antibonding Rydberg state of methane (10 eV above the HOMO of methane in the gas phase) with unoccupied states of the metal. The excitation energy for photodissociation is reduced to about 7 eV with increasing number of metal atoms up to 10. The excitation energy depends strongly on the cluster size because electron redistribution over the metal atoms plays an important role in stabilizing this charge-transfer state.[23]

Another way to understand the excitation mechanism is given by recent slab local density approximation (LDA) calculations on CH_4/Pd(111). The equilibrium distance z between the Pd surface plane and the C nucleus is calculated to be 3 Å.[25] When complete charge transfer to the substrate is assumed in the excited state of methane, the image force stabilizes the excited state by 1.9 eV.[26] The ionization potential of physisorbed methane should then be reduced by 1.9 eV plus the work function of Pd(111). With a work function of 5.6 eV[27] and a gas-phase ionization potential of 12.6 eV,[28] the excitation energy for the complete charge transferred state is calculated to be 5.1 eV, which is accessible with a 6.4 eV photon. Within this model, the increased probability for methane photodissociation at larger clusters can be explained in terms of increased image force expected from the stronger interaction with methane.

In conclusion, adsorption states, photodissociation, and photodesorption of methane at $\lambda = 193$ nm on Pd clusters of various sizes on a thin epitaxial Al_2O_3 film show very pronounced size effects and remarkable differences to the behavior on Pd(111) single-crystal surfaces. These results strongly suggest that metal clusters of different sizes and shapes provide a unique way for controlling both photochemical and thermal reactions of hydrocarbons at metal surfaces.

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[18] At this exposure, a $(\sqrt{3} \times \sqrt{3})$R30° LEED pattern of CD_4 is formed on Pd(111).[10]
[19] The typical irradiation condition was 2.5 mJ cm^{-2} per pulse at 4 Hz and at normal incidence to the surface.
[20] We observed m/z 19 (CD_3H) instead of m/z 20 (CD_4) to avoid spurious desorption signals from parts other than the sample surface. Owing to the high sorptivity of palladium with respect to hydrogen adsorption, residual H_2 in the UHV chamber dissociatively adsorbs on Pd clusters to form hydrogen adsorbates during experiment even at pressures below 10^{-10} mbar. However, this enables the background-free measurement of the recombinative reaction $CD_3(ads) + H(ads) \rightarrow CD_3H(g)$.
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Synthesis, Characterization, and Crystal Structure of Cyclotrisilene: A Three-Membered Ring Compound with a Si=Si Double Bond**

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Akira Sekiguchi*

The synthesis of several compounds with double bonds involving silicon or germanium has been accomplished[1] following the discovery of $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-trimethylphenyl)[2] and $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (Ad = 1-ada-

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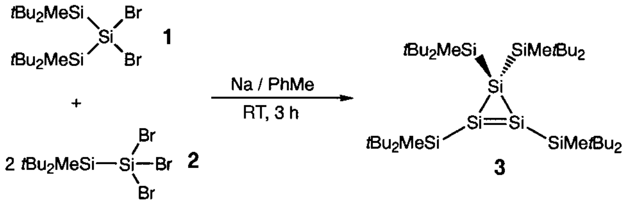
mantyl).[3] Since then, there has been explosive growth in the area of unsaturated compounds of Group 14 elements.[1] In 1996 the first compounds with endocyclic Si–Si double bonds were reported by Kira et al.,[4] and two years later by Wiberg et al. from the reaction of tetrakis(tri-*tert*-butylsilyl)tetrasilatetrahedrane with iodine.[5]

In 1995 we reported the first successful synthesis of cyclotrigermene derivatives containing an unsaturated three-membered ring skeleton and their structural characterization by X-ray crystallography.[6] We have also demonstrated the formation of cyclotrigermenium ions, a free germyl cation with a 2π-electron system, by the oxidation of cyclotrigermenes with trityl tetraarylborates (trityl = triphenylmethyl).[7] Cyclotrisilene (R_4Si_3), analogous to cyclopropene (R_4C_3) and cyclotrigermene (R_4Ge_3), is a very intriguing molecule as it contains a three-membered unsaturated ring. A recent report by Kira et al., which describes the synthesis of cyclotrisilene, prompted us to communicate our own results concerning cyclotrisilene.[8] Herein we report the successful synthesis of symmetrically substituted cyclotrisilene and the first crystal structure of a cyclotrisilene derivative by X-ray crystallography.

For the synthesis of strained molecules, such as cyclotrigermene and cyclotrisilene, it is of prime importance to choose an appropriate protecting group. The stabilization of heavier Main Group element multiple bonds has been largely achieved by using sterically demanding substituents. Theoretical calculations to examine the electronic factor of substituents indicate that electropositive substituents such as silyl groups, are likely to reduce the strain considerably within three-membered rings formed by Group 14 elements.[9] Thus, we have chosen the tBu$_2$MeSi group for protection of the cyclotrisilene ring skeleton.

The reaction of one molar amount of 2,2-dibromo-1,1,3,3-tetra(*tert*-butyl)-1,3-dimethyltrisilane (**1**) and two molar amounts of 2,2,2-tribromo-1,1-di(*tert*-butyl)-1-methyldisilane (**2**) with sodium in toluene led to the immediate formation of a dark red solution which contained tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene (**3**, Scheme 1). The mechanism of the formation of **3** is obscure, although the tBu$_2$MeSi group is essential to the formation of the cyclotrisilene ring. A short reaction time is crucial for the successful isolation of **3**. Prolonged reaction may result in over-reduction. The pure cyclotrisilene **3** was obtained as red-orange crystals by recrystallization from hexane. The cyclotrisilene **3** is air and moisture sensitive, and the color disappears immediately when a solution is exposed to air. However, **3** was thermally stable and melts at 207 °C without decomposition. No reaction occurred with 2,3-dimethyl-1,3-butadiene and *tert*-butyl alcohol at room temperature owing to the large steric congestion.



Scheme 1. Synthesis of **3**.

The structure of **3** was determined by MS and by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as by X-ray crystallography. The NMR data on the structure of **3** in [D$_6$]benzene indicate a highly symmetrical structure. Thus, in the ^{1}H and ^{13}C NMR spectra of **3** in [D$_6$]benzene, only two kinds of signals arising from the tBuMe$_2$Si groups are observed (see experimental section). The ^{29}Si NMR spectrum showed signals at $\delta = -127.3$, 7.9, 27.1, and 97.7. The signal at lowest field ($\delta = 97.7$) is assigned to the unsaturated silicon atoms of tBu$_2$MeSi–*Si*=, and the signal at high field ($\delta = -127.3$) can be assigned to the saturated ring silicon atom of (tBu$_2$MeSi)$_2$*Si*. The mass spectrum showed no molecular ion peaks, but showed a very weak peak at *m/z* 656 [$M^+ - t$Bu] and relatively intense peaks in the mass range of *m/z* 555–560, which are in agreement with the formula $C_{27}H_{63}Si_6$. The latter peaks are attributable to the tris(di-*tert*-butylmethylsilyl)cyclotrisilenium ion by loss of a tBu$_2$MeSi group.

The molecular structure of **3** has been confirmed by X-ray crystallography (Figure 1).[10] The crystal structure shows that, crystallographically, the molecule has no symmetry. The geometry around the Si–Si double bond is not planar, as determined by the sum of the bond angles of the unsaturated silicon atoms (357.5° for Si1 and 358.1° for Si2). The cyclo-

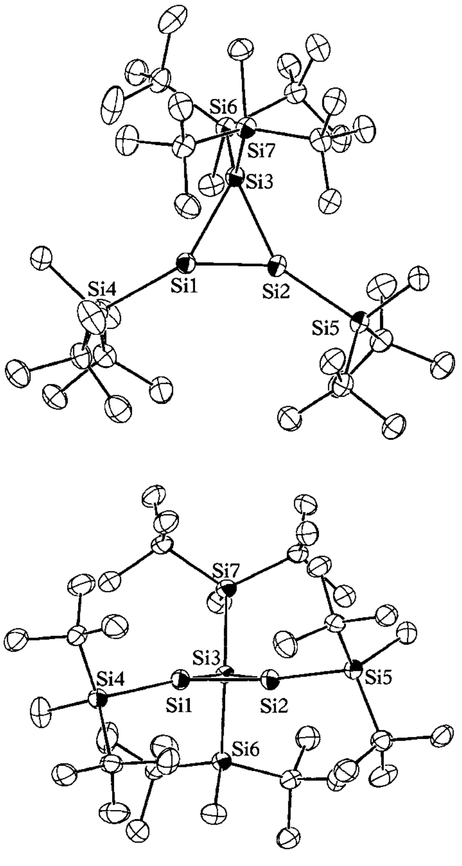


Figure 1. ORTEP representations of the structure of **3**. Top: top view. Bottom: side view (hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angles [°], and torsional angle [°]: Si1–Si2 2.138(2), Si1–Si3 2.364(3), Si1–Si4 2.371(3), Si2–Si3 2.352(3), Si2–Si5 2.367(3), Si3–Si6 2.401(3), Si3–Si7 2.403(3); Si2-Si1-Si3 62.8(1), Si2-Si1-Si4 146.4(2), Si3-Si1-Si4 148.3(1), Si1-Si2-Si3 63.3(1), Si1-Si2-Si5 146.3(2), Si3-Si2-Si5 148.5(2), Si1-Si3-Si2 53.9(1), Si6-Si3-Si7 122.0(1); Si4-Si1-Si2-Si5 31.9(2).

trisilene has a twisted Si–Si double bond probably as a consequence of the eclipsed arrangement of the two tBu$_2$MeSi groups attached to the unsaturated silicon atoms, whereas the tBu$_3$Si-substituted cyclotrigermene has a planar Ge–Ge double bond. The torsional angle of Si4-Si1-Si2-Si5 is 31.9(2)°. The Si=Si bond length of **3** is 2.138(2) Å, which is one of the shortest distances among the Si–Si double-bonded species reported so far (2.138 – 2.261 Å).[11] The Si–Si single bond lengths in **3**, especially the bond distances between the saturated silicon atom in the three-membered ring and the substituents (2.401(3) Å for Si3–Si6 and 2.403(3) Å for Si3–Si7), are somewhat longer than the normal Si–Si bond length (2.34 Å). The three-membered ring is almost an isosceles triangle with bond angles of 62.8(1), 63.3(1), and 53.9(1)°.

Experimental Section

3: A mixture of **1** (1.01 g, 2.01 mmol) and **2** (1.78 g, 4.19 mmol) in toluene (10 mL) was added to a dispersion of sodium (0.95 g, 41.3 mmol) in toluene (10 mL) at room temperature. The reaction was followed by gas chromatography, with **2** disappearing after three hours. At this time 44% of **1** remained. The resulting salts and excess sodium were removed by filtration, and then the solvent was removed in vacuo to give a dark red solid, which contained cyclotrisilene **3** in 34% yield based on the amount of **1** that had reacted. Pure **3** (130 mg, 9.1%) was obtained as red-orange crystals by recrystallization of the reaction mixture from hexane. Air-sensitive red-orange crystals; m.p. 207 – 209 °C; MS (EI, 70 eV): m/z (%): 655 ([$M^+ - t$Bu], 0.2), 555 ([$M^+ - t$Bu$_2$MeSi], 8.6), 73 (100), 59 (11); ^{1}H NMR ([D$_6$]benzene, tetramethylsilane (TMS)): $\delta = 0.42$ (s, 6H), 0.47 (s, 6H), 1.20 (s, 36H), 1.29 (s, 36H); ^{13}C NMR ([D$_6$]benzene, TMS): $\delta = -4.7$, -2.5, 22.2, 23.2, 29.9, 31.2; ^{29}Si NMR ([D$_6$]benzene, TMS): $\delta = -127.3$, 7.9, 27.1, 97.7; UV/Vis (hexane): $\lambda_{\max}$ (ε) = 466 (440), 297 (sh, 1490), 259 (sh, 3610), 223 (7490).

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[8] While our work was in progress we learned that Kira et al. had synthesized 1-tris(*tert*-butyldimethylsilyl)silyl-2,3,3-tris(*tert*-butyldimethylsilyl)cyclotrisilene by a reduction of 1,1-dibromo-3-*tert*-butyl-2,2-di(*tert*-butyldimethylsilyl)-1-chloro-3,3-dimethyltrisilane with KC$_8$. However, no crystal structure is reported and the cyclotrisilene is unsymmetrically substituted, see T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **1999**, *121*, 886.

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[10] A single crystal (0.50 × 0.35 × 0.15 mm) of **3** was sealed in a capillary glass tube, and diffraction data collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The final R factor was 0.071 ($Rw = 0.136$) for 4291 reflections with $I > 3\sigma(I)$. Crystal data: C$_{36}$H$_{84}$Si$_7$, $M_r = 713.67$, monoclinic, space group $P2_1/c$, $a = 24.063(4)$, $b = 11.629(2)$, $c = 17.715(3)$ Å, $\beta = 110.435(1)°$, $V = 4645(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.018$ g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118470. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Kinetic Influences on Enantioselectivity for Non-Diastereopure Catalyst Mixtures

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It has been noted that a partially resolved chiral catalyst or auxiliary may be responsible for a reaction product of significantly higher enantiomeric excess than expected from combination of the separate reactions of the enantiopure catalysts. This nonlinear behavior has been termed an "asymmetric amplification" of product enantioselectivity, and Kagan and co-workers were the first to describe such behavior.[1] Numerous other catalytic and stoichiometric examples have since been reported.[2] This phenomenon has obvious implications for practical organic synthetic strategies, since the cost of producing highly enantiopure catalysts is often cited as a limitation to the broader commercial exploitation of asymmetric catalysis. Indeed, the observation of a nonlinear effect in a chiral borane reagent was recently used to advantage in the pharmaceutical production of an LTD$_4$ antagonist for treatment of asthma (LTD$_4$ = Leukotriene D$_4$).[3]

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