

Chapter 3

Cyclotetrasilanyl and Cyclotetrasilanide:

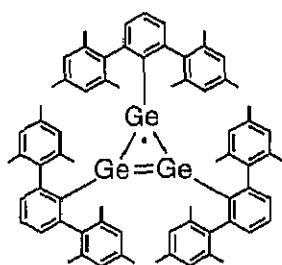
A Reversible Redox system of Cyclotetrasilanyl Cation, Radical, and Anion

Summary

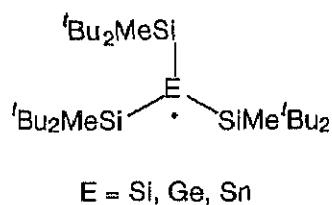
Red-purple crystals of the stable radical, 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl-(methyl)silyl]cyclotetrasilanyl (**11**[•]), were obtained by one-electron reduction of the corresponding cyclotetrasilenylium ion (**11**⁺) with a bulky trialkylsilylsodium or potassium graphite in diethyl ether. The molecular structure of **11**[•] has been unambiguously determined by X-ray crystallography. It shows that **11**[•] is a free silyl radical with an allyl-type delocalized structure. The radical **11**[•] in heptane gives an intense EPR signal ($g = 2.0058$), with accompanying satellite signals due to coupling with the ²⁹Si nuclei of the skeletal silicon atoms. The two-electron reduction of **11**⁺ lead to the formation of the cyclotetrasilanyl anions **11**⁻•M⁺ (M = Li, Na, and K). A unique chemical reversible redox system of the cyclotetrasilanyl cation, radical, and anion is also described.

Introduction

Since the discovery of triphenylmethyl radical by Gomberg in 1903, free radicals have been well-known to be one of the most important classes of reactive intermediates in organic chemistry.¹ Mostly, such radical species have been considered as short-lived species, whose existence was proved by spectroscopic methods or trapping reactions. To date, there are only a few examples of structurally characterized organic radicals.² The heavier analogues of such radical species, e.g., stable silicon- and germanium-centered radicals, were isolated much later than their carbon counterparts, although their formation was suggested a while ago.^{3,4} In 1997, the first isolable germynyl radical, the cyclotrigermenyl radical with a three-membered ring allylic-type structure, was reported by Power et al.⁵ Quite recently, structural characterization of tricoordinated Si-, Ge-, and Sn-centered radicals lacking conjugation with π -bonds were reported by Sekiguchi et al.⁶

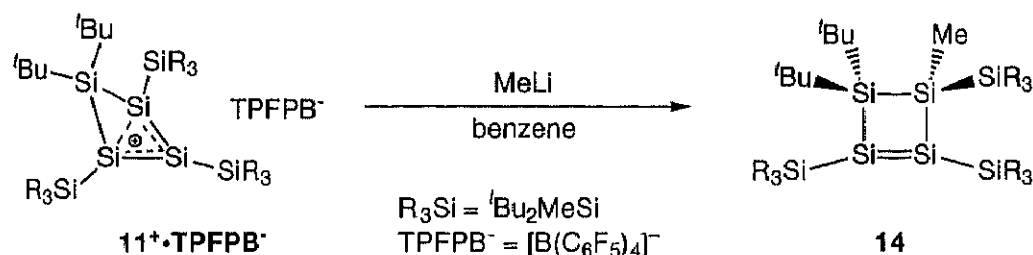


P. P. Power (1997)



A. Sekiguchi (2002)

As described in Chapter 2, the author has succeeded in synthesizing a cyclotetrasilenylium ion (**11**⁺) which is not only a free silyl cation in the condensed phase but also a homoaromatic compound consisting of silicon atoms. It is quite reasonable to assume that the reaction of **11**⁺ with nucleophiles may afford cyclotetrasilene⁷ and/or tetrasilabicyclo[1.1.0]butane derivative.⁸ Indeed, **11**⁺ smoothly reacts with small nucleophile such as methyllithium in diethyl ether, to produce yellow crystals of cyclotetrasilene derivative **14** in 97% yield (Scheme 3-1).



Scheme 3-1

However, the reaction of 11^+ with the bulky trialkylsilylsodium compounds ${}^t\text{Bu}_3\text{SiNa}$ and ${}^t\text{Bu}_2\text{MeSiNa}$ did not produce the corresponding cyclotetrasilene or tetrasilabicyclo-[1.1.0]butane derivatives. Instead, cyclotetrasilenylium radical 11^\bullet was formed as a result of one-electron reduction. This result also prompts the author to investigate the two-electron reduction of 11^+ with alkali metal to give the corresponding cyclotetrasilene anion 11^- . Alkali metal derivatives of organosilicon compounds are useful not only in organosilicon chemistry but also in organic synthesis. The synthesis, reactivity, and structural aspects of silyllithium compounds are the most studied of alkali metal derivatives.⁹ Numerous anionic organosilicon compounds are known, however, knowledge of the chemistry of organosilicon compounds with an interaction between alkali metals and π electrons is very limited. The only examples of such interactions are silole dianions $[\{\text{Li}(\text{thf})_2\}\{\text{Li}(\text{thf})_3\}\{\eta^1, \eta^5\text{-C}_4\text{Ph}_4\text{Si}\}]$, $[\{\text{K}(\text{18-crown-6})\}_2\{\eta^5, \eta^5\text{-C}_4\text{Me}_4\text{Si}\}]$, and related compounds.¹⁰ A recent report by Weidenbruch and co-workers, an unexpected formation of a cyclotetragermenylium derivative by the reaction of tetrakis(2,4,6-triisopropylphenyl)-digermene with lithium in dimethoxyethane,¹¹ prompts the author to communicate the synthesis of the alkali metal derivative of cyclotetrasilenylium anion.

In this chapter, the first isolation and full characterization of the stable silyl radical 11^\bullet which formed by the one-electron reduction of the corresponding cyclotetrasilenylium ion 11^+ are reported. The synthesis, and structure of alkali metal derivatives of cyclotetrasilene

ion $11^{\bullet}M^+$ ($M = Li, Na, K$), and a unique reversible redox system of cyclotetrasilanyl cation, radical, and anion are also described (Chart 3-1).

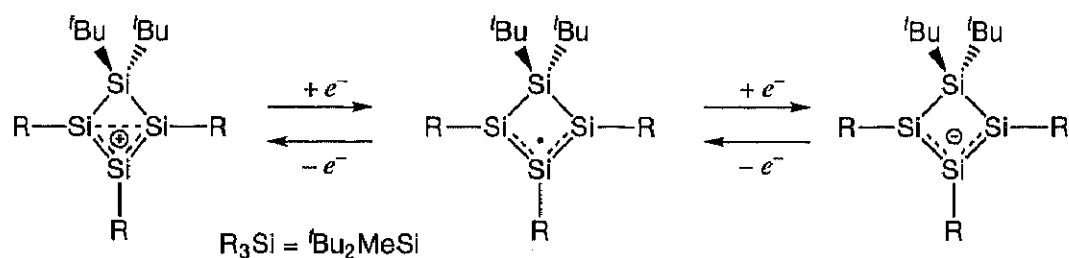
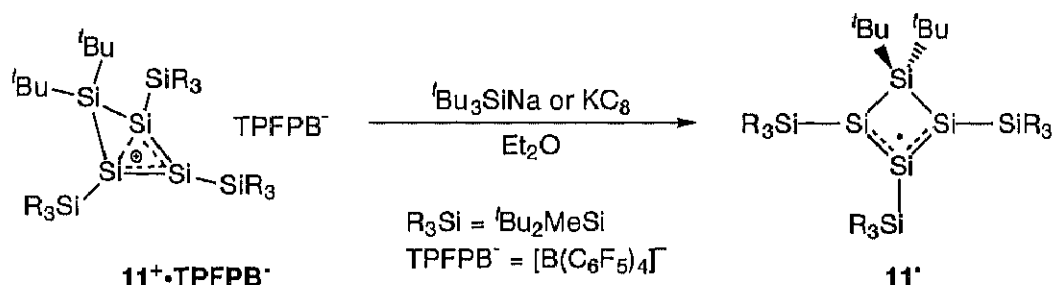


Chart 3-1

Results and Discussion

One-Electron Reduction of Cyclotetrasilenylium Ion

A mixture of $11^+ \cdot \text{TPFPB}^-$ (TPFPB^- = tetrakis(pentafluorophenyl)borate) and ${}^t\text{Bu}_3\text{SiNa}$ in diethyl ether, which was initially a yellow suspension, became a red-purple solution within 5 minutes with stirring at room temperature. The resulting $\text{Na}^+ \cdot \text{TPFPB}^-$ salt was removed by filtration after exchange of solvent to heptane, and subsequent evaporation of heptane gave a red-purple solid containing 11^* . Pure 11^* was obtained as red-purple crystals recrystallized from hexane in 67% yield. One-electron reduction of 11^+ could also be achieved by potassium graphite (KC_8) in diethyl ether, and 11^* was easily isolated in 83% yield (Scheme 3-2). Radical 11^* is quite stable at room temperature in the absence of air and moisture, and an intense ESR signal was observed for both solid 11^* and heptane solution of 11^* .



Scheme 3-2

Structural Characterization of Cyclotetrasilanyl Radical

The structure of **11**[•] was determined by X-ray analysis, and an ORTEP drawing of the molecular structure of **11**[•] and crystal packing are given in Figure 3-1 and Figure 3-2, respectively. The closest intermolecular distances between silicon atoms of the radical part (Si1, Si2, and Si3) range from 8.401(2) to 9.914(2) Å, indicating that cyclotetrasilanyl **11**[•] is a free silyl radical in the solid state. The four-membered ring is almost planar with the dihedral angle between the radical part Si1-Si2-Si3 and Si1-Si4-Si3 being 4.7°. This is in marked contrast to the precursor silyl cation **11**⁺, which has a largely folded four-membered ring (the corresponding folding angle: 46.6°), caused by 1,3-orbital interaction due to the homoaromatic character. The sum of the bond angles around the three coordinated silicon atoms of the radical part (Si1, Si2, and Si3) are 360.0, 359.1, and 356.2°, respectively. The Si1 and Si2 atoms have planar geometry, but the Si3 atom is slightly pyramidalized. A small unsymmetrical feature for the radical part was also found in the bond lengths: Si1-Si2 [2.226(1) Å] is slightly shorter than Si2-Si3 [2.263(1) Å]. However, these Si-Si bond lengths are comparable with the corresponding Si-Si bond lengths of **11**⁺ [2.240(2) and 2.244(2) Å], being intermediate between the Si=Si double bond [2.174(4) Å] and the Si-Si single bond [2.349(4)-2.450(4) Å] in the four-membered ring of hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene.^{7a,12} The bond lengths of Si1-Si4 [2.358(1) Å] and Si3-Si4 [2.364(1) Å] are slightly longer than the corresponding bond lengths of **11**⁺ [2.336(2) and 2.325(2) Å]. The interatomic distance between Si1 and Si3 of **11**[•] [3.225(2) Å] indicates that the 1,3-orbital interaction observed in **11**⁺ is lost by the one-electron reduction.

ESR Spectrum of Cyclotetrasilanyl Radical

Crystalline **11**[•] reveals an intense ESR signal with $g = 2.0058$, which is close to the typical values for tris(trialkylsilyl)silyl radicals (2.0053 – 2.0063).^{3,4} The heptane solution of **11**[•] also gives a strong ESR signal at room temperature as an unresolved broad singlet (g

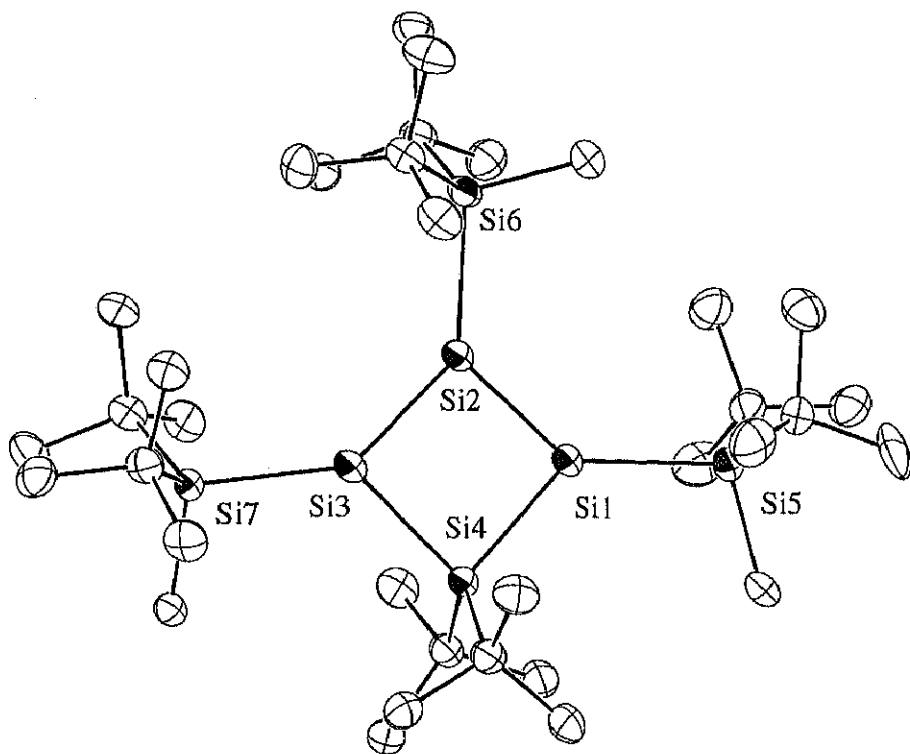


Figure 3-1. ORTEP drawing of 11' (hydrogen atoms are omitted for clarity).

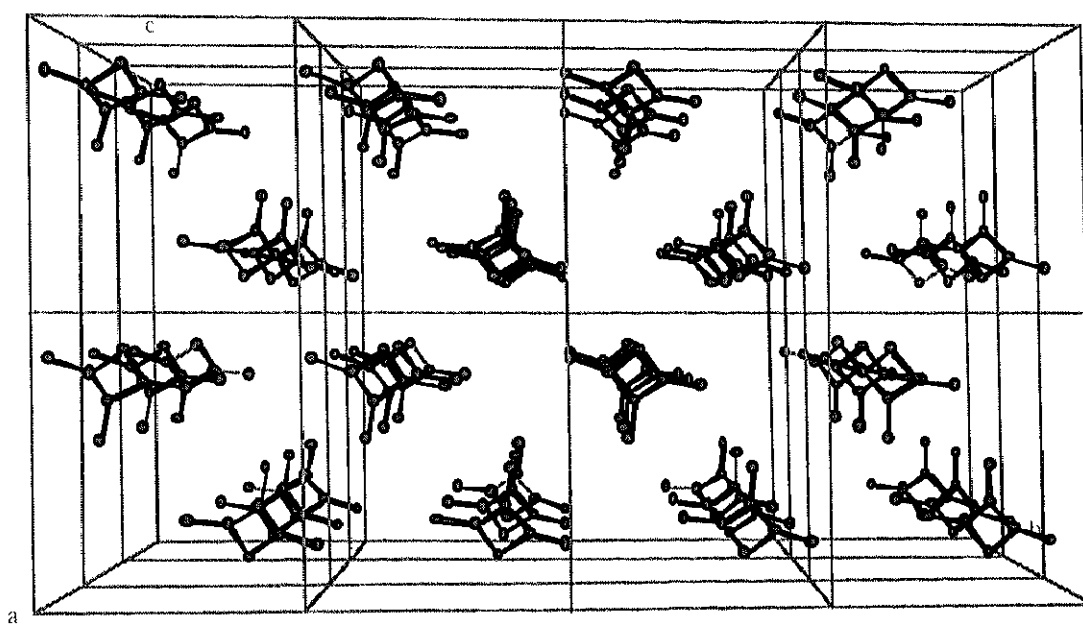


Figure 3-2. Crystal packing of 11' (carbon and hydrogen atoms are omitted for clarity).

= 2.0058) with the definite five doublet satellite signals, as shown in Figure 3-3. Three doublet satellite signals with relatively large hyperfine coupling constants (hfcc) (4.07, 3.74, and 1.55 mT) are evidently due to coupling with the ^{29}Si nuclei, judging from their intensities relative to the central peak. The two doublet satellite signals with hfcc of 4.07 and 3.74 mT are broadened by raising the temperature and coalesce at 370 K due to the rotation of $^t\text{Bu}_2\text{MeSi}$ groups. Since cyclotetrasilanyl radical **11'** is an allyl-type radical, the largest spin density (α spin) should be located on the terminal Si1 and Si3 atoms, and the second largest spin density (β spin), on the central Si2 atom. Therefore, the two hfcc of 4.07 and 3.74 mT can be assigned to coupling with the $^{29}\text{Si1}$ and $^{29}\text{Si3}$ nuclei, and the hfcc of 1.55 mT is assigned to coupling with the $^{29}\text{Si2}$ nucleus. The relatively low hfcc due to Si1 and Si3 atoms are consistent with the delocalization of the unpaired electron in the allylic system.^{13,14}

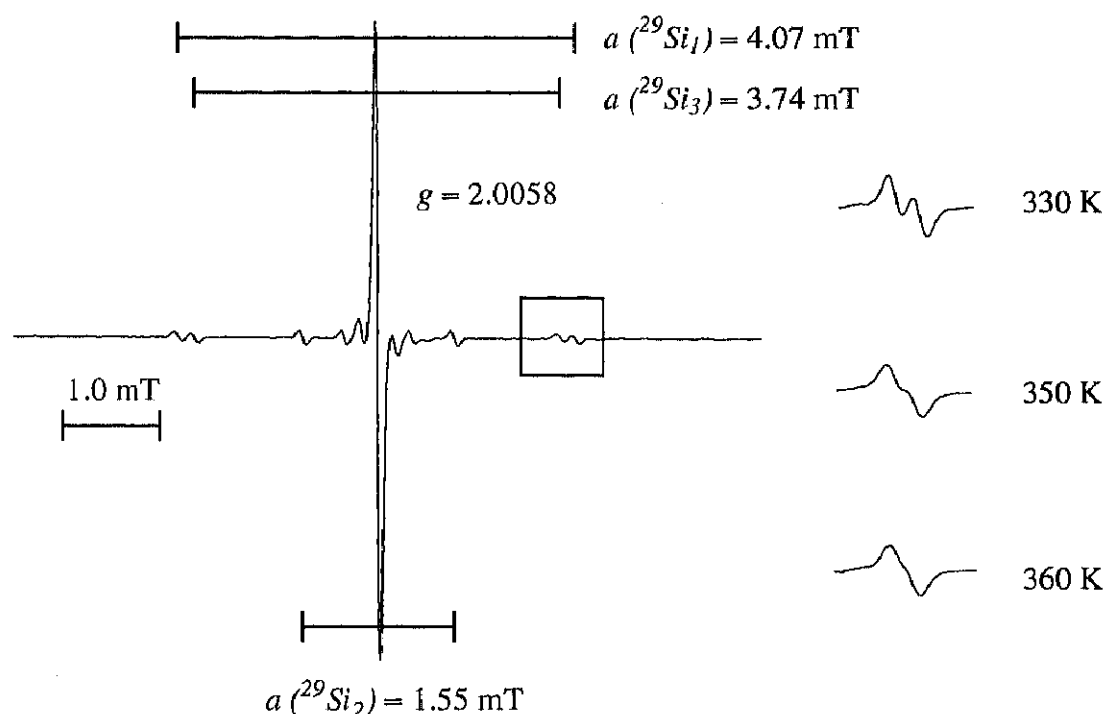
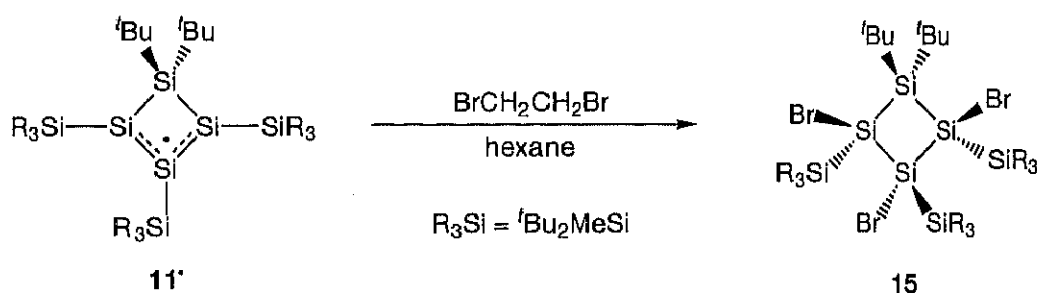


Figure 3-3. ESR spectra of **11'** in heptane solution.

Reactivity of Cyclotetrasilanyl Radical

Reaction with 1,2-Dibromoethane

The high reactivity of silyl radicals toward organic halides is well established.³ The stable silyl radical **11**[•] also readily reacted with 1,2-dibromoethane to give *trans,trans*-1,2,3-tribromo-4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclotetrasilene **15** in 79% yield (Scheme 3-3). This reaction initially occurred bromine abstraction of the terminal radical center of **11**[•] to give a cyclotetrasilene derivative followed by *trans* addition of bromine atoms to Si=Si double bond in the four-membered ring (Scheme 3-3).

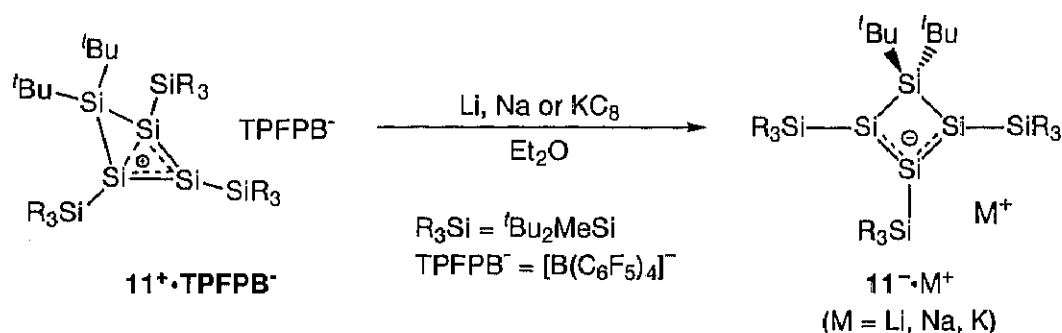


Scheme 3-3

Two-Electron Reduction of Cyclotetrasilenylium Ion

The reaction of **11**⁺•TPFPB⁻ with an excess of lithium in oxygen-free, dry diethyl ether at room temperature led to the immediate formation of a red-purple solution, caused by the formation of **11**[•]. After about 30 minutes, the color of the solution changed to green, caused by the formation of 4,4-di-*tert*-butyl-1,2,3-tetrakis[di-*tert*-butyl(methyl)silyl]cyclotetrasilene **11**⁻ by further reduction. After removal of the solvent in vacuo, hexane was introduced by vacuum transfer. After the excess lithium and resulting Li⁺•TPFPB⁻ had been removed by the filtration, the solution was cooled to afford green crystals of **11**[•]•Li⁺, which contained one equivalent of Et₂O, in 85% yield (Scheme 3-4). Reduction of **11**[•] with lithium in Et₂O at room temperature also produced **11**[•]•Li⁺ cleanly. Compound **11**⁺•TPFPB⁻ also underwent two-electron reduction with sodium or potassium graphite (KC₈) in Et₂O, and the

$11^-\cdot\text{Na}^+$ and $11^-\cdot\text{K}^+$ were obtained in 65% and 75% yields, respectively.



Scheme 3-4

Molecular Structures of Cyclotetrasilene Ion

To determine the exact structure of $11^-\cdot\text{Li}^+$ by X-ray crystallography, the author performed a ligand exchange on the Li^+ ion, from Et_2O to tetrahydrofuran. A single crystal of $11^-\cdot\text{Li}^+$, which contained one equivalent of THF, was obtained by recrystallization from a mixture of hexane and THF, the molecular structure was confirmed by X-ray analysis (Figure 3-3). The lithium cation is located over the four-membered ring, and is coordinated by the three silicon atoms (Si1 , Si2 , and Si3) in the four-membered ring, as well as by the oxygen atom of the THF molecule.

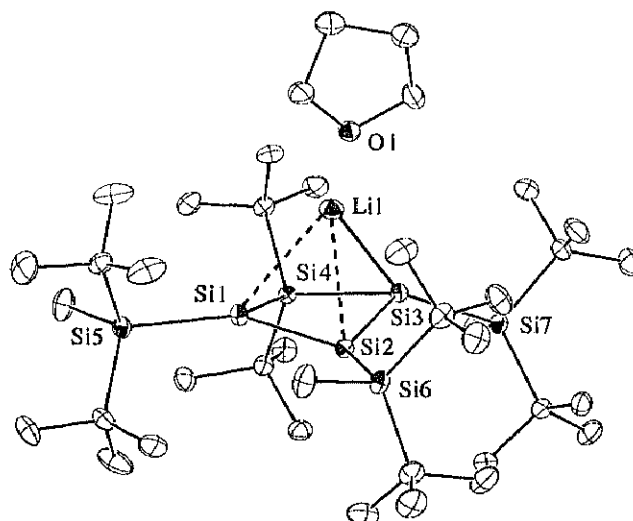


Figure 3-4. ORTEP drawing of $11^-\cdot[\text{Li}(\text{thf})]^+$ (hydrogen atoms are omitted for clarity).

The four-membered ring deviates from planarity, as demonstrated by the dihedral angle of 27.3° between Si2-Si3-Si4/Si2-Si1-Si4 planes. The bond length of Si3-Li1 (2.569(4) Å) lies within the range for typical η^1 -type silyllithium compounds,⁹ whereas the bond lengths of Si1-Li1 (2.789(4) Å) and Si2-Li1 (2.814(4) Å) are significantly longer than that of Si3-Li1 (2.569(4) Å). The bond length of Si1-Si2 is 2.2245(7) Å, which lies in the reported range for Si=Si double bonds (2.138 – 2.289 Å).¹⁵ The bond lengths of Si2-Si3 (2.3135(7) Å) and Si1-Si4 (2.3692(7) Å) lie in the normal region for Si-Si single bond (2.33 – 2.37 Å). The structural features suggest that $\mathbf{11}^-\cdot\text{Li}^+$ has a cyclotetrasilene structure with a Si=Si double bond in the ring, and that the lithium cation is bonded to the Si3 atom and also interacts with the double-bonded Si1 and Si2 atoms. Such an electrostatic interaction leads to elongation of the Si=Si double bond, which is intermediate between Si=Si double bond (2.174(4) Å) and Si-Si single bond (2.349(4) – 2.450(4) Å) in the four-membered ring of hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene.^{7,12}

The molecular structure of $\mathbf{11}^-\cdot\text{Na}^+$ was also determined by X-ray analysis of a single-crystal of $\mathbf{11}^-\cdot\text{Na}^+$ which obtained by recrystallization from a mixture of hexane and THF (Figure 3-5). In contrast to the structure of $\mathbf{11}^-\cdot\text{Li}^+$, the sodium cation is located outside the four-membered ring, and is coordinated by the only one silicon atom (Si1) in the four-membered ring, as well as by the three oxygen atoms of the THF molecules.

The bond length of Si2-Si3 is 2.1992(13) Å, which is slightly shorter than the corresponding Si=Si double bond length (2.2245(7) Å) in $\mathbf{11}^-\cdot\text{Li}^+$. The bond lengths in the four-membered ring (Si1-Si2; 2.352(1), Si1-Si4; 2.410(1); Si3-Si4; 2.351(1) Å) lie in the normal region for Si-Si single bond (2.33 – 2.37 Å). These structural features indicate that $\mathbf{11}^-\cdot\text{Na}^+$ has also cyclotetrasilene structure which is similar to the structure of $\mathbf{11}^-\cdot\text{Li}^+$, but there is no electrostatic interaction between sodium cation and Si=Si double bond. This difference in the structures of $\mathbf{11}^-\cdot\text{Na}^+$ and $\mathbf{11}^-\cdot\text{Li}^+$ is probably due to the ionic radii of

counteractions and the coordination number of THF molecule on the alkali metal.

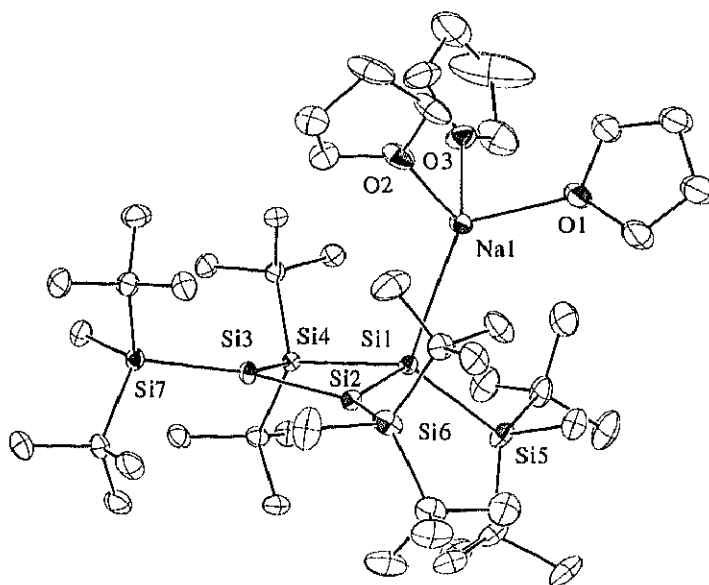


Figure 3-4. ORTEP drawing of $11^{-} \cdot [\text{Na}(\text{thf})_3]^{+}$ (hydrogen atoms are omitted for clarity).

NMR Spectra of Cyclotetrasilene Ion

The NMR spectroscopic data of $11^{-} \cdot \text{Li}^{+}$ in toluene- d_8 indicate that $11^{-} \cdot \text{Li}^{+}$ forms a contact ion pair (CIP) with C_2 symmetry. The two *tert*-butyl groups that are attached to the Si4 atom show chemical shift nonequivalence, caused by coordination of the lithium cation (Figure 3-3). The two *tert*-butyl groups of ${}^t\text{Bu}_2\text{MeSi}$ that are bounded to the Si1 and Si3 atoms are diastereotopic. Thus, the ${}^1\text{H}$ NMR spectrum of $11^{-} \cdot \text{Li}^{+}$ in toluene- d_8 reveals the presence of two methyl groups and five *tert*-butyl groups. The ${}^{13}\text{C}$ NMR spectrum also shows signals arising from two methyl carbons for ${}^t\text{Bu}_2\text{MeSi}$, five methyl carbons for three ${}^t\text{Bu}_2\text{MeSi}$ and two ${}^t\text{Bu}$ groups. In the ${}^{29}\text{Si}$ NMR spectrum, five signals are observed at $\delta = -31.5$ (Si1 and Si3), 13.9 (Si6), 19.0 (Si5 and Si7), 26.0 (Si4), and 273.0 (Si2). The Si1 and Si3 atoms are equivalent, which indicates that the lithium cation is fluxional in solution,

in accordance with an allyl-type anion. The signal appearing at $\delta = -31.5$ is assigned to the Si1 and Si3 atoms, which are shifted upfield because of the negative charge. Of particular interest is the highly deshielded signal at $\delta = 273.0$ arising from Si2 atom, similar to the central carbon atom of allyllithium.¹⁶

However, the Li^+ ion can be separated from the anion to yield a solvent-separated ion pair (SSIP) in a solvating medium such as $\text{THF-}d_8$. Consequently, the skeleton of $\mathbf{11}^-$ has the same environment above and below the ring; the two ^tBu groups attached to the Si4 atom are equivalent. In the ^{29}Si NMR spectrum of $\mathbf{11}^- \cdot \text{Li}^+$ in $\text{THF-}d_8$, five signals are observed at $\delta = -24.7$ (Si1 and Si3), 5.4 (Si6), 7.4 (Si5 and Si7), 77.1 (Si4), and 224.5 (Si2).¹⁷ These chemical shifts are independent of the counter cation (Li, Na, and K), implying that $\mathbf{11}^- \cdot \text{M}^+$ ($\text{M} = \text{Li, Na, and K}$) formed SSIP in the polar solvent, caused by solvation of the counter cations (Figure 3-5).

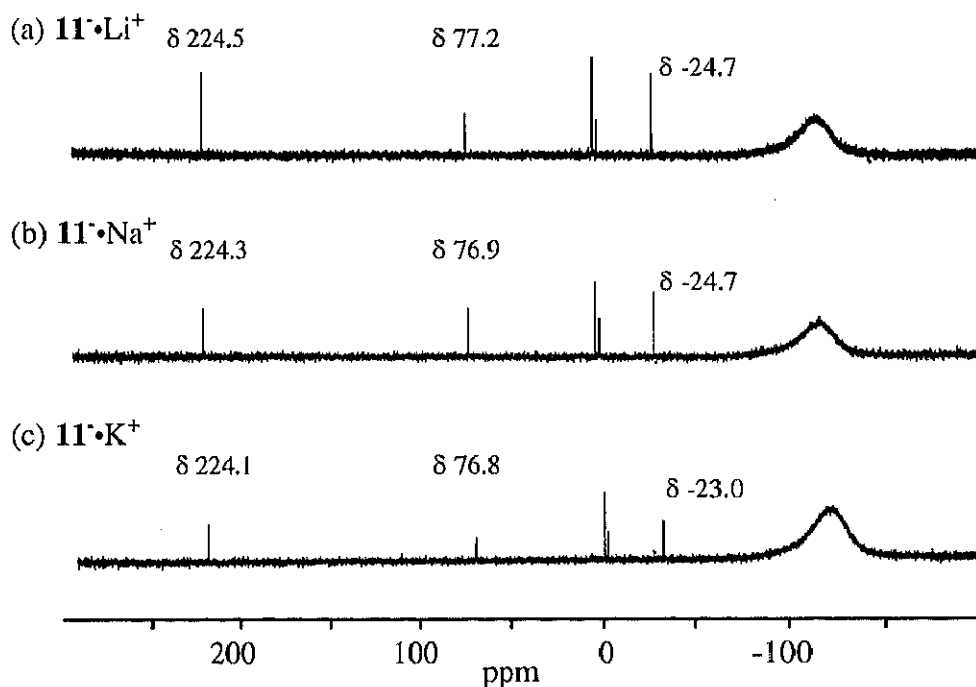
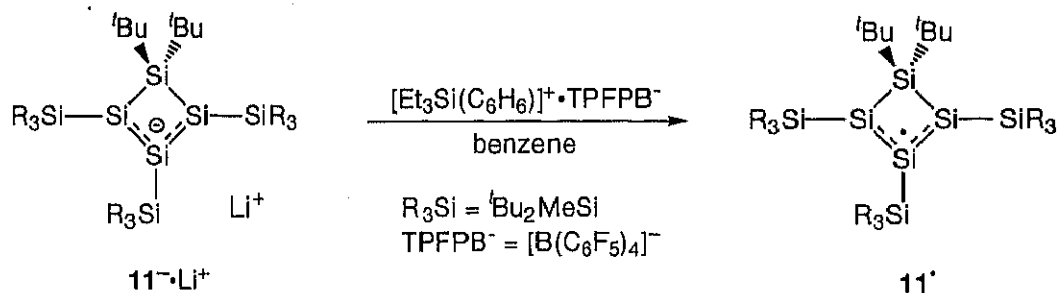


Figure 3-5. ^{29}Si NMR spectra of cyclotetrasilanyl anion ($\text{THF-}d_8$, 293K, using inverse-gate pulse sequence); (a) $\mathbf{11}^- \cdot \text{Li}^+$, (b) $\mathbf{11}^- \cdot \text{Na}^+$, (c) $\mathbf{11}^- \cdot \text{K}^+$.

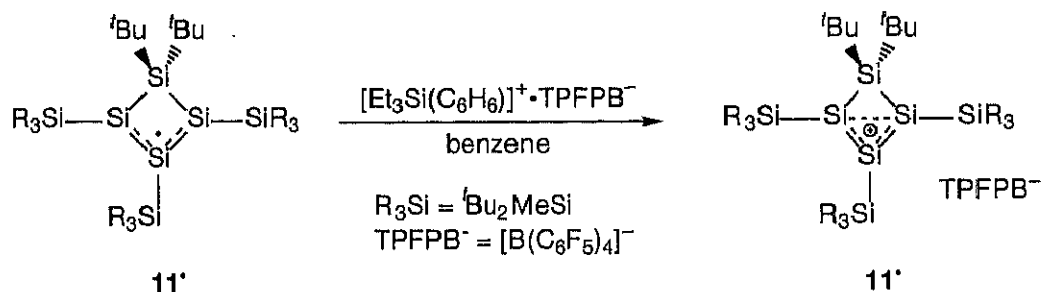
Oxidation of Cyclotetrasilanyl Anion and Radical

One-electron oxidation of the cyclotetrasilanyl anion 11^- and radical 11^\bullet were also investigated. A benzene solution of cyclotetrasilanyllithium $11^-\cdot\text{Li}^+$ was added to a benzene solution of $[\text{Et}_3\text{Si}(\text{benzene})]^+\cdot\text{TPFPB}^-$. A green color of 11^- was immediately disappeared to afford a red-purple solution containing the corresponding cyclotetrasilanyl radical resulting by one-electron oxidation of 11^- (Scheme 3-5).



Scheme 3-5

The radical 11^\bullet also undergoes one-electron oxidation to form 11^+ . Treatment of 11^\bullet with equimolar amount of $\text{Ph}_3\text{C}^+\cdot\text{TPFPB}^-$ in benzene at room temperature, the red-purple color of 11^\bullet immediately disappeared to afford two layers. The lower one consisting of dark red viscous oil was washed with hexane to give starting material of 11^+ in 80% yield (Scheme 3-6). However, reaction of 11^\bullet with $\text{Ph}_3\text{C}^+\cdot\text{TFPB}^-$ (TFPB $^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) did not afford the corresponding cyclotetrasilanylium ion. Thus, abstraction of fluorine atom on CF_3 groups in TFPB $^-$ was occurred by the silyl radical center to give a complex mixture. This result indicates that selection of counteranion is very important to synthesize the highly reactive silyl cation species. Thus, the author has prepared a reversible redox system of the cyclotetrasilanyl cation, radical, anion.



Scheme 3-6

Conclusion

The first isolable silyl radical of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]-cyclotetrasilanyl **11**[•] was obtained by the one-electron reduction of the corresponding cyclotetrasilenylium ion **11**⁺ with bulky trialkylsilylsodium or KC₈. The crystal structure and the ESR spectrum in solution show that **11**[•] is a free radical with allyl-type delocalized structure. Two-electron reduction of **11**⁺ also underwent to afford green crystals of the corresponding alkali metal derivatives of cyclotetrasilanyl anion. The cyclotetrasilenyllithium **11**⁻Li⁺ has a cyclotetrasilene structure with a Si=Si double bond in the ring, and that the lithium cation is interacts with the Si=Si double bond to form asymmetrically bridged η^3 -allyllithium structure.

The oxidation reaction of **11**⁻ and **11**[•] can easily occurred to regenerate **11**[•] and **11**⁺, respectively. Thus, a reversible redox system of cyclotetrasilanyl cation, radical, and anion was successfully prepared.

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. NMR spectra were recorded on a Brüker AC-300FT NMR spectrometer (^1H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). ESR spectrum was recorded on a Brüker EMX-T ESR spectrometer. Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan). $\text{Ph}_3\text{C}^+ \cdot \text{TPFPB}^-$ (TPFPB^- = tetrakis(pentafluorophenyl)borate) was prepared according to the literature procedure.¹⁸

Reaction of $11^+ \cdot \text{TPFPB}^-$ with MeLi

Crystals of $11^+ \cdot \text{TPFPB}^-$ (80 mg, 0.058 mmol) and MeLi (2mg, 0.091 mmol) were placed in a sealed tube with a magnetic stirrer bar. After degassing the tube, dry oxygen-free Et₂O was introduced by vacuum transfer and stirred for 1 h. The solvent was removed in vacuo, the residue was extracted with hexane, and filtered. The reaction mixture was cooled to afford yellow crystal of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]-3-methylcyclotetrasilene **14** (40 mg, 97%). mp 174-177 °C, ^1H NMR (C_6D_6 , δ) 0.37 (s, 3 H), 0.45 (s, 3 H), 0.46 (s, 3 H), 0.85 (s, 3 H), 1.18 (s, 9 H), 1.19 (s, 9 H), 1.197 (s, 9 H), 1.200 (s, 9 H), 1.21 (s, 9 H), 1.24 (s, 9 H), 1.39 (s, 9 H), 1.49 (s, 9 H); ^{13}C NMR (C_6D_6 , δ) -3.3, -3.2, -3.0, 5.2, 21.6, 21.7, 22.0, 22.1, 22.6, 23.1, 23.9, 24.8, 30.1, 30.2, 30.4, 30.5, 30.7, 31.4, 32.9, 33.4; ^{29}Si NMR (C_6D_6 , δ) -34.6, 14.4, 17.3, 19.2, 43.9, 158.1,

182.7; HRMS calcd for C₃₆H₈₄Si₇: 712.4958; found 712.4960.

Synthesis of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilenyli

The crystals of **11**⁺•TPFPB⁻ (70 mg, 0.051 mmol) and KC₈ (7 mg, 0.050 mmol) were placed in a reaction tube with a magnetic stirrer and degassed. Dry oxygen-free diethyl ether (1 mL) was introduced by vacuum transfer, and the mixture was stirred at room temperature to give a purplish-red solution within 5 min. After the solvent was removed in vacuo, degassed heptane was introduced. After the resulting K⁺•TPFPB⁻ salt and graphite had been removed, the solution was cooled to produce red-purple crystals of **11**[•] (29 mg, 83%); UV-Vis (hexane) λ_{max} /nm (ϵ) 241 (sh, 23500), 302 (9600), 331 (sh, 6300), 365 (sh, 4700), 483 (2100), 541 (9400).

X-ray Crystal Structure Determination of **11[•]**

A single crystal of **11**[•] for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo–K α radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 3-1a. The final atomic parameters, the bond length, and the bond angles of **11**[•] are listed in Table 3-1b and Table 3-1c, respectively.

Table 3-1a. Crystal data and structure refinement for **11**

Empirical formula	$\text{C}_{35}\text{H}_{81}\text{Si}_7$	
Formula weight	698.63	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Triclinic, $P\bar{1}$	
Unit cell dimensions	$a = 8.906(1)$ Å $b = 15.076(3)$ Å $c = 16.939(4)$ Å	$\alpha = 90.97(1)$ deg. $\beta = 90.82(1)$ deg. $\gamma = 91.92(1)$ deg.
Volume	$2272.5(8)$ Å ³	
Z, Calculated density	2, 1.021 Mg/m ³	
Absorption coefficient	0.231 mm ⁻¹	
F(000)	778	
Crystal size	0.5 x 0.4 x 0.3 mm	
Theta range for data collection	2.41 to 28.00 deg.	
Limiting indices	$0 \leq h \leq 10$, $-19 \leq k \leq 19$, $-21 \leq l \leq 22$	
Reflections collected / unique	7836 / 7836 [R(int) = 0.0000]	
Completeness to theta = 27.94	71.2%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7836 / 0 / 380	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R1 = 0.0767, wR2 = 0.1862	
R indices (all data)	R1 = 0.1172, wR2 = 0.2148	
Extinction coefficient	0.0089(19)	
Largest diff. peak and hole	0.495 and -0.346 e.Å ⁻³	

Table 3-1b.

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 11'. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	7194(2)	3747(1)	7638(1)	48(1)
Si(2)	7924(2)	2544(1)	6989(1)	42(1)
Si(3)	7025(2)	1639(1)	7937(1)	52(1)
Si(4)	6353(2)	2885(1)	8704(1)	40(1)
Si(5)	7178(2)	5303(1)	7456(1)	44(1)
Si(6)	8849(2)	2366(1)	5688(1)	44(1)
Si(7)	7327(2)	175(1)	8390(1)	40(1)
C(1)	6339(7)	5807(3)	8369(3)	61(2)
C(2)	5868(6)	5604(3)	6599(3)	51(1)
C(3)	4470(8)	4968(5)	6577(4)	82(2)
C(4)	5340(9)	6550(4)	6673(4)	86(2)
C(5)	6585(8)	5517(4)	5781(3)	68(2)
C(6)	9206(7)	5738(3)	7387(3)	54(1)
C(7)	9293(8)	6746(4)	7257(4)	72(2)
C(8)	10055(7)	5287(4)	6730(4)	67(2)
C(9)	10020(8)	5570(5)	8170(4)	81(2)
C(10)	8554(7)	3428(3)	5148(3)	58(1)
C(11)	7650(6)	1473(3)	5144(3)	49(1)
C(12)	5974(7)	1644(4)	5282(3)	60(1)
C(13)	7907(8)	1492(4)	4246(3)	68(2)
C(14)	7980(7)	549(3)	5458(3)	61(1)
C(15)	10971(6)	2181(3)	5744(3)	45(1)
C(16)	11396(7)	1440(3)	6296(3)	55(1)
C(17)	11751(7)	3050(3)	6058(3)	59(1)
C(18)	11592(6)	1977(4)	4912(3)	53(1)
C(19)	6936(6)	237(3)	9480(3)	46(1)
C(20)	5819(6)	-600(3)	7911(3)	49(1)
C(21)	4264(7)	-298(4)	8180(4)	64(2)
C(22)	5996(7)	-1559(3)	8202(3)	61(2)
C(23)	5826(7)	-616(4)	7011(3)	58(1)
C(24)	9352(6)	-215(3)	8295(3)	46(1)
C(25)	9654(7)	-988(4)	8855(3)	60(1)
C(26)	9730(6)	-506(3)	7453(3)	52(1)
C(27)	10422(7)	563(4)	8548(3)	58(1)
C(28)	4210(6)	2914(3)	8862(3)	46(1)
C(29)	3781(7)	3772(3)	9282(3)	58(1)
C(30)	3411(7)	2868(4)	8056(3)	63(1)
C(31)	3620(7)	2116(3)	9332(3)	58(1)
C(32)	7542(6)	3128(3)	9653(3)	44(1)
C(33)	7664(7)	4130(3)	9831(3)	55(1)
C(34)	9160(7)	2812(4)	9515(3)	59(1)
C(35)	6924(7)	2662(3)	10384(3)	56(1)

Table 3-1c. Bond lengths [Å] and angles [deg] for **11**.

Si(1)-Si(2)	2.2260(17)	Si(1)-Si(4)	2.3575(17)	Si(1)-Si(5)	2.3715(18)
Si(2)-Si(3)	2.2625(18)	Si(2)-Si(6)	2.3773(17)	Si(3)-Si(4)	2.3643(17)
Si(3)-Si(7)	2.3717(18)	Si(4)-C(28)	1.933(5)	Si(4)-C(32)	1.936(5)
Si(5)-C(1)	1.886(5)	Si(5)-C(6)	1.907(6)	Si(5)-C(2)	1.920(6)
Si(6)-C(10)	1.880(5)	Si(6)-C(11)	1.907(5)	Si(6)-C(15)	1.922(5)
Si(7)-C(19)	1.885(4)	Si(7)-C(20)	1.912(5)	Si(7)-C(24)	1.923(5)
C(2)-C(4)	1.519(7)	C(2)-C(5)	1.540(7)	C(2)-C(3)	1.545(8)
C(6)-C(8)	1.519(7)	C(6)-C(9)	1.531(8)	C(6)-C(7)	1.539(7)
C(11)-C(14)	1.535(7)	C(11)-C(13)	1.542(7)	C(11)-C(12)	1.544(7)
C(15)-C(16)	1.523(7)	C(15)-C(17)	1.545(7)	C(15)-C(18)	1.551(6)
C(20)-C(23)	1.524(7)	C(20)-C(21)	1.545(7)	C(20)-C(22)	1.547(7)
C(24)-C(26)	1.531(6)	C(24)-C(27)	1.538(7)	C(24)-C(25)	1.542(7)
C(28)-C(30)	1.530(7)	C(28)-C(29)	1.529(6)	C(28)-C(31)	1.536(7)
C(32)-C(35)	1.532(6)	C(32)-C(33)	1.535(6)	C(32)-C(34)	1.553(7)
Si(2)-Si(1)-Si(4)	91.41(6)	Si(2)-Si(1)-Si(5)	138.30(7)	Si(4)-Si(1)-Si(5)	130.29(7)
Si(1)-Si(2)-Si(3)	91.89(6)	Si(1)-Si(2)-Si(6)	130.82(7)	Si(3)-Si(2)-Si(6)	136.35(7)
Si(2)-Si(3)-Si(4)	90.33(6)	Si(2)-Si(3)-Si(7)	139.20(7)	Si(4)-Si(3)-Si(7)	126.67(7)
C(28)-Si(4)-C(32)	113.9(2)	C(28)-Si(4)-Si(1)	113.69(15)	C(32)-Si(4)-Si(1)	111.94(16)
C(28)-Si(4)-Si(3)	112.13(15)	C(32)-Si(4)-Si(3)	116.15(15)	Si(1)-Si(4)-Si(3)	86.18(6)
C(1)-Si(5)-C(6)	108.1(3)	C(1)-Si(5)-C(2)	105.5(3)	C(6)-Si(5)-C(2)	115.7(2)
C(1)-Si(5)-Si(1)	107.13(17)	C(6)-Si(5)-Si(1)	108.32(17)	C(2)-Si(5)-Si(1)	111.61(16)
C(10)-Si(6)-C(11)	106.2(2)	C(10)-Si(6)-C(15)	108.0(2)	C(11)-Si(6)-C(15)	116.4(2)
C(10)-Si(6)-Si(2)	108.02(17)	C(11)-Si(6)-Si(2)	108.78(16)	C(15)-Si(6)-Si(2)	109.13(15)
C(19)-Si(7)-C(20)	107.5(2)	C(19)-Si(7)-C(24)	106.4(2)	C(20)-Si(7)-C(24)	115.0(2)
C(19)-Si(7)-Si(3)	104.93(15)	C(20)-Si(7)-Si(3)	109.41(17)	C(24)-Si(7)-Si(3)	112.97(16)
C(4)-C(2)-C(5)	106.6(5)	C(4)-C(2)-C(3)	108.3(5)	C(5)-C(2)-C(3)	105.8(5)
C(4)-C(2)-Si(5)	112.2(4)	C(5)-C(2)-Si(5)	113.8(4)	C(3)-C(2)-Si(5)	109.7(4)
C(8)-C(6)-C(9)	108.2(5)	C(8)-C(6)-C(7)	108.3(5)	C(9)-C(6)-C(7)	107.0(5)
C(8)-C(6)-Si(5)	112.7(4)	C(9)-C(6)-Si(5)	108.8(4)	C(7)-C(6)-Si(5)	111.6(4)
C(14)-C(11)-C(13)	109.8(4)	C(14)-C(11)-C(12)	108.0(5)	C(13)-C(11)-C(12)	107.5(4)
C(14)-C(11)-Si(6)	110.8(4)	C(13)-C(11)-Si(6)	111.4(4)	C(12)-C(11)-Si(6)	109.2(3)
C(16)-C(15)-C(17)	107.8(4)	C(16)-C(15)-C(18)	108.9(4)	C(17)-C(15)-C(18)	108.0(4)
C(16)-C(15)-Si(6)	113.6(3)	C(17)-C(15)-Si(6)	107.7(4)	C(18)-C(15)-Si(6)	110.7(3)
C(23)-C(20)-C(21)	108.2(5)	C(23)-C(20)-C(22)	108.5(4)	C(21)-C(20)-C(22)	107.1(4)
C(23)-C(20)-Si(7)	114.3(4)	C(21)-C(20)-Si(7)	108.4(3)	C(22)-C(20)-Si(7)	110.1(4)
C(26)-C(24)-C(27)	108.7(4)	C(26)-C(24)-C(25)	108.6(4)	C(27)-C(24)-C(25)	107.2(4)
C(26)-C(24)-Si(7)	113.0(3)	C(27)-C(24)-Si(7)	107.9(3)	C(25)-C(24)-Si(7)	111.3(3)
C(30)-C(28)-C(29)	108.2(4)	C(30)-C(28)-C(31)	107.0(5)	C(29)-C(28)-C(31)	109.2(4)
C(30)-C(28)-Si(4)	108.8(4)	C(29)-C(28)-Si(4)	111.3(4)	C(31)-C(28)-Si(4)	112.1(4)
C(35)-C(32)-C(33)	108.4(4)	C(35)-C(32)-C(34)	108.2(4)	C(33)-C(32)-C(34)	107.1(4)
C(35)-C(32)-Si(4)	113.6(4)	C(33)-C(32)-Si(4)	110.6(3)	C(34)-C(32)-Si(4)	108.6(3)

Reaction of Cyclotetrasilanyl **11'** with 1,2-dibromoethane

An excess of 1,2-dibromoethane (0.1 mL) was added through a vacuum transfer to a hexane solution (1.5 mL) of **11'** (31 mg, 0.045 mmol). Reaction immediately took place, and the color of the reaction mixture was changed from red purple to colorless. The resulting *trans,trans*-1,2,3-tribromo-4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilene **15** was isolate after evaporation of solvent as colorless crystals in 79% (33 mg) yield. mp 82 °C (dec.), ^1H NMR (C_6D_6 , δ) 0.55 (s, 6 H), 0.63 (s, 3 H), 1.25 (s, 18 H), 1.28 (s, 18 H), 1.34 (s, 18 H), 1.45 (s, 9 H), 1.58 (s, 9 H); ^{13}C NMR (C_6D_6 , δ) -2.9, -2.3, 23.0 (2C), 23.2, 23.3, 24.4, 31.0, 31.1, 31.2, 33.4, 34.0; ^{29}Si NMR (C_6D_6 , δ) -8.2, 9.4, 18.6, 26.4, 37.3; MS $m/z(\%)$ 935 (M^+ , 5.0), 700 ($\text{M}^+ - ^t\text{Bu}_2\text{MeSiBr}$), 643 (33), 555 (36), 73 (100); Anal. Calcd for $\text{C}_{35}\text{H}_{81}\text{Br}_3\text{Si}_7$: C, 44.80; H, 8.70. Found: C, 45.12; H, 8.99.

Synthesis of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilenyllithium

Crystals of $\text{11}^+ \cdot \text{TPFPB}^-$ (65 mg, 0.047 mmol) and Li (18mg, 2.6 mmol) were placed in a sealed tube with a magnetic stirrer bar. After degassing the tube, dry oxygen-free Et_2O (2.5 mL) was introduced by vacuum transfer and stirred at room temperature to give a green solution of 11^- within 1 h. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the lithium and resulting TFPBPB- salt had been removed from the tube, the solution was cooled to afford green crystals of $\text{11}^- \cdot [\text{Li}(\text{Et}_2\text{O})]^+$ (31 mg, 85%). ^1H NMR (C_7D_8 , δ) 0.43 (s, 6 H), 0.52 (s, 3 H), 1.03 (t, $J = 7.0$ Hz, 6 H), 1.21 (s, 18 H), 1.26 (s, 18 H), 1.28 (s, 18 H) 1.42 (s, 9 H) 1.75 (s, 9 H) 3.39 (q, $J = 7.0$ Hz, 4 H); ^{13}C NMR (C_7D_8 , δ) -3.1, -1.5, 15.1, 22.0, 22.4, 22.6, 23.4, 25.1, 30.4,

30.71, 30.74, 31.2, 34.8, 66.3; ^{29}Si NMR (C_7D_8 , δ) -31.5, 13.9, 19.0, 26.0, 273.0; ^7Li NMR (C_7D_8 , δ) 1.96.

X-ray Crystal Structure Determination of $11^-\cdot[\text{Li}(\text{thf})]^+$

A single crystal of $11^-\cdot[\text{Li}(\text{thf})]^+$ for X-ray diffraction was grown from a hexane-THF solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 3-2a. The final atomic parameters, the bond length, and the bond angles of $11^-\cdot[\text{Li}(\text{thf})]^+$ are listed in Table 3-2b and Table 3-2c, respectively.

Table 3-2a. Crystal data and structure refinement for 11⁻•[Li(thf)]⁺

Empirical formula	C ₃₉ H ₈₉ LiOSi ₇	
Formula weight	777.67	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	a = 12.2510(3) Å b = 21.7420(4) Å c = 19.5840(5) Å	alpha = 90 deg. beta = 106.088(2) deg. gamma = 90 deg.
Volume	5012.1(2) Å ³	
Z, Calculated density	4, 1.031 Mg/m ³	
Absorption coefficient	0.216 mm ⁻¹	
F(000)	1728	
Crystal size	0.5 x 0.5 x 0.5 mm	
Theta range for data collection	2.16 to 27.95 deg.	
Limiting indices	0 ≤ h ≤ 16, 0 ≤ k ≤ 28, -25 ≤ l ≤ 24	
Reflections collected / unique	50409 / 12000 [R(int) = 0.0320]	
Completeness to theta = 27.94	99.7%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12000 / 0 / 434	
Goodness-of-fit on F ²	1.008	
Final R indices [I > 2sigma(I)]	R1 = 0.0487, wR2 = 0.1281	
R indices (all data)	R1 = 0.0575, wR2 = 0.1349	
Extinction coefficient	0.0053(5)	
Largest diff. peak and hole	1.219 and -0.379 e.Å ⁻³	

Table 3-2b.

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $11\text{-}[\text{Li}(\text{thf})]^+$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	3621(1)	1236(1)	6537(1)	24(1)
Si(2)	4596(1)	457(1)	7150(1)	22(1)
Si(3)	6016(1)	1081(1)	7831(1)	23(1)
Si(4)	5333(1)	1807(1)	6889(1)	20(1)
Si(5)	1924(1)	1394(1)	5624(1)	26(1)
Si(6)	3858(1)	-529(1)	7350(1)	29(1)
Si(7)	7985(1)	874(1)	8293(1)	25(1)
O(1)	3433(1)	1492(1)	8761(1)	33(1)
C(1)	2007(2)	2175(1)	5230(1)	45(1)
C(2)	644(2)	1434(1)	6011(1)	34(1)
C(3)	479(3)	848(1)	6393(2)	59(1)
C(4)	-468(2)	1562(2)	5434(2)	71(1)
C(5)	856(2)	1955(1)	6551(2)	60(1)
C(6)	1824(2)	810(1)	4871(1)	32(1)
C(7)	2850(2)	900(2)	4577(1)	56(1)
C(8)	1851(2)	145(1)	5139(1)	45(1)
C(9)	749(2)	895(1)	4253(1)	48(1)
C(10)	2299(2)	-588(1)	6870(2)	48(1)
C(11)	3947(2)	-588(1)	8343(1)	36(1)
C(12)	3084(3)	-137(1)	8499(2)	57(1)
C(13)	5130(2)	-410(1)	8819(1)	50(1)
C(14)	3660(2)	-1240(1)	8549(2)	50(1)
C(15)	4578(2)	-1174(1)	6961(1)	38(1)
C(16)	4681(3)	-957(1)	6235(1)	52(1)
C(17)	5770(2)	-1328(1)	7433(2)	54(1)
C(18)	3875(2)	-1770(1)	6856(2)	55(1)
C(19)	8793(2)	1481(1)	7942(1)	37(1)
C(20)	8337(2)	1012(1)	9303(1)	36(1)
C(21)	7620(2)	632(1)	9667(1)	50(1)
C(22)	9606(2)	901(1)	9685(1)	48(1)
C(23)	8086(2)	1693(1)	9409(1)	50(1)
C(24)	8537(2)	88(1)	8060(1)	30(1)
C(25)	7998(2)	-54(1)	7272(1)	36(1)
C(26)	8228(2)	-433(1)	8505(1)	37(1)
C(27)	9833(2)	90(1)	8185(1)	43(1)
C(28)	5160(2)	2622(1)	7272(1)	26(1)
C(29)	6311(2)	2872(1)	7723(1)	37(1)
C(30)	4615(2)	3090(1)	6689(1)	37(1)
C(31)	4394(2)	2571(1)	7772(1)	35(1)
C(32)	6056(2)	1859(1)	6118(1)	26(1)
C(33)	7076(2)	2302(1)	6280(1)	35(1)
C(34)	5208(2)	2083(1)	5426(1)	34(1)
C(35)	6461(2)	1215(1)	5977(1)	34(1)
C(36)	2279(2)	1655(1)	8722(1)	47(1)
C(37)	2336(2)	1950(1)	9431(1)	54(1)
C(38)	3236(3)	1582(2)	9922(2)	70(1)
C(39)	4085(2)	1463(2)	9497(1)	57(1)
Li(1)	4087(3)	1395(2)	8003(2)	35(1)

Table 3-2c. Bond lengths [Å] and angles [deg] for 11-•[Li(thf)]⁺

Si(1)-Si(2)	2.2245(7)	Si(1)-Si(5)	2.3617(7)	Si(1)-Si(4)	2.3692(7)
Si(1)-Li(1)	2.789(4)	Si(2)-Si(3)	2.3153(7)	Si(2)-Si(6)	2.4012(7)
Si(2)-Li(1)	2.814(4)	Si(3)-Si(7)	2.3732(7)	Si(3)-Si(4)	2.3955(7)
Si(3)-Li(1)	2.569(4)	Si(4)-C(32)	1.9539(19)	Si(4)-C(28)	1.9578(18)
Si(4)-Li(1)	3.121(4)	Si(5)-C(1)	1.881(2)	Si(5)-C(6)	1.923(2)
Si(5)-C(2)	1.925(2)	Si(6)-C(10)	1.884(2)	Si(6)-C(11)	1.922(2)
Si(6)-C(15)	1.921(2)	Si(7)-C(19)	1.890(2)	Si(7)-C(20)	1.928(2)
Si(7)-C(24)	1.938(2)	O(1)-C(36)	1.439(2)	O(1)-C(39)	1.442(3)
O(1)-Li(1)	1.885(4)	C(2)-C(3)	1.518(3)	C(2)-C(5)	1.523(3)
C(2)-C(4)	1.536(3)	C(6)-C(9)	1.533(3)	C(6)-C(7)	1.532(3)
C(6)-C(8)	1.535(3)	C(11)-C(12)	1.534(3)	C(11)-C(14)	1.540(3)
C(11)-C(13)	1.541(3)	C(15)-C(17)	1.534(3)	C(15)-C(18)	1.537(3)
C(15)-C(16)	1.537(4)	C(20)-C(21)	1.519(4)	C(20)-C(23)	1.538(3)
C(20)-C(22)	1.546(3)	C(24)-C(25)	1.531(3)	C(24)-C(26)	1.541(3)
C(24)-C(27)	1.538(3)	C(28)-C(31)	1.536(3)	C(28)-C(29)	1.541(3)
C(28)-C(30)	1.537(3)	C(31)-Li(1)	2.641(4)	C(32)-C(35)	1.536(3)
C(32)-C(33)	1.540(3)	C(32)-C(34)	1.539(3)	C(36)-C(37)	1.513(3)
C(37)-C(38)	1.480(4)	C(38)-C(39)	1.525(4)		
Si(2)-Si(1)-Si(5)	138.38(3)	Si(2)-Si(1)-Si(4)	86.70(2)	Si(5)-Si(1)-Si(4)	131.86(3)
Si(2)-Si(1)-Li(1)	67.19(8)	Si(5)-Si(1)-Li(1)	130.36(8)	Si(4)-Si(1)-Li(1)	73.94(8)
Si(1)-Si(2)-Si(3)	93.97(2)	Si(1)-Si(2)-Si(6)	126.75(3)	Si(3)-Si(2)-Si(6)	133.37(3)
Si(1)-Si(2)-Li(1)	66.03(8)	Si(3)-Si(2)-Li(1)	59.17(7)	Si(6)-Si(2)-Li(1)	113.28(8)
Si(2)-Si(3)-Si(7)	129.06(3)	Si(2)-Si(3)-Si(4)	84.07(2)	Si(7)-Si(3)-Si(4)	121.30(3)
Si(2)-Si(3)-Li(1)	70.13(8)	Si(7)-Si(3)-Li(1)	151.05(8)	Si(4)-Si(3)-Li(1)	77.80(9)
C(32)-Si(4)-C(28)	111.40(8)	C(32)-Si(4)-Si(1)	111.04(6)	C(28)-Si(4)-Si(1)	113.82(6)
C(32)-Si(4)-Si(3)	119.82(6)	C(28)-Si(4)-Si(3)	110.64(6)	Si(1)-Si(4)-Si(3)	88.34(2)
C(32)-Si(4)-Li(1)	166.16(9)	C(28)-Si(4)-Li(1)	82.28(9)	Si(1)-Si(4)-Li(1)	59.20(7)
Si(3)-Si(4)-Li(1)	53.58(7)	C(1)-Si(5)-C(6)	106.33(11)	C(1)-Si(5)-C(2)	105.25(10)
C(6)-Si(5)-C(2)	116.53(9)	C(1)-Si(5)-Si(1)	107.77(8)	C(6)-Si(5)-Si(1)	109.92(7)
C(2)-Si(5)-Si(1)	110.52(7)	C(10)-Si(6)-C(11)	105.41(12)	C(10)-Si(6)-C(15)	105.44(11)
C(11)-Si(6)-C(15)	116.64(10)	C(10)-Si(6)-Si(2)	110.79(8)	C(11)-Si(6)-Si(2)	107.83(7)
C(15)-Si(6)-Si(2)	110.58(7)	C(19)-Si(7)-C(20)	105.92(10)	C(19)-Si(7)-C(24)	106.10(9)
C(20)-Si(7)-C(24)	112.68(9)	C(19)-Si(7)-Si(3)	107.96(7)	C(20)-Si(7)-Si(3)	106.04(7)
C(24)-Si(7)-Si(3)	117.50(6)	C(36)-O(1)-C(39)	109.15(17)	C(36)-O(1)-Li(1)	127.68(17)
C(39)-O(1)-Li(1)	122.96(18)	C(3)-C(2)-C(5)	107.7(2)	C(3)-C(2)-C(4)	107.6(2)
C(5)-C(2)-C(4)	108.9(2)	C(3)-C(2)-Si(5)	112.92(15)	C(5)-C(2)-Si(5)	107.87(15)
C(4)-C(2)-Si(5)	111.80(17)	C(9)-C(6)-C(7)	107.63(18)	C(9)-C(6)-C(8)	108.44(18)
C(7)-C(6)-C(8)	107.8(2)	C(9)-C(6)-Si(5)	112.60(16)	C(7)-C(6)-Si(5)	108.61(15)
C(8)-C(6)-Si(5)	111.61(14)	C(12)-C(11)-C(13)	108.40(19)	C(12)-C(11)-C(13)	107.6(2)
C(14)-C(11)-C(13)	108.53(19)	C(12)-C(11)-Si(6)	108.06(16)	C(14)-C(11)-Si(6)	111.97(17)
C(13)-C(11)-Si(6)	112.11(15)	C(17)-C(15)-C(18)	107.5(2)	C(17)-C(15)-C(16)	108.4(2)
C(18)-C(15)-C(16)	108.7(2)	C(17)-C(15)-Si(6)	112.71(16)	C(18)-C(15)-Si(6)	111.48(17)
C(16)-C(15)-Si(6)	107.91(16)	C(21)-C(20)-C(23)	107.3(2)	C(21)-C(20)-C(22)	108.8(2)
C(23)-C(20)-C(22)	107.23(18)	C(21)-C(20)-Si(7)	113.80(15)	C(23)-C(20)-Si(7)	106.97(15)
C(22)-C(20)-Si(7)	112.41(16)	C(25)-C(24)-C(26)	108.48(17)	C(25)-C(24)-C(27)	107.37(18)
C(26)-C(24)-C(27)	108.41(17)	C(25)-C(24)-Si(7)	109.52(13)	C(26)-C(24)-Si(7)	111.03(14)
C(27)-C(24)-Si(7)	111.92(14)	C(31)-C(28)-C(29)	106.46(17)	C(31)-C(28)-C(30)	107.72(16)
C(29)-C(28)-C(30)	109.39(16)	C(31)-C(28)-Si(4)	109.26(12)	C(29)-C(28)-Si(4)	111.07(13)

Table 3-2c (continued). Bond lengths [Å] and angles [deg] for **11**-•[Li(thf)]⁺

C(30)-C(28)-Si(4)	112.70(13)	C(28)-C(31)-Li(1)	108.64(14)	C(35)-C(32)-C(33)	108.86(16)
C(35)-C(32)-C(34)	107.73(16)	C(33)-C(32)-C(34)	107.12(16)	C(35)-C(32)-Si(4)	108.90(12)
C(33)-C(32)-Si(4)	113.05(13)	C(34)-C(32)-Si(4)	111.02(13)	O(1)-C(36)-C(37)	105.07(19)
C(38)-C(37)-C(36)	101.8(2)	C(37)-C(38)-C(39)	103.6(2)	O(1)-C(39)-C(38)	105.4(2)
O(1)-Li(1)-Si(3)	137.73(19)	O(1)-Li(1)-C(31)	97.95(16)	Si(3)-Li(1)-C(31)	93.14(12)
O(1)-Li(1)-Si(1)	144.56(18)	Si(3)-Li(1)-Si(1)	76.45(9)	C(31)-Li(1)-Si(1)	86.66(12)
O(1)-Li(1)-Si(2)	139.60(19)	Si(3)-Li(1)-Si(2)	50.70(7)	C(31)-Li(1)-Si(2)	122.32(14)
Si(1)-Li(1)-Si(2)	46.78(6)	O(1)-Li(1)-Si(4)	156.33(18)	Si(3)-Li(1)-Si(4)	48.62(6)
C(31)-Li(1)-Si(4)	58.80(8)	Si(1)-Li(1)-Si(4)	46.85(6)	Si(2)-Li(1)-Si(4)	63.99(7)

Synthesis of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilenylnsodium

Crystals of $11^+ \cdot \text{TPFPB}^-$ (72 mg, 0.052 mmol) and Na (63 mg, 2.7 mmol) were placed in a sealed tube with a magnetic stirrer bar. After degassing the tube, dry oxygen-free Et_2O (2.0 mL) was introduced by vacuum transfer and stirred at room temperature to give a green solution of 11^- within 1 h. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the lithium and resulting TPFPB^- salt had been removed from the tube, the solution was cooled to afford green crystals of $11^- \cdot [\text{Na}(\text{Et}_2\text{O})]^+$ (27 mg, 65%). ^1H NMR ($\text{THF}-d_8$, δ) 0.12 (s, 6 H), 0.34 (s, 3 H), 1.10 (s, 36 H), 1.15 (s, 18 H), 1.45 (s, 18 H); ^{13}C NMR ($\text{THF}-d_8$, δ) -3.8, -2.5, 21.0, 22.1, 24.2, 30.3, 30.6, 32.6; ^{29}Si NMR ($\text{THF}-d_8$, δ) -24.5, 5.4, 7.4, 76.9, 224.3.

X-ray Crystal Structure Determination of $11^- \cdot [\text{Na}(\text{thf})_3]^+$

A single crystal of $11^- \cdot [\text{Na}(\text{thf})_3]^+$ for X-ray diffraction was grown from a hexane-THF solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 3-3a. The final atomic parameters, the bond length, and the bond angles of $11^- \cdot [\text{Na}(\text{thf})_3]^+$ are listed in Table 3-3b and Table 3-3c, respectively.

Table 3-3a. Crystal data and structure refinement for $11^{-}\cdot[\text{Na}(\text{thf})_3]^{+}$

Empirical formula	$\text{C}_{47}\text{H}_{105}\text{NaO}_3\text{Si}_7$	
Formula weight	937.93	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Monoclinic, $P2_1/n$	
Unit cell dimensions	$a = 11.9930(6)$ Å $b = 21.7390(13)$ Å $c = 23.8780(14)$ Å	$\alpha = 90$ deg. $\beta = 102.358(4)$ deg. $\gamma = 90$ deg.
Volume	$6081.1(6)$ Å ³	
Z, Calculated density	4, 1.024 Mg/m ³	
Absorption coefficient	0.197 mm ⁻¹	
F(000)	2080	
Crystal size	0.3 x 0.2 x 0.1 mm	
Theta range for data collection	2.07 to 27.95 deg.	
Limiting indices	$0 \leq h \leq 15$, $0 \leq k \leq 28$, $-31 \leq l \leq 30$	
Reflections collected / unique	56476 / 13554 [$R(\text{int}) = 0.0900$]	
Completeness to $\theta = 27.94$	92.7%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13554 / 0 / 524	
Goodness-of-fit on F^2	1.025	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0810$, $wR2 = 0.2003$	
R indices (all data)	$R1 = 0.1106$, $wR2 = 0.2225$	
Extinction coefficient	$0.0082(8)$	
Largest diff. peak and hole	1.415 and -0.812 e.Å ⁻³	

Table 3-3b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $11\Gamma \cdot [\text{Na}(\text{thf})_3]^+$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	4266(1)	-1160(1)	2826(1)	23(1)
Si(2)	3292(1)	-1214(1)	1861(1)	25(1)
Si(3)	4477(1)	-1874(1)	1602(1)	26(1)
Si(4)	5255(1)	-2051(1)	2579(1)	22(1)
Si(5)	3128(1)	-1116(1)	3535(1)	36(1)
Si(6)	1908(1)	-595(1)	1240(1)	42(1)
Si(7)	4951(1)	-2320(1)	784(1)	28(1)
Na(1)	5646(1)	6(1)	2854(1)	35(1)
O(1)	6291(3)	295(1)	2037(1)	50(1)
O(2)	5212(3)	965(1)	3207(2)	57(1)
O(3)	7468(2)	47(2)	3447(1)	51(1)
C(1)	2398(4)	-334(2)	3420(2)	52(1)
C(2)	1895(4)	-1690(2)	3552(2)	46(1)
C(3)	1258(4)	-1814(2)	2933(2)	52(1)
C(4)	1008(4)	-1438(3)	3874(2)	67(2)
C(5)	2347(4)	-2304(2)	3837(2)	57(1)
C(6)	4152(4)	-1038(2)	4279(2)	49(1)
C(7)	4880(5)	-464(3)	4272(2)	69(2)
C(8)	4971(4)	-1589(3)	4415(2)	62(1)
C(9)	3524(5)	-976(3)	4773(2)	71(2)
C(10)	1776(5)	-837(3)	445(2)	71(2)
C(11)	2432(4)	233(2)	1288(2)	44(1)
C(12)	2800(5)	451(2)	1919(2)	59(1)
C(13)	3486(5)	253(3)	1021(3)	77(2)
C(14)	1556(5)	690(2)	961(2)	58(1)
C(15)	398(4)	-716(2)	1357(2)	54(1)
C(16)	-509(4)	-477(3)	834(3)	74(2)
C(17)	276(5)	-402(3)	1914(2)	66(1)
C(18)	196(5)	-1411(3)	1396(3)	71(2)
C(19)	6172(3)	-2868(2)	1042(2)	40(1)
C(20)	5525(3)	-1715(2)	327(2)	36(1)
C(21)	6720(4)	-1520(2)	653(2)	52(1)
C(22)	4779(4)	-1138(2)	232(2)	45(1)
C(23)	5628(5)	-1972(2)	-259(2)	52(1)
C(24)	3695(3)	-2811(2)	377(2)	35(1)
C(25)	2729(4)	-2403(2)	49(2)	53(1)
C(26)	3224(4)	-3200(2)	811(2)	50(1)
C(27)	4072(4)	-3263(2)	-45(2)	49(1)
C(28)	6906(3)	-1914(2)	2818(1)	26(1)
C(29)	7223(3)	-1395(2)	2450(2)	34(1)
C(30)	7226(3)	-1710(2)	3447(2)	36(1)
C(31)	7647(3)	-2475(2)	2747(2)	37(1)
C(32)	4843(3)	-2874(2)	2785(2)	31(1)

Table 3-3b (continued). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11**-•[Na(thf)₃]⁺. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

C(33)	5276(4)	-2993(2)	3434(2)	41(1)
C(34)	5303(4)	-3380(2)	2448(2)	39(1)
C(35)	3537(3)	-2930(2)	2633(2)	40(1)
C(36)	6585(4)	-98(2)	1602(2)	51(1)
C(37)	6607(5)	302(2)	1092(2)	57(1)
C(38)	6994(7)	903(3)	1378(2)	90(2)
C(39)	6413(6)	934(2)	1893(2)	74(2)
C(40)	4195(5)	1225(3)	3309(4)	105(3)
C(41)	4392(5)	1859(3)	3481(4)	94(3)
C(42)	5609(5)	1973(3)	3534(4)	87(2)
C(43)	6119(5)	1376(3)	3457(3)	82(2)
C(44)	8516(5)	107(4)	3270(3)	90(2)
C(45)	9396(6)	274(4)	3776(5)	134(4)
C(46)	8950(10)	132(6)	4235(5)	201(8)
C(47)	7776(6)	-25(3)	4060(2)	82(2)

Table 3-3c. Bond lengths [\AA] and angles [deg] for **11**-•[Na(thf)₃]⁺

Si(1)-Si(2)	2.3520(12)	Si(1)-Si(5)	2.3934(13)	Si(1)-Si(4)	2.4103(12)
Si(1)-Na(1)	3.0193(17)	Si(2)-Si(3)	2.1992(13)	Si(2)-Si(6)	2.3903(13)
Si(3)-Si(4)	2.3511(12)	Si(3)-Si(7)	2.3557(12)	Si(4)-C(32)	1.947(3)
Si(4)-C(28)	1.963(3)	Si(5)-C(1)	1.904(5)	Si(5)-C(6)	1.939(4)
Si(5)-C(2)	1.942(5)	Si(6)-C(11)	1.903(4)	Si(6)-C(15)	1.908(5)
Si(6)-C(10)	1.946(5)	Si(7)-C(19)	1.886(4)	Si(7)-C(20)	1.927(4)
Si(7)-C(24)	1.930(4)	Na(1)-O(1)	2.335(3)	Na(1)-O(3)	2.337(3)
Na(1)-O(2)	2.349(3)	O(1)-C(39)	1.446(5)	O(1)-C(36)	1.446(6)
O(2)-C(40)	1.412(6)	O(2)-C(43)	1.435(6)	O(3)-C(44)	1.416(6)
O(3)-C(47)	1.440(6)	C(2)-C(3)	1.536(7)	C(2)-C(5)	1.542(6)
C(2)-C(4)	1.541(6)	C(6)-C(7)	1.526(8)	C(6)-C(8)	1.539(7)
C(6)-C(9)	1.536(6)	C(11)-C(14)	1.532(6)	C(11)-C(13)	1.532(7)
C(11)-C(12)	1.551(7)	C(15)-C(17)	1.529(7)	C(15)-C(18)	1.536(7)
C(15)-C(16)	1.559(6)	C(20)-C(22)	1.530(6)	C(20)-C(23)	1.536(5)
C(20)-C(21)	1.538(6)	C(24)-C(25)	1.534(6)	C(24)-C(26)	1.536(6)
C(24)-C(27)	1.541(5)	C(28)-C(29)	1.528(5)	C(28)-C(30)	1.535(5)
C(28)-C(31)	1.538(5)	C(32)-C(34)	1.533(5)	C(32)-C(35)	1.535(5)
C(32)-C(33)	1.546(5)	C(36)-C(37)	1.499(6)	C(37)-C(38)	1.501(8)
C(38)-C(39)	1.540(9)	C(40)-C(41)	1.444(8)	C(41)-C(42)	1.459(8)
C(42)-C(43)	1.463(7)	C(44)-C(45)	1.470(10)	C(45)-C(46)	1.354(15)
C(46)-C(47)	1.422(11)				

Table 3-3c (continued). Bond lengths [\AA] and angles [deg] for $11\text{-}\bullet[\text{Na}(\text{thf})_3]^+$

Si(2)-Si(1)-Si(5)	117.14(5)	Si(2)-Si(1)-Si(4)	83.52(4)	Si(5)-Si(1)-Si(4)	126.16(5)
Si(2)-Si(1)-Na(1)	102.65(5)	Si(5)-Si(1)-Na(1)	110.08(5)	Si(4)-Si(1)-Na(1)	112.61(5)
Si(3)-Si(2)-Si(1)	95.34(4)	Si(3)-Si(2)-Si(6)	126.74(6)	Si(1)-Si(2)-Si(6)	135.42(5)
Si(2)-Si(3)-Si(4)	88.33(4)	Si(2)-Si(3)-Si(7)	141.86(5)	Si(4)-Si(3)-Si(7)	129.80(5)
C(32)-Si(4)-C(28)	111.14(15)	C(32)-Si(4)-Si(3)	109.47(12)	C(28)-Si(4)-Si(3)	115.11(10)
C(32)-Si(4)-Si(1)	120.82(12)	C(28)-Si(4)-Si(1)	109.02(11)	Si(3)-Si(4)-Si(1)	89.97(4)
C(1)-Si(5)-C(6)	103.6(2)	C(1)-Si(5)-C(2)	104.4(2)	C(6)-Si(5)-C(2)	111.9(2)
C(1)-Si(5)-Si(1)	104.37(14)	C(6)-Si(5)-Si(1)	107.86(14)	C(2)-Si(5)-Si(1)	122.76(14)
C(11)-Si(6)-C(15)	115.7(2)	C(11)-Si(6)-C(10)	105.7(2)	C(15)-Si(6)-C(10)	103.0(3)
C(11)-Si(6)-Si(2)	108.62(14)	C(15)-Si(6)-Si(2)	112.77(15)	C(10)-Si(6)-Si(2)	110.67(16)
C(19)-Si(7)-C(20)	105.60(18)	C(19)-Si(7)-C(24)	106.47(18)	C(20)-Si(7)-C(24)	115.21(17)
C(19)-Si(7)-Si(3)	107.31(13)	C(20)-Si(7)-Si(3)	111.53(12)	C(24)-Si(7)-Si(3)	110.19(12)
O(1)-Na(1)-O(3)	93.53(12)	O(1)-Na(1)-O(2)	101.46(13)	O(3)-Na(1)-O(2)	89.92(13)
O(1)-Na(1)-Si(1)	119.04(9)	O(3)-Na(1)-Si(1)	118.87(10)	O(2)-Na(1)-Si(1)	126.24(10)
C(39)-O(1)-C(36)	110.1(4)	C(39)-O(1)-Na(1)	121.7(3)	C(36)-O(1)-Na(1)	128.1(2)
C(40)-O(2)-C(43)	106.6(4)	C(40)-O(2)-Na(1)	133.0(3)	C(43)-O(2)-Na(1)	119.7(3)
C(44)-O(3)-C(47)	105.2(5)	C(44)-O(3)-Na(1)	126.7(4)	C(47)-O(3)-Na(1)	127.9(3)
C(3)-C(2)-C(5)	109.1(4)	C(3)-C(2)-C(4)	106.8(4)	C(5)-C(2)-C(4)	107.6(4)
C(3)-C(2)-Si(5)	108.5(3)	C(5)-C(2)-Si(5)	111.6(3)	C(4)-C(2)-Si(5)	113.1(4)
C(7)-C(6)-C(8)	107.3(4)	C(7)-C(6)-C(9)	108.2(4)	C(8)-C(6)-C(9)	107.5(4)
C(7)-C(6)-Si(5)	108.3(3)	C(8)-C(6)-Si(5)	112.1(3)	C(9)-C(6)-Si(5)	113.2(3)
C(14)-C(11)-C(13)	107.9(4)	C(14)-C(11)-C(12)	108.6(4)	C(13)-C(11)-C(12)	107.9(4)
C(14)-C(11)-Si(6)	113.7(3)	C(13)-C(11)-Si(6)	107.1(3)	C(12)-C(11)-Si(6)	111.6(3)
C(17)-C(15)-C(18)	109.9(5)	C(17)-C(15)-C(16)	111.5(5)	C(18)-C(15)-C(16)	106.5(4)
C(17)-C(15)-Si(6)	109.6(3)	C(18)-C(15)-Si(6)	108.2(4)	C(16)-C(15)-Si(6)	111.0(4)
C(22)-C(20)-C(23)	108.8(3)	C(22)-C(20)-C(21)	107.5(4)	C(23)-C(20)-C(21)	108.2(3)
C(22)-C(20)-Si(7)	112.1(3)	C(23)-C(20)-Si(7)	112.1(3)	C(21)-C(20)-Si(7)	108.0(3)
C(29)-C(28)-C(30)	107.9(3)	C(29)-C(28)-C(31)	107.7(3)	C(30)-C(28)-C(31)	107.9(3)
C(29)-C(28)-Si(4)	107.8(2)	C(30)-C(28)-Si(4)	110.7(2)	C(31)-C(28)-Si(4)	114.7(2)
C(34)-C(32)-C(35)	106.5(3)	C(34)-C(32)-C(33)	109.0(3)	C(35)-C(32)-C(33)	109.3(3)
C(34)-C(32)-Si(4)	112.8(2)	C(35)-C(32)-Si(4)	108.3(2)	C(33)-C(32)-Si(4)	110.9(2)
O(1)-C(36)-C(37)	106.9(4)	C(36)-C(37)-C(38)	101.1(4)	C(37)-C(38)-C(39)	104.7(4)
O(1)-C(39)-C(38)	103.5(5)	O(2)-C(40)-C(41)	109.6(5)	C(40)-C(41)-C(42)	106.6(5)
C(41)-C(42)-C(43)	106.0(5)	O(2)-C(43)-C(42)	107.7(5)	O(3)-C(44)-C(45)	107.7(6)
C(46)-C(45)-C(44)	105.7(7)	C(45)-C(46)-C(47)	110.8(8)	C(46)-C(47)-O(3)	107.1(7)

Synthesis of 4,4-di-*tert*-butyl-1,2,3-tris[di-*tert*-butyl(methyl)silyl]cyclo-tetrasilenyipotassium

Crystals of **11**⁺·TPFPB[−] (82 mg, 0.060 mmol) and KC₈ (16 mg, 0.12 mmol) were placed in a sealed tube with a magnetic stirrer bar. After degassing the tube, dry oxygen-free Et₂O (1.5 mL) was introduced by vacuum transfer and stirred at room temperature to give a green solution of **11**[−] within 30 minutes. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the lithium and resulting TPFPB[−] salt had been removed from the tube, the solution was cooled to afford green crystals of **11**[−]·K⁺ (33 mg, 75%). ¹H NMR (THF-*d*₈, δ) 0.12 (s, 6 H), 0.34 (s, 3 H), 1.10 (s, 36 H), 1.15 (s, 18 H), 1.45 (s, 18 H); ¹³C NMR (THF-*d*₈, δ) −2.8, −1.5, 22.0, 23.1, 25.2, 31.3, 31.6, 33.6; ²⁹Si NMR (THF-*d*₈, δ) −23.0, 5.5, 7.6, 76.8, 224.1.

References and Notes

- [1] F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, Part A: Structure and Mechanisms, 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2000.
- [2] a) P. Andersen and B. Klewe, *Acta Chem. Scand.*, **1967**, *21*, 2599; b) O. Armet, J. Veciana, C. Rovira, J. Riera, J. Castaner, E. Molins, J. Rius, C. Miravittles, S. Olivella, and J. Brichfeus, *J. Phys. Chem.*, **1987**, *91*, 5608; c) H. Sitzmann and R. Boese, *Angew. Chem., Int. Ed. Engl.*, **1991**, *30*, 971; d) B. T. King, B. C. Noll, A. J. McKinley, and J. Michl, *J. Am. Chem. Soc.*, **1996**, *118*, 10902; e) Y. Apeloig, D. Bravo-Zhivotovskii, M. Bendikov, D. Danovich, M. Botoshansky, T. Vakul'skaya, M. Voronkov, R. Samoilova, M. Zdravkova, V. Igonin, V. Shklover, and Y. Struchkov, *J. Am. Chem. Soc.* **1999**, *121*, 8118.
- [3] For reviews on silyl and germyl radicals, see: a) H. Sakurai, *Free Radicals*; J. K. Kochi, Ed.; John Wiley & Sons Ltd.: New York, **1973**; Vol. II; b) C. Chatgililoglu, *Chem. Rev.*, **1995**, *95*, 1229; c) J. Iley, In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, **1995**; Chapter 5.
- [4] For examples of persistent silyl and germyl radicals, see: a) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. (A)*, **1970**, 348; b) J. D. Cotton, C. S. Cundy, D. H. Harris, A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, **1974**, 651; c) A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, **1976**, 2369; d) M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Rivière, and M. Rivière-Baudet, *J. Organomet. Chem.*, **1980**, *202*, 5; e) H. Sakurai, H. Umino, and H. Sugiyama, *J. Am. Chem. Soc.*, **1980**, *102*, 6837; f) A. J. McKinley, T. Karatsu, G. M. Wallraff, R. D. Miller, R. Sooriyakumaran, and J. Michl, *Organometallics*, **1988**, *7*, 2567; g) A. J. McKinley, T. Karatsu, G. M. Wallraff, D. P. Thompson, R. D. Miller, and J.

- Michl, *J. Am. Chem. Soc.*, **1991**, *113*, 2003; h) S. Kyushin, H. Sakurai, T. Betsuyaku, and H. Matsumoto, *Organometallics*, **1997**, *16*, 5386; i) S. Kyushin, H. Sakurai, and H. Matsumoto, *Chem. Lett.*, **1998**, 107; j) M. Kira, T. Obata, I. Kon, H. Hashimoto, M. Ichinohe, H. Sakurai, S. Kyushin, and H. Matsumoto, *Chem. Lett.*, **1998**, 1097; k) Y. Apeloig, D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, and A. I. Shames, *Appl. Magn. Reson.*, **2000**, *18*, 425.
- [5] M. M. Olmstead, L. Pu, R. S. Simons, and P. P. Power, *Chem. Commun.*, **1997**, 1595.
- [6] a) A. Sekiguchi, T. Fukawa, M. Nakamoto, V. Ya. Lee, and M. Ichinohe, *J. Am. Chem. Soc.*, **2002**, *124*, 9865; b) A. Sekiguchi, T. Fukawa, V. Ya. Lee, and M. Nakamoto, *J. Am. Chem. Soc.*, **2003**, *124*, 9250.
- [7] a) M. Kira, T. Iwamoto, and C. Kabuto, *J. Am. Chem. Soc.*, **1996**, *118*, 10303; b) T. Iwamoto and M. Kira, *Chem. Lett.*, **1998**, 277; c) N. Wiberg, H. Auer, H. Nöth, J. Knizek, and K. Polborn, *Angew. Chem. Int. Ed.*, **1998**, *37*, 2869.
- [8] S. Masamune, Y. Kabe, S. Collins, D. J. Williams, and R. Jones, *J. Am. Chem. Soc.*, **1985**, *107*, 5552.
- [9] For reviews on silyllithium compounds, see: a) P. D. Lickiss and C. M. Smith, *Coord. Chem. Rev.*, **1995**, *145*, 75; b) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, **1995**, *38*, 1; c) J. Belzner and U. Dehnert, In *The Chemistry of Organic Silicon Compounds*; Z. Rappoport and Y. Apeloig, Eds.; John Wiley & Sons Ltd.: **1998**; Vol. 2, Part 1, Chapter 14; d) A. Sekiguchi, V. Ya. Lee, and M. Nanjo, *Coord. Chem. Rev.*, **2000**, *210*, 11.
- [10] a) J.-H. Hong, P. Boudjouk, and S. Castellino, *Organometallics*, **1994**, *13*, 3387; b) U. Bankwitz, H. Sohn, D. R. Powell and R. West, *J. Organomet. Chem.*, **1995**, *499*, C7; c) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Müller, *J. Am. Chem. Soc.*, **1995**, *117*, 11608; d) W. P. Freeman, T. D. Tilley, G. P. A. Yap,

- and A. L. Rheingold, *Angew. Chem. Int. Ed. Engl.*, **1996**, 35, 882.
- [11] H. Schäfer, W. Saak, and M. Weidenbruch, *Angew. Chem. Int. Ed.*, **2000**, 39, 3703.
- [12] 3,4-Diiodo-1,2,3,4-tetrakis(tri-*tert*-butylsilyl)cyclotetrasilene has also been reported.^{7c} Its Si=Si double bond length is reported to be 2.257(2) Å, which is significantly elongated due to the steric reasons and/or the $\sigma(\text{Si-I})$ - $\pi(\text{Si=Si})$ hyper conjugation.
- [13] For the similar delocalization of the unpaired electron in the cyclotrigermenyl radical, see ref 5.
- [14] For the carbon allyl-type analogous radical with a silacyclobutenyl skeleton, see: G. Maier, A. Kratt, A. Schick, H. P. Reisenauer, F. Barbosa, and G. Gescheidt, *Eur. J. Org. Chem.* **2000**, 1107.
- [15] M. Kaftory, M. Kapon, and M. Botoshansky, in *The Chemistry of Organic Silicon Compounds*; Z. Rappoport and Y. Apeloig, Eds.; John Wiley & Sons Ltd.: 1998; Vol. 2, Part 1, Chapter 5; b) T. A. Schmedake, M. Haaf, Y. Apeloig, T. Müller, S. Bukalov, and R. West, *J. Am. Chem. Soc.*, **1999**, 121, 9479.
- [16] G. C. Levy, R. L. Lichter, and G. L. Nelson, in *Carbon-13 NMR spectroscopy*, 2nd Ed., Wiley, New York, **1980**.
- [17] Spectral data of **11**-Li⁺ in THF-*d*₈. ¹H NMR (THF-*d*₈, δ) 0.12 (s, 6 H), 0.33 (s, 3 H), 1.09 (s, 36 H), 1.15 (s, 18 H), 1.44 (s, 18 H); ¹³C NMR (THF-*d*₈, δ) -2.8, -1.5, 22.0, 23.1, 25.2, 31.3, 31.6, 33.6; ²⁹Si NMR (THF-*d*₈, δ) -24.7, 5.4, 7.4, 77.1, 224.5; ⁷Li NMR (THF-*d*₈, δ) 2.61.