

Reactivity of Ar'GeGeAr' (Ar' = C₆H₃-2,6-Dipp₂, Dipp = C₆H₃-2,6-*i*Pr₂) toward Alkynes: Isolation of a Stable Digermacyclobutadiene

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Strained rings incorporating heavier group 14 elements have attracted considerable attention in recent years due to their unique structures and reaction patterns.¹ Several three- and four-membered rings with heavier main group elements have been synthesized and characterized. However, stable cyclobutadiene rings containing Si–Pb atoms remain unknown, although in a few cases they have been postulated as reactive intermediates.² This is, of course, consistent with the instability of cyclobutadiene itself for which calculations have indicated an antiaromatic destabilization of 30–60 kcal/mol.³ Moreover, recent experimental results also showed that the cyclic 4π-electron system is destabilized by 55 kcal/mol.⁴ For heavier element derivatives, a few calculations have been carried out on SiC₃H₄,⁵ Si₂C₂H₄,⁶ and their isomers. For Si₂C₂H₄, they have shown

that the silacyclopropene $\text{HCC}(\text{SiH}_3)\text{Si}$ structure is the most stable of the numerous possible isomers with 1,2-disilacyclobutadiene ca. 46 kcal/mol higher in energy. Accordingly, the synthesis and characterization of a stable cyclobutadiene ring containing a heavy group 14 element is of fundamental interest and a formidable synthetic challenge. We previously reported the synthesis and structure of the stable germanium alkyne analogue Ar'GeGeAr' (**1**, Ar' = C₆H₃-2,6-Dipp₂, Dipp = C₆H₃-2,6-*i*Pr₂).⁷ It has a trans-bent geometry in contrast to that of the linear alkynes. The lone pair character and consequent bending at the Ge atoms suggest heightened reactivity, but little is known of the chemistry of these heavier group 14 alkyne analogues. We now report the reaction of the “digermine” **1** with alkynes and the formation of the first stable cyclobutadiene incorporating heavier group 14 elements as shown in Scheme 1.

Upon stirring an *n*-hexane solution of **1** and diphenylacetylene at room temperature for 7 days, the orange red color became deep red.⁸ Cooling the solution at 6 °C overnight afforded black-red crystals of **2**, a 1,2-digermacyclobutadiene, in high yield (Scheme 1). It displayed relatively high thermal stability as indicated by its high melting point (178 °C). Nonetheless, it is extremely air-sensitive both in solution and in the solid state. It was characterized by ¹H NMR, ¹³C NMR, IR, and UV–vis spectroscopies, and by X-ray crystallography. The reaction of **2** with an excess of diphenylacetylene under normal conditions did not result in further addition of alkyne. However, the reaction of **1** with the less crowded terminal alkyne HCCSiMe₃ led to the unusual bicyclic compound **3** (Scheme 1), which was also spectroscopically and structurally characterized.

The structure of **2** is shown in Figure 1.⁹ Its most prominent feature is the four-membered Ge₂C₂ ring which is an almost planar trapezoid (average deviation from the plane 0.026 Å; sum of the internal angles 359.82°). The two terphenyl ligands are disposed above and below the Ge₂C₂ ring such that the Ge centers have pyramidal coordination ($\Sigma^\circ\text{Ge} = 318.0^\circ$ and 317.3° , ClGe1Ge2C31 = 151.4°). The C61–C68 bond length (1.365(7) Å) is consistent with C–C double bonding, and the Ge–C ring distances (ca. 2.00

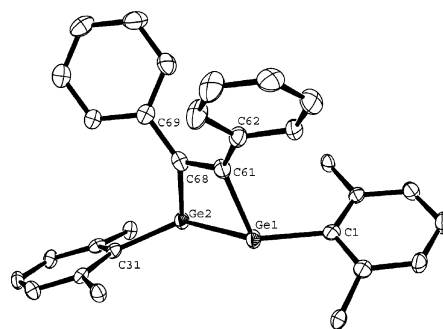
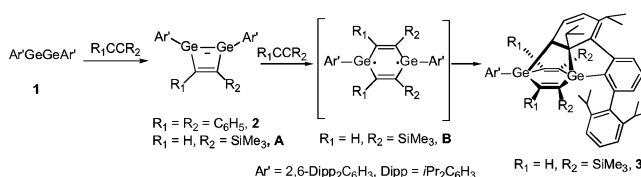


Figure 1. Thermal ellipsoid drawing of **2** (50% probability). Hydrogen atoms and Dipp rings (except *ipso* carbon atoms) are not shown. Selected bond lengths (Å) and angles (deg): Ge1–Ge2 2.4708(9), Ge1–C61 2.022(5), Ge2–C68 2.027(5), C61–C68 1.365(7), Ge1–C1 2.004(5), Ge2–C2 2.003(5); C61–Ge1–Ge2 74.00(15), C68–Ge2–Ge1 74.22(15), Ge1–C61–C68 106.2(4), C61–C68–Ge2 105.4(4), C61–Ge1–C1 109.2(2), C1–Ge1–Ge2 134.8(15), Ge1–Ge2–C31 132.04(14).

Scheme 1



Å) indicate single bonding. The Ge–Ge bond length (2.4708(9) Å) is slightly longer than a single bond (2.44 Å)^{10a} and is just above the known range for “digermenes” (2.21–2.46 Å).^{10b,c} The data for **2** clearly establish the presence of a carbon–carbon double bond and two germanium–carbon single bonds in the central four-membered ring. In addition, the pyramidal Ge environments and the Ge–Ge bond length are consistent with a weak Ge–Ge double bond as seen in several acyclic digermenes.^{10b,c,11}

Compound **3** crystallizes as two crystallographically independent molecules which have similar bond lengths and angles. One of these molecules is shown in Figure 2. The unusual structure results from the addition of a Dipp ring from an Ar' ligand to the postulated diradical intermediate **B** in Scheme 1. The C61–C62 and C66–C67 bond lengths are in the range for alkenes, while C38–C39 (1.555 Å) is close to that of a C–C single bond. The Ge atoms are each coordinated to four carbon atoms and display a distorted tetrahedral geometry. The Ge–Ge separation is 3.076(3) Å, which underlines the breaking of the Ge–Ge bond during the reaction.

The reaction of **1** with PhCCPh or HCCSiMe₃ under ambient conditions underlines its high reactivity in comparison to alkynes. A possible mechanism for the formation of **2** and **3** is shown in Scheme 1. The 1,2-digermacyclobutadienes **2** and **A** are formed initially by a [2+2] cycloaddition of **1** with PhCCPh or HCCSiMe₃. The species **A** is probably more reactive due to the lower steric protection afforded by the hydrogen substituent on the carbon atom. It reacts with another molecule of HCCSiMe₃ to afford the 1,4-

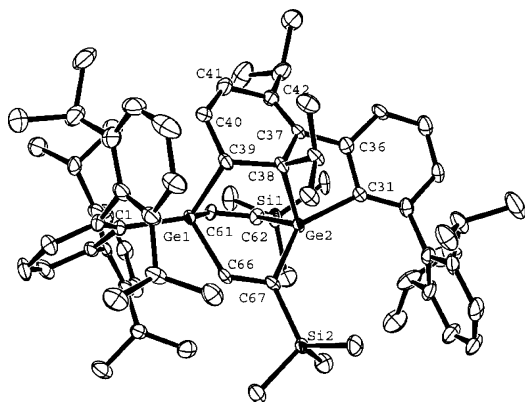


Figure 2. Thermal ellipsoid drawing of **3** (50% probability). Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ge1–C1 1.978(6), Ge1–C39 2.002(6), Ge1–C61 1.945(7), Ge1–C66 1.957(6), Ge2–C31 1.973(6), Ge2–C38 2.017(7), Ge2–C62 1.978(5), Ge2–C67 1.961(6), C66–C67 1.334(9), C61–C62 1.360(9), C38–C39 1.555(9); C39–Ge1–C61 102.1(3), C39–Ge1–C66 104.3(3), C61–Ge1–C66 100.9(3), C1–Ge1–C39 119.8(3), C1–Ge1–C61 119.9(3), C1–Ge1–C66 107.3(3), Ge1–C39–C38 110.8(4), Ge1–C61–C62 117.8(4).

digermbenzene intermediate **B**,¹² followed by the activation of one of the flanking aryl rings on the terphenyl ligands to give **3**. The regioselectivity of this reaction may be attributed to steric effects in which head-to-head coupling of the germanium center with the less hindered carbon atom of the unsaturated C–C units is favored. Although [2 + 2] cycloadditions are common for reactions of unsaturated heavier group 14 element species with unsaturated hydrocarbons,¹³ reaction with a relatively unactivated benzene ring is uncommon, suggesting that the reactive intermediate **B** has considerable diradical character.

In summary, the reactions of PhCCPh or HCCSiMe₃ with Ar'GeGeAr', **1**, show that it is much more reactive than normal alkynes. The heightened reactivity of **1** is very probably due to its incipient diradical character and accessibility of the excited state of this molecule.

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Supporting Information Available: X-ray CIF data for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (b) Lee, V. Y.; Sekiguchi, A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, 2002; Vol. 2, Part 1, Chapter 14. (c) Sekiguchi, A.; Lee, V. Y. *Chem. Rev.* **2003**, *103*, 1429.
- (2) (a) Ohgaki, H.; Fukaya, N.; Ando, W. *Organometallics* **1997**, *16*, 4956. (b) Kon, Y.; Ogasawara, J.; Sakamoto, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9310. (c) Gee, J. R.; Howard, W. A.; McPherson, G. L.; Fink, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 5461. (d) Maier, G.; Born, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1050.
- (3) (a) Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1995**, *99*, 6828. (b) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. (c) Rogers, D. W.; McLafferty, F. J.; Podosenin, A. V. *J. Phys. Chem.* **1996**, *100*, 17148.
- (4) Deniz, A. A.; Peters, K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119.
- (5) (a) Colvin, M. E.; Schaefer, H. F. *Faraday Symp.* **1984**, *19*, 39. (b) Schriver, G. W.; Fink, M. J.; Gordon, M. S. *Organometallics* **1987**, *6*, 1977. (c) Maier, G.; Reisenauer, H. P.; Jung, J.; Pacl, H.; Egenolf, H. *Eur. J. Org. Chem.* **1998**, 1297.
- (6) (a) Holme, T. A.; Gordon, M. S.; Yabushita, S.; Schmidt, M. W. *Organometallics* **1984**, *3*, 583. (b) Maier, G.; Reisenauer, H. P.; Meudt, A. *Eur. J. Org. Chem.* **1998**, 1291.
- (7) (a) Pu, L. H.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626. (b) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.
- (8) All manipulations were carried out under anaerobic and anhydrous conditions. **2**: A mixture of Ar'GeGeAr'⁷ (**1**, Ar' = C₆H₃-2,6-Dipp₂, Dipp = C₆H₃-2,6-*i*-Pr₂, 0.140 g, 0.149 mmol) and diphenylacetylene (0.053 g, 0.30 mmol) in *n*-hexane (30 mL) was stirred at room temperature for 7 days. The resulting deep red solution was concentrated and stored at 6 °C overnight to give dark red crystals of **2** (0.148 g, 77.7%). Mp: 178 °C. ¹H NMR (C₆D₆, 300.08 MHz): δ 0.77 (br, 24H, CHMe₂), 1.07 (br, 24H, CHMe₂), 3.04 (sept, 8H, *J* = 6.6 Hz, CHMe₂), 6.65 (br, 4H, Ar–H), 6.71 (br, 6H, Ar–H), 6.98 (d, 6H, *J* = 7.5 Hz, Ar–H), 7.09–7.21 (m, 6H, Ar–H), 7.29 (d, 4H, *J* = 6.9 Hz, Ar–H). ¹³C NMR (C₆D₆, 100.52 MHz): δ 23.5 (CHMe₂), 26.1 (CHMe₂), 31.1 (CHMe₂), 123.5, 126.4, 127.1, 129.1, 129.3, 130.8, 138.0, 140.2, 145.7, 146.8, 147.5, 159.2 (unsaturated carbon). IR (KBr, Nujol): 1605 (w), 1580 (w), 1570 (w), 855 (w), 757 (s), 735 (m), 711 (s), 688 (m), 452 (m), 367 (s) cm⁻¹. UV-vis (*n*-hexane): 375 nm (shoulder). **3**: This compound was prepared similarly to **2**. After workup, yellow crystals of **3** were obtained at ca. –20 °C from *n*-hexane (0.120 g, 84%). Mp: 225 °C (dec). ¹H NMR (C₆D₆, 300.08 MHz): δ –0.21 (s, 9H, SiMe₃), –0.15 (s, 9H, SiMe₃), 0.24 (d, 6H, CHMe₂), 0.90, 1.01, 1.19, 1.23–1.45 (m, 42H, CHMe₂), 1.68 (br, 1H, C39, H), 2.03 (sept, 1H, *J* = 6.7 Hz, CHMe₂), 2.28 (sept, 1H, *J* = 6.7 Hz, CHMe₂), 2.82 (sept, 2H, *J* = 6.7 Hz, CHMe₂), 3.05 (mult, 3H, *J* = 6.7 Hz, CHMe₂), 3.35 (sept, 1H, *J* = 6.7 Hz, CHMe₂), 5.38 (br, s, 1H, *vi*-CH), 5.76 (br, s, 1H, *vi*-CH), 6.58 (d, 2H, *J* = 7.5 Hz, Ar–H), 6.98–7.24 (m, 13H, Ar–H), 7.50 (d, 2H, *J* = 7.4 Hz, Ar–H). ¹³C NMR (C₆D₆, 75.5 MHz): δ –1.58 (SiMe₃), –1.28 (SiMe₃), 12.95 (CHMe₂), 17.84 (CHMe₂), 19.64 (CHMe₂), 21.64 (CHMe₂), 24.41 (CHMe₂), 29.71 (CHMe₂), 32.78 (CHMe₂), 34.57 (CHMe₂), 50.05 (*vi*-C), 121.67, 122.74, 124.6, 126.08, 130.46, 131.06, 140.48, 145.14, 147.11, 159.21, 163.55 (unsaturated carbon). IR (KBr, Nujol): 1591 (w), 1575 (w), 1554 (w), 1305 (m), 1248 (m), 1154 (m), 1056 (w), 967 (m), 934 (w), 893 (s), 875 (m), 840 (m), 760 (m), 748 (m), 660 (m), 644 (s), 605 (s), 475 (w) cm⁻¹.
- (9) Crystal data for **2** at 130(2) K with Cu Kα radiation (λ = 1.54178 Å): trigonal, space group R $\bar{3}$, *a* = *b* = 43.910(7) Å, *c* = 19.208(7) Å, α = β = 90°, γ = 120°, R1 = 0.0586 for 7378 reflections (*I* > 2σ(*I*)), wR2 = 0.1705 (all data). Crystal data for **3** at 91(2) K with Mo Kα (λ = 0.71073 Å): monoclinic, space group *Ia*, *a* = 33.299(8) Å, *b* = 13.209(3) Å, *c* = 38.495(13) Å, β = 104.211(6)°, R1 = 0.073 for 30 438 reflections (*I* > 2σ(*I*)), wR2 = 0.2380 (all data).
- (10) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; p 1280. (b) Baines, K. M.; Stubbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (c) Escudie, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 114.
- (11) The weakness of the Ge–Ge double bond is underlined by the large torsion (75.7°) and out-of-plane (46.5°) angular parameters. For a discussion of these, see: Power, P. P. *Dalton Trans.* **1998**, 2939.
- (12) For a 1,4-disila or digerma(Dewar-benzene), see: Kabe, Y.; Ohkubo, K.; Ishikawa, H.; Ando, W. *J. Am. Chem. Soc.* **2000**, *122*, 3775. Ohtaki, T.; Ando, W. *Organometallics* **1996**, *15*, 3103.
- (13) For example: (a) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3382. (b) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 12, 770. (c) Apeloig, Y.; Bravov-Zhivotovskii, D.; Zharov, I.; Panov, V.; Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 1398. (d) Bravov-Zhivotovskii, D.; Zharov, I.; Kapon, M.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1625. (e) Fukaya, N.; Ichinohe, M.; Kabe, Y.; Sekiguchi, A. *Organometallics* **2001**, *20*, 3364. (f) Fukaya, N.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3881.

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