

# Polymeric Chain Structures of Substituted (Dimethylfluorenylsilyl)cyclopentadienyl Lithium and Sodium Compounds

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**Summary:** Reaction of the dimethylsilyl-bridged fluorene cyclopentadiene ligand with 1 equiv of *n*-butyllithium or sodium hydride smoothly afforded the corresponding monoalkali-metal salts  $[(\text{FluMe}_2\text{Si})\text{Cp}]_n\text{M}(\text{THF})_n$  ( $\text{Cp} = \text{C}_5\text{H}_4$ ,  $\text{Flu} = \text{C}_{13}\text{H}_9$ ) ( $\text{M} = \text{Li}$  (**1**),  $n = 0$ ;  $\text{M} = \text{Na}$  (**2**),  $n = 1$ ). Complexes **1** and **2** were characterized by single-crystal X-ray structural analyses. These revealed that both of them have similar linear polymeric structural aggregate types in the solid state. In complexes **1** and **2**, the fluorenyldimethylsilyl groups attached to the cyclopentadienyl rings are arranged in gaps and oriented on the same side of the multideck chain.

## Introduction

Due to the rapid development of metallocene chemistry in the 1950s, alkali-metal derivatives of cyclopentadienes have become indispensable starting reagents.<sup>1</sup> Numerous alkyl- and silyl-substituted cyclopentadienyl ligands have been synthesized and characterized in organometallic chemistry, e.g.,  $\text{C}_5\text{H}_5\text{-}n(\text{CMe}_3)_n$  ( $n = 1$  or  $2$ ),  $\text{C}_5\text{H}_5\text{-}m(\text{SiMe}_3)_m$  ( $m = 1$  or  $2$ ), and  $\text{C}_5\text{H}_5\text{-}m(\text{SiMe}_2\text{-}^t\text{Bu})_m$  ( $m = 1$  or  $2$ ), and have been extensively used in the organometallic chemistry of most of the main group and transition metals, as well as for the f-elements.<sup>2</sup> During the past two decades, the study of bridged dicyclopentadienyl metal complexes has been a very important area of research. In recent years, there is also an increasing interest in the synthesis of the transition metal compounds containing bridged dicyclopentadienyl-type ligands with only one of its rings linked to the metal. Organotransition metal complexes of this type are usually considered as potential precursors for the synthesis of binuclear complexes.<sup>3</sup> However, until now no crystal structures of the monoalkali metal derivatives of bridged bis-cyclopentadienyl ligands have been re-

ported. In the framework of our systematic studies of silylated dicyclopentadienyl metallocenes, we now report our latest results on the synthesis and characterization of monolithium and -sodium derivatives of dimethylsilylene-bridged fluorenylcyclopentadienyl systems.

## Experimental Section

All operations with organometallic compounds were carried out under an inert atmosphere of argon using standard Schlenk techniques. Solvents were distilled under argon over sodium benzophenone ketyl prior to use. Mass spectra were recorded on a HP 5989A spectrometer ( $T = 50\text{--}400\text{ }^\circ\text{C}$ , 1.3 kV). The element analysis result of complex **1** was not satisfactory, due to the extreme sensitivity to air and moisture. The solvent THF-*d*<sub>8</sub> was degassed and dried over a Na/K alloy. <sup>1</sup>H NMR spectra were recorded on a Bruker Am-300 (300 MHz) spectrometer.

**Synthesis of  $\{[(\text{C}_{13}\text{H}_9\text{Me}_2\text{Si})\text{C}_5\text{H}_4]\text{Li}\}_n$  (**1**).** *n*-Butyllithium (1.0 mL, 1.8 M in *n*-hexane) was added dropwise to a solution of dimethylsilyl-bridged fluorene cyclopentadiene ligand (510 mg, 1.77 mmol) in diethyl ether (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the evolution of gas finished the reaction mixture was filtered, the filtrate was concentrated to 2 mL, and slowly adding hexane afforded **1** as colorless needle crystals (130 mg, 26%). EI mass spectrum (70 eV, 50–400 °C) *m/z* (relative abundance): 294 (2.7, [M]<sup>+</sup>), 287 (7.8, [M – Li]<sup>+</sup>), 165 (100, [C<sub>13</sub>H<sub>9</sub>]<sup>+</sup>), 123 (34.0, [C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>]<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>):  $\delta$  7.79 (d, 2H,  $J = 8.0$ , Flu), 7.28 (d, 2H,  $J = 7.8$ , Flu), 7.21 (t, 2H,  $J = 6.8$ , Flu), 7.14 (t, 2H,  $J = 7.0$ , Flu), 6.18 (s, 4H, Cp), 4.02 (s, 1H, 9H-Flu), –0.16 (s, 6H, SiMe<sub>2</sub>).

We tried to synthesis compound **1** in THF, but only a brown oily product was obtained.

**Synthesis of  $\{[(\text{C}_{13}\text{H}_9\text{Me}_2\text{Si})\text{C}_5\text{H}_4]\text{Na}\cdot\text{THF}\}_n$  (**2**).** Dimethylsilyl-bridged fluorene cyclopentadiene ligand (1.8 g, 6.25 mmol) was added dropwise to a suspension of sodium hydride (0.164 g, 6.83 mmol) in THF (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the evolution of gas finished, the reaction mixture was filtered, the filtrate was concentrated to 10 mL, and slowly adding hexane by vapor diffusion afforded **2** as colorless needle crystals (1.128 g, 58%). Anal. Calcd for C<sub>28</sub>H<sub>35</sub>SiNaO<sub>2</sub> (**2** + THF): C, 73.96; H, 7.76. Found: C, 73.61; H, 6.83. EI mass spectrum (70 eV, 50–400 °C) *m/z* (relative abundance): 310 (26.9, [M]<sup>+</sup>), 287 (14.6, [M – Na]<sup>+</sup>), 165 (100, [C<sub>13</sub>H<sub>9</sub>]<sup>+</sup>), 123 (59.1, [C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>]<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>):  $\delta$  7.86 (d, 2H,  $J = 7.8$ , Flu), 7.15 (m, 2H, Flu), 7.28 (t, 2H,  $J = 8.0$ , Flu), 7.19 (t, 2H,  $J = 7.9$ , Flu), 6.28 (t, 2H,  $J = 2.6$ , Cp), 6.20 (t, 2H,  $J = 2.5$ , Cp), 4.04 (s, 1H, 9H-Flu), 0.01 (s, 6H, SiMe<sub>2</sub>). FT-Raman (cm<sup>–1</sup>): 3058 (m), 1607 (s), 1475 (m), 1299 (s), 1236 (m), 1221 (m), 1186 (m), 1153 (w), 1045 (m), 1025 (w), 744 (m), 404 (w).

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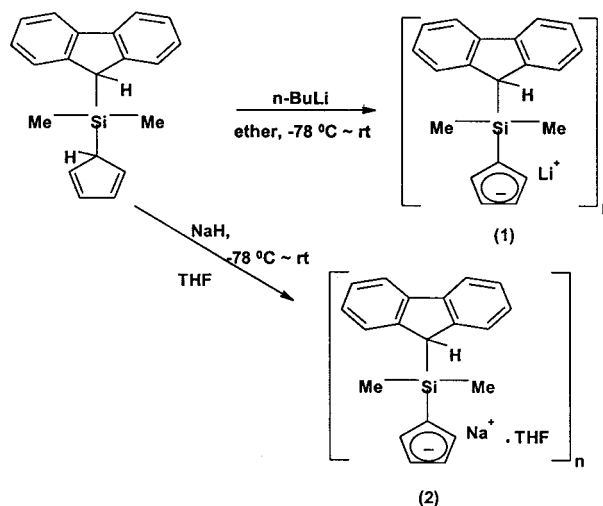
**Table 1. X-ray Diffraction Data Collection Parameters for Complexes 1 and 2**

	1	2
formula	C <sub>40</sub> H <sub>38</sub> Si <sub>2</sub> Li <sub>2</sub>	C <sub>24</sub> H <sub>27</sub> SiONa
fw	588.79	382.55
cryst syst	monoclinic	orthorhombic
space group	<i>P2<sub>1</sub>/a</i>	<i>Pca2<sub>1</sub></i>
<i>a</i> , Å	7.831(2)	18.652(3)
<i>b</i> , Å	15.356(3)	11.852(2)
<i>c</i> , Å	28.476(8)	9.621(3)
$\beta$ , deg	96.73(2)	
<i>V</i> , Å <sup>3</sup>	3400(1)	2126(1)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> , Mg/cm <sup>3</sup>	1.150	1.195
<i>F</i> (000)	1248.00	816.00
$\mu$ , cm <sup>-1</sup>	1.30	1.41
no. reflns	5839	2795
no. observations	3700	1581
no. variables	388	243
final <i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.047; 0.057	0.054; 0.056
peak, hole/e Å <sup>3</sup>	0.24; -0.32	0.23; -0.29

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{0.5}.$$

**Solution and Refinement of the Crystal Structures.**

As the compounds are all air sensitive, crystals were sealed into thin-walled glass capillaries under an argon atmosphere. Crystal data and experimental details are presented in Table 1. The selected bond lengths and angles for complexes **1** and **2** are listed in Tables 2 and 3, respectively. X-ray diffraction data were collected at room temperature using  $\omega$ - $2\theta$  scan technique to maximum  $2\theta$  values of 50.0° and 55.0° for complexes **1** and **2**. The intensities of three representative reflections were measured after every 200 reflections, respectively. During the data collection, the standards decreased by 2.3% and 0.1%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected to eliminate the Lorentz and polarization effects. Both of the structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were put into the calculated positions, but not refined. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation.<sup>4</sup>

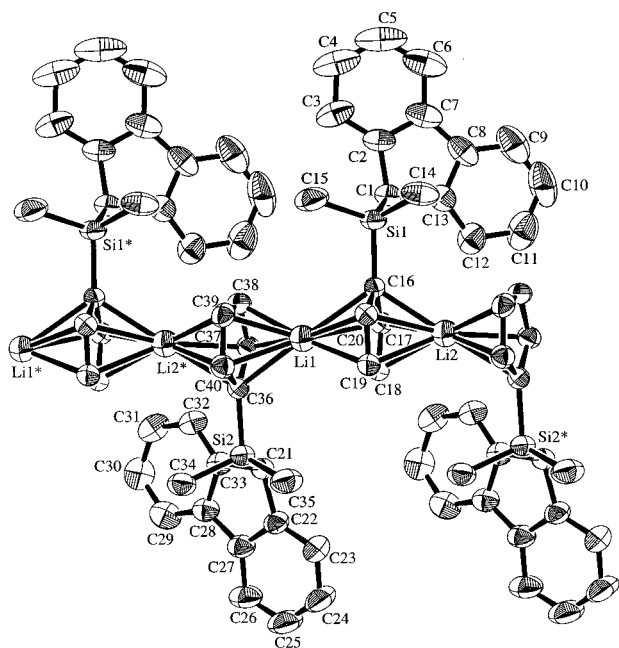
**Scheme 1****Results and Discussion**

**Synthesis.** Preparation of alkali-metal derivatives of the monoalkali-metal salts  $\{[(\text{FluMe}_2\text{Si})\text{Cp}]\text{Li}\}_n$  (**1**) and  $\{[(\text{FluMe}_2\text{Si})\text{Cp}]\text{Na}\cdot\text{THF}\}_n$  (**2**) is given in Scheme 1. The reaction of the dimethylsilyl-bridged fluorene cyclopentadiene ligand with 1 equiv of *n*-butyllithium or sodium hydride smoothly affords the corresponding monoalkali-metal salts **1** and **2**, respectively. Complexes **1** and **2** are extremely air and moisture sensitive. Both of them were characterized by <sup>1</sup>H NMR, elemental analyses, MS, and X-ray analyses.  $\{[(\text{FluMe}_2\text{Si})\text{Cp}]\text{Li}\}_n$  (**1**) was first observed as a byproduct of the reaction of  $\{[(\text{FluMe}_2\text{Si})\text{Cp}]\text{Li}_2\}$  with NdCl<sub>3</sub> in Et<sub>2</sub>O.<sup>5</sup> It is possible that the crystals formed by slow decomposition of an intermediate in this reaction. Any attempts to isolate the early-lanthanide metallocene complexes such as  $\{[(\text{FluMe}_2\text{Si})\text{Cp}]\text{NdCl}\}$  failed.

**Structures.** Crystals of complexes **1** and **2** were grown by a slow addition of *n*-hexane into the concen-

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1**

Bond Lengths			
Li(1)–C(16)	2.400(6)	Li(1)–C(36)	2.370(6)
Li(1)–C(17)	2.297(6)	Li(1)–C(37)	2.287(6)
Li(1)–C(18)	2.224(6)	Li(1)–C(38)	2.234(6)
Li(1)–C(19)	2.252(6)	Li(1)–C(39)	2.255(6)
Li(1)–C(20)	2.349(6)	Li(1)–C(40)	2.328(6)
Li(2)–C(36)	2.347(6)	C(16)–C(17)	1.419(4)
Li(2)–C(37)	2.328(6)	C(16)–C(20)	1.427(4)
Li(2)–C(38)	2.295(6)	C(18)–C(17)	1.406(4)
Li(2)–C(39)	2.287(6)	C(19)–C(20)	1.409(4)
Li(2)–C(40)	2.302(6)	C(19)–C(18)	1.405(4)
C(1)–C(2)	1.522(4)	C(1)–C(13)	1.506(4)
C(21)–C(33)	1.504(4)	C(21)–H(20)	1.02
plane(1) and Li(1)	1.960	plane(1) and Li(2)	1.973
Li(2)–C(16)	2.333(6)	Li(2)–C(17)	2.311(6)
Li(2)–C(18)	2.274(6)	Li(2)–C(19)	2.276(6)
Li(2)–C(20)	2.301(6)	Li(2)–C(37)	1.427(4)
C(36)–C(40)	1.427(4)	C(36)–C(38)	1.403(4)
C(37)–C(38)	1.403(4)	C(39)–C(40)	1.409(4)
C(38)–C(39)	1.412(4)	C(21)–C(22)	1.527(4)
C(21)–C(22)	1.527(4)	C(1)–H(1)	1.00
Bond Angles			
Si(1)–C(1)–H(1)	108.9	Si(2)–C(21)–H(20)	104.1
C(1)–Si(1)–C(16)	112.0(1)	C(21)–Si(2)–C(36)	110.1(1)
C(1)–Si(1)–C(14)	108.2(2)	C(35)–Si(2)–C(34)	109.4(2)
Si(1)–C(16)–C(17)	131.7(2)	Si(2)–C(36)–C(37)	122.8(2)
Si(1)–C(16)–C(20)	122.2(2)	Si(2)–C(36)–C(40)	131.5(2)
C(17)–C(16)–C(20)	106.0(2)	C(37)–C(36)–C(40)	105.7(2)
C(16)–Li(1)–C(17)	35.1(1)	C(16)–Li(2)–C(17)	35.6(1)
C(16)–Li(1)–C(20)	35.0(1)	C(16)–Li(2)–C(20)	35.9(1)
C(18)–Li(1)–C(19)	36.2(1)	C(18)–Li(2)–C(19)	36.0(1)
Dihedral Angles			
plane(1) and (2)	8.30	plane(1) and (3)	71.73
plane(2) and (4)	72.76	plane(3) and (4)	135.47



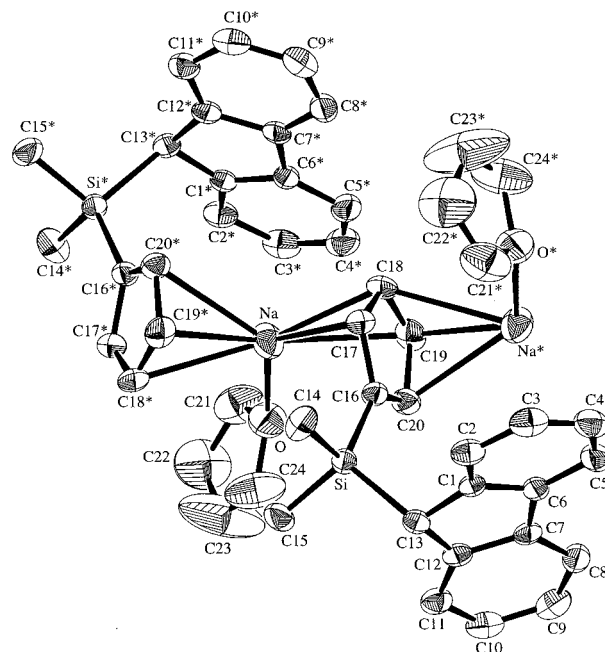
**Figure 1.** Plot of the polymeric structure of (FluMe<sub>2</sub>Si)-CpLi (**1**).

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2****

Bond Lengths					
Na-C(18)	2.651(7)	Na-C(18*)	2.790(8)	C(16)-C(17)	1.432(7)
Na-C(19)	2.762(7)	Na-C(19*)	2.632(7)	C(16)-C(20)	1.412(7)
Na-C(17)	2.830(6)	Na-C(17*)	3.023(6)	C(17)-C(18)	1.391(8)
Na-C(20)	3.008(6)	Na-C(20*)	2.801(7)	C(19)-C(20)	1.430(8)
Na-C(16)	3.056(7)	Na-C(16*)	3.047(6)	C(18)-C(19)	1.390(8)
C1-C(13)	1.484(8)	C(1)-C(6)	1.391(8)	C(6)-C(7)	1.476(8)
C12-C(13)	1.505(8)	C(12)-C(7)	1.413(8)	Na-O	2.320(5)
plane(1)-Na	2.555				
Bond Angles					
Si-C(13)-H(9)	99.5	Si-C(16)-C(17)		124.8(4)	
C(13)-Si-C(14)	107.6(3)	Si-C(16)-C(20)		128.1(4)	
C(13)-Si-C(16)	113.7(2)	C(17)-C(16)-C(20)		106.3(4)	
Dihedral Angles					
plane(1) and (4)	70.36	plane(1) and (5)		57.31	
plane(4) and (5)	81.29				

trated mother liquors. The details of the crystal data and refinements are presented in Table 1. The molecular structures of **1** and **2** are shown in Figures 1 and 2, and the selected structural parameters are listed in Tables 2 and 3, respectively.

The X-ray structural analysis confirms that in the solid state these monoalkali-metal salts **1** and **2** exhibit a similar structural fashion with a parallel oriented high linear infinite unit. Each of these units contains a supersandwich complex, which consists of a repeating sequence of alkali-metal atoms on both sides coordinated to the cyclopentadienyl rings. The unit cell is composed of two crystallographically independent [Cp-(FluMe<sub>2</sub>Si)]M (M = Li, Na) moieties. The fluorenyldimethylsilyl groups attached to the cyclopentadienyl rings are arranged in gaps and situated on one and the same side of the chain. In both cases, the sum of the angles at the bridgehead (i.e., the carbon atom bearing the SiMe<sub>2</sub>Flu substituent) is almost equal to 360.0°. Thus, the bridgehead carbon atom coordination environment



**Figure 2.** Plot of the polymeric structure of (FluMe<sub>2</sub>Si)-CpNa·THF (**2**).

is planar and the silicon atom is in the plane of the cyclopentadienyl ring. The longer bond distances of C(13)-C(12) and C(1)-C(13) (ranging from 1.504 to 1.527 Å for **1**, 1.484 to 1.505 Å for **2**) indicate that the 9-carbon atom in the fluorenyl moiety is saturated.

A weak interchain interaction (the shortest interchain C-C distance between the fluorenyl groups is 3.4 Å) was observed in the unit cell of **1** (graphite-type packing). This crystal packing effect determines the interchain mutual orientation of the dimethylfluorenylsilyl substituent in the solid state.

In complex **1**, the binding of the cyclopentadienyl rings to the lithium atoms is not symmetric. The lithium atoms are facially bonded with lower hapticity. As it can be seen from the extent of the scattering in Li-C (ring) bond distance data listed in Table 2, the Cp ring should be considered rather  $\eta^3:\eta^2$ -type bound than  $\eta^5$ -type with respect to the Li(1) atom. The values of the Li(1)-C(ring) bond distances range from 2.224(6) to 2.400(6) Å, while the Cp ring is  $\eta^5$ -bound to the Li(2) atom, and the values of the Li(2)-C(ring) bond distances range from 2.274(6) to 2.333(6) Å. One can also see that the bond distances between the Li atom and bridgehead C(16) and  $\alpha$ -carbon atoms (C(17), C(20)) are much longer than those between the Li atom and the  $\beta$ -carbon atoms (C(18), C(19)).

The structure of **1** differs significantly from that of solvent-free trimethylsilyl-substituted cyclopentadienyl complexes  $\{[C_5H_4(SiMe_3)Li]_n\}$  (**3**)<sup>6</sup> and  $\{[C_5H_4(SiMe_3)K]_n\}$  (**4**).<sup>7</sup> In complex **3**, the unit cell comprises three crystallographically independent LiC<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub> moieties. The mutual orientation of the SiMe<sub>3</sub> substituents in the trimetallic unit generates a highly ordered interchain structure. In complex **4**, a "weak bonding relationship" between the larger metal atoms of the potassium and

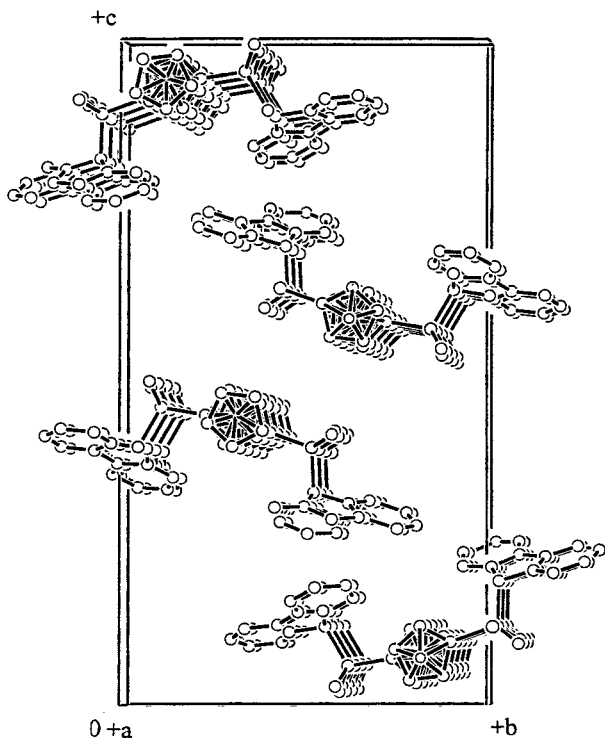
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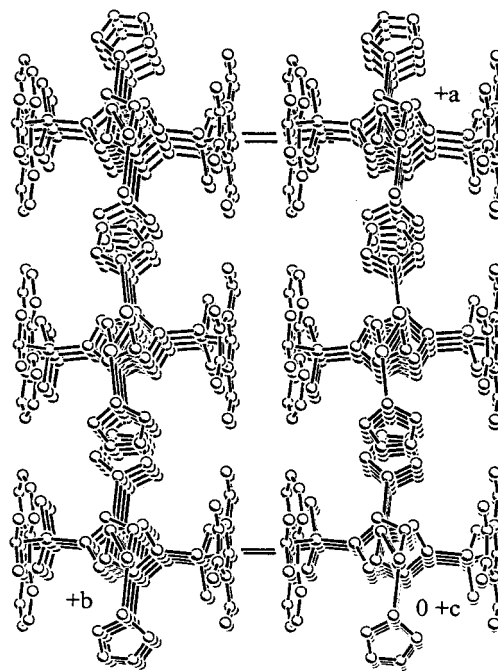




**Figure 3.** Drawing of the unit cell of (FluMe<sub>2</sub>Si)CpLi (**1**) viewed along the *a*-axis.

two carbon atoms of a cyclopentadienyl ring in another chain leads to a zigzag chain containing bent metallocene units, but the “gaps” arrangement of the SiMe<sub>3</sub> substituents in **4** is similar to that observed in **1**. The longer metal–ring centroid distances (1.960 to 1.973 Å) found for **1** are comparable to that in **3** (1.957 to 1.982 Å), reflecting the bridging nature of the cyclopentadienyl rings in **1** and **3**.

In complex **2**, the sodium atoms are exposed to one side and, thus, coordinated here by a Lewis base molecule (THF). Besides the distinct Na–O (THF) coordination (the bond distance of Na–O is 2.320(5) Å), an important feature of complex **2** is the position of the sodium atom with respect to the cyclopentadienyl ring. As it is shown in Figure 2, one can see that in complex **2** the Na–C(18) bond is nearly normal to the Cp ring mean plane, and the ring can be considered to be a  $\eta^3$ : $\eta^2$ -type ligand. The shorter Na–C(17, 18, 19) bond lengths together with shorter C(17)–C(18) and C(18)–C(19) bond distances in complex **2** would seem to indicate this kind of  $\eta^3$ -coordination mode. The Na–C distances (2.651(7)–3.056(7) Å, mean values: 2.86 Å) and the Na–Cp<sub>centroid</sub> distance (2.555 Å) in **2** are much longer compared to those of the polymeric base-free cyclopentadienyl sodium salt (NaCp),<sup>8</sup> in which the Na–C bond distances are 2.631(12)–2.671(6) Å (mean value: 2.649 Å) and the Na–Cp<sub>centroid</sub> distance is 2.357(1) Å. In the polymeric zigzag chain of the com-



**Figure 4.** Drawing of the unit cell of (FluMe<sub>2</sub>Si)CpNa·THF (**2**) viewed along the *c*-axis.

pound [NaCp(tmeda)]<sub>n</sub> (tmeda = (Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>),<sup>9</sup> considerably longer Na–C bond lengths have been observed: 2.829(14)–3.033(12) Å (mean value: 2.924 Å) and Na–Cp<sub>centroid</sub>: 2.667 Å.

In summary, we have successfully synthesized two monoalkali-metal salts (Li and Na) of silylene-bridged fluorenyl cyclopentadienyl ligands and characterized their structural features by X-ray diffraction analyses. Monoalkali-metal salts of this type could be used as precursors for the synthesis of binuclear complexes of the transition metals and f-elements containing a bridged dicyclopentadienyl ligand or complexes with only one of the rings coordinated.

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**Supporting Information Available:** Tables of atomic coordinates, thermal parameters, and interatomic distances and angles for complexes **1** and **2**, and <sup>1</sup>H NMR spectra for complexes **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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