

bath) resulted in a dark green solution. The 300-MHz^{8c} ¹H NMR spectrum at $-85\text{ }^{\circ}\text{C}$ indicated the formation of protonated ether **5** with the following absorptions: δ (¹H) 4.48 (s, H₆, H₇), 4.16 (s, H₉, H₁₀, H₁₁, H₁₂, H₁₃), 4.04 (s, H₅, H₈), 0.78 and 0.35 (s, H₂, H₃), -0.03 (s, Si(CH₃)₃), -3.21 (s, OH). The 75-MHz ¹³C NMR spectrum showed the following peaks: δ (¹³C) 97.9 (s, C₄), 77.9 (d, $J_{\text{CH}} = 181.7$ Hz, C₆, C₇), 77.3 (d, $J_{\text{CH}} = 185.6$ Hz, C₉, C₁₀, C₁₁, C₁₂, C₁₃), 75.5 (d, $J_{\text{CH}} = 182.7$ Hz, C₅, C₈) 60.4 (s, C₁), 17.4 (t, $J_{\text{CH}} = 166.0$ Hz, C₂, C₃), -1.6 (q, $J_{\text{CH}} = 122.1$ Hz, Si(CH₃)₃). Comparison of the ¹³C NMR data with those of the pregenitor **4**^{8a} shows no drastic change, in accordance with the structure of **5**. Indicative of **5** is also the observation of the highly shielded acidic proton on the ether oxygen at δ (¹H) -3.21 , indicating strong agostic¹⁰ interaction with the iron atom.

Allowing the solution to reach $-40\text{ }^{\circ}\text{C}$ in the NMR probe for 8 min followed by obtaining the spectrum by recooling to $-60\text{ }^{\circ}\text{C}$ showed irreversible changes, indicating the formation of 1-ferrocenyl-1-cyclopropyl cation **6**. The ¹³C NMR spectrum (Figure 1) consists of the following absorptions: δ (¹³C) 117.1 (s, C₁), 94.8 (d, $J_{\text{CH}} = 184.6$, C₆, C₇), 94.3 (s, C₄), 84.3 (d, $J_{\text{CH}} = 183.6$ Hz, C₉, C₁₀, C₁₁, C₁₂, C₁₃), 83.5 (d, $J_{\text{CH}} = 190.4$ Hz, C₅, C₈), 7.6 (t, $J_{\text{CH}} = 166.0$ Hz, C₂, C₃). The trimethylsilyl group absorption at δ (¹³C) 1.6 is assigned to trimethylsilyl fluorosulfate. The observation of the cyclopropyl group methylene carbon signals at δ (¹³C) 7.6 supports the formation of a free cyclopropyl cation with extensive charge delocalization into the ferrocenyl moiety as expressed in the resonance structure **6a**. Such delocalization is also supported by the observation of a signal for the carbocationic center at δ (¹³C) 117.1. The C6 and C7 cyclopentadienyl carbons are extensively deshielded (δ (¹³C) 94.8) compared to the C5 and C8 carbons. The assignments are also in accord with previously studied ferrocenyl-substituted carbocations.¹¹ The ¹H NMR data [δ (¹H) 5.76 (s, H₆, H₇), 4.3 (s, H₉, H₁₀, H₁₁, H₁₂, H₁₃), 4.3 (s, H₅, H₈), 1.59 and 1.25 (s, H₂, H₃)] are also in accord with structure **6**. Support for **6** comes from the nonequivalence of H₂ and H₃ cyclopropyl protons as well. Attempts to quench **6** to an intact cyclopropyl product were, however, unsuccessful.¹²

The large shielding of the cyclopropyl methylene carbons in **6** compared to **4** (by ca. 9.5 ppm) can be rationalized in terms of significant double bond character of the C1–C4 bond in the former. In fact, in going from methylcyclopropane to methylenecyclopropane, a shielding (3.2 ppm) of the ¹³C NMR chemical shifts of the cyclopropyl methylene carbons is observed.¹³

(8) (a) Compound **4** was obtained in 63% yield, as a yellow solid, by the cyclopropanation^{9a} of [1-[(trimethylsilyloxy)oxy]ethenyl]ferrocene,^{9b} which was readily available from acetylferrocene by Duboudin's procedure.^{9c} NMR data for **4**: δ (¹H) (CDCl₃) 4.08 (s, H₆, H₇), 4.01 (s, H₉, H₁₀, H₁₁, H₁₂, H₁₃), 3.92 (s, H₅, H₈), 1.11 and 0.92 (m, H₂, H₃); δ (¹³C) (CDCl₃) 94.4 (s, C₄), 69.0 (d, C₉, C₁₀, C₁₁, C₁₂, C₁₃), 67.5 (d, C₆, C₇), 67.2 (d, C₅, C₈), 55.2 (s, C₁), 17.1 (t, C₂, C₃), 1.3 (q, Si(CH₃)₃). (b) Freshly distilled materials were used; FSO₃H was used in 10-fold excess. (c) The NMR studies were carried out on a Varian Associates Model Unity 300 Superconducting NMR spectrometer equipped with a variable-temperature ¹H, ¹⁹F broad band probe using capillary acetone-*d*₆ lock. The chemical shifts are referenced from capillary TMS.

(9) (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* **1968**, 3495–3498. (b) Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864–4870. (c) Cazlau, P.; Moulines, F.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C9–C13.

(10) Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1987.

(11) Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 1849–1850 and references therein. Also see: Braun, S.; Abram, T. S.; Watts, E. *J. Organomet. Chem.* **1975**, *97*, 429–441.

(12) Quenching the solution with excess methanol/K₂CO₃ at $-78\text{ }^{\circ}\text{C}$ gave decomposed products.

(13) Crawford, R. J.; Tokunaga, H.; Schrijver, L. M. H. C.; Goddard, J. C.; Nakashima, T. *Can. J. Chem.* **1978**, *56*, 992–997. Monti, J. P.; Faure, R.; Vincent, E. *J. Org. Magn. Reson.* **1976**, *8*, 611–617.

In conclusion, we have been successful in the generation and observation of the first persistent tertiary cyclopropyl cation under long-lived stable-ion conditions. The cyclopropyl group in **6** remains intact due to substantial positive charge delocalization into the adjacent ferrocenyl moiety.

Acknowledgment. Support of the work at USC by the National Institutes of Health is gratefully acknowledged. H.B. thanks the Hermann Schlosser Stiftung for a predoctoral fellowship.

Structure and Bonding Nature of 2,4,5-Triseleno-1,3-disilabicyclo[1.1.1]pentane: A Novel [1.1.1]Propellane-Type Molecule¹

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The nature of the bridgehead bond of propellanes has been of considerable recent interest;^{3,4} however, only a few isolable group 14 [1.1.1]propellanes and bicyclo[1.1.1]pentanes are known experimentally.⁴ Here, we wish to report the preparation of a novel [1.1.1]propellane-type molecule **1-Se3** (2,4,5-triseleno-1,3-disilabicyclo[1.1.1]pentane) and discuss the nature of the bridgehead bond.

A benzene solution of **1-Se4**⁵ in a sealed tube was irradiated with a low-pressure Hg lamp for 18 h to give **1-Se3**, liberating Se as a reddish brown precipitate.⁶ The title compound **1-Se3**

(1) Yoshida, H.; Ando, W. Presented in part at the 6th Conference on the Chemistry of Selenium and Tellurium, Osaka, Japan, July 8–13, 1991. Chalcanes. 2. For Part 1, see ref 5.

(2) (a) Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan. (b) Production Engineering Research Laboratory, Hitachi Ltd. 292, Yoshida, Totsuka, Yokohama 244, Japan. (c) Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan.

(3) (a) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679. (b) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233. (c) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. (d) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. (e) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247. Schmidt, M. W.; Nguyen, K. A.; Gordon, M. S.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5998. Nguyen, K. A.; Carroll, M. T.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 7924. (f) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408. (g) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878. Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591. (h) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456. Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063. Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. Nagase, S. *Polyhedron* **1991**, *10*, 1299. (i) Streitwieser, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1261. (j) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267. (k) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (l) O'Keefe, M.; Gibbs, G. V. *J. Chem. Phys.* **1984**, *81*, 876. Note that the IUPAC name for [1.1.1]propellane is tricyclo[1.1.1.0^{1,3}]pentane.

(4) (a) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. (b) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454. Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839. (c) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794.

(5) Yoshida, H.; Ando, W. *Organometallics* **1991**, *10*, 27.

(6) Irradiation with a halogen lamp yielded the same product, **1-Se3**, but the rate was very slow. The UV maximum of **1-Se4** (450 nm) is explained by the lone pair–lone pair interaction of two neighboring Se atoms.⁵⁷ This four-electron interaction served to destabilize the molecule; therefore, we expected the photolytic cleavage of the selenium–selenium bond. However, the corresponding sulfur analogue **1-S4** did not show such photochemical reactivity.

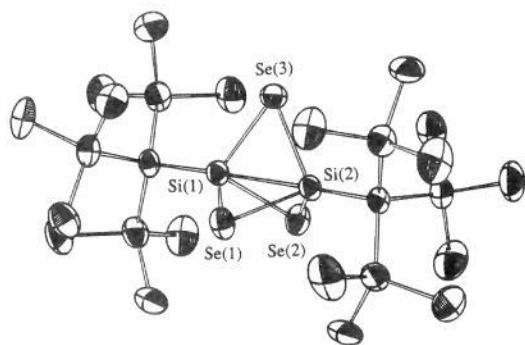


Figure 1. X-ray structure of **1-Se3**. Selected bond lengths (Å) and angles (deg): Si(1)–Se(1), 2.319 (2); Si(1)–Se(2), 2.323 (2); Si(1)–Se(3), 2.326 (2); Si(2)–Se(1), 2.316 (2); Si(2)–Se(2), 2.325 (2); Si(2)–Se(3), 2.327 (2); Si(1)–Si(2), 2.515 (3); Si(1)–C(1), 1.848 (8); Si(2)–C(2), 1.867 (8); Si(1)–Se(1)–Si(2), 65.70 (8); Si(1)–Se(2)–Si(2), 65.51 (8); Si(1)–Se(3)–Si(2), 65.43 (8); Se(1)–Si(1)–Se(2), 93.61 (8); Se(1)–Si(1)–Si(2), 57.09 (8).

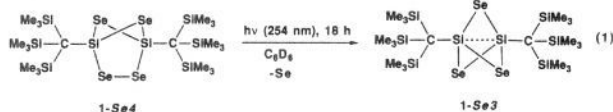
Chart I



Table I. Calculated Geometries of **3-Se3** and **4-Se3** and Bond Orders between Bridgehead Si Atoms

system	distances (Å)		Si–Se–Si angle (deg)	Si...Si bond order
	Si–Se	Si...Si		
3-Se3	2.340	2.457	63.3	0.366
4-Se3	2.339	2.484	64.1	0.366

was isolated by GPC; recrystallization from *n*-hexane afforded an analytically pure sample in 62.5% yield. The structure was determined by X-ray crystal analysis⁸ and examination of its spectral data⁹ (eq 1, Figure 1). The Si₁–Si₃ distance is very short



(2.515 Å) but is within the range of usual Si–Si single bond lengths (2.227–2.697 Å).¹⁰ The Si–Se bond length (2.323 Å) is somewhat longer than a normal Si–Se bond (2.27 Å).¹¹ The most interesting feature is the sharp Si–Se–Si angle (65.43–65.70°), which can be regarded as an angle of a three-membered-ring compound; a normal Si–Se–Si angle is ca. 95°. It is close to the value of a

(7) (a) Linderberg, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 2619. (b) Bergson, G. *Ark. Kemi* **1958**, *13*, 11. Bergson, G. *Ark. Kemi* **1962**, *19*, 195.

(8) Compound **1-Se3**: C₂₀H₅₄Se₃Si₃, FW 756.22; monoclinic; *a* = 15.650 (4), *b* = 13.073 (2), *c* = 17.648 (5) Å, *V* = 3608.4 Å³, *Z* = 4; space group *P*2₁/*C*, *ρ* = 1.39 g/cm³, *μ* = 48.0 cm. The 4855 independent observed reflections [*2θ* ≤ 50°; |*F*_o²| > 3σ(*F*_o²)] were measured on an Enraf-Nonius CAD4 diffractometer using MoK α irradiation and an ω - θ scan. No absorption correction was made. The structures were solved by direct methods, and only silicon and selenium atoms were refined anisotropically to *R* = 0.059 and *R*_w = 0.068.

(9) **1-Se3**: MS *m/e* 758 (M⁺); ¹H NMR (C₆D₆, 500 MHz) δ 0.446 (s); ¹³C NMR (C₆D₆, 125 MHz) δ 5.85 (s), 4.33 (q); ²⁹Si NMR (C₆D₆, 79.4 MHz) δ 0.6 (dect, *J*_{Si–H} = 9.4 Hz; SiMe₃), –59.0 (t, *J*_{Si–Se} = 48.5 Hz; bridgehead Si); ⁷⁷Se NMR (C₆D₆, 76.4 MHz, vs Me₂Se) δ 830.2; UV (*n*-hexane) λ 230.0 nm (s) (ϵ = 3850); exact mass found 755.9849, calcd for C₂₀H₅₄Si₃Se₃, 755.9892. The compound **1-Se3** reacts easily with silica gel, alcohols, and moisture to give a complex mixture, although the raw material **1-Se4** is stable to all of them.⁵

(10) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: 1989; Part 1, Chapter 3.

(11) Barrow, M. J.; Ebsworth, E. A. V. *J. Chem. Soc., Dalton Trans.* **1982**, 211.

Table II. Calculated Lewis–Langmuir Atomic Charges¹⁸

compd	<i>e</i> ^a	<i>e</i> ^{'a}
4-O3	+0.920	–0.613
4-S3	+0.448	–0.299
4-Se3 (or 1-Se3)	+0.351	–0.234

^a *e* represents the Lewis–Langmuir atomic charge of an SiH group and *e*['] represents that of the X atom.

Chart II

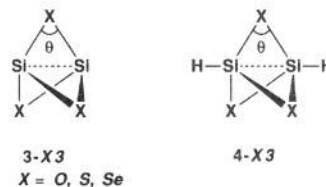


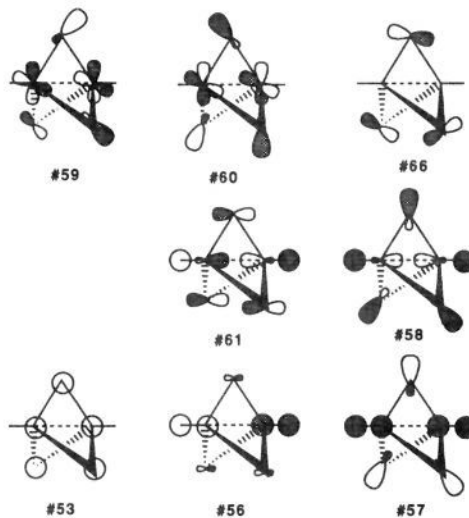
Chart III



Chart IV



Chart V



similar bond in selenadisilirane **2** (59.9°) prepared very recently.¹² The constancy of the ratio of ring bond lengths to bridgehead distances (KMC) in a homologous series was reported by Kabe and Masamune.^{4c,13} The constant KMC for **1-Se3** is calculated to be 1.08, which means **1-Se3** belongs to the same class as three-membered-ring compounds (KMC = 1.0). This result implies that some type of chemical bonding exists between the

(12) Tan, R. P.-K.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 546.

(13) KMC = (Si...Si distance)/(Si–X bond length).^{4c} KMC = 1.0 for trisilasiliranes¹⁴ and selenadisilirane **2**,¹² and KMC = 1.21–1.26 for bicyclo[1.1.1]pentanes.^{4c}

(14) (a) Schäfer, A.; Weidenbruch, M.; Peters, K.; Schnering, H. G. v. *Angew. Chem.* **1984**, *96*, 311. (b) Watanabe, H.; Kato, M.; Okawa, T.; Nagai, Y.; Goto, M. *J. Organomet. Chem.* **1984**, *271*, 225. (c) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

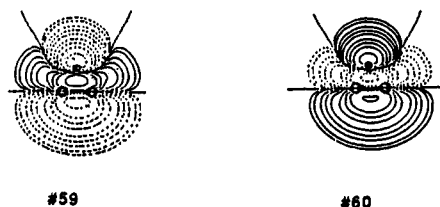


Figure 2. Countour plots of orbitals 59–60 for the plane of a three-membered ring in 4-Se3.

bridgehead Si atoms.¹⁵ It is probably not a conventional σ or π bond;^{3,16} of course the line joining the bridgehead Si atoms does not always mean “a bond path”.¹⁹ An innovative explanation is “ σ -bridged- π ” bonding, which is a three-center bond as shown in Chart I.³⁸

The molecular structures and electronic states were calculated by the ab initio restricted Hartree–Fock method (RHF, DZP) for 3-Se3 and 4-Se3 (Table I).²⁰ The RHF geometry of 4-Se3 is in good agreement with the experimental results²¹ and almost identical with the RHF geometry of 3-Se3. The bond order of the Si₁–Si₃ bond is calculated to be 0.366 for both 3-Se3 and 4-Se3 (Chart II), and the orbital A for 3-Se3 (Chart III) shows little overlap between Si atoms.

The ⁷⁷Se and ²⁹Si NMR studies for 1-Se3 afforded surprising results.²² ⁷⁷Se chemical shifts of normal silaselenanes are generally observed upfield (–199 to –614 ppm) from Me₂Se (0 ppm),^{12,23} yet the ⁷⁷Se chemical shift of compound 1-Se3 is +830 ppm, which is downfield by more than 1000 ppm from the chemical shifts of normal silaselenanes. The ⁷⁷Se signals of 1-Se4 are observed in the middle region (+320.7, +273.2 ppm). On the other hand, the ²⁹Si NMR chemical shift of 1-Se3 is –59.0 ppm, which is similar to the chemical shift of three-membered-ring compound 2 (–64.8 ppm).¹² The values are far different from those of normal four-membered-ring compounds, e.g., tetramethyl-1,3-diselenad-isiletane (⁷⁷Se NMR δ –199 ppm, ²⁹Si NMR δ –8.0 ppm).²³ The $J(^{29}\text{Si}-^{77}\text{Se})$ coupling constant for 1-Se3 ($J = 48.5$ Hz) is smaller than that for 2 ($J = 78$ Hz). It shows that the s character of the Si–Se bond in 1-Se3 is very low.

This result implies two possible explanations: (1) Both in 3-Se3 and in 4-Se3 there is no Si–Si bond which can be defined using the concept of the electron density analysis of Bader and co-

(15) Allen predicted similar geometry in the 1,3-diborabicyclo[1.1.1]pentane system and showed the [1.1.1]propellane-type bonding picture.³⁸

(16) We reported that Streitwieser's ionic model³¹ can apply to the 2,4,5-trisilabicyclo[1.1.1]pentane system;¹⁷ however, the Si–Se–Si angles of 1-Se3 go beyond the optimal value of the ionic model (80°). Clearly, the ionic model cannot be applied to this system. Lewis–Langmuir atomic charges were determined for 4-X3 according to the method reported by Allen¹⁸ (Table II). These data show that the contribution of the ionic bonding in 4-Se3 (or 1-Se3) is smaller than in others (see also ref 21).

(17) Ando, W.; Yoshida, H.; Kurishima, K.; Sugiyama, M. *J. Am. Chem. Soc.* **1991**, *113*, 7790.

(18) (a) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9115. (b) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003. (c) Allen, L. C. Private communication.

(19) It is not unusual, because the same type of descriptions are often used for simplicity. For example, in metallocenes (Chart IV), the straight line joining metal and Cp does not mean a bond path. As for a bond path, see ref 3e,k.

(20) The calculation was carried out by the GAUSSIAN 82 program package. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab-initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986. The basis sets used here for the Se and Si atoms were double zeta plus polarization (DZP) types, which consisted of the Tawewaki–Huzinaga basis sets plus an extra d-function. Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984. For the H atom, the 3-21G function was employed.

(21) The charge distribution is –0.18 for the Si atom and +0.01 for the Se atom. The results from ab initio calculations are reasonable, because the electronegativity difference between Si and Se is smaller than that between Si and carbon.^{18b}

(22) ⁷⁷Se and ²⁹Si NMR spectra were recorded with a Bruker MSL 400 spectrometer with a 10-mm sample tube and multinuclear probehead. The spectral widths were 30 000 and 125 000 Hz operated at 76.4 and 79.4 MHz for ⁷⁷Se and ²⁹Si, respectively.

(23) (a) Boudjouk, P.; Bahr, S. R.; Thompson, D. P. *Organometallics* **1991**, *10*, 778. (b) Thompson, D. P.; Boudjouk, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1466.

workers.^{3e,3k,24} The shorter bridgehead distance is a result of geometrical constraint.^{3e} (2) The bond order is low, which does not reflect the magnitude of the three-center bonding. The bridgehead bond is considerably reinforced with the three-center bonding.²⁵ This type of bond exists both in 3-Se3 and in 4-Se3.

We propose the latter explanation, since the structure and the NMR data of 1-Se3 are far different from those of normal disilaselenanes and rather resemble the selenadisilirane in several points. However, at this moment, we cannot show a clear bonding picture of the mysterious bridgehead bond.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on a Priority Area of Molecular Design with heteroatoms and for General Scientific Research from the Ministry of Education, Science and Culture, Japan. The numerical calculations were carried out on the HITAC M680H at the Production Engineering Research Laboratory, Hitachi Ltd.

Supplementary Material Available: Detailed information of the X-ray crystal analysis, including tables of crystal structure data, positional parameters, displacement parameters, torsional angles, and bond distances and angles (25 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(24) As yet we have never carried out the electron density analysis for 3-Se3 and 4-Se3; however, according to Gordon's paper, no Si–Si bond critical point is found in 3-O3, 4-O3, 3-S3, and 4-S3.^{3e}

(25) The RHF calculation for 4-Se3 afforded some orbitals, which mainly consisted of s orbitals (1s of H, 3s of Si, and 4s of Se, Scheme I, #53, #56–58, #61). They are essentially the same type orbital as the three-center orbitals, which consist of three hydrogen 1s orbitals.²⁶ The acute angle of 4-Se3 and the short Si₁–Si₃ length may be explained on the basis of the same concept as the geometrical distortion of the three-hydrogen system.²⁶ That is, the overlap of the 3s orbitals for the Si atoms lowers the energy of the three-center-bond-type orbitals, which also is consistent with the low s character of Si–Se bonds. The orbital #59–60 can be regarded as a σ -bridged- π bonding type orbital (Figure 2).

(26) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; Chapter 7.

Strong Organometallic “Anomeric” Effects. Long-Range Stereoelectronic Control of Cyclohexanone Conformation via a Transannular Metallacyclobutane Interaction

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The importance of stereoelectronic effects to the configuration and conformation of organic molecules has been generally recognized in a variety of contexts.¹ Here we present evidence for conformational control of the cyclohexanone ring system by a remote transition-metal center, communicated via a transannular electronic interaction across a metallacyclobutane framework. This unprecedented organometallic “anomeric” effect is demonstrated both in the solid state and in solution and is shown to be greater in magnitude than the anomeric effect in carbohydrate acetals.^{1,2} A molecular orbital description for this interaction is proposed and supported by theoretical considerations.

The complexes under investigation, metallacyclobutane-substituted ketone derivatives 2–4, were prepared as previously described³ by the addition of enolates to cationic η^3 -allyl complexes

(1) See: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983.

(2) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: New York, 1983. Szarek, W. A.; Horton, D. *Anomeric Effects*; ACS Symposium Series 87; American Chemical Society: Washington, D.C., 1979.