The occurrence of reaction 1[14] is of fundamental significance since free oximes such as diacetyl monoxime (pK_a = 9.3)[15a] or even carboxylic acids such as *p*-fluorobenzoic acid (pK_a = 4.14)[15b] do not react with $CpCr(NO)_2Me$ under identical experimental conditions. The role of the electrophilic $[CpCr(NO)_2]^+$ cation in activating formaldoxime by coordination is thus to increase substantially its Brønsted acidity above that which it possesses in its free state. Once activated, the bound formaldoxime can then undergo deprotonation by $CpCr(NO)_2Me$ to afford the observed products.[16]

The utility of the $CpCr(NO)_2^+$ cation for effecting the activation of other small molecules of synthetic importance is currently being investigated.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and to the University of British Columbia for the award of a graduate fellowship to G.B.R.-A. We also thank Professor Ross Stewart for helpful discussions.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]BPh_4$ (7 pages); a listing of structure factors for $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]BPh_4$ (33 pages). Ordering information is given on any current masthead page.

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[14] The occurrence of reaction 1 explains why $[\{CpCr(NO)_2\}_2[\mu,\eta^2\text{-}N(CH_2)O\}]PF_6$ is formed as a byproduct during the synthesis of $[CpCr(NO)_2\{N(CH_2)OH\}]PF_6$[4] from $CpCr(NO)_2Me$ and $NOPF_6$ in CH_2Cl_2 if (a) an excess of $CpCr(NO)_2Me$ is used or (b) the insoluble $NOPF_6$ is not finely ground (in effect causing (a) locally).

[15] (a) Krueger, P. J. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley-Interscience: New York, 1975; Part 1, p 167. (b) Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Section 8.

[16] $Cp_2Zr(Cl)Me$ has also been employed recently to deprotonate other organic groups bound to organo-transition-metal centers.[17]

[17] Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

Photochemical Generation of Cyclopropenylsilylenes

Mark J. Fink* and Dhananjay B. Puranik

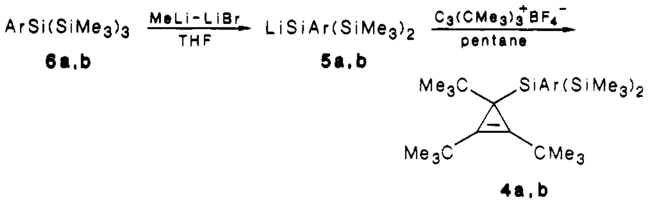
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received February 27, 1987

Summary: Two cyclopropenyltrisilanes have been prepared by the reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with silyllithium reagents. The 254-nm photolysis of one of these compounds in the presence of ethanol gives trapping products indicative of an initially generated cyclopropenylsilylene.

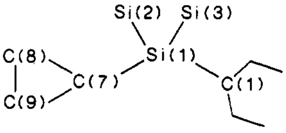
The SiC_3H_4 isomer surface, which includes silatetrahedrane (1) and silacyclobutadiene (2), is a potential paradigm for the interplay of ring strain and antiaromatic delocalization in organosilicon molecules. Calculations by Gordon suggest that silacyclobutadiene is the most stable of the isomers, 33.3 kcal mol^{-1} more stable than silatetrahedrane and 56.3 kcal mol^{-1} more stable than a silyne–alkyne pair.[1] A sophisticated calculation by Schaeffer on the structure and electronic properties of singlet and triplet silcyclobutadiene has also appeared.[2] Despite theoretical interest in these molecules, there is little experimental evidence for their existence.[3]

Scheme I[a]

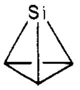


[a] **a**, Ar = Ph; **b**, Ar = Mes (mesityl; 2,4,6-trimethylphenyl).

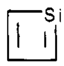
Table I. X-ray Structure of 4a: Selected Bond Lengths and Angles



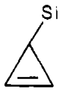
Bond Lengths (Å)			
Si(1)–Si(2)	2.396 (2)	C(7)–C(8)	1.546 (6)
Si(1)–Si(3)	2.398 (2)	C(7)–C(9)	1.536 (6)
Si(1)–C(1)	1.893 (5)	C(8)–C(9)	1.284 (6)
Si(1)–C(7)	1.940 (4)		
Bond Angles (deg)			
C(8)–C(7)–C(9)	49.3 (3)		
C(7)–C(8)–C(9)	64.9 (3)		
C(7)–C(9)–C(8)	65.8 (3)		



1



2



3

In an effort to synthesize analogs of 1 and 2, we have sought to generate derivatives of yet another SiC_3H_4 species, cyclopropenylsilylene (3). Similar low-valent species, most notably cyclopropenyl carbenes and nitrenes, undergo facile rearrangements to give cyclobutadienes and azetes, respectively.[4] Accordingly, cyclopropenylsilylenes may prove to be convenient sources of either 1 or 2. We report herein the synthesis of two photochemical precursors of highly substituted cyclopropenylsilylenes, a solid-state structure, and preliminary photochemistry of one of these compounds.

A convenient route to organosilylenes is the photolysis of 2-aryltrisilanes.[5] Two cyclopropenylaryltrisilanes, **4a** and **4b**, were prepared by the respective addition of silyllithium reagents **5a** and **5b** to a pentane slurry of tri-*tert*-butylcyclopropenium tetrafluoroborate at room temperature. Filtration and removal of solvent in vacuo gave **4a** and **4b** in 65% and 68% yields, respectively. The corresponding lithium reagents were prepared by the action of MeLi–LiBr on the tetrasilanes **6a** and **6b** as shown in Scheme I.

Compounds **4a** and **4b** are white crystalline solids that are stable in refluxing xylene and unreactive toward mild acids. Both **4a** and **4b** show a characteristic cyclopropene C=C stretch at 1815 and 1810 cm^{-1}, respectively. Other spectral data are consistent with the proposed structures.[6]

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[1] Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1980**, 1131–1132.

[2] Colvin, M. E.; Schaeffer, H. III. *Faraday Symp. Chem. Soc.* **1984**, *19*, 39–48.

[3] Gentle, T. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 304–305.

[4] For pertinent examples, see: Masamune, S.; Nakamura, M.; Suda, M.; Ono, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481–8483. Vogelbacher, U.-J.; Regitz, M.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842–843.

[5] Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51–95. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509.

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Table II. Yields of Products from the 254-nm Photolysis of 4b in 3:1 Hexane–Ethanol Mixture at −50 °C[a]

	$Me_3SiSiMe_3$ 7	CypH 8	CypMesSiHOEt 9	$MesSiH(OEt)_2$ 10	$MesSiH_2OEt$ 11
yields, %	>95	21	46	19	6

[a] Cyp ≡ tri-*tert*-butylcyclopropenyl; Mes ≡ mesityl.

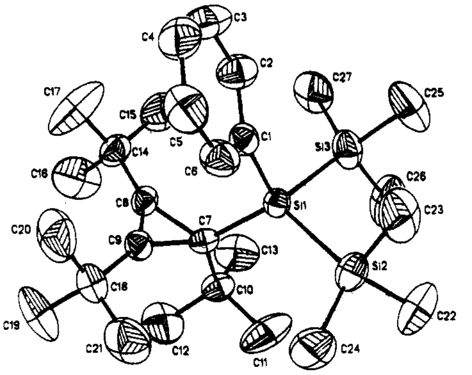
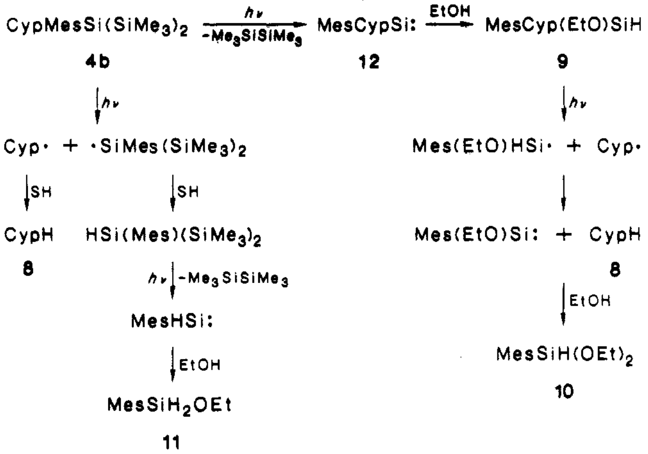


Figure 1. ORTEP drawing of 4a showing all non-hydrogen atoms.

Scheme II[a]



[a] Cyp ≡ tri-*tert*-butylcyclopropenyl; Mes = mesityl; SH = solvent.

An X-ray structural analysis of **4a** was undertaken.[7] An ORTEP drawing of **4a** is shown in Figure 1, and important bond lengths and angles are summarized in Table I. The geminal planes of the cyclopropene and aromatic rings are twisted 45° in respect to each other. The values of bond lengths and endocyclic angles of the cyclopropene ring are in the expected range;[8] however, there is considerable bond elongation around the cyclopropene-substituted silicon atom. Most conspicuous is the silicon–allylic carbon bond length of 1.94 Å, one of the longer silicon–carbon bond lengths known.[9] The silicon–silicon bond lengths (2.40 Å) are also somewhat longer than the typical value of 2.34 Å.[10] These long bond lengths probably reflect the highly crowded environment about this silicon center.

The 254-nm photolysis of **4b** at −50 °C in 3:1 v/v hexane–ethanol mixtures afforded a variety of products: hexamethyldisilane (**7**), tri-*tert*-butylcyclopropene (**8**), mesityl(tri-*tert*-butylcyclopropenyl)ethoxysilane (**9**), mesityldiethoxysilane (**10**), and mesitylethoxysilane (**11**). The GC yields of these products at 85% conversion are shown in Table II.[11]

The near quantitative yield of hexamethyldisilane and the high yield of the expected silylene insertion product **9** strongly suggest the formation of mesityl(tri-*tert*-butylcyclopropenyl)silylene, **12**, as the primary photoproduct as depicted in Scheme II. The initial photochemical formation of the silylene **12** is also supported by the photolysis of **4b** in a rigid 3-methylpentane glass which gives a yellow species with a broad absorption band at 450 nm. The absorption band is quite similar to other related silylenes.[12]

The other products in the solution photolysis seem to arise from competing photochemical reactions of both the trisilane precursor **4a** and the ethanol-trapping product **9**. Independent photolysis of **9** under the same conditions of the original photolysis cleanly gave a 1:1 mixture of **8** and **10** as determined by GC analysis. The formation of these products appear to result from the homolytic cleavage of the silicon–cyclopropene bond followed by

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(6) Characterization. For **4a**: ^1H NMR (δ, $CDCl_3$) 0.23 (s, 18 H), 0.94 (s, 9 H), 1.03 (s, 18 H), 7.17–7.42 (m, 5 H); ^{13}C NMR (δ, $CDCl_3$), 3.67 (CH_3), 31.72 (CH_3), 31.86 (CH_3), 32.08 (q), 38.06 (q), 40.03 (q), 127.16 (CH), 128.19 (CH), 128.92 (q), 139.95 (CH), 138.62 (q); ^{29}Si (δ, $CDCl_3$) −15.02 (Me_3Si), −38.76 (q); IR (CCl_4, cm^{-1}) 3100 (s), 2960 (s), 2900 (m), 815 (w), 1590 (s), 1570 (s), 1250 (s), 900 (s); MS (EI) *m/e* (relative intensity) 443 (1, $-CH_3$), 401 (1.4, −*t*-Bu), 207 (100, $C_3(t\text{-}C_4H_9)_3$), 73 (25, $Si(CH_3)_3$), 57 (6, $t\text{-}C_4H_9$). Anal. Calcd: C, 70.75; H, 10.91. Found: C, 70.93, H, 10.84. For **4b**: ^1H (δ, $CDCl_3$) 0.26 (s, 18 H), 0.96 (s, 9 H), 1.06 (s, 18 H), 2.17 (s, 3 H), 2.53 (s, 6 H), 6.69 (s, 2 H); ^{13}C (δ, $CDCl_3$) 6.16 (CH_3), 20.70 (CH_3), 29.45 (CH_3), 31.37 (CH_3), 31.76 (CH_3), 38.28 (q), 42.02 (q), 128.01 (CH), 129.58 (q), 137.23 (q), 135.12 (q), 145.41 (q); ^{29}Si (δ, $CDCl_3$) −13.96 (Me_3Si), −35.55 (q); IR (CCl_4, cm^{-1}), 3000 (s), 2960 (s), 2900 (s), 1810 (w), 1600 (m), 1550 (s), 1250 (s), 900 (w); MS (EI) *m/e* (relative intensity) 485 (0.6, $-CH_3$), 427 (0.8, $-Si(CH_3)_3$), 207 (100, $C_3(t\text{-}C_4H_9)_3$), 73 (68, $Si(CH_3)_3$), 57 (86, $t\text{-}C_4H_9$). Anal. Calcd: C, 71.92; H, 11.26. Found: C, 71.76; H, 11.23.

(7) Crystal data: dimensions, 0.30 × 0.25 × 0.20 mm; crystal system, monoclinic; space group, $P2_1/c$; a = 16.382 (5) Å, *b* = 11.990 (2) Å, *c* = 15.199 (3) Å, β = 96.70 (2)°; *Z* = 4; absorption coeff 14.8 cm^{-1}; graphite-monochromaticized Cu Kα; scan range 0–59°; 4507 unique reflections measured with 3897 $F_o^2 > 3.0\sigma(F_o^2)$. Structure solution was obtained by direct methods and refined to convergence with full-matrix least squares; $R = 0.071$, $R_w = 0.100$.

(8) Experimentally determined bond lengths for cyclopropene are 1.300 (C=C) and 1.515 Å (C—C), respectively; the endocyclic bond angles are 114.7° and 149.9°: Kasai, P. H.; Myers, R. J.; Eggers, D. F.; Wiberg, K. B. *J. Chem. Phys.* **1959**, *30*, 512–516.

(9) The typical value of the Si–C bond length is 1.89 Å (see ref 10). The longest known Si–C bond length is 2.00 Å found in 1,3-diiodohexakis-*tert*-butylcyclotrisilane: Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 79–80.

(10) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkenson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2.

(11) Compounds **7**, **8**, **10**, and **11** show identical mass spectra and GC retention times as that of commercially available or independently synthesized samples. Compound **9** was isolated by HPLC. Characterization for **9**: ^1H NMR (δ, C_6D_6) 1.06 (s, 9 H), 1.28 (s, 9 H), 1.31 (s, 9 H), 1.06 (t, 3 H), 2.11 (s, 3 H), 2.67 (s, 6 H), 3.49 (q, 2 H), 5.53 (s, 1 H), 6.77 (s, 2 H); ^{13}C NMR (δ, C_6D_6) 15.05 (CH_3), 21.10 (CH_3), 26.13 (CH_3), 30.81 (CH_3), 31.61 (CH_3), 31.67 (CH_3), 31.82 (q), 32.00 (q), 35.59 (CH_3), 36.29 (CH_3), 60.12 (CH_2), 124.06 (q), 126.77 (q), 129.31 (CH), 132.35 (q), 139.28 (q), 144.96 (q); ^{29}Si (δ, C_6D_6) −14.78 (SiH). Anal. Calcd: C, 77.93; H, 11.07; Si, 7.01. Found: C, 76.16; H, 10.91; Si, 6.56.

(12) Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Carlson, C. W.; Welsh, K.; West, R.; Michl, J. *Silicon, Germanium, Tin, Lead Compds* **1986**, *9*, 75–80.

disproportionation of the radical pair to give tri-*tert*-butylcyclopropene, 8, and ethoxymesitylsilylene. The silylene subsequently reacts with the ethanol which is present to give the diethoxysilane, 10.[13] Similarly, we believe that the formation of the monoethoxysilane, 11, results from homolytic cleavage of the starting trisilane to give tri-*tert*-butylcyclopropenyl and mesityl(trimethylsilyl)silyl radicals. Since these radicals cannot undergo the same disproportionation reaction as does the previously discussed radical pair, each of the radicals probably abstracts a hydrogen atom from the solvent system to give 8 and mesitylbis(trimethylsilyl)silane. The silane may then photolyze to give mesitylsilylene which reacts with ethanol to give 11. Although we do not detect the mesityltrisilane in our photolysis mixtures, we have independently shown that this compound photolyzes much more efficiently than our starting trisilane. Considering the small amounts of 11 actually formed in this photolysis (vide infra, minor pathway), it is possible that the steady state concentration of this intermediate would be too small to be detected in our experiment.

Interestingly, we see little evidence for the trapping of valence isomers of the silylene 12. Only when **4b** was photolyzed at near ambient temperatures and at low concentrations of ethanol (0.25% v/v) can several isomers of the silylene-trapped product be detected. The overall yield of these products is less than 1%. We believe that these products arise from the trapping of small amounts of valence isomers, and attempts to characterize these compounds are presently underway.

In conclusion, the cyclopropenylsilylene 12 does not appear to undergo facile isomerization under conditions which would be favorable for the isomerization of the analogous carbenes and nitrenes. The origin of this difference may lie in the relative stability of the silylene in respect to its closed-shell valence partners. Results of a recent ab initio molecular orbital calculation indeed suggest that cyclopropenylsilylene is nearly thermoneutral with silacyclobutadiene and over 30 kcal mol^{-1} more stable than silatetrahedrane.[14] The presence of a significant activation barrier for the isomerization of the silylene would thus account for the apparent thermal stability of 12.

Acknowledgment. We wish to thank Dr. William Pennington and Molecular Structure Corp. for their assistance in the reported X-ray structure. We also wish to thank the Tulane University Committee on Research for support of this project.

Supplementary Material Available: Complete listings of atomic coordinates and bond lengths and angles (24 pages); a listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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(13) A similar disproportionation of silyl radicals to form silylene and silane has been observed in the gas phase. Reimann, B.; Matten, A.; Lavpert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1977,** *81,* 500–504. We favor the radical disproportionation mechanism in our system on the basis of deuterium-labeling experiments. For instance, the photolysis of the Si–D isotopomer of 9 in EtOH gives mostly the C–D isotopomer of 8. Complete details of these labeling experiments will be described in a future paper.

(14) Schriver, G. W.; Fink, M. J.; Gordon, M. S., submitted for publication in *Organometallics.*

Characterization of Bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) Using Extended X-ray Absorption Fine Structure

Kunio Mochida,* Akira Fujii, and Noriko Tsuchiya

Department of Chemistry, Faculty of Science
Gakushuin University
1-5-1 Mejiro, Tokyo 171, Japan

Kazuyuki Tohji and Yasuo Udagawa*

Institute for Molecular Science (IMS)
Okazaki, Aichi 444, Japan

Received June 13, 1986

Summary: Bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) was characterized by extended X-ray absorption fine structure (EXAFS).

Although germylenes R_2Ge have received attention as reactive intermediates in synthetic chemistry and reaction mechanism,[1] there is no report on the direct observation of germylenes in solution. The technique of the direct observation of germylenes has been limited to the matrix isolation until now.[2] In this communication, we report the first direct observation of germylene, bis(2,4,6-tri-*tert*-butylphenyl)germanium(II), in solution by extended X-ray absorption fine structure (EXAFS).

The synthesis of bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) (1) was carried out similarly as described in literatures.[3,4] Thus, after the addition of germanium(II) iodide (0.82 g, 2.5 mmol) to a solution of 2,4,6-tri-*tert*-butylphenyl bromide (1.63 g, 5.0 mmol) in tetrahydrofuran (THF) (20 mL) and *n*-butyllithium (5.0 mmol) in hexane at −78 °C, the resulting mixture was stirred at the same temperature for 2 h and then warmed to room temperature.[4]

EXAFS measurements were performed by using the laboratory EXAFS spectrometer reported elsewhere.[5] The sample was transferred from a reacting vessel to a Pyrex flat cell (path length $\approx$ 2 mm) in an argon atmosphere in order to avoid decomposition by moisture, and the cell was sealed after the sample was degassed.

EXAFS is the most suitable method because it can tell the kinds of interatomic distances in the first several coordination shells surrounding the absorbing atom in a multicomponent system.[6]

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(4) Lange, L. L.; du Mont, W.-W. *Angew. Chem.*, in press (z 2157). Bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) (1) (λ_{max} = 420 nm in THF) can be prepared from GeI_2/BuLi/2,4,6-tri-*tert*-butylphenyl bromide in THF at −78 °C in high yields. Compound 1 was identified by reported ^{1}H and ^{13}C NMR spectra.

(5) For example: Tohji, K.; Udagawa, Y.; Kawasaki, T.; Masuda, K. *Rev. Sci. Instrum.* **1983,** *54,* 1482.

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