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THERMOLYSIS AND PHOTOLYSIS OF (CYCLOPENTADIENE)IRON TRICARBONYL. EVIDENCE FOR A RADICAL MECHANISM INVOLVING IRON(I)

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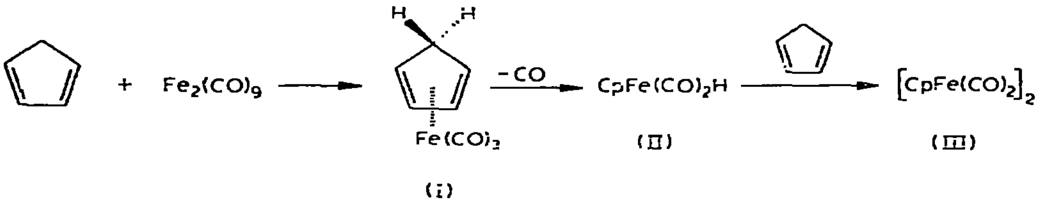
Summary

The thermolysis and photolysis of (η^4-cyclopentadiene)iron tricarbonyl to yield (principally) cyclopentadienyliron dicarbonyl dimer has been studied using the 5-*exo* deuterated compound (produced by cyanoborodeuteride reduction of cyclopentadienyliron tricarbonyl cation) as the principal mechanistic probe. The results of this study are interpreted in terms of a stereospecific free-radical chain abstraction of the deuterium by an Fe^I species as the major pathway for the thermal process. The photochemical process, on the other hand, seems to involve the intramolecular hydrogen transfer pathway previously proposed for the thermal reaction.

Introduction

It has been known for several years [1,2] that cyclopentadiene and its dimer react thermally with iron pentacarbonyl to yield cyclopentadienyliron dicarbonyl dimer III, a useful starting material for a variety of iron-containing compounds. The reaction has been postulated [3,4] to proceed by way of the diene complex I, cyclopentadieneiron tricarbonyl, followed by loss of CO and intramolecular hydrogen transfer to yield cyclopentadienyliron dicarbonyl hydride (II). Although the hydride has been reported [5] to decompose to III with loss of hydrogen, in the presence of excess cyclopentadiene hydrogenation occurs to give III plus cyclopentene and cyclopentane [3].

That the proposed intermediate, cyclopentadieneiron tricarbonyl (I), decomposes under the reaction conditions to III has been confirmed by Kochar and Pettit [6], who synthesized I by reaction of cyclopentadiene with diiron enneacarbonyl under mild conditions and found that heating I in the presence of dicyclopentadiene gave III. A similar sequence has been observed in the ruthenium series, where the Ru analogs of I and II can be isolated. Interestingly, SCHEME 1

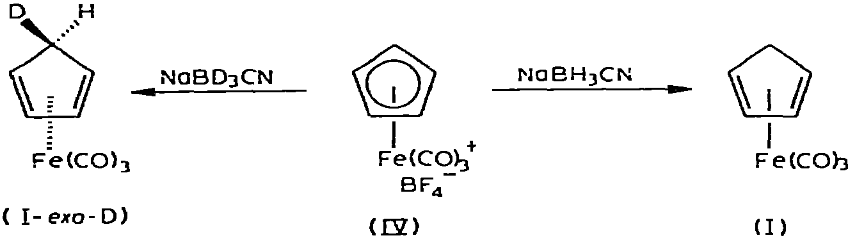


the conversion of the Ru analog of II to dimer occurs only in the presence of oxygen [7].

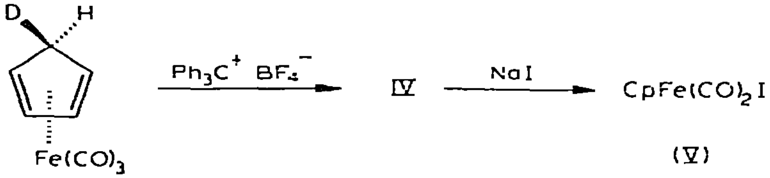
We became interested in this problem for two reasons. First, we wished to investigate the possibility that I might undergo rapid, concerted hydrogen shifts. Since the uncomplexed hydrocarbon undergoes degenerate 1,5 shifts quite readily, it seemed likely that the complex might also rearrange with facility. This chemistry would then contrast sharply with that of other dieneiron complexes, which undergo rearrangement via metal hydride intermediates which are formed in processes with high activation energies [8]. We were also interested in intramolecular metal—ligand hydrogen transfers of the type proposed in Scheme 1, since these reactions seem to be at the heart of a large number of catalytic processes and also are frequently encountered in decomposition reactions of transition metal organometallics. Therefore, we decided to investigate more closely the thermolysis and photolysis of I.

Results and discussion

The mechanism in Scheme 1 predicts that the hydrogen *syn* to iron will be lost. In order to investigate the prediction, a means of stereospecifically labelling I with deuterium was needed. We have found that I (*exo*-D) may be conveniently prepared in high isotopic purity by the reaction of sodium cyanoborodeuteride [9a] with cyclopentadienyliron tricarbonyl cation IV (prepared by a minor modification of King's method [9b]) in THF.



Both I and I (*exo*-D) were prepared for use in this study by reduction of IV. It is interesting that reaction of sodium borohydride and IV gives none of species I, but is reported instead to lead only to mixtures of II and III. The stereochemistry of deuterium in I (*exo*-D) was confirmed both by the absence of the IR band at 2790 cm^{-1}, characteristic of the *exo*-hydrogen, and by hydride abstraction with triphenylmethyl fluoroborate. This reaction resulted in the recovery of IV containing no deuterium, as shown by mass spectroscopic measurements

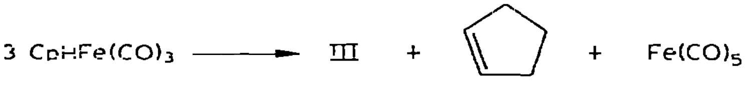


(I-*exo*-D)

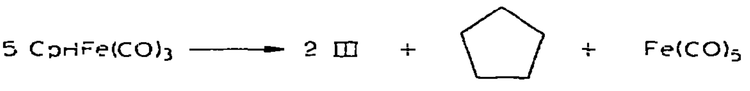
on the derived iodide V[*]. In addition, the NMR of I (*exo*-D) showed the absence of the upfield (δ1.92) half of the AB quartet due to the methylene protons, thus confirming the stereospecificity of the reduction.

Thermolysis of I or I (*exo*-D) in inert solvents (methyl cyclohexane or benzene) led to the formation of dimer III. Isolation of III from the thermolysis of I (*exo*-D), conversion to the iodide V by reaction with molecular iodine in chloroform, and examination of the mass spectrum showed that the cyclopentadienyl rings retained only 15% of the deuterium, in sharp contrast to the prediction of the mechanism in Scheme 1. Control experiments showed that deuterium was not lost in the conversion of dimer to iodide and that no scrambling of the label had taken place in the diene complex. In particular, undeuterated dimer could be converted as above to iodide V in deuterated chloroform with no incorporation of deuterium. Further, recovery of a sample of diene complex from an incomplete (at least 20% conversion) pyrolysis of I (*exo*-D), followed by treatment with triphenylmethyl cation and conversion to the iodide as before, gave V containing no deuterium within experimental error.

Obviously, the reaction mechanism is more complex than indicated in Scheme 1. When the reaction was carried out in a sealed NMR tube, several products other than dimer III could be detected. Even in the absence of excess cyclopentadiene [3], signals due to cyclopentane and cyclopentene were seen (in the ratio of about 1/4) in the NMR spectrum. Integrations of the NMR spectrum of a sample containing an internal standard (anisole) indicated that the stoichiometry of the reaction is probably described by a combination of eqns. 1 and 2.



(1)



(2)

Consistent with these equations, $Fe(CO)_5$ was detected in the reaction mixture by infrared spectroscopy.

Another indication of the complexity of the reaction was obtained during attempts to analyze the kinetics of the decomposition. Samples of I were trans-

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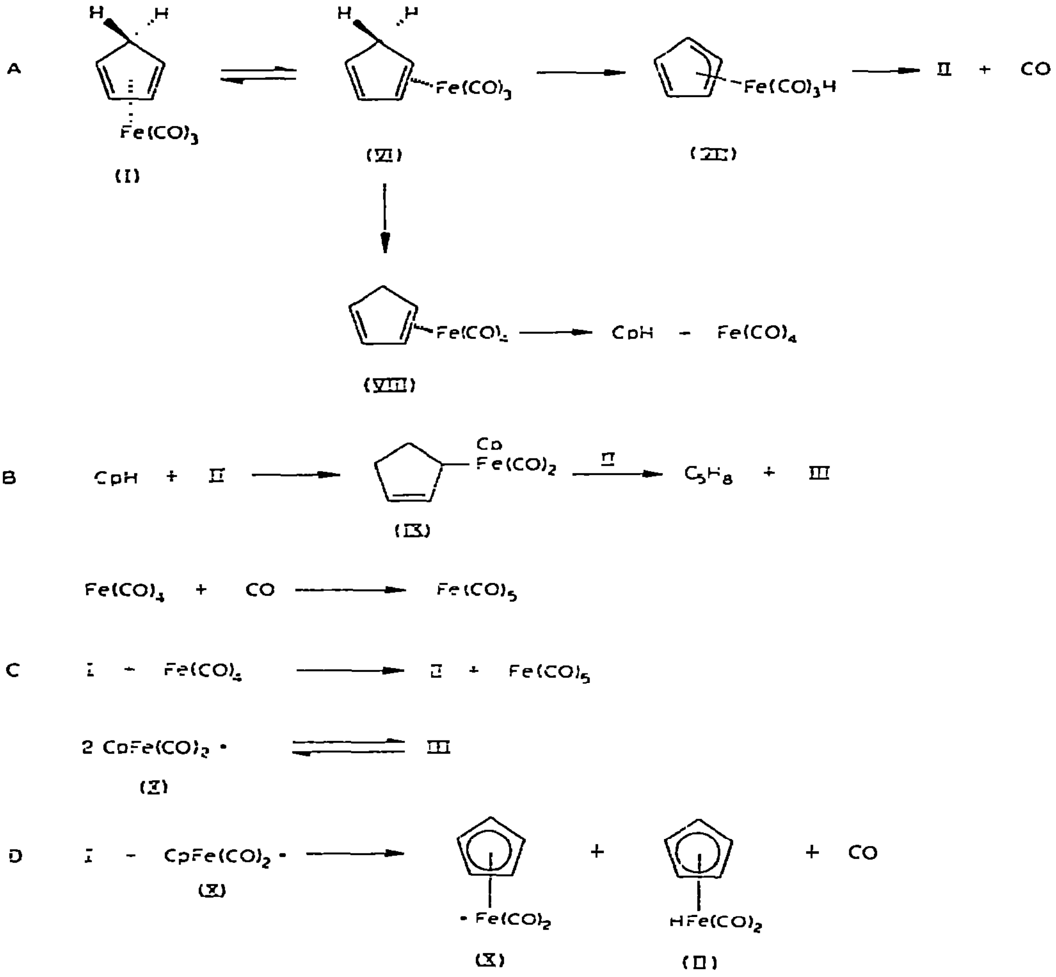
[*] See ref. 10 for a discussion and references to the stereochemistry of hydride addition and elimination in similar species.

ferred on a vacuum line to carefully degassed benzene solutions containing a weighed amount of anisole (as an internal standard) together with various other substances (see below) in a NMR tube. The tube was sealed under vacuum and immersed in a bath held at 100.0°C. Periodically, the tube was removed, cooled to room temperature, and the NMR spectrum recorded.

Two important conclusions could be drawn from the initial rates of disappearance of I under these conditions. First, the reaction does not follow any simple rate law. Second, the rate of the reaction is increased by the addition of dimer III — that is, the reaction is autocatalytic. Addition of azoisobutyronitrile (AIBN) also accelerated the rate, with production of 2-cyanopropane. No inhibitors of the reaction could be found which did not also change the character of the products (see below).

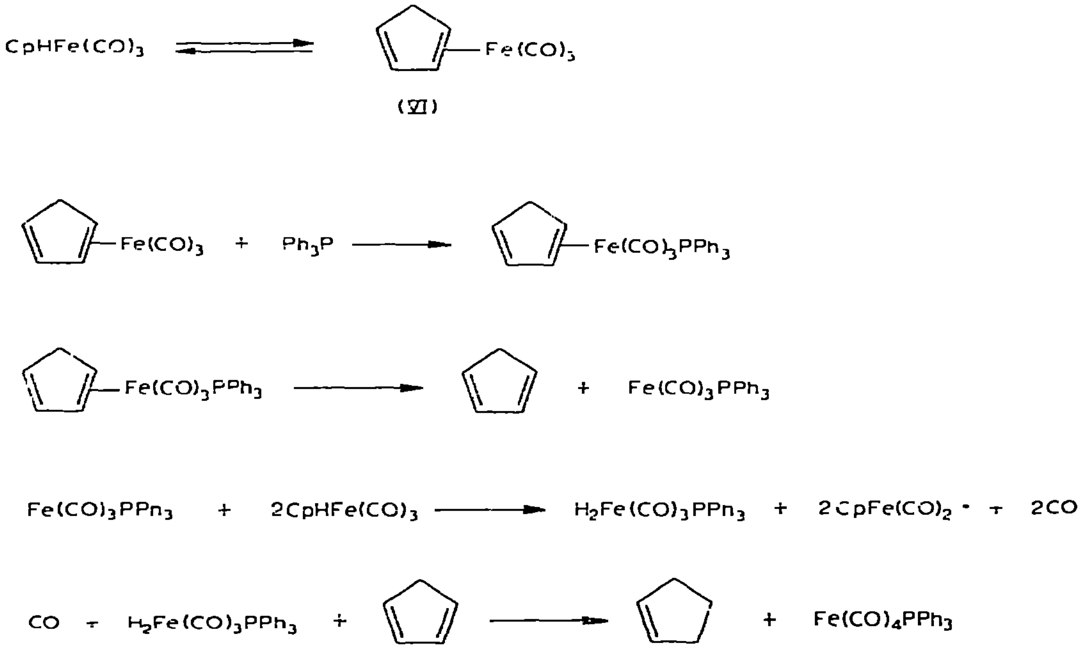
At this point it became clear that the reaction is quite complicated. Further experiments will be discussed in terms of the mechanism in Scheme 2.

SCHEME 2



The sequence A shown in Scheme 2 is based on analogy to our previous work [7,8] on the rearrangements of dieneiron tricarbonyl complexes and is postulated as an initiation sequence and as an explanation of the 15% retention of deuterium in the product. The formation of the coordinatively unsaturated intermediate VI is consistent with the behavior shown by most other dieneiron tricarbonyl complexes [7,8,11]. Thermal loss of CO is usually not observed, and instead dechelation of the conjugated olefin occurs. An intermediate analogous to VI is formed, for example, in the equilibration of 1-phenylcyclohexadieneiron tricarbonyl with the 2-phenyl isomer [8a]. This intermediate can be trapped by triphenylphosphine in competition with hydride migration to the metal [8a]. In sequence A, intermediate VI can either lead to the π-allylmetal hydride VII (which presumably collapses rapidly with CO loss to II) or can react with CO generated in one of several other steps to give the monoolefin complex VIII.

Consistent with these steps is the observation that pyrolysis of I (*exo*-D) in the presence of an equivalent of triphenylphosphine leads to formation of dimer with almost complete loss (98.5%) of the label. Triphenylphosphine apparently reacts efficiently with VI and reduces the importance of sequence A. In a separate experiment, the thermolysis of a dilute solution of I in the presence of two equivalents of triphenylphosphine was observed to yield $Fe(CO)_3(Ph_3P)_2$. In this case the reaction seems to proceed as shown below.



Trapping of VI leads to an olefin complex analogous to VIII, which dissociates. The coordinatively unsaturated fragment can presumably also be trapped by triphenylphosphine, or can initiate the radical chain abstraction process in sequence D (see below). Consistent with the postulated role of coordinatively unsaturated iron moieties is the observation that $Fe_2(CO)_9$ (generally regarded as a source of $Fe(CO)_4$) reacts readily at room temperature with I (*exo*-D) to give dimer III in which once again deuterium loss predominates.

Analogy for the reactions in sequence B can be found in the literature. Metal hydride II is known to react with conjugated olefins to give σ-allyl species similar to IX [12]. Hydrogenolysis of the σ-allyl species by reaction with II has not, to our knowledge, been reported, but it is in fact a facile process. Thus, σ-allyl species XI, isolated as reported [12] from the reaction of butadiene II, reacts readily at 25°C with excess II to yield dimer III. Under these conditions (degassed THF solution) neither II nor XI yields dimer at an appreciable rate. The nature of the olefinic fragment formed was not confirmed in these experiments. However, reaction of cyclopentadiene with (methylcyclopentadienyl)iron dicarbonyl hydride at 100°C was shown to give cyclopentene. In the absence of cyclopentadiene, no methylcyclopentene (or cyclopentene) was formed in this reaction.

$$\mathrm{CpFe(CO)_2^-} \xrightarrow[\text{THF}]{\text{HOAc}} \mathrm{CpFe(CO)_2H}\ \text{(solution in THF)}$$

(II)

(XI)

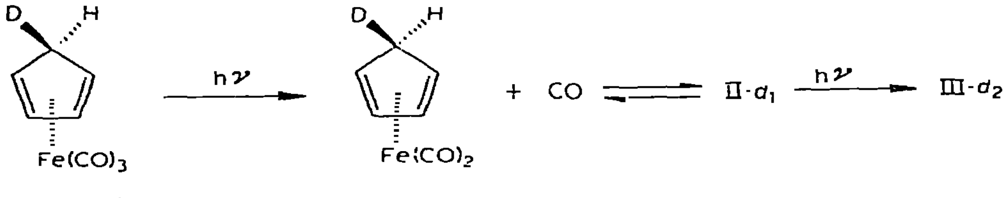
$$\mathrm{XI} + \mathrm{II} \rightarrow \mathrm{III} + (C_4H_8)$$

Evidence for the reversible cleavage of the metal—metal bonds in III as shown in sequence C was obtained from an experiment in which III and (methylcyclopentadienyl)iron dicarbonyl dimer XII were heated in benzene-d_6 at 100°C. After two hours, the NMR of the mixture showed a new peak in the cyclopentadienyl region, and mass spectral studies on the isolated material showed that (methylcyclopentadienyl)(cyclopentadienyl)diiron tetracarbonyl XIII had been formed. Evidence for the homolysis of metal—metal bonds has recently been obtained in other systems as well [13].

$$\underset{\text{(III)}}{[\mathrm{CpFe(CO)_2}]_2} + \underset{\text{(XII)}}{[\mathrm{MeCpFe(CO)_2}]_2} \rightleftharpoons \underset{\text{(XIII)}}{2\,[\mathrm{CpFe(CO)_2Fe(CO)_2MeCp}]}$$

Radical abstraction of hydrogen from I has been demonstrated in the thermolysis of I (*exo*-D) with AIBN, a well-known source of radicals. This reaction leads to stereospecific loss of the deuterium and formation of d_0 dimer at a rate roughly the same as the unimolecular decomposition of AIBN. Deuterium was found in the 2-cyanopropane formed in this reaction. These results suggest the abstraction of hydrogen by cyclopentadienyliron dicarbonyl radical X, as shown in sequence D. As mentioned above, the rate of disappearance of I is accelerated by addition of dimer III. In addition, I (*exo*-D) reacts in the presence of (methylcyclopentadienyl)iron dicarbonyl dimer XII to give III with considerably less deuterium (0.09 deuterium/Cp ring) than in the thermolysis with no additives. Thus, upon addition of product dimer, rate enhancement and an increase in the loss of deuterium are coupled.

In contrast to the thermolysis, photolysis of I gave reasonably clean loss of the *endo* isotope (93.3%) and formation of highly deuterated dimer. We interpret this result as consistent with the mechanism postulated previously for the thermal reaction: loss of CO followed by intramolecular hydrogen transfer to give the hydride II, which eventually forms dimer. The small loss of deuterium observed can be explained by minor intervention of the radical chain path described above.



(I-*exo*-D) (XVII)

The reversibility of the second step is indicated by the fact that scrambling was detected in recovered starting material (to the extent of 4% after ca. 20% conversion). Also, it was observed that photolysis of II led to the efficient formation of dimer III. When $CpFe(CO)_2D$ was similarly photolysed, dimer was formed which contained small amounts of deuterium.

Conclusions

Our experiments show that the decomposition of the diene complex I is much more complex than previously proposed. While previous workers have suggested mechanisms involving CO loss, our results rule out this pathway as the major contributor to the mechanism. We believe that the experimental data may be explained by assuming that I behaves in a manner consistent with other diene complexes, and therefore that the primary thermal reaction is dechelation rather than CO loss. In order to explain the predominant loss of deuterium from I (*exo*-D), additional pathways involving free radical chain abstraction and reaction with coordinatively unsaturated metal species are postulated. Since evidence for cleavage of the metal—metal bond in the dimer III could be obtained, the iron(I) intermediate $CpFe(CO)_2$ is suggested as a reasonable candidate for the chain carrier. In addition, we can detect no trace of thermal hydrogen migrations in I, which means that 1,5 sigmatropic shifts of at least the *endo* hydrogen must be much slower than in the uncomplexed olefin.

Finally, a brief investigation of the photochemistry of I gives results which are interpreted in terms of CO expulsion and hydrogen transfer of the *endo* isotope, the pathway previously postulated for the thermal reaction. This behavior is again typical of metal carbonyls [14], and the contrast between the thermal and photochemical paths lends further credence to the conclusions concerning the mechanism of the thermal reaction.

Experimental

Preparation of cyclopentadienyliron tricarbonyl fluoroborate (IV)

Cyclopentadienyliron dicarbonyl anion was prepared by stirring overnight a solution of cyclopentadienyliron dicarbonyl dimer III (21.2 g, 0.06 mol) in 225 ml THF with 300 g 1% sodium amalgam. The solution of anion was transferred under nitrogen by cannula to another flask and cooled in an ice bath. A deoxygenated solution of ethyl chloroformate (40.7 g, 0.376 mol) in 60 ml THF was added dropwise. The resulting solution was stirred at 0°C for two hours, then allowed to warm to room temperature and stirred overnight. THF was evaporated under reduced pressure and the residue extracted several times with hexane. The hexane solution was treated with 35 ml boron trifluoride etherate. Cyclopentadienyliron tricarbonyl fluoroborate was precipitated upon addition of diethyl ether. The salt was filtered, washed with ether, and dried under vacuum: 29.3 g (84%).

Preparation of cyclopentadieneiron tricarbonyl (I)

A suspension of cyclopentadienyliron tricarbonyl fluoroborate (2.34 g, 8 mmol) and sodium cyanoborohydride (0.50 g, 8 mmol) was stirred in 50 ml THF for 8 h. The solution was decanted, pentane added, and washed with water and saturated aqueous NaCl. The organic layer was dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure. Chromatography on alumina (hexane) gave 340 mg (21%) of I, IR (CS_2) 2785 (CH), 2050, 1975, 1968 (CO) cm^{-1}; NMR (C_6D_6) δ 4.98 (t,2), 2.44 (t,2). 2.14 (AB quartet, 2, $J(AB)$ = 12 Hz, $\Delta\nu$ 24 Hz).

Preparation of cyclopentadieneiron tricarbonyl-d_1 (I-exo-D)

The procedure was similar to that described above for I, using 1.17 g (4 mmol) of cyclopentadienyliron tricarbonyl fluoroborate and 0.27 g (4 mmol) of sodium cyanoborodeuteride. Isolation as above yielded 210 mg (25%), IR (CS_2) 2050, 1975, 1968 (CO) cm^{-1}; NMR (C_6D_6) δ 5.02 (t,2), 2.48 (t,2), 2.37 (br s,1). Isotopic purity up to 92% was attained (analysis by mass spectrometry).

Reaction of triphenylmethyl fluoroborate and I (exo-D)

Triphenylmethyl fluoroborate (0.43 g, 1.3 mmol) in 5 ml methylene chloride was added to I (*exo*-D) (0.27 g, 1.3 mmol) in 2 ml methylene chloride. The precipitate of cyclopentadienyliron tricarbonyl fluoroborate was filtered, washed with ether, and dried, to give 0.24 g (62%). The salt was suspended in 25 ml acetone and treated with potassium iodide (0.14 g, 0.82 mmol). After stirring for three hours, the acetone was evaporated, the residue extracted with chloroform, and the chloroform evaporated under reduced pressure. The residue was sublimed (85°C/0.1 Torr) to yield 0.22 g (87%) of cyclopentadienyliron dicarbonyl iodide, containing no deuterium within experimental error (±0.8%) by mass spectrometry.

Thermolysis of I (exo-D)

(1). A solution of I (*exo*-D) (0.29 g, 1.4 mmol) in 10 ml methylcyclohexane was heated at reflux for 19 h. The solvent was evaporated under vacuum and the solid product cyclopentadienyliron dicarbonyl dimer III extracted with chloroform. Evaporation of the chloroform gave 0.21 g of III (83%). The dimer in 20 ml chloroform was treated with iodine (0.21 g, 0.81 mmol) for one hour at reflux. After cooling to room temperature, the reaction mixture was washed with sodium thiosulfate solution and the chloroform evaporated. Sublimation at 85°C/0.1 Torr gave cyclopentadienyliron dicarbonyl iodide V. Analysis by mass spectrometry indicated that the deuterium content was 85.5 ± 0.8% d_0, 14.5 ± 0.8% d_1.

(2). A solution of I (*exo*-D) (65 mg, 0.31 mmol) in 3.5 ml methyl cyclohexane in a heavy-walled tube was degassed by three freeze-thaw cycles under vacuum, and then sealed. The tube was heated at 130°C for 12 h, and the dimer III isolated (48 mg) and converted to V as before. Deuterium content: 85.0 ± 0.8% d_0, 15.0 ± 0.8% d_1. An experiment in benzene-d_6 gave similar results.

Conversion of III to V in chloroform-d_1

Dimer III (22 mg, 0.062 mmol) and iodine (22 mg, 0.087 mmol) in 2 ml chloroform-d_1 were heated at reflux for 2 h. The chloroform-d_1 was evaporated and the iodide V sublimed at 80°C/0.1 Torr. Mass spectral analysis showed no incorporation of deuterium. Thus, no deuterium loss can occur in the conversion of deuterated III to iodide in chloroform.

Incomplete pyrolysis of I (exo-D)

A solution of I (*exo*-D) (0.21 g, 1.0 mmol) in 10 ml methylcyclohexane was heated at reflux for 7 h. The methylcyclohexane and unreacted I (*exo*-D) were separated from the product III by transfer on the vacuum line. Most of the solvent was fractionally distilled from recovered I at 25°C/10-30 Torr, and the remaining diene complex was treated with triphenylmethyl fluoroborate (0.165 g, 0.50 mmol) in methylene chloride. Filtration of the cyclopentadienyliron tricarbonyl fluoroborate gave 97 mg (0.47 mmol). The salt was converted to the iodide V, and the iodide analysed by mass spectrometry. Deuterium content: 100.4 ± 0.9% d_0. The dimer III isolated from the reaction amounted to 32 mg (18%).

Thermolysis of I (exo-D) with triphenylphosphine

A solution of I (*exo*-D) (52 mg, 0.25 mmol) and triphenylphosphine (66 mg, 0.25 mmol) in enough benzene to make 0.40 ml of solution in a tube was degassed on the vacuum line and sealed under vacuum. The tube was heated at 100°C for 20 h and the benzene removed under vacuum. The dimer III was converted to iodide V as before. Deuterium content: 98.5 ± 0.8% d_0, 1.5 ± 0.8% d_1.

Thermolysis of I (exo-D) with AIBN

A solution of I (*exo*-D) (11 mg, 0.05 mmol) and AIBN (25 mg, 0.15 mmol) in enough benzene-d_6 to make 0.60 ml of solution was degassed and sealed under vacuum. The tube was heated at 100°C for 22 h, the dimer III isolated and converted to iodide V as before. Deuterium content: 99.5 ± 0.8% d_0.

Thermolysis of I (exo-D) with methylcyclopentadienyliron dicarbonyl

A solution of I (*exo*-D) (10 mg, 0.047 mmol) and methylcyclopentadienyliron dicarbonyl dimer (8 mg, 0.021 mmol) in benzene-d_6 was degassed and sealed under vacuum. The tube was heated for 22 h at 100°C. The mixture of dimers was recovered and converted to iodide without separation. Deuterium content of the unsubstituted ring was determined from the cluster of peaks around *m/e* 204. Deuterium content: 90.6 ± 1.0% d_0, 9.4 ± 1.0% d_1.

Thermolysis of I with triphenylphosphine

A solution of triphenylphosphine (157 mg, 0.60 mmol) in benzene to make 2 ml of solution was placed in a glass tube and the solution degassed. The cyclopentadiene complex (58 mg, 0.28 mmol) was distilled in, and the tube sealed under vacuum. It was then heated for 24 h at 100°C, and the benzene removed under vacuum. The remaining yellow solid was extracted with benzene to remove excess triphenylphosphine. The yellow crystals were identified as $Fe(CO)_3(Ph_3P)_2$, 40 mg (21%), IR (benzene) 1885 cm^{-1}.

Isobutyronitrile from reaction of I (exo-D) with AIBN

AIBN (25 mg, 0.15 mmol) in enough benzene to make 1.0 ml of solution was degassed on the vacuum line and the diene complex I (*exo*-D) (80 mg, 0.39 mmol) was distilled. The tube was sealed under vacuum and then heated overnight at 100°C. The benzene solution containing isobutyronitrile was separated from nonvolatile materials on the vacuum line, and the isobutyronitrile isolated by preparative GLPC (10% TCEP, 1/4" × 10', 110°C). The isobutyronitrile contained approximately 35% deuterium by mass spectrometry.

Cyclopentadienyliron dicarbonyl hydride (II)

Dimer III (1.5 g, 4.2 mmol) and 50 g 1% sodium amalgam were stirred for three hours in 40 ml THF. A 5 ml aliquot (1 mmol of anion) was removed and transferred under nitrogen to a centrifuge tube. Acetic acid (60 mg, 1 mmol) was added, and the solution was then centrifuged. The NMR spectrum of the clear supernatant liquid showed resonances at δ 4.90 (CpH) and −11.7 (*m*-H). No appreciable amount of dimer was visible.

Reaction of hydride II with $(\eta^5\text{-}C_5H_5)(\eta^1\text{-2-butenyl})Fe(CO)_2$

To a solution of hydride II (0.25 ml, 0.05 mmol) in THF in a NMR tube was added $(\eta^5\text{-}C_5H_5)(\eta^1\text{-2-butenyl})Fe(CO)_2$ (15 mg, 0.063 mmol) in 0.20 ml THF. Control samples of the hydride and σ-allyl complex were prepared at the same concentration. After four hours, a peak due to dimer III was seen in the NMR spectrum of the mixture of hydride and σ-allyl complex, but the control samples remained unchanged.

Reaction of (methylcyclopentadienyl)iron dicarbonyl hydride with cyclopentadiene

Methylcyclopentadienyliron dicarbonyl hydride was prepared in a manner analogous to II. A solution (0.9 ml, 0.27 mmol) was transferred under nitrogen to a glass tube and cyclopentadiene (20 mg, 0.30 mmol) was added. The solution was degassed and the tube sealed under vacuum. The tube was heated for 4½ h at 95°C, and the volatile components were removed by bulb-to-bulb distillation. Gas chromatography (10% UCW98, 1/8" × 6', 25°C) showed the presence of cyclopentene. A control sample of hydride only produced no methylcyclopentene or cyclopentene.

Reaction of I (exo-D) with $Fe_2(CO)_9$

Deuterated diene complex I (*exo*-D) (43 mg, 0.21 mmol) and $Fe_2(CO)_9$ (100 mg, 0.27 mmol) were stirred in 3 ml diethyl ether for 4 h. The reaction mixture was filtered and the filtrate evaporated to give 37 mg of dimer III (100%). The dimer was converted to the iodide V and analyzed for deuterium. Deuterium content: 89.1 ± 0.8% d_0, 10.9 ± 0.8% d_1.

Scrambling of cyclopentadienyliron dicarbonyl dimers

Cyclopentadienyliron dicarbonyl dimer II (8 mg, 0.023 mmol) and methylcyclopentadienyliron dicarbonyl dimer (10 mg, 0.026 mmol) in enough benzene-d_6 to make 0.35 ml solution was degassed and sealed under vacuum. After heating at 100°C for 2 h, a new methyl peak and a new cyclopentadienyl peak were observed in the NMR spectrum. The mixture of dimers was isolated by evaporation of the solvent, and introduced into the mass spectrometer. A peak at *m/e* 368 was observed, consistent with the formation of the mixed dimer [$MeCpFe(CO)_2CpFe(CO)_2$], which was not present in the spectrum of either $Cp_2Fe_2(CO)_4$ or $(MeCp)_2Fe_2(CO)_4$.

Kinetics and stoichiometry of the thermal reaction

Samples were prepared in NMR tubes on the vacuum line in one of two ways. (1) A solution of a weighed amount of anisole (as an internal standard) plus any additives (e.g. dimer, triphenylphosphine) in benzene-d_6 was degassed by three freeze-thaw cycles. The diene complex was transferred in, and the tube sealed under vacuum. (2) Alternatively, weighed amounts of diene complex, anisole and additives were dissolved in benzene-d_6, degassed, and sealed as before. In either case, the initial concentrations of all species were determined by careful integration vs. the anisole methyl resonance. The volume of solution was estimated by measuring the height of the liquid. The NMR tubes were previously calibrated by addition of known amounts of water. Good agreement (±10%) was obtained in the second method between the values obtained by integration and those calculated from weights. The first method gave variable results due apparently to incomplete transfer of the diene complex. The presence of anisole had no apparent effect on the rate or the products of the reaction.

The kinetic runs were carried out by immersing the NMR tube in an oil bath held at 100.0 ± 0.1°C. Periodically, the tube was removed, cooled quickly to room temperature, and the NMR spectrum recorded and integrated. The rate of dimer formation and diene complex disappearance was calculated from the integrals. Peaks corresponding to cyclopentene and cyclopentane were observed in the NMR spectrum after 1-2 h of thermolysis, identified by chemical shift comparison to authentic samples in benzene-d_6. If these peaks were integrated, > 95% of the C_5 rings could be accounted for. Iron pentacarbonyl was identified by smell and a band in the IR at 1994 cm^{-1} on samples taken from the opened tubes after pyrolysis.

Photolysis of I (exo-D)

A solution of 1 (*exo*-D) (0.19 g, 0.93 mmol) in 14 ml hexane was photolyzed at room temperature for 5 h. Volatile materials were transferred on the vacuum line, leaving a solid residue of 32 mg (19%) of dimer III. Diene complex

(84 mg) was recovered from the distillate after evaporation of the hexane. The dimer III was converted to iodide V, which was determined to contain 93.3% d_1 and 6.7% d_0. The recovered diene complex was treated with triphenylmethyl fluoroborate in methylene chloride yielding 95 mg of IV, which was converted to iodide V as described above. Analysis for deuterium gave values of 4.2% d_1 and 95.8% d_0.

Photolysis of hydride II

A solution of hydride II (0.40 ml, 0.08 mmol) in THF in a NMR tube was photolyzed with water bath cooling. After ten minutes of photolysis, a resonance adjacent to the cyclopentadienyl resonance of the hydride in the NMR spectrum appeared. After one hour of photolysis the hydride resonance at δ -11.7 had disappeared, and only one peak in the cyclopentadienyl region could be seen. This peak (δ 4.9) corresponded to dimer III.

Photolysis of hydride II-d_1

A THF solution of deuteride $CpFe(CO)_2D$ (0.60 ml, 0.12 mmol), prepared by reaction of $CpFe(CO)_2Na$ with CH_3CO_2D, was photolyzed in a NMR tube for 8.75 h at 25°C. The THF was evaporated to give III (24 mg, 0.068 mmol). The dimer was converted to iodide V and analyzed for deuterium. Deuterium content: 95.6 ± 0.8% d_0, 4.4 ± 0.8% d_1.

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References

1 T.S Piper, F.A Cotton and G Wilkinson, J. Inorg. Nucl. Chem , 1 (1955) 165.
2 B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1956) 3030.
3 H.W. Sternberg and I. Wender, Proc. Conf. Coord. Chem. London, 1959, Chem. Soc , Spec Publ. No 13, (1959) 35.
4 A. Davison, M.L.H. Green and G. Wilkinson, J. Chem. Soc., (1961) 3172.
5 M.L.H. Green, C.N. Street and G. Wilkinson, Z. Naturforsch. B, 14 (1959) 738
6 R.K. Kochhar and R. Pettit, J. Organometal. Chem., 6 (1966) 272.
7 A.P. Humphries and S.A.R. Knox, J. Chem. Soc. Chem. Commun., (1973) 327. We thank a referee for bringing this paper to our attention.
8 (a) T.H. Whitesides and J.P. Neilan, J. Amer. Chem. Soc., 95 (1973) 5811
(b) T.H. Whitesides and J.P. Neilan, unpublished observations.
9 (a) R.F. Borch, M.D. Bernstein and H. Dupont Durst, J. Amer. Chem. Soc., 93 (1971) 2897.
(b) R.B. King, M.B. Bisnette and A. Fronzaglia, J. Organometal. Chem., 4 (1965) 256.
10 T.H. Whitesides and R.W. Arhart, J. Amer. Chem. Soc., 93 (1971) 5296
11 H.W. Whitlock and R.L. Markezich, J. Amer. Chem. Soc., 93 (1971) 5290, 5291, H.W. Whitlock, C. Reich and W.P. Woessner, ibid., 93 (1971) 2483; H.W. Whitlock and Y.N. Chuah, ibid., 87 (1965) 3705.
12 M.L.H. Green and P.L.I Nagy, J. Chem. Soc., (1963) 189.
13 J.P. Fawcett, A.J Poe and M.V. Twigg, J Organometal. Chem., 51 (1973) C17 and references therein.
14 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970, p. 324ff