

A Novel Synthesis of a Germene and of a 1,2-Digermacyclobutane via a Peterson-type Reaction

Dmitry Bravo-Zhivotovskii, Ilya Zharov, Moshe Kapon and Yitzhak Apeloig*

Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

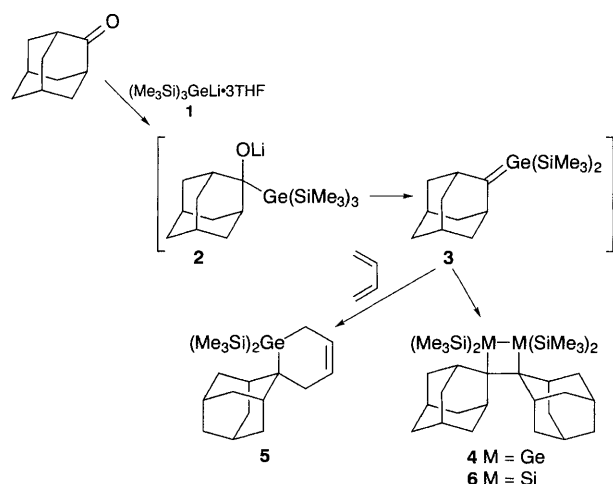
Reaction of $(\text{Me}_3\text{Si})_3\text{GeLi}\cdot 3\text{THF}$ with adamantanone in hexane at -78°C leads via a Peterson-type elimination to bis(trimethylsilyl)adamantylidene germene, which spontaneously dimerizes in a head-to-head fashion to yield 1,1,2,2-tetrakis(trimethylsilyl)-dispiro[3,3',4,4'-biadamantane-1,2-digermacyclobutane] the X-ray structure of which is reported, or which could be trapped by buta-1,3-diene to give the Diels-Alder product.

Exciting progress has been made in the chemistry of Group 14 elements (Si, Ge, Sn) in the past two decades. In particular, several stable compounds with multiple bonds to these elements have been synthesized, isolated and characterized.^{1,2} Germenes, compounds containing a C=Ge double bond,¹ are the focus of this report. The first 'indefinitely' stable germenes were synthesized independently in 1987 by Bernt *et al.* via a coupling reaction between a stable germylene and a carbene,³ and by Satgé *et al.* via elimination of LiF from a lithiated fluorogermene.⁴ Other methods have been used to generate transient germenes.¹ Yet, in spite of these developments, the range of methods available for synthesizing germenes is limited, allowing access to only specific patterns of substitution at the C=Ge bond. Furthermore, not all methods used for synthesizing silenes are also suitable for preparing their higher congeners, the germenes.¹ For example, photolysis of adamantoyl tris(trimethylsilyl)germane does not produce the expected germene,⁵ in contrast to the analogous photolysis of the corresponding silane which yielded a stable silene.⁶

Here we report a novel route, using a Peterson-type reaction, for synthesizing germenes. Furthermore, these germenes have a substitution pattern which was previously unavailable, with two silyl substituents attached to germanium.

Earlier work in our group has shown that the reaction of tris(trimethylsilyl)silyllithium with 2-adamantanone in hexane or benzene yields bis(trimethylsilyl)adamantylidenesilene, which in the absence of trapping reagents gives the corresponding head-to-head dimer.^{7,8} The analogous reaction of a 1:1 ratio of tris(trimethylsilyl)germyllithium·3THF **1** with 2-adamantanone in hexane at -78°C leads after aqueous work-up to 1,2-digermacyclobutane **4** (Scheme 1).[†] In analogy to the silicon case,⁷ we assume that **4** results from the head-to-head dimerization of the germene **3**. The structure of **4** was confirmed by X-ray crystallography (see later).

Further evidence for the intermediacy of the germene **3** was provided by trapping experiments. For example, reaction of **1** with 2-adamantanone in the presence of buta-1,3-diene leads to the expected Diels-Alder product **5**. The structure of **5** was



assigned on the basis of its ^1H and ^{13}C NMR spectra. Two types of allylic protons are observed in the ^1H NMR spectrum: one doublet at δ 1.57, 1.60 (2H) and a second at δ 2.32, 2.36 (2H). As the $(\text{Me}_3\text{Si})_2\text{Ge}$ group shifts β -protons upfield, one can assume that the former doublet δ corresponds to the allylic hydrogens bonded to the germanium [*i.e.* $\text{CH}=\text{CH}-\text{CH}_2-\text{Ge}(\text{SiMe}_3)_2$], while the deshielded signal corresponds to the $\text{CH}=\text{CH}-\text{CH}_2-2\text{-Ad}$ hydrogens. The vinyl protons appear at δ 5.65 and 6.00. The ^{13}C NMR spectrum of **5** confirms the above structural assignment: δ 1.40, 1.77 (Me_3Si); 9.95 [$\text{CH}_2-\text{Ge}(\text{SiMe}_3)_2$]; 28–40 (Ad + $\text{CH}_2\text{-Ad}$); 127.60, 130.00 ($-\text{CH}=\text{CH}-$).

To our best knowledge, **3** is the first reported germene with silicon substituents on germanium, and dimer **4** is the first known 1,2-digermacyclobutane (1,3-digermacyclobutanes are known).[‡] This is also the first example of a head-to-head dimerization of a germene. For example, the transient germene $\text{Me}_2\text{Ge}=\text{C}(\text{SiMe}_3)_2$ produced only the head-to-tail dimer.⁹

Colourless crystals of **4** [mp $237\text{--}260^\circ\text{C}$ (decomp.)] were isolated from pentane at -10°C , but at room temperature they decomposed rapidly. The structure of **4** was assigned unequivocally on the basis of X-ray analysis at 200 K (Fig. 1).[§] In general, the structures of **4** and the sila-analogue **6**⁷ are very similar. The X-ray structure of **4** reveals the substantial structural consequences of its extreme steric congestion: (i) the ring C–C and C–Ge bond lengths of 1.63(1) and 2.097(7) Å, respectively, are among the longest known for such bonds (compare with 1.54 and 1.90–1.98 Å for 'regular' C–C¹⁰ and C–Ge¹¹ bonds, respectively).[¶] The Ge–Ge bond length of 2.422(2) Å is similar to that of 'regular' Ge–Ge distances;¹² (ii) the two adamantyl rings in **4** are nearly perpendicular to each other [*i.e.* the C(2)–C(1)–C(1')–C(2') dihedral angle is -91.0°]; (iii) the 1,2-digermacyclobutane ring is strongly puckered: the angle between the C(1)–Ge(1)–Ge(1') and C(1)–C(1')–Ge(1') planes is 40.7° (similar puckering of 39.6° was found in **6**). The

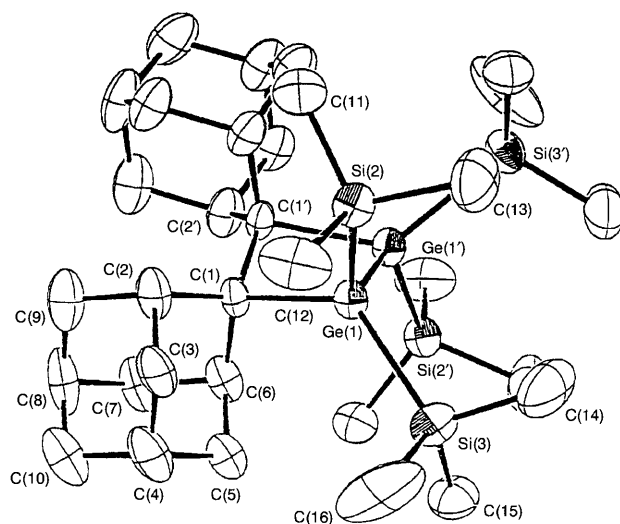
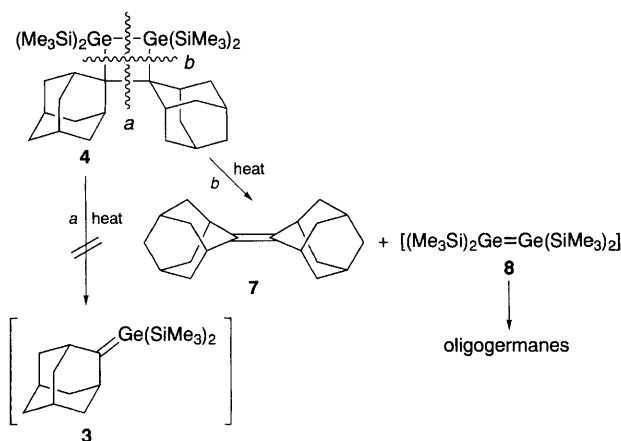


Fig. 1 ORTEP drawing of 1,1,2,2-tetrakis(trimethylsilyl)-dispiro[3,3',4,4'-biadamantane-1,2-digermacyclobutane] **4** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Scheme 2

1,2-digermacyclobutane ring is puckered also in solution at room temperature, as shown by the presence of two different trimethylsilyl groups (at δ 0.25 and 0.32) in its ^1H NMR spectrum.

While the 1,2-disilacyclobutane **6** reverts, upon heating in hexane or benzene, to the corresponding silene, this is not the case with the corresponding 1,2-digermacyclobutane **4**. Heating of **4** in benzene or hexane to 50 °C leads to the isolation of 2,2'-biadamantylidene **7** and of germanium-containing oligomers (Scheme 2). Attempts to observe trapping products of the germene **3** by heating **4** in hexane in the presence of an excess of different trapping reagents (butadienes, styrene, methanol) failed. We therefore suggest that **4** (in contrast to **6**) does not revert upon heating to the germene **3** (Scheme 2, path *a*), but instead undergoes cleavage of the C–Ge bonds to give the digermene **8** (and **7**; Scheme 2, path *b*), which polymerizes before it can be trapped. The reaction in Scheme 2 can also proceed *via* biradicals, bypassing both **3** and **8**. Further studies are in progress in order to establish the mechanism of this interesting reaction.

In conclusion, we have demonstrated that a Peterson-type germylation offers a novel route for synthesizing germenes having a unique pattern of substitution. We are currently studying the scope of this reaction, its mechanism and the nature of the generated transient germenes.

This research was partially supported by German–Israel Binational Science Foundation (GIF), by the Fund for the Promotion of Research at the Technion and by the G.-D. Erteschik Fund for Practical Research (Technion). D. B.-Z. is grateful to the Ministry of Immigrant Absorption, State of Israel, for a scholarship.

Received, 2nd November 1994; Revised manuscript received, 17th May 1995; Com. 4/06705C

Footnotes

† *Procedure*: 2.4 g (4.7 mmol) of $(\text{Me}_3\text{Si})_3\text{GeLi}\cdot 3\text{THF}$ in 20 ml of dry benzene were placed in a Schlenk flask under vacuum and 0.6 g (4.2 mmol) of adamantane in 10 ml of dry benzene were added. The reaction mixture was stirred for 2 h at room temp. saturated aq. NH_4Cl (20 ml) was added to the reaction mixture, the organic layer was separated and dried over MgSO_4 , the volatile materials were evaporated under vacuum and the crude product was washed with 2×10 ml of methanol, yielding 1.6 g (55%) of a clean white powder of **4**. Colourless crystals of **4**, decomposing at room temperature, were obtained by recrystallization from hexane at -10 °C. ^1H NMR (CDCl_3): δ 0.25 (18H, s, Me_3Si); 0.32 (18H, s, Me_3Si); 1.49–2.71 (28H, m, Ad).

‡ *Note added in proof*: A 1,2-digermacyclobutane was reported while this paper was in press; see: H. Ohgaki, Y. Kabe and W. Ando, *Organometallics*, 1995, **14**, 2139.

§ *Crystal data for 4*: $\text{C}_{32}\text{H}_{64}\text{Ge}_2\text{Si}_4$, $M_w = 706.35$, $T = 200$ K, monoclinic, $a = 9.592(4)$, $b = 20.221(8)$, $c = 19.123(8)$ Å, $\beta = 99.33(4)^\circ$, $V = 3660.0$ Å³, space group $C2/c$, $Z = 4$, $F(000) = 1504$, $D_c = 1.282$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 17.2$ cm⁻¹. Intensities of 3419 reflections ($4 < 2\theta < 50^\circ$) were measured at low temperature with a Philips PW 1100/20 four-circle diffractometer using Mo-K α radiation (graphite monochromator, θ – 2θ scan mode). Three standard reflections were measured every 120 min to monitor crystal and apparatus stability, but despite cooling, 15% decay was detected and included in the intensity corrections. Absorption corrections were not applied. The structure was solved by SHELXS86¹³ direct methods and refined by the SHELXL93¹⁴ program package (full-matrix least-squares methods on F^2). All non-hydrogen atoms were refined anisotropically and hydrogens placed in calculated positions were shifted using the riding model [2634 reflections and $F_o \geq 4\sigma(F_o)$]. Convergence was reached at $R = 0.083$. The final difference maps revealed electron density excursions of *ca.* 1.857 e Å⁻³ around the Ge atom. There are four dimer molecules in the unit cell, each located on a crystallographic 2 axis bisecting the bonds Ge(1)–Ge(1') and C(1)–C(1').

Atomic coordinates, bond lengths and angles, and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Other structures with similarly long C–C and C–Ge bonds are known, when these atoms carry bulky substituents. Several examples are: $r(\text{C}–\text{C})$ 1.635 Å in the analogous four-membered ring diazetidine obtained from adamantylideneadamantane and *N*-methyltriazolinedione,¹⁵ and $r(\text{C}–\text{C})$ 1.66 Å in a similar 1,2-disilacyclobutane;⁶ $r(\text{C}–\text{Ge})$ 2.02 Å was reported for $(\text{Bu}^t\text{P})_2(\text{GePh}_2)_2$ ¹⁶ and for cyclo-tetra-*tert*-butyl-1,3-dithia-2,4-digermane.¹⁷ In **4** the C–Ge bond is even longer, as both Ge and C carry very bulky groups.

References

- J. Barrau, J. Escudie and J. Satgé, *Chem. Rev.*, 1990, **90**, 283.
- G. Raabe and J. Michl, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1989, Part 2, p. 1015.
- H. Meyer, G. Baum, W. Massa and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 798; A. Berndt, H. Meyer, G. Baum, W. Massa and S. Berger, *Pure Appl. Chem.*, 1987, **109**, 1011.
- C. Couret, J. Escudie, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.*, 1987, **102**, 4411; M. Lazraq, J. Escudie, C. Couret, J. Satgé, M. Drager and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 828.
- A. G. Brook, F. Abdesaken and H. Sollradl, *J. Organomet. Chem.*, 1986, **299**, 9.
- A. G. Brook, S. C. Nyburg, W. P. Reynolds, Y. C. Poon, Y.-M. Chang, J.-S. Lee and J.-P. Ricard, *J. Am. Chem. Soc.*, 1979, **101**, 6750.
- D. Bravo-Zhivotovski, V. Braude, A. Stanger, M. Kapon and Y. Apeloig, *Organometallics*, 1992, **11**, 2326.
- Similar Peterson-type reactions have been reported by other groups, see: J. Ohshita, Y. Masaoka and M. Ishikawa, *Organometallics*, 1991, **10**, 3775; J. Ohshita, Y. Masaoka and M. Ishikawa, *Organometallics*, 1993, **12**, 876; H. Oehme, R. Wustrack, A. Heine, G. M. Sheldrick and D. Stalke, *J. Organomet. Chem.*, 1993, **452**, 33; C. Krempner, H. Reinke and H. Oehme, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1615.
- N. Wiberg and Ch.-K. Kim, *Chem. Ber.*, 1986, **119**, 2966; D. Seyferth and J. L. Lefferts, *J. Organomet. Chem.*, 1976, **116**, 257.
- E. Osawa, in *Molecular Structure and Energetics*, ed. J. F. Liebman and A. Greenberg, VCH, Deerfield Beach, FL, 1986, vol. 3, p. 329.
- P. Rivière, M. Rivière-Baudet and J. Satgé, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1981, vol. 2, p. 502.
- T. Tsumuraya, S. A. Batcheler and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 902.
- G. M. Sheldrick, SHELXS86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- G. M. Sheldrick, SHELXL93, program for the refinement of crystal structures, University of Göttingen, Germany, 1993.
- C.-C. Cheng, C. A. Seymour, M. A. Petti, F. D. Greene and J. F. Blount, *J. Org. Chem.*, 1984, **49**, 2910.
- K.-F. Tebbe and R. Frohlich, *Z. Anorg. Allg. Chem.*, 1983, **506**, 27.
- M. Wojnowska, M. Noltemeyer, H. J. Fullgrabe and A. Meller, *J. Organomet. Chem.*, 1982, **228**, 229.