Communications to the Editor

Synthesis, Structure, and Stabilities of *trans*-1,2-Diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene

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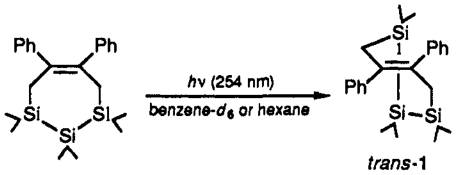
Medium-ring *trans*-cycloalkenes have been the subject of considerable interest as strained cyclic compounds. *trans*-Cyclooctene is well-known as the smallest *trans*-cycloalkene that is stable at room temperature.[1] *trans*-Cycloheptenes have been generated at low temperature and their existence was confirmed by chemical trapping with isobenzofuran[2] or acidic methanol[3] and ^{1}H NMR spectroscopy.[4] Even *trans*-cyclohexene has been generated.[5] However, isolation of the *trans*-cycloheptenes has been unsuccessful except for homoadamant-3-ene stabilized by bulky substituent[6] because of the transient thermal stability caused by the strained structure.[4,7] Recently, we reported the synthesis of pentasilacycloheptyne as the smallest stable polysilacyclic acetylene; it is stabilized by long bond lengths of Si–Si bonds.[8] In the present paper we report the isolation of *trans*-trisilacycloheptene stabilized by long Si–Si bond lengths.

cis-1,2-Diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene (*cis*-**1**) was prepared by the reaction of 2,3-diphenylbutadiene with 1,3-dichlorohexamethyltrisilane in the presence of magnesium in 23% yield. When the benzene-d_6 solution of *cis*-**1** (9.0×10^{-3} M) was irradiated with an 80-W low-pressure mercury lamp through a Quartz NMR tube, it was observed by ^{1}H NMR measurements that the resonances for *cis*-**1** decreased in intensity and new resonances (three singlets at −0.29, 0.37, and 0.39 ppm and an AB quartet at 1.76 and 3.22 ppm, J = 14.0 Hz) appeared upon irradiation. After 5 h, purification by preparative-TLC (hexane) and crystallization gave *trans*-1,2-diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene (*trans*-**1**) in 12.5% yield. Irradiation of a hexane solution of *cis*-**1** also gave *trans* isomer (*trans*-**1**) in 19% yield.



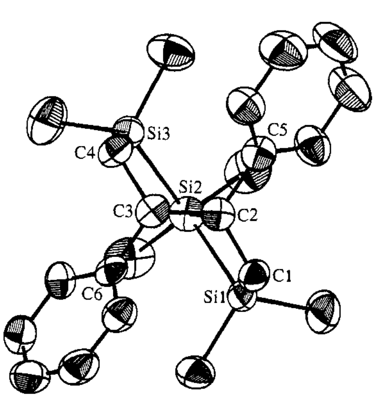


Figure 1. ORTEP plot of *trans*-**1** with hydrogen atoms removed for clarity; selected bond lengths (Å) and bond angles (deg): C(1)–C(2), 1.506 (7); C(2)–C(3), 1.344 (8); C(3)–C(4), 1.515 (8); C(4)–Si(3), 1.905 (6); Si(3)–Si(2), 2.378 (2); Si(2)–Si(1), 2.386 (3); Si(1)–C(1), 1.905 (5); C(1)–C(2)–C(3), 122.4 (5); C(2)–C(3)–C(4), 124.0 (5); C(3)–C(4)–Si(3), 110.0 (3); C(4)–Si(3)–Si(2), 112.9 (2); Si(3)–Si(2)–Si(1), 120.62 (9); Si(2)–Si(1)–C(1), 113.4 (2); Si(1)–C(1)–C(2), 109.6 (4); C(1)–C(2)–C(5), 115.8 (5); C(4)–C(3)–C(6), 113.6 (5); C(3)–C(2)–C(5), 120.5 (5); C(2)–C(3)–C(6), 121.2 (5).

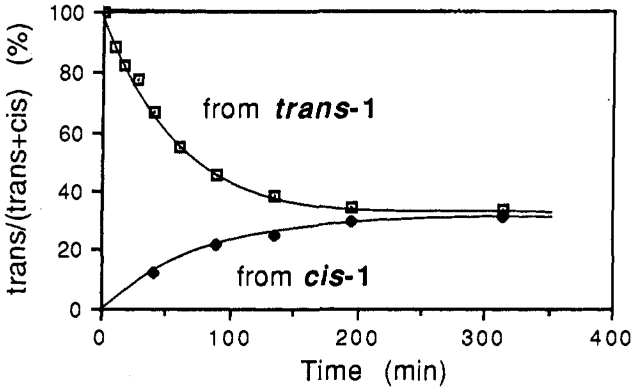


Figure 2. Plot of trans percentage as a function of time for the photo trans–cis isomerization of **1** in benzene-d_6.

The structure of the *trans*-trisilacycloheptene (*trans*-**1**) was determined by NMR, UV, mass, and X-ray analysis.[9,10] The UV spectrum shows characteristic absorption of *trans*-stilbene derivatives at 321 nm (hexane).

The molecular structure of *trans*-**1** was determined by X-ray crystallographic analysis.[10] The X-ray structure of *trans*-**1** is shown in Figure 1. Previously, an unsymmetrical structure was proposed for *trans*-cycloheptene based on ^{1}H NMR measurements[4,11] and force-field calculation.[11] However, the ^{1}H and ^{13}C

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[9] Spectral data of *trans*-**1**: mp 115–117 °C; IR (CCl_4) 3100–2900, 1620–1480, 1250, 1070–1020 cm^{-1}; UV (hexane) 223 (ϵ 7500, sh), 250 (ϵ 2800, sh) 321 (ϵ 2800) nm; ^{1}H NMR (500 MHz, C_6D_6) δ −0.29 (s, 6 H, CH_3), 0.37 (s, 6 H, CH_3), 0.39 (s, 6 H, CH_3), 1.76 (d, J = 14.0 Hz, 2 H, CH), 3.22 (d, J = 14.0 Hz, 2 H, CH), 7.05–7.77 (m, 10 H, Ar); ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.58 (s, 6 H, CH_3), 0.10 (s, 6 H, CH_3), 0.22 (s, 6 H, CH_3), 1.50 (d, J = 14.1 Hz, 2 H, CH), 2.90 (d, J = 14.1 Hz, 2 H, CH), 7.18–7.23 (m, 2 H, Ar), 7.30–7.58 (m, 8 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ −3.4, −0.6, 0.2, 26.6, 126.7, 128.3, 128.4, 136.1, 145.5; ^{29}Si NMR (18 MHz, C_6D_6) δ −44.9 (Si–$\underline{\text{Si}}$–Si), −1.4 ($\underline{\text{Si}}$–Si–$\underline{\text{Si}}$); LRMS, m/e 380, 320, 307, 174, 116; HRMS, m/e calcd for $C_{22}H_{32}Si_3$ 380.1812, found 380.1812.

[10] Crystal data for *trans*-**1**: Compound *trans*-**1** crystallized in the monoclinic space group $P2_1/c$, with a = 8.671 (2) Å, b = 25.238 (0) Å, c = 10.812 (0) Å, β = 101.51 (0)°, V = 2318.6 Å^3, Z = 4, and ρ(calcd) = 1.09 g cm^{-3}. Data were collected on an Enraf-Nonius CAD4 diffractometer at 23 °C. Of the 3184 unique data collected with Mo Kα radiation (λ = 0.70930 Å), the 2022 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield R = 5.2%, R_w = 5.6%.

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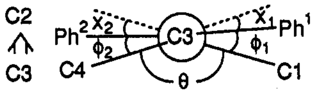
Table I. Time Constants for Thermal Trans–Cis Isomerization of *trans*-Cycloheptenes

compd	solvent	temp, °C	time const, s^{-1}
trans-**1**	DMSO-d_6	80	$1.59\ (\pm 0.10) \times 10^{-6}$
		100	$8.86\ (\pm 0.35) \times 10^{-6}$
		120	$4.72\ (\pm 0.68) \times 10^{-5}$
trans-cycloheptene	MeOH	1.0	1.19×10^{-3}[a]
trans-1-phenylcycloheptene	cyclohexane	ambient	2.77×10^{-3}[b]

[a] Calculated on the basis of ref 15. [b] Calculated on the basis of ref 16.

NMR measurements at room temperature and the X-ray crystallographic analysis of *trans*-**1** show a symmetrical conformation. ^{1}H NMR measurement of *trans*-**1** at low temperature (−70 °C) is also consistent with a symmetrical form. A molecular mechanics calculation (MM2) of *trans*-**1** also supports the symmetrical structure as the one having 11.4 kcal less strain compared with the unsymmetrical form. The most interesting point of the structure of *trans*-**1** is the twisting around the C=C double bond. The torsion angle of C(1)–C(2)–C(3)–C(4) was found to be $180° - \theta = 32.7°$. This value is, however, in fair agreement with the value for the unsymmetrical calculated structure rather than that of the symmetrical form. The twist angle $\Phi\ [=(\phi_1 + \phi_2)/2]$ and the pyramidal deformation $X\ [=(\chi_1 + \chi_2)/2]$ were also found to be 19.6° and 13.2°, respectively. The bond angles around the ring atoms of *trans*-**1** are almost normal except for the expanded Si(1)–Si(2)–Si(3) bond angle. Interestingly, the bond lengths of C(1)–C(2) and C(3)–C(4) are slightly shortened while those of C(1)–Si(1), C(4)–Si(3), Si(1)–Si(2), and Si(2)–Si(3) are stretched from corresponding normal bond lengths. These deformations of the bond angle and lengths must occur to mitigate the twist of the C=C double bond. The C=C double bond [C(2)–C(3) = 1.344 Å] is slightly stretched compared with that of *trans*-stilbene in the solid state (1.228–1.330 Å).[12,13] The expansion of the C=C double bond may result from the twisting of the double bond. Furthermore, two benzene rings incline at 47.3° and 51.1° from the planes of C(3)–C(2)–C(5) and C(2)–C(3)–C(6), respectively, though the torsion angles of *trans*-stilbene are ranged between 3.6 and 5.7° in the solid state.[12]



	θ	ϕ_1	ϕ_2	χ_1	χ_2
X-ray:	**θ = 147.3°**	**ϕ_1 = 19.9°**	**ϕ_2 = 19.2°**	**χ_1 = 12.8°**	**χ_2 = 13.5°**
MM2(symmetrical):	**131.5°**	**42.2°**	**40.7°**	**6.3°**	**7.8°**
MM2(unsymmetrical):	**147.7°**	**31.0°**	**17.2°**	**1.3°**	**15.1°**

Photochemical reaction of *trans*-**1** was examined as a general property of the olefins. Irradiation (254 nm) of *trans*-**1** in benzene-d_6 gave photoisomerized *cis*-**1**. In this isomerization, it was found that a photoequilibrium existed and the photostationary trans/cis ratio was 0.49 (Figure 2). This value is higher than the photosensitized isomerization of *trans*-cycloheptene.[14]

Thermal stabilities of *trans*-**1** were also examined. When a benzene-d_6 solution of *trans*-**1** in an NMR tube was heated at 80 °C, *trans*-**1** was stable even after 72 h. However, heating of the DMSO-d_6 solution at 80 °C tended to initiate the reaction and gave isomerized *cis*-**1**. These results may be explained by stabilization of the transition state caused by solvation with the polar solvent. At several temperatures, the measurements of the trans/cis ratio by ^{1}H NMR at regular time intervals in DMSO-d_6 gave a straight line for a plot of log [*trans*-**1**] as a function of time, and the rate constants obtained are shown in Table I. The rate constants of the thermal trans–cis isomerization are very small compared with those of *trans*-cycloheptene[15] and *trans*-1-phenylcycloheptene.[16] It is found that the introduction of the three silicon atoms in trans-cycloheptene is useful to stabilize the *trans*-trisilacycloheptene. A plot of log κ as a function of reciprocal of temperature also gave a good linear relationship, and the following thermodynamic parameters were obtained: $E_a = 23.2 \pm 1.3$ kcal mol^{-1}, log $A = 8.6 \pm 0.7$, $\Delta G^{\ddagger}_{373} = 30.6 \pm 2.6$ kcal mol^{-1}, $\Delta H^{\ddagger}_{373} = 22.5 \pm 1.3$ kcal mol^{-1}, $\Delta S^{\ddagger}_{373} = -21.7 \pm 11$ cal K^{-1} mol^{-1}. At 120 °C, continued heating gave other minor products, which include 2,3-diphenylbutadiene, *cis*-1,2-diphenyl-4,4-dimethyl-4-silacyclopentene, and *cis*-1,2-diphenyl-4,4,5,5-tetramethyl-4,5-disilacyclohexene which were identified by GCMS and ^{1}H NMR measurements of the mixture and unidentified silicon compounds. These products were found to be formed from *trans*-**1** because the heating of *cis*-**1** under the same conditions gave no reaction.

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Supplementary Material Available: Detailed information of the X-ray crystal analysis of *trans*-**1** including data collection and reductions and structure solution and refinement, the Arrhenius plot for the thermal trans–cis isomerization of **1** in DMSO-d_6, and tables of experimental details, positional and thermal parameters, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, and bond distances and angles (22 pages); listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Observation of a Weakly Bound $Mn(CO)_5^+/CH_4$ Complex

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Intramolecular reductive elimination of an alkane molecule from alkyl hydride organometallic complexes (e.g., $[(Cp)_2Re(H)CH_3]Cl$ and $(Cp)_2W(H)CH_3$) has received considerable attention recently.[1-4] This is partly due to the intense interest in the reverse oxidative addition process, which, in the case of alkanes, results in hydrocarbon activation.[5]

To explain exchange of deuterium from the hydride position with hydrogen in the methyl ligand and an inverse kinetic isotope effect for the elimination of methane, organometallic/methane σ complexes were invoked as intermediates. The structure of the complexes could not be established with certainty, but involvement

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