Preparation and Structure of Alkenyl- and Alkynyl-Substituted Polysila-modules HC(SiMe$_2$SiMe$_3$)$_3$CR

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This paper is dedicated to Professor Teruaki Mukaiyama on the occasion of his 77th birthday.

Abstract: Facile methods for the introduction of alkenyl and alkynyl groups at the bridgehead position of polysilamodule HC(SiMe$_2$SiMe$_3$)$_3$CH are established. Deprotonation of the module with BuLi/–BuOK in THF at $-40\,^\circ\text{C}$ followed by alkylation with bromoacetalddehyde diethyl acetal gives the corresponding acetal, which was hydrolyzed with zinc chloride, yielding a formylmethyl-substituted cage compound. Treatment of the aldehyde with triflic anhydride in the presence of 2,6-di-bromo-4-methylpyridine produced the corresponding enol triflate containing a 4:1 mixture of $E$ and $Z$ isomers. Palladium-catalyzed cross-coupling of the triflate with organometallic reagents afforded alkenyl group-substituted cage molecules in good yields. Meanwhile, lithiation of phenylthio-substituted cage derivative with lithium and subsequent coupling with iodoalkynes allowed us to prepare alkynyl-substituted polysilacage compounds. The structures were determined by X-ray diffraction of single crystals.

Key words: silicon, cage compounds, bicyclo[2.2.2]octane, alkenyl, alkynyl

Since $\pi$-electrons of Si–Si bonds in polysilanes can delocalize, compounds containing Si–Si bonds show unique electronic and optical properties resulting from the delocalization of $\pi$-electrons. Exploration of new silicon-based organic materials has led us to design 2,3,5,6,7,8-hexaethyltricyclo[2.2.2]octane 1 which bundles three parallel Si–Si bonds in a three-dimensional manner and to achieve its facile synthesis (Figure 1). Bridgehead-silylated or -stannylated derivative 2 or 3 exhibited a red shift of UV absorption maxima compared to parent compound 1, while $\sigma$–$\pi$ electronic interaction between the polysilacage moiety and a phenyl group at the bridgehead position was found operative by UV spectra of arylated derivatives C$_2$H$_{2n+1}$C(SiMe$_2$SiMe$_3$)$_3$CAR. To gain further insights into $\sigma$–$\pi$ conjugation between the cage moiety and a $\pi$-conjugated system at the bridgehead position, it is intriguing to connect a $\pi$-conjugated moiety to the polysilacage module via a carbon-carbon unsaturated group. We report herein the facile synthesis of alkenyl- and alkynyl group-substituted polysilacage compounds 5 and 6, respectively, and their molecular structures determined by X-ray diffraction analysis.

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At the outset, we studied the introduction of a carbon-carbon double bond into 1. Since nucleophilic substitution at an sp$^2$ carbon is generally difficult to perform, we designed an indirect strategy for the purpose. Thus, 1 was first deprotonated with BuLi/t-BuOK in THF at $-40\,^\circ\text{C}$ and trapped with bromoacetalddehyde diethyl acetal, giving rise to acetal 7 in 70% yield (Scheme 1). Hydrolysis of 7 with zinc chloride gave formylmethyl-substituted cage compound 8 in 87% yield. Treatment of 8 with triflic anhydride in the presence of 2,6-di-tert-butyl-4-methylpyridine produced enol triflate 9 consisting of a 4:1 mixture of $E$ and $Z$ isomers in 74% yield. Since recrystallization of 9 from hexane afforded $E$-isomer (mp 175.5–176.5 °C) as single crystals, the structure was confirmed by X-ray diffraction analysis.

With 9 in hand, we next studied cross-coupling reaction of 9 with phenylmetal reagent in the presence of Pd(PPh$_3$)$_4$ (Equation 1). The optimization results are summarized in Table 1. Phenylboronic acid reacted with only $(E)$-9 to...
give (E)-styril substituted cage compound 10 in 50% yield based on reacted (E)-9 (entry 1). Triflate (Z)-9 was completely recovered, indicating that oxidative addition of a Pd metal to (Z)-9 was inhibited probably due to a heavy steric hindrance. Phenylzinc chloride and phenylmagnesium bromide gave better results (entries 2 and 3), whereas no compound 10 formed when phenyllithium was employed (entry 4). In this reaction allylde 8 was produced as a sole product. In all cases, (Z)-9 always remained unchanged.

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\text{Equation 1}
\]

The molecular structure of 10 was confirmed by X-ray structure analysis of single crystals obtained by recrystallization from hexane (Figure 2). The C(2)–C(3) bond length (1.278 Å) was much shorter than the average length of C=C bonds (1.34 Å). The bond angles of C(1)–C(2)–C(4) and C(3)–C(2)–C(3)–C(4) were 132.3(2)° and 128.4(2)°, respectively, which were larger than an ideal bond angle of an sp² carbon (120°), probably due to steric repulsion between methyl groups on three silicon atoms and the alkenyl group. The co-planarity of C=C and the phenyl group was confirmed from the dihedral angle of C(2)–C(3)–C(4)–C(5) being 175°. It is noteworthy that the π-plane of the styryl group is almost perpendicular to the C(1)–Si(2) bond of the cage moiety, apparently resulting from a favored conformation for the σ-π conjugation.

When the coupling conditions were applied to the introduction of biphenylyl- and 4-(phenylethynyl)phenyl groups, cage compounds 11 and 12 were obtained in moderate to good yields (Scheme 2).

In brief, we have established a four-step protocol for the incorporation of a C=C group into a bridgehead position of 1, which involves alkylation, hydrolysis, enolization, and Pd-catalyzed cross-coupling reaction.

Next, alkynylation of 1 was examined. As tert-ButLi or carboranyl copper was reportedly alkynylated in one step by treatment of the reagent with phenyl phenylethynyl sulfone or bromoalkyne, respectively, we studied the reaction of hexasilabicyclo[2.2.2]octan-1-yl lithium (14) and -copper (15) with phenylethynyl halides or sulfones 16. Thus, 14 was first generated by reductive lithiation of 1-phenylthio-substituted cage 13 with lithium 4,4′-di-tert-butylbiphenylide in THF at –50 °C. Treatment of 14 or 15 with 13 at –30 °C followed by heating at reflux in THF gave the desired alkynylated cage compound 17. Results are summarized in Table 2. Reaction of 14 with 16a (X = SO₂Ph) produced traces of 17, while 14 was alkynylated with 16b (X = SO₂CF₃) to give 17 in 11% yield (entries 1 and 2). Use of 16c (X = I) resulted in the production of a complex mixture (entry 3). In order to improve the yield of 17, hexasilabicyclo[2.2.2]octan-1-yl-copper (15) was prepared by adding CuI to a THF solution of 14 at –78 °C. The resulting mixture was warmed to 0 °C, treated with 16, and heated at 60 °C. With 16b or 16d, alkynylation of 15 proceeded in a similar way in 11% or 8% yield, respectively (entries 4 and 6). On the other hand, the yield of 17 was slightly improved when 16c or alkynylphenyldionium salt 16e (X = Ph) was employed as an electrophile (entries 5 and 7). Changing the counter anion of the copper salt from iodide to chloride or bromide was not effective enough (entries 8 and 9).

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An ORTEP drawing of 17 is shown in Figure 3.11 The bond angles of C(1)–C(2)–C(3) and C(2)–C(3)–C(4) were 178.83(13)° and 177.21(13)°, respectively, indicating that the carbon-carbon triple bond was almost linear. The average bond length of silicon-silicon bonds in 17 was 2.365 Å, slightly shorter than the average bond length in 1 (2.370 Å), suggesting that substitution of an alkynyl group at the bridgehead position of 1 made the cage framework more rigid. The plane of the phenylethynyl group was found almost perpendicular to the C(1)–Si(4) bond as observed in 10.

This alkynylation method utilizing cage-copper reagent 15 is applicable to 1-iodo-2-trimethylsilylacetylene, giving rise to 18, although the yields remain yet to be improved in further study (Equation 2).

In summary, we have established facile ways for the introduction of carbon-carbon unsaturated groups into polysilacagemodule 1. Studies of photophysical properties of alkenyl- and alkynyl-substituted modules are in progress and will be reported in due course.

All temperatures were not corrected. Melting points were determined using a YANAKO MP-500D apparatus. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). 1H NMR spectra were measured on a Varian Mercury 200 (1H, 200 MHz) spectrometer. Chemical shifts of 1H NMR data are expressed in ppm downfield relative to an internal Me 4Si (δ = 0 ppm) or CDCl3 (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet. 13C NMR spectra were measured on a Varian Mercury 200 (13C, 50 MHz) and JEOL JMN ECP-500 (13C, 125 MHz) spectrometer with Me4Si as an internal standard (δ = 0 ppm). IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. FAB-MS analyses were performed with a JEOL JMS-HX110A spectrometer using 3-nitrobenzyl alcohol or thioglycerol as matrix. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. TLC analyses were performed by means of Merck Kieselgel 60 F254 and Rf values were given. Column chromatography on silica gel was carried out using Wakogel C-200. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAI-GEL-1H and -2H columns (CHCl3 was used as an eluent). Cooling a reaction vessel at –78 °C and –40 °C was effected using acetone with dry ice. Ethereal solvents like THF, and Et2O were distilled from benzophenone and Na under an argon atmosphere.

Entry CuX’ 16 X Yield (%)  
1 – 16a SO2Ph Trace  
2 – 16b SO2CF3 11  
3 – 16c I Complex mixture  
4 CuI 16b SO2CF3 11  
5 CuI 16c I 26  
6 CuI 16d Br 8  
7 CuI 16e I+Ph–OTs 24  
8 CuCl 16c I 18  
9 CuBr 16c I 12
with N-pivaloyl-o-toluidine as an indicator. X-ray crystal structure analyses were carried out using a Bruker SMART APEX CCD diffractometer with Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods on F² with the SHELXL-97. Absorption corrections were applied with SADABS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and placed in idealized positions.

1-(2,2-Diethoxyethyl)-2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (7)

To a solution of 2,3,5,6,7,8-hexasilabicyclo[2.2.2]oct-1-yl)acetaldehyde (8) or 2,2,3,3,5,5,6,6,7,7,8,8-Dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]oct-1-yl)acetaldehyde (8) was added n-BuLi (1.51 M solution in hexane, 2.7 mL, 4.0 mmol) at –40 °C. The mixture was stirred at –40 °C for 1 h before adding a THF solution of bromoacetaldehyde diethyl acetal (0.24 mL, 1.5 mmol) at r.t. After being stirred for 30 min at r.t., the mixture was treated with a solution of NaHCO₃ (1.2 mmol) at r.t. The resulting mixture was refluxed for 2 h, concentrated in vacuo, and washed with hexane. The filtrate was neutralized with cold 1 M HCl, washed with sat. aq NaCl solution, and treated with sat. aq NaCl solution. The organic layer was separated, dried over anhyd K₂CO₃, and concentrated. The resulting crude product was purified by column chromatography on neutral alumina (hexane) to afford 9 (560 mg, 74% yield, E.Z = 4:1) as a colorless solid. Recrystallization of 9 from hexane gave the E isomer as single crystals.

Mp 175.5–176.5 °C; Rf isomer 0.60 (hexane, Al₂O₃); Z isomer 0.53 (hexane, Al₂O₃).

IR (KBr): 2982, 2945, 2897, 2361, 1423, 1258, 1205, 1104, 1069, 1003, 972, 812, 681, 586 cm⁻¹.

1H NMR (200 MHz, CDCl₃): δ = –0.05 (s, 1 H, CH), 0.19 (s, 18 H, SiMe₂), 0.24 (s, 18 H, SiMe₂), 5.98 (d, J = 12.0 Hz, 1 H, CH), 6.39 (d, J = 12.0 Hz, 1 H, CH): Z isomer δ = –0.05 (s, 1 H, CH), 0.21 (s, 18 H, SiMe₂), 0.24 (s, 18 H, SiMe₂), 5.07 (d, J = 6.2 Hz, 1 H, CH), 6.65 (d, J = 6.2 Hz, 1 H, CH).

13C NMR (50 MHz, CDCl₃): δ = 47.9 (SiCH₃), 47.9 (C), 134.2 (CH), 147.2 (CF₃).

HRMS (FAB): m/z (%) = 533 (M⁺ – Me, 4), 73 (100). MS (FAB): m/z (%) = 533 (M⁺ – Me): 533.0953; found: 533.0948.

Si NMR (54 MHz, CDCl₃): δ = –19.3, –21.2.

HRMS (FAB): m/z calc'd for C₁₆H₃₆F₃O₃SSi₆ (M⁺ – Me): 533.0953; found: 533.0948.

2,2,3,3,5,5,6,6,7,7,8,8-Dodecamethyl-1-[(E)-styryl]-2,3,5,6,7,8-hexasilabicyclo[2.2.2]oct-1-ylacetaldehyde (8)

A THF solution of ZnCl₂ (0.5 M in THF, 14.4 mL, 7.2 mmol) was added to a THF solution of tert-ButOK (450 mg, 4.0 mmol) in THF (13 mL) and was washed with sat. aq NaHCO₃ solution, treated with sat. aq NaCl solution, and dried over anhyd MgSO₄. Removal of the organic solvent with a rotary evaporator under reduced pressure followed by column chromatography on silica gel (hexane–CH₂Cl₂, 2:1) gave 8 (370 mg, 70% yield) as a colorless solid.

HRMS (FAB): m/z (%) = 418 (M⁺ + 2.4, 417 (M⁺ + 1.8), 416 (M⁺, 3), 401 (13), 73 (100).

HRMS (FAB): m/z (%) = 416.1695; found: 416.1693.

1H NMR (200 MHz, CDCl₃): δ = –0.05 (s, 1 H, CH), 0.23 (s, 18 H, SiMe₂), 0.24 (s, 18 H, SiMe₂), 6.34 (d, J = 6.0 Hz, 1 H, CH), 6.45 (d, J = 16.0 Hz, 1 H, CH), 7.20–7.26 (m, 5 H, H₅) ppm.

13C NMR (50 MHz, CDCl₃): δ = 6.0 (SiCH₃), 1.0 (CH), 33.9 (SiCH₃), 3.4 (C), 125.3 (C₅), 126.0 (C₅), 128.9 (CH), 130.0 (C₅), 139.2 (C₅).

Si NMR (54 MHz, CDCl₃): δ = –21.0, –21.4.

MS (FAB): m/z (%) = 479 (M⁺ + 3.6, 478 (M⁺ + 2.10), 477 (M⁺ + 1.4, 144, 476 (M⁺, 15), 73 (100).

HRMS (FAB): m/z calc'd for C₁₃H₂₆O₃Si₆: 476.2059; found: 476.2050.
1-[E]-2-Biphenyl-4-ylvinyl]-2,2,3,3,5,5,6,6,7,7,8,8-dodecamethyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane (17)
Prepared from 9 with 2-biphenyl-4-ylmagnesium bromide or -zinc chloride by the same procedure for the preparation of 10 in 55% (16 mg) or 74% (21 mg) yield, respectively; colorless solid.

Mp 219.1–222.0 °C; Rf 0.76 (hexane–EtOAc, 4:1, SiO2).

IR (KBr): 2980, 2943, 2895, 1612, 1254, 1049, 966, 812, 760, 679, 590, 540 cm−1.

1H NMR (200 MHz, CDCl3): δ = −0.06 (s, 1 H, CH), 0.24 (s, 18 H, SiMe2), 0.26 (s, 18 H, SiMe2), 6.38 (d, J = 16.0 Hz, 1 H, CH), 6.52 (d, J = 16.0 Hz, 1 H, CH), 7.32–7.78 (m, 9 H, H arom).

13C NMR (250 MHz, CDCl3): δ = 0.3 (SiCH3), 1.2 (CH), 3.3 (SiCH3), 3.4 (C), 125.7 (Carom), 126.4 (CH), 126.86 (Carom), 126.96 (Carom), 127.02 (C arom), 127.2 (C arom), 128.4 (CH), 128.7 (C arom), 130.4 (C arom), 130.6 (C arom).

29Si NMR (54 MHz, CDCl3): δ = −21.0, −21.4.

MS (FAB): m/z (%) = 555 (M+ + 3, 13), 554 (M+ + 2, 24), 553 (M+ + 1, 41), 552 (M+, 45), 537(15), 77 (11), 73 (100).


1H NMR (200 MHz, CDCl3): δ = −0.01 (s, 1 H, CH), 0.12 (s, 9 H, SiMe3), 0.20 (s, 18 H, SiMe2), 0.22 (s, 18 H, SiMe2).

13C NMR (67.5 MHz, CDCl3): δ = 0.8 (SiCH3), 11.9 (CH), 79.3 (C arom), 81.5 (C arom), 106.7 (C arom), 128.0 (Carom), 131.6 (C arom). 

Si NMR (54 MHz, CDCl3): δ = −21.8, −21.5.

MS (FAB): m/z (%) = 479 (M+ + 5, 1), 478 (M+ + 4, 4), 477 (M+ + 3, 9), 476 (M+ + 2, 23), 475 (M+ + 1, 43), 474 (M+, 76), 459 (100), 401 (78), 73 (58).


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References


(5) Crystallographic data of (E)-9 have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 236989.
(7) Nickel-catalyzed reaction of phenylmagnesium bromide with 9 turned out futile: the reason is not clear.
(8) Crystallographic data of 10 have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 236990: colorless plates: C_{22}H_{44}Si_{6}, M = 477.10, monoclinic, space group P2 \( \bar{1} \)/c, \( a = 16.0000(9), b = 9.4196(5), c = 19.8143(11) \) Å, \( \beta = 106.4620(10)^\circ \), \( V = 2880.0(3) \) Å\(^3\), \( Z = 5 \), \( D_{calc} = 1.375 \) g/cm\(^3\), \( F(000) = 1300 \), \( T = 293 \) K, \( \lambda(Mo-K_\alpha) = 0.71073 \) Å, \( 2\theta_{max} = 54.0^\circ \), \( R_1 = 0.0481 \), \( wR_2 = 0.1208 \), Goodness of fit = 0.895; Number of data = 22549, Number of unique data = 8057 (\( R_{int} = 0.0281 \)).
(10) Since alkynylation at the bridgehead position of adamantane with 16b proceeds in 1,2-dichloroethane at a reflux temperature in the presence of AIBN in 60% yield, 1 was treated with 16b under the same conditions with the results of no reaction: Gong, J.; Fuchs, P. L. J. Am. Chem. Soc. 1996, 118, 4486.
(11) Crystallographic data of 17 have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 236991: colorless prisms: C_{22}H_{42}Si_{6}, M = 475.08, monoclinic, space group P2 \( \bar{1} \)/c, \( a = 15.3584(10), b = 9.6527(6), c = 20.1968(13) \) Å, \( \beta = 110.8280(10)^\circ \), \( V = 2798.5(3) \) Å\(^3\), \( Z = 5 \), \( D_{calc} = 1.128 \) g/cm\(^3\), \( F(000) = 1032 \), \( T = 293 \) K, \( \lambda(Mo-K_\alpha) = 0.71073 \) Å, \( 2\theta_{max} = 54.0^\circ \), \( R_1 = 0.032, wR_2 = 0.087 \), Goodness of fit = 1.036; Number of data = 21622, Number of unique data = 7860 (\( R_{int} = 0.0192 \)).