Photochemistry of the Three Possible Isomeric Cyclic Disilyliron Complexes, $FpSi_2R_5$ (Si_2R_5 = 1,2,2-Trimethyldisilacyclohexyl, (1-Methylsilacyclopentyl)dimethylsilyl, and 1-(Trimethylsilyl)silacyclopentyl, Fp = (η^5-C_5H_5)$Fe(CO)_2$)

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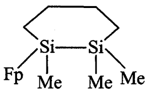
The three cyclic disilyliron complexes $FpSi_2R_5$ (Si_2R_5 = 1,2,2-trimethyldisilacyclohexyl (**3**), (1-methylsilacyclopentyl)dimethylsilyl (**6**), 1-(trimethylsilyl)silacyclopentyl (**9**)) have been synthesized and characterized. Photolysis of these complexes resulted in the formation of $FpSiMe_3$ and $FpSiR_3$ (SiR_3 = methylsilacyclopentyl) in the same ratio of 34:66 via silylene eliminations. Irradiation of **3**, **6**, and **9** independently in the presence of HMPA led surprisingly to the formation of only the unique silylene intermediate [(η^5-C_5H_5)Fe(CO)-(=$SiMe_2$·HMPA)(SiR_3)], **11**, which has been characterized by ^1H, ^{13}C, ^{29}Si, $^{13}C-^1H$ COSY, $^{13}C-^1H$ COLOC, and $^{29}Si-^1H$ COLOC NMR spectroscopy.

Introduction

The activation of the silicon−silicon bond by transition metal complexes is an intriguing area of modern organosilicon chemistry.[1,2] Many oligosilyl derivatives of the transition metals with direct metal−silicon bonds possess the potential ability to undergo α-elimination reactions, resulting in the formation of silyl(silylene) intermediates. These intermediates rapidly form an equilibrium mixture via a series of 1,3-alkyl, -aryl, and -silyl migrations, finally leading to isomerizations and/or silylene eliminations.[3,4] Photolysis of the disilyliron derivatives of the Fp system, Fp = (η^5-C_5H_5)$Fe(CO)_2$, leads exclusively to the formation of monosilyl complexes via silylene eliminations.

The silyl(silylene)iron intermediates have been observed spectroscopically by low-temperature matrix isolation[5] and were isolated, structurally characterized as base- and metal-stabilized species,[4b,f−h,6,7] and observed as intermolecularly HMPA-stabilized complexes.[8] To understand more about the nature of 1,3-migrations in these photoreactions, we report the synthesis and photochemistry of three cyclic isomeric Fp-disilanes, **3**, **6**, and **9**, and the result of their photochemical irradiation in the presence of HMPA ($(Me_2N)_3P$=O).



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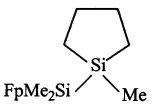

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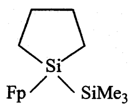

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Experimental Section

All manipulations were carried out under a nitrogen 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, HMPA ($(Me_2N)_3P$=O), Aldrich; CF_3SO_3H, Lancaster; Ph_2SiCl_2, $PhMeSiCl_2$, $Ph_2MeSiCl$, Me_3SiCl, Me_2SiHCl, $PhMe_2SiCl$, Gelest. Other reagents were synthesized by literature procedures or via new methodologies described in the Supporting Information: $Ph_2MeSiSiMe_2H$,[3c] $Ph_2MeSiSiMe_2Cl$,[9] $ClPhMeSiSiMe_2Cl$,[10] 1-methyl-1-phenylsilacyclopentane,[11,12] 1,1-diphenylsilacyclopentane,[11,13] 1-chloro-1-

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methylsilacyclopentane,[11] and 1-chloro-1-phenylsilacyclopentane.[14] 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. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of 1-Phenyl-1,2,2-trimethyl-1,2-disilacyclohexane (1). To a di-Grignard reagent (prepared from 6.6 g (0.27 mol) of magnesium turnings and 32.0 g (0.14 mol) of 1,4-dibromobutane in 200 mL of THF) was added slowly a solution of 24.2 g (0.1 mol) of $ClPhMeSiSiMe_2Cl$ at 0 °C over 30 min. The reaction mixture was then refluxed for 20 h and 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 with the organic layer, washed with water, sodium bicarbonate, and then water, and dried over calcium chloride. The solvent was removed, and the residue was distilled, by using a 20 cm Vigreux column, at 112−113 °C/3 mmHg, to give 18.2 g (78%) of **1** as a colorless oil: NMR (C_6D_6) δ ^{1}H, 0.11, 0.13 (s, s, 3H, 3H, $Si(CH_3)_2$), 0.34 (s, 3H, $SiPhCH_3$), 0.73−1.05 (brm, 4H, $SiCH_2$), 1.54−1.79 (brm, 4H, CH_2), 7.19−7.26 (m, 3H, Ph), 7.51−7.53 (m, 2H, Ph); ^{13}C, −5.06 ($SiPhCH_3$), −3.63 ($Si(CH_3)_2$), 15.6, 17.3, 26.4, 26.5 (CH_2), 128.2, 128.9, 134.5, 138.8 (Ph); ^{29}Si, −24.9 ($SiPhCH_3$), −22.7 ($Si(CH_3)_2$); MS (70 ev) *m/z* 234 M^+, 41; 135 $[Ph(CH_3)_2Si]^+$, 100; 121 $[Ph(CH_3)HSi]^+$, 28; 105 $[PhSi]^+$, 26. Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46. Found: C, 66.65; H, 9.74.

Synthesis of 1-Chloro-1,2,2-trimethyl-1,2-disilacyclohexane (2). To a solution of 16.0 g (68 mmol) of **1** in 25 mL of benzene was added 0.3 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 −25.6 and −23.4 ppm disappeared after 3 h and were replaced by the signals due to the final product **2** at −21.6 and 18.5 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 86−88 °C/23 mmHg to give 11.6 g (88%) of **2** as a colorless oil: NMR (C_6D_6) δ ^{1}H, −0.01, 0.18 (s, s, 3H, 3H, $Si(CH_3)_2$), 0.36 (s, 3H, $SiClCH_3$), 0.72−0.77, 1.60−1.68 (brm, brm, 4H, 4H, CH_2); ^{13}C, −4.91, −4.53 ($Si(CH_3)_2$), 0.51 ($SiClCH_3$), 16.38, 20.9, 25.6, 25.8 (CH_2); ^{29}Si, −20.9 ($Si(CH_3)_2$), 19.3 ($SiClCH_3$).

Synthesis of 3, 6, 9, and 10. Full details are provided for **3**; **6**, **9**, and **10** were synthesized in exactly the same manner using the appropriate chlorosilane. 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 1.85 g (9.6 mmol) of **2** 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, concentrated to 5 mL, and placed on 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 **3** (2.20 g, 67%): NMR (C_6D_6) δ ^{1}H, 0.16, 0.25 (s, s, 3H, 3H, $Si(CH_3)_2$), 0.48 (s, 3H, $SiCH_3$), 0.71−2.09 (brm, 8H, CH_2), 4.14 (s, 5H, Cp); ^{13}C, −2.53, −1.70 ($Si(CH_3)_2$), 1.24 ($SiCH_3$), 18.09, 22.5, 26.8, 27.7 (CH_2), 83.2 (Cp), 215.7, 215.7 (CO); ^{29}Si, −12.8 ($Si(CH_3)_2$), 15.3 (SiFp); IR (ν_{CO}, cm^{-1}) 1997(s), 1945(s); MS (70 ev) *m/z* 334 $[M]^+$, 15; 306 $[M - CO]^+$, 84; 157 $[M - Fp]^+$, 73; 129 $[M - Fp - C_2H_4]^+$, 76; 121 $[CpFe]^+$, 50; 97 $[Si_2C_3H_5]^+$, 100. Anal. Calcd for $C_{14}H_{22}FeO_2Si_2$: C, 50.29; H, 6.63. Found: C, 49.70; H, 6.45.

Compound 6: yellow oil (64%); NMR (C_6D_6) δ ^{1}H, 0.21, 0.52 (s, s, 3H, 6H, $SiCH_3$), 0.63−0.65, 0.86−0.88, 1.66−1.68 (m, m, m, 2H, 2H, 4H, CH_2), 4.16 (s, 5H, Cp); ^{13}C, −1.83 ($SiCH_3$), 3.69 ($FpSiCH_3$), 13.7, 28.5 (CH_2), 83.2 (Cp), 215.7 (CO); ^{29}Si, 2.92 ($SiCH_2$), 16.3 (SiFp); IR (ν_{CO}, cm^{-1}) 1997(s), 1947(s). Anal. Calcd for $C_{14}H_{22}FeO_2Si_2$: C, 50.29; H, 6.63. Found: C, 50.31; H, 6.55.

Compound 9: yellow oil (78%); NMR (C_6D_6) δ ^{1}H, 0.19 (s, 9H, $SiCH_3$), 0.90−0.94, 1.82−1.22, 1.73−1.91 (m, m, m, 2H, 2H, 4H, CH_2), 4.20 (s, 5H, Cp); ^{13}C, 0.11 ($SiCH_3$), 16.8, 29.2 (CH_2), 82.9 (Cp), 215.3 (CO); ^{29}Si, −11.33 ($SiCH_3$), 31.4 (SiFp); IR (ν_{CO}, cm^{-1}) 1997(s), 1944(s). Anal. Calcd for $C_{14}H_{22}FeO_2Si_2$: C, 50.29; H, 6.63. Found: C, 50.37; H, 6.26.

Compound 10: yellow oil (47%); NMR (C_6D_6) δ ^{1}H, 0.41 (s, 3H, $SiCH_3$), 0.88−0.90, 1.75−1.77 (m, m, 4H, 4H, CH_2), 4.09 (s, 5H, Cp); ^{13}C, 7.21 ($SiCH_3$), 20.1, 28.1 (CH_2), 83.2 (Cp), 215.4 (CO); ^{29}Si, 57.4; IR (ν_{CO}, cm^{-1}) 1997(s), 1946(s). Anal. Calcd for $C_{12}H_{16}FeO_2Si$: C, 52.19; H, 5.84. Found: C, 51.78; H, 5.91.

Synthesis of 1-Methyl-1-(dimethylphenylsilyl)silacyclopentane (4). A flask equipped with a magnetic stirring bar and addition funnel was charged with 4.0 g (3.0 mmol) of 1-chloro-1-methylsilacyclopentane and 50 mL of THF. The solution was cooled to 0 °C, and the $PhMe_2SiLi$ solution (prepared from 5.1 g (3.0 mmol) of $PhMe_2SiCl$ and 0.84 g (12 mmol) of Li in 50 mL of THF) was added dropwise. Upon completing the addition the solution was allowed to warm to room temperature and stirred overnight. The solvent was removed at reduced pressure, and the residue was placed on a flash silica gel column. Elution with hexane afforded a colorless oily product upon removing the solvent. The crude product was further purified by distillation at 115−116 °C/5 mmHg to give 6.30 g (90%) of **4**: NMR (C_6D_6) δ ^{1}H, 0.11, 0.35 (s, s, 3H, 6H, $SiCH_3$), 0.55−0.60, 0.81−0.85 (m, m, 2H, 2H, $SiCH_2$), 1.50−1.60 (m, 4H, CH_2), 7.19−7.22 (m, 3H, Ph), 7.46−7.49 (m, 2H, Ph); ^{13}C, −3.66, −3.39 ($SiCH_3$), 12.3, 28.4 (CH_2), 128.1, 128.7, 134.0, 139.4 (Ph); ^{29}Si, −21.5 ($SiPh(CH_3)_2$), −4.95 ($SiCH_3$). Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46. Found: C, 66.05; H, 9.02.

Synthesis of 1-Phenyl-1-(trimethylsilyl)silacyclopentane (7). To 0.84 g (12 mmol) of lithium suspended in 30 mL of THF was added dropwise a solution of 1-chloro-1-phenylsilacyclopentane (6.00 g, 3.05 mmol) in 20 mL of THF. The color of the solution changed from colorless to deep red after 1 h. The reaction mixture was then stirred overnight. The reaction was stopped, and the solution was cautiously transferred to a dropping funnel via a cannula, and the excess lithium was left in the original flask. The solution was then added dropwise to 3.80 g (3.5 mmol) of Me_3SiCl in 50 mL of THF at 0 °C. Upon completing the addition, the solution was allowed to warm to room temperature and stirred overnight. The solvent was removed at reduced pressure, and the residue was placed on a flash silica gel column. Elution with hexane afforded a colorless oily product upon removing the solvent. The crude product was further purified by distillation at 114−115 °C/3 mmHg to give 5.83 g (82%) of **7**: NMR ($CDCl_3$) δ ^{1}H, 0.11 (s, 9H, $SiCH_3$), 0.96 (t, $^3J = 6.95$ Hz, 4H, $SiCH_2$), 1.61−1.69 (m, 4H, CH_2), 7.24−7.26 (m, 3H, Ph), 7.44−7.47 (m, 2H, Ph); ^{13}C, −1.74 ($SiCH_3$), 11.1, 28.3 (CH_2), 127.7, 128.3, 134.2, 138.6 (Ph); ^{29}Si, −19.2 ($SiCH_3$), −5.08 (SiPh). Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.59; H, 9.46. Found: C, 66.38; H, 9.59.

Synthesis of 1-(Chlorodimethylsilyl)-1-methylsilacyclopentane (5) and 1-Chloro-1-(trimethylsilyl)silacyclopentane (8). To a solution of 5.30 g (2.26 mmol) of **4** in 15 mL of benzene was added 0.30 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. After 5 h, ^{29}Si NMR monitoring of the reaction mixture showed the complete disappearance of the starting material and the formation of the product. At this time the reaction was stopped, the solvent was removed under vacuum, and 30 mL of hexane was added

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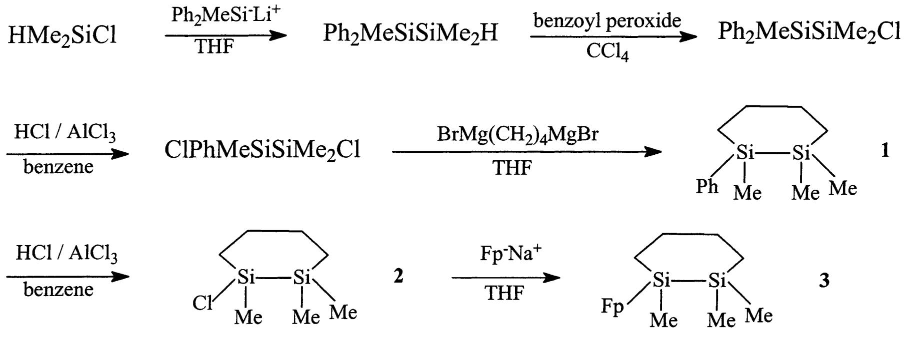
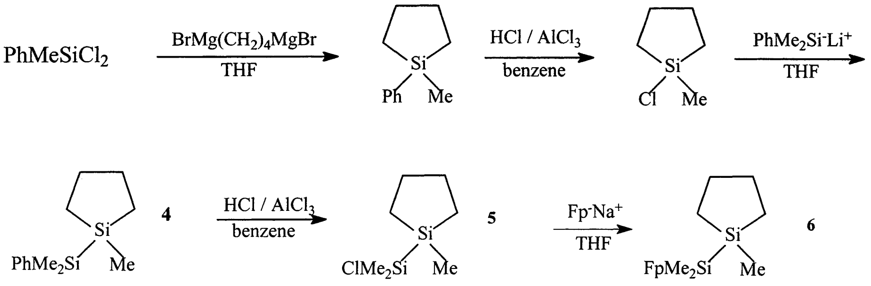
Scheme 1



Scheme 2



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 93−94 °C/30 mm Hg to give 3.80 g (87%) of **5** as a colorless oil: NMR (C$_6$D$_6$) δ ^{1}H, 0.11, 0.37 (s, s, 3H, 6H, SiCH$_3$), 0.54−0.57, 0.83−0.88, 1.52−1.56 (m, m, m, 2H, 2H, 4H, CH$_2$); ^{13}C, −4.68, (SiCH$_2$), 2.52 (SiClCH$_3$), 11.6, 28.3 (CH$_2$); ^{29}Si, −3.90 (SiCH$_3$), 22.8 (SiClCH$_3$).

Compound 8 was prepared in a similar manner from **7** as a colorless liquid: bp 102−104 °C/40 mmHg; NMR (CDCl$_3$) δ ^{1}H, 0.20 (s, 9H, SiCH$_3$), 0.96 (t, ^3J = 7.1 Hz, 4H, SiCH$_2$), 1.55−1.59, 1.77−1.81 (m, m, 2H, 2H, CH$_2$); ^{13}C, −2.53 (SiCH$_3$), 16.1, 26.9 (CH$_2$); ^{29}Si, −17.7 (SiCH$_3$), 37.5 (SiCl). Anal. Calcd for C$_7$H$_{17}$ClSi$_2$: C, 43.60; H, 8.89. Found: C, 43.02; H, 9.18.

Photolysis of 3, 6, and 9. A 5 mm Pyrex NMR tube was charged with 0.10 g (0.3 mmol) of **3** 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. After 67 h, ^{29}Si NMR monitoring showed the disappearance of the starting material and formation of the two major products, FpSiMe$_3$ (41.54 ppm) and **10** (57.35 ppm), in a ratio of 40:60 (GC/MS: 34:66), along with a minor product with a ^{29}Si NMR signal at 47.9 ppm, which we have not yet identified. The solvent was removed under vacuum, and the residue was placed on a 1 × 10 cm silica gel column. Elution with hexane afforded a yellow band, which after removal of the solvent yielded a light yellow oil (55 mg) as a mixture of FpSiMe$_3$ (20.7 mg, 28%) and **10** (34.3 mg, 41%).

Similar photolysis of both **6** and **9** led to the same result as that of **3** except that the reaction time (13 h for **6**, 2 h for **9**) is significantly different. The recovered yields from **6** and **9** were as follows: FpSiMe$_3$ = 31% and 30% and **10** = 46% and 45%, respectively.

Photolysis of 3, 6, and 9 in the Presence of HMPA. A 5 mm Pyrex NMR tube was charged with 0.10 g (0.3 mmol) of **3**, 57 mg (0.32 mmol) of HMPA, 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. After 45 h, NMR monitoring showed the disappearance of the starting material and formation of only the HMPA-stabilized silylene intermediate **11**. **11** has been characterized by ^{1}H, ^{13}C, ^{29}Si, ^{13}C−^{1}H COSY, ^{13}C−^{1}H COLOC, and ^{29}Si−^{1}H COLOC NMR spectroscopy. Similar photolysis of **6** and **9** in the presence of HMPA led to the formation of only **11**, except that the reaction time (9 h for **6**, 2 h for **9**) is significantly different. NMR (C$_6$D$_6$) δ: ^{1}H, 0.61, 0.67 (s, s, 3H, 3H, Fe=Si(C*H*$_3$)$_2$·HMPA), 0.70 (s, 3H, FeSiCH$_3$), 0.87−0.93, 1.12−1.17, 1.42−1.48 (m, m, m, 1H, 2H, 1H, SiCH$_2$), 1.96−2.02 (m, 4H, CH$_2$), 2.18 (d, $^3J_{\mathrm{P-H}}$=10.2 Hz, 18H, Fe=Si(CH$_3$)$_2$·*HMPA*), 4.41 (s, 5H, Cp); ^{13}C, 9.32 (FeSiCH$_3$), 11.8 (Fe=Si(*C*H$_3$)$_2$·HMPA), 13.19 ($^3J_{\mathrm{P-C}}$ = 2.6 Hz, Fe=Si(*C*H$_3$)$_2$·HMPA), 20.6, 24.1 (SiCH$_2$), 28.9, 29.5 (CH$_2$), 36.43 ($^2J_{\mathrm{P-C}}$ = 4.9 Hz, Fe=Si(CH$_3$)$_2$·*HMPA*), 79.4 (Cp), 219.6 (CO); ^{29}Si, 52.01 (FeSiCH$_3$), 114.8 ($^2J_{\mathrm{P-Si}}$ = 29 Hz, Fe=Si(CH$_3$)$_2$·HMPA).

Results and Discussion

Synthesis of Fp-Disilanes. The three isomeric Fp-disilane complexes **3**, **6**, and **9** were successfully synthesized by the multistep synthetic routes outlined in Schemes 1, 2, and 3. Their spectral and analytical data are in accord with the proposed structures.

A significant deshielding effect on ^{29}Si NMR chemical shifts is apparent in cyclic silanes, and the magnitude of the effect is dependent on the ring size, but not the inclusion of single versus double bonds.[9,15−19] In general the silicon atoms of silacyclopentanes are shifted downfield about 11−18 ppm compared to those of the disubstituted dimethylsilanes, and such data facilitate the

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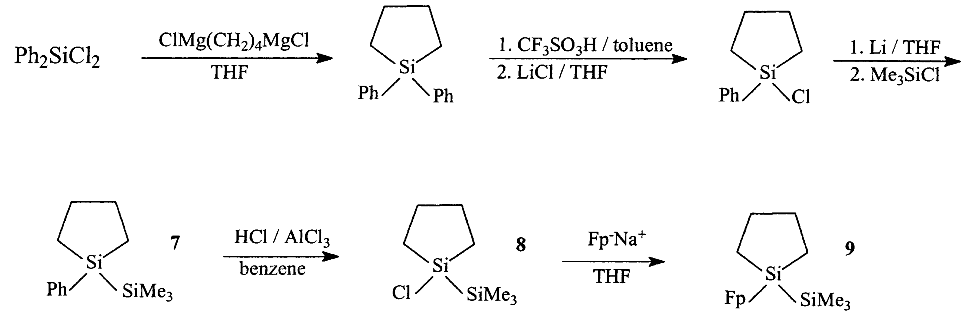
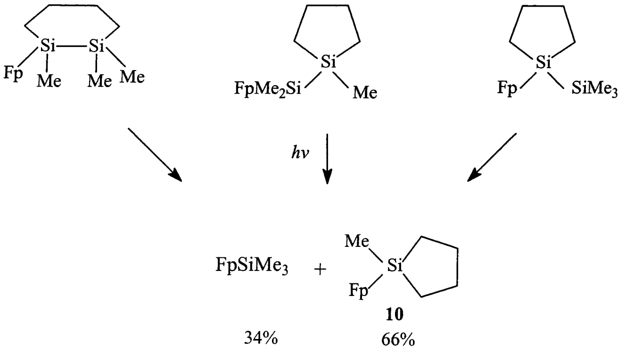
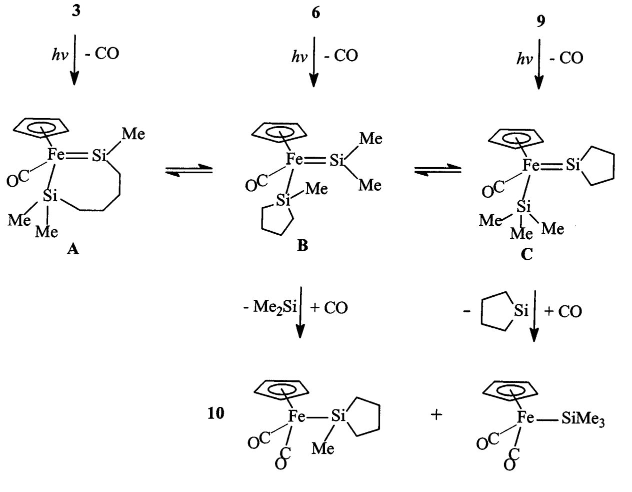
Scheme 3



Scheme 4



Scheme 5

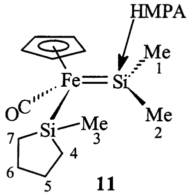


structural assignments of the new complexes involved in this study.

Photochemistry. The progress of the photochemistry of **3** was periodically monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. After 67 h the complete disappearance of **3** and the formation of the expected monosilane compounds **10** and $FpSiMe_3$ (66:34) was observed with a minor product exhibiting a ^{29}Si NMR signal at 47.9 ppm. Similar irradiation of **6** and **9** afforded an identical product distribution as expected (Scheme 4).

The photoreaction of **3** is much slower than that of **6** (13 h) and **9** (2 h). Upon the basis of our previous suggestions,[3b,c] Scheme 5 represents the process occurring during these photolyses. The results obtained suggest that the formation of intermediate **A** needs the higher activation energy; that is, the six-membered ring reinforces the photochemical stability of the Fp-disilanes. We have observed that initial loss of CO is, as expected for photochemical elimination of metal-coordinated carbonyl groups, a reversible process. This reversibility is demonstrated by the initial isomerization of the disilane complex (η^5-indenyl)$Fe(CO)_2SiMe_2SiPh_3$, $IFpSiMe_2SiPh_3$, to a mixture of $IFpSiMePhSiMePh_2$, $IFpSiPh_2SiMe_2Ph$, and $IFpSiMe_2SiPh_3$ complexes prior to ultimate silylene loss and formation of the corresponding IFp-monosilanes upon photolysis.[3h] Thus, the slower photochemical degradation of **3** can be explained by the stability imparted by the six-membered ring to the 16-electron (η^5-C_5H_5)Fe(CO)$SiMeSiMe_2(CH_2)_4$ and its less favored transformation to **A** compared to CO recombination to form starting material. The disilane complexes **3**, **6**, and **9** exhibit a low-energy band in the visible spectra at ~340 nm, without any significant difference in extinction coefficient, $\epsilon = 1500$. These data are essentially the same as those of $FpSiMe_2SiMe_3$; thus the photophysics of the initial CO expulsion is expected to be equivalent for these materials. The preferred formation of **10** suggests that intermediate **B** is more stable than **C** and **A**; however we have no information that permits a precise selection between preferential silylene stabilities and the relative rates of transformation of these intermediates to the varying products that controls the reaction outcome. Since the silylene expulsion is a photochemical event,[5] we favor the former possibility. The unknown species formed along with **10** and $FpSiMe_3$ possibly suggests a minor new pathway.

Photochemistry in the Presence of HMPA. The presence of HMPA during the photolysis of Fp-disilanes is an effective method for stabilizing iron-silylene intermediates.[4i,7d,8,20,21] As noted above, there are three initially formed equilibrating intermediates, **A**, **B**, and **C**. *However, independent irradiation of **3**, **6**, and **9** in the presence of HMPA resulted in the formation of only the intermediate **B** as the HMPA-stabilized form, **11**.* The disappearance of **3**, **6**, and **9** was faster than in the absence of HMPA, suggesting that the back reaction, recoordination of CO to form the starting complex, is strongly inhibited.



11

We find the sole formation of **11** to be an interesting result. We have previously reported that HMPA trapped

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the initially formed silyl(silylene) intermediate (η^5-C_5H_5)Fe(CO)(=$SiMe_2$)$SiMe_2SiMe_2SiMe_3$ upon photochemical irradiation of $FpSiMe_2SiMe_2SiMe_2SiMe_3$ despite the subsequent intermediacy of presumably more stable silylene species in the absence of HMPA; for example, (η^5-C_5H_5)Fe(CO)(=$SiMeSiMe_3$)$SiMe_2SiMe_3$ formed en route to the final rearranged complex FpSi($SiMe_3$)$_3$. Thus, we were prepared to observe three different intermediates as the HMPA-stabilized species formed upon irradiation of **3**, **6**, and **9**. If the rapidly equilibrating silyl(silylene) mechanism is correct, two scenarios are possible. First, intermediate **B** is thermodynamically the most stable and HMPA will trap the most stable intermediate rather than the initially formed one. Alternatively, it may be argued that the HMPA(silylene) complexes have a totally different thermodynamic stability pattern to the "free" silylene complexes, and therefore the observed species is controlled by this feature, not the stability of the free silylene complex. We are currently reinvestigating the various isomeric oligosilyl-Fp complexes (that we previously studied from only a chemical viewpoint) with respect to HMPA trapping experiments. This effort, coupled with appropriate quantum chemical calculations on the various silylene complexes both as free and HMPA-complexed intermediates, also in progress, will permit a more definitive understanding of this important distinction.

We have made no attempt to isolate **11**, which is extremely air- and moisture-sensitive.[8,20] However, **11** has been unambiguously characterized by NMR spectroscopy. The ^{29}Si NMR spectrum exhibits a doublet at 114.8 ppm due to the silylene ligand coupling with the ^{31}P atom of HMPA and a signal at 52.0 ppm due to the iron-attached silacyclopentyl group.[8,20b] The ^{13}C NMR spectrum shows that all the methyl and methylene groups are nonequivalent. It is interesting that there is only one silylene methyl carbon atom coupling with the ^{31}P atom of HMPA. The complete assignment of C and H atoms was confirmed by the ^{13}C−^{1}H COSY spectrum.

As further proof of structure we have used COLOC NMR spectroscopy.[4g,22] In the ^{13}C−^{1}H COLOC spectrum of **11** the two silylene methyl groups (1-Me and 2-Me) show long-range coupling ($^3J_{CH}$) with each other, and the 3-Me shows cross-peaks with both 4-C and 7-C ($^3J_{CH}$), representing the dimethylsilylene and methylsilacyclopentyl groups in the molecule. Several cross-peaks due to the imperfect reduction of $^1J_{CH}$ are present in the spectrum. In the ^{29}Si−^{1}H COLOC spectrum the ^{29}Si atom of the silylene ligand shows cross-peaks with both 1-Me and 2-Me ($^2J_{SiH}$), while the ^{29}Si atom of the silacyclopentyl group shows a cross-peak with 3-Me ($^2J_{SiH}$). All these data support our structural assignment of **11**.

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Supporting Information Available: ^{13}C−^{1}H COSY, ^{13}C−^{1}H COLOC, and ^{29}Si−^{1}H COLOC NMR spectra of **11**; ^{13}C and ^{29}Si NMR spectra for **2** and **5**; alternative syntheses of $ClPhMeSiSiMe_2Cl$,[10] 1-methyl-1-phenylsilacyclopentane,[11,12] 1,1-diphenylsilacyclopentane,[11,13] 1-chloro-1-methylsilacyclopentane,[11] and 1-chloro-1-phenylsilacyclopentane.[14] This material is available free of charge via the Internet at http://pubs.acs.org.

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