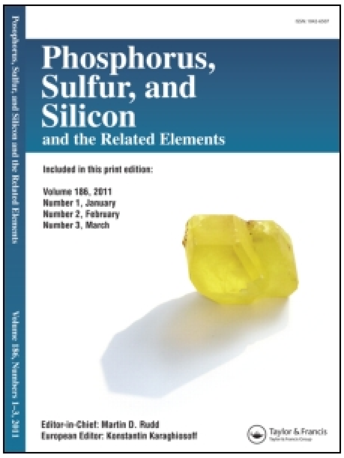

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SYNTHESIS AND REACTIONS OF NOVEL ORGANOSULFUR COMPOUNDS HAVING A HIGHLY STERICALLY BULKY GROUP, 2,4,6-TRIS[BIS(TRIMETHYLSILYL)METHYL]PHENYL

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SYNTHESIS AND REACTIONS OF NOVEL ORGANOSULFUR COMPOUNDS HAVING A HIGHLY STERICALLY BULKY GROUP, 2,4,6-TRIS[BIS(TRIMETHYLSILYL)METHYL]PHENYL

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Abstract Novel cyclic metallatetrasulfides containing Group 14 metals have been synthesized by the thermal reactions of the corresponding metal hydrides substituted by the title new steric protection group. The structure of newly obtained metallacyclopolysulfides is of great interest in comparison with that of the previously reported di-π-cyclopentadienylmetal pentasulfides of titanium(IV) and vanadium(IV). Attempts to prepare the metal-sulfur double bond compounds from the metallacyclopolysulfides are also described.

INTRODUCTION

In recent years, highly reactive and unstable chemical species such as compounds containing multiple bonds of heavier main-group elements have been successfully isolated by taking advantage of kinetic stabilization due to sterically bulky groups (steric protection). In the course of our study on the application of steric protection we have developed an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as **Tb** hereafter),[1] and this new bulky group has been applied to the stabilization of some sulfur-containing highly reactive species.[2] Here, we wish to present a novel formation of new cyclic metallapolysulfides containing Group 14 metals together with their desulfurization reactions leading to the formation of metal-sulfur double bond compounds.

Synthesis of Sterically Crowded Hydrosilanes, Hydrogermanes, and Hydrostannanes

As starting materials **Tb** substituted metal trihalides **1**, **2**, and **3** were synthesized by the reaction of **TbLi**, derived from **TbBr** by the treatment with two equivalent mole of *t*-BuLi in THF,[1,2] with the corresponding metal tetrahalides in moderate to good yields. $\mathbf{TbSiCl_3}$ was found to be too moisture-sensitive to be isolated though the subsequent hydride reduction of the reaction mixture afforded $\mathbf{TbSiH_3}$ in 35% yield.

Further functionalization of the metal trihalides **1**-**3** leading to key substances **4**, **5**, and **6** was readily performed by nucleophilic substitution using appropriate organometallic reagents followed by the $LiAlH_4$ reduction as shown in TABLE I.

In contrast to the facile formation of the dihydrogermanes **5** and dihydrostannanes **6**, nucleophilic substitution of trifluorosilane **1** required rather strong nucleophiles, aryllithiums in the presence of hexamethylphosphoramide (HMPA).

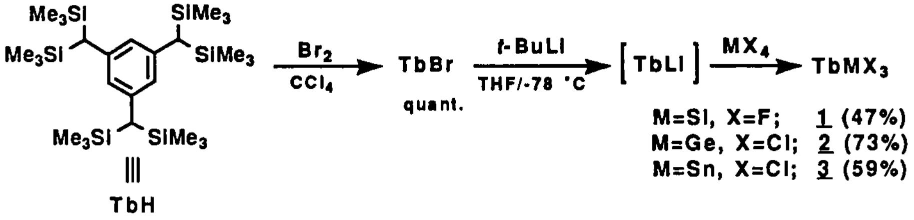


TABLE I Synthesis of Sterically Crowded Group 14 Metal Dihydrides.

$$\mathrm{TbMX_3} \xrightarrow[\text{THF/-78 °C}]{\mathrm{RM}} \xrightarrow[\text{reflux}^{a)}]{\mathrm{LiAlH_4}} \mathrm{Tb(R)MH_2} + \mathrm{Tb(R)_2MH}$$

Substrate	RM	Additive	Products and Yields	
1 (M=Si, X=F)	PhLi (4 eq.)	HMPA (5 eq.)	$\mathrm{Tb(Ph)SiH_2}$ 4a 18%	$\mathrm{Tb(Ph)_2SiH}$ 23%
	MesLi (10 eq.)	HMPA (10 eq.)	$\mathrm{Tb(Mes)SiH_2}$ 4b 24%	$\mathrm{Tb(Mes)_2SiH}$ 0%
2 (M=Ge, X=Cl)	PhMgBr (1.5 eq.)	none	$\mathrm{Tb(Ph)GeH_2}$ 5a 15%	$\mathrm{Tb(Ph)_2GeH}$ 58%
	MesMgBr (2 eq.)	none	$\mathrm{Tb(Mes)GeH_2}$ 5b 54%	$\mathrm{Tb(Mes)_2GeH}$ 0%
3 (M=Sn, X=Cl)	PhMgBr (1 eq.) (2 eq.)	none	$\mathrm{Tb(Ph)SnH_2}$ 6a 39% 6a 0%	$\mathrm{Tb(Ph)_2SnH}$ 1% 30%
	MesMgBr (2 eq.)	none	$\mathrm{Tb(Mes)SnH_2}$ 6b 57%	$\mathrm{Tb(Mes)_2SnH}$ 0%

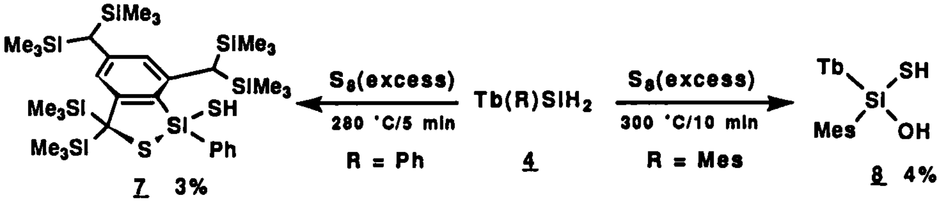
a) In the case of 3 $\mathrm{LiAlH_4}$ reduction was performed at room temperature.

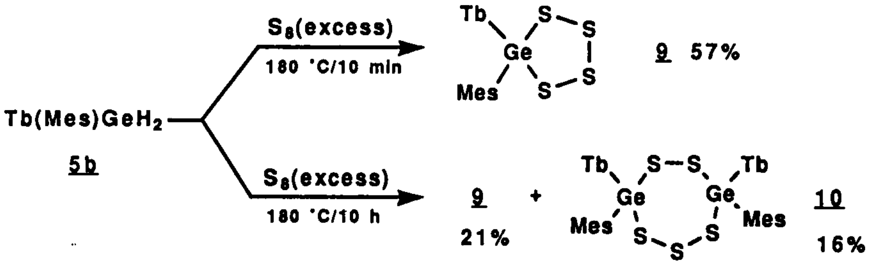
In addition, it is worthy of note that no dimesitylated products were obtained even by the treatment of trichlorides **2** and **3** with an excess amount of mesitylmagnesium bromide in refluxing THF, which suggests severe steric conjestion around the central metal atoms substituted by two bulky aryl groups.

Sulfurization of Group 14 Metal Dihydrides

As for dihydrosilanes, **$\mathrm{Tb(Ph)SiH_2}$ 4a** was quite inert to molten sulfur even at 180 °C. However, the treatment of **4a** with an excess amount of sulfur at 280 °C for 5 min gave an interesting cyclization product **7** and the sulfurization of **$\mathrm{Tb(Mes)SiH_2}$ 4b** also proceeded at 300 °C to afford the hydroxysilanethiol **8** though the yields of **7** and **8** were very low.

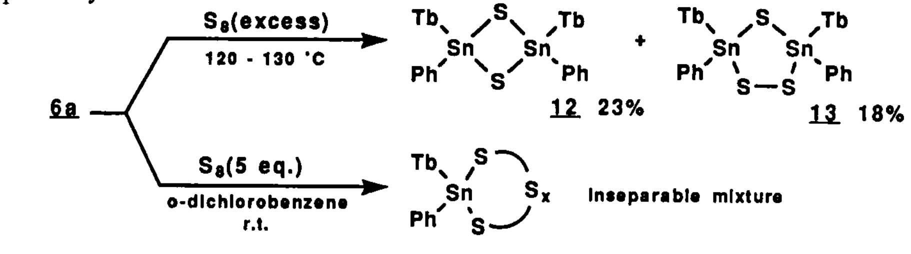
On the other hand, dihydrogermane **5b** was readily sulfurized by heating in excess molten sulfur at 180 °C for 10 min leading to a selective formation of a novel cyclic germatetrasulfide **9** (57%), while the prolongation of reaction time resulted in a formation of another dimeric cyclogermapolysulfide **10** (16%) besides **9** (21%).

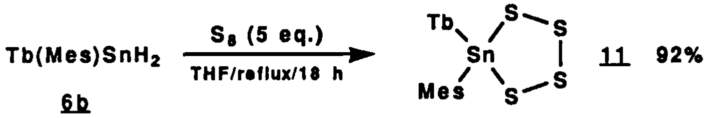




9 was isolated as pale yellow cryatals, and the molecular structure was definitely determined by the X-ray crystallographical analysis along with satisfactory spectral data and elemental analysis. Sulfurization of **Tb(Ph)GeH$_2$ 5a** was also carried out under similar reaction conditions to give an inseparable mixture of cyclic germapolysulfides.

Cyclic stannatetrasulfide **11** was more readily obtained in 92% yield by treatment of the dihydrostannane **Tb(Mes)SnH$_2$ 6b** with sulfur (5 equivalent mole as S_8) in refluxing THF for 18 h. Sulfurization of **Tb(Ph)SnH$_2$ 6a** was also examined to give an inseparable mixture of cyclostannapolysulfides at room temperature as in the case of dihydorgermane **5a**,while treatment of **6a** with molten sulfur at 120-130 °C led to the isolation of two types of dimeric stannapolysulfides **12** and **13** in 23 and 18% yields, respectively.

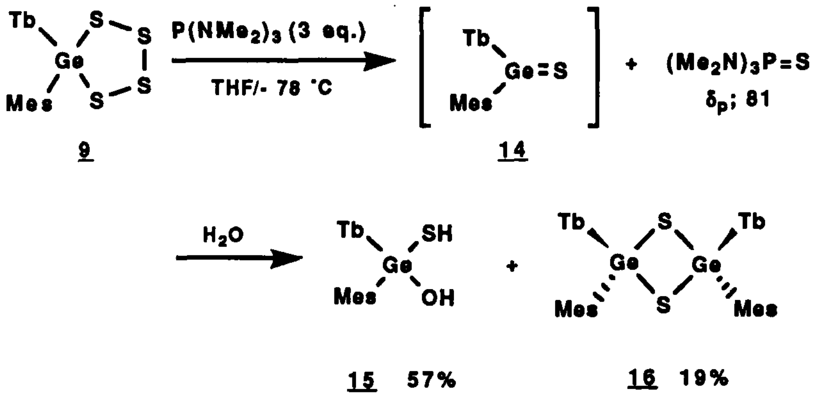




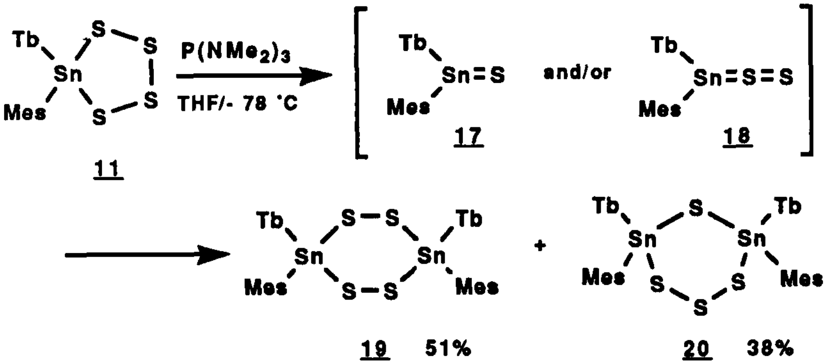
The molecular structure of newly obtained cyclic metallatetrasulfides **9** and **11** is of great interest in comparison with that of previously reported di-π-cyclopentadienylmetal pentasulfides of titanium(VI)[3] and vanadium(VI).[4] In view of the selective formation of tetrasulfides in the sulfurization of mesitylated systems **5b** and **6b** in contrast to the complex sulfurization of **5a** and **6a**, steric requirement due to the **Tb** and mesityl groups might control the number of sulfur atoms in produced cyclic mtallapolysulfides.

Desulfurization of Cyclic Metallatetratetrasulfides

With an expectation of a generation of metal sulfur double bond compounds by desulfurization, cyclic metallatetrasulfides **9** and **11** were treated with hexamethylphosphorous triamide (HMPT).



In the case of **9**, hydroxygermanethiol **15** was obtained in 57% yield together with 1,3-dithiadigermetane **16** (19%). The isolation of **15** and **16** implies the initial formation of gemanethione **14**.[5] **11** was also desulfurized by HMPT to afford two dimeric stannapolysulfides **19** (51%) and **20** (38%) suggesting the possible intermediacy of stannaethione **17** and/or stannathiosulfine **18**.



Attempts to detect and isolate the intermediary metal-sulfur double bond species are now in progress.

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