# *Notes*

## The Question of Aromaticity in the 1-Lithio-1-methyl-1-silafluorenide Anion. Evidence for a Localized Silyl Anion[1]

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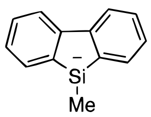
*Summary: The 1-lithio-1-methyl-1-silafluorenide anion (**2**) was prepared in high yield be reductive cleavage of the Si−Si bond from bis(1-methyl-1-silafluorenyl) (**3**) with lithium in THF at room temperature using ultrasonic waves. Treatment of **2** with trimethylchlorosilane produces 1-methy-1-(trimethylsilyl)-1-silafluorene (**4**). NMR parameters ($^1H$, $^{13}C$, $^{29}Si$) of **2** are consistent with localization of charge on the silicon.*

### Introduction

Recently we investigated the chemical and NMR spectral characteristics of the 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion (**1**), finding evidence in the form of $^{29}$Si and $^{13}$C NMR data consistent with significant delocalization of negative charge into the silacyclopentadienide ring.[2] These results are supported by high-level calculations which show that silole anions such as **1** are indeed aromatic and that planarization of the ring and delocalization of $\pi$ electrons are further enhanced when coordination of the lithium ion is taken into consideration.[3]

**1**



**2**

The acidity of cyclopentadiene (p$K_a$ = 16) is attenuated in the fused ring analog fluorene (p$K$ = 23) as a result of reduced $\pi$ delocalization in the conjugate bases of the annelated systems.[4] We wished to explore the question of $\pi$ delocalization in a silicon analogue of the fluorenide anion. In this paper we report the results of our NMR studies of the 1-lithio-1-methyl-1-silafluorenide anion (**2**).[5]

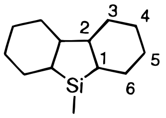
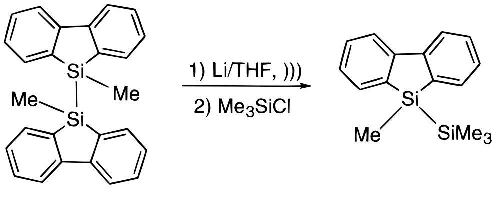


**Figure 1.**

### Results and Discussion

Sonication of bis(1-methyl-1-silafluorenyl) (**3**) and lithium in THF for 8 h gives a dark green solution of **2**. Removal of the unreacted lithium by filtration followed by treatment with an excess of trimethylsilyl chloride produces 1-methyl-1-(trimethylsilyl)-1-silafluorene (**4**) in 66% yield.



**3** **4**

Samples of **2** prepared in an NMR tube gave only one peak in the $^{29}$Si spectrum. The $^{13}$C NMR spectrum shows one methyl and six aromatic carbon peaks, consistent with $C_2$ symmetry (Figure 1).

The $^{29}$Si NMR chemical shift for **2** (−22.09 ppm) is in the range of aryl-substituted silyllithium compounds, which have no delocalization of the negative charge on silicon to the phenyl substituents.[6] $^{29}$Si NMR chemical shifts for two phenylated silyllithium anions and related neutral aryldisilanes[7] are given in Table 1 for comparison. That **2** is upfield from $Ph_2MeSi^-Li^+$ ($\Delta\delta = -1.59$ ppm) is noteworthy because $Ph_2MeSi^-Li^+$ differs from **2** only in the absence of a connecting carbon−carbon bond between the rings. That connection, which enforces planarity in **2**, might be expected to increase $\pi$ delocalization leading to a downfield shift for the $^{29}$Si peak. Analysis of the $^1$H NMR shows the methyl peaks of **2** and **3** have the same chemical shift while the phenyl

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**Table 1. $^{29}$Si NMR Chemical Shifts (δ) for Some Silyl Anions and Disilanes**

| | 1 | 2 | 3 | $Ph_2MeSiLi$[6a] | $(Ph_2MeSi)_2$[7] | $PhMe_2SiLi$[6b] | $(PhMe_2Si)_2$[7] |
|---|---|---|---|---|---|---|---|
| $^{29}$Si | 25.10[a] | −22.09[a] | −18.68[b] | −20.5[c] | −23.21[d] | −27.8[e] | −21.70[d] |

[a] In THF-$d_8$, external $Me_4Si$ as standard. [b] In $CDCl_3$, external TMS as standard. [c] In THF, external $Me_4Si$ as standard. [d] In $CDCl_3$, internal TMS as standard. [e] In THF, internal TMS as standard.

**Scheme 1**

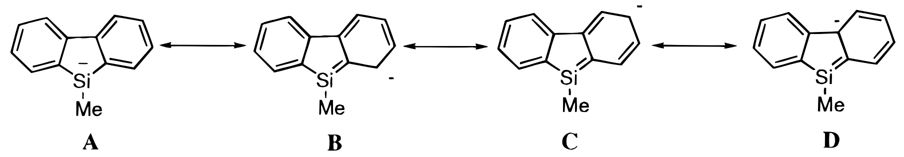

**Table 2. $^1$H NMR Chemical Shifts (δ) for 1-Lithio-1-methyl-1-silafluorenide (2) and Bis(1-methyl-1-silafluorenyl) (3)**

| obsd protons | 2[a] | 3[b] |
|---|---|---|
| $C_6H_5$ | 6.9−7.9 | 7.3−7.95 |
| $CH_3$ | 0.27 | 0.27 |

[a] In THF-$d_8$, reference solvent = 1.73 ppm. [b] In $CDCl_3$, reference = external TMS as standard.

**Table 3. $^{13}$C NMR Chemical Shifts (δ) for 1-Lithio-1-methyl-1-silafluorenide (2) and Bis(1-methyl-1-silafluorenyl) (3)[b]**

| obsd carbons | 2[a] | 3 | | Δ(2−3) |
|---|---|---|---|---|
| $C_1$ | 145.69 | 138.25 | $\Delta C_1$ | 7.44 |
| $C_2$ | 163.40 | 148.27 | $\Delta C_2$ | 15.13 |
| $C_3$ | 123.36 | 129.85 | $\Delta C_3$ | −6.49 |
| $C_4$ | 119.43 | 121.13 | $\Delta C_4$ | −1.70 |
| $C_5$ | 123.10 | 127.18 | $\Delta C_5$ | −4.08 |
| $C_6$ | 132.69 | 133.34 | $\Delta C_6$ | −0.65 |
| $T$[c] | 807.67 | 798.02 | $\Delta T$ | 9.65 |
| $CH_3$ | 1.54 | −6.27 | $\Delta(CH_3)$ | 7.81 |

[a] In THF-$d_8$, reference solvent = 25.30 ppm. [b] In $CDCl_3$, reference = external TMS as standard. [c] Summation of chemical shifts from $C_1$ to $C_6$ in ppm.

protons in **3** undergo an upfield shift upon formation of **2** (Table 2).

Upon metalation of **3** to form **2**, the $C_1$ and $C_2$ carbons of the ring and the methyl carbon are observed to shift downfield [$\Delta\delta(C_1) = 7.44$, $\Delta\delta(C_2) = 15.13$, and $\Delta\delta(Me) = 7.81$ ppm, respectively], while the four carbons, $C_3$−$C_6$, shift upfield (Table 3). The downfield shifts of $C_1$ and the methyl carbon in **2** are similar to the downfield shifts of $C_{ipso}$ and the methyl carbon in $Ph_2MeSi^-Li^+$ relative to $Ph_2MeSiCl$ ([$\Delta\delta(C_{ipso}) = 25.5$ and $\Delta\delta(Me) = 4.2$ ppm].[6a] These downfield shifts can be explained in terms of a field effect induced by the negative charge on silicon.[8] Similar downfield shifts of the ring carbons are observed in $[C_4Me_4GeR]^-$ (R = Ph,[9] $Si(SiMe_3)_3$[10]), in which the negative charge is localized on the germanium atom.

The $^{13}$C NMR chemical shifts of conjugated carbon rings are inversely dependent on the π-electron density on the carbon atoms.[11] Thus, it is important to note that, upon metalation of **3** to form **2**, the total chemical shift change of the phenyl ring carbons is small and downfield ($\Delta T = 9.65$ ppm), which means no additional accumulation of π electron density in the phenyl ring carbons (Table 3).

These NMR data provide an important contrast with the data for **1** in which the $^{29}$Si chemical shift is ∼47 ppm downfield from that in **2**. Moreover, the $^{13}$C chemical shifts of the ring carbons in **1** are upfield from the parent silacyclopentadiene, while the opposite trend exists for **2**.[2] Our interpretation of these observations is that the negative charge in **2** is localized on the silicon and that annelation essentially eliminates π delocalization.

## Conclusion

Analysis of the $^{29}$Si and $^{13}$C NMR data obtained on solutions of 1-lithio-1-methyl-1-silafluorenide anion indicate that the negative charge in the anion is not significantly delocalized as in silole anions but localized as in conventional arylsilane anions. Thus, resonance forms such as B−D (Scheme 1) are not significant contributors to the ground state of the 1-lithio-1-methyl-1-silafluorenide anion.

## Experimental Section

**General Considerations.** All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air-sensitive reagents were transferred in a nitrogen-filled glovebox. THF was distilled from sodium benzophenone ketyl under nitrogen. Hexane was stirred over concentrated $H_2SO_4$ and distilled from $CaH_{20}$ NMR spectra were obtained on JEOL GSX 270 and GSX 400 spectrometers. A common ultrasonic cleaner was used for sonication of synthetic scale reactions and for NMR studies. The sample was placed in a location in the bath that produced maximum cavitation in the reaction flask or NMR tube.[12]

**1-Lithio-1-methyl-1-silafluorenide Anion (2) (NMR Sample).** Sonication of an NMR tube containing **3** (0.100 g, 0.256 mmol) and lithium (0.004 g, 0.571 mmol) in 1.2 mL of THF-$d_8$ for 8 h produced a dark green solution which gave very clean NMR spectra: $^1$H NMR (THF-$d_8$; reference solvent = 1.73 ppm) 0.27 (s, 3H, SiMe), 7.79 (d, 2H, $J$ = 7.8 Hz), 7.66 (d, 2H, $J$ = 5.9 Hz), 7.00 (q with equal intensity, 4H, $J$ = 7.3, 5.9, 6.6 Hz).

**Bis(1-methyl-1-silafluorenyl) (3).** **3** was prepared by the method of Gilman and Gorsich:[5a] Mp 181−182 °C, (lit. mp 180−182 °C); $^1$H NMR ($CDCl_3$, reference solvent = 7.27 ppm), 0.27 (s, 6H, SiMe), 7.91 (d, 2H, Ph, $J$ = 7.32 Hz), 7.65 (d, 2H, Ph, $J$ = 7.32 Hz), 7.49 (t, 2H, Ph, $J$ = 7.32 Hz), 7.32 (t, 2H, Ph, $J$ = 7.32 Hz).

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**1-Methyl-1-(trimethylsilyl)-1-silafluorene (4).** A 100 mL flask containing **2** (0.400 g, 1.026 mmol) and lithium (0.014 g, 2.018 mmol) in 35 mL of THF was placed in an ultrasonic cleaning bath and sonicated for 10 h to give a dark green-brown solution. The solution was filtered to remove excess lithium and added to an excess of trimethylchlorosilane with stirring at room temperature. Stirring for an additional 2 h produced a nearly colorless solution. After the volatiles were removed under vacuum, the residue was extracted with hexane. Evaporation of the hexane gave an oily residue which, after standing for 1 day, gave colorless crystals. **4** was identified by comparison with literature data:[13] Yield 66% (isolated); mp 62.5 °C (lit. mp 57 °C), $^1$H NMR ($CDCl_3$, reference solvent = 7.27 ppm), 0.10 (s, 9H, $SiMe_3$), 0.51 (s, 3H, SiMe), 7.91 (d, 2H, Ph, $J = 7.3$ Hz), 7.68 (d, 2H, Ph, $J = 7.3$ Hz), 7.46 (t, 2H, Ph, $J = 7.3$ Hz), 7.31 (t, 2H, Ph, $J = 7.3$ Hz); $^{13}$C NMR ($CDCl_3$, reference solvent = 77.00 ppm), −6.03 (SiMe), −2.17 ($SiMe_3$), 148.19 ($C_2$), 139.71 ($C_1$), 133.13, 129.40, 126.97, 121.00 (ring carbons); $^{29}$Si NMR ($CDCl_3$, reference external TMS = 0.00 ppm), −17.62 (Si of ring), −18.06 ($SiMe_3$).

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