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A styrene-1% divinylbenzene resin whose phenyl rings have been derivatized with $-PPh_2$ groups serves as an "anchor" for $Fe(CO)_n$ (n = 3,4) groups; the anchor is the Fe-P bond. The photocatalytic activity of suspensions of the polymer-anchored $Fe(CO)_n$ has been compared to homogeneous solutions of $Fe(CO)_n(PPh_3)_{5-n}$ (n = 5,4,3). 1-Pentene isomerization and reaction with $HSiEt_3$ can be effected with each system. Observed quantum yields for 1-pentene isomerization exceed unity for each catalyst precursor and the initial trans- to cis-2-pentene ratio depends on the catalyst precursor, implicating the (over)

retention of the triarylphosphine groups in the actual catalytically active species. Irradiation of $Fe(CO)_n(PPh_3)_{(5-n)}$ (n = 4) results in loss of CO, <u>not</u> PPh_3, suggesting a photoinert anchor to the $Fe(CO)_n$ groups in the polymer systems. These experiments establish the viability of photogenerating catalysts anchored to polymer supports without destruction of the anchor bond in the photogeneration procedure.

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Comparison of the Photocatalytic Behavior of Phosphinated

Polymer-Anchored Iron Carbonyl Species and Homogeneous Phosphine

Substituted Iron Carbonyl Species:

Alkene Isomerization and Reaction with Trialkylsilanes

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January 11, 1979

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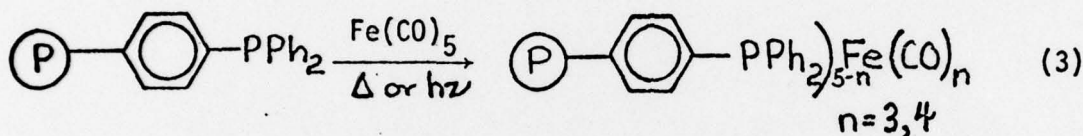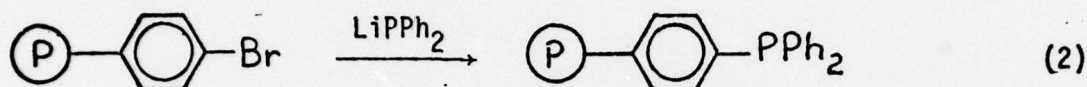[*]Address correspondence to either author.

Abstract: A styrene-1% divinylbenzene resin whose phenyl rings have been derivatized with —PPh$_2$ groups serves as an "anchor" for Fe(CO)$_n$ (n = 3,4) groups; the anchor is the Fe-P bond. The photocatalytic activity of suspensions of the polymer-anchored Fe(CO)$_n$ has been compared to homogeneous solutions of Fe(CO)$_n$(PPh$_3$)$_{5-n}$ (n = 5, 4, 3). 1-Pentene isomerization and reaction with HSiEt$_3$ can be effected with each system. Observed quantum yields for 1-pentene isomerization exceed unity for each catalyst precursor and the initial trans- to cis-2-pentene ratio depends on the catalyst precursor, implicating the retention of the triarylphosphine groups in the actual catalytically active species. Irradiation of Fe(CO)$_n$(PPh$_3$)$_{5-n}$ (n = 4) results in loss of CO, not PPh$_3$, suggesting a photoinert anchor to the Fe(CO)$_n$ groups in the polymer systems. These experiments establish the viability of photogenerating catalysts anchored to polymer supports without destruction of the anchor bond in the photogeneration procedure.

Recent studies have shown that photogenerated coordinatively unsaturated intermediates are capable of serving as catalysts for a variety of reactions involving olefins.[1-10] We have reasoned that it may be possible to generate metal-centered catalysts which are extensively coordinatively unsaturated by irradiation of polymer-anchored, but fully coordinatively saturated, organo-metallic complexes. The simple notion is that the polymer-anchored species may be "matrix-isolated" in the sense that the photogenerated intermediates are incapable of reacting with one another to generate catalytically inactive aggregates. It is well established, for example, that irradiation of mono-nuclear binary metal carbonyls in rigid matrices at low temperature results in extensive loss of CO and in several instances all CO's can be dissociated from the metal to generate elemental metal.[10-21] Consequently, the generation of multiply coordinatively unsaturated species seems a reasonable possibility in the anchored systems. Importantly, such an approach may provide a way to study the reactions of such sites under conditions where sufficient thermal activation energy exists to study catalytic chemistry but at milder conditions than would be required for thermal generation of multiple coordinative unsaturation.

By now the study of polymer-anchored thermal catalysts is well known,[22-37] but polymer-anchored systems exposed to light have received little detailed study. The aim of this report is to describe our results pertaining to the photocatalytic activity of $Fe(CO)_n$ (n = 3,4) species anchored to a phosphinated styrene-divinylbenzene resin. An important component of the results concerns the parallel study of homogeneous "models" of the polymer-anchored systems. Owing to a number of previous photocatalytic studies,[9,10] there is considerable expectation that the $Fe(CO)_n$-based systems could serve as photocatalysts for olefin reactions.

Results

a. Systems Studied. The polymer-anchored $Fe(CO)_n$ system used in this study was prepared according to the procedure indicated in reactions (1)-(3). The

$$\text{(P)}-\bigcirc \xrightarrow[FeBr_3]{Br_2} \text{(P)}-\bigcirc-Br \qquad (1)$$

$$\text{(P)}-\bigcirc-Br \xrightarrow{LiPPh_2} \text{(P)}-\bigcirc-PPh_2 \qquad (2)$$

$$\text{(P)}-\bigcirc-PPh_2 \xrightarrow[\Delta \text{ or } h\nu]{Fe(CO)_5} \text{(P)}-\bigcirc-PPh_2)_{5-n}Fe(CO)_n \qquad (3)$$
$$n=3,4$$
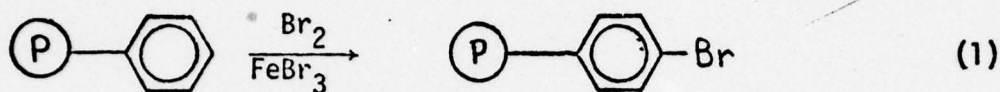
details are given in the Experimental, but we note here that the polymer is a 200-400 mesh styrene-1% divinylbenzene microporous resin.
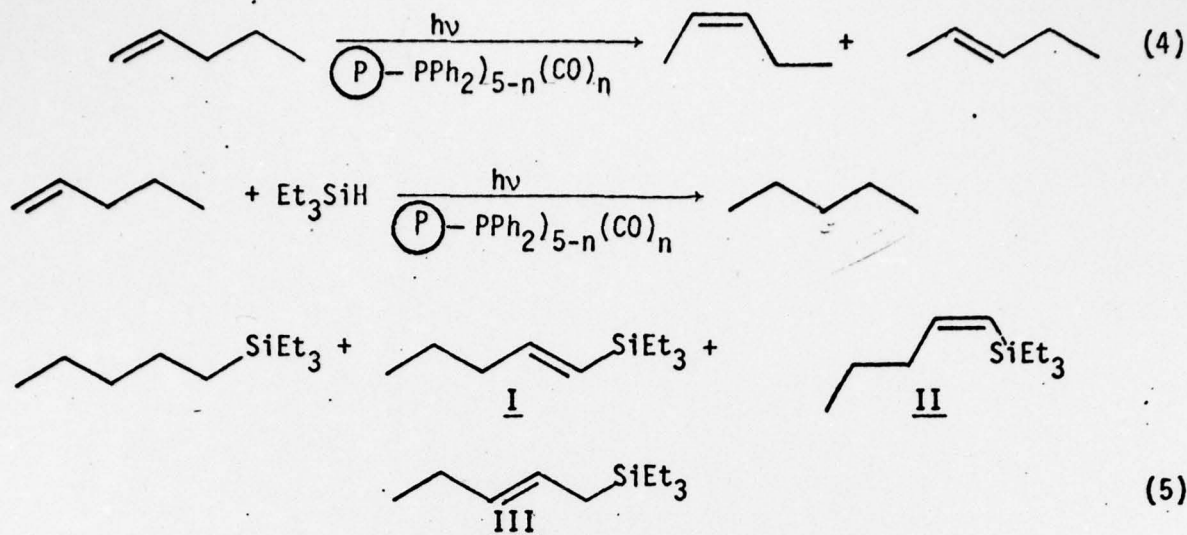
There is some uncertainty concerning the ratio of (P)- $PPh_2)_2Fe(CO)_3$ to (P)-$PPh_2)Fe(CO)_4$ species on the phosphinated polymer, but infrared spectra in in the carbonyl stretching region reveal peaks ascribable to a distribution consisting principally of n = 3 and 4; the iron carbonyl-containing resins exhibit broad, strong carbonyl absorptions at 2045, 1968, and 1932 cm^{-1} for the (P)-$PPh_2)Fe(CO)_4$ sites and a single absorption at 1876 cm^{-1} for (P)-$PPh_2)_2Fe(CO)_3$ sites. These agree well (considering solid phase effects) with the spectra of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ model compounds (see Table I). From the relative absorption intensities of these model compounds, one can estimate the (P)- $PPh_2)Fe(CO)_4/$ (P) - $PPh_2)_2Fe(CO)_3$ ratio to be in the range of 3-5. This ratio is a variable which can be manipulated by - PPh_2 loading, crosslink density, etc. Future studies will be concerned with such variations.

The "anchor" for the catalyst precursor on the polymer is a triaryl-phosphine. Therefore, we have used $Fe(CO)_n(PPh_3)_{5-n}$ (n = 4,3) as homogeneous models for the comparison of catalytic activity. We have also made some direct

comparisons with $Fe(CO)_5$, in order to assess the effect of having the triarylphosphine in the coordination sphere. The electronic absorption properties of the various catalyst precursors have not been studied in detail, but all of the species absorb strongly in the near-uv. The lowest excited states of the complexes logically involve transitions originating from the filled d orbitals $(d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2})$ and terminating in the strongly sigma-antibonding d_{z^2} orbital. This assignment follows from the fact that Fe(0) is d^8 and there is only one empty orbital at low energy; also, $Fe(CO)_5$ has an established[38] d-d assignment for its lowest absorption feature.[3] The d-d assignment provides a general rationale for the photosubstitution lability[39,40] of the metal complexes, but a key question remains as to whether the anchor-Fe bond is photoinert, vide infra.

In our studies of the photocatalytic behavior of the triarylphosphine-iron carbonyl systems we have used alkene isomerization and alkene reaction with trialkylsilane as probe reactions. In particular, we have investigated the photocatalyzed isomerization of 1-pentene and the reactions of 1-pentene with $HSiEt_3$. These substrates have been studied in connection with characterization of the photocatalytic properties of $Fe(CO)_5$.[9,10]

b. Qualitative Photocatalytic Beavhior of Polymer Anchored-$Fe(CO)_n$. All studies of the polymer-anchored $Fe(CO)_n$ system were carried out at 25° using a suspension of the derivatized polymer in a suitable degassed solution. There is little or no catalytic behavior observed at 25° in the dark, with respect to 1-pentene isomerization or 1-pentene/Et_3SiH reactions, nor is there any catalytic activity (light or thermal) associated with the phosphinated, but non-metallated, polymer. However, irradiation of a suspension of the polymer-anchored $Fe(CO)_n$ with near-uv light results in 1-pentene isomerization to cis- and trans-2-pentene and/or reaction with Et_3SiH to yield pentane, (n-pentyl)$SiEt_3$ and several isomers of (pentenyl)$SiEt_3$, reactions (4) and (5). Irradiation of aerated suspensions gives no catalytic chemistry,

$$\diagup\!\!\!\!\diagdown\diagup\diagdown \quad \xrightarrow[\text{(P)}- PPh_2)_{5-n}(CO)_n]{h\nu} \quad \diagup\!\!\!\!\diagup\diagdown \quad + \quad \diagup\diagdown\diagdown \qquad (4)$$

$$\diagup\!\!\!\!\diagdown\diagup\diagdown \quad + Et_3SiH \quad \xrightarrow[\text{(P)}- PPh_2)_{5-n}(CO)_n]{h\nu} \quad \diagup\diagdown\diagup\diagdown$$

$$\diagdown\diagup\diagdown\diagup\diagdown SiEt_3 \quad + \quad \underset{\underline{I}}{\diagdown\diagup\diagdown} SiEt_3 \quad + \quad \underset{\underline{II}}{\diagdown\diagup} SiEt_3$$

$$\underset{\underline{III}}{\diagdown\diagup\diagdown} SiEt_3 \qquad (5)$$

The importance of polymer swelling is reflected in the data given in Table II showing the amount of photocatalyzed 1-pentene isomerization in isooctane vs. benzene solvent. The isooctane yields little or no swelling and we observe little, if any, isomerization. However, in benzene, where the polymer does swell, we observe significant conversion to _cis_- and _trans_-2-pentene on the same time scale. Apparently, high concentrations of the alkene are sufficient to swell the polymer, since the bulk of the work has been successfully carried out in suspensions of the polymer in solutions of initially neat 1-pentene or a 1/1 mole ratio of 1-pentene/Et_3SiH.

Several other qualitative points are worth noting here. The photocatalysis requires continuous irradiation; i.e. when the light is turned off reaction stops, but can be reinitiated by illumination. Additionally, we did not observe reaction of alkene and silane by distilling a 1/1 mole ratio of 1-pentene/Et_3SiH onto the polymer that had been irradiated under vacuum. These observations suggest, but do not prove, that photogenerated coordinative unsaturation of the anchored catalyst does not persist for a very long period. We can report, though, that the polymer anchored catalyst is very durable. We have observed, for example, as many as 2×10^4 molecules reacted per Fe atom present in the alkene-silane photocatalysis. Additionally, the polymer system is easy to handle and can be recovered in useful form subsequent to a photocatalysis experiment.

c. Primary Photoreactions of Phosphine Complexes. A key question concerning the use of polymer-anchored catalyst precursors concerns the photostability of the anchoring bond. In the present instance the question is whether photoexcitation of the (P)-PPh$_2$)$_{5-n}$Fe(CO)$_n$ will break Fe-P bonds. Qualitatively we can state that Fe(CO)$_n$(PPh$_3$)$_{5-n}$ species are not detectable in the solution when (P)-PPh$_2$)$_{5-n}$Fe(CO)$_n$ is irradiated in degassed benzene solutions of 0.1M PPh$_3$, and large turnover numbers are obtained in catalysis experiments without evidence for loss of metal from the polymer. Naturally, this does not mean that the Fe-P bonds are inert; Fe(CO)$_n$ units may be wandering through the polymer with little probability for escape. In such a case we could have catalytic chemistry occurring at non-anchored Fe(CO)$_n$ units. However, the following experiments with the model complexes suggest that the Fe-P bonds are photoinert relative to the Fe-C bonds.

The model complexes, Fe(CO)$_4$PPh$_3$ and Fe(CO)$_3$(PPh$_3$)$_2$, have been irradiated with near-uv light to determine the relative photolability of PPh$_3$ and CO in such complexes. The results should be applicable to the (P)-PPh$_2$)$_{5-n}$Fe(CO)$_n$ system. For Fe(CO)$_4$PPh$_3$ we find that the primary photoreaction is (6). This

$$Fe(CO)_4PPh_3 \xrightarrow{h\nu} Fe(CO)_3PPh_3 + CO \qquad (6)$$
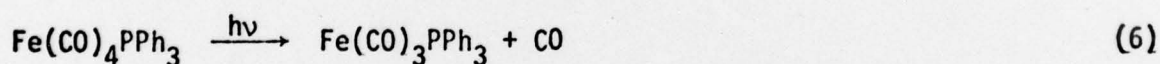
has been determined in several ways. First, irradiation at 366 nm in the presence of 0.1M PPh$_3$ yields Fe(CO)$_3$(PPh$_3$)$_2$ with a quantum yield of 0.4 ± 0.04. The reaction can be followed by ir and the initial chemical yield of Fe(CO)$_3$(PPh$_3$)$_2$ is quantitative. Further, irradiation of isooctane solutions of Fe(CO)$_4$PPh$_3$ in the presence of 0.1M P(OMe)$_3$ initially yields a broad ir absorption centered at 1898 cm^{-1} (presumably Fe(CO)$_3$(PPh$_3$)(P(OMe)$_3$), whereas Fe(CO)$_5$ irradiated in the presence of P(OMe)$_3$ gives peaks initially at 2063(s), 1992(s), 1962(vs), 1949(vs), 1920(vs), and 1910(vs). From Fe(CO)$_5$ a

mixture of $Fe(CO)_n(P(OMe)_3)_{5-n}$ (n = 4, 3) apparently obtains. Literature

values for $Fe(CO)_4P(OMe)_3$ are 2063, 1992, 1963, and 1951 cm^{-1}, and for

$Fe(CO)_3(P(OMe)_3)_2$, 1920 and 1912 cm^{-1} are the reported band positions.[41]

Irradiation of the $Fe(CO)_4PPh_3$ in the presence of $P(OMe)_3$ yields no ir

bands in common with those from $Fe(CO)_5$ (no $Fe(CO)_4P(OMe_3)$ is ir detectable),

indicating that PPh_3 remains coordinated to the Fe. Irradiation of

$Fe(CO)_4PPh_3$ in the presence of 1-pentene results in new bands at 2017, 2002, and

1925 cm^{-1} (presumably $Fe(CO)_3(PPh_3)(pentene)$); again these are non-coincident

with the bands which result from irradiation of $Fe(CO)_5$ in the presence of

1-pentene at 2084 and 1978 cm^{-1} associated with $Fe(CO)_4(pentene)$.[9] Finally,

irradiation of $Fe(CO)_4PPh_3$ in the presence of $HSiEt_3$ results in the growth

of new ir bands at 2032(w) and 1962(vs) cm^{-1} not at 2093(w); 2027(m); 2019(s); and

2006(s) cm^{-1} as found[9] for $HFe(CO)_4SiEt_3$ from irradiation of $Fe(CO)_5$. The

irradiation of $Fe(CO)_4PPh_3$ in the presence of $HSiEt_3$ in C_6D_6 solvent can be

followed by ^1H nmr and a hydride resonance is found at 19.0 τ. This signal is a

doublet with a 26 Hz coupling constant supporting the formulation of the

product as $HFe(CO)_3(PPh_3)(SiEt_3)$. The important point from all these

photochemical results is that a different product results from $Fe(CO)_5$

compared to $Fe(CO)_4PPh_3$, supporting the notion that reaction (6) is the prevailing

primary photoprocess for $Fe(CO)_4PPh_3$.

$Fe(CO)_3(PPh_3)_2$ likewise is photosensitive in solution

in the presence of nucleophiles or oxidative addition substrates. The

disappearance quantum yield at 355nm is approximately 0.2 in the presence of

0.1$\underline{M}$ $P(OMe)_3$ in benzene solution. Spectral changes in the ir are not

clean and reflect some combination of CO and PPh_3 loss. The initial yield

of $Fe(CO)_3(PPh_3)(P(OMe)_3)$ is less than 20% of the products, indicating that

reaction (7) accounts for the bulk of the primary reaction from the excited

state. Prolonged irradiation does result in some loss of PPh_3, but spectral

$$Fe(CO)_3(PPh_3)_2 \xrightarrow{h\nu} Fe(CO)_2(PPh_3)_2 + CO \qquad (7)$$
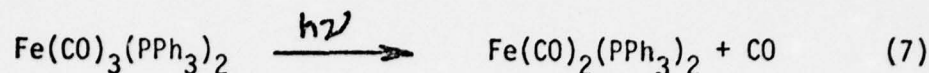
data have not allowed a quantitative measure of its importance. The catalysis results for the 1-pentene reaction are in accord with at least partial retention of both PPh_3 groups in the actual catalytically active species.

d. Photocatalyzed 1-Pentene Isomerization. Irradiation of any of the iron carbonyl species studied results in 1-pentene isomerization. The key results are detailed in Table III. No evidence was found for any reaction of the alkene other than the isomerization. Several important results were found relating to the quantum yield and ratio of primary photoproducts.

We find that the isomerization quantum yield exceeds unity in every case. For the three homogeneous precursors it appears that the degree of PPh_3 substitution is consequential with respect to the observed quantum yields. However, the observed quantum yields likely do not reflect the true differences among the various catalytic species actually produced. Rather, the observed quantum yields likely reflect differences in the efficiency of catalyst generation as well as differences in the rate of isomerization for the actual catalyst. For example, the quantum yield for CO extrusion from $Fe(CO)_5$ is believed to be nearly unity, whereas we find only 0.4 ± 0.04 for CO release from $Fe(CO)_4PPh_3$. The observed quantum yields for the ⓟ-$PPh_2)_5$-$_n$$Fe(CO)_n$ system are the smallest, but the values are lower limits, because we really have no accurate way to determine the fraction of photons which are actually effective in producing electronic excitation. The important finding is that the quantum yields exceed unity, confirming that a catalyst is photogenerated which effects a number of turnovers before requiring reactivation with light. The polymer-anchored catalyst precursor gives quantum yields which approximate the values for the homogeneous analogues.

The second key finding from the alkene isomerization data concerns the initial ratio of the 2-pentenes formed from 1-pentene. Each precursor gives a different ratio, implying that the catalytically active species formed retains the triarylphosphine(s). In particular, it is very evident that the polymer does not approximate $Fe(CO)_5$ but more closely resembles what would be expected from a mixture of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. The change in (trans/cis) ratio with variation in the catalyst precursor along with the results of the photochemical study of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ allow a very important conclusion: the anchoring bond to the photogenerated catalyst is effectively inert to the photocatalysis conditions. At least during the initial stages of the photoreaction, the catalytically active species is very likely anchored to the polymer. There may well be a cage effect tending to prevent net loss of the triarylphosphine in the polymer, but the initial isomerization data provide direct evidence for retention of the phosphine in the coordination sphere during catalysis. Since the ratio of the linear pentenes should approach the same thermodynamic ratio at long irradiation times, we cannot make a comment concerning the long term durability of the Fe-P bonds.

e. Photocatalyzed Reaction of 1-Pentene with $HSiEt_3$. Irradiation of any of the catalyst precursors in the presence of 1-pentene/$HSiEt_3$ gives a distribution of silicon-containing products as indicated in Table IV. n-Pentane is found in amounts equal to the total amount of (pentenyl)$SiEt_3$. Though differences in the product distribution are found, the qualitative findings for each catalyst precursor are similar: the (n-pentyl)$SiEt_3$ is a minor silicon-containing product compared to the (pentenyl)$SiEt_3$ which is found as three isomers in roughly the same ratio in each reaction. These data serve to show that the triarylphosphine groups do not preclude reaction of the alkene with the trialkylsilane. The quantum yields have not been determined, but the irradiation times indicate yields which will be at least of the order of unity. It is surprising that there is not a larger dependence of the product distribution with variation in the catalyst precursor. Apparently, the phosphines exert neither a strong electronic nor steric effect on the formation of the various silicon containing products.

Conclusions

The results outlined in this paper show that $Fe(CO)_n$ (n = 4, 3) attached to a phosphinated styrene-1% divinylbenzene resin is photocatalytically active. Results for photocatalyzed alkene isomerization and alkene reaction with trialkylsilane using the polymer-anchored system are very similar to results found using $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ in homogeneous solution. The photocatalytic activity is logically attributable to the photogeneration of coordinatively unsaturated iron carbonyl species which then follow a mechanism similar to that for $Fe(CO)_5$ itself,[9,10] with the perturbation of having triarylphosphine in the coordination sphere. While the catalytic chemistry is qualitatively the same for the polymer suspensions and for the homogeneous complexes, the results establish the viability of "heterogenizing" photocatalytic systems and designing photostable anchors which can exert some control over catalysis product distribution.

Experimental

Preparation of Polymer-Anchored-Fe(CO)$_n$.

Benzene was distilled from CaH$_2$ and THF was distilled from potassium/ benzophenone under nitrogen prior to use. Styrene-1% divinylbenzene resin was purchased from Bio-Rad Laboratories (SX-1, 200-400 mesh). Microanalytical analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Styrene-divinylbenzene resins were brominated (Br$_2$, FeBr$_3$, dark) and then phosphinated (excess LiPPh$_2$, THF) as previously described.[26,27,42] Elemental analysis shows that 3.3% of the starting polymer's phenyl rings are substituted with -PPh$_2$ groups. Fe(CO)$_n$ was attached by the thermal displacement of CO from Fe(CO)$_5$ by polymer-attached phosphine ligands as follows: Fe(CO)$_5$ (1.78 g, 9.1 mmole) was added to a slurry of the phosphinated polymer (3.00 g, 0.91 mmole P) in 50 ml of deoxygenated benzene and refluxed under N$_2$ for approximately 20 hrs. The resin was then filtered, washed extensively with deoxygenated benzene, and dried in vacuo at 80°C. The catalyst resin analyzed for 0.58% Fe and 0.92% P, which corresponds to a P/Fe ratio of 2.86. This polymer system was used for the reactions with silanes (Table IV). A second polymer with approximately 29% of its phenyl rings substituted with -PPh$_2$ groups (%Fe=4.10; %P=4.47; P/Fe=1.96) which was prepared in a similar manner was shown to give the same distribution of products. The more heavily loaded polymer was used for the quantitative studies of the 1-pentene isomerization, (Table III), but the lightly loaded resin gave similar results.

Preparation of Fe(CO)$_n$(PPh$_3$)$_{5-n}$ (n = 5,4,3).

Fe(CO)$_5$ was obtained commercially and used after distillation. The PPh$_3$ substituted complexes were prepared as described in the literature.[43] Fe(CO)$_4$PPh$_3$ was determined to be free of Fe(CO)$_3$(PPh$_3$)$_2$ and vice versa by ir measurements in the CO stretching region, cf. Table I. The electronic

absorption properties of $Fe(CO)_5$ have been published previously.[38] $Fe(CO)_4PPh_3$ shows only tail absorption below 33,000 cm^{-1} which extends into the visible to give the complex its golden color. In CH_2Cl_2 $Fe(CO)_3(PPh_3)_2$ exhibits a shoulder at 430 nm (ε = 660) and a band maximum at 330 nm (ε = 2540).

Photocatalyzed 1-Pentene Isomerization.

1-Pentene was obtained from Chemical Samples Co. in the highest purity available (~99.9%) and passed through alumina prior to use to remove peroxides. Quantitative analyses for isomer content were conducted using a Varian Series 1400 or 2400 gas chromatograph equipped with a flame ionization detector and a 25 ft x $\frac{1}{8}$ in. column of 20% propylene carbonate on Chromasorb P operated at an oven temperature of 25°C. The irradiation source was a GE Black Lite equipped with two 15W bulbs with output at 355 nm and a width at half-height of ~15 nm. The intensity was determined by ferrioxalate actinometry[44] to be ~2 x 10^{-6} ein/min.

Neat 1-pentene solutions of 2 x $10^{-3}\underline{M}$ $Fe(CO)_5$ or $Fe(CO)_4PPh_3$ were freeze-pump-thaw degassed five times in 13 x 100 mm ampules with constrictions and hermetically sealed. Polymer samples (5.2 mg, 3.8x10^{-3} mmol of Fe in 1.0 ml of 1-pentene) were prepared in the same manner. A small Teflon stirring bar was included in all samples for stirring during irradiation. Samples of 2x$10^{-3}\underline{M}$ $Fe(CO)_3(PPh_3)_2$ were prepared similarly except the solvent was benzene and the 1-pentene concentration was 5.0$\underline{M}$. This procedure was required since $Fe(CO)_3(PPh_3)_2$ is only sparingly soluble in 1-pentene. The sample size in all cases was 1.0 ml and actinometry was carried out under parallel conditions.

Photocatalyzed Reaction of 1-Pentene and $HSiEt_3$.

General procedures for the photocatalyzed 1-pentene/$HSiEt_3$ reactions were the same as those for the isomerization studies. The reaction solutions were typically ~$10^{-3}\underline{M}$ catalyst precursor in neat 1/1 (mole ratio) of 1-pentene/$HSiEt_3$. The catalysis products were those identified previously,[9,10] and they were analyzed quantitatively by gas chromatography using a 10 ft x $\frac{1}{8}$ in. 25% β,β'-oxydipropionitrile on Gaschrome Q column at 50°C.

Photochemistry of $Fe(CO)_n(PPh_3)_{5-n}$ (n = 4, 3).

Irradiation of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ was carried out in freeze-pump-thaw degassed hydrocarbon (C_6D_6, C_6H_6, or isooctane) solution in the presence of PPh_3, $P(OMe)_3$, 1-pentene, or $HSiEt_3$. Irradiation of $Fe(CO)_4PPh_3$ in the presence of PPh_3 yields $Fe(CO)_3(PPh_3)_2$ quantitatively (initially) by ir spectral measurements. The 366 nm reaction quantum yield was determined by irradiation in a merry-go-round[45] equipped with a 550 W Hanovia medium pressure Hg lamp filtered with Corning filter 7-37 to isolate the 366 nm emission. The light intensity was determined by ferrioxalate actinometry. Samples were 3.0 ml in hermetically sealed 13 mm diameter Pyrex ampules.

Spectra.

Infrared spectral data were recorded using a Perkin-Elmer 180 spectrometer using matched pathlength (0.1 or 1.0 mm) NaCl cells. A Cary 17 spectrophotometer was used to record electronic absorption spectra, and a Varian T-60 was used to record the position of the hydride resonances (19.04 τ) in $HFe(CO)_3(SiEt_3)(PPh_3)$ relative to $SiMe_4$.

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Table I. Infrared Bands in CO Stretching Region for Complexes Studied.

Complexes	Bands, cm^{-1} (ϵ, $\ell mol^{-1} cm^{-1}$)[a]
$Fe(CO)_5$	2025 (5470); 2000 (11,830)
$Fe(CO)_4(PPh_3)$	2054 (3500); 1977.5 (2310); 1942 (4870)
trans-$Fe(CO)_3(PPh_3)_2$	1892.5 (5140)
(P)-$PPh_2)_{5-n}Fe(CO)_n$ (n = 3,4)	2045(——); 1968 (——); 1932 (——); 1876 (——)

[a] Isooctane solution, 25°C except where noted otherwise.

[b] KBr Pellet.

Table II. Polymer-anchored Photocatalyzed 1-Pentene Isomerization in Isooctane and Benzene.[a]

Solvent	Irrdn Time, hours	% 1-pentene	% trans-2-pentene	% cis-2-pentene
Benzene	0	100	0	0
	12	70.4	21.4	8.2
Isooctane	0	100	0	0
	12	99.7	0.20	<<1

[a]Degassed 0.1M 1-pentene solutions irradiated at 25°C with near-uv light. Samples were 3.0 ml with benzene or isooctane solvent employing 3.0 mg of polymer (see Experimental) suspended in solution.

Table III. Photocatalyzed Isomerization of 1-Pentene.[a]

Catalyst Precursor	% Conversion (Irrdn Time, min)	Observed Φ[b]	(trans/cis)[c]
$Fe(CO)_5$	6.2 (2)	117	2.92
	11.9 (4)	112	2.93
	31.5 (15)	96	3.29
$Fe(CO)_4PPh_3$	7.8 (5)	71	1.11
	12.7 (10)	58	1.20
	16.3 (15)	50	1.32
	19.8 (21)	43	1.43
	36.2 (60)	28	2.12
$Fe(CO)_3(PPh_3)_2$	8.6 (15)	12	0.56
	11.2 (30)	7.7	0.57
	18.4 (60)	7.7	0.58
(P)$-PPh_2)_{5-n}Fe(CO)_n$	3.9 (30)	6.0	0.71
	6.4 (60)	4.8	0.80
	10.6 (120)	4.0	1.10
	33.8 (720)	2.2	1.76

[a]All reactions are carried out in hermetically sealed, degassed ampules at 25°C. For the homogeneous precursors the concentration was $2 \times 10^{-3}\underline{M}$ in neat 1-pentene as solvent except for $Fe(CO)_3(PPh_3)_2$ which was $5.0\underline{M}$ 1-pentene in benzene as solvent. The polymer suspension was run using 5.2 mg of polymer (see Experimental) in 1.0 ml of 1-pentene (3.8×10^{-3} mmol of Fe per sample).

[b]Φ is the number of 1-pentene molecules isomerized per photon incident on the sample. The irradiation source was a GE Black Lite.

[c]Ratio of trans-2- and cis-2-pentene products.

Table IV. Distribution of Products from Fe Carbonyl Photocatalyzed Reactions of 1-Pentene and Et_3SiH.

Precursor	% Conversion	$(n\text{-Pentyl})SiEt_3$[a]	$(\text{Pentenyl})SiEt_3$[a]		
			I	II	III
$Fe(CO)_5$	2	16.5	21.3 (25.5)	52.4 (62.8)	9.8 (11.7)
	81	17.5	16.1 (19.3)	51.2 (62.5)	15.2 (18.2)
$Fe(CO)_4PPh_3$	8	8.1	16.2 (17.6)	62.0 (67.5)	13.6 (14.8)
	30	10.5	16.0 (17.9)	58.1 (64.9)	15.4 (17.2)
$Fe(CO)_3(PPh_3)_2$	6	19.8	14.8 (18.5)	50.5 (63.0)	14.8 (18.5)
	40	11.1	17.3 (19.5)	57.9 (65.2)	13.6 (15.3)
Ⓟ$-PPh_2)_{5-n}Fe(CO)_n$	20	8.4	21.1 (23.0)	58.7 (64.1)	11.8 (12.9)
	50	14.7	15.5 (18.2)	55.4 (64.9)	14.4 (16.9)

[a] Numbers given are the percent of all Si containing products. Numbers in parentheses are the ratios of the pentenyl isomers given in percent; irradiation of neat 1/1 alkene/silane solutions; ~10^{-3}M precursor. See eq. 5 of text for structures of I, II, and III. See Experimental section for detailed analytical procedures.

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