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Prototropic Rearrangements of Unsaturated Hydrocarbons Promoted by Iron Carbonyls

Dorothy H. Gibson, Tek-Sing Ong and F. G. Khoury
Department of Chemistry, University of Louisville
Louisville, Kentucky 40208 (U.S.A.)

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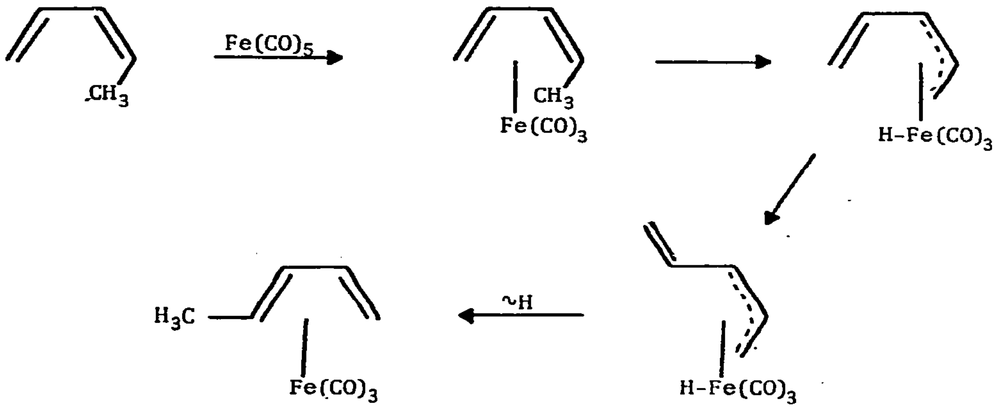
Summary

Results from the thermal and photochemical reactions of cis-1,3-pentadiene and 4-methyl-1,3-pentadiene with iron pentacarbonyl are described together with those obtained from the thermolysis and photolysis of their η^2-iron tetracarbonyl and η^4-iron tricarbonyl complexes. Consideration of these results, and some recent related work of others, allows a new reaction path to be formulated for alkene and diene isomerizations promoted by iron carbonyls.

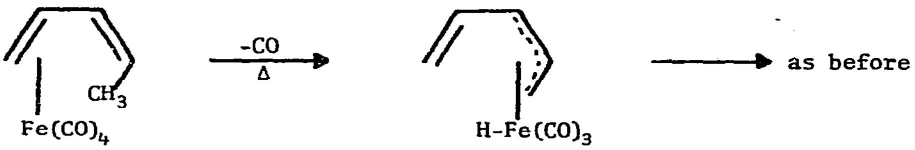
Introduction

Many of the early preparations of dieneiron tricarbonyl complexes were accomplished at high temperatures using iron pentacarbonyl; in some such reactions rearrangement of the diene was found to be extensive.[1] The mechanism first proposed[2] for the rearrangements was a modification of one which had been suggested[3] for alkene isomerizations promoted by $Fe(CO)_5$ and is illustrated for cis-1,3-pentadiene below:

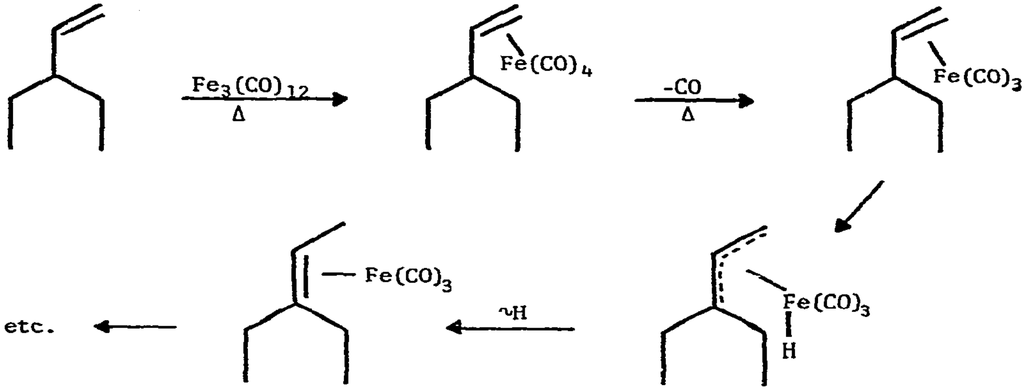
Scheme 1



Much more recently Nelson and Sloan[4] have suggested that the course of the thermal reactions is governed by kinetic factors rather than thermodynamic factors (the kinetic factors being determinative at the time of coordination of an iron tetracarbonyl group to the diene). They suggested that the π-allyl metal hydride was formed in a synchronous manner:



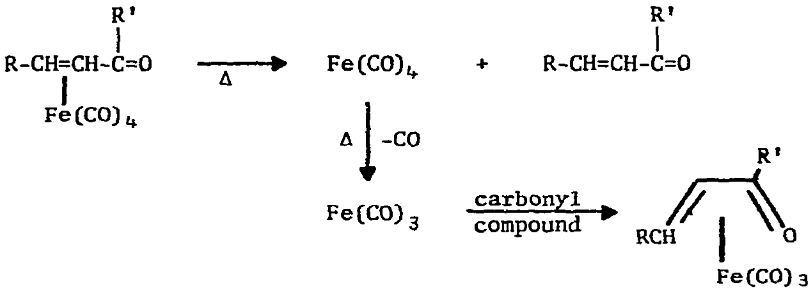
Related to these reactions are the alkene isomerizations promoted by iron carbonyls, the best studied example of which is the work on 3-ethyl-1-pentene and its 3-deuterio analog reported by Casey and Cyr.[5] The path they proposed for isomerization is outlined below:



Since no primary deuterium isotope effect was found, they concluded that the step in which the π-allyl metal hydride is formed cannot be rate determining and suggested that the step likely to be rate determining is the one in which the coordinatively unsaturated (alkene) $Fe(CO)_3$ is formed.

Iron carbonyls also promote hydrocarbon isomerizations under photochemical conditions.[6,7] Very recently Wrighton and Schroeder[8] have reported the results of a study of pentene isomerizations by $Fe(CO)_5$ under photocatalysis conditions; the mechanism suggested for these is much like the one proposed for the thermal reactions, the differences being that light is used to generate $Fe(CO)_4$ and that a substitutionally labile $(alkene)_2\ Fe(CO)_3$ is the species proposed to release the isomerized alkene back into solution.

There has been increasing evidence, however, that an additional iron carbonyl species is present under circumstances where $Fe(CO)_4$ would initially be generated under either thermal or photochemical conditions. Cardaci[9] has studied the mechanism of formation of η^4-complexes of α,β-unsaturated ketones and concluded that such complexes are not produced directly by loss of CO from the η^2-iron tetracarbonyl compound but by an alternate path as shown below:



In studies of (alkene) $Fe(CO)_4$ complexes Cardaci[10] similarly concludes that $Fe(CO)_3$ is produced as a result of alkene-iron bond breaking followed by CO dissociation. The conclusions are based, in both cases, on the kinetics associated with these thermal reactions.

Results

The thermal[1] and photochemical[7] reactions of cis-1,3-pentadiene (1) and 4-methyl-1,3-pentadiene (5) with $Fe(CO)_5$ have been studied briefly by others. We have examined these reactions further and have also examined the thermal and photochemical behavior of their η^2- and η^4- iron carbonyl complexes. The data are presented in Tables 1 and 2 and are summarized below:

a) Reactions of the dienes with $Fe(CO)_5$:

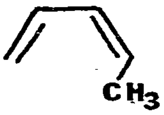
The reactions of 1 and 5 with $Fe(CO)_5$ at high temperatures and extended times lead to η^4- complexes having trans double bonds.[1] The photochemical reactions studied previously,[7] conducted at ambient temperatures and much shorter times than these thermal reactions, show far less diene isomerization. In the photochemical reactions we performed with 5, the η^2- complex 6 is the major product but η^4- complexes 8 and 9, having isomerized diene ligands, are also formed in relatively large amounts in addition to 7. However, in our photochemical studies, diene 1 afforded complexes 2 and 3 only; the isomerization product 4 was not formed.

b) Reactions of the η^2-iron tetracarbonyl complexes:

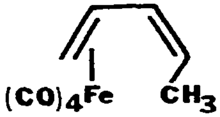
Whether at room temperature or above, thermolysis of 6 yields 7, 8 and 9, but 7 is predominant at all temperatures. Free diene can be observed from an nmr sample of 6 allowed to stand for a few hours at room temperature; however, dissociation is extensive at higher temperatures. Secondary rearrangement of 7 is not responsible for the large amounts of 8 and 9 formed in these reactions; prolonged heating of 7 at 90° yields far less isomerization.

Photochemical reactions of 2 and 6 are quite clean and no more dissociation of the diene ligand takes place than would be expected from room temperature thermolysis during the reaction periods. The sole products observed are 3 and 7, respectively, although small amounts of 4 or 8 and 9 could be present (the limits of detection are about 2-3%).

Table 1. Thermal and Photochemical Reactions Involving <u>cis</u>-1,3-pentadiene or its Iron Complexes



1



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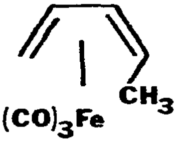


3

4

Compound	Reaction Conditions	Results[a]
1	150-160°, $Fe(CO)_5$ 80 hours[b]	4
1	hν, $Fe(CO)_5$[c]	95% 3, 5% 4
1	hν, $Fe(CO)_5$, 7 hours	65% 2, 35% 3
2	50°, 6 hours	3; low yield, no trans isomer
2	hν, 7 hours	3; high yield, no trans isomer
3	90°, 5 days	stable
3	hν, 7 hours	stable

[a] Percentages shown represent product distributions, not yields.

[b] Data from Pettit, et al, see ref. 1.

[c] Data from Busch and Clark, see ref. 7.

c) Reactions of the η^4-iron tricarbonyl complexes:

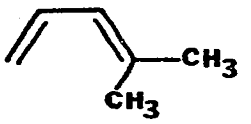
Compound 3 is stable to photolysis under the conditions we employed and to thermolysis at 90° as well. Compound 7 does show some isomerization to 8 and 9 under both sets of conditions. In one instance 7 was photolyzed for 9 hours and showed extensive isomerization, principally to 8. We have repeated this experiment several times and have been unable to repeat those results; since then we have consistently found that little rearrangement of 7 takes place during a 6-9 hour photolysis period.

Discussion

Our results show that rearrangement of diene 1 or that of its complexes 2 and 3 does not take place under conditions which readily promote isomerization of 5 and its complexes. Our results also show that there are only three types of conditions under which isomerization of diene 5 takes place easily: direct thermal or photochemical reactions between 5 and $Fe(CO)_5$ and the thermal reactions of its η^2-complex (6) conducted at elevated temperatures.

The mechanisms previously advanced to explain diene rearrangements promoted by $Fe(CO)_5$ are not adequate to account for the behavior of these systems in the light of our present results. The mechanism proposed by Pettit[1] (see Scheme 1) and supported by others[11] is outlined in terms of secondary

Table 2. Thermal and Photochemical Reactions Involving 4-methyl-1,3-pentadiene or its Iron Complexes



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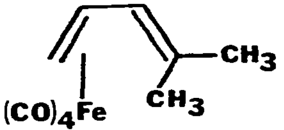
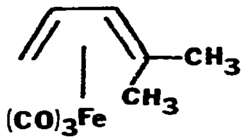


6



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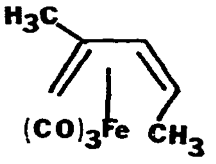

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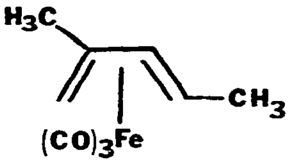

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Compound	Reaction Conditions	Results[a]
5	hν, $Fe(CO)_5$[b]	7, 8, 9 (percentages not reported)
5	hν, $Fe(CO)_5$, 5 hours	51% 6, 35% 7, 10% 8, 4% 9
5	90-100°, $Fe(CO)_5$, 140 hours[c]	9
6	hν, 6 hours	5 (trace), 7
6	ambient, 5 days[d]	91% 7, 6% 8, 3% 9
6	70°, 3 hours[d]	42% 7, 29% 8, 29% 9
6	90°, 2 hours	67% 5, 21% 7, 6% 8, 6% 9
7	90°, 6 hours	90% 7, 5% 8, 5% 9
7	90°, 9 hours (repeat)	86% 7, 7% 8, 7% 9
7	hν, 6 hours	83% 7, 9% 8, 8% 9
7	hν, 9 hours (repeat)	84% 7, 8% 8, 8% 9

[a] Percentages shown represent product distributions, not yields. [b] Data from Busch and Clark, see ref. 7. [c] Data from Pettit, et al., see ref. 1. [d] Sample evaporated to dryness then redissolved in benzene prior to recording the nmr spectrum.

rearrangement of the diene ligand occurring after complex formation; clearly, such secondary rearrangements do occur at high temperatures with η^4-iron tricarbonyl complexes having anti-1-alkyl substituents. However, little or no rearrangement of **3** or **7** takes place under our experimental conditions yet rearrangement products **8** and **9** are formed in rather large amounts in some cases. An alternate mechanism is needed, but the proposal of Nelson and Sloan[4] is not adequate either since their mechanism predicts that isomerization would be caused by reactions of intermediate η^2-iron tetracarbonyl complexes and we have shown that **2** and **6** can be converted to **3** and **7**, respectively, with little attendant formation of the rearrangement products. It is only when **6** is heated to relatively high temperatures or when diene **5** is heated or photolyzed with $Fe(CO)_5$ that substantial amounts of **8** and **9** are formed.

Our studies of these systems now lead us to suggest that diene isomerizations can emanate directly from $Fe(CO)_3$ through a pathway in which coordination and hydride abstraction occur either simultaneously or in rapid succession to yield the π-allyliron tricarbonyl hydride intermediate necessary for diene rearrangement.

Direct evidence for the existence of $Fe(CO)_3$ is available from the work of Poliakoff;[12] prolonged photolysis of matrix isolated $Fe(CO)_5$ yields $Fe(CO)_3$ and small amounts of lower carbonyl fragments. Although these conditions are quite different from those involved in ordinary syntheses where $Fe(CO)_5$ is employed as a reagent, there is secondary evidence that $Fe(CO)_4$ (generated either thermally or photochemically) loses CO and provides $Fe(CO)_3$ in solution. Reactions of phosphines and phosphites with $Fe(CO)_5$ yield mixtures containing $L\,Fe(CO)_4$ and $L_2Fe(CO)_3$ under conditions where the first compound is not attacked by the phosphorous-containing ligand.[13] Also, Wrighton[8] has recently shown that $(Ph_3P)_2Fe(CO)_3$ is a primary photoproduct of the reaction between $Fe(CO)_5$ and triphenylphosphine.

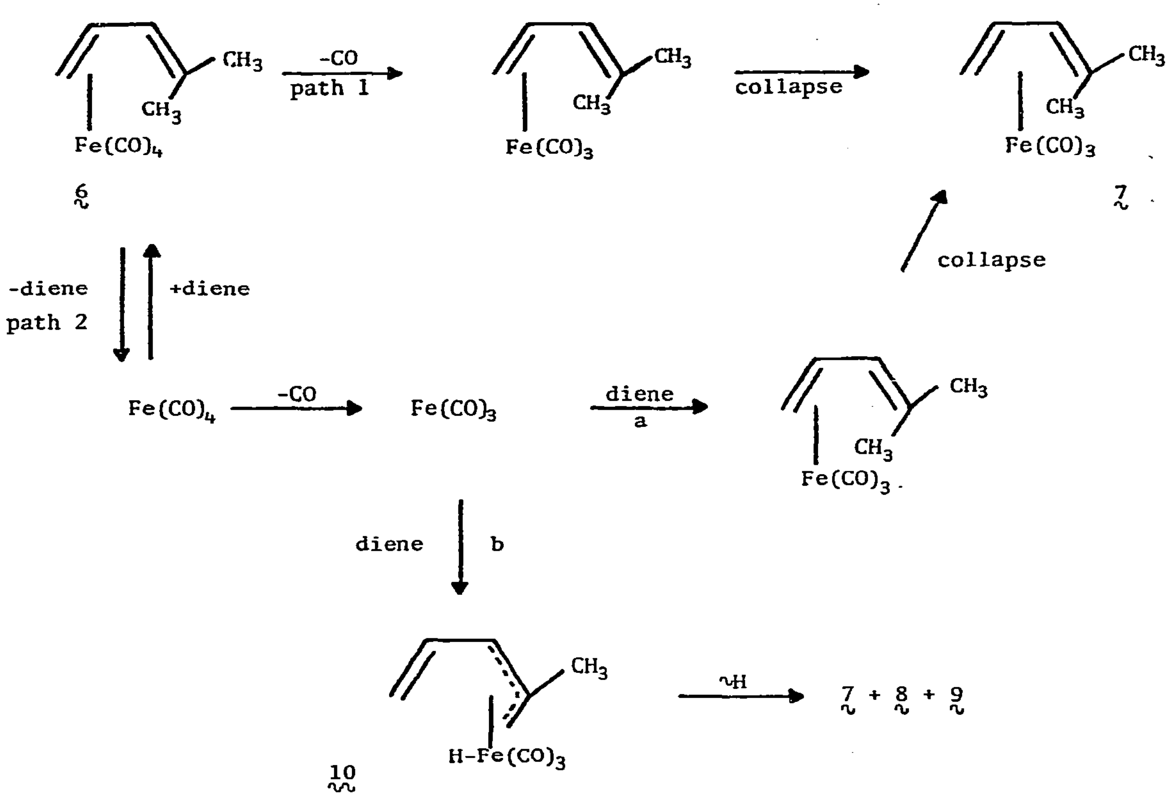
The evidence appears to be fairly strong that $Fe(CO)_3$, or a coordinated form of it, $Fe_2(CO)_7$,[13] is produced from thermal or photochemical reactions in which $Fe(CO)_4$ is generated initially. What has not been identified before is its possible role in promoting isomerizations of alkenes and dienes.

Whatever conditions provide $Fe(CO)_4$ in solution can also be expected to provide some $Fe(CO)_3$; the relative amount of the 14-electron species present, however, should depend greatly on reaction conditions. Loss of CO from $Fe(CO)_4$ should be enhanced as the reaction temperature is increased and the product distribution should reflect this change. In agreement with this, reactions of **6** conducted at elevated temperatures show extensive dissociation of the diene ligand and provide much larger amounts of **8** and **9** than reactions conducted at room temperature. Apart from the thermolyses of **6**, the other reactions which provide large amounts of the rearrangement products from diene **5** are those conducted with $Fe(CO)_5$. Of particular significance is the observation that **8** and **9** are formed in substantial amounts from photolysis of $Fe(CO)_5$ with **5** whereas **6** yields **7**, exclusively, under photolysis.

In consideration of all these observations, we propose the following two paths for reactions of **6**:

The photochemical reactions lead to **7** only and are proposed to follow path 1 exclusively. In the thermolysis of **6**, paths 1 and 2 may be competitive with path 2 taking precedence as the reaction temperature is increased. Whether **8** and **9** are formed directly from **10** (or its rotamer) by a 1,5 hydrogen transfer is not yet known. Strong support has been obtained for a mechanism involving consecutive 1,3 shifts in one case leading to cis → trans isomerization of an η^4-dieneiron tricarbonyl complex, yet similar reactions of η^4-complexes derived from cyclic dienes seem to involve 1,5 shifts.[11]

Scheme 2



Although there is only one entry in Table 2 for the photolysis of $Fe(CO)_5$ with 5, the experiment has been repeated several times with analogous results. These photochemical experiments yield different results in comparison to those involving 6 alone and are proposed to following competing paths related to 1 and 2 above (with the first being predominant).

Our observations about the behavior of the dienes and their complexes have some implications with respect to alkene isomerizations promoted by iron carbonyls. Connor[14] has estimated from enthalpies of thermal decompositions that the iron-alkene bond strength in (ethylene) $Fe(CO)_4$ is less than that of Fe-CO, therefore the isomerization routes for alkenes may parallel the ones we have outlined for the dienes:

$$\begin{tikzcd}
Fe(CO)_4 \arrow[r, shift left, "\substack{+\text{ alkene}\\ \text{path 1}}"] \arrow[d, "\substack{-CO\\ \text{path 2}}"] & (\text{alkene})\ Fe(CO)_4 \arrow[l, shift left, "-\text{ alkene}"] \arrow[r, "-CO"] & (\text{alkene})\ Fe(CO)_3 \arrow[dl] \\
Fe(CO)_3 \arrow[r, "\text{alkene}"] & \pi\text{-allyliron tricarbonyl hydride} &
\end{tikzcd}$$

By analogy to the η^2-dieneiron tetracarbonyl complexes, path 1 should be the predominant course under photolysis conditions. Because of the thermal instability of η^2-alkeneiron tetracarbonyl complexes, path 2 should be predominant under thermolysis conditions. Path 1 is the same one outlined by Casey and Cyr;[5] the slow step for path 2 should be the one in which $Fe(CO)_3$ is formed and would be consistent with their conclusion that hydride abstraction is not involved in the rate determining step.

A number of questions about these reactions remain unanswered at present; work is in progress with alkenes and additional dienes to test and refine the proposed mechanisms further.

EXPERIMENTAL

Instrumentation and Materials

Proton nmr spectra were obtained using a Perkin-Elmer R12A or a Bruker WH90 DS spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. The thermolysis reactions were conducted with the aid of a Fisher Circustat constant temperature bath; temperatures were maintained within 0.2° of the desired setting.

The cis-1,3-pentadiene and 4-methyl-1,3-pentadiene were obtained from Chemical Samples Co. and used without further purification. Iron pentacarbonyl was obtained from Strem Chemical Co. and used directly; diiron nonacarbonyl was prepared by photolysis of iron pentacarbonyl.[15] The iron tricarbonyl complexes 3,4,7,8 and 9 have been characterized previously and were prepared by standard methods;[16] compounds 3 and 7 are best prepared by photolysis of the corresponding η^2-complexes in the manner described below.

Thermolysis Procedures

The compounds to be thermolyzed were dissolved in benzene (or deuteriobenzene) and placed in nmr tubes; the samples were then degassed and sealed under nitrogen and finally immersed in the constant temperature bath.

Photolysis Procedures

The compounds to be photolyzed were dissolved in benzene (or deuteriobenzene) and placed in nmr tubes; the samples were then degassed and sealed under nitrogen. Photolyses were accomplished with an unfiltered 450W Hanovia medium-pressure lamp.

Syntheses of the η^2-Dieneiron Tetracarbonyl Complexes:[17]

A sample of the diene was dissolved in benzene and stirred at room temperature under nitrogen with an equimolar quantity of $Fe_2(CO)_9$ for a short time (usually about 2 hours). The mixture was then filtered through celite and the volatile materials removed on a rotary evaporator. The η^2-complexes are orange-red liquids and were chromatographed on florisil (using hexane as the eluant) when it was necessary to remove small quantities of the corresponding η^4-complex from the sample (the η^2-complex is eluted first). The compounds are oxygen sensitive; all manipulations should be conducted under nitrogen or argon.

Spectral properties:

a) 1,2-η^2-cis-1,3-pentadieneiron tetracarbonyl (2):

IR (hexane) $\nu_{C\equiv O}$ 2080, 2020, 1995 and 1980 cm^{-1}; pmr (C_6D_6) τ 4.78 (m, 2H), 6.02 (m, 1H), 7.75 (d, 2H) and 8.35 (d, 3H).

b) 1,2-η^2-4-methyl-1,3-pentadieneiron tetracarbonyl (**6**):

IR (hexane) $\nu_{C\equiv O}$ 2080, 2002 and 1991 cm^{-1}; pmr (C_6D_6) τ 4.87 (d, 1H), 5.90 (m, 1H), 7.54 (s, 1H), 7.72 (s, 1H), 8.32 (s, 3H) and 8.44 (s, 3H).

Product Analyses

Determination of the composition of each reaction mixture was done by analysis of the pmr spectral data. Although there is extensive overlapping of some of the peaks, there are areas of the spectra which are unique to each component thus allowing the relative amounts of each to be determined. The limit of detectability of the minor components in the mixtures is 2-3%.

Acknowledgments

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15. The synthesis is patterned after King ("Organometallic Syntheses", Vol. 1, J. J. Eisch and R. B. King, ed., Academic Press, N.Y., 1965, p. 93) except acetic anhydride is used as the solvent.

16. See reference 7 and references cited therein.

17. We have reported the preparation of several η^2-dieneiron tetracarbonyl complexes previously: D. H. Gibson and R. L. Vonnahme, *J. Organometal. Chem.*, **70** C33 (1974).