## Syntheses and Photochemically Induced **Rearrangements of Tetrasilyl- and Trisilylgermyl** Complexes of Iron: $(\eta^5 - C_5 R_5) Fe(CO)_2 (SiMe_2)_3 EMe_2 Ph$ (R = H. Me: $\mathbf{E} = \mathbf{Ge}$ . Si)

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Oligosilyl and oligosilylgermyl complexes  $(\eta^5-C_5R_5)Fe(CO)_2(SiMe_2)_3EMe_2Ph$  (R = H (1), Me (2); E = Ge (a), Si (b)) have been synthesized, characterized, and photolyzed. All complexes isomerized cleanly to  $(\eta^5-C_5R_5)Fe(CO)_2E(SiMe_3)_2(SiMe_2Ph)$ . Photolysis of a mixture of  $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(SiMe_{2})_{3}GeMe_{2}Ph$  (2a) and  $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}(SiMe_{2})_{3}SiMe_{3}$  (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  $(\eta^5-C_5R_5)Fe(CO)$  (=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>-SiMe<sub>2</sub>EMe<sub>2</sub>Ph), indicating that silvlene intermediates are key to the rearrangements. Attempts to use this new chemistry to perform the catalytic isomerization Me<sub>3</sub>GeSiMe<sub>2</sub>- $SiMe_2SiMe_2H \rightarrow (Me_3Si)_3GeH$  resulted in high yields of  $(Me_3Si)_3GeSiMe_2H$ . This product indicates the ability of (Me<sub>3</sub>Si)<sub>3</sub>GeH 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 silvlenes (Scheme 1).<sup>1–3</sup> Such intermediates can eliminate silvlenes or undergo rearrangement reactions involving 1,3-alkyl, -aryl, and -silyl migrations. The silylene can be trapped intramolecularly or intermolecularly.<sup>2g,3b,e,5</sup> The chemistry appears to be quite general, and related chemistry is observed with tungsten complexes.<sup>3e</sup> Silylgermyl or germylsilyl Fe analogues were studied in which either the germylene or silvlene 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

We have shown that UV irradiation of  $(\eta^5-C_5H_5)$ Fe-(CO)<sub>2</sub>-SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> resulted in its high-yield

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# Scheme 1 . Fe-SiMe2SiMe2R SiMe<sub>2</sub> =SiMe<sub>2</sub> SiMe<sub>2</sub>R co SiMe 2R со SiMeR SiMeRSiMe 3 SiMea Scheme 2 SiMe2GeMe3 SiMe<sub>2</sub> GeMea



without any silylene elimination.<sup>2d</sup> To understand more about the mechanistic aspects of these rearrangement reactions, we have synthesized the tetrasilane FpSiMe<sub>2</sub>-SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph and the mixed oligosilyl-germyl complexes FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph and Fp\*SiMe<sub>2</sub>-

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SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph (Fp<sup>\*</sup> = ( $\eta^{5}$ -Me<sub>5</sub>C<sub>5</sub>)Fe(CO)<sub>2</sub>). 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).

$$\label{eq:constraint} \begin{split} \mbox{[Fp]Na} + \mbox{Cl(SiMe}_2)_4 \mbox{Ph} \rightarrow \\ \mbox{FpSiMe}_2 \mbox{SiMe}_2 \mbox{SiMe}_2 \mbox{SiMe}_2 \mbox{Ph} + \mbox{NaCl} \ \ (1) \end{split}$$

$$\begin{array}{l} Fp(SiMe_2)_3Cl + [PhMe_2Ge]Li \rightarrow \\ FpSiMe_2SiMe_2SiMe_2GeMe_2Ph + LiCl (3) \end{array}$$

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.

<sup>29</sup>Si NMR spectroscopy is particularly helpful for characterization of the new complexes. For example, the tetrasilyliron complex FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph 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.<sup>1</sup> The low-field signal at 22.9 ppm is due to the silicon atom directly attached to the iron and exhibits an  $\sim$ 40 ppm downfield shift from the permethylated tetrasilane Me<sub>3</sub>SiSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>. The signal at -17.6 ppm is assigned to the terminal -SiMe<sub>2</sub>Ph, the signal at -42.9 is due to  $-SiMe_2SiMe_2Ph$ , and the -32.5 ppm resonance is due to a silicon in the  $\beta$ -position. The latter resonance exhibits an  $\sim 12$  ppm downfield shift compared to the permethylated tetrasilane. In the related germanium complex FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>-Ph, the silicon signal due to -SiMe<sub>2</sub>GeMe<sub>2</sub>Ph 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 silvl analogues.<sup>4</sup>

**Photochemistry.** The oligosilyl and oligosilylgermyl complexes are photochemically labile. The tetrasilyliron complex FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph undergoes a photochemical rearrangement, without silylene elimination, to produce FpSi(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph) (eq 4).

$$FpSiMe_{2}SiMe_{2}SiMe_{2}SiMe_{2}Ph \rightarrow FpSi(SiMe_{3})_{2}(SiMe_{2}Ph)$$
(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.,  $FpSiMe_2SiMe_2SiMe_3 \rightarrow FpSi(SiMe_3)_3$ .<sup>2d</sup>

The photochemistry of the oligosilylgermyl iron complexes is unique. The two complexes FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph and Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph each photochemically rearranged cleanly to yield a single product containing an Fe-Ge bond, i.e., FpGe(SiMe<sub>3</sub>)<sub>2</sub>-(SiMe<sub>2</sub>Ph) and Fp\*Ge(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>Ph. 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.<sup>5</sup> 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<sub>2</sub>SiMe<sub>2</sub>- $SiMe_2ER_3$  (ER<sub>3</sub> = SiMe<sub>3</sub>, SiMe<sub>2</sub>Ph, GeMe<sub>2</sub>Ph) 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>, the <sup>29</sup>Si NMR spectrum of the silvlene complex exhibited a doublet at 114.9 ppm due to coupling with the <sup>31</sup>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 silvlene coordinated to an HMPA molecule, while the other <sup>29</sup>Si signals are comparable to those of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> (i.e., 19.0, -14.7, and -37.9 ppm). The <sup>1</sup>H 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<sub>2</sub> ligand. The signals at 0.58, 0.38, 0.42, and 0.29 are assigned to FeSiMe2, FeSiMe<sub>2</sub>SiMe<sub>2</sub>, and SiMe<sub>3</sub>. The <sup>13</sup>C NMR spectrum shows that all the methyl groups attached to the  $\alpha$ - and  $\beta$ -silicon atoms are nonequivalent. These NMR data support the formula  $(\eta^5 - C_5 H_5)(CO)Fe(=SiMe_2 \cdot HMPA)$ -(SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>) and are compatible with the data reported by the Ogino group. Irradiation of FpSiMe<sub>2</sub>-SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph and FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph in the presence of HMPA provided similar results, with the formation of single products,  $(\eta^5-C_5H_5)(CO)Fe$ -

Table 1. Spectroscopic and Analytical Data for New Complexes<sup>a</sup>

FpSiMe2SiMe2SiMe2SiMe2Ph yield, % 50 mp, °C 43 anal. found (calcd) C, 51.4 (51.8); H, 6.77 (7.04) 22.9 (FpSiMe<sub>2</sub>), -17.6(SiMe<sub>2</sub>Ph), -32.5 (SiMe<sub>2</sub>), -42.9 (SiMe<sub>2</sub>) -4.68, -2.84, -2.44, 5.56 (SiMe<sub>2</sub>), 83.2( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 128.2, 128.9, 134.3, 142.0 (Ph) <sup>29</sup>Si NMR <sup>13</sup>C NMR <sup>1</sup>H NMR 0.52, 0.76 (SiMe<sub>2</sub>), 4.15 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 7.26, 7.29, 7.70 (Ph) v(CO) 1996.6, 1945.8 IR (hexane), cm<sup>-1</sup> FpSi(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph) yield, % 80 mp, °C 45 anal. found (calcd) C, 51.4 (51.8); H, 6.97 (7.04) <sup>29</sup>Si NMR -6.06 (SiMe<sub>3</sub>), 9.16 (SiMe<sub>2</sub>Ph), -82.1 (Fp-Si) <sup>13</sup>C NMR 2.13 (SiMe<sub>2</sub>Ph), 4.14 (SiMe<sub>3</sub>), 83.2 ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 128.5, 128 9, 134.7, 143.1 (Ph) <sup>1</sup>H NMR 0.50 (SiMe<sub>3</sub>), 0.75 (SiMe<sub>2</sub>), 4.14 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 7.26, 7.28, 7.70 (Ph) IR (hexane), cm<sup>-1</sup> v(CO) 1996.6, 1947.9 FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl yield, % 50 122-124/0.02 mmHg Ďp, ℃ anal. found (calcd) C, 40.7 (40.4); H, 6.22 (5.99) <sup>29</sup>Si NMR 27.7 (SiMe<sub>2</sub>Cl), 20.2 (FpSiMe<sub>2</sub>), -35.6 (SiMe<sub>2</sub>) -4.75, 3.37, 4.85 (SiMe<sub>2</sub>),  $83.2 (\eta^{5}-C_{5}H_{5}), 215.6$  (CO) <sup>13</sup>C NMR <sup>1</sup>H NMR 0.30, 0.51, 0.58 (Si-Me), 4.15 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph yield, % 50 (wax) anal. found (calcd) C, 46.6 (47.5); H, 6.75 (6.45) <sup>29</sup>Si NMR 22.6 (Fp-Si), -32.3 (SiMe<sub>2</sub>), -33.6 (SiMe<sub>2</sub>-Ge) <sup>13</sup>C NMR -4.16 (GeMe<sub>2</sub>), -3.18, -3.00, 5.30 (SiMe<sub>2</sub>), 83.1 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 128.3, 128.5, 133.9, 142.5 (Ph), 215.8 (CO) <sup>1</sup>H NMR 0.27 (GeMe<sub>2</sub>), 0.37, 0.59 (SiMe<sub>2</sub>), 4.17 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 7.19, 7.28, 7.52 IR (hexane), cm<sup>-1</sup> v(CO) 1997.1, 1946.1 FpGe(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph) vield, % 82 (wax) C, 47.3 (47.5); H, 6.63 (6.45) anal. found (calcd) 29Si NMR 0.69 (SiMe<sub>3</sub>), -4.81 (SiMe<sub>2</sub>Ph) <sup>13</sup>C NMR 2.27 (SiMe<sub>2</sub>Ph), 4.24 (SiMe<sub>3</sub>), 82.4 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 128.4, 134.3, 143.4 (Ph), 215.7 (CO) <sup>1</sup>H NMR 0.44 (SiMe<sub>3</sub>), 0.69 (SiMe<sub>2</sub>), 4.10 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 7.18, 7.52, 7.64 (Ph) IR (hexane),  $cm^{-1}$ v(CO) 1991.9, 1944.4 Fp\*SiMe2SiMe2SiMe2Cl 56 (oil) yield, % anal. found (calcd) C, 46.7 (47.3); H, 7.54 (7.28) <sup>29</sup> Si NMR 29.17 (SiMe<sub>2</sub>Cl), 18.50 (Fp\*-Si), -35.87 (SiMe<sub>2</sub>) <sup>13</sup>C NMR -4.12, 3.88, 4.26 (SiMe<sub>2</sub>), 10.1 (CH<sub>3</sub>), 95.2 ( $\eta^{5}$ -Me<sub>5</sub>C<sub>5</sub>), 218.0(CO) 0.61, 0.70, 0.75 (SiMe<sub>2</sub>), 1.58 (CH<sub>3</sub>) <sup>1</sup>H NMR IR (hexane), cm<sup>-1</sup> v(CO) 1980.0, 1928.7 Fp\*SiMe2SiMe2SiMe2GeMe2Ph yield, % 38 72 - 73mp, °C anal. found (calcd) C, 51.6 (51.9); H, 7.69 (7.37) 20.6 (Fp-Si), -32.7 (SiMe<sub>2</sub>), -33.0 (SiMe<sub>2</sub>Ge) <sup>29</sup>Si NMR 13C NMR -3.94 (GeMe<sub>2</sub>), -2.83 (SiMe<sub>2</sub>), 4.37 (Fp-Si), 94.8 ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 127.8, 128.2, 133.9, 143.3 (Ph), 218.0 (CO) <sup>1</sup>H NMR 0.52, 0.55, 0.70, 0.73, 1.60 (CH<sub>3</sub>), 7.27, 7.35, 7.62 (Ph) IR (hexane), cm<sup>-1</sup> v(CO) 1978.8, 1927.6 Fp\*Ge(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph) yield, % 80 (wax) anal. found (calcd) C, 51.9 (51.9); H, 8.01 (7.37) <sup>29</sup>Si NMR -1.98 (SiMe<sub>3</sub>), -5.37 (SiMe<sub>2</sub>Ph) 13C NMR 4.23 (SiMe<sub>2</sub>), 5.84 (SiMe<sub>3</sub>), 10.65 (CH<sub>3</sub>), 94.87 (η<sup>5</sup>-Me<sub>5</sub>C<sub>5</sub>), 128.34, 128.51, 135.13, 143.2 (Ph), 219.83 (CO) <sup>1</sup>H NMR 0.64 (SiMe<sub>3</sub>), 0.86 (SiMe<sub>2</sub>), 1.52 (CH<sub>3</sub>), 7.26, 7.82, 7.86 (Ph) IR (hexane), cm<sup>-1</sup> v(CO) 1977.6, 1929.1 PhSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> vield. % 28 bp, °C 145-155/0.05 mmHg anal. found (calcd) C, 51.0 (48.8); H, 8.61 (8.74) <sup>29</sup>Si NMR -17.8 (Ph-Si), -35.8 (SiMe2-GeMe3), -44.0 (SiMe2) 13C NMR -5.08 (SiMe<sub>2</sub>), -4.64 (SiMe<sub>2</sub>), -2.36 (SiMe<sub>2</sub>), -1.52 (GeMe<sub>3</sub>), 128.4, 128.99, 134.3, 140.3 (Ph) <sup>1</sup>H NMR 0.052, 0.085, 0.35 (SiMe2), 0.12 (GeMe3), 7.40, 7.29, 7.28 (Ph)

**Table 1 (Continued)** 

#### HSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> yield, % 44 bp, °C 120-122/0.05 mmHg anal. found (calcd) C, 37.3 (36.9); H, 9.58 (9.62) <sup>29</sup>Si NMR -36.3 (SiMe2-GeMe3), -36.8 (SiMe2H), -44.0 (SiMe2) <sup>13</sup>C NMR -5.73 (SiMe<sub>2</sub>), -5.27 (SiMe<sub>2</sub>), -1.96 (GeMe<sub>3</sub>) <sup>1</sup>H NMR 0.19 (SiMe2H, d),0.20, 0.23 (SiMe2, s), 0.30(GeMe3), 4.05 (SiMe2H, m) (Me<sub>3</sub>Si)<sub>3</sub>GeSiMe<sub>2</sub>H mp, °C 132 - 134 $C_{11}H_{31}Si_4^{74}Ge \ 352.0946 \ (352.0949)$ found (calcd) HRMS, m/z <sup>29</sup>Si NMR -4.61 (Me<sub>3</sub>Si), -29.5 (SiMe<sub>2</sub>H) <sup>13</sup>C NMR -1.24 (SiMe<sub>2</sub>), 3.28 (SiMe<sub>3</sub>) <sup>1</sup>H NMR 4.44 (sept. J = 28 Hz, SiH), 0.358 (d, J = 28 Hz, SiMe<sub>2</sub>), 0.304 (SiMe<sub>3</sub>) IR (hexane), cm<sup>-1</sup> 2090.9 Cp(CO)Fe(=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub>) <sup>29</sup>Si NMR 114.9 (d, J<sub>SiP</sub> = 28.3 Hz, SiMe<sub>2</sub>·HMPA), 13.6 (Fe-SiMe<sub>2</sub>), -15.4 (SiMe<sub>3</sub>), -39.0 (SiMe<sub>2</sub>) <sup>1</sup>H NMR 0.29 (SiMe<sub>3</sub>), 0.38, 0.42 (Fe-SiMe<sub>2</sub>), 0.58 (2 SiMe<sub>2</sub>), 0.63, 0.66 (Fe=SiMe<sub>2</sub>), 2.25 (d, HMPA·SiMe<sub>2</sub>), 2.42 (d, HMPA), 4.35 ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) <sup>13</sup>C NMR -3.20, -3.16 (SiMe<sub>2</sub>), -0.68 (SiMe<sub>3</sub>), 6.02, 6.54 (Fe-SiMe<sub>2</sub>), 11.1, 13.2 (Fe=SiMe<sub>2</sub>), 36.6 (d, HMPA·SiMe<sub>2</sub>) 37.0 (d, HMPA) 79.1 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 219.1 (CO) Cp(CO)Fe(=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph) <sup>29</sup>Si NMR 115.3 (d, J<sub>SiP</sub> = 28.4 Hz, SiMe<sub>2</sub>·HMPA), 14.7 (Fe-SiMe<sub>2</sub>), -17.6 (SiMe<sub>2</sub>Ph), -39.1 (SiMe<sub>2</sub>) 2.35, 2.29 (SiMe<sub>2</sub>), -1.74, -1.69 (SiMe<sub>2</sub>), 7.13, 6.71 (Fe-SiMe<sub>2</sub>), 13.8, 11.7 (Fe=SiMe<sub>2</sub>), <sup>13</sup>C NMR 37.0 (d, HMPA), 36.7 (HMPA·SiMe<sub>2</sub>), 79.6 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 219.7 (CO) <sup>1</sup>H NMR 0.35, 0.41, 0.53, 0.55, 0.57, 0.60, 0.63 (SiMe), 2.21 (d, HMPA·SiMe2), 2.42 (d, HMPA), 4.32 ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.40 (d, J = 3 Hz), 7.19 (d, J = 3 Hz) (Ph) Cp(CO)Fe(=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph) <sup>29</sup>Si NMR 115.6 (d, $\hat{J}_{SiP} = 28.4$ Hz, SiMe<sub>2</sub>·HMPA), 14.9 (Fe–SiMe<sub>2</sub>), -28.9 (SiMe<sub>2</sub>–Ge) -2.23 (GeMe<sub>2</sub>Ph), -1.88, 1.67 (SiMe<sub>2</sub>), 6.42, 6.78 (Fe–SiMe<sub>2</sub>), 11.6, 13.6 (Fe–SiMe<sub>2</sub>), <sup>13</sup>C NMR 36.4 (d, *HMPA*·SiMe<sub>2</sub>) 36.8 (d, HMPA) 79.7 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 145.7, 134.3, 132.9, 127.6 (Ph), 219.5 (CO) <sup>1</sup>H NMR 0.59, 0.60, 0.65, 0.66, 0.69, 0.70, 0.71, 0.72 (SiMe/GeMe), 2.17 (*HMPA* SiMe<sub>2</sub>, 4.38 ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.20 (d, J = 3 Hz), 7.62 (d, J = 3 Hz) (Ph)

<sup>a</sup> NMR spectra in C<sub>6</sub>D<sub>6</sub>, in units of ppm; IR spectra recorded in hexane.

(=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph) and ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)-(CO)Fe(=SiMe<sub>2</sub>·HMPA)(SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph), respectively.

These results confirm that after CO loss these rearrangements involve an  $\alpha$ -elimination. Although trace signals due to other species can be observed in the <sup>1</sup>H NMR, the <sup>29</sup>Si NMR spectra are very clean, as noted in Figure 2. Thus, under our reaction conditions, upon coordination of the silvlene by HMPA, the complexes exhibit no significant further chemistry. This result contrasts with that reported by the Ogino group for the irradiation of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>OMe. Several intramolecularly base-stabilized complexes were obtained involving scrambling of the tetrasilyl chain.<sup>3e</sup> To date, the only stabilized silvlene-Fe complex that exhibits further chemistry involving silvlene elimination is the (arene)Cr(CO)<sub>3</sub> complex we recently reported, ( $\eta^{5}$ - $C_5H_5$ )Fe(CO)(=SiMe<sub>2</sub>)SiMe<sub>2</sub>C<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>2</sub>.<sup>2g</sup>

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.<sup>6</sup> Furthermore, the Tilley group demonstrated intramolecular thiotolyl group transfer from silyl-ruthenium complexes to related silvlene-ruthenium complexes.<sup>7</sup> 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<sub>2</sub>-SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph and FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> 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<sub>3</sub>)<sub>3</sub> or FpGe-(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>Ph).

Catalytic Transformations. We have reported that rearrangements of the type illustrated above can be achieved catalytically, resulting in the isomerization of linear oligosilanes, R<sub>3</sub>Si(R<sub>2</sub>Si)<sub>n</sub>H (Scheme 4).<sup>2f</sup>

Irradiation of M<sub>3</sub>GeMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiH was carried out in the presence of a catalytic amount of FpSiMe<sub>3</sub>, in the hope of obtaining high yields of (M<sub>3</sub>Si)<sub>3</sub>GeH. When following such a reaction by <sup>29</sup>Si NMR spectroscopy, we did indeed observe the formation of (Me<sub>3</sub>Si)<sub>3</sub>-GeH, but only as a low-concentration transient. The major product obtained in the reaction was (Me<sub>3</sub>Si)<sub>3</sub>-GeSiMe<sub>2</sub>H. The same compound was obtained in 70% yield by an independent preparative route (irradiation of FpSiMe<sub>2</sub>SiMe<sub>3</sub> in the presence of (M<sub>3</sub>Si)<sub>3</sub>GeH).

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  $(\eta^5-C_5H_5)$ -Fe(CO)SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub>. This species will rearrange to  $(\eta^5-C_5H_5)Fe(CO)Ge(SiMe_3)_3$  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 SiMe2 into the Ge-H bond. The problem with this explanation is that

<sup>(6)</sup> Horng, K. M.; Wang, S. L.; Liu, C. S. Organometallics 1991, 10, 631.



SiMe<sub>2</sub> elimination has not been observed in the photochemical treatment of either FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> 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<sub>3</sub>Si)<sub>3</sub>GeH (or (M<sub>3</sub>Si)<sub>3</sub>SiH)<sup>2d</sup> the elements of this species are transferred to the germane (silane). This strongly suggests that the SiMe<sub>2</sub> 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  $(\eta^5-C_5H_5)Fe(CO)SiMe_2H(Si-(SiMe_3)_3)(SiMe_2SiMe_2SiMe_3)$  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  $(\eta^5-C_5H_5)Fe(CO)SiMe_2SiMe_3SiMe_3$ , which would either pick up CO to form FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> or continue the silylene elimination chemistry to form FpSiMe<sub>2</sub>SiMe<sub>3</sub> and FpSiMe<sub>3</sub>. Close monitoring of the catalytic reaction did reveal the presence of each of these Fp complexes, i.e., Fp(SiMe<sub>2</sub>)<sub>n</sub>Me (n = 1-3), illustrating the internal consistency of the proposed chemistry. Since photochemical treatment of both FpSiMe<sub>2</sub>SiMe<sub>3</sub> and FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> results in the elimination of SiMe<sub>2</sub>, which can be trapped by (Me<sub>3</sub>Si)<sub>3</sub>GeH, the very high yield of (Me<sub>3</sub>Si)<sub>3</sub>GeSiMe<sub>2</sub>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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl,<sup>2e</sup> PhSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl,<sup>2e</sup> Cl-





**Figure 2.** <sup>29</sup>Si NMR spectra of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>3</sub> (a) prior to photochemistry and (b) after 4 h irradiation.



SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl,<sup>8a</sup> [Me<sub>3</sub>Ge]Li,<sup>8b</sup> and FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl,<sup>3d</sup> were synthesized by known methods. (Me<sub>3</sub>Si)<sub>3</sub>GeH was purchased from Gelest Inc.; [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph.** To a 50 mL THF solution of  $[(\eta^5-C_5H_5)Fe(CO)_2]Na$  (prepared from 1.0 g (2.82 mmol) of  $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ ) was added 1.93 g (5.6 mmol) of PhSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl 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  $2.5 \times 20$  cm silica gel column. The yellow band developed with hexane was collected and after removal of the solvent yielded 1.38 g of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph (51%) as a yellow solid (mp 43 °C).

**Synthesis of Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl.** Using the same procedure as above with a 60 mL THF solution of  $[(\eta^5-C_5Me_5)-Fe(CO)_2]$ Na (prepared from 1.44 g (2.90 mmol) of  $[(\eta^5-C_5Me_5)-Fe(CO)_2]_2$ ) and 1.43 g (5.8 mmol) of ClSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl, Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl (1.5 g, 3.28 mmol, 56%) was obtained as an orange-red waxy solid.

**Synthesis of Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph.** A 30 mL solution of [PhMe<sub>2</sub>Ge]Li in THF (prepared from 0.570 g, 2.6 mmol, of PhGeMe<sub>2</sub>Cl) was added dropwise to 30 mL of a stirred THF solution of 1.20 g (2.60 mmol) of Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph (0.10 mmol, 38% yield) as a waxy orange solid.

**Synthesis of PhSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub>.** [Me<sub>3</sub>Ge]Li, obtained from 3.5 g (22.8 mmol) of Me<sub>3</sub>GeCl in 20 mL of dry ether, was added dropwise to 6.62 g (22.8 mmol) of PhSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Cl 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<sub>4</sub>Cl) 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> as a colorless liquid.

**Synthesis of HSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub>.** 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> 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

<sup>(8) (</sup>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<sub>4</sub> 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<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> as a colorless liquid (0.70 g, 2.38 mmol).

**Photolysis of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph.** 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 <sup>29</sup>Si NMR spectroscopy. The starting material disappeared completely after 1.5 h of irradiation. The solution was placed on a  $2.5 \times 10$  cm silica gel column, and a yellow band was eluted with hexane. Upon removal of solvent in vacuo FpSi(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>Ph (0.13 g, 87%) was obtained as a yellow crystalline solid.

**Photolysis of Fp\*SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph.** 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 <sup>29</sup>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  $2.5 \times 10$  cm silica gel column, and a yellow band was eluted with hexane. Upon removal of solvent in vacuo Fp\*Ge(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>Ph (0.08 g, 80%) was obtained as an orange oil, which became solid when placed in the freezer.

Photolysis of HSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> in the Presence of a Catalytic Amount of FpSiMe<sub>3</sub>. A mixture of HSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>3</sub> (0.120 g, 0.41 mmol) and a 10% equivalent of FpSiMe<sub>3</sub> in 1 mL of  $C_6D_6$  was irradiated in a sealed Pyrex NMR tube. The progress of the reaction was monitored by <sup>29</sup>Si NMR spectroscopy. After 53 h <sup>29</sup>Si NMR analysis showed the presence of signals at -4.61 and -29.5 ppm due to the formation of (Me<sub>3</sub>Si)<sub>3</sub>GeSiMe<sub>2</sub>H and a signal at -16.1 ppm due to Me<sub>3</sub>SiH. Some starting material was also present.

Photolysis of (Me<sub>3</sub>Si)<sub>3</sub>GeH + HSiMe<sub>2</sub>SiMe<sub>3</sub> in the Presence of a Catalytic Amount of FpSiMe<sub>3</sub>. A 5 mm Pyrex NMR tube was charged with 0.3 g (2.24 mmol) of HSiMe<sub>2</sub>-SiMe<sub>3</sub>, 0.3 g (1.02 mmol) of (Me<sub>3</sub>Si)<sub>3</sub>GeH, and 10 mol % of FpSiMe<sub>3</sub> in 1 mL of C<sub>6</sub>D<sub>6</sub> and sealed under vacuum. Photolysis, using a Hanovia 450 W lamp at a distance of 6 cm, was monitored by <sup>29</sup>Si NMR spectroscopy. After 62 h the HSiMe<sub>2</sub>-SiMe<sub>3</sub> had been consumed and resonances associated with the insertion product (Me<sub>3</sub>Si)<sub>3</sub>GeSiMe<sub>2</sub>H were observed (-4.6 and -29.5 ppm) together with that due to Me<sub>3</sub>SiH (-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<sub>3</sub>Si)<sub>3</sub>GeSiMe<sub>2</sub>H (0.71 mmol, 70% yield).

**Photolysis of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph in the Presence of HMPA.** A 5 mm NMR tube was charged with 0.08 g (0.164 mmol) of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph and 0.10 g (0.56 mmol) of HMPA in 1.0 mL of degassed C<sub>6</sub>D<sub>6</sub> and sealed under vacuum. The sealed NMR tube was irradiated with a 450 W medium-pressure mercury lamp, and the reaction was monitored by <sup>29</sup>Si and <sup>1</sup>H NMR spectroscopy. After 3.0 h the starting material had disappeared, and the <sup>29</sup>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 ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(CO)Fe(=SiMe<sub>2</sub>·HMPA)-SiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>Ph. Continued irradiation had no effect upon the spectra obtained.

**Photolysis of FpSiMe<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>GeMe<sub>2</sub>Ph in the Presence of HMPA.** A mixture of 0.10 g (0.19 mmol) of FpSiMe<sub>2</sub>-SiMe<sub>2</sub>GeMe<sub>2</sub>Ph 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 <sup>29</sup>Si NMR spectroscopy. During this time the starting compound disappeared. The <sup>29</sup>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<sub>2</sub>Ph (36.0 ppm) were also observed.

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