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A Study of the Stereochemistry at Iron of Electrophilic Cleavage of the Iron–Carbon σ Bond in Methyl(η⁵-1-methyl-3-phenylcyclopentadienyl)carbonyl(triphenylphosphine)iron(II)

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Abstract: The stereochemistry at iron of electrophilic cleavage, with insertion or elimination, of the Fe–CH₃ σ bond in the diastereomers (used as enantiomeric pairs) of the "pseudotetrahedral" $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (**2**) was investigated by ¹H NMR spectroscopy and X-ray crystallography. The insertion of SO₂ in **2** to yield the corresponding S-sulfinate, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$ (**3**), is essentially stereoselective (>95% stereospecificity) in CH₂Cl₂ solution, and highly (79%) stereospecific in neat SO₂. Eliminative cleavage of **2** by a deficiency of each of HI, I₂, and HgI₂ to afford the iodo complex, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (**4**), proceeds with variable stereospecificity (0–67%). The stereospecificity of this cleavage by a given electrophile is unequal for the two diastereomers of **2** (0–38 and 38–67%), and higher with I₂ (38–67%) than with HI and HgI₂ (0–47%). Unreacted **2** undergoes epimerization during the reaction to an extent (20–42%) which appears to be independent of the diastereomer employed. To elucidate the stereochemistry of these eliminative cleavage reactions crystal structure determinations were carried out of one diastereomer each of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ (**1**) and **4**. The structural results, taken in conjunction with the known stereochemistry of the photochemical decarbonylation of acyl(η⁵-cyclopentadienyl)iron complexes, show that the cleavage of **2** by the iodine-containing electrophiles (EI) proceeds with net retention of configuration at iron. A mechanism is proposed which involves attack of the electrophile at the iron center to generate an ionic intermediate, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)\text{-}[P(C_6H_5)_3](CH_3)E^+I^-$ (**5**), containing a square pyramidal cation. Reductive elimination of CH₃E followed by coordination of iodide or, alternatively, nucleophilic attack of iodide at the ligated CH₃ (when E = I) lead to product **4**. These individual steps are discussed in the context of the observed net retention of configuration at iron and the previously reported stereochemical results at α carbon of such cleavage processes. A possible fluxional behavior of **5** and its relationship to partial epimerization of unreacted **2** are also considered. Crystallographic details follow. Crystals of the iodide complex (**4a**) are monoclinic, space group $P2_1/n$, with $a = 9.773$ (7) Å, $b = 15.635$ (8) Å, $c = 17.235$ (8) Å, $\beta = 92.43$ (4)°, $V = 2631$ (6) Å³, $Z = 4$. The structure, refined to an R value of 0.078 for 2541 reflections, consists of a racemic mixture of molecules having RS and SR configurations. The acetyl complex (**1b**) crystallizes as a benzene solvate in the triclinic space group $P\bar{1}$, with $a = 15.359$ (4) Å, $b = 9.072$ (3) Å, $c = 14.112$ (4) Å, $\alpha = 86.22$ (3)°, $\beta = 119.64$ (2)°, $\gamma = 109.38$ (2)°, $V = 1601$ (2) Å³, $Z = 2$. Final R factor = 0.081 for 2370 reflections. Crystals of the acetyl complex are also racemic, and contain equal numbers of each member of the enantiomeric pair (RR/SS).

Introduction

Cleavage of transition metal–carbon σ bonds, either insertive or eliminative, is a reaction of great importance in catalysis and stoichiometric synthesis, as well as in the identification of organometallic compounds.[2–6] This reaction is often promoted by electrophilic reagents which vary considerably in nature and include, inter alia, protic acids, halogens, covalent oxides, and metal salts. Although the literature abounds in examples of such electrophilic cleavage, relatively little is known about mechanism. A very recent review[7] considers this subject in some detail.

The Ohio State University (OSU) group has for some time been engaged in mechanistic investigations of cleavage reactions of transition metal–carbon σ bonds.[8-10] In order to obtain maximum possible information for a given reaction, organometallic substrates were sought which would lend themselves not only to kinetic studies, but to stereochemical examination at both α carbon and metal as well.

Alkyliron complexes of the type η^5-$C_5H_5Fe(CO)LR$ (L = CO or another neutral monodentate ligand) represent ideal candidates for such substrate compounds for several reasons. First, these complexes are inexpensive and readily accessible organometallic derivatives, known for a variety of alkyl groups R when L is CO, a phosphorus-donor ligand, or an organic isocyanide.[3] Second, they are "18-electron" species which generally show both sufficient stability to decomposition and kinetic inertness to ligand dissociation at ambient temperatures. Third, with L other than CO, the molecules η^5-$C_5H_5Fe(CO)LR$ contain a chiral metal center of high enough configurational stability to allow resolution into enantiomers.[11-13] Because of favorable stability and "pseudotetrahedral" structural simplicity, these compounds are well suited for studies of stereochemical changes at metal in chemical reactions.

Stereochemical studies at iron of reactions involving η^5-$C_5H_5Fe(CO)LR$ or related $(\eta^5$-$C_5H_3R'R'')Fe(CO)LR$ have utilized, with success, both enantiomeric and diastereomeric species of such compositions.[9-16] Diastereomers are obtainable by the introduction of another chiral center into the molecule: in $(\eta^5$-$C_5H_3R'R'')Fe$ (R' $\neq$ R''), L, or R. The use of diastereomers, either as an enantiomeric pair or as a single stereoisomer, offers the advantage of a generally facile separation by physical techniques. Moreover, determination of diastereomeric ratios in mixtures by NMR spectroscopy is often possible without the use of shift reagents. However, varying degrees of asymmetric induction have been observed in reactions that utilized diastereomeric species[9,17] and may, in some cases, detract from the usefulness of this approach.

In this paper we report stereochemical studies at iron of electrophilic cleavage of the iron–carbon σ bond in the diastereomers (each an enantiomeric pair) of $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2) by each of SO_2 (with insertion), HI, I_2, and HgI_2 (with elimination). Iodine-containing electrophiles were selected over their chlorine or bromine counterparts because they afford the organometallic halo product, $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (4), of the highest configurational stability.

1, X = C(O)CH₃
2, X = CH₃
3, X = S(O)₂CH₃
4, X = I
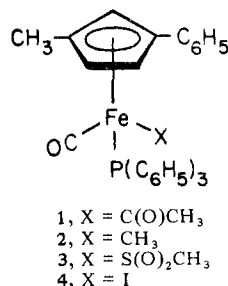
Reactions of η^5-$C_5H_5Fe(CO)LR$ with the aforementioned electrophiles have been the object of previous kinetic and stereochemical investigations. The kinetics of the SO_2 insertion[8,18] and the HgX_2 (X = Cl, Br, I) cleavage[10] in a series of η^5-$C_5H_5Fe(CO)_2R$ complexes was studied in neat SO_2 and organic solutions. The stereochemistry at α carbon of the SO_2 insertion in each of η^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$[19] and η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$[20,21] was found to proceed with inversion of configuration, whereas that of the cleavage by $HgCl_2$ of the same two compounds occurred with retention.[22,23] Halogen (Cl_2, Br_2, I_2, ICl) cleavage of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ takes place with varying

degrees of retention of configuration at α carbon;[24] by contrast, the Br_2 and I_2 cleavage of η^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$ proceeds with inversion.[19] Recently, the SO_2 insertion in η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$,[9] η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C(O)OC_{10}H_{19}$ ($C_{10}H_{19}$ = menthyl),[13] and η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)_2$[16] was shown to occur with high stereospecificity at iron, and with retention of configuration for the last compound. Some studies at iron of the CF_3CO_2H, X_2 (X_2 = Cl_2, Br_2, I_2, ICl), and HgI_2 cleavage of η^5-$C_5H_5Fe(CO)[(C_6H_5)_2PN(CH_3)CH(CH_3)C_6H_5]CH_3$[14] and η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ (R = CH_3, C_2H_5, $CH_2OC_{10}H_{19}$, $CH_2C(O)OC_{10}H_{19}$),[25] communicated subsequent to the publication of certain preliminary aspects of this work,[17] report varying degrees of stereospecificity, most likely retention.

Presented now in detail is our stereochemical study. Also reported as an integral part of this investigation are X-ray crystallographic results on $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)$-$Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ (1) and $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (4) which show that the eliminative cleavage by HI, I_2, and HgI_2 proceeds with varying degrees of *retention* of configuration at iron. Combined with kinetic and α-carbon stereochemical results of the aforementioned, earlier studies, our present findings provide a more complete mechanistic picture of the cleavage reactions in point.

Experimental Section

General Procedures. All reactions of and control experiments on organoiron compounds were conducted under an atmosphere of nitrogen. Unless indicated otherwise, they were done at room temperature. Photochemical experiments were carried out in Pyrex tubes using a Rayonet Model RPR-100 photochemical reactor equipped with 350-nm lamps. Neutral alumina (Ventron) deactivated with distilled H_2O (5%) was used in all chromatographic separations and purifications. Melting points were taken in vacuo on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer or on a Beckman Model IR-9 spectrophotometer. Solution spectra were taken with a pair of matched 0.1-mm KBr cells. A polystyrene film was used for calibration. ¹H NMR spectra were obtained on a JEOL JNM-MH-100 or a Varian A-60A spectrometer. Tetramethylsilane was used as an internal standard in these measurements. Mass spectra were recorded at 70 eV on an AEI MS-9 spectrometer by Mr. C. R. Weisenberger.

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under an atmosphere of nitrogen immediately before use. Reagent grade benzene and technical grade pentane were distilled from CaH_2. Spectroscopic grade $CHCl_3$ and CH_2Cl_2 were used without further purification.

Anhydrous grade sulfur dioxide, from Matheson, was passed through concentrated H_2SO_4 and then through a 24-in. column of $CaCl_2$-P_4O_{10}. Anhydrous HI was prepared by treating 1,2,3,4-tetrahydronaphthalene with I_2.[26] Reagent grade HgI_2 was used as received from General Chemical Co. Methylmercuric iodide (CH_3HgI) was synthesized by the method of Nesmeyanov.[27] Commercial iodine was sublimed before use. Other procured chemicals were used without additional purification.

The preparation of the complexes $[\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)$-$Fe(CO)_2]_2$, $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ (1), and $(\eta^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2), and the separation of the diastereomers of 1, 1a and 1b, and 2, 2a and 2b, followed the published procedures.[15] Crystals for X-ray diffraction study of the less soluble diastereomer of 1, 1b, were grown from 3:2 pentane–benzene at 5 °C[15] by Dr. J. L. Hughey. They were isolated as the benzene solvate of 1b, 1b · C_6H_6, mp 87–88 °C with evolution of benzene vapor. Other, new organoiron complexes were synthesized as detailed below. All infrared and ¹H NMR spectroscopic data of these compounds are set out in Table I.

Table I. Infrared and ^{1}H NMR Spectra of New Organoiron Compounds

compd	IR,[a] cm^{-1}	^{1}H NMR,[b] τ
$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$	$\nu(CO)^c$ 2049 vs, 1989 vs	C_6H_5 2.4–3.0 m (5 H); C_5H_3 5.30 m (1 H), 5.60 m (2 H); CH_3 8.08 s (3 H) (C_6D_6 solution)
$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)\text{-}[P(C_6H_5)_3]S(O)_2CH_3$ (50:50 **3a–3b**)	$\nu(CO)$ 1958 vs; $\nu(SO_2)^d$ 1161, 1031	C_6H_5 2.4–3.0 m (20 H, **3a** and **3b**); C_5H_3 5.15 m (1 H, **3a** and **3b**), 5.32 m (0.5 H, **3a**), 5.50 m (0.5 H, **3a**), 5.66 m (0.5 H, **3b**), 6.01 m (0.5 H, **3b**); SCH_3 7.60 s (1.5 H, **3b**), 7.61 s (1.5 H, **3a**); CCH_3 8.11 s (1.5 H, **3b**), 8.20 s (1.5 H, **3a**) (CDCl$_3$ solution)
$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)\text{-}[P(C_6H_5)_3]I$ (50:50 **4a–4b**)	$\nu(CO)^e$ 1949 vs	C_6H_5 2.4–3.0 m (20 H, **4a** and **4b**); C_5H_3 5.17 m (0.5 H, **4a**), 5.35 m (0.5 H, **4b**), 5.61 m (0.5 H, **4a**), 5.89 m (0.5 H, **4b**), 6.41 m (0.5 H, **4a**), 6.82 m (0.5 H, **4a**); CH_3 7.82 s (1.5 H, **4b**), 8.05 s (1.5 H, **4a**) (C_6D_6 solution)

[a] CHCl$_3$ solution and Perkin-Elmer Model 337 spectrophotometer unless noted otherwise. Abbreviations: vs, very strong. [b] Abbreviations: s, singlet; m, multiplet. [c] CH$_2$Cl$_2$ solution. [d] Nujol mull. [e] Beckman IR-9 spectrophotometer.

Preparation of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$ (3). Sulfur dioxide was condensed (ca. 25 mL of liquid) onto 303 mg (0.586 mmol) of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2) and the resulting solution was maintained at reflux (−10 °C) for 2 h. Excess SO$_2$ was removed first in a stream of nitrogen and then under reduced pressure (27 °C, 20 Torr) to leave a green solid. This residue was dissolved in minimum CH$_2$Cl$_2$ and introduced onto a 2 × 25 cm column of alumina. Upon addition of CH$_2$Cl$_2$ the green band gradually turned orange, and the latter was eluted off with CHCl$_3$. The volume of the effluent was reduced (27 °C, 20 Torr), and addition of pentane with stirring afforded orange crystals of **3** (175 mg, 51% yield), mp 103 (106)–110 °C dec (dependent on the ratio of the diastereomers of **3**, **3a–3b**). Anal. Calcd for C$_{32}$H$_{29}$FeO$_3$PS: C, 66.21; H, 5.04. Found (two samples containing different ratios **3a–3b**): C, 66.15, 66.10; H, 5.20, 5.10.

Preparation of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$. A solution of 2.1 g (4.0 mmol) of $[(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ and 1.5 g (5.8 mmol) of iodine in 25 mL of CHCl$_3$ was maintained at reflux for 30 min, then allowed to cool to room temperature and treated with 5 g of Na$_2$S$_2$O$_3$·5H$_2$O in 20 mL of H$_2$O in two portions. The CHCl$_3$ layer was separated and dried over MgSO$_4$. The solvent was removed (27 °C, 20 Torr) to afford 2.97 g (94% yield) of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$ as a black oil. Attempts to crystallize this product failed. The mass spectrum (source temperature 80 °C) shows peaks (intensities relative to 100 for m/e 56 of Fe$^+$ given in parentheses) at m/e 394 (P$^+$, 83), 366 ((P − CO)$^+$, C$_{24}$H$_{22}$Fe$^+$, 134), 338 ((P − 2CO)$^+$, 400), 211 ((P − 2CO − I)$^+$, 58).

Preparation of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (4). A. From $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$ and P(C$_6$H$_5$)$_3$. A solution of 2.97 g (7.55 mmol) of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$ and 2.35 g (8.95 mmol) of P(C$_6$H$_5$)$_3$ in 150 mL of THF was irradiated for 4.5 h. Solvent was removed (27 °C, 20 Torr) and the residue was dissolved in minimum benzene and chromatographed. Elution with 1:1 pentane–benzene produced two brown bands. The first band, eluted off with pentane–benzene, was shown by infrared spectroscopy to contain unreacted $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$ and P(C$_6$H$_5$)$_3$ whereas the second band, eluted off with benzene, yielded upon concentration of the effluent and addition of pentane 2.31 g (50%) of black crystals of **4**, mp 167 °C (50:50 mixture of the diastereomers of **4**, **4a–4b**). Anal. Calcd for C$_{31}$H$_{26}$FeIOP: C, 59.26; H, 4.17. Found: C, 59.25; H, 4.20.

B. From $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2) and HI. A solution of 115 mg (0.230 mmol) of **2** in 30 mL of CH$_2$Cl$_2$ was treated dropwise with rapid stirring with an approximately equimolar amount of freshly prepared HI in 50 mL of CH$_2$Cl$_2$. Solvent was removed (27 °C, 20 Torr) and the residue was dissolved in benzene and chromatographed. Elution with benzene, concentration of the effluent, and addition of pentane yielded crystalline **4** (101 mg, 72%).

C. From $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2) and I$_2$. A solution of 104 mg (0.412 mmol) of I$_2$ in 40 mL of CH$_2$Cl$_2$ was added dropwise to a rapidly stirred solution of 212 mg (0.412 mmol) of **2** in 15 mL of CH$_2$Cl$_2$. Complex **4** was then isolated as in the preceding reaction, yield 156 mg (60%).

D. From $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2) and HgI$_2$. A solution of 110 mg (0.242 mmol) of HgI$_2$ in 40 mL of THF was added dropwise to a rapidly stirred solution of 125 mg (0.242

mmol) of **2** in 30 mL of THF. The rest of the procedure was the same as above, resulting in the isolation of 131 mg (86% yield) of **4**.

Reaction of the Diastereomers of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2a and 2b) with SO$_2$. A. In CH$_2$Cl$_2$ Solution. Sulfur dioxide (ca. 0.5 mL of liquid, 10 mmol) was introduced into a graduated volumetric flask[8] containing 27 mL of CH$_2$Cl$_2$ at −75 °C, and this solution was added dropwise with stirring to 76-100 mg (0.14-0.194 mmol) of **2** enriched in **2a** or **2b** dissolved in 25 mL of CH$_2$Cl$_2$ at −10 °C. The resulting solution was stirred for 1 h, solvent was removed, and the residue was dissolved in minimum CH$_2$Cl$_2$. Chromatography (1.5 × 20 cm column) eluting with CHCl$_3$ and removal of the solvent from the effluent afforded 66-91 mg (78-80% yield) of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$, **3a–3b**. The stereochemistry of these and other reactions of the diastereomers **2a** and **2b** with electrophilic reagents is presented in Table II.

B. In Neat SO$_2$. Sulfur dioxide (ca. 25 mL of liquid) was added to 75 mg (0.15 mmol) of diastereomerically enriched **2a–2b** at −78 °C and the resulting solution was maintained at ca. −60 °C for 2 h. Excess SO$_2$ was removed in a stream of nitrogen, and workup identical with that described above afforded ca. 45 mg (55% yield) of **3a–3b**.

This reaction was also carried out at −10 °C using ca. 3 mL of liquid SO$_2$. Removal of excess SO$_2$ followed by the same workup gave a 36% yield of **3a–3b**.

C. In Liquid SO$_2$ in the Presence of Iodide. A solution of 5.4 g of $[(n\text{-}C_4H_9)_4N]I$ in 25 mL of liquid SO$_2$ at −75 °C was added to 75-95 mg (0.14-0.19 mmol) of diastereomerically enriched **2a–2b** at −78 °C. The resulting solution was maintained at ca. −60 °C for 15 min and then was allowed to warm to −10 °C and kept at reflux for 1 h. The workup was similar to that described above. Elution of the column with benzene afforded 10-24 mg (11-21% yield) of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)]P(C_6H_5)_3]I$, **4a–4b**. Then elution with CHCl$_3$ gave an undetermined amount of a mixture of **3a–3b** and $[(n\text{-}C_4H_9)_4N]I$.

Reaction of Various Diastereomeric Mixtures of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2a–2b) with HI. Freshly prepared anhydrous HI (ca. 0.05 mmol) in 40 mL of CH$_2$Cl$_2$ was added dropwise to a rapidly stirred, ice-cooled solution of 100 mg (0.194 mmol) of different mixtures **2a–2b** in 35 mL of CH$_2$Cl$_2$. Solvent was removed and the residue was dissolved in minimum benzene and chromatographed (1.5 × 17 cm column). Elution with 1:1 pentane–benzene afforded unreacted **2a–2b** and then elution with benzene gave **4a–4b**. Solvents were evaporated (27 °C, 20 Torr) and the residues were pumped on in vacuo to furnish 50-60 mg (67-80% recovery based on excess) of **2a–2b** and 20-27 mg (67-87% yield based on HI) of **4a–4b**.

Reaction of Various Diastereomeric Mixtures of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2a–2b) with I$_2$. The procedure strictly paralleled that for the preceding reaction, except that I$_2$ (12 mg, 0.049 mmol) was used in place of HI. A 65-70-mg (87-94% based on excess) recovery of **2a–2b** and a 24-25-mg (80-95% based on I$_2$) yield of **4a–4b** were realized.

Reaction of Various Diastereomeric Mixtures of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2a–2b) with HgI$_2$. A solution of 21 mg (0.049 mmol) of HgI$_2$ in 40 mL of THF was added dropwise to a rapidly stirred solution of 100 mg (0.194 mmol) of different mixtures **2a–2b** in 35 mL of THF. After 15 min of additional stirring

Table II. Stereochemistry of Reactions of the Diastereomers of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (**2a** and **2b**) with Various Electrophiles

electrophile	starting 2a–2b	recovered 2a–2b (% retention)	isolated 3a–3b (% stereospecificity)	isolated 4a–4b (% stereospecificity)
SO₂ (in CH₂Cl₂)	97:3	*a*	>95:5 (>95)	
	8:92	*a*	10:90 (95)	
SO₂ (neat, ca. −60 °C)	90:10	*a*	83:17 (82)	
	8:92	*a*	18:82 (76)	
SO₂ (neat, −10 °C)	77:23	*a*	71:29 (78)	
SO₂ (with added I⁻)	90:10	*a*	*b*	37:63
	16:84	*a*	*b*	33:67
HI	90:10	73:27 (58)		53:47 (8)
	50:50	50:50		42:58
	14:86	27:73 (64)		33:67 (47)
I₂	100:0	90:10 (80)		69:31 (38)
	97:3	90:10		67:33
	62:38	54:46		54:46
	50:50	50:50		49:51
	33:67	40:60		40:60
	8:92	20:80 (71)		22:78 (67)
HgI₂	100:0	85:15 (70)		50:50 (0)
	90:10	77:23		50:50
	50:50	50:50		42:58
	8:92	17:83 (79)		34:66 (38)

a No recovery. *b* Diastereomeric ratio not determined; see Experimental Section.

solvent was removed. The rest of the procedure was identical with that described for the corresponding reactions of HI. A 65–69-mg (87–92% based on excess) recovery of **2a–2b** and a 26–29-mg (85–95% based on HgI₂) yield of **4a–4b** were obtained.

Separation of the Diastereomers of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)$-Fe(CO)[P(C₆H₅)₃]I (4a and 4b). The diastereomers **4a** and **4b** were partially separated by a combination of column chromatography and fractional crystallization. The following represents a typical procedure.

Approximately 1.3 g of 50:50 **4a–4b** was dissolved in minimum benzene and chromatographed on a 2.7 × 37 cm column of alumina. With pentane as the eluent, **4a–4b** remained at the top of the column. When the eluent was changed from pentane to 3:2 pentane–benzene the broad brown band moved slowly. This band was eluted and the solvent was removed until 0.39 g of material had been collected. Addition of pentane afforded black crystals of 11:89 **4a–4b**.

The remainder of the band was eluted off with CH₂Cl₂, solvent was removed, the residue (0.91 g) was dissolved in benzene (10 mL)–pentane (15 mL), and the resulting solution was stored under nitrogen at 5 °C for 24 h. The crystals which had formed were collected and washed with pentane to afford 0.59 g of 67:33 **4a–4b**. These crystals were then dissolved in benzene (10 mL)–pentane (13 mL) and again stored under nitrogen at 5 °C for 24 h. The resulting crystals were filtered off and washed with pentane to yield 0.41 g of 83:17 **4a–4b**.

Three additional, similar crystallizations afforded pure **4a** suitable for X-ray diffraction.

Configurational Stability of the Diastereomers of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (2a and 2b). A. In the Presence of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (4a–4b). A rapidly stirred solution of 70 mg (0.14 mmol) of 92:8 **2a–2b** in 30 mL of CH₂Cl₂ was treated dropwise with 45 mg (0.072 mmol) of 26:74 **4a–4b** in 40 mL of CH₂Cl₂. The resulting solution was stirred for an additional 30 min. Usual workup including chromatography led to a complete recovery of **2a–2b** and **4a–4b** of unchanged composition.

B. In the Presence of CH₃HgI. A solution of 12 mg (0.035 mmol) of CH₃HgI in 40 mL of THF was added dropwise to a rapidly stirred solution of 65 mg (0.13 mmol) of 90:10 and 13:87 **2a–2b** in 35 mL of THF. After 30 min of additional stirring, usual workup resulted in a quantitative recovery of unchanged **2a–2b**.

Configurational Stability of the Diastereomers of $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I$ (4a and 4b). A. In CH₂Cl₂ and THF Solution. A solution of 40–50 mg of **4a–4b** (83:17 and 11:89) in 45–55 mL of each of CH₂Cl₂ and THF was stirred for 30–60 min. Removal of the solvent and chromatography led to a quantitative recovery of **4a–4b** of unchanged composition.

B. In the Presence of Iodide. A solution of 4.5 g (12 mmol) of [$(n\text{-}C_4H_9)_4N$]I in 25 mL of liquid SO₂ was treated with 75 mg (0.12 mmol) of 20:80 **4a–4b**. The resulting solution was maintained at ca. −60 °C for 1 h, the SO₂ was evaporated, and the residue was dissolved in minimum CH₂Cl₂ and chromatographed. Elution with benzene and removal of the solvent led to a complete recovery of 20:80 **4a–4b**.

C. In the Presence of Each of HI, I₂, HgI₂, and CH₃HgI. A solution (30–40 mL) of ca. 0.02–0.05 mmol of each of HI, I₂ (in CH₂Cl₂), HgI₂, and CH₃HgI (in THF) was added dropwise to a rapidly stirred CH₂Cl₂ or THF solution (30–40 mL) of approximately fourfold excess (equimolar for the CH₃HgI experiments) of various mixtures **4a–4b** (ranging from 83:17 to 11:89). Stirring was continued for an additional 30 min. Usual workup that followed led to an essentially quantitative recovery of **4a–4b** of unchanged (±1 percent unit) composition.

Determination of the Ratios of the Diastereomers 2a–2b, 3a–3b, and 4a–4b. The ratios of the diastereomers of complexes **2–4** were determined from the respective ¹H NMR spectra recorded on a JEOL JNM-MH-100 spectrometer by measuring peak height of the CH₃ groups on the cyclopentadienyl ring. Peak height measurements were found to give the same ratio as multiple integrations of the signals and have an error of ±1 percent unit. The average of four peak height measurements was taken.

Structure Analysis of $(RS\text{-}SR)\text{-}(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)$-[P(C₆H₅)₃]I (4a). The structure analysis of **4a**, which was actually carried out a year before that of **1b**, will be discussed first. Precession photographs of crystals of **4a** revealed the extinctions $h0l, h + l = 2n + 1$, and $0k0, k = 2n + 1$, indicating that the space group was $P2_1/n$. This is a nonstandard setting of space group number 14, having the following equivalent positions: (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

A crystal of dimensions 0.22 × 0.19 × 0.15 mm was selected for data collection and mounted on a glass fiber. Data collection and preliminary crystallographic experiments were performed on a Nonius CAD-3 automated diffractometer with Mo Kα radiation. General data collection and reduction details are essentially the same as those reported previously.[28] A total of 4936 reflections (±h, ±k, +l) were merged to yield 2541 independent reflections satisfying the criterion $I > 3\sigma(I)$ for subsequent structure solution and refinement. The standard deviation for each intensity reading, $\sigma(I)$, was estimated using the formula $\sigma(I) = [(\text{scan count}) + (\text{background count}) + (0.04)^2 (\text{integrated intensity})^2]^{1/2}$.

The structure was solved by conventional heavy atom methods. Scattering factor tables for I, Fe, P, O, and C (including $\Delta f'$ and $\Delta f''$ for Fe and I) were taken from the "International Tables for X-ray Crystallography".[29] From a three-dimensional Patterson synthesis,

Table III. Crystal Data and Details of Refinement for $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]X$ (X = I, C(O)CH₃)

molecular formula	$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)\text{-}$ $[P(C_6H_5)_3]I$ **(4a)**	$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]C(O)\text{-}$ $CH_3\cdot C_6H_6$ **(1b·C₆H₆)**
stereochemical designation	*RS–SR*	*RR–SS*
space group	$P2_1/n$ (no. 14n)	$P\bar{1}$ (no. 2)
cell constants *a*	9.773 (7) Å	15.359 (4) Å
b	15.635 (8) Å	9.072 (3) Å
c	17.235 (8) Å	14.112 (4) Å
α	90.0°	86.22 (3)°
β	92.43 (4)°	119.64 (2)°
γ	90.0°	109.38 (2)°
V	2631 (6) Å³	1601 (2) Å³
No. of formula units in the unit cell	4	2
mol wt	628.3	622.5
calcd density	1.59 g cm⁻³	1.29 g cm⁻³
obsd density	1.59 g cm⁻³	*a*
data collection limit	2θ = 45°	2θ = 45°
radiation used	Mo Kα	Mo Kα
max and min values for absorption (normalized to unity)	1.154–0.890	1.050–0.950
final agreement factor	*R* = 0.078 (2541 reflections)	*R* = 0.081 (2370 reflections)

a The ease with which **1b·C₆H₆** lost its benzene of crystallization prevented a reproducible density measurement.

the positions of the iron and iodine atoms were obtained and were used to phase a three-dimensional electron density map.[30] Several successive difference-Fourier syntheses, based on structure factor calculations phased by an increasing number of atoms, led to the unambiguous locations of all nonhydrogen atoms.

In the subsequent least-squares cycles, the parameters of this molecule were split into two sets (one set included the phosphine group only, the other set including all other atoms) and refined in two different matrices. Five cycles of least-squares refinement of all positional and thermal parameters (the iron, phosphorus, and iodine atoms anisotropically, all others isotropically) and the scale factor converged to the final agreement factors[31] R_F = 0.078, R_{wF} = 0.091 for 2541 reflections ($I > 3\sigma(I)$). A final difference-Fourier synthesis showed no unexpected features. Crystal data and details of refinement are reported in Table III.

Structure Analysis of (*RR–SS*)-(η^5-1-CH₃-3-C₆H₅C₅H₃)Fe(CO)-[P(C₆H₅)₃]C(O)CH₃·C₆H₆ (1b·C₆H₆). Precession photographs of numerous crystals of **1b·C₆H₆** revealed no symmetry other than an inversion center, indicating the triclinic crystal system. At this point, it was noted that the crystals turned to powder upon exposure to air; therefore all subsequent work was performed on crystals sealed in thin-walled glass capillaries.

Data were collected on a Syntex P2₁ automated diffractometer with Mo Kα graphite-monochromatized radiation. The crystal chosen for data collection exhibited the forms [105], [$\bar{1}0\bar{5}$], [705], [$\bar{7}05$], [02$\bar{1}$], and [0$\bar{2}$1] and was approximately 0.51 × 0.25 × 0.10 mm. At the beginning of data collection, 15 high-angle (19° < 2θ < 33°) general reflections were centered to obtain cell constants and an orientation matrix. Upon termination of data collection, 15 additional reflections were centered (20° < 2θ < 35°). A general least-squares fit of these 30 angle settings provided the cell constants reported in Table III. One hemisphere of data (3988 reflections) was collected by the ω scan technique in the variable scan mode, the scan range being set at 1.0°. Two check reflections were monitored every 60 reflections as a check on crystal and diffractometer stability. These standards showed only minor fluctuations throughout data collection.
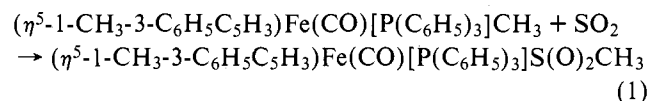
The standard deviation of each intensity reading, $\sigma(I)$, was estimated as before. Only reflections fulfilling the criteria $I > 3\sigma(I)$ were retained for subsequent structure solution (2370). An empirical absorption correction was applied, based on the average normalized variation of four reflections located near χ = 90°. Scattering factors for Fe, P, O, and C were taken from the "International Tables of X-ray Crystallography"[29] and the effects of anomalous dispersion for Fe were included in the calculations.

The subsequent structure solution was carried out in the centrosymmetric space group $P\bar{1}$ because of the known racemic nature of the crystal. The coordinates obtained for the Fe and P atoms were used to phase the data, and successive difference-Fourier syntheses revealed the locations of all nonhydrogen atoms in the crystal, including the benzene of crystallization. Four cycles of full-matrix least-squares

refinement, in which all positional and thermal parameters were varied, resulted in the agreement factors[31] R_F = 0.081 and R_{wF} = 0.076 for 2370 reflections with $I > 3\sigma(I)$. During the least-squares refinement, the Fe and P atoms were allowed to vary anisotropically, all other atoms isotropically. A final difference-Fourier synthesis was essentially featureless. Crystal data and details of refinement are reported in Table III.
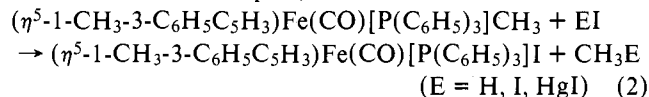
Results

Preparation and Characterization of Diastereomeric Iron Complexes. The previously reported[15] methyliron complex **2** reacts with neat SO₂ at reflux to afford the corresponding *S*-sulfinate, **3**, after workup:

$$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3 + SO_2$$
$$\rightarrow (\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3 \quad (1)$$

Reaction 1 likely proceeds by the intermediacy of the *O*-sulfinate, $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]OS\text{-}(O)CH_3$, as suggested by the isolation of a crude product which turned from green to orange upon chromatography. Sulfur dioxide insertion in complexes $\eta^5\text{-}C_5H_5Fe(CO)(PR'_3)R$ is known[9,32] initially to yield green-colored *O*-sulfinates, $\eta^5\text{-}C_5H_5Fe(CO)(PR'_3)OS(O)R$.

Spectroscopic properties of **3** are set out in Table I. It is of interest that a 50:50 mixture of the diastereomers of **2** (used throughout this work as enantiomeric pairs), **2a** and **2b**, furnished a 50:50 mixture of the diastereomers of **3**, **3a** and **3b**. This is most clearly evidenced by the appearance of two proton magnetic resonances of equal intensity at τ 8.11 and 8.20 for the ring-bonded CH₃ group (Table I). No separation was attempted of **3a** and **3b**.

Reaction of **2** with each of HI, I₂, and HgI₂ in CH₂Cl₂ or THF solution at room temperature rapidly leads to the formation of the iodo complex, **4**:

$$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3 + EI$$
$$\rightarrow (\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I + CH_3E$$
$$(E = H, I, HgI) \quad (2)$$

An alternative synthesis of **4** consists of reaction of $[(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ with I₂ to give $(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I$ followed by photolysis in the presence of P(C₆H₅)₃:

$$[(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2 + I_2$$
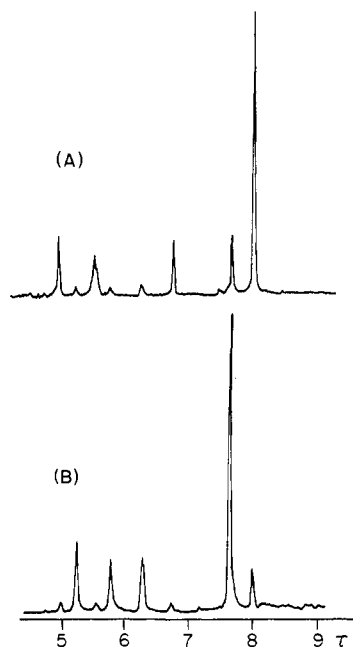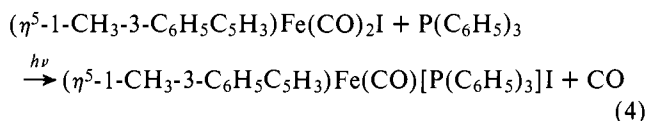$$\rightarrow 2(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I \quad (3)$$
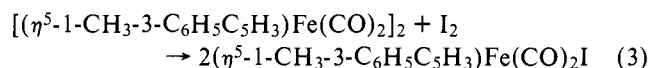
Figure 1. 100-MHz ^{1}H NMR spectra of (A) an 83:17 mixture **4a–4b** and (B) an 11:89 mixture **4a–4b**, both in C_6D_6 solution.

Figure 2. A molecular plot of the acetyl complex **1b** {η^5-1-CH$_3$-3-C$_6$H$_5$C$_5$H$_3$)Fe(CO)[P(C$_6$H$_5$)$_3$]C(O)CH$_3$}. The racemic crystal contains equal numbers of each member of the enantiomeric pair (*RR/SS*); what is actually shown here is the *SS* isomer.

$$(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2I + P(C_6H_5)_3$$

$$\xrightarrow{h\nu} (\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I + CO$$

$$(4)$$

The latter procedure affords **4** approximately as a 50:50 mixture of its diastereomers, **4a** and **4b**. These diastereomers exhibit different NMR spectra, with separate signals for the CH$_3$ and each of the C$_5$H$_3$ protons (Table I), thus allowing determination of their relative amounts in mixtures. The ^{1}H NMR spectra in the region τ 4.5–9 of 83:17 and 11:89 mixtures of **4a** and **4b** are reproduced in Figure 1. The diastereomers were separated by a combination of chromatography on alumina and fractional crystallization from benzene–pentane. An X-ray crystallographic study of the slower eluting **4a** showed it to be the enantiomeric pair *RS–SR*[33] (vide infra).

To elucidate a stereochemical relationship between **2a–2b** and **4a–4b**, the less soluble diastereomer of the acetyl complex **1**, **1b**, was also investigated (as **1b·C$_6$H$_6$**) by X-ray crystallography. Its structure was established as *RR–SS* (vide infra). Crystallographic studies of **2** were precluded by unfavorable stability and difficulties in growing suitable crystals of this methyl complex. Advantage was therefore taken of the higher stability of **1** and of the finding[11] that photochemical decarbonylation of η^5-C$_5$H$_5$Fe(CO)[P(C$_6$H$_5$)$_3$]C(O)R to η^5-C$_5$H$_5$Fe(CO)[P(C$_6$H$_5$)$_3$]R proceeds with inversion of configuration at iron. Accordingly, one may assume with considerable confidence that the photochemical conversion of **1** to **2** also leads to inversion at metal. In this manner the absolute configurations of **2a** and **2b** were inferred.

Description of the Structures of the Diastereomers 1b and 4a. Two views each of **1b** and **4a** are shown in Figures 2–5, and selected distances and angles in the two molecules are given in Table IV. A complete listing of the distances and angles is available as supplementary material, together with the final atomic parameters and the observed and calculated structure factors (see paragraph at end of paper).

Since the space groups are centrosymmetric, each crystal is constrained to contain enantiomeric pairs of molecules. Examination of the figures reveals the stereochemical designations to be *RR–SS* for **1b** and *RS–SR* for **4a**. Although recognition is made somewhat difficult by the various con-
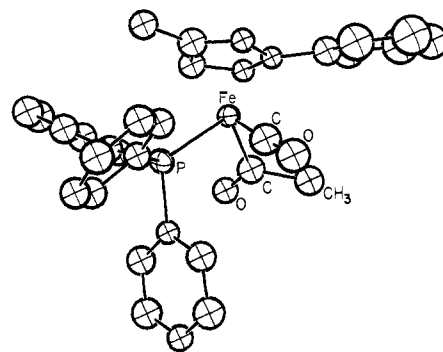
Table IV. Selected[a] Distances and Angles in (η^5-1-CH$_3$-3-C$_6$H$_5$C$_5$H$_3$)Fe(CO)[P(C$_6$H$_5$)$_3$]X [X = I, C(O)CH$_3$]

	1b (X = acetyl)	**4a** (X = iodide)
A. Bond Distances (Å)		
Fe–I		2.599 (2)
Fe–P	2.216 (3)	2.223 (4)
Fe–C(1)	1.700 (14)	1.735 (14)
Fe–C(2)	1.964 (12)	
Fe–C(Cp) av	2.136 (5)	2.125 (11)
P–C(Ph) av	1.844 (12)	1.825 (13)
C(1)–O(1)	1.193 (17)	1.074 (16)
C(2)–O(2)	1.228 (13)	
C(2)–C(3)	1.531 (15)	
C–C(Cp) av	1.428 (6)	1.422 (19)
C–C(Ph) av	1.405 (6)	1.389 (7)
C(6)–C(10)	1.506 (14)	1.508 (18)
C(8)–C(9)	1.537 (16)	1.544 (21)
B. Bond Angles (deg)		
P–Fe–I		94.3 (1)
P–Fe–C(1)	94.6 (4)	91.2 (4)
P–Fe–C(2)	90.6 (3)	
I–Fe–C(1)		91.7 (4)
I–Fe–Cen[b]		119.1 (3)
P–Fe–Cen[b]	122.0 (5)	121.2 (3)
C(1)–Fe–Cen[b]	122.0 (3)	119.0 (5)
C(2)–Fe–Cen[b]	115.0 (4)	
C(1)–Fe–C(2)	92.4 (6)	
Fe–C(1)–O(1)	178.1 (10)	175.2 (12)
Fe–C(2)–O(2)	123.7 (8)	
Fe–C(2)–C(3)	119.7 (8)	
C(3)–C(2)–O(2)	116.4 (10)	
Fe–P–C(Ph) av	115.8 (3)	115.8 (4)
C–P–C(Ph) av	102.4 (5)	102.4 (6)
P–C–C(Ph) av	120.0 (5)	119.7 (7)
C–C–C(Ph) av	119.9 (3)	120.5 (5)
C–C–C(Cp) av	108.0 (8)	108.0 (10)

[a] A full listing of the distances and angles in the two molecules is given in the supplementary material. [b] Cen = centroid of cyclopentadienyl ring.

formations that the cyclopentadienyl ring can adopt about the Fe–Cp axis, one can convince oneself that the molecule shown in Figures 2 and 3 is in fact the one labeled **1b**-*SS* in Scheme I. Similarly, Figures 4 and 5 can be shown to correspond to the molecule **4a**-*SR* in Scheme I. The distances and angles in the two molecules all fall within expected values, and so there are no unusual features in the compounds as far as structural parameters are concerned.

Reactions of Diastereomers of 2 with Electrophiles. The stereochemical results of the reactions of various diastereomeric mixtures **2a–2b** with each of SO$_2$, HI, I$_2$, and HgI$_2$ are summarized in Table II.
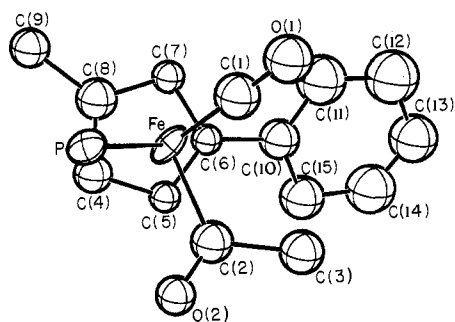
Figure 3. An alternative view of **1b**-*SS*, looking approximately from the Fe atom to the center of the cyclopentadienyl ring. The phenyl rings on the $P(C_6H_5)_3$ ligand have been omitted for clarity.

Scheme I

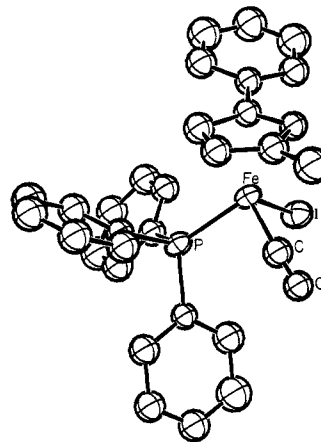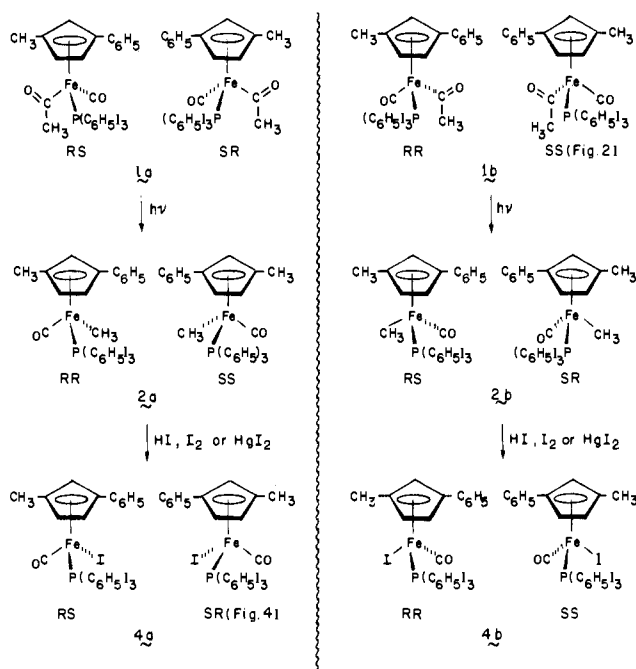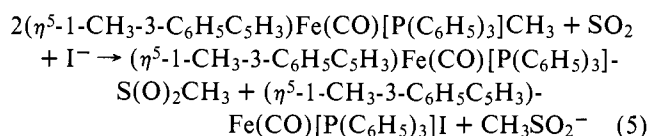**Figure 4.** A molecular plot of the iodide complex **4a** $\{(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]I\}$. As in the case of the acetyl complex, the structure analysis is carried out on a racemic crystal. This diagram shows the *SR* isomer of the (*RS/SR*) pair. The essential conclusion from the structure determination of compounds **1b** and **4a** is that the eliminative cleavage of an iron–carbon bond by HI, I_2, and HgI_2 proceeds with varying degrees of retention (see Scheme I).

Figure 5. The **4a**-*SR* molecule viewed roughly along the Fe–Cp axis. Again, the phenyl groups on the phosphine ligand have been removed for clarity.

The insertion of SO_2 in **2** (eq 1) proceeds with essentially equal stereospecificity at iron[37] for the two diastereomers. In CH_2Cl_2 solution the reaction is almost completely stereoselective ($\gtrsim 95\%$ stereospecificity) whereas in neat SO_2 it exhibits a lower, ca. 79%, stereospecificity. When carried out in neat SO_2 in the presence of a large excess of $[(n\text{-}C_4H_9)_4N]I$, the insertion affords both **3** and **4**:

$$2(\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3 + SO_2$$
$$+ I^- \rightarrow (\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]\text{-}$$
$$S(O)_2CH_3 + (\eta^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)\text{-}$$
$$Fe(CO)[P(C_6H_5)_3]I + CH_3SO_2^- \quad (5)$$

A **2a**–**2b** mixture enriched in **2a** yields the iodide **4**, which is substantially (32% stereospecificity) enriched in **4b**. Surprisingly, **2** enriched in **2b** also gives **4** rich in **4b** (50% stereospecificity). Since **4** is configurationally stable in the presence of $[(n\text{-}C_4H_9)_4N]I$ in liquid SO_2, the observed preferential formation of **4b** must be ascribed to a rather marked asymmetric induction in this substitution reaction. The isolated **3** was not analyzed for diastereomeric composition because of heavy contamination with the $[(n\text{-}C_4H_9)_4N]I$.

Eliminative cleavage reactions of **2a**–**2b** of various compositions with each of HI, I_2, and HgI_2 (eq 2) were carried out in CH_2Cl_2 or THF solution at 0 or 25 °C using a 4:1 ratio of
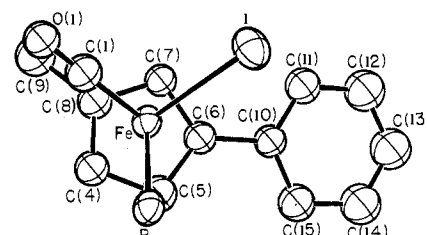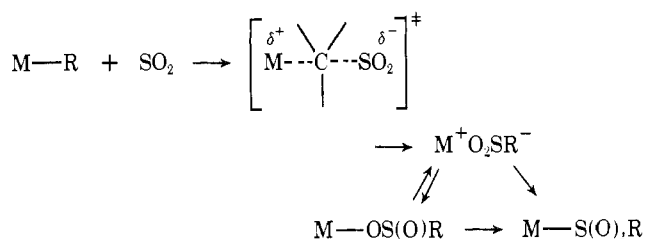
the methyliron complex to the electrophile. The cleavage is rapid, being essentially complete within a period of several minutes required for dropwise addition of the iodine-containing reagent. The use of a deficiency of the cleaving reagent allows isolation of diastereomeric mixtures of both unreacted **2** and product **4**, which were readily separated by chromatography on alumina. Products containing the eliminated CH_3 group (i.e., CH_4, CH_3I, and CH_3HgI from HI, I_2 and HgI_2, respectively) were not characterized in this study; however, they have been identified in related work.[9,10,19,22,24,39] Material balance based on iron is good but not quantitative, ranging from 67 to 95% and being best for the reactions with I_2 and HgI_2.

Unreacted **2** underwent some epimerization at iron in the cleavage reactions by all three electrophiles. The extent of such epimerization is higher in the cleavage by HI (58–64% retention) than in that by I_2 or HgI_2 (70–80% retention). In the cleavage by a given electrophilic reagent, the diastereomers **2a** and **2b** epimerize to a slightly different extent (Table II). However, no regular trend is apparent and the observed variations may not be significant. Control experiments conducted in an earlier study[15] established that **2** is configurationally stable when chromatographed on alumina or stored in CH_2Cl_2 and THF solutions at 25 °C for 4 h. Additional experiments have now revealed configurational stability of **2** in the presence of each of **4** in CH_2Cl_2 solution and CH_3HgI in THF solution.

The isolated iodo complex **4** lost part or all of the diastereomeric enrichment of the starting **2**. The extent of such epimerization in the conversion of **2** to **4** is a function of both the electrophile and the diastereomer of **2**, **2a** or **2b**. Thus cleavage

Scheme II

$$M\text{—}R + SO_2 \longrightarrow \left[\begin{array}{c} \overset{\delta^+}{M}\text{--}\overset{|}{\underset{|}{C}}\text{---}\overset{\delta^-}{SO_2} \end{array} \right]^{\ddagger}$$

$$\longrightarrow M^+O_2SR^-$$

$$M\text{—}OS(O)R \longrightarrow M\text{—}S(O)_2R$$

of **2a–2b** by I_2 to give **4a–4b** is accompanied by a higher stereospecificity (38–67%) than the corresponding cleavage by HI and HgI_2 (8–47 and 0–38% respective stereospecificities). Moreover, appreciable asymmetric induction was observed when using **2a–2b** of different compositions in a given type of reaction. Accordingly, mixtures **2a–2b** enriched in **2a** react to give **4a–4b** with lower stereospecificity (0–38%) than those enriched in **2b** (38–67% stereospecificity). Control experiments have demonstrated that **4** is configurationally stable for at least 1 h in CH_2Cl_2 in THF solutions and during chromatography on alumina. It is also stable with respect to epimerization in the presence of each of **2**, HI, I_2, HgI_2, and CH_3HgI in CH_2Cl_2 or THF solution.

Using the above stereochemical results and the structural data for **1b** and **4a** it can be shown that the cleavage of **2** to **4** by each of HI, I_2, and HgI_2 proceeds with varying degrees of retention at iron. As mentioned earlier, this conclusion requires the assumption that the photochemical decarbonylation of **1** to **2** inverts the configuration at "pseudotetrahedral" metal; this stereochemistry has been indeed demonstrated[11] for a very similar system. The relationships that exist among the diastereomers **1a–1b**, **2a–2b**, and **4a–4b** in these reactions, along with the assignment of the absolute configurations, are presented in Scheme I. In separate and independent studies of the electrophilic cleavage of related chiral iron complexes, Brunner[14] and Flood[25] reached similar conclusions with the aid of some reasonable assumptions.

Discussion

Sulfur Dioxide Insertion. The currently accepted mechanism for the sulfur dioxide insertion reaction of "18-electron" transition metal–alkyl carbonyl complexes (M–R) is presented in Scheme II.[40,41] This mechanism was originally proposed for the insertion in neat SO_2;[8] however, it most likely applies also to the insertion in organic solutions as evidenced by a similarity in the kinetic[8,18] and α-carbon stereochemical[19–21] behavior of η^5-$C_5H_5Fe(CO)_2R$ in various reaction media.

The stereochemical results of this study indicate that the postulated contact ion pair $M^+O_2SR^-$, specifically (η^5-1-CH_3-3-$C_6H_5C_5H_3$)$Fe(CO)[P(C_6H_5)_3]^+O_2SCH_3^-$, must possess substantial configurational stability, especially in CH_2Cl_2 solution. Thus this finding appears to be consistent with the observations of Brunner[42,43] that η^5-$C_5H_5Mn(NO)[P(C_6H_5)_3]C(O)C_6H_5$ undergoes ligand substitution to give η^5-$C_5H_5Mn(NO)(L)C(O)C_6H_5$ by a dissociative process, but with retention of configuration at metal. It is further in accord with the recently reported extended Hückel calculations[44] which suggest that "16-electron" species of the type η^5-C_5H_5MLL' are "pseudopyramidal" (i.e., nonplanar). The observed partial (21%) epimerization accompanying the conversion of **2** to **3** in neat SO_2 may be ascribed to dissociation of the contact ion pair and some epimerization of the resultant cation (η^5-1-CH_3-3-$C_6H_5C_5H_3$)$Fe(CO)[P(C_6H_5)_3]^+$ in this medium.

No structural studies were conducted on **3** to establish the stereochemistry at iron of the insertion. This is because the OSU group learned that an X-ray crystallographic investigation was underway by Flood and co-workers[16] on the stereochemistry of the conversion of η^5-$C_5H_5Fe(C$-

$O)[P(C_6H_5)_3]CH_2CH(CH_3)_2$ to η^5-$C_5H_5Fe(CO)[P(C_6$-$H_5)_3]S(O)_2CH_2CH(CH_3)_2$. Based on the results of these authors and on the mechanism in Scheme II, it seems virtually certain that the stereochemical outcome of reaction 1 is retention.

Iodide appears to trap some of the contact ion pair (η^5-1-CH_3-3-$C_6H_5C_5H_3$)$Fe(CO)[P(C_6H_5)_3]^+O_2SCH_3^-$ to afford **4** in addition to the expected **3**, as observed previously by Wojcicki and co-workers.[45] The formation of **4** enriched in **4b** from either **2a** or **2b** must proceed with net inversion at iron for **2a**, but with net retention of configuration for **2b** (cf. Scheme I). This difference in stereochemistry may be a consequence of the rather robust nature of **4a** caused by the proximity of the bulky $P(C_6H_5)_3$, C_6H_5, and I groups (cf. Figure 4). If the diastereomer **4b** is less sterically crowded, as one would expect, then its preferential formation over **4a** may be rationalized by displacement of the $O_2SCH_3^-$ by iodide from the backside of the contact ion pair derived from **2a**, but from the frontside of the contact ion pair derived from **2b**. The measured ratios **4a–4b** accord with 76% epimerization and 24% inversion at iron in the reaction of **2a**, and 64% epimerization and 36% retention of configuration at iron in the reaction of **2b**.

Eliminative Cleavage by HI, I_2, and HgI_2. An acceptable mechanism for the eliminative cleavage reaction of **2** with each of HI, I_2, and HgI_2 (eq 2) must accommodate the following results. First, it must account for net retention of configuration (or, in some cases, complete epimerization) at iron in the formation of **4** and for partial epimerization (with higher net retention) at iron of unreacted **2**. Second, such mechanism must be in accord with the reported kinetic data for the cleavage of η^5-$C_5H_5Fe(CO)_2R$ by HgX_2[10] and protic acids,[39] and with the observed retention of configuration at α carbon for the reaction of η^5-$C_5H_5Fe(CO)_2CHDCHDR$ (R = $C(CH_3)_3$, C_6H_5) with $HgCl_2$[22,23] but either retention or inversion for the reaction with halogens.[19,24]
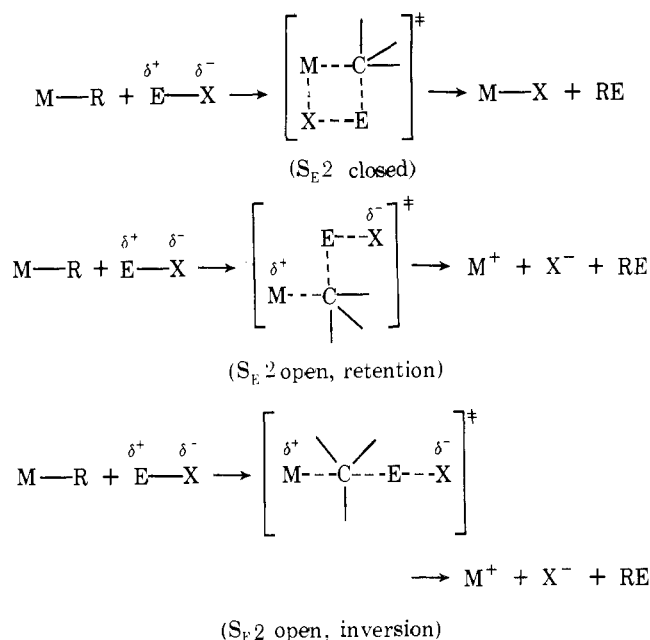
The most frequently invoked mechanism for the cleavage reactions of both representative metal and transition metal alkyls (M–R) involves attack of an electrophile at the α carbon of R.[7,46,47] This type of bimolecular interaction may lead to either retention (S_E2 closed or open, retention) or inversion (S_E2 open, inversion) of configuration at α carbon as depicted in Scheme III.

It is clear, however, that such mechanisms are inconsistent with the combined kinetic and stereochemical results of this and previous studies on η^5-$C_5H_5Fe(CO)LR$ and analogous "pseudotetrahedral" iron complexes. Perhaps the most convincing evidence against attack of the electrophile at the α carbon is derived from examination of reaction products of various η^5-$C_5H_5Fe(CO)LR$ and ICl. This cleavage yields η^5-$C_5H_5Fe(CO)LI$ and RCl,[24,25] rather than η^5-$C_5H_5Fe(CO)LCl$ and RI, as would be expected by the mechanisms in Scheme III. Also arguing against such S_E2 pathways are the observations on the reaction of several η^5-$C_5H_5Fe(CO)_2R$ with HgX_2, which, depending on the nature of R, affords either η^5-$C_5H_5Fe(CO)_2X$ and RHgX or η^5-$C_5H_5Fe(CO)_2HgX$ and RX.[10] The latter products are strongly suggestive of attack of HgX_2 at the metal rather than at the α carbon. Both types of HgX_2 cleavage reaction give the same rate expression and are thought to involve similar intermediates.

The results of this study are best rationalized by a mechanism presented in Scheme IV or by a slight variant thereof.[48]

The proposed electrophilic addition of EI to the metal results in formal oxidation of iron(II) in **2** to iron(IV) in the intermediate **5**. An η^5-cyclopentadienyliron(IV) complex, η^5-$C_5H_5Fe(CO)(SiCl_3)_2H$,[49] structurally similar to **5** has been characterized by X-ray crystallography.[50] The expected square pyramidal geometry of **5**, with η^5-1-CH_3-3-$C_6H_5C_5H_3$ in the

Scheme III

$$M\text{—}R + \overset{\delta^+}{E}\text{—}\overset{\delta^-}{X} \rightarrow \left[\begin{array}{c} M\text{---}C \\ \vdots \quad \vdots \\ X\text{---}E \end{array} \right]^{\ddagger} \rightarrow M\text{—}X + RE$$

(S$_E$2 closed)

$$M\text{—}R + \overset{\delta^+}{E}\text{—}\overset{\delta^-}{X} \rightarrow \left[\begin{array}{c} \overset{\delta^-}{E}\text{---}X \\ \overset{\delta^+}{M}\text{---}C\text{—} \end{array} \right]^{\ddagger} \rightarrow M^+ + X^- + RE$$

(S$_E$2 open, retention)

$$M\text{—}R + \overset{\delta^+}{E}\text{—}\overset{\delta^-}{X} \rightarrow \left[\overset{\delta^+}{M}\text{---}C\text{---}E\text{---}\overset{\delta^-}{X} \right]^{\ddagger}$$

$$\rightarrow M^+ + X^- + RE$$

(S$_F$2 open, inversion)

axial position, can in theory give rise to three geometrical isomers, with each of $P(C_6H_5)_3$, CH_3, and CO being trans to the added E. However, when E is the bulky I or HgI, its preferred position of attack at iron is likely to be between the small ligands CH_3 and CO, thus leading to the depicted stereochemistry of **5**.

The intermediate **5** may then reductively eliminate CH_3E to give a "16-electron" species **6** of expected "pseudopyramidal" (as opposed to planar) structure (Scheme IV, path A). Such a process has previously been proposed for E = H or HgX, and in the latter case receives support from the reported retention of configuration at the α carbon of R.[22,23] Capture of this coordinatively unsaturated cation by iodide, attacking from the "open" side, would yield **4** with net retention of configuration at iron, as noted in the present study. The observed variable loss of stereospecificity during the formation of **4** may result from a combination of epimerization of the "pseudopyramidal" **6** and attack of iodide on **6** from the side opposite the reductively eliminated CH_3E (also vide infra for further discussion of this point). The latter process would arise as a consequence of steric factors and has already been discussed for the reaction of **2** with SO_2 in the presence of iodide. It would account for the noticeable asymmetric induction favoring **4b** over **4a**. The reactions in Scheme IV, along with proposed intermediates **5** and **6**, are entirely in accord with the kinetics of such cleavage processes in $\eta^5\text{-}C_5H_5Fe(CO)_2R$.[10,39]

For the cleavage of **2** by I_2 one must consider, in addition to reductive elimination of CH_3E (i.e., CH_3I), nucleophilic attack of iodide at the coordinated CH_3 in **5** (Scheme IV, path B). Such backside nucleophilic attack has been proposed for reactions of several cationic transition metal–alkyl complexes with halide ion on the basis of observed inversion of configuration at the α carbon of R.[51,52] It has also been invoked for the cleavage of some $\eta^5\text{-}C_5H_5Fe(CO)_2R$ by halogens, including ICl.[25] The higher stereospecificity observed in this study for the formation of **4** from **2** using I_2 compared to HI and HgI_2 suggests that the former reaction may proceed substantially by attack of iodide at the CH_3 of **5**. Since the bulky I^+ is assumed to enter **2** preferentially in a position between the groups CH_3 and CO, the stereochemical result of the iodination would be retention of configuration at iron. The observed partial epimerization may come from attack of some E^+ (i.e., I^+) at **2** from the side between $P(C_6H_5)_3$ and CO or,

Scheme IV

R, R' = CH_3, C_6H_5
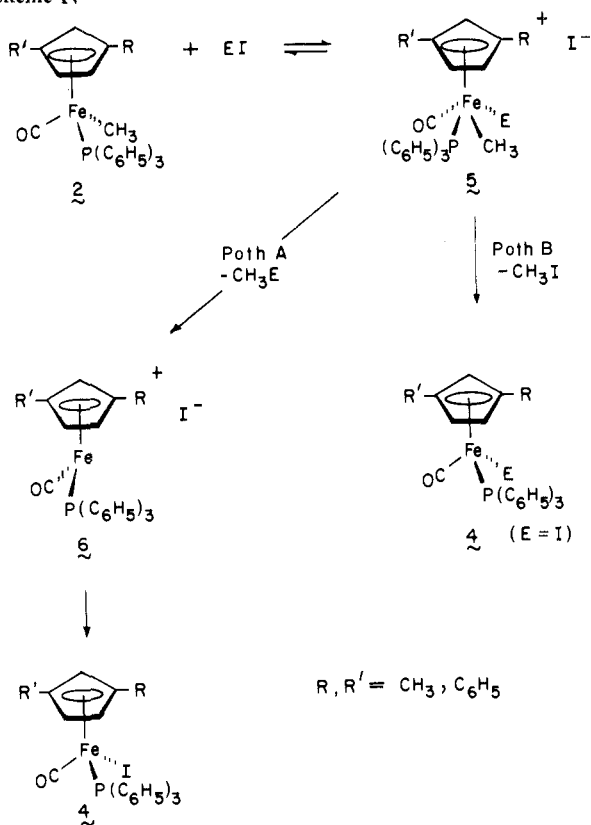
alternatively, from a contribution of the reductive elimination path.

Finally, we wish to address the question of partial epimerization of recovered **2**. The proposed square pyramidal structure of **5** is strictly analogous to that adopted by molybdenum(II) complexes of the type $\eta^5\text{-}C_5H_5MoL_2L'X$ and the protonated derivatives $(\eta^6\text{-}C_6H_xR_{6-x})M(CO)_2(PR_3)H^+$ (M = Cr, Mo, W). A number of such species have been shown to exhibit fluxional behavior,[53-55] even at low temperatures. Therefore it is not unreasonable to propose that **5** may undergo intramolecular epimerization by a similar fluxional process which proceeds at a rate comparable to either reductive elimination of CH_3E or attack by iodide. If indeed operative, such stereochemical nonrigidity would also account, at least in part, for the observed epimerization of product **4**.

There is, however, a troublesome feature of the aforementioned proposal. The observed degrees of epimerization of unreacted **2** from the cleavage by each HI, I_2, and HgI_2 are remarkably similar considering different electronic and steric properties of H, I, and HgI. Thus, a possibility exists that this epimerization may not occur along the reaction path but rather derive its origin from some other interaction of **2** with the electrophile.[25] The nature of such an interaction is not immediately obvious to us. Since stable iron complexes closely resembling **5** are unknown, further tests of the suggested fluxional behavior with a view to resolving this problem are precluded at present.

Conclusion

The present study indicates that stereochemistry at metal can be a valuable mechanistic tool when used as a complement to kinetics and stereochemistry at α carbon in investigations of reactions at metal–carbon σ bonds. Nevertheless, caution must be exercised in interpreting such stereochemical results, since it appears that considerations of geometry and stability applying to species of reduced coordination number of carbon may not extend to transition metals. The determination by

X-ray diffraction techniques of the absolute configuration of the chiral complexes **1b** and **4a** provides a groundwork for further investigations of stereochemistry at iron of reactions of such "pseudotetrahedral" complexes in an attempt to evaluate the usefulness of this mechanistic approach.

Supplementary Material Available: Listings of the final atomic parameters for the molecules **1b** and **4a** (Tables A and B), distances and angles (Tables C and D), and the observed and calculated structure factors (Tables E and F) (18 pages). Ordering information is given on any current masthead page.

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(31) $R_F = \Sigma ||F_{obsd}| - |F_{calcd}||/\Sigma |F_{obsd}|$; $R_{wF} = [\Sigma w(|F_{obsd}| - |F_{calcd}|)^2/\Sigma wF_{obsd}^2]^{1/2}$
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(33) The sequencing rules for establishing *R* and *S* designations associated with the chirality of π complexes are given in the literature.[34,35] Applied specifically to (η⁵-1-CH₃-3-C₆H₅C₅H₃)Fe they involve determination of the absolute configuration of C* (which has a higher priority than C** or any other C in the η⁵-C₅ ring) in
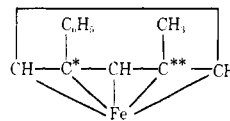
according to standard conventions for tetrahedral centers.[34] The priority sequence for determining *R* and *S* configuration for chiral iron follows the pseudoatom rules of Stanley and Baird[36] and gives I > η⁵-1-CH₃-3-C₆H₅C₅H₃ > P(C₆H₅)₃ > CO > C(O)CH₃ > CH₃. We propose herein to extend the sequencing rules of Stanley and Baird[36] to apply also to the ordering of *R* and *S* designations in a molecule containing more than one chiral center; accordingly, (*R* or *S*)C· precedes (*R* or *S*)Fe consistent with the relative atomic weights, η⁵-C₅ ring (60) > Fe (56).
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