Mechanism of the Thermal Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) Derivatives into (η^5-C_5H_5)Fe(CO)(PPh_3)H and Olefin

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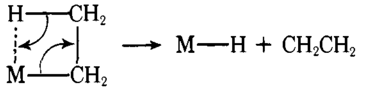
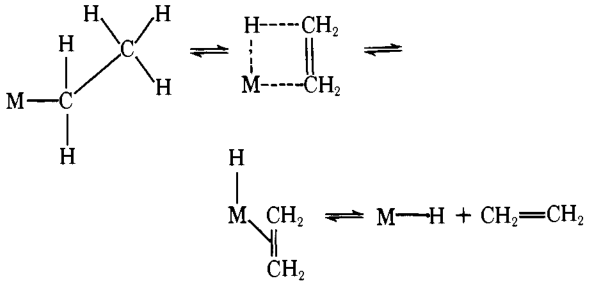
Abstract: The mechanism of the thermal decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) derivatives both in solution and the melt to yield (η^5-C_5H_5)Fe(CO)(PPh_3)H and olefin has been determined. No alkanes are produced in this reaction. The olefins can be isolated in 90% yield and the metal-hydride in about 50% yield. For the *n*-butyl derivative 1-butene, *cis*-2-butene, and *trans*-2-butene are all formed. Studies with *n*-butyl complexes labeled with deuterium at both the α and, separately, the β carbon have shown that the deuteriums are completely scrambled in the butene products as shown mainly by deuterium NMR. The deuteriums are also scrambled in the alkyl chain of recovered starting material. The reactions follow first-order kinetics in solution with the deuterium labeled complexes showing only a small deuterium isotope effect. The reaction is completely inhibited by excess phosphine. A mechanism which is consistent with these data is presented. The main features of the mechanism are dissociation of the phosphine, β-elimination to yield an intermediate of the type (η^5-C_5H_5)Fe(CO)(olefin)H, a series of insertion and elimination steps of this intermediate to scramble the hydrogens, and dissociation of the olefin with association of the phosphine to yield final products.

Interest in the mechanism(s) of the decomposition of transition metal alkyls has been stimulated by the implication of compounds of this type in catalytic systems.[1] The intramolecular mechanism most often cited is β-elimination.[2] Although



this reaction could proceed in a concerted, one-step elimination as shown above, it is generally viewed as going by eq 1.[3] If β-



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elimination takes place by this mechanism, the number of electrons around the metal atom in the intermediate or activated complex is increased by two. Thus, the β-elimination mechanism as generally written requires a transition metal complex that is coordinatively unsaturated or contains labile ligands. The reverse of this reaction, olefin insertion into a metal-hydrogen bond, is frequently proposed as the key step in hydrogenation of olefins and the isomerization of olefins in the presence of transition metal homogeneous catalysts.[1e] As in the forward reaction, in this reverse of reaction 1 the olefin is generally believed to coordinate to the metal before the metal-hydrogen bond adds to the olefin.[3,4]

The most definitive implication of β hydrogens in decomposition reactions of metal alkyls is the work of Whitesides et al.[5] They have decomposed deuterated alkyl copper compounds and studied the alkyl products for retention of deuteriums. The decomposition of *n*-butyl-*1,1*-d_2-(tri-*n*-butylphosphine)copper(I) yields 1-butene-d_2 with none of the d_1 or d_0 species detected. The decomposition of the analogous *2,2*-d_2 compound yields 1-butene-d_1. In these studies, the copper alkyl was not isolated but was characterized in solution. The metal deuteride that is the presumed product of decomposition of the *2,2*-d_2 derivative cannot be isolated because it reacts with the starting alkyl to yield butane-d_3. This secondary reaction, the reduction of alkyl copper(I) compounds by copper(I) hydride, occurs at a rate competitive with the alkyl decomposition and has been shown to proceed via a nonradical mechanism.[6] Thus, the decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I) yields 1-butene (51%) and *n*-butane (49%). A similar mechanism has been proposed for the decomposition of (σ-octyl)IrCO(PPh_3)$_2$.[7]

Another system which has been studied in detail is the thermal decomposition of di-*n*-butylbis(triphenylphosphine)platinum(II).[8] This decomposition reaction also yields approximately equal amounts of alkane and alkene. In this case, deuteration at the 1 or 2 position of the butyl group in the starting material did not determine the location of hydride abstraction. The deuteriums are scrambled in the 1-butene product. This was straightforwardly explained by a fast, reversible equilibrium similar to that shown in reaction mechanism 1. A scrambling of deuteriums was also observed by Chatt et al. in the decomposition of *trans*-[Pt(CD_2CH_3)Br(PEt_3)$_2$].[9] The main feature of the mechanism proposed for the di-*n*-butyl system is the initial dissociation of a phosphine followed by β-elimination of a σ-butyl group. The olefin formed upon β-elimination was shown to remain attached to the platinum. The final step in the mechanism is reductive elimination of butane yielding, presumably, an equal amount of butene as the platinum compound decomposes.

$$L_2Pt(butyl)_2 \underset{+L}{\overset{-L}{\rightleftharpoons}} LPt(butyl)_2 \rightleftharpoons LPt(H)(butyl)(butene)$$

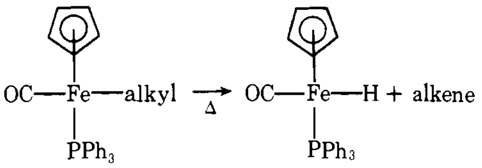
There are other systems in which β-elimination has been proposed as a reasonable mechanism for the decomposition of a transition metal alkyl. For example, Hosokawa and Maitlis[10] have proposed β-elimination for a palladium alkyl. As in the studies by Whitesides, the metal-hydride product was not isolated. Additional evidence is that alkyls containing no β hydrogens are found to be considerably more stable than analogous compounds containing β hydrogens. Particularly stable compounds of this type contain σ-$CH_2Si(CH_3)_3$ groups.[11]

Mechanisms other than β-elimination have also been proposed for the decomposition of metal alkyls. Neophyl(tri-*n*-butylphosphine)copper(I) has been shown to decompose mainly by a free radical mechanism.[12] Sneeden and Zeiss[13] have carried out extensive studies on the decomposition of chromium alkyls. They have proposed that both homolysis and β-elimination are important in the decomposition of these complexes. In addition, from results obtained in a deuteration study, they have suggested the possibility of α-elimination.[14] They also propose some bimolecular mechanisms.[14] As has been frequently the case in systems studied to date, isolation of starting reactant alkyls and/or metal–hydride products has been difficult or impossible. Decomposition of these chromium alkyls usually leads to about a 70–30% mixture of alkane and alkene, respectively.

A recent study on the decomposition of an f-block transition metal-alkyl has given quite different results. Marks et al.[15] have prepared and studied the properties of $(\eta^5\text{-}C_5H_5)_3U$-alkyl compounds. These decompose to yield alkanes exclusively. Deuteration studies showed that the alkyl group abstracts a proton from one of the cyclopentadienyl rings. In a following study[15] on uranium(IV) tetraalkyls, β-elimination was proposed to take place for the saturated alkyls containing β hydrogens although there was a considerable excess of alkane over alkene produced in some cases suggesting another possible mechanism was operative. Marks et al. proposed that the difference between the results for the $(\eta^5\text{-}C_5H_5)_3U$-alkyls and the $(alkyl)_4U$ compounds is a consequence of the fact that the former compounds are most likely coordinatively saturated and thus block a β-elimination mechanism like that shown in eq 1. The latter compounds are presumably not coordinatively saturated and can decompose via mechanism 1. For both of these systems it was not possible to characterize any metal containing products.

Despite this considerable research effort in the area of transition metal alkyls, recent texts[3] and journal articles[10,17] indicate a strong need for model systems that can be studied in detail for mechanistic purposes. It seems apparent that, in particular, a system in which both the starting material and final metal–hydride product are stable enough to be isolated as pure solids and characterized is needed for study.

A system which fits these requirements, as well as having other advantages, is shown in eq 2. The starting σ-alkyl derivatives form red crystals that are stable at room temperature to thermal decomposition and air oxidation. Solutions slowly decompose in air. Although compounds of this type have been prepared previously,[18] we have prepared them directly by reaction 3.[19] The decomposition reaction 2 was first reported for the σ-alkyl derivative in boiling heptane.[18b] The metal-hydride product can be isolated in ca. 45% yield, even when the reaction is carried out in a melt above 125 °C (vide infra). Another advantage of this system for a mechanistic study is that only alkenes are formed. Finally, this system differs from others that have been studied in detail in that the alkyl complexes are coordinatively saturated and at room temperature in solution the ligands are nonlabile. This has been demonstrated by the fact that alkyls of this type that have been resolved at the metal center are stable to racemization in solution at room temperature.[20] Reported here is our mechanistic study of reaction 2.



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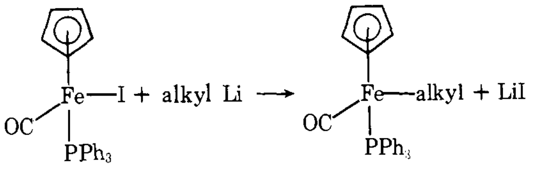

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Experimental Section

General Data. All operations on the iron complexes in solution were carried out under an atmosphere of nitrogen using solvents that were purified and degassed before use. Routine infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. The kinetic data were obtained using a Perkin-Elmer Model 621 spectrometer. Raman spectra were either recorded on a Cary 81 spectrometer equipped with a Spectra Physics Model 123 helium–neon laser with the instrument being calibrated with emission lines from a neon lamp over the spectral range 0–4000 cm^{-1} or on a Beckman Model 700 spectrometer equipped with a Spectra Physics Model 164 Ar$^+$ laser using the 4880-Å line. All Raman samples were run as neat liquids in capillary tubes. Proton NMR spectra were recorded on a Perkin-Elmer R-32 or Varian A-60 spectrometer. Phosphorus and deuterium NMR spectra were recorded on a Varian XL-100-15 spectrometer as were proton spectra used to determine the amount of deuterium incorporation in metal–alkyl complexes. Mass spectra were measured at 70.0 eV on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. All preparative work in synthesis of alkyl(carbonyl)(η^5-cyclopentadienyl)(triphenylphosphine)iron(II) compounds (alkyl = ethyl, *n*-butyl, isobutyl, and *sec*-butyl) has been previously reported.[19]

Preparation of *n*-Butyl-*1,1*-d_2 Chloride. The preparation of 1-butanol-*1,1*-d_2 was similar to the procedure of Friedman and Jurewicz.[21] The alcohol (7.2 g, 94.6 mmol) was converted to the chloride by reaction with zinc chloride (24.0 g, 176 mmol) and concentrated hydrochloric acid (16 ml). The reaction mixture was heated slowly to reflux for 90 min and the *n*-butyl chloride was distilled from the reaction vessel. It was then washed with H_2SO_4 (2 × 5 ml), water (3 × 10 ml), a saturated aqueous solution of sodium carbonate (2 × 5 ml), and water (2 × 5 ml) again and dried over magnesium sulfate (4.56 g, 51%). Deuterium incorporation was 98% as determined by NMR.

Preparation of *n*-Butyl-*2,2,*-d_2 Chloride. Butanoic acid (10 g, 0.114 mol) was converted to butanoic-*2,2*-d_2 acid by the method of Atkinson et al.[22] The acid was converted to the *n*-butyl-*2,2*-d_2 chloride by the method described above in a 28% overall yield. Deuterium incorporation was 97% as determined by NMR.

Preparation of Deuterated Carbonyl(η^5-cyclopentadienyl)triphenylphosphineiron(II) Alkyl Compounds. Complexes were prepared as previously reported[19] with the exception being the substitution of deuterated alkyl–lithium for the undeuterated alkyls in the previous preparations. The synthesis of the (ethyl-*1,1*-d_2)-iron complex has been previously reported.[23]

Decomposition Reactions. (a) Melt. A 0.3-g (0.64 mmol) sample of the alkyl iron compound was placed in a 100-ml round-bottom flask with an extended neck connected to a gas bulb and the entire apparatus evacuated. The round bottom was immersed in a 140 °C oil bath while simultaneously immersing the gas bulb in liquid nitrogen. The red solid melted rapidly to a red liquid which then turned a yellow-green color with considerable frothing. After completion of the reaction (ca. 15 min), the gas bulb is sealed by a vacuum stopcock and saved for future analysis (vide infra). The solid residue that remained in the flask was extracted with benzene (2 ml) and chromatographed (5 × 1.5 cm column of alumina). The single, yellow band that developed was eluted using hexane–ether (2:1 v/v). Concentration of the solution by vacuum evaporation yielded yellow crystals (0.13 g, 51%), of carbonyl(η^5-cyclopentadienyl)hydrido(triphenylphosphine)iron(II). This compound has been reported previously by two groups.[18b,24] The ^{1}H NMR and carbonyl stretching frequency match the reported values: ^{13}C NMR spectrum 210.80 (doublet, J = 27.9 Hz, CO), 138.67 (doublet, J = 42.6 Hz, P-bound phenyl carbons), 133.30 (doublet, J = 10.3 Hz, ortho phenyl carbons), 129.58 (doublet, J = 2.4 Hz, para phenyl carbons), 128.12 (doublet, J = 9.0 Hz, meta phenyl carbons), 80.48 (singlet, $\eta^5\text{-}C_5H_5$); ^{31}P NMR spectrum 55.9 ppm shielded vs. external H_3PO_4 (doublet, J = 72.0 Hz, PPh_3).

(b) Solution. The alkyl-iron complex (0.2 g) was decomposed at 61.2 ° at atmospheric pressure under N_2 in 25 ml of hexane (for the ethyl compounds) or xylene (for the butyl compounds) in a 100-ml flask connected through a water condenser to two cold traps immersed in liquid nitrogen. After 8 h, the solution was freeze–thawed twice to remove any dissolved gases and the volatile products were separated from trace amounts of solvent by standard vacuum line techniques and stored in a gas bulb for future analysis. The metal hydride was isolated from the solution as outlined above (0.65 g, 37.1%). A sample of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ (0.15 g) was heated in xylene as described above for the alkyl complexes. A similar workup of this solution after 8 h yielded a 40% recovery of the metal hydride.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)H$ and Ethylene. The iron hydride (0.05 g, 0.12 mmol) was dissolved in benzene (25 ml) and ethylene bubbled through the solution for 2 h. At this time an infrared spectrum was taken which showed no reaction had taken place, so the reaction vessel was sealed for 24 h with stirring. At the end of this period, another infrared spectrum was taken and again no reaction had taken place.

Reaction of (η^5-C_5H_5)Fe(CO)(PPh_3)H and Cyanoethylene. The iron hydride (0.1 g, 0.24 mmol) was dissolved in 1.5 ml of cyanoethylene. Monitoring the solution by infrared spectroscopy after 15 min showed no reaction had taken place. The solution was then heated for 5 min and another infrared spectrum take in which no reaction was evident.

Partial Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl-*1,1*-d_2). The (*n*-butyl-*1,1*-d_2) iron complex (0.2 g, 0.48 mmol) was dissolved in 20 ml of xylene and heated by an oil bath (ca. 70 °C) for 1 h at which time the solvent was reduced by vacuum evaporation and the solution chromatographed (7 × 1.5 cm column of alumina). Elution with hexane developed two bands that were removed from the column by hexane–ether (2:1 v/v) after initial separation had occurred. The first band was then shown to be the iron hydride (0.05 g) by comparison with an authentic sample. The second band was the starting material (0.12 g) with the deuteriums scrambled throughout the alkyl chain as determined by NMR. A similar result was obtained for the ethyl-*1,1*-d_2 derivative as followed by NMR. In this case, it was determined that extensive scrambling had occurred in less than 0.1 half-life.

Deuterium NMR. Neat 1-Butene. Proton decoupled ^2H NMR spectrum (reported in δ units measured vs. external acetone-d_6), all resonances are singlets: 1.00 (3, $CH_2{=}CHCH_2\mathit{CH_3}$), 2.03 (2, $CH_2{=}CH\mathit{CH_2}CH_3$), 4.89 and 4.95 (2, $\mathit{CH_2}{=}CHCH_2CH_3$), 5.82 (1, $CH_2{=}\mathit{CH}CH_2CH_3$). The spectrum is shown in Figure 2.

Butenes from Solution Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl-*1,1*-d_2). The conditions for obtaining the spectrum of the butenes from the solution decomposition reaction are as follows: sweep width = 1000 Hz (expansion = 200 Hz), sweep offset = 38 434, acquisition time = 1.0 s, pulse delay = 0 s, and the number of transients = 7000. The concentration was ca. 0.015 ml of butene in 0.5 ml of benzene. Proton decoupled ^2H NMR spectrum (δ in C_6H_6 vs. internal natural abundance benzene or external acetone-d_6, which both yield the same results), all resonances are singlets: 1.00 ($CH_2{=}CHCH_2\mathit{CH_3}$), 1.65 (*cis*- and *trans*-$\mathit{CH_3}CH{=}CH\mathit{CH_3}$), 2.02 ($CH_2{=}CH\mathit{CH_2}CH_3$), 5.09 ($\mathit{CH_2}{=}CHCH_2CH_3$), 5.51 (*cis*-$CH_3\mathit{CH}{=}\mathit{CH}CH_3$), 5.37 (*trans*-$CH_3\mathit{CH}{=}\mathit{CH}CH_3$), 5.95 ($CH_2{=}\mathit{CH}CH_2CH_3$). Integration shows that the deuterium are statistically scrambled in each butene. An example is shown in Figure 3.

Kinetic Procedure. All spectral measurements were made in xylene solvent employing a Perkin-Elmer 621 grating spectrophotometer in the expanded mode recording the range 2100–1750 cm^{-1}. One-half millimeter sodium chloride cells were used.

The decomposition reactions were run under nitrogen in a 50-ml round-bottom flask equipped with a rubber septum cap. The reaction flask was placed in a constant temperature oil bath (±0.2 °C). Samples for spectral analysis were withdrawn at regular intervals with a hypodermic syringe. The rates of decomposition of the (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) complexes were followed by observing the decrease in the absorbance of the carbonyl stretching frequency with time. Figure 4 shows results from a typical run. Rate constants were calculated using a linear least-squares computer program for the first-order rate plots of ln (c) vs. time, where c is the concentration at time t. Linear first-order rate plots were observed for all samples over at least *two* half-lives. A representative example is shown in Figure 5.

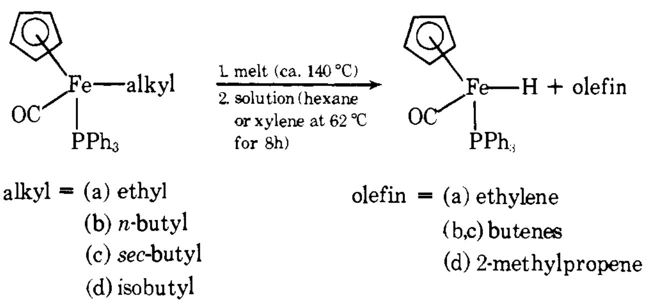
Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl) in a Carbon Monoxide Atmosphere. A xylene (25.0 ml) solution of (η^5-C_5H_5)Fe(CO)(PPh)(*n*-butyl) (0.1146 g, 0.245 mmol) was decomposed at 61.2 °C. The reaction was monitored by infrared spectroscopy as described above for 8 h. The decomposition product proved not to be the iron hydride, but [η^5-C_5H_5)Fe(CO)$_2$]$_2$ by comparison of the infrared spectrum of an authentic sample.

Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl) in the Presence of PPh_3. A xylene (25 ml) solution of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl) (0.1156 g, 0.247 mmol) and 1 equiv (0.0646 g, 0.247 mmol) of triphenylphosphine was placed in a constant temperature oil bath (61.2 °C) and monitored by infrared spectroscopy regularly for 75 h. No reaction occurred over this time period. After 75 h, the temperature was raised to 91.2 °C for 24 h again with similar results; no reaction had taken place. Similar results were obtained with 0.5 equiv of added PPh_3.

Results

Thermal Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) Compounds. The thermal decomposition reaction of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) compounds proceeds as shown in Scheme I. The iron hydride, which has been previously reported,[18b,24] was isolated via chromatography on alumina from the melt as well as from solution reactions in yields of 40–50%. Although other iron containing products were not isolated, a control study showed that these yields are determined mainly from decomposition of the metal hydride product under the conditions of the reaction.

Scheme I



The volatile products from the solution and melt reactions of the iron ethyl compound produced ethylene in ca. 90% yield with no detectable saturated hydrocarbon products as analyzed by mass spectral and infrared spectral data. The volatile products of the iron *n*-butyl and iron *sec*-butyl decomposition reactions were found to be 1-butene, *cis*-2-butene, and *trans*-2-butene (yields ca. 90%). For the xylene solution decomposition of the *n*-butyl compound the ratio of the three butenes is 10.4:1.2:1 when the reaction is carried out at 61.2 °C and 9.6:1:1.9 at 90°, respectively, as determined by a Raman spectroscopic investigation of the carbon–carbon double bond stretching region (1-butene, 1641 cm^{-1}; *cis*-2-butene, 1669 cm^{-1}; *trans*-2-butene, 1681 cm^{-1}).[25] For the xylene solution decomposition of the *sec*-butyl compound at 61.2 °C, the ratio of butenes was essentially identical with those of the *n*-butyl complex. The iron isobutyl complex produced 2-methylpropene as the sole detectable volatile product. Again, mass spectral data gave no indication of saturated hydrocarbon products for any of the iron butyl derivatives.

Deuterium Labeling Study. Decomposition reactions as described above were carried out with (η^5-C_5H_5)Fe(CO)(PPh_3)(ethyl-*1,1*-d_2), (η^5-C_5H_5)Fe(CO)(PPh_3)(ethyl-*2,2,2*-d_3), (η^5-C_5H_5)Fe(CO)(PPh_3)(butyl-*1,1*-d_2), and (η^5-C_5H_5)Fe(CO)(PPh_3)(butyl-*2,2*-d_2). Again the volatile products were collected from the melt and solution reactions with analysis by mass spectroscopy, Raman spectroscopy, and deuterium NMR. Infrared analysis of the volatile products of the decomposition of the deuterated iron ethyl compounds showed scrambling of the deuteriums in the ethylene product. The butene products from the decomposition of the deuterated iron butyl compounds proved more informative. Mass spectral data showed that the butene products from the labeled compounds were mainly butene-d_2 (ca. 95%). In addition, examination of the fragmentation patterns determined that some of the deuteriums had scrambled to the methyl group; however, it was not possible to quantitate the extent of deuterium scrambling. Raman and infrared spectral studies gave no conclusive information on this point either. The Raman spectra from both deuterated samples in the olefin stretching region contain peaks as shown in Figure 1. Peaks are assigned in the figure and demonstrate extensive deuterium scrambling around the double bond in the 1-butene product. Peak locations

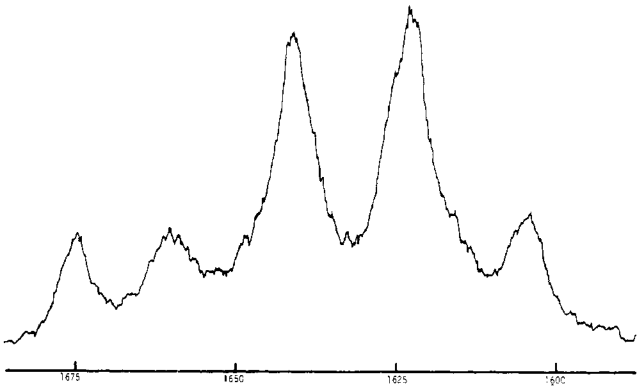


Figure 1. Raman spectrum of the carbon-carbon double bond stretching region for a butene mixture derived from the solution decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl-*1,1*-d_2). Peak assignments are as follows: 1675 cm^{-1}, *trans*-2-butene; 1662 cm^{-1}, *cis*-2-butene; 1641 cm^{-1}, 1-butene with no deuteriums at terminal position; 1624 cm^{-1}, 1-butene with one deuterium at terminal position; and 1605 cm^{-1}, 1-butene with two deuteriums at terminal position.

(cm^{-1}) and average percentages (%) of the butenes are as follows: 1675 (7), 1665 (10), 1671 (33), 1624 (38), and 1605 (12). Assignments given in the figure have been substantiated by deuterium NMR results (vide infra). Proton decoupled, deuterium NMR showed complete scrambling had taken place in these butene samples. The natural abundance, proton decoupled deuterium NMR of neat 1-butene is shown in Figure 2. Assignments of the resonances are straightforward since ^{2}H resonances in parts per million have essentially the same chemical shift as ^{1}H resonances. For 1-butene, analysis of the olefin region is particularly simplified because it is first order, whereas the ^{1}H NMR is second order.[26] The ^{2}H NMR of the butenes obtained from the iron *n*-butyl-*1,1*-d_2 or iron *n*-butyl-*2,2*-d_2 decompositions are the same, and an example is shown in Figure 3. It should be pointed out that under the conditions employed to obtain this spectrum only deuterium enriched samples would be observed. This is graphically seen from the low intensity of the benzene resonance which was used as solvent. Integration of the ^{2}H NMR resonances conclusively shows that the deuteriums are completely scrambled in both the 1-butene and 2-butene products with a ratio of butene products being 3.5:1, respectively. Note that the resonance assigned to the terminal olefin deuteriums are resolved in the neat sample, but not in the samples from the decomposition reactions run in benzene.

Two other results should also be noted. First, when the iron *n*-butyl-*1,1*-d_2 complex was decomposed for one half-life and starting material recovered, the deuteriums had scrambled throughout the alkyl chain. A similar result was obtained for the ethyl-*1,1*-d_2 derivative. In this case, extensive scrambling was observed after 0.1 half-life. Second, attempts to reverse the reaction by mixing excess ethylene or cyanoethylene with the iron hydride failed.

Kinetics. The rate of the decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl) compounds studied follows the first-order rate law

$$\text{rate} = k[(\eta^5\text{-}C_5H_5)\text{Fe(CO)}(\text{PPh}_3)(\text{alkyl})]$$

Values of the rate constants, *k*, calculated from the first-order rate expression, are given in Table I for the compounds studied. Of particular note is the lack of an appreciable deuterium isotope effect. Figure 4 shows the typically observed infrared traces of the disappearance of starting material ν(CO) band (1906 cm^{-1}) with simultaneous appearance of product ν(CO) band (1925 cm^{-1}), while Figure 5 illustrates a typical linear first-order rate plot for ca. 2 half-lives. The apparent[27] activation parameters for the decomposition are: E_{act} = 31 ± 3 kcal, ΔH^* = 30 ± 3 kcal, and the ΔS^* = 20 ± 3 eu, which were calculated from an Arrhenius plot.

Table I. Rate Constants for the Decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl)

alkyl	10^3k (min^{-1})	Temp (°C)
n-Butyl	0.396 ± 0.009	51.0
n-Butyl	2.72 ± 0.03	61.2
n-Butyl	6.10 ± 0.01	74.8
n-Butyl	9.81 ± 0.02	91.0
n-Butyl-*1,1*-d_2	2.10 ± 0.03	61.2
n-Butyl-*2,2*-d_2	2.30 ± 0.04	61.2
sec-Butyl	2.48 ± 0.05	61.2
2-Methylpropyl	1.80 ± 0.02	61.2

The addition of 1.0 or 0.5 equiv of triphenylphosphine causes complete inhibition of the decomposition reaction. Also, when the reaction is done under an atmosphere of CO the decomposition rate is retarded and the product is not the expected iron hydride, (η^5-C_5H_5)Fe(CO)PPh_3(H), but [(η^5-C_5H_5)Fe$(CO)_2$]$_2$. It was found that other Lewis bases (THF, 1,4-dioxane) also caused a decrease in the rate.

Discussion

From the data presented in the Results section it is possible to propose a detailed mechanism for the reaction shown in eq 2, the thermal decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(alkyl), a coordinatively saturated transition metal alkyl, yielding (η^5-C_5H_5)Fe(CO)(PPh_3)H and olefin. The main points of evidence are listed below.

(1) For this reaction carried out in either the melt or in solution, no saturated products have been isolated. Isolated in greater than 90% yield are from the ethyl derivative only ethylene, from the *n*-butyl and *sec*-butyl derivatives 1-butene, *cis*-2-butene, and *trans*-2-butene, and from the isobutyl derivative 2-methylpropene. The ratio of butenes for both the *n*-butyl and *sec*-butyl compound decomposing in xylene solution of 61.2 °C is 10.4:1.2:1, respectively. These ratios change for solution decompositions carried out at higher temperatures in favor of the 2-butenes.

(2) Deuterium NMR, Raman, and mass spectral studies have shown that for the decomposition of both the *n*-butyl-*1,1*-d_2 and -*2,2*-d_2 iron compounds the deuteriums are completely scrambled in the butene products.

(3) Rate data have shown that the reaction follows first-order kinetics. There is only a small deuterium isotope effect for both the butyl-*1,1*-d_2 and *2,2*-d_2 derivatives.

(4) The solution reaction is essentially completely retarded by the addition of excess triphenylphosphine. Other weaker Lewis bases such as THF and dioxane also substantially retard the reaction. In the case of excess CO, the reaction is retarded to a lesser extent with a concomitant change in the metal product to [(η^5-C_5H_5)Fe$(CO)_2$]$_2$.

(5) If the solution reaction is carried out for ca. one half-life and starting material recovered, the deuteriums are scrambled throughout the alkyl chain. Extensive scrambling occurs in as short a time as 0.1 half-life. Also, the reaction could not be reversed in the presence of excess olefin.

A mechanistic scheme that incorporates all of these results is shown for the *n*-butyl derivative (Scheme II). The rate determining steps are collapse of the proposed (η^5-C_5H_5)Fe(CO)(butene)H intermediates with an association of phosphine.

This scheme fits our experimental data in that all three butene derivatives but no alkanes are formed. A shift in product distribution of the butenes would be expected for reactions carried out at different temperatures in favor of the 2-butenes

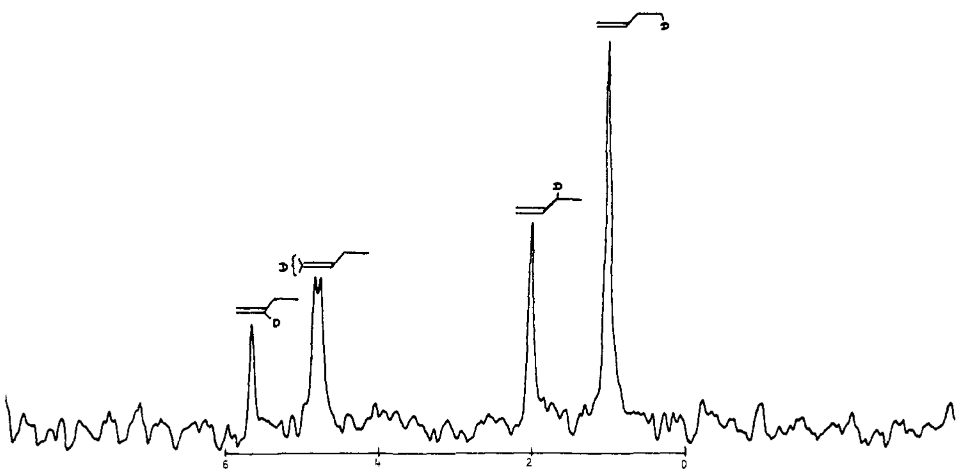


Figure 2. Proton decoupled deuterium NMR of natural abundance neat 1-butene (for chemical shift values see Experimental Section).

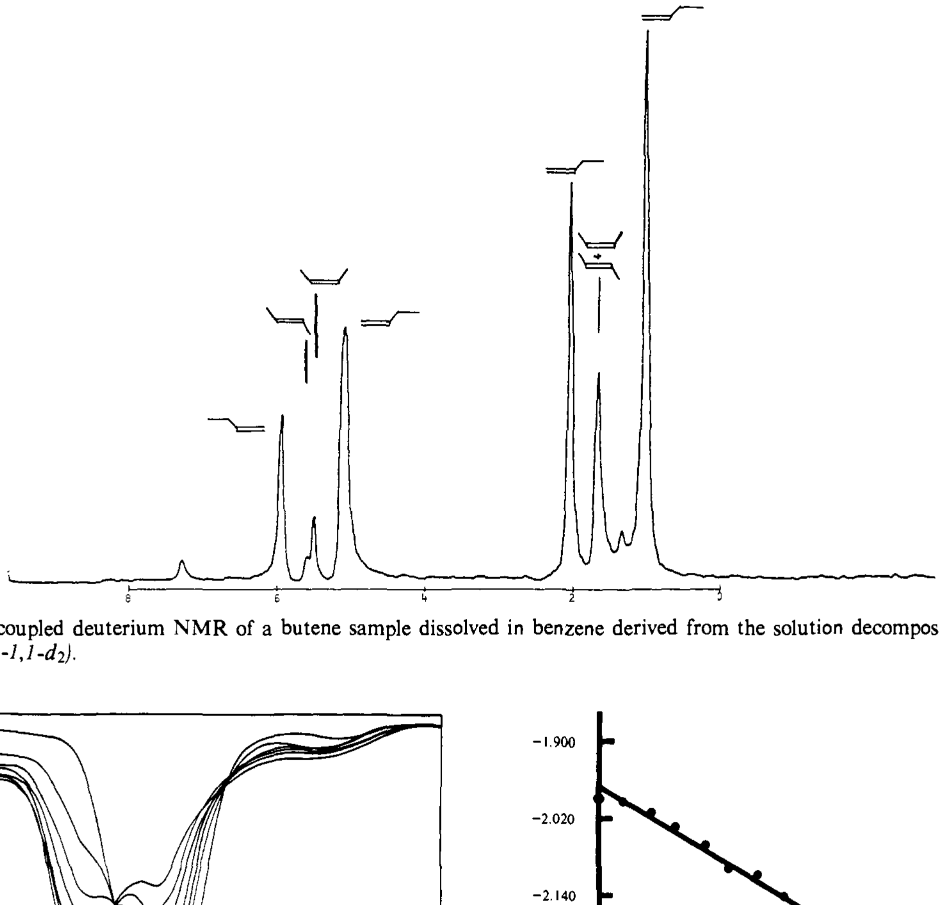


Figure 3. Proton decoupled deuterium NMR of a butene sample dissolved in benzene derived from the solution decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl-*1,1-d$_2$*).

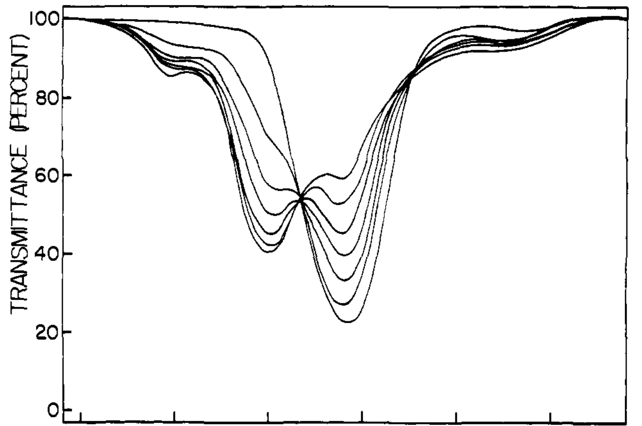


Figure 4. Change of infrared ν(CO) with time for (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl) in xylene solution of 61.2°. The peak at 1906 cm^{-1} is starting material and the peak at 1925 is (η^5-C_5H_5)Fe(CO)(PPh_3)H.

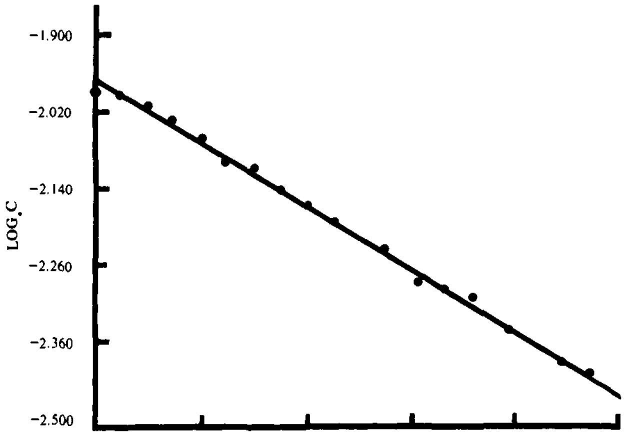
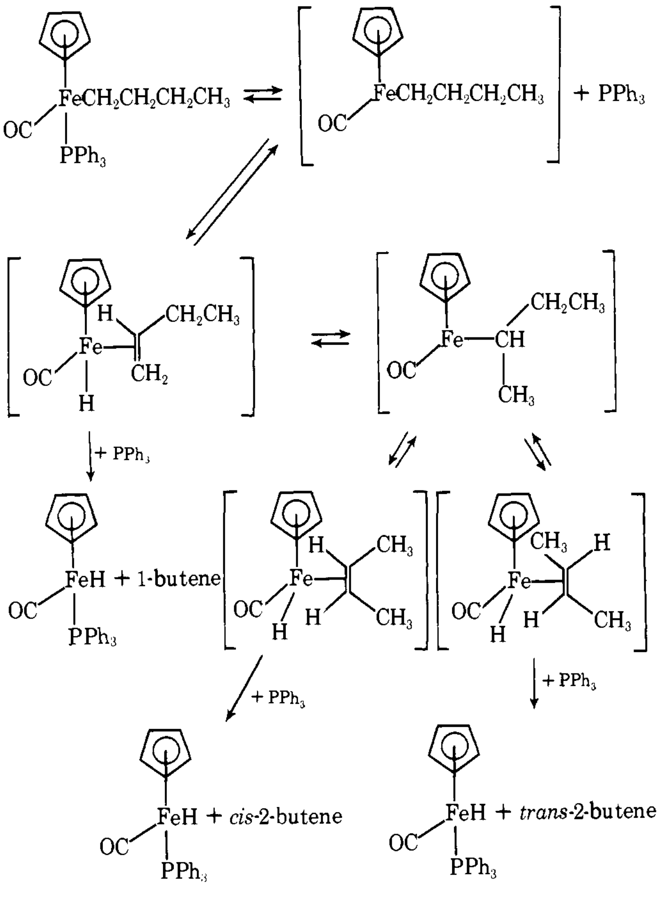


Figure 5. First-order rate plot of the decomposition of (η^5-C_5H_5)Fe(CO)(PPh_3)(*n*-butyl) in xylene at 61.2 °C.

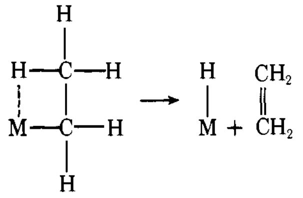
because they would form less stable (η^5-C_5H_5)Fe(CO)(butene)H intermediates.[28] The equilibria before the rate determining steps would completely scramble the deuterium labels in final butene products. This scrambling plus the data that show the deuterium label scrambled in starting material after as little as 0.1 half-life of the reaction support the contention

Scheme II



that the rate determining steps collapse the proposed olefin hydride intermediates. The scheme would follow first-order kinetics and only a small deuterium isotope effect would be expected. Retardation of the reaction by PPh_3 would be expected because it would alter the first equilibrium.

The primary significance of this study is to demonstrate that for the conversion of a transition metal alkyl into a metal hydride and olefin an open coordination site is necessary. It is particularly interesting to note that the direct expulsion of olefin as shown below must be a comparatively high energy process. It does not take place for this system at 90° over a 24-h



period as demonstrated by complete inhibition of the reaction studied here in the presence of excess phosphine. By implication, an open coordination site is also necessary for the reverse reaction, the insertion of an olefin into a metal-hydrogen bond, a reaction important in catalysis.

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