been inferred to involve mercury orbitals of predominantly p character.[14]

Supplementary Material Available: Tables of bond distances and angles, structure factors, and positional and thermal parameters (10 pages). Ordering information is given on any current masthead page.

(14) Dent Glasser, L. S.; Ingram, L.; King, M. G.; McQuillan, G. P. *J. Chem. Soc. A* **1969**, 2501.

Tetrasilabicyclo[1.1.0]butane System: Preparation and Characterization of 1,3-Di-*tert*-butyl-2,2,4,4-tetrakis-(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]butane

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We wish to report herein the synthesis and characterization of the title compound **1** (R = *tert*-butyl in Scheme I), which represents the first tetrasilabicyclo[1.1.0]butane derivative. Although no mention of this system has been made in the literature,[1–3] the anticipated reactivity attributed to its intrinsic strains attracts great interest.[4] It has now been found that the central Si(1)–Si(3) bond of compound **1** is readily susceptible to a variety of external attacks and the puckered ring system itself undergoes rapid inversion (**1** ⇌ **1a**).

Synthesis of 1 (Scheme II). Reaction of trichlorosilane **2** (1 equiv) with (2,6-diethylphenyl)lithium (2 equiv), prepared from the corresponding bromide and *tert*-butyllithium, led to the formation of chlorobis(2,6-diethylphenyl)silane **3** (73% yield),[5] which after metalation with lithium was condensed with *tert*-butyl-chlorosilane (1 equiv)[6] to provide the disilane **4** (41%).[5] Treatment of **4** with chlorine (ca. 3.5 equiv, 2 M, CCl_4) yielded the corresponding trichloro compound **5** of 88% purity (71%)[5] which was

(1) Other strained silicon systems which are known include cyclotrisilanes (a–h) and spiropentasilane (i): (a) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (b) Masamune, S.; Tobita, H.; Murakami, S. *Ibid.* **1983**, *105*, 6524. (c) Murakami, S.; Collins, S.; Masamune, S. *Tetrahedron Lett.* **1984**, *25*, 2131. (d) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333. (e) Dewan, J. C.; Murakami, S.; Snow, J. T.; Collins, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1985**, 892. (f) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *Ibid.* **1983**, 781. (g) Watanabe, H.; Kougo, Y.; Nagai, Y. *Ibid.* **1984**, 66. (h) Schafer, A.; Weidenbruch, M.; Peters, K.; v. Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302. (i) Boudjouk, P.; Sooriyakumaran, R. *J. Chem. Soc., Chem. Commun.* **1984**, 777.

(2) For the 2,4-disilabicyclo[1.1.0]butane system, see: (a) Fritz, G.; Thomas, J. *J. Organomet. Chem.* **1984**, *271*, 107. (b) Fritz, G.; Wartanessian, S.; Matern, E.; Honle, W.; V. Schnering, H. G. *Z. Anorg. Allg. Chem.* **1981**, *475*, 87.
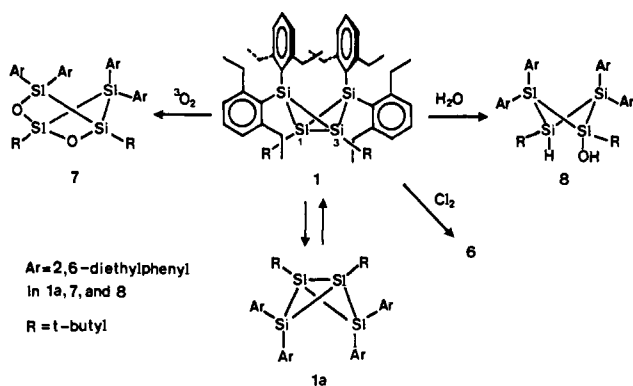
(3) (a) Tetraphospha- and (b) tetraarsabicyclo[1.1.0]butane derivatives have been reported: (a) Niecke, E.; Ruger, R.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 544. (b) Baudler, M.; Wietfeltd-Haltenhoff, S. *Ibid.* **1984**, *23*, 379.

(4) Cf. the chemistry of (carbon) bicyclo[1.1.0]butane. Wiberg, K. B. In "Advances in Alicyclic Chemistry"; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1968; pp 185–205; vol. 2.
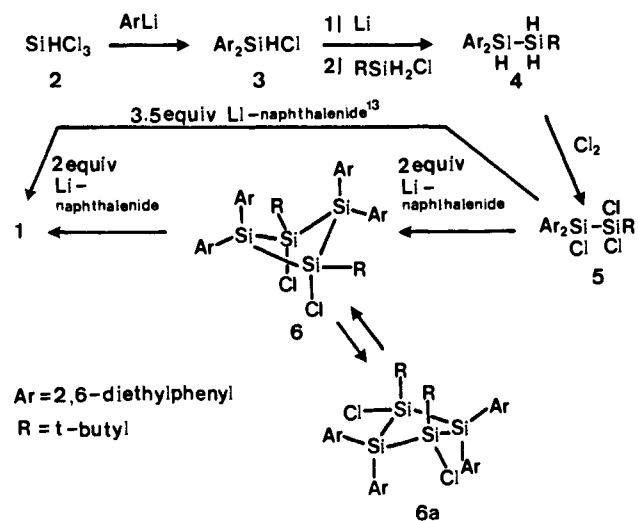
(5) Physical properties of all new compounds and UV and temperature-dependent NMR spectra of **1** are provided in the supplementary material. Complete experimental details for Scheme II are available from S.M. upon request.

(6) Collins, S.; Duncan, J. A.; Kabe, Y.; Murakami, S.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 2837.

Scheme I

Ar=2,6–diethylphenyl
in **1a**, **7**, and **8**

R = t–butyl

Scheme II

Ar = 2,6–diethylphenyl

R = t–butyl

in turn reductively cyclized with 2 equiv of lithium naphthalenide. The resulting compound **6** (see below), the only isolable cyclotetrasilane, has cis-oriented chloro substituents and exists in solution as a ca. 3:1 mixture of two conformers (**6** ⇌ **6a**).[7]

The final step, the formation of the central Si–Si bond of **1**, proceeded quantitatively, but during the entire operation, including workup, the contact of **1** with air and moisture had to be strictly avoided. Thus, addition of a 1 M solution (2 equiv) of lithium naphthalenide in dimethoxyethane to a 6 mM solution of **6** in toluene at 0 °C produced a pale yellow solution containing suspended solids. The solvent was removed in vacuo and dry, degassed hexane was introduced by vacuum transfer. The mixture was filtered, the filtrate concentrated in vacuo, and naphthalene removed by sublimation at 0.005 mmHg. The resulting pale yellow solid residue was dissolved in dry, degassed hexane and filtered again. The filtrate was concentrated upon slow evaporation of the solvent in a glovebox to provide pale yellow thermochromic[8] crystals (decomposition at ~240 °C) that exhibit the following physical and chemical properties fully consistent with the bicyclobutane structure **1**.

Physical Properties of 1. (1) mass spectrum (EI), m/z calcd for $C_{48}H_{70}Si_4$ 758.4555, for $C_{44}H_{61}Si_4$ 701.3851; found 758.4558 (M$^+$, 14.9%), 701.3855 (M$^+$-t-C_4H_9, 100%). (2) UV (cyclo-

(7) **6**: 290–300 °C dec; ^{1}H NMR (250 MHz, C_6D_6, at 25 °C) δ 0.37 ~ 0.58 (12 H, m, CH$_3$), 0.78 (4.5 H, s, t-Bu), 1.22 (13.5 H, s, t-Bu), 1.23 (6 H, t, 7 Hz, CH$_3$), 1.28 (2 H, t, 7 Hz, CH$_3$), 1.45 (1 H, t, 7.4 Hz, CH$_3$), 1.56 (3 H, t, 7.4 Hz, CH$_3$), 2.52~2.94 (8 H, m, CH$_2$), 2.94~3.45 (7 H, m, CH$_2$), 3.58~3.72 (1 H, m, 7.4 Hz, CH$_2$), 6.75~6.93 (8 H, m, meta Ar), 7.10, 7.24 (4 H, m, para Ar); mass spectrum (EI), calcd m/z for $C_{48}H_{70}Si_4Cl_2$ 828.3932, found 828.3925 (M$^+$). Two sets of signals are discernible in the ^{1}H NMR spectrum and any pair of signals that are assignable to the same proton of compound **6** has a relative intensity 3:1 and merges at high temperatures (decalin-d_{18}, 160 °C). This spectral behavior is inconsistent with the assignment of a *trans*-dichloro configuration to **6**.

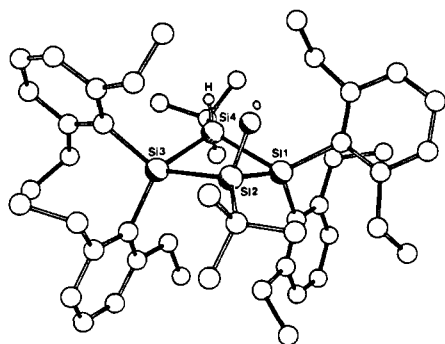(8) Intensely yellow at 170 °C, colorless at –196 °C.

Figure 1. Crystal structure of **8**. Si–Si bond lengths (Å): 2.396 [Si-(1)-Si(2)], 2.428 [Si(1)-Si(4)], 2.411 [Si(2)-Si(3)], 2.400 [Si(3)-Si(4)]. Ring angles (deg): 80.9° [at Si(1)], 93.9° [Si(2)], 81.2° [Si(3)], 93.4° [Si(4)]. Interatomic distance (Å) between Si(2) and Si(4): 3.13. Dihedral angle between Si(1),Si(2),Si(3) and Si(1),Si(4),Si(3) planes (deg): 143.4°. (The silicon numbering shown above does not conform with the IUPAC system.)

hexane, 25 °C) λ_{max} 256 nm (log ϵ, 4.45); $\lambda_{shoulder}$ 275 (4.36), 304 (4.20); tailing off into the visible region.[5] (3) ^{1}H NMR (decalin-d_{18}); the NMR spectra measured at −50–120 °C, all having a singlet assignable to the *tert*-butyl groups of **1**, are temperature dependent and the dynamic behavior of **1** is best analyzed by the inspection of the methylene region (δ 2.2–3.6). Thus, at -31 °C (250 MHz) more than six partially overlapping, well-defined multiplets (of roughly equal intensity) are discernible in this region (250 MHz).[5] Due to the obvious steric congestion of the substituents, the rotation of the aromatic rings along the axis of the carbon–silicon bond is frozen at -31 °C in terms of the NMR time scale. This rotation proceeds at 2 °C to the extent that the molecule attains roughly 2-fold symmetry as indicated by the appearance of the three broad methylene signals (δ 2.45, 2.87, 3.34; relative intensity 1:2:1) (see stereostructure **1**). Signals further coalesce in both the methylene (broad singlet, δ 2.70) and methyl (broad singlet, δ 0.77) regions as the temperature is raised to 60 °C, and the 90-MHz spectrum taken at 115 °C[5] simply consists of an AB$_2$ multiplet (δ 7.06, 6.79; J = 6.5 Hz) for the aromatic protons, a typical quartet–triplet pair (δ 0.80, 2.70; J = 7 Hz) for the ethyl groups, and a singlet (δ 1.21) for the *tert*-butyl groups. Thus, all the aryl rings have become equivalent. This observation is best explained by reversible ring inversion (Scheme I, **1** ⇌ **1a**) involving a planar intermediate or transition state in addition to the rapid rotation of the aryl rings at this temperature.[9] Since the former process is undoubtedly accompanied by significant stretching of the central Si–Si bond, a lower limit for its strength can be roughly estimated to be 15 kcal/mol[10] from the coalescence temperature observed.

Chemical Properties of 1. The reactivity of the central bond is extremely high even with the bulky sustituents present. Thus, **1** instantly reacts with dioxygen to provide as the major product the corresponding dioxo derivative to which structure **7** is assigned based mainly on its ^{1}H NMR spectrum.[11] Addition of degassed water to a solution of **1** at room temperature effects quantitative hydration of **1** to provide *cis*-1,3-di-*tert*-butyl-2,2,4,4-tetrakis-

(2,6-diethylphenyl)-1-hydroxycyclotetrasilane (**8**),[12,13] the crystal structure of which is shown in Figure 1.[14] Treatment of **1** with a equimolar amount of Cl$_2$ in hexane at 0°C regenerates **6** in high yield. Note that both the hydration and the chlorination proceed in a cis fashion. Further studies on the tetrasilabicyclobutane system are in progress.

Supplementary Material Available: Detailed information of the X-ray crystal analysis of **8** and listing of physical properties of all new compounds and UV and temperature-dependent ^{1}H NMR spectra of **1** (12 pages). Ordering information is given on any current masthead page.

(9) Cf.: Gassman, P. G.; Greenlee, M. L.; Dixon, D. A.; Richtsmeier, S.; Gougoutas, J. Z. *J. Am. Chem. Soc.* **1983**, *105*, 5865.

(10) This estimate based on the 2 and 60 °C (250 MHz) spectra is obviously crude since aryl ring rotation is occurring simultaneously. No attempt has been made to separate these processes by line-fitting studies due to the complexity of the system.

(11) **7**: Amorphous solid; IR (KBr) 1450 (ν SiAr), 1050 cm^{-1} (ν SiOSi); ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 0.43 (3 H, t, 7 Hz, CH$_3$), 0.46 (3 H, t, 7 Hz, CH$_3$), 0.78 (3 H, t, 7 Hz, CH$_3$), 0.97 (3 H, t, 7 Hz, CH$_3$), 1.05 (3 H, t, 7 Hz, CH$_3$), 1.13 (9 H, s, *t*-Bu), 1.16 (3 H, t, 7 Hz, CH$_3$), 1.37 (9 H, s, *t*-Bu), 1.42 (3 H, t, 7 Hz, CH$_3$), 1.43 (3 H, t, 7 Hz, CH$_3$), 1.82 (2 H, m, 7 Hz, CH$_2$), 2.43 (2 H, m, 7 Hz, CH$_2$), 2.59 (2 H, q, 7 Hz, CH$_2$), 2.83 (4 H, m, CH$_2$), 3.08 (2 H, m, CH$_2$), 3.45 (2 H, dq, 7 Hz, CH$_2$), 3.61 (2 H, m, CH$_2$), 6.57, 7.24 (12 H, m, meta, para Ar); mass spectrum (EI), calcd m/z for C$_{48}$H$_{70}$-O$_2$Si$_4$ 790.4453, found 790.4455. The ^{1}H NMR spectrum is interpreted as eight nonequivalent methyl and methylene absorptions. Compound **7** is unstable with respect to further oxygenation in solution, so a larger fragment corresponding to C$_{48}$H$_{70}$O$_3$Si$_4$ is detectable in the mass spectrum.

(12) **8**: 209–220 °C dec; IR (KBr) 3600 (ν SiOH), 2040 (ν SiH), 1450 (ν SiAr), 1050 cm^{-1} (ν SiOH); UV (cyclohexane) λ_{max} 274 nm (log ϵ 4.42), 330 (2.90); ^{1}H NMR (250 MHz, C$_6$D$_6$) δ 0.64 (6 H, t, 7 Hz, CH$_3$), 0.75, 1.75 (12 H, brs, CH$_3$), 1.05 (6 H, t, 7 Hz, CH$_3$), 1.08 (9 H, s, *t*-Bu), 1.16(9 H, s, *t*-Bu), 1.53 (1 H, s, SiOH), 2.75, 3.75 (8 H, brs, CH$_2$), 2.87 (8 H, q, CH$_2$), 4.63 (1 H, s, SiH), 6.90~7.24 (12 H, m, para Ar); mass spectrum (EI), calc m/z for C$_{48}$H$_{72}$OSi$_4$ 776.4660, found 776.4651. The ^{1}H NMR spectrum indicates that four of the eight ethyl groups are subject to hindered rotation.

(13) Treatment of **5** in dimethoxyethane with 3.5 equiv. of lithium naphthalenide at 0 °C followed by aqueous workup gave rise to **8** in ca. 41% yield, whereas the isolation of **6** was successful only to the extent of 7% yield.

(14) Crystals of C$_{48}$H$_{62}$OSi$_4$ (**8**) M = 767.3 are monoclinic with a = 11.468 (3) Å, b = 24.025 (8) Å, c = 16.734 (4) Å, β = 94.98 (2)°, U = 4594 Å^3, space group $p2_1/n$, Z = 4, μ(Cu Kα) = 14 cm^{-1}, D_c = 1.11 g cm^{-3}. Data were measured with Cu Kα radiation on a Nicolet R3m diffractometer using ω scans. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically by full-matrix least squares to R = 0.050 for 4477 independent observed reflections [$|F_0| > 3\sigma(|F_0|)$, $\theta \leqslant 50°$]. The X-ray analysis reveals a disordered structure which has an approximate, noncrystallographic, 2-fold axis normal to the plane of the cyclotetrasilane ring. The disorder is confined to the axial hydroxy group which has equal (50%) site occupancies on both Si(2) and Si(4).

Fluxional Behavior in the Solid State: Bullvalene

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The study of dynamical behavior in the crystalline state is of particular interest as—in contrast to the situation in liquid phase—the environment of the single molecule is well-defined and its geometry is often accurately known from X-ray structure studies. In addition, the solid state normally allows a much bigger temperature range to be investigated. In many cases, lattice forces greatly influence the dynamics in solids.[1–6] For example, it has been demonstrated that the Cope rearrangement in semibullvalene, which takes place easily in the liquid state, is drastically hindered in one of the solid phases, whereas in the other phase the de-

(1) Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396.
(2) Macho, V.; Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3735.
(3) Fyfe, C. A. "Solid State NMR for Chemists"; C.F.C. Press: Ontario, 1983.
(4) Shiau, W. I.; Duesler, E. N.; Paul, I. C.; Curtin, D. Y.; Blann, W. G.; Fyfe, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 4546.
(5) Szeverini, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Reson.* **1982**, *47*, 462.
(6) Meier, B. H.; Graf, F.; Ernst, R. R. *J. Chem. Phys.* **1982**, *76*, 767.