7). Thus, the photochemical reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R′Br produces R′·, $[RCo(bpy)_2]^+$, and RBr (eq 7).[43] The benzyl and allyl radicals give mainly the coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) together with small amounts of byproducts derived from the hydrogen abstraction from a solvent (toluene and propene, respectively) as shown in Table II. The carbanion ligand in $[RCo(bpy)_2]^+$ may react readily with R′Br to produce the more stable carbanion ligand, and $[R'Co(bpy)_2]^+$ thus formed may undergo the coupling reaction with R′Br to yield R′–R′ and $[Co(bpy)_2Br]^+$. $[RCo(bpy)_2Br]^+$ may also participate in a cross-coupling reaction with R′Br, which is shown by the broken line in Scheme II, yielding R–R′ as a minor byproduct (ethylbenzene, propylbenzene, 1-butene, and 1-pentene for the *cis*-$[Me_2Co(bpy)_2]^+$–$PhCH_2Br$, *cis*-$[Et_2Co(bpy)_2]^+$–$PhCH_2Br$, *cis*-$[Me_2Co(bpy)_2]^+$–C_3H_5Br, and *cis*-$[Et_2Co(bpy)_2]^+$–C_3H_5Br systems, respectively). According to Scheme II, the stoichiometry of the photoredox reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R′Br is 1:3 (eq 5), in contrast with the case in Scheme I.

The photoredox reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with allyl bromide (Scheme III) is the most complicated case, where the photocleavage reaction occurs to give $[PhCH_2Co(bpy)_2]^+$, which can undergo the exchange, coupling, and cross-coupling reactions with comparable rates, because of similar stabilities between the benzyl and allyl anions to yield 1,2-diphenylethane and 1,5-hexadiene as the homocoupling products as well as 4-phenyl-1-butene as the cross-coupling product (Table II). According to Scheme III, the stoichiometry is 1:1 as the case of Scheme I.

In conclusion, the photocleavage of the cobalt–carbon bond of *cis*-dialkylcobalt(III) complexes produces monoalkylcobalt(II) complexes as reactive intermediates in which the alkyl group has carbanion character, inducing the facile reduction of benzyl and allyl bromides to yield coupling and cross-coupling products depending on the stabilities of the carbanion ligands.

Registry No. *cis*-$[Me_2Co(bpy)_2]^+$, 71697-34-2; *cis*-$[Et_2Co(bpy)_2]^+$, 71697-32-0; *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, 104013-21-0; *trans*-$[Me_2Co(DpnH)]$, 105900-07-0; $[MeCo(DH)_2py]$, 23642-14-0; $[EtCo(DH)_2py]$, 25360-57-0; $PhCH_2Br$, 100-39-0; C_3H_5Br, 106-95-6; PhC_2H_4Ph, 103-29-7; C_6H_{10}, 592-42-7; PhC_4H_7, 768-56-9; $PhCH_3$, 107-35-7.

---

[43] In the initial photochemical step in eq 7, the β-elimination pathway may also give the same species as the homolytic pathway by the facile reaction with R′Br in the presence of water, since the β-elimination pathway may be regarded as β-hydrogen transfer between the geminate radical pair following the homolytic cleavage of the cobalt–carbon bond; see: Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* 1982, *104*, 623. However, the detailed mechanism is not clear at present.

Low-Temperature Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$: Establishment of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the Intermediate in the Rearrangement of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$

Claudia Lewis Randolph and Mark S. Wrighton*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 3, 1986

Near-UV (355-nm) photolysis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in alkane solution under 1 atm of CO or saturated with PPh_3 results in the nearly quantitative formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ (L = CO, PPh_3). The intermediate in this rearrangement is shown to be $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ by low-temperature IR, UV–vis, and NMR studies. Near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 77 K in a 1-pentene or 2-methyltetrahydrofuran matrix results in loss of CO as evidenced by the growth of an IR absorption due to free CO at 2132 cm^{-1}. A 16e $(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2SiMe_2H$ cannot be trapped by the donor matrices, nor can it be detected under any conditions used. Rather, even at 77 K the β-H is transferred from the Si to the Fe as evidenced by the decline of the IR absorption at 2101 cm^{-1} associated with the Si-H bond. Although β-H transfer is the major photoprocess in alkane matrices at 77 K, the direct rearrangement of approximately 20% of the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is evidence for radical formation as a minor primary photoprocess. The $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ resulting from β-H transfer is inert up to 225 K. The ^1H NMR of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ indicates that the complex is not fluxional even at the highest temperature at which it is chemically inert. This finding is consistent with the formulation of the $M(CH_2SiMe_2)$ unit as a metallasilacyclopropane. Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in a 1 M PEt_3 alkane solution at 200 K results only in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$. Warming of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ to 225 K in the presence of 1 atm of CO or PEt_3 results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ (L = CO, PEt_3). The results confirm that $M(CH_2SiMe_2)(H)$ complexes are intermediates in the conversion of $M–CH_2SiMe_2H$ complexes to $M–SiMe_3$ complexes.

We would like to report the establishment of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the intermediate in the rearrangement of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (eq 1 and 2). A similar intermediate

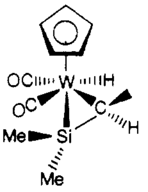
0276-7333/87/2306-0365$01.50/0 © 1987 American Chemical Society

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H \xrightarrow[77 \text{ or } 196 \text{ K}]{h\nu} (\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H + CO \quad (1)$$

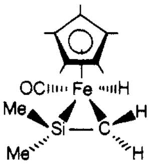
$$(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H \xrightarrow[CO]{225 \text{ K}} (\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 \quad (2)$$

has been proposed in the rearrangement of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$.[1] The lability of other $M\text{-}CH_2SiMe_2H$ complexes[2] has also been attributed to the presence of a reactive Si–H bond in the β-position.[3]

The reaction intermediates in photochemically induced β-H elimination from $(\eta^5\text{-}C_5R_5)W(CO)_3$(alkyl) complexes have been characterized by low-temperature matrix-isolation techniques[4] and by monitoring of the thermal chemistry which occurs upon warming of the matrix. These reaction intermediates include 16e $(\eta^5\text{-}C_5R_5)W(CO)_2$(alkyl) complexes formed via loss of CO at 77 K and, for alkyls containing β-H's, *trans*-$(\eta^5\text{-}C_5R_5)W(CO)_2$(alkene)H formed upon warming of the matrix to 196 K.[4a] More recently *cis*-$(\eta^5\text{-}C_5R_5)W(CO)_2$(alkene)H has been detected from irradiation of the parent tricarbonyls at 12 K.[4] We have employed similar matrix-isolation techniques to study photoinduced β-H transfer from $M\text{-}CH_2SiMe_2H$[5] complexes with the aim of characterizing a metal silaethylene complex. Preliminary results have been published including the characterization of *cis*-$(\eta^5\text{-}C_5R_5)W(CO)_2(CH_2SiMe_2)H$ (R = H, Me).[5] The $W(CH_2SiMe_2)$ unit was characterized as a metallasilacyclopropane (I) without Si–C multiple-bond character. We now report the establishment of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the intermediate in the photochemical rearrangement of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (eq 1 and 2). It is important to note that analogous $(\eta^5\text{-}C_5Me_5)Fe(CO)$(alkene)H complexes have been postulated as reaction intermediates but have not been fully characterized.[6] As in the *cis*-$(\eta^5\text{-}C_5R_5)W(CO)_2(CH_2SiMe_2)H$ complexes,[5] the bonding of the $Fe(CH_2SiMe_2)$ fragment is proposed to be a metallasilacyclopropane (II).



I



II

Experimental Section

Materials. Tetrahydrofuran (THF, reagent grade, MCB) and hexanes (HPLC grade, Baker) were freshly distilled under N_2 from CaH_2. Methylcyclohexane (MCH, Photorex grade, Baker) and 2-methyltetrahydrofuran (2-MeTHF, reagent grade, Aldrich) were freshly distilled from Na under Ar. $ClCH_2SiMe_2Cl$ (Petrarch) and $BrSiMe_3$ (Petrarch) were distilled under Ar prior to use. PPh_3 (Aldrich) was recrystallized from absolute EtOH prior to use. $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (Pressure Chemical) and toluene-d_8 (99.5%, Crescent) were used as received.

Instrumentation. IR spectra were recorded by using either a Nicolet 7199 or a Nicolet 60SX Fourier transform spectrometer. All IR band positions are ± 1 cm^{-1}; spectra were recorded at 2-cm^{-1} resolution. NMR spectra were recorded on either a Bruker 250- or Bruker 270-MHz Fourier transform spectrometer. UV–vis spectra were recorded on either a Cary 17 or Hewlett-Packard Model 8451 A diode array spectrometer.

Irradiations. Irradiations of IR spectroscopy samples were performed by using a Bausch and Lomb SP 200W high-pressure Hg lamp equipped with a Pyrex filter and a 10-cm water filter to suppress IR and short wavelength UV emissions. A Hanovia 550-W medium-pressure Hg lamp was used for the irradiation of NMR samples. Quantum yields at 366 nm were measured by using a merry-go-round[7] with a Hanovia 550-W medium-pressure Hg lamp equipped with Corning glass filters to isolate the 366-nm Hg emission. Ferrioxalate actinometry[8] was used to determine light intensity, typically $\sim 10^{-7}$ einstein/min incident on the 13 × 100 mm Pyrex ampules containing 3.0 mL of the sample.

Low-Temperature Spectra. Low-temperature IR and UV–vis spectra were obtained by using a Precision Cell, Inc., Model P/N 2100 variable-temperature cell with CaF_2 windows. Liquid N_2 or dry ice/acetone were used as coolants. NMR samples were prepared by irradiating the sample in an NMR tube immersed in dry ice/acetone bath contained in a quartz Dewar. The samples were removed from the dry ice/acetone bath and immediately transferred to the cooled probe of the NMR spectrometer.

Syntheses. All manipulations of organometallic complexes were carried out under Ar by using a Vacuum Atmospheres drybox or conventional Schlenk line techniques. $ClCH_2SiHMe_2$ was prepared by a modification of the published synthesis of $ClCH_2SiH_3$.[9] THF solutions of $Na^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$ were prepared by stirring THF solutions of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ over fresh Na for 24 h. Suspended Na was removed from the solution by filtration.

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2)CH_2SiMe_2H$ was synthesized by adding a twofold excess of $ClCH_2SiMe_2H$ to a 100 mL of THF solution of $\sim$0.01 M $Na^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$ and stirring at room temperature for no more than 30 min. Longer reaction times resulted in the rearrangement of the product to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. THF was removed by vacuum and the brown residue extracted with hexanes. The extract was filtered and concentrated. The resulting $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ was purified by passing it through a short Al_2O_3 column (no longer than 3 in.). The yellow product band was eluted with hexanes. Solid $(\eta^5\text{-}C_5Me_5Fe(CO)_2CH_2SiMe_2H$ was isolated by removal of the solvent under vacuum. An NMR of the solid dissolved in toluene-d_8 showed the compound to have some organic impurities. Further purification of the compound by sublimation resulted in removal of organic impurities, but partial ($\sim$5%) rearrangement of the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ also

---

[1] (a) Pannell, K. H. *J. Organomet. Chem.* **1970**, *21*, 17. (b) Bulkowski, J. E.; Miro, N. D.; Sepelak, D.; Van Dyke, C. H. *J. Organomet. Chem.* **1975**, *101*, 267.

[2] For a review of the chemistry of $MSiMe_3$ and MCH_2SiMe_2H complexes see: Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *No. 2*, 253.

[3] Cundy, C. S.; Lappert, M. F.; Pearce, R. *J. Organomet. Chem.* **1973**, *59*, 161.

[4] (a) Wrighton, M. S.; Kazlauskas, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 6005; **1980**, *102*, 1727. (b) Alt, H. G.; Eichner, M. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 78. (c) Mahmoud, K. A.; Narayanaswamy, R.; Rest, A. J. *J. Organomet. Chem.* **1981**, *222*, C9. (e) Klein, B.; Kazalauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 1338. (f) Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175. (g) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 761. (h) Mahmoud, K. A. Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1984**, 187. (i) Alt, H. G.; Mahmoud, K. A.; Rest, A. S. *J. Organomet. Chem.* **1983**, *246*, C37.

[5] Lewis, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 7768.

[6] (a) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. (b) Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. (c) Randolph, C. L.; Wrighton, M. S., unpublished results.

[7] Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

[8] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, 235.

[9] Kaesz, H. D.; Stone, F. G. A. *J. Chem. Soc.* **1957**, 1433.

Table I. IR and UV-Vis Spectral Data for Relevant Complexes

complex	solv	T, K		ν(CO), cm^{-1} (ϵ, M^{-1} cm^{-1}, or rel abs)	UV-vis, nm (ϵ, M^{-1} cm^{-1})
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$	MCH	298		2100 (300)	365 (970)
				1991 (5700)	240 (4400)
				1938 (6300)	250 (sh) (~9100)
		196	ν(Si–H)	2102	
				1990	
				1937	
		77	ν(Si–H)	2103 (360)	363
				1988 (6500)	363
				1934 (7600)	
	2-MeTHF	198	ν(Si–H)	2097	
				1985 (0.9)	
				1930 (1.0)	
		77	ν(Si–H)	2092	
				1977	
				1919	
	1-pentene	298	ν(Si–H)	2101	
				1991 (0.9)	
				1938 (1.0)	
		77	ν(Si–H)	2101	
				1985	
				1929	
$(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$	MCH	77		1922	405, 325 (sh)
		196		1925	
	2-MeTHF	77		1907	
	1-pentene	77		1917	
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$	MCH	298		1980 (6500)	250 (sh) (~9400)
				1927 (7900)	285 (5000)
					333 (1900)
		77		1978 (0.8)	
				1921 (1.0)	
	1-pentene	298		1979	
				1925	
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$	MCH	298		1895	
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PEt_3)SiMe_3$	MCH	298		1892	
$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$	MCH	298		1929 (14700)	533 (1500)
				1962 (8150)	420 (3000)
					362 (10100)

Table II. NMR Data for Relevant Complexes[a]

complex	temp, K	^{1}H,[b] δ	^{13}C,[b,c] δ
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$	298	C_5Me_5, 1.41 (15 s)	CO, 219.5
		$SiMe_2$, 0.37 (6, d, J = 4 Hz)	C_5, 95.1
		CH_2, −0.65 (2, d, J = 4 Hz)	Me_5, 9.1
		SiH, 4.48 (1, m)	$SiMe_2$, 0.1
			CH_2, −16.3
	200	C_5Me_5, 1.26 (15, s)[d]	CO, 220.0
		$SiMe_2$, 0.54 (6, d)	C_5, 95.0
		CH_2, −0.58 (2, d)	Me_5, 9.1
		SiH, 4.72 (1, m)	$SiMe_2$, 0.6
			CH_2, −16.8
$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$	298	C_5Me_5, 1.54 (15, s)	CO, 217.8
		$SiMe_3$, 0.53 (9, s)	C_5, 94.6
			Me_5, 9.8
			$SiMe_3$, 6.7
	200	C_5Me_5, 1.39 (15, s)	CO, 218.1
		$SiMe_3$, 0.66 (9, s)	C_5, 94.4
			Me_5, 9.7
			$SiMe_3$, 6.7
$(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$	200	C_5Me_5, 1.55 (s, 15)	CO, 220.2
		$SiMe_2$, 0.21 (s); 0.18 (s)[d]	C_5, 90.1
		CH_2 ~0.20,[e] −0.62 (1, d, J = 10 Hz)	$SiMe_2$, −1.4, −4.89
		FeH, −16.0 (s, 1)	CH_2, −20.39
$(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$[f]	298	C_5Me_5, 1.42 (s, 15)	
		$SiMe_3$, −0.05 (s, 9)	

[a] All data are for toluene-d_8 solutions unless noted otherwise. [b] Chemical shifts vs. $Si(CH_3)_4$; relative integration, peak multiplicity, and coupling constants are given in parentheses for ^{1}H NMR. [c] Samples contain ~10 mg of $Cr(acac)_3$ as a relaxation agent. Spectra are ^{1}H-decoupled. [d] Total relative integration for this area of the spectrum is seven protons. Decoupling experiments indicate that the resonance for one of the methylene protons is under one of the two inequivalent methyl groups. [e] The resonance for this proton is under that of the resonances for the $SiMe_2$ protons. Decoupling experiments indicate this proton is coupled to the other methylene proton. [f] Cyclohexane-d_{12} solution.

occurs. IR and UV-vis spectral data for $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ are given in Table I. NMR data are given in Table II.

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ was synthesized in the same manner as $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ by using a twofold excess of $BrSiMe_3$ instead of $ClCH_2SiMe_2$ in the reaction with $Na^+[(\eta^5\text{-}$

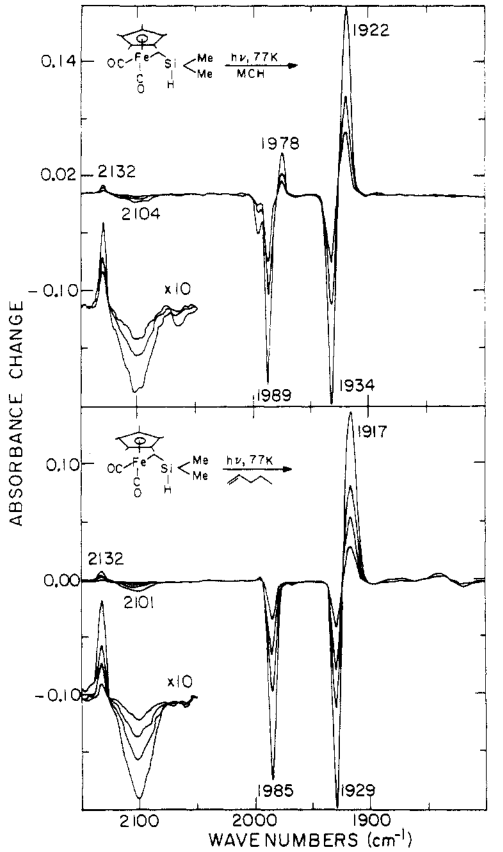


Figure 1. Top: IR difference spectral changes accompanying near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$. Negative peaks show the disappearance of the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ including the loss of the Si–H stretch (~2100 cm^{-1}). Positive peaks are due to free CO (2132 cm^{-1}), $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (1978, 1922 cm^{-1}), and $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ (1922 cm^{-1}). The ratio of the amount of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ formed to the amount of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ formed is ~4:1. Bottom: IR difference spectral changes accompanying near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in 1-pentene at 77 K. Negative peaks show the disappearance of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ including the loss of the Si–H stretch (~2100 cm^{-1}). Positive peaks indicate the appearance of free CO (2132 cm^{-1}) and $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ (1917 cm^{-1}). Note the absence of direct formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$.

$C_5Me_5)Fe(CO)_2]^-$. The resulting compound was purified by sublimation at 40 °C under vacuum. The elemental analysis is satisfactory (Schwarzkopf Microanalytical Laboratory). Anal. Calcd: C, 56.23; H, 7.55. Found: C, 56.22; H, 7.60. IR and UV–vis spectral data for $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ are given in Table I. NMR data are given in Table II.

Results and Discussion

Low-Temperature Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$. Near-UV irradiation of ~10^{-3} M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in a 1-pentene matrix at 77 K results in the IR spectral changes shown in the bottom of Figure 1. Table I gives other relevant spectral data. Disappearance of the spectral bands in the CO stretching region of the starting dicarbonyl is rapid and is associated with the dissociative loss of carbon monoxide as evidenced by the growth of absorption at 2132 cm^{-1} due to uncomplexed CO. An absorbance at 1917 cm^{-1} appears upon irradiation of the dicarbonyl. Comparison of the absorbance changes of the band at 2132 cm^{-1} with the absorbance changes of the bands of the starting dicarbonyl shows that for every molecule of starting material consumed one molecule of CO[10] is produced. The band at 1917 cm^{-1} can then be attributed to a monocarbonyl product. It is important to note that the absorption at ~2100 cm^{-1} associated with the Si–H bond of the starting complex also declines and no new absorbance attributable to a Si–H bond appears. Quantitatively, the absorption associated with Si–H declines in a manner consistent with loss of one Si–H bond per CO released. Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 77 K in 2-MeTHF results in almost the same spectral changes as those in a 1-pentene matrix. Even though 1-pentene and 2-MeTHF are 2e donor ligands, apparently neither can trap the presumed 16e intermediate formed upon loss of CO. The loss of the Si–H absorption concomitant with CO appearance in the matrix is consistent with transfer of the β-H to the Fe. Unfortunately, no absorption characteristic of the Fe–H could be seen, perhaps because it is too weak or because the transfer is incomplete. Attempts to locate the Fe–H stretch of the product by starting with $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2D$ have not been successful.

The spectral changes that are seen upon irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 77 K in a methylcyclohexane matrix are shown in the top portion of Figure 1. As in 1-pentene and 2-MeTHF matrices, the consumption of the starting dicarbonyl is associated with the loss of CO as evidenced by the growth of an absorption at 2132 cm^{-1} due to uncomplexed CO. A monocarbonyl product band, analogous to that seen in 1-pentene and 2-MeTHF, appears at 1922 cm^{-1}. Interestingly, in addition to the 1922 cm^{-1} band attributed to the monocarbonyl a band at 1978 cm^{-1} which is associated with $(\eta^5\text{-}C_5M_5)Fe(CO)_2SiMe_3$ appears. The second band of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, which is at 1921 cm^{-1}, is masked by the absorption of the monocarbonyl product at 1922 cm^{-1}. Comparison of the absorbance changes of the bands at 2132 and 1978 cm^{-1} with the absorbance changes of the bands of the starting dicarbonyl show that for every molecule of starting material consumed either one molecule of CO[10] or one molecule of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is produced. The ratio of CO loss to rearrangement is about 4:1.

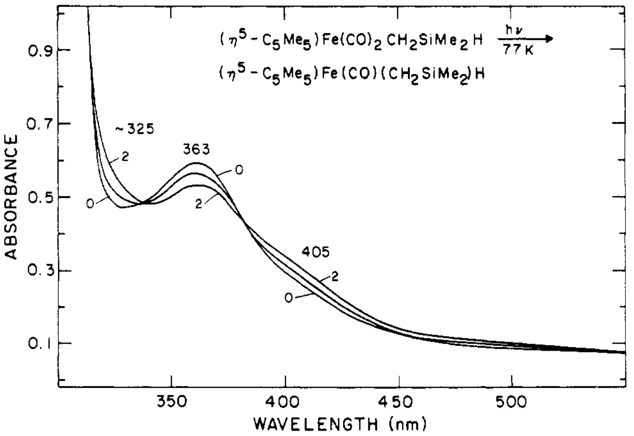


Figure 2. UV–vis spectral changes accompanying near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 77 K in methylcyclohexane. Trace 0 is a spectrum prior to irradiation. Trace 2 is a spectrum after 20 min of irradiation with a Pyrex-filtered high-pressure Hg lamp to give ~50% conversion to $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$.

UV–vis spectral changes accompanying the near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in methylcyclohexane are shown in Figure 2. The spectrum found after photolysis is not that of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (Table I) and must be attributed, in part, to the mono-

---

(10) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* 1985, *24*, 2792.

carbonyl photoproduct. No low-energy visible absorption is detected. The failure to detect a substantially red-shifted absorption suggests that the product monocarbonyl is not coordinatively unsaturated.[4,11] Generally, photogenerated 16e species absorb at much lower energy than their 18e parents, owing to the stabilization of the lowest unoccupied molecular orbital upon loss of a 2e donor ligand. The disappearance of the band at ~2100 cm^{-1} associated with the Si–H bond; the similar (except for small "solvent" shifts) IR spectra of the monocarbonyl photoproduct in a methylcyclohexane, a 1-pentene, and a 2-MeTHF matrix; and the lack of a low-energy visible absorption band for the monocarbonyl product indicate that photoinduced β-H transfer occurs at 77 K resulting in the monocarbonyl product (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H. This photochemistry parallels the photochemistry of (η^5-C_5R_5)W(CO)$_3$CH$_2$SiMe$_2$H complexes (R = H, Me) which also undergo photoinduced loss of CO and β-H transfer at 77 K to form *cis*-(η^5-C_5R_5)W(CO)$_2$H(CH$_2$SiMe$_2$).[5] The relatively small UV–vis spectral changes that accompany photoreaction of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H indicate that secondary photoreaction may be a problem. For this reason IR-monitored photoreactions have been measured at very low extent conversions (<5%) to avoid such difficulty. There is no evidence for problems in interpretation of primary events from irradiation of the initial photoproducts as deduced from IR spectral changes as a function of irradiation time.

The photochemistry of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H at 77 K is in contrast to the photochemistry of certain other (η^5-C_5R_5)Fe(CO)$_2$alkyl complexes.[6] For example, (η^5-C_5R_5)Fe(CO)$_2$Me complexes typically show no productive photochemistry at 77 K in alkane matrices, apparently due to the reversibility of CO loss within the matrix cage. However, with a PVC matrix, where a coordinatively unsaturated species may be "stabilized" by interaction with the matrix, there is evidence of light-induced CO loss from (η^5-C_5H_5)Fe(CO)$_2$Me.[12] The β-Si–H bond of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H acts as an intramolecular trap for the 16e (η^5-C_5Me_5)Fe(CO)CH$_2$SiMe$_2$H. The notion of intramolecular trapping of photogenerated 16e species from (η^5-C_5R_5)Fe(CO)$_2$(η^1-CH$_2$C$_6$H$_5$)[13] and (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5)[14] in alkane matrices also accounts for their low-temperature photochemistry (eq 3 and 4). The η^1-CH$_2$C$_6$H$_5$ and η^1-C$_5$H$_5$ ligands, which are able

$$(\eta^5\text{-}C_5R_5)Fe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5R_5)Fe(CO)(\eta^3\text{-}CH_2C_6H_5) \quad (3)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5) \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_5) \quad (4)$$

to bind in an η^3-fashion upon CO loss, also serve as an intramolecular trap for the 16e intermediate derived upon prompt loss of CO from the parent dicarbonyl.

It is interesting that photochemical rearrangement of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H to (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ occurs in a methylcyclohexane matrix but not in the softer 1-pentene and 2-MeTHF matrices. Presumably, in the softer matrices CO escape is more efficient, allowing CO loss chemistry via the 16e fragment to dominate. In the harder methylcyclohexane matrix net CO loss is less efficient and a relatively inefficient rearrangement, presumably through metal–carbon bond cleavage and radical rearrangement (eq 5–7) emerges as competitive. The point

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H \xrightarrow{h\nu} [(\eta^5\text{-}C_5Me_5)Fe(CO)_2\cdot + \cdot CH_2SiMe_2H] \quad (5)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2\cdot + \cdot CH_2SiMe_2H] \rightarrow [(\eta^5\text{-}C_5Me_5)Fe(CO)_2\cdot + \cdot SiMe_3] \quad (6)$$

$$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2\cdot + \cdot SiMe_3] \rightarrow (\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 \quad (7)$$

is that the approximate 4:1 ratio of CO to (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ likely does not illustrate the real primary ratio of CO loss to homolysis of the Fe–CH$_2$SiMe$_2$H bond. Indeed, at 196 K where methylcyclohexane is fluid, irradiation of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H does not give significant yield of any product other than (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)(H) (vide infra). Light-induced homolysis of the Fe–alkyl bond has been established to be inefficient (compared to CO loss)[13] in fluid solutions, but photochemical homolysis of the Fe–CH$_3$ bond can account[13] for the photochemistry of (η^5-C_5H_5)Fe(CO)$_2$Me in a CO matrix.[15] The rationale for homolysis of the Fe–CH$_3$ bond has been elaborated elsewhere.[13] It should be noted that irradiation of (η^5-C_5H_5)Fe(CO)$_2$CH$_2$SiMe$_3$ in the presence of nitrosodurene gives rise to strong EPR signals assigned to nitrosodurene adducts from ·CH$_2$SiMe$_3$ and (η^5-C_5H_5)Fe(CO)$_2$· radicals,[16] providing support for the radical formation shown in eq 5.

Thermal Chemistry of (η^5-C_5R_5)Fe(CO)(CH$_2$SiMe$_2$)H. Warming of a methylcyclohexane matrix containing photogenerated (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H to 196 K results in no significant IR spectral changes. Irradiation of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H in a methylcyclohexane solution at 196 K also results in the clean formation of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H (Figure 3). The stability of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H at 196 K allows its characterization by ^{1}H and ^{13}C NMR spectroscopies (Table II). The ^{1}H NMR spectrum (Figure 4) shows the (CH$_2$SiMe$_2$) fragment to have two inequivalent Si-Me groups and two inequivalent C–H protons. The C–H protons are coupled to each other, J = 10 Hz. The ^{1}H-decoupled ^{13}C NMR spectrum shows the CH$_2$SiMe$_2$ fragment to have three inequivalent carbons in the high-field region (0 to –30 ppm) of the spectrum. These three carbons cannot be unequivocally assigned since the long acquisition time has precluded the determination of the ^{1}H-coupled ^{13}C NMR spectrum, but it seems reasonable to assign the highest field ^{13}C NMR signal to the methylene carbon bound to both Si and Fe. Both the ^{1}H and ^{13}C NMR are similar to spectra obtained for *cis*-(η^5-C_5R_5)W(CO)$_2$(CH$_2$SiMe$_2$)H complexes.[5] The CH$_2$SiMe$_2$ group of the W complexes also shows two inequivalent methylene protons in the +1.0 to –1.0 ppm region of the ^{1}H NMR spectra and shows three inequivalent carbons in the 0 to –30 ppm region of the ^{13}C NMR spectra. The coupling constants of the methylene protons of the Fe complex and of both of the W complexes are about the same, $J \approx 10$ Hz.

Warming of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H to 225 K results in no change in the ^{1}H NMR spectrum of the

---

(11) Geoffroy, G. O.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

(12) Hooker, R. H.; Rest, A. J.; Whitwell, I. *J. Organomet. Chem.* **1984**, *266*, C27.

(13) Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

(14) Belmont, J. A.; Wrighton, M. S. *Organometallics* **1986**, *5*, 1421.

(15) Fettes, D. J.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2311.

(16) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

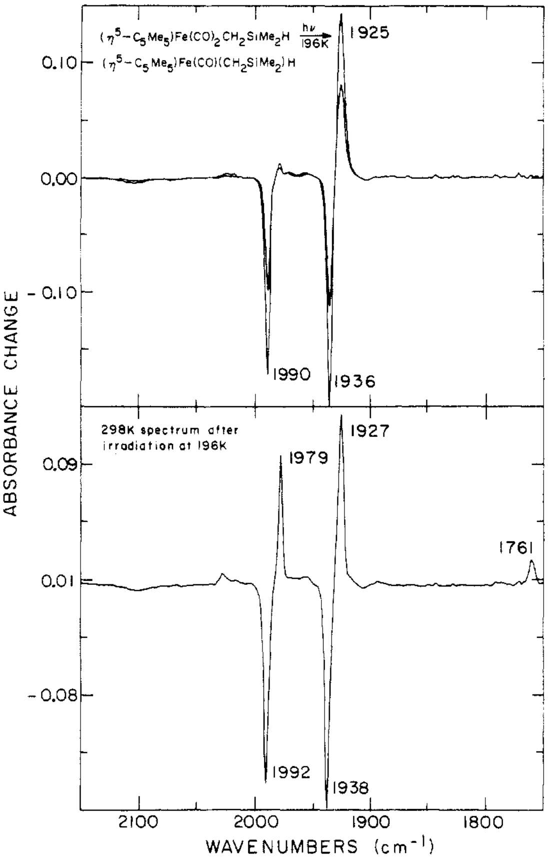


Figure 3. Top: IR difference spectral changes accompanying near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in methylcyclohexane at 196 K showing the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ (1925 cm^{-1}) as the only product. Bottom: Warmup to 298 K yields $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (1979, 1927 cm^{-1}) as the major product and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (1929, 1761 cm^{-1}) as a minor product.

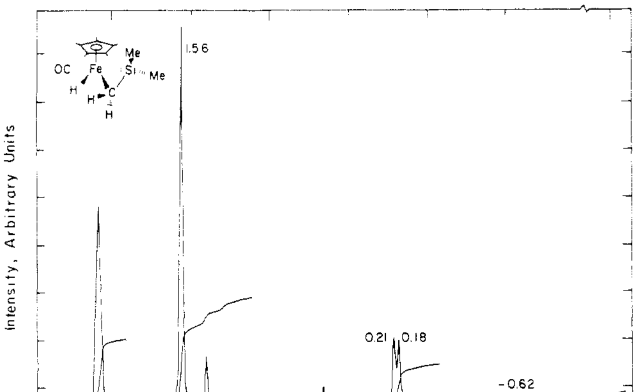


Figure 4. ^1H NMR spectrum at 200 K of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ formed by irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in toluene-d_8 at 196 K. Resonances at 1.39 and 0.66 ppm are due to a small amount of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in solution. For assignments of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ see Table II.

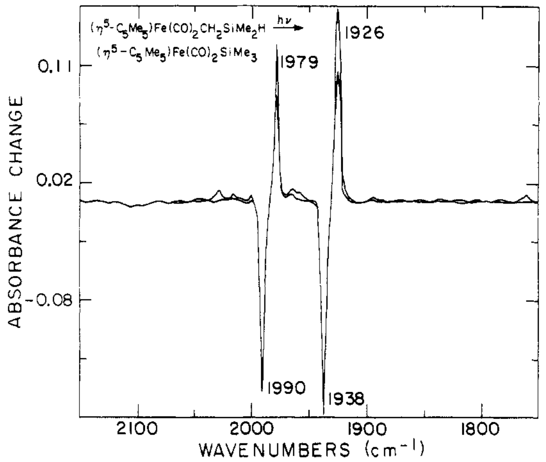


Figure 5. IR difference spectrum associated with the photochemical rearrangement of 5 mM $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ under 1 atm of CO at 298 K to $(\eta^5\text{-}C_5Me_5)Fe(CO_2)SiMe_3$ in methylcyclohexane.

compound. At 225 K the $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ slowly reacts to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (eq 8). The

$$(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H \xrightarrow{>225K} (\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3 \xrightarrow{+CO} (\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 \quad (8)$$

lack of ^1H NMR detected fluxionality in the CH_2SiMe_2 fragment up to the highest temperature at which the compound is inert indicates that the $Fe(CH_2SiMe_2)$ bonding, like that of the *cis*-$(\eta^5\text{-}C_5R_5)W(CO)_2(CH_2SiMe_2)H$,[5] is best described as a metallasilacyclopropane. The W–(alkene) complexes formed by β-H transfer from $(\eta^5\text{-}C_5R_5)W(CO)_3$(alkyl) complexes and by olefin substitution of $(\eta^5\text{-}C_5R_5)W(CO)_3X$ complexes[17] have been shown to have large rotational barriers and are formulated as having metallacyclopropane character. Warming of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_5SiMe_2)(H)$ generated at 196–298 K results in formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ and a small amount (<5%) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)]_2$ (Figure 3). ^1H NMR spectroscopy shows the only organic product to be Si_2Me_6. Relative integrations show that for every molecule of dimer produced one molecule of Si_2Me_6 is produced.

It is important to note that in the reaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ with CO at 225 K the only product formed is $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. No back-reaction to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ can be detected. Thus the Fe–H reductively eliminates to form a more stable C–H bond rather than a less stable Si–H bond. This reaction is analogous to the reductive elimination of alkanes upon photoinduced oxidative addition of R_3SiH to $(\eta^5\text{-}C_5R_5)Fe(CO)_2$(alkyl) complexes.[16]

Room-Temperature Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$. The photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at room temperature is similar to that of its $\eta^5\text{-}C_5H_5$ analogue. Photolysis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in either methylcyclohexane or toluene-d_8 at 298 K results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ and a small amount (<5%) $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. The disappearance quantum yield at 366 nm for 298 K photoreaction in methylcyclohexane is 0.6 ± 0.1 mol/einstein. The formation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ can be suppressed by carrying out the photochemistry under 1 atm of CO (Figure 5). The only product of irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ under high pressure, 2 atm, of CO is $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. The suppression of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ formation and the lack of formation of an $(\eta^4\text{-}C_5Me_5R)Fe(CO)_3$ complex in the presence of CO indicate that $Fe\text{–}CH_2SiMe_2H$ bond cleavage to form CH_2SiMe_2H is not a significant process in the photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$

---

(17) (a) Alt, H. G.; Schwarzel, J. A.; Kreiter, C. G. *J. Organomet. Chem.* **1978**, *153*, C7. (b) Kreiter, C. G.; Nist, K.; Alt, H. G. *Chem. Rev.* 1981, *114*, 1845.

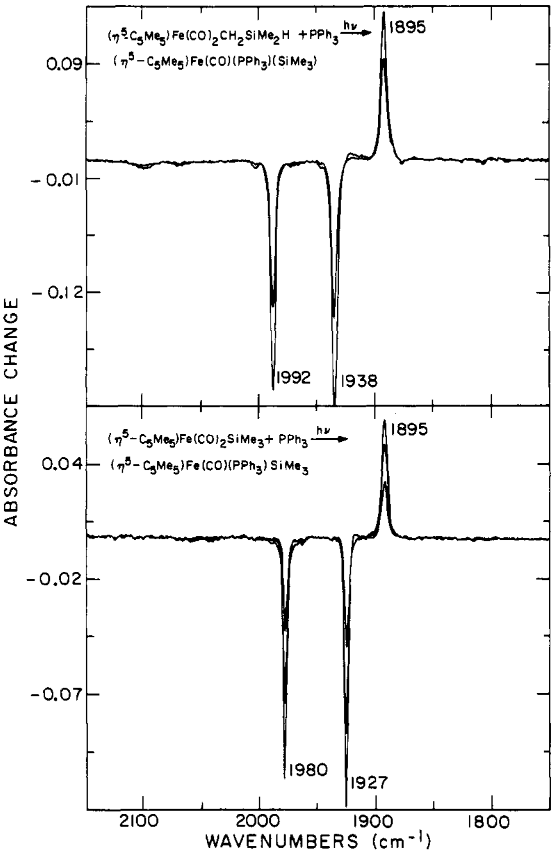


Figure 6. Top: Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in a PPh_3-saturated methylcyclohexane solution at 298 K to form $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$ (1895 cm^{-1}) as the only detectable product. Bottom: irradiation of a PPh_3-saturated methylcyclohexane solution of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ to yield $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$ (1895 cm^{-1}).

at 298 K.[13] Inefficient recombination of CO with the 16e-rearranged CO loss product $(\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3$ is probably responsible for formation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. The process leading to $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ is presently being investigated in detail.

The relatively clean formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is in contrast to the chemistry of $(\eta^5\text{-}C_5R_5)W(CO)_3CH_2SiMe_2H$ complexes.[5] In the W system the principal products of irradiation at 298 K of $(\eta^5\text{-}C_5R_5)W(CO)_3CH_2SiMe_2H$ are $[(\eta^5\text{-}C_5R_5)W(CO)_3]_2$ and $(\eta^5\text{-}C_5R_5)W(CO)_3H$. The rearranged $(\eta^5\text{-}C_5H_5)W(CO)_3SiMe_3$ is only formed by irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2H$ under high pressure of CO. This difference is probably a consequence of the thermal (and photochemical) instability of $(\eta^5\text{-}C_5R_5)W(CO)_3SiMe_3$ complexes.[6c]

Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 298 K in the presence of ligands (L = PPh_3, PEt_3, CO) results in the clean formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ by IR and ^1H NMR spectroscopies. Figure 6 illustrates the IR spectral changes resulting from irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in the presence of PPh_3; the product is the same as that from irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in the presence of PPh_3, $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$. The disappearance quantum yield for $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in a 0.08 M solution of PPh_3 (eq 9) is 0.7 ± 0.1 mol/einstein. This is

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H \xrightarrow[PPh_3]{h\nu} (\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3 \quad (9)$$

consistent with the quantum yield for CO loss from other $(\eta^5\text{-}C_5R_5)Fe(CO)_2(\text{alkyl})$ complexes.[6,13] Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ at 196 K in an alkane solution which is 1 M in PEt_3 results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ as the only product detectable by IR. Warming of the solution to 225 K, the temperature at which $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ has been shown to react to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(PEt_3)SiMe_3$. Interestingly, no $(\eta^5\text{-}C_5Me_5)Fe(CO)(PEt_3)CH_2SiMe_2H$ can be detected even at high (1 M) PEt_3 concentration. The inability to detect $(\eta^5\text{-}C_5Me_5)Fe(CO)(PEt_3)CH_2SiMe_2H$ at high PEt_3 concentration is consistent with the irradiation carried out in pure 2-MeTHF or 1-pentene at low temperature where the presumed 16e $(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2SiMe_2H$ could not be intercepted.

Conclusion

Our findings confirm the mechanism presented in eq 1 and 2 for the rearrangement of $Fe\text{-}CH_2SiMe_2H$ species to $Fe(SiMe_3)$ species. We have found that the $-CH_2SiMe_2H$ group like the $\eta^1\text{-}CH_2C_6H_5$ or $\eta^1\text{-}C_5H_5$ groups[13,14] can "trap" the 16e species formed by CO loss from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R$ species. The resulting $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ complex is inert up to 225 K, unlike analogous $(\eta^5\text{-}C_5Me_5)Fe(CO)(\text{alkene})H$[6] complexes, and can be characterized by NMR spectroscopy. The bonding of the $Fe(CH_2SiMe_2)$ fragment is a metallasilacyclopropane like that of the analogous W complex.[5] $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ undergoes reductive elimination of C–H upon warming in the presence of ligands to form $(\eta^5\text{-}C_5Me_5)Fe(CO)(L)SiMe_3$ complexes.

There are two other rearrangements reported in the literature that can also be postulated to involve similar $Fe(CH_2SiR_2)$ intermediates. These are the thermal rearrangement of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_nCl_{2-n}CH_2Cl$ (n = 2, 1) to $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_nCl_{3-n}$[18] and the photochemical rearrangement of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2SiMe_3$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2CH_2SiMe_3$.[19] These reactions are of particular interest because they involve β-transfer of groups other than H. β-Transfer of an $-SiMe_3$ group has been detected[16] subsequent to photoinduced CO loss from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, and elaboration of this finding is currently in progress.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. II, 106063-04-1; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$, 101493-95-2; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, 101493-92-9; $Na^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$, 52409-74-2; $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$, 101494-05-7; $(\eta^5\text{-}C_5Me_5)Fe(CO)(PEt_3)SiMe_3$, 106040-42-0; $ClCH_2SiMe_2H$, 3144-74-9; $BrSiMe_3$, 2857-97-8.

---

(18) (a) Windus, C.; Sujishi, S.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1951. (b) *J. Organomet. Chem.* **1975**, *101*, 279.

(19) Pannell, K. H.; Rice, J. R. *J. Organomet. Chem.* **1974**, *78*, C35.