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Photochemical Treatment of Transition Metal Substituted Disilanes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Me_4(C_6H_4X)$ (X = Cl, CF_3, NMe_2, OMe, H), Including Trapping of Expelled Silylene

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Abstract: A series of complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Me_4Ar$, $FpSi_2Me_4Ar$ ($Ar = C_6H_4X$; X = H, *p*-Cl, *m*-CF_3, *o*-Me, *p*-OMe, *p*-NMe_2), have been synthesized and characterized. Photochemical treatment of the complexes in inert hydrocarbon solvents led to expulsion of the $SiMe_2$ and/or SiMeAr fragments to yield $FpSiMe_3$ and/or $FpSiMe_2Ar$. The effects of the phenyl group substituents upon the product distribution indicate that in the intermediate silyl–silylene complexes $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMe_2)SiMe_2Ar$ and $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMeAr)SiMe_3$, the silylene portion is highly polar in the form $Fe^-{-}Si^+$. Trapping experiments with Et_3SiH during the photolysis of $FpSiMe_2SiMe_3$ yielded small but reproducible amounts of $Et_3SiSiMe_2H$, confirming the elimination of $SiMe_2$. Significant amounts of siloxanes were also obtained from this photolysis. Photochemical generation of $SiMe_2$ from $(SiMe_2)_6$ in the presence of $FpSiMe_3$ resulted in a similar set of products, not the high yield of $Et_3SiSiMe_2H$ obtained in the absence of $FpSiMe_3$, indicating the great reactivity of $SiMe_2$ with CO to form siloxane materials in the presence of metal complexes. GC/MS analysis of the reaction products from the photolyses of $FpSiMe_2SiMe_2Ar$ also indicated some direct Si–Si bond cleavage to produce radicals that abstract H to form Me_2ArSiH.

Introduction

The placement of the substituent $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, Fp, into oligosilanes permits a series of photochemical rearrangements and de-oligomerizations to be observed that are not characteristic of the parent oligosilanes.[1,2] The reason for such new chemistry is the capacity of the metal center to create a coordinatively unsaturated environment which permits α-eliminations to form intermediate silyl–silylene complexes. Via a series of 1,3-alkyl, -aryl, and -silyl shifts, followed by either re-formation of the Si–Si bond or elimination of the silylene species, the new chemistry may proceed. The exact nature of the intermediate silylene species is unknown. The Ogino–Tobita group have isolated internally base-stabilized complexes by having a methoxy substituent upon the silicon chain, i.e. $(\eta^5\text{-}C_5H_5)Fe(CO)(SiMe_2\text{-}\mu\text{-}OMe\text{-}SiMe_2)$.[2f] This type of complex apparently does not react with CO to form elimination products $FpSiMe_3$ or $FpSiMe_2OMe$. Turner et al. have observed $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMe_2)SiMe_3$ via low-temperature matrix isolation techniques and laser flash photolysis and have demonstrated that the final elimination of $SiMe_2$ is a photochemical event.[3] The nature of the $Fe{=}SiR_2$ species in the systems that leads to rearrangement or deoligomerization is not clear. To date, we have been unable to trap the eliminated SiR_2 fragment; however, there are several examples of base-stabilized and free silylene complexes reported in the literature.[4] To provide further insight into the exact nature of the intermediate in the chemistry of the Fp systems we have synthesized a series of Fp-disilanes containing a substituted phenyl group whose electronic effects should dramatically alter the aptitude for 1,3-migrations needed for the observed chemistry. We report the synthesis and study of these new complexes and also report for the first time our ability to trap the silylene fragment formed upon recombination of the CO ligand.

Experimental Section

All glassware was flame-dried under N_2 before use, and all manipulations were performed in N_2 atmospheres using dry oxygen-free solvents. Me_2SiCl_2 was purchased from Petrarch Systems Inc., and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, from Strem Chemicals. NMR spectra were recorded on a Bruker NR 200 MHz multinuclear spectrometer, and IR spectra, on a Perkin-Elmer 1600 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc.

Typical reactions are described below, and spectral and analytical data are provided in Table I. All Fp complexes were synthesized on the same general scale as the examples provided, and all, with the exception of the *p*-$Me_2NC_6H_4$ derivatives, which are fully described below, involved the reaction sequence outlined in the synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2SiMe_2(p\text{-}MeOC_6H_4)$.

Synthesis of (p-$MeOC_6H_4$)$SiMe_2SiMe_2Cl$. A Grignard reagent was prepared by the dropwise addition of *p*-$MeOC_6H_4Br$ (20 g, 0.107 mol) to Mg turnings (2.71 g, 0.113 mol) in THF (50 mL) with stirring. After complete addition, the reaction mixture was allowed to stir at room temperature for a further 40 min. The Grignard reagent was added slowly to a stirred solution of $ClSiMe_2SiMe_2Cl$[5] (20 g, 0.11 mol) in THF (50 mL), with cooling (ice bath). After complete addition of the Grignard reagent, the reaction mixture was allowed to stir overnight at room temperature. The THF was distilled under reduced pressure, hexane

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Table I. Spectroscopic and Analytical Data of New Fp Complexes:[a] Complex; Yield; Analysis, found (calcd); Mp

$\mathrm{FpSiMe_2SiMe_2(\mathit{p}\text{-}NMe_2C_6H_4)}$; 54%; C 54.5 (55.2), H 6.75 (6.58); 67–70 °C

^{1}H: 0.57 (s, 6H, $\mathrm{Si\mathit{Me}_2C_6H_4NMe_2}$), 0.66 (s, 6H, $\mathrm{Si\mathit{Me}_2Fp}$), 2.52 (s, 6H, p-NMe$_2$), 4.08 (s, 5H, $\eta\text{-}\mathrm{C_5H_5}$), 6.65, 6.69, 7.49, 7.53 ($\mathrm{C_6H_4}$)
^{13}C: −2.24 ($\mathrm{Si\mathit{Me}_2C_6H_4}$), 3.67 ($\mathrm{Si\mathit{Me}_2Fp}$), 39.8 ($\mathit{p}$-NMe$_2$), 83.1 ($\eta^5\text{-}\mathrm{C_5H_5}$), 112.6, 135.1, 151.04, ($\mathrm{C_6H_4}$), 216.1 (CO)
^{29}Si: −16.2 ($\mathrm{SiMe_2(C_6H_4)}$)), 17.0 ($\mathrm{SiMe_2Fp}$)
IR ν(CO): 1995.2, 1943.9

$\mathrm{FpSiMe_2SiMe_2(\mathit{p}\text{-}OMeC_6H_4)}$; 23%; C 53.8 (54.0), H 6.26 (6.04); 52–56 °C

^{1}H: 0.48 (s, 6H, $\mathrm{Si\mathit{Me}_2C_6H_4}$), 0.57 (s, 6H, $\mathrm{Si\mathit{Me}_2Fp}$), 3.34 (s, 3H, p-OMe), 4.04 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 6.84, 6.88, 7.41, 7.44 ($\mathrm{C_6\mathit{H}_4}$)
^{13}C: −2.29 ($\mathrm{Si\mathit{Me}_2C_6H_4}$), 3.60 ($\mathrm{Si\mathit{Me}_2Fp}$), 54.5 ($\mathit{p}$-OMe), 83.0 ($\eta^5\text{-}\mathrm{C_5H_5}$), 114.2, 131.7, 135.4, 160.7, ($\mathrm{C_6H_4}$), 215.9 (CO)
^{29}Si: −15.8 ($\mathrm{SiMe_2(C_6H_4)}$)), 16.6 ($\mathrm{SiMe_2Fp}$)
IR ν(CO): 1996.5, 1945.1

$\mathrm{FpSiMe_2SiMe_2(\mathit{o}\text{-}OMeC_6H_4)}$; 67%; C 53.7 (54.0), H 5.98 (6.04); 88–90 °C

^{1}H: 0.55 (s, 6H, $\mathrm{Si\mathit{Me}_2C_6H_4}$), 0.64 (s, 6H, $\mathrm{Si\mathit{Me}_2Fp}$), 3.33 (s, 3H, o-OMe), 4.06 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 6.46, 6.50, 6.91, 7.42, 7.45 ($\mathrm{C_6\mathit{H}_4}$)
^{13}C: −1.88 ($\mathrm{Si\mathit{Me}_2C_6H_4}$), 4.22 ($\mathrm{Si\mathit{Me}_2Fp}$), 54.2 ($\mathit{o}$-OMe), 83.1 ($\eta^5\text{-}\mathrm{C_5H_5}$), 109.5, 121.1, 130.6, 135.3, 164.1 ($\mathrm{C_6H_4}$), 216.0 (CO)
^{29}Si: −16.9 ($\mathrm{SiMe_2C_6H_4}$), 17.8 ($\mathrm{SiMe_2Fp}$)
IR ν(CO): 1995.2, 1943.9

$\mathrm{FpSiMe_2SiMe_2(\mathit{p}\text{-}ClC_6H_4)}$; 77%; C 51.0 (50.4), H 5.25 (5.23); 35–56 °C

^{1}H: 0.37 (s, 6 H, $\mathrm{Si\mathit{Me}_2C_6H_4}$), 0.47 (s, 6H, $\mathrm{Si\mathit{Me}_2Fp}$), 3.99 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 7.22, 7.23 ($\mathrm{C_6H_4}$)
^{13}C: −2.58 ($\mathrm{Si\mathit{Me}_2C_6H_4}$), 3.49 ($\mathrm{Si\mathit{Me}_2Fp}$), 83.0 ($\eta^5\text{-}\mathrm{C_5H_5}$), 128.4, 135.0, 135.4, 139.8, ($\mathrm{C_6H_4}$), 215.6 (CO)
^{29}Si: −15.1 ($\mathrm{SiMe_2C_6H_4}$), 16.0 ($\mathrm{SiMe_2Fp}$)
IR ν(CO): 1996.8, 1947.1

$\mathrm{FpSiMe(\mathit{p}\text{-}ClC_6H_4)SiMe_3}$; 33%; C 50.2 (50.4), H 5.31(5.23); 117–120 °C

^{1}H: 0.23 (s, 9H, $\mathrm{SiMe_3}$), 0.65 (s, 3H, $\mathrm{Si\mathit{Me}C_6H_4}$), 3.99 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 7.23, 7.39 ($\mathrm{C_6H_4}$)
^{13}C: −0.27 ($\mathrm{SiMe_3}$), 1.50 ($\mathrm{Si\mathit{Me}C_6H_4}$), 83.9 ($\eta^5\text{-}\mathrm{C_5H_5}$), 128.1, 134.1, 135.3, 144.6, ($\mathrm{C_6H_4}$), 215.7 (CO)
^{29}Si: −12.2 ($\mathrm{SiMe_3}$), 12.3 ($\mathrm{SiMeC_6H_4}$)
IR ν(CO): 1998.4, 1947.1

$\mathrm{FpSiMe_2SiMe_2(\mathit{m}\text{-}CF_3C_6H_4)}$; 65%; C 53.1 (52.6), H 5.52 (5.41); Oil

^{1}H: 0.37 (s, 6H, $\mathrm{Si\mathit{Me}_2C_6H_4}$), 0.43 (s, 6H, $\mathrm{Si\mathit{Me}_2Fp}$), 4.00 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 7.07, 7.37, 7.41, 7.49, 7.90 ($\mathrm{C_6H_4}$)
^{13}C: −2.82 ($\mathrm{Si\mathit{Me}_2C_6H_4}$), 3.37 ($\mathrm{Si\mathit{Me}_2Fp}$), 83.0 ($\eta^5\text{-}\mathrm{C_5H_5}$), 125.1, 125.2, 128.3, 130.2, 130.3, 137.3, 143.3 ($\mathrm{C_6H_4}$) 215.4 (CO)
^{29}Si: −14.5 ($\mathrm{SiMe_2C_6H_4}$), 15.8 ($\mathrm{SiMe_2Fp}$)
IR ν(CO): 1999.1, 1948.2

$\mathrm{FpSiMe_2(\mathit{p}\text{-}NMe_2C_6H_4)}$; 25%; 143–145 °C

^{1}H: 0.79 (s, 6H, $\mathrm{SiMe_2}$), 2.60 (s, 6H, $\mathrm{NMe_2}$), 4.07 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 6.68, 7.57 (m, $\mathrm{C_6H_4}$)
^{13}C: 5.94 ($\mathrm{SiMe_2}$), 40.0 ($\mathrm{NMe_2}$), 84.1 ($\eta^5\text{-}\mathrm{C_5H_5}$), 112.3, 132.7, 133.9, 150.6 ($\mathrm{C_6H_4}$), 216.4 (CO)
^{29}Si: 35.0
IR ν(CO): 1995.0, 1942.3

$\mathrm{FpSiMe_2(\mathit{p}\text{-}OMeC_6H_4)}$; 48%; C 55.72 (56.15), H 5.34 (5.30); 64–66 °C

^{1}H: 0.75 (s, 6H, $\mathrm{SiMe_2}$), 3.39 (s, 3H, p-OMe), 4.00 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 6.86, 6.90, 7.55, 7.59 ($\mathrm{C_6H_4}$)
^{13}C: 5.84 ($\mathrm{SiMe_2}$), 54.5 (p-OMe), 84.1 ($\eta^5\text{-}\mathrm{C_5H_5}$), 113.8, 134.2, 138.1, 160.2, ($\mathrm{C_6H_4}$), 216.2 (CO)
^{29}Si: 35.3
IR ν(CO): 1995.2, 1943.9

$\mathrm{FpSiMe_2(\mathit{o}\text{-}OMeC_6H_4)}$; 39%; C 55.81 (56.15), H 5.17 (5.30); 41–42 °C

^{1}H 0.85 (s, 6H, $\mathrm{SiMe_2}$), 3.42 (2, 3H, o-OMe), 4.04 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 6.58, 6.96, 7.17, 7.21 ($\mathrm{C_6H_4}$)
^{13}C: 6.28 ($\mathrm{SiMe_2}$), 54.17 (o-OMe), 83.93 ($\eta^5\text{-}\mathrm{C_5H_5}$), 109.8, 120.7, 130.1, 134.2, 134.6, 163.3 ($\mathrm{C_6H_4}$), 216.2 (CO)
^{29}Si: 33.0
IR ν(CO): 1998.4, 1945.5

$\mathrm{FpSiMe_2(\mathit{p}\text{-}ClC_6H_4)}$; 53%; C 51.55 (51.97), H 4.06 (4.36); 45–48 °C

^{1}H: 0.63 (s, 6H, $\mathrm{SiMe_2}$), 3.88 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 7.16, 7.21, 7.25, 7.35 ($\mathrm{C_6H_4}$)
^{13}C: 5.43 ($\mathrm{SiMe_2}$), 84.0 ($\eta^5\text{-}\mathrm{C_5H_5}$), 128.1, 134.2, 145.8 ($\mathrm{C_6H_4}$), 215.7 (CO)
^{29}Si: 36.1
IR ν(CO): 1998.4, 1947.1

$\mathrm{FpSiMe_2(\mathit{m}\text{-}CF_3C_6H_4)}$; 63%; Oil

^{1}H: 0.61 (s, 6H, $\mathrm{SiMe_2}$), 3.92 (s, 5H, $\eta^5\text{-}\mathrm{C_5H_5}$), 7.10, 7.38, 7.65, 8.01 ($\mathrm{C_6H_4}$)
^{13}C: 5.25 ($\mathrm{SiMe_2}$), 83.9 ($\eta^5\text{-}\mathrm{C_5H_5}$), 124.7, 124.8, 128.2, 129.0, 136.3, 149.2 ($\mathrm{C_6H_4}$), 215.5 (CO)
^{29}Si: 36.8
IR ν(CO): 1998.4, 1948.7

[a] NMR spectra (ppm) were recorded in $\mathrm{C_6D_6}$, and IR spectra (cm^{-1}) were recorded in *n*-hexane.

added, and the mixture filtered under N_2 to remove the magnesium salts. The resulting solution was fractionally distilled (68–76 °C/0.2–0.3 mmHg) to yield 18.5 g (67%) of the title compound.

Synthesis of ($\mathbf{\mathit{p}\text{-}ClC_6H_4}$)$\mathbf{SiMe_2Cl}$. A Grignard reagent was prepared by the dropwise addition of 30 mL of a THF solution of p-$\mathrm{ClC_6H_4Br}$ (20.3 g, 0.11 mol) to Mg turnings (2.73 g, 0.11 mol) in THF (50 mL) with stirring. After complete addition, the reaction mixture was allowed to stir at room temperature for a further 40 min. The Grignard reagent was added slowly to a stirred solution of $\mathrm{Me_2SiCl_2}$ (15 mL, 0.12 mol) in THF (80 mL), with cooling (ice bath). After complete addition of the Grignard reagent, the reaction mixture was allowed to stir overnight at room temperature. Workup as above, followed by fractional distillation, yielded the title product, 8.71 g (40%) (37–41 °C/0.07–0.11 mmHg).

Synthesis of ($\mathbf{\mathit{p}\text{-}ClC_6H_4}$)$\mathbf{SiMeClSiMe_3}$. A Grignard reagent was prepared by the dropwise addition of 15 mL of a THF solution of p-Cl-$\mathrm{(C_6H_4)Br}$ (10.1 g, 0.053 mol) to Mg turnings (1.36 g, 0.06 mol) in THF (25 mL) with stirring. After complete addition, the reaction mixture was allowed to stir at room temperature for a further 40 min. The Grignard reagent was added slowly to a stirred solution of $Cl_2SiMeSiMe_3$[6] (10.3 g, 0.06 mol) in THF (50 mL), with cooling (ice bath). After complete addition of the Grignard reagent, the reaction mixture was allowed to stir overnight at room temperature. Workup as above yielded the title product, 7.23 g (52%) (56–59 °C/0.07–0.05 mmHg).

Synthesis of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$SiMe$_2$(*p*-MeOC$_6$H$_4$). A 250-mL round-bottomed flask equipped with a side arm was charged with 0.13 g (5.7 mmol) of Na, which was amalgamated with 15 g of Hg. To this mixture was added 1.54 g (4.4 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in THF (60 mL). The mixture was shaken vigorously for 1.5 h until formation of the Fp salt was complete. Excess Hg was removed through the side arm, the solution was cooled to 0 °C, ClSiMe$_2$SiMe$_2$(*p*-MeOC$_6$H$_4$) (1.15 g, 4.5 mmol) was added, and the reaction mixture was allowed to stir at room temperature overnight. The THF was removed under reduced pressure, hexane added, the mixture filtered under N_2, and the hexane solution concentrated and applied to a silica gel column. Elution with a 20/80 methylene chloride/hexane solvent mixture yielded a yellow band which upon collection, removal of the solvent under reduced pressure, and recrystallization from hexane yielded 0.42 g (23%) of the yellow crystalline title complex.

Synthesis of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$(*p*-ClC$_6$H$_4$). To a cooled (0 °C) solution of $[Fp]^-Na^+$ formed as above (from 3.0 g (8.6 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in 120 mL THF was added a 2-mL THF solution of ClSiMe$_2$(*p*-ClC$_6$H$_4$) (1.88 g, 9.2 mmol), and the reaction mixture was allowed to stir at room temperature overnight. The THF was removed under reduced pressure, hexane added, the mixture filtered under N_2, and the hexane solution concentrated and applied to a silica gel column. Elution with hexane yielded a yellow band which upon collection, removal of the solvent under reduced pressure, and recrystallization from hexane yielded 1.70 g (53%) of the yellow title complex.

Synthesis of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$SiMe$_2$(*p*-Me$_2$NC$_6$H$_4$). A solution of *p*-Me$_2$N(C$_6$H$_4$)Br (4.93 g, 0.025 mol) dissolved in 20 mL of THF was added dropwise to Mg turnings (0.60 g, 0.025 mol) and ClSiMe$_2$SiMe$_2$Cl (5.0 g, 0.027 mol) in THF (150 mL) with stirring. After complete addition, the reaction mixture was allowed to stir at room temperature for 2 h and then added slowly to a cooled (0 °C) THF solution of $[Fp]^-Na^+$ obtained from 9.17 g (0.026 mol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as described above. The reaction mixture was allowed to stir at room temperature overnight, the THF removed under reduced pressure, hexane added, and the mixture filtered under N_2. The hexane solution was concentrated and applied to a silica gel column. Elution with a 20/80 methylene chloride/hexane solvent mixture yielded a yellow band which upon collection, removal of the solvent under reduced pressure, and recrystallization from hexane yielded 3.5 g (34%) of the yellow crystalline title complex.

Synthesis of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$(*p*-Me$_2$NC$_6$H$_4$). A Grignard reagent was prepared by the dropwise addition of *p*-Me$_2$N(C$_6$H$_4$)Br (5.20 g, 0.026 mol) dissolved in THF (10 mL) to Mg turnings (0.73 g, 0.030 mol) in THF (20 mL) with stirring. After complete addition, the reaction mixture was allowed to stir at room temperature for a further 40 min. The Grignard reagent was added slowly to a stirred solution of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$Cl[7] at 0 °C in 10 mL of THF. After the mixture was stirred overnight, the THF was removed under reduced pressure, hexane added, and the resulting mixture filtered under N_2. The hexane solution was concentrated and applied to a silica gel column. Elution with a 20/80 methylene chloride/hexane solvent mixture yielded a yellow band which upon collection, removal of the solvent under reduced pressure, and recrystallization from hexane yielded 34% of the yellow crystalline title complex.

Photolysis of the FpSiMe$_2$SiMe$_2$(XC$_6$H$_4$) Complexes (X = *p*-NMe$_2$, *p*-OMe, *o*-OMe, H, *p*-Cl, *m*-CF$_3$). The photolysis reactions were carried out under N_2 in dried, degassed solvents, using a medium-pressure mercury lamp and were performed in two distinct manners:

(a) A sample of the appropriate complex (50–80 mg) was dissolved in hexane (20 mL), and the progress of the reaction was monitored directly by reverse-phase HPLC (Econosphere C-18, 5-μm packing, 80/20 CH_3CN/H_2O solvent mixture). For X = *p*-NMe$_2$, a 92/8 MeOH/H$_2$O solvent mixture was used.

(b) A sample of the appropriate complex (200 mg) was dissolved in C_6D_6 (0.5 mL) in a sealed NMR tube, and the progress of the reaction was monitored directly by ^{29}Si NMR (with final HPLC monitoring).

Table II

$$FpSiMe_2SiMe_2(C_6H_4X) \xrightarrow{h\nu} \underset{Y\%}{FpSiMe_3} + \underset{Z\%}{FpSiMe_2(C_6H_4X)}$$

X	Y[a]	Z
p-NMe$_2$	57 (52) [58]	43 (48) [42]
p-OMe	31 (11)	69 (89)
H	13 (5)	87 (95)
p-Cl	12 (4)	88 (96)
m-CF$_3$	8 (2)	92 (98)
o-Me	3 (3)	97 (97)

$$FpSiMe(p\text{-}ClC_6H_4)SiMe_3 \rightarrow \underset{14\%}{FpSiMe_3} + \underset{86\%}{FpSiMe_2(p\text{-}ClC_6H_4)}$$

[a] Relative percent of products determined by using NMR (HPLC) [GC/MS].

Direct comparison of NMR resonances and retention times for the photoproducts and authentic samples of these products permitted accurate product analysis. We also made a final evaluation of the product distribution using GC/mass spectrometry (Hewlett Packard 5890/5871 instrument with ionizing voltage of 70 eV). Product distributions are provided in Table II.

Results and Discussion

Synthesis and Photochemistry of Fp-Disilanes. The Fp complexes were synthesized by the standard routes outlined below in good to moderate yields, and their spectral and analytical data, recorded in Table I, are in total accord with the proposed structures.

$$Fp^-Na^+ + ClSiMe_2SiMe_2Ar \xrightarrow{THF} FpSiMe_2SiMe_2Ar + NaCl \quad (1)$$

$$Fp^-Na^+ + ClSiMe_2Ar \xrightarrow{THF} FpSiMe_2Ar + NaCl \quad (2)$$

In the case of FpSiMe$_2$(*p*-Me$_2$NC$_6$H$_4$), a different route was used (eq 3).

$$Fp^-Na^+ + Cl_2SiMe_2 \xrightarrow{THF} FpSiMe_2Cl + NaCl \quad (3a)$$

$$FpSiMe_2Cl + BrMg(p\text{-}Me_2NC_6H_4) \xrightarrow{THF} FpSiMe_2(p\text{-}Me_2NC_6H_4) \quad (3b)$$

Photochemical treatment of the Fp-disilanes proceeded smoothly in high conversion to the two expected monosilane compounds (eq 4).

$$FpSiMe_2SiMe_2Ar \xrightarrow{h\nu} FpSiMe_3 + FpSiMe_2Ar + [Me_2Si] + [MeArSi] \quad (4)$$

$$Ar = XC_6H_4;\ X = p\text{-}NMe_2, p\text{-}OMe, o\text{-}OMe, H, p\text{-}Cl, m\text{-}CF_3$$

The series of substituents used in this study range from electron-withdrawing to electron-donating; thus any polarity in the transition state involved in the 1,3-alkyl/aryl migrations and polarity of the silylene intermediates should result in significant substituent effects upon the product distribution of eq 4. As noted from Table II, there was indeed a very significant range for the ratio [FpSiMe$_3$]/[FpSiMe$_2$Ar].

The data unambiguously illustrate the capacity of electron-donating substituents on the aromatic ring to facilitate the

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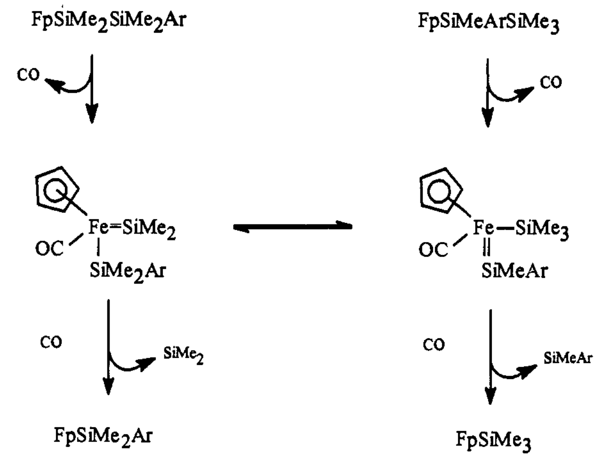
[6] Kumada, M.; Kondo, T.; Mimura, K.; Yamamoto, K.; Ishikawa, M.; Ikeda, S.; Kondo, M. *J. Organomet. Chem.* **1972**, *43*, 293.

[7] King, R. B.; Pannell, K. H.; Bennett, C. R.; Ishaq, M. *J. Organomet. Chem.* **1969**, *19*, 327.

Scheme I



formation of the $FpSiMe_3$ product at the expense of $FpSiMe_2Ar$. Furthermore, the same product distributions obtained for the two isomeric $FpSi_2Me_4(p\text{-}ClC_6H_4)$ complexes confirm our earlier results that the equilibrium between the two silyl–silylene intermediates is rapid and that product distributions are a true reflection of this equilibrium position (Scheme I).

An increased formation of $FpSiMe_3$ reflects the stability of $(\eta^5\text{-}C_5H_5)Fe(CO)(SiMe_3)({=}SiMeAr)$; cf. $(\eta^5\text{-}C_5H_5)Fe(CO)(SiMe_2Ar)({=}SiMe_2)$, and *vice versa*. Thus, our product distribution data indicate that electron-donating groups stabilize the intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(SiMe_3)({=}SiMeAr)$, which in turn suggests that this silylene is significantly polarized in the sense $Fe{=}Si \leftrightarrow Fe^-{-}Si^+$. The fact that the effect is most dramatically illustrated for the $p\text{-}Me_2N$ substituent results from the strong resonance stabilization of positive charge (Figure 1).

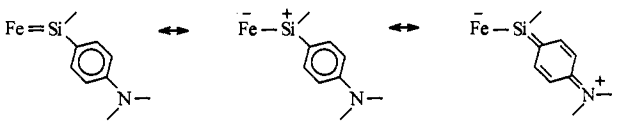


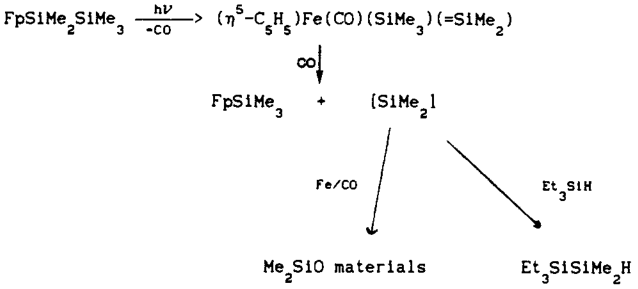
Figure 1.

It is significant that photolysis of $FpSiMe_2SiMe_2(o\text{-}MeOC_6H_4)$ does not provide evidence for enhanced stability of $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMeAr)SiMe_3$ leading to preferred formation of $FpSiMe_3$ as does the *p*-MeO isomer (Table II). We suggest that this is due to the stabilization of $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiMe_2)\{SiMe_2(o\text{-}MeOC_6H_4)\}$ via the same type of intramolecular OMe bridging observed by the Ogino group from photolytic transformation of $FpSiMe_2SiMe_2OMe$.[2f] In the present case, we were unable to isolate such an intermediate, but it seems clear that the formation of $FpSiMe_3$ in only 3% compared to 30% for the related *p*-MeO is best explained in this manner. These results provide an interesting example of the capacity of a substituent to stabilize different intermediates dependent upon whether it is in the ortho or para position of the aromatic group.

In general, our data reinforce the idea that in metal silylenes the silicon atom is electron-deficient. The facile formation and isolation of base-stabilized metal silylenes and isolations of "base-free" silylenes which involve internal base atoms, i.e. S, represent a clear demonstration of the electrophilicity of metal silylenes.

Trapping of Eliminated SiR_2. A major problem with our suggested mechanism involving formation of silyl–silylene intermediates, and ultimate elimination of SiR_2, has been our inability to definitively characterize the fate of the silylene species. We, and the Ogino group, have previously attempted the traditional silylene-trapping experiments without success. However, new results pertain to the reasons for this previous lack of success.

Scheme II



We have re-investigated the study by Kumada *et al.* on the photochemical degradation of $(SiMe_2)_6$ leading to elimination of $SiMe_2$ and formation of both $(SiMe_2)_5$ and $(SiMe_2)_4$.[8] We have verified this classic reaction by cleanly trapping the expelled $SiMe_2$ with Et_3SiH to form $Et_3SiSiMe_2H$. We repeated the process in the presence of 1 equiv of either a simple Fp complex, $FpSiMe_3$, or $Fe(CO)_5$ complexes, from which elimination of CO upon photochemical irradiation is well documented. Irradiation of $(SiMe_2)_6$ in the presence of the metal carbonyls and Et_3SiH resulted in the formation of both $(SiMe_2)_5$ and $(SiMe_2)_4$, **but no Et_3SiMe_2SiH**. This result demonstrates that the silylene species $SiMe_2$ is extremely reactive in the presence of CO. GC mass spectral analysis of the resulting photochemical product mixtures revealed a large number of Si-containing materials that contain the $SiMe_2O$ grouping. Comparison of this product mixture with a sample of a mixture of linear and cyclic $(Me_2SiO)_n$ materials supplied by the Dow Corning Corp. exhibited some overlap, but it was also clear that a range of other materials were present. Photochemical treatment of $(SiMe_2)_6$ and Et_3SiH in a CO-saturated C_6H_6 solution, under a CO atmosphere, resulted in mainly trapping to form $Et_3SiSiMe_2H$; apparently CO solubility problems restricted the efficiency of the $SiMe_2$ reaction with CO. It is also possible that the reaction of CO and Me_2Si in the presence of metal complexes occurs not only because of high local CO concentrations but also because of some more specific Me_2Si/Fe interactions that modify the silylene produced during the photochemical event, however we are unable to address this possibility at the present time.

With the above information at hand, we re-investigated the photochemistry of a cyclohexane solution of $FpSiMe_2SiMe_3$ in the presence of Et_3SiH, examining the product via GC mass spectrometry. Using this technique we were able, for the first time, to observe the formation of $Et_3SiSiMe_2H$, albeit in only approximately 1% yield, along with SiO-containing materials. We observed 11 SiO products, 6 of which were also produced from the photolysis of $(SiMe_2)_6/Et_3SiH/FpSiMe_3$ (or $Fe(CO)_5$) mixtures. Overall, the results may be summarized as in Scheme II.

The definitive formation of $Et_3SiSiMe_2H$, coupled with the above described experiments with $(SiMe_2)_6$, demonstrates the viability of our suggested SiR_2 expulsion. The absence of high-yield trapping experiments is unfortunate but explicable by the ubiquitous presence of photoejected CO, since recovered yields of the photoproducts containing the Fp unit are generally in the range 50–70%. The exact nature of the siloxy products obtained from the reaction between $SiMe_2$ and CO is obscure, except to note that they are many and seem to be linear and branched oligomers. It is of interest that, despite the many studies on the chemistry of $SiMe_2$ and related species in the literature, no definitive reports are available concerning its ultimate reactivity with CO. Both the Arrington[9] and West[10] groups studied the

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(8) (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 612. (b) *J. Organomet. Chem.* **1972**, *42*, 325.

(9) Arrington, C. A.; Petty, J. T.; Payne, S. E.; Haskins, W. C. K. *J. Am. Chem. Soc.* **1988**, *110*, 6240.

(10) Pearsall, M.-A.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 7228.

low-temperature-matrix chemistry of silylenes with CO and concluded that an acid–base complex formed, $R_2Si \leftarrow CO$. Upon an increase in temperature, this complex decomposed, but neither group could determine the nature of the products. In a private communication Professor Arrington informed us that after many hours of studying the dimethylsilylene/CO system the CsI plates used for the matrix study developed a thin film whose IR properties resembled silicone grease, in accord with our general observations.

Formation of SiH Compounds. In their detailed infrared study of the low-temperature-matrix photolysis and flash photolysis of $FpSiMe_2SiMe_3$, the Turner group observed the formation of an SiH-containing material. They reasonably suggested that this may arise from irradiation of $SiMe_2$ to form $Me(H)Si{=}CH_2$, a reaction with literature precedent, which itself leads to dimerization to $Me(H)Si(\mu\text{-}CH_2)_2Si(H)Me$.[11] However, the ν(SiH) reported, 2121 cm^{-1}, was only the average of the bands expected for disilacyclobutane, 2113, 2116, and 2134 cm^{-1}. In our detailed GC/MS analysis of the reaction products obtained from the irradiation of $FpSiMe_2SiMe_3$ and the various $FpSiMe_2SiMe_2Ar$ complexes, we have been unable to observe evidence for such a product, but we have observed significant quantities of Me_2ArSiH, Ar = p-Me_2N-C_6H_4 and p-$MeOC_6H_4$ (together with small amounts of ArH for both complexes). We also observed that these products are formed, in significantly lower yield, from the photolysis of $FpSiMe_2Ar$ over the same photolysis time period as used in the study on Fp-disilanes. These results indicate that photolysis of Fp-disilanes also leads to some direct Si–Si cleavage, possibly involving fortuitous H_2O. When the "dry" solvents used for the photochemical reactions were spiked with H_2O, the yields of Me_2ArSiH were significantly greater. We have not been able to observe the formation of Me_3SiH from $FpSiMe_2SiMe_3$ since this product would be encompassed in the solvent envelope in our experimental setup. The Si–H stretching frequency noted by the Turner group in their experiments with $FpSiMe_2SiMe_3$, 2121 cm^{-1}, is exactly the correct frequency expected for Me_3SiH.[12]

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(11) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1846.

(12) Shevchenko, I. V.; Kovalev, I. F.; Dernova, V. S.; Voronkov, M. G.; Khudobin, Yu. I.; Andreeva, N. A.; Kharitonov, N. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *21*, 98.