drawing of the molecular geometry of **2** is shown in Figure 1, together with the selected bond distances and angles.

In contrast to the prediction from the ab initio results, **2** had a rather normal trigonal-bipyramidal (TBP) structure around the pentacoordinate silicon atom, where the triphenylsilyl group occupied the equatorial position: the distance of the silicon–silicon bond was 240,3 ppm, which was unexpectedly normal in comparison to the usual $Si(sp^3)$–$Si(sp^3)$ bonds.[11] Martin et al. have already reported the X-ray analyses of the fluoro- (**4**)[12] and phenyl- (**5**)[13] substituted silicates having the same residual ligand as **2**.
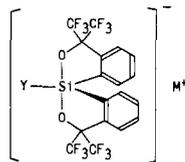
4: Y=F, M⁺=(Me₂N)₃S⁺
5: Y=Ph, M⁺=Me₄N⁺
6: Y=n-Bu, M⁺=Et₄N⁺

Electronegative equatorial ligands should effectively render the silicon atom more electronegative in nature and therefore decrease the atomic radius to result in shortening of the Si–O bonds.[13] In accord with this argument, **2** with an electropositive silyl ligand showed the longest distance of Si–O bonds among **2**, **4**, and **5**. Unexpectedly, the Si–C bond lengths of **2** were even shorter than those of **4** and **5**.

Interestingly, among the known spirobicyclic silicates, **2** has the highest TBP character of the geometry around the pentacoordinate silicon atom (78.2% of TBP character measured by using the dihedral angle method employing unit vectors[14]). The TBP character may depend on the electronic nature of ligands. Further investigation is required for elucidating the relationship as well as its origin.

In the UV spectra, absorption maxima of **2** and **3** appeared at 252 nm (ϵ 17 400, dichloromethane) and 254 nm (ϵ 8800, diethyl ether), respectively. It is clear that the existence of the Si–Si σ bond is responsible for the absorption, because the related pentacoordinate butylsilicate **6**[13] did not show the absorption maxima longer than 200 nm. Both **2** and **3** showed the absorption maxima at longer wavelength than tetracoordinate phenyldisilanes (240 nm for 1,1,2,2-tetraphenyldimethyldisilane and 247 nm for hexaphenyldisilane).[15] The results are suggestive of the high-lying Si–Si σ bonding orbital in the pentacoordinate silylsilicates, because the ^1L_a electronic transition of the phenyldisilanes has been regarded essentially to be the transition from the Si–Si σ bonding orbital to the phenyl π^* orbital.[16]

Further works are in progress.

(10) Crystal data of **2** [$C_{44}H_{43}F_{12}NO_2Si_2$ (fw 901.7)] are as follows: monoclinic space group *Aa*; $a = 19.142$ (2) Å, $b = 18.263$ (2) Å, $c = 12.514$ (1) Å; $\beta = 105.03$ (1); $V = 4225.0$ (9) Å³; $D_{calcd} = 1.41$ g/cm³ ($Z = 4$). A total of 3659 independent reflections were collected on a Rigaku AFC-5R diffractometer using graphite monochromated Mo- Kα radiation. The final R factor was 0.047 for 2792 reflections with $F_o > 3\sigma(F_o)$.

(11) The Si–Si bond orbital would formally be described by the overlap between an sp³ orbital on the tetragonal Si atom and an sp² orbital on the pentacoordinate Si atom. The detailed feature of the Si–Si bonding may be obtained by elucidating the molecular orbitals. Studies along this line are in progress.

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Isolation and Characterization of 1,2-Dilithio[tetrakis(trimethylsilyl)]ethane. The First Crystal Structure of Nonconjugated 1,2-Dilithioethane[1]

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Recently we have reported unusual chemical and physical properties of tetrakis(trimethylsilyl)ethylene (**1**) due to $\sigma(Si–C)$–π mixing resulting from the distorted nonplanar structure in the ground state.[2] An interesting feature of **1** is that a cation radical was readily generated upon oxidation with aluminum trichloride, and also an anion radical and subsequently a dianion were formed by reduction with alkali metals. The existence of the dianion **2** of **1** has been indicated only in solution, though. We now wish to report herein synthesis and characterization of 1,2-dilithio[tetrakis(trimethylsilyl)]ethane, the first stable alkyl-substituted 1,2-dilithioethane derivative as well as its chemical reactions.

The renewed interest in the reactivity, structure, and bonding of organolithium compounds has remarkably increased in recent years.[3] Dilithioalkanes such as 1,3-dilithiopropane, 1,4-dilithiobutane, and higher α,ω-dilithioalkanes are available by the direct lithiation of dihaloalkanes[4] or transmetallations.[5] The structure of dilithium trimethyl[(phenylsulfonyl)methyl]silane, the first 1,1-dilithiomethane derivative, is also demonstrated very recently.[6] Although 1,2-dilithioethane has been briefly described as a black-gray amorphous substance[7] or as a reaction intermediate,[8] the structural proof is ambiguous.

Reduction of **1** (162 mg, 0.51 mmol) with excess lithium metal (ca. 70 mg) in dry-oxygen free THF (10–15 mL) at room temperature under argon at first gives a dark green solution of the anion radical of **1** (λ_{max} 697 nm). Further reduction of the anion radical leads to a dark red solution of the dianion with long tailing of the absorption into a visible region. Reduction to the dianion completes within a few hours. The resulting mixture was filtered, the solvent was removed in vacuo, and then dry degassed hexane was introduced by vacuum transfer. Crystallization at –10 °C in hexane afforded yellow crystals of the tetrahydrofuran adduct

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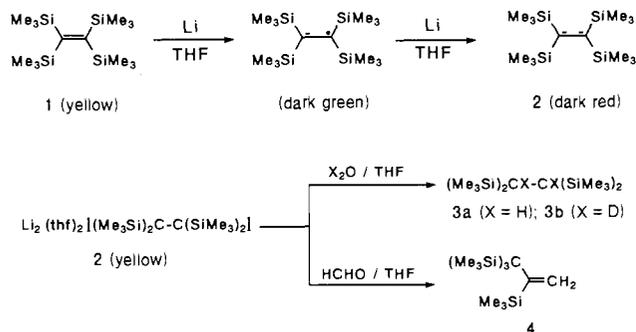
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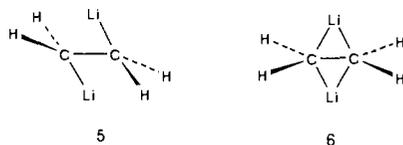
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Scheme I

1 (yellow)   (dark green)   2 (dark red)

Li$_2$(thf)$_2$[(Me$_3$Si)$_2$C-C(SiMe$_3$)$_2$]

2 (yellow)

X$_2$O / THF → (Me$_3$Si)$_2$CX-CX(SiMe$_3$)$_2$
3a (X = H); 3b (X = D)

HCHO / THF → (Me$_3$Si)$_3$C\=CH$_2$
                    Me$_3$Si
                    4

Scheme II

5   6

of 1,2-dilithio[tetrakis(trimethylsilyl)]ethane, Li$_2$(thf)$_2$-[(Me$_3$Si)$_2$C—C(SiMe$_3$)$_2$] (2).[9]

The dilithium compound 2[10] is extremely air and moisture sensitive and immediately reverted to 1 on exposure to traces of air. The reactions with H$_2$O and D$_2$O cleanly produced 3a[11] and 3b,[12] respectively. The reaction with paraformaldehyde afforded 4 (73%)[13] probably via 1,2-anionic rearrangement of the silyl group. In contrast, electron-transfer reactions took place with aromatic ketones.[14]

^{1}H as well as ^{13}C NMR spectroscopy of the yellow crystals reveals that two molecules of the tetrahydrofuran tightly binds to lithium since the values of the chemical shifts of THF are significantly different from those of the free one. An interesting point is that the anionic carbon of 2 was observed at 9.8–10.6 ppm as an unresolved multiplet resulting from ^{13}C and Li spin coupling. The spectra did not change appreciably in the temperature range of 220–298 K (in toluene-d_8). The chemical shift of ^{29}Si slightly shifted to the upfield compared to 1 due to the negative charge (−8.4 ppm for 1, −12.7 ppm for 2). ^{7}Li NMR signal appeared at 1.39 ppm ($\nu_{1/2}$ = 9 Hz) similar to those in alkyllithiums.[15]

The structure of 2 has been unequivocally determined by X-ray crystallography.[16] The lithium atoms are three-coordinated, being

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(9) The synthesis of the dilithium compound requires high-vacuum line techniques and carefully deoxygenated solvents. During the entire manipulations, the contact with air and moisture should be strictly avoided.

(10) Compound 2: ^{1}H NMR (C$_6$D$_6$) δ 0.60 (s, 36 H, SiMe$_3$), 1.25 (m, 8 H, THF), 3.59 (m, 8 H, THF); ^{13}C NMR (C$_6$D$_6$, ^{1}H-decoupled) δ 8.49 (s, SiMe), 9.8–10.6 (m, Li–C), 25.3 (s, THF), 69.3 (s, THF); ^{7}Li NMR (C$_6$D$_6$) δ 1.39 ppm (from LiCl in MeOH); ^{29}Si NMR (C$_6$D$_6$) δ −12.7 ppm. Chemical shifts of ^{1}H, ^{13}C, and ^{29}Si NMR are in δ values down field from tetramethylsilane.

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(12) Compound 3b: ^{1}H NMR (C$_6$D$_6$) δ 0.23 (s, 18 H), 0.32 (s, 18 H); ^{13}C NMR (CDCl$_3$) δ 0.91, 3.14, 10.5 (t, J_{C-D} = 16 Hz); ^{29}Si NMR (CDCl$_3$) δ 1.06, 4.19; high resolution MS calcd for C$_{14}$H$_{36}$D$_2$Si$_4$ 320.2176, found 320.2137.

(13) Compound 4: ^{1}H NMR (C$_6$D$_6$) δ 0.25 (s, 9 H), 0.28 (s, 27 H), 5.88 (s, 1 H), 5.93 (s, 1 H); ^{13}C NMR (C$_6$D$_6$) δ 3.94, 5.52, 23.6, 134.1, 152.7; ^{29}Si NMR (C$_6$D$_6$) δ −1.76, 0.35; MS (20 eV) 330 (M$^+$); high resolution MS calcd for C$_{15}$H$_{38}$Si$_4$ 330.2051, found 330.2051.

(14) The reaction of 2 with benzophenone gave benzophenone anion radical (λ = 626 nm), whereas with acetophenone, 2,3-diphenyl-2,3-butanediol was obtained. In both cases, 1 was produced quantitatively.

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(16) Being extremely air and moisture sensitive, crystals of 2 are sealed in a capillary glass tube for data collection. A total of 2416 data were collected on a Rigaku-Denki automated four-circle diffractometer equipped with a rotating anode (40 kV, 200 mA) using Mo- Kα radiation (λ = 0.71029 Å). Crystal data: mf = C$_{22}$H$_{52}$O$_2$Li$_2$Si$_4$, mw = 474.9, monoclinic, space group P2$_1$, a = 10.436 (3) Å, b = 17.820 (3) Å, c = 9.219 (2) Å, β = 116.18 (2)°, V = 1538.57 (8) Å^3, Z = 2, D$_c$ = 1.025 g/cm^3. The final R factor was 0.072 for 1433 reflections of F$_o$ > 3σ(F$_o$). Atomic positional and thermal parameters are provided as Supplementary Material.
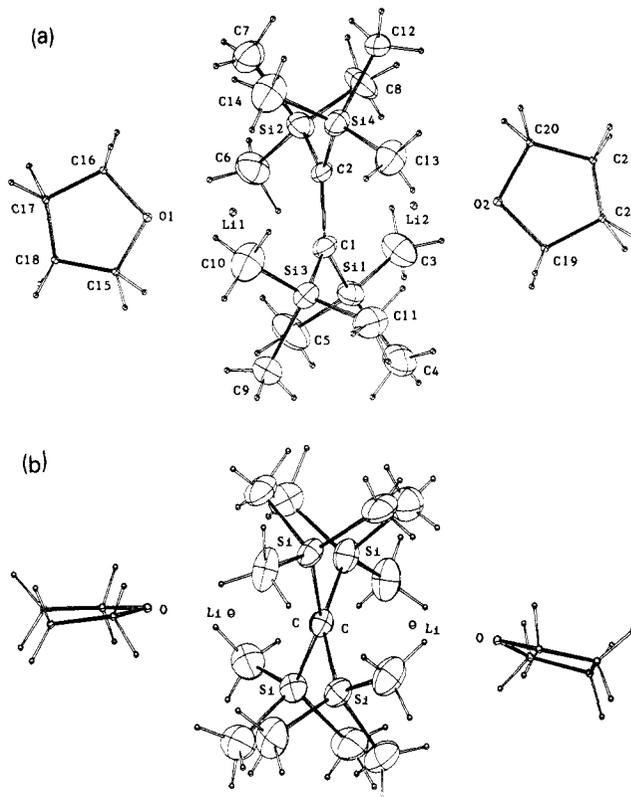
Figure 1. Stereoscopic views of Li$_2$(thf)$_2$[(Me$_3$Si)$_2$C—C(SiMe$_3$)$_2$]. (a) Selected bond lengths (Å): C(1)–C(2) 1.597 (17), Si(1)–C(1) 1.833 (13), Si(2)–C(2) 1.829 (13), Si(3)–C(1) 1.844 (13), Si(4)–C(2) 1.846 (13), C(1)–Li(1) 2.101 (29), C(1)–Li(2) 2.113 (30), C(2)–Li(1) 2.096 (29), C(2)–Li(2) 2.109 (30), O(1)–Li(1) 1.871 (29), O(2)–Li(2) 1.841 (30). (b) Selected bond angles (deg): Si(1)–C(1)–Si(3) 111.7 (7), Si(1)–C(1)–C(2) 124.2 (9), Si(3)–C(1)–C(2) 124.0 (9), Si(2)–C(2)–Si(4) 111.5 (7), Si(2)–C(2)–C(1) 124.1 (9), Si(4)–C(2)–C(1) 124.3 (9). Torsion angle (deg): 33.6.

bonded to the THF in addition to two carbon atoms as shown in Figure 1. Several interesting features for the structure can be pointed out. The bond length of the dianionic C–C bond is significantly increased from 1.368 Å in 1[2c] to 1.597 Å in 2. In contrast, the bond lengths of Si–C bonds (av 1.838 Å) are somewhat shortened with respect to 1 (av 1.915 Å) probably due to the interaction of the anionic carbon with silicon by p–σ* conjugation. The Li–C bond (av 2.105 Å) is similar to that 2.13 Å observed, for example, in a pentamethyldiethylenetriamine complex of LiCH(SiMe$_3$)$_2$.[17] The bond angles of C–C–Si (av 124.2°) and C–Si–C (av 111.6°) are almost the same with those of 1 (124.1 and 111.9°, respectively). The dihedral angle (33.6°) between the Si(1)–C(1)–Si(3) and Si(2)–C(2)–Si(4) planes enlarges to some extent as compared to 29.5° in the parent olefin 1. These structural features indicate that the geometry of 1 is essentially retained after the lithiation.

Although a theoretical calculation of 1,2-dilithioethane is reported,[18] our results provide the first structural characterization of nonconjugated 1,2-dilithioethane.[19] The calculation suggests that a trans conformation 5 (C_{2h}) with partially bridged geometry is the most stable one, although it is also suggested that the

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symmetrically trans doubly bridged structure **6** (D_{2h}) is only 1.9 kcal/mol higher in energy than the most stable one. The present X-ray results of **2** evidently support the trans doubly bridged structure of lithiums.

Further works are in progress.

Supplementary Material Available: Listings of atomic parameters and thermal parameters (Tables I and II), anisotropic temperature factors (Table III), distances for heavy atoms (Table IV), distances for hydrogen atoms (Table V), angles for heavy atoms (Table VI), and angles for hydrogen atoms (Table VII) (7 pages); listing of observed and calculated structure factors (Table VIII) (9 pages). Ordering information is given on any current masthead page.

# Kinetics and Mechanism of the Reaction of Diphenylcarbene with [1.1.1]Propellane[1]

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Molecules with inverted structures at carbon are of considerable interest to theoreticians and experimentalists as a result of the unusual bonding and reactivity properties that result from these highly strained structures.[3–5] [1.1.1]Propellane (**I**) is the smallest member, and perhaps one of the most interesting, of this group of substrates. **I** was first prepared by Wiberg et al. in 1982.[6] More recently Szeimies et al. reported a more convenient synthesis, which has been employed in our work.[7]

I has been reported to react with various substrates by a presumed free-radical mechanism;[8,9] for example, *t*-BuOCl and PhSSPh add readily across the central bond in **I**.[8] Our own kinetic work shows that *tert*-butoxyl and thiophenoxyl radicals are scavenged by **I** with rate constants in excess of 10^6 M^{-1} s^{-1}.[10]

Triplet carbenes add to olefins nonstereospecifically by a biradical mechanism which is believed to involve stepwise formation of the two carbon bonds.[11] We reasoned that reaction of diphenylcarbene with **I** could involve addition of the carbene to one of the bridge positions to yield a biradical (**II**). We report here kinetic and product studies which demonstrate that addition does occur, ultimately leading to the formation of **III**, reaction 1.

$$^3Ph_2C: \quad + \quad \overset{k_1}{\longrightarrow} \quad ^3[Ph_2C\cdot \overset{}{\longrightarrow}\cdot] \quad \longrightarrow \quad Ph_2C = \qquad (1)$$
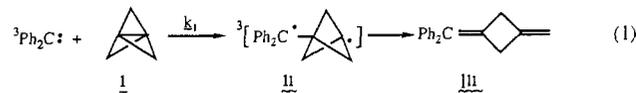
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(10) Rate constants of 2.8×10^6 and 6.2×10^7 M^{-1} s^{-1} were measured for reaction of *tert*-butoxyl and phenylthiyl radicals, respectively, with [1.1.1]propellane. The addition of phenylthiyl is reversible at room temperature.
(11) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984,** *17,* 283.
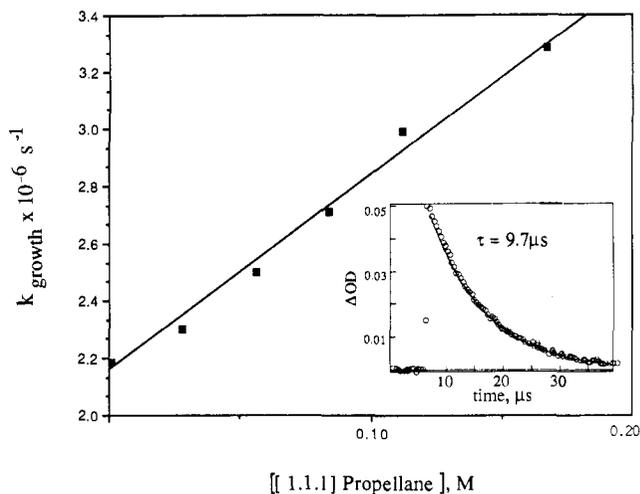
[[1.1.1] Propellane], M

Figure 1. Plot of the growth of benzophenone oxide at 410 nm in benzene saturated with 1% oxygen in nitrogen as a function of [1.1.1]propellane concentration. Insert: decay trace for biradical **II** at 330 nm in Freon-113 under nitrogen.

Irradiation of a solution of 8.1 mM diphenyldiazomethane in benzene containing 0.28 M **I** until the characteristic color of the diazo compound had been discharged leads cleanly to a single product which was isolated and characterized as carbene/propellane adduct **III**. Both ^1H and ^{13}C NMR and GC/MS data are fully consistent with the assigned structure.[12] The NMR spectra of **III** show similar methylenecyclobutane resonances to those which we have observed in the dimer of **I**.[13]

In order to determine the kinetics of the initial step in reaction 1 (k_1) we performed a series of laser flash photolysis experiments. In principle, the carbene may be detected directly ($\lambda_{max} \sim 310$ nm) when dilute solutions (10^{-5}–10^{-4} M) are employed.[14] Under these conditions, however, it is essential to use a flow system in order for the diazo precursor to be continuously replenished. Unfortunately, this is not a viable approach with **I** as a substrate. Even with Szeimies's improved synthesis, this volatile material can only be prepared in small amounts, requires preparative GC purification, and is not indefinitely stable.[15] Quite simply, **I** is not available in the amounts required to prepare the volume of solution (usually ≥100 mL) needed for each flow experiment. In order to employ static cells, and therefore less **I**, higher concentrations of the diazo compound are required, which rendered the solutions opaque in the 310-nm region. Thus, the carbene cannot be monitored directly, and we had to resort to a probe technique using benzophenone oxide which had been employed successfully in earlier work.[16] Thus, the samples were saturated with a custom mixture of 1% oxygen in nitrogen and irradiated with the pulses (337 nm) from a nitrogen laser. Benzophenone oxide, Ph_2COO, formed by reaction of the triplet carbene with oxygen, can be easily monitored at 410 nm.[16] The growth traces follow clean first-order kinetics and lead to a rate constant, k_{growth}, that can be related to the rate constants of interest according to eq 2

$$k_{growth} = k_0 + k_{ox}[O_2] + k_1[I] \qquad (2)$$

(12) ^1H NMR (ppm, CDCl$_3$, 300 MHz) 7.25 (m, 10 H), 4.29 (pent, 2 H, J = 2.5 Hz), 3.55 (t, 4 H, J = 2.5 Hz); ^{13}C NMR (ppm, CDCl$_3$) 144.0, 140.5, 134.1, 134.0, 128.7 (CH), 128.1 (CH), 126.4 (CH), 106.4 (CH$_2$), 41.4 (CH$_2$); GC/MS m/e 232 (M$^+$); mp 86.0–88.5 °C.
(13) ^1H NMR (ppm, CDCl$_3$) 4.98 (pent, 4 H, J = 2.1 Hz), 3.30 (t, 8 H, J = 2.1 Hz); ^{13}C NMR (ppm) 144.5, 124.4, 106.7 (CH$_2$), 38.8 (CH$_2$); GC/MS m/e 132 (M$^+$).
(14) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976,** *98,* 8190 or ref 16.
(15) [1.1.1]Propellane is stored at –78 °C and as described in the literature. Even with these precautions, the dimer and higher oligomers are detectable by GC analysis after several days. The hydrocarbon is remarkably stable, however, in dilute solutions ($\sim$1 molar) at low temperature. Thus, it is usually desirable to purify propellane just prior to use in an experiment. This method can only be used for relatively small amounts (in our case $\sim$500 mg).
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