A NOVEL REACTION OF AN OVERCROWDED GERMYLENE WITH ISOTHIOCYANATE LEADING TO THE FORMATION OF 4-IMINO-1,3,2-DITHIAGERMETANE RING SYSTEM[1]

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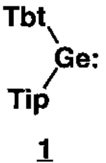
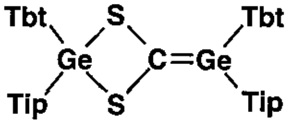
Abstract- A diarylgermylene [Tbt(Tip)Ge:] kinetically stabilized by 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip) groups was allowed to react with phenyl isothiocyanate to afford a germanium-containing four-membered heterocycle, 4-imino-1,3,2-dithiagermetane derivative *via* [2+2]-cycloaddition reaction of initially formed diarylgermanethione [Tbt(Tip)Ge=S], the intermediacy of which was evidenced by electronic spetroscopy.

Germylenes, i. e. divalent germanium species, are among a most fascinating class of reactive organogermanium compounds, and their high reactivity toward unsaturated bonds enables us to synthesize a variety of germanium-containing novel cyclic systems.[2] For example, Ando *et al.* reported the synthesis of the first 3-alkylidene-1,2-thiagermirane derivative by [1+2] cycloaddition reaction of dimesitylgermylene generated by thermolysis of hexamesitylcyclotrigermane with di-*t*-butylthioketene.[3] Although they also described the reactions of less hindered germylenes such as dimethyl- and diphenylgermylenes with di-*t*-butylthioketene leading to the formation of the corresponding 4-alkylidene-1,2,3-thiadigermetane derivatives,[3] there has been no description for cycloaddition of germylenes with other heterocumulenes. Meanwhile, we have already developed new and effective methods for the generation of an extremely hindered diarylgermylene, Tbt(Tip)Ge: (**1**),[4] bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip) groups on the germanium atom, and quite recently we reported the reaction of germylene (**1**) with carbon disulfide which resulted in the first isolation of a novel germaketene-dithioacetal derivative (**2**).[5] Here, we present the reaction of the overcrowded germylene (**1**) with another heterocumulene, i. e. phenyl isothiocyanate, which provides a novel approach to germanium-containing heterocyclic systems.

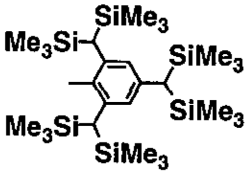


1



2

Tbt=



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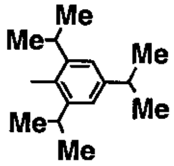
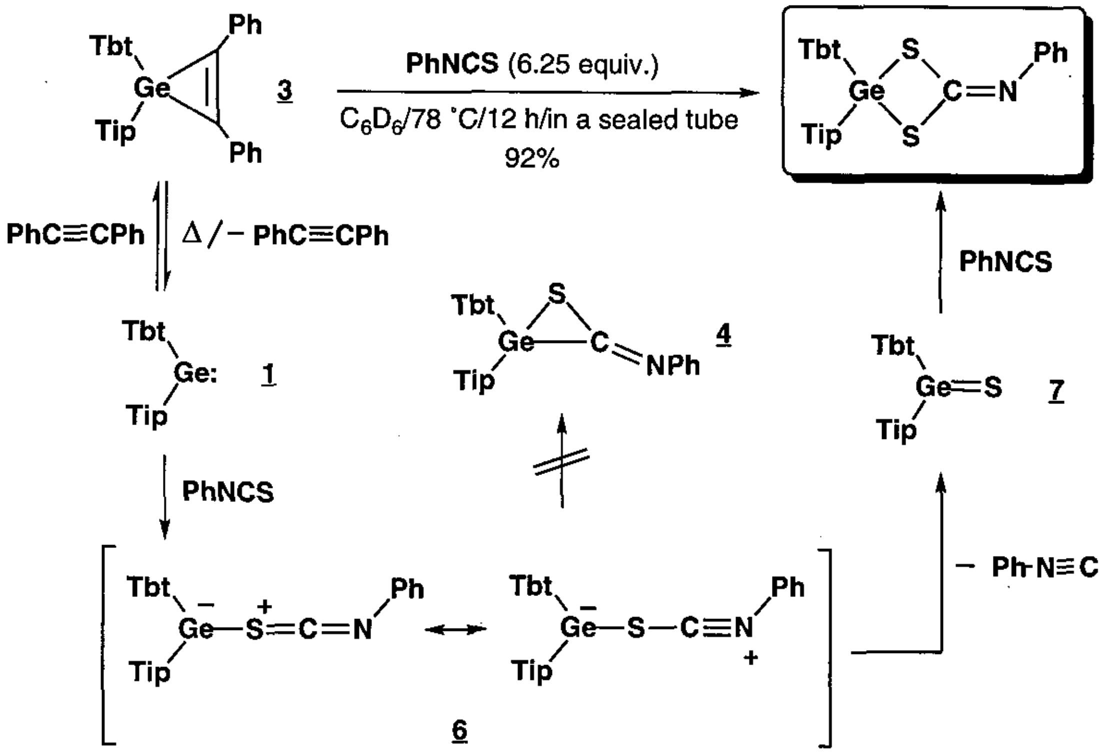
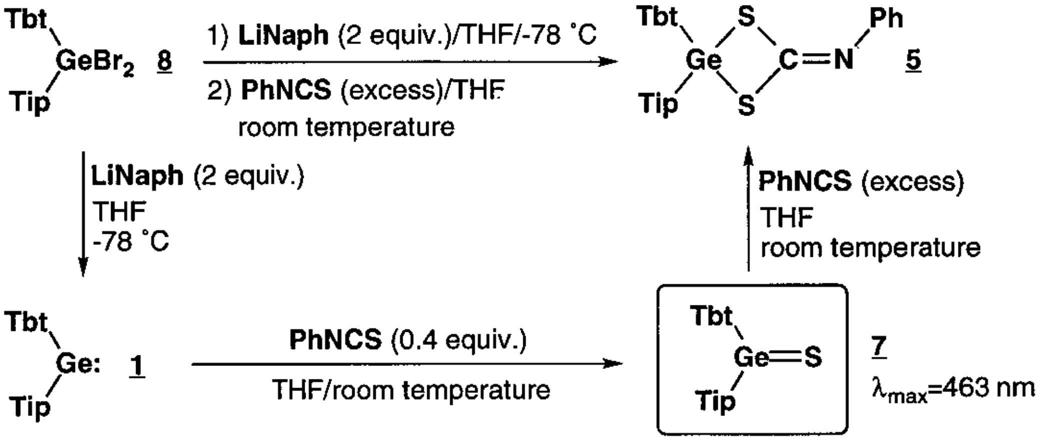


The reaction of 2,3-diphenylgermirene (**3**)(31.8 mg, 0.048 mmol) bearing Tbt and Tip groups on the germanium atom, a good precursor of diarylgermylene (**1**) under neutral conditions,[4c] with an excess amount (0.03 ml, 0.3 mmol, 6.25 equiv.) of phenyl isothiocyanate in benzene at 80 °C for 12 h, did not give the expected [1+2] cycloadduct of **1** with phenyl isothiocyanate, 3-imino-1,2-thiagermirane derivative (**4**), but the four-membered ring system with two sulfur atoms in the skeleton, i. e. 4-imino-1,3,2-dithiagermetane derivative (**5**),[6] as stable colorless crystals in 92% yield (28.9 mg) (Scheme 1).



Scheme 1

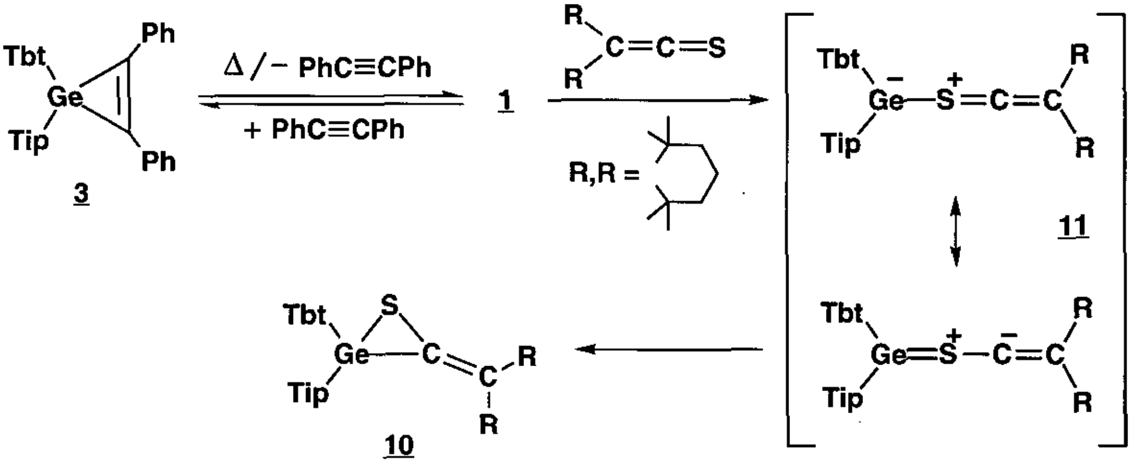
The exclusive formation of **5** is most likely interpreted in terms of the initial addition of germylene (**1**) derived from **3** to phenyl isothiocyanate to give the ylide-type intermediate (**6**) or its valence isomer (**4**) followed by the extrusion of phenyl isocyanide leading to the formation of the germanethione (**7**), which then undergoes [2+2] cycloaddition reaction with excess phenyl isothiocyanate to afford the final product (**5**) (Scheme 1). We have already described the desulfurization of overcrowded tetrathiagermolane Tbt(Tip)GeS_4 with triphenylphosphine leading to the isolation of the first stable germanethione (**7**) with a characteristic absorption maximum in the electronic spectra [λ_{max}(hexane) = 450 nm, λ_{max}(THF) = 463 nm] and its reaction with phenyl isothiocyanate to give **5**.[6] Since the thermal generation reaction of germylene (**1**) together with diphenylacetylene from **3** is a reversible system with the equilibrium being favorable for the starting **3**,[4c] in the above reaction system phenyl isothiocyanate always exists in excess to the intermediary germanethione (**7**) even in the reaction with equimolar amount of phenyl isothiocyanate. Hence, the spectroscopic detection of **7** should be very difficult due to its high reactivity toward [2+2]cycloaddition with the isothiocyanate under the reaction conditions used.



Scheme 2

On the other hand, we previously reported an alternative generation method for germylene (**1**), the blue solution of which was found to be stable at room temperature, by reductive debromination of the corresponding dibromogermane, Tbt(Tip)$GeBr_2$ (**8**), with lithium naphthalenide in THF.[4a,b] Treatment of germylene (**1**) thus generated with an excess amount (15 equiv.) of phenyl isothiocyanate in THF at room temperature also afforded the 4-imino-1,3,2-dithiagermetane (**5**) in 64% isolated yield, suggesting the same reaction mode as was observed for the germylene derived from **3** (Scheme 2). With these results in mind, we next examined the reaction of germylene (**1**) derived from **8** with less than equimolar amount of phenyl isothiocyanate. When 0.4 equivalent molar amount of phenyl isothiocyanate was added to the blue THF solution of **1** at room temperature, the reaction mixture turned orange and the electronic spectra of an aliquot of this reaction solution showed an absorption maxima at 465 nm identical with that of the isolated germanethione (**7**) in THF (Scheme 2). Furthermore, the orange color of this solution disappeared on addition of excess amount of phenyl isothiocyanate.

By contrast, treatment of germylene (**1**) with bulky thioketene (**9**) afforded the corresponding [1+2] cycloadduct, 3-alkylidene-1,2-thiagermirane derivative (**10**),[7] as stable colorless crystals in 65% yield (Scheme 3). The difference between the reactivity of **1** with isothiocyanate and that with thioketene probably arises from the high leaving ability of the isocyanide from the initially formed intermediate (**6**). In the case of the thioketene, intramolecular cyclization of the initially formed germathiocarbonyl ylide (**11**) leading to **10** is expected to be more favorable than dissociation of **11** into germanethione (**7**) and the corresponding alkylidenecarbene R_2C=C: of high energy.



Scheme 3

Finally, we have succeeded in the X-Ray crystallographic analysis of **5** which confirms the regiochemistry of the [2+2] cycloaddition of germanethione (**7**) with phenyl isothiocyanate and provides us with the first example of structural parameters for this germanium-containing heterocyclic system, 4-imino-1,3,2-dithiagermetane.[8] In Figure 1 is shown the ORTEP drawing of **5** together with its intramolecular structural parameters. The central dithiagermetane ring of **5** was found to be planar, the sum of the interior angles being 359.7 °. The sum of the angles around C13 (360 °) clearly showed the completely trigonal planar geometry of the phenylimino group on 4-position of **5**. Furthermore, the geometry of the central 1,3,2-dithiagermetane ring of **5** here revealed is very similar to that of the 1,3,2-dithiagermetane skeleton of germaketenedithioacetal (**2**)[5] though their exo-substituents on 4-positions are quite different.

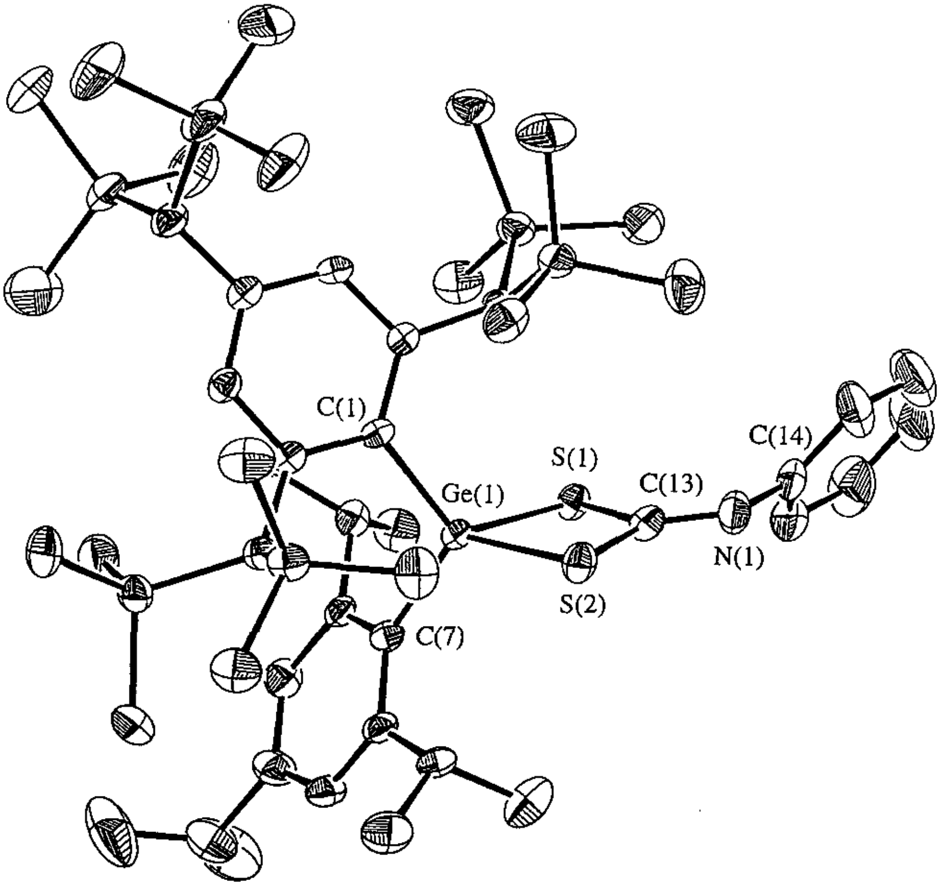


Figure 1. ORTEP drawing of **5** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg); Ge(1)-S(1) 2.271(1), Ge(1)-S(2) 2.266(2), Ge(1)-C(1) 1.980(4), Ge(1)-C(7) 1.961(5), S(1)-C(13) 1.780(5), S(2)-C(13) 1.770(5), C(13)-N(1) 1.269(6), N(1)-C(14) 1.420(7), C(1)-Ge(1)-C(7) 113.6(2), S(1)-Ge(1)-S(2) 79.85(5), Ge(1)-S(1)-C(13) 84.6(2), Ge(1)-S(2)-C(13) 85.0(2), S(1)-C(13)-N(1) 130.1(4), S(2)-C(13)-N(1) 119.7(4), C(13)-N(1)-C(14) 122.3(5).

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   5; white crystals, mp 150-153 °C (decomp.), ^{1}H nmr ($CDCl_3$, 500 MHz, 300 K) δ -0.05 (s, 9H), -0.03 (s, 9H), 0.03 (s, 9H), 0.05 (s, 9H), 0.09 (s, 18H), 1.16 (br s, 3H), 1.20 (br s, 6H), 1.22 (d, J = 6.9 Hz, 6H), 1.32 (br s, 3H), 1.33 (s, 1H), 2.43 (br s, 1H), 2.87 (sept, J = 6.9 Hz, 1H), 3.08 (br s, 3H), 6.33 (s, 1H), 6.51 (s, 1H), 6.92 (s, 1H), 6.93 (s, 1H), 7.04-7.29 (m, 5H); ^{13}C nmr ($CDCl_3$, 125 MHz, 300 K) δ 0.90 (q), 1.58 (q), 1.62 (q), 1.72 (q), 23.12 (br q), 23.85 (q), 28.18 (d), 28.24 (d), 30.82 (d), 34.35 (d), 35.73 (d), 35.85 (d), 121.20 (d), 122.96 (d), 123.81 (d), 124.13 (d), 128.80 (d), 129.03 (d), 129.60 (s), 137.36 (s), 146.16 (s), 149.03 (s), 151.12 (s), 151.68 (s), 151.91 (s), 153.16 (s). Anal. Found: C, 58.64; H, 8.51; N, 1.46; S, 6.39. Calcd for $C_{49}H_{87}NGeS_2Si_6 \cdot 0.5H_2O$ C, 58.59; H, 8.83; N, 1.39; S, 6.38.
7. The assignment of the ^{1}H and ^{13}C nmr spectra of **10** failed due to the severe peak overlapping and broadening of signals resulting from the extremely large steric congestion caused by the bulky substituents, although compound (**10**) was isolated as pure white crystals [mp 148-152 °C (decomp.)] and showed a satisfactory analytical data. High resolution FAB-ms spectra for **10**: obsd m/z 1010.5317, calcd for $C_{53}H_{100}GeSSi_6$ 1010.5373.
8. Crystal data for **5**. $C_{49}H_{87}GeNS_2Si_6$ M = 995.46, monoclinic, space group $P2_1/c$, a = 13.590(4), b = 9.987(3), c = 44.077(2) Å, β = 93.22(1) °, V = 5973(2) Å^3, Z = 4, ρ_{calcd} = 1.017 g cm^{-3}, μ = 7.19 cm^{-1}, $R(R_w)$ = 0.055 (0.065). The intensity data were collected on a Rigaku AFC5R diffractometer with Mo Kα radiation (λ = 0.71069 Å, graphite monochromater), and the structure was solved by direct methods with *SHELXS-86*.[9] All non-hydrogen atoms were refined anisotropically. The final

cycle of full-matrix least-squares refinement was based on 7339 observed reflections [$I > 3.00\sigma(I)$] and 532 variable parameters. Atomic coordinates, thermal parameters, and the complete tables of bond lengths and angles of **5** have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK).

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