Syntheses and Photochemically Induced Rearrangements of Tetrasilyl- and Trisilylgermyl Complexes of Iron: $(\eta^5\text{-}C_5R_5)Fe(CO)_2(SiMe_2)_3EMe_2Ph$ (R = H, Me; E = Ge, Si)

Sneh Sharma† and Keith H. Pannell*

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968-0513

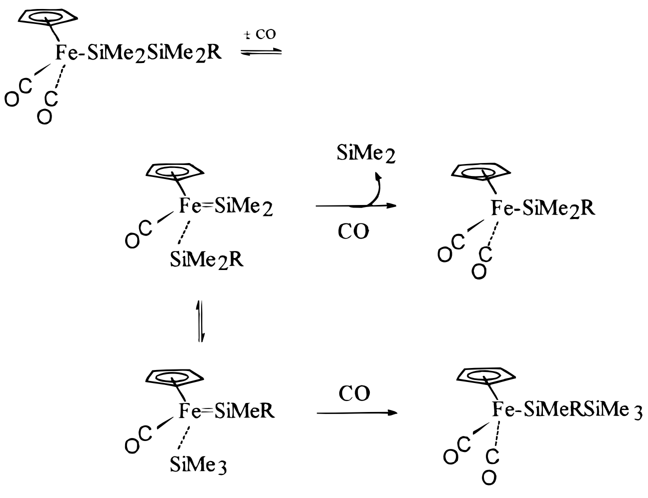
Received November 10, 1999

Oligosilyl and oligosilylgermyl complexes $(\eta^5\text{-}C_5R_5)Fe(CO)_2(SiMe_2)_3EMe_2Ph$ (R = H (**1**), Me (**2**); E = Ge (**a**), Si (**b**)) have been synthesized, characterized, and photolyzed. All complexes isomerized cleanly to $(\eta^5\text{-}C_5R_5)Fe(CO)_2E(SiMe_3)_2(SiMe_2Ph)$. Photolysis of a mixture of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(SiMe_2)_3GeMe_2Ph$ (**2a**) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(SiMe_2)_3SiMe_3$ (**1b**) proved that the rearrangements occur via an intramolecular mechanism. Irradiation of **1** and **2** in the presence of HMPA resulted in the formation of $(\eta^5\text{-}C_5R_5)Fe(CO)({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2EMe_2Ph)$, indicating that silylene intermediates are key to the rearrangements. Attempts to use this new chemistry to perform the catalytic isomerization $Me_3GeSiMe_2SiMe_2SiMe_2H \rightarrow (Me_3Si)_3GeH$ resulted in high yields of $(Me_3Si)_3GeSiMe_2H$. This product indicates the ability of $(Me_3Si)_3GeH$ to intercept the Fe−silylene intermediates.

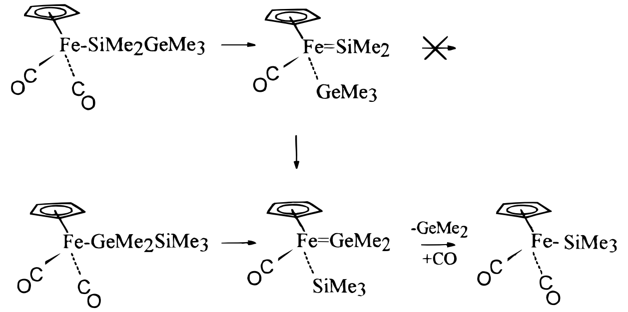
Introduction

The signature chemistry of oligosilyl derivatives of the transition metals that contain direct metal−silicon bonds is their ability to undergo elimination reactions, resulting in the formation of transient silylenes (Scheme 1).[1−3] Such intermediates can eliminate silylenes or undergo rearrangement reactions involving 1,3-alkyl, -aryl, and -silyl migrations. The silylene can be trapped intramolecularly or intermolecularly.[2g,3b,e,5] The chemistry appears to be quite general, and related chemistry is observed with tungsten complexes.[3e] Silylgermyl or germylsilyl Fe analogues were studied in which either the germylene or silylene intermediate was possible. Via the characteristic 1,3-shift, it was the germylene that formed preferentially and it was chemistry of this intermediate that was observed (Scheme 2).[4]

Scheme 1



Scheme 2



We have shown that UV irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2{-}SiMe_2SiMe_2SiMe_2SiMe_3$ resulted in its high-yield transformation to $FpSi(SiMe_3)_3$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) without any silylene elimination.[2d] To understand more about the mechanistic aspects of these rearrangement reactions, we have synthesized the tetrasilane $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ and the mixed oligosilyl−germyl complexes $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$ and Fp^*SiMe_2-

---

[†] Sneh Sharma died in El Paso, TX, May 24, 1999. She was much loved.

(1) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

(2) (a) Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056. (b) Pannell, K. H.; Rozell, J. M.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (c) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (d) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (e) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (f) Pannell, K. H.; Brun, M.-C.; Sharma, H. K.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075. (g) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes-Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315.

(3) (a) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (b) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (c) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (d) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2850. (e) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138.

(4) (a) Pannell, K. H.; Sharma, S. *Organometallics* **1991**, *10*, 1655. (b) Sharma, H.; Pannell, K. H. *Organometallics* **1994**, *13*, 4946. (c) Koe, J. R.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479.

(5) Ueno, K.; Nakano, K, Ogino, H. *Chem. Lett.* **1996**, 459.

10.1021/om990897c CCC: $19.00
Publication on Web 03/01/2000

$SiMe_2SiMe_2GeMe_2Ph$ (Fp* = (η^5-Me_5C_5)$Fe(CO)_2$). The photochemistry of these complexes is reported, including attempted crossover experiments, along with the observation of complexed silylene intermediates. Catalytic transformations of germylsilanes were also accomplished.

Results and Discussion

Synthesis and Characterization. The syntheses of the new iron complexes were accomplished in moderate to good yields by salt-elimination reactions (eqs 1−3).

$$[Fp]Na + Cl(SiMe_2)_4Ph \rightarrow FpSiMe_2SiMe_2SiMe_2SiMe_2Ph + NaCl \quad (1)$$

$$[Fp]Na + Cl(SiMe_2)_3Cl \rightarrow FpSiMe_2SiMe_2SiMe_2Cl + NaCl \quad (2)$$

$$Fp(SiMe_2)_3Cl + [PhMe_2Ge]Li \rightarrow FpSiMe_2SiMe_2SiMe_2GeMe_2Ph + LiCl \quad (3)$$

The new complexes are either low-melting solids or oils. Their spectroscopic and analytical data, recorded in Table 1, are in accord with their proposed structures.

^{29}Si NMR spectroscopy is particularly helpful for characterization of the new complexes. For example, the tetrasilyliron complex $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ exhibits signals in the ^{29}Si NMR spectrum at 22.9, −17.6, −32.5, and −42.9 ppm. These can be assigned on the basis of our previous extensive analysis of oligosilyl Fp complexes.[1] The low-field signal at 22.9 ppm is due to the silicon atom directly attached to the iron and exhibits an ~40 ppm downfield shift from the permethylated tetrasilane $Me_3SiSiMe_2SiMe_2SiMe_3$. The signal at −17.6 ppm is assigned to the terminal $-SiMe_2Ph$, the signal at −42.9 is due to $-\mathit{Si}Me_2SiMe_2Ph$, and the −32.5 ppm resonance is due to a silicon in the β-position. The latter resonance exhibits an ~12 ppm downfield shift compared to the permethylated tetrasilane. In the related germanium complex $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$, the silicon signal due to $-\mathit{Si}Me_2GeMe_2Ph$ is shifted to low field, by about 9.0 ppm, to −33.6 ppm. Similar 7−9 ppm low-field shifts were observed in the silicon NMR spectra of the iron silylgermyl complexes compared to signals for their silyl analogues.[4]

Photochemistry. The oligosilyl and oligosilylgermyl complexes are photochemically labile. The tetrasilyliron complex $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ undergoes a photochemical rearrangement, without silylene elimination, to produce $FpSi(SiMe_3)_2(SiMe_2Ph)$ (eq 4).

$$FpSiMe_2SiMe_2SiMe_2SiMe_2Ph \rightarrow FpSi(SiMe_3)_2(SiMe_2Ph) \quad (4)$$

The reaction is very clean, and no intermediates or significant amounts of any other products were observed in the NMR spectra of the crude product. This result is similar to a rearrangement we have previously reported, i.e., $FpSiMe_2SiMe_2SiMe_2SiMe_3 \rightarrow FpSi(SiMe_3)_3$.[2d]

The photochemistry of the oligosilylgermyl iron complexes is unique. The two complexes $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$ and $Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph$ each photochemically rearranged cleanly to yield a single product containing an Fe−Ge bond, i.e., $FpGe(SiMe_3)_2(SiMe_2Ph)$ and $Fp^*Ge(SiMe_3)_2SiMe_2Ph$. No other significant products were observed by NMR analysis of the crude reaction products.

The formation of complexes containing an Fe−Ge bond reinforces our earlier observations that the germylene−iron intermediates are more stable than their silylene−iron analogues when a dynamic equilibrium between them is possible. A further driving force for the rearrangement is the large enthalpy gain associated with the exchange of three Ge−C bonds for three Si−C bonds. This is presumably greater than any potential loss associated with the transformation of Si−Si bonds to Si−Ge bonds and the Fe−Si to a Fe−Ge bond. Our proposed mechanism for this rearrangement is illustrated in Scheme 3.

Photochemistry in the Presence of HMPA. Ogino and co-workers have shown that when disilyl−Fp species are irradiated in the presence of hexamethylphosphoramide (HMPA), HMPA-stabilized silylene species are generated.[5] Since the mechanisms that we have proposed for the rearrangements of oligosilyl, and now oligosilylgermyl, Fp complexes contain many steps, there is always the possibility that alternative mechanisms to that outlined in Scheme 3 might be important. We have irradiated the new complexes in the presence of HMPA to see if it might be possible to observe at least the first step in the process depicted in Scheme 3. Indeed, monitoring the photolysis of $FpSiMe_2SiMe_2SiMe_2ER_3$ (ER_3 = $SiMe_3$, $SiMe_2Ph$, $GeMe_2Ph$) in the presence of HMPA by NMR spectroscopy showed the formation of silylene·HMPA iron complexes (Figure 1, Table 1).

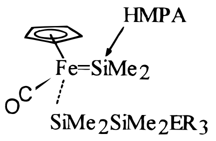


Figure 1.

In the case of $FpSiMe_2SiMe_2SiMe_2SiMe_3$, the ^{29}Si NMR spectrum of the silylene complex exhibited a doublet at 114.9 ppm due to coupling with the ^{31}P atom of HMPA (J = 28 Hz) and signals at 13.6, −15.4, and −39.0 ppm. The doublet nature and low-field shift of the signal at 114.9 ppm compared to that of the starting compound (22.4, −14.8, −32.9, and −43.2 ppm) clearly indicate the formation of a silylene coordinated to an HMPA molecule, while the other ^{29}Si signals are comparable to those of $FpSiMe_2SiMe_2SiMe_3$ (i.e., 19.0, −14.7, and −37.9 ppm). The ^1H NMR spectrum showed two doublets at 2.42 and 2.25 ppm for free and coordinated HMPA molecules, respectively, and resonances at 0.63 and 0.66 ppm, assigned to the methyl groups of the HMPA-coordinated $SiMe_2$ ligand. The signals at 0.58, 0.38, 0.42, and 0.29 are assigned to $FeSiMe_2$, $FeSiMe_2SiMe_2$, and $SiMe_3$. The ^{13}C NMR spectrum shows that all the methyl groups attached to the α- and β-silicon atoms are nonequivalent. These NMR data support the formula (η^5-C_5H_5)(CO)Fe(=$SiMe_2$·HMPA)($SiMe_2SiMe_2SiMe_3$) and are compatible with the data reported by the Ogino group. Irradiation of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ and $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$ in the presence of HMPA provided similar results, with the formation of single products, (η^5-C_5H_5)(CO)Fe-

Table 1. Spectroscopic and Analytical Data for New Complexes[a]

	$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_2Ph}$
yield, %	50
mp, °C	43
anal. found (calcd)	C, 51.4 (51.8); H, 6.77 (7.04)
^{29}Si NMR	22.9 ($\mathrm{FpSiMe_2}$), −17.6($\mathrm{SiMe_2Ph}$), −32.5 ($\mathrm{SiMe_2}$), −42.9 ($\mathrm{SiMe_2}$)
^{13}C NMR	−4.68, −2.84, −2.44, 5.56 ($\mathrm{SiMe_2}$), 83.2(η^5−$\mathrm{C_5H_5}$), 128.2, 128.9, 134.3, 142.0 (Ph)
^{1}H NMR	0.52, 0.76 ($\mathrm{SiMe_2}$), 4.15 (η^5-$\mathrm{C_5H_5}$), 7.26, 7.29, 7.70 (Ph)
IR (hexane), cm^{-1}	ν(CO) 1996.6, 1945.8
	$\mathrm{FpSi(SiMe_3)_2(SiMe_2Ph)}$
yield, %	80
mp, °C	45
anal. found (calcd)	C, 51.4 (51.8); H, 6.97 (7.04)
^{29}Si NMR	−6.06 ($\mathrm{SiMe_3}$), 9.16 ($\mathrm{SiMe_2Ph}$), −82.1 (Fp-Si)
^{13}C NMR	2.13 ($\mathrm{SiMe_2Ph}$), 4.14 ($\mathrm{SiMe_3}$), 83.2 (η^5-$\mathrm{C_5H_5}$), 128.5, 128 9, 134.7, 143.1 (Ph)
^{1}H NMR	0.50 ($\mathrm{SiMe_3}$), 0.75 ($\mathrm{SiMe_2}$), 4.14 (η^5-$\mathrm{C_5H_5}$), 7.26, 7.28, 7.70 (Ph)
IR (hexane), cm^{-1}	ν(CO) 1996.6, 1947.9
	$\mathrm{FpSiMe_2SiMe_2SiMe_2Cl}$
yield, %	50
bp, °C	122−124/0.02 mmHg
anal. found (calcd)	C, 40.7 (40.4); H, 6.22 (5.99)
^{29}Si NMR	27.7 ($\mathrm{SiMe_2Cl}$), 20.2 ($\mathrm{FpSiMe_2}$), −35.6 ($\mathrm{SiMe_2}$)
^{13}C NMR	−4.75, 3.37, 4.85 ($\mathrm{SiMe_2}$), 83.2 (η^5-$\mathrm{C_5H_5}$), 215.6 (CO)
^{1}H NMR	0.30, 0.51, 0.58 (Si−Me), 4.15 (η^5-$\mathrm{C_5H_5}$)
	$\mathrm{FpSiMe_2SiMe_2SiMe_2GeMe_2Ph}$
yield, %	50 (wax)
anal. found (calcd)	C, 46.6 (47.5); H, 6.75 (6.45)
^{29}Si NMR	22.6 (Fp-Si), −32.3 ($\mathrm{SiMe_2}$), −33.6 ($\mathrm{SiMe_2}$−Ge)
^{13}C NMR	−4.16 ($\mathrm{GeMe_2}$), −3.18, −3.00, 5.30 ($\mathrm{SiMe_2}$), 83.1 (η^5-$\mathrm{C_5H_5}$), 128.3, 128.5, 133.9, 142.5 (Ph), 215.8 (CO)
^{1}H NMR	0.27 ($\mathrm{GeMe_2}$), 0.37, 0.59 ($\mathrm{SiMe_2}$), 4.17 (η^5-$\mathrm{C_5H_5}$), 7.19, 7.28, 7.52
IR (hexane), cm^{-1}	ν(CO) 1997.1, 1946.1
	$\mathrm{FpGe(SiMe_3)_2(SiMe_2Ph)}$
yield, %	82 (wax)
anal. found (calcd)	C, 47.3 (47.5); H, 6.63 (6.45)
^{29}Si NMR	0.69 ($\mathrm{SiMe_3}$), −4.81 ($\mathrm{SiMe_2Ph}$)
^{13}C NMR	2.27 ($\mathrm{SiMe_2Ph}$), 4.24 ($\mathrm{SiMe_3}$), 82.4 (η^5-$\mathrm{C_5H_5}$), 128.4, 134.3, 143.4 (Ph), 215.7 (CO)
^{1}H NMR	0.44 ($\mathrm{SiMe_3}$), 0.69 ($\mathrm{SiMe_2}$), 4.10 (η^5-$\mathrm{C_5H_5}$), 7.18, 7.52, 7.64 (Ph)
IR (hexane), cm^{-1}	ν(CO) 1991.9, 1944.4
	$\mathrm{Fp^*SiMe_2SiMe_2SiMe_2Cl}$
yield, %	56 (oil)
anal. found (calcd)	C, 46.7 (47.3); H, 7.54 (7.28)
^{29} Si NMR	29.17 ($\mathrm{SiMe_2Cl}$), 18.50 (Fp*−Si), −35.87 ($\mathrm{SiMe_2}$)
^{13}C NMR	−4.12, 3.88, 4.26 ($\mathrm{SiMe_2}$), 10.1 ($\mathrm{CH_3}$), 95.2 (η^5-$\mathrm{Me_5C_5}$), 218.0(CO)
^{1}H NMR	0.61, 0.70, 0.75 ($\mathrm{SiMe_2}$), 1.58 ($\mathrm{CH_3}$)
IR (hexane), cm^{-1}	ν(CO) 1980.0, 1928.7
	$\mathrm{Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph}$
yield, %	38
mp, °C	72−73
anal. found (calcd)	C, 51.6 (51.9); H, 7.69 (7.37)
^{29}Si NMR	20.6 (Fp-Si), −32.7 ($\mathrm{SiMe_2}$), −33.0 ($\mathrm{SiMe_2Ge}$)
^{13}C NMR	−3.94 ($\mathrm{GeMe_2}$), −2.83 ($\mathrm{SiMe_2}$), 4.37 (Fp−Si), 94.8 (η^5-$\mathrm{C_5H_5}$), 127.8, 128.2, 133.9, 143.3 (Ph), 218.0 (CO)
^{1}H NMR	0.52, 0.55, 0.70, 0.73, 1.60 ($\mathrm{CH_3}$), 7.27, 7.35, 7.62 (Ph)
IR (hexane), cm^{-1}	ν(CO) 1978.8, 1927.6
	$\mathrm{Fp^*Ge(SiMe_3)_2(SiMe_2Ph)}$
yield, %	80 (wax)
anal. found (calcd)	C, 51.9 (51.9); H, 8.01 (7.37)
^{29}Si NMR	−1.98 ($\mathrm{SiMe_3}$), −5.37 ($\mathrm{SiMe_2Ph}$)
^{13}C NMR	4.23 ($\mathrm{SiMe_2}$), 5.84 ($\mathrm{SiMe_3}$), 10.65 ($\mathrm{CH_3}$), 94.87 (η^5-$\mathrm{Me_5C_5}$), 128.34, 128.51, 135.13, 143.2 (Ph), 219.83 (CO)
^{1}H NMR	0.64 ($\mathrm{SiMe_3}$), 0.86 ($\mathrm{SiMe_2}$), 1.52 ($\mathrm{CH_3}$), 7.26, 7.82, 7.86 (Ph)
IR (hexane), cm^{-1}	ν(CO) 1977.6, 1929.1
	$\mathrm{PhSiMe_2SiMe_2SiMe_2GeMe_3}$
yield, %	28
bp, °C	145−155/0.05 mmHg
anal. found (calcd)	C, 51.0 (48.8); H, 8.61 (8.74)
^{29}Si NMR	−17.8 (Ph−Si), −35.8 ($\mathrm{SiMe_2}$−$\mathrm{GeMe_3}$), −44.0 ($\mathrm{SiMe_2}$)
^{13}C NMR	−5.08 ($\mathrm{SiMe_2}$), −4.64 ($\mathrm{SiMe_2}$), −2.36 ($\mathrm{SiMe_2}$), −1.52 ($\mathrm{GeMe_3}$), 128.4, 128.99, 134.3, 140.3 (Ph)
^{1}H NMR	0.052, 0.085, 0.35 ($\mathrm{SiMe_2}$), 0.12 ($\mathrm{GeMe_3}$), 7.40, 7.29, 7.28 (Ph)

Table 1 (Continued)

	$HSiMe_2SiMe_2SiMe_2GeMe_3$
yield, %	44
bp, °C	120−122/0.05 mmHg
anal. found (calcd)	C, 37.3 (36.9); H, 9.58 (9.62)
^{29}Si NMR	−36.3 ($SiMe_2{-}GeMe_3$), −36.8 ($SiMe_2H$), −44.0 ($SiMe_2$)
^{13}C NMR	−5.73 ($SiMe_2$), −5.27 ($SiMe_2$), −1.96 ($GeMe_3$)
^{1}H NMR	0.19 ($SiMe_2H$, d),0.20, 0.23 ($SiMe_2$, s), 0.30($GeMe_3$), 4.05 ($SiMe_2H$, m)
	$(Me_3Si)_3GeSiMe_2H$
mp, °C	132−134
found (calcd) HRMS, *m/z*	$C_{11}H_{31}Si_4{}^{74}Ge$ 352.0946 (352.0949)
^{29}Si NMR	−4.61 (Me_3Si), −29.5 ($SiMe_2H$)
^{13}C NMR	−1.24 ($SiMe_2$), 3.28 ($SiMe_3$)
^{1}H NMR	4.44 (sept. $J = 28$ Hz, SiH), 0.358 (d, $J = 28$ Hz, $SiMe_2$), 0.304 ($SiMe_3$)
IR (hexane), cm^{-1}	2090.9
	$Cp(CO)Fe({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2SiMe_3)$
^{29}Si NMR	114.9 (d, $J_{SiP} = 28.3$ Hz, $SiMe_2{\cdot}HMPA$), 13.6 ($Fe{-}SiMe_2$), −15.4 ($SiMe_3$), −39.0 ($SiMe_2$)
^{1}H NMR	0.29 ($SiMe_3$), 0.38, 0.42 ($Fe{-}SiMe_2$), 0.58 (2 $SiMe_2$), 0.63, 0.66 ($Fe{=}SiMe_2$), 2.25 (d, $HMPA{\cdot}SiMe_2$), 2.42 (d, HMPA), 4.35 (η^5-C_5H_5)
^{13}C NMR	−3.20, −3.16 ($SiMe_2$), −0.68 ($SiMe_3$), 6.02, 6.54 ($Fe{-}SiMe_2$), 11.1, 13.2 ($Fe{=}SiMe_2$), 36.6 (d, $HMPA{\cdot}SiMe_2$) 37.0 (d, HMPA) 79.1 (η^5-C_5H_5), 219.1 (CO)
	$Cp(CO)Fe({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2SiMe_2Ph)$
^{29}Si NMR	115.3 (d, $J_{SiP} = 28.4$ Hz, $SiMe_2{\cdot}HMPA$), 14.7 ($Fe{-}SiMe_2$), −17.6 ($SiMe_2Ph$), −39.1 ($SiMe_2$)
^{13}C NMR	−2.35, 2.29 ($SiMe_2$), −1.74, −1.69 ($SiMe_2$), 7.13, 6.71 ($Fe{-}SiMe_2$), 13.8, 11.7 ($Fe{=}SiMe_2$), 37.0 (d, HMPA), 36.7 ($HMPA{\cdot}SiMe_2$), 79.6 (η^5-C_5H_5), 219.7 (CO)
^{1}H NMR	0.35, 0.41, 0.53, 0.55, 0.57, 0.60, 0.63 (SiMe), 2.21 (d, $HMPA{\cdot}SiMe_2$), 2.42 (d, HMPA), 4.32 (η^5-C_5H_5), 7.40 (d, $J = 3$ Hz), 7.19 (d, $J = 3$ Hz) (Ph)
	$Cp(CO)Fe({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2GeMe_2Ph)$
^{29}Si NMR	115.6 (d, $J_{SiP} = 28.4$ Hz, $SiMe_2{\cdot}HMPA$), 14.9 ($Fe{-}SiMe_2$), −28.9 ($SiMe_2{-}Ge$)
^{13}C NMR	−2.23 ($GeMe_2Ph$), −1.88, 1.67 ($SiMe_2$), 6.42, 6.78 ($Fe{-}SiMe_2$), 11.6, 13.6 ($Fe{=}SiMe_2$), 36.4 (d, *HMPA*$\cdot SiMe_2$) 36.8 (d, HMPA) 79.7 (η^5-C_5H_5), 145.7, 134.3, 132.9, 127.6 (Ph), 219.5 (CO)
^{1}H NMR	0.59, 0.60, 0.65, 0.66, 0.69, 0.70, 0.71, 0.72 (SiMe/GeMe), 2.17 (*HMPA*$\cdot SiMe_2$, 4.38 (η^5-C_5H_5), 7.20 (d, $J = 3$ Hz), 7.62 (d, $J = 3$ Hz) (Ph)

[a] NMR spectra in C_6D_6, in units of ppm; IR spectra recorded in hexane.

$({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2SiMe_2Ph)$ and (η^5-C_5H_5)$(CO)Fe({=}SiMe_2{\cdot}HMPA)(SiMe_2SiMe_2GeMe_2Ph)$, respectively.

These results confirm that after CO loss these rearrangements involve an α-elimination. Although trace signals due to other species can be observed in the ^{1}H NMR, the ^{29}Si NMR spectra are very clean, as noted in Figure 2. Thus, under our reaction conditions, upon coordination of the silylene by HMPA, the complexes exhibit no significant further chemistry. This result contrasts with that reported by the Ogino group for the irradiation of $FpSiMe_2SiMe_2SiMe_2SiMe_2OMe$. Several intramolecularly base-stabilized complexes were obtained involving scrambling of the tetrasilyl chain.[3e] To date, the only stabilized silylene−Fe complex that exhibits further chemistry involving silylene elimination is the (arene)$Cr(CO)_3$ complex we recently reported, (η^5-C_5H_5)$Fe(CO)({=}SiMe_2)SiMe_2C_6H_5Cr(CO)_2$.[2g]

Intramolecular vs Intermolecular Rearrangement. Although the 1,3-migrations described in Scheme 1 have been shown to involve intramolecular mechanisms, the possibility for an intermolecular process cannot be totally ignored. For example, Liu and coworkers have shown that fluoro-substituted iron−silylene complexes dimerize in the absence of a coordinating ligand that can stabilize the species.[6] Furthermore, the Tilley group demonstrated intramolecular thiotolyl group transfer from silyl−ruthenium complexes to related silylene−ruthenium complexes.[7] Therefore, we performed a photochemical experiment to confirm that the rearrangements reported in this study are indeed intramolecular in nature, as our mechanism demands. Irradiation of a mixture of $Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph$ and $FpSiMe_2SiMe_2SiMe_2SiMe_3$ was followed by NMR spectroscopy. Only the two expected products were observed: there was no evidence for any crossover products, i.e., $Fp^*Si(SiMe_3)_3$ or $FpGe(SiMe_3)_2(SiMe_2Ph)$.

Catalytic Transformations. We have reported that rearrangements of the type illustrated above can be achieved catalytically, resulting in the isomerization of linear oligosilanes, $R_3Si(R_2Si)_nH$ (Scheme 4).[2f]

Irradiation of $M_3GeMe_2SiMe_2SiMe_2SiH$ was carried out in the presence of a catalytic amount of $FpSiMe_3$, in the hope of obtaining high yields of $(M_3Si)_3GeH$. When following such a reaction by ^{29}Si NMR spectroscopy, we did indeed observe the formation of $(Me_3Si)_3GeH$, but only as a low-concentration transient. The major product obtained in the reaction was $(Me_3Si)_3GeSiMe_2H$. The same compound was obtained in 70% yield by an independent preparative route (irradiation of $FpSiMe_2SiMe_3$ in the presence of $(M_3Si)_3GeH$).

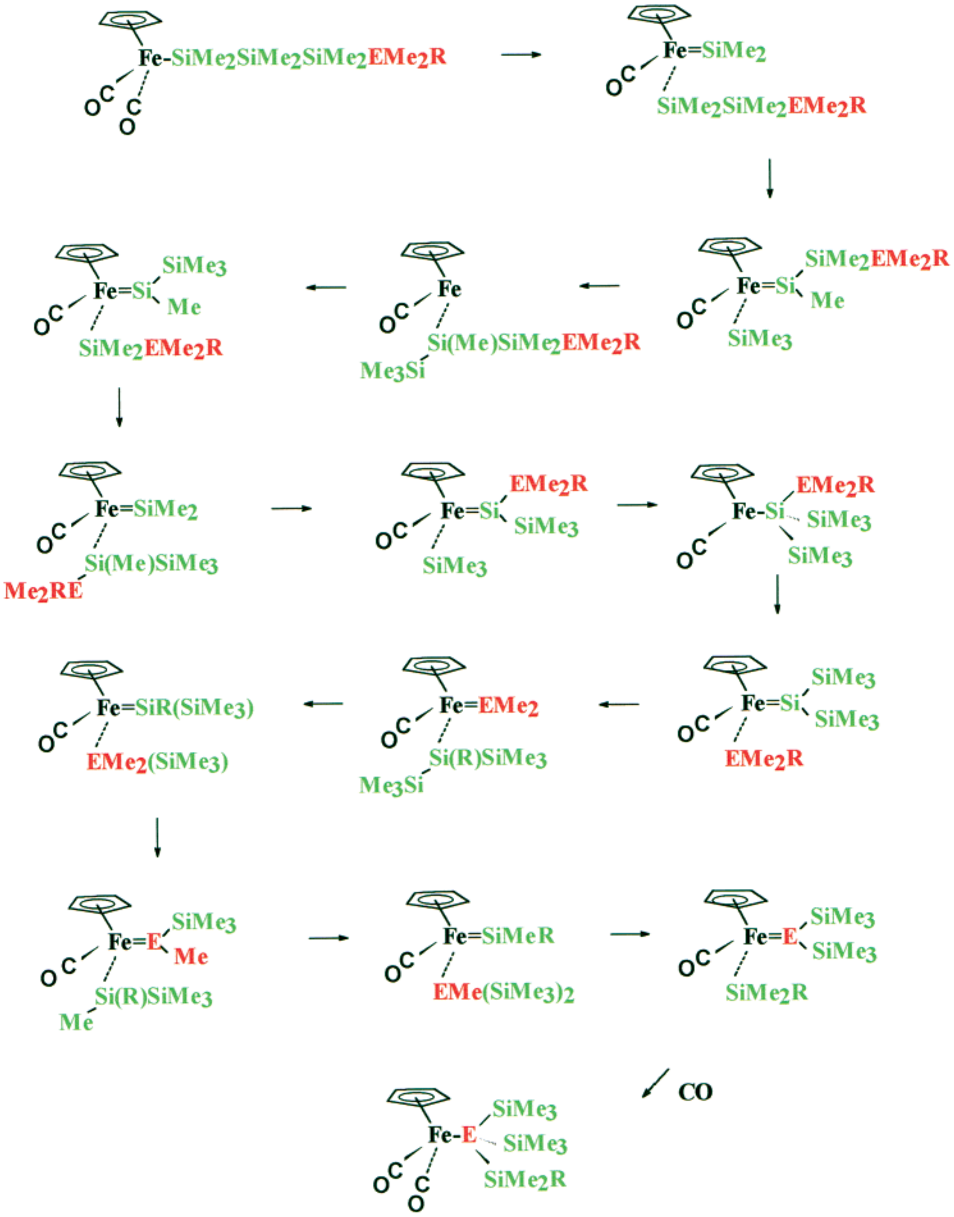
This result is very intriguing. On the basis of Scheme 4, the catalytic process involves a series of oxidative addition/reductive elimination steps to form (η^5-C_5H_5)$Fe(CO)SiMe_2SiMe_2SiMe_2GeMe_3$. This species will rearrange to (η^5-C_5H_5)$Fe(CO)Ge(SiMe_3)_3$ prior to a second oxidative addition/reductive elimination process to yield the rearranged product $(M_3Si)_3GeH$. It is apparent that this product undergoes a further reaction via the insertion of the elements of $SiMe_2$ into the Ge−H bond. The problem with this explanation is that

---

[6] Horng, K. M.; Wang, S. L.; Liu, C. S. *Organometallics* **1991**, *10*, 631.

[7] Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

Scheme 3



SiMe$_2$ elimination has not been observed in the photochemical treatment of either FpSiMe$_2$SiMe$_2$SiMe$_2$SiMe$_3$ or FpSiMe$_2$SiMe$_2$SiMe$_2$GeMe$_3$ and their related analogues containing at least four metalloid atoms in the chain bound to iron. In all cases only rearrangement reactions occurred. The result clearly implies that although no free silylene is liberated from the iron center during the isomerization reactions, in the presence of (M$_3$Si)$_3$GeH (or (M$_3$Si)$_3$SiH)[2d] the elements of this species are transferred to the germane (silane). This strongly suggests that the SiMe$_2$ is transferred via the addition of the germane (silane) to the iron silylene functionality prior to a reductive elimination process to yield the observed product (Scheme 5, path B).

It is also possible that a reverse addition could involve the transient formation of (η^5-C$_5$H$_5$)Fe(CO)SiMe$_2$H(Si(SiMe$_3$)$_3$)(SiMe$_2$SiMe$_2$SiMe$_3$) followed by reductive elimination of the product (path A). Whatever the precise mechanism, which is presently under investigation, this suggestion demands that we also form the transient species (η^5-C$_5$H$_5$)Fe(CO)SiMe$_2$SiMe$_2$SiMe$_3$, which would either pick up CO to form FpSiMe$_2$SiMe$_2$SiMe$_3$ or continue the silylene elimination chemistry to form FpSiMe$_2$SiMe$_3$ and FpSiMe$_3$. Close monitoring of the catalytic reaction did reveal the presence of each of these Fp complexes, i.e., Fp(SiMe$_2$)$_n$Me ($n = 1-3$), illustrating the internal consistency of the proposed chemistry. Since photochemical treatment of both FpSiMe$_2$SiMe$_3$ and FpSiMe$_2$SiMe$_2$SiMe$_3$ results in the elimination of SiMe$_2$, which can be trapped by (Me$_3$Si)$_3$GeH, the very high yield of (Me$_3$Si)$_3$GeSiMe$_2$H in the present study probably results from both processes, i.e., addition to the metal silylene intermediate and direct silylene insertion.

Experimental Section

All reactions were carried out under a nitrogen atmosphere using oxygen-free, dry solvents. Organosilicon compounds, PhSiMe$_2$SiMe$_2$SiMe$_2$Cl,[2e] PhSiMe$_2$SiMe$_2$SiMe$_2$SiMe$_2$Cl,[2e] Cl-

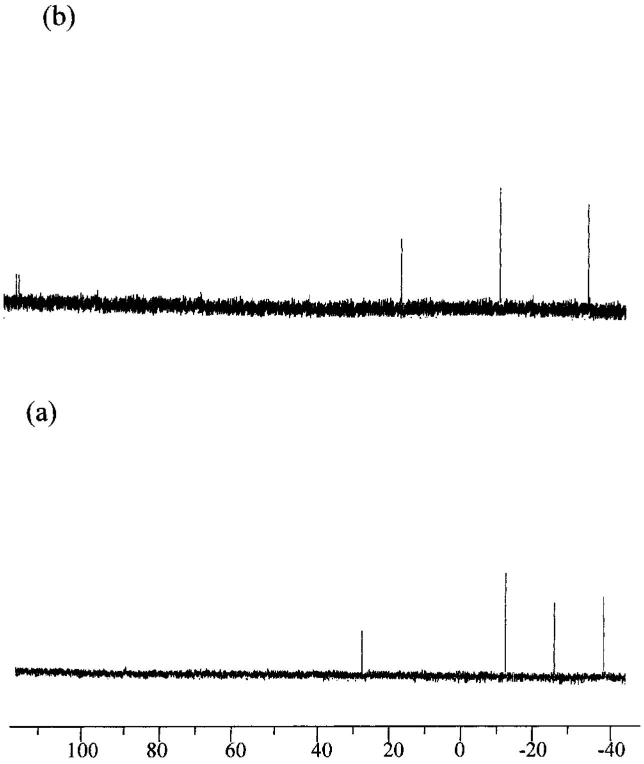
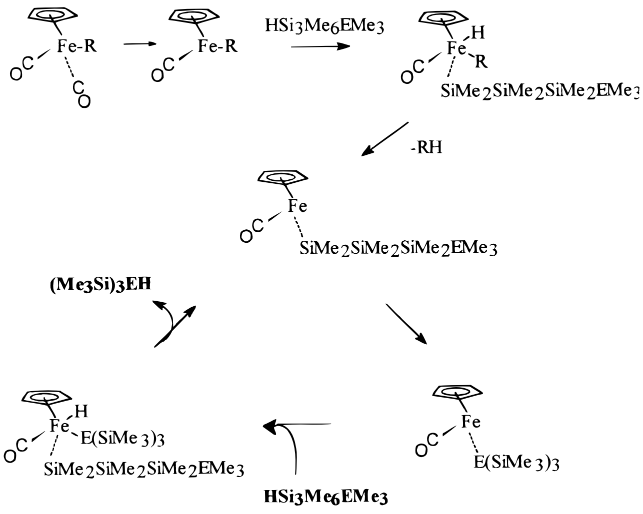


Figure 2. ^{29}Si NMR spectra of $FpSiMe_2SiMe_2SiMe_2SiMe_3$ (a) prior to photochemistry and (b) after 4 h irradiation.

Scheme 4

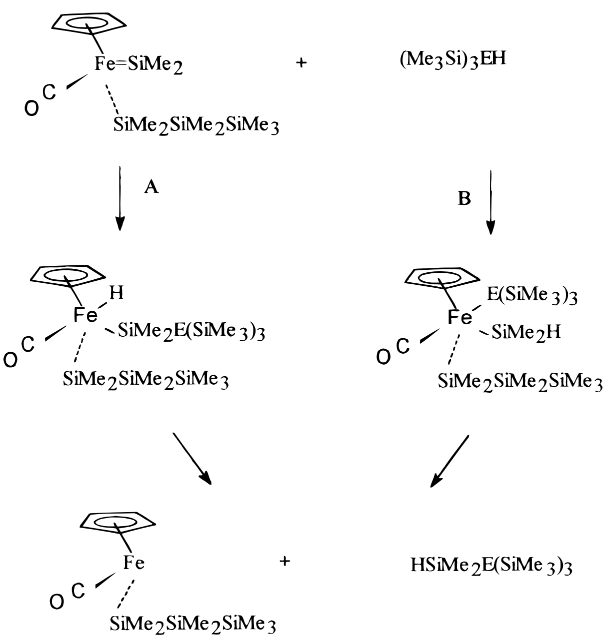


$SiMe_2SiMe_2SiMe_2Cl$,[8a] $[Me_3Ge]Li$,[8b] and $FpSiMe_2SiMe_2SiMe_2Cl$,[3d] were synthesized by known methods. $(Me_3Si)_3GeH$ was purchased from Gelest Inc.; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals, and reagent grade silica gel (60−200 mesh) was purchased from EM Science. NMR spectra were recorded on a Bruker 300 MHz spectrometer and IR spectra on a Perkin-Elmer 1600 FT IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Typical experimental procedures are outlined below.

Synthesis of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$. To a 50 mL THF solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]Na$ (prepared from 1.0 g (2.82 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) was added 1.93 g (5.6 mmol) of $PhSiMe_2SiMe_2SiMe_2SiMe_2Cl$ in 10 mL of THF at 0 °C. The solution was stirred at this temperature for 1 h and then warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue extracted with 60 mL of hexane. This solution was filtered and the filtrate concentrated to 5.0 mL and placed upon a 2.5 × 20 cm silica gel column. The yellow band developed with hexane was collected and after removal of the solvent yielded 1.38 g of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ (51%) as a yellow solid (mp 43 °C).

Scheme 5



Synthesis of $Fp^*SiMe_2SiMe_2SiMe_2Cl$. Using the same procedure as above with a 60 mL THF solution of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]Na$ (prepared from 1.44 g (2.90 mmol) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$) and 1.43 g (5.8 mmol) of $ClSiMe_2SiMe_2SiMe_2Cl$, $Fp^*SiMe_2SiMe_2SiMe_2Cl$ (1.5 g, 3.28 mmol, 56%) was obtained as an orange-red waxy solid.

Synthesis of $Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph$. A 30 mL solution of $[PhMe_2Ge]Li$ in THF (prepared from 0.570 g, 2.6 mmol, of $PhGeMe_2Cl$) was added dropwise to 30 mL of a stirred THF solution of 1.20 g (2.60 mmol) of $Fp^*SiMe_2SiMe_2SiMe_2Cl$ at −25 °C. The reaction mixture was stirred at low temperature for 1 h, and then the temperature was allowed to rise to room temperature. The reaction mixture was stirred at room temperature for 16 h. Subsequently the solvent was removed in vacuo and the residue was extracted with 60 mL of hexane, filtered, and concentrated to 5.0 mL prior to placement on a 2.5 × 20 cm silica gel column, which was developed with hexane. The orange band was collected and after normal workup gave 0.60 g of $Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph$ (0.10 mmol, 38% yield) as a waxy orange solid.

Synthesis of $PhSiMe_2SiMe_2SiMe_2GeMe_3$. $[Me_3Ge]Li$, obtained from 3.5 g (22.8 mmol) of Me_3GeCl in 20 mL of dry ether, was added dropwise to 6.62 g (22.8 mmol) of $PhSiMe_2SiMe_2SiMe_2Cl$ in 20 mL of ether at −78 °C. The solution was warmed to room temperature slowly and stirred overnight and then filtered to remove lithium chloride. After acidic workup (NH_4Cl) the organic layer was dried over magnesium sulfate. The solvent was removed, and the colorless liquid residue was distilled under vacuum. The fraction distilling at 145−150 °C/0.05 mmHg was collected to yield 2.4 g (6.50 mmol, 28%) of $PhSiMe_2SiMe_2SiMe_2GeMe_3$ as a colorless liquid.

Synthesis of $HSiMe_2SiMe_2SiMe_2GeMe_3$. Triflic acid (0.82 g, 5.4 mmol) was added dropwise through a dropping funnel to 2.0 g (5.4 mmol) of neat $PhSiMe_2SiMe_2SiMe_2GeMe_3$ in a 100 mL three-necked flask at 0 °C. The reaction mixture was brought to room temperature slowly and stirred for 2 h. The

---

[8] (a) Oakley, R. T.; Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1978**, *157*, 389. (b) Wickham, G.; Young, D.; Kitching, W. F. *J. Org. Chem.* **1982**, *47*, 4884.

volatiles were removed in vacuo, and a colorless liquid residue was obtained. The latter was dissolved in 10 mL of dry ether and this solution then added slowly to 0.20 g of $LiAlH_4$ in 20 mL of dry ether at 0 °C contained in a 100 mL three-necked flask. The solution was brought to room temperature slowly and stirred overnight. The reaction mixture was immersed in an ice bath, and 20 mL of 10% aqueous ammonium chloride solution was added dropwise. The solution was filtered to remove the salts, and the filtrate was extracted with three portions of 10% ammonium chloride. The organic layer was separated and dried over magnesium sulfate. Filtration and removal of the solvent in vacuo followed by further distillation (120−122 °C/20 mm of Hg) yielded $HSiMe_2SiMe_2SiMe_2GeMe_3$ as a colorless liquid (0.70 g, 2.38 mmol).

Photolysis of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$. A solution of the title compound (0.15 g, 0.31 mmol) in 1.0 mL of degassed C_6D_6 was sealed in a Pyrex NMR tube. The NMR tube was placed 10 cm from a 450 W medium-pressure mercury lamp and irradiated. The progress of the photochemical reaction was monitored by ^{29}Si NMR spectroscopy. The starting material disappeared completely after 1.5 h of irradiation. The solution was placed on a 2.5 × 10 cm silica gel column, and a yellow band was eluted with hexane. Upon removal of solvent in vacuo $FpSi(SiMe_3)_2SiMe_2Ph$ (0.13 g, 87%) was obtained as a yellow crystalline solid.

Photolysis of $Fp^*SiMe_2SiMe_2SiMe_2GeMe_2Ph$. The title compound (0.10 g) in 1.0 mL of degassed C_6D_6 was placed in a Pyrex NMR tube. The sealed NMR tube was placed 8 cm from the 450 W medium-pressure mercury lamp and irradiated. The reaction was followed by ^{29}Si NMR spectroscopy. After 3.5 h the starting material had been consumed; i.e., the resonances at 20.6, −32.7, and −33.0 ppm had disappeared and new signals at −2.0 and −5.4 ppm had appeared. The solution was placed on a 2.5 × 10 cm silica gel column, and a yellow band was eluted with hexane. Upon removal of solvent in vacuo $Fp^*Ge(SiMe_3)_2SiMe_2Ph$ (0.08 g, 80%) was obtained as an orange oil, which became solid when placed in the freezer.

Photolysis of $HSiMe_2SiMe_2SiMe_2GeMe_3$ in the Presence of a Catalytic Amount of $FpSiMe_3$. A mixture of $HSiMe_2SiMe_2SiMe_2GeMe_3$ (0.120 g, 0.41 mmol) and a 10% equivalent of $FpSiMe_3$ in 1 mL of C_6D_6 was irradiated in a sealed Pyrex NMR tube. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 53 h ^{29}Si NMR analysis showed the presence of signals at −4.61 and −29.5 ppm due to the formation of $(Me_3Si)_3GeSiMe_2H$ and a signal at −16.1 ppm due to Me_3SiH. Some starting material was also present.

Photolysis of $(Me_3Si)_3GeH + HSiMe_2SiMe_3$ in the Presence of a Catalytic Amount of $FpSiMe_3$. A 5 mm Pyrex NMR tube was charged with 0.3 g (2.24 mmol) of $HSiMe_2SiMe_3$, 0.3 g (1.02 mmol) of $(Me_3Si)_3GeH$, and 10 mol % of $FpSiMe_3$ in 1 mL of C_6D_6 and sealed under vacuum. Photolysis, using a Hanovia 450 W lamp at a distance of 6 cm, was monitored by ^{29}Si NMR spectroscopy. After 62 h the $HSiMe_2SiMe_3$ had been consumed and resonances associated with the insertion product $(Me_3Si)_3GeSiMe_2H$ were observed (−4.6 and −29.5 ppm) together with that due to Me_3SiH (−16.3 ppm). The contents of the tube were passed through a silica gel column (1 × 2 cm) using hexane as eluant, and the resulting solution was evaporated to dryness. The resulting white solid was recrystallized from dry ethanol to yield 0.25 g of pure $(Me_3Si)_3GeSiMe_2H$ (0.71 mmol, 70% yield).

Photolysis of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ in the Presence of HMPA. A 5 mm NMR tube was charged with 0.08 g (0.164 mmol) of $FpSiMe_2SiMe_2SiMe_2SiMe_2Ph$ and 0.10 g (0.56 mmol) of HMPA in 1.0 mL of degassed C_6D_6 and sealed under vacuum. The sealed NMR tube was irradiated with a 450 W medium-pressure mercury lamp, and the reaction was monitored by ^{29}Si and ^1H NMR spectroscopy. After 3.0 h the starting material had disappeared, and the ^{29}Si NMR spectrum showed a doublet at 115.3 ppm and singlets at 14.7, −17.6, and −39.1 ppm due to the formation of $(\eta^5\text{-}C_5H_5)(CO)Fe({=}SiMe_2{\cdot}HMPA)SiMe_2SiMe_2SiMe_2Ph$. Continued irradiation had no effect upon the spectra obtained.

Photolysis of $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$ in the Presence of HMPA. A mixture of 0.10 g (0.19 mmol) of $FpSiMe_2SiMe_2SiMe_2GeMe_2Ph$ and 0.13 g (0.66 mmol) of HMPA in 1.0 mL of C_6D_6 in a 5 mm sealed Pyrex NMR tube was irradiated for 2.0 h, and the reaction was monitored by ^{29}Si NMR spectroscopy. During this time the starting compound disappeared. The ^{29}Si NMR spectrum at this time showed a doublet at 115.6 ppm due to the silylene ligand coordinated by a HMPA molecule and singlets at 14.9 and −32.6 ppm. Trace amounts of $FpSiMe_2Ph$ (36.0 ppm) were also observed.

Acknowledgment. This research was supported by the NIH-MARC program and the R. A. Welch Foundation, Houston, TX. HRMS measurements were obtained from the Nebraska Center for Mass Spectrometry.

OM990897C