

## ELECTROPHILIC CLEAVAGE OF THE IRON—CARBON SIGMA BOND: MECHANISM AND THE STEREOCHEMISTRY AT IRON

THOMAS C. FLOOD\* and DAVID L. MILES

*Department of Chemistry, University of Southern California, University Park, Los Angeles,  
CA 90007 (U.S.A.)*

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### Summary

Electrophilic cleavage of the iron—carbon sigma bond in the resolved chiral complexes  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{R}$  (where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $-\text{CH}_2\text{CO}_2$  (menthyl), and  $-\text{CH}_2\text{O}$  (menthyl)) by  $\text{I}_2$ ,  $\text{ICl}$ , and  $\text{HgI}_2$  reveals that the reaction proceeds with net retention of configuration at iron, but stereospecificity is not high and is insensitive to the nature of the alkyl group. In every case, recovered starting material is partially racemized, but the source of this is not yet certain. Formation of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  from cleavages using  $\text{ICl}$  indicates that initial electrophilic attack is at the metal. A mechanism is discussed which accounts for net retention at metal in terms of steric and ion pairing rather than electronic effects. Cleavage using  $\text{HO}_2\text{CCF}_3$  forms  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{O}_2\text{CCF}_3$  of ca. 50% enantiomeric excess as shown by the use of an optically active Eu NMR shift reagent, but net retention or inversion at iron cannot be inferred.

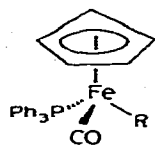
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### Introduction

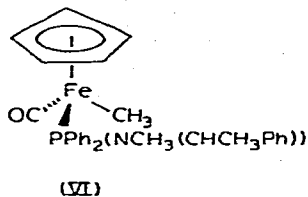
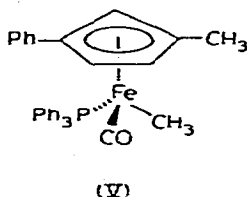
Electrophilic cleavage reactions of metal—carbon sigma bonds find significant use in the removal of organic ligands from metals in a variety of organometallic systems [1]. One principal application of such cleavage has been in the study of mechanisms of formation and reaction of metal—carbon bonds, with the result that the importance of understanding the mechanisms of the cleavage reactions themselves is generally recognized. Carbon stereochemistry has been of considerable use in this regard, [2-4] but while necessary, it is of course not sufficient for development of a detailed mechanistic understanding.

We therefore undertook to evaluate the usefulness of metal stereochemistry in the study of electrophilic cleavage reactions of iron—carbon sigma bonds. This paper describes our results using the resolved chiral iron alkyls I-IV, whose preparation, resolution, and optical assay have been reported elsewhere [5]. During the course of our investigations, other groups have published related work

on similar systems. Attig and Wojcicki [6] have separated the diastereoisomers of V (as pairs of enantiomers) and have cleaved the Fe—CH<sub>3</sub> bond with HI, HgI<sub>2</sub>, and



- (I) R = CH<sub>2</sub>CO<sub>2</sub> (menthyl)  
 (II) R = CH<sub>2</sub>O (menthyl)  
 (III) R = CH<sub>3</sub>  
 (IV) R = CH<sub>2</sub>CH<sub>3</sub>



I<sub>2</sub>. Brunner and Wallner [7] \* have studied the halogen cleavage of one diastereomer of optically pure VI, and have shown by a reaction cycle that it proceeds with net retention of configuration at iron, granting several reasonable assumptions (see below).

In the present studies, both enantiomeric and single enantiomers of diastereomeric iron alkyls with a variety of alkyl groups have been employed. Our results therefore provide additional information from the use of a variety of alkyl groups, the use of several different electrophiles, and the execution of a number of control experiments. The fact that the observed net retention at iron in these reactions is not an electronic requirement of the suggested mechanism is discussed, and some cautionary comments on the current interpretation of starting material racemization in these chiral iron systems are offered.

## Results

Cleavage of the iron—carbon sigma bond has been carried out on alkyls I—IV using I<sub>2</sub>, ICl, HgI<sub>2</sub>, and HOCOCF<sub>3</sub> (see Table 1) with formation of products as shown in Scheme 1. The alkyl products have not been isolated in the present work, but these have been thoroughly characterized in a number of related cases [1c,2,8]. Material balance is reasonable (except in the ICl cleavages) but not quantitative, presumably owing to over-oxidation since the compounds hold up well to isolation procedures. In general, the reaction is not highly stereospecific at iron. *S*-Alkyls (configuration shown in Scheme 1 \*\*) yield iron iodide VII varying in optical purity from nearly racemic to possibly 90% enantiomeric excess (ee) (as an upper limit, see below) which we assign the *R* configuration (shown in Scheme 1, see arguments for this assignment below) in any cleavage reaction using an iodine containing electrophile. When optically active iodide VII is treated with each electrophile under cleavage reaction conditions (benzene, 5°C, up to 30 min) it is recovered with undiminished activity (see Table 2), although it is to be noted that under slightly more vigorous conditions VII was racemized by I<sub>2</sub> or HgI<sub>2</sub> but not by HO<sub>2</sub>CCF<sub>3</sub>.

\* We thank Professor Brunner for communication of results prior to publication.

\*\* In previous publications we have used sequencing rules for the assignment of *R* and *S* designations suggested by Davison and Martinez [24]. Current consensus seems to favor the less ambiguous rules suggested by Stanley and Baird [25], so that the latter rules have been used in the present paper.

TABLE 1  
ELECTROPHILIC CLEAVAGE REACTIONS OF CpFe(CO)(PPh<sub>3</sub>)R

R	FeR (%ee)	Electrophile <sup>a</sup> (FeR/elec)	Conditions	% Yield <sup>b,c</sup>		% Recovered <sup>d</sup> (%ee)	Stereospes. of FeX formation <sup>e</sup>	Retention in FeR recovered (%)	Material <sup>e</sup> balance
				FeX	FeR				
CH <sub>2</sub> CO <sub>2</sub> Men	91	I <sub>2</sub> (2)	25°C, 1/2 h	34	96	(70)	—	77	65
CH <sub>2</sub> OMen	pure	I <sub>2</sub> (1.3)	5°C, 1/2 h	94	0	—	4	—	72
CH <sub>3</sub>	pure	I <sub>2</sub> (2)	5°C, 6 min	69	82	(33)	67	33	76
CH <sub>3</sub>	pure	I <sub>2</sub> (4.1)	5°C, 1/2 h	77	67	(0)	19	0	70
CH <sub>2</sub> OMen	pure	ICl (1.3)	5°C, 1/2 h	67 <sup>f</sup>	0	—	13	—	44
CH <sub>3</sub>	pure	ICl (4.1)	5°C, 6 min	13 <sup>e,f</sup>	53 <sup>e</sup>	(61)	44	61	66
CH <sub>2</sub> CO <sub>2</sub> Men	91	HgI <sub>2</sub> (2)	25°C, 1/2 h	36	100	(76)	—	86	68
CH <sub>2</sub> OMen	pure	HgI <sub>2</sub> (2)	25°C, 1/2 h	46	74	(82)	7	82	60
CH <sub>3</sub>	83	HgI <sub>2</sub> (4)	5°C, 1/2 h	91	71	(32)	15	39	76
CH <sub>3</sub>	pure	HO <sub>2</sub> CCF <sub>3</sub> (2)	5°C, 1/2 h	82 <sup>g</sup>	100	(76)	56	76	97
CH <sub>2</sub> CH <sub>3</sub>	90	HO <sub>2</sub> CCF <sub>3</sub> (2)	5°C, 1/2 h	69 <sup>g</sup>	89	(40)	37	44	79
CH <sub>2</sub> CO <sub>2</sub> Men	91	FeCl <sub>3</sub> · 6 H <sub>2</sub> O (2) <sup>h</sup>	25°C, 1/2 h	—	30 <sup>e</sup>	(92)	—	100	—
CH <sub>2</sub> CH <sub>3</sub>	82	FeCl <sub>3</sub> · 6 H <sub>2</sub> O (2.3) <sup>h</sup>	25°C, 1/2 h	—	37 <sup>e</sup>	(0)	—	0	—
CH <sub>3</sub>	pure	I <sub>2</sub> (2) <sup>i</sup>	5°C, 6 min	100 <sup>j</sup>	36 <sup>j</sup>	(94)	94	—	69

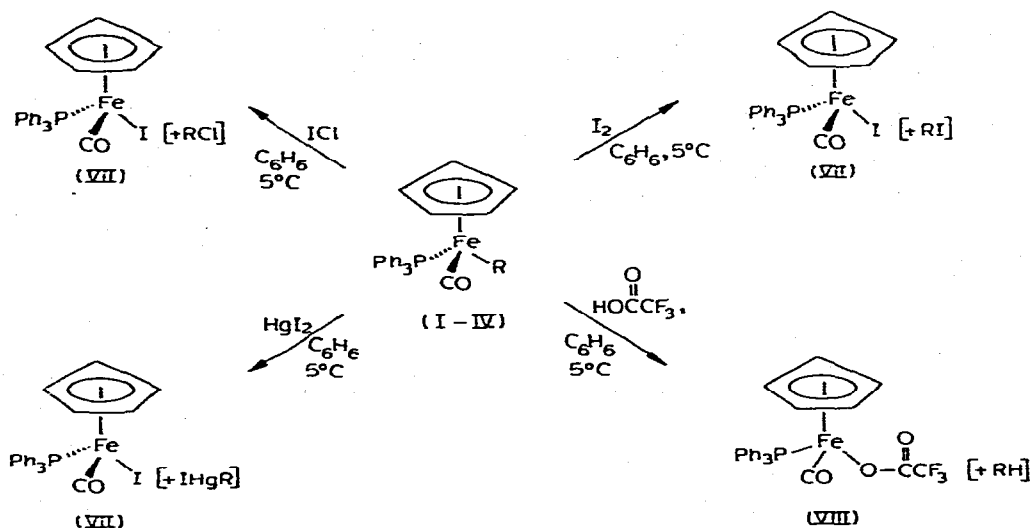
<sup>a</sup> Benzene solvent, FeR ca. 5–10 X 10<sup>-3</sup> M; FeR/elec. is the molar ratio of reactants, <sup>b</sup> Based on electrophile used, <sup>c</sup> These enantiomeric excess and stereospecificity figures are maximum possible values; see the text, <sup>d</sup> Based on molar excess of iron alkyl over electrophile used, <sup>e</sup> Based on total iron used, <sup>f</sup> Product is iron iodide, VII, <sup>g</sup> Product is iron trifluoroacetate, VIII, <sup>h</sup> THF solvent, <sup>i</sup> 10 molar equivalent of P(*p*-tolyl)<sub>3</sub> was added, <sup>j</sup> No replacement of PPh<sub>3</sub> by P(*p*-tolyl)<sub>3</sub> in this product occurred.

TABLE 2  
OPTICAL STABILITY OF  $CpFe(CO)(PPh_3)I$  UNDER VARIOUS CONDITIONS

Conc. of X ( $M \times 10^3$ ) <sup>a</sup>	Conc. of added reagent ( $M \times 10^3$ ) <sup>a</sup>	Time (h)	Temperature (°C)	Racemization of isolated X
1.9	I <sub>2</sub> , 2.0	4	23	racemic
1.9	HI, saturated	4	23	no racemization
1.9	HgI <sub>2</sub> , 3.1	4	23	racemic
5.6	I <sub>2</sub> , 1.4	0.5	5	no racemization
5.6	HgI <sub>2</sub> , 1.3	0.5	5	no racemization
5.2	CF <sub>3</sub> CO <sub>2</sub> H, 1.3	0.5	5	no racemization
1.8	KI in SO <sub>2</sub> , 2.2	4	-10	no racemization
1.3	PPh <sub>3</sub> , 5.5	24	23	no racemization
1.3	R <sub>4</sub> N <sup>+</sup> I <sup>-</sup> , 2.2	24	23	no racemization

<sup>a</sup> Concentration in total reaction mixture in benzene.

SCHEME 1



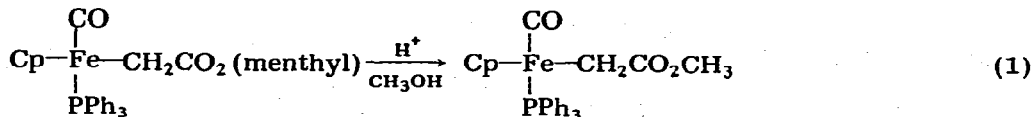
If a deficiency of electrophile is used in reactions of iron alkyls with I<sub>2</sub>, ICl, or HgI<sub>2</sub>, then the excess alkyl may be recovered. In every case, such recovered alkyl is racemized to some extent\*. Neither the amount of racemization of starting material nor of product seems to correlate with the nature of the alkyl group. Alkyl I-IV and iodide VII are optically stable at room temperature to the presence of I<sup>-</sup> and PPh<sub>3</sub> in solution. When I is partially oxidatively destroyed by 1/2 equivalent of FeCl<sub>3</sub> · 6 H<sub>2</sub>O in THF, recovered I showed no loss of optical purity (Table 1), but ethyliron III recovered from the same treatment has suffered complete racemization. Cleavage of methyliron III by 1/4 equivalent of I<sub>2</sub> in ben-

\* Such partial racemization of starting material has also been observed by Wojcicki [6] and Brunner [7].

zene in the presence of 10 molar equivalents of  $P(p\text{-tolyl})_3$  led to formation of iodide VII with no incorporation of  $P(p\text{-tolyl})_3$ .

A further important observation is that when ICl is used as the electrophile, only iodide VII is isolated. Thin layer chromatography of the reaction mixture shows a trace of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$ , but there is always an equilibrium quantity of  $\text{Cl}_2$  of ca. 0.3% present in ICl [9]. Treatment of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  with one equivalent of ICl in benzene for 30 min leads to reisolation of only the chloride, no VII was detected, so that formation of VII must occur during, rather than after, cleavage of the iron alkyl.

Protonic acid does eventually lead to the destruction of I or II, but these compounds have special pathways available to them. Ester I, for example, will undergo rapid transesterification in methanol with a trace of sulfuric acid, but the

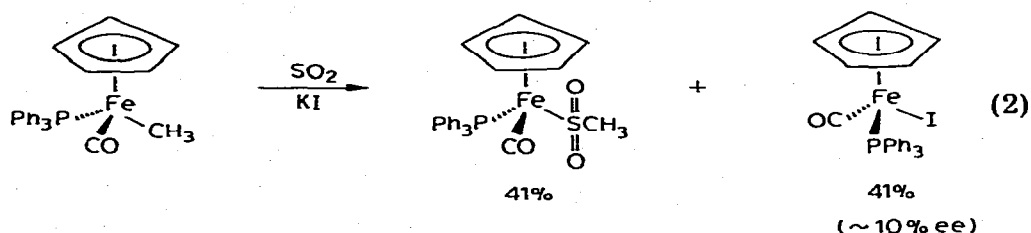


product is totally racemic. Ether II reacts with HX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) to yield  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CH}_2\text{X}$  which is itself rather resistant to cleavage, but slowly extrudes methylene to form  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$  [5]. Ether II reacts with  $\text{HBF}_4$  at low temperature forming a species which is a methylene transfer reagent [10]. Alkyls III and IV, however, react as expected when treated with trifluoroacetic acid leading to the iron trifluoroacetate, VIII, and presumably methane and ethane, respectively. As shown in Table 1, VIII is of 30–60% ee, and if an excess of iron alkyl is employed, the recovered alkyl is significantly racemized. Optical assay of VIII is easily accomplished through the use of NMR spectroscopy and the optically active shift reagent tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III),  $\text{Eu}(\text{opt})_3$ . The trifluoroacetate group is basic enough to complex with  $\text{Eu}(\text{opt})_3$  and this results in the formation of diastereomeric Fe–Eu complexes. The Cp group, normally a doublet ( $J(\text{HP}) \sim 1 \text{ Hz}$ ) at  $\delta$  4.6 ppm for VIII itself, gives rise to two diastereotopic resonances in the presence of  $\text{Eu}(\text{opt})_3$  which are separated by up to  $\delta$  0.2 ppm. Direct integration then yields the desired information. Trifluoroacetate VIII is racemized very slowly in the presence of trifluoroacetic acid at concentrations in excess of that used in the cleavage reaction, so that only very little of the observed racemization of VIII from the cleavage of III or IV can be due to product instability to protic acid. The circular dichroism spectrum of VIII (see below) is significantly different from all of the other spectra of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$  derivatives that we have observed, so that at this point, it cannot be inferred whether VIII is of retained or inverted stereochemistry at iron.

Optical assay of iron iodide VII could not be carried out directly with the use of NMR and a shift reagent because there is no functional group in VII which is sufficiently basic to interact with such a reagent. Neither did optically active solvents (e.g.  $\alpha$ -phenethylamine) lead to diastereotopic chemical shift differences. Crystallization of partially active VII led to the formation of less active crystalline material, so that finally a reasonable lower limit of optical purity could be established by extraction of the more active material into cyclohexene, evaporation of solvent, and re-extraction of the more enriched material. In this way,

a  $[\theta]_{408}$  of  $16.5 \times 10^3$  was reached \* which represents a minimum possible value for the pure material and serves to establish that these cleavage reactions are not highly stereospecific.

The absolute configuration of iron alkyls I–IV is known from the X-ray structure determination of I and II [11] and from the fact that III and IV are prepared from II with no change in configuration at iron [5]. Alkyls having an *S* configuration all exhibit a positive maximum in the 300–350  $m\mu$  region of their CD spectra. Although the absolute configuration of VII has not been shown by crystallography, there is strong evidence to indicate that *S* alkyls yield *R* iodide: (a) the CD spectrum of VII is similar to those of the iron alkyls, except that the maximum of 300–350  $m\mu$  is shifted to 353  $m\mu$ . This maximum is of positive sign for VII derived from *S* alkyls in all the electrophilic cleavage reactions; (b) Methylene extrusion from (*R*)-CpFe(CO)(PPh<sub>3</sub>)CH<sub>2</sub>I [12] \*\* yields (+)<sub>353</sub>-VII, in which process it is difficult to imagine inversion at iron unless one invokes involved bimolecular mechanisms; (c) when the SO<sub>2</sub> insertion is carried out in the



presence of iodide ion, the iron iodide formed is (–)<sub>353</sub>-VII (eq. 2), wherein a retention mechanism is difficult to imagine [5a]. All of these facts taken together argue for retention of configuration at iron upon formation of VII in electrophilic cleavage reactions. In addition, Brunner and Walner [7] have shown by means of a cyclic set of reactions that at least in the case of I<sub>2</sub> and Br<sub>2</sub> cleavage, retention of configuration results from compound VI \*\*\* [7].

## Discussion

Halogen cleavage of CpFe(CO)<sub>2</sub>CHDCHDC(CH<sub>3</sub>)<sub>3</sub> has been shown to proceed with clean inversion of configuration at carbon, while mercuric chloride cleavage leads to retention of configuration at carbon in the alkylmercuric chloride product [2]. Also, kinetic studies of HgCl<sub>2</sub> cleavage of CpFe(CO)<sub>2</sub>CH<sub>3</sub> have shown the reaction to be first order in iron alkyl and second order in HgCl<sub>2</sub> [13]. There is no evidence to suggest that CpFe(CO)<sub>2</sub>R compounds react differently than CpFe(CO)(PPh<sub>3</sub>)R, so that any reasonable mechanism for electrophilic cleavage

\* Iodide VII is deep green in color, and it has been found to be much too strongly absorbing to allow ORD measurements on the Perkin–Elmer 141. Circular dichroism intensities (as molecular ellipticities) at 408  $m\mu$  were therefore measured instead on a Carey 61 CD spectrometer.

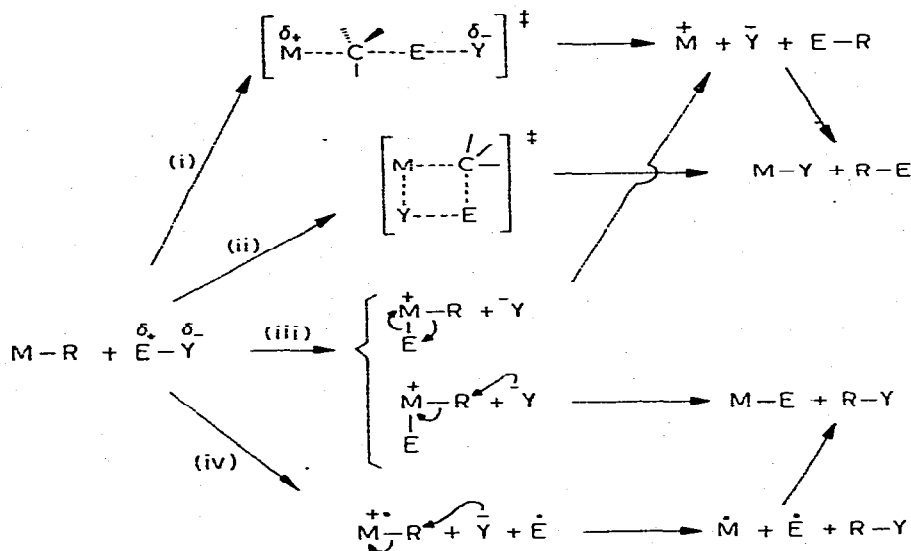
\*\* Note that this *R* molecule has the same absolute configuration as the *S* alkyls, but the presence of the iodide group leads to the reversal of the usual CO > alkyl priority.

\*\*\* Only one diastereomer of VI was used, but stereospecificity was moderately high for this compound, and Attig and Wojcicki [6] found only moderate amounts of asymmetric induction in cleavage reactions of their diastereomers, V. The only other assumption in Brunner's cycles is that the two reactions  $\text{FeR} + \text{I}_2$  (or  $\text{Br}_2$ )  $\rightarrow$   $\text{FeI}(\text{Br})$ , and  $\text{FeI} + \text{Br}_2 \rightarrow \text{FeBr}$  proceed with the same stereochemistry.

must account for the above facts, as well as the partial retention of configuration at iron, and possibly the partial racemization of starting iron alkyls recovered from these reactions.

Four likely cleavage mechanisms are shown in Scheme 2. Paths (i) and (ii) are

SCHEME 2



representations of the classical  $S_E2$  mechanisms leading to inversion ( $S_E2$  open) and retention ( $S_E2$  closed) at carbon respectively. Reactions (iii) and (iv) are what may be called prior oxidation pathways and involve (potentially reversible) formation of intermediates before the M-R bond is actually broken. Stereochemical data for carbon in the halogen cleavage, for example, are consistent with path (i), (iii), or (iv). The fact that starting chiral iron alkyls are recovered partially racemized would rule out path (i) if it could be shown that the racemizing intermediate is on the mechanistic path to cleavage, (see below). There is good evidence from other sources, however, that intermediates are involved in the cleavage of iron-carbon bonds by halogens\* and there is strongly suggestive evidence for this in cleavage by mercuric salts as well\*\*. Furthermore, in the dicarbonyl series,  $\text{CpFe}(\text{CO})_2\text{R}$ , paths (iii) and (iv) appear to be distinctly different since electrophiles such as  $\text{H}^+$ ,  $\text{Hg}(\text{II})$ , and  $\text{I}_2$  or  $\text{Br}_2$  lead to different products than do presumed one-electron oxidants such as  $\text{O}_2$ ,  $\text{Cu}(\text{II})$ , or  $\text{Ce}(\text{IV})$  upon cleavage of Fe-C bonds [1c,2]. This argument is, of course, only suggestive for the phosphine substituted iron compounds I-IV since this dichotomy of behavior has not yet been demonstrated for them.

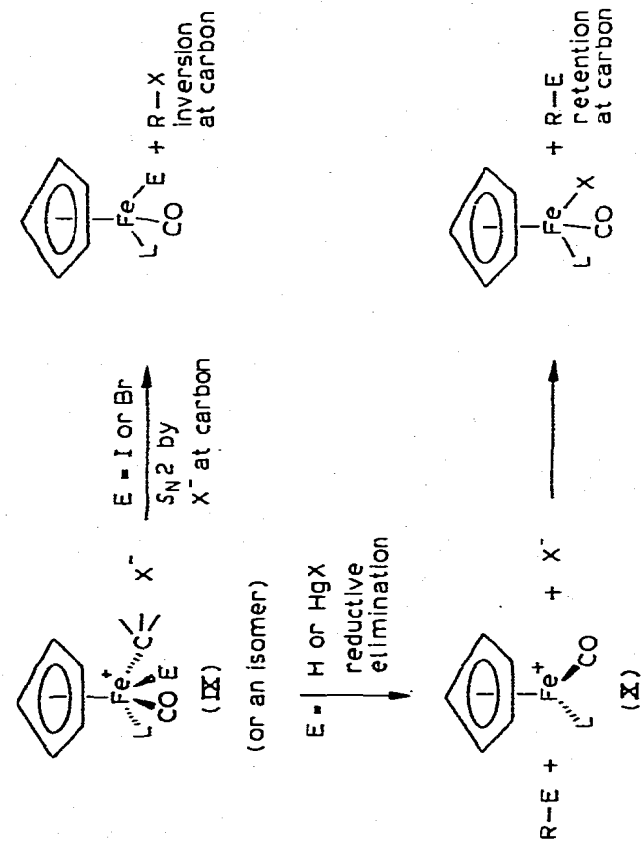
Path (iii) for the iron systems at hand would proceed as in Scheme 3\*\*\*. Di-

\* Cleavage of  $\text{CpFe}(\text{CO})_2\text{CD}_2\text{CH}_2\text{Ph}$  by halogens proceeds via a phenonium ion intermediate [8,26].

\*\* Cleavage of  $\text{CpFe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  by  $\text{HgCl}_2$  affords  $\text{CpFe}(\text{CO})_2\text{HgCl}$ , which is consistent with an Fe-Hg coordinated intermediate [13].

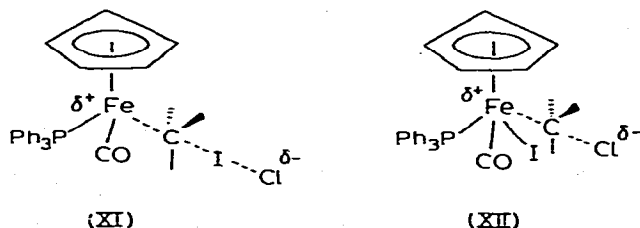
\*\*\* This basic mechanism has also been suggested by others [2,6,15,26].

SCHEME 3



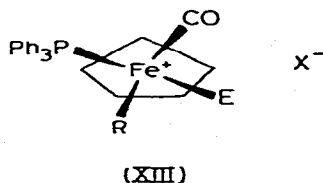


rect oxidative addition of "Br<sup>+</sup>" and "I<sup>+</sup>" [14], H<sup>+</sup> [15,16], and HgX<sub>2</sub> [17] to 18-electron organometallic complexes is well known, and would be expected to give the square pyramidal geometry, as shown for IX in Scheme 3, characteristic of (arene)ML<sub>4</sub> neutral [18] and cationic [19] species. Then, if the electrophile in IX were "Br<sup>+</sup>" or "I<sup>+</sup>", reductive elimination (to form X) would be slow with respect to backside nucleophilic attack at carbon by the anionic counterion. In this regard, the experiment employing ICl is an important one since mechanism (i) of CpFe(CO)(PPh<sub>3</sub>)Cl while path (iii) would produce VII via transition state XII. The fact that only VII is formed argues for path (iii) (or possibly (iv)).



If the electrophile in intermediate IX were H<sup>+</sup> or HgX<sup>+</sup>, then reductive elimination would be fast with respect to backside attack at carbon by the counterion, ion pair X would form, and this would close to product.

Net retention of configuration of VII is not a necessary feature of this mechanism; indeed, totally racemic iodide might reasonably be expected. One possible explanation for retention is that the entering electrophile attacks iron *anti* to the sterically dominating PPh<sub>3</sub> group to give XIII. In iodine cleavage, loss of RX

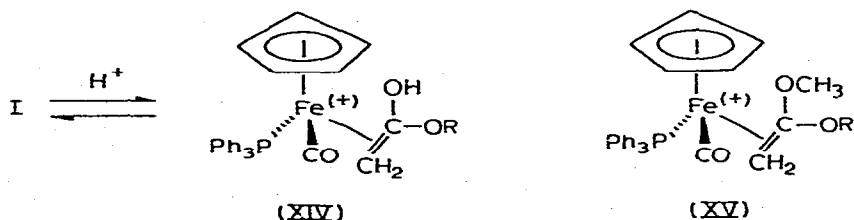


would lead to VII with retention of configuration at iron. In the case of H<sup>+</sup> or Hg<sup>+</sup>X cleavage, reductive elimination of RE would necessarily occur from a *syn* configuration, and ion pairing of X<sup>-</sup> adjacent to E (e.g., hydrogen bonding of X<sup>-</sup> when E = H<sup>+</sup>) might lead to ion pair X wherein X<sup>-</sup> finds itself on the same side of the iron atom from which R-X has left\*.

Reaction of both I and II with protic acids would be expected to take a course different than that of III or IV. Protonation of CpFe(CO)<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub> is known to occur at the acyl oxygen [21]. This, and the fact that protic acid leads to very rapid hydrolysis or transesterification of I without Fe-C cleavage, suggest the predominant site of protonation in I is not the metal, but the acyl oxygen leading to formation of XIV. Our attempts to observe XIV or the alkylated analogue XV (from reaction of I and (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> or CH<sub>3</sub>OSO<sub>2</sub>CF<sub>3</sub>) by NMR over a wide

\* That ion pairs [CpFe(CO)(PPh<sub>3</sub>)<sup>+</sup>X<sup>-</sup>] can have significant optical stability in moderately polar solvents is indicated by the highly stereospecific insertion of SO<sub>2</sub> into I-IV, a reaction which is thought to involve ion pairs [5,20].

temperature range have failed to show well-behaved observable species, while



alkylated dicarbonyl analogues of XV (i.e., [CpFe(CO)<sub>2</sub>(CH<sub>2</sub>=C(OR)<sub>2</sub>)<sup>+</sup>) have been reported to be stable salts [22]. Racemization attendant to reactions of I in acidic media may therefore proceed by reversible dissociation of the olefinic group from intermediate XIV, rather than via metal protonation.

In contrast to I, II undergoes reaction without racemization upon treatment with anhydrous HX in non-protic media to form CpFe(CO)(PPh<sub>3</sub>)CH<sub>2</sub>X [5a]. Excess HCl in these reactions does not racemize the product, but excess HBr does. Since it is difficult to imagine that HCl is less able to protonate iron than HBr, one is led to wonder whether simple metal protonation can account for racemization in these reactions or in cleavage of iron alkyls by HO<sub>2</sub>CCF<sub>3</sub>.

This last question leads us to consider the source of starting material racemization in electrophilic cleavage of iron alkyls. Such racemization has been given the reasonable interpretation [6] that attack by electrophiles results in formation of intermediate IX which in each case may revert to starting material, and that IX itself racemizes by a fluxional process at a rate comparable to progress to products. Rapid configurational lability has been observed in the square pyramidal complexes CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)X, where X = H, alkyl, and halogen [18], and in [(arene)M(CO)<sub>2</sub>(PR<sub>3</sub>)H]<sup>+</sup> where M = Cr, Mo, W [19] but in no case has it been demonstrated that the patterns of motion in these molecules would lead to racemization of a species such as IX. An additional complication is the range of rate constants observed, e.g., for CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)X at 0°C: [18] X = H, *k* ≈ 10<sup>2</sup> sec<sup>-1</sup>; X = CH<sub>3</sub>, *k* ≈ 10<sup>-5</sup>; and X = I, *k* ≈ 10<sup>-8</sup>. That the short lived intermediate IX should proceed to roughly the same degree of racemization independent of the electrophile requires significant coincidence in offsetting differences of rates of racemization vs. different lifetimes of the intermediates. The main difficulty with using starting material racemization as evidence for the existence of intermediate IX lies in establishing that IX uniquely accounts for the racemization of starting material, as opposed to some other species which is not an obligatory intermediate on the cleavage reaction coordinate. The control experiments described above clearly do relate the racemization to the presence of electrophile, but some over-oxidized iron molecule might be the critical species. The fact that I and IV are both partially racemized in I<sub>2</sub> and HgI<sub>2</sub> cleavage reactions, but that IV is recovered totally racemic, while I is recovered optically pure from partial (presumed) one-electron oxidative destruction by FeCl<sub>3</sub> is an ambiguous result and suggests the possibility of several paths for racemization. Furthermore, it may be seen from Table 1 that the extent of racemization of both starting material and product in the I<sub>2</sub> cleavage of III is dependent on reaction time. This would not be true if the only racemization path lay on the cleavage

coordinate, since it is clear from the product yields that reaction is over within five minutes. Alternate paths of starting material racemization might include ligand dissociation (e.g., CO) induced by reversible one-electron oxidation, or ligand exchange via bimolecular reaction with a species such as  $[\text{CpFe}(\text{CO})(\text{PPh}_3)]^+$ .

In conclusion, we believe that the present work contributes to the growing awareness that optical activity at metals is certainly a tractable experimental tool for mechanistic studies in organometallic systems. Metal stereochemistry provided the first indications to us that the cleavage of iron alkyls, for example by mercuric salts, might involve oxidation of the metal prior to M—C bond breaking rather than a single step  $S_E2$  bond rupture. However, interpretation of stereochemical results at metals must be approached with care. Sufficiently little is known at present about racemization mechanisms in chiral low-valent transition metal systems, especially in electron deficient environments, that the espousal of one path over another based on metal stereochemical data alone, (for example, based on starting material racemization as in the above cases) may be premature. Nevertheless, a clear picture of electrophilic cleavage mechanisms appears to be emerging from the combination of metal and carbon [2] stereochemical and structure-reactivity studies, [8,13] at least for iron alkyls. It remains to be seen whether this picture may be generalized to other transition metal alkyls.

## Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen in flamed-out glassware. THF was distilled from a purple solution of benzophenone dianion just before use. Benzene was passed through alumina and degassed by bubbling nitrogen through. All other solvents were reagent grade which were degassed similarly with nitrogen. Preparations of iron alkyls I—IV have been described in detail [5a]. Compounds VII, VIII [23], and  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Cl}$  are all well-known, and were identified in comparison with standard samples and/or published spectral data. Trifluoroacetic acid and ICl were distilled just prior to use;  $\text{I}_2$  and  $\text{HgI}_2$  were reagent grade, used as received. NMR spectra were recorded using a Varian T-60 or XL-100 FT-CW spectrometer. Optical rotations were measured on a Perkin—Elmer 141 polarimeter, and CD spectra were taken on a Cary 61 spectrometer.

### *Cleavage reactions*

These reactions were all carried out as described in Table 1. Typically, 100 mg of iron alkyl was dissolved in 40 ml of benzene, the solution was cooled in an ice bath to the point of freezing, and the electrophile was added ( $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{I}_2$ , and ICl as solutions in a few ml of benzene;  $\text{HgI}_2$  as solid). Light was scrupulously excluded during reaction and workup. After the indicated time, the reaction mixture was diluted with an equal volume of hexane, the mixture was immediately added to an alumina (hexane) column, and forced filtration of the solution through the column eluted unreacted starting material. The electrophilic cleavage product (VII or VIII) was then eluted in normal fashion with  $\text{CH}_2\text{Cl}_2$ . Evaporation of solvents afforded pure crystalline compounds.

### Control experiments

These were carried out as indicated in Tables 1 and 2. Iodide VII or trifluoroacetate VIII of known optical activity was treated under the specified conditions. The reaction mixture was added directly to an alumina column (hexane) and the products were eluted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of solvent under reduced pressure afforded crystalline products, characterized by comparisons with authentic samples.

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