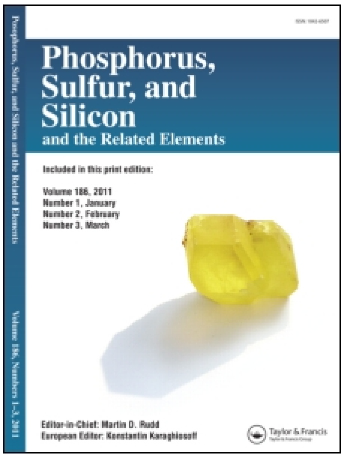

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Tokitoh, Norihiro , Kishikawa, Kuniyuki and Okazaki, Renji(1999) 'Synthesis and Reactions of a 1-Germaallene Kinetically Stabilized by 2,4,6-Tris[Bis(Trimethylsilyl)Methyl]Phenyl Group', Phosphorus, Sulfur, and Silicon and the Related Elements, 150: 1, 137 — 143

To link to this Article: DOI: 10.1080/10426509908546378

URL: http://dx.doi.org/10.1080/10426509908546378

Phosphorus, Sulfur and Silicon, 1999, Vol. 150-151, pp. 137-143
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Printed in Malaysia

Synthesis and Reactions of a 1-Germaallene Kinetically Stabilized by 2,4,6-Tris[Bis(Trimethylsilyl)Methyl]Phenyl Group

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Treatment of an extremely hindered alkylidenetelluragermirane with a large excess amount of hexamethylphosphorous triamide resulted in the formation of the first stable l-germaallene, which was also synthesized 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.

Keywords: alkylidenetelluragermirane; 1-germaallene; reductive dechlorination; (1-chlorovinyl)chlorogermane; steric protection

INTRODUCTION

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

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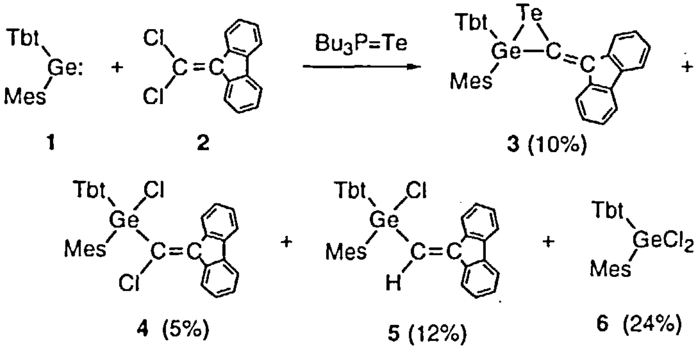
a series of stable double-bond compounds between heavier group 14 and group 16 elements Tbt(R)M=X (M = Si, Ge, Sn; X = S, Se, Te),[2] *i. e.* the heavier congeners of a ketone, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (denoted as Tbt hereafter), 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.

RESULTS AND DISCUSSION

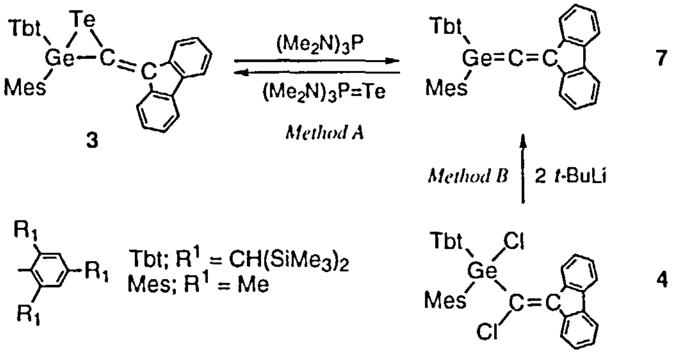
We have recently succeeded in the synthesis of a stable alkylidenetelluragermirane 3 (Mes = mesityl) by the reaction of an overcrowded diarylgermylene 1 and 9-(dichloromethylene)foluorene 2 in the presence of tributylphosphine telluride and revealed the unique molecular structure of 3 by X-ray crystallographic analysis.[6]



Scheme 1.

In this reaction, the alkilidenetelluragermirane **3** was obtained as one of the minor products together with the other non-tellurated products **4–6** as shown in Scheme 1.

Here, we wish to present the synthesis of the first kinetically stabilized 1-germaallene **7** via the following two independent synthetic routes, *i. e.* the detelluration of telluragermirane **3** with trivalent phosphorus reagent (*Method A*) and the reductive dechlorination of (1-chlorovinyl)chlorogermane **4** with *t*-butyllithium (*Method B*) as shown in Scheme 2.[7]

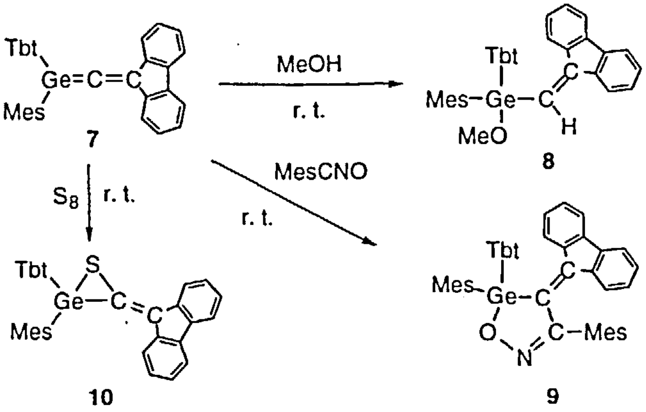


Scheme 2.

When a large excess amount (50 equiv.) of hexamethylphosphorous triamide (HMPT) was added to a C_6D_6 solution of telluragermirane **3** at room temperature, the exclusive formation of 1-germaallene **7** 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 **7** 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 **8** in 72% yield. Interestingly, in detelluration of **3** the ratio of 1-germaallene **7** produced to the starting telluragermirane **3** depends on the amount of the phosphine reagent used. For instance, treatment of **3** with 50 equiv. of HMPT resulted in the exclusive formation of **7**, while the use of 10 equiv. of HMPT gave the mixture of **3** and **7** (**3**/**7** ratio is 1/2 as judged by ^{1}H NMR). Furthermore, the reaction of **1** with 1.2 equiv. of HMPT afforded a 7/2 mixture of **3** and **7**. These results suggest that there is an equilibrium between [**3** + $(Me_2N)_3P$] and [**7** + $(Me_2N)_3P{=}Te$] 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 ^{1}H NMR.

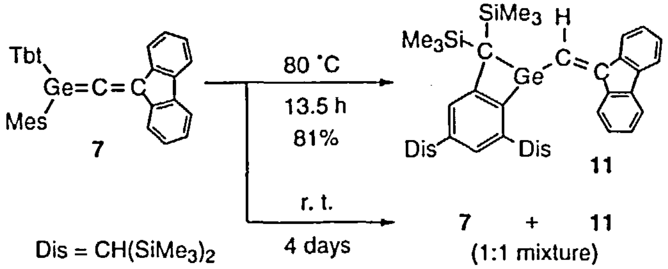
Although we have succeeded in the synthesis of 1-germaallene **7** as a stable compound in solution at room temperature by *Method A*, it is difficult to isolate **7** by this method because of the re-telluration of **7** with the co-existing phosphine telluride via an equilibration. Therefore, we next examined the reductive dechlorination of (1-chlorovinyl)chlorogermane **4** with *t*-butyllithium (2.2 equiv.) in THF at -72 °C (*Method B*)in the hope of isolating **7**. 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 **7**. Although single crystals of **7** suitable for X-ray crystallographic analysis have not been obtained yet unfortunately, **7** was isolated as a colorless solid by slow evaporation of its saturated hexane solution at -35 °C. The C_6D_6 solution of **7** thus obtained showed satisfactory ^{1}H and ^{13}C NMR spectra[9] which were essentially identical with those of **7** synthesized by *Method A*; the central allenic carbon of **7** was again observed at the characteristic low-field (δ_C 243.6).

The structure of 1-germaallene **7** was also proved by its chemical reactivity (Scheme 3). On treatment of **7** obtained by *Method B* with methanol (ca. 6 equiv.) and mesitonitrile oxide (4.5 equiv.), the corresponding addition products, methoxy(vinyl)germane **8** and 4-alkylidene-1,2,5-oxazagermolene **9**, were isolated in 67 and 61% yields, respectively. 1-Germaallene **7** also reacted with elemental sulfur to afford the corresponding [1+2]cycloadduct, alkylidenethiagermirane **10**[6] in 22% yield. Although compound **10** showed satisfactory spectral and analytical data, the molecular geometry of this new ring system was finally determined by its X-ray crystallographic analysis.



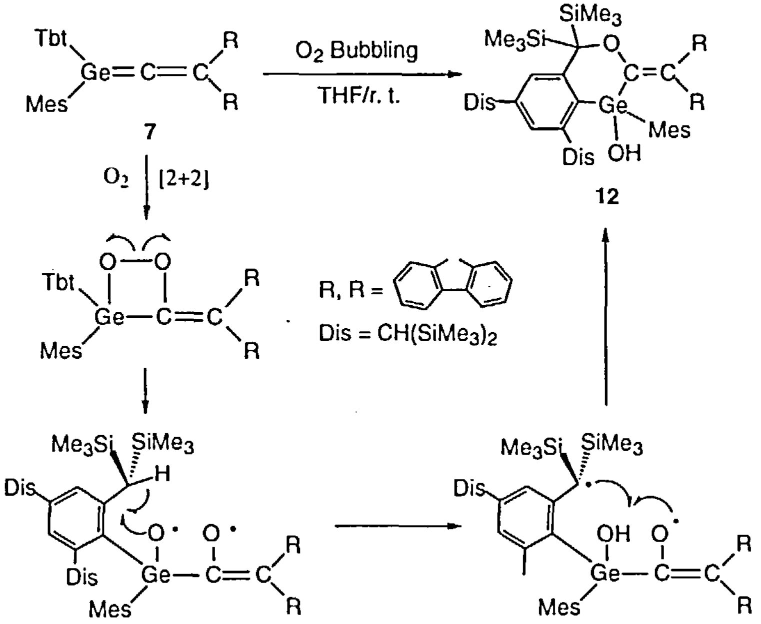
Scheme 3.

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



Scheme 4.

When oxygen gas was bubbled into a THF solution of 1-germaallene **7** prepared from **4** by *Method B*, an interesting oxidation product **12** was obtained as a major product (36% from **4**).



Scheme 5.

The formation of **12** in the oxidation of **7** is most likely interpreted in terms of the initial [2+2]cycloaddition of molecular oxygen with **7** followed by the cleavage of the 1,2-dioxetane ring and further intramolecular cyclization of the resulting biradical species as shown in Scheme 5.

Further investigation on physical and chemical properties of the newly obtained 1-germaallene **7** is currently in progress.

ACKNOWLEDGMENTS This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10874107) from the Ministry of Education, Science, Sports, and Culture of Japan. We are also grateful to Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gift of chlorosilanes and alkyllithiums, respectively.

References

[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, West *et al.* reported the synthesis and structure of stable 1-germaallenes independently. See, B. E. Eichler, D. R. Powell, and R. West, *Organometallics*, **17**, 2147 (1998).

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

[7] K. Kishikawa, N. Tokitoh, and R. Okazaki, *Chem. Lett.*, **1998**, 239.

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

[9] **7**: ^{1}H 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 **7** probably due to the inevitable overlapping with the solvent peak (C_6D_6).