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Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and NMR Characterization of 2,5-Bis(Trimethylsilyl)-3,4-Diphenyl-1-Silacyclopentadienyl Dianion

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SYNTHESIS AND NMR CHARACTERIZATION OF 2,5-BIS(TRIMETHYLSILYL)-3,4-DIPHENYL-1-SILACYCLOPENTADIENYL DIANION

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GRAPHICAL ABSTRACT



Abstract Two new silyl-substituted silolide dianions (**11a**, **11b**) have been synthesized and characterized spectroscopically. Their ${}^{1}H$, ${}^{29}Si$, and ${}^{13}C$ NMR spectra show similarities to the known phenyl- and alkyl-substituted analogues. Reaction with ethyl bromide gave the expected diethylsilol. B3LYP/6-31 + G* geometry optimization revealed equalized CC distances, and also NICS values indicate significant aromaticity.

Figures S1—S5 are available online in Supplemental Materials.

Keywords Aromacity; silolyl dianion; density functional calculation

INTRODUCTION

Silacyclopentadienyl anions—in contrast to the cyclopentadienyl anion—in general exhibit small aromaticity, due to the pyramidality of the silyl anion,¹ similarly to the isoelectronic phospholes.² Silacyclopentadienyl dianions do not suffer from the planarity problem and are considered highly aromatic,³ likewise phospholide anions.⁴ Recently, we have shown⁵ that α -silyl substitution enhances the aromaticity of the monoanion, by increasing the weight of the **b** resonance form (Scheme 1). Having this in mind, we have decided to investigate the aromaticity of the α -substituted silolid dianion as well, in a combined synthetic/theoretical study.

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Dedicated to Professor Louis D. Quin on the occasion of his 86th birthday.

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Scheme 1 Mesomeric structures of silolide anion.

The first silacyclopentadienyl dianon 1b (1,1-disodio-2,3,4,5-tetraphenylsilacyclopen tadienyl dianion) (Scheme 2) was synthetized by Joo and Hong in 1990.⁶ To estimate the extent of aromaticity, ²⁹Si-NMR chemical shifts were also studied in the case of the dilithio-dianion (1a).⁷ In theory, delocalization should result a charge transfer from the silicon toward the butadiene moiety, which is considered to result in a downfield effect on ²⁹Si NMR, and an upfield effect on the ring carbons in ¹³C NMR signals as compared to the signals of the neutral tetravalent synthetic precursors (e.g. dichlorosilols). This charge transfer effect was related to the aromatic character of the dianion.⁷ The X-ray structure was also obtained in the case of 1,1-dilithio-2,3,4,5-tetraphenylsilolide (1b) exhibiting nearly equal CC distances in agreement with the high aromaticity.⁸ Interestingly, while in the solid state $\eta^{1} - \eta^{5}$ -coordinated silolyl dianion was formed, in THF solution ⁷Li-NMR studies indicated $\eta^5 - \eta^5$ -coordination. Tilley's research group was able to obtain the X-ray structure of the crown ether-coordinated 1,1-dipotassio-2,3,4,5-tetramethylsilolide (2b).⁹ Theoretical calculations carried out by Schleyer et al. also approved the high aromaticity of the silolyl dianions and other groups' 14 metallocyclopentadienyl dianions.^{3,10} Some aromatic germoyl dianions were also published during this period and the synthesis of a stannacyclopentadienyl dianion was also reported.^{11–14} Altogether only five different silolyl dianions (Scheme 2) were published due to the limited number of the available dihalo precursors.^{15,16} Despite the limited availability of silolyl dianions, their interesting and unusual chemistry is continuously studied.^{17,18}



Scheme 2 Silol dianions, silafluorenyl dianion, silaindenyl dianions.

Tetraphenylsilolyl dianions (**1a**, **1b**) were produced from 1,1-dichloro-2,3,4, 5-tetraphenylsilol that can be prepared by the reaction of SiCl₄ and 1,4-dilithio-1,2,3,4tetraphenylbuta-1,3-diene.⁶ The latter compound can be obtained from diphenylacetylene and lithium,¹⁹ this reaction, however, is limited to the aryl-substituted derivatives. Tetramethylsilolyl dianions (**2a**, **2b**) can be obtained from the direct reduction of 1,1-dibromo-2,3,4,5-tetramethylsilol or 1,1-dichloro-2,3,4,5-tetramethylsilol. While the former precursor can be synthetized from Cp₂ZrC₄Me₄ and SiBr₄,^{9,20} 1,1-dichloro-2,3,4,5-tetramethylsilol is generated by the reaction of SiCl₄ and 1,1-dilithio-1,2,3,4,tetramethylbuta-1,3-diene which in turn can be produced from the corresponding $Cp_2ZrC_4Me_4$.²¹ The tetraethyl derivative can also be produced by the zirconocene route.²² Silaindenyl and silafluorenyl derivatives were also prepared.^{23,24} Here we report the synthesis and an NMR study of the new 2,5-bis(trimethylsilyl)-substituted silolide dianions.

RESULTS AND DISCUSSION

Synthesis of 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenylsilol was performed by the same route that was published by Tamao's research group (Scheme 3).²⁵ Reaction between bis(diethylamino)dichlorosilane (**6**) and lithium-phenylacetylide in THF solution provides bis(phenylethynyl)bis(diethylamino)silane (**8**). Addition of **8** to a THF solution of lithium-naphtalide, then quenching the mixture with excess amount of trimethylchlorosilane gives 1,1-bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenylsilol (**9**) in high yield. Transformation of the diethylamino- to a chlorine-function can be achieved by bubbling HCl gas through the diethylether solution of the diaminolsilol (**9**).



Scheme 3 (i) 1 molar amount ^{*n*}Buli, THF, 0°C; (ii) 4 molar amount Li/Np, THF, -78° C, 1 h, then 4 molar amount Me₃SiCl, -78° C to RT, 8 h; (iii) 10 molar amount dry HCl gas, Et₂O, -78° C, 1 h.



Scheme 4 Synthesis of dianions and their reaction with EtBr.

10 reacts with sodium in dioxane giving a dark red solution after 12 h at reflux temperature. Applying potassium instead of sodium, the reaction time is decreased to 4 h, while with lithium no reaction occurred. After the filtration of the suspension, the dianion (11a, b) can be isolated as a yellow pyrophoric powder. Both compounds are stable in

Ph Ph Ph Ph Ph Ph Ph Cl Ph Cl 13		Ph Ph Si 2Na ⁺ 1b		$\begin{array}{c} Ph \qquad Ph \\ Me_3Si \qquad Si \qquad Si Me_3 \\ Cl \qquad Cl \\ 10 \end{array}$	Ph Me ₃ Si Si 2Na 11b	∑Ph SiMe₃
	$\delta(\text{CDCl}_3)$	$\delta(\text{THF-}d_8)$	$\Delta\delta$	$\delta(\text{CDCl}_3)$	$\delta(C_6 D_6/THF)$	$\Delta\delta$
Cα	154.7	153.2	-1.5	169.8	149.2	-20.6
C_{β}	132.3	130.7	-1.6	136.2	140.2	4.0
eta-Ph				β -Ph		
Cipso	135.4	146.7	11.3	140.4	143.1	2.7
Corto	129.3	133.4	4.1	128.4	131.0	2.6
C _{meta}	128.2	126.4	-1.8	127.5	125.4	-1.9
Cpara	127.1	121.8	-5.3	127.2	121.2	-6.0
C _{SiMe3}	—	—	_	0.3	5.1	4.8

Table 1 ¹³C NMR chemical shifts in ppm (reference external TMS) of 1b, 10, 11, and 13

nitrogen atmosphere for months, however, they react with air rapidly to form a white powder. Adding EtBr to the THF solution of **11a** or **11b** gives the expected diethylsilol (**12**) in 90% yields. (Scheme 4).

The ²⁹Si NMR signal of the ring silicon of **11a** (49.3 ppm), **11b** (44.9 ppm) is shifted downfield compared to **10** (19.3 ppm) and **12** (2.8 ppm), and is between the reported chemical shift of **1a** (68.5 ppm)⁷ and **2a** (29.8 ppm).^{21 13}C NMR chemical shifts of **10** and **11b** together with that of the tetraphenyl derivatives **13** and **1b** are given in Table 1 (**11a** exhibits similar data—see experimental section). The direct metallation of **10** results in a significant upfield effect on the C_{α} of **11**, while the upfield effect on C_{β} is small. However, chemical shift changes on β -phenyl groups during the reduction are similar in **1b** and **11b** (see Table 1). The ¹³C NMR signals of the trimethylsilyl groups in **11b** with respect to **10** are downfielded (**11b**: 5.1 ppm; **10**: 0.3 ppm). This is probably caused by the ring current of the delocalization, as was already observed on the alkyl signals (¹H, ¹³C) of **2a**, **2b**, and **3**. Interestingly, the ²⁹Si NMR and ¹H NMR signals of the trimetylsilyl group changed to the opposite direction than expected (²⁹Si NMR: **11b**: -19.1 ppm, **10**: -7.9 ppm; ¹H NMR: **11b**: -0.96 ppm, **10**: 0.22 ppm).

Density functional calculations were carried out on **11** for understanding the effect of the trimethylsilyl substituents on the aromaticity of the ring. The optimized structure of **11** is shown in Figure 1. Geometry optimization and NBO calculations were carried out at B3LYP/6-31+G^{*}, whereas for NMR calculations B3LYP/pcS-2 level was used. The CC bond lengths in the silolide ring is nearly the same ($C_{\alpha}C_{\beta}$: 1.439 Å $C_{\beta}C_{\beta}$: 1.436 Å). Indeed $C_{\beta}C_{\beta}$ is shorter than $C_{\alpha}C_{\beta}$ which means that the mesomeric structure is closer to type **b** or **c** (Scheme 1). The phenyl groups exhibit a propeller like arrangement—as an apparent consequence of steric congestion—and therefore the conjugation between the silol ring and the phenyl groups should be decreased as already noted in the case of the tetraphenyl silolides (**1a**, **1b**).^{7,22} Interestingly, NICS values show a moderate aromatic character (NICS(0): -5.9 ppm; NICS(1)_{πzz}: -19.4 ppm) while the planar monoanion ($C_4H_4SiH^-$) has larger NICS (NICS(0): -14.0 ppm; NICS(1)_{πzz}: -26.1 ppm) values.⁵



Figure 1 Optimized structure of 11 at B3LYP/6-31+G* level of theory.

To obtain the mesomeric distribution of **11**, NBO calculations were carried out. The β phenyl groups were removed from the structure for the easier comparison of the mesomeric distribution of **11** with that of the 2,5-disilylsilolide anion.⁵ It is noteworthy that in the absence of the steric repulsion between the phenyl residues, the $C_{\beta}C_{\beta}$ distance decreases (from 1.436 to 1.400 Å) while $C_{\alpha}C_{\beta}$ and the NICS values did not change significantly (see Supporting Information). As expected, the mesomeric distribution of 2,5-bis(trimetilsilyl) dianion (**a**: 7%, **b**: 31%, **c**: 23%, see Scheme 1) is close to that of the planar 2,5-disilylsilolide (**a**: 9%, **b**: 32%, **c**: 23%, see Scheme 1).⁵

EXPERIMENTAL

All reactions were carried out under dry nitrogen atmosphere using standard Schlenk techniques. Dioxane and THF were distilled from sodium benzophenone under nitrogen. Hexane was dried with LiAlH₄ and distilled under nitrogen atmosphere. C_6D_6 was dried over sodium benzophenone and were vacuum transferred to the NMR tube. NMR spectra were recorded on Bruker Avance 300 and Bruker Avance DRX-500 spectrometers in CDCl₃ or C_6D_6 /THF. GC-MS data were obtained on a SHIMADZU GC-MS QP2010 with GC-MS system equipped with ZB-5 capillary column (95% methylpolysiloxane and 5% diphenylpolysiloxane). Quantum chemical calculations carried out with Gaussian 09²⁶ software package at B3LYP/6-31 + G* level of theory. This method was successfully applied earlier to calculate anionic structures converging to wavefunctions with the SOMO not being a spatially diffuse orbital.²⁷ Investigation of the wavefunction of **11** at B3LYP/6-31 + G*, indeed, showed that no electron was placed on the diffuse orbitals. NICS values^{28, 29} were calculated with B3LYP/pcS-2 method. Selected NMR and mass spectra for **11a** and **12** are presented in the Supplemental Materials (Figures S1–S5).

Synthesis of 1,1-dicloro-2,5-bis(trimethylsilyl)-3,4-diphenilsilol (10)

10 was prepared according to the Tamao's procedure.²⁵ Before use **10** was recrystallized from hexane at -40° C. Yield: 3.2 g (81%). ¹H NMR (CDCl₃) δ_{H} : 0.22 (s, 18H, Si(CH₃)₃), 6.77–6.96 (m, 10H, Ph). ¹³C NMR (CDCl₃) δ_{C} : 0.3 (Si(CH₃)₃), 127.2 (Ph- C_{p}), 127.5 (Ph- C_{m}), 128.4 (Ph- C_{p}), 136.2 (C_{β}), 140.4 (Ph- C_{i}), and 169.8 (C_{α}). ²⁹Si NMR (CDCl₃) δ_{Si} : -7.9 (Si(CH₃)₃), 19.3 (SiC₄).

Synthesis of 1,1-dipotassio-2,5-bis(trimethylsilyl)-3,4-diphenilsilol (11a)

1.50 g (3.35 mmol) **10** was dissolved in 5 mL dioxane and 0.66 g (16.8 mmol) potassium was added to the solution under nitrogen. The mixutre was stirred for 8 h at reflux temperature. The mixture became dark red and a thick precipitate formed. Dioxane was removed at reduced pressure and THF (10 mL) was added to the residual. The THF suspension was filtered to remove unreacted sodium. The filtrate was concentrated and hexane (10 mL) was added to the solution. The precipitate was filtered and washed with hexane until the precipitate become yellow. The yellow solid was dried under reduced pressure. Yield: 1.30 g (85%). ¹H NMR (C₆D₆/THF) $\delta_{\rm H}$: 0.23 (s, 18H, Si(CH₃)₃), 6.79–6.83 (m, 2H, *p*-Ph), 6.92–6.97 (m, 4H, *m*-Ph), 7.05–7.15 (m, 4H, *o*-Ph). ¹³C NMR (C₆D₆/THF) $\delta_{\rm C}$: 6.3 (Si(CH₃)₃), 122.7 (Ph-C_p), 126.7 (Ph-C_m), 132.0 ppm (Ph-C_o), 141.3 (C_β), 145.0 (Ph-C_i), and 149.7 (C_α). ²⁹Si NMR (C₆D₆/THF) $\delta_{\rm Si}$:-15.0 (Si(CH₃)₃), 49.3 (SiC₄).

Synthesis of 1,1-disodio-2,5-bis(trimethylsilyl)-3,4-diphenilsilol (11b)

1.50 g (3.35 mmol) **10** was dissolved in dioxane (5 mL) and 0.39 g (16.8 mmol) sodium was added to the solution under nitrogen. The mixture was stirred for 24 h on reflux temperature. The work up process was carried out the same way as for **11a**. Yield: 1.29 g (91%). ¹H NMR (C₆D₆/THF) $\delta_{\rm H}$: -0.96 (s, 18H, Si(CH₃)₃), 6.61-6.63 (m, 2H, *p*-Ph), 6.72-6.78 (m, 4H, *m*-Ph), 6.86-6.90 (m, 4H, *o*-Ph). ¹³C NMR (C₆D₆/THF) $\delta_{\rm C}$: 5.1 (Si(CH₃)₃), 121.2 (Ph-C_p), 125.4 (Ph-C_m), 131.0 (Ph-C_o), 140.2 (C_β), 143.1 (Ph-C_i), 149.2 (C_α). ²⁹Si NMR (C₆D₆/THF) $\delta_{\rm Si}$:-19.1 (Si(CH₃)₃), 44.9 (SiC₄).

Synthesis of 1,1-diethyl-2,5-bis(trimethylsilyl)-3,4-diphenilsilol (12)

130 mg (0.29 mmol) **11a** was dissolved in THF (3 mL) and 0.05 mL (0.58 mmol) EtBr was added to the solution. The dark red solution became light yellow after 1 h. The solvent and the volatiles were removed under reduced pressure and the residual was dissolved in hexane and was filtered. Hexane was removed by vacuum to give a yellow oil. Yield: 112 mg (93%). ¹H NMR (CDCl₃) δ_{H} : 0.39 (s, 18H, Si(CH₃)₃), 1.15 (q, 4H, CH₂CH₃), 1.25 (t, 6H, CH₂CH₃), and 6.95–7.03 (m, 10H, Ph). ¹³C NMR (CDCl₃) δ_{C} : 1.7 (Si(CH₃)₃), 6.0 (CH₂CH₃), 8.0 (CH₂CH₃), 126.9 (Ph-C_p), 127.72 (Ph-C_m), 129.5 (Ph-C_o), 142.4 (C_β), 143.8 (Ph-C_i), 172.3 (C_α). ²⁹Si NMR (CDCl₃) δ_{Si} : -10.0 (Si(CH₃)₃), 2.8 (SiC₄). EI-MS: m/z (M⁺, relative abundance): 434.3 (18.7) [M]⁺, 419.1 (5.6) [M – CH₃]⁺, 405.1 (7.0) [M – C₂H₅]⁺, 361.1 (7.5) [M – 2C₂H₅ – CH₃]⁺, 231.1 (25.3) [M – 2CH₂CH₃ – 2Si(CH₃) + H]⁺.

CONCLUSION

Synthesis of 1,1-disodio-2,5-bis(trimethylsilyl)-3,4-diphenilsilol and 1,1-dipotassio-2,5-bis(trimethylsilyl)-3,4-diphenilsilol has been carried out successfully. The reaction with EtBr produced the expected 1,1-diethyl-2,5-bis(trimethylsilyl)-3,4-diphenilsilol. NMR studies shows that these dianions (**11a**, **11b**) have enhanced aromatic character due to the charge transfer effect that can be observed in ²⁹Si NMR and ¹³C NMR spectra. However, theoretical calculations showed that the aromaticity of the dianions is somehow lesser than the monoanions based on different NICS aromaticity measures, while the optimized structure showed bond length equalization. This indicates that the aromaticity of the silolide anions

and dianions is a complex issue, and it depends strongly on the nature of the substituents on the ring carbons.

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SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

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