Synthesis and Crystal Structure of the First Stable Diarylgermanethione

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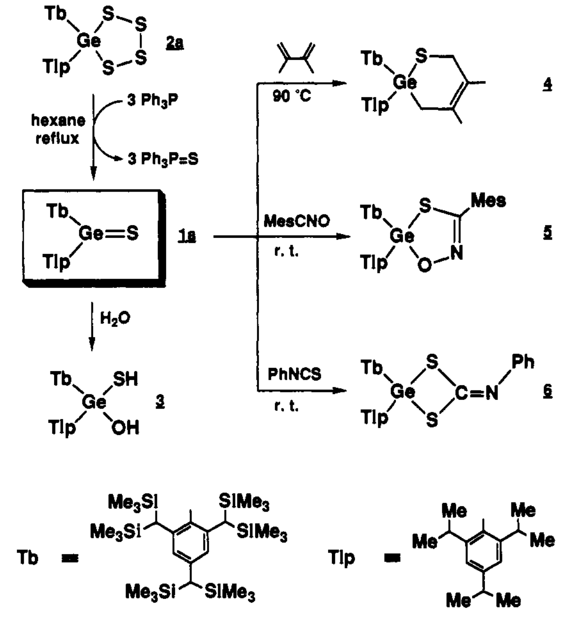
Germanethiones (RR′Ge=S) are among the most fascinating class of multiply bonded organoheteroatom compounds of current interest.[1] Recently, dimethylgermanethione was detected spectroscopically in an argon matrix at cryogenic temperatures,[2] while a germathiourea (germanium–sulfur double-bond compound with two amino groups on the germanium) stabilized by intramolecular complexation has been isolated and crystallographically analyzed.[3] Meanwhile, even the sterically crowded diarylgermanethiones such as dimesitylgermanethione[4] and bis(2,4,6-tri-*tert*-butylphenyl)germanethione[5] have been known as labile systems which suffer from ready dimerization or intramolecular cyclization at ambient temperature, and there have been hitherto no examples of stable germanethiones. We previously reported the synthesis of novel 1,2,3,4,5-tetrachalcogenametallolanes containing group 14 metals, Tb(R)MY$_4$ [R = mesityl (Mes) or 2,4,6-triisopropylphenyl (Tip); M = Si, Ge, Sn; Y = S, Se][6] by taking advantage of a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb hereafter).[7] We delineate here the synthesis of the first stable diarylgermanethione Tb(Tip)Ge=S (**1a**) by desulfurization of 1,2,3,4,5-tetrathiagermolane Tb(Tip)GeS$_4$ (**2a**), together with the X-ray crystallographic analysis of **1a**.

When a pale yellow hexane solution (5 mL) of **2a** (800 mg, 0.837 mmol) and 3 molar equiv of triphenylphosphine (658 mg, 2.51 mmol) was refluxed for 2 h, the solution turned bright yellow and a quantitative amount of triphenylphosphine sulfide was precipitated. After filtration of the phosphine sulfide under argon, the residual bright yellow solution was concentrated in a glovebox filled with argon to give pure germanethione **1a** (718 mg, 99.7%) as orange yellow crystals (Scheme I).

Germanethione **1a** gave satisfactory spectral and analytical data,[8] showing a characteristic strong Raman line at 521 cm^{-1} attributable to the Ge–S stretching of the germathiocarbonyl unit.[9] The molecular structure of **1a** was finally determined by X-ray crystallographic analysis, which also confirmed that **1a** exists as a monomer even in the solid state.[10] As clearly shown in Figure 1, the germanium atom in **1a** is bound to the two aryl groups (Tb and Tip) and a singly coordinated sulfur atom with completely trigonal-planar geometry, the sum of the bond angles around the germanium atom (359.4°) being nearly equal to 360°. Of particular note is the remarkable shortening of the Ge–S bond length [2.049(3) Å], the value of which is the shortest one reported so far for Ge–S distance[11] and distinctly shorter than that of a Ge–S single bond.[12] Dihedral angles between the two aryl planes and the π-plane containing Ge(1), S(1), C(1), and C(2) atoms are 38.9° (for Tb group) and 70.1° (for Tip group), while the two aryl planes are almost perpendicular to each other (89.3°), reflecting the large steric repulsion between them.

Scheme I



Germanethione **1a** was found to be thermally quite stable under inert atmosphere either in the solid state or in solution. For example, **1a** has a sharp melting point at 163–165 °C, and the electronic spectra of **1a** in hexane, which showed a characteristic absorption maximum at 450 nm (ε 100), most likely due to the Ge=S *n*–π* transition, was unchanged, even after the sample was heated at 160 °C for 3 days in a sealed cell.

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(8) **1a**: orange yellow crystals, mp 163–165 °C, ^{1}H NMR (500 MHz, C$_6$D$_6$ at 300 K) δ 0.15 (s, 18H), 0.16 (s, 18H), 0.26 (br s, 18H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.35 (br d, *J* = 6.9 Hz, 6H), 1.48 (d, *J* = 6.9 Hz, 6H), 1.51 (s, 1H), 2.74 (sept, *J* = 6.9 Hz, 1H), 3.18 (br s, 1H), 3.29 (br s, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.65 (br s, 1H), 6.52 (br s, 1H), 6.70 (br s, 1H), 7.07 (s, 2H); ^{13}C NMR (C$_6$D$_6$, 125 MHz at 300 K) δ 1.08 (q), 1.28 (q), 1.61 (q), 22.32 (q), 24.11 (q × 2), 27.68 (d), 29.56 (d), 29.60 (d), 31.74 (d), 34.83 (d), 37.52 (d), 122.30 (d), 123.89 (d), 128.29 (d), 128.98 (d), 132.57 (s), 142.25 (s), 144.96 (s), 149.98 (s), 150.99 (s), 151.27 (s × 2), 152.30 (s); FABMS *m/z* 861.4042 ([M + H]$^+$), calcd for $C_{42}H_{83}{}^{74}GeSSi_6$ 861.4043; UV (hexane) λ_{max} 229 (ε 52 000), 340 (5000), 450 (100) nm; FT-Raman spectrum in solid (excitation; Nd: YAG laser 1064 nm) 521 cm^{-1} ($\nu_{Ge=S}$).

(9) The value of the Ge–S stretching for **1a** (521 cm^{-1}) is in good agreement with that (518 cm^{-1}) for Me$_2$Ge=S reported in ref 2b.

(10) Crystallographic data for **1a**: $C_{42}H_{82}GeSSi_6$, *M* = 860.27, triclinic, a = 13.508(4), b = 20.722(8), and c = 9.740(3) Å, α = 96.96(3)°, β = 90.01(3)°, γ = 81.87(3)°, V = 2679(3) Å^3, Z = 2, space group $P\bar{1}$, d_c = 1.066 g cm^{-3}, μ = 7.56 cm^{-1}. The intensity data were collected through a capillary glass on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å), and the structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3454 observed reflections [$I > 4.00\sigma(I)$] and 451 variable parameters with R (R_w) = 0.065 (0.076). Intermolecular S–S and Ge–Ge distances between the nearest molecule in the crystal were found to be 5.284(8) and 7.094(4) Å, respectively. Full details for the crystallographic analysis of **1a** are described in the supplementary material.

(11) The Ge–S bond length of the Veith's germathiourea, which is the shortest one reported so far, is 2.063(3) Å; see ref 3a.

(12) The values for common Ge–S single bonds are varied within a range of 2.21 ± 0.04 Å. For example, see: (a) Benno, R. H.; Frichie, C. J. *J. Chem. Soc., Dalton Trans.* **1973**, 543. (b) Jutzi, P.; Steiner, W.; König, E.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1978**, *111*, 606. (c) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *Inorg. Chem.* **1987**, *26*, 2885. (d) Ando, W.; Kadowaki, T.; Kabe, Y.; Ishii, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 59.

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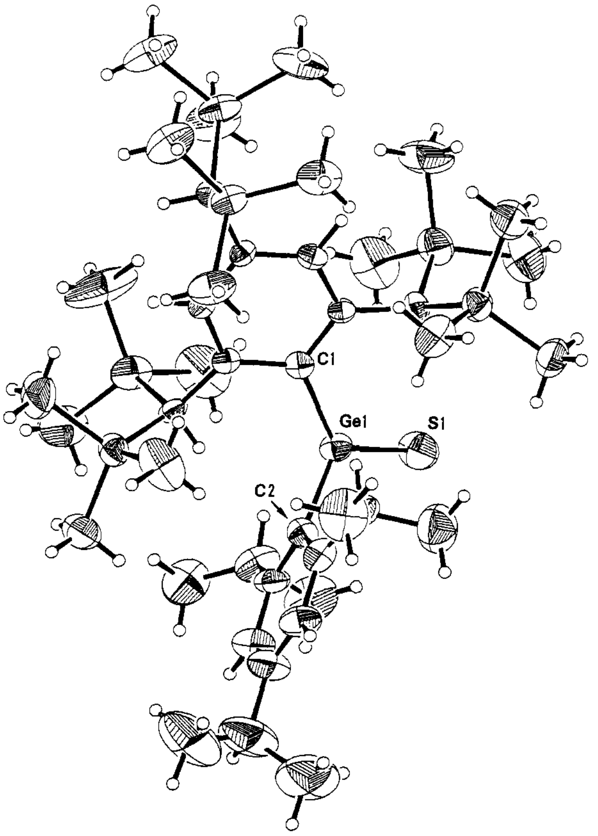
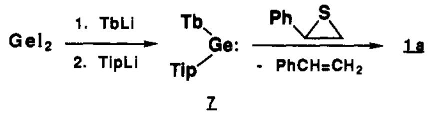


Figure 1. ORTEP drawing of Tb(Tip)Ge=S (**1a**) with thermal ellipsoid plot (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Ge(1)–S(1) 2.049(3), Ge(1)–C(1) 1.953(9), Ge(1)–C(2) 1.91(1), S(1)–Ge(1)–C(1) 124.8(3), S(1)–Ge(1)–C(2) 116.2(3), C(1)–Ge(1)–C(2) 118.4(4).

The germathiocarbonyl unit in **1a**, however, has a high chemical reactivity toward water. Exposure of **1a** to the open air resulted in an instantaneous and quantitative formation of the hydroxymercaptogermane **3**.[13] Furthermore, **1a** underwent ready cycloaddition reactions with 2,3-dimethyl-1,3-butadiene, mesitonitrile oxide, and phenyl isothiocyanate to give the corresponding cycloadducts **4**, **5**, and **6** in 84, 99, and 84% yields, respectively (Scheme I).[13] These cycloaddition reactions are of great importance from the viewpoint of elucidating the intrinsic nature of a germanium-sulfur double bond. Especially striking is the [2 + 4] cycloaddition reaction with 2,3-dimethyl-1,3-butadiene, which represents the first example of a [2 + 4] cycloaddition reaction of germanium-sulfur double-bond compounds and demonstrates that the germanethione has a considerable extent of ene character like its carbon analogues, such as thioketones and thioaldehydes.[14]

Scheme II



We have also examined an alternative synthetic route for germanethione **1a** starting from the corresponding sterically protected diarylgermylene Tb(Tip)Ge: (**7**), derived from diiodogermylene and bulky aryllithiums (TbLi and TipLi).[15] Treatment of a dark red hexane solution of **7** with styrene episulfide afforded an orange solution of **1a**, the electronic spectrum of which was identical with that of **1a** prepared by the desulfurization of **2a**, and **1a** thus obtained was also trapped with phenyl isothiocyanate to give **6** (31% yield based on GeI_2) (Scheme II).

Since less hindered diarylgermanethione Tb(Mes)Ge=S (**1b**) (Mes = mesityl) generated by desulfurization of the corresponding tetrathiagermolane Tb(Mes)GeS_4 (**2b**) under the reaction conditions similar to those for the synthesis of **1a** underwent a ready head-to-tail dimerization to give the corresponding *cis*-substituted 1,3,2,4-dithiadigermetane[16] exclusively (95%), even in the presence of a trapping reagent such as dimethylbutadiene or phenyl isothiocyanate, the outstanding stability of the germanethione **1a** is obviously due to the steric demand of the combination of Tb and Tip groups.

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Supplementary Material Available: Spectral and analytical data of **3**–**6** and X-ray crystallographic data for **1a** (42 pages). Ordering information is given on any current masthead page.

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(13) Physical properties of the reaction products **3**, **4**, **5**, and **6** are described in the supplementary material.

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(16) For the stereospecific [2 + 2] cycloaddition of germanethione **1b** and the crystallographic structure analysis of the resulting 1,3,2,4-dithiadigermetane, see: Tokitoh, N.; Matsumoto, T.; Ichida, H.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6877.