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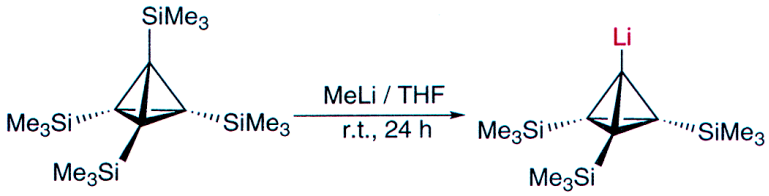

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Tetrahedranyllithium: Synthesis, Characterization, and Reactivity

Akira Sekiguchi* and Masanobu Tanaka

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

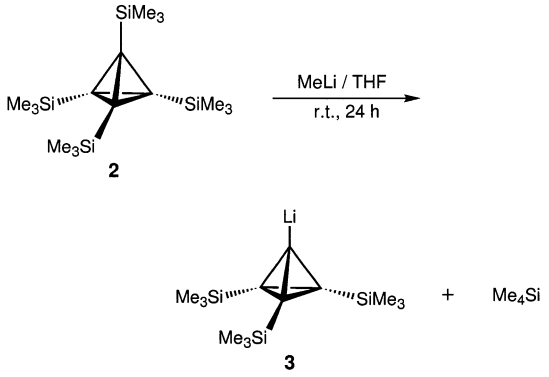
Received August 1, 2003; E-mail: sekiguch@staff.chem.tsukuba.ac.jp

Tetrahedrane is the smallest and most strained cage compound, and its highly symmetrical structure and unusual bonding nature attract organic chemists.[1] However, many attempts to isolate the parent tetrahedrane have been unsuccessful because of the high reactivity and very short lifetime caused by the strain in this molecule.[1,2] In 1978, Maier and co-workers succeeded in synthesizing tetrakis(*tert*-butyl)tetrahedrane (**1**),[3] in which the four bulky ^{t}Bu-substituents kinetically stabilize the tetrahedrane skeleton from ring-opening bond cleavage, the so-called "corset effect". However, if one of the *tert*-butyl substituents in **1** is replaced with a smaller group, this effect is lost. Indeed, phenyl- and methyl-substituted tetrahedrane derivatives were not detected, even under matrix isolation conditions.[4] Recently, we succeeded in synthesizing tetrakis(trimethylsilyl)tetrahedrane (**2**) by the photochemical isomerization of tetrakis(trimethylsilyl)cyclobutadiene.[5,6] The "corset effect" in **2** is smaller than that in **1** because of the longer C−Si bonds. However, the four σ-donating trimethylsilyl groups of **2** electronically stabilize the highly strained tetrahedrane skeleton.[7,8] This influence dramatically increases the thermal stability of **2** despite the enormous strain energy expected for a tetrahedral skeleton.[5]

Electropositive lithium is also an electron-donating atom and therefore was expected to stabilize tetrahedrane in a way similar to that by the Me_3Si groups in **2**.[5] In this work, we synthesized tris(trimethylsilyl)tetrahedranyllithium (**3**) by the reaction of **2** with MeLi. Compound **3** was characterized by NMR spectroscopy and X-ray crystallography. This is the first stable example of a lithium derivative of tetrahedrane. Furthermore, we were successful in the derivatization of **3** with cyclopentadiene and dimethyl sulfate to form new, hydrogen- and methyl-substituted tetrahedranes, respectively.

Tris(trimethylsilyl)tetrahedranyllithium (**3**) was synthesized by the reaction of **2** with excess methyllithium in THF at room temperature and was isolated as a colorless solid in 67% yield (Scheme 1).[9,10] Compound **3** is air and moisture sensitive, but

Scheme 1



thermally stable. The ^{1}H and ^{13}C NMR spectra of **3** in benzene-d_6 demonstrated its C_{3v} symmetry. Only one signal at −0.03 ppm was observed for the trimethylsilyl groups in the ^{1}H NMR spectrum, and three signals appeared at −27.0 (ring C−Li), −22.0 (ring C), and 1.6 ($SiMe_3$) ppm in the ^{13}C NMR spectrum. The large upfield shift of the ring C atom is typical for tetrahedrane.[3,5,8] The Li-substituted skeletal carbon atom shows a remarkable upfield shift relative to that of **2** (−20.5 ppm) because of its carbanion character.

The molecular structure of **3** has been unambiguously characterized by X-ray crystallography, as shown in Figure 1. We were able to grow single crystals by changing the ligand from THF to tetramethylethylenediamine (TMEDA).[11] Three TMEDA molecules are coordinated to two tetrahedranyllithium molecules, and one of three TMEDA molecules bridges two tetrahedranyllithium units.

Compared with the regular tetrahedral structure of **2**, the structure of **3**·$(TMEDA)_{1.5}$ represents a stretched tetrahedron with Li−C bond length of 2.076(2) Å. The endocyclic C(Li)−C($SiMe_3$) bond lengths range from 1.5408(15) to 1.5441(15) Å (av 1.5425(15) Å), and are longer than the endocyclic C($SiMe_3$)−C($SiMe_3$) bond lengths, which range from 1.4961(15) to 1.5009(15) Å (av 1.4986(15) Å).

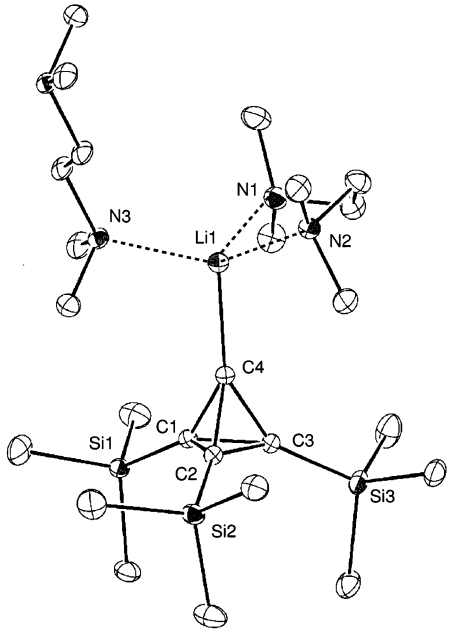


Figure 1. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1−C2 = 1.4961(15), C1−C3 = 1.5009(15), C1−C4 = 1.5441(15), C2−C3 = 1.4988(15), C2−C4 = 1.5426(15), C3−C4 1.5408(15), C4−Li1 = 2.076(2). Selected bond angles (deg): C1−C2−C4 = 61.06(7), C1−C4−C2 = 57.98(7), C2−C1−C4 = 60.96(7), C3−C2−C4 = 60.86(7), C2−C3−C4 = 60.98(7), C2−C4−C3 = 58.17(7), C3−C1−C4 = 60.77(7), C1−C3−C4 = 61.00(7), C1−C4−C3 = 58.23(7), C2−C1−C3 = 60.01(7), C1−C2−C3 = 60.15(7), C1−C3−C2 = 59.83(7).

Tetrahedranyllithium **3** readily undergoes reaction with a variety of electrophiles, which allowed us to introduce a methyl group onto the tetrahedrane skeleton. The methyl group is the smallest alkyl group and was not expected to exert appreciable steric or electronic

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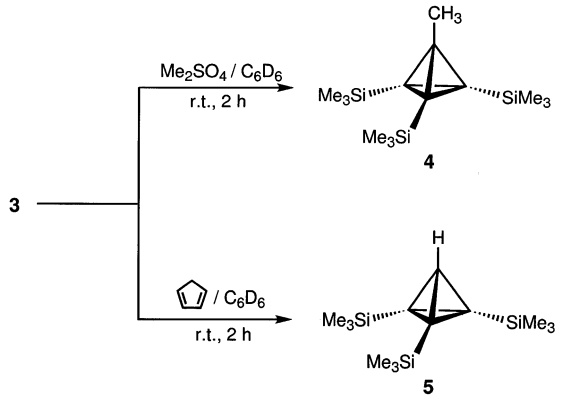
influences. Reaction of **3** with an equivalent amount of dimethyl sulfate in C_6D_6 at room temperature produced methyltris(trimethylsilyl)tetrahedrane (**4**) as a colorless oil in 20% yield (Scheme 2).[10,12] Methyl-substituted tetrahedrane **4** is less sterically protected compared with **2**; however, no decomposition of **4** was observed upon standing in air or after heating at 100 °C for 3 h.

Scheme 2



This surprising result prompted us to introduce a hydrogen substituent on tetrahedrane, since unsubstituted tetrahedrane has been among the most attractive synthetic challenges. Tris(trimethylsilyl)tetrahedrane (**5**) was prepared by the reaction of **3** with cyclopentadiene as a colorless oil in 32% yield (Scheme 2).[10,13] In the ^{1}H NMR spectrum, the signal of the proton attached to the tetrahedrane skeleton appeared at 2.85 ppm, being deshielded because of the high *s*-character of the ring C−H bond. The C−H coupling constant ($^1J_{C-H}$ = 255.6 Hz) is comparable to that of acetylene ($^1J_{C-H}$ = 249.0 Hz).[14] From the empirical correlation ($^1J_{C-H} = 5.70s - 18.4$ Hz),[15] we estimated the *s*-character of the ring C−H bond to be 48% ($sp^{1.08}$). Hydrogen-substituted tetrahedrane is also air- and thermally stable up to 100 °C. The stability of tetrahedrane derivatives **4** and **5** is surprising in light of previous reports.[4] The most important stabilizing factor should be attributed to the electronic effect of the trimethylsilyl groups.

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Supporting Information Available: Experimental procedures, spectral data, tables of crystallographic data including atomic positional and thermal parameters for **3** (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Spectral data of **3**: ^{1}H NMR (THF-d_8, δ) −0.03 (s, 27 H, $SiMe_3$); ^{13}C NMR (THF-d_8, δ) −27.0 (ring C), −22.0 (ring C), 1.6 ($SiMe_3$); ^{29}Si NMR (THF-d_8, δ) −0.22; ^{7}Li NMR (THF-d_8, δ) 1.32.
(10) For the experimental procedures of **3**, **4**, and **5**, see the Supporting Information.
(11) Crystal data for **3**·$(TMEDA)_{1.5}$ at 120 K: MF = $C_{22}H_{51}LiN_3Si_3$, MW = 448.87, monoclinic, $P2_1/n$, a = 9.1390(2) Å, b = 15.1390(5) Å, c = 22.1150(6) Å, β = 94.278(2)°, V = 3051.20(15) Å^3, Z = 4, D_{calcd} = 0.977 g/cm^3. The final R factor was 0.0368 (R_w = 0.1054 for all data) for 7253 reflections with $I > 2\sigma(I)$. GOF = 1.033.
(12) Spectral data of **4**: ^{1}H NMR (C_6D_6, δ) 1.75 (s, 3 H, CH_3), 0.18 (s, 27 H, $SiMe_3$); ^{13}C NMR (C_6D_6, δ) −19.6 (ring C), −2.9 (ring C), −0.1 ($SiMe_3$), 5.6 (CH_3); ^{29}Si NMR (C_6D_6, δ) −2.1; HRMS calcd for $C_{14}H_{30}Si_3$ 282.1655, found 282.1647.
(13) Spectral data of **5**: ^{1}H NMR (C_6D_6, δ) 2.85 (s, 1 H, CH), 0.18 (s, 27 H, $SiMe_3$); ^{13}C NMR (C_6D_6, δ) −26.7 (ring C), −12.7 ($^1J_{C-H}$ = 255.6 Hz, ring C), −0.4 ($SiMe_3$); ^{29}Si NMR (C_6D_6, δ) −1.8; HRMS calcd for $C_{13}H_{28}Si_3$ 268.1499, found 268.1499.
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