**Abstract:** The reductive cleavage of the Si-Si bond in 1,1-bis(1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene) [(C₄Ph₄SiMe)₂] (1) with either Li or Na in THF gives the silole anion [MeSiC₄Ph₄]⁻ (2). The head-to-tail dimerization of the silole anion 2 gives crystals of the disilatricyclic diallylic dianion [(C₄Ph₄SiMe)₂]⁻² (3). The derivatization of 3 (crystals) with bromoethane (gas) under reduced pressure provides [(MeSiC₄Ph₄Et)₂] (4) quantitatively. The reverse addition of 3 in THF to trimethylsilyl chloride, hydrogen chloride, and bromoethane in THF gives 1-methyl-1-trimethylsilyl-1-silole [Me₃SiMeSiC₄Ph₄] (6), 1-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentenyl-1-methyl-1-silole [C₄Ph₄H₂SiMe-MeSiC₄Ph₄] (7), and 1-methyl-2,5-diethyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentenyl-1-methyl-1-silole [C₄Ph₄Et₂SiMe-MeSiC₄Ph₄] (8), respectively. The reaction products unambiguously suggest that the silole anion [MeSiC₄Ph₄]⁻ is generated by coordination of the chloride ion at the silicon atom in 3 or by the nucleophilic substitution of either chloride or bromide ion at one of two silicon atoms in 3. The quenching reaction of 3 dissolved in THF with water gives 1,2,3,4-tetraphenyl-2-butene, the disiloxane of 1-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentenyl [O(MeSiC₄Ph₄)₂] (10) and methyl silicate.

**Keywords:** silole anion; silacyclopentadiene; aromaticity; dimer; tricyclic diallylic dianion
1. Introduction

Since the first silacyclopentadienide anion, 5-methylbenzosilole anion, was prepared in 1958 by Gilman [1], the chemistry of group 14 metalloles has developed enormously [2-7], in particular the chemistry of silole and germole dianion [8]. Among the pioneering work reported are the first synthesis of silole dianion [9] and germole dianion [10], including synthesis and trapping reactions with halides, the NMR-characterization of the aromaticity in the silole/germole dianions [10-12], the X-ray crystallography of the silole/germole dianions [13-22], and their computational theoretical study [23,24]. All of the silole dianion and germole dianions are reported as highly delocalized systems, regardless of their C-substituents [8]. In contrast, there have been few reports of delocalized silole anions since NMR studies of [t-Bu-SiC₄Ph₄] were reported [25]. For example, the NMR data of the transition metal complex (η⁵-C₅Me₅)Ru[η⁵-(Me₃Si)₃SiSiC₄Me₄] [26] and X-ray crystallography of the transition metal complex, (η⁵-C₅Me₅)MCl₂[η⁵-(Me₃Si)₃SiEC₄Me₄] (E=Si, Ge, M = Hf, Zr) [27,28], dimerization of [MeSiC₄Ph₄] to the disilatricyclic diallylic dianion [29], and the theoretical study of the silole anion [C₄H₄SiH] [30-33]. Years ago, even the heavy analogue of CpLi, 1,2-disila-3-germacyclopentadienide anion, has been reported [34]. Meanwhile there has been no additional information concerning the dimerization of the silole anion and the reactivity of this anion and its dimer. Here we report the novel generation of the silole anion [MeSiC₄Ph₄] from the disilatricyclic diallylic dianion [(MeSiC₄Ph₄)₂]²⁻.

2. Results and Discussion

The reductive cleavage in THF of the Si-Si bond in 1,1-bis(1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene) [(MeSiC₄Ph₄)₂] (1) by either lithium or sodium gives silole anion [C₄Ph₄SiMe] (2, Scheme 1). Upon standing at r.t. the dark blue solution of 2 gives black crystals of the respective silole anion dimer [(MeSiC₄Ph₄)₂]²⁻ (3) whose unique disilatricyclic diallylic dianion structure has been determined by x-ray crystallography [29]. The tricyclic structure of 3 is maintained during the derivatization of 3 (crystals) with bromoethane (gas) under reduced pressure, whereupon the derivative [(MeSiC₄Ph₄Et)₂] (4) is obtained quantitatively. In the case of iodomethane (gas) the analogous derivative [(MeSiC₄Ph₄Me)₂] (5) is also obtained quantitatively (Scheme 1).

Scheme 1. Synthesis of 3 and its derivatization with RX (EtBr, MeI).

Surprisingly no product is obtained from the reaction of 3 (crystalline solid) with trimethylchlorosilane (gas) under reduced pressure. This can be attributed to the bulkiness of the trimethylsilyl group. It has been observed that even the smaller dimethylsilyl group exhibits hindered...
rotation about the bond to the ring carbon due to its steric hindrance when the dimethylsilyl group is introduced into the similar allylic anion in 1-methyl-2-dimethylsilyl-2,3,4,5-tetraphenyl-1-silacyclo-2-pentene [MeHSiC₄Ph₄H(SiHMe₂)] [35].

Interestingly, the addition of the trimethylchlorosilane to 3 dissolved in THF provides only 1,1-bis(1-methylsilole) [(MeSiC₄Ph₄)₂] (1) along with hexamethyldisilane (Scheme 2). Moreover the reverse addition of 3b in THF to trimethylchlorosilane in THF for an extended reaction time gives [Me(Me₂Si)SiC₄Ph₄] (6) in 65% yield (Scheme 2). These results indicate that the disilatricyclic diallylic dianion 3b is dissociated into the silole anions 2 in THF solution. A similar dissociation of the gallole dimer [(C₄Me₄Ga-t-Bu)₂] in benzene was previously reported [36].

**Scheme 2.** Reaction of 3 with trimethylchlorosilane.

Furthermore, reverse addition of 3 in THF to an excess of dry hydrogen chloride in THF affords neither a disilatricyclic derivative or the silole [Me(H)SiC₄Ph₄], but instead only the disilane [C₄Ph₄H₂SiMe-MeSiC₄Ph₄] (7). This disilane 7 has a 1-methylsilole moiety [MeSiC₄Ph₄] and a 1-methyl-1-silacyclo-3-pentene moiety [MeSiC₄Ph₄H₂], which is the hydrogenated derivative at the allylic 2 and 5-carboanions in the silole ring (Scheme 3).

**Scheme 3.** Reaction of 3 with hydrogen chloride.

In the case of bromoethane the disilane derivative [C₄Ph₄Et₂SiMe-MeSiC₄Ph₄] (8) was obtained in 65~75 % yield, along with a minor amount of the disilatricyclic derivative [(C₄Ph₄EtSiMe₂)] (4). The disilane 8 has a 1-methylsilole moiety [MeSiC₄Ph₄] and the ethylation derivative at the allylic 2 and 5-carboanions in the silole ring such as 7 (Scheme 4).

**Scheme 4.** Reaction of 3 with bromoethane.
The minor product 4 unambiguously indicates that some of the unique disilatricyclic structure in 3 is sustained during the reaction. However, the major products of the disilanes 7 and 8 clearly suggest that in THF the silole anion 2 and the silyl halide [R₂Ph₄C₄SiMeX] (R=H, X=Cl for 7, R=Et, X=Br for 8) are generated in a ratio of 1:1 from 3, as indicated in Scheme 5:

**Scheme 5. Suggested mechanism for the formation of disilanes (7 and 8).**

The coupling reaction of an allylic anion in one of two 5-membered rings with RX releases above the C₄Si ring the latter’s halide ion, which is easily associated with the vicinal silicon atom of the silicon in 3. This association easily induces ring opening in the highly strained 1,3-disilacyclobutane via a pentacoordinated state since the angles of the C-Si-C bonds in both C₄Si ring and 1,3-silacyclobutane ring are nearly 90 degrees [29]. The nucleophilic substitution at the silicon atom produces a [Si=C] double bond in the other 5-membered ring to generate the novel silole anion [C₄Ph₄SiMe]⁻ (9) via a pentacoordinated anionic intermediate, in which the methyl group and one Si-C bond of the C₄Si ring occupy pseudo-axial positions and two bonds of X-Si-C and the other Si-C bond of the C₄Si ring occupy pseudo-equatorial positions. Simultaneously the pushing of the electron pair in the other Si-C bond of 1,3-disilacyclobutane ring to the Cₐ carbon produces an allylic carbanion, which immediately reacts with RX. The just generated silole anion 9 is beneath the silicon atom of the C₄Si ring, so coordination of the double bond [Si=C] to the silicon atom above of the C₄Si ring would be an alternative mechanism involving a pseudo-pentacoordinated intermediate to stabilize the [Si=C] moiety of the silole anion 9, such as in (η⁵-C₅Me₅)(PR₃)RuH(η²-CH₂=SiPh₂) [37,38] and H₂(PMe₃)₃Ru(η²-CH₂=SiMe₂) [39]. However, the preferred mechanism is a coupling reaction of the silole anion 9 with the halide. Then the nuclopilic substitution at the silicon provides the Si-Si bond of 7 or 8 while the allylic anion is rearranged to form a C=C double bond in the other C₄Si ring to lead the silole moiety [MeSiC₄Ph₄].

Similar pseudo-pentacoordinated silole intermediates lacking highly electronegative atoms on the silicon atom have been proposed, and are produced by the apical attack of methyl lithium, diphenylmethylsilyl lithium [40,41], sodium bis(trimethylsilyl)amide [42], and potassium hydride [35].
on the less hindered SiC₄ ring. Even the neutral pseudo-pentacoordinate silole [Me(Me₂NNp)SiC₄Ph₄] has been reported [44]. In those pentacordinated anionic intermediates it was suggested that the SiC₄ ring occupies one axial and one equatorial position during its pseuderotation and substitution reactions [45].

For some reason the reverse addition of 3 in THF to an excess of trimethylchlorosilane in THF produces chloride ion from the trimethylchlorosilane. Then, the association of the chloride ion to the silicon atom of 3 induces ring opening dissociation in the highly strained 1,3-disilacyclobutane to form [Si=C] bonds in two silole anions 9 via a pentacoordinated state, in which the methyl group and one Si-C bond of the C₄Si ring occupy pseudo-axial positions and two bonds of X-Si-C and the other Si-C bond of the C₄Si ring occupy pseudo-equatorial positions. Then the cation coordination enhances the stability by the delocalization in the silole ring [32]. The silole anion 9 is not consumed instantly by the reaction with trimethylchlorosilane to produce [Me(Me₃Si)SiC₄Ph₄] (6) due to the bulkiness of trimethlysilyl group [35]. Therefore, only from the reverse addition of 3 in THF to an excess of trimethylsilylchloride for the extended reaction time 6 could be obtained (Scheme 6).

**Scheme 6. Suggested mechanism for the formation of 1.**

Meanwhile the weak Si-Si bond of 6 is easily attacked by the other silole anion 9 or one-electron oxidation of 9 with trimethylsilylchloride to produce only 1,1-bis(1-methylsilole) [(MeSiC₄Ph₄)₂] (1) when trimethylsilylchloride is added to 3 in THF since the reaction rate of the silole anion 9 with trimethylchlorosilane is much slower than that of the anion 9 with the Si-Si bond of 6. Alternatively, the silole anion 9 is persistent in the solution for a while due to the lower reactivity of the bulky trimethylsilylchloride. A similar result in the form of a radical reaction of 1,1-bis(1-phenylsilole) [(PhSiC₄Ph₄)₂] has been reported by Jutzi and Karl [46].

The quenching reaction of 3 dissolved in THF with water gives no 1,2,3,4-tetraphenyl-1,3-butadiene, which should be obtained if 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl moiety [MeSiC₄Ph₄] were present in the THF solution [47]. Instead, the disiloxane [O(MeSiC₄Ph₄H₂)] (10), 1,2,3,4-tetraphenyl-2-butene, and methylsilicate are obtained (Scheme 7).
Scheme 7. Hydrolysis reaction of 3.

![Scheme 7](image)

The disiloxane 10 is the condensation product of 1-methyl-1-hydroxy-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene [MeHOSiC₄Ph₄H₂] (11), which is produced from the protonation of the allylic anions and the hydrolysis cleavages of two Si-C bonds in 1,3-disilacyclobutane ring of 3. 1,2,3,4-Tetraphenyl-2-butene and methylsilicate are the hydrolysis products of 10 and/or 11. These reaction products unambiguously indicate that there is no 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl moiety, but rather the disilatricyclic diallylic dianion species in the THF solution of 3 and/or the silole anion 9. However, the self dissociation of 3 in THF to the silole anion 9 is not plausible since there is no derivatization at the silicon atom from the reaction of 3 with hydrogen chloride. Therefore it is suggested that the disilatricyclic diallylic dianion of 3 is sustained in THF solutions of 3 without halide ion to give its hydrolysis products (Scheme 8). An alternative mechanism would involve a bent η²-chloride bridge between two silicon atoms of 1,3-disilacyclobutane in 3 to lead the silole anion 9 [48].

Scheme 8. Suggested mechanism for the hydrolysis reaction of 3.

![Scheme 8](image)

There are five resonance forms for the silole anion [C₄Ph₄SiMe]- (2). From the reaction products the resonance form A (Scheme 9) can be proposed as a prominent contributor to the silole anion. The other four resonance forms are reduced to two sets of the symmetric resonance forms (B and E, C and D), which have the allylic carbanion and silaethene moiety. The coordination of the cation, especially lithium, to the silole anion 2 enhances the delocalization in the silole ring [32], then the negative charge or electron density of the silicon atom moves to the carbons in the ring to induce some silicon-carbon double character. Consequently, the silicon atom becomes more electrophilic or less nucleophilic than that of the silyl anion A. It is reasoned that the the silole anion 2 has considerable Si=C double bond character and it dimerizes by head-to-tail [2 + 2] cycloaddition, which is known as silenes [49]. A t-Bu [25] or Si(SiMe₃)₃ [26] substituent on the silicon hinders the dimerization, in addition the electronic effect of the substituents on the silicon and on the carbons may be critical for the planarity of the silole anion to induce a stable 2-silaallylic anion in it (Scheme 9). It is noteworthy that the novel silole anion 9 coincides with resonance forms B and D or E and C of the silole anion 2 and it is an analogue of 2H or 3H-silole.
3. Experimental

**General**

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Air sensitive reagents were transferred in a nitrogen-filled glove box. THF and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. Pentane was stirred over concentrated H₂SO₄ and distilled from CaH₂. NMR spectra were recorded on Bruker WP SY and Bruker AM 200 FT-NMR spectrometers. MS data were obtained on a mass spectrometer DMX 300. IR spectra were recorded as KBR pellets on a Shimazu IR 440 and melting points were measured on a Wagner & Meunz Co. capillary type apparatus. Elemental analyses were done using a Yanaco elemental analyzer at the Analytic Center of College of Engineering, Seoul National University.

**[(MeSiC₄Ph₄)₂]** (1): Stirring of 1-chloro-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene [MeClSiC₄Ph₄] (4.58 g, 10 mmol) and sodium (0.23 g, 10 mmol) in THF (170 mL) at room temperature for 10 hrs produced a pale green precipitate. After evaporating THF from the mixture, the remaining solid was treated with water and dichloromethane. Removal of dichloromethane under reduced pressure from the organic suspension, gave a pale green solid. The solid was washed with ether for purification. It was identified by the comparison of its analytical data with an authentic sample [50]. Yield: 3.69 g (90%); mp 322-329 °C (lit. [50] mp > 300 °C), ¹³C-NMR (CDCl₃, ref; ext. 77.00 ppm), −6.09 (SiMe), 154.49, 143.25, 139.76, 138.69 (Cᵦ, Cα and Cᵢ of Cᵦ and Cα), 130.18, 129.34, 127.81, 127.28 (C₀ and Cₘ of Cᵦ and Cα), 126.16, 125.52 (Cₚ of Cᵦ and Cα).

**Crystalization of 3**: From the dark purple THF solution, the volume of the solution reduced to a half under reduced pressure. After standing for a week it provided black crystals of 3a and 3b, respectively.

**[(MeSiC₄Ph₄Et)₂]** (4): The silole anion crystals (1.42 g, 1.7 mmol for the lithium salt, 1.48 g, 1.70 mmol for the sodium salt) was exposed to ethyl bromide vapor for 2 hrs under reduced pressure. After evacuating the unreacted bromoethane, the resulting yellow solid was extracted with dichloromethane. Concentration and storage of the solution at −15 °C for a day gave yellow crystals of 4. Yield: 1.38 g (95%) for the lithium salt, 1.38 g (95%) for the sodium salt, mp 296−300 °C; ¹H-NMR (CDCl₃, ref; ext. TMS = 0.00 ppm), 0.65 (s, 6H, SiMe), 0.70 (brd t, 6H, Me, J = 6.96Hz), 2.23 (brd q, 4H, CH₂, J = 6.96Hz), 6.6-7.1 (brd m, 40H, Ph). ¹³C-NMR (CDCl₃, ref; solvent = 77.00 ppm), −1.26 (SiMe₃), 11.71 (Me), 32.48 (CH₂), 46.33 (q-C-Ph), 43.12 (q-C-Et), 148.90, 145.01, 141.65, 141.43, 140.99, 140.62 (ethenyl C and Cᵢ), 132.16, 131.44, 131.09, 130.28, 127.04, 126.93, 126.62, 126.32 (C₀ and Cₘ),
126.09, 125.86, 125.28, 123.06 (C_\beta); IR (cm\(^{-1}\)), \(\delta_{\text{Si-Me}} = 1255\); MS (M\(^+\), relative abundance), 856 (M\(^+\), 65), 797 (M\(^+\)-59, 10), 428 (M\(^+\)/2, 95), 135 (100); Anal. Calcd. for C\(_{62}\)H\(_{56}\)Si\(_2\): C, 86.88; H, 6.59, Found: C, 86.86; H, 6.58.

\([\text{MeSiC}_4\text{Ph}_4\text{Me}]_2\) (5): Silole anion crystals (1.42 g, 1.7 mmol for the lithium salt, 1.48 g, 1.70 mmol for the sodium salt) was exposed to methyl iodide vapor for 2 hrs under reduced pressure. After evacuating the unreacted methyl iodide, the residual yellow solid was extracted with ether. Concentration and storage at \(-15^\circ\text{C}\) for 1 day gave yellow crystals of 4. Yield: 0.85 g (60%) for 3a, 1.22 g (87%) for 3b; mp 334–338 °C (lit. [29] 336–339 °C). The NMR data of 5 agreed with those reported earlier [30].

\([\text{Me}_2\text{SiC}_4\text{Ph}_4\text{Me}]\) (6): After all volatile reagents were removed under reduced pressure, the residue was extracted with pentane. Several recrystallizations from pentane gave pure green crystals of 6 [51]. Yield: 1.15 g (65%) for the lithium salt and 1.13 g (64%) for the sodium salt, mp 130–132 °C; \(^1\)H-NMR (CDCl\(_3\), ref: solvent = 7.27 ppm), 0.03 (s, 9H, SiMe\(_3\)), 0.58 (s, 3H, SiMe), 6.80-7.15 (brd m, 20H, Ph); \(^{13}\)C-NMR (CDCl\(_3\), ref: solvent = 77.00 ppm), –7.43 (SiMe\(_2\)), –1.88 (SiMe), 153.84 (C\(_\beta\)), 143.62(C\(_\alpha\)), 140.21 (Ci of C\(_\beta\)), 139.26 (Ci of C\(_\alpha\)), 130.12, 127.27, 127.39, 127.82 (C\(_o\) and C\(_m\)), 126.05, 125.36 (C\(_p\)); \(^{29}\)Si-NMR (CDCl\(_3\), ref: ext. TMS=0.00), –8.13 (ring Si), –15.50 (SiMe\(_3\)); MS (M\(^+\), relative abundance), 474 (M\(^+\)+2, 21), 473 (M\(^+\)+1.45), 472 (M\(^+\), 100), 457 (M\(^+\)-15, 42), 400 (M\(^+\)-73, 5), 379 (48), 279(25), 221 (47), 135 (21), 105 (61), 73 (27); Anal Calcd. for C\(_{32}\)H\(_{32}\)Si\(_2\): C, 81.32 ; H, 6.83, Found: C 81.52; H, 6.84.

\([\text{C}_4\text{Ph}_4\text{H}_2\text{SiMe-MeSiC}_4\text{Ph}_4]\) (7): Addition with stirring at room temperature of the purple solution of 3 to THF saturated with dry HCl gave a yellow solution. After removing the THF, the residue is extracted with pentane. Pentane was replaced with diethyl ether, and crystallization of the solution at \(-10^\circ\text{C}\) for 1 day gave green crystals. Yield: 0.88g (65%) for the lithium salt, 0.85g (63%) for the sodium salt; mp 215–218 °C; \(^1\)H-NMR (CDCl\(_3\), ref: ext. TMS = 0.00 ppm), –0.07 (s, 3H, SiMe of butene), 0.58 (s, 3H, SiMe of butadiene), 3.53(s, 2H, CH), 6.5–7.1 (brd m, 40H, Ph); \(^{13}\)C-NMR (CDCl\(_3\), ref: ext. 77.00 ppm), –7.69 (SiMe of butene), –2.71 (SiMe of butadiene), 48.41 (CH), 138.80, 140.89, 141.86, 143.01, 143.45, 155.22 (ethylene, C\(_i\)), 129.96, 129.27, 129.12, 129.00, 128.09, 127.94, 127.52, 127.10 (C\(_o\) and C\(_m\)), 126.25, 125.98, 125.44, 124.69 (C\(_p\)); Anal Calcd for C\(_{58}\)H\(_{48}\)Si\(_2\): C,86.96; H,6.04, Found: C, 86.60; H, 6.02.

\([\text{C}_4\text{Ph}_4\text{Et}_2\text{SiMe-MeSiC}_4\text{Ph}_4]\) (8): Yield: 0.87 g (60%) for the lithium salt and 1.02 g (70%) for the sodium salt; mp 288–290 °C; \(^1\)H-NMR (CDCl\(_3\), ref: solvent = 7.27 ppm), 0.11 (s, 3H, SiMe of butene), 0.16 (s, 6H, Me, J = 6.96Hz), 0.70 (s, 3H, SiMe of butadiene), 1.86 (brd q, 4H, CH\(_2\)), 6.6–7.2 (brd m, 40H, Ph); \(^{13}\)C-NMR (CDCl\(_3\), ref: solvent = 77.00 ppm), –4.66 (SiMe of butene), 10.56 (Me), 27.75 (CH), 49.69 (q-C), 154.85, 147.59, 144.32, 142.52, 139.52, 139.32, 139.15 (three sp\(^2\) C and four C\(_i\)), 130.78, 130.61, 130.31, 129.90, 127.42, 127.35, 126.59, 126.12 (four C\(_o\) and four C\(_m\)), 125.61, 125.28, 125.21 (C\(_p\)); IR (cm\(^{-1}\)), \(\delta_{\text{Si-Me}} = 1245\); MS (M\(^+\), relative abundance), 856 (M\(^+\), 38), 457 (M\(^+\)-Me-silole, 100), 442 (65), 427 (35), 197 (70); Anal Calcd for C\(_{62}\)H\(_{56}\)Si\(_2\): C, 86.88; H, 6.59, Found: C, 87.20; H, 6.60.
(C₄Ph₄H₂SiMe)₂O (10): Aqueous HCl (0.10N) was added to a THF solution of 3 with stirring at room temperature until the pH of the mixture reached neutrality. Filtration of the hydrolyzed mixture gave a white solid, which was insoluble in organic solvents and water, did not melt when heated to over 300 °C, and showed a broad band at 1000–1100 cm⁻¹ in the IR spectrum. After THF was removed from the filtrate, the residue was extracted with diethyl ether. The concentrated ether solution was kept at −20 °C for 1 day and pale green crystals of 10 were obtained. The mother solution was concentrated and after standing at −20 °C for 1 day it yielded colorless crystals of 1,2,3,4-tetraphenyl-2-butene (yield: 0.72 g, 40%), whose spectral data agreed with those reported earlier [9]. Yield(10): 1.35 g (33%) for 3a and 1.23 g (30%) for 3b; mp 292 °C; ¹H-NMR (CDCl₃ ref.: ext. TMS = 0.00 ppm), −0.45 (s, 6H, SiMe), 3.15 (s, 4H, CH), 6.8–7.3 (brd m, 40H, Ph); MS (M⁺, relative abundance), 818 (M⁺, 100), 650 (M⁺, 18), 537 (60), 460 (50), 445 (25), 383 (40), 382 (30); Anal Calcd for C₅₈H₅₀Si₂O: C, 85.05; H, 6.16, Found: C, 84.82; H, 6.12.

4. Conclusions

The pathway for generation of the silole anion 9 is dependent on the reactivity of the alkyl halide used. Two silole anions 9 are generated from the disilatricyclic diallylic dianion 3 in THF by the coordination of the chloride ion to the silicon atom in it; the reaction of 9 with trimethylchlorosilane provides [(MeSiC₄Ph₂-Me₂)] (5) or [Me(Me₃Si)SiC₄Ph₄] (6) according to the method of the addition. From the reverse addition of 3 in THF to bromoethane or hydrogen chloride in THF the silole anion 9 and the silyl halide [R₂Ph₄C₄SiMeX] (R=H, X=Cl for 7, R=Et, X=Br for 8) are generated in a ratio of 1:1, then the coupling reaction of the two produces the corresponding disilane [C₄Ph₄R₂SiMe-MeSiC₄Ph₄] (R=H, X=Cl for 7, R=Et, X=Br for 8).

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Conflict of Interest

The author declares no conflict of interest.

References and Notes

1. Gilman, H.; Gorsich, R.D. Cyclic Organosilicon Compounds. I. Synthesis of Compounds Containing the Dibenzosilole Nucleus. J. Am. Chem. Soc. 1958, 80, 1883-1886.
2. Corey, J.Y. Organometallic Benziheterocycles. Adv. Organomet. Chem. 1975, 13, 139-271.
3. Barton, T.J. Carbacyclic Silanes. In Comprehensive Organometallic Chemistry; Wilkinson, G.; Stone, F.G.A.; Abel, E.W., Eds.; Pergamon Press: Oxford, UK, 1982; Volume 2, pp. 205, 250-261.
4. Dubac, J.; Laporterie, A.; Manuel, G. Group 14 metalloles. 1. Synthesis, organic chemistry, and physicochemical data. Chem. Rev. 1990, 90, 215-282.
5. Colomer, E.; Corriu, R.J.P.; Lheureux, M. Group 14 metalloles. 2. Ionic species and coordination compounds. Chem. Rev. 1990, 90, 265-282.

6. Dubac, J.; Guerin, C.; Meunier, P. In The Chemistry of Organosilicon Compounds; Patai, S., Rappoport, Z., Eds.; Willey-Interscience: Chichester, UK, 1998; Volume 2, p. 1961.

7. Hissler, M.; Dyer, P.W.; Reau, R. Linear organic π-conjugated systems featuring the heavy Group 14 and 15 elements. Coord. Chem. Rev. 2003, 244, 1-44.

8. Saito, M.; Yoshioka, M. The anions and dianions of group 14 metalloles. Coord. Chem. Rev. 2005, 249, 765-780.

9. Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E. Synthesis and reactivity of 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopentadiene. J. Organomet. Chem. 1990, 391, 27-36.

10. Hong, J.-H.; Boudjouk, P. Synthesis and characterization of a delocalized germanium-containing dianion: dilithio-2,3,4,5-tetraphenyl-germole. Bull. Soc. Chim. Fr. 1995, 132, 495-498.

11. Hong, J.-H.; Boudjouk, P.; Castellino S. 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. Organometallics 1994, 13, 3387-3389.

12. Hong, J.-H. Synthesis and NMR-Study of the 2,3,4,5-Tetraethylsilole Dianion [SiC₄Et₄]²⁻•2[Li⁺]. Molecules 2011, 16, 8033-8040.

13. West, R.; Sohn, H.; Bankwitz, U. Calabrese, J.; Apeloig, T.; Mueller, T. Dilithium Derivative of Tetraphenylsilole: An η¹⁻η⁵ Dilithium. J. Am. Chem. Soc. 1995, 117, 11608-11609.

14. Freeman, W.P.; Tilley, T.D.; Yap, G.P.A.; Rheingold, A.L. Siloyl Anions and Silole Dianions: Structure of [K([18]crown-6)]₂[C₄Me₄Si²⁻]. Angew. Chem. Int. Ed. 1996, 35, 882-884.

15. West, R.; Sohn, H.; Powell, D.R.; Mueller, T.; Apeloig, Y. Dianion of Tetraphenylgermole is Aromatic. Angew. Chem., Int. Ed. 1996, 35, 1002-1004.

16. Freeman, W.P.; Tilley, T.D.; Liable-Sands, L.M.; Rheingold, A.L. Synthesis and Study of Cyclic π-Systems Containing Silicon and Germanium. The Question of Aromaticity in Cyclopentadienyl Analogues. J. Am. Chem. Soc. 1996, 118, 10457-10468.

17. Choi, S.-B.; Boudjouk, P.; Hong, J.-H. Unique Bis-η⁵/η¹ Bonding in a Dianionic Germole. Synthesis and Structural Characterization of the Dilithium Salt of the 2,3,4,5-Tetraethyl Germole Dianion. Organometallics 1999, 18, 2919-2921.

18. Choi, S.-B.; Boudjouk, P. Synthesis and characterization of dibenzannulated silole dianions. The 1,1-dilithiosilafluorene and 1,1'-dilithiobis(silafluorene) dianions. Tetrahedron Lett. 2000, 41, 6685-6688.

19. Liu, Y.L.; Stringfellow, C.; Ballweg, D.; Guzei, I.A.; West, R. Structural and chemistry of 1-silafluorenyl dianion. Its derivatives, and an organosilicon diradical dianion. J. Am. Chem. Soc. 2002, 124, 49-57.

20. Choi, S.-B.; Boudjouk, P.; Wei, P. Aromatic benzannulated silole dianions. The dilithio and disodio salts of a silaindenyl dianion. J. Am. Chem. Soc. 1998, 120, 5814-5815.

21. Choi, S.-B.; Boudjouk, P.; Qin, K. Aromatic Benzannulated Germole Dianions. The Dilithio and Disodio Salts of a Germaindenyl Dianion. Organometallics 2000, 19, 1806-1809.

22. Liu, Y.; Ballweg, D.; Müller, T.; Guzei, I.A.; Clark, R.W.; West, R. Chemistry of the Aromatic 9-Germanfluorenyl Dianion and Some Related Silicon and Carbon Species. J. Am. Chem. Soc. 2002, 124, 12174-12181.
Molecules 2011, 16

23. Goldfuss, B.; Schleyer, P.v.R.; Hampel, F. Aromaticity in Group 14 Metalloles: Structural, Energetic, and Magnetic Criteria. *Organometallics* 1996, 15, 1755-1757.

24. Schleyer, P.v.R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N.J.R.v.E. Nucleus-Independent Chemical shifts: A simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* 1996, 118, 6317-6318.

25. Hong, J.-H.; Boudjouk, P. A Stable Aromatic Species Containing Silicon. Synthesis and Characterization of the 1-tert-Butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide Anion. *J. Am. Chem. Soc.* 1993, 115, 5883-5884.

26. Freeeman, W.P.; Tilley, T.D.; Rheingold, A.L. Stable Silacyclopentadienyl Complexes of Ruthenium: (η5-C5Me5)Ru[η5-Me4C4SiSi(SiMe3)3] and X-ray Structure of Its Protonated Form. *J. Am. Chem. Soc.* 1994, 116, 8428-8429.

27. Dysard, J.M.; Tilley, T.D. η5-Silolyl and η5-Germolyl Complexes of d0 Hafnium. Structural Characterization of an η5-Silolyl Complex. *J. Am. Chem. Soc.* 1998, 120, 8245-8246.

28. Hong, J.-H.; Boudjouk, P. Synthesis and Characterization of a Novel Pentavalent Silane: 1-Methyl-1,1-dihydro-2,3,4,5-tetraphenyl-1-silacyclopentadiene Silicate, [Ph4C4SiMeH2]•[K+]. *Organometallics* 1995, 14, 574-576.

29. Gordon, M.S.; Boudjouk, P.; Anwari, F. Are the silacyclopentadienyl anion and the silacyclocoprophenyl cation aromatic? *J. Am. Chem. Soc.* 1983, 105, 4972-4976.

30. Damewood, J.R. Pyramidal inversion and electron delocalization in the silacyclopentadienyl anion. *J. Org. Chem.* 1986, 51, 5028-5029.

31. Goldfuss, B.; Schleyer, P.v.R. The Siloyl Anion C4H4SiH- is Aromatic and the Lithium Silolide C4H4SiLi Even More So. *Organometallics* 1995, 14, 1553-1555.

32. Lee, V.Y.; Kato, R.; Ichinohe, M.; Sekiguchi, A. The Heavy Analogue of CpLi: Lithium 1,2-Disila-3-germacyclopentadienide, a 6π-Electron Aromatic System. *J. Am. Chem. Soc.* 2005, 127, 13142-13143.

33. Campion, B.K.; Heyn, R.H.; Tilley, T.D.; Rheingold, A.L. Synthesis and study of the ruthenium-silene complexes (η2-C5Me5)[PR3]RuH(η2-CH2SiPh2). *J. Am. Chem. Soc.* 1999, 121, 8391-8392.
40. Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. Chemistry of siloles. The reactions of siloles with organolithium reagents. *J. Organomet. Chem.* **1983**, *250*, 109-119.

41. Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. Unexpected behavior of siloles toward organolithium regagents. *J. Organomet. Chem.* **1981**, *218*, C21-C24.

42. Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. Chemistry of siloles. 1-Methyl dibenzosilacyclopentadienide anion. *Organometallics* **1983**, *2*, 351-352.

43. Pan, Y.; Hong, J.-H.; Choi, S.-B.; Boudjouk, P. Surprising Reaction of Non-Nucleophilic Bases with 1-Hydrosiloles: Addition and Not Deprotonation. *Organometallics* **1997**, *16*, 1445-1451.

44. Tamao, K.; Asahara, M.; Kawachi, A. The differing modes of reaction of 1-(8-dimethylamino-1-naphthyl)-1-hydrodisilane and 1-(1-naphthyl)-1-hydrodisilane in nickel-catalyzed reactions with acetylene: formation of a pseudo-pentacoordinate silole via Si-Si bond cleavage vs. hydrosilation without Si-Si bond cleavage. *J. Organomet. Chem.* **1996**, *521*, 325-334.

45. Choi, S.-B.; Boudjouk, P.; Pan, Y. Mechanistic Studies of the Reaction of Hydrosiloles with Nucleophiles. Crystal Structures of the Enantiomers of 1-Methyl-2-(dimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene and 1-(Bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene. *Organometallics* **1999**, *18*, 3813-3817.

46. Jutzi, P.; Karl, A. Synthesis and reactions of some 1-R-1-R’-2,3,4,5-tetraphenyl-1-silacyclopentadienes. *J. Organometa. Chem.* **1981**, *214*, 289-302.

47. Balasubramanian, R.; Gerge, M.V. Alkali metal, alkaline and acidic decomposition of silacyclopentadienes. *J. Organomet. Chem.* **1975**, *85*, 311-316.

48. Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. Tautomeric Equilibrium between Penta- and Hexacoordinate Silicon Chelates. A Chloride Bridge between Two Pentacoordinate Silicons. *J. Am. Chem. Soc.* **2001**, *123*, 4709-4716.

49. Brook, A.G.; Brook, M.A. The Chemistry of Silenes. *Adv. Organomet. Chem.* **1996**, *39*, 71-158.

50. Sekiguchi, A; Zigler, S.S.; West, R. A synthon for the silicon-silicon triple bond. *J. Am. Chem. Soc.* **1986**, *108*, 4241-4242.

51. [Me(Me₃Si)SiC₄Ph₄] (6) has been synthesized, however, the physical property and the spectral data were not provided: Wakahara, T.; Ando, W. Reaction of hydrosilanes with lithium. Formation of silole anions from 1-methylsilole via carbodianion. *Chem. Letter.* **1997**, *11*, 1179-1180.

*Sample Availability:* Samples of the derivatives of the silole anion [MeSiC₄Ph₄]⁻ are available from the author.

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