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PENTACARBONYLIRON(0) PHOTOCATALYZED REACTIONS OF TRIALKYLSILANES WITH ALKENES

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Summary

We report results of the near-ultraviolet irradiation of $Fe(CO)_5$ in the presence of R_3SiH (R = Me or Et) and an alkene. Good conversion to a mixture of alkane, (alkyl)SiR_3, and (alkenyl)SiR_3 products obtains. For terminal alkenes, conversion to products generally exceeds 80%. The distribution of products depends on the alkene/R_3SiH ratio and on the reaction temperature (0—50°C). Terminal, sterically unhindered alkenes react fastest, and give organosilicon products which result from addition of the R_3Si moiety to the terminal carbon. With R_3SiD starting silane extensive protium/deuterium exchange can be detected in the starting alkene and silane at intermediate stages of the reaction. Quantum yields for consumption of the starting materials exceed unity, implicating photocatalysis. The key photogenerated species is proposed to be (H)(R_3Si)$Fe(CO)_3$(alkene) which can be used to rationalize the formation of all products. Also, this intermediate accommodates a temperature dependent photocatalysis as well as a reagent concentration ratio dependence on the final product distribution. At low temperature and low alkene/silane ratio the alkylsilane product dominates, but at higher temperatures and high alkene/silane ratio the alkenylsilane is the dominant product. The temperature dependence in the range 0—50°C is consistent with a thermal rate-limiting step in the photocatalytic cycle which is crucial to the final product distribution.

Photocatalysis refers to a situation where a catalyst is generated by irradiation of some appropriate precursor [1]. Phenomenologically, observed substrate reaction quantum yields which exceed unity and/or continued substrate reactions after cessation of irradiation are the telltale signs of photocatalysis. The rate and

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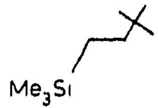
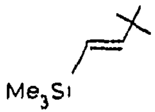
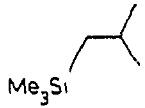
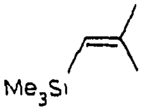
TABLE 1

$Fe(CO)_5$ PHOTOCATALYZED REACTIONS OF TRIALKYLSILANES WITH ALKENES[a]

Starting alkene	Starting silane	Irradiation time(h)	Conversion (%) to products	Product distribution (% of products)		
				Alkane	Alkylsilane	Alkenylsilane(s)
Ethylene[b]	$HSiEt_3$	12[b]	>99	None (<1)	$SiEt_4$(>99)	None (<1)
Propylene	$HSiMe_3$	12	>90	Propane (~5)	$(n\text{-}C_3H_7)SiMe_3$ (~90)	$(allyl)SiMe_3$ $(trans\text{-}C_3H_5)SiMe_3$ $(cis\text{-}C_3H_5)SiMe_3$ } (~5)
1-Butene	$HSiMe_3$	12	>90	n-Butane (~40)	$(n\text{-}C_4H_9)SiMe_3$ (~20)	$C_4H_7SiMe_3$(~40) (3 isomers)
1-Pentene	$HSiMe_3$	12	>90	n-Pentane (~40)	$(n\text{-}C_5H_{11})SiMe_3$ (~20)	$(trans\text{-}1\text{-}C_5H_9)SiMe_3$ (~12) $(cis\text{-}1\text{-}C_5H_9)SiMe_3$ (trace) isomer I (~22) isomer II (~6)
Cyclopentene	$HSiMe_3$	168	~5	Cyclopentane (~25)	$(cyclo\text{-}C_5H_9)SiMe_3$ (~50)	$(cyclo\text{-}C_5H_7)SiMe_3$ (~25)
t-Butylethylene	$HSiMe_3$	96	~20	2,2-Dimethylbutane (~5)	 (~90)	 (~5%)
Isobutylene	$HSiMe_3$	168	>80	Isobutane (~10)	 (~80)	 (~10)

[a] Reactions were run at 25—35°C using the neat substrates in a 1 : 1 mole ratio with 0.003 *M* $Fe(CO)_5$ and a total solution volume of 3.0 ml. All products indicated are separable by VPC. A sample of each product was VPC purified and was then analyzed by mass spectroscopy. Comparison of VPC retention times, mass spectrum, and NMR with authentic samples was used to identify most products, cf. Experimental Section. [b] Reaction run with 7 ml Et_3SiH and 0.008 *M* $Fe(CO)_5$ under 10 psig of ethylene, irradiated with Hg arc lamp filtered to isolate the 300—380 nm region. The reaction temperature was 25°C.

nature of any substrate transformations depends on the properties of the photogenerated catalyst. Hopefully, photogeneration techniques will lead to catalysts having unique properties.

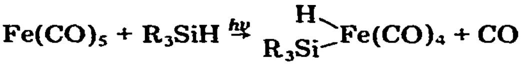
We have recently shown that examples of true photocatalysis include $Cr(CO)_6$ photocatalyzed hydrogenation [2] and hydrosilation [3] of 1,3-dienes and $Fe(CO)_5$ photocatalyzed [4] isomerization and hydrogenation of olefins. In each of these cases it is possible to run the same substrate reactions thermally, but the thermal conditions are significantly more stringent, since formation of the actual catalyst very likely involves loss of at least one CO from the starting metal carbonyl. It is well known [5] that irradiation of mononuclear metal carbonyls leads to efficient dissociative loss of CO to yield coordinatively unsaturated, 16-electron, intermediates. Thus, when such intermediates are involved, it is expected that irradiation can significantly alter the conditions necessary for the desired chemistry. One interesting consequence of the irradiation may be to change the nature of the thermally rate-limiting step from catalyst generation and/or regeneration to a step which is more crucial to the actual substrate transformation. The point is, that while the same catalyst may be formed by forcing thermal conditions and at ambient conditions by irradiation, the catalyst may well be more discriminating (or discriminate differently) under mild conditions. Additionally, if steps which are normally termed "fast" actually become rate limiting then one may better characterize the mechanism of catalytic processes.

In this report we wish to outline our results for the $Fe(CO)_5$-photocatalyzed reactions of trialkylsilanes with alkenes. It is known [6] that $Fe(CO)_5$ is a thermal catalyst for silane/alkene reactions as in reaction 1. Additionally, the photolysis of $Fe(CO)_5$ in the presence of alkene or a trialkylsilane is known to proceed

$$C_2H_4 + Et_3SiH \xrightarrow[130^\circ C]{Fe(CO)_5} Et_4Si + Et_3Si(CH{=}CH_3) \qquad (1)$$

according to reaction 2 [7] or 3 [8], respectively. Our knowledge of reactions 1—3; our discovery [4] of the $Fe(CO)_5$ photocatalyzed hydrogenation of alkenes;

$$Fe(CO)_5 + \text{alkene} \xrightarrow{h\nu} Fe(CO)_4(\text{alkene}) + CO \qquad (2)$$



$$Fe(CO)_5 + R_3SiH \xrightarrow{h\nu} \begin{matrix} H \searrow \\ R_3Si \nearrow \end{matrix} Fe(CO)_4 + CO \qquad (3)$$

and the similarity of H_2 and R_3SiH in the $Cr(CO)_6$ system [2,3] make the $Fe(CO)_5$ photocatalyzed reactions of trialkylsilanes and alkenes a very reasonable venture.

Results

a. Irradiation of Fe(CO)$_5$ in the presence of trialkylsilanes and alkenes

Near-UV irradiation of ~0.01 *M* $Fe(CO)_5$ in room temperature degassed mixtures of an alkene and a trialkylsilane generally results in the organic and organosilicon products indicated in reaction 4. Alkenes and silanes used and their $Fe(CO)_5$ photocatalysis products are set out in Table 1. For every case except

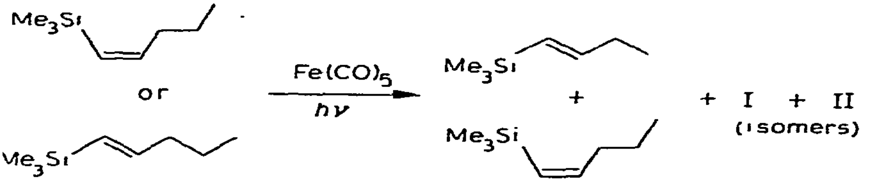
$$\text{alkene} + R_3SiH \xrightarrow[\text{UV, degassed solution, } 25^\circ C]{Fe(CO)_5} \text{alkane} + \text{alkylsilane} + \text{alkenylsilane} \qquad (4)$$

ethylene + Et_3SiH we observed a mixture of products, and this exception will be discussed below. The distribution of products depends significantly on reaction conditions, vide infra, but at this point it is important to note that the yield of alkane is essentially equivalent to the total yield of alkenylsilanes.

This point was established quantitatively for reaction of Me_3SiH and 1-pentene as a function of reaction time, substrate concentration, and silane/alkene ratio. Within 20% the pentane equalled the total of the C_5H_9- $SiMe_3$ products. At large conversion there is some tendency to see conversion of the (alkenyl)-SiR_3 to the (alkyl)SiR_3, presumably by a mechanism like that resulting in the alkane from the alkene. The alkyl- and alkenyl-silanes are obtained in the thermal catalysis, reaction 1, and it is very reasonable to expect that the alkane is also formed, but the analytical procedures employed [6] precluded detection of the alkane.

In most cases listed in Table 1 the reaction was carried out using neat substrates in a 1 : 1 mole ratio. For cases where the starting alkene has a terminal double bond the extent conversion can be >90%, but even for the terminal alkenes the conversion rate depends markedly on the starting olefin. For example, in 10 h propylene can be consumed by about 90% while t-butylethylene requires 48 h to reach ~10% conversion at the same conditions. The terminal double bond seems crucial. We detected little or no reaction between cyclohexene and Et_3SiH, and reaction with cyclopentene is very slow. Seven days of photoreaction yielded only a few percent consumption. These qualitative observations point to the fact that structural factors evert a large influence on rate. This was also found in the $Fe(CO)_5$ photoassisted hydrogenation of alkenes [4].

We generally find that the alkenylsilanes are present as several isomers, where such are possible. This is no surprise since it is known that $Fe(CO)_5$ is an effective alkene isomerization photocatalyst [4]. Indeed, to demonstrate that alkenylsilanes are not exceptional, we have carried out reaction 5. Importantly, irrespective of the starting isomer, the distribution of alkenylsilanes at equilibrium from the $Fe(CO)_5$ photocatalysis is the same within experimental error as the ratio for these alkenylsilane products listed in Table 1.



(5)

We have demonstrated that the reaction indicated in eq. 4 is an example of true photocatalysis by measuring the quantum yield for reaction 6. We find

$$\text{1-pentene} + Me_3SiH \xrightarrow[\text{near-UV } 25^\circ C]{Fe(CO)_5} C_5H_{12} + (C_5H_{11})SiMe_3 + (C_5H_9)SiMe_3 \qquad (6)$$

quantum yields which exceed 7 for this process, providing unequivocal evidence for the photogeneration of a catalyst capable of operating at 25°C. The quantum yield of 7 was simply measured by determining the total number of einsteins incident on the sample in the 300—380 nm region and the number of moles of Me_3SiH consumed. This was determined as a function of time and the maximum quantum yield was observed to be 7 at 25°C for initially 1 : 1 mole ratio of 1-pentene/Me_3SiH and 10^{-2} M $Fe(CO)_5$.

b. Experiments with $DSiMe_3$ and $DSiEt_3$

Irradiation of $Fe(CO)_5$ in a mixture of 1-pentene and $DSiMe_3$ leads to the normal types of products. However, mass-spectroscopic analyses of the products indicated extensive deuterium exchange with little discrimination. The products indicated in reaction 7 were detectable by a combination of gas chromatographic

$$\text{1-pentene} + \text{DSiMe}_3 \xrightarrow[\text{near-UV } 25^\circ\text{C}]{\text{Fe(CO)}_5} (\text{n-C}_5\text{H}_{11})\text{SiMe}_3\text{-}d_n\ (n = 0\text{—}5)$$

$$+ (\text{C}_5\text{H}_9)\text{SiMe}_3\text{-}d_n \quad (n = 0\text{—}5) + \text{pentane-}d_n \quad (n = 0\text{—}4) + \text{pentenes-}d_n \quad (n = 0\text{—}4) \tag{7}$$

separations and mass spectroscopy, Table 2. Since the silane is not amenable to mass spectroscopic analysis, separate experiments were carried out to determine whether any $HSiR_3$ is formed at intermediate stages of a reaction like 7. PMR analysis clearly shows that the exchange does occur as indicated in reaction 8. The experiment was carried out by irradiating a 1 : 1 mole ratio of $DSiEt_3$ and

$$\text{1-pentene} + \text{DSiEt}_3 \xrightarrow[\text{near-UV } 25^\circ\text{C}]{\text{Fe(CO)}_5} \text{HSiEt}_3 + \text{other products} \tag{8}$$

1-pentene containing 0.05 *M* $Fe(CO)_5$. An NMR tube containing 1.0 ml of the solution was degassed and irradiated for a period of two hours with the near-UV source. Within the limits of the PMR analysis, $DSiEt_3$ was converted to $HSiEt_3$ before significant formation of pentyl- or pentenyl-silanes. A similar irradiation with no alkene present yields no formation of $HSiEt_3$. That Si—C bond formation is not reversible under reaction conditions is seemingly demonstrated by the inertness of authentic $(n\text{-}C_3H_7)SiMe_3$ in solutions of $Fe(CO)_5$ exposed to near-UV light. Even with added propylene the tetraalkylsilane was found to be inert. Experiments on the $Fe(CO)_5$-photocatalyzed isomerization of alkenylsilanes gave no evidence for any products arising from Si—C bond cleavage.

TABLE 2

DISTRIBUTION OF DEUTERATED PRODUCTS FROM $Fe(CO)_5$ PHOTOCATALYZED REACTION OF $DSiMe_3$ AND 1-PENTENE[a]

Product	Relative abundance					
	d_0	d_1	d_2	d_3	d_4	d_5
n-Pentane	100	45	24	6.7	3.8	—
Linear pentenes (equilibrium distribution of isomers)	100	16	7.8	4.6	1.8	—
$Me_3Si(n\text{-}C_5H_{11})$	100	61	33	20	9.3	5.3
$Me_3Si(n\text{-}1\text{-}C_5H_9)$	100	54	31	15	5.4	3.1
isomer I [$Me_3Si(n\text{-}1\text{-}C_5H_9)$	100	53	29	15	5.8	1.9
isomer II [$Me_3Si(n\text{-}1\text{-}C_5H_9)$]	100	53	31	17	5.9	3.5

[a] Sample initially 3.0 ml of 1 : 1 $DSiMe_3$/1-pentene, 10^{-2} *M* $Fe(CO)_5$. Degassed sample irradiated for 24 h with near-UV output from GE Blacklite at 25°C. Conversion corresponds to consumption of ~80% of silane. Unreacted pentenes are equilibrated (~3% 1-pentene, ~77% *trans*-2-pentene, ~20 *cis*-2-pentene). Pentenylsilane products are in ratio indicated in Table 1, and pentylsilane/pentenylsilane ratio is ~30/70. The amount of pentane formed is equal to total amount of pentenylsilanes. Relative abundance of deuterated products determined on products purified by preparative VPC using an Hitachi Perkin—Elmer RMU-6 mass spectrometer.

c. Dependence of product distribution on initial substrate ratio

We have found that the distribution of products depends significantly on the ratio of the starting alkene and silane. Some convincing data are given in Table 3 showing that the ratio of alkyl- to alkenyl-silane can be varied from a dominance of one to the other by variation in the initial alkene to trialkylsilane ratio. With a starting excess of trialkylsilane the dominant product is tetraalkylsilane. This can be used to explain why the reaction of ethylene + $HSiEt_3$ yields essentially only $SiEt_4$. In our experiment, ethylene at ~10 psi was exposed to neat $HSiEt_3$ giving a very large excess of the trialkylsilane compared to the alkene. This parallels nicely the $Fe(CO)_5$ thermal catalysis [6b].

d. Temperature dependence on the $Fe(CO)_5$ photocatalysis

Data in Table 4 show that there is a marked temperature effect on the photocatalyzed reaction even over a very modest temperature range near ambient temperature. Lower temperatures favor the formation of the alkylsilane, while higher temperatures favor the formation of the alkenylsilane. Moreover, we find that lower temperatures slow down the overall photocatalyzed reaction. This result is consistent with the fact that a photo-generated thermal catalysis is actually responsible for the reactions observed.

e. Nature of the photogenerated-Fe-containing species

Near-UV irradiation of 0.003 *M* $Fe(CO)_5$ in a degassed isooctane solution containing 0.1 *M* 1-pentene and 1.0 *M* $HSiMe_3$ initially yields a mixture of $Fe(CO)_4(C_5H_{10})$ and $(H)(SiMe_3)Fe(CO)_4$ as determined by infrared spectral changes in the CO stretching region: infrared bands at 1980 and 2080 cm^{-1} associated with $Fe(CO)_4(C_5H_{10})$ [4] and at 2090 m, 2025 m, 2015 s, and 2000 s for $(H)(SiMe_3)Fe(CO)_4$. The four band pattern for the $(H)(SiMe_3)Fe(CO)_4$ is consistent with the reported [8] spectra of $(H)(SiR_3)Fe(CO)_4$ (R = Cl or C_6H_5). Thus, photolysis

TABLE 3

CONCENTRATION DEPENDENCE OF $Fe(CO)_5$ PHOTOASSISTED REACTIONS OF $HSiMe_3$ WITH 1-PENTENE: EFFECT ON THE RELATIVE RATES OF ALKYLSILANE AND ALKENYLSILANE FORMATION[a]

1-Pentene (*M*)	$HSiMe_3$ (*M*)	Concentrations ratio 1-Pentene/$HSiMe_3$	Alkylsilane[b] (%)	Alkenylsilane[b] (%)
0.9	7.5	0.12	66.7	33.3
1.6	6.8	0.24	56.2	43.8
4.8	4.0	1.2	27.3	72.7
7.7	1.3	5.8	3.1	96.9
8.4	0.7	12.0	1.3	98.7
0.9[c]	0.1	9.0	1.8	98.2
0.1[c]	0.9	0.11	44.8	55.2

[a] Degassed, sealed ampoules containing 3.0 ml of the alkene and silane with 0.008 *M* $Fe(CO)_5$ were exposed simultaneously to the output of a black light equipped with two 15W GE Black Light bulbs. The reaction temperature was 30°C. After two hours of irradiation the samples were analyzed by VPC. Conversion of the starting materials to silicon-containing products was approximately 50%, based on the least concentrated reagent as the limiting reagent. [b] Percent of total silicon-containing products. [c] Degassed, sealed ampoules containing 7.0 ml of a benzene solution of the alkene and silane with 0.006 *M* $Fe(CO)_5$ exposed to 300—380 nm light for 70 minutes at a reaction temperature of 25°C.

TABLE 4

TEMPERATURE DEPENDENCE OF $Fe(CO)_5$ PHOTOASSISTED REACTION OF $HSiMe_3$ WITH 1-PENTENE: EFFECT ON RELATIVE RATES OF ALKYLSILANE AND ALKENYLSILANE FORMATION[a]

Temperature (°C)	Time of irradiation (min)	Alkylsilane[b] (%)	Alkenylsilane[b] (%)
0	960	60.6	39.4
25	240	38.1	61.9
50	100	27.1	72.9

[a] Degassed, sealed ampoules, containing 7 ml of an equimolar mixture of the alkene and silane with 0.008 *M* $Fe(CO)_5$, were exposed to 300—380 nm light under conditions which were identical except for irradiation time and temperature. Yields in all cases were approximately 60% based on pentene disappearance. [b] Percent of total silicon-containing products.

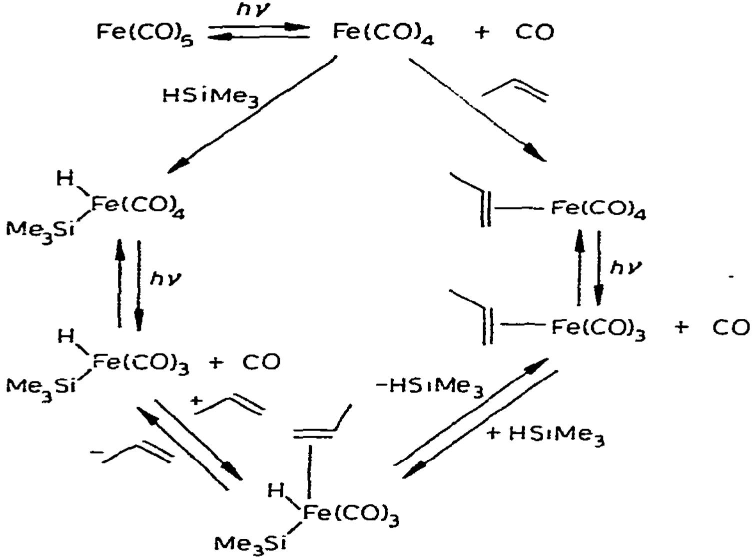
of $Fe(CO)_5$ in the presence of $HSiMe_3$ and 1-pentene results in spectral changes consistent with the formation of both oxidative addition and simple substitution products. Neither of these species leads to reaction of the alkene and silane. For example, $(H)(SiMe_3)Fe(CO)_4$ was synthesized and treated with 1-pentene at 0°C for 14 h. After this period no alkene isomerization or hydrosilation was detectable. However, irradiation of the $(H)(SiMe_3)Fe(CO)_4$ does lead to the chemistry indicated in reaction 4. Likewise $Fe(CO)_4(C_5H_{10})$ is not a thermal catalyst under typical photocatalysis conditions, but upon irradiation of $Fe(CO)_4(C_5H_{10})$ in the presence of a 1 : 1 mole ratio of $HSiEt_3$ and 1-pentene the products indicated in Table 1 are formed.

Discussion

The results presented support the conclusion that $Fe(CO)_5$-photocatalyzed reaction of alkenes with trialkylsilanes can be carried out under mild conditions. The truly photocatalytic nature of the reactions is proven by the quantum yields which exceed unity and the strong temperature effects on the photocatalysis. From the data in the Tables we typically observe hundreds of product molecules per $Fe(CO)_5$ molecule initially present. Thus, the reactions can be carried out on a synthetic scale. But, the products synthesized are by no means unique. What we emphasize here is the procedure by which the products can be made and the extent of control of product formation rate and product distribution. It is important to realize that the reactions carried out here simply do not occur in the dark by $Fe(CO)_5$ catalysis at comparable temperatures. While the hydrosilation of acetylenes is a well known route to alkenylsilanes, we note that the generation of alkenylsilanes by reaction of silanes with alkenes is not a typical result [9]. Thus, in this respect, the formation of alkenylsilanes may prove useful. Indeed, there is, of course, no acetylene precursor to the alkenylsilane obtained here from isobutylene or cyclopentene.

The results allow some comments concerning the mechanism of the $Fe(CO)_5$-photocatalyzed reactions. The lack of reaction with either $(H)(SiMe_3)Fe(CO)_4$ or $(alkene)Fe(CO)_4$ rules these out as the key intermediates. We propose that the direct precursor to products is in fact the species $(H)(R_3Si)Fe(CO)_3(alkene)$ which can be photogenerated according to Scheme 1 (for $HSiR_3 = HSiMe_3$ and

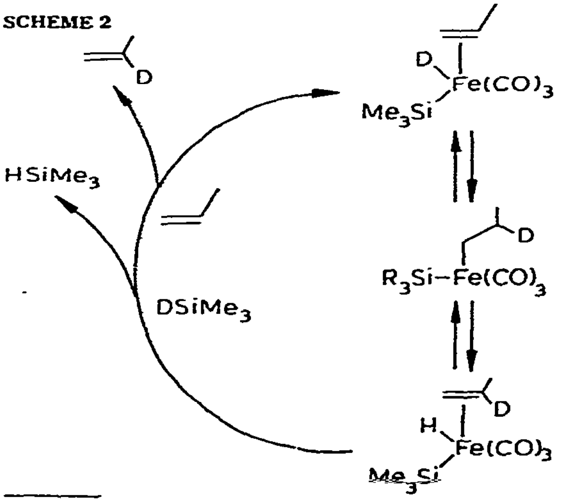
SCHEME 1



alkene = propylene). Such a species has not been observed, but we feel that its intermediacy can account for all of our results.

First, we must invoke the notion that $(H)(R_3Si)Fe(CO)_3$(alkene) is very labile with respect to reductive elimination of the silane and loss of the alkene *. These are necessary properties to account for efficient production of $HSiEt_3$ by irradiation of $Fe(CO)_5$ in the presence of 1-pentene and $DSiEt_3$. The actual exchange can occur by the processes indicated in Scheme 2. The crucial fact is that the $(D)(SiR_3)Fe(CO)_3$(alkene) → $(SiR_3)Fe(CO)_3$(alkyl) conversion is reversible by a β-elimination process, scrambling the H and D.

SCHEME 2



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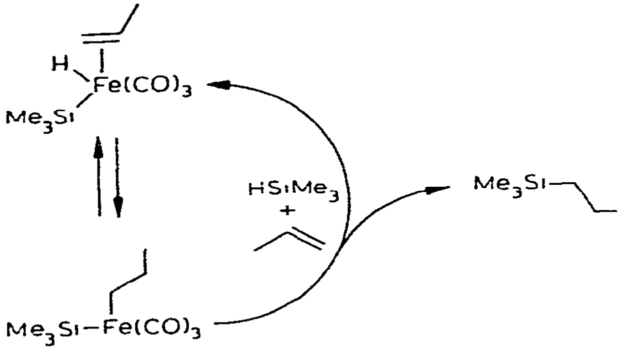
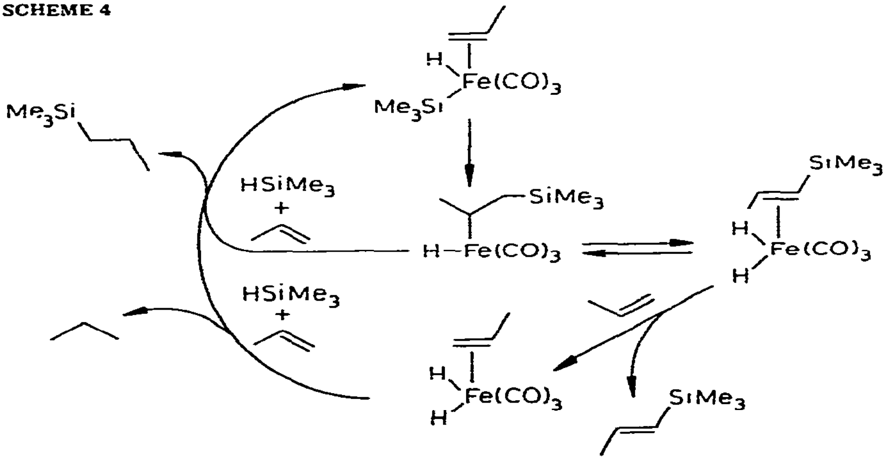
* The processes in the Schemes in the remainder of the discussion have ample precedence in organometallic chemistry; cf. ref. 16.

The $(R_3Si)Fe(CO)_3$(alkyl) can also competitively reductively eliminate to yield net hydrosilation (alkylsilane) products as indicated in Scheme 3. Again, the reversibility of $(H)(R_3Si)Fe(CO)_3$(alkene) → $(R_3Si)Fe(CO)_3$(alkyl) can account for extensive deuterium incorporation in the hydrosilation (alkylsilane) product. The intermediate $(H)(R_3Si)Fe(CO)_3$(alkene) can react in yet another way to ultimately yield alkenylsilane products as shown in Scheme 4. We regard the transfer of the R_3Si moiety to the alkene as irreversible since no evidence exists in our system for the activation of the C—Si bonds. The relative amounts of alkyl- and alkenylsilane are determined, in part, by the relative rate of reductive and β-elimination from the $(H)(alkyl)Fe(CO)_3$ species. The generation of $(H_2)Fe(CO)_3$(alkene) accompanies alkenylsilane formation, and this species is believed [4] to lead to alkane formation.

SCHEME 3



SCHEME 4



Schemes 1—4 show that it is possible to account for all of the products of the photocatalysis by invoking the "$Fe(CO)_3$" species as the repeating unit. The temperature dependence on alkyl-/alkenyl-silane product ratios is accommodated by the mechanism, also. In Scheme 4 there are two thermal routes out of (H)-

(alkyl)$Fe(CO)_3$; one path leads to alkylsilane, the other leads to alkenylsilane. We can simply invoke different thermal parameters for these two processes, and, in the right temperature range, one should be able to see different amounts of the resulting products. At least in the range 0—50°C with the photocatalysis procedure, one is able to conveniently observe the temperature effect. We should note here that we also observed [4] a temperature effect on the $Fe(CO)_5$-photocatalyzed reactions of alkenes with D_2, reaction 9, which can be rationalized in a manner analogous to the alkene/silane reactions.

$$\text{alkene} \xrightarrow[h\nu,\, D_2]{Fe(CO)_5} \text{alkane-}d_n + \text{alkene-}d_n \qquad (9)$$

The Schemes 1—4 can also be used to rationalize the dependence of the starting alkene/silane ratio on the product ratio. One only needs to invoke a degree of alkene assistance to β or reductive elimination processes or the like. At this point, though, we are not in a position to provide details on the molecularity of the crucial steps of the catalytic cycle. It is certainly not unreasonable, however, to expect some interaction of alkenes or trialkylsilanes with species like (H)(alkyl)$Fe(CO)_3$ which is a 16-electron intermediate.

From the mechanistic schemes outlined one might expect catalytic activity to continue indefinitely after cessation of the irradiation. Indeed, one does generally observe some dark after effects, but these normally cease after a short period [4]. The logical reasoning is that in the hermetically sealed systems described here the CO present simply ultimately back reacts to generate $Fe(CO)_4$(alkene) or $(H)(R_3Si)Fe(CO)_4$ complexes which are the infrared detected species through a significant portion of the reaction. Thus, continuous irradiation is needed to maintain a steady-state concentration of the catalytically active "$Fe(CO)_3$" species. Removal of CO allows easy formation of polynuclear, inactive iron carbonyl species. We are now probing the photocatalysis behavior of such clusters, and preliminary results from these laboratories show that $Fe_3(CO)_{12}$ is a photocatalyst, but not a thermal catalyst, for the hydrosilation at 25°C.

Experimental Section

Starting materials

Alkenes obtained from Chemical Samples Co., Matheson Gas Co., and Aldrich Chemical Co. were used as received unless contaminated with peroxides. Peroxides were removed by passage through grade I Woelm alumina. Et_3SiH was obtained from PCR, Inc. and was used as received. Me_3SiH and Me_3SiD were synthesized by the literature method [10] using $LiAlH_4$ (Alfa-Ventron) or $LiAlD_4$ (Stohler Isotope Chemicals), respectively. The Et_3SiD was prepared in a manner analogous to the preparation of Me_3SiD. $Fe(CO)_5$ was obtained from Pressure Chemical Co., and used without further treatment. Benzene and isooctane were of spectroscopic grade, and all other solvents were of reagent grade. Solvents were used as received except for benzene and tetrahydrofuran, which were distilled from sodium-benzophenone under nitrogen.

Instrumental

All vapor phase chromatography (VPC) was done with a Varian Series 2400 gas chromatograph equipped with flame ionization detectors. Separation of components of the reaction mixtures was accomplished on a 25' × 1/8" column of 20% propylene carbonate on Chromosorb P or a 25' × 1/8" column of 25% β,β'-oxydipropionitrile on Gaschrome Q, and preparative VPC was done on a 25' × 1/4" column of 20% propylene carbonate on Chromasorb P.

Qualitative IR spectra were obtained using a Perkin—Elmer 337 grating infrared spectrometer with 0.1 mm pathlength cells obtained from Perkin—Elmer Corp. Mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6 mass spectrometer. A Forma-Temp, Jr. Bath and circulator was used for thermostatted experiments.

The PMR data were collected using a Varian T-60 instrument. The PMR was calibrated prior to running each sample using a $SiMe_4$ standard. The $SiMe_4$ was not added to the sample directly as an internal standard, to avoid complications associated with the $SiMe_3$ signal which falls close to that for $SiMe_4$. Consequently, the error (±0.2 ppm) in the PMR resonance position is more than usual, and we have relied on integrations which we estimate to have errors of ±20%.

Irradiation procedure

Three ml aliquots of the $Fe(CO)_5$ and substrates solution in pyrex test tubes (13 × 100 mm) with constrictions were degassed by four freeze-pump-thaw cycles and were then hermetically sealed. The quantum yield and temperature dependence experiments were done with 7 ml aliquots in 15 × 125 mm test tubes with constrictions. Continuous photolysis experiments were done either with a black light source equipped with two GE black light bulbs or with a 550 W medium pressure Hanovia Hg lamp filtered with a Corning CS 7-54 filter to isolate the 300—380 nm region. Light intensities were determined for the latter by ferrioxalate actinometry [11] and were found to be of the order of 10^{-5} ein/min.

Product identification and analysis

Each product listed in Table 1 was purified by preparative gas chromatography and then subjected to mass spectroscopic analysis using an Hitachi—Perkin—Elmer RMU-6 spectrometer. Every product exhibited a parent peak consistent with its formulation. The alkane products were identified (1) by co-injection with an authentic sample on the gas chromatograph and (2) comparison of mass spectrum with the authentic samples which are all readily available materials.

Alkylsilanes

$SiEt_4$ from reaction of Et_3SiH and ethylene was identified by mass spectral analysis, PMR and VPC retention time compared to an authentic sample prepared by the literature procedure [12]. The PMR is complex ($\tau \sim 8.5$ ppm center) but the CH_2 to CH_3 integration is 0.68, or very close to the expected 0.67. Likewise the other (n-alkyl)$SiMe_3$ products in Table 1 were identified by comparison (VPC retention time, mass spectrum) with authentic (n-alkyl)$SiMe_3$ prepared by the procedure in ref. 12. (Cyclo-C_5H_9)$SiMe_3$ was identified only by mass spectrum. The (i-C_4H_9)$SiMe_3$ was identified by mass spectrum and the PMR of a VPC purified sample: $Si(CH_3)_3$ singlet, τ 9.8 ppm; Si—CH_2—C, doublet, $\tau \sim 9.4$ ppm; $C\underline{H}(CH_3)_2$, multiplet, τ 8.2 ppm; and $CH(C\underline{H}_3)_2$, doublet, $\tau \sim 9.0$

ppm, integrating in a 9 : 2.3 : 1.1 : 7.0 ratio, or very nearly that for the expected 9 : 2 : 1 : 6. Similarly, $Me_3SiCH_2CH_2C(CH_3)_3$ was identified by mass spectral and PMR analysis. The prominent feature of the PMR being two singlets integrating to 1 : 1, $SiMe_3$ (τ 9.9 ppm); $C(CH_3)_3$ (τ 9.0 ppm).

Alkenylsilanes

(Cyclo-C_5H_7)$SiMe_3$ was identified by mass spectrum only. The $(CH_3)_3CCH{=}CHSiMe_3$ was identified by mass spectrum and NMR. On the basis of steric considerations, we feel that the compound is the *trans* isomer. The compound is known [13] and is prepared by catalyzed reaction of 3,3-dimethyl-1-butyne and Cl_3SiH followed by alkylation with MeMgBr. Using benzoyl peroxide as the catalyst one usually obtains a thermodynamic mixture of the olefin isomers, and for this case only the *trans*-isomer was found [13]. This likely reflects the thermodynamic ratio. Since the present system appears to give thermodynamically controlled products, it is very likely that the isomer generated here is the *trans*. The $(CH_3)_2CCHSiMe_3$ was identified by mass spectrum and its PMR which shows the $SiMe_3$ resonance at ($\tau \sim 9.9$ ppm), the vinyl proton ($\tau \sim 5.3$ ppm) and a $C(CH_3)_2$ at $\tau \sim 8.0$ ppm. The ratio of signals for $SiMe_3$ to $C(CH_3)_2$ is 9 : 6.3, or very close to the expected 9 : 6. The three isomers of the formula $Me_3SiC_4H_7$ from reaction of 1-butene and $HSiMe_3$ were shown to be isomers of this formula by mass spectra of the collected fractions. A sample of *cis*-($CH_3CH{=}CHCH_2SiMe_3$) was available from a previous study [3], and its PMR, mass spectral properties and VPC retention time corresponds to one of the three products. The other two products have PMR spectra consistent with the formulation as isomers of $(C_4H_7)SiMe_3$. No authentic samples were prepared to rigorously identify these alkenylsilanes, but from the $(C_3H_5)SiMe_3$ and $(C_5H_9)SiMe_3$ products (vide infra) we believe the $(C_4H_7)SiMe_3$ to be the isomers where the $SiMe_3$ moiety is attached to a terminal carbon.

The $(C_3H_5)SiMe_3$ products were identified first by mass spectrum and then by PMR, VPC retention time, and mass spectral comparison with authentic samples. (Allyl)$SiMe_3$ is a well known compound and was synthesized by reaction of (allyl)MgX and Me_3SiCl. The formation of (i-C_3H_5)$SiMe_3$ in our reaction was ruled out by the fact that none of the photocatalysis products has the same VPC retention time as an authentic sample. Authentic (i-C_3H_5)$SiMe_3$ was prepared by reaction of $SiCl_4$ with (i-C_3H_5)MgBr to yield (i-C_3H_5)$SiCl_3$ followed by treatment with MeLi to give (i-C_3H_5)$SiMe_3$. Mass spectral analysis showed it to have the correct composition, but from the VPC retention time it does not correspond to any of the photocatalysis products. The other photocatalysis products were *cis*- and *trans*-(1-C_3H_5)$SiMe_3$. An authentic sample was prepared by Pt/C catalyzed reaction of Cl_3SiH with propyne which yields mainly *trans*-(1-C_3H_5)$SiCl_3$ which was then treated with MeLi to yield essentially pure (1-C_3H_5)$SiMe_3$. This procedure is essentially that outlined in ref. 13, except for the alkylation procedure. Our alkylation procedure using MeLi has good precedence [9]. A small amount of the *cis* isomer was also formed and the *trans*-isomer could be converted partially to the *cis* by benzene-photosensitized isomerization of the *trans*-isomer. Benzene-sensitized alkene isomerization is well documented [14]. The two isomers are separable by VPC and each has a retention time corresponding to one of the photocatalysis products. The *cis*- and *trans*-isomers prepared here have NMR and VPC retention properties as reported previously [15]. Thus, we ruled out the (i-C_3H_5)$SiMe_3$ and showed that the three other possible Me_3Si-(propenyl) isomers coincide with products.

The (C_5H_9)$SiMe_3$ compounds were identified in a manner analogous to the (C_3H_5)$SiMe_3$ products. Authentic *cis*- and *trans*-(1-C_5H_9)$SiMe_3$ were prepared [13]. The *trans* compound was prepared by Pt/C-catalyzed reaction of Cl_3SiH and 1-pentyne followed by treatment with MeLi, and a mixture of the *cis*- and *trans*-isomers was prepared by benzoyl peroxide-catalyzed reaction of Cl_3SiH and 1-pentyne followed by treatment with MeLi. The compounds are separable by VPC. These authentic samples could be isomerized to other isomers denoted as I and II in the text and in Tables 1 and 2. The isomerization was effected by irradiation of $Fe(CO)_5$ in the presence of the *cis*- and *trans*-(1-C_5H_9)$SiMe_3$. In other cases, such a procedure is known to yield double bond migration isomers [4], and we tentatively assign I and II as such.

Quantitative analysis

For the product ratios indicated in the tables, we have assumed that isomers have the same relative response on the VPC. Relative response of the alkene, alkane, and various silanes was determined by injection of solutions of known composition. Where no authentic samples were prepared, estimates of relative response were made on the basis of the molecular weights. Conversion percentages were determined by disappearance of starting materials relative to an inert alkane internal standard.

Handling volatile substrates

Low boiling substrates, like propane, $HSiMe_3$, etc., were handled either on a vacuum line or in a cold room (~4°C). Solutions of such substrates were prepared in all cases by volume. Concentrations given are estimated to be only ±10%, owing to the difficulty in metering out the substrates.

Thermal $(OC)_4Fe(H)(SiMe_3)$ reactions

A solution of 5.5 ml (6.0×10^{-2} moles) of $HSiMe_3$ and 0.34 ml (0.25×10^{-2} moles) of $Fe(CO)_5$ was freeze-pump-thaw degassed four times on a high vacuum line in a 250 ml flask. This solution was then irradiated with a Pyrex filtered 200 Watt Bausch and Lomb high pressure Hg arc lamp, until the bright yellow color disappeared leaving a pale tan solution. At this point all $Fe(CO)_5$ was consumed, according to the IR, giving a material having an NMR spectrum consistent with $(OC)_4Fe(H)(SiMe_3)$; τ(Fe—H), 19.55 ppm, τ(Si—Me), 9.48 ppm. The solution was then freeze-pump-thaw degassed three times to remove the CO. Previously degassed 1-pentene (6 ml, 6.0×10^{-2} moles) was transferred by bulb-to-bulb distillation and this mixture was then allowed to stand for 14 hours at 0°C in the dark. After this time it was analyzed by VPC.

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