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The thermolysis of dicarbonylcyclopentadienyliron dimer: the formation of biferrocene

The thermolysis of dicarbonylcyclopentadienyliron dimer in a sealed tube at 300°C has been reported to produce ferrocene, carbon monoxide, carbon dioxide, cyclopentadiene and elemental iron. We observe in addition to these products the production of biferrocene and elemental carbon. Thermolysis of carbonylcyclopentadienyliron tetramer (produced from the dimer by thermolysis in refluxing xylene) produces ferrocene, iron and carbon monoxidre; no biferrocene, carbon dioxide or elemental carbon are produced. A scheme is proposed to account for these products.

Keywords: Dicarbonylcyclopentadienyliron dimer, monocarbonylcyclopentadienyliron tetramer, flame retardant, thermolysis

INTRODUCTION

The thermolysis of the dicarbonylcyclopentadienyliron dimer ($[\eta\text{-}C_5H_5Fe(CO)_2]_2$; $[CpFe(CO)_2]_2$; Fp_2) has been reported to produce two different products depending upon the temperature and the atmosphere in which the thermolysis is conducted. At low temperatures,[1–5] in solvent under a nitrogen atmosphere the product is reported to be the monocarbonylcyclopentadienyliron tetramer [$(\eta\text{-}C_5H_5Fe(CO))_4$; $(CpFeCO)_4$] at higher temperatures in a sealed tube the reported product is ferrocene.[6–8] Little detail has been provided about these reactions, but it has been suggested that the initial step is a dissociation of the dimer to produce monomer radicals.[8] The yield of ferrocene is 86% based upon cyclopentadiene (CpH) and 43% based upon iron.[7] The reaction is stated to be promoted at lower temperatures by the presence of hydrocarbon solvents. The yield is increased somewhat by the addition of free cyclopentadiene and unsymmetrical ferrocenes are obtained in the presence of substituted cyclopentadienes.[7] Thermolysis of the tetramer also produces ferrocene.[1–5] There is one report that suggests that the tetramer, upon thermolysis, leads first to the dimer and thence to ferrocene.[9]

We are interested in the potential utilization of this and similar compounds as flame retardants, especially for poly(methyl methacrylate). It is important to know the identity of the species that are produced upon thermolysis of the dimer alone, to be able to delineate a scheme for the reaction of the dimer with a polymer. In this paper we report on the thermolysis of the dimer and suggest a scheme which can lead to the observed products.

RESULTS

The thermolysis of Fp_2 in refluxing xylene produces only tetramer [$(\eta\text{-}C_5H_5Fe(CO))_4$; $(CpFe(CO))_4$] in relatively modest yields. Heating of the dimer to 160°C for 24 hr in a sealed tube causes no decomposition, and only starting material is recovered. Thermolysis of Fp_2 at 300°C in a sealed tube for 2 hr causes the complete decomposition of the dimer and an iron mirror forms on the walls of the reaction vessel.

The products that are observed for the thermolysis of the dimer at 300°C in a sealed tube are carbon monoxide, carbon dioxide, cyclopenetadiene, iron, carbon, ferrocene and biferrocene. From 1 mol of dimer, 3 mol of carbon monoxide, 1 mol each of iron and ferrocene are obtained and also approximately 0.1 mol of carbon dioxide, carbon, cyclopentadiene and biferrocene. Previous workers[6–9] have noted all of the above products except elemental carbon and biferrocene, both of which are produced in low yields.

In order to assist in the understanding of the reaction, the pyrolysis of methy dicarbonylcyclopentadienyliron dimer ($MeFp_2$) and pentamethyl dicarbonylcyclopentadienyliron dimer (Me_5Fp_2) were studied. Thermolysis of $MeFp_2$ alone produces both dimethylferrocene and tetramethylbiferrocene; thermolysis of an equimolar mixture of the unsubstituted Fp_2 and the monomethyl-substituted compound, $MeFp_2$, leads to the formation of ferrocene, methylferrocene, dimethylferrocene and mono-. di-, tri-, and tetra-methyl biferrocene. Thermolysis of Me_5Fp_2, on the other hand, produces only decamethylferrocene; no biferrocenes are observed.

The thermolysis of the tetramer proceeds quite differently from that of the dimer. It is reported in the literature that the product is ferrocene; one assumes that iron and carbon monoxide are also produced. In this laboratory, we observe that only half of the potential carbon monoxide is evolved; the remainder is left as insoluble residue. From 1 mol of tetramer, 2 mol of ferrocene and 2 mol of carbon monoxide are obtained. The residue consists of elemental iron (2 mol) with some carbon and oxygen in an unknown form. Heating of the tetramer with an excess of carbon monoxide to a temperature of 200°C for some time causes the formation of the dimer in modest yield. When the time of heating is increased the yield of dimer increases.

Thermogravimetric analysis

When 8 mg of dimer (Fp_2) is subjected to thermogravimetric analysis (TGA), 21% of the material is observed as residue. This residue is clearly elemental iron as its appearance is quite similar to that seen in the sealed-tube reactions. The volatiles from the TGA experiment were captured on a filter and analyzed by GC MS. The volatiles consist of three components: two which have a mass of 130 amu as well as ferrocene.

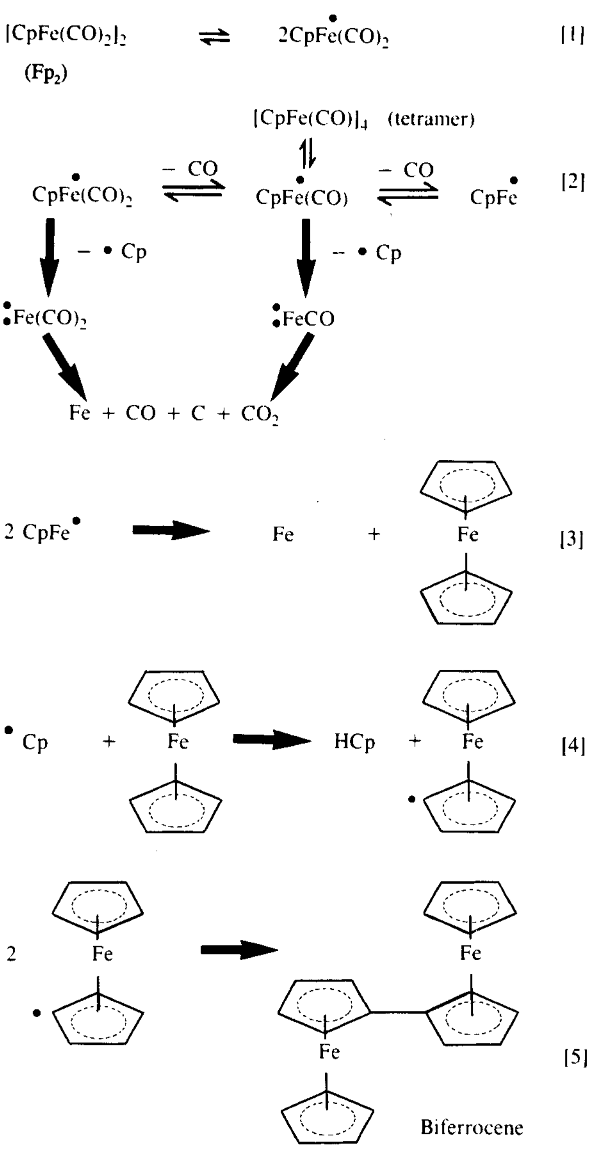
TGA analysis of the tetramer $[(\eta\text{-}C_5H_5Fe(CO))_4$; $(CpFe(CO))_4]$ is critically dependent on the amount of starting material. An 8 mg charge leads to about 50% residue, a 4 mg charge leads to 40% residue, and a 2 mg charge leads to 30% residue. Again the volatiles were captured on a filter and then analyzed by GC MS. The same three components were observed as for the dimer; ferrocene was more abundant for the thermolysis of the tetramer, whilst the two peaks with molecular weight 130 were more abundant for the thermolysis of the dimer.

DISCUSSION

It is apparent that there are at least three distinct pathways for the thermolysis of the dicarbonylcyclopentadienyliron dimer (Fp_2). These are: (1) formation of the tetramer; (2) formation of ferrocene; and (3) formation of biferrocene. Thermolysis under conditions which allow the escape of CO seem to favor the production of the tetramer, whereas in a sealed tube the tetramer is not obtained. The initial step has been suggested to form $Fp^\bullet$ radicals. The loss of carbon monoxide from this radical would produce a $CpFeCO^\bullet$ radical which could recombine with carbon monoxide to give $Fp^\bullet$ radical or tetramerize to give the tetramer. Presumably the equilibrium is more favorable for recombination in the presence of carbon monoxide. When the carbon monoxide is removed, recombination is no longer a viable reaction and only further reactions or association, to produce tetramer, are possible. As noted above, the reaction of the tetramer with an excess of carbon monoxide at 200°C produces the dimer.

The results from the thermolysis of an equimolar mixture of Fp_2 and the $MeFp_2$ indicate that the process is an intermolecular reaction. The lack of a biferrocene formation from the pentamethyl derivative indicates that the presence of at least one hydrogen atom on the cyclopentadiene ring is required. The observation that 1 mol of iron, 2 mol of carbon monoxide, and 1 mol of ferrocene are produced from 1 mol of dimer probably means that these materials are produced by one step in the pathway; the other materials that have been observed to arise from this thermolysis are present in much lower concentrations (about 10% of the amount of ferrocene observed) and these probably arise from another branch of the pathway.

Thermolysis of the tetramer $[(CpFe(CO)_4)_4]$ leads only to the formation of carbon monoxide, iron and ferrocene; no biferrocene is ever obtained from the tetramer regardless of the temperature. The appearance of the products from tetramer thermolysis is quite different from those of dimer thermolysis. The dimer produces an iron mirror which covers much of the surface of the tube, whereas the tetramer yields only a black deposit in the bottom of the tube, not unlike the deposit of carbon from the dimer. Psaro[9] has reported that heating a potassium bromide (KBr) pellet containing the tetramer to 200°C for 24 h results in the formation of the dimer. In this laboratory the tetramer was heated alone to 200°C for 20 h; ferrocene but no



Scheme 1

dimer was observed. When the tetramer is heated in the presence of carbon monoxide, dimer and ferrocene are observed. Psaro's result must be attributed to a matrix effect; perhaps decomposition of the tetramer produces carbon monoxide which is trapped in the matrix and then reacts to produce dimer.

A reaction pathway must account for the formation of all of the products and explain the differences in thermolysis of the dimer and tetramer. The fact that all of the carbon monoxide is evolved from the dimer and only half is evolved from the tetramer must also be addressed. It should be noted that ferrocene is quite stable thermally. In this laboratory it has been heated to 400°C in a sealed tube and recovered unchanged; thus ferrocene decomposition cannot be an important step in the pathway. The pathway shown in Scheme 1 is proposed to account for the observations.

The initial step is likely to be the dissociation of the dimer [(CpFe(CO)$_2$)$_2$] to prouce monomer radicals (Eqn [1]), as suggested by other workers.[8] This initial radical has two pathways open to it: it may lose carbon monoxide and give the CpFeCO$^\bullet$ radical or it may lose a Cp$^\bullet$ radical and give a dicarbonyliron diradical (Eqn [2]). The CpFeCO$^\bullet$ radical under mild conditions reacts with itself and gives the tetramer, whilst in the presence of carbon monoxide, dimer is produced. Under more severe conditions this material may lose a second carbon monoxide and produce the CpFe$^\bullet$ radical. The interaction of two CpFe$^\bullet$ radicals can form ferrocene with the elimination of iron (Eqn [3]). This process requires only the interaction of two radicals and is clearly an intermolecular process, as required by the thermolysis of the mixture of unsubstituted and methyl-substituted dimers. The CpFe$^+$ cation is a particularly abundant peak in the mass spectrum of Fp$_2$ and is postulated to arise by the same process.[10] It should also be noted that a CpNi$^\bullet$ radical is obtained upon flash-vacuum pyrolysis of nickelocene (Cp$_2$Ni).[11]

This scheme is also in agreement with the results of previous workers. Hallam[7] has observed that the addition of substituted cyclopentadienes gives rise to the production of unsymmetrical ferrocenes. Certainly the reaction of a CpFe$^\bullet$ radical with a cyclopentadiene molecule would produce a ferrocene. The by-product hydrogen radical would undergo further reaction and would not be detected.

An alternative scheme for the formation of ferrocene would be the interactrion of two CpFeCO$^\bullet$ radicals to produce η^5–CpFe(CO)$_2\eta^1$–Cp and iron metal. Loss of 2 mol of carbon monoxide from the iron complex will yield ferrocene. Alternatively the CpFe$^\bullet$ radical may interact with Fp$^\bullet$ radical or Fp$_2$; the elimination of carbon monoxide and iron may yield ferrocene. Both routes seem inconsistent with the observation of Hallam[7] that unsymmetrical ferrocenes are produced in the presence of substituted cyclopentadienes, since either would require the formation of a new substituted CpFeCO$^\bullet$ radical.

As noted above, the initial CpFe(CO)$_2^\bullet$ radical may also lose a cyclopentadienyl (Cp$^\bullet$) radical. The loss of a $Cp^{\bullet}$ radical from metallocenes has previously been reported.[11] Nickelocene under flash vacuum pyrolysis conditions gives 9,10-dihydrofulvalene by coupling of two $Cp^{\bullet}$ radicals. The fact that cyclopentadiene is observed as a product of the reaction, and the observation by TGA MS that indicates the formation of rearranged fulvenes, provide ample proof for this reaction. The loss of a $Cp^{\bullet}$ radical from $CpFe(CO)_2^{\bullet}$ yields the $Fe(CO)_2^{2\bullet}$ diradical. Since the amounts of cyclopentadiene, carbon dioxide, and carbon are similar, they are likely to be produced by the same process. Thermolysis[12] of $Fe(CO)_5$ produces elemental carbon and carbon dioxide as well as iron and carbon monoxide; thus $Fe(CO)_2^{2\bullet}$ diradical decomposes to produce, in equimolar amounts, iron, carbon dioxide, and elemental carbon (Eqn [2]).

Alternatively, the $CpFeCO^{\bullet}$ radical may be the species that loses a $Cp^{\bullet}$ radical to give an $FeCO^{2\bullet}$ diradical. This suggestion is supported by the observation that both dimer and tetramer thermolysis produce rearranged fulvenes. It is impossible to identify if one or both of these species, $CpFe(CO)_2$ or $CpFeCO^{\bullet}$, gives rise to the $Cp^{\bullet}$ radical.

The $Cp^{\bullet}$ radical may attack the ferrocene produced by the major branch of the pathway, giving neutral cyclopentadiene and a ferrocene radical (Eqn [4]). Dimerization of these radicals accounts for the formation of the biferrocene (Eqn [5]). It should be noted that this last reaction requires that the ferrocene have at least one hydrogen present for abstraction by the $Cp^{\bullet}$ radical. The termolysis of the pentramethyl derivative yields only decamethylferrocene; no biferrocene is produced since no hydrogen abstraction is possible from the completely substituted ferrocene.

The preparation of biferrocene has been accomplished by an Ullmann reaction of iodoferrocene and copper bronze[13] and by the coupling of mono- and dilithioferrocene with tri-n-hexylbromosilane.[14] Both reactions probably involve the coupling of two ferrocenyl radicals, as proposed in our Scheme.

Another scheme that has been considered for the formation of biferrocene is the reaction of either the $CpFe(CO)_2^{\bullet}$ radical or the $CpFeCO^{\bullet}$ radical with ferrocene. In the first case this may produce FpH and a ferrocenyl radical. Since FpH is known to decompose to Fp_2 and hydrogen (H_2), this decomposition will not lead to CpH, carbon and carbon dioxide. The reaction of $CpFeCO^{\bullet}$ radical with ferrocene could give a ferrocenyl radical and CpFe(CO)H. This unknown species may decompose to give CpH and a $FeCO^{\bullet}$ radical and the latter may then produce iron, carbon and carbon dioxide, analogous to the above case for the $Fe(CO)_2^{2\bullet}$ diradical. This latter pathway is thought to be unlikely because the observation of species with a molecular weight of 130 amu can only be explained by the dimerization of two $Cp^{\bullet}$ radicals and subsequent rearrangement of the fulvenes.

It is worthwhile to note that a GC MS study of Fp_2 shows ferrocene but not biferrocene. Under these conditions the cyclopentadienyl radical is more likely to encounter other reactive materials than a ferrocene molecule so the lack of production of biferrocene is not surprising. The $CpFe^{\bullet}$ radical may also encounter other reactive species; however no stable species are produced from these encounters so this radical should survive until it encounters a reaction partner. GC MS of a mixture of Fp_2 and $MeFp_2$ yields the spectrum of ferrocene, methylferrocene, and dimethylferrocene; even on the column the reaction is apparently intermolecular. This suggests that decomposition occurs immediately upon injection and ferrocene and cyclopentadiene are formed at the injector. GC MS of the tetramer yields only the spectrum of ferrocene and no other products are observed. In both cases the retention time is identical with that obtained when ferrocene is injected; this indicates that all reactions occur at the injection port. The mass spectrum of Fp_2 has been reported,[10] but we do not observe this spectrum under any conditions since thermolysis occurs upon injection and ferrocene is obtained. Ferrocene is a product of the electron impact study of Fp_2 and it is suggested that the formation of ferrocene occurs by an intramolecular process. Either the mass-spectral experiments are quite different from those reported in this work or the route to ferrocene needs to be re-examined.

As noted above, the TGA curves are unusually dependent upon the initial charge of material for the analysis. The literature reports about 50% residue[5,9] and suggests that this is due to the evolution of all ligands, cyclopentadiene and carbon monoxide as free ligands and that the iron is oxidized as it is formed to iron oxide by the oxygen impurity present in the helium. It is very unlikely that the amount of oxygen present in the helium is sufficient to oxidize the iron at all, and even more unlikely that the iron will all be oxidized as it is formed, and not at higher temperature. These workers also noted the formation of an orange deposit (ferrocene) on the walls of the container, which suggested that some iron is evolved in their experiment.

We reject this hypothesis and suggest instead that the decomposition does indeed proceed to form iron and ferrocene, as observed by GC MS analysis of the volatiles produced in the TGA experiment. The large sample (58 mg) used by Braunsten[5] permits either ferrocene or starting material to be trapped by the iron that is formed and leads to high residue content. Verification for this comes from a variation of the initial charge for the analysis and the observation that the amount of residue does decrease as the initial charge is decreased. Since the amount of iron produced is decreased, the possibility of trapping either starting material or product by the iron is lessened. Sealed-tube reactions (noted above) lead to a 19% residue for the dimer and 28% for the tetramer, in reasonable agreement with the TGA results which lead to 21% for the dimer and 30% for the tetramer.

Analysis of the volatiles from the TGA experiment indicate the presence of two components with molecular weights of 130. Analysis of the mass spectrum suggests that the compounds are substituted indenes. The scheme reported above for the decomposition of the dimer indicates the evolution of the cyclopentadienyl radical. Should this radical be evolved in the TGA experiment it will dimerize to give a dihydrofulvalene. Hedaya has reported that 9,10-dihydrofulvalene is produced by the flash-vacuum pyrolysis of nickelocene and that this material has a half-life for rearrangement to another dihydrofulvene of about 50 min at 30°C in heptane solution.[15] The fulvalene is no doubt unstable at 300°C and will undergo further rearrangement.

The differences in the decomposition pathways of the dimer and tetramer may be explained since, in the dimer pathway, the reactive species are CpFeCO$^{2\bullet}$ and CpFe(CO)$_2^\bullet$ radicals. For the tetramer pathway both tetramer and monomer (CpFeCO$^\bullet$) radicals may be important and they may react differently. Since no carbon dioxide or elemental carbon is formed in tetramer decomposition, the formation of these species must be attributed to some species not produced in the thermolysis of the tetramer and this is most likely to be the CpFe(CO)$_2^\bullet$ radical. According to the above scheme, if CpFeCO$^\bullet$ were the only reactive species in tetramer decomposition then only iron and ferrocene would be expected. The observation of an iron carbide/iron oxide mixture must arise from reaction of the tetramer, rather than the monomer radical, since it is not observed in dimer decomposition where only the monomer radical is present. The fact that more ferrocene and less rearranged fulvenes arise from the tetramer may also indicate that the tetramer reacts without prior decomposition.

It has been suggested[9] that the tetramer decomposes to produce dimer first which then leads to ferrocene. Such a scheme seems unlikely and the observations are explained by the above scheme. The tetramer gives monomer radical which may either combine with carbon monoxide to give the Fp$^\bullet$ radical (and hence dimer) or it may lose carbon monoxide to give the CpFe$^\bullet$ radical and hence ferrocene.

CONCLUSION

A scheme has been presented which accounts for the thermolysis of Fp$_2$ and indicates that several radicals are produced in the decomposition. Any thermal reaction of the dimer with a substrate must take into account these radicals as possible reactants with the substrate on the path to products. We are currently examining reactions of Fp$_2$ with various substrates to determine which of the radicals produced by its thermolysis are involved in the reaction.

EXPERIMENTAL

A 1.0 g sample of dimer [(CpFe(CO)$_2$)$_2$]; was placed in a thoroughly evacuated vessel and the vessel was once again thoroughly evacuated for several hours. The tube was sealed off from the vacuum line and placed in a muffle furnace which had been preheated to 300°C for 2 h. After 2 h, the oven was turned off and allowed to cool to room temperature. (*Caution. Tubes have been known to explode from gas pressure and care must be exercised.*) Upon removal from the oven, a metallic sheen might be noted within the tube. The tube was cooled in liquid nitrogen, then opened. The contents of the tube were washed repeatedly with chloroform (100 cm^3) to remove all soluble materials. The solvent was removed from this fraction on a rotary evaporator and the fractions were separated by column chromatography on silica. Ferrocene could be removed with hexane (250 cm^3) whilst biferrocene was removed with chloroform (250 cm^3). Ferrocene was identified by melting point, mixed melting point, and spectroscopic methods. Biferrocene was identified by mass spectroscopy and a crystal structure determination. The structure was obtained and refined as previously described.[17] The structure was identical to that previously reported.[16t] The chloroform-insoluble fraction was added to nitric acid (100 cm^3, 0.10 mol dm^{-1}) and allowed to remain overnight. The solution was decanted, reduced to the divalent state with zinc (5 g) and titrated with potassium permanganate (0.1 mol dm^{-1}). The appearance of the nitric acid-insoluble residue indicated it to be carbon but it was nonetheless combusted with oxygen and the effluent was passed into a calcium hydroxide solution and calcium carbonate was precipitated to confirm that this material was indeed elemental carbon.

Some experiments were performed in vessels equipped with break-seals. After the tube was removed from the oven, it was re-attached to the vacuum line and the break-seal was opened. Non-volatiles were quantiated by pressure–volume–temperature measurements and identified by infrared spectroscopy. After removal of the non-volatiles, the tube was allowed to warm to room temperature and the volatiles were pumped into a U-tube. Infrared spectroscopy was used to identify this as a mixture of cyclopentadiene and carbon dioxide. The carbon dioxide was separated by vacuum line techniques[18] and each gas was independently determined. The cyclopentadiene was also identified by mass spectroscopy. The tube was then removed from the vacuum line and worked up as above.

These procedures led to the following results. A 1.0 g sample of $[(CpFe(CO)_2]_2$ dimer (2.8 mmol) gave 0.23 g (8.3 mmol) CO, 0.17 g (3.0 mmol) iron, 0.42 g (2.2 mmol) ferrocene, 0.07 g (0.2 mmol) biferrocene, 0.006 g (0.1 mmol) C_5H_6, 0.01 g (0.23 mmol) CO_2, and 0.03 g (2.5 mmol) elemental carbon. The result for carbon is given as the residue that was left in the vessel after completion of the experiment and is undoubtedly in error. Total recovery is about 93% for the best case. The results for ferrocene and biferrocene were obtained by integration of the gas chromatogram for the entire soluble fraction. Very small amounts of other compounds were observed by gas chromatography–mass spectroscopy (GC MS). These products are more volatile than biferrocene and contain iron. These were presumably products from other radical reactions but proceeded in amounts too small to permit characterization.

The recoveries may be expressed as functionalities. A 1.0 g sample of Fp_2 contains 5.6 mmol iron, 5.6 mmol Cp, and 11.2 mmol CO. Recoveries are 5.6 mmol iron (100%), 5.3 mmol Cp (95%), 8.9 mmol oxygen (80%), and 10.3 mmol carbon (92%). The recoveries of iron, cyclopentadiene and carbon are reasonable, whilst the result for oxygen is uncomfortably low. It should be noted that the tube contains a small amount of black residue which cannot be removed. This residue could not be analyzed but is postulated to contain the materials that were not recovered.

The thermolyses of the methyl and pentamethyl derivatives were conducted in an identical fashion. These reactions were performed in standard vessels and the amount of gas produced was not measured. After separation of the soluble and insoluble fractions the soluble fraction was analyzed by GC MS.

The tetramer was prepared according to the procedure of Landon and Rheingold[3] and its purity was ascertained by infrared spectroscopy. A 0.50 g (0.84 mmol) sample of the tetramer was thermolyzed at 300°C for 2 h in a vessel equipped with a break-seal. Upon removal from the oven an orange vapor filling the tube could be observed (presumably ferrocene), and also a black deposit at the bottom of the tube. There was no iron mirror formed like that observed with the dimer. After re-attachment to the vacuum line, the break-seal was opened and 1.7 mmol of gas was determined by pressure–volume–temperature measurements and identified as carbon monoxide by infrared spectroscopy. All volatiles were removed from the tube by pumping and a trace (less than 0.1 mmol) of volatile material was obtained. This was identified as cyclopentadiene by infrared and mass spectroscopy. The vessel was removed from the vacuum line, chloroform was added to the contents, and the solution was filtered to leave a soluble fraction (0.30 g), identified as ferrocene by mass spectroscopy, and an insoluble fraction (0.14 g). The insoluble portion was analyzed for carbon, oxygen and iron and was found to contain 21% oxygen, 9% carbon, and the balance was found to be iron. The mass balance for this is excellent; 0.05 g carbon monoxide, 0.14 g insolubles, 0.30 g solubles, and 0.006 g HCp are recovered for an initial charge of 0.50 g. The recovery is much better for the tetramer than it is for the dimer. In mole terms, one-half of the carbon monoxide is recovered as vapor and one-half in the insoluble fraction in an unknown form. Almost all of the cyclopentadiene is recovered as ferrocene with only a trace present as free cyclopentadiene and one-half of the iron is observed as free iron with the balance as ferrocene.

In order to test whether the tetramer may be converted to the dimer in the presence of carbon monoxide, a tube was charged with 0.10 g $(CpFeCO)_4$ (0.17 mmol) and about 1 mmol of carbon monoxide. The tube was heated for 2 h at 200°C. Upon removal from the oven, weak carbonyl bands at 1760, 1935, and 1993 cm^{-1}, in addition to the tetramer vibration at 1620 cm^{-1}, are observed in the infrared spectrum. The same sample was heated for 24 h at 200°C with the same amount of carbon monoxide. Upon removal from the oven, an orange vapor was observed. Infrared spectroscopy showed more intense dimer carbonyl vibrations and the presence of ferrocene.

A 1.0 g sample of ferrocene was placed in an evacuated vessel and heated to 400°C for 2 h. After the vessel cooled, it was removed from the oven and opened. Analysis by chromatography and mass spectroscopy confirmed that the ferrocene was unchanged by this treatment.

Infrared spectra were obtained on an Anelect FX-6200 FT-IR spectrometer. ^1H NMR spectra were obtained on a Varian EM-360 spectrometer; ^{13}C NMR spectra were obtained on a JEOL FX-60 spectrometer. Mass spectra were obtained with a Hewlett–Packard 5890A gas chromatograph with a 5970 mass selective detector. Thermogravimetric analysis was carried out on a Perkin–Elmer model TGA-7 instrument. The volatiles were trapped on a porous filter and this trap was used for GC MS analysis. The sample was desorbed with a Chemical Data Systems model CDS-330 desorber interfaced to a Finnegan 4023 GC MS system.

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