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Synthesis, Structure, and Reactivity of a Thermally Stable Dialkylgermylene[#]

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Abstract

The dialkylgermylene Trp_2^*Ge : (Trp*: peripherally extended sterically demanding alkyl groups based on the triptycene (Trp) framework), was obtained from the reaction of Trp*Li with GeCl₂·dioxane. The structure of Trp*₂Ge: was unequivocally determined by NMR and UV-vis spectroscopy, mass spectrometry, and a single-crystal X-ray diffraction analysis. Moreover, the reactivity of Trp*₂Ge: was examined.

Keywords: Germylene, Steric Protection, X-ray Analysis

1. Introduction

Since the first stable germylene has been reported by Lappert *et al.*,¹ the chemistry of divalent organogermanium compounds and related congeners has been developed steadily.² Due to the high intrinsic reactivity and instability of germylenes,^{2k} most of the hitherto reported isolated germylenes are stabilized kinetically by bulky substituents on the germanium atom,^{3,4} albeit that some thermodynamically stabilized germylenes have also been reported (Chart 1).⁵ The first stable germylene, Dis₂Ge:, is monomeric in solution, but dimerizes in the solid state (Chart 1a).^{1b}



HermannMellerDriessDippChart 1. a)Lappert's germylene $Dis_2Ge:$. b)Selectedkineticallystabilizedgermylenes.c)Selectedthermodynamically stabilized germylenes.

When one Dis group in Dis₂Ge: is exchanged with Tsi, DisTsiGe: exists as a monomer in the solid state (Chart 2).^{3a} Moreover, Kira *et al.* have reported a stable dialkylgermylene that bears helmet ligands on the germanium atom.^{3b} But despite numerous studies conducted on aryl-substituted germylenes,⁴ only two isolated monomeric dialkylgermylenes³ are listed in the Cambridge Structural Database,⁶ and synthetic examples of germylenes with aliphatic carbon-based ligands on the germanium atom remain scarce.^{2c,e,h-o,3}



Chart 2. Hitherto reported dialkylgermylenes.

Recently, our group has designed and synthesized Trp*, i.e., a novel triptycene (Trp)-based aliphatic bulky group that bears bulky fused ring-type substituents at the periphery of the Trp framework.⁷ Using Trp*, we have demonstrated that it is possible to synthesize and isolate highly reactive species, such as an alkylsulfenic acid (Trp*SOH)^{7a} and a tetraalkyldisilenes ([Trp*CH₂(Trp)Si]₂)^{7b}. In the present study, we took advantage of the steric protection of the Trp* group to synthesize the thermally stable germylene Trp*₂Ge: (1), in which the divalent germanium atom is bound to aliphatic carbon ligands.



Chart 3. A stable alkylsulfenic acid (Trp*SOH) and a stable tetraalkyldisilene ([Trp*CH₂(Trp)Si]₂) with Trp* substituent(s).

2. Results and Discussion

The synthesis of germylene **1** was achieved by the reaction of GeCl₂·dioxane with 2 equiv. of Trp*Li, which was obtained from Trp*Br and *tert*-BuLi at -78 °C. After removal of the volatiles *in vacuo*, the residue was dissolved in benzene and filtered to eventually afford **1** as an orange solid in 55% yield (Scheme 1). Although isolated **1** is moisture-sensitive, it is thermally extremely stable (mp > 300 °C), and the ¹H NMR spectrum of **1** in toluene-*d*₈ remained unchanged after one week at 110 °C.⁸



Single crystals of **1** were obtained from recrystallization from benzene, and the solid-state structure of **1** was determined by a single-crystal X-ray diffraction analysis. The molecular structure showed a two-coordinate Ge atom and intermolecular contacts around the Ge atom were not observed (shortest intermolecular Ge...Ge distance: 14.3899(6) Å), which indicates that the germylene is monomeric in the solid state. The bond lengths [Ge-C1: 2.055(2); Ge-C2: 2.048(3) Å] and the bond angles [C1-Ge-C2: 110.4(1) °] around the Ge atom are comparable to those of previously reported germylenes.³ The front view of the space-filling model of **1** (Figure 1) seems to exhibit sufficient space for reactions around the Ge atom. The side and bottom views show an inter-meshing of the Trp* groups that should provide effective steric protection. The UV-vis spectrum of a THF solution of **1** showed an absorption maximum at 458 nm ($\varepsilon = 500$), which was assigned to the n(Ge)-4p π (Ge) transition as it is close to that of a previously reported diakygermylene.^{3b} Again, this result indicates that **1** is monomeric in solution.⁹



Figure 1. a) ORTEP drawing of **1** with thermal ellipsoids at 50% probability. b) Space-filling models of **1**.

In the ¹H and ¹³C NMR spectra of a benzene- d_6 solution of 1, only one set of Trp* signals was observed and the six aromatic rings of the two Trp* groups are magnetically equivalent at room temperature. Line-broadening was not observed, not even at -60 °C in toluene- d_8 . These phenomena are probably due to the correlative rotation around the two C-Ge bonds given the meshing-gear conformation of the Trp* groups.



Figure 2. ¹H NMR spectrum of **1**. All aromatic protons are labeled with the corresponding colored circles and squares.

Isolated **1** exhibited the characteristic reactivity of a divalent group-14-element species (Scheme 2). Reactions of **1** with an excess of MeOH or H₂O afforded the corresponding adducts **3** and **4**, whereby the formation of $\text{Trp*}_2\text{GeH}_2$ was not observed.^{10,11} In the reaction of **1** with EtBr, the C-Br bond-insertion product **5** was obtained in good yield. The reaction of **1** with CS₂ furnished three-membered thioxothiagermirane **6** (74% yield), whose thioxothiagermirane structure was experimentally confirmed for the first time (Figure 3).¹² Such three-membered ring systems have been postulated as reactive intermediates in the reaction between the *in-situ*-generated germylene and CS₂, by Okazaki *et al.*^{12b,c} Treatment of **1** with acetylene afforded the

three-membered germacyclopropene (germirene) 7 via a [1 + 2]-cycloaddition.¹³ Isolated 7 is air-stable, and single crystals were obtained from recrystallization from benzene, which allowed determining the molecular structure of 7 (Figure 3). During the solid-state thermal reaction of 7 at 200 °C *in vacuo*, detectable quantities of 1 were regenerated, although 6 is thermally very stable.



Scheme 2. Reactivity of 1 with small molecules.



Figure 3. ORTEP drawing of 6 (left) and 7 (right) with thermal ellipsoids at 50% probability.

3. Conclusions

Dialkylgermylene $\text{Trp}^*_2\text{Ge:}(1)$ was synthesized and isolated thanks to the kinetical stabilization of the Trp^* group. The structure of 1 was fully characterized. Isolated 1 exhibits remarkable thermal stability and reacts with MeOH, H₂O, EtBr, CS₂, and acetylene. Further studies into the reactivity of 1 and the synthesis of other reactive main-group-element compounds with Trp* groups are currently in progress in our laboratory.

4. Experimental

Synthesis of Trp*2Ge: (1). A THF solution (20 mL) of 2 (492 mg, 0.743 mmol) at -78 °C was treated with tert-BuLi (1.00 mL, 1.56 mmol, 1.56 M in pentane) and stirred for 5 min. Then the mixture was stirred for 2.5 min at -50 °C. This THF solution of Trp*Li was cooled to -78 °C and treated with a THF solution (3 mL) of GeCl₂·dioxane (122 mg, 0.520 mmol). The reaction mixture was allowed to warm to room temperature, where it was stirred for 1 h. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from benzene to give 1 (253 mg, 0.204 mmol, 55%) as orange crystals, which were isolated by filtration: mp > 300 °C; ¹H NMR (400 MHz, C₆D₆): δ 0.85 (s, 36H), 1.17 (s, 36H), 1.40-1.42 (m, 12H), 1.45-1.48 (m, 12H), 5.54 (s, 2H), 7.59 (s, 6H), 7.75 (s, 6H); ¹³C NMR (100 MHz, C₆D₆): δ 32.0, 32.1, 34.3, 34.4, 35.5, 35.6, 55.4, 64.9, 122.1, 122.4, 140.9, 141.2, 146.3, 146.7; UV-vis (THF) $\lambda_{max} = 458 \text{ nm} (\varepsilon = 500 \text{ cm}^{-1} \text{ M}^{-1});$ HRMS-FAB (m/z): [M] calcd. for $C_{88}H_{110}^{-74}$ Ge, 1240.7819; found, 1240.7774.

X-ray Crystal Structure Analysis. The single-crystal X-ray diffraction analyses of **1**, **6**, and **7** were carried out at the BL40XU and BL02B1 beam lines of the SPring-8 synchrotron. All frame images (Dectris) were converted to the SFRM format using *Henkankun-R*.¹⁴ Data reduction was performed using Bruker SAINT. Structures were solved by direct methods (*SHELXT*) and refined against F^2 by weighted full-matrix least-squares (*SHELXL*). Crystallographic data of **1**, **6**, and **7** were deposited at the CCDC under reference numbers 1966229-1966231.

Supporting Information

General experimental procedures and materials, as well as X-ray crystallographic and spectroscopic data are available in the Supporting Information. This material is available on http://dx.doi.org/10.1246/ bcsj.201XXXXX.

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8. For example, $Mes_2Ge:$ decomposes at room temperature to release Mes^*H ; *cf*. ref. 4b.

9. DFT calculations at the TDDFT-B3PW91/6-311G (2d,p)//B3PW91/6-31G(d) level of theory suggest a λ_{max} values of 493 nm for 1 (Fig. S7 in SI).

10. The result suggests a singlet ground state for 1; this hypothesis was supported by the results of DFT calculations, i.e., the singlet state of 1 is by 19.1 kcal mol⁻¹ more stable than the corresponding triplet state (Table S2 in SI).

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