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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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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 that of homogeneous solutions of $Fe(CO)_n(PPh_3)_{5-n}$ (n = 3–5). 1-Pentene isomerization and reaction with $HSiEt_3$ can be affected 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, organometallic 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 mononuclear 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

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

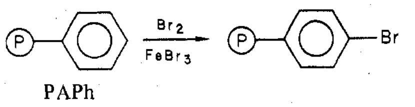
complexes	bands, cm^{-1} (ϵ, L mol^{-1} cm^{-1})[a]
$Fe(CO)_5$	2025 (5470), 2000 (11 830)
$Fe(CO)_4(PPh_3)$	2054 (3500), 1977.5 (2310), 1942 (4870)
trans-$Fe(CO)_3(PPh_3)_2$	1892.5 (5140)
$[(PAPh)-PPH_2]_{5-n}$-$Fe(CO)_n$ (n = 3,4)[b]	2045 (-), 1968 (-), 1932 (-), 1876 (-)

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

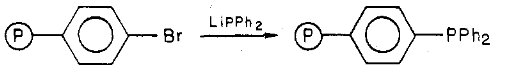
considerable expectation that the $Fe(CO)_n$-based systems could serve as photocatalysts for olefin reactions.

Results

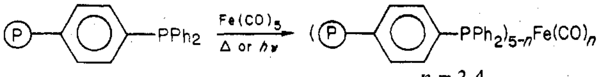
a. Systems Studied. The polymer-anchored (PA) $Fe(CO)_n$ system used in this study was prepared according to the procedure indicated in reactions 1–3. The details are given in the Experimental Section, but we note here that the polymer is a 200–400 mesh styrene–1% divinylbenzene microporous resin.



(1)



(2)



(3)

There is some uncertainty concerning the ratio of $[(PAPh)-PPh_2]_2Fe(CO)_3$ to $[(PAPh)-PPh_2]Fe(CO)_4$ species on the phosphinated polymer, but infrared spectra 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 $[(PAPh)-PPh_2]Fe(CO)_4$ sites and a single absorption at 1876 cm^{-1} for the $[(PAPh)-PPh_2]_2Fe(CO)_3$ 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 $[(PAPh)-PPh_2]Fe(CO)_4/[(PAPh)-PPh_2]_2Fe(CO)_3$ ratio to be in the range of 3–5. This ratio is a variable which can be manipulated by PPh_2 loading, cross-link density, etc. Future studies will be concerned with such variations.

The "anchor" for the catalyst precursor on the polymer is a triarylphosphine. Therefore, we have used $Fe(CO)_n(PPh_3)_{5-n}$ (n = 3, 4) 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 σ-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–iron bond is photoinert; vide infra.

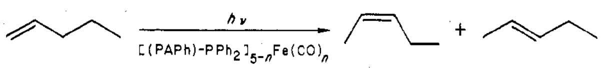
In our studies of the photocatalytic behavior of the triarylphosphine–iron carbonyl systems we have used alkene isomerization and alkene reaction with trialkylsilane as probe reactions. In particular, we have investigated the photocatalyzed isomerization of 1-pentene and the reactions of 1-pentene with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

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

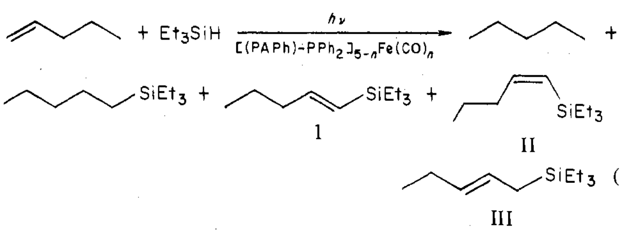
solvent	irrdn time, h	% 1-pentene	% *trans*-2-pentene	% *cis*-2-pentene
benzene	0	100	0	0
	12	70.4	21.4	8.2
isooctane	0	100	0	0
	12	99.7	0.20	<<1

[a] Degassed 0.1 M 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 Section) suspended in solution.

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



(4)



(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/triethylsilane.

Several other qualitative points are worth noting here. The photocatalysis requires continuous irradiation; i.e., when the light is turned off, the reaction stops, but the reaction 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/triethylsilane 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/Fe atom present in the alkene–silane photocatalysis. Additionally, the polymer system is easy to handle and can be recovered in a 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 $[(\mathrm{PAPh})\text{–}\mathrm{PPh_2}]_{5-n}\mathrm{Fe(CO)}_n$ will break Fe–P bonds. Qualitatively we can state that $\mathrm{Fe(CO)}_n(\mathrm{PPh_3})_{5-n}$ species are not detectable in the solution when $[(\mathrm{PAPh})\text{–}\mathrm{PPh_2}]_{5-n}\mathrm{Fe(CO)}_n$ is irradiated in degassed benzene solutions of 0.1 M $\mathrm{PPh_3}$, 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; $\mathrm{Fe(CO)}_n$ units may be wandering through the polymer with little probability for escape. In such a case we could have catalytic chemistry occurring at nonanchored $\mathrm{Fe(CO)}_n$ 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 $\mathrm{Fe(CO)_4PPh_3}$ and $\mathrm{Fe(CO)_3(PPh_3)_2}$ have been irradiated with near-UV light to determine the relative photolability of $\mathrm{PPh_3}$ and CO in such complexes. The results should be applicable to the $[(\mathrm{PAPh})\text{–}\mathrm{PPh_2}]_{5-n}\mathrm{Fe(CO)}_n$ system. For $\mathrm{Fe(CO)_4PPh_3}$ we find that the primary photoreaction is (6). This has been determined in several ways.

$$\mathrm{Fe(CO)_4PPh_3} \xrightarrow{h\nu} \mathrm{Fe(CO)_3PPh_3} + \mathrm{CO} \qquad (6)$$

First, irradiation at 366 nm in the presence of 0.1 M $\mathrm{PPh_3}$ yields $\mathrm{Fe(CO)_3(PPh_3)_2}$ with a quantum yield of 0.4 ± 0.04. The reaction can be followed by IR spectroscopy and the initial chemical yield of $\mathrm{Fe(CO)_3(PPh_3)_2}$ is quantitative. Further, irradiation of isooctane solutions of $\mathrm{Fe(CO)_4PPh_3}$ in the presence of 0.1 M $\mathrm{P(OMe)_3}$ initially yields a broad IR absorption centered at 1898 $\mathrm{cm^{-1}}$ (presumably $\mathrm{Fe(CO)_3(PPh_3)(P(OMe)_3)}$), whereas $\mathrm{Fe(CO)_5}$ irradiated in the presence of $\mathrm{P(OMe)_3}$ gives peaks initially at 2063 (s), 1992 (s), 1962 (vs), 1920 (vs), and 1910 (vs) $\mathrm{cm^{-1}}$. From $\mathrm{Fe(CO)_5}$ a mixture of $\mathrm{Fe(CO)}_n(\mathrm{P(OMe)_3})_{5-n}$ (n = 3, 4) apparently obtains. Literature values for $\mathrm{Fe(CO)_4P(OMe)_3}$ are 2063, 1992, 1963, and 1951 $\mathrm{cm^{-1}}$, and for $\mathrm{Fe(CO)_3(P(OMe)_3)_2}$, 1920 and 1912 $\mathrm{cm^{-1}}$ are the reported band positions.[41] Irradiation of $\mathrm{Fe(CO)_4PPh_3}$ in the presence of $\mathrm{P(OMe)_3}$ yields no IR bands in common with those from $\mathrm{Fe(CO)_5}$ (no $\mathrm{Fe(CO)_4P(OMe_3)}$ is IR detectable), indicating that $\mathrm{PPh_3}$ remains coordinated to the Fe. Irradiation of $\mathrm{Fe(CO)_4PPh_3}$ in the presence of 1-pentene results in new bands at 2011, 1945, and 1916 $\mathrm{cm^{-1}}$ (presumably $\mathrm{Fe(CO)_3(PPh_3)(C_5H_{10})}$); again these are noncoincident with the bands which result from irradiation of $\mathrm{Fe(CO)_5}$ in the presence of 1-pentene at 2084 and 1978 $\mathrm{cm^{-1}}$ associated with $\mathrm{Fe(CO)_4(C_5H_{10})}$.[9] Finally, irradiation of $\mathrm{Fe(CO)_4PPh_3}$ in the presence of $\mathrm{HSiEt_3}$ results in the growth of new IR bands at 2032 (w) and 1962 (vs) $\mathrm{cm^{-1}}$ but not at 2093 (w), 2027 (m), 2019 (s), and 2006 (s) $\mathrm{cm^{-1}}$ as found[9] for $\mathrm{HFe(CO)_4SiEt_3}$ from irradiation of $\mathrm{Fe(CO)_5}$. The irradiation of $\mathrm{Fe(CO)_4PPh_3}$ in the presence of $\mathrm{HSiEt_3}$ in $\mathrm{C_6D_6}$ solvent can be followed by ^{1}H NMR spectroscopy and a hydride resonance is found at τ 19.0. This signal is a doublet with a 26-Hz coupling constant supporting the formulation of the product as $\mathrm{HFe(CO)_3(PPh_3)(SiEt_3)}$. The important point from all these photochemical results is that a different product results from $\mathrm{Fe(CO)_5}$ than from $\mathrm{Fe(CO)_4PPh_3}$, supporting the notion that reaction 6 is the prevailing primary photoprocess for $\mathrm{Fe(CO)_4PPh_3}$.

$\mathrm{Fe(CO)_3(PPh_3)_2}$ likewise is photosensitive in solution in the presence of nucleophiles or oxidative addition substrates. The disappearance quantum yield at 355 nm is approximately 0.2 in the presence of 0.1 M $\mathrm{P(OMe)_3}$ in benzene solution. Spectral changes in the IR are not clean and reflect some combination of CO and $\mathrm{PPh_3}$ loss. The initial yield of $\mathrm{Fe(CO)_3(PPh_3)(P(OMe)_3)}$ is less than 20% of the products, indicating that reaction 7 accounts for the bulk of the primary

$$\mathrm{Fe(CO)_3(PPh_3)_2} \xrightarrow{h\nu} \mathrm{Fe(CO)_2(PPh_3)_2} + \mathrm{CO} \qquad (7)$$

reaction from the excited state. Prolonged irradiation does result in some loss of $\mathrm{PPh_3}$, but spectral 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 $\mathrm{PPh_3}$ groups in the actual catalytically active species.

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

catalyst precursor	% cnvrsn (irrdn time, min)	obsd ϕ[b]	trans/cis[c]
$\mathrm{Fe(CO)_5}$	6.2 (2)	117	2.92
	11.9 (4)	112	2.93
	31.5 (15)	96	3.29
$\mathrm{Fe(CO)_4PPh_3}$	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
$\mathrm{Fe(CO)_3(PPh_3)_2}$	8.6 (15)	12	0.56
	11.2 (30)	7.7	0.57
	18.4 (60)	7.7	0.58
$[(\mathrm{PAPh})\text{–}\mathrm{PPh_2}]_{5-n}\mathrm{Fe(CO)}_n$	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 were carried out in hermetically sealed, degassed ampules at 25 °C. For the homogeneous precursors the concentration was 2×10^{-3} M in neat 1-pentene as solvent except for $\mathrm{Fe(CO)_3(PPh_3)_2}$ which was 5.0 M 1-pentene in benzene as solvent. The polymer suspension was run using 5.2 mg of polymer (see Experimental Section) in 1.0 mL of 1-pentene (3.8×10^{-3} mmol of Fe/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.

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 $\mathrm{PPh_3}$ 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 $\mathrm{Fe(CO)_5}$ is believed to be nearly unity, whereas we find only 0.4 ± 0.04 for CO release from $\mathrm{Fe(CO)_4PPh_3}$. The observed quantum yields for the $[(\mathrm{PAPh})\text{–}\mathrm{PPh_2}]_{5-n}\mathrm{Fe(CO)}_n$ 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-

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

precursor	% cnvrsn	(*n*-pentyl)-$SiEt_3$[a]	(pentenyl)$SiEt_3$[a]		
			I	II	III
$Fe(CO)_5$	2	16.5	21.3	52.4	9.8
			(25.5)	(62.8)	(11.7)
	81	17.5	16.1	51.2	15.2
			(19.3)	(62.5)	(18.2)
$Fe(CO)_4PPh_3$	8	8.1	16.2	62.0	13.6
			(17.6)	(67.5)	(14.8)
	30	10.5	16.0	58.1	15.4
			(17.9)	(64.9)	(17.2)
$Fe(CO)_3(PPh_3)_2$	6	19.8	14.8	50.5	14.8
			(18.5)	(63.0)	(18.5)
	40	11.1	17.3	57.9	13.6
			(19.5)	(65.2)	(15.3)
$[(PAPh)\text{-}PPh_2]_{5-n}\text{-}Fe(CO)_n$	20	8.4	21.1	58.7	11.8
			(23.0)	(64.1)	(12.9)
	50	14.7	15.5	55.4	14.4
			(18.2)	(64.9)	(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; $\sim 10^{-3}$ M precursor. See eq 5 of text for structures of I, II, and III. See Experimental Section for detailed analytical procedures.

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/triethylsilane 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)triethylsilane. Though differences in the product distribution are found, the qualitative findings for each catalyst precursor are similar: (*n*-pentyl)triethylsilane is a minor silicon-containing product compared to (pentenyl)triethylsilane 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 = 3, 4) 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 by 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 Section

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, N.Y.

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 mmol) was added to a slurry of the phosphinated polymer (3.00 g, 0.91 mmol of P) in 50 mL of deoxygenated benzene and refluxed under N_2 for approximately 20 h. 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 ratio 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 = 3–5). $Fe(CO)_5$ was obtained commercially and used after distillation. The PPh_3 substituted complexes were prepared as described in the literature.[43] $Fe(CO)_4PPh_3$ 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 region 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 × 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 15-W 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 $\sim 2 \times 10^{-6}$ einstein/min.

Neat 1-pentene solutions of 2×10^{-3} M $Fe(CO)_5$ or $Fe(CO)_4PPh_3$ were freeze–pump–thaw degassed five times in 13 × 100 mm ampules with constrictions and hermetically sealed. Polymer samples (5.2 mg, 3.8×10^{-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 2×10^{-3} M $Fe(CO)_3(PPh_3)_2$ were prepared similarly except the solvent was benzene and the 1-pentene concentration was 5.0 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/triethylsilane reactions were the same as those for the isomerization studies. The reaction solutions were typically ~10^{-3} M catalyst precursor in neat 1/1 (mole ratio) 1-pentene/triethylsilane. The catalysis products were those identified previously,[9,10] and they were analyzed quantitatively by gas chromatography using a 10 ft × 1/8 in. 25% β,β'-oxydipropionitrile on Gaschrome Q column at 50 °C.

Photochemistry of $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3, 4$). 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, 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 path length (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 (τ 19.04) in $HFe(CO)_3(SiEt_3)(PPh_3)$ relative to $SiMe_4$.

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References and Notes

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