

Synthesis and dimerization of 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene. Structure determination of 2,3,12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene by x-ray crystallography

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Synthesis and Dimerization of 2,3-Dimethyl-5-silaspiro[4.4]nona-2,7-diene. Structure Determination of 2,3,12,13-Tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca- 2,7,12,16-tetraene by X-ray Crystallography

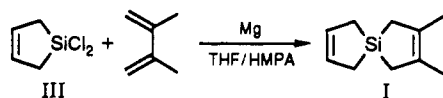
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Unsymmetrical 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene (I) has been prepared by a dissolving-metal reaction between 1,1-dichloro-1-silacyclopent-3-ene (III) and 2,3-dimethyl-1,3-butadiene. Ring-opening reactions of I catalyzed by alkyllithium reagents and hexamethylphosphoramide (HMPA) have been explored. High yields of the dimer 2,3,12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II) are formed in these reactions. The structure of II has been determined by X-ray crystallography. II lies on a crystallographic inversion center. It crystallizes in space group $P\bar{1}$ (triclinic) with unit cell parameters $a = 7.826$ (3) Å, $b = 9.415$ (3) Å, $c = 7.421$ (3) Å, $\alpha = 94.11$ (3)°, $\beta = 114.56$ (3)°, $\gamma = 89.34$ (3)°, $V = 496.0$ (3) Å³, and $Z = 1$.

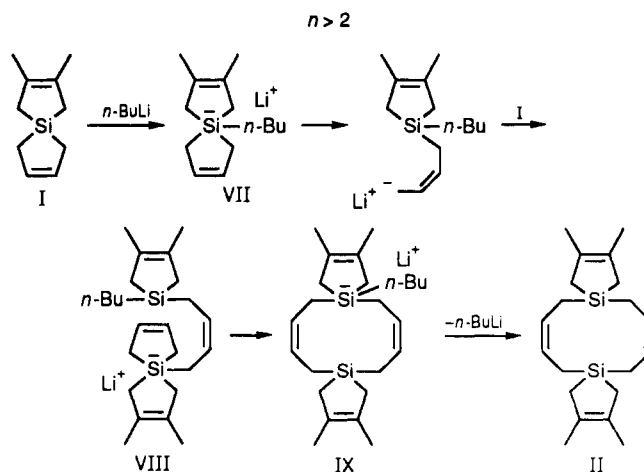
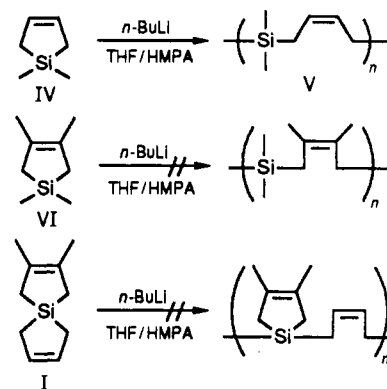
While a few symmetrical 5-silaspiro[4.4]nona-2,7-dienes have been prepared,¹⁻³ no unsymmetrically substituted examples of this ring system are known. We have prepared unsymmetrical 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene (I) by the dissolving-metal reaction of 2,3-dimethyl-1,3-



butadiene with 1,1-dichloro-1-silacyclopent-3-ene (III) and magnesium in THF and HMPA. The recently reported preparation of III from readily available starting materials makes this synthetic route feasible.⁴

We anticipated that treatment of I with catalytic amounts of alkyllithium reagent and HMPA in THF at low temperature would result in a polymer formed by the selective ring opening of the unsubstituted 1-silacyclopent-3-ene ring of I. Such a polymer, poly((3,4-dimethyl-1-silacyclopent-3-en-1-ylene)-*cis*-but-2-en-1,4-ylene), would have 1,4-(*cis*-but-2-ene) units bonded to the silicon atoms of the 3,4-dimethyl-1-silacyclopent-3-ene rings. This expectation was based on our previous work, which has shown that while 1,1-dimethyl-1-silacyclopent-3-ene (IV) undergoes polymerization under these conditions to yield poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (V),⁵ 1,1,3,3-tetramethyl-1-silacyclopent-3-ene (VI) does not.⁶

To our surprise, treatment of I under these conditions led to almost quantitative formation of a dimer, 2,3,12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II). The central ring of II is the first



example of the 1,6-disiladeca-3,8-diene ring system of which we are aware. We believe that II is formed by anionic attack on the silyl center of I by an alkyllithium reagent to form a pentacoordinate hypervalent silicon species (VII). We have no information that would permit us to determine whether VII is an intermediate or a transition state. Ring opening of the unsubstituted ring of VII occurs to generate a *cis*-allyl anion, which reacts with another molecule of I to form a new hypervalent silicate (VIII) species. This process must occur faster than rotation about the partial carbon-carbon double bonds of the *cis*-

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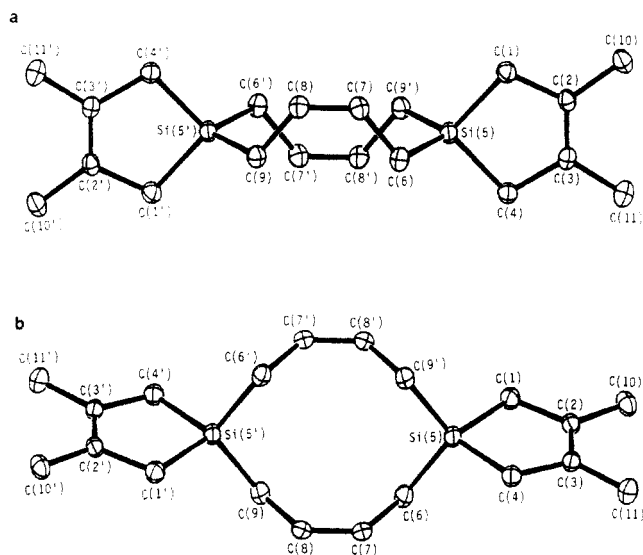


Figure 1. ORTEP diagrams of II: (a) side view; (b) top view.

allyl anion, which would convert it into a *trans*-allyl anion. This appears reasonable since energy barriers of between 10 and 17 kcal/mol have been measured for this type of isomerization process.⁷⁻⁹ Ring opening of the unsubstituted five-membered ring of VIII leads to a new *cis*-allyl anion intermediate that reacts intramolecularly with the other silicon atom of VIII faster than it reacts with another molecule of I. This process forms the central 10-membered ring of II and yields a new hypervalent silicate species (IX), which loses a molecule of alkyllithium to give II. Thus alkyllithium reagents *catalyze* the conversion of I to II. Precipitation of II from the reaction medium (THF) may drive the reaction.

It was not possible to definitely assign the structure of II on the basis of NMR spectroscopy. Thus, ¹H, ¹³C, and ²⁹Si NMR spectra were consistent with two highly symmetrical structures: II and 7,8,16,17-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene. The chemical shifts of the vinyl protons and carbons favor II. In particular, the ¹H NMR signals for the vinyl protons of IV are found at 5.73 ppm, while those for V are found at 5.29 ppm. Similarly, the ¹H NMR resonance for the vinyl protons of I comes at 5.91 ppm, while those for II are found at 5.30 ppm. The ¹³C NMR signals assigned to the vinyl carbons of II are found at 130.58 and 122.92 ppm. These resonances can be compared to the vinyl carbon resonances for IV at 130.74 ppm and that for V, which is found at 123.22 ppm. The ¹³C NMR signals assigned to the nonequivalent vinyl carbons of I are found at 131.16 and 130.87 ppm. Similarly, the vinyl carbon resonance of VI is found at 130.56 ppm. Finally, the ²⁹Si resonance in I is found at 25.54 ppm, while that of the dimer II is observed at 11.87 ppm. This upfield shift is similar in magnitude to that observed when one compares the ²⁹Si NMR resonance of IV at 16.5 ppm to that of V, which is found at 2.17 ppm.

The structure of the dimer was confirmed by X-ray crystallography. II lies on a crystallographic inversion center. The Si-C bonds of II are between 1.872 and 1.878 Å, while the C-C single bonds are between 1.487 and 1.516 Å in length. The C-C double bonds are between 1.325 and 1.327 Å. The C-Si-C bond angle in the five-membered

Table I. Final Atomic Coordinates for 2,3,12,13-Tetramethyl-5,10-disila[4.4.4.4]octadeca-2,7,12,16-tetraene

atom	x	y	z
Si5	0.2718 (1)	0.1925 (1)	0.1046 (1)
C1	0.5295 (3)	0.1823 (2)	0.1654 (4)
C2	0.6007 (3)	0.3338 (2)	0.2349 (3)
C3	0.4776 (3)	0.4342 (2)	0.2257 (3)
C4	0.2721 (3)	0.3908 (2)	0.1493 (4)
C6	0.2106 (3)	0.0975 (2)	0.2840 (4)
C7	0.2255 (3)	-0.0600 (2)	0.2658 (3)
C8	0.0879 (3)	-0.1563 (2)	0.2130 (3)
C9	0.1157 (3)	0.1295 (3)	-0.1585 (4)
C10	0.8087 (4)	0.3575 (3)	0.3070 (5)
C11	0.5233 (4)	0.5891 (3)	0.2839 (4)
H1A	0.554 (3)	0.150 (2)	0.056 (3)
H1B	0.589 (3)	0.121 (2)	0.260 (3)
H4A	0.202 (3)	0.433 (2)	0.035 (3)
H4B	0.2228 (29)	0.4178 (22)	0.2407 (33)
H6A	0.2929 (30)	0.1346 (22)	0.4077 (34)
H6B	0.0891 (31)	0.1256 (22)	0.2689 (31)
H7	0.3457 (30)	-0.0936 (22)	0.2945 (31)
H8	0.1190 (28)	-0.2521 (23)	0.2047 (31)
H9A	0.1371 (28)	0.0324 (24)	-0.1787 (31)
H9B	0.1554 (29)	0.1756 (23)	-0.2340 (32)
H10A	0.8506 (30)	0.3342 (22)	0.2050 (33)
H10B	0.8795 (30)	0.3018 (23)	0.4060 (33)
H10C	0.8473 (29)	0.4569 (24)	0.3444 (32)
H11A	0.4672 (29)	0.6450 (23)	0.1794 (33)
H11B	0.4812 (29)	0.6236 (22)	0.3830 (33)
H11C	0.6522 (31)	0.6095 (22)	0.3408 (32)

Table II. Important Bond Distances (Å) and Angles (deg) for 2,3,12,13-Tetramethyl-5,10-disila[4.4.4.4]octadeca-2,7,12,16-tetraene

Si5-C1	1.878 (2)	Si5-C6	1.874 (2)
Si5-C4	1.872 (2)	Si5-C9	1.877 (2)
C2-C1	1.512 (3)	C7-C8	1.325 (3)
C3-C2	1.327 (3)	C8-C9	1.495 (3)
C3-C4	1.516 (3)	C2-C10	1.501 (3)
C6-C7	1.487 (3)	C3-C11	1.495 (3)
C1-Si5-C4	95.2 (1)	C6-Si5-C4	112.3 (1)
C1-Si5-C9	113.9 (1)	C6-Si5-C9	110.8 (1)
C6-Si5-C1	111.4 (1)	C9-Si5-C4	112.4 (1)
Si5-C1-C2	103.7 (1)	Si5-C6-C7	114.2 (2)
Si5-C4-C3	103.9 (1)		
C1-C2-C10	116.0 (2)	C3-C2-C10	125.4 (2)
C2-C3-C4	118.2 (2)	C4-C3-C11	116.2 (2)
C2-C3-C11	125.6 (2)	C6-C7-C8	127.4 (2)
C3-C2-C1	118.6 (2)		

silacyclopent-3-ene ring is 95.2° (see Tables I and II). For comparison, this is slightly larger than the C-Si-C bond angle of 92.6° that is found in 1,1-dimethyl-2,3,4,5-tetra-phenylsilole.^{10,11}

Experimental Section

X-ray Structure Analysis of II. Crystals suitable for an X-ray structure analysis were grown by cooling a concentrated THF solution of II in a refrigerator. A crystal of dimensions 0.5 × 0.3 × 0.2 mm was used for data collection.

X-ray data were collected at room temperature by using a Nicolet/Syntex P2₁ diffractometer with Mo K α radiation and a maximum 2 θ angle of 50°. The orientation matrix and unit cell parameters were determined from the angular settings of 15 well-centered reflections. Three check reflections showed no significant change in intensity during the period of data collection. A total of 1809 reflections were measured. The data were corrected for Lorentz and polarization effects, but not for absorption, since

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the intensity of an axial reflection showed less than 5% variation as a function of ψ . Details of the crystal data and of structural analysis are summarized in Tables I and II.

Compound II crystallizes in space group $P\bar{1}$ (triclinic) with unit cell parameters $a = 7.826$ (3) Å, $b = 9.415$ (3) Å, $c = 7.421$ (3) Å, $\alpha = 94.11$ (3)°, $\beta = 114.56$ (3)°, $\gamma = 89.34$ (3)°, and $V = 496.0$ (3) Å³. Application of direct methods¹² yielded the position of the silicon atoms; the other non-hydrogen atoms were located from a series of structure factor calculation/difference Fourier calculations. Full-matrix least-squares refinement¹² (including hydrogen atoms whose initial positions were calculated) yielded a final agreement factor of 3.3% for 1478 nonzero reflections ($I > 3\sigma(I)$). Unit weights were used in the least-squares refinement. For details of the X-ray structure and its determination, see the supplementary material.

¹H, ¹³C, and ²⁹Si NMR spectra were recorded on an IBM-Bruker 270-SY or Bruker AM-360 spectrometer operating in the Fourier transform mode. ¹³C NMR spectra were run with broad-band proton decoupling. A DEPT pulse sequence was used to obtain ²⁹Si NMR spectra. This was effective since all the silicon atoms have at least one methylene group bonded to them.¹³ Identical ²⁹Si NMR spectra could be obtained by use of a heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 30 s.¹⁴ ¹³C and ²⁹Si NMR spectra were obtained on 10–15% solutions in chloroform-*d*. ¹H NMR spectra were obtained on 5% solutions. Chloroform was utilized as an internal standard for ¹H and ¹³C NMR spectra. ²⁹Si NMR spectra were externally referenced to TMS.

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer. Spectra of oils were taken as neat films on NaCl plates. IR spectra of solids were taken as KBr pellets.

Low-resolution mass spectra were obtained on a Finnigan Mat Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer. High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Tetrahydrofuran (THF) was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over activated 4-Å molecular sieves. 2,3-Dimethyl-1,3-butadiene and active magnesium powder were purchased from Aldrich Chemical Co., Inc.

All glassware was dried overnight in an oven at 120 °C. It was assembled and was flame-derived under an atmosphere of purified argon. All reactions and transfers were conducted under an atmosphere of purified argon.

2,3-Dimethyl-5-silaspiro[4.4]nona-2,7-diene (I). In a 500-mL three-neck round-bottom flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar was placed magnesium powder (2.48 g, 0.1 mol), 2,3-dimethyl-1,3-butadiene (8.4 g, 0.1 mol), THF (63 mL), and HMPA (17 mL).¹⁵ The flask and its contents were cooled to 0 °C. III (10.4 g, 68 mmol)⁴ and THF (20 mL) were placed

in the addition funnel. This solution was added dropwise to the vigorously stirred suspension of magnesium powder over 1 h. The reaction mixture was warmed to room temperature and was stirred for 72 h. Pentane (100 mL) was added. Saturated aqueous ammonium chloride (100 mL) was then added dropwise with vigorous stirring. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and filtered. The organic solvents were removed by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. The residue was transferred to a smaller flask, and the distillation was continued under reduced pressure. A fraction with bp 108–110 °C (11 mm) was obtained (4.4 g, 40% yield). It had the following properties. ¹H NMR (δ): 1.45 (d, 4 H, $J = 1.0$ Hz), 1.51 (d, 4 H, $J = 1.1$ Hz), 1.72 (t, 6 H, $J = 1.0$ Hz), 5.91 (t, 2 H, $J = 1.0$ Hz). ¹³C NMR (δ): 16.54, 19.18, 24.13, 130.87, 131.16. ²⁹Si NMR (δ): 25.54. IR (ν): 3020, 2970, 2890, 2880, 1605, 1440, 1395, 1205, 1175, 1090, 940, 820, 760, 725, 615 cm⁻¹. GC/MS (m/e (relative intensity)): 166 (3.5), 165 (12.9), 164 (82.4) [M]⁺, 149 (4.0) [M - 15]⁺, 136 (4.4), 123 (3.2), 122 (10.0), 112 (3.7), 111 (12.6), 110 (100.0) [M - C₄H₆]⁺, 97 (4.0), 96 (9.8), 95 (83.2) [M - C₄H₆ - 15]⁺, 84 (2.1), 82 (25.6) [M - C₆H₁₀]⁺, 71 (2.2), 70 (3.7), 69 (17.2), 68 (8.9), 67 (28.3), 66 (5.8), 65 (2.7), 59 (1.7), 58 (1.8), 57 (3.5), 56 (5.3), 55 (34.7), 54 (16.5), 53 (26.8), 51 (2.5), 50 (1.1). High-resolution MS (m/e): calcd for C₁₀H₁₆Si, ([M]⁺) 164.1021; found, 164.1023. Anal. Calcd for C₁₀H₁₆Si: C, 73.09; H, 9.82. Found: C, 72.59; H, 10.20.

Reaction of I with *n*-Butyllithium. I (1.5 g, 9.1 mmol), THF (40 mL), and 30 μ L of HMPA were placed in a flame-dried 100-mL Schlenk flask equipped with a Teflon-covered magnetic stirring bar. The flask was sealed with a rubber septum and was cooled to -78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M, 100 μ L, 0.25 mmol) was added slowly to the well-stirred reaction mixture, which became yellowish and milky. The reaction mixture was stirred for 3 h. It was quenched by addition of 10 mL of saturated aqueous ammonium chloride while the solution was maintained at -78 °C. Ether (300 mL) was added to dissolve the product. The organic layer was washed with water (3 × 50 mL), dried over anhydrous calcium chloride, and filtered, and the volatile organic solvents were removed by evaporation under reduced pressure. In this way, 1.45 g (97% yield) of II was obtained. It was recrystallized from hot THF; mp 160–162 °C. It had the following spectral properties. ¹H NMR (δ): 1.38 (d, 8 H, $J = 0.9$ Hz), 1.56 (d, 8 H, $J = 6.6$ Hz), 1.69 (s, 12 H), 5.30 (d of d, 4 H, $J = 6.8$ and 0.9 Hz). ¹³C NMR (δ): 14.06, 19.34, 22.99, 122.92, 130.58. ²⁹Si NMR (δ): 11.87. IR (KBr, ν): 2996, 2973, 2943, 2909, 2884, 2869, 2775, 1635, 1439, 1408, 1393, 1375, 1366, 1268, 1178, 1151, 1124, 1055, 1025, 986, 932, 766, 730, 694, 685, 672, 636 cm⁻¹. GC/MS (m/e (relative intensity)): 330 (3.9), 329 (11.7), 328 (40.7) [M]⁺, 274 (2.7), 273 (6.7), 272 (4.2), 246 (2.5), 245 (4.9), 244 (2.6), 218 (1.0), 166 (4.0), 165 (11.2), 164 (62.7) [C₁₀H₁₆Si]⁺, 163 (3.6), 151 (1.5), 150 (2.6), 149 (7.2), 147 (1.5), 138 (3.6), 137 (15.1), 136 (12.0), 135 (5.8), 125 (1.9), 124 (3.5), 123 (13.5), 122 (17.4), 121 (7.2), 113 (1.1), 112 (4.9), 111 (21.0), 110 (100.0) [C₆H₁₀Si]⁺, 109 (37.5), 108 (11.0), 97 (4.7), 96 (6.1), 95 (47.9), 94 (3.9), 84 (2.4), 83 (12.7), 82 (15.4), 71 (3.3), 70 (2.5), 69 (14.2), 68 (3.1), 67 (10.2), 58 (1.5), 57 (1.3), 56 (0.6), 55 (12.2), 54 (3.1). High-resolution MS (m/e): calcd for C₂₀H₃₂Si₂ ([M]⁺): 328.2042; found, 328.2036. Anal. Calcd for C₂₀H₃₂Si₂: C, 73.09; H, 9.81. Found: C, 73.30; H, 9.98.

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Supplementary Material Available: Listings of crystal data and refinement results, temperature factors, and bond distances and angles involving H atoms (4 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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