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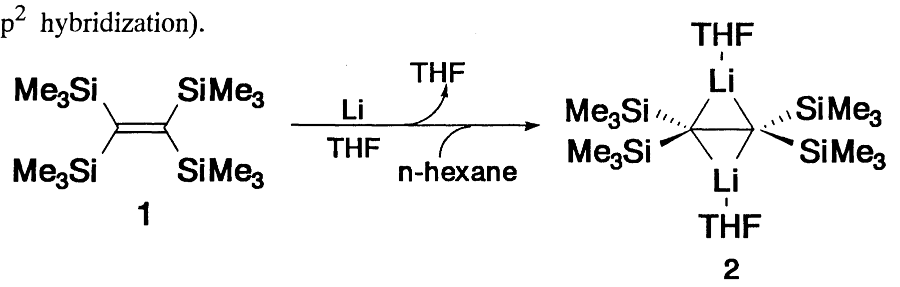
Structure of 1,2-Dilithio[tetrakis(trimethylsilyl)]ethane in Solution. Observation of Lithium-Bridged Structures and Unexpected Anionic Rearrangement[1)]

Akira SEKIGUCHI, Masaaki ICHINOHE, Tetsuo NAKANISHI, and Hideki SAKURAI
Department of Chemistry and Organosilicon Research Laboratory,
Faculty of Science, Tohoku University, Aoba-ku, Sendai 980

^{6}Li and ^{13}C NMR spectra of 1,2-dilithio[tetrakis(trimethylsilyl)]ethane revealed a doubly bridged π-structure in aromatic solvents similar to that observed in the crystals. However, the dianion in THF, which was found to exist as a solvent-separated ion pair of $Li^+(THF)_4$ and a species bridged by one Li atom, was highly reactive to undergo anionic rearrangement.

Recently, we have reported the isolation and characterization of 1,2-dilithio[tetrakis(trimethylsilyl)]-ethane **2** obtained by the reduction of tetrakis(trimethylsilyl)ethylene **1** with lithium as the first stable 1,2-dilithioethane without aryl substituents.[2)] The structure of **2**, determined by the X-ray crystallographic analysis, revealed the existence of three-coordinated lithium atoms which bridged to the two carbon atoms and were coordinated by one molecule of THF.[2)] The geometry of **2** around the carbon framework was essentially the same as that of **1**[3)] and the carbon atoms attached to the lithium atoms adopt trigonal geometry (sp^2 hybridization).



Because of current intense interests in theoretical and experimental structures of lithium compounds,[4)] it seems important and interesting to investigate whether the lithium-bridged structure found in crystals is maintained in solution. NMR data are most informative of the structure in solution, and particularly observation of ^{13}C-^{6}Li scalar coupling is useful. Then we have examined various NMR spectra of **2** and report herein the evidence for the existence of two type structures; a doubly-bridged structure in aromatic solvents and a singly bridged one in THF.[5)]

^{1}H, ^{13}C, ^{29}Si, ^{7}Li, and ^{6}Li NMR spectra of **2** in aromatic solvents indicate a symmetric structure containing two molecules of THF which bind to the lithium atoms.[6)] The ^{7}Li NMR signal appears at 1.39 ppm ($\nu_{1/2}$ = 7 Hz) as a sharp singlet in benzene-d$_6$ and toluene-d$_8$ at 293 K. The spectrum did not change appreciably in the temperature range of 220 - 298 K in toluene-d$_8$. An anionic carbon of **2** was observed at 9.8 - 10.6 ppm in ^{13}C NMR as an unresolved multiplet due to the coupling with ^{7}Li (I = 3/2).

However, the spectra were simplified by the use of ^{6}Li (I = 1). The anionic carbon now appeared at 10.4 ppm as a quintet due to two ^{6}Li with a coupling constant of 3.1 Hz (Fig. 1). The very small coupling constant between ^{13}C and ^{6}Li reflects quite small contribution of the s-character. The ^{6}Li resonance was observable at 1.42 ppm ($\nu_{1/2}$ = 0.15 Hz) with satellite signals due to the ^{13}C coupling (J = 3.1 Hz). These spectral features suggest that the species doubly bridged by lithium for the carbon framework, similar to that found in the solid state, exists also in aromatic solvents (Fig. 1).

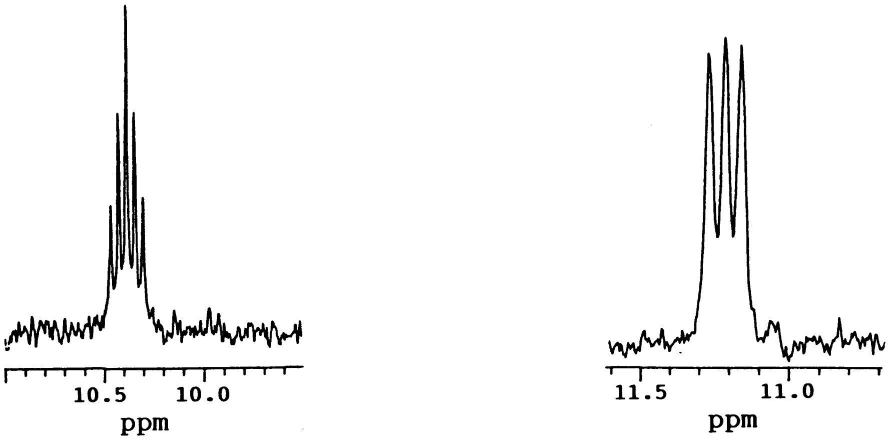


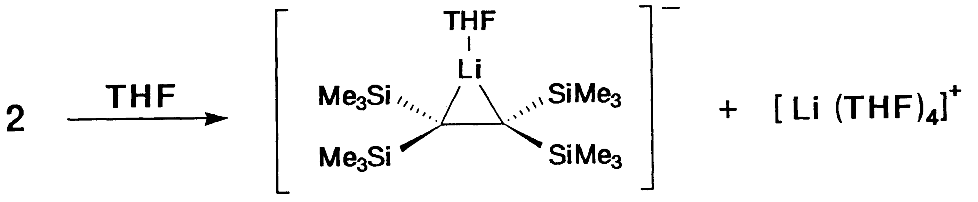
Fig. 1. ^{13}C NMR spectra (75.5 MHz) of the anionic carbon of dianions prepared from **1** and ^{6}Li: in toluene-d_8 at 298 K (left) and in THF-d_8 at 220 K (right).

In a solvating medium such as THF, however, the NMR spectra changed considerably from those in aromatic solvents.$^{6)}$ Thus, ^{1}H, ^{13}C, and ^{29}Si NMR signals of the crystals of **2** dissolved in THF-d_8 shifted significantly to a high field due to the increased ionic character.$^{6)}$ The anionic carbon in THF-d_8 at 220 K appeared at 11.2 ppm as a triplet signal (Fig. 1). This implies that only one lithium atom binds to the carbon. The coupling constant between ^{13}C and ^{6}Li was very small (4.1 Hz) as found in toluene-d_8.

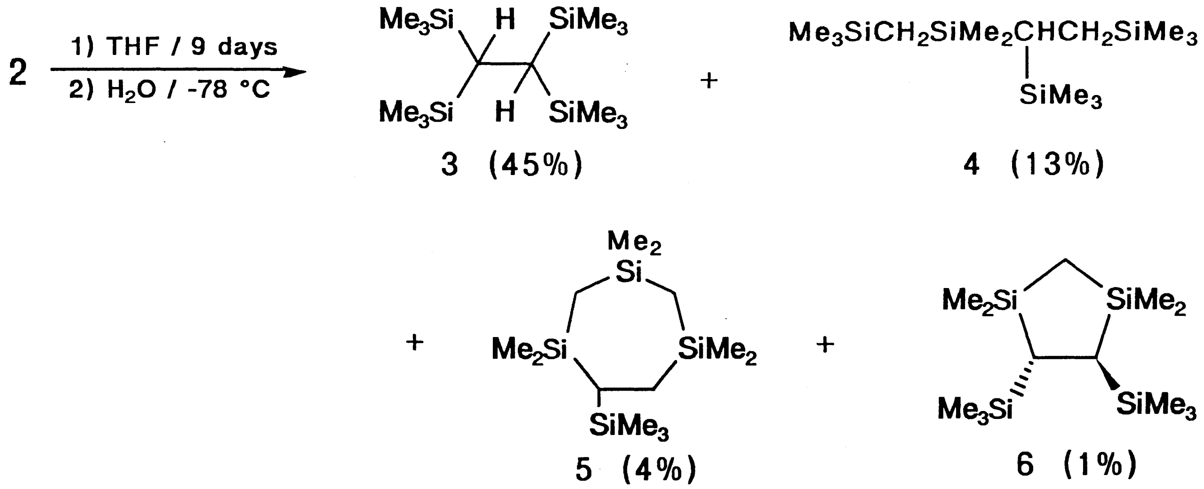
The most dramatic change was observed for the ^{6}Li NMR spectrum (220 K) which yielded two different signals at 1.43 ppm ($\nu_{1/2}$ = 1.7 Hz) and -0.39 ppm ($\nu_{1/2}$ = 1.7 Hz). It is interesting to note that the satellite signals due to the ^{13}C coupling (J = 4.1 Hz) were observed for the lower field signal at 1.43 ppm, whereas no coupling could be found for the signal at -0.39 ppm. The signal at 1.43 ppm should be assigned to a singly-bridged lithium derived by the cleavage of the doubly bridged species **2**. The signal at -0.39 ppm can be assigned to a solvent-separated lithium ion, $Li^+(THF)_4$, since no coupling with ^{13}C was observed. The large solvation energy of the Li^+ ion should be the driving force to lead to the formation of the solvent-separated ion pair.

The ratio of intensity of these two signals was independent of the temperature (220 - 290 K) and almost unity. By raising temperature, the signals became wide and ultimately a very broad single peak (0.53 ppm, $\nu_{1/2}$ = 55.6 Hz) at 320 K due to the exchange between two lithiums. The dynamic process was reversible and the coalescence temperature (Tc) was 315 K, giving $\Delta G^‡$ = 63.6 kJ mol^{-1} and $\Delta S^‡$ = 123 J mol^{-1}K^{-1} for the lithium interconversion. The large positive activation entropy is probably ascribed to the loss of THF molecules from $Li^+(THF)_4$ in the transition state. Thus, upon dissolving crystals of **2** in THF, a solvent-separated ion pair of a singly-bridged species and $Li^+(THF)_4$ must be produced.

Structural features in crystals indicated that the π–bonding of the lithium could be described by the overlap between the lithium p–orbital and low–lying π*–orbital of **1**. A theoretical study on 1,2–dilithioethane, however, suggested that the most stable structure was not a symmetrically doubly–bridged one (D_{2h}), but a partially bridged one (C_{2h}); the former was 7.9 $kJmol^{-1}$ higher in energy than the latter. The orthogonal structure was calculated to be much higher in energy than either D_{2h} or C_{2h} structure.[7)]



The dianion is highly reactive in THF to undergo intramolecular anionic rearrangement to give 2,2,4,4,7,7–hexamethyl–5–trimethylsilyl–2,4,7–trisilaoctane **4**.[8)] Thus after prolonged standing (9 days), quenching the THF solution of the dianion with water led to the formations of **3** and **4** together with small amounts of cyclic compounds (**5** and **6**).[9)] The reaction was accelerated appreciably by addition of 12–crown–4; **4** and **6** were obtained in 52 and 11% yield, respectively, after 14 h. These unusual products may be derived by anionic rearrangement involving the intramolecular proton abstraction from a methyl group on silicon as the initial step followed by subsequent anionic rearrangement. Intramolecular cyclization of the rearranged anion may lead to the cyclic compounds (**5** and **6**) and methyllithium.



In conclusion, the dilithioethane **2** exists as a symmetrically lithium–bridged species in non polar solvents, whereas in polar solvents solvation accelerates dissociation to a solvent–separated ion pair. The high reactivity of the latter toward proton abstraction is interesting in relation to the function of basic solvents in organolithium reactions.

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6) NMR spectra of **2**: ^{1}H NMR (toluene-d_8, δ) 0.49 (s, 36H), 1.28 - 1.36 (m, 8H, THF), 3.52 - 3.60 (m, 8H, THF); ^{13}C NMR (toluene-d_8, δ) 8.6 ($SiMe_3$), 10.4 (quintet, J = 3.1 Hz, C-Li), 25.6 (THF), 69.2 (THF); ^{29}Si NMR (toluene-d_8, δ) -12.9; ^{6}Li NMR (toluene-d_8, δ) 1.42. ^{1}H NMR (THF-d_8, δ) -0.07 ($SiMe_3$); ^{13}C NMR (THF-d_8, δ) 7.3 ($SiMe_3$), 11.2 (t, J = 4.1 Hz, C-Li); ^{29}Si NMR (THF-d_8, δ) -17.3; ^{6}Li NMR (THF-d_8, 220 K, δ) -0.39, 1.43. For NMR data in benzene-d_6 see Ref. 2. ^{6}Li NMR spectra were recorded at 44.2 MHz with an external standard (LiCl in MeOH).

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8) Compound **4**: ^{1}H NMR ($CDCl_3$, δ) -0.35 (s, 2H), -0.33 (t, 1H, J = 5 Hz), -0.12 (s, 9H), -0.10 (s, 9H), -0.08 (s, 15H), 0.47 (d, 2H, J = 5 Hz); ^{13}C NMR ($CDCl_3$, δ) -0.69 ($SiMe_3$), 0.33 ($SiMe_3$), 0.77 (SiMe), 0.79 (SiMe), 1.55 ($SiMe_3$), 3.55 (CH_2), 7.06 (CH), 10.2 (CH_2). ^{29}Si NMR ($CDCl_3$, δ) 0.45, 2.78, 3.37, 3.70; Ms m/z 318 (M^+, 0.1), 303 (0.3), 215 (15), 158 (59), 145 (99), 141 (15), 85 (15), 73 (100); high-resolution MS Found: 318.2055. Calcd for $C_{14}H_{38}Si_4$: 318.2051. The compound **4** was independently prepared by the hydrosilylation of 1,2-bis(trimethylsilyl)ethylene with dimethyl(trimethylsilylmethyl)silane with hydrogen hexachloroplatinate as a catalyst.

9) Compound **5**: NMR ($CDCl_3$, δ) -0.38 (d,d, 2H, J = 13 Hz), -0.23 (d,d, lH, J = 8.5 Hz), -0.16 (d,d, 2H, J = 14 Hz), -0.05 (s, 3H), -0.02 (s, 9H), -0.01 (s, 3H), -0.005 (s, 3H), 0.01 (s, 3H), 0.03 (s, 6H), 0.45-0.65 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) -0.63 (Me), -0.39 (Me), 0.51 (Me), 2.00 (Me), 2.76 (Me), 3.02 (CH_2), 3.17 (Me), 5.10 (CH_2), 7.07 (CH), 11.0 (CH_2). H-H as well as C-H COSY plots also support the assigned structure. ^{29}Si NMR ($CDCl_3$, δ) 0.51, 3.58, 3.90, 4.32; high-resolution MS Found: 302.1721. Calcd for $C_{13}H_{34}Si_4$: 302.1738. Compound **6**: NMR ($CDCl_3$, δ) -0.343 (s, 2H), -0.020 (s, 18H), 0.066 (s, 2H), 0.079 (s, 6H), 0.174 (s, 6H); ^{13}C NMR ($CDCl_3$, δ) 0.124 (Me), 1.92 (CH_2), 2.02 (Me), 2.62 (Me), 12.16 (CH); ^{29}Si NMR ($CDCl_3$, δ) 2.18, 16.4; high-resolution MS Found: 302.1753. Calcd for $C_{13}H_{34}Si_4$: 302.1738.

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