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Formation of 1,2,4-Trisilacyclopentanes by Photolysis of $FpCH_2SiR_2SiR_2SiR_2CH_2Fp$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$)

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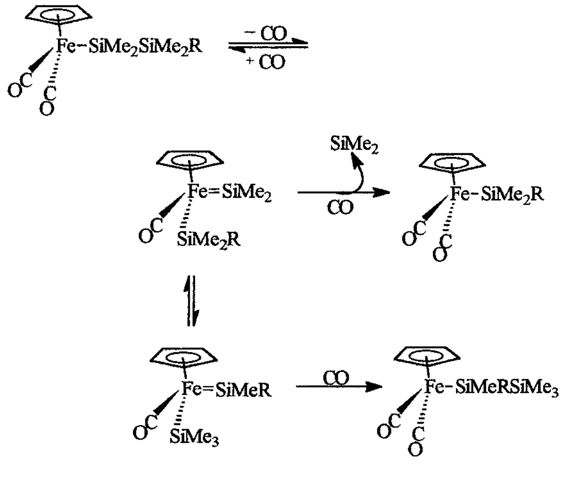
Photolysis of $FpCH_2SiMe_2SiMe_2SiMe_2CH_2Fp$ (**1**), $Fp = [(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, resulted in almost quantitative formation of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane (**2**) and Fp_2. Similar treatment of $FpCH_2Me_2SiMeSiEtSiMe_2CH_2Fp$ (**6**) afforded 1-ethyl-1,2,2,4,4-pentamethyl-1,2,4-trisilacyclopentane (**7**), indicating that the central silicon of the trisilane remains associated with the silicon−silicon bond of the product. Irradiation of $FpCH_2PhMeSiSiMe_2SiMe_2CH_2Fp$ (**11**) led to the formation of the two positional isomers (ratio 4:3), 1,1,2,2,4-heptamethyl-4-phenyl-1,2,4-trisilacyclopentane (**12a**) and 1,1,2,4,4-heptamethyl-2-phenyl-1,2,4-trisilacyclopentane (**12b**), indicating that either one of the two terminal silicon atoms of the trisilane remains in the Si−Si bond of the product while the other becomes the silicon atom of the product at 4-position. A mechanism for the formation of 1,2,4-trisilacyclopentane is suggested. Irradiation of **11** also produced a small amount the rearranged product $FpPhMeSiCH_2SiMe_2CH_2SiMe_2Fp$ (**13**), whereas photochemical treatment of the tetrasilane analogue, $FpCH_2SiMe_2SiMe_2SiMe_2SiMe_2CH_2Fp$ (**15**), resulted in only the high-yield rearrangement product $FpMe_2SiCH_2SiMe_2SiMe_2CH_2SiMe_2Fp$ (**17**) with an absence of elimination products.

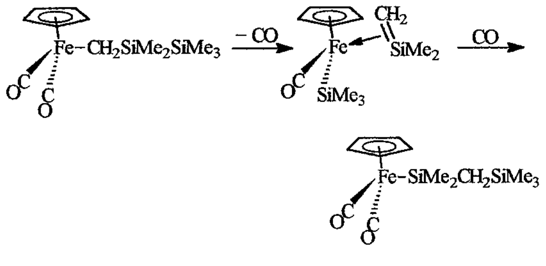
Introduction

The activation of the silicon−silicon bond by transition metal complexes is an important area of modern organosilicon chemistry.[1] Photolysis of oligosilyl and oligosilylmethyl derivatives of the transition metals results in the formation of transient silylene and silene complexes via α- and β-elimination processes, respectively (Schemes 1 and 2).[2−4] These intermediates lead to either silylene (or silene) eliminations or rearrangements. There are now many examples of silylene and silene transition metal complexes reported.[5]

Scheme 1



Scheme 2



By way of contrast, we recently reported that UV irradiation of $FpCH_2RMeSiSiMeRCH_2Fp$ ($Fp = (\eta^5$-

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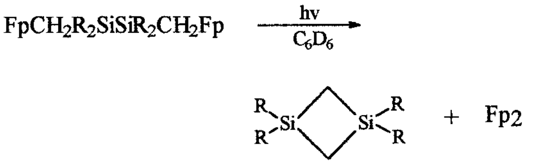
$C_5H_5)Fe(CO)_2$; R = Me, Ph) resulted in the formation of 1,3-disilacyclobutanes and Fp_2, stereospecifically in the case of R_2 = MePh (eq 1).[6]



(1)

To understand more about the nature of these photoreactions, we have synthesized the related trisilane complexes $FpCH_2SiR_2SiR_2SiR_2CH_2Fp$ and the tetrasilane complex $FpCH_2SiMe_2SiMe_2SiMe_2SiMe_2CH_2Fp$ and report the results of their photochemical irradiation.

Experimental Section

All manipulations were carried out under an argon atmosphere or under high vacuum. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. The following reagents were used as received from the suppliers named, silica gel (grade 62, 60−200 mesh), anhydrous HCl, $BrCH_2Cl$, Aldrich; CF_3SO_3H, Lancaster; $Ph_2MeSiCl$, $MeEtSiCl_2$, Me_2SiHCl, $PhMe_2SiCl$, Gelest. Other reagents were synthesized by literature procedures: $ClCH_2SiMe_2SiMe_2SiMe_2CH_2Cl$,[7] $ClMe_2SiSiMe_2Cl$,[8] $Ph_2MeSiSiMe_2H$,[2c] $ClMe_2SiSiMe_2SiMe_2SiMe_2Cl$.[9] Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer, and infrared (IR) spectra were obtained using hexane as solvent on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra were obtained from the Nebraska Center for Mass Spectrometry. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of $FpCH_2SiMe_2SiMe_2SiMe_2CH_2Fp$ (1). To 50 mL of a THF solution of $[CpFe(CO)_2]^-Na^+$ (prepared from 2.00 g (5.60 mmol) of Fp_2) was added 1.45 g (5.30 mmol) of $ClCH_2SiMe_2SiMe_2SiMe_2CH_2Cl$ at 0 °C. The solution was stirred at low temperature and then allowed to warm to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered and concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band, which was collected and after solvent removal afforded a yellow crystalline solid. The solid was recrystallized from hexane to yield **1**, 0.79 g (27%) as yellow crystals. Mp: 52−4 °C. NMR (C_6D_6): δ ^1H, 0.06 (s, 2H, CH_2), 0.37 (s, 6H, $SiSiMe_2Si$), 0.40 (s, 12H, $\mathit{Me}_2SiSiMe_2Si\mathit{Me}_2$), 4.18 (s, 10H, Cp); ^{13}C, −23.34 ($FpCH_2$), −5.43 ($SiSiMe_2Si$), 0.80 ($\mathit{Me}_2SiSiMe_2Si\mathit{Me}_2$), 84.96 (Cp), 218.15 (CO); ^{29}Si, −46.40 ($Si\mathit{Si}Si$), −2.55 ($\mathit{Si}Si\mathit{Si}$). IR (ν_{CO}, cm^{-1}): 2009(s), 1958(s). Anal. Calcd for $C_{22}H_{32}Fe_2O_4Si_2$: C, 47.49; H, 5.80. Found: C, 46.85; H, 5.86.

Photolysis of 1: Formation of 1,1,2,2,4,4-Hexamethyl-1,2,4-trisilacyclopentane (2). A 5 mm Pyrex NMR tube was charged with 0.17 g (0.3 mmol) of **1** and 1 mL of C_6D_6 and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ^1H, ^{13}C, and ^{29}Si NMR. The color of the solution changed from yellow to dark red upon irradiation, and after 2 h complete disappearance of **1** and formation of 1,2,4-trisilacyclopentane **2** and iron dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were noted, along with a trace of ferrocene. The solvent was then removed under vacuum, and the residue was placed upon a 1 × 15 cm silica gel column. Elution with hexane afforded a colorless oily product, **2** (48 mg, 79%). Elution with a mixture of hexane and benzene (4:1) yielded 98 mg (92%) of violet-red solid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Compound **2** has been previously synthesized by cyclization of $(BrMe_2SiCH_2)_2SiMe_2$ in the presence of Na−K alloy.[10] ^1H NMR (C_6D_6): δ −0.25 (s, 4H, CH_2), 0.13 (s, 6H, $SiMe_2$), 0.19 (s, 12H, Si_2Me_4). ^{13}C NMR (C_6D_6): δ −0.97 (Si_2Me_4), 2.06 ($SiMe_2$), 3.19 (CH_2). ^{29}Si NMR (C_6D_6): δ −12.86 (Si_2Me_4), 9.45 ($SiMe_2$). MS (70 eV): *m/z* 202 (M^+, 33), 187 (M^+ − Me, 100), 28 (Si^+, 60).

Synthesis of $PhMe_2SiMeSiEtSiMe_2Ph$ (3). A flask equipped with a magnetic stirring bar and addition funnel was charged with 10.9 g (76 mmol) of $MeEtSiCl_2$ and 100 mL of THF. The solution was cooled to 0 °C, and the $PhMe_2SiLi$ solution (prepared from 27.0 g (0.16mol) of $PhMe_2SiCl$ and 4.45 g (0.64mol) of Li in 150 mL of THF) was added dropwise. Upon complete addition the solution was allowed to warm to room temperature and stirred overnight and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled, by using a 20 cm Vigreux column, at 138−140 °C/2 mmHg to give 16.6 g (64%) of **3** as a colorless oil. NMR (C_6D_6): δ ^1H, 0.13 (s, 3H, $SiEtSi\mathit{Me}Si$), 0.30, 0.31 (s, s, 12H, $\mathit{Me}_2SiEtSiMeSi\mathit{Me}_2$), 0.69 (q, ^3J = 7.0 Hz, 2H, $\mathit{C}H_2CH_3$), 0.92 (t, ^3J = 7.5 Hz, 3H, $CH_2\mathit{C}H_3$), 7.16−7.20 (m, 6H, Ph), 7.35−7.38 (m, 4H, Ph); ^{13}C, −8.21 ($SiEtSi\mathit{Me}Si$), −2.14 ($\mathit{Me}_2SiEtSiMeSi\mathit{Me}_2$), 4.49, 10.35 (Et), 128.15, 128.84, 134.18, 140.01 (Ph); ^{29}Si, −43.48 ($Si\mathit{Si}Si$), −19.70 ($\mathit{Si}Si\mathit{Si}$). MS (70 eV): *m/z* 342 (M^+, 10), 327 (M^+ − Me, 3), 207 (M^+ − $SiMe_2Ph$, 15), 179 ($PhMe_2SiSiMeH^+$, 65), 135 ($PhMe_2Si^+$, 100), 130 ($MeEtSi{=}SiMe_2^+$, 48), 105 ($MeEtSi{=}SiMe^+$, 25). Anal. Calcd for $C_{19}H_{30}Si_3$: C, 66.59; H, 8.82. Found: C, 66.26; H, 9.03.

Synthesis of $ClMe_2SiMeSiEtSiMe_2Cl$ (4). To a solution of 12.5 g (36 mmol) of **3** in 40 mL of benzene was added 0.4 g of aluminum chloride. Dry hydrogen chloride was passed slowly through the reaction mixture at room temperature. The progression of the reaction was monitored by ^{29}Si NMR spectroscopy. The signals due to the starting material at −43.5 and −19.7 ppm disappeared after 2 h and were replaced by the signals due to the final product **4** at −39.8 and 24.1 ppm, indicating the completion of the reaction. At this time the reaction was stopped, the solvent was removed under vacuum, and 50 mL of hexane was added to the residue. The solution was filtered to remove the catalyst, the solvent was removed at 50 mmHg, and the residue was distilled, by using a 20 cm Vigreux column, at 68−70 °C/1 mm Hg to give 16.6 g (64%) of **4** as a colorless oil. NMR (C_6D_6): δ ^1H, 0.15 (s, 3H, $SiEtSi\mathit{Me}Si$), 0.42 (s, 12H, $\mathit{Me}_2SiEtSiMeSi\mathit{Me}_2$), 0.75 (q, ^3J = 7.9 Hz, 2H, $\mathit{C}H_2CH_3$), 0.98 (t, ^3J = 7.8 Hz, 3H, $CH_2\mathit{C}H_3$); ^{13}C, −9.56 ($SiEtSi\mathit{Me}Si$), 3.88 ($\mathit{Me}_2SiEtSiMeSi\mathit{Me}_2$), 3.27, 9.77 (Et); ^{29}Si, −39.83 ($Si\mathit{Si}Si$), 24.10 ($\mathit{Si}Si\mathit{Si}$). Anal. Calcd for $C_7H_{20}Cl_2Si_3$: C, 32.41; H, 7.77. Found: C, 32.61; H, 7.90.

Synthesis of $ClCH_2Me_2SiMeSiEtSiMe_2CH_2Cl$ (5). Into a 250 mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 5.50 g (21.1 mmol) of **4** and $BrCH_2Cl$ (5.48 g, 42.2 mmol) in 100 mL of dry THF. To this mixture, maintained between −78 and −70 °C, was added on the cold wall of the flask, via syringe over 30 min, 26.4 mL (42.2 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was allowed to warm to room temperature and stirred overnight and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled, by using a 20 cm Vigreux column, at 108−110 °C/2 mmHg to give 5.70 g (94%) of **5**. NMR (C_6D_6): δ ^1H, 0.05 (s, 3H, $SiEtSi\mathit{Me}Si$), 0.11 (s, 12H, $\mathit{Me}_2SiEtSiMeSi\mathit{Me}_2$), 0.64 (q, ^3J = 7.9 Hz, 2H, $\mathit{C}H_2CH_3$), 0.91 (t, ^3J = 7.6 Hz, 3H, $CH_2\mathit{C}H_3$), 2.70 (s, 4H, CH_2Cl);

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^{13}C, −8.51 (SiEtSi*Me*Si), −3.31 (*Me*$_2$SiEtSiMeSi*Me*$_2$), 4.20, 10.30 (Et), 31.51 (CH_2Cl); ^{29}Si, −44.09 (Si*Si*Si), −12.32 (*Si*Si*Si*). MS (70 eV): *m/z* 237 ($M^+ - CH_2Cl$, 13), 179 ($M^+ - Me_2SiCH_2Cl$, 10), 151 ($ClCH_2MeHSiSiEtH^+$, 100), 73 ($SiMe_3^+$, 33). Anal. Calcd for $C_9H_{24}Cl_2Si_3$: C, 37.61; H, 8.42. Found: C, 38.01; H, 8.69.

Synthesis of $FpCH_2Me_2SiMeEtSiSiMe_2CH_2Fp$ (6). To 50 mL of a THF solution of $[CpFe(CO)_2]^-Na^+$ (prepared from 2.00 g (5.6 mmol)of Fp_2) was added 1.38 g (4.8 mmol) of **5** at 0 °C. The solution was stirred at low temperature and then allowed to warm to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered and concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band, which was collected and after solvent removal afforded a yellow oily product of **6** (1.22 g, 44%). NMR (C_6D_6): δ ^{1}H, 0.10 (s, 4H, FpC*H*$_2$), 0.35 (s, 3H, SiEtSi*Me*Si), 0.43 (s, 12H, *Me*$_2$SiEtSiMeSi*Me*$_2$), 0.95, 1.27 (bd s, bd. s, 5H, Et), 4.21 (s, 10H, Cp); ^{13}C, −22.67 (Fp*C*H$_2$), −7.70 (SiEtSi*Me*Si), 1.45 (*Me*$_2$SiEtSiMeSi*Me*$_2$), 5.34, 11.07 (Et), 84.98 (Cp), 218.22 (CO); ^{29}Si, −40.34 (Si*Si*Si), −2.46 (*Si*Si*Si*). IR (ν_{CO}, cm^{-1}): 2009(s), 1957(s). HRMS (FAB): calcd for ($C_{23}H_{34}Fe_2O_4Si_3 + Na$) *m/z* 593.0363, found *m/z* 593.0389. HRMS (EI): calcd for $C_{22}H_{31}Fe_2O_4Si_3$ ($M - CH_3$) *m/z* 555.0226, found *m/z* 555.0233. LRMS (EI): *m/z* 555.0 ($M^+ - Me$, 21), 235 ($FpSiMe_2^+$, 97), 186 (Fc^+, 70), 121 ($CpFe^+$, 100), 73 (Me_3Si^+, 29).

Photolysis of 6: Formation of 1-Ethyl-1,2,2,4,4,-pentamethyl-1,2,4-trisilacyclopentane (7). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.18 mmol) of **6** and 1 mL of C_6D_6 and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ^{1}H, ^{13}C, and ^{29}Si NMR. The color of the solution changed from orange to dark red upon irradiation, and after 2 h complete disappearance of **6** and formation of **7** and iron dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were noted, along with a trace of ferrocene. The solvent was removed under vacuum, and the residue was subjected to a 1 × 10 cm silica gel column. Elution with hexane afforded a colorless oil of **7** (25 mg, 67%) upon removing the solvent very cautiously. Elution with a mixture of benzene/hexane (1:3) developed a red band, which was collected and after solvent removal afforded 46 mg (74%) of violet crystals of iron dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. For **7**: NMR ($C_6D_6$): δ ^{1}H, −0.25 (m, 4H, CH_2), 0.13, 0.15, 0.16, 0.20, 0.21 (s, s, s, s, s, 15H, SiMe), 0.65 (q, ^3J = 7.9 Hz, 2H, *C*H$_2$CH$_3$), 1.03 (t, ^3J = 7.8 Hz, 3H, CH$_2$*C*H$_3$); ^{13}C, −3.54 (EtSi*C*H$_3$), −0.73, −0.59 (SiSi*Me*$_2$), 0.78 (EtMeSi*C*H$_2$SiMe$_2$), 2.03, 2.22 (CH$_2$Si*Me*$_2$CH$_2$), 3.38 (Me$_2$Si*C*H$_2$SiMe$_2$), 7.92 (*C*H$_2$CH$_3$), 8.79 (CH$_2$*C*H$_3$); ^{29}Si, −12.76 (Si*Si*Me$_2$), −8.28 (MeEt*Si*Si), 9.67 (SiMe$_2$). HRMS (EI): calcd for $C_9H_{24}Si_3$ *m/z* 216.1186, found *m/z* 216.1181. LRMS (EI): *m/z* 216.1 (M^+, 40), 201.1 ($M^+ - Me$, 23), 187.1 ($M^+ - Et$, 100), 173.1 ($M^+ - C_3H_7$, 47). Anal. Calcd for $C_9H_{24}Si_3$: C, 49.92; H, 11.17. Found: C, 48.92; H, 11.40.

Synthesis of $Ph_2MeSiSiMe_2Cl$. A flask equipped with a magnetic stirring bar and a refluxing condenser was charged with 20.0 g (0.078 mol) of $Ph_2MeSiSiMe_2H$ and 1.0 g (4 mmol) of benzoyl peroxide in 100 mL of CCl_4. The solution was refluxed for 10 h and was permitted to cool to room temperature. The solvent was removed under vacuum, and 100 mL of hexane was added to precipitate the catalysts. The hexane solution was filtered to remove the precipitate and the hexane solution concentrated under vacuum. The residue was distilled, by using a 20 cm Vigreux column, at 148−150 °C/2 mmHg (lit.[2c] 106−108 °C/0.2 mm Hg) to give 20.2 g (89%) of $Ph_2MeSiSiMe_2Cl$ as a colorless oil.

Synthesis of $Ph_2MeSiSiMe_2SiMe_2Ph$ (8). A flask equipped with a magnetic stirring bar and addition funnel was charged with 19.6 g (67.5 mmol) of $Ph_2MeSiSiMe_2Cl$ and 70 mL of hexane. The solution was cooled to 0 °C, and the $PhMe_2SiLi$ solution (prepared from 11.5 g (67.5 mmol) of $PhMe_2SiCl$ and 1.89 g (270 mmol) of Li in 120 mL of THF) was added dropwise via the addition funnel. Upon completing addition the solution was allowed to warm to room temperature and stirred overnight and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled at 234−236 °C/2 mmHg to give 17.7 g (67%) of **8** as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.23, 0.25 (s, s, 12H, Si*Me*$_2$Si*Me*$_2$Ph), 0.53 (s, 3H, Si*Me*Ph$_2$), 7.16−7.48 (m, 15H, Ph). ^{13}C NMR (C_6D_6): δ −5.29 (Ph*Me*$_2$Si), −3.61 (Ph$_2$*Me*Si), −2.88 (SiSi*Me*$_2$Si), 128.28, 128.39, 128.94, 129.29, 134.29, 135.38, 137.84, 139.52 (Ph). ^{29}Si NMR (C_6D_6): δ −43.48 (Si*Si*Si), −19.64, −19.21 (*Si*Si*Si*). MS (70 eV): *m/z* 390 (M^+, 4), 375 ($M^+ - Me$, 2), 255 ($M^+ - SiMe_2Ph$, 39), 197 (Ph_2MeSi^+, 100), 178 ($PhMeSiSiMe_2^+$, 42), 135 ($PhMe_2Si^+$, 91). Anal. Calcd for $C_{23}H_{30}Si_3$: C, 70.70; H, 7.34. Found: C, 70.59; H, 7.97.

Synthesis of $ClPhMeSiSiMe_2SiMe_2Cl$ (9). A flask equipped with a magnetic stirring bar and addition funnel was charged with 14.7 g (37.7 mmol) of **8** and 50 mL of toluene. The solution was cooled to −30 °C, and 11.3 g (75.4 mmol) of trifluoromethane sulfonic acid was added dropwise via the addition funnel. Upon completing addition, the solution was allowed to warm to room temperature and stirred for an additional 2 h. ^{29}Si NMR monitoring of the reaction mixture indicated the disappearance of **8**. The new resonance signals appearing at −46.81, 29.31, 44.15 ppm were assigned to the complex $(CF_3SO_3)PhMeSiSiMe_2SiMe_2(CF_3SO_3)$. The reaction mixture was added dropwise to a solution of 3.20 g (75.4 mmol) of LiCl in 40 mL of THF at 0 °C. Upon completing addition, the solution was permitted to warm to room temperature and stirred for an additional 2 h. The solvents were removed under vacuum, and 100 mL of hexane was added to precipitate the salts. The hexane solution was filtered and the filtered material washed with an extra 50 mL of hexane. The hexane fractions were concentrated under reduced pressure, and the residue was distilled, by using a 20 cm Vigreux column, at 136−140 °C/2 mmHg to give 3.7 g (32%) of **9** as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.22, 0.23, 0.30, 0.39 (s, s, s, s, 12H, Si*Me*$_2$Si*Me*$_2$Cl), 0.68 (s, 3H, Si*Me*PhCl), 7.19−7.21 (m, 3H, Ph), 7.58−7.60 (m, 2H, Ph). ^{13}C NMR (C_6D_6): δ −7.13, −7.09 (SiSi*Me*$_2$Si), −1.78 (SiPh*Me*Cl), 3.07, 3.21 (SiMe$_2$Cl), 128.62, 130.46, 133.66, 136.26 (Ph). ^{29}Si NMR (C_6D_6): δ −44.10 (Si*Si*Si), 14.30 (SiPhMeCl), 24.38 (SiMe$_2$Cl).

Synthesis of $ClCH_2PhMeSiSiMe_2SiMe_2CH_2Cl$ (10). Into a 250 mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 2.76 g (9.0 mmol) of **9** and $BrCH_2Cl$ (2.33 g, 18.0 mmol) in 70 mL of dry THF. To this mixture, maintained between −78 and −70 °C, was added on the cold wall of the flask, via syringe over 30 min, 11.3 mL (18.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was allowed to warm to room temperature and stirred overnight and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled at 164−170 °C/2 mmHg to give 2.38 g (79%) of **10**. ^{1}H NMR (C_6D_6): δ 0.08 (s, 6H, SiSi*Me*$_2$Si), 0.20, 0.22 (s, s, 6H, Si*Me*$_2$CH$_2$Cl), 0.47 (s, 3H, Si*Me*PhCH$_2$Cl), 2.64 (s, 2H, SiMe$_2$*CH*$_2$Cl), 2.98 (AB, ^2J = 13.6 Hz, 2H, SiMePh*CH*$_2$Cl), 7.20−7.22 (m, 3H, Ph), 7.38−7.40 (m, 2H, Ph). ^{13}C NMR (C_6D_6): δ −6.01 (Si*Me*PhCH$_2$Cl), −5.76, −5.58 (SiSi*Me*$_2$Si), −4.30 (SiMe$_2$CH$_2$Cl), 29.99, 31.30 (CH$_2$Cl), 128.54, 129.76, 134.39, 136.01 (Ph). ^{29}Si NMR (C_6D_6): δ −48.90 (Si*Si*Si), −16.12 (SiPhMeCH$_2$Cl), −12.15 (SiMe$_2$CH$_2$Cl). MS (70 eV): *m/z* 285 ($M^+ - CH_2Cl$, 6), 227 ($M^+ - Me_2SiCH_2Cl$, 37), 191 ($M^+ - Me_2SiCH_2Cl{-}HCl$, 95), 165 ($M^+ - MePhSiCH_2Cl$, 100), 135 ($ClCH2MeSi{=}SiMe^+$, 82), 73 ($SiMe_3^+$, 93). Anal. Calcd for $C_{13}H_{24}Cl_2Si_3$: C, 46.24; H, 7.21. Found: C, 45.81; H, 7.40.

Synthesis of $FpCH_2PhMeSiSiMe_2SiMe_2CH_2Fp$ (11). To 50 mL of a THF solution of $[CpFe(CO)_2]^-Na^+$ (prepared from 1.3 g (3.64 mmol) of Fp_2) was added 0.9 g (2.7 mmol) of **10** at

0 °C. The solution was stirred at low temperature and then allowed to warm to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered and concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band, which was collected and after solvent removal afforded a yellow oily product of **11** (1.01 g, 60%). ^{1}H NMR (C$_6$D$_6$): δ −0.14, −0.03 (s, m, 4H, CH$_2$), 0.26, 0.40 (s, s, 12H, SiMe$_2$), 0.69 (s, 3H, Si*Me*PhCH$_2$Fp), 4.05, 4.13 (s, s, 10H, Cp), 7.15−7.22 (m, 3H, Ph), 7.56−7.67 (m, 2H, Ph). ^{13}C NMR (C$_6$D$_6$): δ −26.26, −23.43 (FpCH$_2$), −5.16, −5.07 (SiSiMe$_2$Si), −1.63 (FpCH$_2$Si*Me*Ph), 0.62 (Si*Me*$_2$CH$_2$Fp), 84.64, 85.99 (Cp), 128.16, 128.51, 134.52, 142.77 (Ph), 217.93, 218.01, 218.11 (CO). ^{29}Si NMR (C$_6$D$_6$): δ −46.52 (Si*Si*Si), −7.20 (FpCH$_2$PhMeSi), −3.32 (FpCH$_2$Me$_2$Si). IR (ν_{CO}, cm^{-1}): 2009(s), 1958(s). HRMS (FAB): calcd for (C$_{27}$H$_{34}$Fe$_2$O$_4$Si$_3$ + Na) *m*/*z* 641.0361, found *m*/*z* 641.0363.

Photolysis of 11: Formation of 1,2,4-Trisilacyclopentane (12a and 12b) and FpPhMeSiCH$_2$SiMe$_2$CH$_2$SiMe$_2$Fp (13). A 5 mm Pyrex NMR tube was charged with 0.15 g (0.24 mmol) of **11** and 1 mL of C$_6$D$_6$ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The ^{29}Si signals due to the starting material at δ −46.52, −7.20, −3.32 ppm disappeared after 2 h and were replaced by eight new resonance signals, which were assigned to the complexes **12a** (−12.95, 5.60 ppm), **12b** (−13.68, −11.86, 9.97 ppm), and **13** (1.45, 36.84, 42.84 ppm), respectively. The solvent was removed under vacuum, and the residue was subjected to a 1 × 10 cm silica gel column. Elution with hexane afforded a colorless oil of **12** (44 mg, 69%) upon removing the solvent very cautiously. ^{1}H NMR and GC/MS spectra of **12** indicate that the two positional isomers, **12a** and **12b**, exist as a ratio of 4:3 in the mixture. Elution with a mixture of benzene/hexane (1:10) developed a yellow band, which was collected and after solvent removal afforded 16 mg (16%) of **13** as a yellow oil. Further elution with a mixture of benzene/hexane (1:3) developed a red band, which was collected and after solvent removal afforded 64 mg (75%) of violet crystals of iron dimer [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$. For **12**: ^{1}H NMR (C$_6$D$_6$): δ −0.15 (AB, ^2J = 13.97 Hz, CH$_2$, **12b**), 0.06 (AB, ^2J = 13.89 Hz, CH$_2$, **12a**), 0.07 (AB, ^2J = 14.22 Hz, CH$_2$, **12b**), 0.16, 0.19, 0.26, 0.29, 0.33, 0.45 (s, s, s, s, s, SiMe), 7.16−7.31, 7.54−7.61 (m, m, Ph). ^{13}C NMR (C$_6$D$_6$): δ −1.83 (Ph*Me*SiSi, **12b**), −1.03, 0.96 (*Me*$_2$SiSi*Me*$_2$, **12a**), −0.81, −0.42 (PhMeSiSi*Me*$_2$, **12b**), 1.31 (Me$_2$Si*C*H$_2$SiMe$_2$, **12b**), 1.41 (PhSi*Me*, **12a**), 1.65 (CH$_2$, **12a**), 2.09, 2.34 (CH$_2$Si*Me*$_2$CH$_2$, **12b**), 3.29 (Me$_2$Si*C*H$_2$SiMePh, **12b**), 128.18, 129.22, 134.03, 141.56 (Ph, **12a**), 128.31, 128.88, 134.54, 139.95 (Ph, **12b**). ^{29}Si NMR (C$_6$D$_6$): δ −12.95 (Si$_2$Me$_4$, **12a**), 5.60 (PhSiMe, **12a**), −13.68, −11.86 (PhMeSiSiMe$_2$, **12b**), 9.97 (SiMe$_2$, **12b**). Anal. Calcd for C$_{13}$H$_{24}$Si$_3$: C, 59.01; H, 9.14. Found: C, 58.54; H, 9.62. For **13**: ^{1}H NMR (C$_6$D$_6$): δ 0.13 (s, 3H, Me), 0.20 (s, 2H, CH$_2$), 0.21 (s, 3H, Me), 0.33 (s, 2H, CH$_2$), 0.61, 0.63 (s, s, 6H, FpSiMe$_2$), 0.90 (s, 3H, FpSi*Me*Ph), 3.94, 4.06 (s, s, 10H, Cp), 7.16−7.27 (m, 3H, Ph), 7.68−7.71 (m, 2H, Ph). ^{13}C NMR (C$_6$D$_6$): δ 3.10, 3.46 (CH$_2$Si*Me*$_2$CH$_2$), 6.35 (FpSi*Me*Ph), 8.76, 8.81 (FpSi*Me*$_2$), 12.05 (FpSiMePh*C*H$_2$), 14.87 (FpSiMe$_2$*C*H$_2$), 83.93, 84.50 (Cp), 128.09, 128.32, 133.15, 148.03 (Ph), 216.63, 217.02 (CO). ^{29}Si NMR (C$_6$D$_6$): δ 1.45 (CH$_2$SiCH$_2$), 36.84 (FpSiPhMe), 42.84 (FpSiMe$_2$). IR (ν_{CO}, cm^{-1}): 1995(s), 1943(s). HRMS (FAB): calcd for (C$_{27}$H$_{34}$Fe$_2$O$_4$Si$_3$ + Na) *m*/*z* 641.0381, found *m*/*z* 641.0363.

Photolysis of 13. A 5 mm Pyrex NMR tube was charged with 30 mg (0.05 mmol) of **13** and 1 mL of C$_6$D$_6$ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. The signals due to the starting material at δ 1.45, 36.84, 42.84 ppm disappeared after 24 h and was replaced by several new resonance signals at δ 2.23, 2.32, 27.39, 32.81, 33.74, 33.82 ppm. We could not identify these new species at present.

Synthesis of ClCH$_2$Me$_2$SiSiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Cl (14). Into a 250 mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 6.50 g (21.5 mmol) of ClMe$_2$SiSiMe$_2$SiMe$_2$SiMe$_2$Cl and 5.55 g (43 mmol) of BrCH$_2$Cl in 100 mL of dry THF. To this mixture, maintained between −78 and −70 °C, was added on the cold wall of the flask, via syringe over 30 min, 26.8 mL (43 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was allowed to warm to room temperature and stirred overnight and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over CaCl$_2$. The solvent was removed, and the residue was distilled at 100−104 °C/1 mmHg to give 6.34 g (89%) of **14**. ^{1}H NMR (C$_6$D$_6$): δ 0.12, 0.13 (s, s, 12H, SiMe$_2$), 2.70 (s, 4H, CH$_2$Cl). ^{13}C NMR (C$_6$D$_6$): δ −5.34, −3.96 (SiMe$_2$), 31.37 (CH$_2$Cl). ^{29}Si NMR (C$_6$D$_6$): δ −47.58 (Si*SiSi*Si), −13.59 (*Si*SiSi*Si*). MS (70 ev): *m*/*z* 281 (M$^+$ − CH$_2$Cl, 1), 223 (M$^+$ − SiMe$_2$CH$_2$Cl, 87), 165 (SiMe$_2$SiMe$_2$CH$_2$Cl$^+$, 65), 73 (Me$_3$Si$^+$, 100). Anal. Calcd for C$_{10}$H$_{28}$Cl$_2$Si$_4$: C, 36.62; H, 8.51. Found: C, 37.13; H, 8.84.

Synthesis of FpCH$_2$Me$_2$SiSiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Fp (15). To 60 mL of a THF solution of [CpFe(CO)$_2$]$^-$Na$^+$ (prepared from 2.00 g (5.6 mmol) of Fp$_2$) was added 1.56 g (4.7 mmol) of **14** at 0 °C. The solution was stirred at low temperature and then permitted to warm to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with hexane. The solution was filtered and concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band, which was collected and after solvent removal afforded a yellow crystalline product of **15** (1.31 g, 45%). Mp: 120−2 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.04 (s, 4H, CH$_2$), 0.40, 0.42 (s, 24H, SiMe$_2$), 4.16 (s, 10H, Cp). ^{13}C NMR (C$_6$D$_6$): δ −23.54 (Fp*C*H$_2$), −4.47, 0.84 (SiMe$_2$), 84.98 (Cp), 218.10 (CO). ^{29}Si NMR (C$_6$D$_6$): δ −43.54 (Si*SiSi*Si), −1.84 (*Si*SiSi*Si*). IR (ν_{CO}, cm^{-1}): 2010(s), 1959(s). Anal. Calcd for C$_{24}$H$_{38}$Fe$_2$O$_4$Si$_4$: C, 46.90; H, 6.23. Found: C, 47.16; H, 6.69.

Photolysis of 15: Formation of FpMe$_2$SiCH$_2$SiMe$_2$SiMe$_2$CH$_2$SiMe$_2$Fp (17). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.24 mmol) of **15** and 1 mL of C$_6$D$_6$ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The color of the solution changed from yellow to violet-red upon irradiation, and after 1 h complete disappearance of **15** and formation of **17** was noted, along with a small amount of the intermediate product **16**. We made no attempt to isolate **16** since it was a low-concentration transient. Irradiation was continued for 2 h and NMR monitoring showed the complete disappearance of **16**. The solvent was then removed under vacuum, and the residue was subjected to a 1 × 10 cm silica gel column. Elution with hexane developed a yellow band, which was collected and after solvent removal afforded 83 mg (83%) of **17** as yellow crystals. For **16**: ^{13}C NMR (C$_6$D$_6$): δ −23.64 (Fp*C*H$_2$), −5.78, 0.28, 0.75, 9.08 (SiMe$_2$), 10.82 (SiCH$_2$Si), 83.89, 85.00 (Cp), 216.59, 218.11 (CO). ^{29}Si NMR (C$_6$D$_6$): δ −46.53 (SiCH$_2$Si*Si*SiCH$_2$), −13.85 (SiCH$_2$*Si*SiSiCH$_2$), −2.72 (SiCH$_2$SiSi*Si*CH$_2$), 44.84 (*Si*CH$_2$SiSiSiCH$_2$). For **17**: Mp: 80−2 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.34 (s, 16H, C*H*$_2$*Me*$_2$SiSi*Me*$_2$C*H*$_2$) 0.63 (s, 12H, FpSi*Me*$_2$), 4.11 (s, 10H, Cp). ^{13}C NMR (C$_6$D$_6$): δ −0.46, 9.09 (SiMe$_2$), 9.76 (CH$_2$), 83.91 (Cp), 216.61 (CO). ^{29}Si NMR (C$_6$D$_6$): δ −17.35 (SiCH$_2$*SiSi*CH$_2$Si), 44.64 (*Si*CH$_2$SiSiCH$_2$*Si*). IR (ν_{CO}, cm^{-1}): 1996(s), 1942(s). Anal. Calcd for C$_{24}$H$_{38}$Fe$_2$O$_4$Si$_4$: C, 46.90; H, 6.23. Found: C, 46.70; H, 6.51.

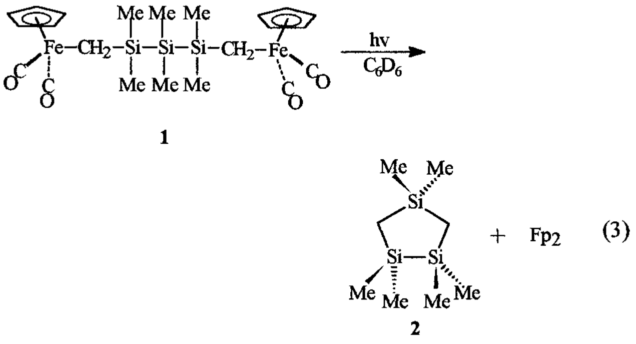
Results and Discussion

Synthesis and Photolysis of FpCH$_2$SiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Fp (1). Complex **1** was readily prepared by reacting $ClCH_2SiMe_2SiMe_2SiMe_2CH_2Cl$ with $[Fp]^-Na^+$ in THF (eq 2).

$$[Fp]^-Na^+ + ClCH_2(SiMe_2)_3CH_2Cl \rightarrow FpCH_2(SiMe_2)_3CH_2Fp \quad (2)$$

The ^{29}Si NMR spectrum of **1** exhibits two signals at −2.55 and 46.4 ppm, which are assigned to the Si atoms β and γ with respect to the Fe atom, i.e., the terminal and central atoms of the trisilane unit, respectively. Comparison of the ^{29}Si NMR chemical shifts of **1** with the permethylated analogue Me_8Si_3 shows that the Si_β and Si_γ atoms are characteristically shifted downfield 13.6 and 2.2 ppm, respectively,[1] and the ^{13}C NMR spectrum exhibits a diagnostic signal for the CH_2 moiety at −23.4 ppm.[4c]

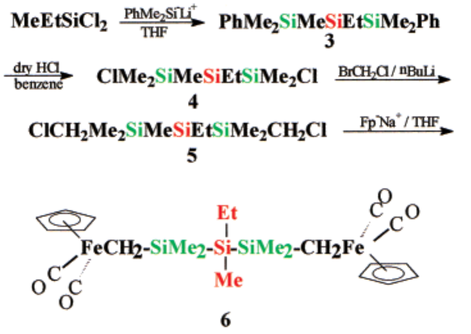
A C_6D_6 solution of **1** in a flame-sealed Pyrex NMR tube was irradiated using a 450 W medium-pressure Hg lamp. The progress of the reaction was periodically monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The spectra obtained after 2 h showed the complete disappearance of **1** and the almost quantitative formation of 1,1,2,2,4,4-hexamethyl-1,2,4-trisilacyclopentane (**2**)[10] and Fp_2 (eq 3).



This reaction is an unprecedented photochemical formation of 1,2,4-trisilacyclopentane from the linear trisilane. In comparison with the linear trisilane **1**, a new structural arrangement occurs in the product **2** with one silicon−silicon bond and one 4-positional silicon atom in the molecule. Since all the silicon atoms have the same substituents, it is not possible to know if there is any specificity to the Si positional transformation.

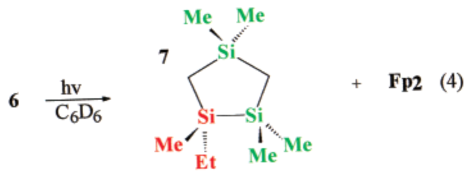
It is well known that a significant deshielding effect on ^{29}Si chemical shifts occurs with the ring strain in cyclic systems.[11] The ^{29}Si NMR spectrum of **2** exhibits two resonance signals at −12.9 and 9.45 ppm representing downfield shifts of 6.84 and 9.45 ppm compared to the acyclic permethylated analogues (Me_6Si_2 and Me_4Si, respectively). These shifts are much smaller than that observed in related cyclic silanes ($\Delta\delta = 16.77$ ppm for silacyclopentane[12] and $\Delta\delta = 16.5$ ppm for silacyclopentene[13]), indicating that incorporation of several silicon atoms in a ring decreases the effect of the ring strain substantially.

Scheme 3



Synthesis and Photolysis of $FpCH_2SiMe_2MeSiEtSiMe_2CH_2Fp$ (6). To examine the fate of Si_γ (the initially central atom of the trisilane chain), we have synthesized complex **6**, where this atom contains both a methyl and an ethyl substituent, Scheme 3. The ^{29}Si NMR spectrum of **6** shows the expected two chemical shifts at −2.55 and −46.4 ppm, and the ^{13}C NMR spectrum has the CH_2 group resonance at −23.4 ppm.

Photochemical irradiation of **6** was monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, and after 2 h **6** had completely disappeared with an almost quantitative formation of 1-ethyl-1,2,2,4,4-heptamethyl-1,2,4-trisilacyclopentane (**7**) and Fp_2, eq 4.



We did not observe the formation of the positional isomer of **7**, 4-ethyl-1,1,2,2,4-heptamethyl-1,2,4-trisilacylcopetane, thereby indicating that the central SiMeEt group is exclusively incorporated as one of the Si atoms in the Si−Si bond of the product.

Synthesis and Photolysis of $FpCH_2PhMeSiSiMe_2SiMe_2CH_2Fp$ (11). The above result suggests that at least one of the terminal Si atoms of the trisilane must transform to the 4-position of the 1,2,4-trisilacyclopentane. However, it is not clear if only one, or both, of these terminal atoms can be transformed. To resolve this ambiguity, we have synthesized and irradiated complex **11**, with only one of the two terminal silicon atoms distinguished with different substituents. A successful synthesis is illustrated in Scheme 4. The ^{29}Si and ^{13}C NMR data for **11** are in accord with the structural assignment exhibiting the expected three resonances (−46.5, −7.20, −3.32 ppm) and two $Fe-CH_2$ resonances at −26.26 and −23.43 ppm, respectively.

Photochemical irradiation of **11** led to a smooth reaction with production of two isomeric 1,2,4-trisilacyclopentanes (**12a** and **12b**), Fp_2, and a new product, $FpPhMeSiCH_2SiMe_2CH_2SiMe_2Fp$ (**13**), eq 5. The latter complex, formed in low yield (16%), results from two β-elimination rearrangement reactions of the type previously noted for disilylmethyl- and trisilylmethyl-Fp complexes and indicates that the presence of the phenyl group can play a very subtle role in determining the outcome of these photochemical reactions. The formation of the two isomers 1,1,2,2,4-heptamethyl-4-phenyl-

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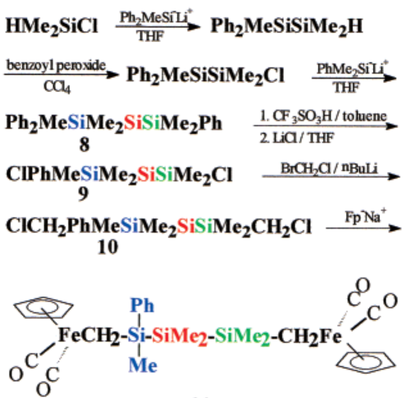
[11] Williams, E. A. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd: New York, 1989; pp 511−555.

[12] Scholl, R. G.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376.

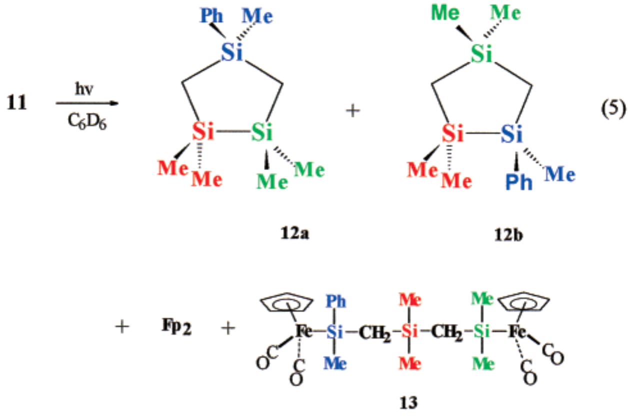
[13] Filleux-Blanchard, M.-L.; An, N. D.; Manuel, G. *Org. Magn. Reson.* **1978**, *11*, 150.

Scheme 4



11

1,2,4-trisilacyclopentane (**12a**) and 1,1,2,4,4-heptamethyl-2-phenyl-1,2,4-trisilacyclopentane (**12b**) indicates that either one of the two terminal silicon atoms of the initial trisilane can be incorporated into the silicon−silicon bond and/or 4-position of the product. It could be argued that the introduction of the phenyl group changes the mechanism for the formation of the 1,2,4-trisilacyclopentanes; that is, the phenyl group is not an innocent substituent. While the formation of **13** certainly indicates that other reaction pathways are possible with this substituent, Occam's Razor leads us to doubt that a totally new mechanistic route is offered for the formation of the cyclopentanes.

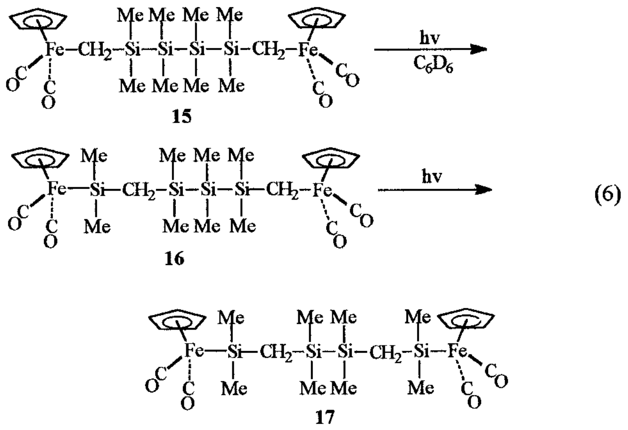


The ^{29}Si NMR spectrum of **12** exhibits five signals at −13.7, −12.9, −11.9, 5.60, and 9.97 ppm. The two signals at −12.9 and 9.97 ppm are assigned to **12a**, and the other three to **12b**. Comparison of the ^{29}Si NMR chemical shifts to its acyclic permethylated analogues indicates that the deshielding effect due to the ring strain still exists.

The ^{29}Si NMR spectrum of **13** exhibits three signals at 1.45, 36.8, and 42.8 ppm. The two downfield signals at 42.8 (FpSiMe$_2$) and 36.8 ppm (FpSiMePh) are close to those of FpSiMe$_3$ and FpSiMe$_2$Ph, respectively. Surprisingly, complex **13** is photochemically labile, and irradiation for 24 h resulted in the formation of new species which, to date, we have been unable to identify. However, we did not observe the formation of **12**, indicating that the formation of **13** is not reversible and is not involved in the initial formation of **12**. We continue to investigate this aspect of the present work.

Synthesis and Photolysis of FpCH$_2$SiMe$_2$SiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Fp (15). The chemistry of the Fp-substituted oligosilanes can be readily distinguished based upon the length of the oligosilane chain. Thus, whereas for disilanes and trisilanes the overall chemistry involves silylene elimination and ultimate formation of Fp-monosilanes, the linear tetrasilanes undergo a molecular rearrangement to form FpSi(Si)$_3$ complexes.[1] Given the variety of chemistry observed for the various 1,3-bis-Fpmethyltrisilanes, including the rearrangement to **13**, it was natural to extend the silicon chain to four atoms.

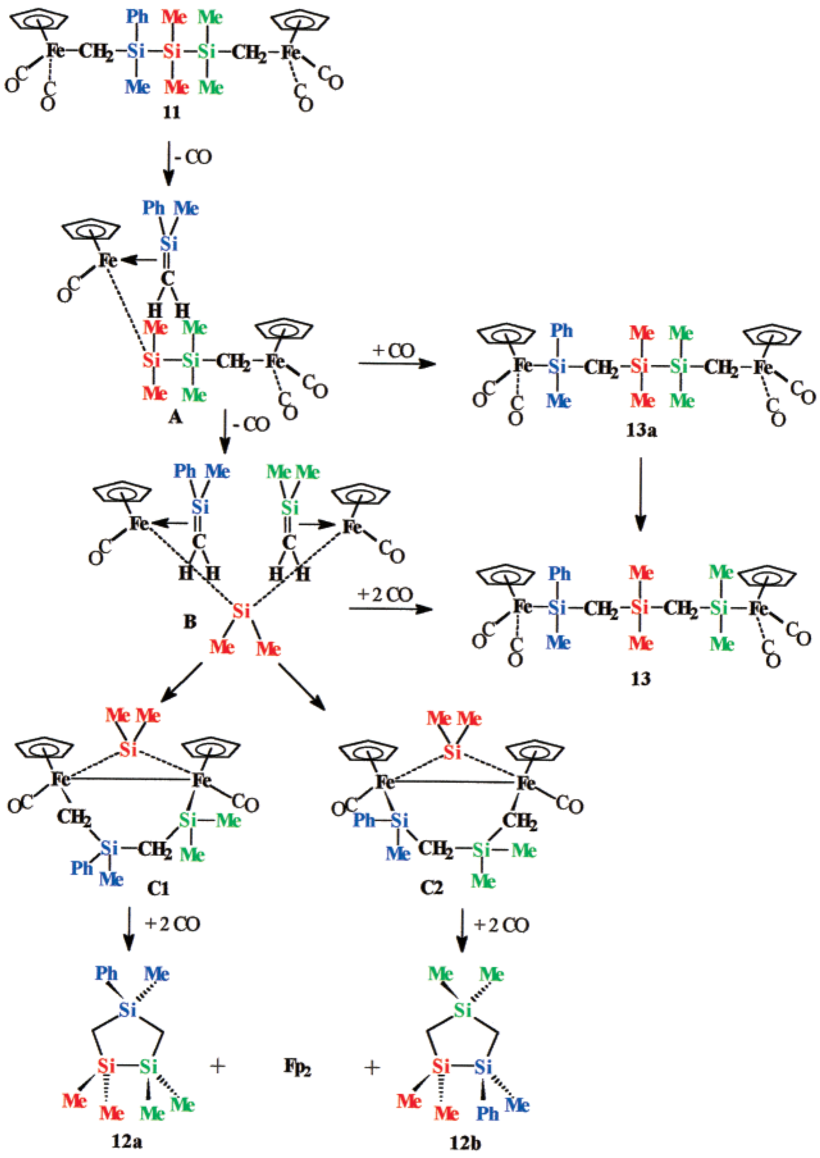
Therefore we have synthesized complex **15** via the reaction between ClCH$_2$SiMe$_2$SiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Cl and [Fp]$^-$Na$^+$ in THF. All spectral and analytical data are in accord with the proposed structure. Photochemical irradiation of **15** resulted in a straightforward high-yield transformation, but unlike the disilyl and trisilyl analogues we observed no elimination chemistry. Only the rearrangement chemistry typical of the di- and trisilylmethylFp complexes occurred to yield **17**, eq 6. Following the photochemical reaction by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy we observed the transient formation of FpMe$_2$SiCH$_2$SiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Fp (**16**), indicating the overall tranformation **15** → **17** was stepwise. We made no attempt to isolate **16** since it existed only as a low-concentration transient.



The ^{29}Si NMR spectrum of **16** exhibits four different signals at −46.5, −13.9, −2.72, and 44.8 ppm. The low-field signal at 44.8 ppm is due to the silicon atom directly attached to the iron, Fp-*Si*; −46.5 ppm is the central Si atom of the trisilyl group, FpCH$_2$Si*Si*Si; −2.72 is FpCH$_2$*Si*; and 13.9 is FpSiC*Si*. All these assignments are in total accord with previous studies on the chemical shifts of oligosilyl Fp complexes. The ^{13}C NMR spectrum of **16** exhibits the high-field signal at −23.6 ppm associated with the Fp-*CH*$_2$ unit. The final product **17** exhibits two signals in the ^{29}Si NMR spectrum at −17.4, 44.6 ppm, and the former resonance exhibits a small downfield shift (2.4 ppm) from the permethylated disilane. Unlike the trisilyl rearranged product **13**, **17** is photochemically stable, which given the presence of a Si−Si bond is somewhat surprising; however, irradiation of **17** for 2 days did not lead to any change except for a little decomposition to Fp$_2$.

Mechanism. We have shown that photolysis of FpCH$_2$MePhSiSiMePhCH$_2$Fp resulted in the stereospecific formation of 1,3-disilacyclobutane and suggested a mechanism involving bis(silene-iron) intermediates.[6] In the present examination of the chemistry of **1**, **6**, and

Scheme 5



11 the formation of 1,2,4-trisilacyclopentanes suggests a related mechanism. Furthermore, since we have demonstrated that there is some specificity to the product formation, the γ-positional silicon atom of **6** does not transform to the 4-position of the product, the mechanism must take this into account. Our present suggestion is presented in Scheme 5.[14]

The formation of **12** is involved in three possible intermediates, **A**, **B**, and **C**. **B** can be considered as bis(silene-iron) intermediates with a bridging silylene unit, structurally similar to known μ-silylene (μ-germylene or μ-stannylene) bimetallic complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2\text{-}ER_2$ (E = Si, Ge, Sn), however also containing silene ligands.[15] Such complexes photochemically rearrange to μ-carbonyl μ-silylene bridged diiron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{(\mu\text{-}SiR_2)(\mu\text{-}CO)_2\}$,[16] indicating that the transformation from **B** to **C** is possible. The assumed intermediates **C** are structurally analogous to the known bimetallic bis(μ-silylene) complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMe_2)_2$.[17,18] The distinction is that one of the bis(μ-silylene) bridges is replaced by the μ-$SiR_2CH_2SiR_2$-CH_2 bridge. The relative ratio of **12a** and **12b** is closely related to the stability of the intermediates **C1** and **C2**. It is clear that the formation of **C1** from **B** is more favorable presumably since the phenyl group in the **C1** molecule is more distant from the metal center (**12a**:**12b** = 4:3).

Although photolysis of the tetrasilane complex **15** resulted in the stepwise formation of the rearranged product **17** via the transient product **16**, we cannot rule

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[14] The Scheme 5 illustrates a possible pathway where the initial CO loss occurs at the terminal silicon atom with a phenyl substituent. However, this does not rule out the possibility that the initial CO loss occurs at the other terminal silicon atom with two methyl groups.

[15] (a) Malisch, W.; Ries, W. *Chem. Ber.* **1979**, *112*, 1304. (b) Aylett, B. J.; Colquhoun, H. M. *J. Chem. Res., Synop.* **1977**, 148. (c) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Denisov, F. S. *Izv. Akad. Nauk SSSR Ser. Khim.* **1966**, 2246. (d) Bush, M. A.; Woodward, P. *J. Chem. Soc. A* **1967**, 1833. (e) Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1972**, *34*, C15. (f) Bir'yukov, B. P.; Struchkov, Yu. T.; Anisimov, K. N.; Kolobova, N. E.; Skripkin, V. V. *Chem. Commun.* **1968**, 159. (g) Zhang, Y.; Xu, S.; Tian, G.; Zhang, W.; Zhou, X. *J. Organomet. Chem.* **1997**, *544*, 43.

[16] Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120.

[17] (a) Pannell, K. H.; Sharma, H. K. *Organometallics* **1991**, *10*, 954. (b) Sharma, H. K.; Pannell, K. H. *Organometallics* **1994**, *13*, 4946.

[18] (a) Uneo, K.; Hamashima, N.; Ogino, H. *Organometallics* **1991**, *10*, 959. (b) Uneo, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435.

out the possibility of the concerted formation of **13** from **B** since we did not observe the formation of the transient product **13a** by closely following the photolysis via ^{29}Si NMR spectroscopy. Photolysis of **1** and **6** did not result in the formation of the rearranged products, while similar irradiation of **11** afforded a significant amount of the rearranged product, indicating that the phenyl group possibly stabilizes the silene intermediates via the electronic delocalization.

Overall, we can now understand that in the general system $FpCH_2(SiR_2)_nCH_2Fp$ the elimination chemistry is essentially restricted to the shorter chain lengths containing five or less atoms. The ability of the two terminal iron systems to be in close proximity is undoubtedly a key factor in this restriction. We are continuing our studies on such systems containing other transition metals and/or other group 14 elements, i.e., Ge and Sn.

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Supporting Information Available: ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopic data for complexes **6**, **9**, **11**, **12a/b**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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