Photochemical Reactions of $(\eta^5$ -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

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Abstract: Near-UV irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ 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 $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ at 298 K is shown to be at least 0.22 ± 0.03 mol/einstein as measured by the photosubstitution yield for formation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ at 298 K is shown to be at least 0.22 ± 0.03 mol/einstein as measured by the photosubstitution yield for formation of $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)PPh_3$ in methylcyclohexane containing ~0.05 M PPh₃. Photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in the presence of HSiR'₃ (R' = Me, Et in alkane solution, or pure HSiEt₃) results in the loss of CO and the oxidative addition of HSiR'₃ to form trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(SiR'_3)H$ 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$ in C_2H_4 saturated alkane solution results in the formation of $(\eta^5 - C_5 Me_5)Fe(CO)(C_2H_4)SiMe_3$, as evidenced by the growth of a single band in the IR spectrum and the ¹³C NMR when 99% ¹³C-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 -C₅Me₅)Fe(CO)₂H and Me₃Si(CH=CH₂). In the presence of CO (η^5 -C₅Me₅)Fe- $(CO)_2CH_2CH_2SiMe_3$ is formed. $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ has been isolated and characterized. Near-UV photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in an alkane solution at 298 K results in both β -hydrogen and β -SiMe₃ transfer. This is evidenced by the appearance of both Me₃Si(CH=CH₂) and C₂H₄ in the ¹H NMR. The ratio of β -hydrogen transfer to β -SiMe₃ transfer is ~2:1. Photolysis of (η^5 -C₅Me₅)Fe(CO)₂R (R = Me, Et) in an alkane solution containing HSiR'₃ results in the formation of RH and trans-(η^5 -C₅Me₅)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 $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(Me)H$ at 173 K by photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in the presence of HSiMe₃. 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2 R$ complexes, R = Me, Et, $CH_2 CH_2 SiMe_3$, and SiMe₃, 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 $(\eta^5-C_5Me_5)$ -Fe(CO)₂SiMe₃, (ii) transfer of either the -SiMe₃ group or a β -H group upon photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, and (iii) reductive elimination of alkane, RH, upon photoinduced oxidative addition of HSiR'₃ (R' = Me, Et) to $(\eta^5-C_5Me_5)Fe$ - $(CO)_2R$, R = Me, Et.

A commonly proposed mechanism¹ for transition metal-catalyzed hydrosilation of olefins, eq 1, involves the key steps of

$$= \left\langle + HSiR'_3 \xrightarrow{\text{cotalyst}}_{H} \xrightarrow{H} \right\rangle$$

insertion of the olefin into the M-H bond of an R₃Si-M-H complex, eq 2, followed by the reductive elimination of the alkyl

$$\xrightarrow{M-SiR'_3} + \xrightarrow{M-SiR'_3}$$
 (2)

group and the silyl group to form an alkylsilane, eq 3. This

$$\xrightarrow{M-SiR'_3} \xrightarrow{M} + \xrightarrow{H}$$
 (3)

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)(SiR₃),⁵ but it should be noted that the rate at 298 K is slow.

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 R₃SiCo(CO)₄⁸ photocatalyzed hydrosilation. This mechanism involving olefin insertion into the M-Si bond as a key step was

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Scheme I. Proposed Mechanism for Hydrosilation Catalysis via C₂H₄ 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

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, β -H elimination from M-CH2CH2SiR3 complexes has not been studied.

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

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3} \xrightarrow{\eta\nu}_{C_{2}H_{4}}$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3} \quad (5)$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3} \xrightarrow{\Delta}$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}CH_{2}CH_{2}SiMe_{3}$$
 (6)

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

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}CH_{2}CH_{2}SiMe_{3} \xrightarrow{h\nu} \\ (\eta^{5}-C_{5}Me_{5})Fe(CO)CH_{2}CH_{2}SiMe_{3}$$
(7)
$$(\eta^{5}-C_{5}Me_{5})Fe(CO)CH_{2}CH_{2}SiMe_{3} \xrightarrow{\Delta}$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}H + Me_{3}Si(CH=CH_{2})$$
 (8)

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)CH_{2}CH_{2}SiMe_{3} \xrightarrow[+CO]{} +cO$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3} + C_{2}H_{4} (9)$$

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have also found that loss of CO from $(\eta^5-C_5Me_5)Fe(CO)_2(alkyl)$ 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

$$(\pi^{5}-C_{5}Me_{5})Fe(CO)_{2}R \xrightarrow{A\nu}_{HSiR'_{3}} [(\pi^{5}-C_{5}Me_{5})Fe(CO)(R)(SiR'_{3})H] + CO$$

 $\downarrow \Delta, HSiR'_{3}$
trans - $(\pi^{5}-C_{5}Me_{5})Fe(CO)(SiR'_{3})_{2}H + RH$ (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 CaH₂. 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. ¹³C-enriched (99%) CO and C_2H_4 were obtained from Cambridge Isotopes. $(\eta^5-C_5Me_5)Fe(CO)_2R$, R = Me, Et,¹⁰ CH₂SiMe₂H,¹¹ and SiMe₃,¹¹ and $(\eta^5-C_5H_5)Fe(CO)_2$ SiMe₃¹¹ 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. Room temperature samples in NMR tubes were irradiated by using two General Electric blacklight bulbs (355 \pm 20 nm). Quantum yields for PPh₃ and alkene substitution and HSiR', addition were measured at 366 nm in a merry-go-round¹² 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 $[(\eta^5 - C_5 Me_5)Fe(CO)_2]_2$ from $(\eta^5 - C_5 Me_5)Fe(CO)_2]_2$ $C_5Me_5)Fe(CO)_2Me$ and $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ 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 actioometry¹³ was used to determine light intensity, typically $\sim 10^{-7}$ eins. in/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 CaF₂ windows. Liquid N₂ 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. $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was prepared by 5 h of irradiation (with a Hanovia 550-W Hg lamp) of a ~ 0.002 M solution (50 mL) of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in C_2H_4 -saturated methylcyclo-

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⁽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 $(\eta^5-C_5Me_5)Fe(CO)_2H$ (~20%), $(\eta^5-C_5Me_5)Fe(CO)_2CH_2SiMe_3$ (~50%), $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ (~20%), and $[(\eta^5-C_5Me_5)Fe(CO)_2]_2$. CCl₄ (5 mL) was added to the solution to react with $(\eta^{5}-C_{5}Me_{5})Fe$ - $(CO)_2H$ to form $(\eta^5-C_5Me_5)Fe(CO)_2Cl$. 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 $(\eta^5$ -C₅Me₅)Fe(CO)₂CH₂CH₂SiMe₃. The remaining fractions were a mixture of $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ and $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3}$. The $[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}]_{2}$ and the $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}]_{2}$ $C_5Me_5)Fe(CO)_2Cl$ remained at the top of the column. The solutions containing pure $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was combined and reduced to dryness, leaving the $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ as a yellow powder. The $(\eta^5 C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ was further purified by sublimation at 40 °C (~10⁻³ atm). The $(\eta^5 - C_5Me_5)Fe^{-1}$ $(CO)_2CH_2CH_2SiMe_3$ 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 ¹³C NMR spectra of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ are as expected.

 $(\eta^5 - C_5 Me_5)Fe(CO)_2 CH_2 Si Me_2 H$ was also used as a precursor to $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. A C_2H_4 -saturated solution of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ was irradiated at 198 K for 1 h to form $(\eta^5 - C_5 Me_5)Fe(CO)(CH_2SiMe_2)H^{11}$ This solution was then warmed to and left at ~225 (dry ice/acetonitrile) for about 1 h to allow the rearrangement of the $(\eta^5 \cdot C_5 M e_5)Fe(CO)(CH_2SiM e_2)H$ to $(\eta^5 \cdot C_5 M e_5)Fe(C$ $(CO)(C_2H_4)SiMe_3$. 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$. The product was identified as $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ by its ¹H NMR spectrum. Attempts to synthesize $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ from the

reaction of $Na^+[(\eta^5-C_5M_5)Fe(CO)_2]^-$ with $ClCH_2CH_2SiMe_3$ were not successful. Apparently the $Na^+[(\eta^5-C_5Me_5)Fe(CO)_2]^-$ is a strong enough nucleophile to cause the ClCH2CH2SiMe3 to undergo an elimination, a reaction typical of β -halosilanes.¹⁴

Results and Discussion

Photochemistry of $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$: Relative Importance of CO Loss and Fe-Si Homolysis. Near-UV irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ (typically 5×10^{-3} M) at 298 K in the presence of PPh₃ results in the clean, quantum-efficient formation of $(\eta^5 - C_5 Me_5)Fe(CO)(PPh_3)SiMe_3$, eq 11. The

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3} + PPh_{3} \xrightarrow[-CO]{-CO} (\eta^{5}-C_{5}Me_{5})Fe(CO)(PPh_{3})SiMe_{3} (11)$$

quantum yield for this reaction at 366 nm in alkane with 0.07 M PPh₃ is 0.21 ± 0.03 mol/einstein and with 0.04 M PPh₃ is 0.22 \pm 0.03 mol/einstein. The lack of significant change in the quantum yield for PPh₃ substitution of $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$ with change in the PPh₃ concentration suggests that the mechanism for this reaction is dissociative loss of CO. The photosubstitution of $(\eta^5-C_5H_5)Fe(CO)_2SiMe_3$ by phosphines is wellknown,¹⁵ and dissociative loss of CO from various (η^5 -C₅R'₅)- $Fe(CO)_2R$ complexes is known to be efficient.^{10,16}

In an attempt to observe the $16e^{-}(\eta^{5}-C_{5}Me_{5})Fe(CO)SiMe_{3}$, the parent dicarbonyl was irradiated in an alkane matrix at low temperature. The IR spectral changes in the CO region accompanying reaction of $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$ 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 $(\eta^5$ -C₅Me₅)Fe(CO)SiMe₃ grows in at 1902 cm⁻¹. As is the case for other $(\eta^5-C_5R_5)Fe(CO)_2R'$ complexes, the low-temperature matrix photoreaction of $(\eta^5-C_5Me_5)Fe$ -



Figure 1. IR difference spectral changes accompanying near-UV irradiation of ~0.005 M (η^{5} -C₅Me₅)Fe(CO)₂SiMe₃ at 77 K in methyl-cyclohexane 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), (η^5 -C₅Me₅)Fe(CO)SiMe₃.

(CO)₂SiMe₃ is very slow.^{10,16,17} In fact, $(\eta^5$ -C₅Me₅)Fe(CO)₂SiMe₃ is the only $(\eta^5 - C_5 R'_5) Fe(CO)_2 R$ 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., $R' = \eta^1 - CH_2C_6H_5^{16}$ 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 (η^{5} - C_5Me_5)Fe(CO)₂CH₂SiMe₂H, for example, can be substantially (>50%) converted to $(\eta^5 - C_5 Me_5)Fe(CO)(CH_2SiMe_2)H$ in 1 min.¹¹

Near-UV irradiation of 5×10^{-3} M (η^5 -C₅Me₅)Fe(CO)₂SiMe₃ at 298 K in alkane solution (no added ligands) results in the formation of $[(\eta^5-C_5Me_5)Fe(CO)_2]_2$ in about 75% yield. The disappearance quantum yield for 355-nm excitation is 0.05 ± 0.01 mol/einstein. Irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ under similar conditions, but in a CO-saturated alkane solution, results in little net photochemistry. Irradiation in a ¹³CO-saturated alkane solution results in the rapid formation of $(\eta^5-C_5Me_5)Fe_5$ $(CO)(^{13}CO)SiMe_3$, 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 Me₃Si radicals cannot be unambigously ruled out. Formation of M-M bonded products via photogenerated 16e⁻ species has been implicated in photoreactions of $(\eta^5-C_5H_5)MO(\dot{CO})_3Me^{19}$ and $(\eta^5-C_5Me_5)Fe(\dot{CO})_2H^{.20}$ This is in contrast to the photochemistry of other $(\eta^5 - C_5 R_5)$ 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 $(\eta^5$ - C_5Me_5)Fe(CO)₂SiMe₃ is very quantum inefficient in comparison to light-induced loss of CO.

Photochemistry of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in the Presence of HSiR₃: Formation of $(\eta^5 - C_5 Me_5)Fe(CO)(SiR_3)_2H$ Complexes. Near-UV irradiation of $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$ in a 0.03 M HSiMe₃ methylcyclohexane solution results in the oxidative ad-

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Table I.	IR and	UV-vis	Spectral	Data	for	Relevant	Complexes
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complex	temp, (K)	ν (CO), cm ⁻¹ (ϵ , M ⁻¹ cm ⁻¹ or rel Abs)	λ , nm (ϵ , M ⁻¹ cm ⁻¹)	
$(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$	298	1980 (6500) 1927 (7900)	250 (sh) (~9400) 285 (5000) 223 (1000)	
$(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$	77	1978 (0.8) 1921 (1.0)	333 (1900)	
$(\eta^5-C_3Me_3)Fe(CO)SiMe_3$	77	1902		
$(\eta^5 - C_1 Me_3) Fe(CO)(PPh_3) SiMe_3$	298	1895		
trans- $(\eta^5$ -C ₅ Me ₅)Fe(CO)(SiMe ₃) ₂ H	298	1926	~ 275 (sh), 320, ~ 400 (sh)	
trans- $(\eta^5$ -C ₅ Me ₅)Fe(CO)(SiMe ₃) ₂ H	173	1925	$(320, \sim 400 \text{ (sh)})$	
$(\eta^5 - C_5 Me_5) Fe(CO)_2 CH_2 CH_2 Si Me_3$	298	1985 (0.8), 1932 (1.0)		
$(\eta^5 - C_5 Me_5) Fe(CO)(SiMe_3)(Me)H$	173	1925	318, 510	
$(\eta^5 - C_5 Me_5)Fe(CO)(C_2 H_4)SiMe_3$	198	1929		
$(\eta^5 - C_5 Me_5 Fe(CO)(C_2 H_4)SiMe_3$	298	1929		
$(\eta^5-C_5Me_5)Fe(CO)(1-pentene)SiMe_3$	298	1920		
$(\eta^5 - C_5 Me_5) Fe(CO)_2 Me$	298	1993 (7700) 1939 (7750)		
$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}H$	298	2002 (6210) 1945 (6060)	340 (1500)	
$[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}]_{2}$	298	1930 (12700) 1761 (7400)	533 (1520), 420 (2980) 362 (10100)	
$(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$	298	1977 1925		

^aAll data for alkane solutions.

Table II. NMR Data for Relevant Complexes⁴

compound	¹ H NMR	δ ppm ^b	¹³ C NMR	δ ppm ^b
$(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$	C5Me5 SiMe2	1.53 (s, 15) 0.53 (s, 9)	C5 Mes	94.6 9.8
	,		SiMe ₃	6.7
$(x^{\frac{1}{2}} \cap M_{2}) \mathbb{E}_{2}(\mathbb{C} \cap M_{2})$	C Ma	1 42 (* 15)	CO	217.8
$(\eta^2 - C_5 Me_5) Fe(CO)_2 Me$	Csivics Me	1.42 (s, 15) 0.06 (s, 3)		
(n ⁵ -C ₄ Me ₄)Fe(CO) ₂ H	C.Me.	1.61(s, 15)		
(1/ 03:103): 0(00)2:1	Fe-H	-11.5 (s, 1)		
$(\eta^5$ -C ₅ Me 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
	-SiMe3	0.12 (s, 9)	SiMe ₃	-1.7
			CH ₂ CH ₂ CO	26.1, 7.5 220.0
$(\eta^5-C_5Me_5)Fe(CO)(PPh_3)SiMe_3^d$	C ₅ Me ₅	1.40 (s, 15)		
	SiMe ₃	0.38 (s, 9)		
$(\eta^{5}-C_{5}Me_{5})Fe(CO)(PPh_{3})CH_{2}CH_{2}SiMe_{3}$	C ₅ Me ₅	1.46 (s, 15)		
	SiMe ₃	0.01 (s, 9)		
$(\eta^3 - C_5 Me_5) Fe(CO)(C_2 H_4) Si Me_3 (200 \text{ K})$	C ₅ Me ₅	1.28 (s, 15)		
	SiMe ₃	0.75 (s, 3)		
		0.68(s, 3)		
	0.14	0.20 (s, 3)		
$(\eta^2 - C_5 Me_5) Fe(CO)(C_2 H_4) SiMe_3 (298 K)$	C ₅ Me ₅	1.39 (s, 15)		
$(1,5,0,M_{0}) = (0,0) (S;M_{0}) H$	Sime ₃	$0.37(s, 9)^2$	<u>^</u>	04.0
$(\eta^2 - C_5 Me_5) Fe(CO)(SiMe_3)_2 H$	(SiMa)	1.45(8, 15)	C ₅	94.0
	$(Sinvie_3)_2$	-13.31(s, 16)	(SiMe)	0.6
	1.0-11	-13.31 (8, 1)	$(SiMe_3)_2$	215.6
				412.0

^a All data for toluene- d_8 solutions at 298 K unless otherwise noted. ^b Chemical shifts vs. Si(CH₃)₄; peak multiplicity and relative integration are given in parentheses for ¹H NMR. ^c An AA':BB' system, see Figure 4. ^d Benzene- d_6 solution. ^e This is a broadened singlet.

dition of HSiMe₃ to yield *trans*- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$, eq 12, as indicated by the disappearance of the absorption at 2120

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3} + HSiMe_{3} \xrightarrow{h\nu}_{-CO}$$

trans- $(\eta^{5}-C_{5}Me_{5})Fe(CO)(SiMe_{3})_{2}H$ (12)

cm⁻¹ associated with the Si-H bond of HSiMe₃ 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 -C₅Me₃)Fe(CO)₂SiMe₃ molecule reacted. The ¹H 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 -SiMe₃ groups. The integration of the ¹H NMR resonances is consistent with the proposed structure. The same reaction has been reported for (η^5 -C₅H₅)Fe(CO)₂SiCl₃ in the presence of HSiCl₃ to yield fully characterized *trans*-(η^5 -C₅H₅)Fe(CO)- $(SiCl_3)_2H$.²¹ Attempts to isolate the *trans*- $(\eta^5-C_5Me_5)$ Fe-(CO) $(SiMe_3)_2H$ have not been successful. The complex is labile with respect to loss of HSiMe₃ in the absence of HSiMe₃. In the presence of 1 atm CO, the complex gradually reacts (~25% in 2 h at 298 K) to form only $(\eta^5-C_5Me_5)$ Fe(CO)₂SiMe₃, consistent with reductive elimination of HSiMe₃ followed by CO uptake as the mechanism for reaction. There is no evidence for formation of $(\eta^5-C_5Me_5)$ Fe(CO)₂H in the reaction, ruling out reductive elimination of Si₂Me₆. No Si₂Me₆ is detected by ¹H NMR.

elimination of Si₂Me₆. No Si₂Me₆ is detected by ¹H NMR. Irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in methylcyclohexane solution which is 0.8 M in HSiEt₃ results in the growth of a single IR band at 1922 cm⁻¹. We assign the 1922-cm⁻¹ feature to *trans*- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(SiEt_3)H$, 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 (η^5 -C₅Me₅)Fe(CO)₂SiMe₃ at 196 K in C₂H₄-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 (η^5 -C₅Me₅)Fe(CO)(C₂H₄)SiMe₃.

 $(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$ 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 $(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$ from reductive elimination of HSiMe3 and reaction with CO. The low-energy band of $(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$ (1925 cm⁻¹) overlaps the single band of trans- $(\eta^5-C_5Me_5)Fe(CO)(SiR'_3)_2H$. Irradiation of a toluene- d_8 solution of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ which is ~ 0.05 M in HSiEt₃ 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 $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(SiEt_3)H$ and $(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$. Free HSiMe₃ also appears in the NMR spectrum, confirming that silane exchange occurs. Slow conversion to $(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$ is ultimately found. The quantum yield for disappearance of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ when photolyzed at 366 nm in an alkane solution which is 0.1 M in HSiEt₃ is 0.20 ± 0.02 mol/einstein.

Photochemistry of $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2SiMe_3$ in the Presence Formation of an Alkene Insertion Product (η^5 of C₂H₄: $C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. The IR spectral changes accompanying near-UV photolyhsis of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in an C₂H₄-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 $(\eta^5-C_5Me_5)Fe(CO)(C_2H_4)$ -SiMe₃. The band at 1929 cm⁻¹ persists upon warming of the solution to 298 K. The same spectrum is obtained when $(\eta^5$ -C₅Me₅)Fe(CO)₂SiMe₃ is irradiated at 298 K in an C₂H₄-saturated methylcyclohexane solution, Figure 3. Within 5 min at 298 K, thermal reaction of $(\eta^5-C_Me_5)Fe(CO)(C_2H_4)SiMe_3$ occurs to the extent of $\sim 50\%$ 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 $(\eta^5-C_5Me_5)Fe_5$ $(CO)_2H$. The two larger bands at 1985 and 1932 cm⁻¹ appear to be a new $(\eta^5 - C_5 Me_5)Fe(CO)_2 R$ complex. The photochemistry was carried out on a synthetic scale, resulting in the isolation of $(\eta^5-Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, a species having IR absorptions at 1985 and 1932 cm⁻¹. The ¹H- and ¹³C NMR spectra of at 1985 and 1932 cm⁻¹. $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, 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 $(\eta^5 C_5Me_5)Fe(CO)_2SiMe_3$ in the presence of C_2H_4 .

The reaction of $(\eta^5 \cdot \hat{C}_5 Me_5)Fe(CO)_2SiMe_3$ with C_2H_4 has been investigated by ¹H NMR spectroscopy at 298 and 200 K in order to more fully characterize the labile $(\eta^5 \cdot C_5 Me_5)Fe(CO)(C_2H_4)$ -SiMe₃. Near-UV irradiation of $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2SiMe_3$ in



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Figure 3. IR difference spectral changed resulting from near-UV photolysis of 0.01 M (η^5 -C₅Me₅)Fe(CO)₂SiMe₃ at 298 K in C₂H₄-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 (η^5 -C_{Me₃})Fe(CO)(C₂H₄)SiMe₃. 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 (η^5 -C₅Me₅)Fe(CO)₂H. The absorptions at 1985 and 1932 cm⁻¹ are due to (η^5 -C₅Me₅)Fe(CO)₂CH₂CH₂SiMe₃.



Figure 4. The ¹H- and ¹³C (inset) NMR spectra of $(\eta^5-C_5Me_5)$ Fe-(CO)₂CH₂CH₂SiMe₃ in toluene- d_8 at 298 K. Cf. Table II for assignments.

 C_2H_4 -saturated toluene- d_8 solution at 200 K results in the appearance of a new (η^5 - C_5Me_5) resonance at 1.28 ppm. Three new resonances, each of which integrates as three protons relative to the (η^5 - C_5Me_5) resonance, also appear at 0.75, 0.68, and 0.20 ppm. These are assigned to the -SiMe_3 protons of (η^5 - 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 (η^5 - C_5Me_5)Fe(CO)₂SiMe_3 in the toluene- d_8 at 200 K in the presence of 99% ¹³C-enriched C_2H_4 monitored by ¹³C 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 (η^5 - C_5Me_5)Fe(CO)(C_2H_4)SiMe_3 rests on the 1929



Figure 5. IR difference spectral changes resulting from near-UV photolysis of a methylcyclohexane solution of 0.01 M (η^5 -C₃Me₅)Fe-(CO)₂SiMe₃ under ~0.05 atm of ¹³CO and ~0.5 atm of C₂H₄. 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 -C₅Me₅)-Fe(CO)(¹³CO)SiMe₃. The absorbance at 1930 cm⁻¹ is attributed to (η^5 -C₅Me₅)Fe(CO)(C₂H₄)SiMe₃. 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 -C₅Me₅)Fe(CO)(¹³CO)CH₂CH₂SiMe₃ at the expense of (η^5 -C₅Me₅)Fe-(CO)(C₂H₄)SiMe₃.

cm⁻¹ IR feature, the ¹³C NMR, and the analogy to ¹³CO and PPh₃ substitution of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ (vide supra).

An ¹H NMR spectrum of a 200-K sample of $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$ warmed to 298 K or a sample prepared by near-UV photolysis of $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}SiMe_{3}$ in an $C_{2}H_{4}$ saturated toluene- d_{8} solution at 298 K shows a sharp resonance at 1.39 ppm assigned to the $(\eta^{5}-C_{5}Me_{5})$ protons. A broad resonance $(-SiMe_{3})$ which integrates as nine protons relative to the $(\eta^{5}-C_{5}Me_{5})$ resonance also appears at 0.37 ppm. As for the 200-K experiment, no resonance for coordinated $C_{2}H_{4}$ could be detected. The broad $-SiMe_{3}$ resonance and the lack of a resonance for coordinated $C_{2}H_{4}$ indicate that the $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})$ -SiMe₃ may be fluxional at 298 K. Within about 5 min at 298 K the ¹H NMR spectrum shows features due to Me_{3}Si(C_{2}H_{3}), $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}H$, and $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$ formation at the expense of $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$. When the 200-K sample of $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$ is warmed to 298 K and monitored by ¹³C NMR, the $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}^{13}CH_{2}^{13}CH_{2}SiMe_{3}$ is clearly observed.

Interestingly, the $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ complex can be produced from the photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in the presence of C₂H₄. Near-UV irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2SiMe_2H$ in C₂H₄ (or ¹³C₂H₄)-saturated toluene-d₈ at 200 K results only in the formation of $(\eta^5-C_5Me_5)Fe(CO)(CH_2SiMe_2)H$, as shown by ¹H NMR and ¹³C NMR spectroscopy.¹¹ Warming the sample to 225 K and then recooling the sample to 200 K results in an ¹H NMR spectrum which is the same as that obtained when $(\eta^5-C_5Me_5)Fe(CO)(CH_2SiMe_2)H$ has already been shown to rearrange at 225 K and react with ligands to form $(\eta^5-C_5Me_5)-Fe(CO)(L)(SiMe_3)$, L = CO, PPh₃, PEt₃.¹¹

The insertion of the C₂H₄ into the Fe–Si bond at room temperature has been investigated by the photolysis of $(\eta^5-C_5Me_5)$ -Fe(CO)₂SiMe₃ in a methylcyclohexane solution under an atmosphere of about 0.5 atm C₂H₄ and about 0.5 atm ¹³CO, Figure 5. Upon photolysis both $(\eta^5-C_5Me_5)$ Fe(CO)(¹³CO)SiMe₃ and $(\eta^5-C_5Me_5)$ Fe(CO)(C₂H₄)SiMe₃ are formed. The $(\eta^5-C_5Me_5)$ - Scheme II. The Photochemistry of $(\eta^5\mbox{-}C_5\mbox{Me}_5)\mbox{Fe}(CO)_2\mbox{Si}\mbox{Me}_3$ in the Presence of C_2H_4



Fe(CO)(C₂H₄)SiMe₃ then reacts with the ¹³CO to form (η^5 -C₅Me₅)Fe(CO)(¹³CO)CH₂CH₂SiMe₃, 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 -C₅Me₅)Fe(CO)(¹³CO)SiMe₃ 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 -C₅Me₅)Fe(CO)(¹³CO)(¹³CO)CH₂CH₂SiMe₃ is consistent with relatively slow C₂H₄ insertion into the Fe–Si bond.

Interestingly, we observe no features in the IR spectrum that can be assigned to $(\eta^5-C_5Me_5)Fe(CO)(C_2H_4)CH_2CH_2SiMe_3$ upon irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ in a C_2H_4 -saturated alkane solution. Such would be expected, but the species may be too labile with respect to formation of $(\eta^5-C_5Me_5)Fe-(CO)_2CH_2CH_2SiMe_3$ to allow detection.

Near-UV irradiation of $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2SiMe_3$ in 1-pentene at 298 K results in the formation of $(\eta^5 \cdot C_5 Me_5)Fe(CO)(1$ pentene)SiMe₃, 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 $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2H$. 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 $(\eta^5 \cdot C_5 Me_5)Fe(CO)_2SiMe_3$ 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 PPh₃.

Our findings concerning the photochemistry of $(\eta^{5}-C_{5}Me_{5})$ -Fe(CO)₂SiMe₃ in the presence of C₂H₄ are summarized in Scheme II. The primary photoprocess of $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)₂SiMe₃ is CO loss to form first $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)SiMe₃. This species can be detected in low-temperature matrices and can be scavenged by CO, PPh₃, C₂H₄, or HSiR'₃. In the presence of C₂H₄, for example, $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)(C₂H₄)SiMe₃ is formed upon photoreaction of $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)₂SiMe₃. This assertion is supported by the quantum yield for the reaction and by the reaction of $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)(CH₂SiMe₂)H in the presence of C₂H₄ at 225 K to give the same product, $(\eta^{5}-C_{5}Me_{5})$ Fe(CO)(C₂H₄)SiMe₃.

⁽²²⁾ The correct assignment of these bands was determined from the positions of the bands for naturally abundant $(\eta^5-C_5Me_5)Fe(CO)(^{13}CO)-CH_2CH_2SiMe_3$ in the IR spectrum of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$.

 $(\eta^{5}-C_{5}Me_{5})Fe(CO)(CH_{2}SiMe_{2})H$ can be considered a precursor for the thermal formation of $16e^{-}(\eta^{5}-C_{5}Me_{5})Fe(CO)SiMe_{3}$ at 225 K.¹¹ We propose that the conversion of $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$ to the $(\eta^{5}-C_{5}Me_{5})Fe(CO)CH_{2}CH_{2}SiMe_{3}$ (16e⁻) intermediate is the rate-determining step in forming $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}CH_{2}CH_{2}SiMe_{3}$. However, an incoming ligand-assisted insertion of the bound olefin into the Fe–Si bond cannot be completely ruled out. The thermal formation of $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}H$ and $Me_{3}Si(CH=CH_{2})$ from $(\eta^{5}-C_{5}Me_{5})Fe(CO)(C_{2}H_{4})SiMe_{3}$ does suggest, however, that insertion occurs by a nonassociative mechanism. In the absence of sufficient CO to trap the $16e^{-}$ insertion complex, $(\eta^{5}-C_{5}Me_{5})Fe(CO)-CH_{2}CH_{2}SiMe_{3}$, β -hydride elimination occurs, vide infra.

Preliminary results showing the insertion of C₂H₄ into the Fe-Si of $(\eta^5 - C_4 H_5) Fe(CO)_2 SiMe_3$ 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 C₅Me₅ complex. Irradiation of $(\eta^5-C_5H_5)Fe(CO)_2SiMe_3$ in C_2H_4 -saturated alkane results in the formation of $(\eta^5-C_5H_5)Fe(CO)(C_2H_4)SiMe_3$, as evidenced by the appearance of a single IR band at 1944 cm⁻¹. Thermal reaction of the $(\eta^5-C_5H_5)Fe(CO)(C_2H_4)SiMe_3$ in the presence of 1 atm CO has been monitored by IR. After 8 h, approximately 25% of the $(\eta^5-C_5H_5)Fe(CO)(C_2H_4)SiMe_3$ reacts, as evidenced by the decline in intensity of the 1944-cm⁻¹ band. Carbonyl bands of a new $(\eta^5-C_5H_5)Fe(CO)_2R$ complex appear at 2005 and 1951 cm^{-1} . By analogy to the chemistry of the C₅Me₅ complex, we attribute these bands to $(\eta^5 - C_5H_5)Fe(CO)_2CH_2CH_2SiMe_3$. Photolysis of the solution containing the $(\eta^5 - C_5 H_5)$ Fe-(CO)₂CH₂CH₂SiMe₃ results in IR changes consistent with the formation of some $(\eta^5 - C_5 H_5)Fe(CO)_2H$ from $(\eta^5 - C_5 H_5)Fe$ - $(CO)_2CH_2CH_2SiMe_3$ by β -hydrogen transfer in analogy to the photochemistry of the C₅Me₅ analogue described below.

Photochemistry of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$. The photochemistry of the insertion complex $(\eta^3-C_5Me_5)Fe-(CO)_2CH_2CH_2SiMe_3$ 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 $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}CH_{2}CH_{2}SiMe_{3}$ in either toluene- d_{8} or benzene- d_{6} results in the formation of Me₃Si(CH=CH₂) and $(\eta^5$ -C₅Me₅)- $Fe(CO)_2H$. 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 (n⁵-C₅Me₅)Fe(CO)₂H and Me₃Si(CH=CH₂), near-UV irradiation of $(\eta^5 - C_5 Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ also results in the formation of $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ and $(\eta^5-C_5Me_5)Fe (CO)(C_2H_4)SiMe_3$. The free C_2H_4 apparently arises from a β -SiMe₃ transfer to form (η^5 -C₅Me₅)Fe(CO)(C₂H₄)SiMe₃ which reacts with CO to form $(\eta^5 - C_5 Me_5)Fe(CO)_2SiMe_3$. [(ŋ⁵- $C_{SMe_{S}Fe(CO)_{2}}$ is formed as a secondary irradiation product from $(\eta^5 - C_5 Me_5)Fe(CO)_2H$. The relative yields, by integration of the ¹H NMR of Me₃Si(CH=CH₂), $(\eta^5$ -C₅Me₅)Fe(CO)₂SiMe₃, and $(\eta^5-C_5Me_5)Fe(CO)_2(C_2H_4)SiMe_3$ are 65%, 14%, and 15%, respectively, from near-UV irradiation of $(\eta^5-C_5Me_5)Fe$ - $(CO)_2CH_2CH_2SiMe_3$ in alkane solution.

Irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ in benzene- d_6 which is ~0.1 M in PPh₃ results in the suppression of both C_2H_4 formation and Me₃Si(CH=CH₂) formation. The major product, $(\eta^5-C_5Me_5)Fe(CO)(PPh_3)CH_2CH_2SiMe_3$, has resonances in the ¹H NMR spectrum at 1.46 and 0.01 ppm which integrate as 15 to 9. Resonances attributable to $(\eta^5-C_5Me_5)Fe(CO)(PPh_3)SiMe_3$ were not detected. thus, the photochemistry of $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ 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.

The suppression of the formation of Me₃Si(CH=CH₂) from $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$ by carrying out the irradiation in the presence of PPh₃ is consistent with the photochemistry of the $(\eta^5-C_5R_5)Fe(CO)_2(alkyl)$ complexes.¹⁰ The room temperature photochemistry of these complexes has been shown to be dominated by CO loss. PPh₃ is able to trap the 16e⁻, CO-loss inter-



Figure 6. ¹H NMR spectrum at 298 K of trans- $(\eta^5-C_5Me_5)Fe(CO)$ -(SiMe₃)₂H and $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ generated by the photolysis of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in toluene- d_8 containing ~0.01 M HSiMe₃. The resonance at 0.18 ppm is due to CH₄. The resonance at 1.53 and 0.53 ppm are due to the C₅Me₅ and -SiMe₃ protons of $(\eta^5-C_5Me_5)Fe$ -(CO)₂SiMe₃ formed via reaction of CO with trans- $(\eta^5-C_5Me_5)Fe$ -(CO)(SiMe₃)₂H which has the hydride resonance at -13.3 ppm. Cf. Table II for assignments.

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



mediate, $(\eta^5 - C_5 R_5)$ Fe(CO)(alkyl), thus inhibiting β -H transfer. The inhibition of C₂H₄ formation from $(\eta^5 - C_5 Me_5)$ Fe-(CO)₂CH₂CH₂SiMe₃ by PPh₃ shows that β -SiMe₃ transfer likely also arises from a CO-loss process.

The photochemistry of $(\eta^{5} \cdot C_{5}Me_{5})Fe(CO)_{2}CH_{2}CH_{2}SiMe_{3}$ 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 C₂H₄ into the M-Si bond. Our results indicate that the insertion of C₂H₄ can be a reversible process.

Photochemistry of $(\eta^5-C_5Me_5)Fe(CO)_2$ (alkyl) Complexes in the Presence of HSiR'₃. The ¹H NMR spectrum of the product from near-UV irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in a toluene- d_8 solution that is ~0.01 M in HSiMe₃ is shown in Figure 6. Interestingly, the spectrum shows that the Fe-containing product is *trans*- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$, the same as that obtained when $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ is irradiated in the presence of HSiMe₃. The spectrum also shows the growth of a singlet at 0.18 ppm which is assigned to CH₄. Eq 10 thus describes the photochemistry of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in the presence of HSiMe₃. Irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in the presence of HSiEt₃

Irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in the presence of HSiEt₃ also yields a disilyl hydride compound, *trans*- $(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$, as evidenced by the initial appearance of a band at 1920 cm⁻¹ in the IR spectrum of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ photolyzed in pure HSiEt₃. Subequently, in the dark, the 1920-cm⁻¹ band declines and two new bands appear at 1977 and

$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}$ -Alkyl and -Silyl Complexes

1925 cm⁻¹. These are attributed to $(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$. The 366-nm quantum yield for the disappearance of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in alkane solution which is 0.1 M in HSiEt₃ is 0.58 ± 0.03 mol/einstein. This quantum yield is in good agreement with the quantum yields obtained for CO-loss from various $(\eta^5-C_5R_5)Fe(CO)_2R$ compounds.^{10,16,17} We can, therefore, postulate the mechanism outlined in eq 13–16 for the photoreaction of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ with HSiR'₃.

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}Me \stackrel{h\nu}{\underset{\Delta}{\leftarrow}} (\eta^{5}-C_{5}Me_{5})Fe(CO)Me + CO$$
(13)

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)Me + HSiR'_{3} \rightleftharpoons$$

 $(\eta^{5}-C_{5}Me_{5})Fe(CO)(SiR'_{3})(Me)H$ (14)

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)(SiR'_{3})(Me)H \rightarrow (\eta^{5}-C_{5}Me_{5})Fe(CO)SiR'_{3} + MeH (15)$$

$$(\eta^{5}-C_{5}Me_{5})Fe(CO)(SiR'_{3}) + HSiR'_{3} \rightleftharpoons (\eta^{5}-C_{5}Me_{5})Fe(CO)(SiR'_{3})_{2}H (16)$$

Some evidence for the formation of $(\eta^5-C_5Me_5)Fe(CO)$ -(Me)(SiMe₃)H postulated in eq 14 can be seen in the UV-vis spectral changes that occur when $(\eta^5 - C_5 Me_5)Fe(CO)_2 Me$ is irradiated in methylcyclohexane containing 0.01 M HSiMe₃, 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 $[(\eta^5 C_5Me_5$ $Fe(CO)_2]_2$, 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 $(\eta^5$ -C₅Me₅)Fe(CO)₂Me in the presence of HSiMe₃ at 298 K to form trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ 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- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ by the growth of a band at 1926 cm⁻¹. A UV-vis spectrum of a sample of trans- $(\eta^5 - \eta^5)$ $C_5Me_5)Fe(CO)(SiMe_3)_2H$ prepared by irradiation of $(\eta^5 C_5Me_5$)Fe(CO)₂SiMe₃ in methylcyclohexane containing 0.01 M in HSiMe₃ at 298 K is the same as the spectrum of *trans*- $(\eta^5$ - C_5Me_5)Fe(CO)(SiMe_3)₂H formed from (η^5 - C_5Me_5)Fe(CO)₂Me. 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 $(\eta^5-C_5Me_5)Fe(CO)_2Me$ is irradiated at 173 K in the presence of HSiMe₃ is not trans- $(\eta^5-C_5Me_5)Fe(CO)$ - $(SiMe_3)_2H$. We assign the absorption at 510 nm to $(\eta^5 C_5Me_5)Fe(CO)(Me)(SiMe_3)H$. Unfortunately, a ¹H 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2 Me$ to yield CH₄ following oxidative addition of Si-H to a monocarbonyl is analogous to the photoreactivity of $(\eta^5-C_5Me_5)Fe_-$ (CO)₂CH₂SiMe₂H.¹¹ This complex undergoes oxidative addition of the β -Si-H at 77 K to form (η^5 -C₅Me₅)Fe(CO)(CH₂SiMe₂)H. The Fe(CH₂SiMe₂) is formulated as a metallasilacyclopropane having Fe-Si and Fe-C σ -bonds. The single CO absorption of $(\eta^5 - C_5 Me_5)Fe(CO)(CH_2SiMe_2)$ is at ~1926 cm⁻¹—very close to that for the feature found at 1925 cm⁻¹ from irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in HSiMe₃ at 173 K. The similarity of the CO absorption suggests that the $(\eta^5-C_5Me_5)Fe(CO)(Me)$ -(SiMe₃)H is very similar electronically to the $(\eta^5-C_5Me_5)$ Fe-(CO)(CH₂SiMe₂)(H). But surprisingly, the $(\eta^5-C_5Me_5)$ Fe-(CO)(CH₂SiMe₂)H is less labile than the $(\eta^5$ -C₅Me₅)Fe(CO)-(Me)(SiMe₃)H. Only above approximately 225 K does (η^{5} - C_5Me_5)Fe(CO)(CH₂SiMe₂)H undergo active reductive elimination of C-H and reaction with CO to form $(\eta^5-C_5Me_5)$ Fe-(CO)₂SiMe₃. Interestingly, no reductive elimination of Si-H to reform $(\eta^5 - C_5 Me_5) Fe(CO)_2 CH_2 Si Me_2 H$ can be detected.¹¹ Presumably, geometric factors dominate the lability of $(\eta^5$ - $C_5Me_5)Fe(CO)(Me)(SiMe_3)H$ compared to $(\eta^5-C_5Me_5)Fe_5$ (CO)(CH₂SiMe₂)H.



Figure 7. UV-vis spectral changes accompanying the photochemical reaction of $(\eta^5-C_5Me_5)Fe(CO)_2R$; R = Me, SiMe₃ with HSiMe₃. 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 $(\eta^5 - C_5 Me_5)Fe(CO)_2 Me (0.002 M)$ in methylcyclohexane containing ~0.01 M HSiMe, at 173 K. Trace 0 is the spectrum of $(\eta^5-C_5Me_5)Fe(CO)_2Me$. Trace 2 shows the changes occurring upon irradiation. The absorption at 510 nm is attributed to $(\pi^5-C_5Me_3)Fe(CO)(SiMe_3)(Me)H$. 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 $(\pi^5-C_5Me_3)Fe(CO)_2SiMe_3$ (0.004 M) in methylcyclohexane at 173 K. Trace 1 shows the UV-vis spectrum of trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ at 173 K. The trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ was generated by photolysis of $(\eta^5$ -C₅Me₅Fe(CO)₂SiMe₃ (0.004 M) in the presence of 0.01 M MSiMe₃ at 173 K to effect 90% conversion of the $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ to trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$. Bottom: The UV-vis spectral changes accompanying the near-UV irradiation at 298 K of $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$. C_5Me_5)Fe(CO)₂Me (0.001 M) in methylcyclohexane containing ~0.01 M HSiMe₃. Trace 0 shows the spectrum of $(\eta^5-C_5Me_5)Fe(CO)_2Me$. Trace 2 shows the spectrum of *trans*- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ 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 -C₅Me₅)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 -C₅Me₅)Fe(CO)- (Me)(SiR'₃)H, it would give rise to $(\eta^5-C_5Me_5)Fe(CO)H$. We have found²⁰ that photoreaction of $(\eta^5-C_5Me_5)Fe(CO)_2H$ gives CO loss to form $(\eta^5-C_5Me_5)Fe(CO)H$, but in the presence of HSiEt₃ $[(\eta^5-C_5Me_5)Fe(CO)_2]_2$ results, and there is no evidence for the formation of $(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$. Note that trans- $(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$ is the only product formed from 298 K irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ in the presence of HSiEt₃. In the presence of HSiMe₃, irradiation of $(\eta^5-C_5Me_5)Fe(CO)_2Me$ is the only for all of the reacted Fe-Me species. Thus, for the case at hand, $(\eta^5-C_5Me_5)Fe(CO)(Me)(SiR'_3)H$, it appears that reductive elimination of alkane (CH₄) 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 -C₅Me₅)Fe(CO)R complexes appears general. Near-UV irradiation of either $(\eta^5 - C_5 Me_5)Fe(CO)_2C_2H_5$ or (n⁵-C₅Me₅)Fe(CO)₂CH₂CH₂SiMe₃ in pure HSiEt₃ 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 $(\eta^5-C_5Me_5)$ - $Fe(CO)(SiEt_3)_2H$. The intermolecular addition of $HSiR'_3$ to $(\eta^5 - C_5 Me_5)$ Fe(CO)R is, however, in competition with intramo-Irradiation of $(\eta^5-C_5Me_5)Fe_5$ lecular β -elimination. (CO)₂CH₂CH₂SiMe₃ complexes in alkane with moderate HSiMe₃ concentration (~ 0.05 M) results in formation of both trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$ and $(\eta^5-C_5Me_5)Fe(CO)_2H$. ¹H NMR spectroscopy shows that irradiation of $(\eta^5-C_5Me_5)$ Fe- $(CO)_2C_2H_5$ in toluene- d_8 which is about 0.01 M in HSiMe₃ does result in the formation of C_2H_6 and trans- $(\eta^5-C_5Me_5)Fe(CO)$ - $(SiMe_3)_2H$, as evidenced by the appearance of an ¹H NMR resonance at 0.82 ppm for C_2H_6 and 0.51 and -13.31 for trans- $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$. There is, however, a significant yield of $(\eta^5-C_5Me_5)Fe(CO)_2H$ and C_2H_4 arising from β -H elimination.

The reductive elimination of alkylsilane, $H-CH_2CH_2SiMe_3$, from the ($\eta^5-C_5Me_5$)Fe(CO)(SiR'_3)(CH_2CH_2SiR'_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 $(\eta^5-C_5Me_5)Fe(CO)_2R$ 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 $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$ has been demonstrated. In addition, the reaction of $(\eta^5 - C_5 Me_5)Fe(CO)_2 CH_2 CH_2 SiMe_3$ upon photolysis to form $(\eta^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$ is evidence that the insertion of C₂H₄ into an M-Si bond is a reversible reaction and should be drawn as such. Reductive elimination of R-H, R =Me, Et, CH₂CH₂SiMe₃, following oxidative addition of HSiR'₃, R' = Me, Et, to photogenerated $(\eta^5-C_5Me_5)Fe(CO)R$ has also been demonstrated. Interestingly, the intermediate in this reaction, $(\eta^5-C_5Me_5)Fe(CO)(SiR'_3)(R)H$, does not eliminate R-SiR'₃. Such an elimination, though very slow, has been demonstrated for $(CO)_4FeR(SiMe_3)^5$ 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.

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Registry No. $(\eta^5-C_5Me_5)Fe(CO)_2SiMe_3$, 101493-92-9; $(\eta^5-C_5Me_5)-Fe(CO)_2CI$, 101493-93-0; $(\eta^5-C_5Me_5)Fe(CO)_2CH_2CH_2SiMe_3$, 101493-94-1; $[(\eta^5-C_5Me_5)Fe(CO)_2]_2$, 35344-11-7; $(\eta^5-C_5Me_5)Fe(CO)_2CH_2SiMe_2H$, 101493-95-2; $trans-(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)_2H$, 101493-96-3; $trans-(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(SiEt_3)H$, 101493-97-4; $(\eta^5-C_5Me_5)Fe(CO)_2SiEt_3$, 101493-98-5; $(\eta^5-C_5Me_5)Fe(CO)(^{13}CO)-SiMe_3$, 101493-99-6; $(\eta^5-C_5Me_5)Fe(CO)(^{13}CO)-CH_2CH_2SiMe_3$, 101493-99-6; $(\eta^5-C_5Me_5)Fe(CO)(^{13}CO)-CH_2CH_2SiMe_3$, 101494-00-2; $(\eta^5-C_5Me_5)Fe(CO)(B)SiMe_3$ (B = 1-pentene), 101494-01-3; $(\eta^5-C_5Me_5)Fe(CO)_2H$, 80409-91-2; $(\eta^5-C_5Me_5)Fe(CO)(PPh_3)-CH_2CH_2SiMe_3$, 101494-02-4; $(\eta^5-C_5Me_5)Fe(CO)_2Me$, 52409-66-2; $trans-(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$, 101494-03-5; $(\eta^5-C_5Me_5)Fe(CO)-SiMe_3$, 101494-02-4; $(\eta^5-C_5Me_5)Fe(CO)_2Me$, 52409-66-2; $trans-(\eta^5-C_5Me_5)Fe(CO)(SiEt_3)_2H$, 101494-03-5; $(\eta^5-C_5Me_5)Fe(CO)-SiMe_3$, 101494-04-6; $(\eta^5-C_5Me_5)Fe(CO)(PPh_3)SiMe_3$, 101494-04-6; $(\eta^5-C_5Me_5)Fe(CO)(PPh_3)SiMe_3$, 101494-05-7; $(\eta^5-C_5Me_5)Fe(CO)(SiMe_3)(Me)H$, 101494-06-8; $(\eta^5-C_5Me_5)Fe(CO)(C_2H_4)SiMe_3$, 101494-07-9; C_2H_4 , 74-85-1; $Me_3Si(CH=CH_2)$, 754-05-2.