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Preparation, Resolution, and Sulfur Dioxide Insertion Reactions of Chiral Iron Alkyl Complexes[1]

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Two chiral pseudotetrahedral iron alkyls, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ (**3**, R = $CH_2CO_2(Men)$ (Men = menthyl); **4**, R = $CH_2O(Men)$), have been prepared and resolved. Ether derivative **4** is converted by HCl to $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Cl$, **5**, which in turn is an active alkylating agent which couples with nucleophiles. Action of Grignard reagents on **5** provides good yields of primary iron alkyls. These alkyls undergo insertion of SO_2 in CH_2Cl_2 or DMF to form $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)S(O)_2R$ whose optical purity may be shown by the use of NMR spectroscopy in conjunction with optically active europium shift reagents, so that all of the foregoing transformations are demonstrated to proceed stereospecifically at iron. An unusual insertion of SO_2 into the C–O bond of **4** is found which forms $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2S(O)_2O(Men)$. For the iron alkyl where R = $CH_2\text{-c-}C_3H_5$, SO_2 insertion leads to formation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)S(O)_2CH_2CH_2CH{=}CH_2$ with only 40% stereospecifity at iron.

Introduction

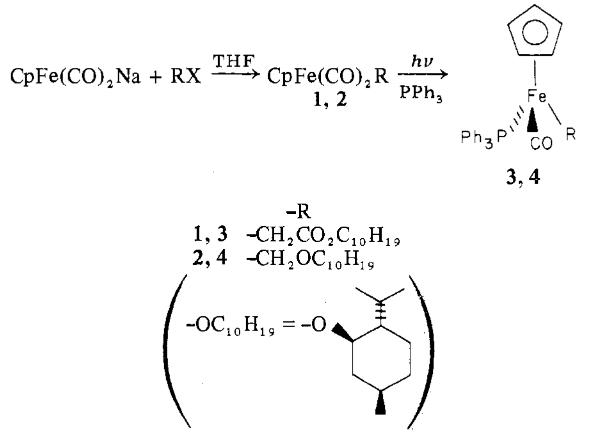
Stereochemistry of reaction centers has classically been an invaluable tool for mechanistic investigations. While configuration at carbon[2-8] and at some octahedral metals[9-11] has been extensively examined in organo(transition metal) systems, until recently very little attention has been given to the stereochemical outcome of reactions at metal centers in other than octahedral complexes. At the time that we began our investigations, most of the extant knowledge of stereochemical behavior of pseudotetrahedral and square-pyramidal organometallic complexes was from the work of Brunner and co-workers.[12,13] Recently, however, increased attention has been given to the preparation and resolution of chiral low-valent complexes by other groups.[15-18]

It is now clear that the carbon–metal σ bond is of central importance in virtually all metal-catalyzed chemistry involving changes at carbon,[19] and the above-mentioned stereochemical studies of carbon have been valuable in the examination of reactions of this bond.[2-8] Since it is evident from Brunner's work that chiral pseudotetrahedral metal molecules may be resolved, we set about to provide the first examples of resolved iron molecules containing an sp^3 carbon–metal bond and to use these molecules to evaluate the usefulness of metal stereochemistry as a tool in mechanistic investigations of reactions of this important bond.

Iron molecules of the type $CpFe(CO)(PPh_3)R$ (Cp = $\eta^5\text{-}C_5H_5$ = cyclopentadienyl) are ideally suited to these purposes because they are "18-electron" or "saturated" complexes which are kinetically inert to ligand dissociation under ambient conditions. They have a geometry which has been called "pseudotetrahedral," i.e., four different ligands in a nonplanar arrangement, and so are chiral and resolvable into separate enantiomers. Such a geometry has several advantages over octahedral complexes: chirality at metal is much easier to generate synthetically with only four ligands rather than six, and the only possible stereochemical outcome upon changing one of four ligands is retention, inversion, or some degree of racemization; cis–trans isomerism, present in octahedral systems, is not a complicating factor. Pseudopentacoordinate alkyl complexes such as $CpMo(CO)_2LR$ appear to be characterized by high stereochemical lability[14] and so have not proved to be useful as yet for mechanistic studies based on resolution.

In general, one may employ an enantiomer, one enantiomer of a diastereomer, or an enantiomeric pair of a single diastereomer in any given experiment. The difficulty with the use of an enantiomer is that of measuring its optical purity. On the other hand, in using a diastereomer, asymmetric induction may be incurred which can be as large as the inherent stereospecificity of the reaction being investigated. If both enantiomers of a diastereomer are employed, then one loses the use of ORD and CD spectroscopy as analytical tools. Several of these different approaches have been utilized concurrently in different laboratories. Wojcicki and co-workers[17] have employed unresolved diastereomers with good results but have not had the use of CD spectroscopy and have observed significant asymmetric induction in some reactions.[17b] Davison and co-workers have used resolved iron molecules,[15] for example, in their elegant acyl decarbonylation experiments.[15c]

Scheme I



This paper describes our efforts toward the general preparation of a series of resolved primary alkyliron complexes, their optical assay, and their sulfur dioxide insertion reactions. The approach used involves both enantiomeric and diastereomeric complexes. Electrophilic cleavage chemistry of the Fe–R bond and x-ray crystallographic and circular dichroism spectroscopic investigations will be described in subsequent papers.[20]

Results

Preparation and Resolution of Iron Alkyls. Complexes **3** and **4** have been prepared by the standard techniques shown in Scheme I. Alkylation of the iron anion provided **1** and **2** in 30% and 90% yields, respectively. Incorporation of triphenylphosphine proceeded readily to form **3** upon irradiation of **1** by a sun lamp in benzene–pentane with ca. 20% excess of the phosphine. However in preparing **4**, heating of the photolysis solution of **2** by the sun lamp caused predominant carbonyl insertion into the iron–alkyl bond so that all subsequent photolyses were carried out in an immersion well (Pyrex filter) maintained at ambient temperature.

Table I. Nucleophilic Displacement Reactions of (+)-$CpFe(CO)(PPh_3)CH_2Cl$, **5a**

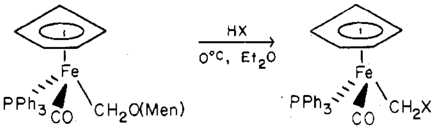
-R in $CpFe(CO)(PPh_3)R$	Reagent/solvent	Reagent:**5** ratio	Yield,^{a,b} %	$[\alpha]^{25}_{578}$, deg^h	Mp, °C
$-CH_3$ (**8**)	$NaBH_4$/DME	Excess	71	+90^c	173–174
$-CH_2OCH_3$ (**14**)	KOAc/CH_3OH	Excess	52	*d*	156–157.5
$-CH_2CN$	KCN/C_6H_6–H_2O^e	Excess	33	*d*	170–172
$-CH_2CH_3$ (**9**)	CH_3Li/Et_2O–THF	1.1	67 (0.12)	+95	140–142 dec
$-CH_2CH_3$ (**9**)	CH_3MgBr/Et_2O–THF	2.0	78 (0.35)	+89	140–142 dec
$-CH_2CH_3$ (**9**)	CH_3MgBr/Et_2O–THF	1.1	75 (8)	*d*	151.5–152
$-CH_2CH_2CH_3$ (**10**)	CH_3CH_2MgBr/Et_2O–THF	1.9	56 (0.28)	+93	117.5–118
$-CH_2CH(CH_3)_2$ (**11**)	*i*-PrMgBr/Et_2O–THF	1.9	74^f (0.27)	+71	131–132^g
$-CH_2C_6H_5$ (**12**)	C_6H_5MgBr/THF	1.8	63 (0.31)	−165	79–83
$-CH_2C_6H_5$ (**12**)	C_6H_5Li/Et_2O–C_6H_6–THF	1.0	13 (0.12)	*d*	135–137
$-CH_2$-*c*-C_3H_5 (**13**)	*c*-C_3H_5MgBr/THF	1.5	40^f (0.14)	+176	126–126.5^g

[a] Grams of isolated product given in parentheses as an indication of reaction scale. [b] Recrystallized yield based on starting **5**. [c] Taken in CH_2Cl_2; see footnote 26. [d] Prepared from racemic **5**. [e] Tetra-*n*-butylammonium bromide catalyst. [f] Yield of oil; this compound would not crystallize. [g] Melting point of crystalline racemic material. [h] In benzene; ~1 mg/ml.

Crystallization of compound **3** from hexane after purification by column chromatography yielded one diastereomer, (+)**3b**,[21] which after several recrystallizations exhibited a constant rotation and melting point. Diastereomer (−)**3a** had solubility very similar to (+)**3b** and so could be purified in the same way. Isolation of complex (+)**4a** was achieved easily by crystallization from hexane. The much more soluble (−)**4b** was crystallized with difficulty from hexane and was rendered pure by recrystallization.

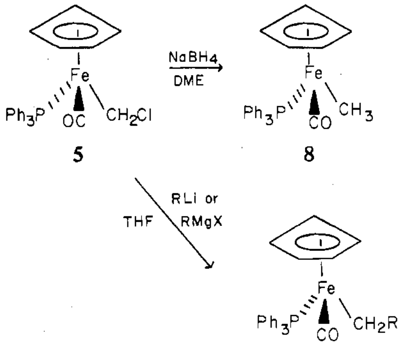
Assessment of the degree of resolution of (−)**3a** and (+)**3b** was readily achieved as described previously[1a] by the use of the lanthanide NMR shift reagent tris(dimethylheptafluorooctanedionato)europium(III)-d_{27} (Eu(fod)$_3$-d_{27}) which induces a diastereotopic chemical shift difference between the resonances of the Cp groups of the two diastereomers which otherwise appear as a single doublet. Compounds (+)**4a** and (−)**4b** also showed a single Cp NMR resonance, in this case at δ 4.4 ppm, but the addition of Eu(fod)$_3$-d_{27} had no effect on the spectrum. Presumably the relative weakness of an ether as a ligand for europium[22] combined with the extreme crowding around this oxygen precludes complexation leading to pseudocontact shifts. While the classical criteria of purity, constant melting point and constant rotation, were convincing for (+)**4a** and (−)**4b**, it was later found that their SO_2 insertion products provided conclusive proof (vide infra).

Several different attempts were made to remove the menthyl group from compounds (−)**3a** and (+)**3b** in order to eliminate the potential for asymmetric induction in subsequent reactions. Treatment of (−)**3a** or (+)**3b** with dilute HCl in aqueous THF at 60 °C for several hours does convert the ester to carboxylic acid but the acid was totally racemic. Reaction of resolved **3** with a trace of sulfuric acid in methanol at room temperature for a few minutes produced crystalline methyl ester which also was totally racemic. Complex **3** was not stable to basic hydrolysis conditions.



5, X = Cl
6, X = Br
7, X = I

Scheme II



5
8

9, R = CH_3
10, R = CH_2CH_3
11, R = $CH(CH_3)_2$
12, R = C_6H_5
13, R = *c*-C_3H_5

On the other hand, **4** has proven to be very versatile in synthesis. Upon treatment with anhydrous HCl or HBr, halomethyliron complexes **5** and **6** are formed in good yield as crystalline solids,[23] **5** being significantly more thermally stable than **6** and the iodomethyl analogue, **7**, being so unstable that we have not sought to characterize it.[24] In solution all of these derivatives **5**–**7** are substantially less stable. Gaseous HCl effects the **4** to **5** conversion well. Gaseous HBr, however, leads to formation of **6** with varying amounts of racemization and so is apparently too acidic. Controlled addition of a stoichiometric amount of HBr dissolved in benzene provides optically pure **6** (vide infra).

Chloromethyl compound **5** is quite reactive toward nucleophilic substitution at carbon (see Table I). For example, KCN and **5** in benzene–water under phase-transfer conditions lead to the formation of $FeCH_2CN$, and **5** in methanol–ether in the presence of KOAc provides $FeCH_2OCH_3$.

Grignard and alkyllithium reagents in reactions with **5** in THF provide good yields of primary alkyliron derivatives such as **9**–**13** (Scheme II), with Grignards generally giving the higher yields. While primary or secondary Grignards alkylate **5** normally, *t*-BuLi or *t*-BuMgCl only lead to reduction of **5** producing methyliron compound **8**. Sodium borohydride in DME converts **5** to **8** in good yield. The alkylation reaction provides the best yields when ca. 50% excess of the Grignard reagent is used for up to 2 g of **5**. For larger scale reactions, a **5**:RMgX molar ratio closer to 1 gives better yields. This reaction is also very well suited to larger scale preparations of racemic alkyliron species of the type **9**–**13** especially when starting material **5** is made from $CpFe(CO)(PPh_3)CH_2OCH_3$, **14**, which is obtained in high yield in a manner completely analogous to the preparation of **3** and **4** as shown in Scheme I.

The sequence of converting **4** to **5** and then **5** to alkyls **8**–**13** has been carried out using pure diastereomers of **4**. Each of the alkyls (except **13**) has been shown, through the use of NMR and lanthanide shift reagents on its corresponding SO_2 insertion product, to be formed as a pure enantiomer (vide infra). Reagent acidity, however, can be a problem in the Grignard alkylation of optically active **5**. Normally, addition

Table II. Sulfur Dioxide Insertion Reactions of $CpFe(CO)(PPh_3)R$

Substrate, -R	Alkyl optical purity,[a] %	Reaction conditions	Sulfinate yield, %	Sulfinate $[\alpha]^{25}{}_{578}$,[b] deg	Sulfinate optical purity,[a] %	Stereo-specificity of the insertion, %
3b, $-CH_2CO_2(Men)$	82[c]	SO_2(l), −10 °C	54	+206	78	95
9a, $-CH_2CH_3$	Pure	SO_2-CH_2Cl_2, 0 °C	69	−255	Pure	>95
10a, $-CH_2CH_2CH_3$	Pure	SO_2-CH_2Cl_2, 0 °C	42	−250	Pure	>95
11a, $-CH_2CH(CH_3)_2$	>95	SO_2-CH_2Cl_2, 0 °C	16	−229	95	>95
12a, $-CH_2C_6H_6$	Pure	SO_2-CH_2Cl_2, 0 °C	61	−275	Pure	>95
13a, $-CH_2$-c-C_3H_5	*d*	SO_2-CH_2Cl_2, 0 °C	44[e]	−57	40	~40[f]
8a, $-CH_3$	Pure	SO_2-CH_2Cl_2, 0 °C	43	−196	Pure	>95
8a, $-CH_3$	93[g]	SO_2(l), −10 °C	95	−138	70	75
8b, $-CH_3$	Pure[g]	SO_2(l), −78 °C	73	+166	88	88
8a, $-CH_3$	94[g]	SO_2-DMF, 25 °C	17	−177	90[h]	96
8a, $-CH_3$	94[g]	SO_2(l), −10 °C, with KI	41[i]	−179	91[h]	97
9a, $-CH_2CH_3$	87	SO_2(l), −78 °C	47		80	92
9a, $-CH_2CH_3$	89	SO_2(l), 10 °C, with KI	41[i]		84	95
9a, $-CH_2CH_3$	Pure	SO_2-DMF, 0 °C	56		Pure	>95

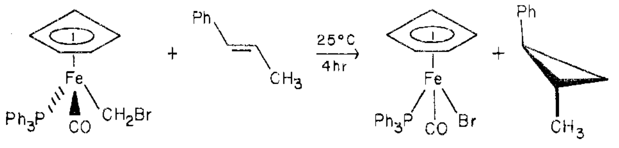
[a] As determined by NMR using $Eu(opt)_3$ on the sulfinate derivative. "Pure" means none of the Cp resonance of the second enantiomer could be detected (i.e., greater than 95% ee). [b] In CH_2Cl_2; ~1 mg/ml. [c] Determined directly by NMR and Eu(fod)-d_{27}. [d] Could not be directly determined because the sulfinate product did not form stereospecifically. [e] The major product was $CpFe(CO)(PPh_3)S(O)_2CH_2CH_2$-$CH{=}CH_2$. [f] Assuming that alkylation of **5** to form **13** is stereospecific as in all of the other cases. [g] Determined by specific rotation measurement in comparison to that of demonstrably pure **8**. [h] Determined by specific rotation measurement in comparison with demonstrably pure sulfinate **15**. [i] A second product, $CpFe(CO)(PPh_3)I$, was formed in 35–40% yield.

of the Grignard reagent is carried out at 0 °C, followed after a few minutes by rapid filtration of the reaction mixture on an alumina column or removal of the solvent at reduced pressure in the cold and then chromatography. If the crude reaction mixture is allowed to stand at room temperature for several hours and then is worked up, the isolated iron alkyl is nearly racemic. This racemization is apparently associated with the acidic MgX_2 salts, since a THF solution of optically pure **9** (~10^{-3} M) and $MgBr_2$ (~10^{-2} M) is ca. half-racemized after 2 h at 25 °C in the dark.

X-ray crystallographic structure determination[20b] of both (+)**3b** and (+)**4a** has established their absolute configuration at iron to be as shown in Scheme I, i.e., *R*.[25] The absolute configuration of all compounds reported here, with the exception of the iron sulfinates, is therefore known unequivocally.

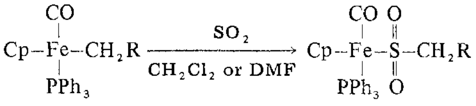
In the crystalline form under nitrogen atmosphere in the cold (~10 °C) and in absence of light, virtually all of these molecules are indefinitely chemically and optically stable. In solution at room temperature (under nitrogen, no light) the alkyliron compounds are optically stable over a period of hours (e.g., **8** showed no decrease in specific rotation upon heating in benzene at 48 °C overnight). In chlorocarbon solvents, for reasons which are not known, some racemization was occasionally observed, especially for **8** when attempting to take CD spectra. For this reason chlorocarbon solvents were avoided, and optical measurements were made in benzene or hexane.[26] Alkoxymethyliron **4** slowly changes to other unidentified products on standing over a period of weeks in solution or in contact with solvent.

Halomethyls **5**–**7** in solution all extrude methylene with resultant formation of $CpFe(CO)(PPh_3)X$ (X = Cl, Br, I), the iodide doing so very rapidly. In this connection, it is noteworthy that (+)**6a** is a reasonably efficient methylene-transfer reagent, at least toward one substrate.[27] Upon treatment of solid (+)**6a** with a sevenfold excess of *trans*-β-methylstyrene, a 55% yield of *trans*-1-phenyl-2-methylcyclopropane was formed and was found to contain a 9% enantiomeric excess of (+)-(1*S*,2*S*)-cyclopropane.[28]



(+)**6a** (1*S*,2*S*)

Sulfur Dioxide Insertion. Insertion of SO_2 has been carried out on iron alkyls **8**–**12** and in each case yields the expected Fe–S bonded sulfinate.



$$Cp{-}\overset{\displaystyle CO}{\underset{\displaystyle PPh_3}{Fe}}{-}CH_2R \xrightarrow[CH_2Cl_2 \text{ or } DMF]{SO_2} Cp{-}\overset{\displaystyle CO}{\underset{\displaystyle PPh_3}{Fe}}{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}CH_2R$$

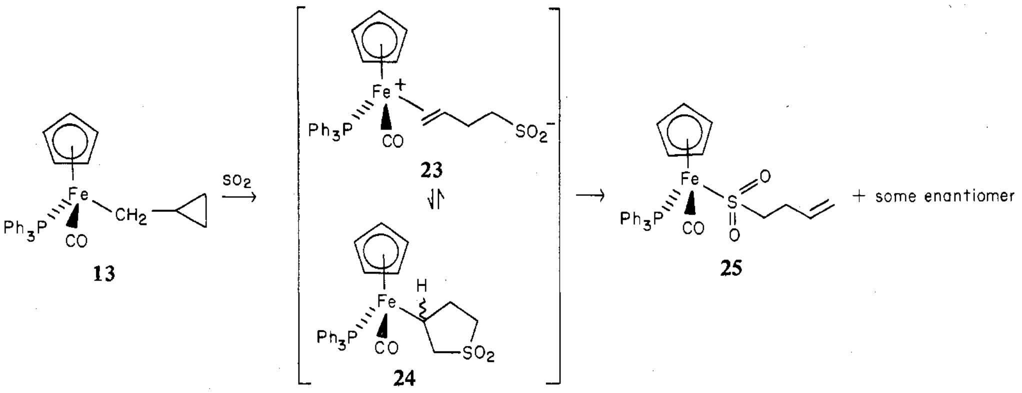
8-12 **15-19**

	R
8, 15	H
9, 16	CH_3
10, 17	CH_2CH_3
11, 18	$CH(CH_2)_3$
12, 19	C_6H_5

The insertion reaction of (+)- or (−)**3** has been reported to proceed with >90% stereospecificity in refluxing (−10 °C) SO_2 as established by NMR spectroscopy through the use of lanthanide shift reagents on the diastereomeric products.[1a] In a similar way, this NMR technique has been employed to establish the optical purity of enantiomeric sulfinates. Shift reagents interact very strongly with the sulfinate group, and when an optically active reagent such as tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III), $Eu(opt)_3$, is used with a racemic iron sulfinate, diastereomeric substrate–shift reagent complexes are formed and are found to exhibit diastereotopic cyclopentadienyl (Cp) resonances at different chemical shifts. Optical assay is then achieved by direct peak integration.[29]

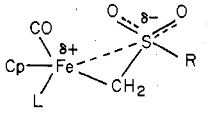
Concurrent with our work on the SO_2 insertion stereochemistry of **3**, Attig and Wojcicki observed that an analogous iron alkyl suffered partial racemization upon insertion in liquid SO_2 at −10 °C but formed sulfinate with >95% stereospecificity in dilute SO_2 solution in CH_2Cl_2.[17b] We have found that methyliron **8** also provides product from liquid SO_2 solution whose optical purity depends on the reaction temperature (Table II) but that it undergoes >95% stereospecific SO_2 insertion when carried out in CH_2Cl_2 or DMF solution and that all of the other iron alkyls (**9**–**12**) undergo stereospecific insertion in CH_2Cl_2 solution as determined by the NMR-shift reagent technique.[30] Thus the stereospecific nature of each step in the sequence from **4** to halomethyl derivatives **5** and **6** to alkyls **8**–**12** to their sulfinates **15**–**19** has been shown directly.

The racemization component of the reaction in liquid SO_2 appears to be dependent on the alkyl group. At −78 °C in SO_2(l), the methylsulfinate (**15**) forms with 15% racemization, Scheme III



the ethylsulfinate (**16**) with ca. 8%, and the isobutylsulfinate (**18**) with no more racemization than in CH_2Cl_2 solution. As stated above, the sulfinate of ester **3** forms in SO_2(l) at −10 °C with less than 5% racemization. When iodide ion (KI) is added to the liquid SO_2 reaction medium, at −10 °C substantial amounts of product are diverted to the formation of $CpFe(CO)(PPh_3)I$ with no pronounced change in the stereospecificity of formation of the alkylsulfinate, except in the case of the methylsulfinate (**15**) whose stereospecificity goes up (see Table II).[31]

Attempts to insert SO_2 into the Fe–C bond of **4** and its methyl analogue $CpFe(CO)(PPh_3)CH_2OCH_3$, **14**, in each case led to the formation of a compound which was different from that expected, $CpFe(CO)(PPh_3)CH_2(SO_3)R$ (**20**, R = menthyl; **21**, R = methyl). These formed very rapidly and could be isolated presumably owing to the much slower further insertion into the Fe–C bond because of the highly electronegative SO_3R group. It is evident that CH_2 is still bonded to iron in **20** and **21** since its NMR spectrum comprises an ABX pattern which can be phosphorus decoupled to an AB pattern and since its circular dichroism spectrum is significantly different from those of Fe–S sulfinates (vide infra). Two chemically reasonable structures are likely for **20** and **21**, $FeCH_2S(O)_2OR$ (A) and $FeCH_2OS(O)OR$ (B). We favor structure A on the basis of the ir and ^{13}C NMR data given in Table III. Structure B should exhibit one S=O stretching band at ca. 1200 cm^{-1} (as for dimethyl sulfite) but instead shows two at 1320 and 1150 cm^{-1}. The 30-cm^{-1} drop in frequency for these two bands (with respect to the corresponding methyl methanesulfonate bands) is readily attributable to a strong β interaction, as in structure **22**, of the type which is well precedented for acyl groups β to a metal.[32] For comparison, note the size of the α effect in the decreases of 200 and 150 cm^{-1} for the two S=O bands of $CpFe(CO)(PPh_3)SO_2CH_3$ with respect to those of $CH_3S(O)_2OCH_3$.



22

Table III. Spectroscopic Data Relevant to the SO_2 Insertion of $CpFe(CO)(PPh_3)CH_2OR$

	$\nu_{S=O}$, cm^{-1}	^{13}C NMR, ppm[a]
$CH_3S(O)_2OCH_3$	1350, 1180	56.8 (OCH_3) 37.2 (SCH_3)
$CH_3OS(O)OCH_3$	1200	49.1 (OCH_3)
$CpFe(CO)(PPh_3)CH_2(SO_3)CH_3$ (**21**)	1320, 1150	54.7 (OCH_3) 20.2[b] ($FeCH_2$)
$CpFe(CO)(PPh_3)S(O)_2CH_3$ (**15**)	1150, 1030	58.9 (SCH_3)
CH_3OCH_3		59.4[c] (OCH_3)
$CpFe(CO)(PPh_3)CH_2OCH_3$ (**14**)		62.4 (OCH_3) 70.0[b] ($FeCH_2$)
CH_4		−2.3[c]
$CpFe(CO)(PPh_3)CH_3$ (**8**)		−22.6[b] ($FeCH_3$)

[a] Downfield from tetramethylsilane. [b] Doublet; $^2J_{CP} \simeq 20$ Hz. [c] G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972.

From examination of the ^{13}C NMR data of Table III its seems likely that the methyl group of **21** ($-OCH_3$, 54.7 ppm) is bonded to oxygen (cf. $CH_3SO_3CH_3$, 56.8 ppm, vs. $CH_3SO_3CH_3$, 37.2 ppm). Otherwise, the chemical shift data for carbon σ bonded to iron show a substantial lack of consistency; e.g., $\Delta\delta$ for methane vs. $FeCH_3$ in **8** is +20.3 ppm, while $\Delta\delta$ for dimethyl ether vs. $FeCH_2-$ in **14** is −10.6 ppm. Furthermore, $\Delta\delta$ for $CH_3S(O)_2OCH_3$ vs. $FeCH_2-$ in **21** is +17.0 ppm and for CH_3O in dimethyl sulfite vs. $FeCH_2-$ in **21** is +28.9 ppm. Sufficiently little is presently known about sources of chemical shifts of carbon bonded to metals that we do not feel justified in drawing conclusions from these numbers. Nevertheless from the infrared data it seems most likely that these derivatives are of structure A.

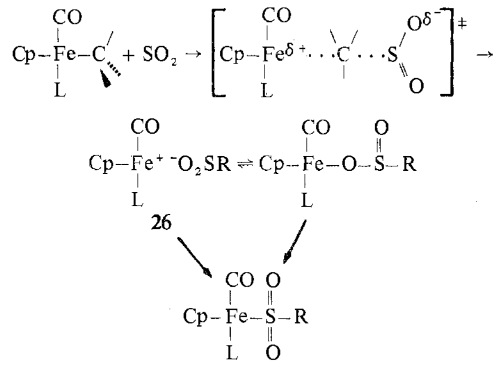
It should also be noted that derivatives **20** and **21** serve as well for optical assay as do the normal sulfinate derivatives **15**–**19** using NMR spectroscopy and $Eu(opt)_3$.

The cyclopropylcarbinyl derivative **13** undergoes SO_2 insertion reactions (Scheme III) which appear to be analogous to those reported for $CpFe(CO)_2CH_2$-c-C_3H_5.[33] At higher temperatures (e.g., ambient) and longer times (several hours) the predominant product from either liquid SO_2 or SO_2–CH_2Cl_2 was the butenylsulfinate **25**. At shorter times or lower temperatures the predominant product was an orange oil whose instability and air sensitivity rendered its characterization difficult. On standing either as an oil or, more rapidly, in CH_2Cl_2 solution, this compound rearranged to **25**. Based on analogy with the dicarbonyl analogues,[33] **24** is one likely structure to assign to this unstable intermediate. In any case, the overall process of conversion of the chloromethyliron **5** to the cyclopropylcarbinyliron **13** to the sulfinate **25** proceeds with 40% net stereospecificity, again, as shown by NMR with the use of $Eu(opt)_3$.

Discussion

Preparation and Resolution. The incorporation of menthol-containing alkyl groups has served well for the resolution of chiral iron compounds **3** and **4**. Initially, we were concerned that the presence of the excess chirality of menthol in these diastereomers might lead to substantial complicating asymmetric induction in reactions at the iron–carbon bond, but this has not as yet been observed. Although **3** was first prepared and resolved, the presence of the β-acyl group may render it atypical of an alkyliron compound in its reactions. The well-known "β effect"[32] is clearly evident in this compound since the stretching frequency of the acyl group is lowered some 90 cm^{-1}, to 1650 cm^{-1}. For this reason and because of the fact that stereospecific transformations were not readily carried

Scheme IV



out on the acyl group, the synthesis of **4** was undertaken.[34]

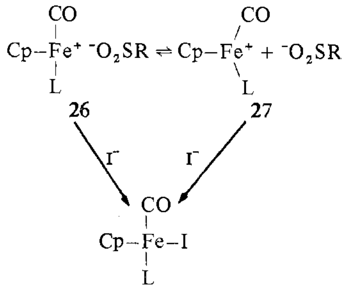
Ether compound **4** has been very versatile in synthesis by virtue of its stereospecific conversion to the chloromethyliron **5**. It was not clear that this transformation would be stereospecific since there is evidence that strong Lewis acids racemize pseudotetrahedral complexes of iron.[17b,20a] The fact that gaseous HBr results in partially racemized bromomethyliron, **6**, while HCl yields optically pure **5** is most easily explained by the relative acidity of the two acids. The ether oxygen presumably is the kinetically favored site of protonation, but HBr is sufficiently acidic that any excess leads to metal protonation with resultant racemization.[17b,20a]

Racemic chloromethyliron, **5**, may be prepared in multigram quantities from the more readily available CpFe(CO)(PPh$_3$)CH$_2$OCH$_3$, **14**, which in turn we have prepared in 100-g quantities from [CpFe(CO)$_2$]$_2$ in ca. 65% yield. Because of this availability of **5**, *alkylation of* **5** *by Grignard reagents is the method of choice for the preparation of CpFe(CO)(PPh$_3$)CH$_2$R whenever -CH$_2$R contains a β hydrogen.* This synthetic path is free of β elimination encountered in the photochemical approach from CpFe(CO)$_2$R and PPh$_3$ and offers better yields than from the action of Grignard reagents on CpFe(CO)(PPh$_3$)I in which yields are generally very poor.

In any event, this alkylation procedure is a valuable means of preparing a variety of primary alkyliron complexes which now may also be obtained optically pure. Whether the same approach will be applicable to other alkylmetal systems is currently under investigation.

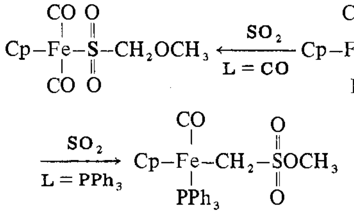
Sulfur Dioxide Insertion. The mechanism of the sulfur dioxide insertion into transition metal–carbon σ bonds has been extensively studied, primarily by Wojcicki and his co-workers.[31,35] It may be said that attack at carbon is electrophilic, the reaction is sensitive to steric bulk at the backside of the metal-bonded carbon, a metal–oxygen bonded sulfinate is generally an intermediate,[31,35] and insertion of SO$_2$ into CpFe(CO)$_2$CHDCHDC(CH$_3$)$_3$ proceeds with clean inversion at carbon.[2] The mechanism of Scheme IV has been proposed by Wojcicki.[35] This proposal is consistent with our stereochemical results at iron described above and with some similar results from Wojcicki's laboratories.[17] In solvents such as methylene chloride or dimethylformamide, the tight ion pair **26** does not dissociate but instead collapses to the *O*-sulfinate, the kinetic product, without racemization. Rearrangement of the *O*-sulfinate to the *S*-sulfinate (concertedly or dissociatively) is stereospecific at iron. In liquid SO$_2$ the contact ion pair dissociates to some extent (Scheme V) and leads to partial racemization of the final product, depending on the alkyl group. In the presence of iodide ion, **27** is efficiently trapped but **26** is only partially trapped. As a result, all of the sulfinate product formed is from the contact ion pair and so is not significantly racemized. Evidence for the presence of an Fe–O bonded sulfinate has been provided by Wojcicki and coworkers.[31] In the present phosphine-substituted iron system, the intermediate is apparent because of its deep green color in contrast to the red-orange Fe–S bonded sulfinate. Overall, then, these mechanistic schemes are at least consistent with the extant experimental facts.

Scheme V



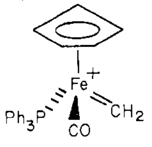
Whether the SO$_2$ insertion proceeds with inversion or retention of configuration at iron is not yet certain. For the above mechanism to be correct, retention of configuration at iron would be required. A tentative empirical argument can be made using circular dichroism (CD) spectroscopy that this is actually true. The CD spectra of resolved molecules CpFe(CO)(PPh$_3$)X are all quite similar in the range of 3000–5500 Å, the major and most reproducible feature being an intense ([θ] = (2–4) × 10^4) maximum in the range of 3000–3500 Å.[1a,12,13,15,20] For those molecules whose absolute configuration is known by crystallographic determination[20b,36] or can be shown therefrom, all of those having the absolute configuration shown in Scheme I (*R*) have a positive sign for this intense maximum. The CD spectra for all of the normal sulfinates (**15–19**) are essentially superimposable and, for sulfinates prepared from (*R*)-alkyls, also have a positive maximum at 3300 Å. These spectral results suggest retention of configuration at iron, but definite corroboration by x-ray structure determination of a sulfinate is planned.[37]

The abnormal SO$_2$ insertion into the C–O bond of **4** and **14** is in contrast to the normal insertion reported for the dicarbonyl analogue.[35] This may be understood as a reflection of the increased electron density at the metal center which is provided by PPh$_3$, which increases the stability of the polar contributor [CpFe(CO)(L)=CH$_2$]$^+$OR$^-$ to the ground-state bonding. In fact, we have not been successful in isolating CpFe(CO)(PPhMe$_2$)CH$_2$O(Men) but instead isolate only CpFe(CO)(PPhMe$_2$)CH$_3$ which we believe arises from redox chemistry of a dissociated cationic iron intermediate.[38]



21

While we have no evidence for the intermediacy of cation **28**, it is reasonable to anticipate its existence as a transient intermediate, in either the SO$_2$ insertion or the conversion of **4** to **5** by HCl, in the light of the indirect characterization of cationic carbene complex **29** at low temperatures.[39]



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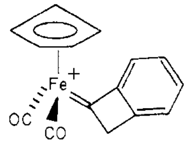

29

The sulfinate of cyclopropylcarbinyliron (**25**) is the only sulfinate which is formed with substantial racemization in

CH_2Cl_2–SO_2. Since the action of Grignard reagents on chloromethyliron (**5**) has led to optically pure product in five cases, it is highly likely that cyclopropylcarbinyliron (**13**) is also formed without racemization. The 60% racemate in **25** therefore probably arises from the insertion (Scheme III). The CD spectrum of **25** shows that this insertion proceeds with the same stereochemistry as for the other alkyls, probably retention of configuration at iron. These results are consistent with dissociation of the zwitterion **23** to an ion pair in which $CH_2{=}CHCH_2CH_2SO_2^-$ would already be significantly solvent separated (more like **27** than **26**) and so more racemic sulfinate product would form. A dissociative rearrangement of **23** to **25** is also consistent with our preliminary results on the nucleophilic substitution chemistry of optically active $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-}CH_2{=}CH_2)^+\ BF_4^-$.[38]

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under an atmosphere of prepurified nitrogen. THF and DME were distilled from a purple solution of benzophenone dianion just before use. All other solvents were degassed by vigorously bubbling a stream of nitrogen through them. Cyclopentadienyldicarbonyliron dimer[40a] and THF solutions of $Na[CpFe(CO)_2]$[40b] were prepared by standard procedures. Sulfur dioxide was passed through P_4O_{10} prior to use. Melting points (Thomas-Hoover apparatus) are uncorrected. NMR spectra were recorded using a Varian T-60 or XL-100 FT-CW spectrometer; chemical shifts are reported in parts per million downfield from tetramethylsilane for both ^1H and ^{13}C spectra. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Preparative photolyses, unless otherwise noted, were performed using a Hanovia 450-W medium-pressure mercury arc lamp in a quartz immersion apparatus, using a Pyrex filter sleeve. Microanalyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

Preparation of $BrCH_2CO_2((-)_D\text{-}Men)$. A solution of 100 g of $BrCH_2COBr$ in 200 ml of ether was cooled to 0 °C, and a solution of 70 ml of *N,N*-dimethylaniline and 80 g of menthol in 300 ml of ether was added dropwise with vigorous stirring over a period of ca. 35 min. The solution was allowed to warm to 25 °C and was then warmed at 30–40 °C for 1.5 h. The solution was decanted from the white precipitate, washed five times with cold 10% H_2SO_4 and two times with water, and dried ($MgSO_4$). Distillation, after collection of foreruns of menthol, afforded 80 g (58%) of clear oil: bp 110–115 °C (0.1 mm); NMR (CCl_4) δ 0.4–2.2 (m, 18), 3.6 (s, 2), 4.6 (m, 1); $[\alpha]^{25}{}_D$ −57.8° (benzene, *c* 1.0). Anal. Calcd for $C_{12}H_{21}O_2Br$: C, 51.99; H, 7.64. Found: C, 52.11; H, 7.54.

Preparation and Resolution of $CpFe(CO)(PPh_3)CH_2CO_2((-)_D\text{-}Men)$ ((−)3a and (+)3b). Over a period of 15 min, a solution of $Na[CpFe(CO)_2]$ (from 19 g of dimer) in 225 ml of THF was added to 27.3 g of menthyl bromoacetate in 150 ml of THF. After stirring of the mixture at 25 °C for 12 h, the solvent was removed under reduced pressure. The residue was taken up in 200 ml of pentane, the solution filtered, and the solvent removed. Chromatography of the oil (alumina, hexane) upon elution with 2–10% acetone–hexane afforded $CpFe(CO)_2CH_2CO_2(Men)$ (11.2 g, 30%) as an amber oil. This was used without further purification: NMR ($CDCl_3$) δ 0.5–2.2 (m, 20), 4.4 (m, 1), 4.8 (s, 5); ir (neat) 2020, 1970 (C≡O), 1680 (C=O) cm^{-1}.

$CpFe(CO)_2CH_2CO_2(Men)$ (11.2 g) and PPh_3 (15 g) were dissolved in benzene (100 ml) and pentane (600 ml) in a 1-l. flask. This was irradiated for 2 h with a sun lamp. Solvent was removed, CH_3I (ca. 5 ml) was added, and this mixture was warmed (40–50 °C) for 30 min. The oil was filtered to remove phosphonium salt, the solid was washed with pentane, and the solvent was removed. Chromatography (alumina, hexane) upon elution with 0–20% $CHCl_3$–hexane afforded 8.5 g of red-orange oil which was contaminated with some starting material (ca. 45% yield).

This material was fractionally crystallized with some difficulty from pentane, affording small portions of crystals enriched in each diastereomer. Repeated recrystallizations (generally four or five) gave low yields of pure diastereomers: (+)**3b**, $[\alpha]_{578}$ +330°, mp 129–130°; (−)**3a**, $[\alpha]_{578}$ −309° (benzene, *c* 0.1), mp 115–116.5°. Spectra were indistinguishable for the two diastereomers: NMR ($CDCl_3$) δ 0.6–2.4 (m, 21), 4.4 (d, J_{PH} = 1.2 Hz, 5), 4.6 (m, 1), 7.3 ppm (m, 15); ir ($CHCl_3$) 1930, 1650 cm^{-1}. Anal. Calcd for $C_{36}H_{41}FeO_3P$: C, 71.05; H, 6.79. Found: C, 70.96; H, 6.90.

Preparation of Chloromethyl Menthyl Ether. Following the procedure of Andrianov et al.,[41] $(-)_D$-menthol (205 g) was powdered and mixed thoroughly with paraformaldehyde (42.4 g). Dry HCl was passed through the mixture at 0 °C for 8 h. Distillation of the upper layer afforded 228 g (84%) of the ether: bp 60 °C (0.08 mm) [lit.[41] bp 78–82 °C (0.5 mm)]; NMR ($CDCl_3$) δ 0.2–0.4 (m, 18), 3.50 (m, 1), 5.53 (s, 2); $[\alpha]^{25}{}_D$ −189° (benzene, *c* 1.0) [lit.[41] $[\alpha]^{25}{}_D$ −177°].

Preparation and Resolution of $CpFe(CO)(PPh_3)CH_2O((-)_D\text{-}Men)$ ((+)4a and (−)4b). A solution of $Na[CpFe(CO)_2]$ (from 44.2 g of dimer) in 750 ml of THF was added by forced siphon through a stainless steel cannula to a stirred, cooled (−78 °C) solution of chloromethyl menthyl ether (50.9 g) in 150 ml of THF. After addition, the solution was allowed to warm to 25 °C and stirred 3 h more, and the solvent was removed under reduced pressure. Pentane (800 ml) was added and the slurry was filtered through a cake of anhydrous $MgSO_4$. Solvent removal and chromatography of the residue (alumina, hexane), upon elution with 10% ether–hexane, afforded $CpFe(CO)_2CH_2OC_{10}H_{19}$ as an amber oil: 78.5 g, 91%; NMR ($CDCl_3$) δ 0.6–2.6 (m, 19), 2.9 (m, 1), 4.4–5.1 (m, 2), 4.82 (s, 5); ir (neat) 2000, 1945 cm^{-1} (CO).

$CpFe(CO)_2CH_2OC_{10}H_{19}$ (29.5 g) and PPh_3 (30 g) dissolved in 80 ml of benzene and 120 ml of pentane were irradiated through a Pyrex filter in the immersion apparatus for 2 h. Solvent was removed, methyl iodide (ca. 4 g) was added, and the mixture was warmed (40–50 °C) for 45 min. Pentane was added and the slurry was filtered through a cake of $MgSO_4$. Solvent was removed from the filtrate and the residue was again filtered, this time on an alumina column (ca. 7 × 7 cm, hexane). Elution with 30% ether–hexane, concentration to a volume of ca. 300 ml, and cooling (0 °C) overnight afforded 12.6 g of red-orange crystals. Recrystallization from hexane gave 11.9 g (22%) of pure (+)**4**: mp 146–146.5 °C; $[\alpha]^{25}{}_{578}$ +209° (benzene, *c* 0.1).

The concentrated supernatant, upon storage at 0 °C for 1 week, afforded 13 g of crystalline (−)**4** which when recrystallized (hexane) gave 11.1 g of pure (−)**4**: mp 119–120 °C; $[\alpha]^{25}{}_{578}$ −407° (benzene, *c* 0.1); NMR (indistinguishable for (+)- or (−)**4**) ($CDCl_3$) δ 0.62–1.92 (m, 18), 2.60 (m, 1), 4.08–4.52 (m, 2), 4.44 (d, 5, $J_{HP} \approx$ 1 Hz), 7.16–7.95 (m, 15); ir (benzene) 1900 cm^{-1} (CO). Anal. Calcd for $C_{35}H_{41}FeO_2P$: C, 72.41; H, 7.12. Found: C, 72.57; H, 7.16.[42]

Preparation of $CpFe(CO)(PPh_3)CH_2OCH_3$ (14). $CpFe(CO)_2CH_2OCH_3$[23] (60.8 g) and PPh_3 (76 g) were dissolved in 250 ml of benzene in a 2-l. round-bottomed flask, and 750 ml of pentane was added. The Pyrex flask, fitted with a reflux condenser, was irradiated externally by a Hanovia 450-W mercury arc lamp, without stirring the solution, until crystals of product coated the walls. The solution was transferred to a new flask by forced siphon, and the photolysis was continued. The crystals were collected, washed with ether, and dried in vacuo. This process was continued until no more crystalline product appeared. The remaining solution was cooled 2 days at 0 °C to induce further crystallization. Finally the mother liquor was concentrated to an oil under reduced pressure and chromatographed (alumina, hexane). Elution with 50% ether–hexane afforded 7 g more for a total yield of 112 g (89%), of >95% purity according to its NMR spectrum: mp 145–148 °C; NMR ($CDCl_3$) δ 3.02 (s, 3), 4.44 (d, 5, $J_{HP} \approx$ 1 Hz), 4.06–4.64 (m, 2), 7.4 (m, 15); ir ($CHCl_3$) 1895 cm^{-1} (CO).

A recrystallized sample melted at 156–157.5 °C. Anal. Calcd for $C_{26}H_{25}FeO_2P$: C, 68.44; H, 5.52. Found: C, 68.32; H, 5.61.[42]

Preparation of $CpFe(CO)(PPh_3)CH_2Cl$ (5). (a) From Racemic 14. A 11.4-g amount of finely powdered **14** was partially dissolved in 250 ml of vigorously stirred ether maintained at 0 °C in a 500-ml flask. Anhydrous HCl was slowly fed into the flask via a needle in the septum, for about 10 min, until the suspended solid became more granular and bright orange and the solution became light orange (but not green). After an additional 10 min of stirring at 0 °C, the solid was collected on a filter in the air and washed several times with a minimum of ether. The vacuum-dried orange crystalline product weighed 8 g (70%); mp 123–124°.

(b) From Optically Pure $CpFe(CO)(PPh_3)CH_2OMen$ (4). One gram of (−)**4b** dissolved in 10 ml of ether was cooled to 0 °C and a slow stream of dry HCl was bubbled in until formation of a precipitate just became visible (ca. 1 or 2 min). The solution was then allowed to stir at 0 °C for 5 min and was filtered, and the solid was washed with ether: yield of orange solid (−)**5b** 0.56 g (71%); mp 115 °C dec; $[\alpha]^{25}_{578}$ −380° (benzene, *c* 0.1); NMR (benzene-d_6) δ 4.33 (d, 5, $J_{HP} \approx 1$ Hz), 4.4 (m, 2), 6.9 (m, 15); ir (benzene) 1930 cm^{-1} (CO). Anal. Calcd for $C_{25}H_{22}ClFeOP$: C, 65.17; H, 4.81. Found: C, 65.09; H, 4.88.[42]

The (+)$_{578}$ enantiomer, (+)**5a**, was similarly prepared: $[\alpha]^{25}_{578}$ +383°; mp 115 °C dec.

Preparation of CpFe(CO)(PPh$_3$)CH$_2$Br (6). (a) From (+)4a. One gram of (+)**4a** in 10 ml of ether cooled to 0 °C was treated in one portion with 4.6 ml of 0.349 N HBr in benzene. The mixture was allowed to warm to room temperature and was then evaporated to half-volume, 10 ml of hexane was added, and the resultant mixture was cooled to 0 °C. The orange solid was collected and washed with hexane: yield 0.47 g (54%); mp 129 °C dec; $[\alpha]^{25}_{578}$ +280° (EtOAc, *c* 0.1); NMR (CDCl$_3$) δ 4.22 (d, 2), 4.47 (s, 5), 7.4 (m, 15); ir (benzene) 1930 cm^{-1} (CO). Anal. Calcd for $C_{25}H_{22}BrFeOP$: C, 59.44; H, 4.39. Found: C, 58.98; H. 4.34.

The optical purity of (+)**6a** was shown by its reduction to the methyliron compound (+)**8a** by NaBH$_4$ as described below. Gaseous HBr could not be used for the preparation of optically active **6** because it led to the formation of racemic product.

(b) From Racemic 14. The procedure was the same as that given in preparation (b) of **5**, except that racemic **14** was used as starting material and gaseous HBr was employed. Typical yields of 70–80% were achieved; mp 124–128 °C dec.

Preparation of *trans*-1-Methyl-2-phenylcyclopropane. A slurry of bromomethyliron, **6** (shown to be optically pure as described above) (2.23 g), in 3.6 g of *trans*-β-methylstyrene was stirred for 4 h in the dark. The mixture was diluted with hexane and filtered, and the solid was washed with hexane. Distillation of the volatiles and GLC analysis in comparison with a standard mixture indicated that 0.27 g of the cyclopropane was present (47% based on **6**). Pure cyclopropane was isolated by preparative GLC and identified by comparison with an authentic sample;[43] $[\alpha]^{25}_{D}$ +10.0° (hexane, *c* 0.6) corresponds to ca. 10% ee (enantiomeric excess), depending on the literature value taken for the pure material,[44] with the 1*S*,2*S* isomer predominating.[45]

The solid from the reaction mixture was chromatographed on alumina, and elution with CH$_2$Cl$_2$ afforded 1.34 g of CpFe(CO)-(PPh$_3$)Br (62% based on **6**), identified by comparison of its NMR and TLC data with those of an authentic sample;[46] mp 159–162 °C.

Preparation of CpFe(CO)(PPh$_3$)CH$_2$CN. To a benzene solution (10 ml) of chloromethyliron **5** (100 mg) was added a solution of 450 mg of KCN and 50 mg of tetrabutylammonium bromide in 1 ml of H$_2$O. The mixture was stirred vigorously for 45 min. The benzene layer was separated and chromatographed (alumina, hexane) and the product was eluted with ether: 32 mg (33%); mp 170–172 °C [lit.[47] mp 164–165 °C]; NMR and ir spectra agreed with those published.[47]

Preparation of CpFe(CO)(PPh$_3$)CH$_2$OCH$_3$ (14) from 5. The chloromethyliron compound **5** (0.5 g) was stirred overnight in 35 ml of methanol and 10 ml of ether containing 120 mg of KOAc. After solvent removal, the residue was taken up in chloroform and chromatographed (alumina, hexane). Elution with 50% ether–hexane afforded 258 mg (52%) of racemic **14**, mp 156–157.5 °C, characterized as above.

Preparation of CpFe(CO)(PPh$_3$)CH$_3$ (8). (a) From (+)5a. A cooled (0 °C) solution of 30 mg of NaBH$_4$ in 10 ml of DME was added in one portion to the chloromethyliron compound (+)**5a** (320 mg) suspended in 3 ml of DME at 0 °C. The stirred mixture was allowed to warm to 25 °C and was diluted with hexane (20 ml), and this solution was chromatographed (alumina, hexane). Elution with 40% ether–hexane afforded 210 mg (71%) of **8a**: mp 173–174 °C; $[\alpha]^{25}_{578}$ +50° (benzene, *c* 0.1); NMR (CDCl$_3$) δ −0.18 (d, 3, J_{HP} = 6.5 Hz), 4.29 (d, 5, $J_{HP} \approx 1$ Hz), 7.43 (m, 15); ir (CHCl$_3$) 1905 cm^{-1} (CO).

(b) From (+)6a. To the bromomethyliron (+)**6a** (0.46 g) was added a 0 °C solution of 30 mg of NaBH$_4$ in 10 ml of methanol. The mixture was allowed to warm to room temperature and the product, (+)**8a**, was purified as above: 130 mg (33%); mp 173–174 °C [lit.[46] mp 152 °C (racemic)]; $[\alpha]^{25}_{578}$ +91° (CH$_2$Cl$_2$, *c* 0.1).[26]

Preparation of Iron Alkyls, CpFe(CO)(PPh$_3$)R. General Procedure. To the chloromethyliron **5** dissolved in THF (15–20 ml for each 0.5 g of **5**) in a 0 °C bath was added 1.1–2 equiv of Grignard reagent, depending on the reaction scale (see Table I), or 1 equiv of RLi (at −78 °C). The solution was stirred for ca. 10 min at 0 °C, and most of the solvent was removed under reduced pressure, keeping the solution cold. In the presence of magnesium salts solutions of the iron alkyls are especially light sensitive toward racemization, so that light must be scrupulously excluded throughout these procedures. The concentrated solution was chromatographed (alumina, hexane). Elution with 20–30% ether–hexane followed by evaporation of the solvent afforded the pure product as an oil which could be crystallized (except isobutyliron) from hexane. See Table I for reactant ratios, yields, specific rotations, and melting points. Data for new compounds follow. **Propyliron (10)**: NMR (CDCl$_3$) δ 0.4–1.6 (m, 7), 4.1 (d, 5, $J_{PH} \approx 1$ Hz), 7.4 ppm (m, 15); ir (CHCl$_3$) 1905 cm^{-1}. Anal. Calcd for $C_{27}H_{27}FePO$: C, 71.38; H, 5.99. Found: C, 71.40; H, 6.16. **Isobutyliron (11)**: NMR (CDCl$_3$) δ 0.3–1.8 (m, 9; includes triplet centered at 0.8 ppm, *J* = 7 Hz, and m centered at 1.5 ppm), 4.2 (d, 5, $J_{PH} \approx 1$ Hz), 7.4 ppm (m, 15); ir (CHCl$_3$) 1920 cm^{-1}. Anal. Calcd for $C_{28}H_{29}FePO$: C, 71.81; H, 6.24. Found: C, 71.44; H, 6.03. **Cyclopropylcarbinyliron (13)**: NMR (CDCl$_3$) δ −0.2 to +1.0 (m, 6), 1.8 (m, 1), 4.4 (d, 5, $J_{PH} \approx 1$ Hz), 7.4 ppm (m, 15); ir (CHCl$_3$) 1900 cm^{-1}. Anal. Calcd for $C_{28}H_{27}FePO$: C, 72.12; H, 5.84. Found: C, 72.21; H, 5.86.

Sulfur Dioxide Insertion Reactions. (a) Ester 3b in Liquid SO$_2$. Ester **3b** ($[\alpha]_{578}$ +295°; 110 mg) was added to ca. 12 ml of SO$_2$ at reflux (−10 °C) and this solution was stirred under reflux (dry ice condenser) for 3 h during which time the red-orange color gradually changed to yellow-orange. The solvent was allowed to evaporate and the residue was taken up in CHCl$_3$ and chromatographed on alumina. Some starting material was eluted with CHCl$_3$, and then EtOAc–hexane (1:1) eluted the product, a yellow-orange amorphous glass: 54% yield; $[\alpha]^{25}_{578}$ +206° (EtOAc, *c* = 0.2). A rechromatographed sample was characterized: NMR (CDCl$_3$) δ 1.6–2.4 (m, 18), 3.6 (s, 2), 4.6 (d, 5, $J_{HP} \approx 1$ Hz), 4.7 (m, 1, >CH–O–), 7.4 ppm (m, 15); ir (film) 1970 (C≡O), 1710 (C=O), 1175, 1040 (S=O) cm^{-1}. Anal. Calcd for $C_{36}H_{41}FeO_5PS$: C, 64.28; H, 6.14. Found: C, 64.29; H, 6.32.

Insertion was carried out in an identical way on 31.4 mg of **3a** ($[\alpha]^{25}_{578}$ −304°) in 12 ml of SO$_2$ at reflux. Sulfinate was isolated in 53% yield as a glass; $[\alpha]^{25}_{578}$ −270° (EtOAc, *c* 0.2). Spectra of the (+) and (−) sulfinate diastereomers were indistinguishable except, in the case of NMR, in the presence of europium shift reagents (Table II).

(b) Racemic Alkyls in Liquid SO$_2$. The racemic iron alkyl (**8–12**, ca. 0.5 g) was dissolved in liquid SO$_2$ (5–10 ml). After ca. 10 min at reflux the SO$_2$ was allowed to evaporate and the deep green oil was taken up in CHCl$_3$ and submitted to chromatography (alumina). Elution with acetonitrile afforded product as a yellow-orange oil which could be crystallized from ether. The methylsulfinate **15** and benzylsulfinate **19** were identified by their properties in comparison with published data.[48] Data for new compounds follow. **Ethylsulfinate (16)**: yield 70%; mp 169–169.5 °C; ir (CHCl$_3$) 1945 (CO), 1170, 1040 (S=O) cm^{-1}; NMR (CDCl$_3$) δ 1.1 (t, 3, *J* = 7 Hz), 2.7 (m, 2), 4.6 (d, 5, $J_{HP} \approx 1$ Hz), 7.5 ppm (m, 15). Anal. Calcd for $C_{26}H_{25}FeO_3PS$: C, 61.92; H, 5.00. Found: C, 61.59; H, 5.04. **Propylsulfinate (17)**: yield 57%; mp 167.5–168 °C; ir (CDCl$_3$) 1950 (CO), 1170, 1045 (S=O) cm^{-1}; NMR (CDCl$_3$) δ 0.8 (t, 3, *J* = 7 Hz), 1.7 (m, 2), 2.6 (m, 2), 4.6 (d, 2, $J_{HP} \approx 1$ Hz), 7.5 ppm (m, 15). Anal. Calcd for $C_{27}H_{27}FeO_3PS$: C, 62.56; H, 5.25. Found: C, 62.32; H, 5.34. **Isobutylsulfinate (18)**: yield 65%; mp 171.5–172; ir (CHCl$_3$) 1950 (CO), 1175, 1040 (S=O) cm^{-1}; NMR (CDCl$_3$) δ 0.8 (t, 3, *J* = 6 Hz), 0.9 (t, 3, *J* = 6 Hz), 1.8–2.7 (m, 3), 4.6 (d, 4, $J_{HP} \approx 1$ Hz), 7.6 ppm (m, 15). Anal. Calcd for $C_{28}H_{29}FeO_3PS$: C, 63.17; H, 5.49. Found: C, 62.84; H, 5.39.

(c) Optically Active Alkyls in CH$_2$Cl$_2$ or DMF. In a typical procedure, ca. 100 mg of iron alkyl was dissolved in 15 ml of CH$_2$Cl$_2$ or DMF (DMF was freshly distilled from BaO), the solution was cooled to 0 °C, and SO$_2$ was slowly bubbled through (without reflux) for 2 min. The reaction mixture was stirred at 0 °C for 30 min and the solvent was removed at reduced pressure. The residue was taken up in CH$_2$Cl$_2$ and chromatographed (alumina). Elution with acetonitrile afforded the product which upon removal of the solvent formed a glass. The optically active sulfinates, which were not readily crystallized, were identified by comparison with the racemic compounds characterized above. Specific rotations, optical assay, reaction conditions, and yields are given in Table II.

(d) SO$_2$ Insertion in the Presence of KI. Typically, thoroughly dried KI (ca. 60 mg) was dissolved in ca. 25 ml of SO$_2$ at reflux (dry ice condenser), and to this was added ca. 200 mg of iron alkyl. After 10 min in the case of the methyliron **8** or the ethyliron **9** or after 3 h for ester **3**, the solvent was allowed to evaporate. The residue was taken up in a minimum of $CHCl_3$ and chromatographed (alumina, hexane). Elution with $CHCl_3$ afforded a 35–40% yield (in every case) of $CpFe(CO)(PPh_3)I$, while further elution with acetonitrile led to isolation of the sulfinate product. In the case of ester (+)**3b**, the sulfinate was isolated in 31% yield and was shown to have undergone insertion with ca. 94% stereospecificity as calculated from specific rotations. The results from the other two alkyls are shown in Table II.

(e) SO_2 Insertion into $CpFe(CO)(PPh_3)CH_2OR$. In a typical reaction, 100 mg of optically pure (–)-menthoxymethyliron (**4b**) was dissolved in 25 ml of SO_2 at –10 °C. After 2 h at reflux, the solvent was allowed to evaporate, the residue was taken up in $CHCl_3$, and this was chromatographed (alumina). Elution with $CHCl_3$, removal of solvent, and vacuum drying afforded 94 mg (82% yield) of product [mp 169–171 °C; $[\alpha]^{25}{}_{578}$ +80° (CH_2Cl_2, *c* 0.1)] assigned the structure $CpFe(CO)(PPh_3)CH_2S(O)_2O(Men)$ (**20**) based on its spectral data: ir ($CHCl_3$) 1940 (CO), 1310, 1150 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 0.5–2.4 (m, 19, with a d of d of ca. 1 H superimposed at δ 1.6, J_{AB} = 11 Hz, J_{HP} = 11 Hz), 2.7 (d of d, 1, J_{AB} = 11 Hz, J_{HP} ≈ 1 Hz), 4.2 (m, 1, CH–O), 4.4 (d, 5, J_{HP} ≈ 1 Hz), 7.4 ppm (m, 15). Additional relevant spectral data are given in Table III. Anal. Calcd for $C_{35}H_{41}FeO_4PS$: C, 65.22; H, 6.41. Found: C, 65.10; H, 6.40.

$CpFe(CO)(PPh_3)CH_2S(O)_2OCH_3$ (**21**) was prepared from racemic **14** in an identical manner; mp 152–153 °C; 77% yield; ir ($CHCl_3$) 1940 (CO), 1320, 1150 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 1.7 (apparent t, irradiation of P caused collapse to a d, 1 H, J_{AB} = 11 Hz, J_{HP} = 11 Hz), 2.6 (d of d, irradiation of P caused collapse to a d, 1 H, J_{AB} = 11 Hz, J_{HP} ≈ 1 Hz), 3.4 (S, 3), 4.5 (d, 5, J_{HP} = 1.4 Hz), 7.4 ppm (m, 15). Anal. Calcd for $C_{26}H_{25}FeO_3PS$: C, 60.01; H, 4.84. Found: C, 60.05; H, 4.90.

(f) Reaction of Cyclopropylcarbinyliron 13 with SO_2. SO_2 (ca. 10 ml) was condensed onto 1.3 g of racemic **13**, and the solution was stirred at reflux for 30 min. The solvent was allowed to evaporate, and the residue was taken up in CH_2Cl_2 and was chromatographed (5% deactivated alumina). Elution with 30% acetone–ether afforded 800 mg (54% yield) of orange solid, mp 164–166 °C, identified as the butenylsulfinate **25**: ir ($CHCl_3$) 1950 (CO), 1160, 1040 (S=O) cm^{-1}; NMR ($CDCl_3$) δ 2.3–2.8 (m, 4), 4.7–5.2 (m, 3), 4.7 (d, 5, J_{HP} ≈ 1 Hz), 7.6 ppm (m, 15). Anal. Calcd for $C_{28}H_{27}FeO_3PS$: C, 63.41; H, 5.13. Found: C, 63.27; H, 5.14.

Further elution of the column with methanol yielded 240 mg (16% assuming structure **24**) of an orange oil which eluted as a single band but was too unstable to obtain interpretable NMR spectra. After standing as an oil for 3 days at room temperature, the polar oil (0.75 g) was rechromatographed as above. Acetone–ether eluted 230 mg (31%) of the butenylsulfinate **25** and 5% CH_3OH–CH_3CN afforded 360 mg (48% recovery) of the polar product. When 220 mg of the polar oil was left standing for 2.5 h in 10 ml of CH_2Cl_2 saturated with SO_2 at room temperature, chromatography led to the isolation of **25**, 120 mg (55%), and 90 mg (41%) of the oil.

Cyclopropylcarbinyliron **13** (400 mg), prepared from optically pure **5**, was dissolved in 15 ml of CH_2Cl_2 and SO_2 was slowly bubbled through the solution for $^1/_2$ h at room temperature. After standing an additional 1 h, the solution was concentrated and the residue was chromatographed on 10% deactivated alumina. The isolated **25** [200 mg (44%); $[\alpha]^{25}{}_{578}$ –57° (CH_2Cl_2, *c* 0.1)], was shown by NMR and $Eu(opt)_3$ to be of 40% ee.

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Registry No. **1**, 59349-66-5; **2**, 56977-53-8; (–)**3a**, 42936-43-6; (+)**3b**, 42992-04-1; (+)**4a**, 53584-63-7; (–)**4b**, 53521-53-2; **5**, 53521-54-3; (+)**5a**, 56907-95-0; (–)**5b**, 56907-96-1; **6**, 59349-64-3; (+)**6a**, 59433-06-6; **8**, 12100-51-5; (+)**8a**, 56907-97-2; (–)**8b**, 53318-87-9; **9**, 32824-72-9; (+)**9a**, 53318-85-7; **10**, 53683-99-1; (+)**10a**, 56907-98-3; **11**, 59367-58-7; (+)**11a**, 56861-24-6; **12**, 33135-99-8; (–)**12a**, 56907-99-4; **13**, 56861-25-7; (+)**13a**, 59433-07-7; **14**, 53521-55-4; **15**, 31811-87-7; (–)**15a**, 59367-39-4; (+)**15b**, 59367-40-7; **16**, 56861-28-0; (–)**16a**, 59367-41-8; **17**, 56861-29-1; (–)**17a**, 59367-42-9; **18**, 56861-30-4; (–)**18a**, 59367-34-9; **19**, 31811-66-2; (–)**19a**, 59367-35-0; (+)**20b**, 59349-67-6; **21**, 59349-65-4; **25**, 59331-92-9; (–)**25a**, 59367-36-1; $BrCH_2CO_2((-)_D\text{-men})$, 55284-67-8; $BrCH_2COBr$, 598-21-0; menthol, 2216-51-5; $Na[CpFe(CO)_2]$, 12152-20-4; PPh_3, 603-35-0; chloromethylmenthyl ether, 26127-08-2; $CpFe(CO)_2CH_2OCH_3$, 12108-35-9; $CpFe(CO)(PPh_3)CH_2CN$, 53897-01-1; (+)-(1*S*,2*S*)-*trans*-1-methyl-2-phenylcyclopropane, 53403-04-6; *trans*-β-methylstyrene, 873-66-5; CH_3Li, 917-54-4; CH_3Br, 74-83-9; CH_3CH_2Br, 74-96-4; *i*-PrBr, 75-26-3; C_6H_5Br, 108-86-1; C_6H_5Li, 591-51-5; c-C_3H_5Br, 4333-56-6; (+)$CpFe(CO)(PPh_3)CH_2COS(O)_2O(men)$, 59367-37-2; (–)$CpFe(CO)(PPh_3)CH_2COS(O)_2O(men)$, 59367-38-3; SO_2, 7446-09-5; $CH_3S(O)_2OCH_3$, 66-27-3; $CH_3OS(O)OCH_3$, 616-42-2; ^{13}C, 14762-74-4.

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(27) This type of reactivity is precedented for the nonchiral analogue $CpFe(CO)_2CH_2Cl$.[23b]

(28) Davison and co-workers have found that treatment of (+)**4a** (same configuration as (+)**6a**) with HBF_4 also leads to cyclopropanation of this same olefin, but in this case the (−)-(1*R*,2*R*)-cyclopropane predominates.[15b]

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Reactivity of the Radical and Anion of $C_3H_5Fe(CO)_2P(C_6H_5)_3$: The Debromination of Vicinal Organic Dibromides

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Tetrahydrofuran solutions of the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ radical and the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ anion were generated from η^3-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ using zinc dust and sodium amalgam, respectively. The solutions of these species free from reducing agents were found to be effective debromination reagents for vicinal organic dibromides. The stereochemistry of the debromination reactions was studied using racemic (*R*,*R* and *S*,*S*) and (*R*,*S*)-3,4-dibromohexane. The radical does not react stereospecifically but the anion can react stereospecifically with anti elimination.

Since the synthesis[1-3] of the η^3-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) system, principally structural[4] and spectral properties[5,6] of the allyliron derivatives have been investigated. The salient chemical feature of the system is the existence of both a stable radical[7] $C_3H_5Fe(CO)_3$ and anion[8] $C_3H_5Fe(CO)_3^-$. The iron atom in the monomeric radical has an effective atomic number of 17 while in the anion it has the inert gas configuration. The radical species was suggested[7] and recently unequivocally confirmed[9] to be in equilibrium with its dimer $[C_3H_5Fe(CO)_3]_2$. In the case of monophosphine substituted derivatives of the radical $C_3H_5Fe(CO)_2L$ (L = $P(C_6H_5)_3$, $P(C_4H_9)_3$), the equilibrium favors the monomeric radical.[7,9] Both the radical and anion exhibit an affinity toward halogen to regenerate the parent η^3-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) system. This paper reports the ability of both the radical and the anion to debrominate vicinal organic dibromides and compares the reactivity to the two related species. The principal comparison involves the stereochemistry of the debromination reaction.

Experimental Section

Chemicals were purchased from the following sources: triphenylphosphine, Pressure Chemical Co., iron pentacarbonyl, Alfa Inorganics; 3-bromopropene, Aldrich; *cis*- and *trans*-3-hexene, Chemical Samples Co. Tetrahydrofuran was purified by distillation under nitrogen from Vitride. The photochemical preparation of η^3-$C_3H_5Fe(CO)_3Br$ and the preparation of η^3-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ from η^3-$C_3H_5Fe(CO)_3Br$ were by the method of Heck.[1] The racemic (*R*,*R* and *S*,*S*) and (*R*,*S*)-3,4-dibromohexanes were synthesized by the method of Stokr and Doskocilova.[10] Photochemical reactions were run under nitrogen in a Rayonet photochemical reactor equipped with a magnetic stirrer. Infrared spectra were obtained using a Perkin-Elmer 137 spectrophotometer while ^1H NMR spectra were obtained using a Varian A60A Spectrometer. Gas chromatographs were obtained on a Model 700 Hewlett-Packard Chromatograph.

Preparation of the $C_3H_5Fe(CO)_2P(C_6H_5)_3$ Radical (I). The radical was prepared under nitrogen either in a drybox or in a Schlenk flask. A 0.742-g (1.5 mmol) sample of η^3-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ was mixed with an excess of zinc dust, 0.327 g (5.0 mmol), and 20 ml of tetrahydrofuran was added. The brown solution was stirred until a dark green color appeared. The mixture was filtered to remove excess Zn and the resulting solution was used to study the reaction of the radical, ν_{CO}(THF) = 1960, 1897 cm^{-1}.

Preparation of the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ Anion (II). The anion was prepared under nitrogen either in a drybox or using a Schlenk flask. A 0.742-g (1.5 mmol) sample of η^3-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ in 20 ml of tetrahydrofuran was added to Na(Hg) containing 0.12 g of sodium (5 mmol). After about 3 min of stirring the green color of the radical appeared and within 15 min a deep red-brown color appeared. The mixture was then filtered through Celite to remove excess sodium amalgam and the filtrate used to study reactions of the anion ν_{CO}(THF) = 1960, 1890 cm^{-1}.

Reaction of 3,4-Dibromohexane with the Radical and the Anion of $C_3H_5Fe(CO)_2P(C_6H_5)_3$. The procedure for the reaction of either $C_3H_5Fe(CO)_2P(C_6H_5)_3$ or $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$ with the stereoisomers of 3,4-dibromohexane was the same. This procedure is illustrated for the radical. A solution of 1.5 mmol of the radical in tetrahydrofuran was prepared as described above. The solution was placed under nitrogen in a single necked flask modified with a side