Synthesis and Reactions of the First Stable 1-Germaallene†

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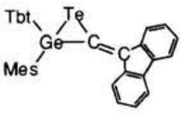
The first stable 1-germaallene was synthesized by treatment of an extremely hindered alkylidenetelluragermirane with a large excess amount of hexamethylphosphorous triamide or by reductive dechlorination of the corresponding overcrowded (1-chlorovinyl)chlorogermane with *t*-butyllithium in THF. The germaallene was isolated as a colorless solid by the latter synthetic method and found to be fairly stable even in solution at room temperature, although it underwent an intramolecular cyclization at 80 °C in benzene.

In recent decades, much attention has been paid to the chemistry of low-coordinate compounds containing heavier group 14 elements because of its unique structure and reactivities, and a number of stable examples have been reported for the doubly bonded species of this class, such as silenes (Si=C), disilenes (Si=Si), germenes (Ge=C), and digermenes (Ge=Ge).[1] We have also reported the synthesis of a series of stable double-bond compounds between heavier group 14 and group 16 elements Tbt(R)M=X (M = Si, Ge, Sn; X = S, Se, Te),[2] *i. e.* the heavier congeners of a ketone, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), developed in our group.[3] By contrast, as for the cumulative doubly bonded compounds containing heavier group 14 elements several stable 1-silaallenes (Si=C=C) were recently synthesized and characterized by X-ray analysis,[4] but there have been no reports on the synthesis of 1-germaallene (Ge=C=C),[5] a novel class of germanium–carbon double-bond compounds.



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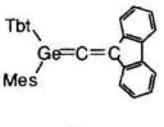

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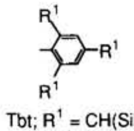
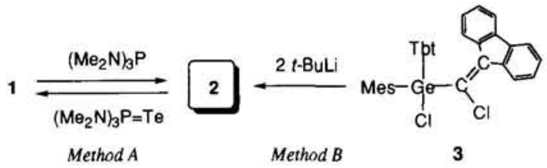


Tbt; R^1 = $CH(SiMe_3)_2$
Mes; R^1 = Me

Meanwhile, we have recently reported the synthesis and X-ray crystallographic analysis of the stable alkylidenetelluragermirane **1** bearing Tbt and mesityl (Mes) groups on the germanium atom.[6] Here, we wish to present the synthesis of the first kinetically stabilized 1-germaallene **2** via the following two independent synthetic routes, *i. e.* the detelluration of telluragermirane **1** with trivalent phosphorus reagent (Method A) and the reductive dechlorination of (1-chlorovinyl)chlorogermane **3**[7] with *t*-butyllithium (Method B).

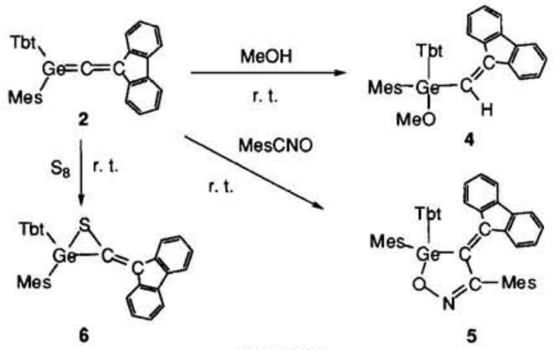
When a large excess amount (50 equiv.) of hexamethylphosphorous triamide (HMPT) was added to a C_6D_6 solution of telluragermirane **1** at room temperature, the exclusive formation of 1-germaallene **2** was observed by ^1H and ^{13}C NMR; the ^{13}C NMR spectra showed a quaternary carbon signal at very low field (δ_C 243.5) which is characteristic of an allenic carbon. Similar low-field shifts have already been reported for the allenic carbon of the first examples of stable 1-silaallene (δ_C 226)[4a] and germaphosphaallene $Mes_2Ge=C=PMes^*$ (δ_C 281; Mes* = 2,4,6-tri-*t*-butylphenyl).[8] The formation of **2** in high yield was confirmed by the trapping experiment with excess methanol leading to the isolation of the corresponding 1,2-addition product, methoxy(vinyl)germane **4** in 72% yield. Interestingly, in detelluration of **1** the ratio of 1-germaallene **2** produced to the starting telluragermirane **1** depends on the amount of the phosphine reagent used. For instance, treatment of **1** with 50 equiv. of HMPT resulted in the exclusive formation of **2**, while the use of 10 equiv. of HMPT gave the mixture of **1** and **2** (**1**/**2** ratio is 1/2 as judged by ^1H NMR). Furthermore, the reaction of **1** with 1.2 equiv. of HMPT afforded a 7/2 mixture of **1** and **2**. These results suggest that there is an equilibrium between [**1** + $(Me_2N)_3P$] and [**2** + $(Me_2N)_3P=Te$] and the rate of interconversion among them is slow enough on the NMR time scale for each species to be observed at room temperature by ^1H NMR.



Scheme 1.

Although we have succeeded in the synthesis of 1-germaallene **2** as a stable compound in solution at room temperature by Method A, it is difficult to isolate **2** by this method because of the re-telluration of **2** with the co-existing phosphine telluride via an equilibration. Therefore, we next examined the reductive dechlorination of (1-chlorovinyl)chlorogermane **3** with *t*-butyllithium (2.2 equiv.) in THF at -72 °C in the hope of isolating **2**. The removal of volatile materials under reduced pressure followed by solvent exchange to hexane, filtration of insoluble inorganic materials, and slow evaporation in a glovebox filled with argon gave the crude sample of expected 1-germaallene **2**. Although single crystals of **2** suitable for X-ray crystallographic analysis have not been obtained yet unfortunately, **2** was isolated as a colorless solid by slow evaporation of its saturated hexane solution at -35 °C. The C_6D_6 solution of **2** thus obtained showed satisfactory ^1H and ^{13}C NMR spectra[9] which were essentially identical with those of **2** synthesized by Method A; the central allenic carbon of **2** was again observed at the characteristic low-field (δ_C 243.6).

The structure of 1-germaallene **2** was also proved by its chemical reactivity (Scheme 2). On treatment of **2** obtained by Method B with methanol (ca. 6 equiv.) and mesitonitrile oxide (4.5 equiv.), the corresponding addition products, methoxy(vinyl)germane **4** and 4-alkylidene-1,2,5-oxazagermolene **5**, were isolated in 67 and 61% yields, respectively.[10] 1-Germaallene **2** also reacted with elemental sulfur to afford the corresponding [1+2]cycloadduct, alkylidenethiagermirane **6**[6] in 22% yield.



Scheme 2.

Although compound **5** showed satisfactory spectral and analytical data, the molecular geometry of this new ring system was finally determined by its X-ray crystallographic analysis as shown in Figure 1.[11]

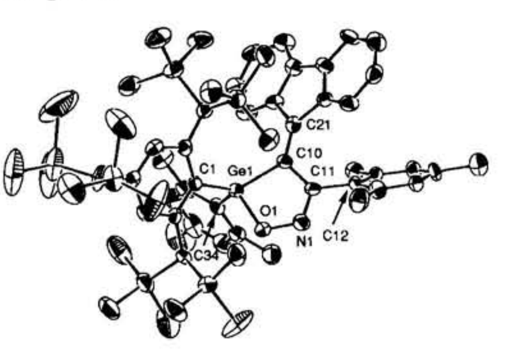
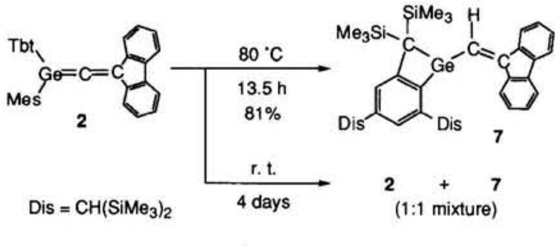


Figure 1. ORTEP drawing of **5** with thermal ellipsoid plot (30% probability). The solvent (CH_2Cl_2) was omitted for clarity. Selected bond lengths (Å) and angles (deg); Ge1-O1 1.85(1), Ge1-C10 1.99(2), O1-N1 1.39(2), N1-C11 1.29(2), C10-C11 1.48(2), C10-C21 1.36(2), O1-Ge1-C10 87.1(6), Ge1-C10-C21 132(1), C11-C10-C21 124(1), C10-C11-N1 119(1), C11-N1-O1 112.1(9), C1-Ge1-C34 109.3(4).

In the absence of a trapping reagent, 1-germaallene **2** was found to undergo a slow intramolecular cyclization to give the corresponding benzogermacyclobutene derivative **7**. The rate of isomerization of **2** into **7** was relatively slow at room temperature (the ratio of **2**/**7** reached 1/1 after 4 days), while the isomerization was completed after heating of the C_6D_6 solution of **2** at 80 °C for 13.5 h giving **7** in 81% yield (Scheme 3).[11]



Scheme 3.

Further investigation on physical and chemical properties of the newly obtained 1-germaallene **2** is currently in progress.

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References and Notes

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1 F. G. A. Stone and R. West, Eds., *Adv. Organomet. Chem.*, **39**, 71, 232, and 275 (1996).

2 a) N. Tokitoh, T. Matsumoto, K. Manmaru, and R. Okazaki, *J. Am. Chem. Soc.*, **115**, 8855 (1993). b) T. Matsumoto, N. Tokitoh, and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **33**, 2316 (1994). c) H. Suzuki, N. Tokitoh, S. Nagase, and R. Okazaki, *J. Am. Chem. Soc.*, **116**, 11578 (1994). d) N. Tokitoh, T. Matsumoto, and R. Okazaki, *Chem. Lett.*, **1995**, 1087. e) M. Saito, N. Tokitoh, and R. Okazaki, *Organometallics*, **15**, 4531 (1996). f) N. Kano, N. Tokitoh, and R. Okazaki, *Chem. Lett.*, **1997**, 277. g) N. Tokitoh, T. Matsumoto, and R. Okazaki, *J. Am. Chem. Soc.*, **119**, 2337 (1997). h) M. Saito, N. Tokitoh, and R. Okazaki, *J. Am. Chem. Soc.*, **119**, 11124 (1997), and references cited therein.

3 R. Okazaki, N. Tokitoh, and T. Matsumoto, in "Synthetic Methods of Organometallic and Inorganic Chemistry", ed by N. Auner and U. Klingebiel, Thieme, New York, (1996) Vol. 2, pp. 260-269.

4 a) G. E. Miracle, J. L. Ball, D. R. Powell, and R. West, *J. Am. Chem. Soc.*, **115**, 11598 (1993). b) M. Trommer, G. E. Miracle, E. Eichler, D. R. Powell, and R. West, *Organometallics*, **16**, 5737 (1997).

5 Quite recently, another type of stable 1-germaallene has been synthesized and characterized by R. West et al. R. West, private communication.

6 K. Kishikawa, N. Tokitoh, and R. Okazaki, *Organometallics*, **16**, 5127 (1997).

7 Compound **3** was prepared by the reaction of the germylene Tbt(Mes)Ge: with 9-(dichloromethylene)fluorene. See, ref. 7.

8 H. Ramdane, H. Ranaivonjatovo, and J. Escudié, *Organometallics*. **15**, 3070 (1996).

9 **2**: ^1H NMR (500 MHz, C_6D_6, 300 K) δ 0.18 (s, 18H), 0.21 (s, 36H), 1.54 (s, 1H), 2.08 (s, 3H), 2.69 (s, 1H), 2.73 (s, 6H), 2.76 (s, 1H), 6.68 (s, 1H), 6.74 (s, 2H), 6.78 (s, 1H), 7.26 (t, J=7.4 Hz, 2H), 7.34 (t, J=7.4 Hz, 2H), 7.61 (d, J=7.4 Hz, 2H), 8.13 (d, J=7.4 Hz, 2H); ^{13}C NMR (126 MHz, C_6D_6, 300 K) δ 0.94 (q), 1.07 (q), 1.30 (q), 20.95 (q), 27.30 (q), 31.07 (d), 31.90 (d), 32.24 (d), 120.26 (d), 122.85 (d), 123.32 (d), 127.29 (d), 127.89 (d), 128.65 (d), 128.86 (d), 131.61 (s), 136.00 (s), 136.69 (s), 138.46 (s), 139.66 (s), 140.41 (s), 142.34 (s), 145.47 (s), 150.79 (s), 243.56 (s). At this stage, we are not able to assign one quaternary carbon for compound **2** probably due to the inevitable overlapping with the solvent peak (C_6D_6).

10 Newly obtained reaction products **4**, **5**, and **7** showed satisfactory spectral and analytical data.

11 The crystal data of **5**•$0.5CH_2Cl_2$ are as follows; **5**•$0.5CH_2Cl_2$: $C_{60.5}H_{90}ClGeNOSi_6$, M = 1124.44, a = 14.380(4), b = 13.570(6), c = 35.836(3) Å, β = 99.04(1)°, V = 6906(3) $Å^3$, monoclinic, space group $P2_1/c$, Z = 4, D_c = 1.081 gcm^{-3}, final R = 0.074, R_w = 0.090 for 3102 [$I > 4\sigma(I)$] observed reflections and 646 variable parameters. Although the structure of **5**•$0.5CH_2Cl_2$ was solved with a partial disorder concerning one of the chlorine atom of solvent molecule (CH_2Cl_2) and a part of the trimethylsilyl group in the *p*-substituent of the Tbt group, the disordered atoms were omitted in Figure 1 for clarity. Full details will be described elsewhere.