Article

Synthesis and NMR-Study of 1-Trimethylsilyl Substituted Silole Anion [Ph$_4$C$_4$Si(SiMe$_3$)]$^-$•[Li]$^+$ and 3-Silolenide 2,5-carbodianions {[Ph$_4$C$_4$Si(*n*-Bu)$_2$]$^{-2}$•2[Li]$^+$, [Ph$_4$C$_4$Si(*t*-Bu)$_2$]$^{-2}$•2[Li]$^+$} via Silole Dianion [Ph$_4$C$_4$Si]$^{-2}$•2[Li]$^+$

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[†] Dedicated to Professor Wan-Chul Joo on the occasion of his 89th birthday.

Abstract: 1-Trimethylsilyl, 1-R (R = Me, Et, *i*-Bu)-2,3,4,5-tetraphenyl-1-silacyclopentadiene [Ph$_4$C$_4$Si(SiMe$_3$)R] are synthesized from the reaction of 1-trimethylsilyl,1-lithio-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion [Ph$_4$C$_4$SiMe$_3$]$^-$•[Li]$^+$ (**3**) with methyl iodide, ethyl iodide, and *i*-butyl bromide. The versatile intermediate **3** is prepared by hemisilylation of the silole dianion [Ph$_4$C$_4$Si]$^{-2}$•2[Li]$^+$ (**2**) with trimethylsilyl chloride and characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy. 1,1-bis(R)-2,3,4,5-tetraphenyl-1-silacyclopentadiene [Ph$_4$C$_4$SiR$_2$] {R = *n*-Bu (**7**); *t*-Bu (**8**)} are synthesized from the reaction of **2** with *n*-butyl bromide and *t*-butyl bromide. Reduction of **7** and **8** with lithium under sonication gives the respective 3-silolenide 2,5-carbodianions {[Ph$_4$C$_4$Si(*n*-Bu)$_2$]$^{-2}$•2[Li]$^+$ (**10**) and [Ph$_4$C$_4$Si(*t*-Bu)$_2$]$^{-2}$•2[Li]$^+$ (**11**)}, which are characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy. Polarization of phenyl groups in **3** is compared with those of silole anion/dianion, germole anion/dianion, and 3-silolenide 2,5-carbodianions **10** and **11**.

Keywords: silacyclopentadiene; silole; anion; dianion; silyation; 3-silolenide; aromaticity; NMR

1. Introduction

Cyclopentadienyl anion, the most representative aromatic compound, has for a long time played important roles in organic and organometallic chemistry [1–3]. Therefore it has been a challenge

to synthesize the analogue framework [4–7], in which one of carbon atoms is replaced by a heavier group 14 atom, and the ultimate question is to find out how its aromaticity changes and is maintained [8–15]. Since the first silacyclopentadienide dianion was reported [16], the aromaticity of sila- and germa-cyclopentadienide dianion has been suggested by NMR chemical shift changes upon reduction [17,18]. Their aromatic structures [19,20] and the related structures have been confirmed by X-ray crystallography [21–27]. Heavier metallic dianion equivalents, the stannacyclopentadienide dianion [28–30] and plumbacyclopentadienide dianion [31], are also reported to display aromaticity [32–37].

The principal heavier congener of the cyclopentadienide anion, 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion, has been reported to have aromaticity according to NMR chemical shift changes upon reduction [38]. Meanwhile 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion was synthesized and crystallized in THF as a [2+2] dimer of its Si = C bond in aromatic ring structures [39], the dimer of which is dissociated to the original silole anions when it is reacted with alkyl halides or trimethylchlorosilane in THF [40]. Even the analogue frameworks of trimetallic anion {[C_2GeSi_2]$^-$, [C_2Si_3]$^-$} and divalent germanium containing anion {[C_3NGe:]$^-$}, in which more than one carbon atom of the cyclopentadienyl anion are replaced by heavier group 14 atoms of Si and/or Ge, are synthesized and characterized to have aromaticity [41–43], making it possible to form heavy analogues of ferrocene with them [44,45].

In contrast spectroscopic and X-ray crystallographic data [22,23] for 1-trimethylsilyl-tetramethyl/ethyl-1-silacyclopentadienide anions have revealed that they possess pyramidal silicon centers and bond localization in their butadiene moieties. Nevertheless the heavy analogues of ferrocene are synthesized with them [24,27,46,47]. Therefore it is interesting to study 1-trimethylsilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion [$Ph_4C_4Si(SiMe_3)$]$^-$ to compare it with other metallole anions [48].

There are several routes for silole syntheses, via 1,4-dilithio-butadienides by using diphenylacetylene [16,17,49] and 1,4-dihalobutadienes [23,50,51], the intramolecular reductive cyclization of diethynylsilanes [52,53], metallacyclic transfer reactions [54], and organoboration [55–58]. However those synthetic methods are not applicable to synthesizing of various siloles derivatives at the Si atom, especially for preparing 1-trimethylsilyl group substituted siloles due to the feasibility of the nucleophilic attack on the Si-Si bond by carbanions [22,24,27,59,60] and silole anion [39]. Coversely all metallole dianions are potential and useful intermediates for the synthesis of various di-substituted metallole derivatives, polysiloles, and silole-containing polymers [61–66].

Herein we report that silole dianion is a versatile intermediate to synthesize [$Ph_4C_4Si(SiMe_3)(R)$] (R = Me, Et, *i*-Bu) via [$Ph_4C_4Si(SiMe_3)$]$^-$, which is prepared by hemisilylation of the silole dianion and characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy, and [$Ph_4C_4SiR_2$] (R = *i*-Bu, *t*-Bu).

2. Results and Discussion

2.1. Preparation of 1-Trimethylsilyl,1-lithio-2,3,4,5-tetraphenyl-1-silacyclopentadienide Anion (**3**) and Its Reaction with Methyl Iodide, Ethyl Iodide and i-Butyl Bromide

1-Trimethylsilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion [$Ph_4C_4Si(SiMe_3)$]$^-$•[Li]$^+$ (**3**) was prepared from the reaction of the silole dianion [Ph_4C_4Si]$^{-2}$•2[Li]$^+$ (**2**) with one equivalent of

trimethylsilyl chloride. The silole dianion **2** was generated by the sonication of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene [Ph$_4$C$_4$SiCl$_2$] (**1**) with lithium in THF [17]. Compound **3** in THF was reacted with the alkyl halides of methyl iodide, ethyl iodide, and *i*-butyl bromide to provide [Ph$_4$C$_4$Si(SiMe$_3$)(R)] [R = Me (**4**) , Et (**5**), *i*-Bu (**6**)], respectively (Scheme 1).

**Scheme 1.** Synthesis and alkylation of **3** via silole dianion **2**.
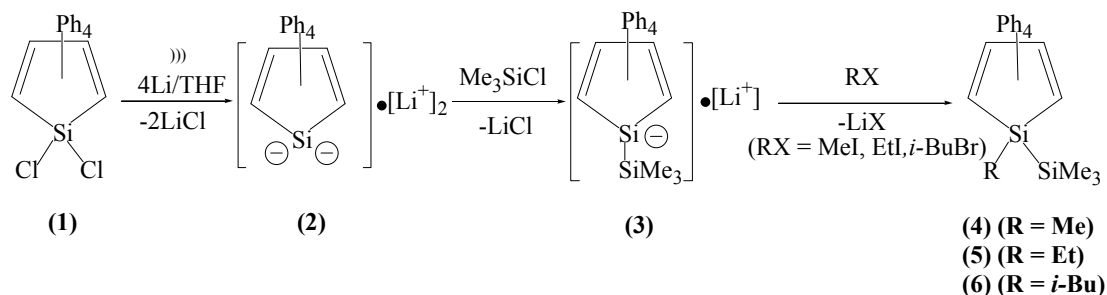
Silylation of **2** with trimethylsilyl chloride is a novel reaction to synthesize 1-trimethylsilyl substituted silole anion **3**; the similar alkylation of stannole dianion with *t*-butyl chloride was reported to give 1-*t*-butyl substituted stannole anion, oxidation of which in the air provided 1,1-bis(1-*t*-butyl-stannole) [67,68]. Oxidation of stannole dianion were reported to give bistannole-1,2-dianion or terstannole-1,3-dianion [69,70]. But the silole anion **3** decomposes in the air to give the ring opening products of 1,2,3,4-tetraphenylbutadiene and silicate. Preparation of **4** is interesting since addition of trimethylsilyl chloride to the silole anion [Ph$_4$C$_4$Si(Me)]$^-$•[M]$^+$ (M = Li, Na) in THF has given 1,1-bi(1-methyl-silole) [Ph$_4$C$_4$Si(Me)]$_2$, but addition of the silole dianion to trimethylsilyl chloride in THF has provided [Ph$_4$C$_4$Si(SiMe$_3$)(Me)] (**4**) [40].

2.2. Synthesis of 1,1-Bis(n-butyl/t-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene and NMR-Study of 3-Silolenide-2,5-carbodianions

1,1-bis(*n*-Butyl/*t*-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene {[Ph$_4$C$_4$Si(*n*-Bu)$_2$] (**7**) and [Ph$_4$C$_4$Si(*t*-Bu)$_2$] (**8**)} are prepared in good yield from the reactions of silole dianion **2**, which is generated by the sonication of **1** with lithium in THF, with *n*-bromobutane and *t*-butyl bromide. In the case of *t*-butyl bromide, [Ph$_4$C$_4$Si(*t*-Bu)$_2$] (**8**) is produced along with 1,1-bi[(*t*-Bu)SiC$_4$Ph$_4$] (**9**) in the ratio of **3** to **1** (Scheme 2). Until now there is one report of the synthesis of 1,1-bis(*t*-butyl)-substituted silole, which has been prepared photochemically in low yield [71].

1,1-bis(*n*-Butyl/*t*-butyl)-2,3,4,5-tetraphenyl-1-silacyclopentadiene {[Ph$_4$C$_4$Si(*n*-Bu)$_2$] (**7**) and [Ph$_4$C$_4$Si(*t*-Bu)$_2$] (**8**)} are sonicated in THF-*d$_8$* with lithium in the 5 mm NMR tube for 2 h. During this time the color of the mixture becomes red and/or purple. The NMR study of the reduced species in THF-*d$_8$* shows clearly that the only one species is formed and is assigned to the respective reduced 3-silolenes with 2,5-carbodianions {[Ph$_4$C$_4$Si(*n*-Bu)$_2$]$^{-2}$•2[Li]$^+$ (**10**) and [Ph$_4$C$_4$Si(*t*-Bu)$_2$]$^{-2}$•2[Li]$^+$ (**11**)}. Each of their ^{13}C-NMR spectra presents ten peaks, consistent with C_2 symmetry, and the ^{29}Si spectrum of each compound shows only one resonance. The respective ^{1}H-NMR spectrum of **10** and **11** shows two kinds of protons, 20 phenyl protons and 18 butyl protons. Even if they are sonicated further, they show the same peaks with no change.

Scheme 2. Synthesis of **7** and **8** and their reduction to **10** and **11**.
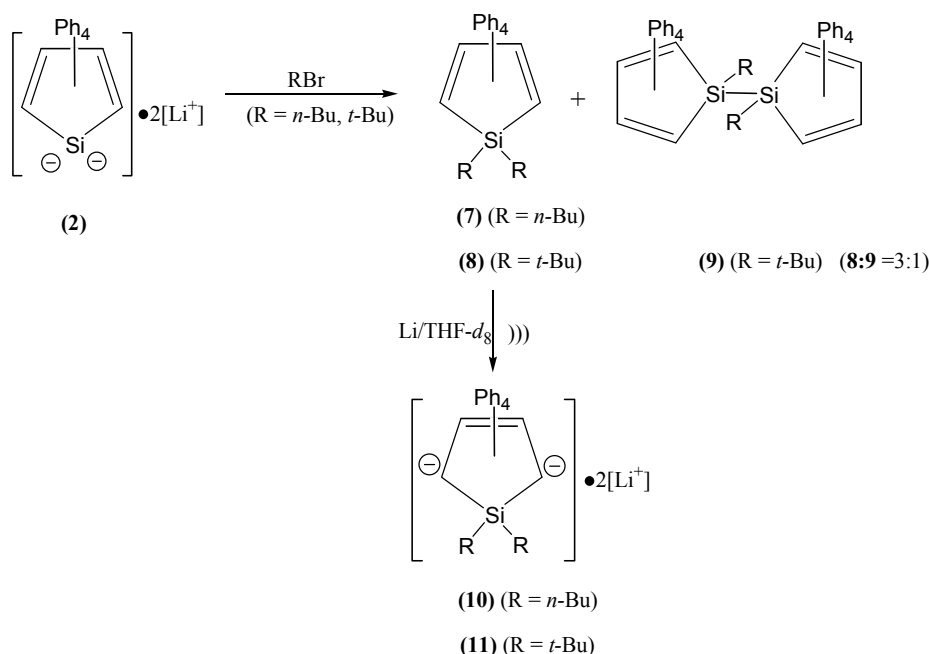
Both chemical shifts of the two *tert*-C$^-$ groups (73.18 ppm for (**10**), 78.12 ppm for (**11**)) are consistent with those of the reported 3-silolenides with 2,5-carbodianions, $[Ph_4C_4Si(R_1)(R_2)]^{-2}$ (77.4 ppm for $R_1 = R_2 = Me$ [72], 76.42 ppm for $R_1 = Me$, $R_2 = H$ [73]), and 1,1-R_1,R_2-2-lithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide anion (77.78 ppm for $R_1 = R_2 = H$ [74]). The ^{13}C-NMR chemical shifts of two $C_{i\alpha}$, $C_{i\beta}$ and two $C_{p\alpha}$, $C_{p\beta}$ show at 151.51, 147.68 ppm and 108.49, 120.80 ppm for **10** and at 152.59, 147.36 ppm and 110.87, 120.25 ppm for **11** (Table 1). The localized carbanions polarize the phenyl groups more than those of the aromatic silole/germole dianions and silole anions. The extent of polarization [Sum(C_i-C_p)/2] in those species shows in narrow range: 3-silolenides 2,5-carbodianions (34.42 to 35.00 ppm), silole/germole dianions $[Ph_4C_4E]^{-2}$ [E = Si (2), Ge] (28.60 to 28.64 ppm), and silole anion $[Ph_4C_4Si(t\text{-}Bu)]^-$ (24.65 ppm). In case of the phenyl group on germanium atom in the localized germole anion $[Me_4C_4GePh]^-\cdot[Li]^+$ [75], the extent of polarization {[Sum(C_i-C_p)/2] = 35.3 ppm} is very close to those of the localized 3-silolenide 2,5-carbodianions (Tables 1 and 2).

Upon lithiation of **8** to **11** the ^{29}Si-NMR chemical shift of **11** is not changed much (16.49 ppm (**8**) to 13.69 ppm (**11**)) since there is no change of its hybridization with the same substituents on the silicon atom (Table 1).

*2.3. NMR Study of 1-Trimethylsilyl,1-lithio-2,3,4,5-tetraphenyl-1-silacyclopentadienide Anion (**3**)*

$[Ph_4C_4SiCl_2]$ (**1**) is sonicated in THF-d_8 with lithium in a 5 mm NMR tube for 2 h, whereby the color of the mixture becomes red and/or purple. NMR study of the species in THF-d_8 clearly indicates that only one species of silole dianion $[Ph_4C_4Si]^{-2}\cdot2[Li]^+$ (**2**) is generated. Upon adding one equivalent of trimethylsilyl chloride to **2** the ^{29}Si-NMR chemical shift changes from 68.54 ppm (for **2**) to −13.22 ppm with another new resonance peak of the trimethylsilyl group at −15.54 ppm {$[Ph_4C_4Si(SiMe_3)]^-\cdot[Li]^+$ (**3**)}. The ^{13}C-NMR spectrum of **3** shows ten peaks in the aromatic region, consistent with C_2 symmetry, and one peak for the trimethylsilyl group (Table 1). In its ^{1}H-NMR

spectrum of it there are two kinds of protons, 20 protons corresponding to four phenyl groups and 9 protons of one trimethylsilyl group.

Table 1. $^{13}C/^{29}Si$-NMR chemical shifts of the localized 3-silolenides and germole anions.

3-Silenes 2,5-carbanion	$[Ph_4C_4SiMe_2]^{-2} \cdot 2[Li]^+$	$[Ph_4C_4SiMeH]^{-2} \cdot 2[Li]^+$	$[Ph_4C_4Si(n\text{-}Bu)_2]^{-2} \cdot 2[Li]^+$ (10)	$[Ph_4C_4Si(t\text{-}Bu)_2]^{-2} \cdot 2[Li]^+$ (11)	$[Me_4C_4GePh]^- \cdot [Li]^+$
C_α	77.4	76.42	73.18	78.12	138.7
C_β	128.5	128.82	128.06	130.34	151.5
Sum ($C_\alpha + C_\beta$)	205.9	205.24	201.24	208.46	290.2
Sum ($C_\beta - C_\alpha$)	51.1	52.40	73.18	78.12	12.8
	Ph	Ph	Ph	Ph	Ph
C_i	150.6, 147.3	150.33, 147.82	151.51, 147.68	152.59, 147.36	159.6
C_o	123.3, 125.8	132.47, 126.62	132.88, 126.61	132.75, 127.75	136.4
C_m	126.5, 132.4	123.05, 125.98	123.58, 126.61	125.77, 125.93	127.3
C_p	107.8, 120.5	107.65, 120.53	108.49, 120.80	110.87, 120.25	124.3
Sum ($C_i - C_p$)/2	69.6/2 = 34.8	69.97/2=35.00	69.90/2 = 34.95	68.83/2 = 34.42	35.3 [a]
^{29}Si-Ring	–	-34.14	-0.27	13.69	–
CH_3, *tert*-C	–	2.58	14.70, 18.88, 27.34, 29.08	31.5, 33.3 (brd d)	–
Reference	72 [b]	73 [b]	This Work [b]	This Work [b]	75 [b]

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

Table 2. $^{13}C/^{29}Si$-NMR chemical shifts of silole/germole dianions and silole anions.

	$[Ph_4C_4Si]^{-2} \cdot 2[Li]^+$ (2)	$[Ph_4C_4Ge]^{-2} \cdot 2[Li]^+$	$[Ph_4C_4Si(t\text{-}Bu)]^- \cdot [Li]^+$	$[Ph_4C_4SiSiMe_3]^- \cdot [Li]^+$ (3)
Ring carbons	151.22, 129.71 [a]	165.57, 129.92 [a]	155.76, 139.51	159.67, 139.30
	Ph	Ph	Ph	Ph
C_i	151.67, 145.83	152.17, 146.30	149.29, 144.72	148.81, 145.72
C_o	129.97, 133.43	129.92, 133.49	130.50, 132.56	129.81, 132.85
C_m	126.38, 126.38	126.38, 126.38	126.40, 126.51	126.30, 126.46
C_p	119.48, 121.83	119.29, 121.91	121.38, 123.34	120.86, 122.86
Sum($C_i - C_p$)/2	56.19/2 = 28.10	57.27/2 = 28.64	49.29/2 = 24.65	40.81/2 = 20.41
CH_3, *tert*-C	–	–	32.78(CH_3), 23.58(*tert*-C)	-0.23 [$Si(CH_3)_3$]
^{29}Si-Ring	68.54	–	25.10	−13.22
Refenence	17 [b]	18 [b]	38 [b]	This Work [b]

[a] The reported assignments were revised [76], the chemical shifts did not coincided with each other [77]. [b] In THF-d_8, reference = 25.30 ppm.

Upon adding trimethylsilyl chloride to **2** the chemical shifts of C_α and C_β in **2** are shifted far downfield from 151.22 ppm and 129.71 ppm to 159.67 ppm and 139.30 ppm in **3**. The chemical shifts of $C_{i\alpha}$ and $C_{i\beta}$ in **3** are observed at 145.72 ppm and 148.81 ppm, while the chemical shifts of $C_{p\alpha}$ and $C_{p\beta}$ in **3** are observed at 122.86 ppm and 120.86 ppm respectively. These carbon peaks of four phenyl groups indicate that the phenyl groups of **3** are still polarized, and the average chemical shift difference of C_i and C_p is 20.41 ppm [Sum($C_i - C_p$)/2] (Table 2). Such polarizations of phenyl groups are generally observed due to the absence of the significant π-conjugation between their phenyl groups and 5-membered ring because of their bulkiness and the congestion of four phenyl groups. The average chemical shift difference of 20.41 ppm for **3** is smaller than those of the silole dianion $[Ph_4C_4Si]^{-2} \cdot 2[Li]^+$ (**2**) (28.10 ppm) [17], $[Ph_4C_4Si]^{-2} \cdot 2[Na]^+$ (29.17 ppm) [16], the germole dianion

$[Ph_4C_4Ge]^{-2} \cdot 2[Li]^+$ (28.64 ppm) [18], and even the silole anion $[Ph_4C_4Si(t\text{-}Bu)]^{-} \cdot [Li]^+$ (24.65 ppm) [38]. The difference is also significantly smaller than those of the localized 3-silolenes (the reduced siloles to 2,5-carbodianions); $[Ph_4C_4SiMe_2]^{-2} \cdot 2[Li]^+$ (34.8 ppm) [72], $[Ph_4C_4SiHMe]^{-2} \cdot 2[Li]^+$ (35.00 ppm) [75], $[Ph_4C_4Si(n\text{-}Bu)_2]^{-2} \cdot 2[Li]^+$ (34.95 ppm) (**10**), $[Ph_4C_4Si(t\text{-}Bu)_2]^{-2} \cdot 2[Li]^+$ (34.42 ppm) (**11**), and that of the phenyl group in the localized germole anion $[Me_4C_4GePh]^{-} \cdot [Li]^+$ (35.3 ppm) [75] (Table 1). This trend implies that the electron density in the silole ring carbons of **3** is significantly lower than those in the rings of the localized 3-silolenes, the high aromatic silole/germole dianions $\{[Ph_4C_4Si]^{-2}, [Ph_4C_4Ge]^{-2}\}$ and the silole anion $[Ph_4C_4Si(t\text{-}Bu)]^{-}$ due to its low aromaticity and/or sp^3 hydridization character on Si atom in **3**.

X-ray crystallographic data for 1-trimethylsilyl-2,3,4,5-tetramethyl/ethyl-1-silacyclopentadienide anion) $[R_4C_4Si(SiMe_3)]^{-}$ (R = Me, Et) have revealed that the anionic rings possess a pyramidal silicon center and bond localization in the butadiene moiety of the ring, the ^{29}Si-NMR chemical shifts of these pyramidal ring Si atoms in those anions are observed from −41 ppm to −54 ppm [23]. However in the case of **3** the ^{29}Si-NMR chemical shift is observed at −13.22 ppm, far downfield from those of the pyramidal Si atoms in the localized silole anions and far upfield from those of silole dianions and silole anion (Table 3).

Table 3. ^{29}Si-NMR chemical shifts of silole anions and dianion.

Silole Anion	$[Me_4C_4SiSiMe_3]^{-} \cdot [M]^+$				$[Et_4C_4SiSiMe_3]^{-} \cdot$ $[M]^+$		$[Et_4C_4Si]^{-2} \cdot$ $2[M]^+$	$[Ph_4C_4SiSiMe_3]^{-} \cdot [M]^+$ (**3**)
M	Li		K		Li	K	Li	Li
^{29}Si-Ring	−45.38	−43.96	−42.70	−41.52	−53.12 [c]	−47.38	24.96	−13.22
^{29}Si-Ring with crown ether	−	12-CE-4	−	18-CE-6	12-CE-4	−	−	−
^{29}Si-SiMe₃	−12.47	−11.68	−12.44	−11.00	−14.27	−14.22	−	−15.54
Reference	22 [a]	22 [b]	22 [a]	22 [b]	22 [c]	22 [c]	51 [c]	This work [c]

[a] In $CH_2Cl_2\text{-}d_2$. [b] In Benzene-d_6. [c] In THF-d_8.

The ^{13}C-NMR and ^{29}Si-NMR chemical shifts of **3** do not support its aromaticity, the introduction of trimethylsilyl group on the silicon atom might decrease aromaticity of silole anion with the substituent effect of the trimethylsilyl group enhancing the s-character of the lone pair on the silicon atom and decreasing the s-character of the Si-Si bond in **3** [23,48].

3. Experimental

General Procedures

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air sensitive reagents were transferred in a nitrogen-filled glove box. THF and ether were distilled from sodium benzophenone ketyl under nitrogen. Hexane and pentane were stirred over concentrated H_2SO_4 and distilled from CaH_2. NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers. GC-MS and solid sample MS data were obtained on a Hewlett-Packard 5988A

GC-MS system equipped with a methyl silicon capillary column. Elemental analyses were done by Desert Analytics (Tucson, AZ, USA).

[Ph₄C₄Si(SiMe₃)(R)] (R = Me (**4**), Et (**5**), *i*-Bu (**6**)). [Ph₄C₄SiCl₂] (**1**) (0.57 g, 1.25 mmol) was sonicated in THF with an excess of lithium for 5 h. Then the remaining lithium was removed by filtration to give a red-purple solution. The solution was added to methyl iodide in THF with stirring at room temperature for 4 h to give a yellow solution. After removing the solvent under vacuum the remaining yellow solid was extracted with hexane. The concentrated solution was kept in a refrigerator for a couple of days to provide yellow crystals.

[Ph₄C₄Si(SiMe₃)(Me)] (**4**). Yield: 0.38 g (65%); mp. 130–132 °C (lit. [40], mp. 130–132 °C).

[Ph₄C₄Si(SiMe₃)(Et)] (**5**). Yield: 0.54 g (59%); mp. 100–102 °C, ^{1}H-NMR (CDCl$_3$, ref; ext. TMS = 0.00 ppm), 0.05 (s, SiMe$_3$, 9H), 1.0–1.2 (brd m, ethyl, 5H), 6.68–7.15 (m, 20H); ^{13}C-NMR (CDCl$_3$, ref; solvent = 77.00 ppm), −1.40 (SiMe$_3$), 3.06 (CH$_2$), 8.64 (CH$_3$); ^{29}Si-NMR (CDCl$_3$, ref; ext. TMS = 0.00), −2.53 (ring Si), −16.15 (SiMe$_3$); Anal. Calcd. for C$_{33}$H$_{34}$Si$_2$: C, 81.42; H, 7.04, Found: C, 81.59; H, 7.19.

[Ph₄C₄Si(SiMe₃)(i-Bu)] (**6**). Yield: 0.44 g (68%); mp. 154–156 °C, ^{1}H-NMR (CDCl$_3$, ref; ext. TMS = 0.00 ppm), 0.03 (s, SiMe$_3$, 9H), 0.92 (d, CMe$_2$, 6H), 1.16 (d, CH$_2$, 2H), 1.85 (m, CH, 1H), 6.68–7.15 (m, 20H); ^{29}Si-NMR (CDCl$_3$, ref; ext. TMS = 0.00), −6.49 (ring Si), −15.88 (SiMe$_3$); Anal. Calcd. for C$_{35}$H$_{38}$Si$_2$: C, 81.65; H, 7.44, Found: C, 81.76; H, 7.31.

[Ph₄C₄Si(n-Bu)₂] (**7**). [Ph₄C₄SiCl₂] (**1**) (0.57 g, 1.25 mmol) was sonicated with an excess of lithium for 5 h. Then the remaining lithium was removed by filtration to give a red-purple solution of the silole dianion. The solution was added to a THF solution of 1-bromobutane with stirring at room temperature for 10 h to give a yellow solution. After removing the solvent under vacuum the remaining yellow solid was extracted with hexane. The concentrated solution was kept in a refrigerator for a couple of days to provide yellow crystals. Yield: 0.56 g (90%); mp. 85 °C (lit. [78] mp. 81 °C).

[Ph₄C₄Si(t-Bu)₂] (**8**). [Ph₄C₄SiCl₂] (**1**) (0.55 g, 1.21 mmol) was sonicated with an excess of lithium in THF for 5 h. Then the remaining lithium was removed by filtration to give a red-purple solution of **2**. The solution was added to a THF solution of *t*-butyl bromide with stirring at room temperature for 24 h to give a yellow solution. After removing the solvent under vacuum the remaining yellow solid was extracted with ether. The concentrated solution was kept in a refrigerator for a couple of days to provide pale yellow crystals of bissilole 1,1-bi[(*t*-Bu)SiC₄Ph₄] [14]. The filtered solution was concentrated under vacuum, then it was kept in a refrigerator for a couple of days to give yellow crystals of [Ph₄C₄Si(*t*-Bu)₂] (**8**). Yield: 0.33 g (54%); mp. 169-171 °C, ^{1}H-NMR (CDCl$_3$, ref; ext. TMS = 0.00 ppm), 1.16 (s, Me, 18H), 6.68–7.15 (m, 20H), ^{29}Si-NMR (CDCl$_3$, ref; ext. TMS=0.00), 16.49 (ring Si); Anal. Calcd. for C$_{36}$H$_{38}$Si$_1$: C,86.69; H,7.68, Found: C, 86.71; H, 7.75.

1,1-Bi[(t-Bu)SiC₄Ph₄] (**9**). Yield: 0.19 g (18%); mp. 295–307 °C (lit. [16] mp. 296-307 °C), ^{29}Si-NMR (THF-*d*8, ref; ext. TMS = 0.00), 3.62 (ring Si).

1,1-Bis(R)-2,5-dilithio-2,3,4,5-tetraphenyl-1-silacyclopenta-3-enide anion [R = *n*-Bu (**10**), R = *t*-Bu (**11**)]. The respective [Ph_4C_4Si(*n*-Bu)$_2$] (**7**) (0.025 g, 0.05 mmol) and [Ph_4C_4Si(*t*-Bu)$_2$] (**8**) (0.025 g, 0.05 mmol) was transferred into 5 mm NMR tube, they were sonicated with an excess of lithium in THF-d_8 for 2 h to give a red-purple solution. Then ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopic study was performed.

[$Ph_4C_4Si(n$-$Bu)_2]^{-2}$•2[Li]$^+$ (**10**); ^{1}H-NMR (THF-d_8, ref; ext. TMS = 0.00 ppm), 0.83 (t, CH$_3$, 6H), 0.90 (m, CH$_2$, 4H), 1.36 (sept, CH$_2$, 4H), 1.52 (m, CH$_2$, 4H), 6.68–7.15 (m, 20H), ^{29}Si-NMR (THF-d_8, ref; ext. TMS = 0.00), −0.27 (ring Si). *[$Ph_4C_4Si(t$-$Bu)_2]^{-2}$•2[Li]$^+$* (**11**); ^{1}H-NMR (THF-d_8, ref; ext. TMS = 0.00 ppm), 1.21 (brd s, Me, 18H), 6.68-7.15 (m, 20H), ^{29}Si-NMR (THF-d_8, ref; ext. TMS = 0.00), 13.69 (ring Si).

4. Conclusions

Silole dianion [Ph_4C_4Si]$^{-2}$ (**2**) is a versatile intermediate to prepare symmetrically substituted siloles of [$Ph_4C_4SiR_2$] (R = *n*-Bu, *t*-Bu) and unsymmetrically substituted siloles of [$Ph_4C_4Si(SiMe_3)$(R)] (R = Me, Et, *i*-Bu). The formers are synthesized from the reaction of silole dianion **2** with the corresponding alkyl bromides, while the latter are synthesized via [$Ph_4C_4Si(SiMe_3)$]$^-$•[Li]$^+$ (**3**) by hemsilylation of **2** with trimethylsilyl chloride and then by alkylation of **3** with the corresponding alkyl halides. The silole anion **3** and the reduced 3-silolenide 2,5-carbodianions {[$Ph_4C_4Si(n$-$Bu)_2$]$^{-2}$•2[Li]$^+$ (**10**) and [$Ph_4C_4Si(t$-$Bu)_2$]$^{-2}$•2[Li]$^+$ (**11**)} are characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopy.

Acknowledgments

Conflicts of Interest

The authors declare no conflict of interest.

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Sample Availability: Not Available.