A Stable Aromatic Species Containing Silicon. Synthesis and Characterization of the 1-*tert*-Butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide Anion

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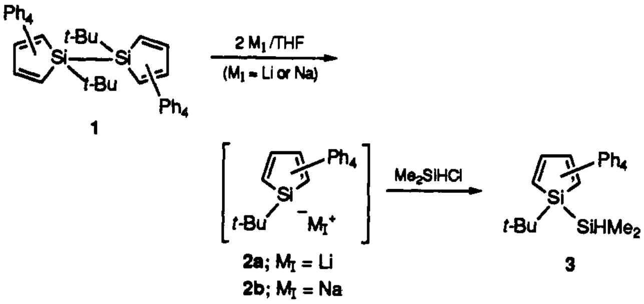
Although silacyclopentadienide anions have long been of interest,[1] there are only a few reports dealing with their chemistry.[2] Theoretical calculations on a model system have predicted that they are approximately 25% as aromatic as the all-carbon analogue[3a] and have essentially the same pyramidality as H_3Si^-.[3b] As a part of our study of the silacyclopentadiene system, we now report the preparation and characterization of 1-*tert*-butyl-1-M_I-2,3,4,5-tetraphenyl-1-silacyclopentadienide anions (**2a**, M_I = Li, **2b**, M_I = Na).



Stirring bis(1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)[4] (**1**, 0.500 g, 0.567 mmol) with sodium (0.026 g, 1.134 mmol) in THF at room temperature produces a dark purple solution. After removal of the unreacted metal, addition of this solution to an excess of dimethylchlorosilane gave 1-*tert*-butyl-1-dimethylsilyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**3**)[5] in 74.5% yield. The formation of **3** clearly indicates that the Si–Si bond in **1** was cleaved by sodium to give the silacyclopentadienide anion **2b**. In an NMR tube, **1** (0.107 g, 0.12 mmol) and Na (0.005 g, 0.218 mmol) were sonicated for 1 h in THF-d_8, to give the same purple solution.

Table I. ^{29}Si NMR Chemical Shifts for the Neutral **1**,[a] Silole Anions **2a** and **2b**,[a] and Other Silyl Anions

1	2a	2b	$(Ph_3Si)_2$[b]	Ph_3SiLi[c]	$(Me_3Si)_2$[c]	Me_3SiK[c]
3.62	25.10	26.12	−26.61	−30.0	−19.7	−34.4

[a] In THF-d_8, external Me_4Si as standard. [b] In C_6D_6, external Me_4Si as standard. Reference 6a. [c] Ph_3SiLi in THF, external Me_4Si as standard. $Me_3SiSiMe_3$ and Me_3SiK in HMPA solvent, which was used as the internal standard. Reference 6b.

Table II. ^{1}H NMR Chemical Shifts[a] for the Neutral **1** and Silole Anions **2a** and **2b**

	1	2a	2b
Ph	6.8–7.2	6.6–7.2	6.6–7.3
CH_3	0.87	0.82	0.81

[a] In THF-d_8, reference; THF-d_8 = 1.73 ppm.

Table III. ^{13}C NMR Chemical Shifts[a] for the Neutral **1** and Silole Anions **2a** and **2b**

	1	2a	2b
C_α	144.77	139.51	139.61
C_β	158.04	155.76	156.33

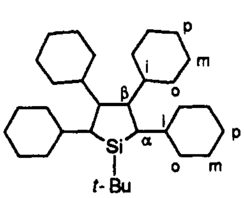
	1		2a		2b	
	αPh	βPh	αPh	βPh	αPh	βPh
C_i	140.33	142.26	144.72	149.29	144.46	148.96
C_o	131.46	127.99	132.56	130.50	132.47	130.47
C_m	131.32	128.34	126.51	126.40	126.55	126.33
C_p	126.30	126.86	121.38	123.34	121.64	123.47

	1	2a	2b
C_i	22.58	23.58	23.48
CH_3	30.19	32.78	32.57

[a] In THF-d_8, reference; THF-d_8 = 25.30 ppm.

The ^{29}Si NMR chemical shift was observed at 26.12 ppm for **2b**, a large downfield shift compared to **1** ($\Delta\delta$ = 22.50 ppm). Only upfield shifts have been reported when neutral organosilanes are converted to silylanions (Table I).[6] Our observation is similar to that for phospholylanions in which the ^{31}P resonances are 60–80 ppm downfield from the neutral phospholes. The ^{31}P deshielding has been attributed to the delocalization of the negative charge, thus lending some phosphaalkene character to these species.[7]

^{1}H NMR analysis of this solution showed phenyl protons over a broader region than in **1** (from 7.2–6.8 to 7.3–6.6 ppm), and *tert*-butyl protons were shifted upfield from 0.87 ppm in **1** to 0.81 ppm in **2b** (Table II). In the ^{13}C NMR spectrum of **2b**, the *tert*-butyl carbons were deshielded. The C_α and C_β of the butadiene moiety are shifted upfield, the C_i and C_o of the phenyl groups are shifted downfield, and the C_m and C_p of the phenyl groups are shifted upfield (Tables III and IV).



Sonication of **1** with Li in THF-d_8 also gave a purple solution, and NMR data showed trends similar to those found for **2b**. All the corresponding ^{13}C and ^{29}Si chemical shifts between **2a** and **2b** are within approximately 1 ppm (Table I, III).

The most important factors affecting the chemical shifts of silicon in ^{29}Si NMR are thought to be hybridization and the

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(1) (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.

(2) (a) Hagen, V.; Rühlmann, K. *Z. Chem.* **1967**, *7*, 462. (b) Corriu, R. J. P.; Gue'rin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973. (c) Han, B.-H.; Boudjouk, P. *Chungnam Kawhak Yonguchi* **1984**, *11*, 101; *Chem. Abstr.* **1986**, *105*, 6549u. Recently, we reviewed the reaction of 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene with KH.[2c] However, we could not obtain evidence for the formation of its silole anion as reported. We did observe as the major product (1-methyl-1,1-dihydro-2,3,4,5-tetraphenyl-1-silacyclopentadiene)silicate potassium by ^{1}H, ^{13}C, and ^{29}Si NMR. We will report our results in due course. Several silafluorenes have been prepared and considered as substituted siloles: (d) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3243. (e) Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. *Organometallics* **1983**, *2*, 351.

(3) (a) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972. (b) Damewood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5028.

(4) Compound **1** was prepared by a known procedure: Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

(5) Compound **3**: pale green crystals, mp 122–123 °C, yield 0.423 g (74.5%); ^{1}H NMR ($CDCl_3$, ref; $CDCl_3$ = 7.27 ppm) δ 0.26 (d, 6H, SiMe, J = 4.40 Hz), 1.02 (s, 9H, CMe), 4.24 (sept, 1H, J = 4.40 Hz), 6.73–7.15 (br m, 20H, Ph); ^{13}C NMR ($CDCl_3$, ref; $CDCl_3$ = 77.00 ppm) δ −5.71 (SiMe), 20.82 (t-C), 28.61 (t-CMe), 155.72 (C_β), 142.90 (C_α), 141.58 (C_i of C_β), 138.88 (C_i of C_α), 130.220 (C_o of C_β), 129.32 (C_o of C_α), 127.63 (C_m of C_β), 127.02 (C_m of C_α), 125.86 (C_p of C_β), 125.09 (C_p of C_α); ^{29}Si NMR ($CDCl_3$, ref; external TMS = 0.00) δ 2.08 (ring Si), −39.92 ($SiMe_2H$); MS (M^+, relative abundance) 502 (M^+ + 2, 8), 501 (M^+ + 1, 14), 500 (M^+, 29), 443 (M^+ − 57, 54), 356 (40), 135 (45), 105 (100), 59 (48). Anal. Calcd for $C_{34}H_{36}Si_2$: C, 81.54; H, 7.25. Found: C, 81.59; H, 7.19.

(6) (a) Söllradl, H.; Hengge, E. *J. Organomet. Chem.* **1983**, *243*, 257. (b) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989.

(7) Mathey, F. *Chem. Rev.* **1988**, *88*, 429 and references therein.

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Table IV. ^{13}C NMR Chemical Shift Changes[a] upon Reaction of **1** To Form **2a** and **2b**

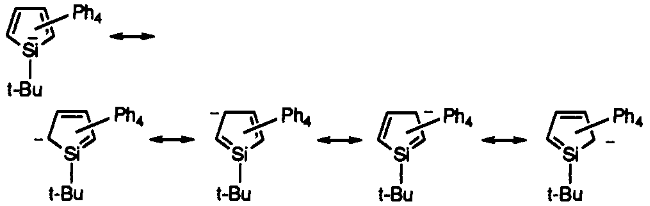
	2a	**2b**
ΔC_α	-5.26	-5.16
ΔC_β	-2.28	-1.71

	2a		**2b**	
	αPh	βPh	αPh	βPh
ΔC_i	4.39	7.03	4.13	6.70
ΔC_o	1.10	2.51	1.01	2.48
ΔC_m	-4.81	-1.94	-4.77	-2.01
ΔC_p	-4.92	-3.52	-4.66	-3.39

	2a	**2b**
ΔC_t	1.00	0.90
ΔCH_3	2.59	2.38

[a] In ppm.

presence of a negative charge.[6] The downfield shifts of **2a** and **2b** in the ^{29}Si NMR strongly suggest an incorporation of silicon p-orbitals to diffuse and/or delocalize the negative charge into the butadiene moiety. This would require a change in the geometry from the neutral **1** (sp^3 hybrid) to the silole anion **2** (sp^2 hybrid) to maximize delocalization.



The shielding of C_α and C_β in **2** indicates that there is an increase in π-electron density at these positions. Increasing electron density on the C_α and C_β positions of **2** cause the C_i to be deshielded, the C_o to be deshielded less than C_i, the C_m to be shielded, and the C_p to be shielded. The magnitude of shielding at C_p, as indicated by changes in chemical shift, is similar to that observed for C_p in $Ph_nMe_{3-n}SiCl$ or $Ph_nMe_{3-n}SiH$ when converted to $Ph_nMe_{3-n}Si^-Li^+$ ($\Delta\delta(C_p) = -1.5$ to -7.8 ppm).[6] The major effect of the increased electron density on C_α and C_β is polarization of the attached phenyl rings,[8] significant delocalization being ruled out because of the nearly perpendicular geometry of the phenyl groups with respect to the silole ring.[9]

An analogous reaction has been carried out to synthesize the 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion by Joo *et al.*[10] They obtained the [2 + 2] head-to-tail dimer of 1-methyl-5-lithio- or -sodio-2,3,4,5-tetraphenyl-1-silacyclo-1,3-diene, which was formed by 1,5-rearrangement of the anion in the silole ring. This resistance to dimerization is attributed to the inhibiting effect of the *tert*-butyl group.

Our NMR data support delocalization of the negative charge in **2** onto the butadiene moiety, justifying an aromatic resonance contributor. The data also suggest that the four phenyl groups on the ring provide additional stabilization of the silacyclopentadienide anion through polarization. We are presently exploring the reactivity of **2**.

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(10) (a) Joo, W.-C.; Hong, J.-H.; Son, H.-E.; Kim, J. H. *Proceedings of the 9th International Symposium on Organosilicon Chemistry*; University of Edinburgh, UK, July 16–20, 1990; p B8. (b) Hong, J.-H. Ph.D. Thesis, Sung Kyun Kwan University, Seoul, Korea, 1989.