Synthesis and Structure of the First Germaketenedithioacetal

Norihiro Tokitoh, Kuniyuki Kishikawa and Renji Okazaki*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Treatment of an overcrowded diarylgermylene Tbt(Tip)Ge: **1** {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl} with carbon disulfide affords the first germaketenedithioacetal derivative **3** as a stable orange crystalline compound, for which the molecular structure is established by X-ray crystallographic analysis.

Divalent germanium compounds, *i.e.* germylenes, are known to be highly reactive chemical species and are widely employed as useful building blocks for the syntheses of a variety of organogermanium compounds having new skeletons *via* their insertion and/or cycloaddition reactions.[1] Meanwhile, we have recently succeeded in the synthesis of a new type of kinetically stabilized diarylgermylene, Tbt(Tip)Ge: **1** (Tip = 2,4,6-triisopropylphenyl),[2] by taking advantage of a new steric protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), which has been applied to the kinetic stabilization of a variety of highly reactive chemical species.[3] We report herein a novel reaction of this overcrowded germylene **1** with carbon disulfide which leads to the first isolation and characterization of a germaketenedithioacetal derivative.

Although in our previous papers we prepared the germylene **1** by the sequential nucleophilic substitution of germanium(II) iodide with TbtLi and TipLi in the presence of hexamethylphosphorous triamide,[2,3b] the yield and reproducibility of this method were not sufficient to be applied to the synthesis and isolation of unstable organogermanium compounds. Therefore, we developed an alternative synthetic method for **1** by reduction of the corresponding dibromogermane **2** with lithium naphthalenide, which gave 68% yield of the [1 + 4]cycloadduct of **1** in the presence of 2,3-dimethylbuta-1,3-diene.

When a blue solution of the diarylgermylene **1**, prepared by reduction of the corresponding dibromogermane **2** (212 mg, 0.22 mmol) with lithium naphthalenide (0.54 mol dm^{-3}, 0.9 ml, 0.49 mmol) in THF, was treated with carbon disulfide (0.13 ml, 2.2 mmol) at room temperature, the reaction mixture turned orange. After removal of the volatile materials under reduced pressure the residual brown oil was separated using low-temperature flash column chromatography (SiO_2–pentane, −10 °C) to afford 85.3 mg of an adduct **3** (0.29 mmol, 46% from **2**) as air-sensitive orange crystals (Scheme 1).

Although the ^1H and ^{13}C NMR spectra of this adduct **3** were extremely complicated suggesting the severe steric congestion, the molecular composition of **3** was confirmed to be a 2:1 adduct of **1** to carbon disulfide by high resolution FABMS (found, *m/z* 1732.7942; calc. for $C_{85}H_{164}Ge_2S_2Si_{12}$, *m/z* 1732.7962). Since pure orange crystals of the adduct **3** (mp 115–118 °C, decomp.) were obtained by recrystallization (benzene–hexane, 1:1) in a glovebox filled with argon, the molecular structure of **3** was finally determined by X-ray crystallographic analysis,[†] which showed a novel germaketenedithioacetal skeleton as shown in Fig. 1.

The length of the Ge(1)–C(1) bond [1.771(16) Å] was found to be consistent with the calculated values for a parent germene $H_2Ge{=}CH_2$ [1.71–1.81 Å][4] but somewhat shorter than those in the previously reported germene derivatives **4** [1.827(4) Å] and **5** [1.803(4) Å],[5] which are the only two examples of germenes thus far crystallographically analysed. The sums of the bond angles around Ge(1) and C(1) of **3** were 359.7 and 360.0°, respectively, suggesting the trigonal planar geometry of the germene unit. The twist angle of the Ge(1)–C(1) double bond of **3** was found to be 4°, while those for **4** and **5** are reportedly 36 and 6°, respectively.[5] As can be seen in Fig. 1, **3** was closely surrounded by the four steric protecting groups, which make the germene unit inert towards methanol even in refluxing benzene, in contrast to the other stable germene **5** which readily reacts with methanol to afford the corresponding methoxygermane.[5c] In the electronic spectra the germaketenedithioacetal **3** showed a characteristic absorption maximum at 396 nm (ε 2600 dm^3 mol^{-1} cm^{-1}) in hexane attributable to the π–π* transition of the germene unit.

The formation of **3** can be reasonably interpreted in terms of the intermediacy of thiagermiranethione **7**, as shown in Scheme 2. Germylene **1** reacts with carbon disulfide to produce **7** *via* an initially formed ylide **6**. The second attack of **1** onto the

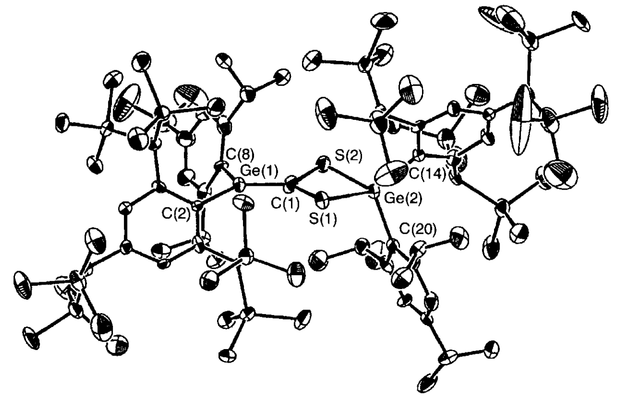
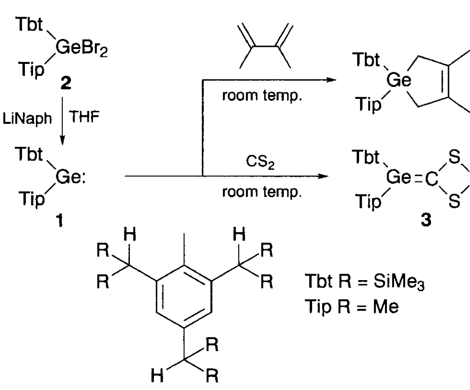
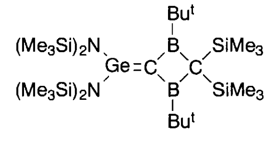


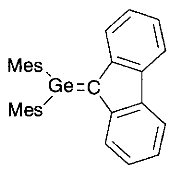
Fig. 1 ORTEP drawing of germaketenedithioacetal **3** with thermal ellipsoid plot (20% probability). The fragment of solvated benzene was omitted for clarity. Selected bond lengths (Å) and angles (°) Ge(1)–C(1) 1.771(16), Ge(1)–C(2) 1.92(1), Ge(1)–C(8) 1.96(2), Ge(2)–S(1) 2.285(5), Ge(2)–S(2) 2.268(5), Ge(2)–C(14) 1.99(2), Ge(2)–C(20) 1.99(2), C(1)–S(1) 1.81(2), C(1)–S(2) 1.81(2), C(1)–Ge(1)–C(2) 130.5(7), C(1)–Ge(1)–C(8) 116.4(7), C(2)–Ge(1)–C(8) 112.8(7), S(1)–C(1)–Ge(1) 134.3(10), S(2)–C(1)–Ge(1) 120.2(10), S(1)–C(1)–S(2) 105.5(8), C(14)–Ge(2)–C(20) 110.4(6).



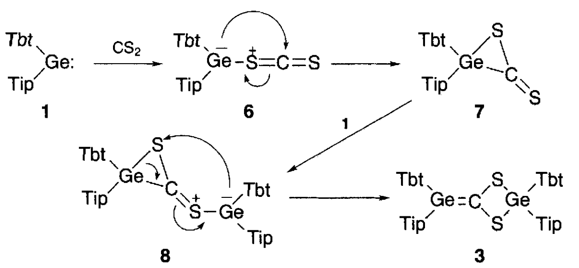
Scheme 1



4



5



Scheme 2

thiocarbonyl sulfur atom of **7** leads to the formation of another germathiocarbonyl ylide **8**, which eventually gives a germaketenedithioacetal skeleton by intramolecular cyclization. Although a similar reaction with carbon disulfide has been reported for silicocene (η^5-$C_5Me_5)_2Si$ by Jutzi and Möhrke,[6] in that case the intermediary thiasiliranethione undergoes a ready dimerization to afford the cyclic thioester. The lack of such a dimerization product of **7** again suggests the effectiveness of our steric protection system, while the exclusive formation of **3** without any 1 : 1 reaction product, even in the presence of an excess amount of carbon disulfide, implies a much higher reactivity of the thiocarbonyl unit of **7** toward germylene **1** than that of carbon disulfide.

The formation of **3** here described should be noted not only from the viewpoint of the first isolation and characterization of a germaketenedithioacetal derivative, but also as the novel mode of formation of a germanium–carbon double bond system (germene).

This work was partially supported by Sumitomo Foundation (N. T.) and a Grant-in-Aid for Scientific Research (No. 05236102) from the Ministry of Education, Science and Culture, Japan. We are grateful to ASAI Germanium Research Institute, Shin-etsu Chemical Co. Ltd and Tosoh Akzo Co. Ltd, for the generous gifts of tetrachlorogermane, chlorosilanes and alkyllithiums, respectively.

Received, 21st April 1995; Com. 5/02541I

Footnote

† *Crystal data* for **3**·0.5C_6H_6: $C_{88}H_{167}Ge_2S_2Si_{12}$, M = 1771.61, orthorhombic, space group $P2_12_12_1$, a = 20.880(6), b = 27.730(9), c = 19.165(8) Å, V = 11096(5) Å^3, Z = 4, D_c = 1.060 g cm^{-3}, μ = 7.44 cm^{-1}. The intensity data were collected through a glass capillary on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods with SHELXS-86.[7] All the non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4350 observed reflections [$I > 3\sigma(I)$] and 917 variable parameters with $R(R_w)$ = 0.055 (0.065). Structure refinement without the benzene solvate gave poorer results than those described above. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283; W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311; P. Jutzi, A. Becker, H. G. Stammler and B. Neumann, *Organometallics*, 1991, **10**, 1647 and references cited therein.

2 N. Tokitoh, K. Manmaru and R. Okazaki, *Organometallics*, 1994, **13**, 167.

3 (*a*) N. Tokitoh, M. Saito and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 2065; (*b*) N. Tokitoh, T. Matsumoto, K. Manmaru and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 8855; (*c*) H. Suzuki, N. Tokitoh, S. Nagase and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11578.

4 (*a*) J. Barrau, G. Rima and J. Satgé, *J. Organomet. Chem.*, 1983, **252**, C73; (*b*) M. J. S. Dewar, G. L. Grady and E. F. Healy, *Organometallics*, 1987, **6**, 186.

5 H. Meyer, G. Baum, W. Massa and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 798; (*b*) A. Berndt, H. Meyer, G. Baum, W. Massa and S. Berger, *Pure Appl. Chem.*, 1987, **59**, 1011; (*c*) C. Couret, J. Escudié, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.*, 1987, **109**, 4411; (*d*) M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 828.

6 P. Jutzi and A. Möhrke, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 762.

7 G. M. Sheldrick, SHELXS-86, University of Göttingen, Göttingen, Germany, 1986.