Synthesis and Characterization of Two Aromatic Silicon-Containing Dianions:The 2,3,4,5-Tetraphenylsilole Dianion and the 1,1'-Disila-2,2',3,3',4,4',5,5'-Octaphenylfulvalene Dianion

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Synthesis and Characterization of Two Aromatic Silicon-Containing Dianions:[1] The 2,3,4,5-Tetraphenylsilole Dianion and the 1,1'-Disila-2,2',3,3',4,4',5,5'-octaphenylfulvalene Dianion

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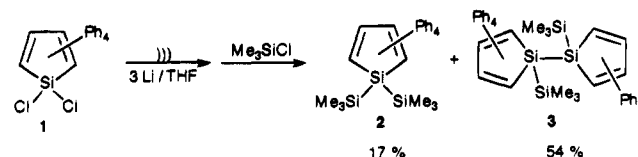
Summary: Sonication of 1,1-dichloro-TPSCp (TPSCp = 2,3,4,5-tetraphenyl-1-silacyclopentadiene) with lithium in a 1:3 ratio in THF gives the 1,1'-disila-2,2',3,3',4,4',5,5'-octaphenylfulvalene dianion {[TPSCp⁻]₂·2[Li⁺]} as the major product. Further sonication of [TPSCp⁻]₂·2[Li⁺] in the presence of lithium gives the 2,3,4,5-tetraphenyl-silole dianion {[TPSCp²⁻]·2[Li⁺]} exclusively. NMR studies (¹H, ¹³C, ²⁹Si) of these anions show significant delocalization of the negative charges to the silole rings.

There is considerable interest[2] in anionic siloles because of their potential aromaticity.[3] Several types of neutral siloles are known,[2] but only a few anionic derivatives of C-phenylated siloles[4] or silafluorenes[5] have been reported. Recently, we presented evidence, in the form of ²⁹Si chemical shifts, that 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anions possessed significant aromaticity.[6] Continuing our search for additional silicon-containing aromatic systems, we examined the silicon analogs of two well-known aromatic structures, the fulvalene dianion and the pyrrole anion. In this paper we report the preparation and characterization of the novel salts of the 1,1'-disila-2,2',3,3',4,4',5,5'-octaphenylfulvalene dianion {[TPSCp⁻]₂·2[Li⁺]}, a silicon analog to the fulvalene dianion,[7] and the 2,3,4,5-tetraphenylsilole dianion {[TPSCp²⁻]·2[Li⁺]}, which is isoelectronic with the pyrrole anion.

Sonication of **1** with 3 equiv of lithium in THF produces a dark red brown solution which, after removal of unreacted lithium and treatment with an excess of Me₃SiCl, gives 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphen-yl-1-silacyclopentadiene (**2**)[4c] and bis(1-(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (**3**).[8] Soni-

cation of **1** with more than 4 equiv of Li followed by quenching with Me₃SiCl gives only **2**.[9] Attempts to produce **3** exclusively by varying the amount of lithium were unsuccessful.

An NMR study of the reaction mixture from **1** and excess lithium revealed the presence of only one species to which we assign the structure **4**. The ¹³C NMR spectrum showed ten peaks, consistent with C_2 symmetry, and the ²⁹Si spectrum had only one resonance at 68.54 ppm. Treatment of **4** with Me₃SiCl produced **2** as the only product in 73% yield.
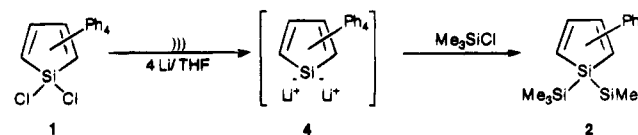
Typically, upfield shifts are observed for ²⁹Si nuclei when organochlorosilanes are converted to silyl anions[10] and downfield shifts are observed when a negative charge is delocalized.[6] Thus, the large downfield shift observed [$\Delta\delta(4-1) = 61.74$ ppm] in the ²⁹Si spectrum

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(1) This work has been presented in part: Hong, J.-H.; Boudjouk, P.; Castellino, S. XXVIIth Organosilicon Symposium, Troy, NY, March 18–19, 1994; Abstract, P-23. Hong, J.-H.; Boudjouk, P. 206th National Meeting of the American Chemical Society, Chicago, IL, August 22–27, 1993; Abstract, INOR 492. Hong, J.-H.; Boudjouk, P.; Castellino, S. XXVIth Organosilicon Symposium, Indianapolis, IN, March 26–27, 1993; Abstract, P-50.

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(8) Sonication of **1** (3.00 g, 6.59 mol) with 3 equiv of Li (0.137 g, 19.77 mmol) and 80 mL of THF for 8 h gives a dark red-brown solution. The solution was filtered and added to an excess of chlorotrimethyl-silane with stirring at room temperature for 20 h. After the volatile reagents were removed under reduced pressure, the yellow residue was extracted with ether. Cooling this ether solution to −20 °C gave yellow crystals of **3**. From the decantated solution, ether was removed and the residue was extracted with hexane; crystallization in hexane gave **2**. All yields were calculated by proton NMR. **2**: yield 17%.[4c] **3**: yield 54%; mp does not melt at 265 °C; ¹H NMR (CDCl₃, ref; CDCl₃ = 7.27 ppm) −0.23 (s, 18H, SiMe₃), 6.8–7.1 (brd m, 40 H, Ph); MS (M⁺, relative intensity) m/z 457 (M⁺/2, 8), 458 (M⁺/2 + 1, 3), 459 (M⁺/2 + 2, 1), 379 (9), 279 (8), 135 (19), 105 (27), 73 (100). Anal. Calcd for C₆₂H₅₈-Si₄: C, 81.34; H, 6.39. Found: C, 81.07; H, 6.29.

(9) Sonication of **1** (0.120 g, 0.264 mol) with an excess of Li (0.011 g, 1.571 mmol) and 1.5 mL of THF-d₈ in a 5-mm NMR tube for 5 h gives a dark brown solution. NMR spectra (¹H, ¹³C, and ²⁹Si) show that only **4** is formed. An excess of Me₃SiCl was added, followed by shaking, to give a yellow solution. NMR spectra (¹H, ¹³C, and ²⁹Si) show that **2** is formed (yield, 73%). Spectral data for **4** matched those of the yellow solid isolated from large scale reactions. Addition of TMEDA does not alter the spectrum. **4**: ¹H NMR (THF-d₈, ref; THF-d₈ = 1.73 ppm) 7.04 (d, Hₒ, 4H, J = 7.3 Hz), 6.83 (d, Hₒ, 4H, J = 7.3 Hz), 6.73 (t, Hₘ, 4H, J = 7.3 Hz), 6.70 (t, Hₘ, 4H, J = 7.3 Hz), 6.64 (d, Hₚ, 2H, J = 7.3 Hz), 6.52 (d, Hₚ, 2H, J = 7.3 Hz).

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Table 1. Silicon-29 Chemical Shifts (ppm)

cpd	ring	SiMe₃	cpd	ring	SiMe₃	cpd	ring
1[a]	6.80		3[a]	−9.08	−29.91	5[b]	−4.13
2[a]	−12.16	−27.46	4[b]	68.54			

[a] In CDCl₃, reference; external TMS = 0.00 ppm. [b] In THF-d_8, reference; external TMS = 0.00 ppm.

Table 2. Carbon-13 Chemical Shifts (ppm)

	1[a]		3[a]		4[b]		5[b]	
SiMe			−1.27					
C_α	132.28		145.79		129.71		134.94	
C_β	154.74		154.88		151.22		135.04	
	αPh	βPh	αPh	βPh	αPh	βPh	αPh	βPh
C_i	135.37	136.67	139.73	140.34	145.83	151.67	146.25	147.97
C_o	129.27	129.48	130.09	130.46	133.43	129.97	130.95	133.38
C_m	128.24	127.84	127.39	127.76	126.38	126.38	126.35	126.51
C_p	127.10	127.37	125.49	126.02	119.48	121.83	120.17	122.41
C_i-C_p	8.27	9.30	14.24	14.32	26.35	29.84	26.08	25.56
ppm[c]	8.79		14.28		28.10		25.82	

[a] In CDCl₃, reference; CDCl₃ = 77.00 ppm. [b] In THF-d_8, reference; THF-d_8 = 25.30 ppm. [c] The average chemical shift differences of C_i and C_p.

of **4** is remarkable considering the presence of two negative charges in the molecule (Table 1). It is further downfield than the ²⁹Si shift of 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide (25.10 ppm)[6] but in the range of silenes (40−140 ppm).[11] This large downfield shift in **4** must be due to the change in the hybridization of silicon and to a different electron distribution which substantially changes the shielding terms of the ²⁹Si chemical shift.[12]

In addition to the downfield shift in the ²⁹Si NMR of **4**, we observed upfield shifts of the C_α and C_β atoms in the ring (Table 2).[13] Upfield shifts of C_α and C_β are generally observed for five-membered ring compounds
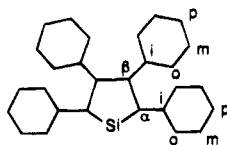
having aromatic contributors such as cyclopentadienyl anions[14] and group 15 heterole anions,[14,15] relative to the corresponding neutrals. In contrast, downfield shifts are observed for the ring carbons [$\Delta\delta(C_\alpha)$ = 10.5 ppm and $\Delta\delta(C_\beta)$ = 2.6 ppm] of the 1-phenyl-1-lithio-2,3,4,5-tetramethyl-1-germacyclopentadienide anion, in which the negative charge localized on the germanium atom induces an anionic field effect, compared to 1-phenyl-2,3,4,5-tetramethyl-1-germacyclopentadiene.[16]

Upon metalation of **1** to form **4**, the peaks of C_α and C_β shift upfield [$\Delta\delta(C_\alpha)$ = −2.57 and $\Delta\delta(C_\beta)$ = −3.52 ppm] and all carbons of the two phenyl groups are strongly polarized [$\Delta\delta(C_i)$ = 10.46 and 15.00 ppm, $\Delta\delta$-

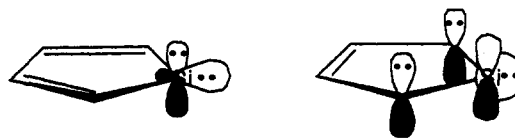**Table 3. Comparison of Carbon-13 Chemical Shift Differences**

	4−1		5−3	
ΔC_α	−2.57		−10.85	
ΔC_β	−3.52		−19.84	
	αPh	βPh	αPh	βPh
ΔC_i	10.46	15.00	6.52	7.63
ΔC_o	4.16	0.49	0.86	2.92
ΔC_m	−1.86	−1.46	−1.04	−1.25
ΔC_p	−7.62	−5.54	−5.32	−3.61

[a] In ppm.

(C_o) = 4.16 and 0.49 ppm, $\Delta\delta(C_m)$ = −1.86 and −1.46 ppm, $\Delta\delta(C_p)$ = −7.62 and −5.54 ppm] (Table 3). The nearly perpendicular orientation of the phenyl groups with respect to the silole ring rules out significant π-resonance between the phenyls and the silole ring.[17] However, the downfield shifts of the ipso and ortho carbons and the upfield shifts of the meta and para carbons are evidence of π-polarization of the phenyl groups by the increased electron density in the silole ring (Table 3). The upfield shifts for C_α and C_β in the ¹³C NMR and the downfield shifts in the ²⁹Si NMR are consistent with significant charge delocalization from silicon onto the ring.
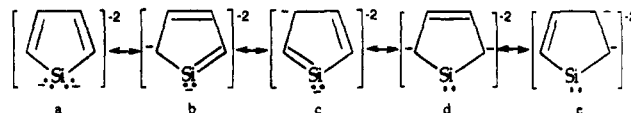
There are two reasonable models for the electronic structure of **4** whose orbital pictures may be useful to understanding the structure of **4**. One is based on the known phospholyl anions, which are isoelectronic with

4 and which have ³¹P resonances 60−80 ppm downfield from the neutral phospholes.[18] The electronic structure of the phospholyl anion is similar to that of cyclopentadienide anions.[19] If the hybridization of the phosphorus atom is given as sp², then a simplified view of these isoelectronic species is that one pair of electrons resides in the in-plane sp² orbital and the other pair of electrons is in the pπ orbital that participates in the extended π-system.

Another possibility is the model suggested for the novel 6 π-electron ring system, 1,3-di-*tert*-butyl-2,3-dihydro-1H-1,3,2-diazasilol-2-ylidene[20] which calls for silicon using nearly pure p orbitals in the Si−N bonds and an s orbital to hold the lone pair like divalent silylenes.[21] A ²⁹Si NMR chemical shift of 78.3 ppm was observed. The molecular orbital model of **4** is better

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approximated by the diazasiloylidene species.[20] Resonance form d is viewed as a major contributor because it is consistent with the electron density as interpreted by NMR data (^{29}Si = 68.54 ppm, upfield shifts of C_α and C_β), and also because it places the two negative charges on the more electronegative carbon atoms.

Sonication of **1** with 3 equiv of Li gives two products. The ^{13}C NMR spectrum shows two sets of ten peaks: the larger set is assigned to **5**, and the smaller group is attributed to **4**. The ^{29}Si NMR spectrum has two peaks,
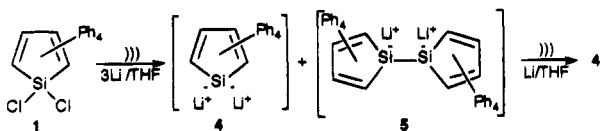
one from **4** at 68.54 ppm and the other at −4.13 ppm which we assign to **5**. Further reaction with lithium using sonication produced **4** exclusively. We were unable to manipulate the stoichiometry or the reaction conditions to produce **5** without some traces of **4**.[22]

The chemical shift (−4.13 ppm) of **5** is in the range of neutral siloles and is downfield from the ring silicon atoms in bis(1-(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (**3**) (−9.08 ppm) and 1,1-bis(trimeth-

ylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**2**) (−12.16 ppm). Comparisons of the ^{29}Si NMR chemical shifts among **2**, **3**, and **5**, suggest that the negative charge in **5** is delocalized into the silole rings. In the carbon spectrum, the α and β carbon atoms in **5** are upfield from those in **3** [$\Delta\delta(C_\alpha)$ = −10.85 and $\Delta\delta(C_\beta)$ = −19.84 ppm]. The carbon atoms in the phenyl rings are polarized as indicated by the change in chemical shifts (Table 3). This pattern of change in chemical shifts is similar to that observed in the 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion,[6] the silole dianion **4**, and the carbon analogs $Ph_4C_5H^-Li^+$ and $Ph_5C_5^-Li^+$.[23]

1,1-Dichloro-2,3,4,5-tetraphenylsilole (**1**) is a precursor to two silicon-containing dianions, the 2,3,4,5-tetraphenylsilole dianion, [TPSCp^{2-}]·2[Li$^+$] (**4**) and the 1,1′-disila-2,2′,3,3′,4,4′,5,5′-octaphenylfulvalene dianion, [TPSCp$^-$]$_2$·2[Li$^+$] (**5**), both of which give ^{13}C and ^{29}Si spectra consistent with a high degree of π-delocalization. Both dianions form stable derivatives in good yields when treated with trimethylchlorosilane.

(22) Sonication of **1** (0.105 g, 0.231 mmol) and lithium (5 mg, 0.714 mmol) with 1.5 mL of THF-d_8 in a 5-mm NMR tube for 6 h gave a dark red solution. NMR spectra (^{1}H, ^{13}C, and ^{29}Si) show that **4** and **5** are formed with the relative intensities of 1:5 (**4**:**5**) in ^{13}C NMR. **5**: ^{1}H NMR (THF-d_8, ref; THF-d_8 = 1.73 ppm) 6.96 (d, H$_o$, 8H, J = 7.3 Hz), 6.84 (d, H$_o$, 8H, J = 7.3 Hz), 6.52−6.80 (overlapped t, H$_m$, 16H), 6.50 (d, H$_p$, 4H, J = 7.3 Hz), 6.47 (d, H$_p$, 4H, J = 7.3 Hz).

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