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Synthesis and characterization of dibenzannulated silole dianions. The 1,1-dilithiosilafluorene and 1,1'-dilithiobis(silafluorene) dianions¹

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Abstract

Stirring of 1,1-dichloro-SiFl (1), (SiFl, silafluorene) in THF with excess lithium for 1 h gave a dark green solution of 1,1-dilithio-SiFl (2) in high yield. The dark red solution of the intermediate 1,1'-dilithio-(SiFl)₂ (3) was also observed from this reaction within 10 min. Treatment of 2 with excess trimethylchlorosilane gave the 1,1-bis(trimethylsilyl)-SiFl derivative (4) in 95% yield. Treatment of the dark red solution of 3 and 2 with excess methyliodide gave the 1,1'-dimethyl-bis(SiFl) (5) and 1,1-dimethyl-SiFl (6) derivatives in a 4:1 ratio. The upfield locations of the ²⁹Si resonances of dianions 2 and 3 (-1.09 ppm and -39.25 ppm, respectively) are consistent with π -electron localization on the silicon atoms. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: dianion; lithio; silacyclopentadiene; silafluorenyl; silole.

The silole framework has been the focal point of considerable interest because it is a readily accessible model for studying the impact of silicon on aromatic systems.² Siloles not only serve as precursors to the silicon analogs of cyclopentadienides³ but also to silicon analogs isoelectronic, and therefore dianionic,⁴ with the highly delocalized pyrrole and phosphole anions. Silaindenyl and silafluorenyl structures can be viewed as benzannulated siloles and are logical subjects for study as potentially aromatic silicon compounds. Indeed, we have shown that the negative charges in silaindenyl and silafluorenyl monoanions reside mostly on the silicon atoms.^{3e,5} However, the silaindene dianion, which is isoelectronic with the highly delocalized phosphindolyl anion,⁶ has a high degree of aromaticity in the silicon-containing ring.⁷



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We report here the synthesis and characterization of the 1,1-dilithio-SiFl (2) and 1,1'-dilithiobis(SiFl) (3) dianions. Stirring 1,1-dichloro-1-SiFl with excess lithium powder for 1 h in THF produced a dark green solution. After removal of unreacted lithium, treatment of this solution with excess trimethylchlorosilane gave 1,1-bis(trimethylsilyl)-1-SiFl⁸ (4) in 95% yield. However, if the reaction is quenched with methyl iodide after only 10 min (dark red solution), two products are obtained: bis(1-methyl-1-SiFl)^{3e} (5) and 1,1-dimethyl-1-SiFl⁹ (6) in a 4:1 ratio (total yield 90%). We ascribe these results to the exclusive formation and trapping of dianion 2 in the first case and the trapping of both anions 2 and 3 in the second experiment. Additional stirring of the dark red solution in the presence of excess lithium for 1 h gives a dark green solution of 1,1-dilithio-SiFl (2) in high yield. Clearly, anion 3 leads to 2 via lithium-induced cleavage of the silicon-silicon bond. The results are summarized in Scheme 1.



Scheme 1. Synthesis and trapping reactions of 2 and 3

¹³C and ²⁹Si NMR data for some dianionic siloles and precursors are given in Table 1 and Table 2. It is noteworthy that the ²⁹Si chemical shifts for 2 (-1.09 ppm) are slightly upfield from that of 1 (6.84 ppm).

In addition, we observed downfield shifts for the five-membered ring carbons in the ¹³C NMR spectra of **2** (Table 2).¹³ These trends in the chemical shifts for the ²⁹Si and ¹³C nuclei are in the opposite direction to those for the aromatic silole and silaindene systems. Thus, our interpretation for the upfield shifts in the ²⁹Si NMR and downfield shifts in the ¹³C NMR spectra of **2** is that the

²⁹ Si chemical shifts (ppm) for dianionic siloles and their neutral precursors						
silole-X ₂	$\delta_1(X=Cl)$	$\delta_2(X=Li)$	$\Delta (\delta_2 - \delta_1)$	references		
C ₄ Et ₄ Si	8.30	24.96	16.66	Boudjouk 10		
C ₄ Me ₄ Si	8.14	29.77	21.63	West 11		
C ₄ Ph ₄ Si	6.80	68.54	61.74	Boudjouk 12		

29.19

-1.09

23.27

-7.93

 Table 1

 ²⁹Si chemical shifts (ppm) for dianionic siloles and their neutral precursors

BPSI = 3-n-butyl-2-phenyl-1-silaindene

5.92

6.84

BPSI

2

Table 2
¹³ C chemical shifts (ppm) for dianionic siloles and their neutral precursors

silole-X ₂	$\delta_1(X=Cl)$	$\delta_2(X=Li)$	$\Delta \; (\delta_2 \text{ - } \delta_1)$	references
C4Et4Si	143.03	138.84	- 4.19	Boudjouk ¹⁰
C ₄ Me ₄ Si	138.17	129.47	- 8.70	West ¹¹
C_4Ph_4Si	143.51	140.46	-3.05	Boudjouk ¹²
2	139.03	149.88	10.85	this work

 $\delta_n = \{\delta(C_\alpha) + \delta(C_\beta)\}/2$

negative charge in 2 is localized on the silicon atom and that annelation essentially excludes π delocalization.

In 1990, Lagow et al. proposed, based on trapping reactions, that a dianionic silicon species was generated in the gas phase from the pyrolysis of LiSi(SiMe₃)₃.¹⁴ Spectroscopic data were not reported. Sekiguchi et al. recently generated a 1,1-dilithiosilane by reduction of silacyclopropene with excess lithium metal and observed a significant upfield chemical shift (-282.0 ppm) in the ²⁹Si NMR spectrum.¹⁵ Tamao et al. has reproduced the generation and trapping reaction of **2** with halosilanes.¹⁶ Liu and West also reported that the lithium potassium mixed salts of sila-fluorene exhibit a peak at 29.0 ppm in the ²⁹Si NMR spectrum.¹⁷

The ¹³C and ²⁹Si NMR spectra for 3^{18} have the same patterns as those for 1,1'-disodio-bis(SiFl),¹⁹ which was prepared by treatment of 1 with excess sodium. The ²⁹Si chemical shifts for 3 and 1,1'-disodio-bis(SiFl) (-39.25 ppm and -38.22 ppm, respectively) are in the range of arylsubstituted silyllithium compounds which have no delocalization of negative charge from silicon to the phenyl substituents. For simple silyl monoanions, the ²⁹Si nuclei typically resonate at -25 to -35 ppm.²⁰

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- NMR Study of 1,1'-disodio-bis(SiFl): 1 (50 mg, 0.2 mmol) and Na (55 mg, 2.4 mmol) were placed in a 5-mm NMR tube followed by THF-*d8* (0.75 ml). Sonication for 12 h gave a dark red solution. ¹H NMR (THF-*d8*, ref; THF-*d8* = 1.72 ppm): 7.10 (bs, 4H), 8.11 (bs, 4H). ¹³C NMR (THF-*d8*, ref; THF-*d8* = 24.63 ppm): 168.39 (C), 145.31 (C), 134.16 (CH), 122.17 (CH), 120.94 (CH), 120.48 (CH). ²⁹Si NMR (THF-*d8*, ref: ext. TMS = 0.00): -38.22.
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