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Functional Group Transformations and Stereochemistry of Silicon-functionalized 7-Silabenzonorbornadienes

Atsushi Kawachi,* Masahiro Okimoto, and Yohsuke Yamamoto

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526

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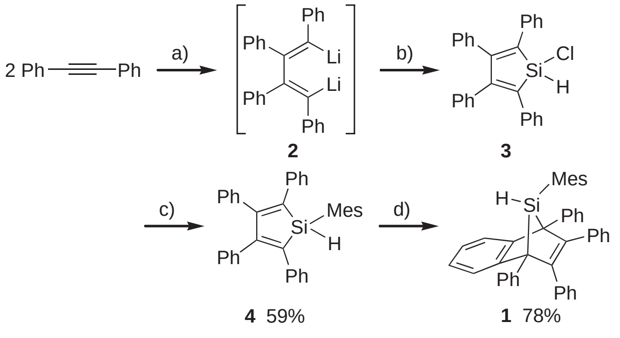
Functional group transformations of 7-silabenzonorbornadiene derivatives have been investigated. The 7-mesityl-7-silanorbornadiene **1** was prepared and converted into the 7-chloro derivative **5**. Reductive lithiation of **5** with lithium naphthalenide afforded the silyllithium **6**, which reacted with Me_3SiCl and MeI. The reactions of **5** with *n*-BuLi and PhNHLi gave the 7-butyl derivative **9** and the 7-amino derivative **10**, respectively. Each stereochemistry during these transformations was determined by X-ray crystallographic analysis.

The 7-silanorbornadienes have been attractive species since they show unique reactivity attributed to their heavily strained skeletons.[1] Thermolysis or photolysis of the 7-silanorbornadienes may produce divalent silylene species with the elimination of arenes, the former of which undergoes reactions with dienes, alkynes, hydrosilanes, and alcohols.[2] Thus the 7-silanorbornadienes are potential precursors of a variety of silicon compounds, and the introduction of functional groups on the bridging silicons will increase their synthetic utility. Functional group transformations of the 7-silanorbornadienes, however, have been scarcely investigated. We report here the preparations and stereochemical aspects of silicon-functionalized 7-silabenzonorbornadienes, starting from the 2,3-benzo-1,4,5,6-tetraphenyl-7-mesityl-7-silanorbornadiene (**1**).

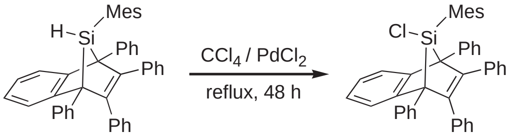
A parent compound, the 7-hydro derivative **1**, was prepared in a manner similar to the reported procedure,[3] as shown in Scheme 1 [Mes = Mesityl (2,4,6-trimethylphenyl)]. The reaction of 1,4-dilithiotetraphenylbutadiene **2** with trichlorosilane gave the 1*H*-1-chloro-1-silacyclopentadiene **3**.[3a] The crude **3** was subsequently treated with mesitylmagnesium bromide to afford the 1*H*-1-mesityl-1-silacyclopentadiene **4** in 59% yield.[3b] The [4 + 2] cycloaddition between **4** and benzyne prepared in situ gave the silanorbornadiene **1** as a diastereoisomer in 78% yield.[3c,4] The X-ray crystallographic analysis of **1** revealed that the hydrogen at the silicon is syn with respect to the annulated benzene.[4] The steric bulkiness of the mesityl group in **1** determines the stereochemistry during the [4 + 2] cycloaddition.



(a) Li / Et_2O / room temp, 12 h. (b) $HSiCl_3$ / –196 °C to room temp.
(c) MesMgBr / THF / room temp, 12 h.
(d) Mg, *o*-C_6H_4FBr / THF / room temp, 48 h.

Scheme 1.

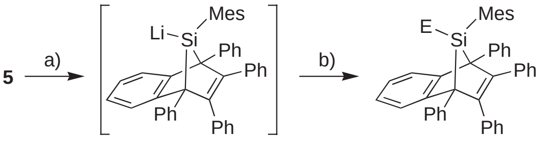
The chlorination of **1** with refluxing carbon tetrachloride in the presence of palladium dichloride (30 mol %) successfully afforded **5** in 90% yield (Eq 1).[5,6] There have been very few examples of the 7-chloro-7-silanorbornadienes, all of which were prepared by the [4 + 2] cycloaddition.[1c] The stereochemistry of **5** was confirmed to be syn by an X-ray crystallographic analysis.[6] This proves that the chlorination reaction proceeds with retention of its configuration at the silicon. The observed stereochemistry is consistent with the trend that reactions of organosilanes involving the intermediate silyl radicals proceed with the predominant retention of the configuration at the silicon.[7]



(1)

1 **5** 90%

The lithiation of **5** was also successful, giving a nucleophilic silanorbornadiene species. The exposure of **5** to lithium naphthalenide (4 molar amounts) in THF–benzene at −78 °C for 4 h produced the corresponding silyllithium **6** (Eq 2).[8,9] Excess amount of lithium naphthalenide was required to consume **5** completely. The silyllithium **6** reacted with methyl iodide and chlorotrimethylsilane to form the 7-methyl derivative **7** in 45% yield and the 7-trimethylsilyl derivative **8** in 52% yield, respectively.[10,11] This is the first example of silicon-lithiated silanorbornadienes whereas there have been a few examples of those having a transition metal fragment on the silicon atom.[12] The syn stereochemistry of **8** was determined by X-ray crystallographic analysis.[11,13] Thus the formation and reaction of **6** undergo the net retention of the configuration at the silicon. This is in good agreement with the known aspects that the reductive lithiation of chlorosilanes and subsequent reactions with the electrophiles proceed with the predominant retention of the configuration at the silicon during each step.[14]



(2)

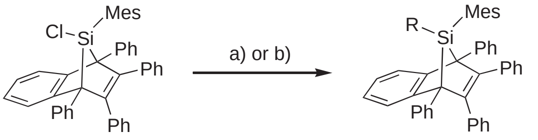
6

7: E = Me 45%
8: E = Me_3Si 52%

(a) Lithium naphthalenide (x 4) / THF–benzene / –78 °C, 4 h.
(b) MeI or Me_3SiCl / –78 °C to room temp.

The nucleophilic substitution reactions of **5** were also examined. The treatment of **5** with butyllithium and lithium phenylamide in THF–benzene gave the 7-butyl derivative **9** and the

7-amino derivative **10** in 53% yield and 52% yield, respectively (Eq 3).[15,16] The X-ray crystallographic analysis of **10** displayed its syn stereochemistry,[13,16] indicating the retention of configuration at the silicon during the amination reaction. It is noted that although the nucleophilic displacements of chlorosilanes mainly undergo inversion at the silicon, the stereochemistry tends towards retention when the silicon is included in a strained ring.[7a]



(3)

5

9: R = *n*-Bu 53%
10: R = PhNH 52%

(a) *n*-BuLi (x 2) / 0 °C, 3 h. (b) PhNHLi (x 1.2) / room temp, 2 h.

In summary, the Si–H functionality in **1** was converted into the Si–Cl functionality (**5**) and then the Si–Si (**8**) and Si–N (**10**) functionalities. These transformations proceed with predominant retention of configuration at the bridging silicons due to the rigid skeletons. The nucleophilic and electrophilic silanorbornadienes prepared here will serve as versatile silicon reagents.

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References and Notes

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4 Compound **1**: colorless crystals (from $CDCl_3$/hexane), mp 223–224 °C (decomposed). ^1H NMR ($CDCl_3$, δ) 2.19 (s, 6H), 2.23 (s, 3H), 5.01 (s, 1H), 6.72 (s, 2H), 6.89–7.00 (m, 8H), 7.04–7.09 (m, 4H), 7.10–7.14 (m, 8H), 7.16–7.20 (m, 2H), 7.58–7.65 (m, 2H). ^{13}C NMR ($CDCl_3$, δ) 21.3, 24.6, 59.9, 122.5, 124.0, 125.3, 126.0, 126.3, 127.1, 127.6, 128.5, 129.9, 130.6, 137.5, 137.8, 140.6, 145.6, 147.1, 148.0. ^{29}Si NMR ($CDCl_3$, δ) 32.9 (d, $^1J_{Si\text{–}H} = 206$ Hz). MS (EI): m/z 580 (M^+, 48), 432 [(tetraphenylnaphthalene)$^+$, 100]. Anal. Calcd for $C_{43}H_{36}Si$: C, 88.92; H, 6.25%. Found: C, 88.79; H, 6.62%. Crystal data for **1** at 173 K (Mac Science DIP2030) (CCDC 270940); see Supporting Information.

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6 Compound **5**: colorless crystals (from $CDCl_3$/hexane), mp 252–253 °C (decomposed). ^1H NMR ($CDCl_3$, δ) 2.08 (s, 6H), 2.24 (s, 3H), 6.29–6.45 (br, 2H), 6.72–6.78 (br, 2H), 6.80–7.04 (m, 8H), 7.09–7.22 (m, 12H), 7.51–7.58 (m, 2H). ^{13}C NMR ($CDCl_3$, δ) 21.1, 25.6, 61.7, 123.4, 124.4, 125.4, 125.8, 126.3, 127.2, 127.6, 129.0, 130.1, 131.3, 136.0, 137.4, 140.9, 145.5, 146.8, 147.5. ^{29}Si NMR ($CDCl_3$, δ) 30.3. MS (EI): m/z 616 (M + 2, 21), 614 (M^+, 45), 432 [(tetraphenylnaphthalene)$^+$, 100]. Anal. Calcd for $C_{43}H_{35}ClSi$: C, 83.94; H, 5.73%. Found: C, 83.88; H, 5.79%. Crystal data for **5** at 173 K (Mac Science DIP2030) (CCDC 270941); see Supporting Information.

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9 The ^{29}Si resonance of **6** could not be confirmed even at low temperatures perhaps due to the low concentration of the solution of **6** prepared under the present conditions.

10 Compound **7**: colorless crystals (from $CHCl_3$/hexane/CH_3CN), mp 234–235 °C (decomposed). ^1H NMR ($CDCl_3$, δ) 0.20 (s, 3H), 2.05 (s, 6H), 2.24 (s, 3H), 6.25–6.50 (br, 2H), 6.68–7.25 (m, 22H), 7.50–7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, δ) 0.5, 21.1, 25.1, 61.6, 122.8, 123.9, 125.2, 125.8, 127.0, 127.5, 128.6, 128.7, 129.9, 130.4, 131.1, 137.7, 138.2, 139.5, 145.1, 147.8, 148.2. ^{29}Si NMR ($CDCl_3$, δ) 51.9. MS (EI): m/z 594 (M^+, 37), 579 ($M^+ - Me$, 5), 432 [(tetraphenylnaphthalene)$^+$, 100]. HRMS (EI): m/z found 594.2742; calcd for $C_{44}H_{38}Si$: 594.2743.

11 Compound **8**: colorless crystals (from $CDCl_3$/hexane), mp 243–244 °C (decomposed). ^1H NMR ($CDCl_3$, δ) −0.30 (s, 9H), 2.07 (s, 6H), 2.23 (s, 3H), 6.17–6.28 (m, 2H), 6.66–7.22 (m, 22H), 7.68–7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, δ) 1.4, 21.1, 25.0, 63.1, 123.1, 123.8, 125.3, 125.6, 126.8, 127.0, 128.3, 129.5, 129.6, 130.5, 132.1, 138.1, 138.5, 138.9, 144.6, 148.2, 149.9. ^{29}Si NMR ($CDCl_3$, δ) −15.9, 56.2. MS (EI): m/z 652 (M^+, 19), 579 ($M^+ - SiMe_3$, 29), 432 [(tetraphenylnaphthalene)$^+$, 43], 205 ($MesSiMe_2Si^+$, 100). HRMS (EI): m/z found 652.2982; calcd for $C_{46}H_{44}Si_2$, 652.2982. Crystal data for **8** at 298 K (Bruker SMART-APEX) (CCDC 270942); see Supporting Information.

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15 Compound **9**: white solid, mp 223–224 °C (decomposed). ^1H NMR ($CDCl_3$, δ) 0.60 (t, 3H, J =7 Hz), 0.71 (t, 2H, $J = 7$ Hz), 0.87 (sext, 2H, $J = 7$ Hz), 0.97 (quint, 2H, $J = 7$ Hz), 2.01 (s, 6H), 2.23 (s, 3H), 6.23–6.41 (br, 2H), 6.68–7.22 (m, 22H), 7.54–7.66 (m, 2H). ^{13}C NMR ($CDCl_3$, δ) 13.5, 16.4, 21.1, 24.7, 26.4, 26.6, 62.0, 122.8, 123.9, 125.1, 125.7, 126.9, 127.3, 128.1, 128.5, 129.7, 130.4, 131.4, 137.9, 138.4, 139.2, 145.1, 148.3, 148.4. ^{29}Si NMR ($CDCl_3$, δ) 55.2. MS (EI): m/z 636 (M^+, 71), 579 ($M^+ - Bu$, 31), 432 [(tetraphenylnaphthalene)$^+$, 100]. HRMS (EI): m/z found 636.3211; calcd for $C_{47}H_{44}Si$, 636.3212.

16 Compound **10**: colorless crystals (from $CDCl_3$/hexane), mp 192–193 °C (decomposed). ^1H NMR (C_6D_6, δ) 2.01 (s, 3H), 2.20 (s, 6H), 4.20 (br, 1H), 6.30–6.40 (m, 2H), 6.52–6.90 (m, 13H), 6.92–7.13 (m, 10H), 7.45–7.56 (m, 4H), 7.70–7.79 (m, 2H). ^{13}C NMR (C_6D_6, δ) 21.2, 24.9, 61.6, 118.7, 119.8, 124.3, 125.1, 125.6, 126.5, 127.6, 127.8, 128.1, 128.3 129.0, 129.5, 131.3, 138.6, 139.3, 140.7, 145.1, 146.6, 147.1, 149.3. ^{29}Si NMR (C_6D_6, δ) 21.6. MS (EI): m/z 672 (MH^+, 5), 671 (M^+, 8), 432 [(tetraphenylnaphthalene)$^+$, 100]. Anal. Calcd for $C_{49}H_{41}NSi$: C, 87.59; H, 6.15; N, 2.08%. Found: C, 87.22; H, 6.11; N, 2.48%. Crystal data for **10** at 298 K (Bruker SMART-APEX) (CCDC 270943); see Supporting Information.

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