Synthesis and Crystal Structure of 9,10-Disilatriptycenes

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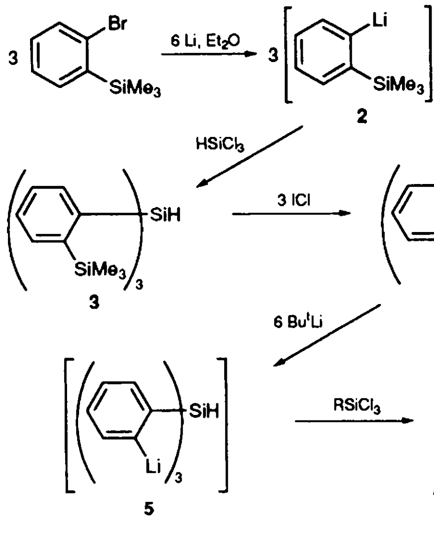
9,10-Disilatriptycenes **1a–1c** have been synthesized by a novel route *via* *o*-trimethylsilylphenyllithium, a novel synthetic equivalent of *o*-halogenophenyl anion; the structure of the 9-methyl-10-hydroxy derivative **1c** was determined by X-ray crystallography.

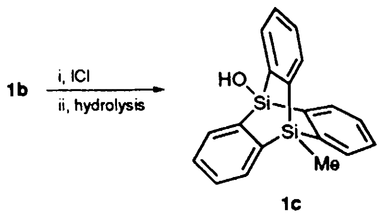
Triptycenes have been investigated extensively because of their unique structures,[1] whereas heterotriptycenes in which bridgehead (9 and/or 10) positions are substituted by group 14 and 15 elements of the third or higher row have received much less attention. The sole known example of a heterotriptycene having a heavier group 14 element is a disilatriptycene derivative with tetrafluorinated *o*-phenylene vanes.[2] While the present work was in progress, the formation of **1a** in the co-pyrolysis of 5,10-dihydro-5,10-silaanthrene and *o*-dichlorobenzene was reported by a Russian group.[3] It is difficult to obtain a reasonable amount of **1a** by this reaction however.

The paucity of examples of disilatriptycenes is mainly due to the difficulty in preparing suitable precursors. We report here a general and efficient synthetic route to 9,10-disilatriptycenes **1** *via* a key intermediate, *o*-trimethylsilylphenyllithium **2**, which is applicable to the synthesis of other heterotriptycenes as well. We also describe the first X-ray crystallographic analysis of a 9,10-disilatriptycene derivative.

Although the reaction of trichlorosilane and *o*-iodophenyl anion seems to be a reasonable route to **4**, a logical precursor of **1**, it is impractical in fact, because of the high propensity of *o*-halogenophenyl anions to form benzyne. We have found that *o*-trimethylsilylphenyl anion **2** can serve as an efficient synthetic equivalent of *o*-iodophenyl anion by taking advan-



Scheme 1



Scheme 2

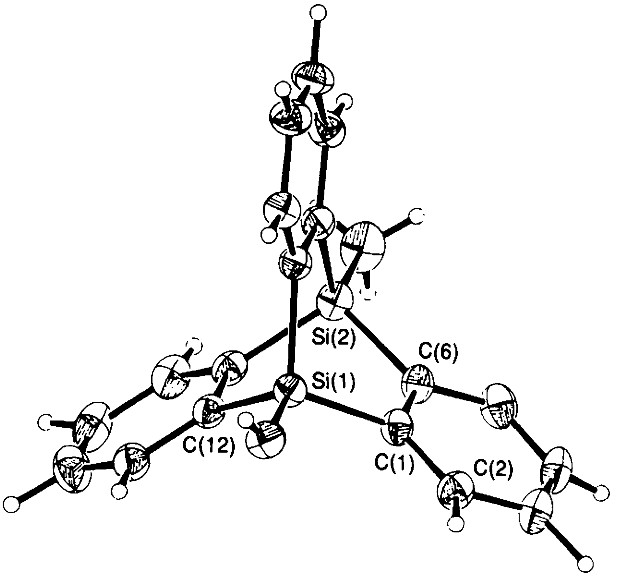


Fig. 1 ORTEP drawing of 9,10-disilatriptycene **1c**

tage of the fact that a trimethylsilyl group is readily transformed into a halogeno group by treatment with halogens[4] (Scheme 1).

The reaction of 1-bromo-2-trimethylsilylbenzene[5] with 1 equivalent of lithium dispersion in refluxing diethyl ether for 30 min afforded an ethereal solution of *o*-trimethylsilylphenyllithium **2**. When the solution of **2** (90.0 mmol) was added to an ethereal solution of trichlorosilane (15.0 mmol) and the resulting solution was stirred at room temperature for 20 h, tris(*o*-trimethylsilylphenyl)silane **3** was obtained in 88% yield. Treatment of **3** (16.3 mmol) with iodine monochloride (48.8 mmol) in dichloromethane at 0 °C for 2 h afforded tris(*o*-iodophenyl)silane **4** in high yield (91%).

Lithiation of **4** (10.0 mmol) with *tert*-butyllithium (63.0 mmol) at −78 °C in diethyl ether–benzene (3 : 1) gave trianion **5** cleanly as shown by deuteriation experiment with D_2O. The reaction of **5** with trichloromethylsilane at −78 °C for 2 h followed by slow warming of the reaction mixture to room temperature afforded 5,10-dihydro-5-methyl-5,10[1′,2′]-benzenosilaanthrene **1b**, which was purified by chromatography on silica gel followed by recrystallization from cyclohexane or hexane (16%). Similar reaction of **5** with trichlorosilane gave **1a** (11%). Although **1a** is decomposed on silica gel, it was purified by direct recrystallization of the crude product from hexane. Both **1a** and **1b** were obtained as colourless cubic crystals and their structures were confirmed by spectroscopic data (NMR, UV, and MS) and elemental analyses.†

^{1}H NMR signals at δ *ca.* 5.5 for **1a** and **1b** flanked by symmetric satellites are assignable to Si–H and the chemical shift is close to that of triphenylsilane (δ 5.47). The ^{1}H NMR signal due to the methyl group of **1b** (δ 1.10) appeared at lower fields than that of methyltriphenylsilane **6** (δ 0.87), whereas the ^{13}C NMR signal of the methyl carbon of **1b** (δ −13.4) shifted to higher field by about 10 ppm compared to **6** (δ −3.4). Similar changes in ^{1}H and ^{13}C NMR chemical shifts of the methyl groups were observed in the case of 1,1,1-triphenylethane **7** and 9-methyltriptycene **8** (**7**: δ_H 2.19, δ_C 30.5; **8**: δ_H 2.36, δ_C 13.2). ^{29}Si NMR signals of **1b** appeared at δ_{Si} −43 and −52, at substantially higher field than those of triphenylsilanes (Ph_3SiMe: δ_{Si} −8, Ph_3SiH: δ_{Si} −21).[6] It is also interesting that the weak absorptions at 270 nm in the UV spectrum of triptycene shifted to slightly longer wavelength for **1a** and **1b** (**1a**: 286 nm, **1b**: 284 nm), suggesting a possible increase of inter-vane charge transfer interaction compared to triptycenes.[7]

For X-ray structural analysis, **1b** was converted to the hydroxy compound **1c** by the reaction with ICl followed by hydrolysis (Scheme 2). Recrystallization from hexane gave single crystals of **1c**·$0.5H_2O$, the molecular structure of which was determined by X-ray crystallographic analysis (Fig. 1).‡

The triptycene skeleton of **1c** has a slightly squashed shape with the silicon atoms closer compared with normal aromatic *ortho*-substituted atoms. The bond angles subtended at the bridgehead Si atoms [C(1)–Si(1)–C(12) *etc.*] are 102.1–105.5°, being less than the usual tetrahedral value of 109.5°, and 1–2° smaller than those of triptycene derivatives (104.0–106.5°).[8] The external [Si(1)–C(1)–C(2) *etc.*] and internal [Si(1)–C(1)–C(6) *etc.*] angles of the disilabicyclooctane rings are 125.2–127.0 and 113.6–115.9°, respectively, substantially different from 120° [triptycenes: 125.0–127.4° (external), 112.1–114.5° (internal)].[8]

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† *Spectroscopic data* for **1a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.56 (s, 2 H), 7.22 (m, 6 H), 7.80 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 127.7, 133.3, 143.6. For **1b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.10 (s, 3 H), 5.53 (s, 1 H), 7.20 (m, 6 H), 7.67 (m, 3 H), 7.80 (m, 3 H); ^{13}NMR ($CDCl_3$, 100 MHz) δ −13.4, 127.3, 127.4, 131.4, 133.1, 144.2, 145.1.

‡ *Crystal data* for **1c**: $C_{19}H_{16}OSi_2 \cdot 0.5H_2O$, M = 325.51, tetragonal cell, space group $I4_1/a$, a = 28.162(7), c = 9.09(1) Å, V = 7211(9) Å^3, Z = 16, D_c = 1.199 g cm^{-3}, μ = 1.93 cm^{-1}. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2415 observed reflections [$I > 3.00\sigma(I)$] and 255 variable parameters with $R(R_W)$ = 0.061(0.0092).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The distance between the bridgehead Si atoms is 2.984(2) Å, which is longer than Si–Si bond length in disilanes (2.33–2.37 Å), but substantially shorter than the sum of van der Waals radius of silicon atoms (4.2 Å),[9] suggesting a possible through-space interaction between the bridgehead Si atoms; this is now under investigation.

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