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Silole Silylene Route to NHC-Stabilized Fused 1-Silabicycles and 1,1'-Spirobisiloles

Tianhao Li,^[a] Jianying Zhang,^[a] and Chunming Cui ^{*[a,b]}

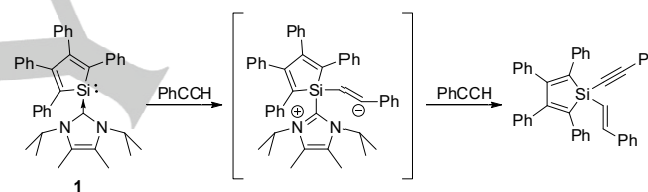
Abstract: The reaction of an NHC-stabilized silole silylene (**1**, 1-silacyclopentadienylidene) with one equivalent of internal acetylenes resulted in the formation of NHC-stabilized 1-silabicyclo[3.2.0]hepta-1,3,6-trienes, which subsequently reacted with one equivalent of the acetylene to yield aryl-substituted 1,1'-spirobisilole (SBS). The SBSs can be alternatively prepared by the reaction of the NHC-stabilized silole silylene **1** with two equivalents of the acetylenes in good yields. The electronic structures of these SBSs have been studied by UV-vis and emission spectroscopy as well as DFT calculations.

Introduction

Over the past several decades, the reactions of silylenes have drawn a great deal of attention owing to their synthetic potentials for novel silicon compounds.^[1] Recent studies have shown that transient silylenes can be stabilized by a Lewis base to form isolable Lewis-base stabilized silylenes, which exhibited distinctive chemistry and properties. We have recently reported the synthesis and reactions of an NHC-stabilized silole silylene and an aminochlorosilylene, which are highly nucleophilic and exhibit interesting reaction patterns towards unsaturated organic substrates.^[2,3]

Organic heterocycles incorporating a silicon atom constitute an attractive class of organosilanes with favorable photophysical properties for luminescent and electronic materials. For example, siloles are remarkable luminescent materials and have been extensively studied.^[4] Bicyclic 1,1'-spirobisiloles (SBSs) with the orthogonal π -system are of considerable interest in view of their potential electronic applications.^[5,6] Although the closely related spirosilabiindenes and spirosilabifluorenes with fused phenyl rings have been investigated as luminescent materials,^[5,7] SBSs have been much less studied due to the lack of efficient synthetic strategies. It was reported that the reaction of 1,4-dilithiotetraphenylbutadiene with silicon tetrachloride only yielded ca. 0.7% octaphenyl-1,1'-spirobisilole.^[8] This situation hampered the detailed investigation of their properties and applications in material chemistry.^[6,9]

In the previous studies, we have shown that the reaction of the NHC-stabilized silole silylene **1** with two equivalents of phenylacetylenes resulted in the formation of the 1-alkenyl-1-alkynylsilole (Scheme 1).^[2a] It was reasoned that the reaction might go through an alkenyl anion intermediate via the nucleophilic addition of **1** to one equivalent of phenylacetylene. Motivated by the results, we are interested in the investigation of reaction of **1** with internal alkynes for the isolation of the possible intermediates and synthesis of spirosilacycles. Herein, we report the synthesis of several aryl-substituted 1,1'-spirobisiloles by the reaction of **1** with aryl-substituted internal alkynes. Notably, this protocol also enabled the isolation of the novel reactive intermediate, the NHC-stabilized 1-silabicyclo[3.2.0]hepta-1,3,6-trienes **3a-b**, a new class of spirosilacycles with a formal NHC-stabilized endocyclic Si=C double bond.



Scheme 1. The reaction of **1** with phenylacetylene.

Results and Discussion

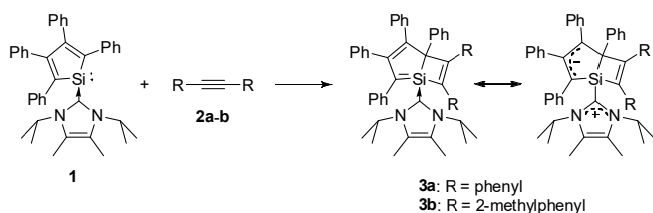
Our initial investigation of the reaction of **1** with one equivalent of diphenylacetylene (**2a**) at room temperature led to a mixture containing two major products as indicated by NMR analysis. However, by the careful addition of **2a** to **1** at low temperatures, the NHC-stabilized 2,3,4,5,6,7-hexaphenyl-1-silabicyclo[3.2.0]hepta-1,3,6-triene **3a** could be isolated as black-green solid in 43% yield (Scheme 2). Compound **3a** is not stable in solution and slowly decomposed to unidentified products in several days. Attempts to grow single crystals of **3a** were unsuccessful to date. Thus, 1,2-di-*o*-tolylethyne (**2b**) was employed for the reaction with the expectation for the stabilization of this type of intermediates by the steric effects. As expected, the similar reaction of **1** with **2b** resulted in the formation of the similar compound **3b** (Scheme 2) in good yield. It was isolated as dark-green crystals and is much more stable than **3a** in solution. Compounds **3a-b** have been fully characterized by ¹H, ¹³C and ²⁹Si NMR spectroscopic methods. The ²⁹Si NMR spectra of **3a** and **3b** exhibit the resonance at -17.2 and -7.6 ppm, respectively, which are close to those observed in Lewis base-stabilized silenes,^[10] indicating that the structure might contain the NHC-stabilized silene fragment. The single crystals of **3b** suitable for X-ray diffraction studies were

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obtained from THF. Its molecular structure has been confirmed by X-ray single crystal analysis.



Scheme 2. Synthesis of NHC-stabilized 1-silabicyclo[3.2.0]hepta-1,3,6-triene **3**.

The structure of **3b** features a fused bicyclic structure with a C–Si bridgehead single bond. The fused SiC₄ five- and SiC₃ four-membered rings are both essentially planar with the dihedral angle of 111.5(4)° (Figure 1). The NHC is coordinated to the silicon atom with the C–Si bond distance of 1.919(3) Å. The endocyclic C1–Si1 bond length of 1.801(3) Å is noticeably shorter than a C–Si single bond, which is comparable to those observed in Lewis base-stabilized silenes,^[10,11] indicating the double bond character. The shortened C1–C2 single bond length of 1.444(3) Å and lengthened C2–C3 double bond length of 1.409(3) Å suggest the significant electron delocalization in the C1–C2–C3 moiety.

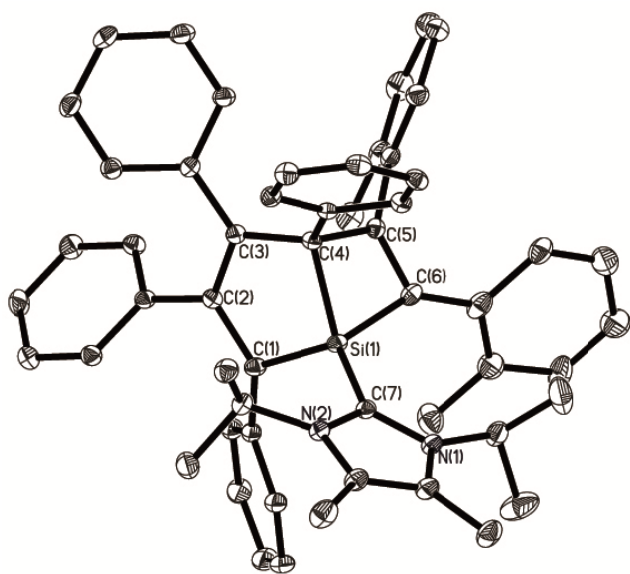
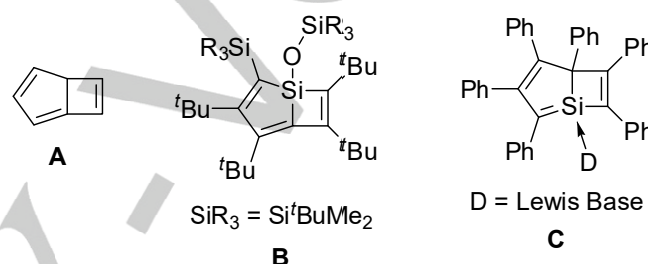


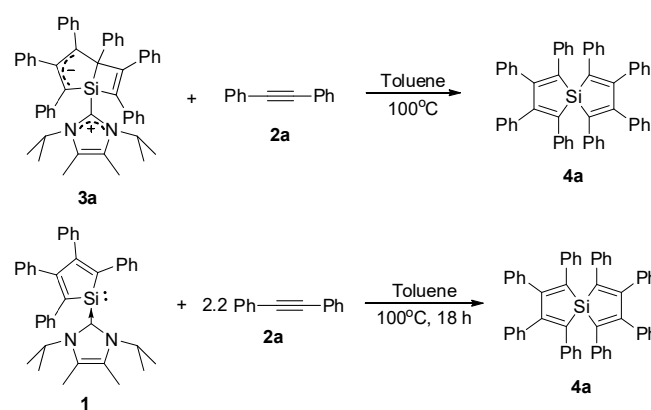
Figure 1. Molecular structure of **3b**. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si1–C1 1.801(3), Si1–C4 1.914(2), Si1–C6 1.858(3), Si1–C7 1.919(3), C1–C2 1.444(3), C2–C3 1.409(3), C3–C4 1.527(3), C4–C5 1.548(3), C5–C6 1.366(3); C1–Si1–C4 96.3(2), C1–Si1–C7 117.0(8), C4–Si1–C6 78.1(6), C6–Si1–C7 118.6(7), Si1–C1–C2 105.9(9), C1–C2–C3 120.1(0), C2–C3–C4 114.1(2), Si1–C4–C3 102.8(7), Si1–C4–C5 82.2(1), C3–C4–C5 112.6(3), C4–C5–C6 109.2(1), Si1–C5–C6 89.2(9).

Bicyclo[3.2.0]hepta-1,3,6-triene (**A** in Scheme 3) and its derivatives are highly reactive molecules arising from the highly strained bridgehead C=C double bond in the fused bicyclic system. Its rearrangements and dimerization processes have been theoretically studied.^[12] However, this type of molecules has not been isolated. In 2003, Kira and co-workers succeeded in the isolation of 5-silabicyclo[3.2.0]hepta-1,3,6-triene (**B** in Scheme 3), which was kinetically stabilized by the peripheral bulky groups.^[13] By taking advantage of Lewis base stabilization concept in low valent main group chemistry, the fused silabicyclic species **3a-b** were isolated and fully characterized. This represents an alternative strategy for the stabilization of highly strained fused ring systems that contain main group elements.



Scheme 3. Bicyclo[3.2.0]hepta-1,3,6-triene and its silicon congeners.

In the reaction of **1** with **2a**, the formation of octaphenyl-1,1'-spirobisilole (**4a**) was also observed by NMR analysis. It is envisioned that the strained species **3a** is very likely to be the intermediate for **4a**. Thus, the reaction of **3a** with one equivalent of **2a** has been investigated. As expected, stirring a mixture of **3a** and **2a** in toluene at 100 °C led to the isolation of the spirobisilole **4a** (Scheme 4). Alternatively, **4a** can be prepared by reaction of the silole silylene **1** with two equivalents of **2a** in good yield (Scheme 4).



Scheme 4. Synthesis of **4a**.

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The formation of **4a** was unambiguously confirmed by X-ray single crystal analysis (Figure S1 in the SI). Its structure is essentially the same as reported previously.^[6d] To extend this methodology for the synthesis of other substituted spirobisiloles with different internal alkynes, the solvent and temperature effects for the reaction of **1** with two equivalents of **2a** have been carefully optimized by the variation of these parameters. As shown in Table 1, the reactions in THF and DME led to the relatively low yields. Increasing the temperatures in THF and DME to 80 °C and 120 °C, respectively, in a sealed tube led to the decrease of the yields. It was reasoned that the decreased yield at the higher temperature is very likely due to the decomposition of the intermediate **3a**. The best yield of 71% was obtained in toluene at 100 °C.

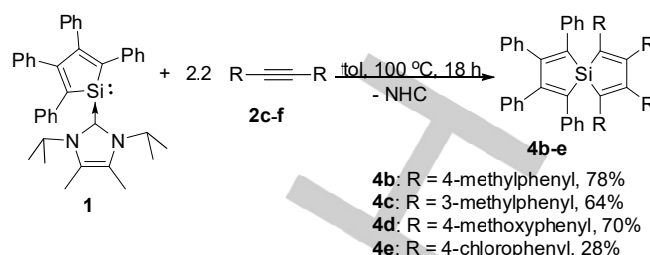
Table 1. Effects of temperature and solvent on yields.

Entry ^[a]	Solvent	T (°C)	Yield (%) ^[b]
1	THF	80	23
2	Toluene	80	49
3	DME	80	4
4	THF	100	36
5	Toluene	100	71
6	DME	100	24
7	Toluene	120	44

^[a]Reaction conditions: NHC stabilized 1-silacyclopenta-2,4-dienylidene **1** (0.53 mmol), diphenyl acetylene **2a** (1.17 mmol), solvent (10 mL), heating in a sealed reaction tube for 18 h. ^[b]Isolated yields.

Under the optimized conditions, several different types of internal acetylenes were examined. As shown in Scheme 5, the reaction of **1** with two equivalents of 1,2-di-*p*-tolylethyne **2c** and 1,2-di-*m*-tolylethyne **2d** afforded the corresponding SBSs **4b-c** in 78% and 64% yields, respectively, with the elimination of the NHC. The introduction of a methoxy group on the para positions of the phenyl ring provided the SBS **4d** in 70% yield, whereas di(4-chloro-phenyl)acetylene **2f** gave the corresponding product **4e** in 28% yield probably due to the side reaction involving the chloride substitute. The other internal alkynes 1,2-di-*o*-tolylethyne **2b**, 1,2-bis(4-fluorophenyl)ethyne, 1,2-bis(4-bromophenyl)ethyne, 1,2-bis(perfluorophenyl)ethyne were also employed for the reaction, but the corresponding products can't be isolated in pure form.

Since **4a** could be formed by the reaction of diphenylacetylene with **3a** (Scheme 4), the tentative mechanism for the formation of **4a** might be similar to that proposed previously for the reaction of **1** with phenylacetylene (Scheme 1).^[2a] It is assumed that **3a** might easily undergo the strained four-membered ring opening to give an alkenyl anion intermediate, which could attack the incoming diphenylacetylene, leading to the C–C bond formation and ring closure with the elimination of the NHC.



Scheme 5. Synthesis of **4b-e**.

The SBS **4a-e** were characterized by ¹H NMR, ¹³C NMR, ²⁹Si NMR and high resolution mass spectrum (HRMS). The structures of **4b** were determined by single-crystal X-ray diffraction analysis, and the molecular structure in the crystal of **4b** is shown in Figure 2. In the crystal structure of **4b**, two mean planes of five-membered rings around the Si atom are almost perpendicular to each other with a dihedral angle of 90.7(0)°.

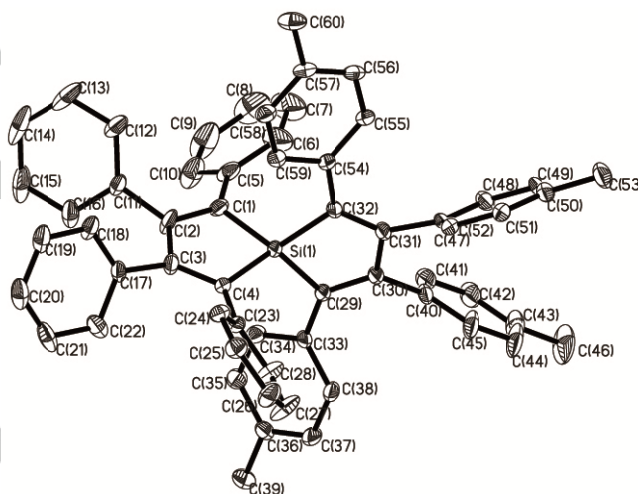


Figure 2. Molecular structure of **4b**. Ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Si1–C1 1.856(2), Si1–C4 1.865(2), C1–C2 1.352(3), C2–C3 1.511(3), C3–C4 1.352(3), C1–C5 1.486(3), C2–C11 1.484(3); C1–Si1–C4 93.3(4), C1–Si1–C29 117.2(3), C1–Si1–C32 118.3(0), Si1–C1–C2 107.2(9), C1–C2–C3 116.1(2), C2–C3–C4 116.3(9), C3–C4–Si1 106.8(1).

Table 2. Electrochemical Properties of **4a**.

	$E_{\text{onset}}^{\text{ox}}$ (V) ^[a]	$E_{\text{onset}}^{\text{red}}$ (V) ^[a]	E_{HOMO} (eV) ^[b]	E_{LUMO} (eV) ^[b]	E_g (eV) ^[c]
4a	0.71	-2.09	-5.51	-2.71	2.8 (2.5)

^[a]Determined by differential pulse polarography in CH₂Cl₂ (0.001 M) using Ag/AgNO₃ as a reference electrode at a scan rate of 100 mV/s. ^[b]HOMO and LUMO levels were estimated using the equations: E_{HOMO} (eV) = $-e(E_{\text{onset}}^{\text{ox}} + 4.8)$, E_{LUMO} (eV) = $-e(E_{\text{onset}}^{\text{red}} + 4.8)$. ^[c]HOMO-LUMO gap, the value in parenthesis referred to the calculated HOMO-LUMO gap.

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The electrochemical properties of **4a** were measured using differential pulse polarography (DPP) versus Ag/AgNO₃ with a ferrocene/ferrocenium internal standard. An estimate of their HOMO and LUMO energy levels was deduced from their redox potentials. As shown in Figure 3, the DPP of **4a** exhibits the double reduction and triple oxidation waves. The cyclic voltammetry showed that all of the processes are chemically irreversible (Figure S2 in the Supporting Information). The onset potentials of oxidation and reduction for **4a** were determined to be 0.71 and -2.09 V, respectively (vs Ag/AgNO₃), which are corresponding to the HOMO and LUMO levels of -5.51 and -2.71 eV, respectively (Table 2). The calculated HOMO-LUMO gap of 2.5 eV is close to that (2.8 eV) determined experimentally. The calculated frontier orbitals for **4a** are shown in Figure 4 and are similar to those of siloles. The LUMO of the silole ring displays a typical $\sigma(\text{Si-C}_{\text{exocyclic}})^*-\pi(\text{butadiene})^*$ hyperconjugation in the system.

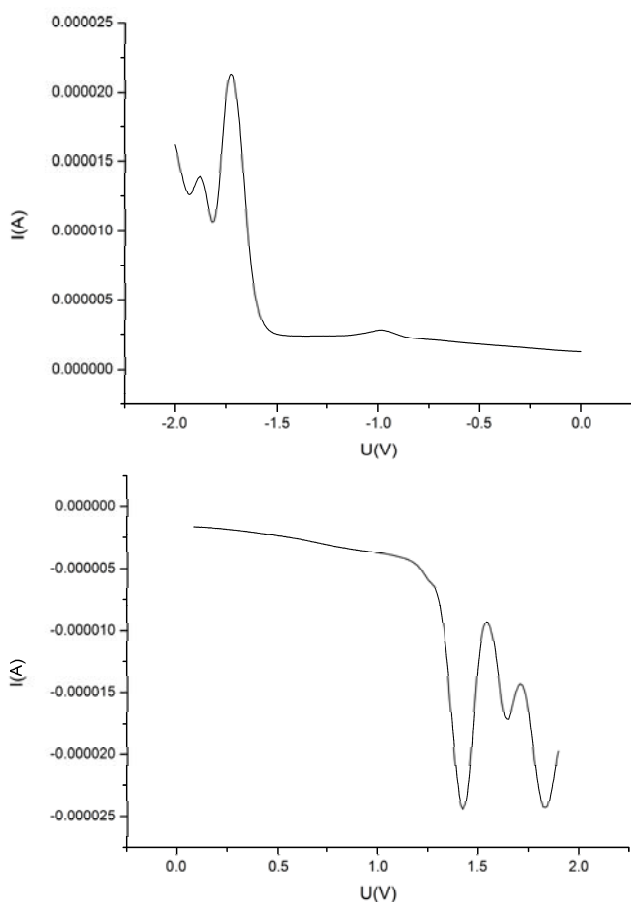


Figure 3. Differential pulse polarography of **4a** measured in CH₂Cl₂ (0.001 M).

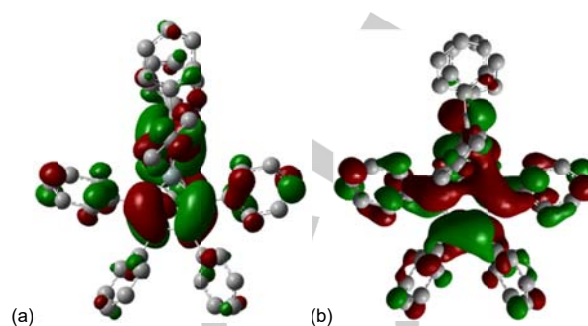


Figure 4. Kohn-Sham frontier orbitals of **4a** [isovalue = 0.02; (a): HOMO; (b): LUMO]

The melting temperatures (T_m) of the SBSs were determined by the differential scanning calorimetry (DSC), and the decomposition temperatures (T_d) were determined by thermogravimetric analysis (TGA) (Table 3). It is obvious that the introduction of the asymmetry character in the molecules reduces the melting points, while the chlorophenyl substituted derivative **4e** is thermally unstable.

Table 3. Thermal properties of 1,1'-spirobisilole (SBS).

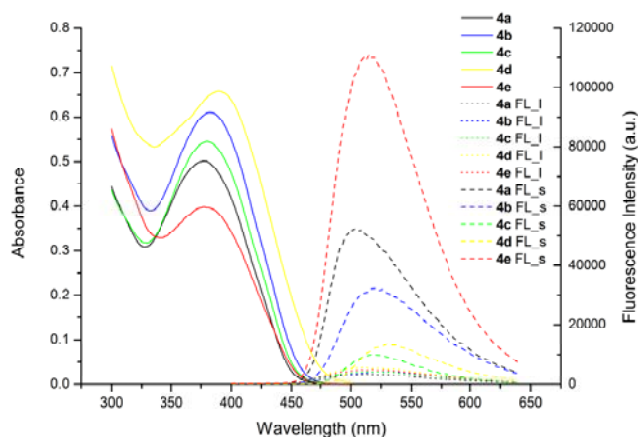
Entry	SBS	T_m (°C)	T_d (°C)
1	4a	231	341
2	4b	223	349
3	4c	152	326
4	4d	197	382
5	4e	-	231

The optical properties of the SBSs **4a-e** have been studied by UV-Vis and emission spectroscopy. The UV-Vis absorption spectra and fluorescence spectra are shown in Figure 5. The substituents on the phenyl groups only have very small effects on the absorption maxima. The fluorescence spectra of **4a-e** were recorded in CH₂Cl₂ and in the solid state. The photoluminescence quantum yields in solution were very low (0.01-0.02), while the solid-state photoluminescence quantum yields were found between 0.04 and 0.23, suggesting that the SBSs are aggregation-induced emission (AIE) active molecules. Compared to peripherally aryl-substituted common siloles,^[14] the spirobisiloles exhibit very similar UV-vis absorptions, whereas the emission maxima of the SBSs are slightly red-shifted.

Table 4. Optical properties of 1,1'-spirobisilole (SBS).

	λ_{abs} (nm)		λ_{pl} (nm)		Φ_{pl}
	CH_2Cl_2	$\text{CH}_2\text{Cl}_2^{[\text{a}]}$	Solid ^[a]	$\text{CH}_2\text{Cl}_2^{[\text{a}]}$	
4a	377.0	513	502	0.01	0.23
4b	382.5	534	521	0.01	0.16
4c	380.0	514	517	0.01	0.04
4d	389.5	510	530	0.02	0.07
4e	377.5	507	515	0.01	0.16

[a] Excited at 326 nm.

**Figure 5.** UV/Vis absorption and fluorescence emission of 1,1'-spirobisiloles (SBS).

Conclusions

The reaction of the silole silylene **1** with internal alkynes enabled the isolation of the NHC-stabilized 1-silabicyclo[3.2.0]hepta-1,3,6-trienes **3a-b** and high-yield synthesis of peripheral aryl-substituted spirobisilole derivatives **4a-e**. Compounds **3a-b** represent a new class of fused silabicycles featuring an NHC-stabilized silene fragment and strained SiC₃ four-membered ring. Reaction of **1** with two equivalents of internal acetylene resulted in the synthesis of spirobisiloles in modest to good yields. These reactions indicated that the silole silylene **1** is synthetically useful for the construction of novel silabicycles. Further investigation of **1** with various organic unsaturated systems is undertaken in our laboratory.

Experimental Section

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Synthesis of 3a-b.

3a: To a solution of the NHC stabilized silole silylene **1** (0.30 g, 0.53 mmol) in THF (10 mL) was added a solution of diphenylacetylene **2a** (0.09 g, 0.53 mmol) in 10 mL of THF at -78 °C. The mixture was slowly warmed up to room temperature and was stirred overnight. It was concentrated to 5 mL and stored at -40 °C overnight to give black-green solid of **3a** (0.17 g, 43%). ¹H NMR (400 MHz, C₆D₆): δ 7.97 (d, J = 7.6 Hz, 2H, PhH), 7.80 (d, J = 6.7 Hz, 2H, PhH), 7.63-7.43 (m, 4H, PhH), 7.21 (m, 3H, PhH), 7.08 (m, 3H, PhH), 6.98 (m, 5H, PhH), 6.90 (m, 2H, PhH), 6.84 (m, 3H, PhH), 6.78 (d, J = 8.0 Hz, 2H, PhH), 6.72 (t, 2H, PhH), 6.56 (dd, J = 12.3, 6.9 Hz, 2H, PhH), 5.43 (m, 2H, NCHMe₂), 1.04 (s, 6H, C=CCH₃), 0.90 (d, J = 6.8 Hz, 6H, CH₃), 0.83 (d, J = 6.9 Hz, 6H, CH₃). ¹³C NMR (101 MHz, C₆D₆): δ 155.73, 147.95, 147.57, 146.79, 146.61, 146.04, 144.67, 132.12, 131.66, 130.36, 129.27, 128.65, 128.30, 127.58, 127.16, 126.73, 126.31, 125.58, 123.05, 122.83, 120.60, 115.81, 105.56, 82.04, 67.68, 52.27, 14.65, 9.71. ²⁹Si NMR (59.62 MHz, C₆D₆): δ -17.20. **3b:** prepared similarly using **1** (0.30 g, 0.53 mmol) and 1,2-di-*o*-tolylethyne **2b** (0.11 g, 0.53 mmol). It was isolated as black-green solid (0.19 g, 49%). ¹H NMR (400 MHz, C₆D₆): δ 8.01 (d, 2H, PhH), 7.88 (m, 2H, PhH), 7.78 (m, 2H, PhH), 7.39 (m, 1H, PhH), 7.28 (m, 3H, PhH), 7.20 (m, 1H, PhH), 7.01-6.69 (m, 11H, PhH), 6.67 (m, 4H, PhH), 6.40 (m, 2H, PhH), 5.07-4.97 (m, 2H, CHMe₂), 2.33 (s, 3H, CH₃), 2.12 (s, 3H, CH₃), 1.25 (d, 3H, CH₃), 1.06 (d, 6H, CH₃), 0.89 (d, 3H, CH₃), 0.73 (d, 3H, CH₃), 0.41 (d, 3H, CH₃). ¹³C NMR (101 MHz, THF-*d*₈): δ 156.94, 151.50, 148.93, 148.43, 148.04, 147.23, 146.21, 144.88, 143.66, 142.26, 140.07, 138.97, 137.85, 137.20, 136.58, 132.40, 131.6, 131.11, 130.90, 130.73, 129.61, 128.48, 128.43, 128.13, 127.82, 127.36, 127.01, 126.87, 126.60, 126.28, 126.04, 125.81, 125.18, 123.94, 123.34, 122.01, 121.76, 119.17, 118.42, 115.88, 111.88, 105.90, 103.01, 82.28, 61.79, 54.71, 53.00, 48.87, 30.82, 22.58, 22.45, 21.81, 21.53, 20.84, 10.68, 9.07. ²⁹Si NMR (59.62 MHz, C₆D₆): δ -7.55.

Synthesis of 4a-e.

4a: To a solution of **1** (0.30 g, 0.53 mmol) in toluene (10 mL) at -78 °C was added a solution of diphenyl acetylene **2a** (0.21 g, 1.17 mmol) in 10 mL of toluene. The mixture was warmed up to room temperature, and then heated up to 100 °C for 18 h. The solvent was removed and the remaining solid was purified by silica gel column chromatography (hexane/dichloromethane : 20/1) to give a bright yellow powder of **4a** (0.28 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.08-7.06 (m, 16H, PhH), 7.03 (t, J = 6.5 Hz, 16H, PhH), 6.86-6.84 (m, 8H, PhH). ¹³C NMR (101 MHz, CDCl₃): δ 158.52, 139.16, 138.53, 134.65, 129.67, 129.45, 128.06, 127.89, 126.80, 126.25. ²⁹Si NMR (59.62 MHz, CDCl₃): δ 6.94. HRMS: 740.2895. Calcd for C₅₆H₄₀Si: 740.2899. **4b-e** were synthesized similarly using different internal alkynes. **4b:** using 1,2-di-*p*-tolylethyne **2c** (0.24 g, 1.17 mmol), bright yellow powder (0.33 g, 78%). ¹H NMR (400 MHz, CDCl₃): δ 7.07-6.98 (m, 16H, PhH), 6.93-6.84 (m, 16H, PhH), 6.72 (s, 2H PhH), 6.70 (s, 2H, PhH), 2.24 (s, 6H, PhCH₃), 2.21 (s, 6H, PhCH₃). ¹³C NMR (101 MHz, CDCl₃): δ 158.23, 158.05, 139.35, 138.64, 136.55, 136.12, 135.81, 135.68, 135.42, 133.34, 129.70, 129.49, 129.38, 128.78, 128.62, 127.97, 127.36, 126.70, 126.09, 21.44, 21.28. ²⁹Si NMR (59.62 MHz, CDCl₃): δ 6.84. HRMS: 796.3522. Calcd for C₆₀H₄₈Si: 796.3525. **4c:** using 1,2-di-*m*-tolylethyne **2d** (0.24 g, 1.17 mmol), bright yellow powder (0.27 g, 64%). ¹H NMR (400 MHz, CDCl₃): δ 7.09-6.93 (m, 20H, PhH), 6.91-6.83 (m, 10H, PhH), 6.75 (d, J = 7.7 Hz, 2H, PhH), 6.64-6.62 (m, 4H, PhH), 2.17 (s, 6H, PhCH₃), 2.12 (s, 6H, PhCH₃). ¹³C NMR (101 MHz, CDCl₃): δ 158.85, 157.97, 139.46, 139.29, 138.64, 138.40, 137.30, 137.20, 135.97, 133.22, 130.83, 130.15, 129.66, 129.51, 128.02, 127.92, 127.79, 127.69, 127.34, 126.97, 126.74, 126.53, 126.21, 126.14, 21.58, 21.39. ²⁹Si NMR (59.62 MHz, CDCl₃): δ 7.27. HRMS: 796.3524. Calcd for C₆₀H₄₈Si: 796.3525. **4d:** using 1,2-bis(4-methoxyphenyl)ethyne **2e** (0.28 g, 1.17 mmol), bright yellow powder (0.32 g, 70%). ¹H NMR (400

MHz, CDCl₃): δ 7.08-6.96 (m, 20H, PhH), 6.87-6.85 (m, 4H, PhH), 6.75 (d, *J* = 8.4 Hz, 4H, PhH), 6.65-6.61 (m, 8H, PhH), 3.74 (s, 6H, OCH₃), 3.72 (s, 6H, OCH₃). ¹³C NMR (101 MHz, CDCl₃): δ 158.25, 158.03, 157.85, 157.05, 139.28, 138.66, 135.65, 132.28, 132.02, 131.45, 130.94, 130.69, 129.69, 129.43, 127.97, 127.86, 126.72, 126.09, 113.52, 113.44, 55.20, 55.19. ²⁹Si NMR (59.62 MHz, CDCl₃): δ 6.55. HRMS: 860.3320. Calcd for C₆₀H₄₈O₄Si: 860.3322. **4e**: using 1,2-bis(4-chlorophenyl)ethyne **2f** (0.29 g, 1.17 mmol), bright yellow powder (0.13 g, 28%). ¹H NMR (400 MHz, CDCl₃): δ 7.09-7.06 (m, 20H, PhH), 6.91 (d, *J* = 7.7 Hz, 4H, PhH), 6.86 (d, *J* = 8.4 Hz, 4H, PhH), 6.80 (d, *J* = 5.7 Hz, 4H, PhH), 6.71 (d, *J* = 8.2 Hz, 4H, PhH). ¹³C NMR (101 MHz, CDCl₃): δ 159.36, 156.85, 138.58, 138.09, 136.60, 136.43, 135.01, 133.42, 133.37, 132.46, 130.92, 130.43, 129.54, 129.21, 128.62, 128.59, 128.24, 128.02, 127.11, 126.58. ²⁹Si NMR (59.62 MHz, CDCl₃): δ 6.57. HRMS: 876.1338. Calcd for C₅₆H₃₆Cl₄Si: 876.1340.

X-ray structural determination.

See supporting information for details. CCDC-1043819 and 1525521 for **3b** and **4b** have been deposited.

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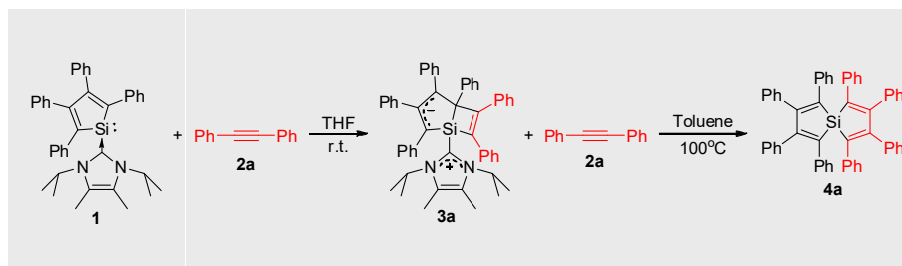
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**Silole Silylene Route to NHC-
Stabilized Fused 1-Silabicycles and
1,1'-Spirobisiloles**

Silabicycles: Reaction of the NHC-stabilized silole silylene 1 with internal acetylenes resulted in the formation of NHC-stabilized 1-silabicyclo[3.2.0]hepta-1,3,6-trienes and 1,1'-spirobisiloles depending on the reaction conditions and stoichiometry.