

The First Metalladiene of Group 14 Elements with a Silole-Type Structure with Si=Ge and C=C Double Bonds

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1,3-Butadiene derivatives and their cyclic analogues constitute one of the most fundamental classes of conjugated organic compounds. After the discovery of the stable metallocenes and dimetallenes of Group 14 elements,¹ experimental efforts have been focused on the synthesis of the Group 14 elements containing metalladienes. However, only two examples of the isolable metalladienes of Group 14 elements have been reported to date: hexakis(2,4,6-triisopropylphenyl)tetrasila-1,3-butadiene and hexakis(2,4,6-triisopropylphenyl)tetragerma-1,3-butadiene.² Theoretical calculations on the model 2,3-digerma-1,3-butadiene, $H_2C=GeH-GeH=CH_2$, have predicted about half the degree of conjugation compared with that of 1,3-butadiene.³ We report here the synthesis, full characterization, X-ray structure, and reactivity of the first cyclic metalladiene consisting of Group 14 elements of the type $-M=M'-C=C-$ ($M = Si, M' = Ge$). This compound represents also the previously unknown metallole with an unsymmetrically composed skeleton, as well as the first example of the structurally characterized Si=Ge double bond. The reaction mechanism to form the metalladiene and the question of conjugation of the two double bonds will also be described.

The reaction of tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**1a**)⁴ with excess phenylacetylene in deuteriobenzene at room temperature in 5 h cleanly afforded an orange-red reaction mixture, which exhibits a downfield signal in the ²⁹Si NMR at +75.8 ppm. Recrystallization from hexane gave air- and moisture-sensitive bright orange crystals of 1,1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]-4-phenyl-1,2-disila-3-germacyclopenta-2,4-diene **4a** (Scheme 1).⁵ The ²⁹Si NMR spectrum revealed five resonances, of which three belong to the silyl substituents (19.4, 26.6, and 30.1 ppm); the downfield signal at +75.8 ppm is attributable to the double bonded silicon atom, and the upfield signal at -45.6 ppm corresponds to the endocyclic sp³ Si atom.

The molecular structure of compound **4a** was established by X-ray crystallography (Figure 1).⁶ The five-membered ring is almost planar, although the Si=Ge double bond has a twisted (*trans*-bent) configuration with a torsion angle Si(6)–Ge(1)–

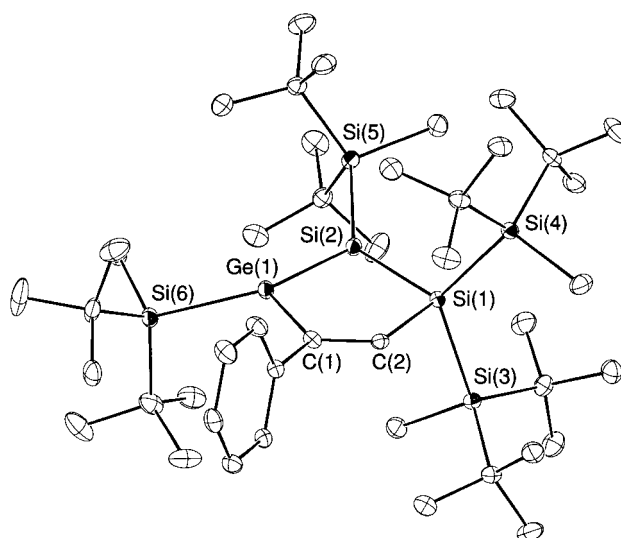
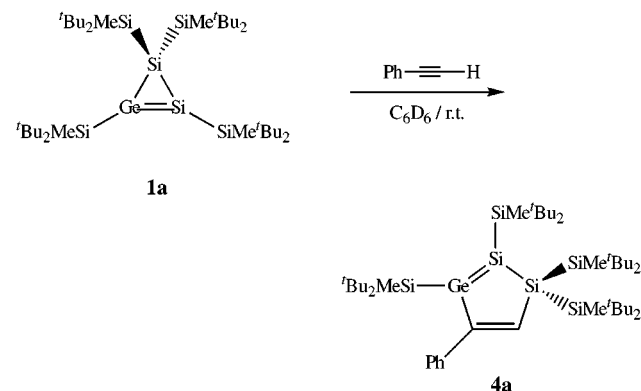


Figure 1. ORTEP drawing of **4a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ge(1)–Si(2) 2.250(1), Si(1)–Si(2) 2.364(1), Si(1)–C(2) 1.888(3), C(1)–C(2) 1.343(5), Ge(1)–C(1) 1.972(3), Si(1)–Si(3) 2.431(1), Si(1)–Si(4) 2.432(1), Si(2)–Si(5) 2.380(1), Ge(1)–Si(6) 2.418(1). Selected bond angles (deg): C(1)–Ge(1)–Si(2) 101.8(1), Ge(1)–Si(2)–Si(1) 95.2(0), C(2)–Si(1)–Si(2) 98.1(1), C(1)–C(2)–Si(1) 126.9(2), C(2)–C(1)–Ge(1) 117.9(2), Si(3)–Si(1)–Si(4) 124.7(0).

Scheme 1



Si(2)–Si(5) of 38.6(1)°. The phenyl ring is almost perpendicular to the plane of the silole ring, which is usual for phenyl-substituted metalloles.⁷ The Si=Ge double bond length is 2.250(1) Å, which is intermediate between the typical values for Si=Si and Ge=Ge double bond lengths.⁸ This value is close to that of the theoretically predicted 2.180 Å (MP2) for **1a**.⁴ It is instructive to estimate the degree of conjugation of the two double bonds in the silole ring system. The length of the Ge(1)–C(1) bond is 1.972(3) Å, which is in the normal range for Ge–C bond lengths of 1.95–2.00 Å.⁹ For the Si(2)=Ge(1) double bond length, it was impossible to compare with other examples, since no previous

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(8) Typical values for a Si=Si double bond length range from 2.138 to 2.289 Å, whereas Ge=Ge double bond lengths lie in the region of 2.213–2.460 Å: see, for example, ref 1b and the following: Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

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(2) (a) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503. (b) Schäfer, H.; Saak, W.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3703.

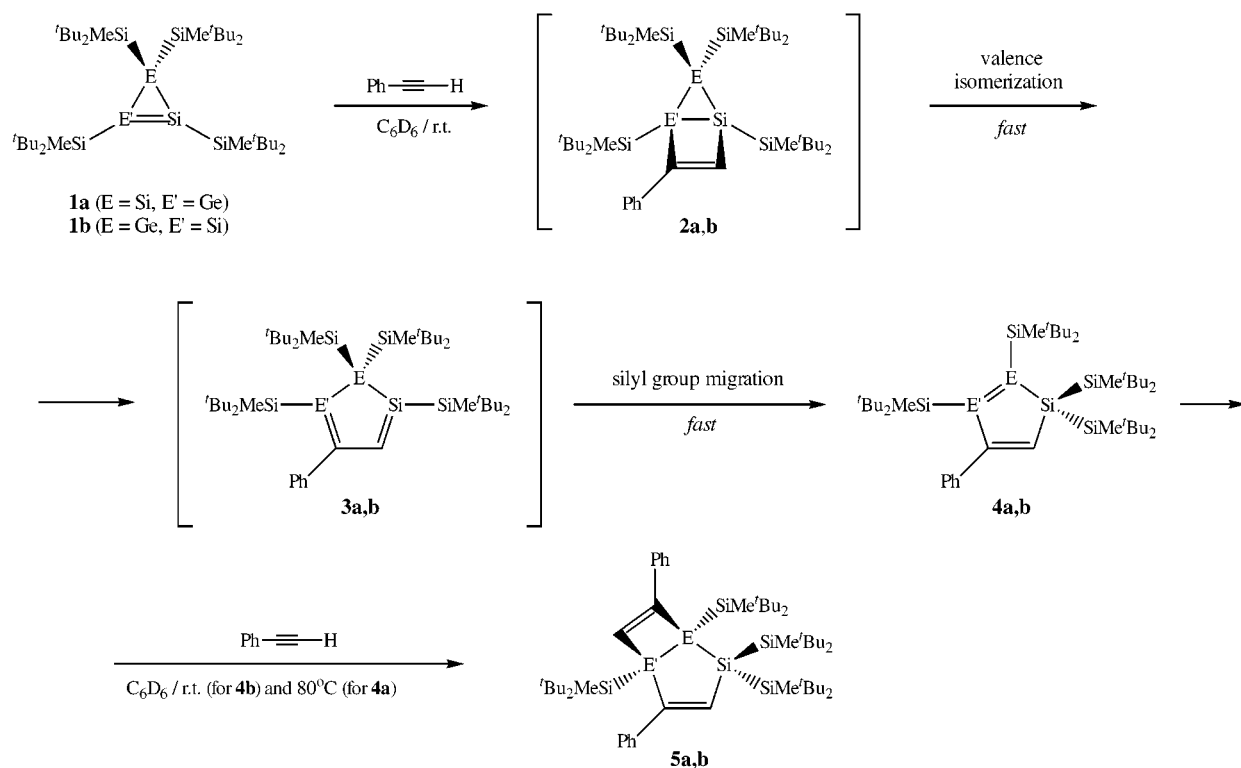
(3) Jouany, C.; Mathieu, S.; Chaubon-Deredempt, M. A.; Trinquier, G. *J. Am. Chem. Soc.* **1994**, *116*, 3973.

(4) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034.

(5) Spectral data for **4a**: bright orange crystals; mp 161–163 °C; ¹H NMR (C₆D₆, δ) 0.37 (s, 6 H), 0.40 (s, 3 H), 0.59 (s, 3 H), 0.99 (s, 18 H), 1.15 (s, 18 H), 1.19 (s, 18 H), 1.31 (s, 18 H), 7.06–7.09 (m, 1 H, ArH), 7.19–7.24 (m, 2 H, ArH), 7.34 (s, 1 H, C=CH), 7.42 (dd, *J*₁ = 8.24 Hz, *J*₂ = 8.15 Hz, 2 H, ArH); ¹³C NMR (C₆D₆, δ) -2.9, -2.3 (3C), 22.1, 22.5, 23.2, 23.7, 29.9, 30.96, 31.12, 31.4, 126.3, 126.8, 128.6, 149.8 (C=CH), 151.7 (ipso C), 173.3 (C=CH); ²⁹Si NMR (C₆D₆, δ) -45.6, 19.4, 26.6, 30.1, 75.8; MS (EI, 70 eV) 856–866 (M⁺ cluster, 31), 803 (M⁺ - 'Bu, 2), 703 (M⁺ - SiMe'Bu₂, 4), 73 (100); UV/vis (hexane) λ_{max}/nm (ε) 243 (37330), 307 (6570), 472 (5540).

(6) Crystal data for **4a** at 120 K: MF = C₄₄H₉₀GeSi₆, MW = 860.29, triclinic, *P*1, *a* = 12.2070(8) Å, *b* = 13.214(1) Å, *c* = 18.815(1) Å, α = 74.551(4)°, β = 73.514(5)°, γ = 64.841(5)°, *V* = 2596.7(4) Å³, *Z* = 2, *D*_{calcd} = 1.100 g·cm⁻³. The final *R* factor was 0.0562 for 7813 reflections with *I*_o > 2σ(*I*_o) (*R*_w = 0.1277 for all data, 10815 reflections), GOF = 1.015.

Scheme 2



structural data were available. The C(1)=C(2) double bond length is 1.343(5) Å, which is similar to that of 2,4-cyclopentadiene derivatives and 1-sila-2,4-cyclopentadienes (1.34–1.35 Å).^{7a} None of these data give any evidence for noticeable conjugation between the Si=Ge and C=C double bonds in the cyclopentadiene unit of **4a**, despite the planarity of the five-membered ring. The same conclusion has been drawn from the UV/vis spectrum of **4a**, which showed no significant bathochromic shift in comparison with an isolated Si=Ge double bond in compound **1a** (472 vs 467 nm, respectively).

For the mechanism of the formation of **4a**, the following reaction sequences can be considered (Scheme 2). In the first step, [2+2] cycloaddition of one molecule of phenylacetylene occurs across the Si=Ge double bond to form the bicyclic compound **2a**.¹⁰ This compound then quickly undergoes valence isomerization to form the silole type structure **3a** with one Si=C and one Ge=C double bond, which in turn rapidly isomerizes to give the thermodynamically more stable silole **4a** with one Si=Ge and one C=C double bond.^{11,12} Cycloaddition of a second molecule of phenylacetylene to the Si=Ge double bond of silole **4a** can be achieved only at elevated temperature. Thus, heating at 80 °C for 6 h caused the complete disappearance of **4a** and formation

of the new bicyclic compound 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diphenyl-1,2-disila-5-germabicyclo[3.2.0]hepta-3,6-diene (**5a**) in 55% yield.¹³ It is interesting that the regiochemistry of the PhCCH cycloaddition to the Si=Ge double bond of **4a** is different from the expected one; according to the polarity of the Si=Ge double bond one can expect the opposite regioselectivity.¹⁰ Apparently, in this case the reaction is governed by a steric effect, rather than an electronic one. Since there is no conjugation in a silole ring system, it is not surprising that **4a** and a second molecule of phenylacetylene react by the [2+2] rather than the [4+2] cycloaddition mechanism. That is, silole **4a** represents an unusual system with two formally conjugated, but actually isolated double bonds, in which one (Si=Ge) possesses a much higher reactivity than the other (C=C).

The reaction of 1-disilagermirene (**1b**) with phenylacetylene proceeds in a similar way at room temperature finally to give the bicyclic compound, 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diphenyl-2,5-disila-1-germabicyclo[3.2.0]hepta-3,6-diene **5b**, in 63% yield (Scheme 2).¹³ Even at room temperature, **4b** was not observed.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **4a**, **5a**, and **5b**, as well as the experimental procedure and spectral data of **4a**, **5a**, and **5b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) For the spectral data and X-ray structures of **5a** and **5b**, see Supporting Information.

(10) The cycloaddition of phenylacetylene to the transient germasilenes was found to be regioselective to form only one isomer, in which the phenyl group-substituted carbon atom is attached to a germanium atom, which is in accordance with the polarity of the Si=Ge double bond, see: Baines, K. M.; Dixon, C. E.; Langridge, J. M.; Liu, H. W.; Zhang, F. *Organometallics* **1999**, *18*, 2206.

(11) Such a type of isomerization was found for the first time for 1-methyl-1-trimethylsilyl-2,5-diphenyl-1-silacyclopenta-2,4-diene, which undergoes isomerization at 150 °C through a 1,5-silyl shift to form 1-methyl-2,5-diphenyl-5-trimethylsilyl-1-silacyclopenta-1,3-diene. The last compound is unstable and was evidenced only by trapping reactions, see: Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733.

(12) The stability of the isomeric compounds **2a**, **3a**, and **4a** was evaluated by ab initio calculations of the parent compounds (hydrogen atoms instead of all substituents) at the B3LYP/6-31G* level. This theory predicted the most stable compound to be **4a**. Compound **2a** is less stable by 13.4 kcal/mol and compound **3a** is the most unfavorable isomer by 14.3 kcal/mol.