

Synthesis and Photochemistry of the Three Isomeric Si₂C₂ Diiron Complexes FpCH₂SiR₂SiR₂CH₂Fp, FpCH₂SiR₂CH₂SiR₂Fp, and FpSiMe₂CH₂CH₂SiMe₂Fp (Fp = (η⁵-C₅H₅)Fe(CO)₂): Stereospecific Formation of 1,3-Disilacyclobutanes

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Photolysis of FpCH₂SiMe₂SiMe₂CH₂Fp (**1**; Fp = (η⁵-C₅H₅)Fe(CO)₂) for 4 h resulted in the quantitative formation of 1,3-tetramethyldisilacyclobutane (**9**) and Fp₂. Similar irradiation of *meso*-FpCH₂SiMePhSiMePhCH₂Fp (**2a**) led to *trans*-1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (**10t**), while photolysis of the racemic isomer (**2b**) afforded only *cis*-1,3-disilacyclobutane (**10c**) and Fp₂. Photolysis of a mixture of **1** and **2a** proved that the process was intramolecular. Irradiation for 35 h of FpCH₂SiMe₂CH₂SiMe₂Fp (**3**), an isomer of **1**, led to clean conversion to **9** and Fp₂ and irradiation of FpCH₂SiMePhCH₂SiMePhFp, a 1:1 mixture of the two diastereomers **6a** and **6b**, afforded a mixture of **10t** and **10c** (1:1). The third isomer of **1**, FpSiMe₂CH₂CH₂SiMe₂Fp (**7**), is photochemically inert. Photolysis of the tungsten analogue of **1**, WpCH₂SiMe₂SiMe₂CH₂Wp (**8**; Wp = (η⁵-C₅H₅)W(CO)₃), produced a complex mixture of products.

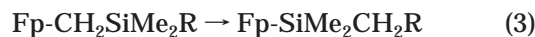
Introduction

The activation of the silicon–silicon bond by transition metals has implications in catalysis and materials science.¹ The family of oligosilyl Fp derivatives (Fp = (η⁵-C₅H₅)Fe(CO)₂) containing direct iron–silicon bonds exhibit photochemically induced α-elimination reactions, resulting in the formation of silyl(silylene) intermediates, (η⁵-C₅H₅)Fe(CO)(SiR₃) (=SiR₂). These intermediates lead to either silylene eliminations (eq 1) or rearrangements (eq 2).^{2,3}



The oligosilylmethyl Fp complexes FpCH₂(SiMe₂)_nMe have the potentially labile silyl group in the β-position

with respect to the metal center, and thus β-elimination chemistry results in the transient formation of iron–silene intermediates that lead to rearrangements (eq 3; R = H, (SiMe₂)_nSiMe₃, GeMe₃). In the specific case of R = GeMe₃ and Wp = (η⁵-C₅H₅)W(CO)₃ (eq 4) a unique silene elimination occurs.⁴



The silene iron intermediates in these photochemically induced β-elimination reactions have been characterized only by low-temperature matrix-isolation techniques;⁵ however, many stable transition-metal silene complexes have been isolated and structurally characterized.⁶

We recently communicated that the photolysis of the diiron complexes FpCH₂SiR₂SiR₂CH₂Fp (R₂ = Me₂ (**1**), MePh (**2**)) resulted in stereospecific formation of 1,2-disilacyclobutanes.⁷ To further study the factors that control such chemistry, we now present the synthesis and photochemical treatment of FpSiR₂CH₂SiR₂CH₂Fp

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(R₂ = Me₂ (**3**), MePh (**6**)) and FpMe₂SiCH₂CH₂SiMe₂Fp (**7**) complexes, where the chains bridging the two Fe atoms are isomeric with **1**, together with a tungsten analogue of **1**, WpCH₂Me₂SiSiMe₂CH₂Wp (**8**).

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, Br(CH₂)₄Br, and BrCH₂Cl, Aldrich; Ph₂MeSiCl, ClMe₂SiCH₂Cl, Cl₂MeSiCH₂Cl, PhMeHSiCl, Me₃SiSiMe₃, and ClMe₂SiCH₂CH₂SiMe₂Cl, Gelest. Other reagents were synthesized by literature procedures with some modifications: ClCH₂Me₂SiSiMe₂CH₂Cl,⁸ PhMeHSiCH₂Cl,⁸ ICH₂Me₂SiSiMe₂CH₂I,⁹ Ph₂MeSiSiMePh₂,¹⁰ ClPhMeSiCH₂Cl,¹¹ and ClSiMe₂CH₂SiMe₂CH₂Cl.¹² Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer. Infrared (IR) spectra were obtained on a Perkin-Elmer 1600 series FT-IR spectrometer using hexane as solvent. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of ClPhMeSiSiMePhCl. To a solution of Ph₂MeSiSiMePh₂ (20.0 g, 50.8 mmol) in 100 mL of toluene was added dropwise trifluoromethanesulfonic acid (15.2 g, 101.6 mmol) at –30 °C. The reaction mixture was warmed to room temperature over 1 h and was stirred for an additional 2 h. The reaction mixture was transferred to a dropping funnel and was slowly added to a solution of lithium chloride (6.48 g, 159 mmol) in 70 mL of THF at 0 °C. The reaction mixture was then stirred overnight at room temperature. The solvents were removed under vacuum. 300 mL of hexane was added to the residue, and this solution was then filtered to remove the lithium salts. The solvent was removed from the filtrate by rotary evaporation, and the residue was distilled at 128–132 °C/0.7 mmHg (lit.¹³ 141–146 °C/2 mmHg) to afford 10.1 g (64%) of the crystalline product ClPhMeSiSiMePhCl as a mixture of two isomers (1:1).

This compound was also prepared by reacting Cl₂MeSiSiMeCl₂ with the Grignard reagent PhMgBr.¹³ ¹H NMR (C₆D₆): δ 0.65 (s, 6H, SiMe), 0.71 (s, 6H, SiMe), 7.09–7.19 (m, 12H, Ph), 7.49–7.52 (m, 4H, Ph), 7.62–7.65 (m, 4H, Ph). ¹³C NMR (C₆D₆): δ 0.23 (SiMe), 128.65, 128.75, 130.90, 130.97, 133.95, 134.03, 134.14, 134.19 (Ph). ²⁹Si NMR (C₆D₆): δ 6.60, 6.82.

Synthesis of ClCH₂PhMeSiSiMePhCH₂Cl. Into a 250 mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 6.22 g (0.02 mol) of ClPhMeSiSiMePhCl and 5.18 g (0.04 mol) of BrCH₂Cl 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, 25 mL (0.04 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was warmed to room temperature, stirred overnight, and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over CaCl₂. The solvent was removed, and the residue was distilled, by using a 20-cm Vigreux column at 150–152 °C/0.7 mmHg to give 5.70 g (85%) of ClCH₂MePhSiSiPhMeCH₂Cl as a mixture of two isomers (10:7).

Synthesis of FpCH₂MeRSiSiRMeCH₂Fp (R = Me (1**), Ph (**2**)).** To 50 mL of a THF solution of [CpFe(CO)₂][–]Na⁺

(prepared from 2.00 g (5.60 mmol) of [(η⁵-C₅H₅)Fe(CO)₂]₂) was added 1.14 g (5.30 mmol) of ClCH₂Me₂SiSiMe₂CH₂Cl at 0 °C. The solution was stirred at low temperature and then warmed to room temperature and further stirred overnight. The solvent was removed under vacuum, and the residue was extracted with a mixture of hexane and methylene chloride (90/10). The solution was filtered and concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with the same solvent mixture developed a yellow band that was collected and after solvent removal afforded a yellow crystalline solid. The solid was recrystallized from a mixture of hexane/methylene chloride to yield 1.70 g (64%) of orange-yellow crystals of **1**.

Complex **2** was similarly synthesized as a mixture (*meso/dl* = 5:1) of two isomers in 23% yield by treatment of [CpFe(CO)₂][–]Na⁺ with ClCH₂MePhSiSiPhMeCH₂Cl in THF. Recrystallization of **2a** and **2b** from a mixture of CH₂Cl₂ and hexane yielded cubic prisms (**2a**, *meso*) and rectangular prisms (**2b**, *dl*) that were separated mechanically.

Synthesis of FpCH₂SiMe₂CH₂SiMe₂Fp (3**).** To 50 mL of a THF solution of [CpFe(CO)₂][–]Na⁺ (prepared from 2.00 g (5.6 mmol) of Fp₂) was added 1.14 g (5.3 mmol) of ClCH₂SiMe₂CH₂SiMe₂Cl at 0 °C. The solution was warmed to room temperature and 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 then placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band that was collected and after solvent removal afforded a yellow crystalline product of **3** (0.91 g, 35%). Mp: 78–80 °C. ¹H NMR (C₆D₆): δ 0.15 (s, 2H, FpCH₂) 0.32 (s, 6H, SiMe₂), 0.40 (s, 2H, SiCH₂Si), 0.68 (s, 6H, FpSiMe₂), 4.14 (s, 10H, Cp). ¹³C NMR (C₆D₆): δ –21.20 (FpCH₂), 3.70, 8.99 (SiMe₂), 15.83 (SiCH₂Si), 83.98, 85.21 (Cp), 216.84, 218.42 (CO). ²⁹Si NMR (C₆D₆): δ 9.66 (FpCH₂SiMe₂), 43.01 (FpSiMe₂). IR (ν_{CO}, cm^{–1}): 2011 (s), 1995 (s), 1959 (s), 1941 (s). Anal. Calcd for C₂₀H₂₆Fe₂O₄Si₂: C, 48.21; H, 5.26. Found: C, 47.77; H, 5.33.

Synthesis of ClCH₂SiPhMeCH₂SiPhMeH (4**).** To 30 mL of a THF solution of 7.06 g (34.4 mmol) of ClPhMeSiCH₂Cl was slowly added a Grignard reagent (prepared from 1.18 g (48.6 mmol) of magnesium turnings and 8.0 g (44.2 mmol) of PhMeHSiCH₂Cl in 110 mL of THF) at 0 °C. The reaction mixture was warmed to room temperature and then refluxed for 20 h. The reaction mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride. The organic layer was separated, and the aqueous phase was extracted with ether (2 × 30 mL). The extracts were combined and the organic layer was washed with water, sodium bicarbonate, and then water and dried over calcium chloride. The solvent was removed, and the residue was distilled using a 20 cm Vigreux column at 150–156 °C/0.7 mmHg to give 7.20 g (68%) of **4**, existing as a mixture of two diastereomers (1:1). ¹H NMR (C₆D₆): δ 0.21, (d, ³J = 3.66 Hz, 3H, SiMePhH), 0.25 (d, ³J = 3.72 Hz, 3H, SiMePhH), 0.34 (s, 3H, SiMePhCH₂Cl), 0.36 (s, 3H, SiMePhCH₂Cl), 0.33–0.44 (m, 4H, SiCH₂Si), 2.76 (AB, ²J = 13.6 Hz, 2H, CH₂Cl), 2.80 (s, 2H, CH₂Cl), 4.64 (m, 2H, SiMePhH), 7.20–7.25 (m, 12H, Ph), 7.42–7.48 (m, 8H, Ph). ¹³C NMR (C₆D₆): δ –4.19, –3.94 (SiMePhH), –3.42, –3.40 (SiCH₂Si), –2.45 (SiMePhCH₂Cl), 30.87, 30.94 (CH₂Cl), 128.34, 128.39, 128.41, 129.77, 129.81, 130.03, 130.06, 134.35, 134.37, 134.54, 136.42, 136.43, 137.67, 137.72 (Ph). ²⁹Si NMR (C₆D₆): δ –16.57, –16.47 (SiMePhH), –3.06, –3.04 (SiMePhCH₂Cl). MS (70 eV): *m/z* 289 [M – Me]⁺, 1; 255 [M – CH₂Cl]⁺, 88; 211 [M – Me – C₆H₆]⁺, 22; 177 [M – CH₂Cl – C₆H₆]⁺, 100; 135 [PhMeSiHCH₂]⁺, 18; 121 [PhMeSiH]⁺, 20; 91 [C₇H₇]⁺, 30; 65 [C₅H₅]⁺, 12. Anal. Calcd for C₁₆H₂₁ClSi₂: C, 63.01; H, 6.94; Found: C, 62.36; H, 6.95.

Synthesis of ClCH₂SiPhMeCH₂SiPhMeCl (5**).** A flask equipped with a magnetic stirring bar and a reflux condenser was charged with 6.2 g (20.8 mmol) of ClCH₂SiPhMeCH₂SiPhMeH (**4**) and 0.32 g (1.3 mmol) of benzoyl peroxide in 20 mL of CCl₄. The solution was refluxed for 10 h and was cooled to room temperature. The solvent was removed under vacuum,

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and 50 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 using a 20 cm Vigreux column at 170–174 °C/0.7 mmHg to give 6.1 g (86%) of **5** as a mixture of two diastereomers (1:1). Compound **5** was previously prepared by a ring-opening reaction of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane with Cl₂.¹⁴ ¹H NMR (C₆D₆): δ 0.30, 0.41, 0.42, 0.44 (s, s, s, 12H, SiMe), 0.65 (AB, ²J = 14.0 Hz, 2H, SiCH₂Si), 0.67 (AB, ²J = 14.2 Hz, 2H, SiCH₂Si), 2.75 (AB, ²J = 13.8 Hz, 2H, CH₂Cl), 2.80 (s, 2H, CH₂Cl), 7.18–7.24 (m, 12H, Ph), 7.35–7.39 (m, 4H, Ph), 7.46–7.49 (m, 4H, Ph). ¹³C NMR (C₆D₆): δ -3.95, -3.89 (SiMePhCH₂Cl), 2.87, 3.05 (SiCH₂Si), 3.13 (SiMePhCl), 30.77 (CH₂Cl), 128.38, 128.48, 130.21, 130.69, 133.54, 133.56, 134.37, 135.77, 135.81, 136.91, 137.03 (Ph). ²⁹Si NMR (C₆D₆): δ -4.27, -4.17 (SiMePhCH₂Cl), 19.47, 19.49 (SiMePhCl).

Synthesis of FpCH₂SiPhMeCH₂SiPhMeFp (6). To 50 mL of a THF solution of [CpFe(CO)₂]⁻Na⁺ (prepared from 2.00 g (5.6 mmol) of Fp₂) was added 1.60 g (4.7 mmol) of ClCH₂-SiPhMeCH₂SiPhMeCl at 0 °C. The solution was stirred at low temperature for 30 min and then warmed to room temperature and 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 then placed upon a 2.5 × 20 cm silica gel column. Elution with hexane developed a yellow band that was collected and after solvent removal afforded a yellow oily product of **6** (2.08 g, 71%) as a mixture of two diastereomers (**6a:6b** = 1:1). ¹H NMR (C₆D₆): δ -0.08 (AB, ²J = 13.6 Hz, 2H, FpCH₂), 0.04 (AB, ²J = 12.5 Hz, 2H, FpCH₂), 0.39, 0.51 (s, s, 6H, FpCH₂SiPhMe), 0.64, 0.91 (s, s, 6H, FpSiPhMe), 1.11 (AB, ²J = 14.1 Hz, 2H, SiCH₂Si), 1.13 (AB, ²J = 14.0 Hz, 2H, SiCH₂Si), 3.96, 3.97, 3.98 (s, s, s, 20H, Cp), 7.20–7.33 (m, 12H, Ph), 7.57–7.79 (m, 8H, Ph). ¹³C NMR (C₆D₆): δ -23.19, -22.01 (FpCH₂), 0.03, 0.76, (FpCH₂SiPhMe), 6.07, 6.76 (FpSiPhMe), 12.06, 12.24 (SiCH₂Si), 84.47, 84.83, 84.93 (Cp), 127.86, 127.96, 128.01, 128.10, 128.24, 128.59, 128.77, 133.20, 133.24, 143.96, 144.22, 148.01, 148.29 (Ph), 216.72, 216.76, 217.03, 217.06, 218.02, 218.08 (CO). ²⁹Si NMR (C₆D₆): δ 4.94, 5.13 (SiMePhCH₂Fp), 36.72, 36.74 (FpSiMePh). IR (ν_{CO}, cm⁻¹): 2010 (s), 1994 (s), 1959 (s), 1942 (s). Anal. Calcd for C₃₀H₃₀Fe₂O₄Si₂: C, 57.89; H, 4.86. Found: C, 58.22; H, 4.99.

Synthesis of WpCH₂Me₂SiSiMe₂CH₂Wp (8). To a solution of [CpW(CO)₃]⁻Na⁺ (8.5 mmol) in 60 mL of THF was added 1.5 g (3.75 mmol) of ICH₂Me₂SiSiMe₂CH₂I in 10 mL of THF, and the solution was stirred overnight. Infrared monitoring of the reaction showed the presence of unreacted tungsten carbonylate, and therefore, the solution was heated to reflux for 24 h. This resulted in the completion of the reaction. The solvent was removed, and the resulting yellowish brown liquid residue was extracted with a mixture of hexane and methylene chloride (90/10). The solution was filtered, concentrated to 5 mL, and placed upon a 2.5 × 20 cm silica gel column. Elution with the same solvent mixture developed a yellow band that was collected and after solvent removal afforded an orange crystalline solid. The solid was recrystallized from a mixture of hexane and methylene chloride to yield 2.04 g (67%) of yellow crystals of **8**, mp 124–126 °C. ¹H NMR (C₆D₆): δ 0.24 (s, 4H, CH₂), 1.12 (s, 12H, SiMe₂), 4.56 (s, 10H, Cp). ¹³C NMR (C₆D₆): δ -38.40 (CH₂), 0.98 (SiMe₂), 91.62 (Cp), 218.90, 230.69 (CO). ²⁹Si NMR (C₆D₆): δ -6.28. IR (ν_{CO}, cm⁻¹): 2015 (s), 1927 (s). Anal. Calcd for C₂₂H₂₆O₆Si₂W₂: C, 32.61; H, 3.23; Found: C, 31.95; H, 3.26.

Synthesis of FpMe₂SiCH₂CH₂SiMe₂Fp (7). A solution of [CpFe(CO)₂]⁻Na⁺ was prepared by reacting 2.00 g (5.60 mmol) of [(η⁵-C₅H₅)Fe(CO)₂]₂ with Na–Hg amalgam in 50 mL of THF. The solvent was removed completely under vacuum, and 70 mL of hexane was then added to the residue to produce a

slurry. To this mixture was slowly added 1.07 g (5.0 mmol) of ClMe₂SiCH₂CH₂SiMe₂Cl via syringe at 0 °C. The solution was stirred for 24 h. The solvent was removed under vacuum, and the residue was extracted with a mixture of hexane and methylene chloride (90/10). The solution was filtered, concentrated to 5 mL, and placed upon a 2.5 × 20 cm silica gel column. Elution with the same solvent mixture developed a light yellow band that was collected and after solvent removal afforded a yellow crystalline solid. The solid was recrystallized from a mixture of hexane and methylene chloride to yield 0.55 g (22%) of pale yellow crystals of **7**, mp 146–148 °C. ¹H NMR (C₆D₆): δ 0.56 (s, 12H, SiMe₂), 1.12 (s, 4H, CH₂), 4.14 (s, 10H, Cp). ¹³C NMR (C₆D₆): δ 4.97 (SiMe₂), 19.06 (CH₂), 83.49 (Cp), 216.48 (CO). ²⁹Si NMR (C₆D₆): δ 43.25. IR (ν_{CO}, THF, cm⁻¹): 1988 (s), 1931 (s). Anal. Calcd for C₂₀H₂₆Fe₂O₄Si₂: C, 48.21; H, 5.26; Found: C, 48.78; H, 5.84.

Photolysis of 1: Formation of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (9). A 5 mm Pyrex NMR tube was charged with 0.15 g (0.3 mmol) of **1** and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp at a distance of 2–5 cm. The progression of the reaction was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 4 h complete disappearance of **1** and formation of **9** and Fp₂ was noted, along with traces of ferrocene. After removal of the solvent the resulting violet-red solid Fp₂ was washed twice with cold hexane and dried under vacuum. Yield: 95 mg (89%). **9** and the solvent C₆D₆ could not be separated by distillation, but a solution of **9** in C₆D₆ could be obtained by distillation under vacuum. **9** was characterized by ¹H, ¹³C, and ²⁹Si NMR and GC/MS (temperature 140 °C, solvent delay 2 min).¹⁸

Photolysis of 1 in the Presence of CH₃OH (or *t*-BuOH). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.2 mmol) of **1**, 76 mg (2.4 mmol) of CH₃OH, and 1 mL of C₆D₆. The solution was subjected to three freeze–pump–thaw cycles and then sealed under vacuum. Irradiation was carried out as above. The progression of the reaction was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 2 h the starting material **1** completely disappeared and **9** was formed with Fp₂. Similar treatment of 0.10 g (0.2 mmol) of **1** and 150 mg (2 mmol) of *t*-BuOH afforded the same result as above.

Photolysis of 2a and 2b: Formation of 1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane (10). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.16 mmol) of **2a** and 1 mL of C₆D₆ and sealed under vacuum. The sample was irradiated as above, and the reaction was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 2 h complete disappearance of **2a** and formation of the trans isomer **10t** and Fp₂ was noted, along with traces of ferrocene. The solvent was removed under vacuum, and the residue was extracted with hexane. The extracts were placed upon a silica gel column. Elution with hexane afforded complex **10t**. The violet-red solid left after extraction was dried under vacuum to afford 46 mg (82%) of Fp₂. Compound **10t** was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy and GC/MS.

Similar photolysis of **2b** afforded only the cis isomer **10c** and Fp₂. **10c** was also characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy and GC/MS.¹⁹

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(16) Pannell, K. H.; Lin, S.-H.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

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

(14) Derine, A. M.; Griffin, P. A.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. *J. Chem. Soc., Dalton Trans.* **1975**, 1822.

Table 1. Crystallographic Data for 1, 2a, and 2b

	1	2a	2b
empirical formula	C ₂₀ H ₂₆ Fe ₂ O ₄ Si ₂	C ₃₀ H ₃₀ Fe ₂ O ₄ Si ₂	C ₃₀ H ₃₀ Fe ₂ O ₄ Si ₂
fw	498.3	622.4	622.4
cryst size (mm)	0.32 × 0.50 × 0.60	0.16 × 0.22 × 0.36	0.28 × 0.08 × 0.36
group syst	monoclinic	triclinic	monoclinic
cryst space	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
unit cell dimens			
<i>a</i> (Å)	8.867(2)	8.607(2)	12.490(6)
<i>b</i> (Å)	6.873(2)	9.509(2)	18.956(8)
<i>c</i> (Å)	19.038(4)	9.819(2)	13.856(8)
α, deg	90	86.84(2)	90
β, deg	98.15(2)	64.95(1)	112.11(4)
γ, deg	90	86.58(2)	90
<i>V</i> (Å ³)	1148.5(5)	726.3(3)	3039(3)
<i>Z</i>	2	1	4
<i>d</i> _{calcd} (g cm ⁻³)	1.441	1.423	1.360
μ, cm ⁻¹	13.86	11.11	10.62
2θ range (deg)	3.5–45.0	3.5–50.0	3.5–45.0
scan type	ω	2θ-θ	ω
scan speed (deg/min)	4–20	3–15	4–20
scan range (ω) (deg)	1.20	1.20	1.20
std rflns		3 measd every 197 rflns	
index ranges			
<i>h</i>	0–9	0–10	–13 to 13
<i>k</i>	0–7	–11 to 11	–20 to 20
<i>l</i>	–20 to 20	–10 to 11	–14 to 14
no. of rflns collected	1624	2771	8578
no. of indep rflns	1510	2581	3989
no. of obsd data	1382 (<i>F</i> > 4.0σ(<i>F</i>))	2181 (<i>F</i> > 3.0σ(<i>F</i>))	3270 (<i>F</i> > 3.0σ(<i>F</i>))
abs cor	n/a	semiempirical	semiempirical
final <i>R</i> indices (obsd data) (%)			
<i>R</i>	4.17	3.33	6.46
<i>R</i> _w	6.35	4.34	7.48
goodness of fit	1.69	1.03	1.59

Photolysis of 1 and 2a. A 5 mm Pyrex NMR tube was charged with 30 mg (0.05 mmol) of **2a**, 24 mg (0.05 mmol) of **1**, and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 2 h the starting materials **2a** and **1** completely disappeared and the trans isomer **10t** and **9** were formed along with Fp₂. No crossover product was detected.

Photolysis of 3: Formation of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (9). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.2 mmol) of **3** and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 35 h complete disappearance of **3** and formation of **9** and Fp₂ was noted. After removal of the solvent, the resulting violet-red solid Fp₂ was washed twice with cold hexane and dried under vacuum (65 mg, 92%). **9** and the solvent C₆D₆ could not be separated by distillation, but a solution of **9** in C₆D₆ could be obtained by distillation under vacuum. **9** was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy and GC/MS.

Photolysis of 3 in the Presence of CH₃OD (or PPh₃). A 5 mm Pyrex NMR tube was charged with 0.10 g (0.2 mmol) of **3**, 24 mg (0.73 mmol) of CH₃OD, and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The color of the solution changed from yellow to dark red upon irradiation, and after 45 h the complete disappearance of **3** and only the formation of **9** and Fp₂ was noted.

Similar photolysis of **3** in the presence of PPh₃ for 3 h resulted in the disappearance of the starting material and the formation of several new unidentified products (²⁹Si NMR, 43.09, 43.03, 10.20, 10.16, 6.67, 0.29, –23.66, –23.70 ppm). Only trace amounts of **9** and Fp₂ were observed.

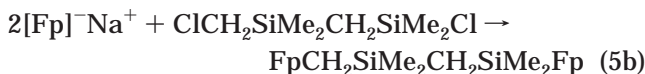
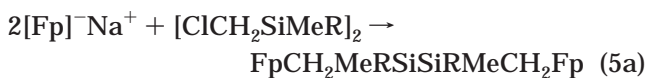
Photolysis of 6: Formation of 1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane (10). A 5 mm Pyrex NMR tube was charged with 0.18 g (0.29 mmol) of **6** (**6a:6b** = 1:1) and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp. The progress of the reaction was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. After 11 h ²⁹Si NMR spectroscopy indicated the complete disappearance of the starting material **6** and the formation of **10** as a mixture of the cis and trans isomers (**10t:10c** = 1:1). The solvent was removed under vacuum, and the residue was placed onto a 1 × 10 cm silica gel column. Elution with hexane afforded a colorless oil of **10** (69 mg, 89%) upon removing the solvent. Elution with a mixture of benzene and hexane (1:3) developed a red band, which was collected and after solvent removal afforded 78 mg (76%) of violet crystals of Fp₂.

Photolysis of 3 and 6. A 5 mm Pyrex NMR tube was charged with 30 mg (0.05 mmol) of **6**, 24 mg (0.05 mmol) of **3**, and 1 mL of C₆D₆ and sealed under vacuum. Irradiation was monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. After 12 h the starting materials **6** and **3** had completely disappeared and **9** and **10** were formed along with Fp₂. No crossover product was detected.

X-ray Diffraction Studies. Crystals (**1**, **2a**, and **2b**) suitable for X-ray diffraction analysis were obtained from hexane solution. Intensity data were collected on a Nicolet-Siemens R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω-scan technique was applied in the 2θ range 3.5° ≤ 2θ ≤ 45.0° with variable scan speeds except for complex **2a** (3.5° ≤ 2θ ≤ 50.0°). The structures were refined by anisotropic, full-matrix least squares. Hydrogen atomic positions were generated from the assumed geometry. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are presented in Tables 2 (**1**), 3 (**2a**), and 4 (**2b**).

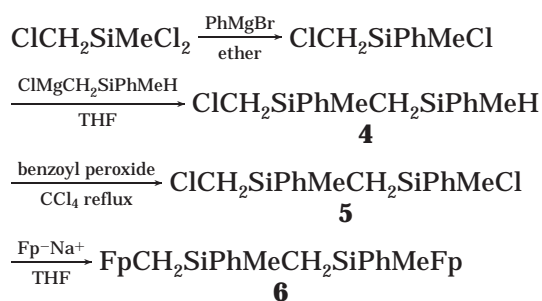
Results and Discussion

Synthesis and Spectroscopic Properties of the Fp Derivatives. The compounds FpCH₂MeRSiSiRMeCH₂Fp (R = Me (**1**), Ph (**2**)) and FpCH₂SiMe₂CH₂SiMe₂Fp (**3**) were readily prepared in THF by the salt-elimination reactions outlined in eq 5.



The compound FpCH₂MePhSiCH₂SiMePhFp (**6**) was also synthesized in an overall 33% yield via the multi-step process outlined in Scheme 1.

Scheme 1



The tungsten analogue of **1**, WpCH₂Me₂SiSiMe₂CH₂Wp (**8**), was readily synthesized in good yield (67%) by reacting ICH₂Me₂SiSiMe₂CH₂I with Wp⁻Na⁺ in THF. Similar treatment of ClMe₂SiCH₂CH₂SiMe₂Cl with [Fp]⁻Na⁺ in THF failed to yield the expected product FpMe₂SiCH₂CH₂SiMe₂Fp (**7**); however, it was obtained in 22% yield from the same reagents when hexane was used as the solvent.

²⁹Si NMR spectroscopy is useful for structural analysis of metal-substituted oligosilanes. In general, silicon atoms directly attached to the metal atom are significantly shifted downfield compared to those of their permethylated analogues; this shift is reduced as the two atoms become separated, and the effect is also additive when the two ends of the silicon atom are attached by the metal-containing substituents. The ²⁹Si NMR spectrum of **1** exhibits one resonance signal at -6.03 ppm, which is shifted downfield over 13 ppm compared to the resonance at -19.5 ppm for the permethylated disilane Me₃SiSiMe₃. The downfield shift was also observed in the ²⁹Si NMR spectra of **2** (-9.00, -9.07 ppm) and **8** (-6.28 ppm). The ²⁹Si NMR spectrum of **3** exhibited two distinct resonances, which were assigned to Fp-Si (43.0 ppm) and FpCH₂-Si (9.66 ppm), respectively. Compound **6** is a mixture of two diastereomers, and the ²⁹Si signals at 36.72 and 36.74 ppm are assigned to Fp-Si, and the signals at 4.94 and 5.13 ppm are due to FpCH₂-Si. These downfield shifts are in the range of the normal shifts (Δδ = 35–45 ppm) for the α-Si atoms and (Δδ = 5–13 ppm) for the β-Si atoms with respect to the Fe atoms.¹

The ¹³C NMR spectra for these complexes were useful for characterization of the CH₂ moiety directly bonded to the transition-metal atom. This carbon atom is significantly shifted upfield (-23.6 ppm (**1**); -26.6,

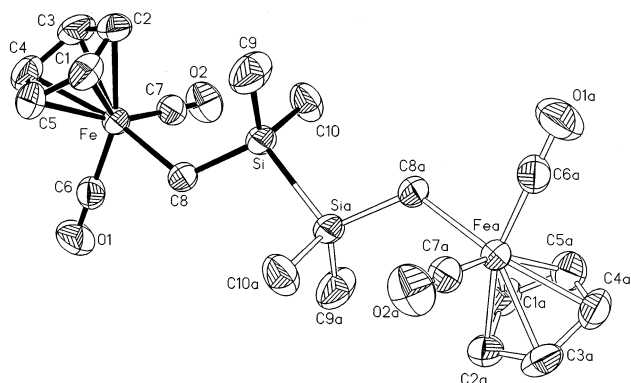


Figure 1. Molecular structure of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Fe-C(6)	1.755(4)	Fe-C(7)	1.747(4)
Fe-C(8)	2.098(4)	Si-SiA	2.354(2)
Si-C(8)	1.873(4)	Si-C(9)	1.874(5)
O(1)-C(6)	1.147(5)	O(2)-C(7)	1.151(5)
C(1)-Fe-C(2)	38.8(1)	C(1)-Fe-C(3)	65.4(2)
C(6)-Fe-C(7)	93.9(2)	C(6)-Fe-C(8)	85.9(2)
C(7)-Fe-C(8)	91.1(2)	Fe-C(8)-Si	121.5(2)
C(8)-Si-SiA	107.8(1)	C(9)-Si-C(10)	107.5(2)

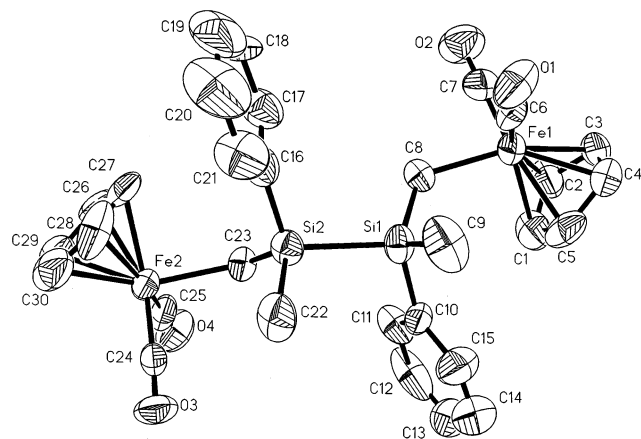
-26.8 ppm (**2**); -21.20 ppm (**3**); -23.19, -22.01 ppm (**6**); -38.4 ppm (**8**), in accord with monoiron analogues.^{4b,c} In all cases the carbonyl groups exhibit distinctive resonances and it is possible to distinguish the Fp-alkyl and Fp-silyl portions of the new complexes.

The infrared spectra of **3** and **6** also clearly indicated the two distinct Fp groups existing in the molecules. The stretching frequencies for the Fp-SiMe₂ group and the Fp-CH₂ group are typical of Fp-silyl and Fp-alkyl complexes and the Fp-alkyl groups exhibit higher stretching frequencies than the Fp-silyl groups.

¹H, ¹³C, and ²⁹Si NMR spectra of **2** indicate a mixture of two diastereomers, with one diastereomer dominant (*meso/dl* = 5:1). Recrystallization of **2** from a mixture of CH₂Cl₂ and hexane yields prisms, and the isomers **2a** (*meso*) and **2b** (*dl*) could be separated mechanically. In the ¹H NMR spectra of **2a** and **2b**, the two chemically inequivalent hydrogen atoms of the CH₂ moiety attached to the chiral silicon atom exhibited an AB system with a large coupling constant (²J = 12.6 Hz (**2a** and **2b**)). ¹H, ¹³C, and ²⁹Si NMR spectra of **4-6** showed that each was a mixture of two diastereomers in a ratio of 1:1. The ¹H NMR spectrum of **6** revealed an AB system for all CH₂ moieties in the two diastereomers.

Overall the accumulated spectral data are in total accord with the proposed structures of the new materials; however, we have confirmed several of the new complexes via single-crystal X-ray diffraction.

Crystal Structures of 1, 2a, and 2b. The single-crystal structure of **1** is illustrated in Figure 1. Selected bond distances and angles are summarized in Table 2. The molecule consists of two identical [(η⁵-C₅H₅)Fe(CO)₂-CH₂SiMe₂] moieties bonded by a Si-Si bond and has C_i symmetry. The Fe-C(8) bond distance (2.098(4) Å) is in the range of normal Fe-C(sp³) bond distances (2.08–2.16 Å).¹⁵ The Si-Si bond length (2.354(2) Å) is slightly shorter than those in LFeSiMe₂SiMe₃ (2.361–2.364 Å)¹⁶ and much shorter than that of the bimetallic complex FpSiMe₂SiMe₂Fp (2.390(4) Å).¹⁷

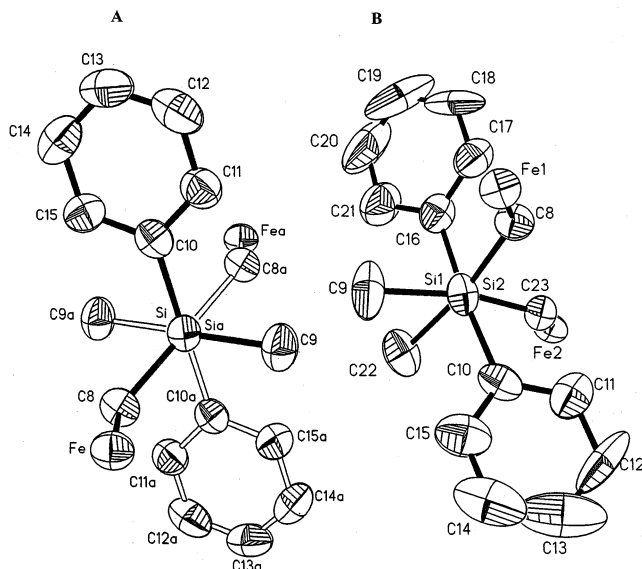
**Figure 2.** Molecular structure of **2b**.**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2a**

Fe–C(6)	1.743(3)	Fe–C(7)	1.749(4)
Fe–C(8)	2.092(3)	Si–SiA	2.359(1)
Si–C(8)	1.865(3)	Si–C(9)	1.875(4)
Si–C(10)	1.888(2)	O(1)–C(6)	1.149(4)
O(2)–C(7)	1.143(5)		
C(1)–Fe–C(2)	38.3(1)	C(1)–Fe–C(3)	64.9(1)
C(6)–Fe–C(7)	93.6(1)	C(6)–Fe–C(8)	86.4(1)
C(7)–Fe–C(8)	90.7(1)	Fe–C(8)–Si	120.5(1)
C(8)–Si–SiA	107.7(1)	C(8)–Si–C(10)	112.3(1)
C(8)–Si–C(9)	113.7(1)	C(9)–Si–C(10)	107.4(1)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 2b

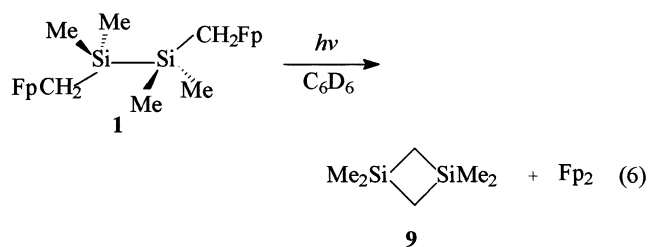
Fe(1)–C(6)	1.745(8)	Fe(1)–C(7)	1.735(6)
Fe(1)–C(8)	2.095(6)	Si(1)–Si(2)	2.373(3)
Si(1)–C(8)	1.853(6)	Si(1)–C(10)	1.900(6)
Fe(2)–C(24)	1.745(6)	Fe(2)–C(25)	1.756(8)
Fe(2)–C(23)	2.106(6)	Si(2)–C(23)	1.861(6)
Si(2)–C(16)	1.899(6)	Si(2)–C(22)	1.871(6)
O(1)–C(6)	1.156(9)	O(2)–C(7)	1.156(7)
O(3)–C(24)	1.150(7)	O(4)–C(25)	1.146(10)
C(1)–Fe(1)–C(2)	38.2(3)	C(1)–Fe(1)–C(3)	64.5(3)
C(6)–Fe(1)–C(7)	94.0(3)	C(6)–Fe(1)–C(8)	92.2(3)
C(7)–Fe(1)–C(8)	85.1(3)	Fe(1)–C(8)–Si(1)	122.2(2)
C(8)–Si(1)–Si(2)	112.0(2)	C(9)–Si(1)–C(10)	108.2(3)
C(8)–Si(1)–C(9)	111.6(3)	C(24)–Fe(2)–C(25)	93.1(3)
C(23)–Fe(2)–C(24)	89.4(2)	C(23)–Fe(2)–C(25)	85.7(3)
Fe(2)–C(23)–Si(2)	118.8(3)	C(23)–Si(2)–Si(1)	112.8(2)

The single-crystal structure of **2a** has been presented in a preliminary communication.⁷ Selected bond distances and angles are summarized in Table 3. The molecular structure of **2b** is shown in Figure 2. Selected bond distances and angles are summarized in Table 4. The molecule consists of two identical $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-CH}_2\text{SiMePh}]$ moieties bonded by a Si–Si bond and is asymmetric. This is also reflected in the dihedral angle (8.5°) between the two Cp ring planes. The Si–Si bond length (2.373(3) Å) is longer than those in $\text{LFeSiMe}_2\text{-SiMe}_3$ ¹⁶ but still shorter than the upper limit of the Si–Si bond in the bimetallic complex $\text{FpSiMe}_2\text{SiMe}_2\text{Fp}$.¹⁷ The projections of **2a** (*meso*) and **2b** (*rac*) about the Si–Si bond are presented in Figure 3. The silicon substituents in **2a** are absolutely staggered and trans relative to one another. However, the silicon substituents in **2b** are not completely staggered relative to one another (the larger C–Si–Si–C torsion angles fall in the range of $167.8(3)\text{--}175.0(3)^\circ$). The two phenyl substituents adopt

**Figure 3.** Projections of **2a** (A) and **2b** (B) about the Si–Si bond. The Fp groups are omitted for clarity.

a *trans* conformation, possibly reducing the repulsion between each other.

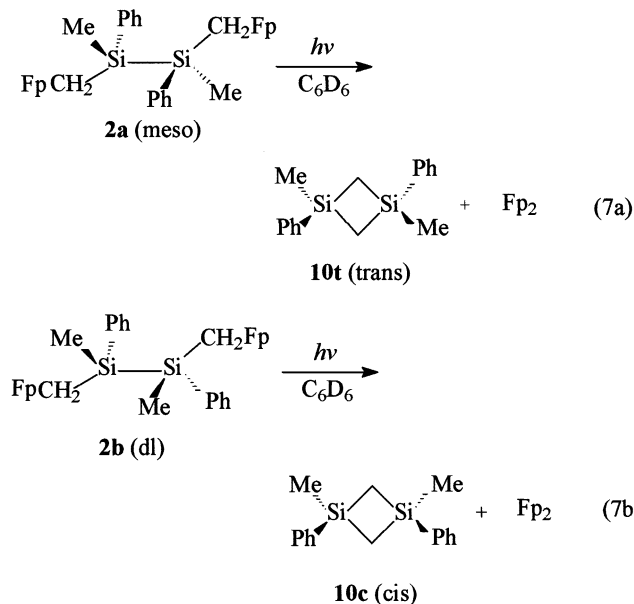
Photolysis of 1, 2, and 8. A C_6D_6 solution of **1** in a sealed Pyrex NMR tube was irradiated using a 450 W medium-pressure Hg lamp and led to the quantitative formation of 1,3-tetramethyldisilacyclobutane (**9**)¹⁸ and Fp_2 (eq 6).



Similarly, irradiation of **2a** (*meso*) resulted in the quantitative formation of *trans*-1,3-diphenyl-1,3-disilacyclobutane (**10t**) and Fp_2 , while similar photolysis of **2b** (*dl*) afforded *cis*-1,3-diphenyl-1,3-disilacyclobutane (**10c**),¹⁹ along with Fp_2 (eqs 7a and 7b). The photoreactions are therefore stereospecific.

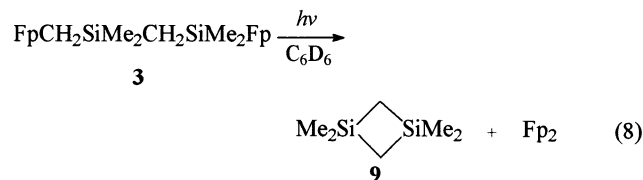
We have photolyzed a mixture of **1** and **2a** and observed no crossover products; the photoreactions proceed via an intramolecular pathway.

This is an unprecedented photoreaction leading to the quantitative formation of 1,3-disilacyclobutanes. In an initial attempt to extend this chemistry to other transition metals, we synthesized and irradiated the analogous tungsten system. We have reported that photolysis of oligosilylmethyl–tungsten complexes $\text{LM-CH}_2(\text{SiMe}_2)_n\text{Me}$ led to a facile rearrangement to $\text{LM-SiMe}_2\text{CH}_2(\text{SiMe}_2)_{n-1}\text{Me}$ complexes, a behavior that parallels Fp chemistry.^{4b} The ditungsten analogue $\text{WpCH}_2\text{Me}_2\text{SiSiMe}_2\text{CH}_2\text{Wp}$ (**8**) was readily prepared by the appropriate salt-elimination reaction; however, photolysis of **8** failed to result in the formation of 1,3-disilacyclobutanes and ^1H , ^{13}C , and ^{29}Si NMR monitoring of the photolysis indicated the formation of many products that could not be identified.



Photolysis of 3, 6, and 7. To further explore the nature and scope of the above photoreactions, the two possible positional isomers of **1**, FpCH₂SiMe₂CH₂SiMe₂Fp (**3**) and FpSiMe₂CH₂CH₂SiMe₂Fp (**7**), and the positional isomer of **2**, FpCH₂SiPhMeCH₂SiPhMeFp (**6**), were synthesized and evaluated.

Photochemical irradiation of **3** resulted in the quantitative formation of disilacyclobutane (**9**) and Fp₂ (eq 8). Even though this reaction took much longer than



the corresponding photolysis of **1**, the transformation was very clean, and we did not observe the formation of trace amount of any side products even after photolysis for 35 h (Figure 4). Under similar photochemical conditions, but with much less irradiation time, photolysis of **1** usually gave trace amounts of ferrocene.

Complex **6** was prepared as a mixture of two diastereomers (**6a** and **6b**). Despite many attempts, we have been unable to separate them; therefore, photolysis was performed on a mixture of the two. Photochemical irradiation of **6a** and **6b** (1:1) for 11 h led to a smooth reaction with production of Fp₂ and the two isomeric 1,3-disilacyclobutanes (**10t** and **10c**) in a ratio of 1:1, equivalent to the ratio of the two starting isomers (eq 9). In comparison with the photolysis of **3**, it is evident

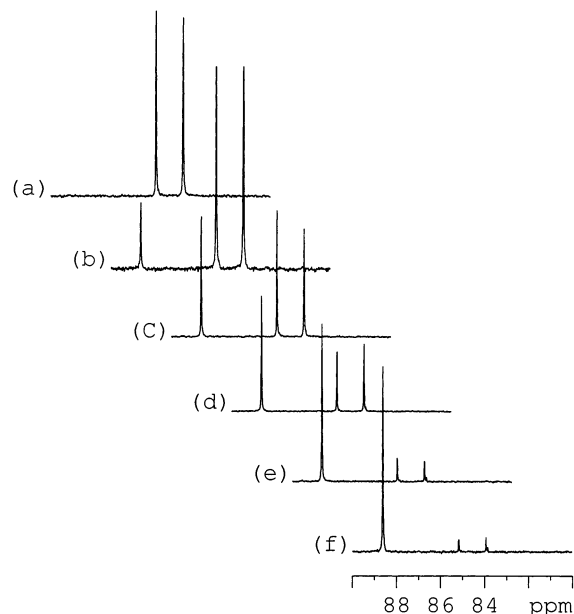
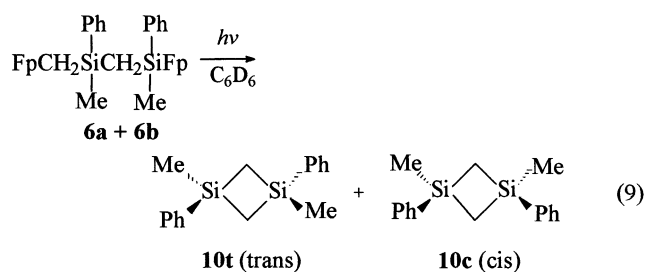


Figure 4. ¹³C NMR spectral changes in the cyclopentadienyl region during photolysis of **3**: (a) prior to photolysis; (b) after 2 h; (c) after 6 h; (d) after 11 h; (e) after 24 h; (f) after 35 h.

that the introduction of the phenyl groups into the system accelerates the photoreaction process (11 h/35 h).

As noted above, the photolysis of **1** proceeds via an intramolecular pathway. In a separate experiment we irradiated a mixture of **3** and **6** and examined the photoproducts by NMR spectroscopy. Such irradiation resulted in the formation of only **9**, **10c**, and **10t**. Since no crossover products were observed, we can conclude that, as with **1** and **2**, the photochemical transformations of their positional isomers proceed via intramolecular processes.

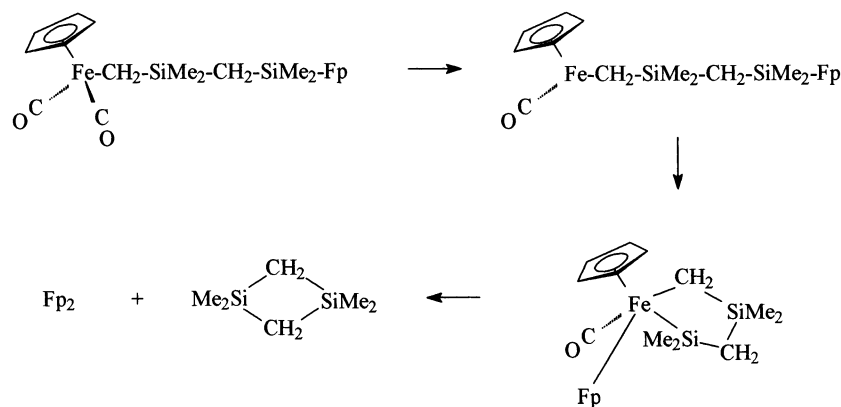
Complex **7** was determined to be photochemically inert, since irradiation of a C₆D₆ solution of **7** in a sealed Pyrex NMR tube for 5 days did not result in any change except for a slight decomposition to Fp₂ with no other observable products.

Mechanism of 1,3-Disilacyclobutane Formation. It has been reported that "unstable" silenes carrying small alkyl substituents readily dimerize in a head-to-tail fashion to form 1,3-disilacyclobutanes,²⁰ while "stable" silenes, e.g. (Me₃Si)₂Si=C(OSiMe₃)R, preferentially produce the head-to-head dimers, 1,2-disilacyclobutanes.²¹ Since the photoreactions involving free silenes yield a mixture of the cis and trans isomers of 1,3-disilacyclobutanes, it is unlikely that free silene was produced by photolysis of **1** and **2**.²² Photolysis of **1** in the presence of *t*-BuOH and MeOH led only to the formation of 1,3-

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Scheme 4



(trimethylsilyl)methyl]platinum via the intermediacy of η^2 -silene complexes formed by a β -CH₃ elimination process.²⁷ Another apparent β -CH₃ migration involving the cleavage of Si-C bonds was also observed in the reaction of Ru(η^5 -C₅H₅)(η^3 -C₃H₅)(CH₂SiMe₃)Br with AgF to yield Ru(η^5 -C₅H₅)(η^3 -C₃H₅)(CH₂SiMe₂F)Me.²⁸ Both these precedents seem to justify our suggestion, as outlined in eq 10, that photolysis of **3** may proceed via a bis(silene-iron) intermediate analogous to that in the photolysis of **1** (Scheme 3).²⁹

However, an alternative suggestion is outlined in Scheme 4. In this case, after loss of CO from the Fe-C end of the FeCSiCSiFe chain an intramolecular oxidative addition of the Fe-Si bond can be envisaged, followed by elimination of the disilacyclobutane. To back up this possible mechanism, we can report that related intermolecular chemistry has been observed in our laboratory. Thus, photochemistry of a mixture of FpCH₃ and FpSiMe₃ leads to the significant formation of only Fp₂ and SiMe₄ within 3 h under the identical experimental conditions reported here. Since photochemistry of the two complexes alone does not yield either ethane or Me₆Si₂ in any reasonable time period (days), there is indeed a new type of chemistry operating consistent

with oxidative addition of Fp-SiMe₃ to (η^5 -C₅H₅)Fe(CO)CH₃ formed upon photochemical elimination of CO from Fp-CH₃ and subsequent elimination of SiMe₄ upon recoordination of CO.³⁰

Notwithstanding all the above chemistry, it is also arguable that the formation of disilacyclobutanes is related to a free radical pathway. This pathway may involve (i) irradiation of **3** leading to the initial homolysis of the Fe-CH₂ bond to form iron radicals and silylmethyl radicals, (ii) the silylmethyl radical intramolecularly attacking at the other silicon atom to produce disilacyclobutanes and the other iron radicals, and (iii) the coupling of the two iron radicals to afford Fp₂.

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Supporting Information Available: Listings of crystal data and data collection and solution and refinement details, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **1**, **2a**, and **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) This scheme only illustrates that initial CO expulsion to form a 16e intermediate occurs at the CH₂-Fe end of the Fp group, since the Fe-C_{carbonyl} bond at this end is weaker.

(30) The generality, and full implications, of this new chemistry is the subject of a forthcoming publication.