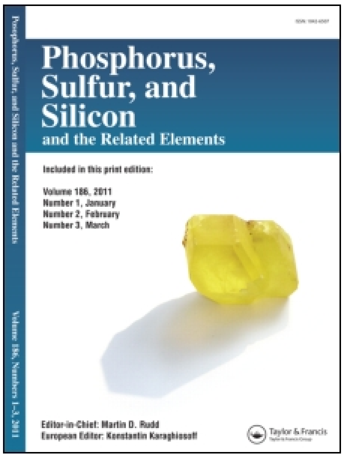

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SYNTHESIS AND REACTIONS OF THE FIRST STABLE 1-GERMAALLENE 1,2-TELLURIDE AND ITS SULFUR AND SELENIUM ANALOGUES

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The first stable 1-germaallene 1,2-telluride and its sulfur and selenium analogues are synthesized by the addition of chalcogen source to the reaction mixture of germanium divalent species such as Tbt(Mes)Ge: (Tbt = 2,4,6-tris[bis(trimethylsilyl) methyl]-phenyl; Mes = mesityl) and α,α-dichloroalkene.

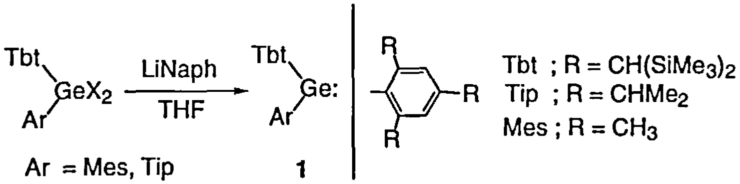
Keywords: 1-germaallene 1,2-chalcogenides; steric protection; germylene; 1-germaallene; X-ray analysis

INTRODUCTION

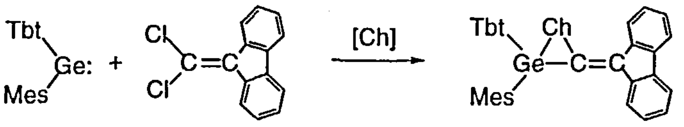
Special interest has been focused on the synthesis and reactions of three-membered rings bearing an exocyclic double bond, since the introduction of an exomethylene group to a three membered ring is expected to increase the strain energy. We present here the syntheses and reactions of the first stable 1-germallene 1,2-telluride and its sulfur and selenium analogues.

SYNTHESIS OF CHALCOGENAGERMIRANES

Divalent germanium compounds (germylene) are known to be highly reactive species and have been widely employed as useful building blocks for the synthesis of a variety of organogermanium compounds. Meanwhile, we have recently reported the synthesis and reactions of overcrowded diarylgermylenes, Tbt(Ar)Ge: (**1**; Ar = Tip, Mes), which was generated by reductive dehalogenation of the corresponding dihalogermanes [Tbt(Ar)GeX$_2$ (X = Cl, Br); Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropyl-phenyl, Mes = mesityl] with lithium naphthalenide in THF.[1] In this paper, we describe the synthesis and reactions of 1-germaallene 1,2-telluride and its sulfur and selenium analogues (chalcogenagermiranes) derived from Tbt(Mes)Ge: **1a**.



Chalcogenagermiranes **2-4** were obtained by the reaction of **1a** with α,α-dichloroalkene **5** followed by the addition of elemental sulfur, selenium and tributylphosphine telluride to the reaction mixture, respectively. Compounds **2-4** are stable even upon exposure to the atmospheric oxygen and moisture. The structure of telluragermirane **4** was established by X-ray crystallographic analysis.



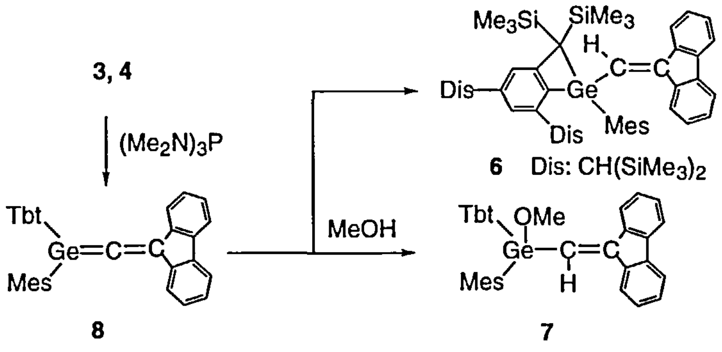
1a **5** **2, 3, 4**: Ch = S, Se, Te

REACTION OF CHALCOGENAGERMIRANES WITH TRIS(DIMETHYLAMINO)PHOSPHINE (HMPT)

Thiagermirane **2** did not react with tris(dimethylamino)-phosphine (HMPT) even at 150 °C, whereas under the same conditions selenagermirane **3** gave a benzogermacyclobutane derivative **6** together with the corresponding phosphine selenide. The structure of **6** was confirmed by X-ray crystallographic analysis.

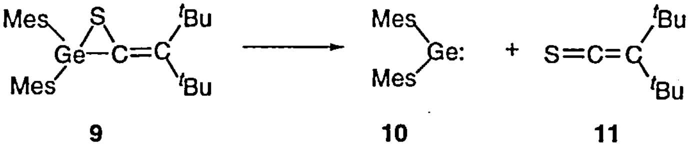
The formation of **6** from selenagermiranes **4** can be interpreted in terms of the initial dechalcogenation of **3** leading to an intermediary germaallene **8**, which is too reactive to be isolated under the reaction conditions, but readily undergoes an intramolecular C-H insertion to give the final product **6** .

On the other hand, 1-germaallene **8** was observed by ^{13}C-NMR (δ_C 246 ppm) at room temperature in the reaction of telluragermirane **5** and HMPT in C_6D_6. A similar lowfield chemical shift is reportedly observed for the allenic carbon of $Mes_2Ge=C=PAr$ (280.9 ppm).[2] The structure of **8** was also proved by its chemical reactivity. Thus, addition of MeOH to the reaction mixture of telluragermirane **4** and HMPT at room temperature gave a methoxygermane **7**, which is an addition product of methanol with **8**.



THERMOLYSIS OF CHALCOGENAGERMIRANES

Thia- and selena-germiranes **2,3** were stable up to 200 °C, whereas telluragermirane **4** decomposed at 120 °C to give the germacyclobutene derivative **6**. On the other hand, thermolysis of **4** in the presence of methanol gave the methoxygermane **7**. These results are in sharp contrast to the fact that 1-germaallene 1,2-sulfide **9** undergoes cycloreversion during pyrolysis (at 500 °C) to produce germylene**10** and thioketene **11**.[3]



Acknowledgments

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