J. Am. Chem. Soc. 1986, 108, 3366–3374

Photochemical Reactions of (η^5-Pentamethylcyclopentadienyl)dicarbonyliron–Alkyl and –Silyl Complexes: Reversible Ethylene Insertion into an Iron–Silicon Bond and Implications for the Mechanism of Transition-Metal-Catalyzed Hydrosilation of Alkenes

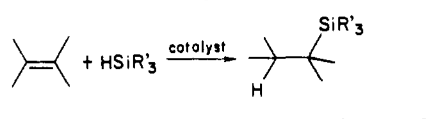
Claudia L. Randolph and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 16, 1985*

Abstract: Near-UV irradiation of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ in a methylcyclohexane matrix at ~77 K results in dissociative loss of CO, as evidenced by the appearance of an absorption at 2132 cm^{-1} due to free CO in the IR spectrum. The 366-nm quantum yield for CO loss from (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ at 298 K is shown to be at least 0.22 ± 0.03 mol/einstein as measured by the photosubstitution yield for formation of (η^5-C_5Me_5)$Fe(CO)(SiMe_3)PPh_3$ in methylcyclohexane containing ~0.05 M PPh_3. Photolysis of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ in the presence of $HSiR'_3$ (R′ = Me, Et in alkane solution, or pure $HSiEt_3$) results in the loss of CO and the oxidative addition of $HSiR'_3$ to form *trans*-(η^5-C_5Me_5)$Fe(CO)(SiMe_3)(SiR'_3)H$ which has been characterized by IR and ^1H NMR. The 366-nm quantum yield for this reaction is 0.20 ± 0.02 mol/einstein. Photolysis of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ in C_2H_4 saturated alkane solution results in the formation of (η^5-C_5Me_5)$Fe(CO)(C_2H_4)SiMe_3$, as evidenced by the growth of a single band in the IR spectrum and the ^{13}C NMR when 99% ^{13}C-enriched C_2H_4 is used. The C_2H_4 then inserts reversibly into the Fe–Si bond. In the absence of added $2e^-$ donor ligands the C_2H_4 insertion product can undergo β-hydrogen transfer to form (η^5-C_5Me_5)$Fe(CO)_2H$ and $Me_3Si(CH{=}CH_2)$. In the presence of CO (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$ is formed. (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$ has been isolated and characterized. Near-UV photolysis of (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$ in an alkane solution at 298 K results in both β-hydrogen and β-$SiMe_3$ transfer. This is evidenced by the appearance of both $Me_3Si(CH{=}CH_2)$ and C_2H_4 in the ^1H NMR. The ratio of β-hydrogen transfer to β-$SiMe_3$ transfer is ~2:1. Photolysis of (η^5-C_5Me_5)$Fe(CO)_2R$ (R = Me, Et) in an alkane solution containing $HSiR'_3$ results in the formation of RH and *trans*-(η^5-C_5Me_5)$Fe(CO)(SiR'_3)_2H$. The 366-nm quantum yield for this process, 0.7 ± 0.1, is consistent with CO loss as the primary step. Preliminary evidence based on the growth of a visible absorption in the UV–vis spectrum is given for the formation of (η^5-C_5Me_5)$Fe(CO)(SiMe_3)(Me)H$ at 173 K by photolysis of (η^5-C_5Me_5)$Fe(CO)_2Me$ in the presence of $HSiMe_3$. The results reported here provide examples of all the reactions postulated to occur in the hydrosilation of alkenes by a mechanism which involves olefin insertion into a M–Si bond as a key step.

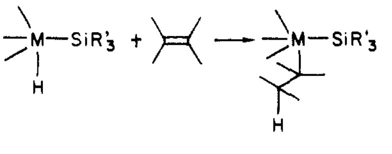
We wish to report three aspects of the photochemistry of (η^5-C_5Me_5)$Fe(CO)_2R$ complexes, R = Me, Et, $CH_2CH_2SiMe_3$, and $SiMe_3$, which relate to a proposed mechanism for hydrosilation catalysis. These aspects are the following: (i) photochemically induced insertion of C_2H_4 into the Fe–Si bond of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$, (ii) transfer of either the –$SiMe_3$ group or a β-H group upon photolysis of (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$, and (iii) reductive elimination of alkane, RH, upon photoinduced oxidative addition of $HSiR'_3$ (R′ = Me, Et) to (η^5-C_5Me_5)$Fe(CO)_2R$, R = Me, Et.

A commonly proposed mechanism[1] for transition metal-catalyzed hydrosilation of olefins, eq 1, involves the key steps of



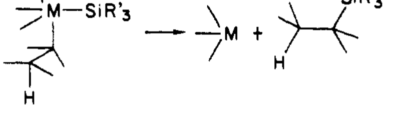
(1)

insertion of the olefin into the M–H bond of an R_3Si–M–H complex, eq 2, followed by the reductive elimination of the alkyl



(2)

group and the silyl group to form an alkylsilane, eq 3. This mechanism has been favored, in part, because olefin insertion into M–H bonds is well documented.[2] A few examples exist for olefin insertion into M–C bonds,[3] and although a few examples of the insertion of fluoroalkenes and fluoroalkynes have been found,[4] there are no examples of insertion of unactivated olefins into a M–Si bond. Precedent for the second key step of the commonly proposed mechanism, reductive elimination of alkylsilane, has recently been reported for $Fe(CO)_4(alkyl)(SiR_3)$,[5] but it should be noted that the rate at 298 K is slow.



(3)

A second mechanism, Scheme I, has been postulated for the $Fe(CO)_5$ photocatalyzed hydrosilation of alkenes.[6] It has also been suggested as a mechanism in $M_3(CO)_{12}$ (M = Fe, Ru, Os)[7] and $R_3SiCo(CO)_4$[8] photocatalyzed hydrosilation. This mechanism involving olefin insertion into the M–Si bond as a key step was

---

(1) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(2) (a) Green, M. L. Hj.; Mahtab, R. *J. Chem. Soc., Dalton Trans* **1979**, *262*. (b) Mahmoud, A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1984**, *187*. (c) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (d) Roe, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 771.

(3) (a) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003. (b) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (c) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

(4) (a) Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *J. Organomet. Chem.* **1970**, *24*, 145. (b) Clark, H. C.; Hauw, T. L. *J. Organomet. Chem.* **1972**, *42*, 429. (c) Schrieke, R. R.; West, B. O. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 141.

(5) (a) Blakeney, A. J.; Gladysz, J. A. *Inorg. Chim. Acta* **1980**, *53*, L25. (b) Brinkman, K. C.; Blankeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *9*, 1325.

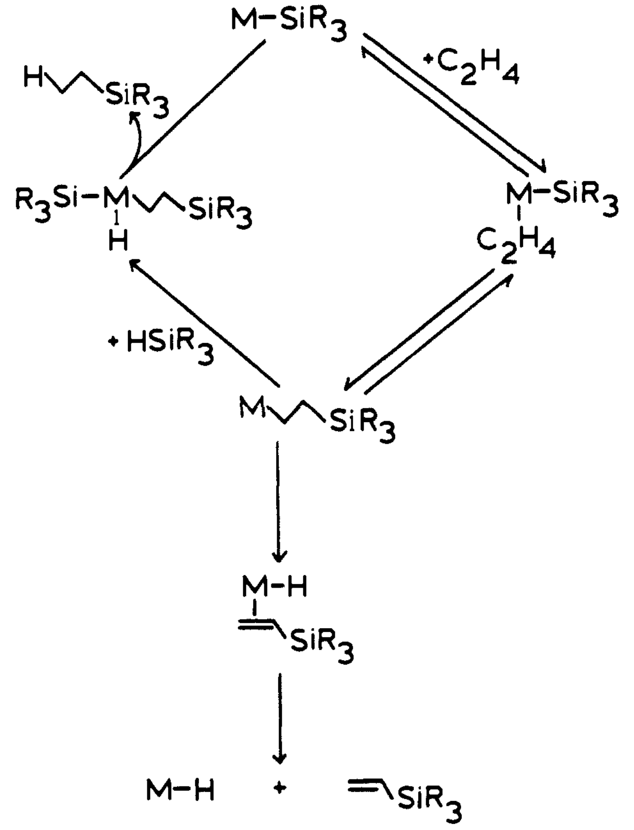
(6) (a) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (b) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wiley: New York, 1977; Vol. 2 pp 690–693. In paticular see the product distribution from thermal catalysis of alkene hydrosilation by $Fe(CO)_5$: Friedlina, R. K.; Chukovskays, E. C.; Tsao, J.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 374. Nesmeyanov, A. N.; Friedlina, R. K.; Chukovsksya, E. C.; Petrova, R. G.; Belyavksy *Tetrahedron* **1961**, *17*, 61.

(7) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *168*, 189.

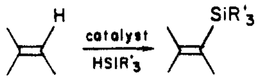
(8) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858.

0002-7863/86/1508-3366$01.50/0

Scheme I. Proposed Mechanism for Hydrosilation Catalysis via C_2H_4 Insertion into a M–Si Bond Adapted from Ref 6



postulated to explain the formation of vinylsilanes as significant products under hydrosilation conditions, eq 4. In some cases the



(4)

yield of the vinylsilane product substantially exceeds the yield of the alkylsilane (based on Si) depending on the catalyst and reaction conditions.[6-8] No precedent has, however, existed in the literature for the insertion of alkenes into M–Si bonds. Although β-H elimination from M-alkyl complexes is well documented,[9] β-H elimination from $M-CH_2CH_2SiR_3$ complexes has not been studied.

In the course of our study of the photochemistry of (η^5-C_5Me_5)$Fe(CO)_2R$ complexes, we have found examples of insertion of C_2H_4 into a M–Si bond, eq 5 and 6. The reverse reaction,

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 \xrightarrow[C_2H_4]{h\nu} (\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3 \quad (5)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3 \xrightarrow[CO]{\Delta} (\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3 \quad (6)$$

β-Si transfer, competes with, β-H transfer following light-induced extrusion of CO from the alkene insertion product, eq 7–9. We

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3 \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5Me_5)Fe(CO)CH_2CH_2SiMe_3 \quad (7)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2CH_2SiMe_3 \xrightarrow[CO]{\Delta} (\eta^5\text{-}C_5Me_5)Fe(CO)_2H + Me_3Si(CH{=}CH_2) \quad (8)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2CH_2SiMe_3 \xrightarrow[+CO]{\Delta} (\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 + C_2H_4 \quad (9)$$

have also found that loss of CO from (η^5-C_5Me_5)$Fe(CO)_2$(alkyl) species in the presence of $HSiR'_3$ yields irreversible loss of alkane, *not* the formation of (alkyl)SiR'_3, eq 10. the results reported here

$$\begin{tikzcd} (\eta^5\text{-}C_5Me_5)Fe(CO)_2R \arrow[r, "h\nu", "HSiR'_3"'] & {[(\eta^5\text{-}C_5Me_5)Fe(CO)(R)(SiR'_3)H] + CO} \arrow[d, "{\Delta,\ HSiR'_3}"] \\ & trans\text{-}(\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3)_2H + RH \end{tikzcd} \quad (10)$$

R = Me, Et R' = Me, Et

suggest that a hydrosilation mechanism involving alkene insertion into a M–Si bond may be more important than previously throught, and at least, the results provide an example of each of the essential steps in the mechanism shown in Scheme I.

Experimental Section

Materials. Hexanes (HPLC grade, Baker) were freshly distilled under Ar from CaH_2. Methylcyclohexane (MCH, Photorex grade, Baker) was freshly distilled from Na under Ar. 1-Pentene (99.5%, Baker) and triethylsilane (Aldrich) were passed through neutral activated alumina prior to use. Trimethylsilane (Petrarch) and CO (CP grade, Matheson) were used as received. Triphenylphosphine (Aldrich) was recrystallized from absolute EtOH prior to use. ^{13}C-enriched (99%) CO and C_2H_4 were obtained from Cambridge Isotopes. (η^5-C_5Me_5)$Fe(CO)_2R$, R = Me, Et,[10] CH_2SiMe_2H,[11] and $SiMe_3$,[11] and (η^5-C_5H_5)$Fe(CO)_2SiMe_3$[11] were available from previous work. All manipulations of organometallic complexes were carried out under Ar by using a Vacuum Atmospheres dry box or conventional Schlenk line techniques.

Instrumentation. IR spectra were recorded by using either a Nicolet 7199 or a Nicolet 60SX Fourier transform spectrometer. NMR spectra were recorded on either a Bruker 250 MHz (proton) or Bruker 270 MHz (proton) Fourier transform spectrometer. UV–vis spectra were recorded on either a Cary 17 or Hewlett-Packard Model 8451A Diode Array spectrometer.

Irradiations. Irradiations of samples in IR cells were performed by using a Bausch and Lomb SP208 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 in the irradiations of low-temperature samples in NMR tubes and in the synthesis of (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$. Room temperature samples in NMR tubes were irradiated by using two General Electric blacklight bulbs (355 ± 20 nm). Quantum yields for PPh_3 and alkene substitution and $HSiR'_3$ addition were measured at 366 nm in a merry-go-round[12] by using a Hanovia 550-W medium-pressure Hg lamp equipped with Corning glass filters to isolate the 366-nm Hg emission. For the 366-nm quantum yields 3.0-mL, freeze–pump–thaw degassed, samples in hermetically sealed 13 × 100 nm Pyrex ampules were used. Quantum yields for formation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ from (η^5-C_5Me_5)$Fe(CO)_2Me$ and (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ were measured at 355 ± 20 nm by using a General Electric blacklight bulb (355 ± 20 nm) with the 3.0-mL samples postioned about 1 in. from bulb. Ferrioxalate actinometry[13] was used to determine light intensity, typically $\sim 10^{-7}$ einstein/min for 366-nm emission of the Hanovia in the merry-go-round and $\sim 10^{-6}$ einstein/min for the blacklight.

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. Low-temperature NMR samples were prepared by irradiating the sample in an NMR tube immersed in a dry ice/acetone bath contained in a quartz dewar. Samples were removed from the dry ice/acetone bath and immediately transferred to the cooled probe of the NMR spectrometer.

Syntheses. (η^5-C_5Me_5)$Fe(CO)_2CH_2CH_2SiMe_3$ was prepared by 5 h of irradiation (with a Hanovia 550-W Hg lamp) of a ~0.002 M solution (50 mL) of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$ in C_2H_4-saturated methylcyclo-

---

(9) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(10) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602.

(11) Randolph, C. L.; Wrighton, M. S. *Organometallics*, to be submitted for publication. (b) Randolph, C. L. Ph.D. Thesis, MIT, 1985. In these reports near-UV irradiation of (η^5-C_5Me_5)$Fe(CO)_2CH_2SiMe_2H$ at 77 K in alkane is shown to yield (η^5-C_5Me_5)$Fe(CO)(CH_2SiMe_2)H$ (a β-H transfer product) without an observable 16e⁻ intermediate. Warmup (to 295 K) of this hydride in the presence of CO yields quantitative formation of (η^5-C_5Me_5)$Fe(CO)_2SiMe_3$; warmup (to 225 K) in the presence of C_2H_4 yields (η^5-C_5Me_5)$Fe(CO)(C_2H_4)SiMe_3$.

(12) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

(13) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London,A* **1956**, 235.

hexane contained in a Pyrex vessel at 196 K. The solution was then warmed to room temperature under a vigorous CO purge. The CO purge was continued for approximately 15 min after the solution reached room temperature. An IR spectrum then showed the presence of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ (~20%), $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ (~50%), $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (~20%), and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. CCl_4 (5 mL) was added to the solution to react with $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Cl$. The solution was then concentrated to about 10 mL and chromatographed on an alumina column. Elution with hexanes give a single yellow band which was fractionated into 5-mL portions as it came off of the column. IR showed the first four fractions to be pure $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. The remaining fractions were a mixture of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. The $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ and the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Cl$ remained at the top of the column. The solutions containing pure $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was combined and reduced to dryness, leaving the $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ as a yellow powder. The $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was further purified by sublimation at 40 °C (~10^{-3} atm). The $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was characterized by mass spectroscopy ($M^+ = 349$) and elemental analysis (Schwarzkopf). Anal. Calcd: C, 58.60; H, 8.12. Found: C, 58.63; H, 8.15. The ^1H and ^{13}C NMR spectra of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ are as expected.

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ was also used as a precursor to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. A C_2H_4-saturated solution of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ was irradiated at 198 K for 1 h to form $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$.[11] This solution was then warmed to and left at ~225 (dry ice/acetonitrile) for about 1 h to allow the rearrangement of the $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ to $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$. The solution was then warmed to room temperature under a vigorous CO purge. The workup was the same as that used for the synthesis from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. The product was identified as $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ by its ^1H NMR spectrum.

Attempts to synthesize $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ from the reaction of $Na^+[(\eta^5\text{-}C_5M_5)Fe(CO)_2]^-$ with $ClCH_2CH_2SiMe_3$ were not successful. Apparently the $Na^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-$ is a strong enough nucleophile to cause the $ClCH_2CH_2SiMe_3$ to undergo an elimination, a reaction typical of β-halosilanes.[14]

Results and Discussion

Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$: Relative Importance of CO Loss and Fe–Si Homolysis. Near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ (typically 5×10^{-3} M) at 298 K in the presence of PPh_3 results in the clean, quantum-efficient formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$, eq 11. The

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 + PPh_3 \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3 \quad (11)$$

quantum yield for this reaction at 366 nm in alkane with 0.07 M PPh_3 is 0.21 ± 0.03 mol/einstein and with 0.04 M PPh_3 is 0.22 ± 0.03 mol/einstein. The lack of significant change in the quantum yield for PPh_3 substitution of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ with change in the PPh_3 concentration suggests that the mechanism for this reaction is dissociative loss of CO. The photosubstitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ by phosphines is well-known,[15] and dissociative loss of CO from various $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ complexes is known to be efficient.[10,16]

In an attempt to observe the $16e^-$ $(\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3$, the parent dicarbonyl was irradiated in an alkane matrix at low temperature. The IR spectral changes in the CO region accompanying reaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ induced by near-UV photolysis in methylcyclohexane matrix at 77 K are shown in Figure 1. The disappearance of starting material is accompanied by the appearance of CO, as evidenced by the growth of an absorption at 2132 cm^{-1} due to uncomplexed CO. An absorbance assigned to $(\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3$ grows in at 1902 cm^{-1}. As is the case for other $(\eta^5\text{-}C_5R_5)Fe(CO)_2R'$ complexes, the low-temperature matrix photoreaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is very slow.[10,16,17] In fact, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is the only $(\eta^5\text{-}C_5R'_5)Fe(CO)_2R$ complex from which photoinduced dissociative loss of CO can be detected at 77 K in an alkane matrix,[10,16] except in those cases where R′ can act as intramolecular trap for the $16e^-$ species, e.g., R′ = $\eta^1\text{-}CH_2C_6H_5$[16] and CH_2SiMe_2H.[11] An hour of irradiation with a high pressure Hg lamp equipped with a quartz filter results in the comsumption of only ~1% of the starting material; under these conditions $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2SiMe_2H$, for example, can be substantially (>50%) converted to $(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ in 1 min.[11]

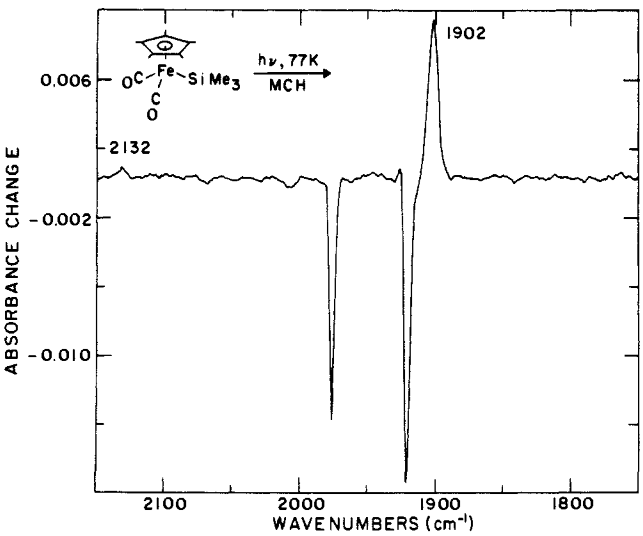


Figure 1. IR difference spectral changes accompanying near-UV irradiation of ~0.005 M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ at 77 K in methylcyclohexane matrix for 1 h. The loss of bands due to the dicarbonyl (1978, 1921 cm^{-1}) is accompanied by the appearance of bands due to free CO (2132 cm^{-1}) and a monocarbonyl product (1902 cm^{-1}), $(\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3$.

Near-UV irradiation of 5×10^{-3} M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ at 298 K in alkane solution (no added ligands) results in the formation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in about 75% yield. The disappearance quantum yield for 355-nm excitation is 0.05 ± 0.01 mol/einstein. Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ under similar conditions, but in a CO-saturated alkane solution, results in little net photochemistry. Irradiation in a ^{13}CO-saturated alkane solution results in the rapid formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(^{13}CO)SiMe_3$, as evidenced by the growth of two bands at 1965 and 1896 cm^{-1} in the IR spectrum.[18] The suppression of dimer formation by CO indicates that the mechanism of dimer formation involves a $16e^-$ intermediate arising from CO loss, but low quantum yield for formation of Me_3Si radicals cannot be unambigously ruled out. Formation of M–M bonded products via photogenerated $16e^-$ species has been implicated in photoreactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$[19] and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$.[20] This is in contrast to the photochemistry of other $(\eta^5\text{-}C_5R_5)Fe(CO)_2R$ complexes in which Fe–Fe bonded product has been shown, at least in part, to arise from M–C bond cleavage.[16] In any event, light-induced homolysis of the Fe–Si bond in $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is very quantum inefficient in comparison to light-induced loss of CO.

Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in the Presence of $HSiR_3$: Formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(SiR_3)_2H$ Complexes. Near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in a 0.03 M $HSiMe_3$ methylcyclohexane solution results in the oxidative ad-

---

[14] Eaborn, C. *Organosilicon Compounds*; Butterworth Scientific Publications: London, 1960.

[15] (a) Chan, T. M.; Connolly, J. W.; Hoff, C. D.; Millich, F. *J. Organomet. Chem.* **1978**, *152*, 287. (b) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77. (c) Cerveau, G.; Chauviere, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1981**, *210*, 343.

[16] Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[17] Randolph, C. L.; Blaha, J. P.; Wrighton, M. S., unpublished results; however, note that $(\eta^5\text{-}C_5H_5)Fe(CO)Me$ has been claimed to be observed upon photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ at 12 K in polyvinylchloride: Hooker, R. H.; Rest, A. J.; Whitwell, I. *J. Organomet. Chem.* **1984**, *266*, C27.

[18] The correct assignment of these bands was determined from the positions of the bands for the naturally abundant $(\eta^5\text{-}C_5Me_5)Fe(CO)(^{13}CO)SiMe_3$ in the IR spectrum of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$.

[19] Tyler, D. R. *Inorg. Chem.* **1979**, *172*, 309.

[20] Randolph, C. L.; Wrighton, M. S. *Organometallics*, to be submitted for publication. Randloph, C. L. Ph.D. Thesis, MIT, 1985.

Table I. IR and UV-vis Spectral Data for Relevant Complexes[a]

complex	temp, (K)	ν(CO), cm^{-1} (ϵ, M^{-1} cm^{-1} or rel Abs)	λ, nm (ϵ, M^{-1} cm^{-1})
(η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$	298	1980 (6500) 1927 (7900)	250 (sh) (~9400) 285 (5000) 333 (1900)
(η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$	77	1978 (0.8) 1921 (1.0)	
(η^5-C_5Me_5)Fe(CO)SiMe$_3$	77	1902	
(η^5-C_5Me_5)Fe(CO)(PPh$_3$)SiMe$_3$	298	1895	
trans-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H	298	1926	~275 (sh), 320, ~400 (sh)
trans-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H	173	1925	(320, ~400 (sh)
(η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$	298	1985 (0.8), 1932 (1.0)	
(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)(Me)H	173	1925	318, 510
(η^5-C_5Me_5)Fe(CO)(C$_2$H$_4$)SiMe$_3$	198	1929	
(η^5-C_5Me_5Fe(CO)(C$_2$H$_4$)SiMe$_3$	298	1929	
(η^5-C_5Me_5)Fe(CO)(1-pentene)SiMe$_3$	298	1920	
(η^5-C_5Me_5)Fe(CO)$_2$Me	298	1993 (7700) 1939 (7750)	
(η^5-C_5Me_5)Fe(CO)$_2$H	298	2002 (6210) 1945 (6060)	340 (1500)
[(η^5-C_5Me_5)Fe(CO)$_2$]$_2$	298	1930 (12700) 1761 (7400)	533 (1520), 420 (2980) 362 (10100)
(η^5-C_5Me_5)Fe(CO)$_2$SiEt$_3$	298	1977 1925	

[a] All data for alkane solutions.

Table II. NMR Data for Relevant Complexes[a]

compound	^{1}H NMR	δ ppm[b]	^{13}C NMR	δ ppm[b]
(η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$	C$_5$Me$_5$	1.53 (s, 15)	C$_5$	94.6
	SiMe$_3$	0.53 (s, 9)	Me$_5$	9.8
			SiMe$_3$	6.7
			CO	217.8
(η^5-C_5Me_5)Fe(CO)$_2$Me	C$_5$Me$_5$	1.42 (s, 15)		
	Me	0.06 (s, 3)		
(η^5-C_5Me_5)Fe(CO)$_2$H	C$_5$Me$_5$	1.61 (s, 15)		
	Fe–H	−11.5 (s, 1)		
(η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$	C$_5$Me$_5$	1.46 (s, 15)	C$_5$	94.6
	–CH$_2$CH$_2$	1.25 (m, 4.5)[c]	Me$_5$	9.1
	–SiMe$_3$	0.12 (s, 9)	SiMe$_3$	−1.7
			CH$_2$CH$_2$	26.1, 7.5
			CO	220.0
(η^5-C_5Me_5)Fe(CO)(PPh$_3$)SiMe$_3$[d]	C$_5$Me$_5$	1.40 (s, 15)		
	SiMe$_3$	0.38 (s, 9)		
(η^5-C_5Me_5)Fe(CO)(PPh$_3$)CH$_2$CH$_2$SiMe$_3$	C$_5$Me$_5$	1.46 (s, 15)		
	SiMe$_3$	0.01 (s, 9)		
(η^5-C_5Me_5)Fe(CO)(C$_2$H$_4$)SiMe$_3$ (200 K)	C$_5$Me$_5$	1.28 (s, 15)		
	SiMe$_3$	0.75 (s, 3)		
		0.68 (s, 3)		
		0.20 (s, 3)		
(η^5-C_5Me_5)Fe(CO)(C$_2$H$_4$)SiMe$_3$ (298 K)	C$_5$Me$_5$	1.39 (s, 15)		
	SiMe$_3$	0.37 (s, 9)[e]		
trans-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H	C$_5$Me$_5$	1.45 (s, 15)	C$_5$	94.0
	(SiMe$_3$)$_2$	0.51 (s, 18)	Me$_5$	10.1
	Fe–H	−13.31 (s, 1)	(SiMe$_3$)$_2$	9.6
			CO	215.6

[a] All data for toluene-d_8 solutions at 298 K unless otherwise noted. [b] Chemical shifts vs. Si(CH$_3$)$_4$; peak multiplicity and relative integration are given in parentheses for ^{1}H NMR. [c] An AA′:BB′ system, see Figure 4. [d] Benzene-d_6 solution. [e] This is a broadened singlet.

dition of HSiMe$_3$ to yield *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H, eq 12, as indicated by the disappearance of the absorption at 2120 cm^{-1} associated with the Si–H bond of HSiMe$_3$ and the growth of a single band in the IR spectrum of 1926 cm^{-1}. Quantitative analysis of the IR spectral changes shows that one Si–H bond is consumed for every (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ molecule reacted. The ^{1}H NMR spectrum, Table II, is consistent with the formulation of the product as a trans isomer. In particular, a hydride resonance is observed, and there is only one resonance for the two –SiMe$_3$ groups. The integration of the ^{1}H NMR resonances is consistent with the proposed structure. The same reaction has been reported for (η^5-C_5H_5)Fe(CO)$_2$SiCl$_3$ in the presence of HSiCl$_3$ to yield fully characterized *trans*-(η^5-C_5H_5)Fe(CO)(SiCl$_3$)$_2$H.[21] Attempts to isolate the *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H have not been successful. The complex is labile with respect to loss of HSiMe$_3$ in the absence of HSiMe$_3$. In the presence of 1 atm CO, the complex gradually reacts (~25% in 2 h at 298 K) to form only (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$, consistent with reductive elimination of HSiMe$_3$ followed by CO uptake as the mechanism for reaction. There is no evidence for formation of (η^5-C_5Me_5)Fe(CO)$_2$H in the reaction, ruling out reductive elimination of Si$_2$Me$_6$. No Si$_2$Me$_6$ is detected by ^{1}H NMR.

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3 + HSiMe_3 \xrightarrow[-CO]{h\nu} trans\text{-}(\eta^5\text{-}C_5Me_5)Fe(CO)(SiMe_3)_2H \quad (12)$$

Irradiation of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in methylcyclohexane solution which is 0.8 M in HSiEt$_3$ results in the growth of a single IR band at 1922 cm^{-1}. We assign the 1922-cm^{-1} feature to *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)(SiEt$_3$)H, though some *trans*-

---

(21) (a) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *918* 3375. (b) Manojlovic-Miur, L.; Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 447. (c) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

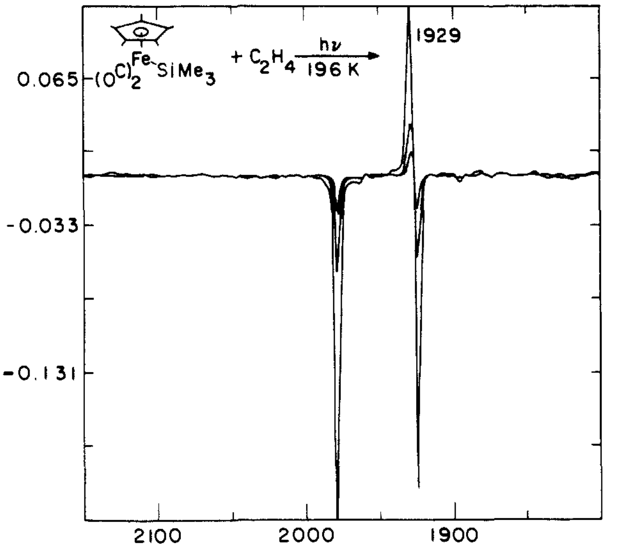


Figure 2. IR difference spectral changes accompanying near-UV irradiation of 0.01 M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ at 196 K in C_2H_4-saturated methylcyclohexane solution. Three irradiation times are shown. The loss of bands due to the dicarbonyl is accompanied by the appearance of a band at 1929 cm^{-1} assigned to $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$.

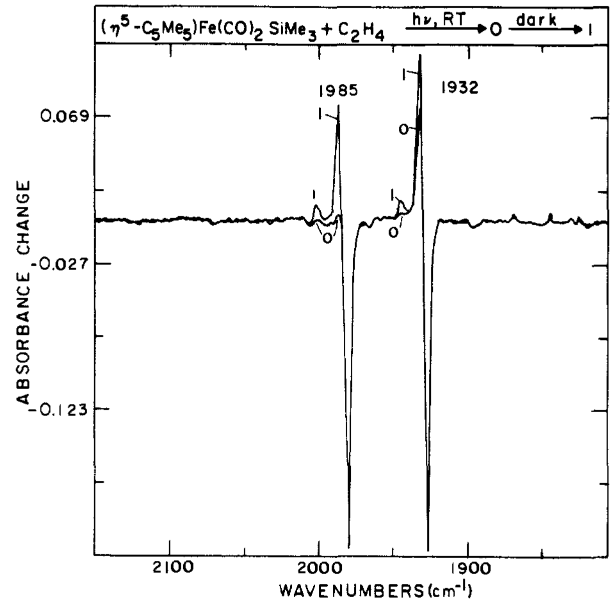


Figure 3. IR difference spectral changed resulting from near-UV photolysis of 0.01 M $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ at 298 K in C_2H_4-saturated methylcyclohexane. Trace 0 shows the spectrum taken immediately after 30 s photolysis. The only absorption appearing in the spectrum is at 1929 cm^{-1} and is assigned to $(\eta^5\text{-}C_{M}e_5)Fe(CO)(C_2H_4)SiMe_3$. Trace 1 shows the thermal chemistry which occurs within 5 min after irradiation. The small absorptions at 2002 and 1945 cm^{-1} are attributed to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$. The absorptions at 1985 and 1932 cm^{-1} are due to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$.

$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiEt_3)_2H$ may also be present, vide infra. When the solution stands in the dark, a second IR band at 1977 cm^{-1} grows. This band is attributed to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiEt_3$ from reductive elimination of $HSiMe_3$ and reaction with CO. The low-energy band of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiEt_3$ (1925 cm^{-1}) overlaps the single band of *trans*-$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3)_2H$. Irradiation of a toluene-d_8 solution of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ which is ~0.05 M in $HSiEt_3$ results in the growth of two Fe–H resonances at −13.35 and −13.31 ppm in the ^1H NMR spectrum. These resonances are attributed to $(\eta^5\text{-}C_5Me_5)Fe(CO)(SiMe_3)(SiEt_3)H$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)(SiEt_3)_2H$. Free $HSiMe_3$ also appears in the NMR spectrum, confirming that silane exchange occurs. Slow conversion to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiEt_3$ is ultimately found. The quantum yield for disappearance of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ when photolyzed at 366 nm in an alkane solution which is 0.1 M in $HSiEt_3$ is 0.20 ± 0.02 mol/einstein.

Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in the Presence of C_2H_4: Formation of an Alkene Insertion Product $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. The IR spectral changes accompanying near-UV photolyhsis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in an C_2H_4-saturated methylcyclohexane solution at 198 K are shown in Figure 2. The IR spectral bands associated with the starting dicarbonyl decline, and a single IR band at 1929 cm^{-1} appears. This band is attributed to $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$. The band at 1929 cm^{-1} persists upon warming of the solution to 298 K. The same spectrum is obtained when $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is irradiated at 298 K in an C_2H_4-saturated methylcyclohexane solution, Figure 3. Within 5 min at 298 K, thermal reaction of $(\eta^5\text{-}C_{M}e_5)Fe(CO)(C_2H_4)SiMe_3$ occurs to the extent of ~50% disappearance. Four new features appear in the IR spectrum: 2001, 1943, 1985, and 1932 cm^{-1}. The two smaller bands at 2001 and 1943 cm^{-1} are attributed to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$. The two larger bands at 1985 and 1932 cm^{-1} appear to be a new $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R$ complex. The photochemistry was carried out on a synthetic scale, resulting in the isolation of $(\eta^5\text{-}Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, a species having IR absorptions at 1985 and 1932 cm^{-1}. The ^1H- and ^{13}C NMR spectra of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, Table II and Figure 4, are consistent with the formulation of the C_2H_4 insertion product. Thus, eq 5 and 6 summarize the results of irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in the presence of C_2H_4.

The reaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ with C_2H_4 has been investigated by ^1H NMR spectroscopy at 298 and 200 K in order to more fully characterize the labile $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$. Near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in C_2H_4-saturated toluene-d_8 solution at 200 K results in the appearance of a new $(\eta^5\text{-}C_5Me_5)$ resonance at 1.28 ppm. Three new resonances, each of which integrates as three protons relative to the $(\eta^5\text{-}C_5Me_5)$ resonance, also appear at 0.75, 0.68, and 0.20 ppm. These are assigned to the $-SiMe_3$ protons of $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$. The $-Me$ groups are apparently inequivalent at 200 K. Unfortunately the ^1H resonances of the complexed C_2H_4 cannot be detected. Thus, ^1H NMR spectroscopy does not provide additional characterization of the C_2H_4 photosubstitution product. However, irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ in the toluene-d_8 at 200 K in the presence of 99% ^{13}C-enriched C_2H_4 monitored by ^{13}C NMR shows a signal consistent with bound C_2H_4. The spectrum shows two inequivalent (but coupled) carbons at 36 and 40 ppm relative to Me_4Si with a J_{CC} of 43 Hz. The formulation of $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$ rests on the 1929

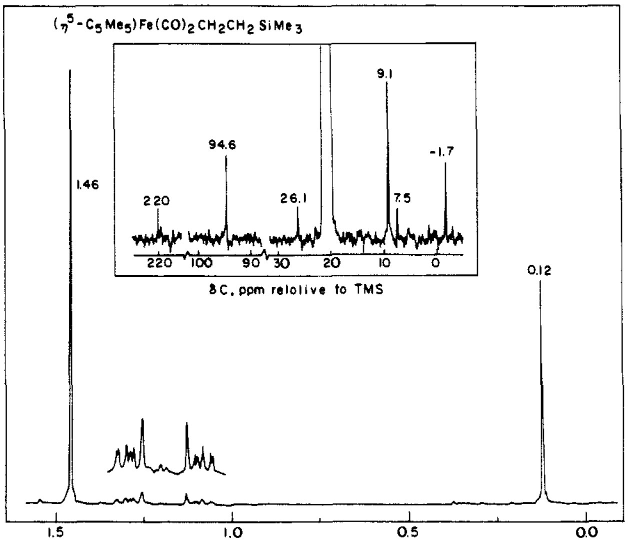


Figure 4. The ^1H- and ^{13}C (inset) NMR spectra of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in toluene-d_8 at 298 K. Cf. Table II for assignments.

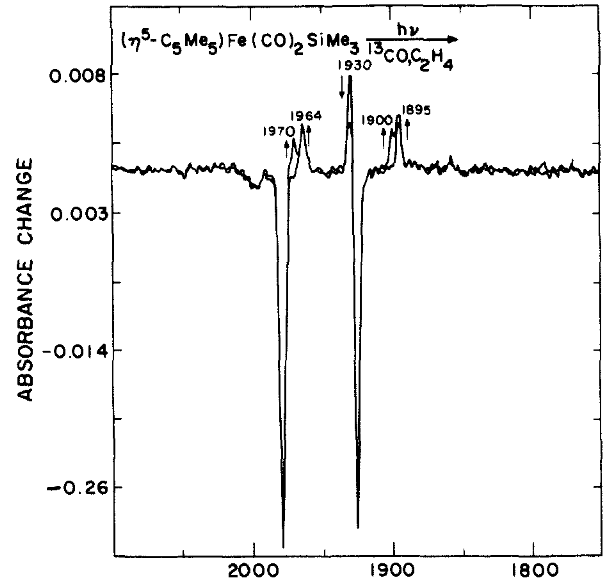


Figure 5. IR difference spectral changes resulting from near-UV photolysis of a methylcyclohexane solution of 0.01 M (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ under ~0.05 atm of ^{13}CO and ~0.5 atm of C_2H_4. Trace 0 shows the spectrum taken immediately after 30 s photolysis. The absorbances appearing at 1964 and 1895 cm^{-1} are due to (η^5-C_5Me_5)Fe(CO)(^{13}CO)SiMe$_3$. The absorbance at 1930 cm^{-1} is attributed to (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$. With time, as indicated by the arrows, the absorption at 1930 cm^{-1} declines, and two new bands at 1970 and 1900 cm^{-1} appear due to thermal formation of (η^5-C_5Me_5)Fe(CO)(^{13}CO)CH$_2$CH$_2$SiMe$_3$ at the expense of (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$.

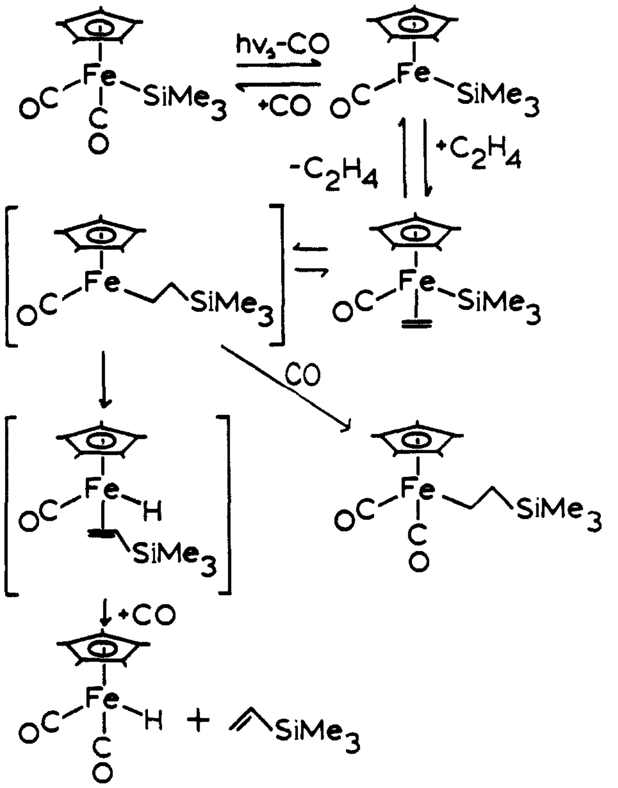
cm^{-1} IR feature, the ^{13}C NMR, and the analogy to ^{13}CO and PPh$_3$ substitution of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ (vide supra).

An ^{1}H NMR spectrum of a 200-K sample of (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$ warmed to 298 K or a sample prepared by near-UV photolysis of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in an C_2H_4-saturated toluene-d_8 solution at 298 K shows a sharp resonance at 1.39 ppm assigned to the (η^5-C_5Me_5) protons. A broad resonance (–SiMe$_3$) which integrates as nine protons relative to the (η^5-C_5Me_5) resonance also appears at 0.37 ppm. As for the 200-K experiment, no resonance for coordinated C_2H_4 could be detected. The broad –SiMe$_3$ resonance and the lack of a resonance for coordinated C_2H_4 indicate that the (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$ may be fluxional at 298 K. Within about 5 min at 298 K the ^{1}H NMR spectrum shows features due to Me$_3$Si(C_2H_3), (η^5-C_5Me_5)Fe(CO)$_2$H, and (η^5-C_kMe_5)(CO)$_2$CH$_2$CH$_2$SiMe$_3$ formation at the expense of (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$. When the 200-K sample of (η^5-C_5Me_5)Fe(CO)($^{13}C_2H_4$)SiMe$_3$ is warmed to 298 K and monitored by ^{13}C NMR, the (η^5-C_5Me_5)Fe(CO)$_2$^{13}CH$_2$^{13}CH$_2$SiMe$_3$ is clearly observed.

Interestingly, the (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$ complex can be produced from the photolysis of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H in the presence of C_2H_4. Near-UV irradiation of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H in C_2H_4 (or $^{13}C_2H_4$)-saturated toluene-d_8 at 200 K results only in the formation of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H, as shown by ^{1}H NMR and ^{13}C NMR spectroscopy.[11] Warming the sample to 225 K and then recooling the sample to 200 K results in an ^{1}H NMR spectrum which is the same as that obtained when (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ is irradiated in the presence of the C_2H_4 at 200 K. (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H has already been shown to rearrange at 225 K and react with ligands to form (η^5-C_5Me_5)Fe(CO)(L)(SiMe$_3$), L = CO, PPh$_3$, PEt$_3$.[11]

The insertion of the C_2H_4 into the Fe–Si bond at room temperature has been investigated by the photolysis of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in a methylcyclohexane solution under an atmosphere of about 0.5 atm C_2H_4 and about 0.5 atm ^{13}CO, Figure 5. Upon photolysis both (η^5-C_5Me_5)Fe(CO)(^{13}CO)SiMe$_3$ and (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$ are formed. The (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$ then reacts with the ^{13}CO to form (η^5-C_5Me_5)Fe(CO)(^{13}CO)CH$_2$CH$_2$SiMe$_3$, as indicated by the appearance of bands at 1970 and 1900 cm^{-1} in the IR spectrum.[22] A small additional amount of (η^5-C_5Me_5)Fe(CO)(^{13}CO)SiMe$_3$ is also formed, as indicated by the slight growth of the bands at 1964 and 1895 cm^{-1}. The lack of any primary formation of (η^5-C_5Me_5)Fe(CO)(^{13}CO)CH$_2$CH$_2$SiMe$_3$ is consistent with relatively slow C_2H_4 insertion into the Fe–Si bond.

Scheme II. The Photochemistry of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in the Presence of C_2H_4



Interestingly, we observe no features in the IR spectrum that can be assigned to (η^5-C_5Me_5)Fe(CO)(C_2H_4)CH$_2$CH$_2$SiMe$_3$ upon irradiation of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in a C_2H_4-saturated alkane solution. Such would be expected, but the species may be too labile with respect to formation of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$ to allow detection.

Near-UV irradiation of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in 1-pentene at 298 K results in the formation of (η^5-C_5Me_5)Fe(CO)(1-pentene)SiMe$_3$, as evidenced by the growth of a single band at 1920 cm^{-1} in the IR spectrum. Monitoring of the subsequent thermal chemistry by IR spectroscopy shows the formation of (η^5-C_5Me_5)Fe(CO)$_2$H. These results are interpreted as evidence that 1-pentene will also insert into the Fe–Si bond. The insertion complex has not, however, been detected. The 366-nm quantum yield for 1-pentene substitution of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in an alkane solution which is 0.1 M in 1-pentene is 0.21 ± 0.02 mol/einstein, the same value as for photosubstitution by PPh$_3$.

Our findings concerning the photochemistry of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in the presence of C_2H_4 are summarized in Scheme II. The primary photoprocess of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ is CO loss to form first (η^5-C_5Me_5)Fe(CO)SiMe$_3$. This species can be detected in low-temperature matrices and can be scavenged by CO, PPh$_3$, C_2H_4, or HSiR'$_3$. In the presence of C_2H_4, for example, (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$ is formed upon photoreaction of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$. This assertion is supported by the quantum yield for the reaction and by the reaction of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H in the presence of C_2H_4 at 225 K to give the same product, (η^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe$_3$.

---

[22] The correct assignment of these bands was determined from the positions of the bands for naturally abundant (η^5-C_5Me_5)Fe(CO)(^{13}CO)CH$_2$CH$_2$SiMe$_3$ in the IR spectrum of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$.

$(\eta^5\text{-}C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ can be considered a precursor for the thermal formation of $16e^-$ $(\eta^5\text{-}C_5Me_5)Fe(CO)SiMe_3$ at 225 K.[11] We propose that the conversion of $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$ to the $(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2CH_2SiMe_3$ ($16e^-$) intermediate is the rate-determining step in forming $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. However, an incoming ligand-assisted insertion of the bound olefin into the Fe–Si bond cannot be completely ruled out. The thermal formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ and $Me_3Si(CH{=}CH_2)$ from $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$ does suggest, however, that insertion occurs by a nonassociative mechanism. In the absence of sufficient CO to trap the $16e^-$ insertion complex, $(\eta^5\text{-}C_5Me_5)Fe(CO)CH_2CH_2SiMe_3$, β-hydride elimination occurs, vide infra.

Preliminary results showing the insertion of C_2H_4 into the Fe–Si of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ have also been obtained. The conversion of the C_2H_4 complex to the $-CH_2CH_2SiMe_3$ complex is much slower than that of the C_5Me_5 complex. Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ in C_2H_4-saturated alkane results in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)SiMe_3$, as evidenced by the appearance of a single IR band at 1944 cm^{-1}. Thermal reaction of the $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)SiMe_3$ in the presence of 1 atm CO has been monitored by IR. After 8 h, approximately 25% of the $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)SiMe_3$ reacts, as evidenced by the decline in intensity of the 1944-cm^{-1} band. Carbonyl bands of a new $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ complex appear at 2005 and 1951 cm^{-1}. By analogy to the chemistry of the C_5Me_5 complex, we attribute these bands to $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_2SiMe_3$. Photolysis of the solution containing the $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_2SiMe_3$ results in IR changes consistent with the formation of some $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH_2SiMe_3$ by β-hydrogen transfer in analogy to the photochemistry of the C_5Me_5 analogue described below.

Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. The photochemistry of the insertion complex $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ is of particular interest since β-H elimination from such complexes has been proposed as the source of vinylsilane products in the photocatalyzed hydrosilation of olefins.[4-6] ^1H NMR spectroscopy shows that near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in either toluene-d_8 or benzene-d_6 results in the formation of $Me_3Si(CH{=}CH_2)$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$. In addition, a sharp resonance at 5.24 ppm in the ^1H NMR spectrum indicates the formation of a significant amount of C_2H_4. Analysis of the 0–2 ppm region of the ^1H NMR spectrum (Cf. Table II) shows that in addition to the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$ and $Me_3Si(CH{=}CH_2)$, near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ also results in the formation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$. The free C_2H_4 apparently arises from a β-$SiMe_3$ transfer to form $(\eta^5\text{-}C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$ which reacts with CO to form $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$. $[(\eta^5\text{-}C_5Me_5Fe(CO)_2]_2$ is formed as a secondary irradiation product from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2H$. The relative yields, by integration of the ^1H NMR of $Me_3Si(CH{=}CH_2)$, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$, and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(C_2H_4)SiMe_3$ are 65%, 14%, and 15%, respectively, from near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in alkane solution.

Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in benzene-d_6 which is $\sim$0.1 M in PPh_3 results in the suppression of both C_2H_4 formation and $Me_3Si(CH{=}CH_2)$ formation. The major product, $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)CH_2CH_2SiMe_3$, has resonances in the ^1H NMR spectrum at 1.46 and 0.01 ppm which integrate as 15 to 9. Resonances attributable to $(\eta^5\text{-}C_5Me_5)Fe(CO)(PPh_3)SiMe_3$ were not detected. thus, the photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ is summarized by eq 7–9 where the photoinduced CO-loss step leads to a $16e^-$ species that can be trapped by added $2e^-$ ligands.

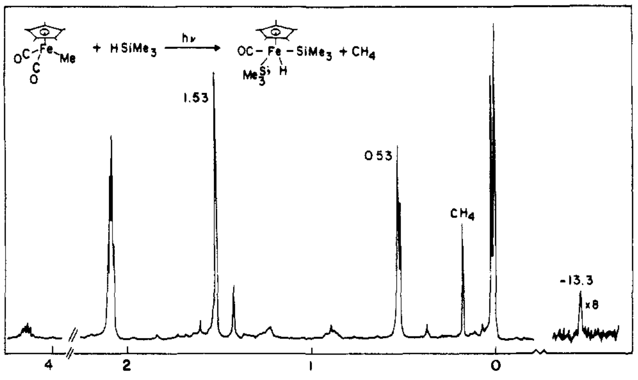
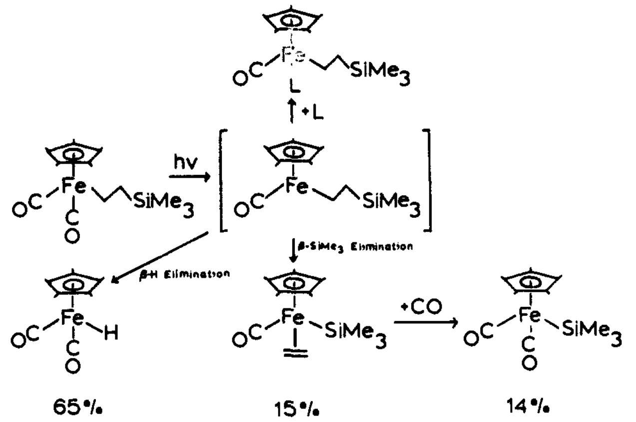


Figure 6. ^1H NMR spectrum at 298 K of *trans*-$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiMe_3)_2H$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ generated by the photolysis of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ in toluene-d_8 containing $\sim$0.01 M $HSiMe_3$. The resonance at 0.18 ppm is due to CH_4. The resonance at 1.53 and 0.53 ppm are due to the C_5Me_5 and $-SiMe_3$ protons of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ formed via reaction of CO with *trans*-$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiMe_3)_2H$ which has the hydride resonance at −13.3 ppm. Cf. Table II for assignments.

Scheme III. The Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$



The suppression of the formation of $Me_3Si(CH{=}CH_2)$ from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ by carrying out the irradiation in the presence of PPh_3 is consistent with the photochemistry of the $(\eta^5\text{-}C_5R_5)Fe(CO)_2(alkyl)$ complexes.[10] The room temperature photochemistry of these complexes has been shown to be dominated by CO loss. PPh_3 is able to trap the $16e^-$, CO-loss intermediate, $(\eta^5\text{-}C_5R_5)Fe(CO)(alkyl)$, thus inhibiting β-H transfer. The inhibition of C_2H_4 formation from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ by PPh_3 shows that β-$SiMe_3$ transfer likely also arises from a CO-loss process.

The photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ is summarized in Scheme III. The product distribution resulting from β-H and β-$SiMe_3$ transfer is 2.1:1.0, a ratio not significantly different from the ratio of β-hydrogens to β-$SiMe_3$ groups, 2:1. Thus it appears that the CO-loss intermediate does not discriminate with respect to β-transfer between a β-H and a β-$SiMe_3$ group. The transfer of a β-$SiMe_3$ group is of particular importance to the proposed mechanism of hydrosilation involving insertion of C_2H_4 into the M–Si bond. Our results indicate that the insertion of C_2H_4 can be a reversible process.

Photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(alkyl)$ Complexes in the Presence of $HSiR'_3$. The ^1H NMR spectrum of the product from near-UV irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ in a toluene-d_8 solution that is $\sim$0.01 M in $HSiMe_3$ is shown in Figure 6. Interestingly, the spectrum shows that the Fe-containing product is *trans*-$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiMe_3)_2H$, the same as that obtained when $(\eta^5\text{-}C_5Me_5)Fe(CO)_2SiMe_3$ is irradiated in the presence of $HSiMe_3$. The spectrum also shows the growth of a singlet at 0.18 ppm which is assigned to CH_4. Eq 10 thus describes the photochemistry of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ in the presence of $HSiMe_3$.

Irradiation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ in the presence of $HSiEt_3$ also yields a disilyl hydride compound, *trans*-$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiEt_3)_2H$, as evidenced by the initial appearance of a band at 1920 cm^{-1} in the IR spectrum of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me$ photolyzed in pure $HSiEt_3$. Subequently, in the dark, the 1920-cm^{-1} band declines and two new bands appear at 1977 and

1925 cm^{-1}. These are attributed to (η^5-C_5Me_5)Fe(CO)$_2$SiEt$_3$. The 366-nm quantum yield for the disappearance of (η^5-C_5Me_5)Fe(CO)$_2$Me in alkane solution which is 0.1 M in HSiEt$_3$ is 0.58 ± 0.03 mol/einstein. This quantum yield is in good agreement with the quantum yields obtained for CO-loss from various (η^5-C_5R_5)Fe(CO)$_2$R compounds.[10,16,17] We can, therefore, postulate the mechanism outlined in eq 13–16 for the photoreaction of (η^5-C_5Me_5)Fe(CO)$_2$Me with HSiR'$_3$.

$$(\eta^5\text{-}C_5Me_5)Fe(CO)_2Me \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta^5\text{-}C_5Me_5)Fe(CO)Me + CO \quad (13)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)Me + HSiR'_3 \rightleftharpoons (\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3)(Me)H \quad (14)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3)(Me)H \rightarrow (\eta^5\text{-}C_5Me_5)Fe(CO)SiR'_3 + MeH \quad (15)$$

$$(\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3) + HSiR'_3 \rightleftharpoons (\eta^5\text{-}C_5Me_5)Fe(CO)(SiR'_3)_2H \quad (16)$$

Some evidence for the formation of (η^5-C_5Me_5)Fe(CO)(Me)(SiMe$_3$)H postulated in eq 14 can be seen in the UV–vis spectral changes that occur when (η^5-C_5Me_5)Fe(CO)$_2$Me is irradiated in methylcyclohexane containing 0.01 M HSiMe$_3$, Figure 7. Upon irradiation at 173 K a significant visible absorption band appears at about 510 nm. A band at 318 nm also appears. An IR spectrum of the sample does not show the presence of [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$, a possible decomposition product with a significant visible absorption. The only product band appearing in the IR spectrum is at 1925 cm^{-1}. Warming of the sample to 298 K results in the loss of visible absorption. Irradiation of (η^5-C_5Me_5)Fe(CO)$_2$Me in the presence of HSiMe$_3$ at 298 K to form *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H does not result in the growth of a visible absorption. Only an absorption at 320 nm appears. An IR spectrum of the sample confirms the formation of *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H by the growth of a band at 1926 cm^{-1}. A UV–vis spectrum of a sample of *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H prepared by irradiation of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ in methylcyclohexane containing 0.01 M in HSiMe$_3$ at 298 K is the same as the spectrum of *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H formed from (η^5-C_5Me_5)Fe(CO)$_2$Me. Cooling of the sample to 173 K does not result in the growth of a visible absorption at 510 nm. Thus, the visible absorption that appears when (η^5-C_5Me_5)Fe(CO)$_2$Me is irradiated at 173 K in the presence of HSiMe$_3$ is not *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H. We assign the absorption at 510 nm to (η^5-C_5Me_5)Fe(CO)(Me)(SiMe$_3$)H. Unfortunately, a ^{1}H NMR of the species could not be obtained owing to low solubility of starting material and low temperature necessary to observe the 510-nm absorption.

The photochemical reaction of (η^5-C_5Me_5)Fe(CO)$_2$Me to yield CH$_4$ following oxidative addition of Si–H to a monocarbonyl is analogous to the photoreactivity of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H.[11] This complex undergoes oxidative addition of the β-Si–H at 77 K to form (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H. The Fe(CH$_2$SiMe$_2$) is formulated as a metallasilacyclopropane having Fe–Si and Fe–C σ-bonds. The single CO absorption of (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$) is at ~1926 cm^{-1}—very close to that for the feature found at 1925 cm^{-1} from irradiation of (η^5-C_5Me_5)Fe(CO)$_2$Me in HSiMe$_3$ at 173 K. The similarity of the CO absorption suggests that the (η^5-C_5Me_5)Fe(CO)(Me)(SiMe$_3$)H is very similar electronically to the (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)(H). But surprisingly, the (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H is less labile than the (η^5-C_5Me_5)Fe(CO)(Me)(SiMe$_3$)H. Only above approximately 225 K does (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H undergo active reductive elimination of C–H and reaction with CO to form (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$. Interestingly, no reductive elimination of Si–H to reform (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$SiMe$_2$H can be detected.[11] Presumably, geometric factors dominate the lability of (η^5-C_5Me_5)Fe(CO)(Me)(SiMe$_3$)H compared to (η^5-C_5Me_5)Fe(CO)(CH$_2$SiMe$_2$)H.

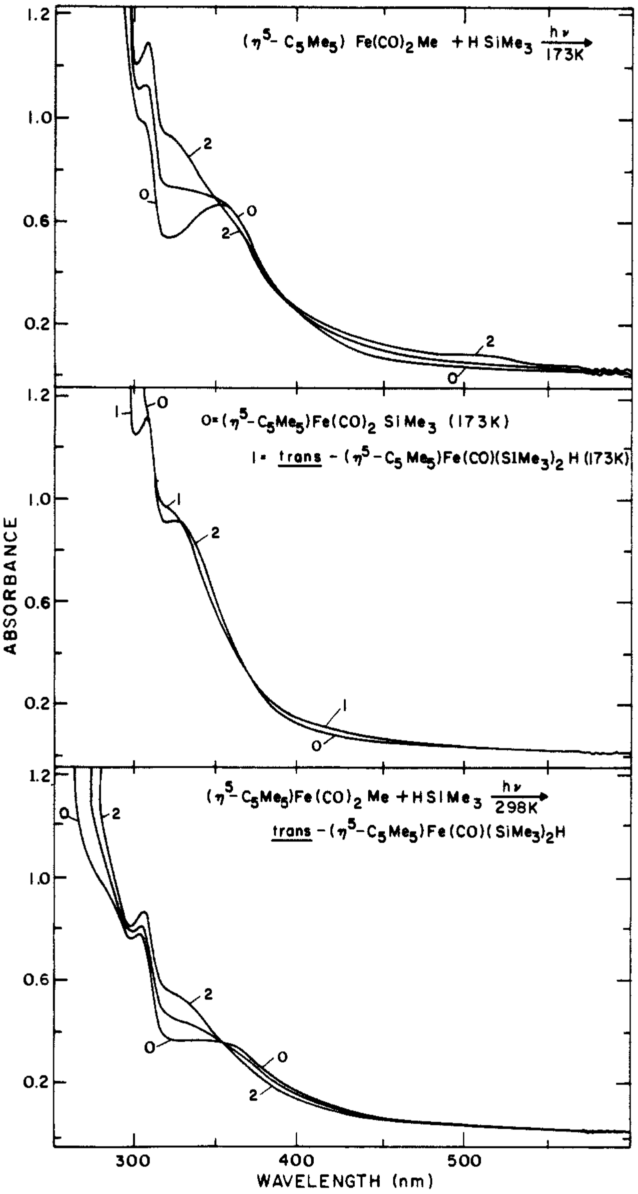


Figure 7. UV–vis spectral changes accompanying the photochemical reaction of (η^5-C_5Me_5)Fe(CO)$_2$R; R = Me, SiMe$_3$ with HSiMe$_3$. It should be noted that the sharp band at 305 nm in all spectra is an artifact of the cell. Top: The UV–vis spectral changes accompanying the near-UV irradiation of (η^5-C_5Me_5)Fe(CO)$_2$Me (0.002 M) in methylcyclohexane containing ~0.01 M HSiMe$_3$ at 173 K. Trace 0 is the spectrum of (η^5-C_5Me_5)Fe(CO)$_2$Me. Trace 2 shows the changes occurring upon irradiation. The absorption at 510 nm is attributed to (η^5-C_5Me_5)Fe(CO)(SiMe$_3$)(Me)H. An IR spectrum of the sample shows a single product band at 1925 cm^{-1}. The extent of conversion is ~50%. Middle: Trace 0 shows the UV–vis spectrum of (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ (0.004 M) in methylcyclohexane at 173 K. Trace 1 shows the UV–vis spectrum of *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H at 173 K. The *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H was generated by photolysis of (η^5-C_5Me_5Fe(CO)$_2$SiMe$_3$ (0.004 M) in the presence of 0.01 M MSiMe$_3$ at 173 K to effect 90% conversion of the (η^5-C_5Me_5)Fe(CO)$_2$SiMe$_3$ to *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H. Bottom: The UV–vis spectral changes accompanying the near-UV irradiation at 298 K of (η^5-C_5Me_5)Fe(CO)$_2$Me (0.001 M) in methylcyclohexane containing ~0.01 M HSiMe$_3$. Trace 0 shows the spectrum of (η^5-C_5Me_5)Fe(CO)$_2$Me. Trace 2 shows the spectrum of *trans*-(η^5-C_5Me_5)Fe(CO)(SiMe$_3$)$_2$H generated upon photolysis. An IR spectrum of the sample shows a single product band at 1926 cm^{-1}. The extent conversion is 95%.

It is important to note that evidence for the reductive elimination of MeSiR'$_3$ from (η^5-C_5Me_5)Fe(CO)(Me)(SiR'$_3$)H has not been found. The elimination of RSiR'$_3$ from R–M–SiR'$_3$ complexes is a crucial step in the postulated mechanism for hydrosilation that involves alkene insertion into the M–H bond.[1] If reductive elimination of MeSiR'$_3$ did occur from (η^5-C_5Me_5)Fe(CO)-

(Me)(SiR$'_3$)H, it would give rise to (η^5-C$_5$Me$_5$)Fe(CO)H. We have found[20] that photoreaction of (η^5-C$_5$Me$_5$)Fe(CO)$_2$H gives CO loss to form (η^5-C$_5$Me$_5$)Fe(CO)H, but in the presence of HSiEt$_3$ [(η^5-C$_5$Me$_5$)Fe(CO)$_2$]$_2$ results, and there is no evidence for the formation of (η^5-C$_5$Me$_5$)Fe(CO)(SiEt$_3$)$_2$H. Note that *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiEt$_3$)$_2$H is the only product formed from 298 K irradiation of (η^5-C$_5$Me$_5$)Fe(CO)$_2$Me in the presence of HSiEt$_3$. In the presence of HSiMe$_3$, irradiation of (η^5-C$_5$Me$_5$)Fe(CO)$_2$Me yields no SiMe$_4$; CH$_4$ accounts for all of the reacted Fe–Me species. Thus, for the case at hand, (η^5-C$_5$Me$_5$)Fe(CO)(Me)(SiR$'_3$)H, it appears that reductive elimination of alkane (CH$_4$) is much more facile than elimination of Me–SiR$'_3$.

The reductive elimination of alkane following oxidative addition of HSiR$'_3$ to 16e$^-$ (η^5-C$_5$Me$_5$)Fe(CO)R complexes appears general. Near-UV irradiation of either (η^5-C$_5$Me$_5$)Fe(CO)$_2$C$_2$H$_5$ or (η^5-C$_5$Me$_5$)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$ in pure HSiEt$_3$ at 298 K results in the growth of a single IR band at 1920 cm^{-1}. This IR spectral change is consistent with the formation of (η^5-C$_5$Me$_5$)Fe(CO)(SiEt$_3$)$_2$H. The intermolecular addition of HSiR$'_3$ to (η^5-C$_5$Me$_5$)Fe(CO)R is, however, in competition with intramolecular β-elimination. Irradiation of (η^5-C$_5$Me$_5$)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$ complexes in alkane with moderate HSiMe$_3$ concentration ($\sim$0.05 M) results in formation of both *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)$_2$H and (η^5-C$_5$Me$_5$)Fe(CO)$_2$H. ^{1}H NMR spectroscopy shows that irradiation of (η^5-C$_5$Me$_5$)Fe(CO)$_2$C$_2$H$_5$ in toluene-d_8 which is about 0.01 M in HSiMe$_3$ does result in the formation of C$_2$H$_6$ and *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)$_2$H, as evidenced by the appearance of an ^{1}H NMR resonance at 0.82 ppm for C$_2$H$_6$ and 0.51 and −13.31 for *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)$_2$H. There is, however, a significant yield of (η^5-C$_5$Me$_5$)Fe(CO)$_2$H and C$_2$H$_4$ arising from β-H elimination.

The reductive elimination of alkylsilane, H–CH$_2$CH$_2$SiMe$_3$, from the (η^5-C$_5$Me$_5$)Fe(CO)(SiR$'_3$)(CH$_2$CH$_2$SiR$'_3$)H complexes is an example of a crucial step in the hydrosilation of alkenes via alkene insertion into the M–SiR$'_3$ bond. Our results show that this a facile reaction. In addition, our results show that oxidative addition of silane to 16e$^-$ M–R complexes is in competition with β-H elimination from these complexes. This competition is consistent with reports that in the hydrosilation of olefins, the yields of vinylsilane, eq 4, (compared to alkylsilane, eq 1) are inversely proportional to the concentration of silane.[6]

Conclusions

The photochemistry of (η^5-C$_5$Me$_5$)Fe(CO)$_2$R complexes in the presence of silanes and olefins provides a precedent for all of the reactions postulated to occur in catalytic hydrosilation of olefins via alkene insertion into a M–Si bond, the mechanism shown in Scheme I. Photoinduced alkene insertion into the Fe–Si bond of (η^5-C$_5$Me$_5$)Fe(CO)$_2$SiMe$_3$ has been demonstrated. In addition, the reaction of (η^5-C$_5$Me$_5$)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$ upon photolysis to form (η^5-C$_5$Me$_5$)Fe(CO)(C$_2$H$_4$)SiMe$_3$ is evidence that the insertion of C$_2$H$_4$ into an M–Si bond is a reversible reaction and should be drawn as such. Reductive elimination of R–H, R = Me, Et, CH$_2$CH$_2$SiMe$_3$, following oxidative addition of HSiR$'_3$, R$'$ = Me, Et, to photogenerated (η^5-C$_5$Me$_5$)Fe(CO)R has also been demonstrated. Interestingly, the intermediate in this reaction, (η^5-C$_5$Me$_5$)Fe(CO)(SiR$'_3$)(R)H, does not eliminate R-SiR$'_3$. Such an elimination, though very slow, has been demonstrated for (CO)$_4$FeR(SiMe$_3$)[5] and is a crucial step in a hydrosilation mechanism via olefin insertion into an M–H bond. While our results do not rule out this traditional mechanism for hydrosilation, they do demonstrate that a mechanism involving olefin insertion into an M–Si bond is viable and must be considered as an alternative.

Acknowledgment. We thank the National Science Foundation and the Office of Naval Research for partial support of this research.

Registry No. (η^5-C$_5$Me$_5$)Fe(CO)$_2$SiMe$_3$, 101493-92-9; (η^5-C$_5$Me$_5$)Fe(CO)$_2$Cl, 101493-93-0; (η^5-C$_5$Me$_5$)Fe(CO)$_2$CH$_2$CH$_2$SiMe$_3$, 101493-94-1; [(η^5-C$_5$Me$_5$)Fe(CO)$_2$]$_2$, 35344-11-7; (η^5-C$_5$Me$_5$)Fe(CO)$_2$CH$_2$SiMe$_2$H, 101493-95-2; *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)$_2$H, 101493-96-3; *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)(SiEt$_3$)H, 101493-97-4; (η^5-C$_5$Me$_5$)Fe(CO)$_2$SiEt$_3$, 101493-98-5; (η^5-C$_5$Me$_5$)Fe(CO)(^{13}CO)SiMe$_3$, 101493-99-6; (η^5-C$_5$Me$_5$)Fe(CO)(^{13}CO)CH$_2$CH$_2$SiMe$_3$, 101494-00-2; (η^5-C$_5$Me$_5$)Fe(CO)(B)SiMe$_3$ (B = 1-pentene), 101494-01-3; (η^5-C$_5$Me$_5$)Fe(CO)$_2$H, 80409-91-2; (η^5-C$_5$Me$_5$)Fe(CO)(PPh$_3$)CH$_2$CH$_2$SiMe$_3$, 101494-02-4; (η^5-C$_5$Me$_5$)Fe(CO)$_2$Me, 52409-66-2; *trans*-(η^5-C$_5$Me$_5$)Fe(CO)(SiEt$_3$)$_2$H, 101494-03-5; (η^5-C$_5$Me$_5$)Fe(CO)SiMe$_3$, 101494-04-6; (η^5-C$_5$Me$_5$)Fe(CO)(PPh$_3$)SiMe$_3$, 101494-05-7; (η^5-C$_5$Me$_5$)Fe(CO)(SiMe$_3$)(Me)H, 101494-06-8; (η^5-C$_5$Me$_5$)Fe(CO)(C$_2$H$_4$)SiMe$_3$, 101494-07-9; C$_2$H$_4$, 74-85-1; Me$_3$Si(CH=CH$_2$), 754-05-2.