path of CC coupling via an intramolecular dinuclear replacement reaction has been found.

Acknowledgment. We acknowledge Prof. K. Isobe for valuable discussions. All the calculations were carried out at the Computer Center of IMS.

Appendix

Electronic Structure of CpRh(PH$_3$). The ground state of CpML with the formal electron count of d^8 has so far been discussed by the extended Hückel method,[28a,b] the ab initio SCF method,[28b] and the density functional.[28c] Its d levels are schematically shown in Figure 11. Since 3a″ and 5a′ are close in energy, one anticipates three low-lying electronic states: a closed shell singlet (3a″)^2, an open-shell singlet, and a triplet (3a″)^1(5a′)^1. We optimized the structure of CpRh(PH$_3$) with the RHF and the singlet and triplet UHF methods, as shown in Figure 12, under the constraint of C_s symmetry with the nine valence electron ECP and the DZ basis functions for Rh[14a] and the 3-21G for Cp and PH$_3$.[15b,29]

In the RHF-optimized structure, two C^2–C^3 bonds of the Cp ring are much shorter than the other C–C bonds. In the closed-shell singlet state, the antibonding 3a″ is doubly occupied and thus the Cp π_A orbital does not contribute to the RhCp bonding interaction. Only the electron donation from π_S to d$_{xy}$ is responsible for the RhCp bonding interaction. Therefore, representing the bond order in π_S, the C^2–C^3 bonds are shorter than the C^1–C^2 and C^3–C$^{3'}$ bonds.

In the open-shell states, on the other hand, 3a″ and 5a′ are singly occupied, and π_A and π_S interact with d$_{yz}$ and d$_{xy}$ equivalently. Therefore, the five CC distances in the Cp ring are close to each other.

In Table IV we show the relative energies calculated at the several levels with a larger basis set: [2s2p3d]/(3s3p4d) for Rh, [4s3p]/(11s8p) for P, [3s2p]/(8s5p) for C, and [2s]/(4s) for H.[14a,30,31] At all the levels of calculation, the triplet is the ground state of CpRh(PH$_3$). At the highest level of calculation, MP4SDTQ, the closed-shell singlet is 8 kcal/mol higher in energy than the triplet. The open-shell singlet is the most unstable. These results are different from the density functional calculations,[28c] which gives the closed-shell singlet of CpML (M = Ir, Rh; L = CO, PH$_3$) as being more stable, than the triplet by 1–6 kcal/mol.

---

(28) (a) Hofmann, P.; Radmanabhan, M. *Organometallics* **1983**, *2*, 1273. (b) Veillard, A.; Dedieu, A. *Theor. Chim. Acta* **1980**, *63*, 339. (c) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

(29) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(30) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian basis sets for molecular calculations*; Elsevier: Amsterdam, 1984.

(31) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(32) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theor. Chim. Acta* **1988**, *73*, 337.

(33) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

Synthesis and Photochemical Reactivity of Transition-Metal-Disubstituted Disilanes LMSiMe$_2$SiMe$_2$ML (LM = (η^5-C$_5$H$_5$)Fe(CO)$_2$ and (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$))[1]

Keith H. Pannell* and Hemant Sharma

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

Received June 27, 1990

Three transition-metal-disubstituted disilanes, [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$SiMe$_2$SiMe$_2$ (FpSiMe$_2$SiMe$_2$Fp, I), [(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)]$_2$SiMe$_2$SiMe$_2$ (FcSiMe$_2$SiMe$_2$Fc, II), and FpSiMe$_2$SiMe$_2$Fc (III), have been synthesized, characterized, and studied photochemically. Complex I undergoes rearrangement to (η^5-C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-SiMeSiMe$_3$) (IV) as well as smaller amounts of FpSiMe$_3$. Complex II is photochemically inert in nonpolar solvents but undergoes an oxidative methanolysis reaction in MeOH in the presence of O$_2$ to form FcSiMe$_2$OMe (V) as the only product. Complex III, which contains the activating Fp group and the deactivating Fc group, reacts photochemically to form FpSiMe$_2$Fc (VI) and FpSiMe$_3$ in the ratio 3:1. Photolysis of FpSiMe$_2$SiMe$_2$Cl was also performed and produced FpSiMe$_2$Cl and FpSiMe$_3$ in the ratio 4:1. The various results illustrate that loss of SiMe$_2$ is much favored compared to loss of SiMeR, R = Ph, Cl, and Fc, where competition is possible. The various ferrocenylsilanes were prepared from the appropriate chlorosilanes and Fc$^-$Li$^+$ prepared from the transmetalation reaction between (chloromercurio)ferrocene and *n*-butyllithium. The yields, in the 70% range, were far superior to published values of approximately 10% obtained by using Fc$^-$Li$^+$ prepared directly from ferrocene.

Introduction

The photochemical properties of oligo- and polysilanes have been well studied, and in particular the photochemistry of aryldisilanes and related compounds has been an area of active research.[2] In general, such photolyses are thought to involve an excited state that leads to cleavage of the Si–Si bond to form the corresponding silyl radicals, which may either recombine or be trapped by appropriate agents. We have an ongoing interest in the chemical and

---

[1] Organometalloidal Derivatives of the Transition Metals. 26. Part 25: Pannell, K. H.; Lin, H.-S.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

(2) (a) For a review of the area, see: Ishikawa, M.; Kumada, M. *Advances In Organometallic Chemistry*; Ed. F. G. A., Stone, R., West, Eds.; Academic Press: New York, 1981; Vol. 19, p 51. (b) For a recent article concerning related photochemical studies, see: Hu, S-S.; Weber, W. F. *J. Organomet. Chem.* **1989**, *369*, 155.

0276-7333/91/2310-0954$02.50/0 © 1991 American Chemical Society

photochemical properties of transition-metal-substituted oligo- and polysilanes.[3,4] Previous studies in this arena have shown that the substituent (η^5-C_5H_5)Fe(CO)$_2$ (Fp) has a dramatic activating effect upon oligosilanes when directly bound to the silicon chain via a Fe–Si σ bond. Thus, in a series of Fp–oligosilane complexes, oligosilane isomerization and/or SiR_2 elimination reactions occur via the intermediacy of silylsilyleneiron complexes.[3] Furthermore, we have observed that when ferrocenyl (Fc) substituents are placed upon the silicon chain in high molecular weight polysilanes, a significant photochemical stability is imparted to the polymer.[4b] In order to better understand the different effects of these two distinct transition-metal substituents upon the photochemistry of oligo- and polysilanes, we are investigating the properties of disilanes, trisilanes, tetrasilanes, etc. containing the two metal substituents Fp and Fc. We now report the results of such an initial investigation on the disilane system $FpSiMe_2SiMe_2Fp$, $FpSiMe_2SiMe_2Fc$, and $FcSiMe_2SiMe_2Fc$.

Results and Discussion

The starting complexes $LMSiMe_2SiMe_2ML$, LM = (η^5-C_5H_5)Fe(CO)$_2$ (Fp) and (η^5-C_5H_5)Fe(η^5-C_5H_4) (Fc), are readily synthesized by the reactions outlined in eqs 1–4.[5-7,10a]

$$Fp^-Na^+ + ClSiMe_2SiMe_2Cl \xrightarrow{C_6H_{12}} \underset{X}{FpSiMe_2SiMe_2Cl} \quad (1)$$

$$2Fp^-Na^+ + ClSiMe_2SiMe_2Cl \xrightarrow{THF} \underset{I}{FpSiMe_2SiMe_2Fp} \quad (2)$$

$$Fc^-Li^+ + FpSiMe_2SiMe_2Cl \xrightarrow{THF} \underset{III}{FcSiMe_2SiMe_2Fp} \quad (3)$$

$$2Fc^-Li^+ + ClSiMe_2SiMe_2Cl \xrightarrow{THF} \underset{II}{FcSiMe_2SiMe_2Fc} \quad (4)$$

All the complexes are crystalline materials that may be handled in the air for short periods. Spectroscopic properties recorded in Table I are unexceptional, but as is usual with transition-metal-substituted silanes, ^{29}Si NMR spectroscopy is useful for characterization. Complex I should exhibit a single ^{29}Si resonance that is both α and β to the Fp group. From our previous studies this should exhibit a single resonance approximately 50 ppm downfield of $Me_3SiSiMe_3$, i.e. due to the sum of the α-effect of the Fp group (38 ppm) and the β-effect (12 ppm).[8] The observed resonance at 29.2 ppm indeed represents a shift ($\Delta\delta$) of 49 ppm. Similarly, the $\Delta\delta$ values observed for $FcSiMe_2SiMe_2Fc$, −3 ppm, and $FpSiMe_2SiMe_2Fc$, 35.8 ppm

Table I. Spectral Data for the Complexes[a,b]

	$FpSiMe_2SiMe_2Fp$ (I)
IR	ν(CO) 2001.6, 1992.1, 1944.9, 1936.5
^1H NMR	0.64 (12 H, s, $SiMe_2$); 4.27 (10 H, s, C_5H_5)
^{13}C NMR	6.68 ($SiMe_2$); 83.5 (C_5H_5); 216.6 (CO)
^{29}Si NMR	29.19
	$FcSiMe_2SiMe_2Fc$ (II)
^1H NMR	0.35 (12 H, s, $SiMe_2$); 4.03, 4.18 (18 H, m, Fc)
^{13}C NMR	−2.54 ($SiMe_2$); 68.4, 71.1, 73.4 (Fc)
^{29}Si NMR	−22.41
	$FpSiMe_2SiMe_2Fc$ (III)
IR	ν(CO) 1996.0, 1944.6
^1H NMR	0.55 (6 H, s, $SiMe_2$); 0.50 (6 H, s, $SiMe_2$); 4.07, 4.09, 4.11–4.13 (14 H, s, m, C_5H_5, Fc)
^{13}C NMR	−2.00 ($SiMe_2$); 3.81 ($SiMe_2$); 68.7, 69.6, 71.2, 73.4 (Fc); 83.3 (C_5H_5); 216.0 (CO)
^{29}Si NMR	16.3 (Fe–Si); −14.9 (Si–Fc)
	(η^5-C_5H_5)$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-SiMeSiMe$_3$) (IV)
IR	ν(CO) 2005.6, 1997.3 (sh), 1976.3, 1961.3, 1945.1, 1793.9, 1784.9
^1H NMR	0.33, 0.47 ($SiMe_3$); 1.28, 1.33 (μ-SiMe); 4.08, 4.12, 4.23, 4.40 (C_5H_5)
^{13}C NMR	0.98, 1.36, 1.97 ($SiMe_3$); 9.08, 10.8, 12.2 (μ-SiMe); 83.7, 84.6, 85.3, 88.6 (η^5-C_5H_5); 213.2, 213.8 (CO_{ter}), 274.3, 276.6 (CO_{bdg})
^{29}Si NMR	−6.72, −5.56, −4.70 ($SiMe_3$); 229.5, 239.6, 242.4 (μ-SiMe)
	$FcSiMe_2OMe$ (V)
IR	ν(Si–O–C) 1092.5
^1H NMR	0.33 (6 H, s, $SiMe_2$); 3.31 (3 H, s, OCH_3); 4.00, 4.06, 4.20 (9 H, m, Fc)
^{13}C NMR	−1.28 ($SiMe_2$); 50.4 (OCH_3); 68.5, 71.7, 73.7 (Fc)
^{29}Si NMR	10.7 (12.4)[c]
	$FpSiMe_2Fc$ (VI)
IR	ν(CO) 1995.7, 1943.0
^1H NMR	0.61 (6 H, s, $SiMe_2$); 4.08, 4.11, 4.13, 4.48 (14 H, s, m, C_5H_5, Fc)
^{13}C NMR	6.20 ($SiMe_2$); 68.7, 70.6, 72.2, 81.5 (Fc); 84.3 (C_5H_5); 215.95 (CO)
^{29}Si NMR	35.6
	$FcSiMe_2Fc$ (VII)
^1H NMR	0.50 (6 H, s, $SiMe_2$); 4.02, 4.19, 4.20 (18 H, m, Fc)
^{13}C NMR	−0.34 ($SiMe_2$); 68.7, 71.2, 71.8, 73.6 (Fc)
^{29}Si NMR	−7.00
	$FcSiMe_2Cl$ (VIII)
^1H NMR	0.62 (6 H, s, $SiMe_2$); 4.19, 4.39, 4.41 (9 H, m, Fc)
^{13}C NMR	3.24 ($SiMe_2$); 69.1, 72.1, 73.2 (Fc)
^{29}Si NMR	22.47
	$FcSiMe_2H$ (IX)
IR	ν(Si–H) 2118.0 (2112.1)[b]
^1H NMR	0.29 (6 H, d, $SiMe_2$, J = 3.6 Hz); 4.12, 4.22 (9 H, m, Fc); 4.66 (1 H, m, Si–H)
^{13}C NMR	−2.68 ($SiMe_2$); 68.75, 73.80, 74.11 (Fc)
^{29}Si NMR	−18.8
	$FpSiMe_2SiMe_2Cl$ (X)
IR	ν(CO) 2000.1, 1949.4
^1H NMR	0.57 (12 H, s, $SiMe_2$); 4.31 (5 H, s, C_5H_5)
^{13}C NMR	3.58 ($SiMe_2$); 3.63 ($SiMe_2$); 83.5 (C_5H_5); 215.3 (CO)
^{29}Si NMR	16.9 (Fe–Si); 28.5 ($SiMe_2Cl$)

[a] NMR spectra were recorded in C_6D_6 except V and IX, which were in $CDCl_3$. Values are in ppm. IR spectra were recorded in hexane. Values are in cm^{-1}. [b] IR spectrum recorded in methanol. [c] ^{29}Si NMR spectrum was recorded in 1:1 mixture by volume of C_6D_6 and CH_3OH.

---

(3) (a) Pannell, K. H.; Rice, J. R. *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) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (f) Ueno, K.; Tobita, H.; Simoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (g) Pannell, K. H.; Rozell, J. M.; Vincenti, S. P. In *Silicon-Based Polymer Science: A Comprehensive Resource*; Zeigler, J. M., Fearon, G. W., Eds.; Advances in Chemistry Series No. 224; American Chemical Society: Washington, DC, 1990.

(4) (a) Lin, J.; Wen, X.; Du, Z. *Shandong Daxue Xuebao, Ziran Kexueban* **1987**, *22*, 115; *Chem. Abstr.* **1988**, *108*, 56695w. (b) Pannell, K. H.; Rozell, J. M.; Zeigler, J. M. *Macromolecules* **1988**, *21*, 276.

(5) King, R. B.; Pannell, K. H.; Ishaq, M.; Bennett, C. R. *J. Organomet. Chem.* **1969**, *19*, 327.

(6) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1.

(7) Malisch, W. *J. Organomet. Chem.* **1974**, *82*, 185.

(8) Pannell, K. H.; Cervantes, J.; Parkanyi, L.; Cervantes-Lee, F. *Organometallics* **1990**, *9*, 859.

(9) Rausch, M. D.; Schloemer, G. C. *Org. Prep. Proc.* **1969**, *1*, 131.

(10) (a) Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Kondo, M. *J. Organomet. Chem.* **1972**, *43*, 293. (b) Kumada, M.; Kondo, T.; Mimura, K.; Yamamoto, K.; Ishikawa, M. *J. Organomet. Chem.* **1972**, *43*, 307. (c) Kondo, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1972**, *43*, 315.

(Fp–Si) and 4.6 ppm (SiFc), are in the expected ranges.

In general, the reactions of Fc^-Li^+ with the chlorosilanes discussed in this paper are modifications of literature procedures.[9,10a] In our hands the published procedures, although entirely reproducible, provided very low yield reactions (10%). This is almost certainly associated with the formation of the Fc^-Li^+ directly from FcH, under which conditions it is not possible to obtain only the monolithiated species, the dilithiated species $Fc^{2-}2Li^+$ being an important side product. The transmetalation reaction involving the use of (chloromercurio)ferrocene and *n*-butyllithium is far superior and resulted in yields of 60–70%, a most significant improvement.[11]

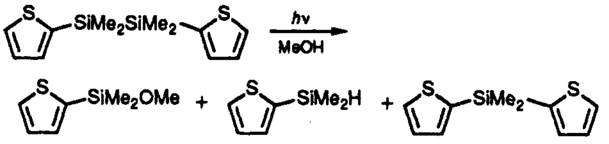
All three disubstituted complexes exhibit distinctive photochemical activity. In general ferrocene acts as a quencher of triplet states in many diverse systems.[12] With respect to the photochemistry of organosilicon compounds, we have previously established that the Fc group inhibits the photochemical reactivity of both polysilanes and acylsilanes.[4b,13] In keeping with these observations, II is photoinert in hydrocarbon solvents under a N_2 atmosphere. Thus, irradiation of a benzene solution of II for 25 h resulted in no apparent change when monitored by NMR spectroscopy. However, addition of methanol, e.g. 50% by volume, resulted in very slow loss of starting material and, as monitored by ^{29}Si NMR spectroscopy, the formation of a single product that exhibits a resonance at 12.4 ppm. No other material was observed. By independent synthesis (eq 5) this photoproduct was identified as $FcSiMe_2OMe$.

$$Fc^-Li^+ + Me_2SiCl_2 \xrightarrow{THF} FcSiMe_2Cl \xrightarrow{MeOH} FcSiMe_2OMe \quad (5)$$

Intensive study of the system showed that trace amounts of O_2 were responsible for the slow photochemical reaction. If O_2 was deliberately added to the system, the photochemical transformation occurred rapidly, <15 h, whereas extremely rigorous exclusion of O_2, and use of Ar as the inert atmosphere, resulted in the total absence of photochemical Si–Si bond cleavage. Such chemistry is reminiscent of the acid-catalyzed alcoholysis and oxidative alcoholysis of disilylferrocenes reported by Kumada et al.[10b,c] This group showed that ferrocene complexes containing a Si–Si bond are very prone to methanolysis in the presence of $FeCl_3$ and/or O_2/HCl. The requirement for both O_2 and HCl was suggested to be due to the formation of a ferrocenium ion intermediate that could activate the Si–Si bond with respect to methanolysis. No methanolysis occurred in the presence of only O_2, or only HCl, which is similar to our observation that both photolysis *and* O_2 are required for the formation of $FcSiMe_2OMe$. In our initial experiments with trace O_2 present we did not observe any coloration due to ferrocenium ion species; however, upon deliberate addition of O_2 pale green coloration was indeed observed during the photolysis. Complex II is stable in the dark under the conditions of the photolysis reactions, even with adition of O_2; however, extremely rapid methanolysis, <5 min, occurs when catalytic amounts of $FeCl_3$ are added to a methanol/benzene solution of II. It is clear therefore that the chemistry we observe is an oxidative methanolysis occurring under photolytic conditions.

$$FcSiMe_2SiMe_2Fc \xrightarrow[MeOH]{O_2/h\nu} 2FcSiMe_2OMe \quad (6)$$

Hu and Weber have observed that methnol reacts with 1,2-bis(2-thienyl)-1,1,2,2-tetramethyldisilane primarily via the photoexcited Si–Si bond to form the corresponding 2-thienyldimethylmethoxysilane and 2-thienyldimethylsilane, along with significant amounts of bis(2-thienyl)dimethylsilane (eq 7).[2]



(7)

We therefore anticipated formation of the related silane $FcSiMe_2H$ as a coproduct from our photochemical reaction; however, no such product was obtained. In a separate experiment, photolysis of $FcSiMe_2H$ under the same reaction conditions used for II, i.e. presence of O_2, caused its transformation to $FcSiMe_2OMe$ at a rate faster than the formation of $FcSiMe_2OMe$ from II. We observed no evidence for the formation of $FcSiMe_2Fc$ (VII), the complex that would be formed via the loss of $SiMe_2$, and in a separate experiment showed that this complex is stable under the photochemical conditions used. Since the photochemistry of 1,2-diphenyltetramethyldisilane and 1,2-bis(2-thienyl)tetramethyldisilane is both reported to yield R_2SiMe_2, R = Ph and 2-thienyl, our results represent a significant distinction between the two aromatic substituents, phenyl and thienyl, and the ferrocene substituent used in our study.

Overall the results observed for the 1,2-bis(ferrocenyl)-1,1,2,2-tetramethyldisilane system may be understood in terms of the reaction of methanol with the excited state of a ferroceniumyldisilane to form $FcSiMe_2OMe$.

By way of contrast the photolysis of complex I in hydrocarbon solvents, e.g. C_6D_6, proceeded smoothly and after 3.5 h greater than 80% of I had been transformed. The reaction is quite clean; only two major complexes were observed along with starting material. Via ^{29}Si NMR monitoring we noted a resonance at 41.2 ppm due to $FpSiMe_3$ and a series of resonances at −4.5, −5.5, −6.5, 229.5, 239.6, and 242.4 ppm due to the presence of the major product from this reaction, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$. This latter complex can exist as a pair of isomers, cis and trans, with respect to the orientation of the two cyclopentadienyl groups, with a further possible pair of isomers due to the orientation of the Me_3Si group, toward or away from the cis-cyclopentadienyl groups. Indeed, the spectral data indicate three isomers present. In an accompanying article Ogino and co-workers have determined the crystal structure of one of these isomers and examined the further photochemistry of the new complex.[14]

The formation of the μ-$SiMeSiMe_3$ complex agrees with the general mechanism we have proposed for the photochemical expulsion of SiR_2 groups from Fp–disilane complexes and, with reference to the present system, is outlined in Scheme I. The results also demonstrate the lability of the Si–Si bond in I suggested by the recent structural analysis, which exhibited a long Si–Si bond in this complex.[8] We also observe significant but minor production of $FpSiMe_3$ upon photolysis, an observation not made by the Ogino group. We are unable to resolve this distinction at the present time, but it may be due to the

---

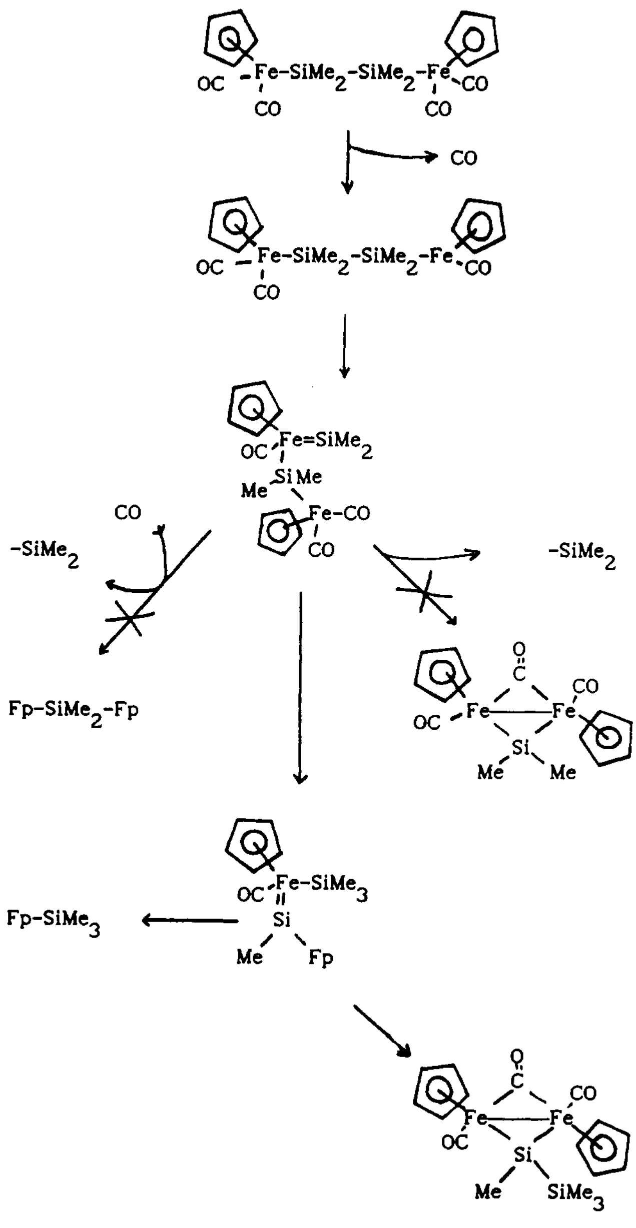
(11) Seyferth, D.; Hofmann, H. P.; Burton, R.; Helling, J. F. *Inorg. Chem.* **1962**, *1*, 227.

(12) (a) Kikuchi, M.; Kikuchi, K.; Kokubun, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1331. (b) Karmilo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575.

(13) Sharma, H. K.; Vincenti, S. P.; Vicari, R.; Cervantes-Lee, F.; Pannell, K. H. *Organometallics* **1990**, *9*, 2109.

(14) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics*, following paper in this issue.

Scheme I



wavelength distribution of our respective photolytic equipment. We are attempting to study this matter in more detail.

The formation of the μ-silyl complex is in accord with several previous studies by the Malisch[15] and Curtis[16] groups. Both have observed the formation of cis- and trans-mono(μ-silyl)(germyl) complexes upon photochemical treatment of complexes of the type LM–ER$_2$–ML, LM = (η^5-C$_5$H$_5$)Fe(CO)$_2$, Mn(CO)$_5$, etc., and E = Si and Ge. Furthermore, there are many examples of bis(μ-silyl)(germyl) complexes of tungsten, rhenium, and ruthenium in the literature.[17]

From Scheme I one may see that the recombination of the Si–Si bond from the intermediate silyl–silylene complex FpMeSi=Fe(CO)(SiMe$_3$)(η^5-C$_5$H$_5$) is the most favored reaction, with only minor products derived from loss of the coordinated silylene species, i.e. FpSiMe$_3$. No loss of SiMe$_2$ seems to occur from the isomeric intermediate Me$_2$Si=Fe(CO)(SiMe$_2$Fp)(η^5-C$_5$H$_5$). This is reminiscent of the chemistry of the systems (η^5-C$_5$H$_5$)Fe(CO)(=SiMeR′)SiR$_3$, where R′ = Me$_3$Si and Me$_5$Si$_2$, which we have recently reported lead to isomerized Fp–oligosilanes, e.g. eqs 8a,b.[3d]

$$\mathrm{FpSiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSiMe(SiMe_3)_2} \quad (8a)$$

$$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSi(SiMe_3)_3} \quad (8b)$$

The re-formation of the Si–Si bond reported herein for complex I is the first example of such a re-formation for an Fp–disilane. Other studies in our laboratory have shown that changing the η^5-C$_5$H$_5$ ligand for the η^5-C$_9$H$_7$, π-indenyl, ligand results in a similar recombination in (η^5-C$_9$H$_7$)Fe(CO)$_2$–disilanes leading to isomerization reactions. These results, illustrated in eq 9, will be the focus of a future publication.

$$(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Fe(CO)_2SiMePhSiMe_3} \rightarrow (\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Fe(CO)_2SiMe_2SiMe_2Ph} \quad (9)$$

The photochemistry of the mixed-metal-substituted disilane III, FpSiMe$_2$SiMe$_2$Fc, is dominated by the capacity of the Fp system to photoeject a CO ligand, thereby activating the disilane ligand. Two major products are observed from photochemical treatment of III, FpSiMe$_2$Fc, VI, and FpSiMe$_3$ (eq 10). Both complexes are stable

$$\mathrm{FpSiMe_2SiMe_2Fc} \xrightarrow{h\nu} \mathrm{FpSiMe_2Fc}\ (75\%) + \mathrm{FpSiMe_3}\ (25\%) \quad (10)$$

under the reaction conditions, i.e. photochemical treatment for 2–4 h, but prolonged irradiation leads to Fe–Si bond cleavage as determined by the formation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$. No stabilization of the Si–Si bond is imparted by the Fc group in this system. The fate of the silicon-containing portion of the complexes is unknown at this time.

The mixed-metal silane VI was conveniently synthesized by a more direct method for further proof of structure (eq 11).

$$\mathrm{FcSiMe_2Cl} + \mathrm{Fp^-Na^+} \xrightarrow{\mathrm{THF}} \mathrm{FpSiMe_2Fc} + \mathrm{NaCl} \quad (11)$$

Photolysis of FpSiMe$_2$SiMe$_2$Cl in inert solvents is also a facile process and would be expected to lead to two major Fp products, FpSiMe$_3$ and FpSiMe$_2$Cl. As monitored by ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy, these two products are obtained in the ratio 1:4. Trace amounts of (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl are also observed via infrared monitoring [ν(CO) (THF) 2045, 1980 cm^{-1}]; however, we made no attempt to isolate this complex.

It is becoming clear that the photochemistry of disilane groups bonded to the Fp system exhibit a range of chemistry dependent upon the nature of the other groups attached to the disilane. This is partially understandable in the light of recent observations by the Turner group that suggest the loss of SiMe$_2$ from the intermediate silyl–silylene complex (η^5-C$_5$H$_5$)Fe(CO)(=SiMe$_2$)SiMe$_3$ is a photochemical event; i.e., in the dark it is a stable species in the presence of both excess CO and PPh$_3$.[18]

From the various results obtained above, and also from the results previously published using the general system (η^5-C$_5$H$_5$)Fe(CO)$_2$Si$_2$Ph$_n$Me$_{5-n}$,[3b] it seems that when FpSiMe$_3$ is one of the expected products from SiR$_2$ expulsion from Fp–disilane complexes, the yield obtained is generally lower than the alternative FpSiR$_3$ complexes.

---

[15] Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120.

[16] Job, R. C.; Curtis, M. D. *Inorg. Chem.* **1973**, *12*, 2514.

[17] (a) Henken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747. (b) Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1977**, *16*, 2321. (c) *Ibid.* **1977**, *16*, 2325. (d) Bennett, M. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156. (e) Elder, M. *Inorg. Chem.* **1970**, *9*, 762.

[18] Haynes, A. Ph.D. Thesis, University of Nottingham. We wish to thank Dr. Jim Turner for a copy of this Thesis prior to publication.

This suggests that when the various silyl–silylene intermediate complexes involve an equilibrium between $Fe{=}SiMe_2$ and $Fe{=}SiMeR$, R = Ph, Fc, and Cl, it is the $SiMe_2$ group that is preferentially lost upon recoordination of the CO ligand, although that is clearly not true for the system studied here where R = Fp. This observation may be of use in devising strategies for the isolation of pure silylene complexes of the type $LM{=}SiR_2$.

Experimental Section

All reactions were performed in dry, oxygen-free solvents in atmospheres of N_2 or Ar. Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2{}^-Na^+$,[19] $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4){}^-Li$,[11] $ClSiMe_2SiMe_2Cl$,[20] $FpSiMe_2SiMe_2Cl$,[7] and $FpSiMe_2SiMe_2Fp$[5] were performed by using literature procedures. Starting silicon compounds Me_2SiCl_2 and Me_2SiHCl were purchased from Petrarch Systems, Inc. Transition-metal complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and (chloromercurio)ferrocene were purchased from Strem Chemicals.

NMR spectra were recorded on a Bruker NR 200 MHz spectrometer, and IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of $FcSiMe_2SiMe_2Fc$ (II). To a stirred solution of 1,2-dichlorotetramethyldisilane (1.4 g, 7.5 mmol) in 25 mL of THF at −25 °C was added slowly a 60-mL solution of ferrocenyllithium obtained from 6.3 g (15 mmol) of (chloromercurio)ferrocene. The reaction mixture was stirred at this temperature for 30 min and then brought to room temperature and stirred for 20 h. The solvent was removed, the orange residue was extracted with 50 mL of hexane, and the mixture was filtered. The filtrate was concentrated, and vacuum sublimation of the residue at 50 °C (0.2 mmHg) removed the impurity of Bu_2Hg. The residue was recrystallized from hexane to yield orange crystals of II, 1.05 g (29%), mp 124–125 °C. Anal. Calcd for $C_{24}H_{30}Fe_2Si_2$: C, 59.21; H, 6.16. Found: C, 59.58; H, 6.32.

Synthesis of $FpSiMe_2SiMe_2Fc$ (III). To 60 mL of a cooled (0 °C) THF solution of ferrocenyllithium, obtained from 2.0 g (4.75 mmol) of (chloromercurio)ferrocene, was added dropwise 1.56 g (4.75 mmol) of $FpSiMe_2SiMe_2Cl$ in 15 mL of THF. The solution was stirred at 0 °C for 1 h, permitted to warm to room temperature, and stirred for 20 h. The solvent was removed under vacuum, the residue was extracted with 50 mL of hexane, and the mixture was filtered. The filtrate, after concentration to 10 mL, was placed upon silica gel column, 2.5 × 25 cm. Elution with hexane yielded an orange yellow band, which was collected. After removal of the solvent, an orange liquid was obtained, which also had an impurity of Bu_2Hg that was removed by vacuum sublimation at 50 °C (0.2 mmHg). The residue was recrystallized from 80:20 hexane/methylene chloride solvent mixture to give orange-yellow crystals of III, 0.86 g (38%), mp 104 °C. Anal. Calcd for $C_{21}H_{28}Fe_2O_2Si_2$: C, 52.72; H. 5.44. Found: C, 53.09; H, 5.68.

Synthesis of $FpSiMe_2Fc$ (VI). To 60 mL of a THF solution of $[\eta^5\text{-}C_5H_5Fe(CO)_2]^-Na^+$ obtained from 1.0 g (2.82 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ was added dropwise 1.65 g (5.92 mmol) of $FcSiMe_2Cl$ (VIII) in 10 mL of THF at −25 °C. After 30 min the temperature was raised to room temperature and the reaction mixture was stirred for an additional 18 h. The solvent was removed under vacuum, and the residue was extracted with 50 mL of hexane. Salts were filtered off, and the filtrate was concentrated to 10 mL and chromatographed on a silica gel column (2.6 × 20 cm). Elution with hexane produced a yellow band, which gave 0.12 g of ferrocene. The second fraction produced an orange-yellow band, which after removal of solvent gave an orange-yellow solid that was recrystallized from 90:10 hexane/methylene chloride solvent mixture to yield orange crystals of VI, 1.38 g (58%), mp 101–102 °C. Anal. Calcd for $C_{19}H_{20}Fe_2O_2Si$: C, 54.28; H, 4.76. Found: C, 54.20; H, 4.72.

Synthesis of $FcSiMe_2Cl$ (VIII). Ferrocenyllithium, prepared from 6.3 g (15 mmol) of (chloromercurio)ferrocene and 31.0 mmol of *n*-butyllithium in 60 mL THF, was added slowly and dropwise at −25 °C to 7.8 g (60.5 mmol) of Me_2SiCl_2 in 20 mL of THF. The mixture was stirred for 30 min and then allowed to stir at room temperature for 20 h. Excess of Me_2SiCl_2 and solvent were removed under vacuum, the orange slurry was extracted with hexane (50 mL), and the mixture was filtered. The solvent was evaporated from the filtrate, and the resulting red oil was distilled through a small column. A trace amount of ferrocene that had sublimed into the distillation head was removed. Two fractions were collected, the first of which was light orange in color composed of di-*n*-butylmercury together with traces of ferrocene, bp 61–62 °C/0.5 mmHg. The second fraction produced VIII as a dark red oil, bp 98–100 °C/0.5 mmHg (3.25 g, 78%) [lit.[9] bp 135–138 °C/1.5 mmHg (yield 10%)].

Synthesis of $FcSiMe_2Fc$ (VII). To 10 mL of a THF solution of VIII (1.5 g, 5.4 mmol) at −25 °C was added slowly, with vigorous stirring, 40 mL of ferrocenyllithium, prepared from 2.26 g (5.4 mmol) of (chloromercurio)ferrocene and 11.0 mmol of *n*-butyllithium. The addition was conducted over a period of 45 min. The mixture was stirred for 30 min and then allowed to warm to room temperature. After the mixture was stirred for an additional 20 h, the solvent was evaporated and the resulting orange slurry was extracted with 40 mL of hexane. Lithium chloride was filtered off and the filtrate concentrated to 10 mL. Chromatography of resulting orange oil on silica gel column, 2 × 10 cm, with hexane produced first a small amount of ferrocene and a second band that produced an orange solid, which after recrystallization from hexane gave 1.10 g (48% yield) of the desired compound, mp 76 °C. Anal. Calcd for $C_{22}H_{24}Fe_2Si$: C, 61.68; H, 5.60. Found: C, 61.45; H, 5.53.

Synthesis of $FcSiMe_2H$ (IX). Ferrocenyllithium prepared from 6.3 g (15 mmol) of (chloromercurio)ferrocene and 31.0 mmol of *n*-butyllithium in 60 mL of THF was added dropwise to 2.01 g (21.3 mmol) of dimethylchlorosilane in 15 mL of THF at −25 °C. The solution was permitted to warm to room temperature and stirred for 20 h. Workup as described above produced 2.4 g (66%) of the dark red liquid ferrocenyldimethylsilane (IX), bp 65–66 °C/0.5 mmHg [lit.[9] bp 160 °C/19 mmHg (yield 11%)].

Synthesis of $FcSiMe_2OMe$ (V). At 0 °C, a solution 0.74 g (23 mmol) of methanol in 10 mL THF was added over a period of 40 min with stirring to a solution of 2.06 g (7.4 mmol) of $FcSiMe_2Cl$ (VIII) and 0.75 g (7.4 mmol) of triethylamine dissolved in 40 mL of THF. A white precipitate of triethylamine hydrochloride started separating immediately. After the mixture was stirred for 2 h at room temperature, the solvent was evaporated and 20 mL of hexane was added to complete precipitation of triethylamine hydrochloride. After filtration the solvent was evaporated and the resulting oil was distilled through a small column to produce ferrocenyldimethylmethoxysilane (X), bp 104–106 °C/2 mmHg (1.12 g, 55%) [lit.[10a] bp 102–105 °C/2 mmHg (5.4% yield)].

Photochemical Treatment of Complexes. Photolyses were performed by using a 450-W Hanovia medium-pressure mercury lamp on degassed solutions in hexane, C_6D_6, or mixtures of MeOH and C_6D_6 solutions, either in Pyrex NMR tubes or in quartz test tubes. Argon atmospheres were used in preference to N_2.

Photolysis of I. In a typical reaction $FpSiMe_2SiMe_2Fp$ (I) (0.3 g, 0.64 mmol) in 2 mL of C_6D_6 was irradiated and the reaction monitored by ^{29}Si NMR spectroscopy, and after 4 h all the starting material was consumed. The solvent was removed under vacuum, the residue was extracted in hexane, and the mixture was placed upon a silica gel column (1 × 5 cm). Elution with hexane produced first a yellow band, which on collection yielded $FpSiMe_3$, 35 mg (22%), and a second yellow band that was eluted with 50:50 mixture of hexane/methylene chloride and produced traces of an unidentified yellow oil [IR ν(CO) (hexane) 1988 cm^{-1}]. Finally, a red band was eluted with pure methylene chloride, which on evaporation yielded 120 mg (43%) of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$, mp 140 °C. Anal. Calcd for $C_{17}H_{22}Fe_2O_3Si_2$: C, 46.2; H, 5.02. Found: C, 46.8; H, 5.45.

Photolysis of $FpSiMe_2SiMe_2Fc$ and $FpSiMe_2SiMe_2Cl$. A 0.1–0.15-g sample in 1 mL of C_6D_6 was irradiated for 1 h in a Pyrex NMR tube. The reaction was monitored by ^{29}Si NMR spectroscopy. The spectral data of various monosilyl complexes formed were compared with authentic complexes.

Photolysis of II. A solution of II, 0.22 g (0.45 mmol), was dissolved in 2 mL of C_6D_6 in a quartz tube and irradiated over

---

(19) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(20) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493.

a period of 25 h. No reaction was observed.

In a second experiment, 0.31 g (0.64 mmol) of II was dissolved in a mixture of 2 mL of C_6D_6 and 2 mL of MeOH in a quartz tube and the solution photolyzed under an argon atmosphere. The reaction was monitored by ^{29}Si NMR and IR spectroscopy. After 54 h no new products were observed. When the reaction was repeated under an O_2 atmosphere with O_2-saturated solvents, all the starting material had disappeared after 15 h and the ^{29}Si NMR spectrum exhibited a single new resonance at 12.4 ppm assignable to $FcSiMe_2OMe$ (V).

Photolysis of IX. A 0.12-g (0.49-mmol) sample of IX in a mixture of 1 mL of C_6D_6 and 1 mL of MeOH in a quartz tube was photolyzed over a period of 32 h under scrupulously O_2-free conditions. IR and ^{29}Si NMR monitoring of the reaction showed that no reaction occurred. When the reaction was repeated in an O_2 atmosphere complete conversion to V was observed.

Acknowledgment. Support of this research by the Robert A. Welch Foundation and the NSF (Grant RII-88-02973), via establishment of a Minority Research Center of Excellence in Materials Science, is gratefully acknowledged. K.H.P. thanks Professor M. Kumada for enjoyable and valuable discussions and suggestions.

Photochemical Conversion of a Disilanylene-Bridged Iron Dimer to Silylene-Bridged Iron Dimers

Keiji Ueno, Nagato Hamashima, Mamoru Shimoi, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

Received June 27, 1990

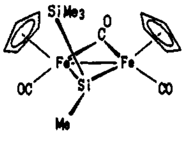
Photolysis of $FpSiMe_2SiMe_2Fp$ (Fp = $CpFe(CO)_2$; Cp = η-C_5H_5) in C_6D_6 afforded, in the early stages of photolysis, a mixture of the geometric isomers $[CpFe(CO)]_2(\mu\text{-}CO)\{\mu\text{-}SiMe(SiMe_3)\}$ and $[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$ (a small amount). Prolonged photolysis gave *cis*- and *trans*-$[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$ almost quantitatively. The structure of a geometric isomer of $[CpFe(CO)]_2(\mu\text{-}CO)\{\mu\text{-}SiMe(SiMe_3)\}$ was determined by X-ray crystallography. Crystal data: $C_{17}H_{22}Fe_2O_3Si_2$, triclinic in the space group $P\bar{1}$, a = 9.555 (3) Å, b = 14.031 (3) Å, c = 7.986 (2) Å, α = 91.18 (3)°, β = 113.56 (3)°, γ = 101.72 (3)°, V = 955.5 (4) Å^3, Z = 2, and $R(F_o)$ = 0.040 for 3792 reflections with $|F_o| > 3\sigma(F_o)$.

Introduction

Photolytic rearrangement of disilanyliron complexes $FpSi_2R_5$ (Fp = $CpFe(CO)_2$; Cp = η-C_5H_5; R = alkyl, aryl) has been proposed to proceed via a mechanism containing silyl(silylene)iron complexes $CpFe(CO)(SiR_3)(=SiR_2)$ as key intermediates.[1,2] Rapid alkyl or aryl scrambling (1,3-alkyl or -aryl migration) occurs in the silyl(silylene)iron intermediates. The proposed mechanism has been strongly supported by the observation that isomeric $FpSi_2R_5$ compounds produce the same relative proportions of $FpSiR_3$[1d,e] and also our recent study on the photolysis of alkoxy-substituted disilanyliron complexes $FpSi_2R_{5-m}(OR)_m$, which leads to the formation of the alkoxy-bridged bis(silylene)iron complexes.[3] This paper describes the photolysis of $FpSiMe_2SiMe_2Fp$ (1).[4] Judging from the findings accumulated for the photolysis of disilanyliron complexes, several products had been expected to be formed as follows: $FpSiMe_3$, $FpSiMe_2Fp$, and/or $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}SiMe_2)$. However, actual photolysis did *not* give these products *at all* but $[CpFe(CO)]_2(\mu\text{-}CO)\{\mu\text{-}SiMe(SiMe_3)\}$ (2) and $[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$ (3).

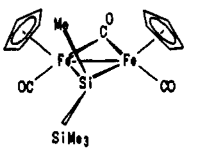
Results and Discussion

A C_6D_6 solution of 1 in a flame-sealed Pyrex NMR tube was irradiated by using a 450-W medium-pressure Hg lamp. The ^1H NMR spectral change upon the irradiation is shown in Figure 1. The spectrum obtained after 2 h irradiation (Figure 1b) shows that 1 disappears almost completely. In turn, all possible geometrical isomers for 2 (2a–c) are formed. Figure 1b also shows the formation of small amounts of 3a and 3b. Further irradiation results



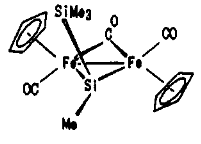
cis-SiMe$_3$

2a



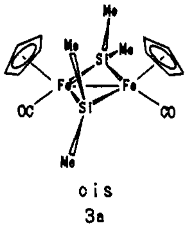
cis-Me

2b



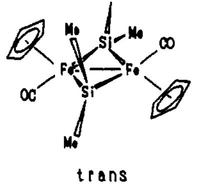
trans

2c



cis

3a



trans

3b

---

(1) (a) Pannell, K. H.; Rice, J. R. *J. Organomet. Chem.* **1974**, *78*, C35. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (c) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777. (d) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797. (e) Pannell, K. H.; Rozell, J. M., Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (f) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (g) Pannell, K. H.; Rozell, J. M., Jr.; Vincenti, S. *Adv. Chem. Ser.* **1990**, *No. 224*, 329.

(2) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550.

(3) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

(4) Pannell and Sharma also report the photolysis of $FpSiMe_2SiMe_2Fp$: Pannell, K. H.; Sharma, H. *Organometallics*, preceding paper in this issue.

0276-7333/91/2310-0959$02.50/0