Thermal Retrocycloaddition of Overcrowded Germirenes. A New Method for the Generation of Germylenes

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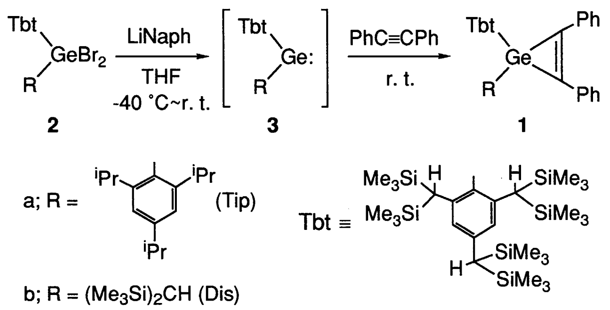
Thermolysis of overcrowded 2,3-diphenylgermirenes bearing bulky substituents on the germanium atom in benzene affords the corresponding kinetically stabilized germylenes, the efficient formation of which is evidenced by the trapping experiments with 2,3-dimethyl-1,3-butadiene. This provides a new and mild method for the generation of germylenes.

It has been reported that germylenes and other divalent species of heavier group 14 elements (silylenes and stannylenes) can be generated from strained small ring compounds,[1] among which the most fascinating class of compounds are silicon, germanium, and tin analogues of cyclopropenes. There have been many reports on the chemistry of silirenes (silacyclopropenes), from which silylenes are generated by photolysis or thermolysis.[2] On the contrary, no cycloreversion of a germirene (germacyclopropane) into a germylene has been described although several isolable germirenes are known.[3,4] Meanwhile, Gordon et al. have recently reported a theoretical study on the thermodynamics of the reaction $MH_2+HC{\equiv}CH{\rightarrow}c\text{-}[H_2MC_2H_2]$ (M = C, Si, Ge, Sn),[5] where the formation of cyclopropene from CH_2 and acetylene is the most exothermic reaction. As one proceeds from M = C to Sn, the reaction exothermicity steadily decreases. This trend is due to both a decrease in stability of the metallacyclopropenes and an increase in that of divalent species MH_2. These theoretical studies are supported by the properties of the first stannacyclopropene derivative, $\Delta^{1,7}$-2,2,6,6-tetramethyl-4-thia-8,8-bis[bis(trimethylsilyl)methyl]-8-stannabicyclo[5.1.0]octane, which was observed to be in thermal equilibrium in solution with its parent stannylene and an acetylene fragment, with the latter being favored at temperatures above -16 °C.[6] These results suggest the possibility of the thermal generation of germylenes from the corresponding germirenes.

Here, we present the thermal reactions of overcrowded germirenes **1a,b** bearing 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted as Tbt in this paper) group, a new and efficient steric protection group developed by us,[7] on the germanium atom, which lead to the first thermal cycloreversion of a germirene into a germylene.

Germirenes **1a,b** were synthesized in 91 and 77% by the reaction of diphenylacetylene (1.5 equiv) with germylenes **3a,b** which were prepared by reduction of the corresponding dibromogermanes **2a,b** with lithium naphthalenide (2.4 equiv) in THF (Scheme 1). These germirenes are kinetically stable owing to the bulky groups in contrast to the previously reported germirenes which are known to be hydrolyzed rapidly in the open air.[3,4] Since no structural analysis of a non-fused germirene has been described so far, we carried out the X-ray crystallographic analysis of **1a** as shown in Figure 1,[8] where one can recognize the central germirene ring of **1a** closely surrounded by the bulky Tbt and Tip (2,4,6-triisopropylphenyl) groups.



Scheme 1.

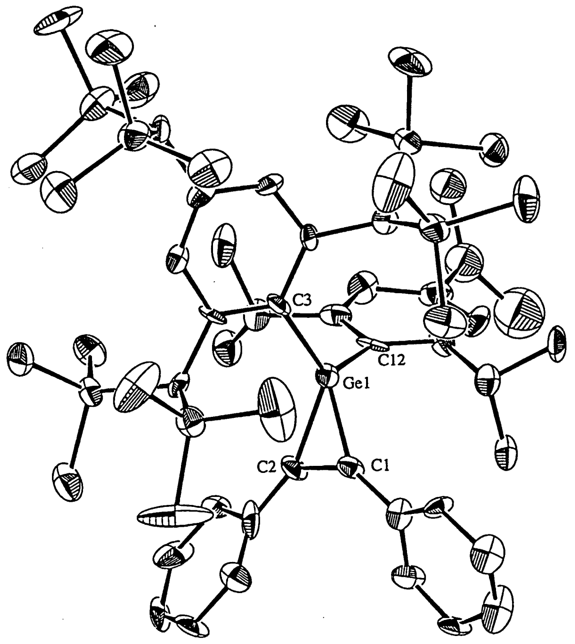
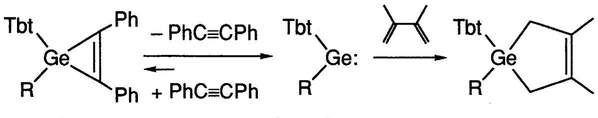


Figure 1. ORTEP drawing of **1a** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg); Ge(1)-C(1) 1.94(20, Ge(1)-C(2) 1.92(2), Ge(1)-C(3) 2.00(2), Ge(1)-C(12) 1.93(3), C(1)-C(2) 1.35(3), C(1)-Ge(1)-C(2) 41.0(9), C(1)-Ge(1)-C(3) 127.6(10), C(1)-Ge(1)-C(12) 115(1), C(2)-Ge(1)-C(3) 124.1(10), C(2)-Ge(1)-C(12) 111.4(9), C(3)-Ge(1)-C(12) 115.4(10).

Since the thermal lability of germirene **1a** was indicated by decomposition at 118–120 °C in the solid state, a benzene-d_6 solution of **1a** and an excess amount of 2,3-dimethyl-1,3-butadiene (8.2 equiv) in an NMR tube was heated while being monitored by ^1H NMR. Only slight change was observed at 50

°C, but heating up to 70 °C for 9 h gave germacyclopentene **4a** (95%) and diphenylacetylene (100%) with complete consumption of the starting **1a** (Scheme 2). This cheletropic reaction is reversible; in the absence of the trapping reagent, the colorless solution of **1a** in hexane at room temperature turns pale blue at 50 °C (λ_{max}=581 nm), showing the generation of germylene **3a**, and becomes colorless again on cooling. Germirene **1b** having a bis(trimethylsilyl)methyl (denoted as Dis hereafter) group on the germanium atom together with the Tbt group also underwent a similar thermal cycloreversion at 80 °C into the corresponding germylene **3b**, which was trapped with 2,3-dimethyl-1,3-butadiene to give an expected cycloadduct **4b** (71%) and diphenylacetylene (97%) (Scheme 2).



1 Δ **3** **4**

Scheme 2.

These results indicate that germirenes **1a,b** are useful precursors for overcrowded germylenes **3a,b**. Although we have already found that germylene **3a** can be prepared as a stable species in solution by either the nucleophilic substitution of germanium(II) iodide with TbtLi and TipLi[7b,9] or the reductive debromination of the dibromogermane **2a** with lithium naphthalenide,[10] these methods have some disadvantages; e. g., i) low reproducibility of the generation of **3a** because of the multi-steps of reactions, ii) basic reaction conditions resulting from the lithium reagents used, iii) inevitable existence of impurities such as lithium halides. The present method for the generation of germylenes **3a,b** is superior to the previous methods from the standpoints of not only its simplicity and high efficiency but also its clean and neutral reaction conditions.

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8 Crystal data for **1a**: $C_{56}H_{92}GeSi_6$; *MW* = 1006.45; *monoclinic*; space group $P2_1/c$; a = 13.672(6), b = 21.181(7), c = 21.569(6) Å; β = 93.21(3)°; V = 6236(3) Å^3; Z = 4; D_c = 1.072 g cm^{-3}; μ(Mo Kα) = 6.37 cm^{-1}. $R(R_w)$ = 0.102(0.113).

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