Organometallics 1992, *11*, 3464-3468

Table I. ^{1}H NMR (400 MHz, Toluene-d_8, −90 °C) Data for Compound 7

	isomers			
	7a	7b	7c	7d
$(CH_3)_2Sn$				
δ[a]	−0.94, −0.31	−0.25, −0.16	−0.96, 0.27	−0.02, 0.01
$^2J(^{119/117}Sn–^1H)$, Hz	53.5, 54.4	53.7, 53.1	52.8, 53.2	b
$(CH_3)_3C$				
δ[a]	1.30	1.35	1.34	b
$(CH_3)_2C$				
δ[a]	~1.59, 1.81	~1.80, 1.64	1.58, 1.47	b
H–C(3a), H–C(4a)				
δ[c]	3.77, 3.93	3.49, 3.70	3.60, 3.88	b
$^2J(^{119/117}Sn–^1H)$, Hz	97.0, 92.5	97.4, 93.1	b	b
H (Cp)				
δ[d]	5.65–6.65			

[a] Singlet. [b] Cannot be measured. [c] Broadened multiplet. [d] Group of overlapping multiplets.

warmed to room temperature, the solution was decanted, THF and hexane were removed, and the resultant brownish red oil was extracted with pentane three times. On removal of pentane and distillation 6.25 g of a yellowish oil was obtained: bp 110 °C/5 × 10^{-2} mmHg; yield 60.5%. Anal. Calcd for $C_{19}H_{28}Sn$: C, 60.83; H, 7.52. Found: C, 60.57; H, 7.61. ^{1}H NMR (400 MHz, toluene-d_8, 26 °C): δ 6.29–6.23 (m, 3 H); 5.87–5.86 (m, 2 H); 5.40–4.70 and 4.15–3.85 (very br signals, 2 H); 1.58 (s, 3 H); 1.41 (s, 3 H); 1.19 (s, 9 H); 0.31, 0.06, −0.53, −0.54 (br s, 6 H). ^{1}H NMR at −90 °C: see Table I.

Compound 4. A solution of 1.44 g (4.51 mmol) of 1 and 1.24 g (4.51 mmol) of $BrMn(CO)_5$ in 20 mL of THF was mixed at room temperature over 12 h. The gaseous products were removed periodically. After THF was removed, the resultant oil was treated with pentane to give 4 as a crystalline precipitate: yield 2.25 g (93%). Anal. Calcd for $C_{18}H_{20}BrMnO_3Sn$: C, 40.19; H, 3.75. Found: C, 40.35; H, 3.63. ^{1}H NMR (400 MHz, THF-d_8, 27 °C): δ 6.43 (m, 2 H); 5.37 (m, $^2J_{H-Sn}$ = 56.5 Hz, 2 H); 4.98 (m, 2 H); 4.64 (m, 2 H); 1.49 (s, 6 H); 0.52 (s, 6 H). ^{13}C NMR (100 MHz, THF-d_8, 27 °C): δ 226.43; 153.78; 125.82; 116.42; 93.47 ($^1J_{C-Sn}$ = 59.2 Hz); 85.12; 80.82; 35.83; 29.96; −1.41.

Compound 8. The reaction was performed similarly to that described above. Above 0.73 g (1.95 mmol) of 7 and 0.54 g (1.95 mmol) of $BrMn(CO)_5$ 1.05 g of orange oil 8 was obtained (yield 91%). All attempts to crystallize the product failed. Anal. Calcd for $C_{22}H_{28}BrMnO_3Sn$: C, 44.49; H, 4.75. Found: C, 44.11; H, 4.69. ^{1}H NMR (400 MHz, THF-d_8, 27 °C): δ 6.55 (m, 1 H); 6.50 (m, 1 H); 5.03 (m, 1 H); 4.98 (m, 1 H); 4.78 (m, 1 H); 4.68 (m, 2 H); 1.51 (s, 3 H); 1.49 (s, 3 H); 1.21 (s, 9 H); 0.61 (br s, 3 H); 0.55 (br s, 3 H). ^{13}C NMR (100 MHz, THF-d_8, 27 °C): δ 226.38; 156.76; 153.37; 124.72; 116.51; 102.67; 85.25; 85.12; 80.82; 80.60; 36.11; 33.39; 31.67; 30.41; 29.75; 0.47; −0.31.

OM910717I

Reactions of 2-Lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with Benzaldehyde, Benzoyl Chloride, and Benzonitrile

Dietmar Seyferth* and Jennifer L. Robison

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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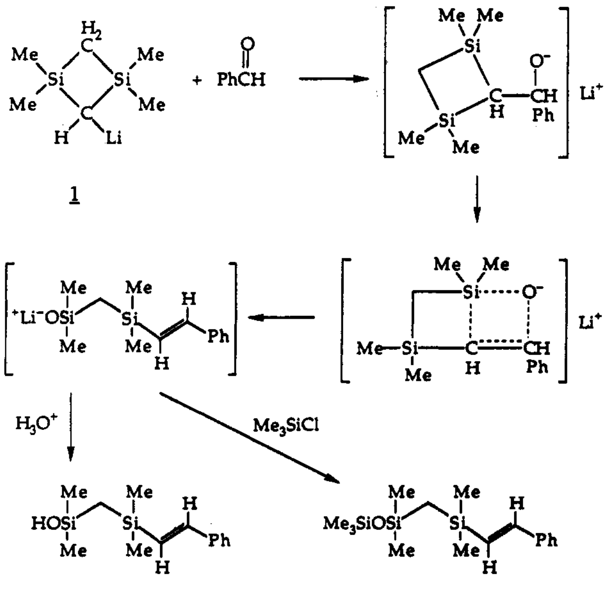
Summary: Reaction of the title cyclic organolithium compound with benzaldehyde gave a ring-opened product. With benzoyl chloride the expected ketone was produced (which underwent ring expansion rearrangement when heated to 140 °C). Reaction of the title organolithium compound with benzonitrile resulted in isolation of a ring-expanded product. The latter, when heated to 140 °C, underwent a ring contraction rearrangement.

Introduction

The reactions of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (1) with benzaldehyde, benzoyl chloride, and benzonitrile, followed by hydrolytic workup (or methanolic workup in the case of PhCN), gave ring-opened or ring-expanded products.[1] In the case of the 1/PhCHO reaction a modified Peterson olefination process appears to be involved (Scheme I). The reaction of 1 with PhC(O)Cl most likely involved initial formation of the β-ketosilane which then underwent a modified Brook rearrangement to give the ring-expanded product (Scheme II). The course of the 1/PhCN reaction is believed to involve first addition to the C≡N bond. Anionic rearrangement, as shown in Scheme III, then gives the six-membered cyclic lithium

Scheme I



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(1) Seyferth, D.; Robison, J. L.; Mercer, J. *Organometallics* 1990, *9*, 2677.

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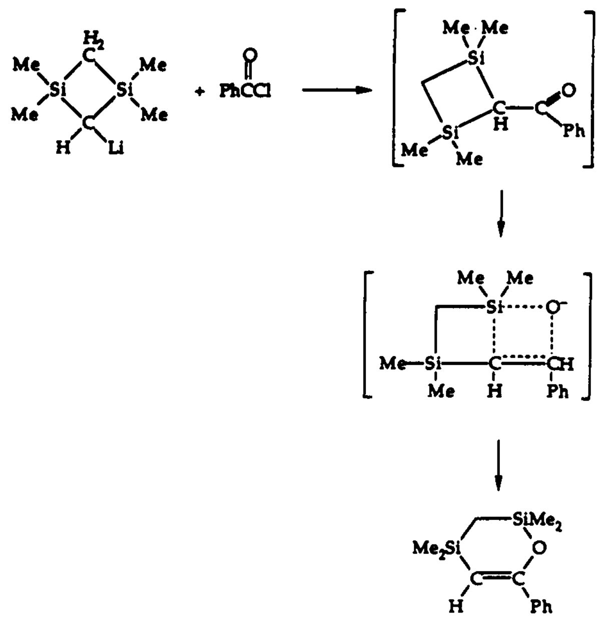
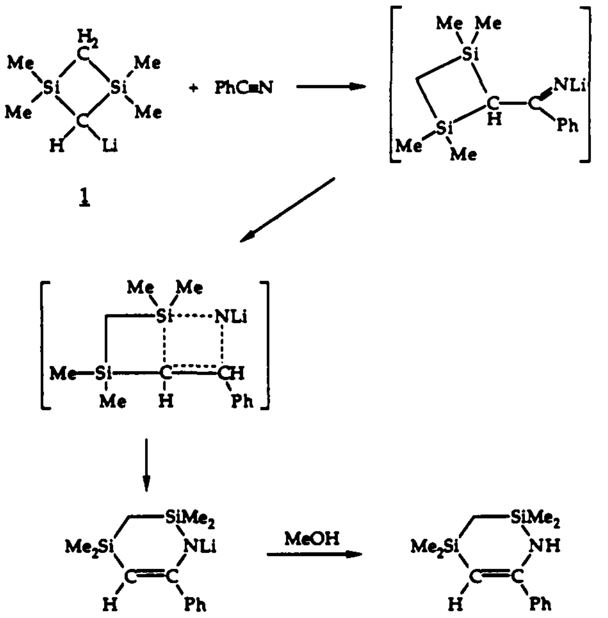
Scheme II



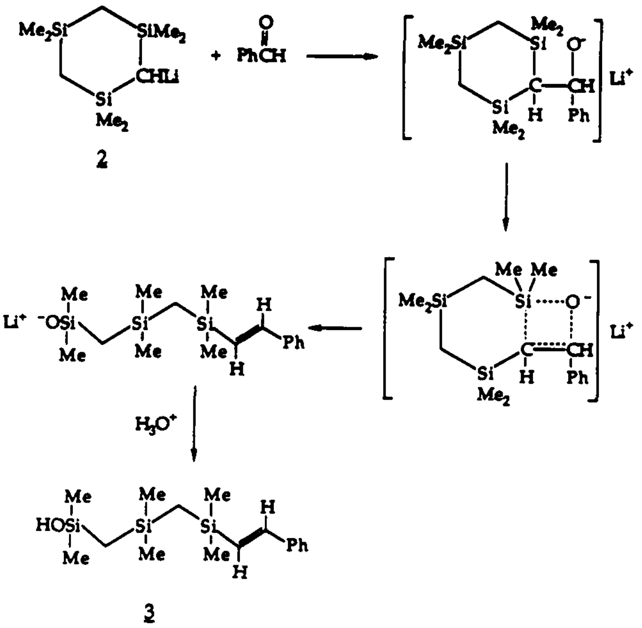
Scheme III



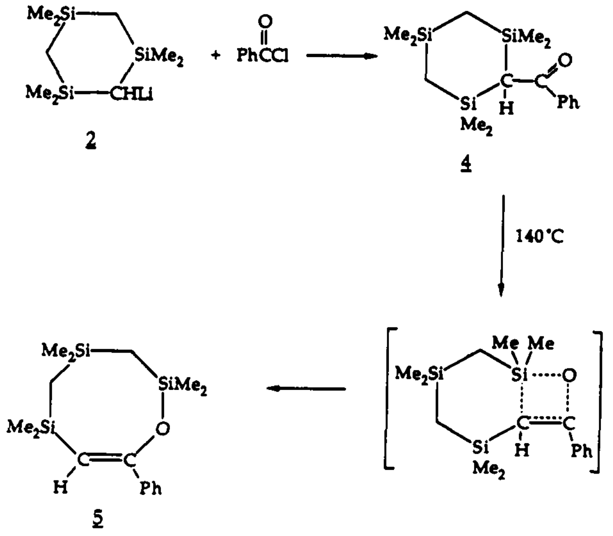
amide which the methanol quench then converts to the observed product.[2] It was suggested that these ring-opening and ring-expansion reactions were facilitated by the strain present in the 1,3-disilacyclobutyl substituent.

The availability of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane as a byproduct in the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane[3] and its known conversion to 2-lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane[4] (**2**) gave us the opportunity of examining the reaction of a less strained organolithium reagent analogous to **1** with the same organic substrates. We report here the reactions of **2** with PhCHO, PhC(O)Cl, and PhC≡N. In carrying out these reactions with the less-strained **2**, we hoped that the intermediates formed in these reactions might be isolable.

Scheme IV



Scheme V



Results and Discussion

Organolithium reagent **2** was prepared as described by Fritz et al.[4] by lithiation of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with *n*-butyllithium/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) reagent in hexane. Such a solution was added to an excess of benzaldehyde in diethyl ether at −78 °C. Following an aqueous NH_4Cl quench, GLC analysis of the organic layer showed the presence of organosilicon starting material in 17% yield and a higher boiling product (43% yield). The latter was isolated by thin-layer chromatography (TLC) on large plates and was identified as the trans ring-opened silanol **3** (Scheme IV). Even though the reaction conditions were mild (reaction temperature at room temperature or below), the less strained lithium α-(1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexyl)benzyl alkoxide underwent rearrangement to give the ring-opened product.

The ^1H, ^{13}C, and ^{29}Si NMR spectral data for **3** are given in Table I. The NMR spectral data support the assignment for the ring-opened structure of **3**. The trans con-

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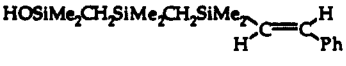
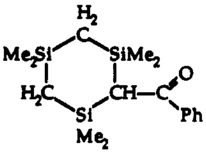
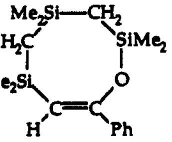
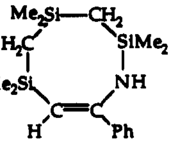
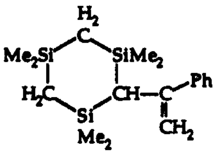
(2) This reaction course originally was suggested to involve rearrangement *after* the MeOH quench.[1] However, on further consideration, especially in view of the results of the present study, we wish to modify the suggested reaction course as shown in Scheme III, i.e., in terms of a rearrangement of the *anionic* intermediate.

(3) Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601.

(4) Fritz, G.; Neutzner, J.; Volk, H. *Z. Anorg. Allg. Chem.* **1983**, *497*, 21.

Table I. Spectroscopic Data

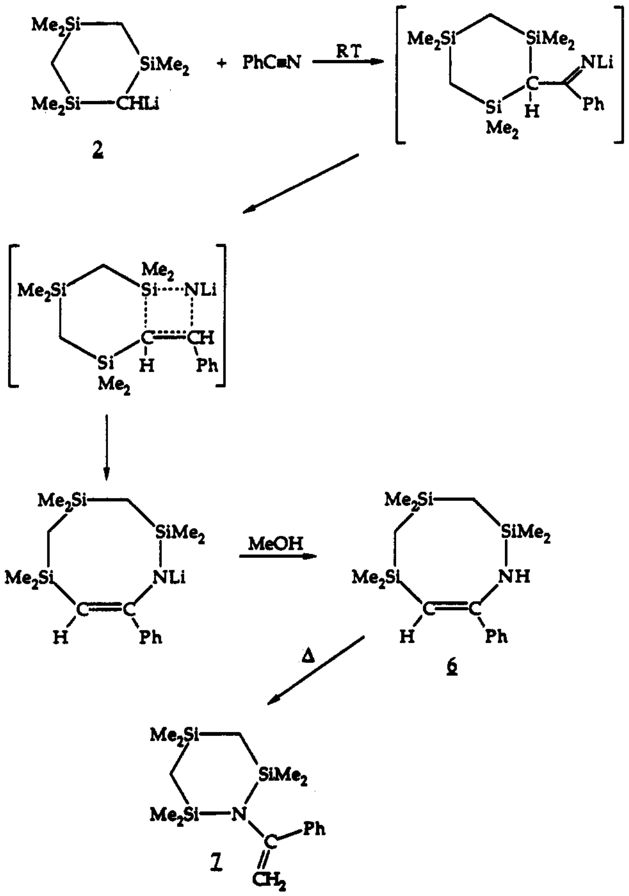
compound	^{1}H NMR (300 MHz), ppm	^{13}C NMR (75.4 MHz), ppm	^{29}Si NMR (59.59 MHz), ppm	IR (thin film), cm^{-1}
 3	−0.15 (s, 4 H, CH$_2$) 0.035, 0.041, 0.07 (s, each 6 H, Me$_2$Si) 6.41, 6.77 (AB, J = 18.8 Hz, 2 H) 7.14–7.38 (m, 5 H, Ph)	−0.45 (q, J = 119.4 Hz, Me$_2$Si) 1.95 (q, J = 118.6 Hz, Me$_2$Si) 2.31 (q, J = 118.4 Hz, Me$_2$Si) 4.02 (t, J = 104.5 Hz, CH$_2$) 7.41 (t, J = 108.8 Hz, CH$_2$) 130.72 (d, J = 133.7 Hz, =CHSi) 143.54 (d of d, ^1J = 151.4 Hz, ^2J = 4.4 Hz, PhCH=) 126.54–138.67 (m, Ph)	−6.26 (s, Si—O) 0.08 (s, CH$_2$SiCH$_2$) 16.74 (s, Si—CH=)	3078 (w), 3058 (w), 3021 (w), 2952 (s), 2898 (m), 2862 (m), 1690 (w), 1643 (w), 1596 (s), 1573 (s), 1490 (m), 1445 (m), 1404 (m), 1354 (m), 1313 (s), 1299 (s), 1278 (s), 1253 (s), 1204 (m), 1062 (m, broad), 1027 (s), 980 (m), 919 (m), 883 (s), 832 (s, broad), 805 (s), 772 (s), 754 (s), 696 (s), 670 (m)
 4	−0.25 (d, J = 13.8 Hz, 4 H, CH$_2$) 0.10 (s, 12 H, Me$_2$Si) 0.29 (s, 6 H, Me$_2$Si) 3.04 (s, 1 H, CH) 7.47–7.85 (m, 5 H, Ph)	0.62, 1.59, 1.68, 2.26, 2.88 (all m, CH$_2$ and (CH$_3$)$_2$Si) 35.99 (d, J = 114.0 Hz, CH) 203.06 (s, C=O) 128.06–132.12 (m, Ph) 140.42 (s, ipso Ph)	−0.06 (s, 1 Si) 2.97 (s, 2 Si)	[neat, NaCl] 3255 (w), 3100 (m), 3090 (s), 3010 (m), 2955 (s), 2880 (s), 2875 (s), 1942 (w), 1918 (w), 1910 (w), 1720 (m), 1632 (s), 1605 (s), 1596 (s), 1584 (s), 1578 (s), 1490 (m), 1445 (s), 1433 (m), 1406 (s), 1372 (m), 1351 (s), 1332 (s), 1316 (s), 1307 (s), 1246 (s), 1170 (s), 1100 (m), 1040 (s), 962 (m), 750 (s, very broad)
 5	−0.09 (s, 4 H, CH$_2$) 0.02, 0.07, 0.10 (s, each 6 H, Me$_2$Si) 5.20 (s, 1 H, HC=) 7.23–7.52 (m, 5 H, Ph)	1.22 (q, J = 117.1 Hz, Me$_2$Si) 1.41 (q, J = 119.5 Hz, Me$_2$Si) 2.73 (q, J = 117.1 Hz, Me$_2$Si) 4.03 (t, J = 110.8 Hz, CH$_2$) 4.36 (t, J = 109.3 Hz, CH$_2$) 107.35 (d, J = 135.4 Hz, HC=) 161.68 (s, C—O) 126.16–128.21 (m, Ph) 140.23 (s, ipso Ph)	−9.90 (s, 1 Si, Si—O) 0.27 (s, 1 Si, CH$_2$SiCH$_2$) 18.94 (s, 1 Si, Si—CH=)	[neat, NaCl] 3070 (w), 3058 (w), 3021 (w), 2898 (m), 2862 (m), 1690 (w), 1643 (w), 1596 (s), 1573 (s), 1490 (m), 1445 (m), 1404 (m), 1354 (m), 1313 (s), 1299 (s), 1278 (s), 1253 (s), 1204 (m), 1062 (m, broad), 1027 (s), 980 (m), 919 (m), 883 (s), 832 (s, broad), 805 (s), 772 (s), 754 (s), 696 (s), 670 (m)
 6	−0.18 (s, 4 H, CH$_2$) 0.038, 0.044, 0.14 (s, each 6 H, Me$_2$Si) 3.05 (s, 1 H, N—H) 5.01 (s, 1 H, HC=) 7.26–7.49 (m, 5 H, Ph)	0.92 (m, Me$_2$Si) 1.43 (m, Me$_2$Si) 2.74 (m, Me$_2$Si) 4.19 (m, CH$_2$) 4.24 (m, CH$_2$) 109.89 (d, J = 137.5 Hz, HC=) 157.75 (s, Ph—C=) 127.74–128.35 (m, Ph) 143.28 (s, ipso Ph)	−10.89 (s, 1 Si, SiNH) 2.89 (s, 1 Si, CH$_2$SiCH$_2$) 7.10 (s, 1 Si, Si—CH=CH$_2$)	
 7	−0.08 (s, 4 H, CH$_2$) 0.01 (s, 12 H, Me$_2$Si) 0.13 (s, 6 H, Me$_2$Si) 4.74, 5.27 (s, 2 H, =CH$_2$) 7.25–7.55 (m, 5 H, Ph)	2.62 (q, J = 118.5 Hz, Me$_2$Si) 2.97 (q, J = 117.8 Hz, Me$_2$Si) 4.06 (t, J = 112.0 Hz, CH$_2$) 107.14 (t, J = 156.0 Hz, H$_2$C=) 150.98 (s, Ph—C=) 126.88–127.67 (m, Ph) 141.93 (m, ^2J = 6.0 Hz, ipso Ph)	−1.81 (s, 1 Si, Me$_2$Si) 4.26 (s, 2 Si, Me$_2$SiN)	[neat, NaCl] 3100 (w), 3079 (w), 3058 (w), 3025 (w), 2954 (s), 2905 (m), 2872 (m), 1605 (m), 1574 (m), 1490 (m), 1445 (m), 1408 (m), 1356 (m), 1250 (s), 1105 (s), 1038 (s, broad), 946 (s), 916 (m), 822 (s, broad), 775 (s)

figuration of the olefin is evidenced in the ^{1}H NMR spectrum of 3. The olefin proton signal is an AB pattern with a spin–spin coupling constant of 18.8 Hz, indicative of a trans configuration. The ^{29}Si NMR spectrum oif 3 shows three resonances of equal intensity at δ_{Si} −6.26, +0.08, and +16.74 ppm. These may be assigned to the Me$_2$SiOH, CH$_2$SiMe$_2$CH$_2$, and Me$_2$SiCH=CHPh units, respectively.

The reaction of lithium reagent 2 with benzoyl chloride resulted in formation of a stable β-ketosilane, 4 (Scheme V), which could be isolated by TLC and fully characterized. In particular, the ^{1}H and ^{13}C NMR spectra of 4 were fully in accord with the structure shown. When 4 was heated under argon to 140 °, it underwent ring expansion as shown in Scheme V to give quantitatively the cyclic enoxysilane 5. This product also was isolated and characterized. Noteworthy was the presence of a C=O function in 4 (ν(C=O) 1632 cm^{-1}, δ_c 203.06 ppm) and its absence in 5, as well as the absence of an olefin C resonance in the ^{13}C NMR spectrum of 4 and the presence of such a signal at δ_c 107.35 ppm for 5. The ^{29}Si NMR spectral data for 4 and 5 support the assignment of the isomers. For 4 two resonances are observed for the two chemically inequivalent Si atoms in the silacyclohexane ring. These resonances at −0.06 and +2.97 ppm integrate correctly for a ratio of 1:2, respectively. As is expected for 5, three equal-intensity resonances are observed for the three chemically inequivalent silicon atoms at −9.90, +0.27, and +18.94 ppm. Attempted distillation of 4 (104 °C at 0.03 Torr) gave a distillate whose proton NMR spectrum showed the presence of a mixture of 4 and 5.

Finally, the reaction of lithium reagent 2 with benzonitrile was investigated. A solution of 2 was added dropwise to benzonitrile in hexane at −78 °C. A room-temperature methanol quench was followed by GLC analysis of the organic phase. One major product was present, but its isolation by TLC proved not to be possible. ^{1}H NMR analysis of the product mixture was not illuminating with regard to the products present. Vacuum distillation of the product mixture gave a mixture of two isomers which spectroscopic analysis showed to be 6 and 7 (Scheme VI). When this mixture was heated at 160 °C for 3 h, 6 was converted quantitatively to 7. Careful comparison of the ^{1}H and ^{13}C NMR spectra of pure 7 with those of the mixture of 6 and 7 led to the structure assignment for 6. The ^{1}H NMR spectrum of 6 showed the presence of only one olefin proton (δ 5.01 (s)), an amine proton (δ 3.05 (s)), and three separate Si(CH$_3$)$_2$ singlet resonances (δ 0.038,

Scheme VI



0.044, and 0.14). The proton NMR spectrum of 7, on the other hand, showed the presence of two olefin protons (δ 4.74, 5.27 (s)) and two $Si(CH_3)_2$ singlet resonances (δ 0.01 (12 H), 0.13 (6 H)). No N–H signal was observed.

Contrary to our expectations, in two of these reactions the initially formed product containing the 2-(1,3,5-trisilacyclohexyl) ring undergoes ring opening and in both of these reactions the initial intermediate was anionic. In the reaction of (1,3,5-trisilacyclohexyl)lithium with benzoyl chloride the initial intermediate was neutral and did not undergo ring opening until it was heated to 140 °C. Since the 1,3,5-trisilacyclohexyl ring is only mildly strained (if at all) in comparison with the 1,3-disilacyclobutyl ring it would appear that in *anionic* systems, such as those involved in the reactions of 2 with benzaldehyde and benzonitrile, factors other than ring strain are important.

The reactions of 2 with benzonitrile was complicated by a further thermal rearrangement of the product obtained upon methanolysis of the reaction mixture 6. Thus the reaction sequence was one of ring expansion and ring contraction and the starting C_3Si_3 ring with an exo nitrogen substituent was converted to a C_2NSi_3 ring with an exo carbon substituent. The 6 → 7 ring contraction possibly proceeded via a transannular N → Si interaction.

Experimental Section

General Comments. All reactions were performed under an argon atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Petrarch Systems, Inc. or Silar and distilled from magnesium chips before use. *tert*-Butyllithium was purchased from Aldrich and titrated for RLi content by the Gilman double-titration method. Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled from calcium hydride before use. 1,1,3,3,5,5-Hexamethyl-1,3,5-trisilacyclohexane was obtained as a byproduct in the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane by the method of Kriner.[3]

Gas chromatographic (GLC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6-ft., 0.25-in. column packed with 10% SE-30 silicone rubber gum on Chromosorb P. The internal standard (C_{14}) method was used in yield determinations with a temperature program of 10 °C/min from 40 to 275 °C.

Proton NMR spectra were obtained with a Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ or C_6D_6/C_6H_6 as a reference at 7.24 ppm or 7.15 ppm downfield from tetramethylsilane, respectively. ^{13}C NMR spectra, both proton coupled and decoupled, were obtained using a Varian XL-300 NMR spectrometer operating at 75.4 MHz in $CDCl_3$ or C_6D_6. ^{29}Si NMR spectra were obtained using a Varian XL-300 NMR spectrometer operating at 59.59 MHz in $CDCl_3$ or C_6D_6 using tetramethylsilane (0.00 ppm) as the external standard.

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of 2-Lithio-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (2). This reagent was prepared by the method of Fritz et al.[4] A 100-mL Schlenk flask equipped with a rubber septum and magnetic stir-bar was evacuated and back-filled with argon and then was charged with 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane and 1.6–1.9 molar equiv of *n*-butyllithium (2.3–2.5 M in pentane). TMEDA (1.4 molar equiv) then was added dropwise. The resulting mixture was stirred at room temperature under argon for 3–4 days.

Reaction of 2 with Benzaldehyde. The solution of 2 was prepared as described above from 3.273 g (0.0151 mol) of 1,1,3,3,5,5,-hexamethyl-1,3,5-trisilacyclohexane, 2.5 mL (0.0166 mol) of TMEDA, and 9.3 mL (2.5 M in hexane, 0.0232 mol) of *n*-butyllithium. A 250-mL three-necked round-bottomed flask equipped with two septa, a magnetic stir-bar, and a gas inlet tube (connected to an oil bubbler on a Schlenk line) was charged with 10 mL of diethyl ether and 2.4 mL (0.0236 mol) of benzaldehyde and cooled to −78 °C (dry ice/acetone bath). By cannula the solution of 2 was added over 5 min. After the addition was complete, the reaction mixture was stirred at −78 °C for 30 min. The yellow solution turned green after 10 min and then turned yellow again after an additional 10 min. After stirring at room temperature for 12 h, a saturated aqueous NH_4Cl solution was added slowly until the organic layer became clear. After separation from the aqueous layer, the organic layer was dried over anhydrous $MgSO_4$ and filtered. Removal of the solvents by trap-to-trap distillation (room temperature, 40 Torr) was followed by GLC analysis, which showed the presence of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane in 17% yield and of a higher boiling product 3 (43% yield). Thin-layer chromatography on large plates of silica gel was used to isolate 3 from the reaction mixture. Pentane eluted two clear bands in minor yield which were discarded, followed by a large clear band of impure 3 which was collected. Compound 3 was purified further by thin-layer chromatography on large plates of silica gel. Pentane eluted a clear band in minor yield which was discarded, followed by a large clear band, 3, which was collected. Anal. Calcd for $C_{16}H_{28}O_1Si_3$: C, 59.93; H, 8.80. Found: C, 60.26; H, 8.62.

Reaction of 2 with Benzoyl Chloride. A solution of 2 was prepared as above by reaction of 3.575 g (0.0165 mol) of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with 11 mL of 2.5 M *n*-butyllithium in pentane (0.0275 mol) and 3.6 mL (0.0238 mol) of TMEDA. A 250–mL, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, gas inlet/outlet tube connected to an oil bubbler on a Schlenk line, a rubber septum, and a magnetic stir-bar was evacuated and back-filled with argon and then was charged with 3.4 mL (0.0293 mol) of benzoyl chloride and 15 mL of Et_2O. The flask was cooled to −78 °C before dropwise addition of the solution of 2 through the addition funnel. After the addition was complete, the mixture was warmed to room temperature and stirred for 1 h. A standard hydrolytic workup was performed. Removal of solvent at 43 Torr was followed by GLC analysis of the residue which showed the presence of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane (23%) and 4 (77%). Removal of any remaining volatiles at reduced pressure (0.04 Torr) then was followed by TLC on large plates of silica gel to purify 4. Pentane eluted a small clear band and a small yellow band which were discarded, followed by a large

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clear band, 4, which was collected. Anal. Calcd for $C_{16}H_{28}O_1Si_3$: C, 59.98; H, 8.80. Found: C, 60.26; H, 8.62.

Thermal Rearrangement of 4. A 100-mL Schlenk flask equipped with a rubber septum and magnetic stir-bar was charged with 0.9 g of 4 and heated under argon for 4 h at 140 °C to give 5 quantitatively (as observed by ^1H and ^{13}C NMR). Anal. Calcd for $C_{16}H_{28}O_1Si_3$: C, 59.98; H, 8.80. Found: C, 60.34; H, 8.75.

Reaction of 2 with Benzonitrile. A solution of 2 was prepared as above by reaction of 4.13 g (0.0183 mol) of 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane with 13 mL of 2.5 M *n*-butyllithium in pentane (0.0325 mol) and 3.9 mL (0.0258 mol) of TMEDA. A 250-mL Schlenk flask was charged with 3.6 mL (0.0353 mol) of benzonitrile and 20 mL of hexane and then cooled to −78 °C in a dry ice/acetone bath. The solution of 2 was added over 5 min with a fine cannula. After the addition was complete, the mixture was warmed to room temperature and stirred for 1 h. Methanol (2 mL, 0.0494 mol) was added dropwise and the solution turned from orange to yellow and a white precipitate formed. The solution was filtered through a Celite-packed Schlenk frit and volatiles were removed by trap-to-trap distillation (room temperature, 30 Torr). GLC analysis showed one major peak (46% yield) and numerous smaller yield products. Separation of the major product was not possible by TLC, and ^1H NMR analysis of the product mixture was too complex for identification of any products. Distillation at 0.03 Torr afforded on fraction between 93 and 96 °C which was determined to be a mixture of isomers 6 and 7. The isomers could not be separated by TLC. However, when the mixture was heated at 160 °C for 3 h, quantitative conversion to 7 was achieved. By careful comparison of the NMR spectral data for the mixture of compounds 6 and 7 with the data obtained for a pure sample of 7, the spectral data for 6 could be determined. Anal. Calcd for $C_{16}H_{29}N_1Si_3$ (7): C, 60.10; H, 9.16. Found: C, 60.42; H, 9.28.

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Interaction of Iron Ethynyl and Ethynediyl Complexes with $Cp_2Ni_2(CO)_2$: Formation of Tri- and Tetranuclear Adducts with a Multiply Bridging C_2H Ligand[†]

Munetaka Akita,* Masako Terada, Masako Tanaka, and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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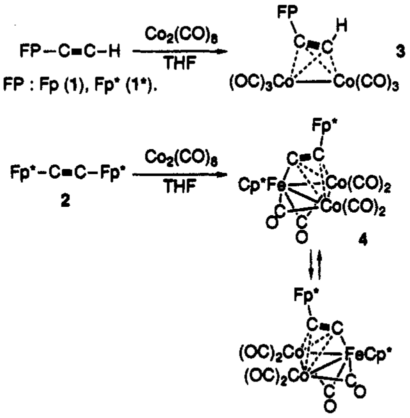
Summary: Reaction of ethynyliron complexes Fp—C≡C—H [FP = Fp (**1**), Fp* (**1***)] with $Cp_2Ni_2(CO)_2$ (**5**) affords the expected adducts $Cp_2Ni_2(\mu\text{-}\eta^2{:}\eta^2\text{-FP—C≡C—H})$ [FP = Fp (**6**), Fp* (**6***)] with a tetrahedral C_2Ni_2 core together with tetranuclear adducts $(CPFe)(CpNi)_2Ni(CO)_2(\mu\text{-}CO)(\mu_4\text{-}C_2H)$ [CP = CP (**7**), Cp* (**7***)] with a quadruply bridging C_2H ligand. **7** (**7***) is formed by a formal capping reaction of **6** (**6***) with a Ni(CO) fragment. On the other hand, reaction of an ethynediyldiiron complex Fp*—C≡C—Fp* (**2**) with **5** affords a dinuclear complex, $Cp^*FeCpNi(\mu\text{-}CO)_2(CO)$ (**10**), without the C_2 ligand, the fate of which is not known. The molecular structures of **6**, **7**, and **10** have been determined by X-ray crystallography.

Introduction

Coordination structure and chemical properties of C2 species ($C_2H_mO_n$) incorporated in a polymetallic system have attracted much attention in connection with corresponding C2 surface species which may be formed after coupling of C1 species in catalytic CO hydrogenation. We[1] also have been studying chemical properties of polymetallic C_2 and C_2H complexes derived from parent acetylides, i.e. ethynyliron complexes FP—C≡C—H [FP = Fp (1), Fp* (1*)] and an ethynediyldiiron complex Fp*—C≡C—Fp* (2). Treatment of 1–2 with mono- and dinuclear species such as $[Fp^{*+}(THF)]BF_4$[1a] and $Co_2(CO)_8$[1d] successfully produced polynuclear complexes with a multiply bridging C_2H or C_2 ligand, and some of the resulting adducts exhibited unusual properties which had not been observed for analogues containing an organic substituent (e.g. Ph, alkyl, COOR) at the C_2 terminus. For example, interaction of 1 and 1* with $Co_2(CO)_8$ resulted in the formation of the normal expected $\mu\text{-}\eta^2{:}\eta^2$-adducts 3, whereas the reaction of 2 afforded a rare example of a cluster compound (4) which is fluxional via a reversible metal—metal bond scission and recombination process (Scheme I).

Scheme I



As an extention, herein we wish to report results of interaction of 1–2 with a dinuclear nickel complex $Cp_2Ni_2(CO)_2$ (5), which has been known to react with various alkynes to afford adducts with a tetrahedral C_2Ni_2 core.[2,3]

[†] Abbreviations: Fp = $CpFe(CO)_2$; Cp = $\eta^5\text{-}C_5H_5$; Fp* = $Cp^*Fe(CO)_2$; Cp* = $\eta^5\text{-}C_5Me_5$.

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