4946 *Organometallics* **1994,** *13,* 4946–4951

Synthesis and Photochemistry of Germylsilyl, Germylstannyl, and Stannylgermyl Derivatives of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (Fp) System: $FpSiMe_2GeMe_2Fp$, $FpGeMe_2SnMe_3$, and $FpSnMe_2GeMe_3$

Hemant Sharma and Keith H. Pannell*

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

Received April 11, 1994⊗

New silicon, germanium, and tin complexes of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (Fp) system containing silylgermyl and germylstannyl groups are reported, $FpSiMe_2GeMe_2Fp$ (**4**), $FpGeMe_2SnMe_3$ (**5**), and its isomer $FpSnMe_2GeMe_3$ (**6**). The bimetallic complex **4** undergoes photochemical transformation to three equilibrating isomers of an intermediate germylene bridged complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}GeMeSiMe_3)$ (**7a**). No evidence was obtained for the formation of the isomeric silylene bridged intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}SiMeGeMe_3)$ (**7b**), confirming the enhanced stability of germylene versus silylene intermediates. Complex **7a** transforms slowly to a mixture of the *cis* and *trans* isomers of the doubly bridged germylene silylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMe_2)(\mu\text{-}GeMe_2)$ (**8**). The germylstannyl complex **5** photoisomerizes to **6** prior to photoelimination of Me_2Ge and Me_2Sn to form $FpSnMe_3$ (40%) and $FpGeMe_3$ (60%), respectively. The same photoproduct distribution was obtained from the photochemical treatment of **6**, but no isomerization to **5** was observed.

Introduction

Significant progress has been made in elucidating the photochemistry of oligosilyl derivatives of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ (Fp) system. Subsequent to initial loss of CO, silyl(silylene) intermediates, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(=SiR_2)(SiR'_3)$, are formed by α-elimination. These intermediates rapidly form an equilibrium mixture via a series of 1,3 alkyl, aryl, and silyl migrations leading to isomerizations and/or silylene expulsions, eqs 1 and 2.[1,2]

$$\mathrm{FpSiMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe_3 + SiMe_2} \tag{1}$$

$$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} FpSi(SiMe_3)_3} \tag{2}$$

Isomeric silylgermyl and germylsilyl Fp complexes behave in similar manner, with a pronounced favoring of the germylene intermediates, eq 3.[3,4]

$$\mathrm{FpSiMe_2GeMe_3 \xrightarrow{h\nu} FpSiMe_3\ (95\%) + FpGeMe_3\ (5\%)} \tag{3a}$$

$$\mathrm{FpGeMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe_3\ (95\%) + FpGeMe_3\ (5\%)} \tag{3b}$$

On the basis of the chemistry described above, both silylene transfer and oligosilane isomerization of linear oligosilanes to their branched isomers may be performed catalytically. Thus, using $FpSiR_3$ as catalyst, photochemical silylene expulsion from disilanes or isomerization may be effected, whereas the phosphine-substituted analog $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiR_3$ may be used to thermally isomerize oligosilanes.[1g]

The bimetallic disilyl complex $FpSiMe_2SiMe_2Fp$ (**1**) photochemically rearranged to the three possible isomers of the carbonyl silylene bridged diiron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{\mu\text{-}SiMe(SiMe_3)(\mu\text{-}CO)\}$ (**2**). Prolonged irradiation of **2** transformed it into the *cis* and *trans* isomers of the bis(silylene)-bridged complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{(\mu\text{-}SiMe_2)\}_2$ (**3**) eq 4.[5,6]

$$\begin{tikzcd}
\mathrm{FpSiMe_2SiMe_2Fp} \arrow[r, "h\nu"] & \mathrm{[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{\mu\text{-}SiMe(SiMe_3)(\mu\text{-}CO)\}} \arrow[d, "h\nu"] \\
 & \mathrm{[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMe_2)_2}
\end{tikzcd} \tag{4}$$

Such reactions also proceed via equilibrating silyl(silylene) intermediates. In order to better understand the effects of the different group 14 elements on the relative stabilities of the coordinated silylenes, germylenes, and stannylenes in these transition metal environments, we report the synthesis and photochem-

---

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1994.

[1] (a) Pannell, K. H.; Rice, J. *J. Organomet. Chem.* **1974**, *78*, C35. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056. (c) Pannell, K. H.; Rozell, J. M.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (d) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (e) Jones, K.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (f) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (g) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075.

[2] 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) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1990**, 1. (d) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

[3] Pannell, K. H.; Sharma, S. *Organometallics* **1991**, *10*, 1655.

[4] Koe, J. R.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479.

[5] Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954.

[6] (a) Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120. (b) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959. (c) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435.

0276-7333/94/2313-4946$04.50/0

istry of $FpSiMe_2GeMe_2Fp$ (**4**), and of the isomeric $FpGeMe_2SnMe_3$ (**5**) and $FpSnMe_2GeMe_3$ (**6**).

Results and Discussion

Synthesis. 1,2-Dichloro-1,1,2,2-tetramethylsilylgermane,[4] $ClSiMe_2GeMe_2Cl$, was prepared in a single step by direct chlorination of $PhMe_2GeSiMe_2H$. The chlorination was best monitored directly by ^{29}Si NMR in C_6H_6. The monochloro intermediate $PhMe_2GeSiMe_2Cl$ was observed spectroscopically, but no attempt was made to isolate it during the present study. Subsequent treatment of $ClSiMe_2GeMe_2Cl$ with Fp^-Na^+ in THF yielded $FpSiMe_2GeMe_2Fp$ (**4**) (54%), eq 5.

$$2Fp^-Na^+ + ClSiMe_2GeMe_2Cl \rightarrow FpSiMe_2GeMe_2Fp + 2NaCl \quad (5)$$

The germylstannyl complex $FpGeMe_2SnMe_3$ (**5**) was synthesized in excellent yield by the salt elimination reaction between $FpGeMe_2Cl$ and Me_3SnLi in THF, eq 6.

$$FpGeMe_2Cl + Me_3SnLi \rightarrow FpGeMe_2SnMe_3 + LiCl \quad (6)$$

Analysis of the crude reaction products by GC/mass spectrometry and ^1H and ^{119}Sn NMR spectroscopy showed traces of $FpSnMe_3$ to be present. The analogous reaction between $FpSnMe_2Cl$ and Me_3GeLi in a THF/HMPA mixture at different temperatures (from −78 °C to room temperature) did not result in the formation of the desired complex, $FpSnMe_2GeMe_3$ (**6**). The only product isolated under these reaction conditions was $FpSnMe_2Fp$. We attempted reductive coupling of $FpSnMe_2Cl$ and Me_3GeBr with lithium or sodium−naphthalene in THF, and low yields of **6** were obtained along with ferrocene, $FpGeMe_3$, and $FpSnMe_3$. Significantly higher yields were obtained by utilizing the milder reducing agent Mg, eq 7.

$$FpSnMe_2Cl + Mg + BrGeMe_3 \rightarrow FpSnMe_2GeMe_3 + MgClBr \quad (7)$$

GC/mass spectral analysis of the crude product showed a 90% yield of the desired complex along with traces of $FpGeMe_3$ and $FpSnMe_3$. Another complex was observed in 8−9% yield, which on the basis of the mass and ^{119}Sn spectra was tentatively identified as $FpGeMe_2GeMe_2SnMe_3$; however, we have not been able to isolate sufficient material to perform a complete analysis. A molecular ion peak was observed for this complex at *m/e* 546 (10%), and major fragments were observed at *m/e* 429 $[FpGeMe_2SnMe_2]^+$, *m/e* 369 $[GeMe_2GeMe_2SnMe_3]^+$, *m/e* 281 $[FpGeMe_2]^+$, *m/e* 221 $[GeMe_2GeMe_3]^+$, and *m/e* 119 $[Me_3Ge]^+$. The ^{119}Sn NMR spectrum exhibited a resonance at −80.0 ppm which rules out the possibility of direct Fe−Sn bonding (*vide infra*).

Spectral Properties. The ^{29}Si and ^{119}Sn NMR data for the new iron complexes are useful for structural assignments. Compound **4** exhibits a signal at 39.9 ppm in the ^{29}Si NMR spectrum. Previous studies of ^{29}Si NMR data of Fp−silyl complexes suggest that it should exhibit a resonance ≈50 ppm downfield of $Me_3SiGeMe_3$. The observed resonance at 39.9 ppm indeed represents a shift ($\Delta\delta$) of 49.7 ppm and may be compared to a $\Delta\delta$ value of 49 ppm for the related complex $FpSiMe_2SiMe_2Fp$ (**1**), cf. $Me_3SiSiMe_3$.[5] Substitution of a germanium for a silicon atom in the iron complexes causes an 8−11 ppm downfield shift.

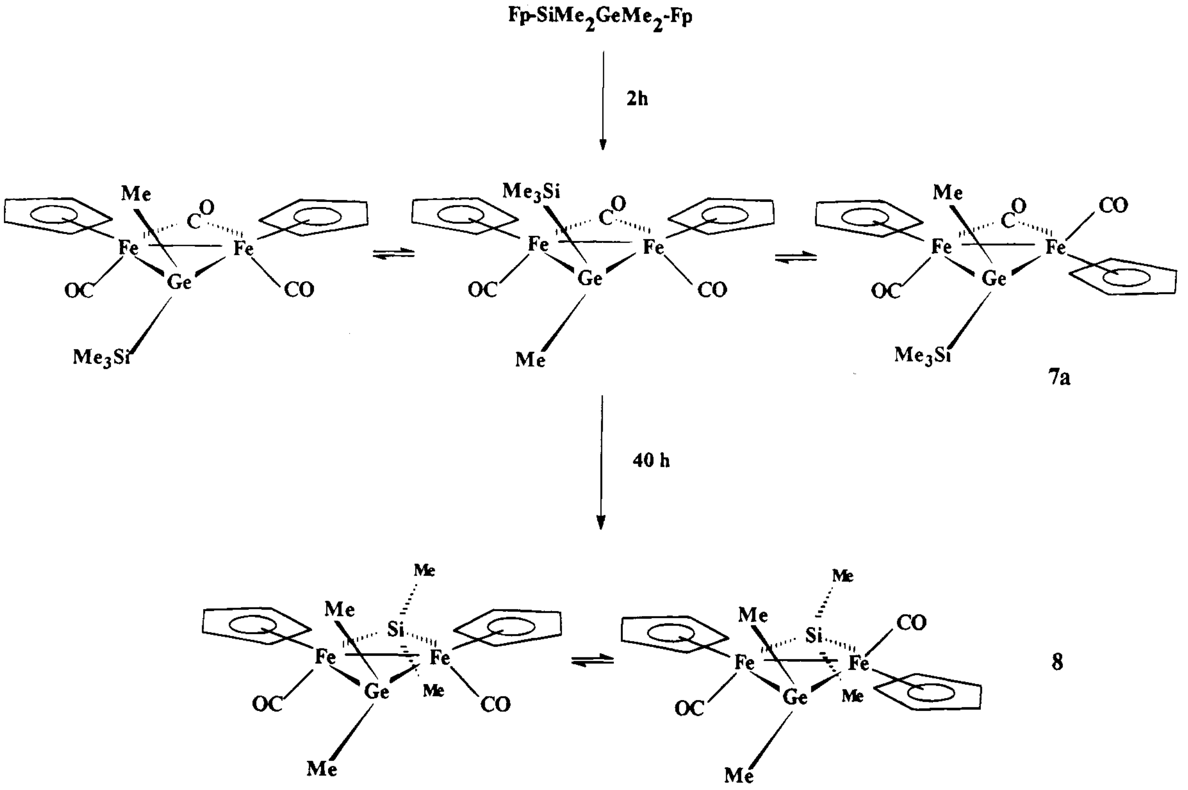
Related, but larger, downfield shifts were observed in the ^{119}Sn NMR spectra of Fp−tin derivatives. Substitution of Fp for Me in $MeSnMe_3$ results in a chemical shift of 147 ppm and when a second Me group is replaced by another Fp substituent, i.e., $FpSnMe_2Fp$, the resonance is observed at 330 ppm, indicating that a direct Fe−Sn bond in Fp−tin complexes causes a downfield shift of ~150−165 ppm. For **5**, in which the Sn atom is situated at a β-position with respect to the Fp group, a resonance is observed at −69.2 ppm with respect to tetramethyltin which represents a $\Delta\delta$ value of 26 ppm compared to $Me_3SnGeMe_3$ (^{119}Sn NMR = −95.2 ppm). In the isomeric complex **6**, the Sn atom which is directly bonded to Fe exhibits a resonance at 49.7 ppm, $\Delta\delta$ = 145 ppm.

The mass spectra of the Ge−Sn bonded complexes **5** and **6** are interesting with respect to the general ability to rapidly distinguish such a pair of isomers. Complex **5** exhibits a major fragment at *m/e* 281 due to $[FpGeMe_2]^+$ which constitutes the base peak obtained by the direct heterolytic cleavage of the Ge−Sn bond and presumably corresponds to a germylene ion species, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(=GeMe_2]^+$. In **6**, the major fragmentations were observed at *m/e* 327, $[FpSnMe_2]^+$, the stannylene analog, and at *m/e* 185, $[C_5H_5Sn]^+$.

Photochemistry of $FpSiMe_2GeMe_2Fp$. A C_6D_6 solution of **4** in a flame-sealed Pyrex NMR tube was irradiated using a 450 W medium-pressure Hg lamp. The progress of the reaction was periodically monitored by ^1H and ^{29}Si NMR spectroscopy. The spectra obtained after 2 h showed the complete disappearance of **4** and formation of the three geometrical isomers of **7a** along with the trace amounts of the *cis* and *trans* isomers of **8**, Scheme 1. These results are analogous to those obtained in the photochemistry of $FpSiMe_2SiMe_2Fp$ (**1**).[5,6] Further irradiation for 40 h resulted in the complete disappearance of **7a** and quantitative formation of **8**. The ^{29}Si NMR spectrum of **7a** exhibits three resonances at 4.78, 5.89, and 6.53 ppm which can be assigned to three isomers in which the $SiMe_3$ group is at the terminal position rather than the bridging position. These resonances are 11 ppm lower than that of the corresponding complex **2** obtained from the photolysis of $FpSiMe_2SiMe_2Fp$ (**1**). For complex **8**, two Si resonances observed at 230.8 and 244.7 ppm can be assigned to the bridging silylene unit in the *cis* and *trans* isomers. These resonances are comparable with those observed in $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMe_2)_2$ (**3**) at 229.5 and 243.8 ppm, respectively.[6]

The formation of complexes **7a** and **8** in the photolysis of 4, Scheme 1, agrees with the general mechanism we and the Ogino group have proposed with respect to the disilyl system, **1**, which is illustrated in Scheme 2. We have no evidence for the formation of the isomer **7b**, i.e., $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{(\mu\text{-}SiMe(GeMe_3)(\mu\text{-}CO)\}$, which contains a bridging silylene group. The exclusive formation of **7a** suggests that the reaction does not react the various intermediates on the left of Scheme 2, i.e., the equilibrium between the germylene and silylene intermediates **9a** and **9b** greatly favors the germylene species **9a**. This result is in accord with earlier findings

Scheme 1



that the germylene intermediates are preferred to the silylene counterparts in systems in which both are possible. The two types of equilibration noted in Scheme 2, A and B, result from the 1,3-migration of either Fp or Me groups.

The isomer formation for **7a** is related to that observed by Malisch and Ries for the compounds $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\{(\mu\text{-}SiMeX)(\mu\text{-}CO)\}$, X = H, Cl,[6a] and Ogino and co-workers have studied the mechanistic aspects of such isomerizations in complex **2**.[6b,c] Basing our studies upon their analysis, we have briefly observed the related isomerization of **7a**. Upon dissolving **7a** in C_6D_6 and recording its ^1H NMR spectrum within 15 min, a mixture of all the three possible isomers in the molar ratios of *trans*:*cis*-$SiMe_3$:*cis*-Me of 10:60:30 was observed. The isomers equilibrated over a 2 h time period at room temperature and the ^1H spectrum recorded after 2 h shows the increase of *trans* and the *cis*-Me isomer and the new ratio is *trans*:*cis*-$SiMe_3$:*cis*-Me 20:40:40. We have not unambiguously assigned the ^{13}C and ^{29}Si NMR data to the respective isomers of either **7a** or **8**.

Photochemistry of $FpGeMe_2SnMe_3$ (5) and $FpSnMe_2GeMe_3$ (6). Separate irradiation of these isomers in sealed Pyrex NMR tubes, monitoring via ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy, led to similar but slightly different results. Irradiation of **5** gave a product distribution involving four metal-containing species after a period of several hours, namely, **5**, **6**, $FpGeMe_3$, and $FpSnMe_3$. Continued irradiation gave only $FpGeMe_3$ and $FpSnMe_3$ as final products in the ratio 60:40, respectively, determined via ^1H NMR and GC/mass spectral analysis (Scheme 3). Tetramethyltin was also an observed product, probably due to disproportionation of Me_2Sn. Irradiation of **6** alone resulted in the disappearance of this complex together with the formation of $FpGeMe_3$ and $FpSnMe_3$. No evidence was observed for the isomerization **6** → **5**.

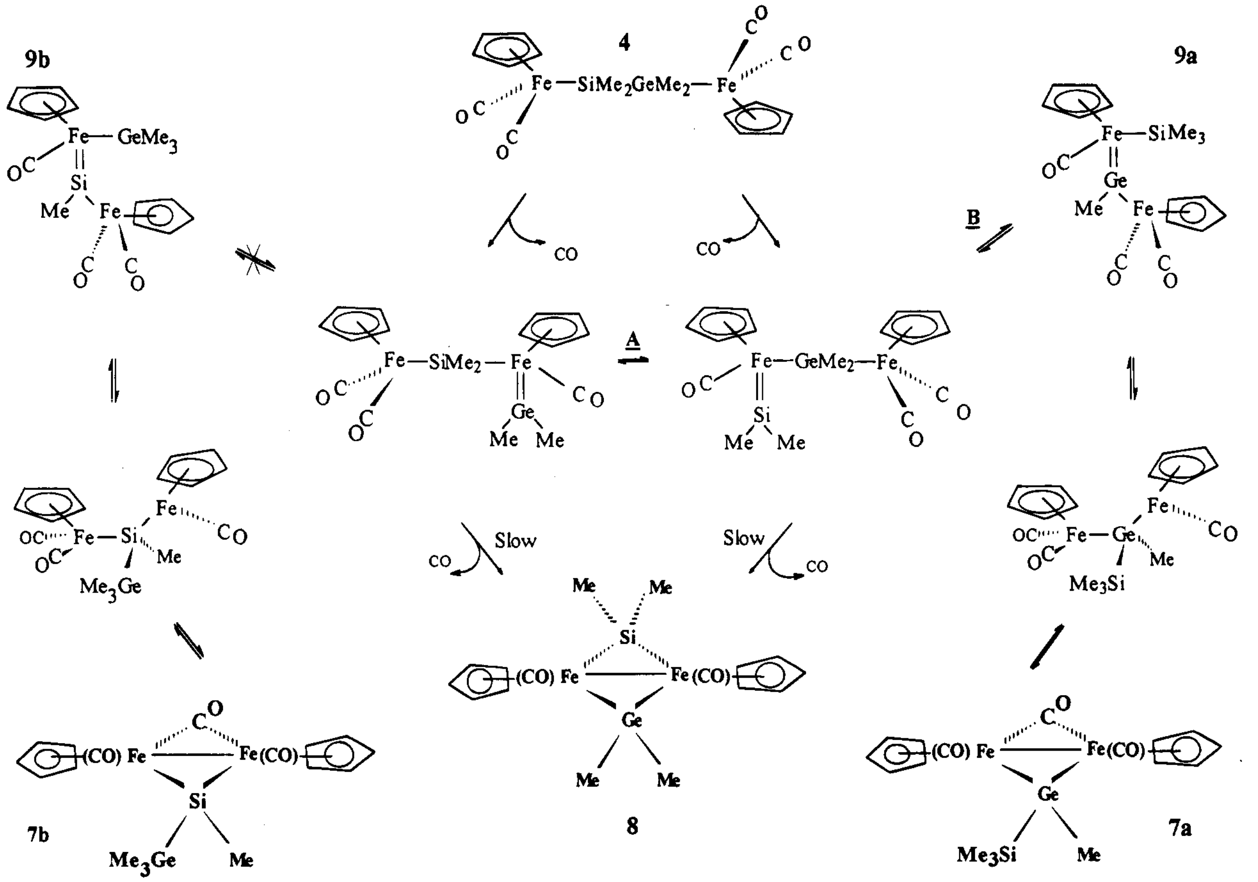
These photochemical conversions are closely related to those observed for the corresponding $FpGeMe_2SiMe_3$ and $FpSiMe_2GeMe_3$ complexes. The ultimate photoproducts, i.e., $FpGeMe_3$ and $FpSnMe_3$, result from the loss of Me_2Sn and Me_2Ge, respectively. It is clear that in this system the equilibrium between germylene and stannylene intermediates marginally favors the stannylene isomer. In the case of equilibrating silylene/germylene systems derived from $FpGeMe_2SiMe_3$ and $FpSiMe_2GeMe_3$ the equilibrium greatly favored germylene formation. However, the relative stabilities of Ge(II) and Sn(II) would suggest a more evenly balanced equilibrium, and the results are in accord with such expectations. The observation of isomerization of **5** to **6** is of interest and represents the first time that the photolysis of any $FpER_2ER_3$, E = Si, Ge, or Sn, has resulted in isomerization. As noted in the Introduction, this occurs for Fp-trisilanes, -tetrasilanes, etc., and has also been noted for indenyliron analogs of disilanes, e.g., $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMePh_2$, as a result of the reformation of the Si−Si bond in silyl(silylene) intermediates. The Turner group has established that the release of the silylene from these intermediates is a photochemical event[7] and clearly factors that control the competition between fission and recombination of the Si−Si (or Si−Ge, Ge−Ge, and Ge−Sn) bond are quite subtle.

It is possible that the formation of **6** from **5** occurred by $SnMe_2$ insertion into $FpGeMe_3$ since both are photoproducts of the reaction. In order to evaluate such ideas we have performed separate experiments aimed at trapping germylene or stannylene intermediates with $FpER_3$, E = Ge, Sn, complexes. Two separate experi-

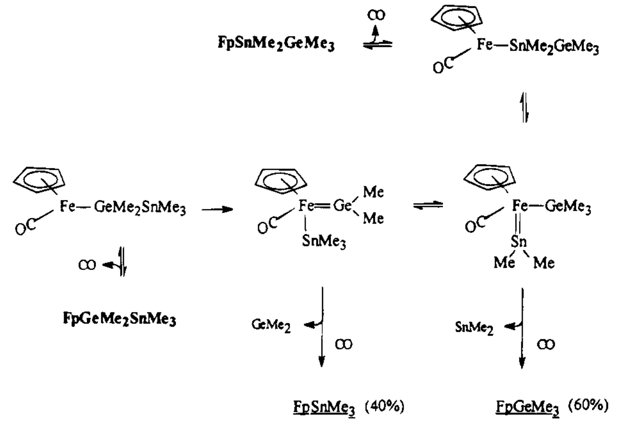
---

[7] Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113*, 2011.

Scheme 2



Scheme 3



ments were performed: (1) Photolysis of FpGeMe$_2$GeMe$_3$ in the presence of FpSnMe$_3$. This resulted the formation of a mixture of FpGeMe$_3$ and FpSnMe$_3$ only. Neither **5** nor **6** was observed. (2) Photolysis of FpGeMe$_2$SnMe$_3$ in the presence of FpGeMe$_2$Ph. This experiment resulted in the formation of FpGeMe$_3$ and FpSnMe$_3$ as noted above (in addition to unreacted FpGeMe$_2$Ph), and the transient formation of the isomer **6**. No production of FpSnMe$_2$GeMe$_2$Ph was observed.

These experiments rule out the possibility of germylene/stannylene insertion into Fe−Sn and Fe−Ge bonds in these systems. Therefore, it is reasonable to propose that the isomerization noted occurs via recombination of the Sn−Ge bond subsequent to 1,3-methyl migration in the (germylene)stannyl iron intermediate as noted in Scheme 3.

The GC/mass spectral analysis of the photoproducts of **5** also showed traces of FpGeMe$_2$GeMe$_3$ and FpGeMe$_2$GeMe$_2$H. The formation of trace amounts of these complexes indicate yet another minor, possibly radical, product formation pathway for these photochemical reactions.

In order to trap the liberated Me$_2$Ge and Me$_2$Sn fragments, the photochemical experiment was performed in the presence of a 10-fold excess of 2,3-dimethyl-1,3-butadiene. The GC/MS analysis of the photoproducts showed the formation of two Fp complexes, FpGeMe$_3$ (70%) and FpSnMe$_3$ (30%) (a slightly different ratio to that observed in the absence of the butadiene trap), but did not provide evidence for the 1,4-addition of germylenes/stannylenes to the butadiene. No transformation **5** → **6** was observed. The Satgé group has reported efficient trapping of Me$_2$Ge produced upon irradiation of FpGeR$_2$GeR$_2$H in the presence of dimethyl disulfide.[8] We have tried this trap in the present system and the results, obtained from GC/MS analysis after 80% removal of **5**, are outlined below.

$$\mathrm{FpGeMe_2SnMe_3 + MeSSMe \xrightarrow{h\nu}}$$
$$\underset{(17\%)}{\mathrm{MeSGeMe_3}} + \underset{(3\%)}{\mathrm{MeSSnMe_3}} + \underset{(21\%)}{\mathrm{MeSGeMe_2SnMe_3}} + \underset{(30\%)}{\mathrm{FpGeMe_3}} +$$
$$\underset{(2\%)}{\mathrm{FpSnMe_3}} + \underset{(7\%)}{\mathrm{(C_5H_5)_2Fe}}$$

There are several points of interest. No trapping products, MeSEMe$_2$SMe, E = Ge, Sn, were observed;

---

[8] Castel, A.; Rivière, P.; Ahbala, M.; Satgé, J.; Soufiaoui, M.; Knouzi, N. *J. Organomet. Chem.* **1993**, *447*, 123.

no isomerization to **6** was noted; and the ratio of FpGeMe$_3$:FpSnMe$_3$ changed from the "normal" value of 60:40 to 93:6. The considerable amounts of (methylthio)germanium and -tin compounds suggest direct cleavage of the Fe–Ge, Fe–Sn, and/or Ge–Sn bonds. Taken together it seems that introduction of the trapping agent, MeSSMe or butadiene, changes the nature of the reaction and suggests a direct interaction of the trap with the starting materials and intermediates. We have previously reported that Me$_2$Si is best trapped using (Me$_3$Si)$_3$SiH, although use of Et$_3$SiH resulted in small amounts of the trapping product Et$_3$SiSiMe$_2$H.[1e,g,9] A more detailed analysis of the various modes of trapping, ER$_2$, E = Si, Ge, Sn, from the photolysis FpER$_2$ER$_3$ complexes will be published elsewhere.

Experimental Section

All manipulations were carried out under an argon atmosphere or under high vacuum. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. The following reagents were used as received from the suppliers named, [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$, Strem Chemicals; silica gel (grade 950, 60–200 mesh), MCB; Me$_3$GeBr, Gelest; Me$_3$SnCl, Aldrich. Other reagents were synthesized by literature procedures: Me$_2$GeCl$_2$,[10] PhGeMe$_2$SiMe$_2$H,[4] FpGeMe$_2$Cl,[11] FpSnMe$_2$Cl,[12] Me$_3$GeLi.[13]

High-resolution mass spectra were obtained from Midwest Center for Mass Spectrometry, Lincoln, NE. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of ClSiMe$_2$GeMe$_2$Cl. Into a 250 mL Schlenk flask containing 3.7 g (15.5 mmol) of PhMe$_2$GeSiMe$_2$H and 100 mg of AlCl$_3$ in 30 mL of benzene was slowly bubbled hydrogen chloride at room temperature. The reaction mixture became warm. Samples of the solution were periodically withdrawn and their ^{29}Si NMR spectra were recorded. The signal due to the starting material at −32.5 ppm gradually disappeared and was replaced by signals at −10.3 and at 27.0 ppm. After 30 min only a single resonance was observed at 24.3 ppm. At this time the reaction was stopped and 5 mL of dry acetone was added to deactivate the catalyst. The solution was filtered, solvents were distilled at 50 mmHg, and ClSiMe$_2$GeMe$_2$Cl (3.1 g, 13.3 mmol, 86%) was distilled at 66–68 °C/20 mmHg (lit.[4] 68 °C/20 mmHg).

Synthesis of FpSiMe$_2$GeMe$_2$Fp (4). To 75 mL of a THF solution of [CpFe(CO)$_2$]$^-$Na$^+$ (prepared from 3.54 g (10.0 mmol) of Fp$_2$) was added 2.4 g (10.3 mmol) of ClSiMe$_2$GeMe$_2$Cl in 20 mL of THF at −20 °C. The solution was stirred at low temperature for 30 min and then permitted to warm to room temperature and further stirred for 12 h. The solvent was removed *in vacuo* and the residue was extracted with a mixture of 90:10 hexane/methylene chloride. The solution was filtered and concentrated to 10 mL and placed upon a 2.5 × 20 cm silica gel column. Elution with the same solvent mixture developed a bright yellow band which was collected and subsequent to solvent removal produced a yellow crystalline solid. The solid was recrystallized from a mixture of hexane/methylene chloride to yield **4** (2.78 g, 5.40 mmol, 54%), mp 148 °C. ^{1}H NMR (C$_6$D$_6$): 0.82 (6H, s, Me); 0.85 (6H, s, Me); 4.35 (5H, s, C$_5$H$_5$); 4.37 (5H, s, C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): 5.23 (SiMe$_2$); 6.93 (GeMe$_2$); 82.6 (C$_5$H$_5$); 83.43 (C$_5$H$_5$); 215.9 (CO); 217.0 (CO). ^{29}Si NMR (C$_6$D$_6$): 39.9. IR (ν(CO), cm^{-1}, hexane): 2005.5, 1990.0, 1945.0, 1936.1. Anal. Calcd for C$_{18}$H$_{22}$Fe$_2$GeO$_4$Si: C, 42.0; H, 4.30. Found: C, 41.56; H, 4.05. LRMS (FAB): *m/z* 515.9 [M$^+$], 432.0 [M − 3CO]$^+$, 338.9 [FpSiMe$_2$GeMe$_2$]$^+$, 235.0 [FpSiMe$_2$]$^+$, 73.0 [Me$_3$Si]$^+$.

Photolysis of 4: Formation of [(η^5-C$_5$H$_5$)Fe(CO)]$_2${μ-GeMe(SiMe$_3$)(μ-CO)} (7a). A 5 mm Pyrex NMR tube was charged with 0.1 g (0.19 mmol) of **4** and 0.5 mL of C$_6$D$_6$ and sealed under vacuum. Irradiation was carried out with a 450 W medium-pressure Hg lamp at a distance of 4 cm. The progress of the reaction was monitored by ^{1}H and ^{29}Si NMR spectroscopy. The color of the solution changed from yellow to violet-red upon irradiation and after 2 h complete disappearance of **4** and formation of **7a** was noted, along with traces of **8**. After removal of the solvent the resulting violet-red solid was washed twice with cold hexane and dried under vacuum. Yield: 40 mg (0.08 mmol, 42%). ^{1}H NMR (C$_6$D$_6$): 0.35, 0.39, 0.50 (SiMe$_3$); 1.32, 1.39, 1.48 (μ-GeMe), 4.08 (*cis*-Me, C$_5$H$_5$), 4.21 (*cis*-SiMe$_3$, C$_5$H$_5$), 4.27, 4.42 (*trans*, C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): 1.28, 1.56, 2.05 (SiMe$_3$), 8.94, 10.50, 11.51 (μ-GeMe), 82.8, 83.6, 83.7, 84.5 (C$_5$H$_5$), 212.6, 213.1, 213.3 (terminal CO), 274.6, 276.0 (bridging CO). ^{29}Si NMR (C$_6$D$_6$): 4.48, 5.89, 6.53 (SiMe$_3$). IR (ν(CO) cm^{-1}, hexane): 2004, 1975, 1961, 1935, 1793, 1781. HRMS (EI): calcd for C$_{17}$H$_{22}$Fe$_2$GeO$_3$Si *m/z* 487.92551, found *m/z* 487.92431.

Photolysis of 4: Formation of [(η^5-C$_5$H$_5$)Fe(CO)]$_2${(μ-GeMe$_2$)(μ-SiMe$_2$)} (8). In an experimental set up the same as that above, irradiation was continued for 40 h or until NMR monitoring showed the complete disappearance of **4** and **7a** and the formation of **8**. The solvent was evaporated, and the violet-red solid was washed two times with cold hexane and dried under vacuum to yield **8**: 35 mg (0.07 mmol, 39%). ^{1}H NMR (C$_6$D$_6$): 1.18, 1.25, 1.30, 1.35, 1.49 (μ-SiMe$_2$, μ-GeMe$_2$), 3.89 (*cis*-C$_5$H$_5$), 4.03 (*trans*-C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): 13.80, 14.80, 15.61, 15.92, 16.31, 16.48 (μ-SiMe$_2$, μ-GeMe$_2$), 79.9, 80.6 (C$_5$H$_5$), 213.6, 214.5 (CO). ^{29}Si NMR (C$_6$D$_6$): 230.8, 244.7 (μ-SiMe$_2$). IR (ν(CO) cm^{-1}, hexane): 1945, 1915. HRMS (EI): calcd for C$_{16}$H$_{22}$Fe$_2$GeO$_2$Si *m/z* 459.9306, found *m/z* 459.9320. Anal. Calcd: C, 41.89; H, 4.83. Found: C, 41.31; H, 4.11.

Synthesis of FpGeMe$_2$SnMe$_3$ (5). To 2.2 g (6.98 mmol) of FpGeMe$_2$Cl in 30 mL of THF was added slowly 30 mL of a THF solution of Me$_3$SnLi (prepared from 1.40 g (7.01 mmol) of Me$_3$SnCl and 0.1 g (14.2 mmol) of Li in 20 mL of THF) at −78 °C. The mixture was stirred at low temperature for 2 h and then warmed to room temperature and further stirred for 16 h. At this time the solvent was removed *in vacuo* and the residue was extracted with 50 mL of hexane. After filtration, the solution was concentrated to 5 mL and placed upon a 2.5 × 20 cm silica gel column. The orange band was eluted with hexane and subsequent to evaporation of solvent yielded 2.1 g (4.72 mmol, 68%) of **5** as an orange wax. ^{1}H NMR (C$_6$D$_6$): 0.38 ($^2J_{\mathrm{Sn-H}}$ = 44 Hz, 9H, s, SnMe$_3$); 0.83 ($^3J_{\mathrm{Sn-H}}$ = 28 Hz, 6H, s, GeMe$_2$); 4.24 (5H, s, C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): −9.28 ($^1J_{\mathrm{Sn-C}}$ = 214 Hz, SnMe$_3$); 4.88 (($^2J_{\mathrm{Sn-C}}$ = 55 Hz, GeMe$_2$); 83.1 (C$_5$H$_5$); 215.8 (CO). ^{119}Sn NMR (C$_6$D$_6$): −69.2. IR (ν(CO) cm^{-1}, hexane): 1996.0, 1947.7. MS (70 eV) *m/z*: 444 [M]$^+$, 4; 429 [M − Me]$^+$, 4; 281 [FpGeMe$_2$]$^+$, 100; 185 [C$_5$H$_5$Sn]$^+$, 68; 135 [SnMe]$^+$, 45; 121 [C$_5$H$_5$Fe]$^+$, 25; 89 [GeMe]$^+$, 3. Anal. Calcd for C$_{12}$H$_{20}$FeGeO$_2$Sn: C, 32.50; H, 4.54. Found: C, 32.80; H, 4.64.

Attempted Synthesis of FpSnMe$_2$GeMe$_3$ (6). (a) Reaction of FpSnMe$_2$Cl with Me$_3$GeLi To Produce FpSnMe$_2$-Fp. A flame-dried 250 mL three-necked flask equipped with stirring bar and dropping funnel was charged with 2.0 g (5.53 mmol) of FpSnMe$_2$Cl in 30 mL of THF. The flask was cooled to −78 °C and a solution of Me$_3$GeLi (prepared in a separate 100 mL Schlenk flask from 1.1 g (5.56 mmol) of Me$_3$GeBr and 0.2 g Li metal in 10 mL HMPA and 25 mL THF) was transferred via cannula into the dropping funnel and then added slowly to the FpSnMe$_2$Cl solution at −78 °C over a period of 45 min. The reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 16 h. THF was

---

(9) Recent studies in our laboratory have shown that photolysis of FpSiMe$_2$SiMe$_3$ in the presence of a 2-fold excess of (Me$_3$Si)$_3$SiH leads to formation of (Me$_3$Si)$_3$SiSiMe$_2$H in a 60% yield, plus (Me$_3$Si)$_3$SiSiMe$_2$SiMe$_2$H (5%).

(10) Lee, M. E.; Bobbitt, K. L.; Lei, D.; Gaspar, P. P. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 77.

(11) Job, R. C.; Curtis, M. D. *Inorg. Chem.* **1973**, *12*, 2514.

(12) Bichler, R. E. J.; Clark, H. C.; Hunter, B. K.; Rake, A. T. *J. Organomet. Chem.* **1974**, *69*, 367.

(13) Wickham, G.; Young, D.; Kitching, W. K. *J. Org. Chem.* **1982**, *47*, 4884.

removed *in vacuo* and the solution was subjected to flash distillation at 0.05 mmHg to remove HMPA. The red, viscous residue was extracted with 50 mL of hexane and filtered. The solution was concentrated and subjected to silica gel chromatography. The yellow band was eluted with hexane and upon evaporation of solvent 200 mg of $FpSnMe_2Fp$ was obtained. ^1H NMR (C_6D_6): 0.87 ($^2J_{Sn-H}$ = 36 Hz, 6H, s, $SnMe_2$); 4.25 (10H, s, C_6H_5). ^{13}C NMR (C_6D_6): 1.40 ($SnMe_2$), 82.20 (C_5H_5); 216.42 (CO). ^{119}Sn NMR (C_6D_6): 329.7 ppm. This complex was also synthesized independently by the reaction between 2 equiv of $[Fp]^-Na^+$ and Me_2SnCl_2.[14]

(b) Reductive Coupling of $FpSnMe_2Cl$ and Me_3GeBr with Lithium. A 100 mL Schlenk flask was charged with 0.9 g (2.48 mmol) of $FpSnMe_2Cl$ in 15 mL of THF. To this were added 0.49 g (2.48 mmol) of Me_3GeBr and 0.2 g of lithium metal. The reaction mixture was stirred vigorously overnight at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted with 30 mL of hexane and filtered. The solvent was concentrated and the residue was placed upon a 2.5 × 10 cm silica gel column. The yellow band which developed was eluted with hexane. Evaporation of solvent from the eluate yielded 200 mg of an orange oil. GC/mass spectral analysis showed it to be a mixture of ferrocene (20%), $FpGeMe_3$ (50%), $FpSnMe_3$ (20%), and $FpSnMe_2GeMe_3$ (10%). The reproducibility of this reaction was variable and no attempt was made to purify complex **6** from this mixture.

(c) Reductive Coupling of $FpSnMe_2Cl$ and Me_3GeBr with Sodium. The reaction above was repeated using Na instead of Li. GC/mass spectral analysis of the resulting orange oil showed it to be a mixture of ferrocene (9%), $FpGeMe_3$ (31%), $FpSnMe_3$ (6%), $FpSnMe_2GeMe_3$ (33%), and $FpGeMe_2GeMe_2SnMe_3$ (2%).

(d) Reductive Coupling of $FpSnMe_2Cl$ and Me_3GeBr with Magnesium. A 100 mL Schlenk flask was charged with 1.0 g (2.76 mmol) of $FpSnMe_2Cl$ in 15 mL of THF. To this were added 0.54 g (2.73 mmol) of Me_3GeBr, 0.03 g of magnesium metal, and a catalytic amount of iodine to activated the magnesium. The reaction mixture was stirred vigorously overnight at room temperature. The solvent was evaporated *in vacuo*, the residue was extracted with 30 mL of hexane, and this solution was filtered. The solvent was concentrated and the residue was placed upon a 2.5 × 10 cm silica gel column. The yellow band developed was eluted with hexane. After removal of the solvent, 0.3 g of an orange viscous oil was obtained. GC/mass spectral analysis showed it to be comprised of **6** (90%), $FpGe_2Me_4SnMe_3$ (8%), and traces of $FpGeMe_3$ and $FpSnMe_3$. Fractional sublimation at 40 °C/0.03 mmHg removed $FpGeMe_3$ and $FpSnMe_3$, and the residue was extracted with hexane and subjected to another chromatography. The yellow-orange band which developed was eluted with hexane. Evaporation of the solvent yielded $FpSnMe_2GeMe_3$ (**6**), 0.2 g (0.45 mmol, 16%) as an orange oil. ^1H NMR (C_6D_6): 0.44 (9H, s, $GeMe_3$); 0.49 (6H, s, $SnMe_2$); 4.13 (5H, s, C_5H_5). ^{13}C NMR (C_6D_6): −8.30 ($SnMe_2$); 0.75 ($GeMe_3$); 81.4 (C_5H_5); 215.7 (CO). ^{119}Sn NMR (C_6D_6): 49.7. IR (ν(CO) cm^{-1}, hexane): 1991.8, 1943.7. MS (70 eV) *m/z* 444 $[M]^+$, 4; 429 $[M - Me]^+$, 12; 327 $[FpSnMe_2]^+$, 40; 281 $[FpGeMe_2]^+$, 20; 185 $[C_5H_5Sn]^+$, 100; 135 $[SnMe]^+$, 60; 119 $[Me_3Ge]^+$, 20; 89 $[GeMe]^+$, 3. Anal. Calcd for $C_{12}H_{20}FeGeO_2Sn$: C, 32.50; H, 4.54. Found: C, 32.28; H, 4.46.

Photolysis of 5. (a) A 9-in. long, 5 mm Pyrex NMR tube was charged with 0.2 g (0.45 mmol) of **5** and 1 mL of C_6D_6. The tube was sealed under vacuum and irradiated with a 450 W medium-pressure Hg lamp at a distance of 4 cm. The progress of the reaction was monitored by ^1H and ^{119}Sn NMR spectroscopy and together with the formation of the photoproducts $FpGeMe_3$ and $FpSnMe_3$ formation of **6** was observed. After 7 h, when only a small amount of starting material was left, the photolysis was stopped and a GC/mass spectrum was recorded. Analysis showed the presence of $FpGeMe_3$, $FpSnMe_3$, (ratio 6:4), and $FpSnMe_2GeMe_3$ (**6**) along with starting material, Me_4Sn, and traces of $FpGeMe_2GeMe_3$ and $FpGeMe_2GeMe_2H$.

(b) Photolysis of 5 in the Presence of 2,3-Dimethyl-1,3-butadiene. A 5 mm Pyrex NMR tube was charged with 0.15 g (0.33 mmol) of **5** and 1 mL of C_6D_6 and a 10-fold excess of 2,3-dimethyl-1,3-butadiene. The sample tube was sealed and irradiated with a 450 W medium-pressure Hg lamp at a distance of 4 cm. The progress of the reaction was monitored by ^1H and ^{119}Sn NMR spectroscopy. After 4 h the photolysis was stopped and the GC/mass spectrum was recorded. The GC/MS did not show any trapping of germylene/stannylene; the only products observed were starting material, $FpGeMe_3$, $FpSnMe_3$, and Me_4Sn. Complex **6** was not observed.

Photolysis of 6. A 5 mm Pyrex NMR tube was charged with 0.15 g (0.33 mmol) of **6** and 1 mL of C_6D_6. The sample tube was sealed and irradiated with a 450 W medium-pressure Hg lamp at a distance of 4 cm. The progress of the reaction was monitored by ^1H and ^{119}Sn NMR spectroscopy. After 3 h the photolysis was stopped and GC/mass spectral analysis showed the presence of $FpGeMe_3$ (60%), $FpSnMe_3$ (40%), Me_4Sn, and starting material. Complex **5** was not observed.

Acknowledgment. Support of this research by the NSF (Grant No. RRII-880-2973) and the R. A. Welch Foundation, Houston, TX, is gratefully acknowledged. We also acknowledge the Midwest Center for Mass Spectrometry with partial support by the NSF Biology Division (Grant No. DIR9017262).

OM9402776

---

[14] Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 488.