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PHOTOACTIVATION OF POLYMER-ANCHORED CATALYSTS: IRON CARBONYL-CA--ETC(U)
NOV 78 R D SANNER, R G AUSTIN, M S WRIGHTON N00014-75-C-0880
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Photoactivation of polymer-anchored iron carbonyl catalysts is reported. Prototypic reactions are 1-pentene isomerization and reaction of 1-pentene with HSiEt ₃ which can be photocatalyzed at 25°C by near-uv irradiation of suspensions of the polymer-anchored catalyst systems. The basic polymer system is a styrene/1% divinylbenzene resin derivatized either with -PPh ₂ or -P(Ph)CH ₂ CH ₂ PPh ₂ anchoring sites for catalyst precursors. Fe(CO) _n (n = 3,4) are attached to the phosphine sites by reaction with Fe ₃ (CO) ₁₂ . The polymer-anchored catalysts show turnover numbers exceeding 2 x 10 ⁴ in some			

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20. ABSTRACT (continued)

cases, and observed quantum yields exceed unity, evidencing the photogeneration of a thermal catalyst. The data allow the conclusion that the anchoring Fe-P bond is relatively photoinert and that the catalysis is initiated by the photoinduced dissociation of CO from the $Fe(CO)_n$ moieties. The catalytic chemistry for the polymer systems parallels that found using homogeneous $Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3,4$) model photochemical catalyst precursors.

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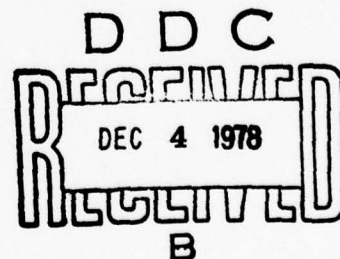
Photoactivation of Polymer-Anchored
Catalysts: Iron Carbonyl-Catalyzed Reactions
of Alkenes

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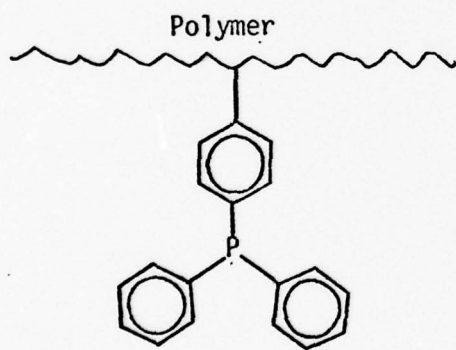
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Coordinatively unsaturated transition metal organometallic complexes are believed to play a key role in homogeneous catalytic processes.¹ Coordinative unsaturation can be generated photochemically by light-induced ligand dissociation and metal-metal bond cleavage,^{2,3} and such photochemistry has been exploited to initiate catalytic processes under relatively mild thermal conditions.⁴⁻⁶ Light-generated catalysts may be genuinely unique, since the catalyst is the result of some excited state decay process. Further, catalytic processes which are run at lower temperature may yield greater selectivity in product distribution where more than one product can be formed. Light also offers a degree of control over catalytic processes not necessarily attainable in conventional catalytic systems, since the product formation depends on two stimuli, light and heat. Examples of organometallic photocatalysis have amply demonstrated the concept of initiating catalysis under relatively mild conditions in the reactions of olefins with hydrogen and silicon hydrides and in unimolecular isomerization reactions of olefins.⁴⁻⁶

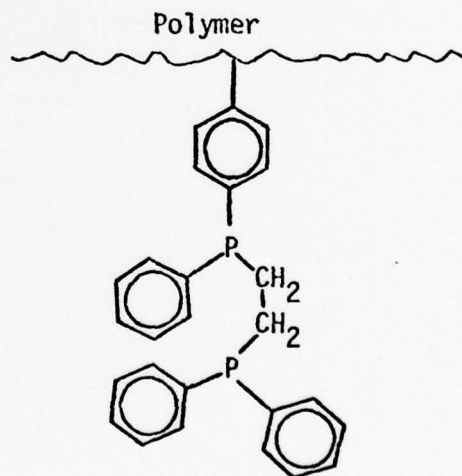
In this report we summarize our recent findings⁷ on the exploitation of photochemical catalyst generation in situations where the catalyst precursor is anchored to a polymer. Additionally, we present new data to add to the characterization of such systems. A large number of examples of thermally activated polymer-anchored catalyst systems have been studied.⁸⁻¹⁰ Anchoring a catalyst to a polymer allows one to take advantage of the molecular specificity of organometallic catalysts while still being able to easily separate the products from the catalyst system. Viewing the polymer as a ligand, albeit an unusual one, one can also effect some control over the catalytic processes by the nature of the polymer-anchoring system. Photochemical activation of polymer-anchored catalyst systems may allow the generation of unique catalyst systems, since it has been demonstrated that extensive, multiple, coordinative unsaturation can be photogenerated by

irradiating metal carbonyls in situations where the complexes are matrix isolated.¹¹⁻¹³ The polymer-anchored complex can be viewed as a situation where the complex can be "matrix isolated", provided the rigidity of the polymer is great enough and the density of complexes on the polymer is low enough. But the exploitation of any photoactivation of a polymer-anchored catalyst depends on the photoinertness of the anchor bond. Photoinduced selective loss of ligands other than the polymer ligand is the objective.

Detailed results have been obtained for $\text{Fe}(\text{CO})_n$ ($n = 3,4$) bound to a phosphinated styrene/divinylbenzene resin. Two types of anchoring sites have been used and are represented in I and II. Most of the work thus



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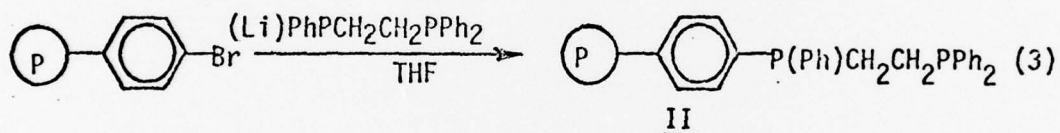
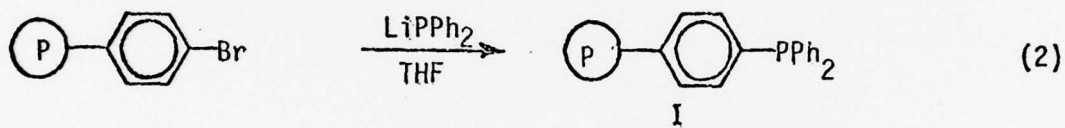
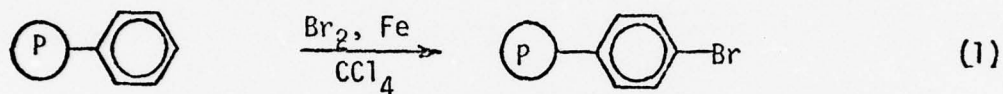


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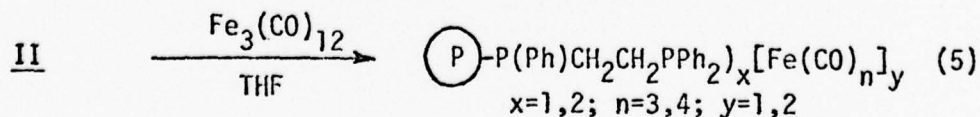
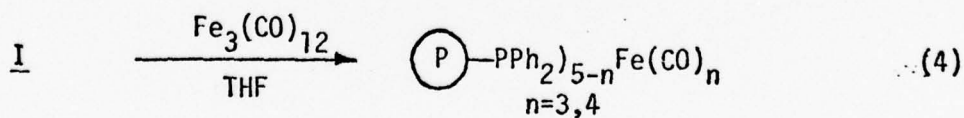
far has involved the phosphinated polymer I. This anchoring system approximates a triphenylphosphine ligand, and consequently, the $\text{Fe}(\text{CO})_n(\text{PPh}_3)_{5-n}$ ($n = 3,4$) complexes have been used as homogeneous models for the polymer-anchored system. A direct comparison of these phosphine derivatives with $\text{Fe}(\text{CO})_5$ has also been made in order to assess the effect of having the phosphine ligand(s) in the coordination sphere. The probe catalytic chemistry is 1-pentene isomerization and reaction with HSiEt_3 . Both of these reactions can be photocatalyzed using $\text{Fe}(\text{CO})_5$ as the catalyst precursor.⁶

Results and Discussion

a. Polymer Systems Studied. The polymer used in this work is a commercially available (Bio-Rad Laboratories SX-1, 200-400 mesh) styrene-1% divinylbenzene microporous resin. It was brominated and functionalized according to the procedures represented in equations (1)-(3). The phosphinated material



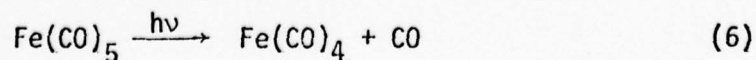
I and II was reacted thermally with $\text{Fe}_3(\text{CO})_{12}$ in THF to incorporate $\text{Fe}(\text{CO})_n$ ($n = 3,4$) by attachment to the phosphine ligands, equations (4) and (5).



Thermal reaction of $\text{Fe}_3(\text{CO})_{12}$ with phosphine ligands is known to produce mononuclear iron carbonyl species.¹⁴ Elemental analyses (Schwarzkopf Microanalytical Laboratories) and infrared spectra in the carbonyl region has been used to characterize these systems.

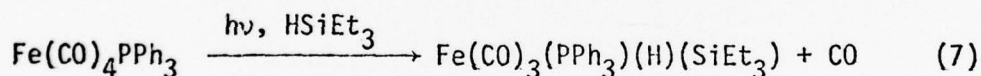
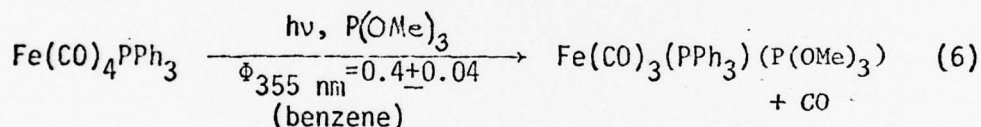
Table I summarizes the essential analytical results for the several polymer catalyst systems described herein, and Table II gives infrared spectral data for polymer systems and other relevant complexes. The infrared data (band positions and relative intensities) for anchoring system I reveal that there is a ratio of $\text{P}-\text{PPh}_2\text{Fe}(\text{CO})_4$ to trans- $\text{P}-\text{PPh}_2)_2\text{Fe}(\text{CO})_3$ in the range 3-5 where the $\text{Fe}(\text{CO})_3$ unit can serve as a cross-linking agent. The distribution of $\text{Fe}(\text{CO})_n$ species for anchoring system II is more complex, owing to the possibility that the diphosphine anchor may or may not be a chelating reagent. Comparison of the infrared spectra for catalyst systems C-F suggest that there are certainly attached $\text{Fe}(\text{CO})_4$ units. The band at 1880 or 1885 cm^{-1} suggests that $\text{Fe}(\text{CO})_3$ serves as a cross linking reagent as in system I mimicking the model trans- $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ species. The data seem to rule out an important contribution from anchoring system II as a chelate to bind $\text{Fe}(\text{CO})_3$ in the systems studied. Deliberate variation in the distribution of the coordination sphere of the attached iron in I and II is clearly achievable by careful control at the functionalization stages, but the work to date has focused mainly on first establishing some of the quantitative photocatalytic behavior in these systems.

b. Primary Photoprocesses in Fe Carbonyl Complexes. It is well known that equation (6) represents the primary chemical result of optically exciting



$\text{Fe}(\text{CO})_5$.^{2,11,12} The reaction occurs efficiently and such is believed to be the primary step in the $\text{Fe}(\text{CO})_5$ photocatalyzed isomerization,¹⁵ hydrogenation,¹⁵ and hydrosilation⁶ of alkenes. But in these cases it has been postulated that absorption of an additional photon by some $\text{Fe}(\text{CO})_4(\text{alkene})$ or $\text{Fe}(\text{CO})_4(\text{H})(\text{R})$ ($\text{R} = \text{H}, \text{Si}(\text{alkyl})_3$) is required in order to effect the alkene chemistry.^{6,15}

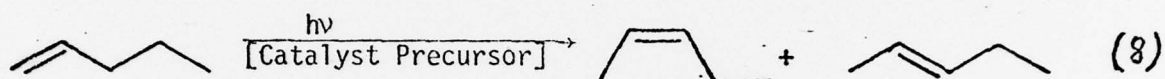
The crucial question here with respect to polymer-anchored $\text{Fe}(\text{CO})_n$ species is whether the Fe-P bond is photoinert. If the Fe-P is cleaved photochemically then the anchored species can be released to the bulk solution and simply effect the same chemistry as that found beginning with $\text{Fe}(\text{CO})_5$ in solution. Three lines of evidence support the conclusion that the Fe-P bond is relatively photoinert for the catalyst systems studied here. First, equations (6) and (7) represent the chemistry occurring upon



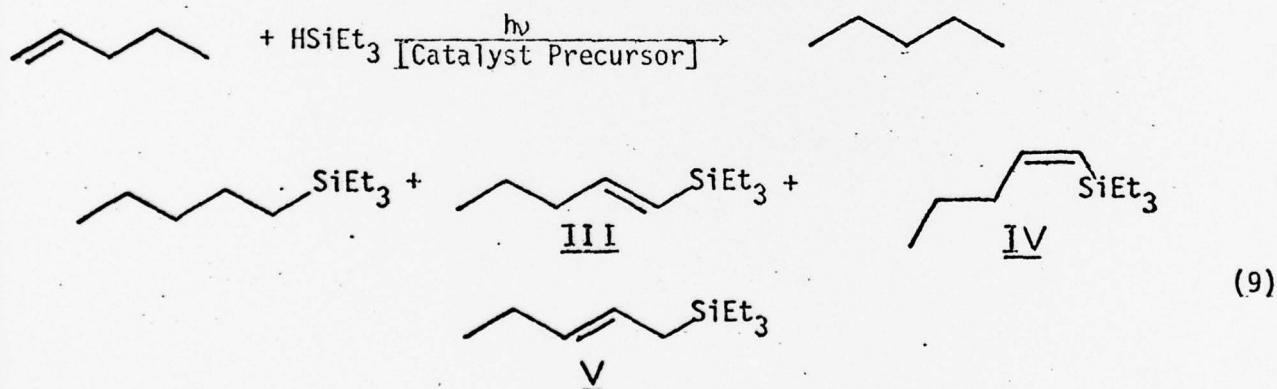
near-uv photoexcitation of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in the presence of $\text{P}(\text{OMe})_3$ and HSiEt_3 , respectively; in the former no $\text{Fe}(\text{CO})_4(\text{P}(\text{OMe})_3)$ was detectable and in the latter no $\text{Fe}(\text{CO})_4(\text{H})(\text{SiEt}_3)$ was found.⁷ Thus, for $\text{Fe}(\text{CO})_4(\text{phosphine})$ it appears that extrusion of CO is the principal result of optical excitation. Similar results appear to obtain for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, but loss of PPh_3 here may have an efficiency of $\sim 1/10$ that for CO loss. Second, irradiation of the polymer-anchored $\text{Fe}(\text{CO})_n$ species does not lead to detectable amounts of $\text{Fe}(\text{CO})_n$ complexes in solution even when the solution contains PPh_3 as a potential sequestering reagent. Finally, the catalytic chemistry for the

polymer-anchored systems is inconsistent with that obtained from $\text{Fe}(\text{CO})_5$; the data suggest the retention of at least one phosphine in the coordination sphere during actual catalytic reactions.

c. Qualitative Photocatalytic Behavior. Polymer-anchored $\text{Fe}(\text{CO})_n$ species have been shown to serve as photochemical sources of catalytically active species capable of effecting 1-pentene isomerization, equation (8), and



1-pentene reaction with HSiEt_3 according to equation (9). The catalytic



chemistry can be induced with near-uv (355 nm) irradiation at 25°C where there is no detectable dark reaction, and no photo-induced reaction of the 1-pentene is found by irradiating suspensions of the anchoring material prior to attachment of the $\text{Fe}(\text{CO})_n$ units. Solvent interactions have been found to be substantial but have not yet been fully evaluated. The importance of polymer solvation is reflected in the fact that 0.1M 1-pentene in an isooctane suspension of polymer system A undergoes <<1% isomerization after 12 h of irradiation whereas >25% isomerization obtains under the same conditions when

benzene is the solvent. For the work described here the solutions are generally neat 1-pentene or a neat 1/1 mole ratio of 1-pentene/ HSiEt_3 .

Catalytic action depends on the rigorous exclusion of O_2 and reactions were run in hermetically sealed, freeze-pump-thaw degassed, ampules. Sustained catalysis requires continuous irradiation; i.e. when the light is turned off reaction appears to stop, but can be re-initiated by light. Quantum yields often exceed unity, though, indicating that irradiation does produce a thermally active catalyst capable of effecting a number of turnovers prior to needing reactivation with light. Except for catalyst systems D, E, and F, we have been able to observe a large amount of substrate reaction compared to the number of Fe atoms initially present. We have observed $>2 \times 10^4$ 1-pentene molecules reacted per Fe atom present. Finally, the catalyst system is used as a stirred suspension in the substrate solution, and this fact results in difficulty in measuring the quantum yields. Since the suspension may scatter light, we take the reaction quantum yields as the number of 1-pentene molecules consumed per photon incident on the sample. These quantum yields are thus a lower limit for the actual quantum yield. Table III shows the quantum yields as a function of the amount of polymer system B suspended in the neat 1-pentene. For the range 10-40 mg there is little change in the observed quantum yield recorded at ~30% conversion. Below 5 mg the quantum yields do fall off, consistent with substantial transmission of the incident irradiation. Even though suspensions are used, good reproducibility has been found.

d. 1-Pentene Isomerization. Data for the photocatalyzed isomerization of neat 1-pentene for several catalyst precursors are shown in Table IV. All of the catalyst precursors having a phosphine in the coordination sphere yield an initial ratio of 2-pentenes which is different from that when $\text{Fe}(\text{CO})_5$ is used as the catalyst precursor. This result unequivocally establishes that the

phosphine complexes do retain the phosphine in the coordination sphere during the actual isomerization process. Further, in the polymer systems it is gratifying that the ratio of the 2-pentenes is between that found for the $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ species, consistent with the distribution of such species anchored to the polymer. The observed decline in isomerization quantum yield

$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2 < \text{Fe}(\text{CO})_4\text{PPh}_3 < \text{Fe}(\text{CO})_5$ is interesting, and perhaps suggestive, but not quantitatively interpretable in terms of catalyst turnover rate, since there may be large differences in the efficiency of catalyst generation.

All of the catalyst precursors studied, except polymer systems D, E, and F, are capable of effecting substantial isomerization of neat 1-pentene. The inactivity of polymer systems D, E, and F is not easily explicable and is currently under study. A plausible rationale is that the amount of uncomplexed diphosphine chelate is great enough and the polymer sufficiently flexible that the catalytically active sites are capped by the coordinating phosphines. Excess triphenylphosphine in solution substantially suppresses the isomerization activity of the homogeneous photocatalysts. One fact that is very interesting is that to the extent that any isomerization does take place on D, E, and F we see a trans/cis product ratio in accord with the fact that there appears to be more than one phosphine group in the Fe coordination sphere.

Table V shows the variation in isomerization quantum yields as the 1-pentene concentration is varied for polymer system B using benzene as co-solvent. There is more than a ten-fold change in the initial quantum yields with variation in the 1-pentene concentration. Such an effect has been reported previously using $\text{Fe}(\text{CO})_5$ in homogeneous solution.¹⁵ It is interesting to note that there appears to be a modest change in the initial trans/cis ratio with variation in 1-pentene concentration. This effect may be due to differences in steric effects owing to change in the degree of polymer swelling by benzene and 1-pentene. Alternatively, the variation in

trans/cis ratio may indicate some effect from pentene not coordinated to Fe, perhaps associatively directing decay of the proposed¹⁵ π -allyl hydride intermediate for isomerization.

e. Photocatalyzed Reaction of 1-Pentene with HSiEt₃. Table VI shows the distribution of Si-containing products resulting from the various photocatalysts. Except for some minor variations the distribution of products seems to be essentially independent of the catalyst precursor or the extent conversion. The amount of n-pentane in each case is initially equal to the total (pentenyl)SiEt₃ yield. These data testify to the ability to effect catalytic chemistry of some consequence synthetically using the polymer-anchored catalyst precursors. The interesting products here are the (pentenyl)SiEt₃ species which are not generally formed in catalyzed reactions of alkenes with silicon hydrides.¹⁶ Since the product distribution does not vary greatly with any of the precursors we cannot unequivocally conclude that the phosphines are retained in the Fe coordination sphere, but nor is there any evidence that the phosphine is lost. The catalytic reaction may simply not be too sensitive to catalyst structure; the Si-containing products are likely generated by competitive β - and reductive-elimination processes^{4,6} which may not be as sensitive to the steric environment as is decay of the π -allyl hydride intermediate¹⁵ for isomerization.

Summary

Polymer-anchored $\text{Fe}(\text{CO})_n$ ($n = 3,4$) units are effective photocatalysts for alkene isomerization and reaction with a silicon hydride. The catalytic chemistry parallels that found for appropriate homogeneous model complexes. Primary photoprocesses for the models and the distribution of photocatalytic products reveal that the anchoring bond attaching the catalyst to the polymer is relatively photoinert. While quantum yields for catalytic reactions substantially exceed unity, long-lived catalytic activity in the dark does not obtain, even for polymer-anchored systems.

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Experimental

The general procedures and synthesis associated with polymer system I have been detailed elsewhere,⁷ including the synthesis and characterization of the derivatized polymer. The irradiation source in the experiments described herein was a GE Blacklite equipped with two 15W bulbs with principal output at 355 nm; the intensity at the sample (stirred for polymer systems) was $\sim 10^{-6}$ ein/min. measured by ferrioxalate actinometry.¹⁷ The samples themselves were solutions or suspensions of the catalyst precursor in neat 1-pentene (Chemical Samples Co., >99.9%) such that $\sim 10^{-3} M$ Fe was present. Sample size was typically 1.0 ml and were placed in 13 x 100 mm ampules and freeze-pump-thaw degassed and hermetically sealed prior to illumination at 298°K. Analyses were all by gas chromatography using equipment described previously.⁷

Polymer system II has not been previously described and its synthesis is described below. THF was distilled from potassium/benzophenone under nitrogen. All other solvents and chemicals were used as received except for diphenylvinylphosphine which was prepared by the reaction of chlorodiphenylphosphine with vinyl magnesium bromide according to the literature method.¹⁷ Styrene-1%-divinylbenzene beads were purchased from Bio-Rad Laboratories (SX-1, 200-400 mesh) and were brominated according to literature methods.¹⁸ Microanalytical analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. All reactions and manipulations involving phosphines were carried out under nitrogen.

Preparation of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$

A neat solution of phenylphosphine (36.0 g, 0.33 mole) and diphenylvinylphosphine (36.8 g, 0.17 mole) containing AIBN (0.30 g) was irradiated under nitrogen for 2 hours with a 100 watt Hanovia uv lamp. The

excess diphenylphosphine was distilled from the resulting solution at atmospheric pressure and the 1-phenylphosphine-2-diphenylphosphinoethane was vacuum distilled at 190-195°/0.05 torr, yield: 35.0 g (63%). The only other major byproduct was bis(2-diphenylphosphinoethyl)phenylphosphine produced by the reaction of two moles of diphenylvinylphosphine per mole of phenylphosphine. The ratio of the two products formed by this reaction is very sensitive to the ratio of the two reactants, with an excess of phenylphosphine favoring production of bis chelate phosphine.

Preparation of $\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$

Lithium metal (5.0 g, 0.72 moles) was suspended in THF (25 ml) and a solution of 1-phenylphosphino-2-diphenylphosphinoethane (22.0 g, 58.3 mmol) dissolved in THF (50 ml) was added dropwise. A yellow solution initially formed and slowly became dark red. The reactants were stirred together for two days at room temperature and then refluxed for 1 day. The excess lithium metal was removed, and the solution was added dropwise to a brominated styrene-1%-divinylbenzene (11.9 g, ~30% of the polystyryl rings brominated). The mixture was stirred for 2 days at room temperature and then refluxed for 1 day. The mixture was cooled and hydrolyzed slowly with 100 ml of deoxygenated water, filtered and washed with 500 ml portions of the following deoxygenated solvents: water, acetone-water (1:1), acetone, benzene, and methanol. The phosphinated resin beads were dried in vacuo at room temperature for 24 hours. Analysis found 0.37% Br and 5.16% P which corresponds to 11.9% of the polystyryl rings containing a bound

$-\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ group.

A similar procedure was followed to prepare a phosphinated resin containing bound- $\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ groups with 3.1% of the polystyryl rings substituted.

Preparation of $\text{P} \text{---} \text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2]_x [\text{Fe}(\text{CO})_n]_y$

$\text{Fe}_3(\text{CO})_{12}$ (0.55 g, 3.28 mmole Fe) was dissolved in 25 ml of THF and reacted with 1.0 g of a phosphinated resin containing bound $\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$ groups (11.9% of the rings substituted, 1.67 mmole P). The mixture was refluxed for 1 hour, cooled, and filtered. The resin beads were then repeatedly washed with alternate portions of dry, deoxygenated THF and methanol, and then dried in vacuo at 80° for 24 hours. Analysis found: 3.91% P and 6.79% Fe corresponding to a P/Fe ratio of 1.0.

Three other polymer-attached catalyst resins were similarly prepared except that different $\text{Fe}_3(\text{CO})_{12}$ /phosphinated resin ratios were used. Catalyst resin D was prepared by the reaction of $\text{Fe}_3(\text{CO})_{12}$ (0.10 g, 5.0 mmole Fe) with phosphinated resin (2.0 g, 3.1% rings substituted, 1.08 mmole P). Catalyst resin E was prepared by the reaction of $\text{Fe}_3(\text{CO})_{12}$ (0.032 g, 0.19 mmole Fe) with phosphinated resin (1.0 g, 11.9% rings substituted, 1.67 mmole Fe). Catalyst resin F was prepared by the reaction of $\text{Fe}_3(\text{CO})_{12}$ (0.023 g, 0.13 mmole Fe) with phosphinated resin (2.0 g, 3.1% rings substituted, 1.08 mmole P).

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Table I. Analytical Data for Polymer Catalyst Systems.

Anchoring ^a System	% of Phenyl Rings Substd.	Catalyst System	%P	%Fe	P/Fe
<u>I</u>	3.3	A	0.92	0.58	2.9
<u>I</u>	29	B	4.47	4.10	2.0
<u>II</u>	11.9	C	3.91	6.79	1.0
<u>II</u>	3.1	D	1.73	1.40	2.2
<u>II</u>	11.9	E	4.32	1.10	7.1
<u>II</u>	3.1	F	1.51	0.42	6.5

^aSee text.

Table II. Infrared Band Maxima in CO Stretching Region for Fe Carbonyl/Phosphine Complexes.^a

Complex	Band Maxima, cm^{-1} (ϵ)
$\text{Fe}(\text{CO})_5$	2025(5470); 2000(11,830)
$\text{Fe}(\text{CO})_4\text{PPh}_3$	2054(3500); 1978(2310); 1942(4870)
<u>trans</u> - $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	1893(5140)
$\text{P}(\text{PPh}_2)_{5-n}\text{Fe}(\text{CO})_n$ ($n = 3, 4$) (A and B)	2045(----); 1968(----); 1932(----); 1876(----)
$\text{Fe}(\text{CO})_4\text{P}(\text{Ph})_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Fe}(\text{CO})_4^b$	2049(----); 1976(----); 1934(----)
$(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})_3^b$	1992(----); 1923(----); 1901(----)
$\text{P}(\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2)_x[\text{Fe}(\text{CO})_n]_y$ ($x = 1, 2$; $n = 3, 4$; $y = 1, 2$)	
(C)	2055(----); 1982(----); 1934(----)
(D)	2050(----); 1975(----); 1935(----); 1880(----)
(E)	2050(----); 1980(----); 1935(----)
(F)	2040(----); 1975(----); 1935(----); 1885(----)

^aPolymer systems measured as Nujol mulls; all other complexes measured in hydrocarbon solution.

^bA. Reckziegel and M. Bigorgne, J. Organomet. Chem., **3**, 341 (1965) and T.A. Manuel, Inorg. Chem., **2**, 854 (1963).

Table III. Dependence of Observed Quantum Yield for 1-Pentene Reaction on Weight of Polymer Used.^a

Wt. of Polymer	% Conv.	ϕ^b	(<u>trans/cis</u>) ^c
5	33.8	2.2	1.76
10	25.4	5.3	1.78
20	30.8	6.5	1.71
30	31.6	6.7	1.68
40	29.4	6.2	1.47

^aStirred suspensions of polymer system B in 1.00 ml of degassed in 1-pentene irradiated at 25°C using a GE Blacklite (355 nm) irradiation source.

^bObserved quantum yield for consumption of 1-pentene; number of 1-pentene molecules consumed per photon incident on the sample.

^cObserved ratio of trans- to cis-2-pentene products.

Table IV. Photocatalyzed Isomerization of 1-Pentene.^a

Catalyst Precursor	% Conv. (Irrdn Time, min)	ϕ^b	(trans/cis) ^c	
Fe(CO) ₅	6.2 (2)	117	2.92	
	31.5 (15)	96	3.29	
Fe(CO) ₄ PPh ₃	7.8 (5)	71	1.11	
	36.2 (60)	28	2.12	
Fe(CO) ₃ (PPh ₃) ₂ ^d	8.5 (15)	12	0.56	
	18.4 (60)	7.7	0.58	
⊙-PPh ₂) _{5-n} Fe(CO) _n (B) ^e	3.9 (30)	6.0	0.71	
	33.8(720)	2.2	1.76	
⊙-P(Ph)CH ₂ CH ₂ PPh ₂) _x [Fe(CO) _n] _y (x = 1,2; n = 3,4; y = 1,2)	(C)	1.3 (15)	3.8	0.80
		2.5 (30)	3.8	0.86
		7.6 (45)	7.7	1.50
		19.6(120)	7.5	2.01
	(D)	2.6(360)	0.2	0.93
		2.5(1680)	0.0 ₄	0.92
	(E)	3.2(360)	0.3	0.42
		3.2(1680)	0.0 ₆	0.45
	(F)	No detectable isomerization(<0.5%)		

^aReactions carried out at 25°C using 1.0 ml of degassed neat 1-pentene solution containing 10⁻³M catalyst precursor. Samples were stirred throughout irradiation period. The irradiation source was a GE Blacklite (355 nm).

^bObserved quantum yield for 1-pentene consumption; number of molecules of 1-pentene consumed per photon incident on sample.

^cRatio of trans- to cis-2-pentene products.

^dCarried out in 5.0M 1-pentene in benzene as co-solvent.

^eComparable results obtained for polymer system A.

Table V. Dependence of Quantum Yield on 1-Pentene Concentration.^a

1-Pentene Conc., M	% Conv.	ϕ^b	(trans/cis) ^c
0.3	9.0	0.3	1.6
0.3	20.7	0.4	1.6
1.0	14.7	0.9	1.8
1.0	19.8	0.8	1.8
2.5	8.4	1.2	1.7
2.5	10.3	1.0	1.8
5.0	8.5	1.7	1.5
9.1 [neat]	6.4	4.8	0.8
9.1 [neat]	10.6	4.0	1.0

^aIrradiation of 5 mg of polymer system B suspended in 1.0 cc of degassed

benzene/1-pentene solution. Solutions are stirred throughout the irradiation period. Reaction is carried out at 25°C using a GE Blacklite (355 nm) irradiation source.

^bObserved quantum yield for 1-pentene disappearance; number of 1-pentene molecules consumed per photon incident on the sample.

^cRatio of trans- to cis-2-pentene products.

Table VI. Product Distribution in Photocatalyzed Reaction of 1-Pentene and HSiEt₃.^a

Catalyst Precursor	% Conv.	(Penteny1)SiEt ₃ ^a				
		(n-Penty1)SiEt ₃	III	IV	V	
Fe(CO) ₅	2	16.5	21.3	52.4	9.8	
	80	17.5	16.1	51.2	15.2	
Fe(CO) ₄ PPh ₃	8	8.1	16.2	62.0	13.6	
	30	10.5	16.0	58.1	15.4	
Fe(CO) ₃ (PPh ₃) ₂	6	19.8	14.8	50.5	14.8	
	40	11.1	17.3	57.9	13.6	
(P-PPh ₂) _{5-n} Fe(CO) _n (n = 3,4) (A or B)	20	8.4	21.1	58.7	11.8	
	50	14.7	15.5	55.4	14.4	
(P-P(Ph)CH ₂ CH ₂ PPh ₂) _x [Fe(CO) _n] _y ^b (C) (X = 1,2; n = 3,4; y = 1,2)	27	11.3	16.4	55.0	17.3	

^aNumbers given are the percent of all Si-containing products. Products generated from irradiation of neat 1/1 alkene/silane solutions containing 10⁻³M catalyst precursor. Cf. text, eq. (9), for structure of (penteny1)SiEt₃ isomers III, IV, and V.

^bExperiments with C were conducted in m-xylene solutions of 1.1 M 1-pentene and 1.1M HSiEt₃.

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