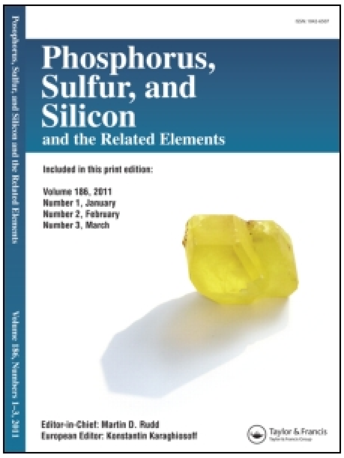

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Cyclic Chalcogenides Containing Group 13–15 Elements

RENJI OKAZAKI

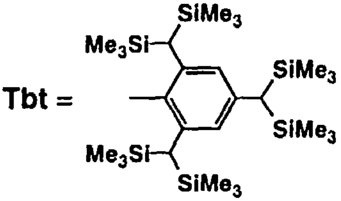
Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, 2–8–1, Mejirodai, Bunkyoku Tokyo 112–8681, Japan

Novel cyclic polychalcogenides containing a variety of heavier main group elements of groups 13, 14, and 15 as ring members have been synthesized as stable crystalline compounds by taking advantage of an effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted as Tbt in this article). The molecular structures of tetrachalcogenametallolanes of group 14 elements, Tbt(R)ME_4 (M = Si, Ge, Sn, and Pb; E = S, Se), and some polysulfides containing antimony or boron atom as a ring member were analyzed by X-ray crystallography to elucidate the skeletal features of these novel ring systems. Dechalcogenation reactions of these cyclic polychalcogenides with trivalent phosphorus reagents provide new and useful synthetic methods for the doubly bonded compounds between the corresponding heavier main group element and a chalcogen atom, a novel class of low-coordinate compounds in the main group element chemistry.

Keywords: Sulfur; Selenium; Group 13–15 elements; X-ray crystallography

INTRODUCTION

Polychalcogenido complexes of transition metals have been extensively studied for the past few decades because of their unique structural features, synthetic utility, and biological activities.[1] For example, there have been reported the syntheses and structures of some monocyclic polysulfides such as Cp_2TiS_5, Cp_2VS_5, Cp_2MoS_4, Cp_2WS_4, $Cp^*_2TiS_3$, and $Cp^*_2ZrS_3$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$), and some of their selenium analogues such as Cp_2TiSe_5 and Cp_2VSe_5, have been prepared and characterized. Zinc-containing cyclic polychalcogenides, $(N\text{-MeIm})_2ZnS_6$ and $(N\text{-MeIm})_2ZnSe_4$, have also been successfully synthesized by direct chalcogenation of zinc dust in *N*-methylimidazole (*N*-MeIm). However, polychalcogenides containing heavier main group elements such as group 13, 14, and 15 metals have been much less explored. In this paper, we describe the synthesis, structures, and reactivities of these cyclic chalcogenides by taking advantage of bulky substituents, particularly 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group which is a new and efficient steric protection group developed by us.[2]

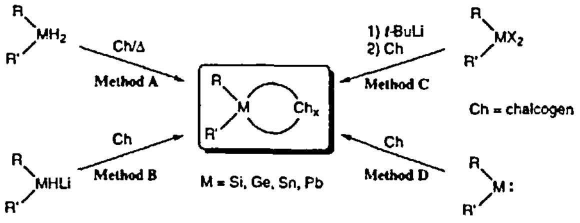


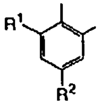
SYNTHESIS

Cyclic Polychalcogenides Containing a Group 14 Element

We have developed the following four different synthetic routes for the synthesis of stable cyclic polychalcogenides containing a heavier group 14 element as shown below;[3] Method A: direct reactions of Tbt-substituted group 14 metal dihydrides with elemental chalcogens, Method B: reactions of the corresponding hydrometallanyllithiums with chalcogens, Method C: successive reactions of the group 14 metal dihalides with *t*-butyllithium and elemental chalcogens, and Method

D: chalcogenation reactions of the Tbt-substituted divalent species of group 14 metals.



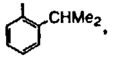


Mes: $R^1 = R^2 = Me$

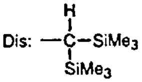
Dep: $R^1 = Et,\ R^2 = H$

Dip: $R^1 = CHMe_2,\ R^2 = H$

Tip: $R^1 = R^2 = CHMe_2$

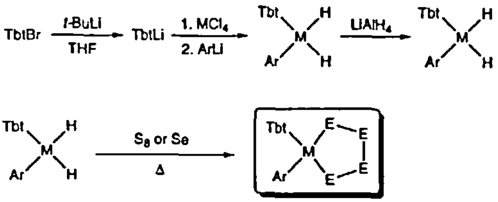
Ditp: $R^1 =$ , $R^2 = H$

Tbt: $R^1 = R^2 = CH(SiMe_3)_2$



$\mathrm{Dis{:}\ {-}C(H)(SiMe_3)SiMe_3}$

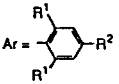
Tetrachalcogenides synthesized by Method A are shown below.



M = Si, Ar = Mes
M = Si, Ar = Tip
M = Ge, Ar = Mes
M = Ge, Ar = Dep
M = Ge, Ar = Tip
M = Sn, Ar = Mes
M = Sn, Ar = Tip

E = S
M = Si, Ar = Mes
M = Ge, Ar = Mes
M = Ge, Ar = Dep
M = Ge, Ar = Tip
M = Sn, Ar = Mes
M = Sn, Ar = Tip

E = Se
M = Sn, Ar = Mes
M = Sn, Ar = Tip



Mes: $R^1 = R^2 = Me$
Dep: $R^1 = Et,\ R^2 = H$
Tip: $R^1 = R^2 = CHMe_2$
Tbt: $R^1 = R^2 = CH(SiMe_3)_2$

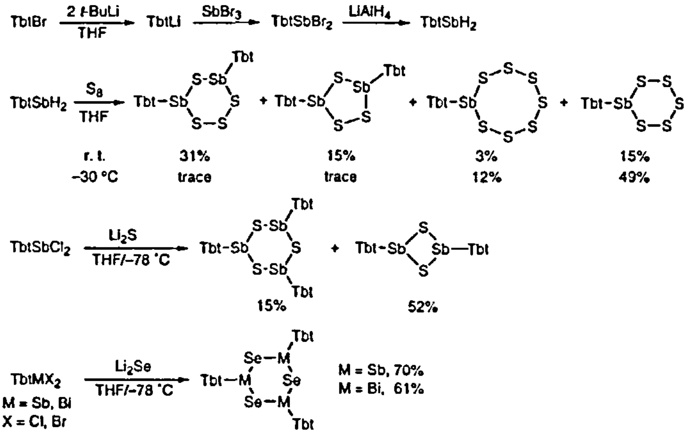
The reactivity of the starting hydrides increases on going from Si to Sn, reflecting the higher reduction ability in metals with higher atomic numbers.

Methods B and C are suitable for the synthesis of germanium and tin tetrasulfide and tetraselenides, while Method D is applicable to all group 14 elements (C, Si, Ge, Sn, and Pb). Method D is a method of choice particularly for the synthesis of silicon and lead tetrasulfides since these sulfides are difficult to be synthesized by other methods.

Cyclic Polychalcogenides Containing Heavier Group 15 Elements

Although there have been several examples of cyclic polysulfides containing a phosphorus or an arsenic atom, *e. g.*, RP(=S)S_n (R = Me or *t*-Bu; n = 5, 6, and 7)[4] and MeAsS_n (n = 5, 6, and 7), [5] as for cyclic antimony polysulfides only one example of a salt of antimony polysulfide anion, [Mg(*N*-MeIm)$_6$][Sb_2S_{15}], [6] has been isolated and characterized and no neutral species of antimony polysulfides have been reported.

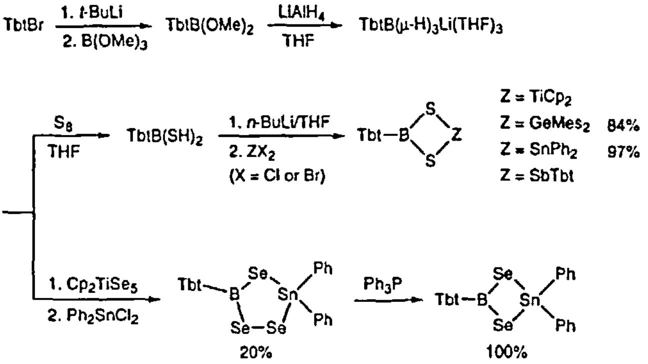
Some cyclic sulfides and selenides of antimony and bismuth were



prepared either by the reaction of hydrides with sulfur or halides with Li_2S or Li_2Se.[7]

Boracycles Containing Chalcogens

We found that lithium aryltrihydroborate $Tbt(\mu\text{-}H)_3Li(THF)_3$ is a good precursor for the synthesis of boracycles containing sulfur and selenium. Dimercaptoborane $TbtB(SH)_2$ can be converted into various 4-membered boracycles containing another metal such as Ti, Ge, Sn, and Sb. 1,3,2,4-Diselenastannaboretane was also synthesized from the aryltrihydroborate.[8]



STRUCTURES

Molecular Geometry of Tetrachalcogenametallolanes of Group 14 Elements

The molecular structures of six tetrachalcogenametallolanes of heavier group 14 elements, $RR'ME_4$ (M = Si, Ge, Sn, Pb; E = S, Se) and a diselenastannirane were determined by X-ray crystallogaraphic analysis. The former tetrachalcogenides have a distorted half-chair conformation, although the extent of the deformation depends on hte metals. The ORTEP drawings of $Tbt(Tip)PbS_4$[3j] and $Tbt(Ditp)SnSe_2$ [9] and are shown in Figure 1.

Molecular Structure of Chalcogen-containing Cyclic Group 15 Element Compounds

The structures of some cyclic chalcogenides containing group 15 elements were established by X-ray crystallography and the ORTEP drawing of heptathiastibocane $TbtSbS_7$ is shown in Figure 2. [10]

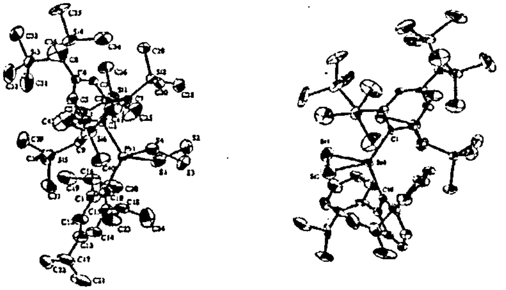


FIGURE 1 The molecular structures of $Tbt(Tip)PbS_4$ (left) and $Tbt(Ditp)SnSe_2$ (right).

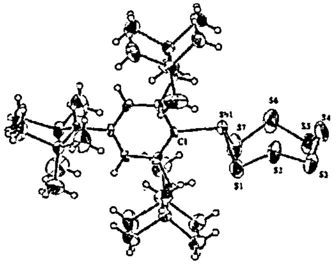


FIGURE 2 The molecular structure of $TbtSbS_7$.

Molecular Structure of 1,3,2,4-Dichalcogenametallaboretanes

Four 1,3,2,4-dichalcogenametallaboretanes ($TbtBS_2TiCp_2$, $TbtBS_2GeMes_2$, $TbtBS_2SnPh_2$, $TbtBSe_2SnMes_2$) have been analyzed by X-ray crystallography. The ORTEP drawing of $TbtBS_2TiCp_2$ is shown in Figure 3. [8a]

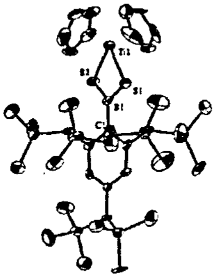
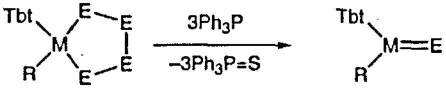


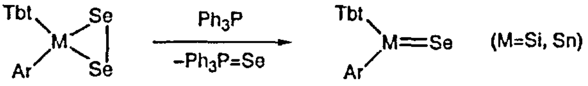
FIGURE 3 The molecular structure of $TbtBS_2TiCp_2$.

REACTIVITY

Metallacycles containing chalcogens show a variety of interesting reactivities. We have carried out dechalcogenation and reactions with transition metal complexes as well as with various reagents such as diphenyldiazomethane, dimethyl acetylenedicarboxylate, and *m*-chloroperbenzoic acid. In this paper we confine ourselves to dechalcogenation reactions leading to the synthesis of stable low-coordinate compounds of new types.

The dechalcogenation of tetrachalcogenametallolane was found to be an excellent synthetic approach to stable group 14-group 16 double-bond compounds, heavier congeners of a ketone, which we refer to as "heavy ketones". In some cases, three-membered diselenides can be also good precursors of selenium-containing heavy ketones.

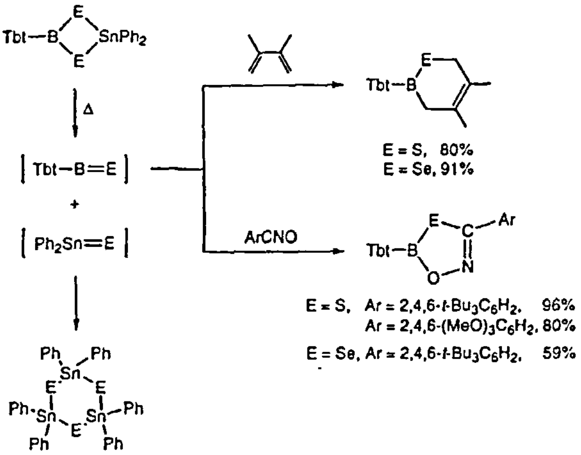




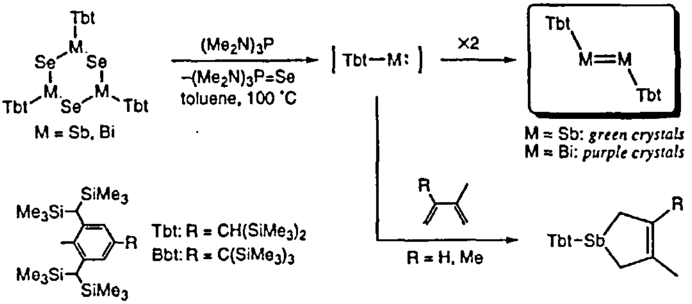
The following heavy ketones have been synthesized by this methods: M=Si, E=S, Se; M=Ge, E=S, Se, Te; M=Sn, E=S, Se. [11]

The X-ray structural analyses of these heavy ketones have revealed that they have a trigonal planar structure and distinctively shorter metal-chalcogen bond length than the corresponding metal-chalcogen single bond, indicating that heavy ketones have structural features essentially similar to those of a ketone.

The boracycles containing chalcogens underwent retro[2+2]cycloaddition reaction to give an intermediate Tbt-B=S or Tbt-B=Se depending on the starting material. These intermediates were trapped by 2,3-dimethylbutadiene or a nitrile oxide to give new types of boracycles. [12]



The cyclic selenides containing antimony and bismuth were found to be an excellent precursor for the synthesis of the first stable distibene (Tbt-Sb=Sb-Tbt)[13] and dibismuthene (Tbt-Bi=Bi-Tbt), [14] both structures of which were established by X-ray diffraction. The deselenation most probably proceeds via intermediacy of monovalent species Tbt-M (M=Sb Bi) because in the presence of a diene five membered trapped products were obtained.



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