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Surprising Reaction of Non-Nucleophilic Bases with 1-Hydrosiloles: Addition and Not Deprotonation[1]

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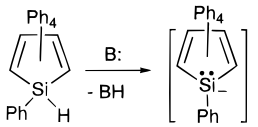
The reaction of 1-R-(Ph$_4$-silole), (R = Ph (**1**), Me (**2**), (Ph$_4$-silole = 2,3,4,5-tetraphenyl-1-silacyclopentadiene), with sodium bis(trimethylsilyl)amide in THF yields only nucleophilic substitution products, 1-R-1-(bis(trimethylsilyl)amino)-(Ph$_4$-silole). 1-H-(Ph$_4$-silole) (**3**) reacts with sodium bis(trimethylsilyl)amide in THF to give the observed anionic intermediate, 1-bis(trimethylsilyl)amino-2-sodio-2,3,4,5-tetraphenyl-1-silacyclopent-3-ene (**14**), the result of hydride migration of the initially formed pentacoordinate intermediate. Quenching of **14** with methyl iodide gives two geometrical isomers of 1-(bis(trimethylsilyl)amino)-5-methyl-2,3,4,5-tetraphenyl-1-silacyclopent-3-ene (**9a**,**b**) in a ratio of 1:1. When a good leaving group (R = Cl, **4**) is on the silicon, displacement of the chloride by the bis(trimethylsilyl)amide group takes place, affording 1-(bis(trimethylsilyl)amino)-(Ph$_4$-silole) (**10**). The substitution products can be explained by a pathway involving pentacoordinate anionic intermediates that undergo psuedorotation. No evidence for deprotonation of 1-H-(Ph$_4$-silole) derivatives was obtained.

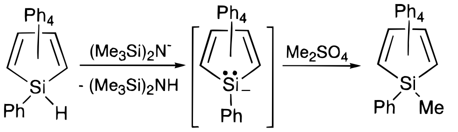
Introduction

Deprotonation of siloles, driven by the stable configuration of 6 π electrons in the product silole anions, should be a convenient route to aromatic silicon-containing species (eq 1).[2,3] The merit of this approach seems reinforced by our finding that the *tert*-butyl-1-(Ph$_4$-silole) anion (Ph$_4$-silole = 2,3,4,5-tetraphenyl-1-silacyclopentadiene), prepared by reductive cleavage of a disilane, is stable in solution and has NMR spectral characteristics consistent with significant aromaticity.[4] Recent calculations indicate that silole anions are aromatic and that lithium coordination increases delocalization of the π electrons.[5]



(1)

Rühlmann observed that 1-phenyl-(Ph$_4$-silole), when treated with phenyllithium or sodium bis(trimethylsilyl)amide, produced a deep purple solution but did not isolate or assign a structure to the species generated.[6] Later he reported that sodium bis(trimethylsilyl)amide deprotonates 1-phenyl-(Ph$_4$-silole) to give 1-methyl-1-phenyl-(Ph$_4$-silole) when treated with methyl sulfate (eq 2).[7]



(2)

Curtis examined the reaction of 1-phenyl-(Ph$_4$-silole) with *n*-butyllithium obtaining spectral data consistent with substitution of hydride by the butyl group and subsequent LiH addition to the silole ring to give a carbanion that could account for the highly colored solution.[8] However, no products were isolated from this reaction. Jutzi and Karl also studied the reaction of *n*-butyllithium with 1-phenyl-(Ph$_4$-silole) and related silole derivatives finding that butyl substitution and subsequent LiH addition were indeed the important steps in this reaction as evidenced by the isolation of silacyclopent-3-ene products (eq 3).[9]

A similar substitution reaction was described by Dubac *et al.* when they prepared 1-R-1,3,4-trimethylsilole by Si−H substitution using RLi (R = *n*-Bu, Ph, allyl, Et$_2$N) from 1,3,4-trimethylsilole (eq 4).[10] They had

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[1] Preliminary results have been presented: (a) Pan, Y.; Hong, J.-H.; Boudjouk, P. The 28th Great Lakes Regional Meeting of the American Chemical Society, La Crosse, WI, June 5−8, 1995; Abstract 216. (b) Pan, Y.; Hong, J.-H.; Boudjouk, P. 29th Organosilicon Symposium, Chicago, IL, March 22−23, 1996; Abstract P15.

[2] (a) Gilman, M.; Steudel, W. *Chem. Ind.* **1959**, 1094. (b) Corriu, R. J. P.; Guérin, C. *J. Chem. Soc. Chem. Commun.* **1980**, 168. (c) Corriu, R. J. P.; Guérin, C.; Kolani, B. *Bull. Soc. Chim. Fr.* **1985**, 973.

[3] (a) Lambert, J. B.; Schulz, W. J., Jr. in *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 16, p 1007. (b) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (c) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265. (d) Grüntzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 295.

[4] (a) Hong J. H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883. b) A recent NMR study demonstrates that the lithio-1-(trimethylsilyl)-2,3,4,5-tetraethylsilole anion is pyramidal with a barrier to inversion of 8.4 kcal/mol: Tilley, T. D. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

[5] (a) Goldfuss, B; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1555. (b) Earlier low-level theoretical calculations on this system give different results. One predicts that silole anions are approximately 25% as aromatic as the all-carbon analogs: Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972. Another indicates that silole anions have essentially the same pyramidality as H_3Si^-: Dame-wood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5028. c) Calculations showing delocalization in isomeric dilithiosilole dianions have recently been reported: West, R.; Sohn, H., Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608.

[6] Rühlmann, K. *Z. Chem.* **1965**, *5*, 354.

[7] Hagen, V.; Rühlmann, K. *Z. Chem.* **1967**, *7*, 462.

[8] Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011.

[9] Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, *214*, 289.

[10] Béteille, J.-P.; Laporterie, A.; Dubac, J. *Organometallics* **1989**, *8*, 1799.

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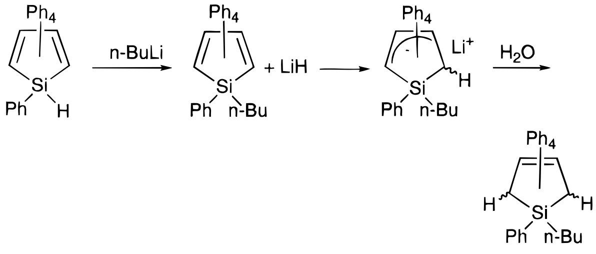
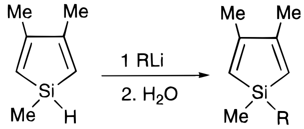


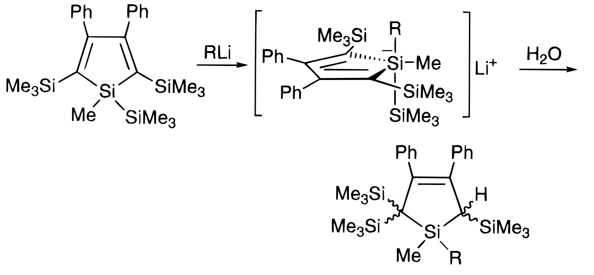
(3)

also reported that even methyl groups can be displaced from the silicon atom using *n*-butyllithium, phenyllithium, and *tert*-butyllithium.[11]



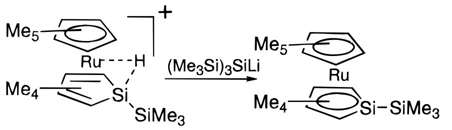
(4)

Ishikawa *et al.* suggested a pentavalent anion intermediate when a trimethylsilyl-substituted silole is treated with methyllithium or (diphenylmethylsilyl)lithium (eq 5). However, when a trimethylsilyl-substituted silafluorene is reacted with alkyllithium or phenyllithium, the trimethylsilyl group is substituted by the alkyl or phenyl group, presumably through a similar pentavalent anion intermediate.[12]



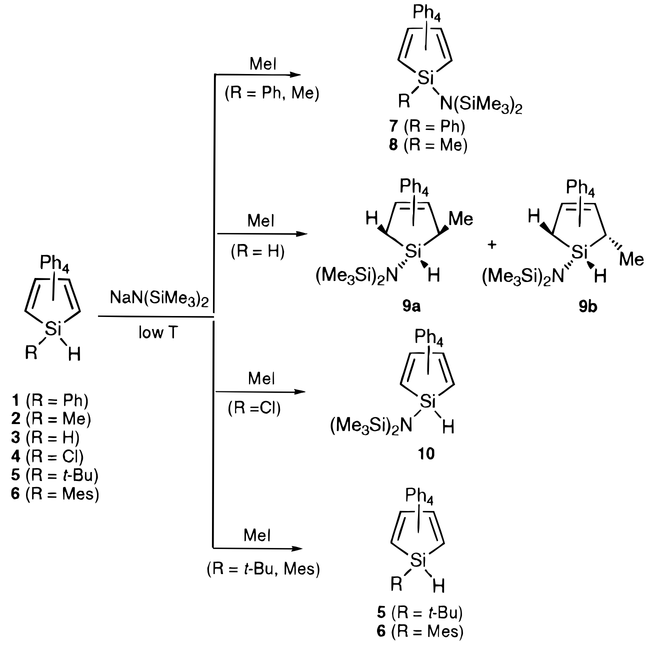
(5)

Complexed siloles appear to open a mechanistic alternative. Tilley *et al.*[13] recently provided persuasive evidence that (tris(trimethylsilyl)silyl)lithium removed the agostic hydrogen in a novel ruthenium complex (eq 6).

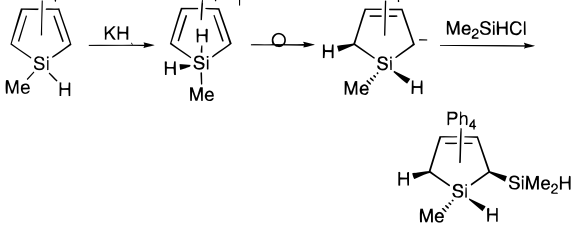


(6)

Scheme 1. Reactions of 1-Hydrotetraphenylsiloles with Sodium Bis(trimethsilylamide) and Methyl Iodide



Recently we described the reaction of potassium hydride with 1-methyl-(Ph$_4$-silole), demonstrating that the primary product is the result of the addition of hydride ion to the silicon center to form a pentacoordinate silicon anion in which the axial and equatorial hydrogens are distinguishable.[14] It was also shown that the resulting carbanion reacts readily with electrophiles to give only one isomer of silacyclopent-3-ene (eq 7).



(7)

In this paper we report the results of our continuing efforts in this area. Herein we describe our investigations of the reaction of non-nucleophilic bases such as sodium bis(trimethylsilyl)amide and potassium hydride with several 1-R-(Ph$_4$-silole) derivatives.

Results

Stirring of 1-phenyl-(Ph$_4$-silole) (**1**) with sodium bis(trimethylsilyl)amide in THF at −25 °C for 4 h and then at room temperature for 2 h produced a deep violet solution. The addition of this solution to methyl iodide resulted in a color change (to yellow) and the evolution of methane. Workup led to the isolation of 1-(bis(trimethylsilyl)amino)-1-phenyl-(Ph$_4$-silole) (**7**) in 58% yield. A similar result was obtained when 1-methyl-(Ph$_4$-silole) (**2**) was treated with sodium bis(trimethylsilyl)amide in the same fashion giving 1-(bis(trimethylsilyl)amino)-1-methyl-(Ph$_4$-silole) (**8**) in 61% yield (Scheme 1).

However, when the 1,1-dihydro derivative, **3**, was treated with sodium bis(trimethylsilyl)amide in the same way, we found that neither simple displacement of the H−Si in **3** by the bis(trimethylsilyl)amide nor a product arising from deprotonation was detected. Instead, a mixture of isomeric silacyclopent-3-enes (**9a**,**b**) resulting from hydride migration was obtained in a ratio of 1:1.

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[11] Dubac, J.; Iloughmane, H.; Laporterie, A.; Roques, C. *Tetrahedron Lett.* **1985**, *26*, 1315.

[12] (a) Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1983**, *250*, 109. (b) Ishikawa, M.; Tabohashi, T.; Ohashi, H.; Kumada, M.; Iyoda, J. *Organometallics* **1983**, *2*, 351. (c) Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *218*, C21.

[13] Freeman, W. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 8428.

[14] (a) Hong, J.-H.; Boudjouk, P. *Organometallics* **1995**, *14*, 574. Other dihydrosiliconates have been investigated: (b) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *368*, C25. (c) Corriu, R. J. P.; Guérin, C.; Henner, B.; Wang, Q. *Organometallics* **1991**, *10*, 3574. (d) Corriu, R.; Guérin, C.; Henner, B.; Wang, Q. *Inorg. Chem. Acta* **1992**, *198*−200, 705.

Table 1. Crystal Data, Data Collection, and Refinement of 6 and 7

	compd	
	6	**7**
molecular formula	$C_{37}H_{32}Si$	$2 \times C_{40}H_{43}NiSi_3 + CH_3OH + Et_2O$
fw	504.7	1350.2
color, habit	yellow rectangle	yellow rectangle
cryst size, mm	0.6 × 0.2 × 0.2	1.2 × 0.8 × 0.6
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	12.875(3)	12.496(2)
b, Å	16.577(2)	15.048(2)
c, Å	15.015(2)	22.683(3)
α, deg		107.900
β, deg	114.110	97.940
γ, deg		92.100
V, $Å^3$	2924.9(8)	4006.0(12)
Z	4	2
d(calcd), g/cm^3	1.146	1.11.9
abs coeff, mm^{-1}	0.103	0.150
F(000)	1072	1448
T, K	298	298
2θ range, deg	3.5−45.0	3.5−45.0
scan type	$2\theta-\theta$	$2\theta-\theta$
scan speed, deg/min	variable; 8.00−60.00 in ω	variable; 8.00−60.00 in ω
scan range (ω), deg	0.39	0.52
index ranges	$-13 \le h \le 13$, $-2 \le k \le 17$, $-16 \le l \le 15$	$-1 \le h \le 13$, $-15 \le k \le 15$, $-24 \le l \le 24$
reflcns collcd	4794	12 007
indepdt reflcns	3823 (R_{int} = 6.97%)	10 298 (R_{int} = 3.43%)
obsd reflcns	1937 ($F > 4.0\sigma(F)$	7879 ($F > 4.0\sigma(F)$)
R, R_w, %	5.64, 5.54	5.06, 5.06
goodness of fit	1.76	1.53

When a good leaving group, such as chloride in **4**, is on silicon, displacement of the chloride by bis(trimethylsilyl)amide prevails, the Si−H bond remains intact, and **10** is isolated in 54% yield. The Si−H bond is also left intact when siloles with bulky groups on the silicon such as1-*tert*-butyl-(Ph_4-silole) (**5**) or 1-mesityl-(Ph_4-silole) (**6**) are treated with bis(trimethylsilyl)amide and then methyl iodide.

The new compounds **7**, **8**, **9a**,**b**, and **10** were characterized by spectroscopic methods and elemental analyses. The structures of **9a**,**b** are tentatively assigned on the basis of IR, ^1H, ^{13}C, and ^{29}Si NMR, and MS spectra. **9a** shows a Si−H absorption at 2150 cm^{-1} in the IR. Two singlets at −0.18 (18H), 1.38 (3H) and two doublets at 4.13 (1H, d, $^3J_{H-H}$ = 4.6 Hz), 4.88 (1H, d, $^3J_{H-H}$ = 4.6 Hz) were observed in the ^1H NMR. Thus, the protons of CH_3− and $(Me_3Si)_2N$− are not coupled to other protons and the two coupled hydrogens must be located at silicon and carbon atoms adjacent to each other. The *cis*-orientation of the two hydrogens is confirmed by the coupling constant, $^3J_{H-H}$ = 4.6 Hz.[15] $^{13}C\{^1H\}$ NMR displays corresponding 4 sp^3 hybrid carbons and 18 sp^2 hybrid carbons. $^{29}Si\{^1H\}$ NMR gives two peaks at −2.49 (s) and 5.81 ppm (s). The mass spectrum (EI, 70 eV) shows a molecular ion at 561 amu and a fragment (546 amu, 10%) corresponding to the loss of a methyl group from the molecular ion. Isomer **9b** displays a similar pattern. Detailed spectral data are given in the Experimental Section.

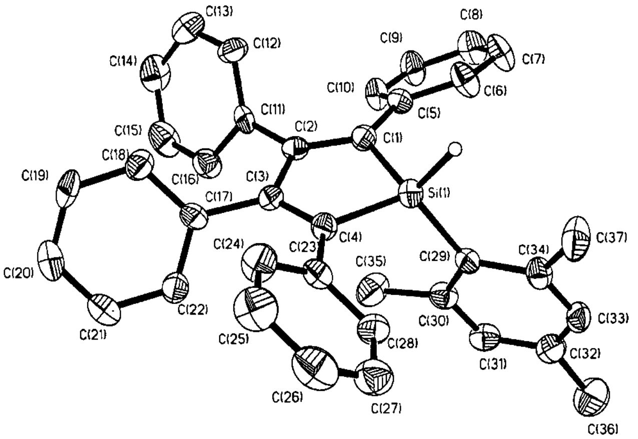

Figure 1. ORTEP view of the molecular structure of compound **6**.

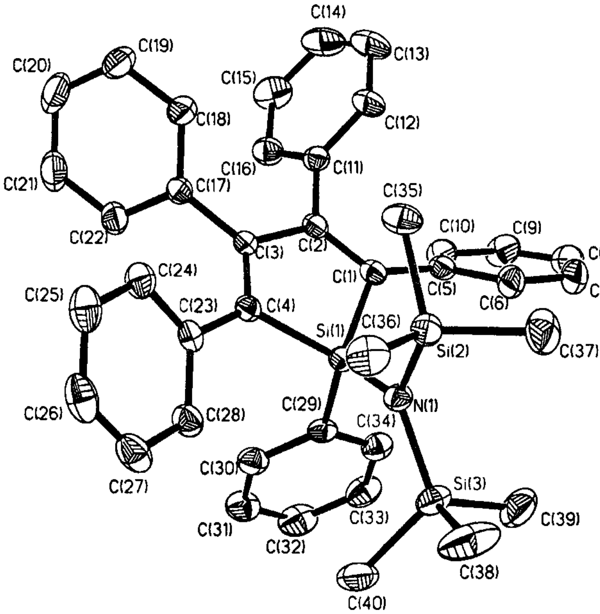

Figure 2. ORTEP view of the molecular structure of compound **7**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6

Si(1)−C(1)	1.872(7)	Si(1)−C(4)	1.869(6)
Si(1)−C(29)	1.891(8)	Si(1)−H(1)	1.474
C(1)−C(2)	1.363(8)	C(2)−C(3)	1.507(9)
C(3)−C(4)	1.364(9)		
C(1)−Si(1)−C(4)	92.6(3)	C(4)−Si(1)−C(29)	117.5(3)
C(29)−Si(1)−H(1)	109.1(4)	C(1)−Si(1)−H(1)	113.8(4)
C(4)−Si(1)−H(1)	111.1(4)	C(1)−Si(1)−C(29)	112.1(3)
Si(1)−C(1)−C(2)	107.4(4)	C(1)−C(2)−C(3)	116.4(5)
C(2)−C(3)−C(4)	115.7(5)	C(3)−C(4)−Si(1)	107.8(4)

The structures of **6** and **7** were confirmed by X-ray crystal structure determination. Crystallographic data are listed in Table 1. The structure of **6** is shown in Figure 1, and selected bond lengths and bond angles are summarized in Table 2. Two molecules of **7** are in the independent unit which differ only slightly in bond distances and bond angles. A representative molecule is given in Figure 2 for which selected bond lengths and bond angles are summarized in Table 3.

The coordination about the ring silicon in **7** is a slightly distorted tetrahedron with a Si(1)−N(1) distance of 1.725 (1.733) Å, which is shorter than Si(2)−N(1) [1.771 (1.765) Å] and Si(3)−N(1) [1.766 (1.765) Å]. Three silicon atoms and the nitrogen atom are in the same plane (the angle around the nitrogen atom: 360°).

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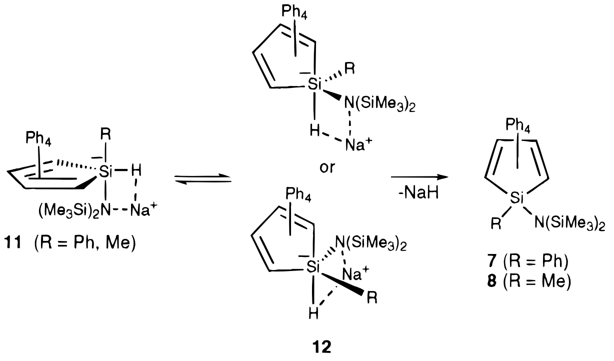
[15] Gunter, H. In *NMR Spectroscopy*; John Wiley & Sons: New York, 1980; Chapter IV, pp 106−113.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 7

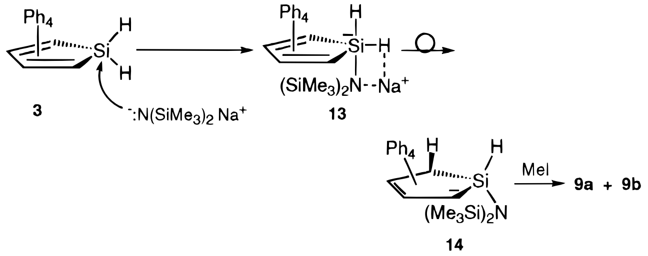
	7a	7b		7a	7b
Si(2)−N(1)	1.771(3)	1.765(3)	Si(3)−N(1)	1.766(3)	1.765(3)
Si(1)−N(1)	1.725(3)	1.733(4)	Si(1)−C(29)	1.876(4)	1.877(4)
Si(1)−C(1)	1.883(4)	1.872(4)	Si(1)−C(4)	1.877(4)	1.872(3)
C(1)−C(2)	1.346(5)	1.362(5)	C(2)−C(3)	1.507(5)	1.504(5)
C(3)−C(4)	1.358(4)	1.356(5)			

	7a	7b		7a	7b
N(1)−Si(1)−C(1)	120.8(2)	117.1(2)	N(1)−Si(1)−C(4)	116.5(1)	119.2(1)
N(1)−Si(1)−C(29)	113.2(1)	114.1(2)	C(29)−Si(1)−C(1)	102.5(2)	107.7(2)
C(29)−Si(1)−C(4)	109.5(2)	103.2(2)	C(4)−Si(1)−C(1)	91.8(2)	92.3(2)
Si(1)−C(1)−C(2)	107.3(3)	106.8(2)	C(1)−C(2)−C(3)	116.2(3)	115.8(3)
C(2)−C(3)−C(4)	116.1(3)	116.4(3)	C(3)−C(4)−Si(1)	107.3(3)	107.0(2)
Si(1)−N(1)−Si(2)	117.8(2)	117.9(2)	Si(1)−N(1)−Si(3)	123.6(2)	122.7(2)
Si(2)−N(1)−Si(3)	118.6(1)	119.4(2)			

Scheme 2. Mechanism for Substitution in 1-Hydrotetraphenylsiloles



Scheme 3. Mechanism for Hydride Migration



The bond distances in the five-membered ring of **6** or **7** are similar to those in silacyclopentadiene and are consistent with highly localized π bonds.[16]

Discussion

Our results show that, in spite of the stability of the product anions that would result from deprotonation of siloles **1**−**6**, treatment of these hydrosiloles with a base, even one that is not a strong nucleophile, is not necessarily a facile route to silole anions. Analysis of the products from the reactions of **1**−**3** with sodium bis(trimethylsilyl)amide, followed by treatment with methyl iodide, clearly indicates that the preferred pathway involves addition of the sodium bis(trimethylsilyl)amide to the silicon center in the first step. Subsequent steps resulting in substitution for **1** and **2** giving **7** and **8**, respectively, or hydrogen migration for **3** leading to **9a**,**b**, can be explained in terms of the geometries of precursor intermediates.

Mechanistic Considerations. Hydride Displacement. The preference for substitution may be explained by the sequence of steps outlined in Scheme 2 for the less hindered siloles **1** and **2**. The first step is apical attack[17] at the least hindered face of **1** by the bis(trimethysilyl)amide anion to form the pentavalent anion **11** in which the sodium ion is coordinated to the amide nitrogen and the silole hydrogen.

The C−Si−C angles in all known siloles are near 90°;[18] thus the trigonal bipyramidal geometry of **11** in which the silole ring is in the equatorial plane would be substantially distorted from the ideal equatorial bond angles of 120°. Thus, rearrangement to the enantiomers, **12**, in which the silole ring is part axial and equatorial with bond angles much closer to 90°, should be favored. Intermediates like **12**, probably the essential precursors to **7** and **8** because they place the hydride in the favored apical position for leaving groups,[19] are readily accessible from **11** via pseudorotation. The suggested intermediate **12** is very similar to the known potassium [η^4-(1,4-diphenylbutadienylene)tricarbonyl]iron trifluorosilicate, in which the silole ring is part axial and equatorial and the potassium cation is coordinated to two fluorides, one in the apical position and the other in the equatorial position.[20]

Hydride Migration. The reaction takes a different pathway when two hydrogens are attached to silicon. We isolated the silacyclopent-3-enes **9a**,**b** from the reaction of **3** with sodium bis(trimethylsilyl)amide followed by quenching with methyl iodide. Hydride migration from silicon to an adjacent ring carbon leading to carbanion formation is the preferred mechanism, as opposed to substitution.

A mechanism is proposed that accounts for hydride migration and the *cis* arrangement of the H−Si−C−H linkage (Scheme 3). Initially, **3** follows the same path as **1** and **2**, forming a pentavalent intermediate (**13**) with sodium coordinated to one of the silicon hydrides and the amide nitrogen. Pseudorotation of **13** to a trigonal bipyramid like **12** appears to be circumvented by hydride migration to form **14**, an intermediate which relieves ring strain and which we were able to detect by NMR spectroscopy. Methylation produced a 1:1 ratio of **9a**,**b**, consistent with the structure of **14**.

The intermediate **14** was directly observed as the major product from the reaction of **3** with sodium bis-

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(16) (a) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755. (b) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715. (c) Parkanyl, L. *J. Organomet. Chem.* **1981**, *216*, 9.

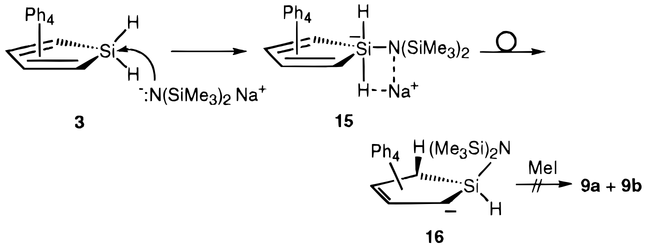
(17) Reference 3b, pp 252−3.

(18) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215.

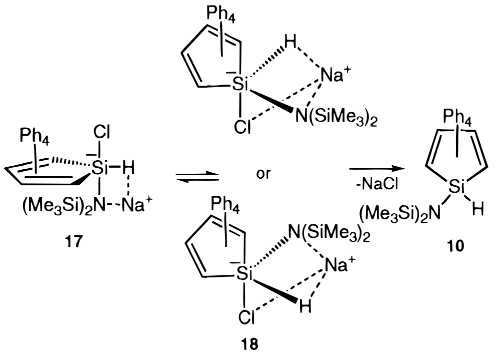
(19) Bassindale, A. R.; Taylor, P. R. in *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 13, pp 854−856.

(20) Carré, F. H.; Corriu, R. J. P.; Guérin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1988**, *347*, C1.

Scheme 4. Edge Attack at Silicon Leading to *trans* H−Si−C−H Orientation



Scheme 5. Possible Mechanism for Substitution with a Good Leaving Group



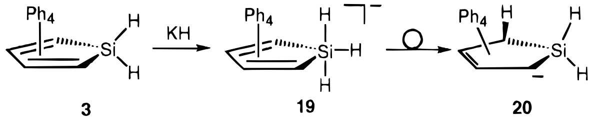
(trimethylsilyl)amide in THF-d_8. In the ^{1}H-NMR, two peaks assigned to H−Si−C−H in **14** appear at 3.32 ppm (1H, d, SiH, $^3J_{\mathrm{H-H}} = 4.4$ Hz) and 5.49 (1H, d, CH, $^3J_{\mathrm{H-H}} = 4.4$ Hz). In the ^{13}C{^{1}H} NMR, the negatively charged carbon adjacent to the silicon and the hydrogen bearing ring carbon, also adjacent to the silicon atom, are observed at 89.77 and 45.38 ppm, respectively. Both absorptions are in the expected regions.[13] In the ^{29}Si-NMR spectrum, peaks were observed at −7.58 ppm (ring-Si, dd, $^1J_{\mathrm{Si-H}} = 183$ Hz and $^2J_{\mathrm{Si-H}} = 9$ Hz) and at 1.57 ppm (m, SiMe$_3$).

Attack at silicon by the nucleophile along a path that is in the plane of the ring and perpendicular to the edge defined by the two hydrogens gives intermediate **15** which cannot lead to the observed **14** nor products **9a**,**b** (Scheme 4).[21] Instead, hydride migration would produce **16**, which, upon methylation, would give a product with a *trans* H−Si−C−H linkage.

In contrast, treatment of the chloride **4** with sodium bis(trimethylsilyl)amide followed by methyl iodide gave only the substitution product **10**. No evidence for hydride migration was detected. S$_N$2 substitution is feasible with very good leaving groups, i.e., apical attack to form **17** coupled with facile apical departure to form **10** directly.[22] It is also reasonable to consider, in light of the results obtained with **3**, that pseudorotation follows the formation of **17** to give **18** and that Cl$^-$ departs to form **10** as shown in Scheme 5.

Less likely, it seems, is an attack pathway by the amide that places chlorine in an equatorial position. Molecular models indicate that the phenyl groups inhibit this route to a much greater extent than the pathway to **17**. Initially, **4** follows the same path as do **1**−**3**, forming a pentavalent intermediate (**17**). Pseudorotation of **17** to form **18**, which relieves ring strain and which accommodates the greater apicophilicity of chloride,[18] is the likely precursor to **10**. However, S$_N$2 type substitution cannot be excluded.

Scheme 6. Potassium Hydride Addition to 1,1-Dihydrotetraphenylsilole



Consistent with these mechanisms, which call for apical attack cis to the hydride, is our observation that siloles with large groups on the silicon, such as *tert*-butyl and mesityl in **5** and **6**, respectively, undergo neither substitution nor hydride migration when treated with sodium bis(trimethylsilyl)amide followed by methyl iodide. In both cases, the addition of the base led to a change in color, to a dark blue, but, following addition of methyl iodide and workup, starting material was recovered in nearly quantitative yields. Inspection of models derived from the X-ray structure of **6** strongly suggest that an apical approach *cis* to the hydride and *trans* to the mesityl group that forms a pentacoordinate anion is feasible but results in an intermediate in which there appears to be repulsion between the phenyl groups on the ring and the mesityl group as well as repulsion resulting from ortho methyl groups on the mesityl group and the silacyclopentadiene π cloud. More importantly, pseudorotation, which would generate a less strained pentacoordinate intermediate in which one Si−C$_\alpha$ bond is axial and the other is equatorial (Figure 1) and would place the leaving group in the apical position, is apparently also blocked by bulky groups, thus cutting off pathways to both substitution and hydride migration.

On the basis of our earlier study of **2** with potassium hydride,[13] we hoped to prepare stable solutions of the hydride addition product.[23] However, when **3** was treated with KH, we were not able to observe the primary product **19** but only the carbanion **20** formed from rearrangement of **19** (Scheme 6). This is additional evidence in support of axial hydride migration in silole.

The decoupled ^{29}Si{H}NMR of **20** shows only one peak at −17.72 ppm. In the ^{13}C{H}NMR spectrum, 20 carbon peaks are observed including two peaks at 77.78 ppm and 40.97 ppm assigned to the carbanion and the hydrogen-bearing ring carbon, respectively. In the ^{1}H-NMR, three alkyl protons, in addition to the phenyl protons, are observed at 1.32 ppm (d, 1H, SiH$_{cis}$, $^3J_{\mathrm{H-H}} = 4.4$ Hz), 4.20 ppm (d, 1H, SiH$_{trans}$, $^3J_{\mathrm{H-H}} = 14.7$ Hz), and 5.20 ppm (dd, 1H, CH, $^3J_{\mathrm{H-H}} = 4.4$ and 14.7 Hz). The *cis* and *trans* conformations in the H$_2$Si−C−H linkages are confirmed by the two coupling constants of 4.4 and 14.7 Hz, respectively.

Conclusions

Our study demonstrates that hydrogens attached to silicon in 2,3,4,5-tetraphenyl-substituted siloles are not deprotonated by sodium bis(trimethylsilyl)amide or

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[21] For studies treating mechanisms that involve edge attack, see: (a) Corriu, R. J. P.; Guérin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (b) Corriu, R. J. P.; Guérin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265. (c) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43.

[22] (a) Dubac, J.; Mazerolles, S. B. *Tetrahedron* **1974**, *30*, 749, 759. (b) Corriu, R. J. P., Massé, *J. Organomet. Chem.* **1972**, *34*, 221.

[23] Corriu, R. J. P.; Royo, G.; De Saxce, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892.

potassium hydride. For siloles with one hydrogen on the silicon, displacement of a hydride by the nucleophile dominates, whereas, for siloles with two hydrogens, 1,5-migration of hydride from silicon to carbon is the preferred course. Pentavalent intermediates are proposed as essential species in both pathways. These different pathways can be understood in terms of common steps: the addition of nucleophile, pseudorotation, and substitution or 1,5-migration of hydride depending on the number and orientation of the hydrogen(s) on silicon. The structures of the isolated products and direct detection of some intermediates support apical attack on the silicon in siloles and rule out edge or side attack. That siloles with bulky substituents on the silicon which restrict pseudorotation undergo neither substitution nor hydride migration when treated with sodium bis(trimethylsilyl)amide is consistent with these observations.

Experimental Section

General Procedures. All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air-sensitive reagents were transferred in a nitrogen-filled glovebox. THF and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. Toluene, hexane, and pentane were stirred over concentrated H_2SO_4 and distilled from CaH_2. NMR spectra were recorded on JEOL GSX270 and GSX 400 spectrometers. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR chemical shifts are relative to external TMS or $CDCl_3$. IR spectra were recorded on a Mattson 2020 Galaxy FT-IR instrument. GC-MS and solid sample MS data were obtained on a Hewlett-Packard 5988A GC-MS system equipped with a methyl silicone capillary column. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Compounds **1**−**4** were prepared according to literature procedures.[24]

1-Phenyl-(Ph_4-silole) (1): Mp 198−200 °C (lit.[6] 200 °C); ^1H NMR 5.50 (s, 1H, SiH), 7.32−7.42 and 7.68−7.73 (brd m, 5H, SiPh), 6.82−7.10 (brd m, 20H, Ph); $^{13}C\{^1H\}$ NMR 156.93, 138.74, 137.41, 135.65. 130.46, 130.27, 129.76, 129.30, 128.38, 127.87, 127.61,126.54, 125.91;^{29}Si NMR −13.49.

1-Methyl-(Ph_4-silole) (2): Mp 224−226 °C (lit.[6] 225−226 °C); ^1H NMR 0.57 (d, 3H, CH_3, J = 4.15), 5.00 (q, 1H, J = 4.5), 6.80−7.15 (brd m, 20H, Ph); $^{13}C\{^1H\}$ NMR 155.66, 138.94, 139.21, 138.76, 129.81, 129.16, 128.00, 127.53, 1126.39, 125.83; ^{29}Si NMR −11.81.

1-Hydro-(Ph_4-silole) (3): Mp 195−198 °C (lit.[25] 209−210 °C); ^1H NMR 4.91 (s, 2H, SiH), 6.8−7.2 (brd m, 20H, Ph); $^{13}C\{^1H\}$ NMR 157.47, 138.70, 138.65, 135.16, 129.61, 129.35, 128.08, 127.71, 126.63, 126.20; ^{29}Si NMR −35.48.

1-Chloro-(Ph_4-silole) (4): Mp 211−214 °C (lit.[26] 212−216 °C); ^1H NMR 5.78 (s, 1H, SiH), 6.8 −7.3 (brd m, 20H, Ph); $^{13}C\{^1H\}$ NMR 156.54, 137.57, 136.83, 134.08, 129.51, 129.40, 128.46, 127.79, 127.08, 126.73; ^{29}Si NMR −4.82.

1-*tert*-Butyl-(Ph_4-silole) (5): A 1.6 mL (2.40 mmol) volume of *tert*-BuLi (1.5 M in pentane) was slowly added by syringe to 1.00 g (2.38 mmol) of **4** in 20 mL of ether and 10 mL of hexane at −78 °C. The mixture was allowed to warm to room temperature slowly and stirred for 2 h. Two drops of MeI were added to destroy unreacted *tert*-BuLi. Filtration, followed by solvent removal, afforded a bright yellow solid of **2** (1.00 g, 95%): Mp 167 °C; ^1H NMR 0.93 (s, 9H), 5.01 (s, 1H), 6.85 −7.20 (brd m, 20H); $^{13}C\{^1H\}$ NMR 18.31, 27.40, 140.16, 138.70, 156.91, 138.47, 129.85, 129.45, 127.74, 127.21, 126.18, 125.57; ^{29}Si NMR −1.09; MS (EI, 70 ev) *m/e* 442 (M^+, 30), 385 ($M^+ - C_4H_9$, 100); IR (KBr, cm^{-1}) ν(Si−H) 2115 (vs). Anal. Calcd for $C_{32}H_{30}Si$: C, 86.83; H, 6.83. Found: C, 86.05; H, 7.07.

1-Mesityl-(Ph_4-silole) (6): 1,4-Dilithiotetraphenylbutadiene (5 mmol) was added slowly by cannulation to 3.30 g (15 mmol) of dichloromesitylsilane in 10 mL of THF at room temperature. Heat was evolved, and the color of the mixture became yellow at the end of the addition. The mixture was stirred at room temperature for 16 h followed by removal of the volatiles under vacuum. Toluene (40 mL) was added to the resulting residue, and the suspension was filtered to give a clear yellow solution. Under reduced pressure 35 mL of toluene was removed from that solution followed by the addition of 30 mL of pentane. A 1.64 g (65.1%) amount of **6** was obtained after cooling of toluene and pentane suspension at −20 °C: Mp 178−180 °C (lit.[9] 179 °C); ^1H NMR 2.28 (s, 3H), 2.59 (s, 6H), 5.74 (s, 1H), 6.8−7.1 (brd m, 20H); $^{13}C\{^1H\}$ NMR 21.22, 23.03, 129.62, 129.16, 127.90, 127.64, 126.42, 125.82, 155.76, 146.11, 140.24, 139.17, 139.09, 138.73,128.84, 124.62; ^{29}Si NMR −26.09.

1-(Bis(trimethylsilyl)amino)-1-phenyl-(Ph_4-silole) (7): **1** (1.39 g, 3 mmol) was dissolved in 30 mL of THF and cooled to −25 °C. To this was added 3.75 mL (2.5 mmol) of $Na[N(SiMe_3)_2]$ in THF immediately producing a deep violet color. The mixture was stirred at −25 to −20 °C for 4 h and then warmed to room temperature. After being stirred in this temperature range for 2 h, the violet solution was added to excess MeI (0.5 mL, 8 mmol) in 10 mL of THF at room temperature by cannulation. This mixture was stirred at room temperature for 2 h forming a yellow solution. The volatiles were evaporated slowly under reduced pressure, and 20 mL of ether was added to the residue. After filtration, ca. 15 mL of ether was removed from the solution and MeOH (20 mL) was added. A 0.82 g (58.08 %) amount of **7** was isolated by cooling to −20 °C: Mp 140 °C; ^1H NMR 0.12 (s, 18H), 6.78−7.58 (m, 20H); $^{13}C\{^1H\}$ NMR 4.80, 125.78, 126.19, 127.44, 127.60, 127.64, 129.60, 129.66, 130.11, 135.32, 137.40, 139.22, 139.47, 142.00, 152.36; ^{29}Si NMR 6.25, 10.11; MS (EI, 70 ev) *m/e* 621 (M^+, 22%), 606 ($M^+ - CH_3$, 8), 544 ($M^+ - C_6H_6$, 6), 73 ($SiMe_3^+$, 100). Anal. Calcd for $C_{40}H_{43}NSi_3$: C, 77.23; H, 6.97. Found: C, 76.98; H, 6.85.

1-(Bis(trimethylsilyl)amino)-1-methyl-(Ph_4-silole) (8): **2** (0.80 g, 2 mmol) was dissolved in 40 mL of THF and cooled to −25 °C. To this was added $Na[N(SiMe_3)_2]$ (2.5 mL, 2.5 mmol) in THF immediately producing a deep violet color. The mixture was stirred at −25 to −20 °C for 4 h and then warmed to room temperature. After being stirred in this temperature range for 4 h, the violet solution was added to excess MeI (0.5 mL, 8 mmol) in 10 mL of THF at room temperature by cannulation. This mixture was stirred at room temperature for 45 min forming a yellow solution. The volatiles were slowly evaporated under reduced pressure, and 20 mL of ether was added to the residue. After filtration, ca. 15 mL of ether was removed from the solution and 20 mL of MeOH was added. A 0.68 g (60.82%) amount of **8** was isolated by cooling to −20 °C: Mp 162 °C; ^1H NMR 0.41 (br, 18H), 0.68 (s, 3H), 6.78−7.10 (m, 20H); $^{13}C\{^1H\}$ NMR 1.79, 4.96, 125.57, 126.11, 127.44, 127.67, 129.27, 129.68, 139.00, 143.51, 150.91; ^{29}Si NMR −1.84, 5.94; MS (EI, 70 ev) *m/e* 559 (M^+, 20), 544 ($M^+ - CH_3$, 6), 466 ($M^+ - C_6H_6 - CH_3$, 20), 73 ($SiMe_3^+$, 100). Anal. Calcd for $C_{35}H_{41}NSi_3$: C, 75.07; H, 7.38. Found: C, 75.19; H, 7.54.

1-(Bis(trimethylsilyl)amino)-2-methyl-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (9a,b): **3** (0.77 g (2 mmol) was dissolved in 35 mL of THF and cooled to −78 °C. To this was added 2.0 mL (2 mmol) of Na[N(SiMe3)2] in THF immediately forming a deep violet color. After being stirred at −78 °C for 2 h, this violet solution was added to excess MeI (0.50 mL, 8 mmol) in 10 mL of THF at room temperature by cannulation. The mixture was stirred at room temperature for 30 min forming a yellow solution. The volatiles were evaporated slowly under reduced pressure, and 20 mL of pentane was added to the residue. After filtration, ca. 15 mL of pentane was removed from the solution and 20 mL of MeOH was added

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(24) Joo, W.-C.; Hong, J.-H.; Choi, S.-B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

(25) Müller, R. *Z. Chem.* **1968**, *8*, 262.

(26) Hagen, V.; Rühlmann, K. *Z. Chem.* **1968**, *8*, 114.

leading to the precipitation of a white solid, **9a** (0.38 g, 34%): Mp 177−178°C; ^{1}H NMR −0.18 (s, 18H), 1.38 (s, 3H), 4.13 (d, 1H, $^3J_{H-H}$ = 4.6 Hz), 4.88 (d, 1H, $^3J_{H-H}$ = 4.6 Hz), 7.08−7.75 (m, 20H); ^{13}C{^{1}H} NMR 4.01, 25.31, 41.17, 42.67, 124.22, 124.94, 126.26, 126.44, 127.42, 127.60, 127.84, 128.11, 128.32 , 128.40, 129.82, 130.54, 139.50, 140.66, 140.79, 141.18, 146.74, 146.86; ^{29}Si NMR −2.49, 5.81; MS (EI, 70 ev) *m*/*e* 561 (M$^+$, 8), 546 (M$^+$ − CH$_3$, 6), 483 (M$^+$ − C$_6$H$_6$, 8), 250 (100); IR (KBr, cm^{-1}) ν(Si−H) 2150 (vs, br). Anal. Calcd for $C_{35}H_{43}NSi_3$: C, 74.80; H, 7.71. Found: C, 74.78; H, 7.48.

After cooling of the supernate to −20 °C, a white solid was obtained, **9b** (0.22 g, 20%): Mp 128−130 °C; ^{1}H NMR 0.42 (s, 18H), 1.71 (s, 3H), 3.96 (d, 1H, $^3J_{H-H}$ = 4.6 Hz), 4.63 (d, 1H, $^3J_{H-H}$ = 4.6 Hz), 6.95−7.54 (m, 20H); ^{13}C{^{1}H} NMR 4.04, 23.98, 41.42, 42.48, 124.45, 124.81, 125.83, 126.11, 127.05, 127.08, 127.10, 127.77, 128.00, 128.10, 128.35, 128.43, 129.71, 130.68, 138.86, 141.44, 142.67, 146.14; ^{29}Si NMR −0.92, 8.61; MS (EI, 70 ev) *m*/*e* 561 (M$^+$, 8), 483 (M$^+$ − C$_6$H$_6$, 10), 250 (100); IR (KBr, cm^{-1}) ν(Si−H) 2140 (vs, br); Anal. Calcd for $C_{35}H_{43}NSi_3$: C, 74.80; H, 7.71. Found: C, 74.84; H, 7.49.

1-(Bis(trimethylsilyl)amino)-(Ph$_4$-silole) (10): **4** (0.84 g, 2 mmol) dissolved in 40 mL of THF was cooled to −78 °C. To this was added 2.5 mL (2.5 mmol) of Na[N(SiMe$_3$)$_2$] in THF immediately forming a brown solution. The mixture was stirred at −78 °C for 4 h followed by the addition of excess MeI (0.5 mL, 8 mmol). The volatiles were evaporated slowly under reduced pressure, and 40 mL of pentane was added to the residue. The filtrate was cooled to −20 °C, and 0.59 g (54.0%) of **10** was isolated as yellow crystals: Mp 164 °C; ^{1}H NMR 0.12 (s, 9H), 2.20 (s, 9H), 5.38 (s, 1H), 6.82−7.08 (m, 20H); ^{13}C{^{1}H} NMR 3.83, 4.46, 126.20, 126.76, 127.95, 128.16, 129.93, 130.06, 139.13, 139.34, 140.50, 153.69; ^{29}Si NMR 7.34, 7.55, 14.48; MS (EI, 70 ev) *m*/*e* 545 (M$^+$, 100), 530 (M$^+$ − CH$_3$, 70), 467 (M$^+$ − C$_6$H$_6$, 25); IR (KBr, cm^{-1}) ν(Si−H) 2153 (vs). Anal. Calcd for $C_{34}H_{39}NSi_3$: C, 74.80; H, 7.20. Found: C, 74.59; H, 7.47.

NMR Study of the Reaction of 1-H-(Ph$_4$-silole) (3) with Na[N(SiMe$_3$)$_2$]: **1** (78 mg, 0.2 mmol) and Na[N(SiMe$_3$)$_2$] (46 mg, 0.25 mmol) were placed in a 5-mm NMR tube followed by THF-d_8 (1 mL). Sonication of the NMR tube for 45 min changed the color of the solution from yellow to a deep violet. Selected data for 1-(bis(trimethylsilyl)amino)-2-sodio-2,3,4,5-tetraphenyl-1-silacyclo-3-pentene (**14**): ^{1}H-NMR (THF-d_8; ref, solvent 1.73 ppm) 0.23 (s, 18H, SiMe$_3$), 3.32 (d, 1H, SiH, $^3J_{H-H}$ = 4.4 Hz), 5.49 (d, 1H, CH, $^3J_{H-H}$ = 4.4 Hz), 5.9−7.5 (m, 20H, Ph); ^{13}C NMR (THF-d_8; ref, solvent 25.30 ppm) 89.77 (C$^-$), 45.38 (CH); ^{29}Si NMR (THF-d_8; ref, external TMS) −7.58 (dd, ring Si, $^1J_{Si-H}$ = 183 Hz and $^2J_{Si-H}$ = 9 Hz), 1.57 (m, SiMe$_3$).

NMR Study of the Reaction of 1-H-(Ph$_4$-silole) (3) with KH: **1** (150 mg, 0.39 mmol) and KH (15.6 mg, 0.39 mmol) were placed in a 5-mm NMR tube followed by the addition of THF-d_8 (1 mL). Sonication of the NMR tube in a conventional ultrasonic cleaning bath for 5 h changed the color of the solution from yellow to a deep violet. The anion **20** was formed exclusively. ^{1}H-NMR (THF-d_8; ref, solvent = 1.73 ppm) 1.32 (d, 1H, SiH$_{cis}$, $^3J_{H-H}$ = 4.4 Hz), 4.20 (d, 1H, SiH$_{trans}$, $^3J_{H-H}$ = 14.7 Hz), 5.20 (dd, 1H, CH, $^3J_{H-H}$ = 4.4 and 14.7 Hz), 5.82 (t, 1H, C$^-$−Ph−H$_p$, J =7.3 Hz), 5.97 (d, 2H, C$^-$−Ph−H$_o$, J = 7.3 Hz), 6.0−7.5 (brd m, 17 H, Ph); ^{13}C{^{1}H} NMR (THF-d_8; ref, solvent = 25.30 ppm) 158.27, 150.82, 149.26, 146.94, 145.91, 131.05, 128.60, 128.41, 127.57, 127.51, 126.75, 125.66, 125.11, 123.89, 123.26, 115.75, 112.82, 111.08, 77.78 (C$^-$), 40.97 (CH); ^{29}Si NMR (THF-d_8; ref, external TMS) −17.72.

X-ray Structure Determination: X-ray-quality crystals of **6** were grown from a concentrated toluene solution of **6** at −20 °C. The crystals of **7** were obtained by slowly cooling a concentrated ether and methanol solution of **7** at −20 °C. A single crystal of **6** or **7** was mounted in thin-walled glass capillary tube and sealed under nitrogen. Data were collected on a Siemens R 3m/V diffractometer at $2\theta = 3.5-45.0°$ using graphite-monochromated Mo Kα radiation. All calculations were performed using Siemens SHELXTL PLUS (VMS) programs. The structures of **6** and **7** were solved by Patterson and refined by the least squares to final R values of 0.0564 (R) and 0.0554 (R_w) for **6** and 0.0506 (R) and 0.0506 (R_w) for **7**, respectively. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. Details on machine parameters, crystal data, data collection, and refinement are given in Table 1.

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Supporting Information Available: Tables of atomic coordinates and U values, bond distances and angles, hydrogen atom coordinates, and anisotopic thermal parameters for **6** and **7** (17 pages). Ordering information is given on any current masthead page.

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