Pentacarbonyliron(0) Photocatalyzed Hydrogenation and Isomerization of Olefins

Mark A. Schroeder and Mark S. Wrighton*

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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Abstract: Photocatalyzed alkene isomerization and olefin hydrogenation using $Fe(CO)_5$ as the photocatalyst have been investigated. Observed quantum efficiency for 1-pentene to 2-pentene isomerization approaches 500, implicating the generation of a thermally active catalyst. The catalytically active species is proposed to be $HFe(CO)_3(\pi\text{-allyl})$. Olefin hydrogenation occurs under mild conditions, 25°C (1 atm H_2), by irradiation of $Fe(CO)_5$ in the presence of olefin. At lower temperatures, use of D_2 reveals that deuterium is incorporated into an alkene competitively with alkane formation. Hydrogenation is proposed to proceed through the sequence:

$$H_2Fe(CO)_3(\text{alkene}) \rightleftarrows HFe(CO)_3(\text{alkyl}) \xrightarrow[\text{alkene, } H_2]{} H_2Fe(CO)_3(\text{alkene}) + \text{alkane}$$

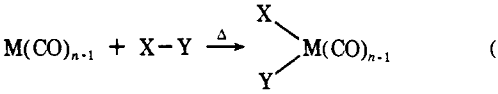
There is good selectivity for the least sterically hindered alkene, and turnover numbers for Fe exceed 10^3 in favorable cases.

Reactive intermediates formed by irradiation of transition metal complexes may be important as catalysts or reagents in organic chemical reactions.[1-6] Among several possible types of intermediates, coordinatively unsaturated metal carbonyls are very common and, in some cases, such species are well characterized structurally.[7-9] Generally, it may be said that mononuclear metal carbonyls undergo reaction 1 with high quantum efficiency.[10] Capture of the

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO \qquad (1)$$

coordinatively unsaturated $M(CO)_{n-1}$ by either nucleophiles, L, reaction 2, or by oxidative addition substrates, X-Y, reaction 3 can occur to give high chemical yields of

$$M(CO)_{n-1} + L \xrightarrow{\Delta} M(CO)_{n-1}L \qquad (2)$$



$$M(CO)_{n-1} + X{-}Y \xrightarrow{\Delta} (X)(Y)M(CO)_{n-1} \qquad (3)$$

the products indicated.[10] In this report we describe our results on $Fe(CO)_5$ photoassisted and photocatalyzed reactions of olefins where we have attempted to exploit reactions 1-3.

Photochemically induced reactions involving $Fe(CO)_5$ all appear to originate with reaction 4 which occurs even in

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \qquad (4)$$

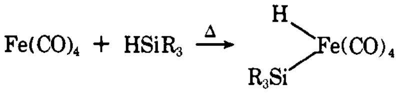
low-temperature matrices.[7] The C_{2v} $Fe(CO)_4$ itself is also photosensitive in the matrices and $Fe(CO)_3$ and lower carbonyls can be formed by prolonged irradiation.[7] In solution and in the absence of other substrates, reaction 5 occurs

$$Fe(CO)_4 + Fe(CO)_5 \xrightarrow{\Delta} Fe_2(CO)_9 \qquad (5)$$

with good efficiency.[11] In the presence of nucleophiles such as pyridine substituted derivatives of $Fe(CO)_5$ can be formed[12]

$$Fe(CO)_4 + \text{pyridine} \xrightarrow{\Delta} Fe(CO)_4(\text{pyridine}) \qquad (6)$$

and in the presence of oxidative addition substrates such as $HSiR_3$, reaction 7 obtains.[13] Even the reactions of olefins



$$Fe(CO)_4 + HSiR_3 \xrightarrow{\Delta} (H)(R_3Si)Fe(CO)_4 \qquad (7)$$

induced by irradiation of $Fe(CO)_5$[14-16] are logically associated with the primary photogeneration of $Fe(CO)_4$. Olefin isomerization,[14] acetylene reactions,[15] and the reactions of halogen containing species[16,17] all likely begin by the photoproduction of $Fe(CO)_4$. However, beyond this, relatively little is known about the possible role of light in these systems, and little information is available concerning mechanism or, in some cases, even about the characteristics of the reaction itself except to say that the product has been identified. Thermally $Fe(CO)_5$ catalyzed reactions of olefins are also known,[14a,b,18] and the elevated temperature required to carry out the catalysis is consistent with the production of $Fe(CO)_4$ by a thermal dissociation of CO from $Fe(CO)_5$. Hydrogenation of olefins in particular requires ~160°C and ~100 psi of H_2.[19]

The aim of the present work is to add substantial, new results to the $Fe(CO)_5$ photoinduced reactions of olefins which help clarify the mechanism subsequent to $Fe(CO)_4$ generation. Detailed studies of linear pentene isomerization and olefin hydrogenation under mild conditions are described herein.

Results and Discussion

(a) Linear Pentene Isomerization. Near-ultraviolet irradiation of $Fe(CO)_5$ in the presence of one of the linear pentenes leads to isomerization to give a common equilibrium mixture of the alkenes irrespective of the starting isomer. Plots of percent conversion against irradiation time are shown in Figure 1, and the equilibria established are given in Table I. The equilibrium value found here for the pentenes is very close to the expected thermodynamic ratio of the alkenes previously measured.[20] Further, we have found that neat solutions of 1-pentene can be equilibrated by initial concentrations of $Fe(CO)_5$ of only 0.011 *M* giving no less than 800 isomerizations per Fe initially present with no obvious loss in activity.

Initial isomerization rates appear to show a short induction period. But it is still appropriate to determine an observed quantum yield for the $Fe(CO)_5$ photoinduced isomerization to determine whether the reaction is catalytic with respect to the number of photons absorbed. We have measured the 366-nm quantum yield for reaction 8 as a function of 1-pentene concentration. Quantum yield values are given in Table II for the portion of the reaction where ex-

$$\text{1-pentene} \xrightarrow[366\ \text{nm}]{Fe(CO)_5} \textit{cis}\text{-2-} + \textit{trans}\text{-2-pentene} \qquad (8)$$

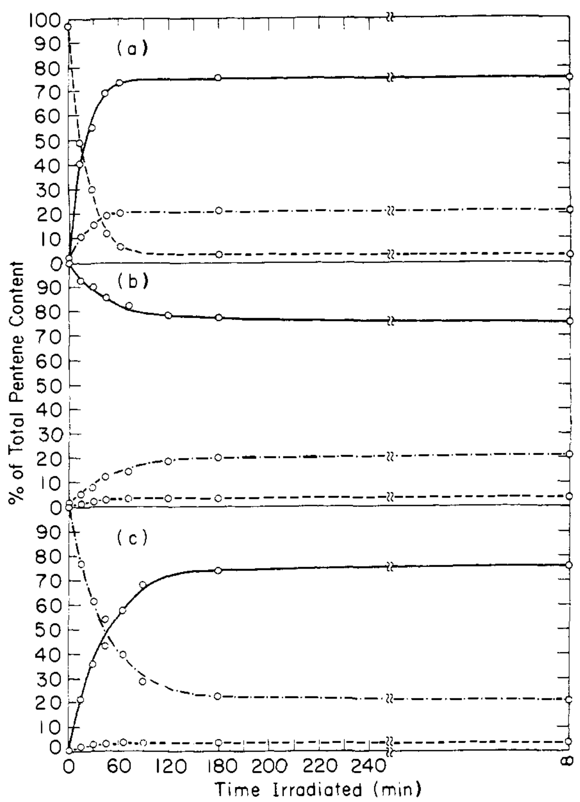


Figure 1. (a) Plot of 1-pentene (- - -) disappearance and *cis*- (— • —•) and *trans*-2-pentene (—) formation; (b) plot of *trans*-2-pentene (—) disappearance and *cis*-2-pentene (— • — •) and 1-pentene (- - -) formation; and (c) plot of *cis*-2-pentene (— • — •) disappearance and *trans*-2-pentene (—) and 1-pentene (- - -) formation as a function of near-ultraviolet irradiation time of 0.1 *M* alkene, 0.011 *M* $Fe(CO)_5$ degassed benzene solutions at 20°C.

Table I. $Fe(CO)_5$ Photocatalyzed Linear Pentene Equilibration[a]

	Equilibrium solution, 20°		
Starting isomer	% 1-pentene	% *cis*-2-pentene	% *trans*-2-pentene
1-Pentene	3.0	21.0	76.0
cis-2-Pentene	3.3	20.7	76.1
trans-2-Pentene	3.3	21.0	75.8

[a] Degassed benzene solution of 0.1 *M* alkene and 0.011 *M* $Fe(CO)_5$ irradiated with near-ultraviolet light.

Table II. Observed Quantum Yields for $Fe(CO)_5$ Photocatalyzed 1-Pentene Isomerization

[1-Pentene], *M*	Φ ± 10%[a]
0.04	1.1
0.1	1.5
0.5	14.5
2.0	67.8
5.0	215
9.14 (neat)	429

[a] Quantum yield for formation at 20° of *cis*- + *trans*-2-pentene using 366-nm light at ~1.4 × 10^{-7} einstein/min in benzene with $Fe(CO)_5$ at 0.011 *M*. The quantum yield reported here is the limiting quantum yield after the induction period (cf. text and Figure 1).

Table III. Attempted $Fe(CO)_5$ Photoassisted Movement away from the Thermodynamic Mixture of Linear Pentenes[a]

Irradiation time, min	% 1-pentene	% *cis*-2-pentene	% *trans*-2-pentene
0	3.31	20.71	75.95
	3.30	20.76	75.92
5	3.18	20.56	76.23
	3.10	20.33	76.46
10	3.18	20.23	76.59
	3.25	20.27	76.47
15	3.33	20.01	76.66

[a] Near-ultraviolet irradiation of degassed benzene solution 0.1 *M* in alkene and 0.011 *M* $Fe(CO)_5$.

tent of conversions appears to be approximately linear with irradiation time. Quantum yields are unquestionably far in excess of unity, particularly at the higher concentrations, suggesting that the role of the light is to generate, at least in part, a species which is a true catalyst. We have attempted to move a prepared mixture of the pentenes away from the thermodynamic ratio to determine whether there is any excited state component to the isomerization at the outset of the reaction. The negative results are summarized in Table III showing that, within experimental error, the prepared thermodynamic mixture is unchanged in the initial stages of the photoreaction. Thus, all data (Tables I-III) are consistent with the notion that the isomerization of the alkenes is actually a thermal process occurring *after* the photogeneration of an isomerization catalyst. Though sustained alkene isomerization subsequent to irradiation is inefficient and somewhat irreproducible, the dark reactivity of the photogenerated catalyst at room temperature is detectable. In a typical experiment (repeated three times), two 3.0-ml samples of 0.011 *M* $Fe(CO)_5$ in neat 1-pentene were irradiated for 30 min at 366 nm (1.3 × 10^{-7} einstein/min). One sample was analyzed immediately subsequent to irradiation and showed 4.0% isomerization, while the other sample was placed in the dark at room temperature and analyzed 18 hr later showing 5.2% isomerization. Two other sets of experiments also show that a catalyst is photogenerated which can, to some extent, sustain isomerization in the dark subsequent to its photogeneration. In the first set of experiments, continuously N_2 purged solutions of $Fe(CO)_5$ and 4.0 *M* cyclohexene were irradiated at −78°C for 15 min. To this solution N_2 purged 1-pentene was added after the irradiation was terminated. The resulting solution was kept at −78°C with an N_2 purge in the dark. Aliquots of the solution were removed and analyzed for the linear pentenes. Typical data are given in Table IV. In a second set of experiments, degassed $Fe(CO)_5$ solutions of pure 1-pentene were immersed in liquid nitrogen and irradiated. The solutions were warmed to room temperature and analyzed for the linear pentenes with the results shown in Table IV. Since diffusion at −196°C is extremely slow (1-pentene is glassy), it is fairly clear that isomerization of the 1-pentene occurs in the warm up of the solution in the dark. Data in Table IV show that several hundred isomerizations can be obtained per Fe initially present by forming the catalytically active species at −196°C by irradiation.

The nature of the catalytically active iron-containing species generated by the light has been probed by several experiments. Since $Fe(CO)_4$ is the primary photoproduct from $Fe(CO)_5$, it is at first a viable candidate for the catalytically active species. Several facts, however, are inconsistent with the conclusion that $Fe(CO)_4$ is the principal alkene isomerization catalyst: (1) we find a short induction period for the alkene isomerization; (2) the rates reported for alkene substitution in $Fe(CO)_4$(alkene) are too slow near room temperature[21] to accommodate the rates of isomerization that we find where the catalyst is generated at low temperatures; (3) there are claims[21c] that complexes such as $Fe(CO)_4$(1-hexene) can be isolated free of either the 2- or 3-hexene complexes; and (4) $Fe(CO)_4L$ complexes in general undergo further photoinduced loss of CO,[10] particularly when L is a good π-acceptor ligand such as an alkene. Despite these facts, though, we find that Fe-

Table IV. Low-Temperature Generation of 1-Pentene Isomerization Catalyst by Irradiation of $Fe(CO)_5$

Expt No.	$Fe(CO)_5$ present, mmol	Irradiation time, min	1-Pentene added, mmol	Reaction time, min	2-Pentene formed, mmol
		(a) Preparation at −78°C[a]			
1	2.5	20	30	5	4.5
				35	7.2
2	0.25	10	30	5	7.7
				35	8.9
		(b) Preparation at −196°C[b]			
3	0.0011	1.0	0.91	10	0.073
4	0.0011	2.0	0.91	11	0.14
5	0.0011	2.0	0.91	22	0.20
6	0.0011	4.0	0.91	12	0.38

[a] A 25-ml solution of $Fe(CO)_5$ and 4.0 *M* cyclohexene in isooctane was irradiated at −78°C using near-ultraviolet light, while the solution was continually purged with N_2. After photolysis, the 1-pentene was added and the mixture allowed to react in the dark at −78°C. Samples for analysis were removed by syringe and allowed to warm to 20° and were analyzed for alkene isomerization as quickly as possible. [b] A neat, degassed 1-pentene solution of 0.011 *M* $Fe(CO)_5$ was irradiated for the indicated time at −196°C in a liquid nitrogen dewar. The irradiation source was the 351, 364 nm emission ($\sim 10^{-6}$ einstein/min) of an argon ion laser.

Table V. Infrared Maxima in CO Stretching Region for Iron Carbonyl Complexes in Isooctane at 298 K

Complex	Bands, cm^{-1} (ϵ, $l.\ mol^{-1}\ cm^{-1}$)
$Fe(CO)_5$	2025 (5470); 2000 (11830)
$Fe(CO)_4(PPh_3)$	2054 (3500); 1977.5 (2310); 1942 (4870)
trans-$Fe(CO)_3(PPh_3)_2$	1892.5 (5140)
$Fe(CO)_4$(ethylene)[a]	2088; 2007; 2013; 1986
$Fe(CO)_4$(1-pentene)[b]	2084; *c*; *c*; 1977.5
$Fe(CO)_4$(*cis*-2-pentene)[b]	2079.5; *c*; *c*; 1972.0
$Fe(CO)_4$(*trans*-2-pentene)[b]	2080.0; *c*; *c*; 1973.0
$Fe(CO)_4$(mixed pentene)[d]	2079.0; *c*; *c*; 1973.5
$Fe(CO)_4$(mixed pentene)[e]	2079.5; 1966 (br); 1973.5

[a] From "Organic Synthesis *via* Metal Carbonyls", Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968, p 111. [b] Initial band positions for the complex formed by short irradiations of $Fe(CO)_5$ (0.001 *M*) and 0.1 *M* pentene in degassed isooctane solution at 298 K. [c] Obscured by $Fe(CO)_5$ absorptions. [d] Initial band positions for mixture of complexes formed in short irradiation of $Fe(CO)_5$ (0.001 *M*) and 3% 1-pentene, 76% *trans*-2-pentene, and 21% *cis*-2-pentene (total pentene is 0.1 *M*) in degassed isooctane solution at 298 K. [e] Infrared band maxima for solution initially 0.0011 *M* $Fe(CO)_5$ and 0.1 *M* 1-pentene in isooctane which was irradiated for 14 hr at 366 nm ($\sim 10^{-7}$ einstein/min) to equilibrate the alkene to: 2.6% 1-pentene; 78.5% *trans*-2-pentene; 18.9% *cis*-2-pentene.

Table VI. Irradiation of $Fe(CO)_5$ in the Presence of PPh_3[a]

	Micromoles of		
Irradiation time, min	$Fe(CO)_5$	$Fe(CO)_4(PPh_3)$	*trans*-$Fe(CO)_3(PPh_3)_2$
0	4.08	0.00	0.00
15	3.70	0.22	0.04
30	3.55	0.37	0.09
45	3.25	0.55	0.17
60	3.16	0.67	0.25
75	2.97	0.78	0.32

[a] Initially 0.01 *M* PPh_3, 0.0011 *M* $Fe(CO)_5$ in degassed isooctane solution. Irradiation is at 366 nm in a merry-go-round at 10^{-7} einstein/min. Micromoles of $Fe(CO)_5$, $Fe(CO)_4(PPh_3)$, and *trans*-$Fe(CO)_3(PPh_3)_2$ were measured by ir (cf. Table V).

$(CO)_4$(pentene) is the only infrared detectable product even when the starting pure 1-pentene has been essentially equilibrated to the thermodynamic ratio of linear pentenes irradiating at 20°C and for a hermetically sealed sample. Table V shows the infrared spectral band maxima in the CO stretching region for $Fe(CO)_5$ and a number of derivatives. Irradiation of $Fe(CO)_5$ in the presence of the thermodynamic mixture of the linear pentenes yields the same band maxima initially as found after prolonged irradiation of $Fe(CO)_5$ in the presence of initially pure 1-pentene. Importantly, analysis of the pentenes after the prolonged irradiation showed them to be equilibrated, and the total amount of $Fe(CO)_4$(alkene) was equal to the amount of $Fe(CO)_5$ originally present. Phenomenologically, then, $Fe(CO)_4$(alkene) is the catalyst, but the facts above point to some other species as that actually responsible for the isomerization.

We find that short irradiation of $Fe(CO)_5$ in the presence of one of the pentene isomers yields CO stretching bands which are different for each of the three isomers. Moreover, short irradiation of $Fe(CO)_5$ in a 1:1:1 mole ratio of the three linear pentenes yields a spectrum which is clearly a composite of a mixture of $Fe(CO)_4$(1-pentene), $Fe(CO)_4$(*cis*-2-pentene), and $Fe(CO)_4$(*trans*-2-pentene). The latter result proves that the alkene substitution rate in $Fe(CO)_4$(pentene) is fairly slow. This conclusion is certain since one would expect the $Fe(CO)_4$(1-pentene) to be substantially more stable, and, hence, would ultimately be the dominant $Fe(CO)_4$(alkene) species present if alkene exchange were rapid. The fact that each pentene isomer yields a spectroscopically different $Fe(CO)_4$(alkene) proves beyond reasonable doubt that interaction with $Fe(CO)_4$ alone does not extensively isomerize the pentene. We have found, however, that pure, isolated samples of a particular isomer of $Fe(CO)_4$(pentene) are difficult to obtain. Repeated attempts to prepare $Fe(CO)_4$(1-pentene) by reacting 1-pentene at 25°C with $Fe_2(CO)_9$ invariably resulted in extensive alkene isomerization. Thermal reaction of 1-pentene and $Fe_2(CO)_9$ may also occur via the coordinatively unsaturated $Fe(CO)_4$ intermediate since ultimately $Fe(CO)_4$(alkene) is obtained. Reaction of $Fe(CO)_4$(propene) in neat 1-pentene at 25°C also yields slow 1-pentene isomerization and the generation of $Fe(CO)_4$(pentene). The half-time of the exchange reaction is greater than 4 hr, but the isomerization observed shows again that the $Fe(CO)_4$ can phenomenologically serve as the catalyst.

In one sense, the infrared spectral studies of the initial $Fe(CO)_4$(alkene) photoproducts differ from the initial product studies for irradiation of $Fe(CO)_5$ in the presence of PPh_3. Table VI shows that both $Fe(CO)_4(PPh_3)$ and *trans*-$Fe(CO)_3(PPh_3)_2$ are *primary* photoproducts. For the alkene case, we found infrared evidence for only $Fe(CO)_4$(alkene). From the low intensity irradiation results in Table VI, and from a flash photolysis ($\leq 10^{-5}$ sec 500-J flash) of a mixture of $Fe(CO)_5$ and PPh_3, we find a ratio of $Fe(CO)_4(PPh_3)$:*trans*-$Fe(CO)_3(PPh_3)_2$ of about 3:1. The formation of a disubstituted primary photoproduct is unusual but is consistent with the recent thermal subtitution studies of $Fe(CO)_4L$ complexes where $Fe(CO)_3L'_2$ complexes were observed[21] as primary thermal products. In part, the lack of observable $Fe(CO)_3(alkene)_2$ products is likely due to the expected facility of reaction 9. No simple

$$Fe(CO)_3(alkene)_2 \xrightarrow{CO} Fe(CO)_4alkene + alkene \qquad (9)$$

alkene complexes of the stoichiometry $Fe(CO)_3(alkene)_2$ have been reported, but $Fe(CO)_3(methylacrylate)_2$ has been isolated at low temperatures and decomposes above −5°C[22] presumably initiated by dissociative loss of an olefin.

We propose that the presence of a very substitutionally labile $Fe(CO)_3(alkene)_2$ complex is actually the species re-

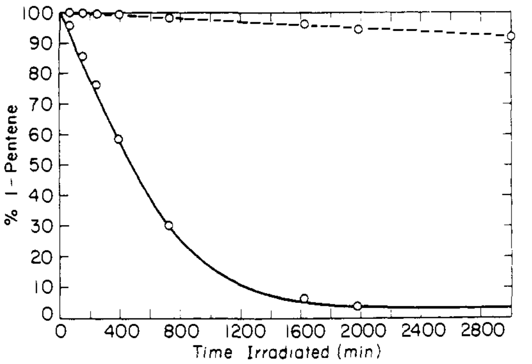
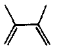
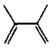
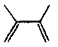
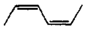
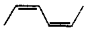
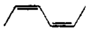


Figure 2. Plot of 1.0 *M* 1-pentene disappearance (—) and disappearance of 1.0 *M* 1-pentene in the presence of 1.0 *M* 2,3-dimethyl-1,3-butadiene (- - -) by irradiation of $Fe(CO)_5$ (0.001 *M*) in each case resulting in 2-pentene formation. In the absence of the diene, the initial ratio of *trans*- to *cis*-2-pentene is 3.7 while, in the presence of the diene, this ratio is 2.1.

Table VII. Quenching of $Fe(CO)_5$ Photocatalyzed Linear Pentene Isomerization by 1,3-Dienes[a]

[1-Pentene], *M*	Quencher (*M*)	Irradiation time, min	% conversion to 2-pentene
1.0	None	120	10.2
1.0	 (0.01)	120	6.0
1.0	 (0.1)	120	1.1
1.0	 (1.0)	120	0.2_3
1.0	 (0.01)	120	8.9
1.0	 (0.1)	120	6.2
1.0	 (1.0)	120	1.8

[a] All samples were irradiated in parallel in a 366-nm merry-go-round (~10^{-7} einstein/min) at 20°C. The 3.0-ml degassed ampules contained 0.011 *M* $Fe(CO)_5$ in benzene.

Scheme I

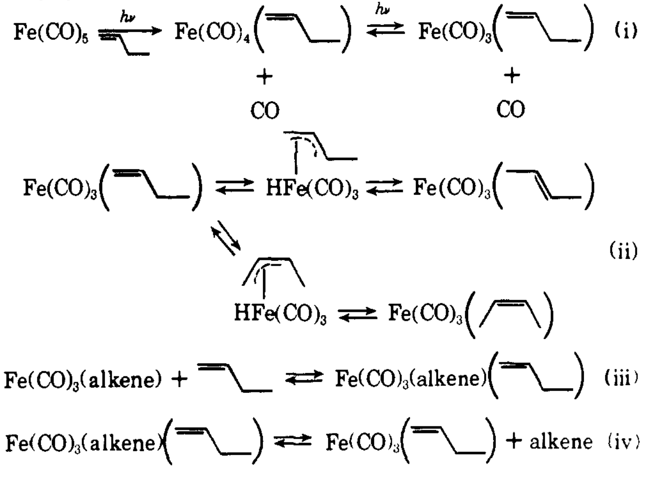


Table VIII. $Fe(CO)_5$ Photoassisted Hydrogenation of Olefins[a]

Starting olefin	Irradiation time, min	Product (% conversion)
Ethylene[b]	60	Ethane (16.7)
Propylene[c]	60	Propane (46.7)
cis-3-Hexene	60	*n*-Hexane (30.8)
2-Methyl-2-butene	60	2-Methylbutane (26.9)
cis-3-Methyl-2-pentene	110	3-Methylpentane (32.0)
2,3-Dimethyl-2-butene	60	2,3-Dimethylbutane (13.6)
Cyclopentene	60	Cyclopentane (47.0)
Cyclohexene	60	Cyclohexane (33.1)
Cycloheptene[d]	60	Cycloheptane (53.2)
cis-Cyclooctene[d]	60	Cyclooctane (53.5)
1-Methylcyclopentene	60	Methylcyclopentane (26.3)
Methylenecyclopentane	70	Methylcyclopentane (40.0)
1,2-Dimethylcyclopentene	60	No reaction
1,2-Dimethylcyclohexene	60	No reaction
α-Methylstyrene	60	No reaction
2,3-Pentadiene	60	No reaction
2-Cyclohexen-1-one	180	Cyclohexanone (4.1)
cis-1,3-Pentadiene	300	Pentenes (4)
trans-1,3-Pentadiene	400	Pentenes (8.5)
cis,cis-2,4-Hexadiene	315	Linear hexenes (30.0) *n*-Hexane (4.7)
trans,trans-2,4-Hexadiene	305	Linear hexenes (35.0) *n*-Hexane (4.7)
Acetylene[e]	35	Ethylene (0.4)
Diethylacetylene	60	Linear hexenes (~6.0)
Diphenylacetylene[f]	160	*cis*-Stilbene (5.0) *trans*-Stilbene (3.5)
Acetaldehyde	60	No reaction
Acetonitrile	60	No reaction

[a] Irradiation with near-uv (300–380 nm) light ~10^{-5}–10^{-6} einstein/min; $Fe(CO)_5$ is initially 0.011 *M*; temperature is 25°C; solvent is benzene; olefin is 0.1 *M*, and H_2 is at 10 psi, unless noted otherwise. [b] Olefin concentration is 0.04 *M*. [c] Olefin concentration is 0.06 *M*. [d] Solvent is 2-methylbutane. [e] Olefin concentration is 0.025 *M*. [f] Solvent is 2,2,4-trimethylpentane.

sponsible for alkene isomerization. A reasonable mechanism is shown in Scheme I. Scheme I and reaction 9 are consistent with all of the known facts. And finally, in support of Scheme I, we have carried out experiments using 1,3-dienes as potential traps of the catalytically active $Fe(CO)_3$ unit. The results are shown in Table VII and Figure 2 and reveal that the photocatalyzed isomerization is very effectively quenched by 1,3-dienes. The 2,3-dimethyl-1,3-butadiene is particularly effective compared with *cis,cis*-2,4-hexadiene perhaps because the former can easily achieve the s-cis conformation, while this conformation is sterically crowded for *cis,cis*-2,4-hexadiene. Quenching of alkene isomerization by the 1,3-diene is accompanied by the formation of $Fe(CO)_3$(1,3-diene), which, apparently, is not an effective photocatalyst for alkene isomerization. The formation of the $Fe(CO)_3$(1,3-diene) complex was monitored by ir spectral measurements in the CO stretching region.

The mechanism in Scheme I is very analogous to that proposed for photocatalyzed pentene isomerization by $M(CO)_6$ (M = Mo, W).[1c] Key to the mechanism is the generation of a coordinatively unsaturated metal carbonyl-alkene complex, resulting in oxidative addition reaction to form a π-allylhydride intermediate. In the Fe carbonyl system, the formation of the $Fe(CO)_3$(alkene) could occur, at least in part, by the absorption of one quantum according to reaction 10.[23] Reaction of $Fe(CO)_4$ with a nucleophile as

$$\begin{array}{ccccc} \mathrm{Fe(CO)_5} & \xrightleftharpoons{h\nu} & \mathrm{Fe(CO)_4} & \xrightarrow[\Delta]{\text{alkene}} & \mathrm{Fe(CO)_3(alkene)} \\ & & + & & + \\ & & \mathrm{CO} & & \mathrm{CO} \end{array} \tag{10}$$

shown in (10) accommodates the primary formation of the coordinatively stable *trans*-$Fe(CO)_3(PPh_3)_2$ as well as the observation that induction periods for isomerization are short. However, the $Fe(CO)_4$ is obviously fairly effectively scavenged without further loss of CO since the infrared results show efficient formation of $Fe(CO)_4$(alkene) with stereochemical integrity of the alkene retained.

(b) Irradiation of $Fe(CO)_5$ Mixtures in the Presence of Hydrogen. Near-ultraviolet irradiation of $Fe(CO)_5$ in the presence of an olefin and H_2 (~1 atm) leads to olefin hydrogenation at room temperature or below. Substrates which were tested are given in Table VIII, and it is appar-

Table IX. Competitive $Fe(CO)_5$ Photoassisted Alkene Hydrogenation[a]

[Propylene], M	Alkene (M)	Propane, %	Alkane, %
0.087	Cyclopentene (0.1)	14.3	6.5
0.084	1-Pentene (0.1)	10.0	2.6
0.082	2,3-Dimethyl-2-butene (0.1)	11.0	0.3_8
0.089	2-Methyl-2-butene (0.1)	24.6	0.2_0
0.079	Cyclohexene (0.1)	20.4	<0.07
0.076	Cycloheptene (0.1)	9.8	~0

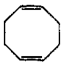
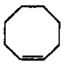
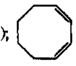
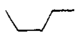
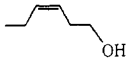
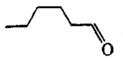
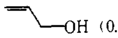
[a] Each solution contains propylene and an alkene in a degassed benzene solution of 0.011 M $Fe(CO)_5$; the H_2 pressure is 10 psi. Irradiations were carried out at 20°C with near-ultraviolet light.

Table X. H_2 Pressure Dependence of $Fe(CO)_5$ Photoassisted Hydrogenation[a]

H_2 pressure, atm	% cyclohexene → cyclohexane
1.0	6.5
1.5	10.0
2.0	10.8
2.5	14.4
3.0	16.6
3.5	17.2

[a] All samples irradiated for 60 min at 20°C with near-ultraviolet light; solvent is benzene and cyclohexene concentration is 0.1 M and $Fe(CO)_5$ is 0.011 M.

Table XI. $Fe(CO)_5$ Photoassisted Hydrogenation vs. Isomerization[a]

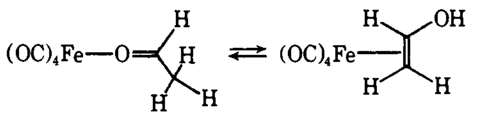
Olefin (M)	Irradiation time, min	Product(s) (% conversion)
 (0.1)	60	 (8.9);  (7.3)
 (0.1)	60	 (30.8); linear hexenes (5.2)
 (0.183)[b]	15	 (5.6);  (17.8);  (71.0)
 (0.1)	60	 (~100)
 (0.1)	60	 (~100)

[a] 25°C, 0.011 M $Fe(CO)_5$ in benzene or toluene, 10–14 psi H_2, near-uv irradiation. [b] D_2 used; data from first entry in Table X.

ent that simple alkenes are most effectively hydrogenated. Quite a range of olefins, however, can be hydrogenated. Table IX shows that, when two alkenes are present in solution, there is a great deal of steric selectivity in that propylene is selectively hydrogenated in every case. The specificity for sterically unhindered alkenes is reminiscent of the behavior of other d^8 catalysts such as $HRh(CO)(PPh_3)_3$[24] and $HRuCl(PPh_3)_3$.[25]

Reasonably, we find that increasing the H_2 pressure increases the initial rate of alkene hydrogenation (Table X). Though the observed quantum efficiency of the hydrogenation reaction has an ill-defined meaning, we have determined that the $Fe(CO)_5$ photocatalyzed hydrogenation can occur with a quantum efficiency which exceeds 1.0. Near-uv irradiation of 0.01 M $Fe(CO)_5$ in neat cyclopentene with 20 psi H_2 at 25°C yields cyclopentane with an observed quantum efficiency of 1.5. Hydrogenation thus proceeds catalytically with respect to the number of photons incident and, moreover, substantial fractions (>20%) of neat alkene can be hydrogenated using 0.001 M $Fe(CO)_5$, showing that the turnover number with respect to Fe exceeds 10^3.

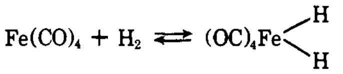
To complete some qualitative aspects of the photocatalytic activity of the $Fe(CO)_5 + H_2$, we investigated the relative importance of hydrogenation and isomerization (Table XI). The H_2 is not *required* for isomerization, nor do we find the isomerization of 1-pentene to be accelerated significantly by irradiation of $Fe(CO)_5$ in the presence of H_2. For the simple alkenes, hydrogenation and isomerization are somewhat comparable in rate, but, for the alkenols, formation of the aldehydes was quantitative by irradiation with or without H_2. The aldehydes are not hydrogenated, and this result may suggest that the equilibrium indicated in reaction 11 is a relatively unimportant consideration.[26]


(11)

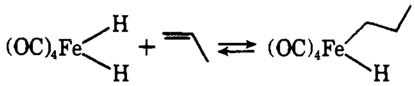
Experiments carried out with D_2 rather than H_2 reveal that reaction 12 obtains, especially at lower temperatures

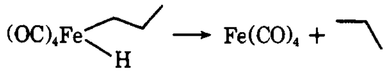
$$\text{1-pentene} \xrightarrow[\substack{Fe(CO)_5 \\ D_2}]{h\nu} \begin{array}{c} \text{linear pentenes-}d_0\text{, -}d_1\text{, -}d_2 \\ + \\ n\text{-pentane-}d_2\text{, -}d_1\text{, -}d_0 \end{array} \qquad (12)$$

(Table XII). Particularly, at the lowest temperature, the amount of deuterium incorporation in the alkene can be greater than the amount of hydrogen incorporation to yield non- or partially deuterated alkane. Appearance of deuterium in the alkenes demands a mechanism featuring a reversible hydrogen transfer. A possible catalytically active species is again $Fe(CO)_4$ as in reactions 13–15. The revers-


(13)

$$Fe(CO)_4 + H_2 \rightleftarrows (OC)_4Fe\begin{smallmatrix} H \\ H \end{smallmatrix} \qquad (13)$$


(14)


(15)

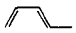
ibility of reaction 14 would allow for deuterium incorporation into the alkene. A direct test of the mechanism has been carried out by examining the reactivity of $Fe(CO)_4H_2$ with neat 1-pentene. Condensation of the 1-pentene (previously degassed) onto $Fe(CO)_4H_2$ at −196°C is followed by warm-up to a desired reaction temperature, say −20°C. The mixture was allowed to stand at the reaction tempera-

Table XII. Temperature Dependence of $Fe(CO)_5$ Photoassisted Reaction of 1-Pentene Exposed to 16 psi of D_2[a]

T, °C	Irradiation time, min	% pentane	Pentane d_2	Pentane d_1	Pentane d_0	% 1-pentene	% *cis*-2-pentene	% *trans*-2-pentene	Pentene d_0	Pentene d_1	Pentene d_2
25	15	5.6	94.8	5.2	0	5.6	17.8	71.0	100	0	~0
16	15	6.8	83.4	12.9	3.6	9.3	19.6	64.3	99.4	0.6	~0
6	15	3.4	62.8	27.7	9.6	4.6	18.6	73.4	98.7	1.3	~0
−5	20	2.3	41.5	41.9	16.6	5.4	20.7	71.6	97.6	2.4	~0
−18	25	1.2	17.2	73.0	9.7	19.8	17.1	61.8	96.8	3.2	~0

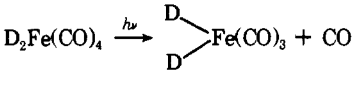
[a] Toluene solutions of 1-pentene at 0.183 M and $Fe(CO)_5$ 0.011 M exposed to 16 psi D_2 after deoxygenation by freeze–pump–thaw degassing. The desired temperature is achieved by placing the sample in a thermostated aluminum block with a window for near-uv irradiation.

Table XIII. Quenching of $Fe(CO)_5$ Photoassisted Hydrogenation of Alkenes by Added 1,3-Dienes[a]

Alkene (*M*)	Quencher (*M*)	% conversion to alkane	% hydrogenation of quencher
Cyclopentene (0.1)	None	47.0	
	 (0.1)	1.1	3.1
	 (0.1)	11.0	1.2
cis-Cyclooctene (0.1)	None	53.5	
	 (0.1)	2.7	3.0
	 (0.1)	12.6	2.3
	 (0.1)	0	0
	 (0.1)	0	0

[a] Each degassed benzene solution was 0.011 *M* $Fe(CO)_5$, was exposed to 10 psi H_2, and was irradiated with near-ultraviolet light at 20°C.

ture for 20 min, and the organic material was distilled away from the iron-containing compounds and analyzed for alkene isomerization and hydrogenated products. Surprisingly,[27] the $Fe(CO)_4H_2$ was found to be virtually unreactive if not allowed to warm significantly above −10°C. Neither hydrogenation nor isomerization at −20°C was effective; 2 *M* $Fe(CO)_4D_2$ in neat 1-pentene at −20°C yielded ~1% isomerization and ≤0.1% pentane. The reaction with $Fe(CO)_4D_2$ did not yield substantial amounts of deuterated pentene. The amount of hydrogenation never exceeded ~1% in any case (up to ~10°C) but, as the temperature is increased more extensive (nearly complete equilibration), 1-pentene to 2-pentene conversion obtains. We attribute this isomerization to thermal decomposition products of $Fe(CO)_4H_2$ which may, or may not, have properties in common with the photogenerated isomerization catalyst.[27] It is fairly clear though, that, if carefully handled below its decomposition temperature, $Fe(CO)_4H_2$ is neither an effective isomerization catalyst nor an efficient stoichiometric hydrogenation agent. It is very clear from Table XII that photoinduced hydrogenation and isomerization do occur rather effectively at temperatures as low as −18°C. Interestingly, near-ultraviolet irradiation of 2 *M* $Fe(CO)_4D_2$ in neat 1-pentene at −20°C does yield substantially more hydrogenation, isomerization, and deuterium–hydrogen exchange than the same system thermally. These photoeffects are consistent with the occurrence of reactions 16 and/or 17. Photodissociation of coordinated CO certainly has precedence and the photoinduced reductive elimination of D_2 has precedence in that a series of Ir(III) dihydrides have recently been shown[28] to undergo chemically efficient photoinduced reductive elimination of H_2.

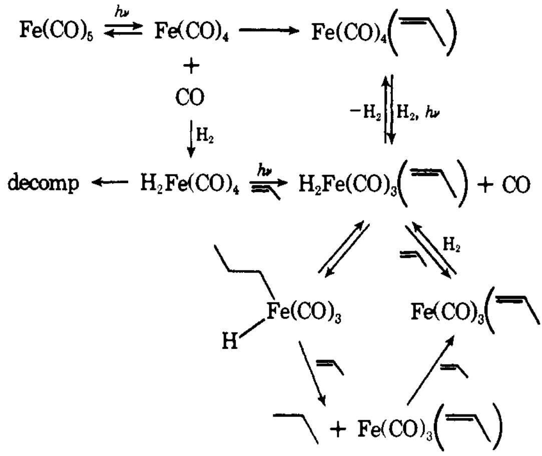
 (16)

$$D_2Fe(CO)_4 \xrightarrow{h\nu} D_2Fe(CO)_3 + CO \quad (16)$$

$$D_2Fe(CO)_4 \xrightarrow{h\nu} Fe(CO)_4 + D_2 \quad (17)$$

All results are consistent with the mechanism given in Scheme II.[29] The key repeating Fe unit is again $Fe(CO)_3$ as we proposed for the photocatalyzed isomerization (Scheme I). And as with the isomerization, we find that 1,3-dienes are good quenchers of the $Fe(CO)_5$ photoinduced hydrogenation (Table XIII). Dienes capable of achieving the s-cis conformation are very effective quenchers consistent with scavenging of "$Fe(CO)_3$" units to form stable (1,3-diene)$Fe(CO)_3$ molecules which are, apparently, not particularly effective photoassistance agents. It is unlikely that "$Fe(CO)_3$" per se exists in solutions of alkene, but the substitution lability of complexes such as $Fe(CO)_3(alkene)_2$ provides a pathway for hydrogenation quantum yields which exceed unity.

Scheme II



Summary

$Fe(CO)_5$ photocatalyzed alkene isomerization is very efficient with respect to quantum yield and turnover number for Fe. The key isomerization intermediate implicated is $HFe(CO)_3(\pi\text{-allyl})$ which can be formed by irradiation of $Fe(CO)_4(alkene)$ or by thermal dissociation of an alkene from $Fe(CO)_3(alkene)_2$. Hydrogenation of alkenes can also be photocatalyzed under mild conditions where the important steps are $H_2Fe(CO)_3(alkene) \rightleftarrows HFe(CO)_3(alkyl) \rightarrow Fe(CO)_3 + alkane$. Considerable selectivity for hydrogenation of the least sterically hindered alkenes obtains.

Experimental Section

Materials. Alkenes were obtained from Chemical Samples Co., Matheson Gas Co., and Aldrich Chemical Co. and were used as received unless contaminated with peroxides. Peroxides were removed by distillation from Na/K alloy or by passage through grade I Woelm alumina. Benzene, isooctane, and pentane were of spectroscopic grade; 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. Triphenylphosphine was sublimed prior to use. Hydrogen (Airco) and deuterium (Matheson Gas Co,) were used without further treatment. $Fe(CO)_5$ was obtained from Pressure Chemical Co. and used without further treatment. $Fe_2(CO)_9$,[11] $Fe_3(CO)_{12}$,[30] $Ph_3PFe(CO)_4$,[31] and $(Ph_3P)_2Fe(CO)_3$[31] were prepared and purified by literature methods. D_2O (Stohler Isotope Chemicals) and P_2O_5 were used as received.

Instrumental. All vapor phase chromatography (VPC) was done with Varian Series 1400 or 2400 gas chromatographs equipped with flame ionization detectors. Separation of components of alkene reaction mixtures was accomplished on a 25 ft × ⅛ in. column of 20% propylene carbonate on Chromosorb P, a 25 ft × ⅛ in. column of 25% β,β'-oxydipropionitrile on Gaschrome Q, or a 10 ft × ⅛ in. column of 5% Carbowax 20M on Chromosorb G, with preparative analyses on a 25 ft × 0.25 in. column of 20% propylene carbonate on Chromosorb P.

All quantitative ir spectra were obtained using a Perkin-Elmer 521 grating infrared spectometer with matched 0.1-mm or 1.0-mm pathlength NaCl cells obtained from Perkin-Elmer Corp. Qualitative ir spectra were obtained on a Perkin-Elmer 337 grating infrared spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

A Forma-Temp, Jr Bath and circulator was used for thermostated experiments unless otherwise inidcated.

Irradiation Procedure in the Absence of H_2. Three-milliter aliquots of the $Fe(CO)_5$ and substrate solution in Pyrex test tubes (13

× 100 mm) with constrictions were degassed by four freeze–pump–thaw cycles and were then hermetically sealed. Continuous photolysis experiments were carried out using 450- or 550-W medium-pressure Hanovia Hg lamps filtered with the appropriate Corning glass filters to isolate the 366- and 550-nm Hg lines and the 300–380 nm region. Ampules to be irradiated were placed in a merry-go-round apparatus.[32] Light intensities were determined by ferrioxalate actinometry[33] and were found to be of the order of 10^{-7} einstein/min for the 366-nm line and 10^{-5} einstein/min for the 300–380 nm region. Analysis was performed by gas chromatography for the olefin substrates or by ir spectral analysis for the iron carbonyl species.

Flash photolysis was carried out on degassed ampules of $Fe(CO)_5$ and substrate using a Xenon Corp. Model F-710 flash photolysis apparatus as the light source, with subsequent analysis by ir spectroscopy.

Irradiation Procedures in the Presence of H_2. A 7-ml aliquot of the $Fe(CO)_5$ and substrate solution and a 3 × 10 mm Teflon coated magnetic stirbar were placed in a 15-mm demountable reaction tube equipped with a high vacuum valve and degassed by three freeze–pump–thaw cycles. The reaction tube was then transferred to a photohydrogenation apparatus consisting of a gas manifold, an insulated thermostated aluminum block with a 40 × 9 mm port to admit light from a 550-W filtered Hanovia Hg source. The aluminum block rested on a magnetic stirrer. The manifold was then evacuated and flushed with H_2 or D_2 three times, and then H_2 or D_2 was admitted to the reaction tube at the desired pressure and allowed to saturate the solution before a shutter was removed to begin the irradiation. The solution was analyzed by VPC after the reaction tube was disconnected.

$H_2Fe(CO)_4$ and $D_2Fe(CO)_4$ Experiments. Sodium tetracarbonyl ferrate was synthesized by reduction of $Fe_3(CO)_{12}$ in THF by sodium, followed by removal of the solvent under reduced pressure.[30] The 95% D_3PO_4 (99% + D) or 95% H_3PO_4 was obtained by addition of a known amount of D_2O or H_2O, respectively, to a known amount of P_2O_5 in a flask under nitrogen. The volatile $Fe(CO)_4H_2$ or $Fe(CO)_4D_2$ was synthesized and manipulated on a high vacuum line. A 250-ml three-necked flask containing a Teflon coated magnetic stirbar was fitted with an airless filter frit, a stopper, and a straight drying tube filled with a mixture of $CaCl_2$ and P_2O_5 between two glass wool plugs. The latter was connected to the vacuum line, and the entire appartus was evacuated to 10^{-5} Torr. Nitrogen was then admitted to the flask, and 30 ml of the 95% H_3PO_4 or D_3PO_4 was added to the filter frit. Degassing was accomplished by reverse passage of nitrogen through the acid in the filter frit for 20 min, and then stopcocks at the top and bottom of the frit were closed. The stopper was replaced with a solid addition tube containing 1 g of $Na_2Fe(CO)_4$. The apparatus was then evacuated, and the bottom stopcock on the frit was opened to admit the acid to the flask. The acid was stirred under a vacuum for 5 min to release dissolved nitrogen. The $Na_2Fe(CO)_4$ was then slowly tapped into the acid and the $H_2Fe(CO)_4$ or $D_2Fe(CO)_4$ gas passed through the drying column to a trap maintained at −196°C, yielding $\sim 1.7 \times 10^{-3}$ mol of a yellow solid, which melts above −78°C. After the $H_2Fe(CO)_4$ or $D_2Fe(CO)_4$ had been transferred from the reaction flask, 1.0 ml of previously degassed 1-pentene was distilled into the −196°C trap. The trap was then isolated from the vacuum line and warmed to the desired temperature, which was maintained by the appropriate slush bath or thermostated isopropyl alcohol. After a set period of time, the reaction mixture in the trap was distilled through a −78°C trap (for fractional condensation of iron compounds from alkenes) to a −196°C trap. Portions of the reaction mixture left in the reaction trap and the −78°C trap were discarded, and the residue in the −196°C trap was transferred to previously degassed 2,3-dimethyl-1,3-butadiene to scavenge any remaining iron compounds. This solution was then analyzed by VPC.

$Fe_2(CO)_9$ Experiments. All attempted thermal $Fe(CO)_4$(1-pentene) synthesis was done on a vacuum line. The 1-pentene, 40 ml (~0.4 mol), was dried over P_2O_5 and freeze–pump–thaw degassed, followed by bulb-to-bulb distillation onto 7.3 g (~0.2 mol) of $Fe_2(CO)_9$.[34] This mixture was stirred for 20 hr in subdued room light and then slowly distilled and fractionally condensed through a −20°C trap to a −196°C trap. A yellow liquid condensed into the −20°C trap which slowly decomposed to a green solution at room temperature. The materials in the −20 and −196°C traps were analyzed by VPC, and the material in the −20°C trap was analyzed by ir spectroscopy. The latter showed a spectrum typical of $Fe(CO)_4$(alkene) complexes and free of $Fe(CO)_5$.

The $Fe(CO)_4$(propylene) was obtained by freeze–pump–thaw, degassing 50 ml of isopentane followed by bulb-to-bulb-distillation onto 3.7 g (~0.01 mol) of $Fe_2(CO)_9$ in a 250-ml flask. This mixture was then placed under 18 psig of propylene and stirred in subdued room light for 12 hr. At the end of this time, the solution was green with little or no solid material left in the flask. The solution was then slowly distilled and fractionally condensed through a −40°C trap to a −196°C trap. Material in the −196°C trap was then discarded. Contamination by $Fe(CO)_5$ was considered unimportant for the purposes of the following exchange reaction, and the $Fe(CO)_4$(propylene) was therefore used without further purification.

Degassed 1-pentene, 15 ml (0.15 mol), was transferred to the $Fe(CO)_4$(propylene), and the trap was isolated from the vacuum line and allowed to stand in subdued room light at room temperature for 4 hr. At the end of this time, the solution was still golden yellow containing a small amount of uncharacterized, white flocculent material. This solution was then slowly distilled and fractionally condensed by passage through a −40°C trap to a −196°C trap. The contents of both of these traps were then analyzed by VPC.

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Alkylation of Tetracyanoethylene. Reaction with Grignard Reagents

Hugh C. Gardner and Jay K. Kochi*

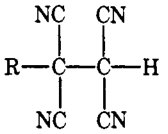
Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received June 10, 1975*

Abstract: The alkylation of tetracyanoethylene has been achieved by the slow addition of 1 equiv of Grignard reagent at low temperatures to produce a series of 1:1 adducts, which on neutralization with trifluoroacetic acid afford a variety of alkyltetracyanoethanes in excellent yields. The reaction of primary alkyl Grignard reagents with 2 equiv of TCNE produces the 1:2 adducts, 3-alkylhexacyanopentadienide salts, with the loss of 2 equiv of HCN. An x-ray crystal structure of the 3-isopropyl analog shows it to be in a twisted **U** conformation in contrast to a planar **W** form previously established for the parent 1,1,2,4,5,5-hexacyanopentadienide ion. A mechanistic scheme is presented for the addition of Grignard reagent to TCNE via nucleophilic and electron transfer routes. The metastability of the initial 1:1 adducts due to loss of HCN leads to tricyanoallyl carbanions, which can be exploited in the preparation of a variety of 3-alkyl-1,1,2,4,5,5-hexacyanopentadienide ions in high yields. The latter are electrochemically readily reduced to poly anions, and they undergo an irreversible rearrangement to a new series of 4-alkyl-2,3,5,6-tetracyanoanilines.

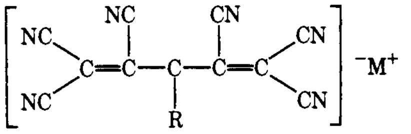
Polycyanoolefins such as tetracyanoethylene (TCNE) are highly electrophilic due to the delocalization of the π-electron density into the cyano substituents. Alkylation reactions of TCNE represent a limiting case of the attack of a nucleophile on such an activated olefin.[1]

The chemistry of polycyanocarbons has been actively investigated for the past 15 years,[2,3] and research has recently gained added impetus from their use in organic metals.[4] The unusual reactivity of TCNE is shown by its high reactivity toward many nucleophiles and rapid formation of cycloadducts with various alkenes.[5-8] TCNE also readily inserts into carbon-hydrogen bonds in ketones and arenes, as well as transition metal-carbon bonds.[7,9-11] These systems all involve nucleophiles less powerful than the substitution-labile organometals such as alkyllithium and magnesium reagents. However, in spite of the extensive and varied studies carried out on TCNE, the reaction with Grignard reagents has not been reported. Indeed, the poor yields and incomplete stoichiometry obtained with organometals in a few cited cases have been attributed to the high reactivity of TCNE and its primary products.[10] The participation of multiple reaction paths and the well-known tendency of cyanoolefins to form tarry materials have also discouraged study heretofore.

The diversity of reactions shown by TCNE suggests that it may react by a variety of mechanisms. Thus, the facile formation of the anion radical [$TCNE\cdot^-$] and the ubiquitous charge-transfer complexes[12] lend support to one-electron processes as alternatives to the more common two-electron or nucleophilic routes. These complications are compounded during the exposure of TCNE to potent nucleophiles such as Grignard reagents which are also electron donors. We report, however, that under proper experimental conditions the direct alkylation of TCNE with Grignard reagents can be carried out in high yields for the convenient synthesis of two interesting classes of polycyanocarbons: 1,1,2,2-tetracyanoalkanes and 1,1,2,4,5,5-hexacyanopentadienide salts.



$R{-}C(CN)_2{-}C(CN)_2{-}H$



Mechanistic routes for the formation of these new series of cyanocarbons will also be described, together with the formation of a novel class of polycyano aromatic compounds, 4-alkyl-2,3,5,6-tetracyanoanilines, by the spontaneous rearrangement of the hexacyanopentadienide ions.

Results

1,1,2,2-Tetracyanoalkanes from 1:1 Adducts. The slow addition of 1 equiv of phenylmagnesium bromide to a sus-