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π-Cages — Syntheses and Properties of Cyclic Siladiynes and Bicyclic Disilatriynes.[1]

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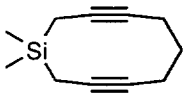
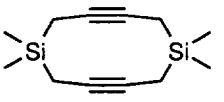
Abstract: The syntheses of 1,1-dimethyl-1-silacyclodeca-3,8-diyne (**1**), 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**2**), 1,6-dimethyl- (**3**) and 1,6-diphenyl-1,6-disilabicyclo[4.4.4] tetradeca-3,8,12-triyne (**4**) are reported.

Cage compounds have fascinated chemists for many years, not only because many of them are highly symmetrical but also because they provide ideal models to study interactions or reactions between sterically fixed functional groups.[2]

In the last few years we have focused our interests on medium-sized cyclic diynes which proved to be excellent models for the study of the interactions of two triple bonds[3] and for the syntheses of superphanes and strained cage compounds.[4] Recently we reported the syntheses of cyclic diynes with a hexamethyldisila-bridge on one side of the ring system.[5] In continuation of this work we report the syntheses of 1,1-dimethyl-1-silacyclodeca-3,8-diyne (**1**), 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diyne (**2**), and the related cage compounds 1,6-dimethyl-1,6-disilabicyclo[4.4.4]tetradeca-3,8,12-triyne (**3**) and the 1,6-diphenyl congener **4**.



1



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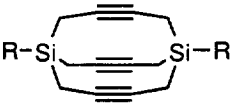
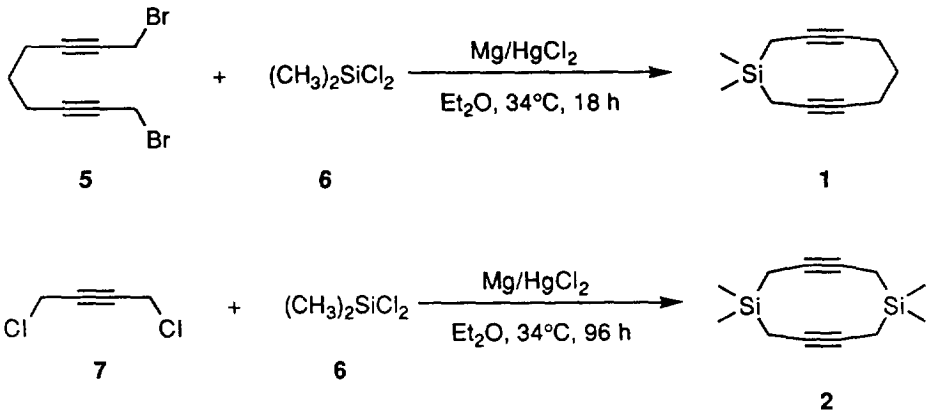


R = CH_3 **3**

R = C_6H_5 **4**

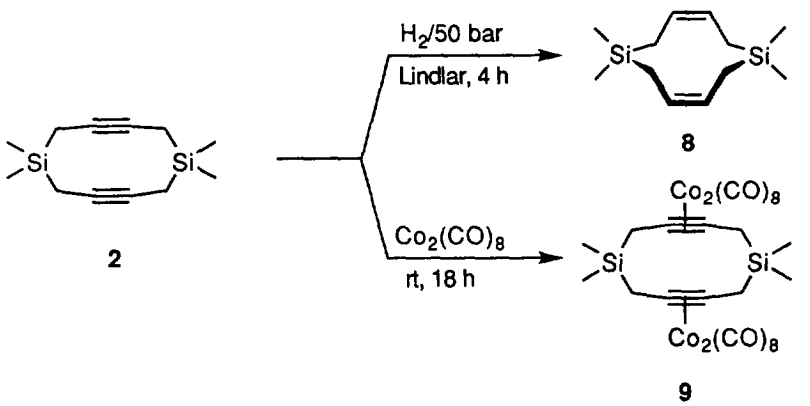
The syntheses of all four compounds could be achieved by a Barbier-type reaction[6] in which an *in situ* generated Grignard reagent reacted with a chlorosilane. In Scheme 1 the synthesis for the cyclic species and in Scheme 3 that for the bicyclic compounds is shown.

Scheme 1



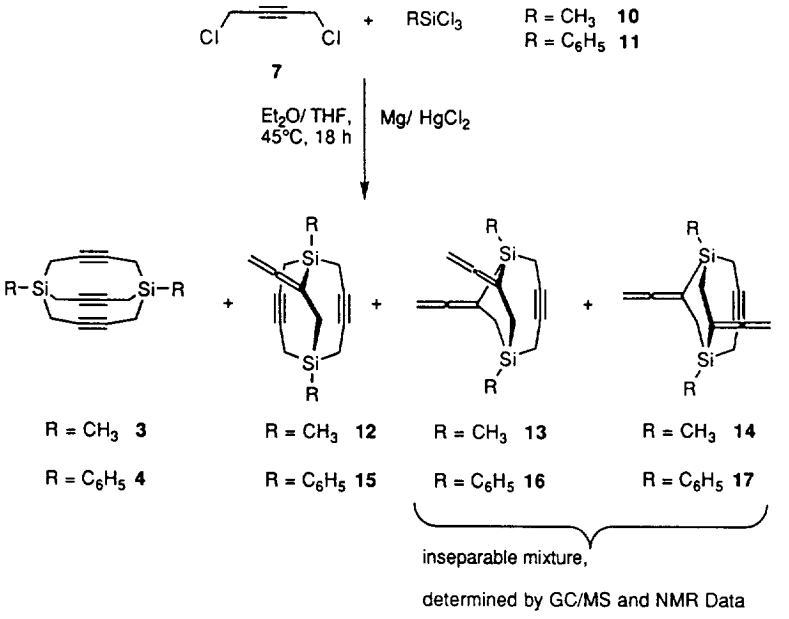
Heating of 1,9-dibromonona-2,7-diyne (**5**)[7] with dimethyldichlorosilane (**6**) in presence of $Mg/HgCl_2$ for 18 h in diethyl ether led to **1**[8] in 5% yield. In an analogous fashion, the heating of 1,4-dichloro-2-butyne (**7**),[9] **6** and Mg / $HgCl_2$ in ether for 96 h gives **2**[8] in 12% yield. As shown in Scheme 2 the ten-membered ring in **2** was hydrogenated to the corresponding diene **8**,[8] it reacted (reluctantly) with Co_2CO_8 to the *bis*(dicobalthexacarbonyl) complex **9**.[8]

Scheme 2



Heating methyltrichlorosilane (**10**) or phenyltrichlorosilane (**11**) with **7** in diethyl ether/THF for 18 h led to the cage compounds **3** and **4** (Scheme 3) in low yield (0.5 - 0.6%). Besides the latter we could identify the side products **12** - **14** and **15** - **17** by NMR spectroscopy (Table 1 and Scheme 3).

Scheme 3



The generation of the isomers **12** - **17** can be rationalized under the assumption that an S_N2' mechanism competes with the S_N2 process in the reaction of the propargyl-Grignard species with R-$SiCl_3$. Compounds **3** and **4** complete the series of new cage-type molecules which we synthesized recently.[10]

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Table 1. Spectroscopic data of 1 - 4, 8, 9 and 12 - 17

1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 6 H), 1.58 (t, 4 H), 1.65 (quintett, 2 H), 2.27 (tt, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -3.55 (q), 6.94 (t), 19.92 (t), 26.29 (t), 79.12 (s), 80.25 (s).

2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 12 H), 1.54 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -3.40 (q), 6.84 (t), 76.17 (s).

3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.12 (s, 6 H), 1.75 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -3.22 (q), 6.73 (t), 76.75(s); HRMS (EI): calcd. 242.0947, found 242.0897.

4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.1 (s, 12 H), 7.3 - 7.4 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.7 (t), 76.9 (s), 128.3 (d), 130.2 (d), 132.9 (d), 134.6 (s); HRMS (EI): calcd. 366.1260, found 366.1283.

8: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 12 H), 1.42 (d, 8 H), 5.28 (t, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -3.06 (q), 15.73 (t), 122.80 (d).

9: ^{1}H NMR (200 MHz, C_6D_6): δ = 0.06 (s, 12 H), 2.29 (s, 8 H); ^{13}C NMR (50 MHz, C_6D_6): δ = -1.89 (q), 25.32 (t), 94.68 (s), 201.00 (s).
12: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 3 H), 0.23 (s, 3 H), 1.4 -1.7 (m, 8 H), 2.0 (t, 2 H), 4.4 (t, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -1.4 (q), - 0.5 (q), 6.8 (t), 6.9 (t), 21.3(t), 68.7 (t), 83.57 (s), 83.64 (s), 92.0 (s), 211.0 (s); HRMS (EI): calcd. 242.0947, found 242.0903.
13/14: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 3 H), 0.21 (s, 3 H), 0.26 (s, 6 H), 1.4 -2.1 (m, 16 H), 4.3 (dd, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = - 4.2 (q), - 3.0 (q), -2.0 (q), 8.0 (t), 8.2 (t), 17.1 (t), 17.2 (t), 68.0 (t), 68.1 (t), 86.77 (s), 86.88 (s), 88.4 (s), 209.6 (s); HRMS (EI): calcd. 242.0947, found. 242.0903.
15: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.7 - 2.2 (m, 8 H), 2.4 (t, 2 H), 4.3 (t, 2 H), 7.3 - 7.5 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 6.0 (t), 6.3 (t), 20.3 (t), 70.0 (t), 83.7 (s), 83.7 (s), 90.1 (s), 127.7 (d),.128.2 (d),.129.7 (d),.129.8 (d),.133.3 (d),.134.1 (d),.135.6 (s), 137.0 (s), 212.1 (s); HRMS (EI): ber. 366.1260, gef . 366.1239
16/17: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.8 -2.3 (m, 16 H), 4.1 - 4.5 (m, 8 H), 7.3 -7.5 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 6.9 (t), 7.0 (t), 7.1 (t), 16.6 (t), 16.7 (t), 69.0 (t), 69.1 (t), 86.9 (s), 87.0 (s), 87.1 (s), 127.5 (d), 127.9 (d), 128.2 (d), 129.8 (d), 129.9 (d), 133.5 (d), 134.1 (d), 134.8 (d), 135.9 (s), 136.5 (s), 137.8 (s), 210.1 (s), 211.0 (s); HRMS (EI): calcd. 366.1260, found 366.1266.

References and Footnotes

1 3rd communication on π-cages. For the 1st and 2nd communication see ref. 10.

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8 Satisfactory elemental analyses were obtained from **1** - **4**, **8** and **9**.

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