account for all of the experimental observations if some tendency for dissociation of isocyanide ligands in coordinating solvents is assumed in order to rationalize the low molecular weight determinations in methyl ethyl ketone. The single resonance for the *tert*-butyl isocyanide protons can arise from stereochemical nonrigidity of the seven-coordinate molybdenum(I) atom or the rapid reversible dissociation of the *tert*-butyl isocyanide ligands.

In an attempt to prepare a cyclopentadienylmolybdenum-*tert*-butyl isocyanide derivative related to those studied in the previous paper[1] the reaction of $[(Me_3CNC)_4MoCl]_2$ with sodium cyclopentadienide in boiling tetrahydrofuran was investigated. However, this reaction gave an intractable product.

The reactions between various alkyl isocyanides and $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ provide an unusual example of a system where the choice of the alkyl isocyanide can greatly affect the type of metal complex formed. The reaction between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and methyl isocyanide to replace allyl chloride forming *cis*-$(CH_3NC)_4Mo(CO)_2$ after removal of the acetonitrile ligands contrasts significantly with the reaction between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and *tert*-butyl isocyanide to replace the carbonyl groups and finally the allyl group with retention of the chlorine to form $[(Me_3CNC)_4MoCl]_2$. The sensitivity of the reactions between $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ and alkyl isocyanides to changes in the alkyl isocyanide as compared with the reported reactions[10] between other transition metal complexes and alkyl isocyanides can be a consequence of the four different types of ligands in $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$ which are potentially replaceable by alkyl isocyanides. Transition metal complexes previously used for reactions with alkyl and aryl isocyanides have not contained such a variety of different ligands as $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$.

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Registry No. $C_3H_5Mo(CO)_2(CH_3CN)_2Cl$, 33221-75-9; $C_3H_5Mo(CO)_2(MeNC)_2Cl$, 51933-93-8; $C_3H_5Mo(CO)_2(EtNC)_2Cl$, 51933-94-9; $C_3H_5Mo(CO)_2$(*i*-PrNC)$_2$Cl, 51933-95-0; $C_3H_5Mo(CO)_2$(*t*-BuNC)$_2$Cl, 51933-96-1; $C_3H_5Mo(CO)_2$(*neo*-PentNC)$_2$Cl, 51933-97-2; $C_3H_5Mo(CO)_2$(*c*-HexNC)$_2$Cl, 51933-98-3; $C_3H_5Mo(CO)$(*t*-BuNC)$_3$Cl, 51933-99-4; $C_3H_5Mo(CO)$(*neo*-PentNC)$_3$Cl, 52022-17-0; [(*t*-BuNC)$_4$MoCl]$_2$, 52022-18-1; *cis*-$(MeNC)_4Mo(CO)_2$, 51933-82-5; *cis*-$(EtNC)_4Mo(CO)_2$, 51933-83-6.

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Stereochemical Studies at Pseudotetrahedral, Chiral Metal of the Decarbonylation, Carbonylation, and Sulfur Dioxide Insertion Reactions

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The stereochemistry of insertion and elimination reactions at the metal center in pseudotetrahedral, chiral organoiron complexes was investigated by ^1H nmr spectroscopy. The acyl complex $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ was synthesized by treatment of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH(CH_3)C_6H_5$ with $P(C_6H_5)_3$ and was separated into two diastereomerically related pairs of enantiomers by a combination of column chromatography and crystallization from benzene–pentane. The photochemical decarbonylation of each pair of enantiomers of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ in benzene solution proceeds with high stereospecificity (>64% retention or inversion) but is complicated by unequal stabilities of the isomers of the alkyl product $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$. The carbonylation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ in acetonitrile at 25° and under 4 atm of CO provided no stereochemical information on the reaction owing to configurational instability of the starting alkyl complex under these conditions. By contrast, the SO_2 insertion reaction of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ in neat SO_2 or in a *ca.* 2 *M* solution of SO_2 in CH_2Cl_2 takes place with high stereospecificity (⩾90% retention or inversion) to yield $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_2CH(CH_3)C_6H_5$. The implications of these results to the mechanism of the respective reactions are considered and discussed.

Introduction

Organometallic insertion and elimination reactions at transition metal–carbon σ bonds have attracted considerable interest in recent years.[1-3] This is largely attributable to their occurrence in a number of important stoichiometric and catalytic processes, *e.g.*, hydroformylation and polymerization.[4-6]

In this context, much attention has focused on the mechanism. Kinetic studies have been carried out on the carbonylation,[2] decarbonylation,[2] and sulfur dioxide insertion[3,7] in several different types of complexes containing transition metal–carbon σ bonds. Stereochemical investigations have established that the mechanism of the carbonylation and the decarbonylation is consistent with migration of the alkyl group onto the nearest coordination site of the metal.[2,8] For the SO_2 insertion, gross stereochemistry was found to be preserved in the formation of *cis*-$Mn(CO)_4[P(C_6H_5)_3]S(O)_2$-

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CH_3[9] and *trans*-η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]S(O)_2CH_3$[10] from the corresponding metal alkyls and SO_2. Retention of configuration at the α carbon has been observed in the carbonylation and decarbonylation reactions,[11,12] whereas inversion at the α carbon was noted in the SO_2 insertion.[11]

The foregoing summary of reported mechanistic data serves to emphasize a highly stereospecific nature of the insertion and elimination processes. To complete a stereochemical picture and to shed more light on the mechanism we endeavored to explore configurational changes at metal in a pseudotetrahedral (nonplanar), chiral environment which occur during the aforementioned types of transformation.

Synthesis, resolution, and reactions of chiral, four-coordinate transition metal complexes have received much attention recently,[13-16] principally from Brunner and coworkers.[13,14] Proton magnetic resonance studies have established that the chiral alkyl η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$[17] and the chiral acyl η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2C_6H_5$[18] possess high configurational stability at iron. These observations enhanced prospects of the feasibility of our proposed stereochemical study.

Although mixtures of enantiomers of general formula η^5-$C_5H_5Fe(CO)(PR'_3)R$ are readily accessible synthetically,[2] their resolution presents a formidable problem. For this reason we elected to work with structurally analogous diastereomers. Diastereomers, unlike enantiomers, are often readily separable by physical techniques, and their ratios in mixtures can in some cases be determined by nmr spectroscopy through measurements on diastereotopic (by external comparison) protons.

Diastereomeric alkyl compounds of the desired composition and structure can be designed by the introduction of another chiral center in η^5-$C_5H_5Fe(CO)(PR'_3)R$. We chose to introduce the second asymmetric center in the β position of the alkyl ligand, R. Such a location makes unlikely any possibility of epimerization at this center during transformations at the Fe–C σ bond. The compound η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ designed for the proposed stereochemical studies further promised a reasonable degree of stability, generally associated with the presence of a primary carbon–iron σ bond, and two diastereotopic (by external comparison) kinds of protons of low multiplicity, *viz.*, C_5H_5 and CH_3, in the nmr spectrum.

Herein we describe the synthesis and the separation of diastereomers of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ and of the corresponding acyl, η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$, together with studies on the stereochemistry of the carbonylation, decarbonylation, and SO_2 insertion involving these complexes. The decarbonylation of the acyl complex was mentioned briefly in a preliminary communication.[19]

Experimental Section

General Procedures. All reactions of organoiron compounds were conducted under an atmosphere of nitrogen. Photochemical experiments were carried out in a Rayonet Model RPR-100 photochemical reactor using 3500-Å lamps. The alumina used in chromatographic separations and purifications was deactivated with H_2O (5%). Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany.

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Acetonitrile was purified by distillation from P_4O_{10}. Sulfur dioxide, from Matheson, was passed through a column packed with $CaCl_2$ and P_4O_{10}. Other commercially procured solvents and common chemicals were of reagent grade or equivalent quality. They were used as received.

$(-)_D$-Menthol ($C_{10}H_{19}OH$), $C_6H_5CH(CH_3)CH_2COOH$, and $C_6H_5CH(CH_3)COOH$ were purchased from Aldrich Chemical Co. $(-)_D$-3-Phenylbutanoic acid was obtained by the reaction of racemic $C_6H_5CH(CH_3)CH_2COOH$ with $(-)_D$-menthol, resolution of the resultant ester, and base hydrolysis:[20] $[\alpha]^{21}D$ −57.9° (*c* 3.0, benzene) [lit.[21] $[\alpha]^{25}D$ −58.5° (*c* 3.0, benzene), for *optically pure* acid]. Both racemic and $(-)_D$-3-phenylbutanoic acid were converted virtually quantitatively to $C_6H_5CH(CH_3)CH_2COCl$ by treatment with $SOCl_2$.

Hydratropic acid, $C_6H_5CH(CH_3)COOH$, on treatment with $LiAlH_4$ in dry ether yielded $C_6H_5CH(CH_3)CH_2OH$ (86%, bp 116° at 12 Torr). This alcohol was converted to $C_6H_5CH(CH_3)CH_2Br$ by the reaction with $P(C_6H_5)_3$ and Br_2 in *N,N*-dimethylformamide;[22] yield 76%, bp 114° at 12 Torr.

The complexes η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$,[23] η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$,[24] η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$,[24] and η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_2C_6H_5$[24] were synthesized as described in the literature. $Rh[P(C_6H_5)_3]_3Cl$ was supplied by Strem Chemicals. Solutions of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ in THF, used for the preparation of iron–alkyl and –acyl complexes, were obtained by a reported procedure.[25]

Preparation of η^5-$C_5H_5Fe(CO)_2C(O)CH_2CH(CH_3)C_6H_5$ (1). To a cooled (−70°) THF solution (150 ml) of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ from 5.3 g (15 mmol) of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ was added with stirring over 10 min 5.5 g (30 mmol) of $C_6H_5CH(CH_3)CH_2COCl$ in 50 ml of THF. Stirring was continued for *ca.* 1 hr while the mixture was allowed to warm to room temperature. The solvent was then removed, the residue was dissolved in minimum $CHCl_3$, and the resulting solution was filtered through a thin layer of alumina. The filtrate was evaporated to dryness to give 9.3 g of a yellowish-brown solid which was recrystallized from 70 ml of 2.5:1 pentane–benzene. The yield of yellow crystals of **1** was 7.0 g (72%).

The optically active $(-)_D$-η^5-$C_5H_5Fe(CO)_2C(O)CH_2CH(CH_3)C_6H_5$, **1A**, was prepared similarly using the optically pure $C_6H_5CH(CH_3)CH_2COCl$. Analyses, melting points, and spectroscopic data for these and other new iron complexes prepared herein are provided in Table I.

Preparation of η^5-$C_5H_5Fe(CO)_2CH_2CH(CH_3)C_6H_5$ (2). (a) Decarbonylation of η^5-$C_5H_5Fe(CO)_2C(O)CH_2CH(CH_3)C_6H_5$ (1). A solution of 3.0 g (9.2 mmol) of **1** in 250 ml of benzene was irradiated for 1 hr in a Pyrex tube. Solvent was then removed, the residue was dissolved in pentane, and the resulting solution was chromatographed on an alumina column (2.7 × 25 cm). Pentane eluted yellow **2**, whereas 1:1 benzene–pentane and eventually pure benzene eluted *ca.* 0.9 g of a mixture of **1** and $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. **2** was rechromatographed with pentane to afford 1.3 g (48% yield) of pure, solid product. The yield may be improved (by *ca.* 15%) by repeating the decarbonylation on recovered **1**.

The optically active **1A** reacted similarly to give the optically active $(-)_D$-η^5-$C_5H_5Fe(CO)_2CH_2CH(CH_3)C_6H_5$, **2A**.

The decarbonylation was also effected by reaction of **1A** (3.0 g,

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Table I. Analyses, Melting Points, and Spectroscopic Data for New Iron Complexes

Compd	Mp, °C	% C		% H		% P or (S)		$[\alpha]^{23}D^a$	Ir, cm^{-1}			Nmr,^{d} τ				
		Calcd	Found	Calcd	Found	Calcd	Found		$\nu_{C\equiv O}{}^b$	$\nu_{C=O}{}^b$	$\nu_{SO}{}^c$	CH_3	CH_2	CH	C_5H_5	C_6H_5
1	106–107	63.00	63.11	4.98	4.90				2017, 1954	1648		8.81 d (7)	6.81 m,c		5.35 s	2.80 s
1A	73.5–75							–30.6° (1.0)								
2	49–50	64.88	64.87	5.46	5.45				1998, 1940			8.68 d (6.5)	8.25^g	7.34 m,c	5.39 s	2.80 s
2A	33–34							–77.8° (0.8)								
3a (90:10 **3a-3b**)	149–151								1910	1608		9.23 d (6.5)	7.60–6.37 c		5.82 d (1.3)	2.67 m,c
3b (9:91 **3a-3b**)	159–164 dec								1910	1608		8.91 d^h (6.5)	7.55–6.60 c		5.66 d (1.3)	2.66 m,c
3A	155–157 dec							–41.0° (0.48)								
3Aa (94:6 **3Aa-3Ab**)	50–61	73.13	74.00	5.60	5.54	5.55	5.45	–127.0° (0.35)								
3Ab (8:92 **3Aa-3Ab**)	54–66	73.13	73.00	5.60	5.45	5.55	5.64	+48.5° (0.35)								
4a (98:2 **4a-4b**)	123–125 dec	74.71	75.27	5.90	5.82	5.84	5.95		1895			8.85 d (6.5)	9.37–7.91 c	7.36 m,c	5.97 d (1.3)	2.67 m,c
4b (9:91 **4a-4b**)	123–125 dec	74.71	74.58	5.90	5.75	5.84	5.83		1898			8.75 d (6.5)	9.25–8.01 c	7.45 m,c	5.74 d (1.3)	2.70 m,c
4Aa (95:5 **4Aa-4Ab**)	123–126 dec							*f*								
4Ab (14:86 **4Aa-4Ab**)	124–126 dec							*f*								
5a (95:5 **5a-5b**)	66–83^e								1957		1180, 1160, 1035	8.63 d (6.5)	7.36–6.24 c		5.42 d (1.3)	2.66 m,c
5b (16:84 **5a-5b**)	55–71^e								1956		1180, 1160 1035	8.77 d (6.5)	7.53–6.37 c		5.42 d (1.3)	2.62 m,c
5Aa (95:5 **5Aa-5Ab**)	149–155^e	66.67	67.51	5.26	5.12	(5.39)	(5.18)									
5Ab (26:74 **5Aa-5Ab**)	69–84	66.67	67.59	5.26	5.21	(5.39)	(4.90)									

[a] In $CHCl_3$ solution; concentrations in parentheses. [b] In CH_2Cl_2 solution, Beckman IR-9 spectrophotometer. [c] As KBr pellets, Perkin-Elmer Model 337 spectrophotometer. [d] In $CDCl_3$ solution; coupling constants (Hz) in parentheses. Abbreviations: s, singlet; d, doublet; c, complex multiplet or other pattern; m,c, center of a complex multiplet. [e] Amorphous, glassy substance sinters. [f] Could not be measured because of low stability. [g] AB part of an ABX pattern. [h] Doublet showing some additional lines; see, for example, F. A. L. Anet, *Can. J. Chem.*, 39, 2262 (1961).

9.2 mmol) with $Rh[P(C_6H_5)_3]_3Cl$ (8.5 g, 9.2 mmol) in 200 ml of CH_2Cl_2. The mixture was stirred at 25° for 1.5 hr, concentrated to 75 ml, and filtered to remove $Rh(CO)[P(C_6H_5)_3]_2Cl$. The filtrate was evaporated to dryness and the residue was extracted with pentane (3 × 50 ml). Chromatography of the extract on alumina eluting with pentane gave two overlapping bands which were collected in three fractions. The first fraction contained pure **2A** (1.2 g, 44% yield), the second showed **2A** and an unidentified impurity, whereas the third was mostly impurity.

(b) Reaction of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ with $C_6H_5CH(CH_3)CH_2Br$. A THF solution (150 ml) of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ from 1.77 g (5.00 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ was treated with 1.99 g (10.0 mmol) of $C_6H_5CH(CH_3)CH_2Br$ in 20 ml of THF and the resulting mixture was stirred at 25° for 1 hr. Solvent was removed, the residue was extracted with 1:1 benzene-pentane, and the extract was filtered through alumina. The extract was then evaporated to dryness and the residue was chromatographed on alumina eluting with pentane. The single mobile yellow band yielded 1.65 g (56%) of **2**.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ (3). A solution of 1.63 g (5.50 mmol) of **2** and 1.44 g (5.50 mmol) of $P(C_6H_5)_3$ in 30 ml of CH_3CN was heated at 65 ± 2° for 15 hr. The mixture was then cooled to room temperature and the precipitated product (*ca.* 1.2 g) was collected by filtration and washed with pentane. The filtrate was evaporated to dryness and the residue was dissolved in 1:1 benzene-pentane. Chromatography on alumina yielded a narrow yellow band of unreacted **2**, which was eluted with 1:1 benzene-pentane, and a broad yellow-orange band of **3**, which was eluted with benzene. Total yield of **3** was 2.64 g (86%). The ^1H nmr spectrum of the product showed it to be approximately a 53:47 mixture of the diastereomers **3a** and **3b**. However, this ratio varies somewhat depending on the completeness of elution of the band containing **3**.

The optically active **2A** reacted in a strictly analogous fashion to afford the optically active $(-)_D\text{-}\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$, **3A**.

The above reaction was also conducted in THF at reflux. A comparable yield of the product was obtained; however, the reaction required 48 hr for completion.

Separation of Diastereomers of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ (3a and 3b). **3** enriched in the less soluble diastereomer **3b** was obtained by fractional crystallization from benzene-pentane of a 53:47 mixture of **3a-3b**. **3a-3b** (6.0 g, 53:47 mixture) was dissolved in 50 ml of benzene at 25°, 80 ml of pentane was added, and the solution was stored overnight at *ca.* 5°. Crystals were filtered off (4.35 g) and dissolved in benzene (40 ml), and the solution was diluted with pentane (80 ml) and stored for 8 hr at *ca.* 5°. The collected crystals weighed 3.22 g. This general procedure was continued with the indicated modifications and yields of crystals. Third crystallization: benzene (25 ml), pentane (50 ml), yield 2.49 g. Fourth crystallization: benzene (20 ml), pentane (50 ml), yield 1.97 g. Fifth crystallization: benzene (20 ml), pentane (30 ml), yield 1.28 g. The final batch of crystals was identified by nmr spectroscopy as a 9:91 mixture of **3a-3b**.

3 enriched in **3a** was obtained by two successive chromatographies on a 2.7 × 25 cm column of alumina, eluting with 1:1 benzene-pentane, of the concentrated mother liquor from the first crystallization above. The leading three-fourths of the broad yellow-orange band was collected, concentrated, and rechromatographed collecting again the front three-fourths of the band. Upon removal of the solvent 0.86 g of a 90:10 mixture of **3a-3b** was isolated.

The diastereomers of **3A**, **3Aa** and **3Ab**, crystallize as a 50:50 mixture and therefore could not be separated by fractional crystallization. Their separation was effected as follows.

3Aa-3Ab (3.0 g, 53:47 mixture) was chromatographed on a 2.7 × 25 cm column of alumina eluting first with 1:1 benzene-pentane and eventually with pure benzene. Three fractions were collected, *viz.*, (1) front, 0.9 g of a 64:36 mixture of **3Aa-3Ab**; (2) middle, 0.7 g; and (3) back, 1.3 g of a 40:60 mixture of **3Aa-3Ab**;

The front fraction was chromatographed again (2.1 × 22 cm column) using 1:1 benzene-pentane as eluent. The leading one-third of the band was collected; removal of the solvent left 0.28 g of **3Aa-3Ab** as an 84:16 mixture. This solid was dissolved in *ca.* 8 ml of 3:1 pentane-benzene and the solution was cooled at *ca.* 5°. The collection of resultant crystals (0.10 g) left a mother liquor which upon removal of the solvent yielded 0.18 g of a 94:6 mixture of **3Aa-3Ab**.

The back fraction (3 above) was chromatographed on a 2.1 × 22 cm column of alumina eluting first with 1:1 benzene-pentane and finally with pure benzene. The last three-fourths of the band was collected; removal of the solvent left *ca.* 0.9 g of a 34:66 mixture of

Table II. Stereochemical Results of the Decarbonylation of **3a** and **3b**[a]

Starting **3a–3b**	Recovered **3a–3b**	Isolated **4a–4b** (% stereospecificity)	Rechromatographed **4a–4b**
90:10, 400 mg	91:9, 65 mg	82:18 (78), 195 mg	90:10, 160 mg
12:88, 500 mg	15:85, 160 mg	32:68 (51), 240 mg	33:67, 200 mg

[a] *Ca.* 15 mg of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ also isolated.

3Aa–3Ab. This material was crystallized from 20 ml of 3:1 pentane–benzene at *ca.* 5°. The crystals (0.4 g) were filtered off and the filtrate yielded 0.45 g of a 25:75 mixture of **3Aa–3Ab** upon evaporation of the solvent. The crystallization was repeated on the 25:75 mixture, and the filtrate furnished 0.28 g of **3Aa–3Ab** in a ratio 8:92 upon removal of the solvent.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4). (a) Photochemical Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH(CH_3)C_6H_5$ (2) with $P(C_6H_5)_3$. **2** (1.18 g, 4.00 mmol) and $P(C_6H_5)_3$ (1.05 g, 4.00 mmol) in 200 ml of benzene were irradiated for 1 hr in a Pyrex tube. Solvent was removed and the residue was dissolved in pentane–benzene and chromatographed on alumina; 4:1 pentane–benzene eluted unreacted **2** and $P(C_6H_5)_3$, and then 1:1 pentane–benzene removed the bands containing **4** and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. The yield of somewhat impure **4** was 1.13 g. Purification may be achieved by an additional chromatography on alumina using 3:1 pentane–benzene as the eluent and crystallization from the same solvent mixture.

(b) Photochemical Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2C(O)CH_2CH(CH_3)C_6H_5$ (1) with $P(C_6H_5)_3$. **1** (1.62 g, 5.00 mmol) and $P(C_6H_5)_3$ (1.31 g, 5.00 mmol) in 200 ml of benzene were irradiated for 1 hr in a Pyrex tube. Removal of the solvent was followed by chromatography and crystallization as described in the preceding experiment. Yield 0.70 g (26%).

1A reacted strictly analogously to afford optically active $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$, **4A**.

(c) Decarbonylation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ (3). A solution of **3** (1.67 g, 3.00 mmol) in 225 ml of benzene was irradiated for 2 hr in a Pyrex tube. Solvent was evaporated and the residue was chromatographed on alumina using 3:1 pentane–benzene to remove first trace amounts of $P(C_6H_5)_3$ and **2** and then a broad red band containing **4**. Pentane–benzene (1:1) eluted a small quantity of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and 1% acetone in benzene eluted unreacted **3**. The yield of **4** was 0.84 g (53%). The compound may be purified by an additional chromatography using 3:1 pentane–benzene as the eluent.

Decarbonylation of Diastereomers of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ (3a and 3b). The reactions were carried out photochemically for 1 hr using 0.40–0.50 g of **3** enriched in **3a** or **3b** in 100–125 ml of benzene. The work-up was the same as that described for **3**. Stereochemical results of these experiments are given in Table II.

Carbonylation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4). A CH_3CN solution (25 ml) of 150 mg (0.283 mmol) of **4** (37:63 mixture of **4a–4b**) in a stainless steel vessel (Model HDF4-76-304, equipped with a 16 DKMK-F4-A314 valve, from Whitey Research Tool Co., Emeryville, Calif.) was pressurized with 4 atm of CO at 25° and maintained at these conditions for 25 hr. The vessel was vented and the reaction mixture was transferred to a round-bottom flask. Removal of the solvent and chromatography of the residue on alumina eluting with pentane–benzene afforded 39 mg (25% yield) of **3** (49:51 mixture of **3a–3b**) and 90 mg (60% recovery) of unreacted **4** (52:48 mixture of **4a–4b**).

Separation of Diastereomers of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4a and 4b). Separation of **4a** and **4b** was effected by a combination of chromatography on alumina and fractional crystallization from pentane–benzene. **4** slightly enriched in **4a** (*ca.* 54:46 **4a–4b**) is obtained upon the decarbonylation of **3** and subsequent chromatography eluting with 3:1 pentane–benzene (*vide supra*). The last portion of the band containing **4** is usually discarded because of contamination with $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

Chromatography of 1.5 g of **4** (54:46 mixture of **4a–4b**) on a 2.0 × 22 cm column of alumina eluting with 3:1 pentane–benzene afforded a broad red band which was collected in three fractions. The front fraction afforded 400 mg of a 95:5 mixture of **4a–4b** upon removal of the solvent and crystallization from 4:1 pentane–benzene. The last fraction was evaporated to dryness, the residue (630 mg) was dissolved in 25 ml of 5:1 pentane–benzene, and the solution was maintained at *ca.* 5° for 8 hr. The crystals (453 mg) were filtered off and dissolved in 5:1 pentane–benzene, and the crystallization procedure was repeated. The collected crystals (250 mg) were identified as a 13:87 mixture of **4a–4b**.

Table III. Stereochemical Results of Sulfur Dioxide Insertion in **4a**, **4b**, **4Aa**, and **4Ab**

Procedure[a]	Starting **4a–4b** (or **4Aa–4Ab**)	Isolated **5a–5b** (or **5Aa–5Ab**)[b]	% stereospecificity
A	97:3	95:5	96
B	97:3	93:7	91
A	(95:5)	(95:5)	100
A	9:91	16:84	83
B	11:89	17:83	85
A	(19:81)	(26:74)	77

[a] See Experimental Section for notations. [b] Yield 60–70%.

Table IV. Stereochemical Results of Thermolysis of **3**, **3a**, and **3b**

Starting **3a–3b**	Reaction time, hr	Recovered **3a–3b**
90:10	70	66:34
90:10	163	60:40
52:48	163	58:42
9:91	70	48:52
9:91	237	58:42

Separation of **4A** into mixtures enriched in **4Aa** and **4Ab** was performed analogously.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_2CH(CH_3)C_6H_5$ (5). A solution of **4** (300 mg, 0.566 mmol) in 50 ml of neat SO_2 was maintained at reflux for 5 hr. SO_2 was removed in a stream of nitrogen, the residue was treated with 5 ml of benzene, and the solution was evaporated to dryness *in vacuo*. The product was chromatographed on a 1.0 × 18 cm column of alumina eluting first with 5% and then with 15% acetone in CH_2Cl_2. A broad red band was collected and the solvent was removed to give 235 mg (70% yield) of **5**.

Sulfur Dioxide Insertion in Diastereomers of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4a, 4b, 4Aa, and 4Ab). The insertion was carried out either as described above (procedure A) or by dissolving 150 mg of **4a** or **4b** in a solution containing *ca.* 8 ml of liquid SO_2 in 70 ml of CH_2Cl_2 and maintaining the resultant mixture at 20° for 2 hr (procedure B). Usual work-up followed in each case. Stereochemical results of these experiments are presented in Table III.

Thermal Treatment of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$ (3) and Its Diastereomers 3a and 3b. Solutions of **3**, **3a**, and **3b** (60 mg) in CH_3CN (1 ml) were kept in sealed tubes at 80° for various periods of time. Solvent was evaporated and the residue was chromatographed on alumina eluting with 1:1 pentane–benzene. Removal of the solvent furnished 40–45 mg (67–75% recovery) of **3a–3b** and *ca.* 5 mg of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Stereochemical results of these experiments are given in Table IV.

Irradiation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4). A benzene solution (125 ml) of 460 mg of **4a** (97:3 **4a–4b**) was irradiated for 25 min in a Pyrex tube. Solvent was removed and the residue was chromatographed on alumina eluting with 3:1 pentane–benzene. Considerable amount of an uncharacterized decomposition material remained at the top of the column. The mobile red band was eluted and upon evaporation of the solvent afforded 260 mg (56% recovery) of an 89:11 mixture of **4a–4b**.

Configurational Stability of Iron Complexes 3, 4, and 5. Solutions of each of **3b**, **4a**, **4b**, and **5a** in $CDCl_3$, prepared for nmr spectra, were kept in the dark at 25° for several days. **3b** and **5a** showed no signs of epimerization after 10 days. **4a** and **4b** epimerized gradually: a 91:9 mixture of **4a–4b** became 80:20 after 48 hr and 75:25 after 96 hr; a 22:78 mixture of **4a–4b** became 32:68 after 48 hr and 44:56 after 96 hr.

Cleavage of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$ (4) with HCl. Hydrogen chloride gas was passed into a solution of **4** (580 mg, 1.1 mmol) in 40 ml of CH_2Cl_2. After 20 min the solution was concentrated to *ca.* 5 ml and diluted with 50 ml of pentane. The precipitated $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ was filtered off and the filtrate was passed through a thin layer of alumina on a glass frit. Solvent was evaporated to leave 64 mg (48% yield) of cumene, characterized by nmr spectroscopy.

Table V. Infrared and ^1H Nmr Spectra of Various η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ Complexes

R	Ir,[a] cm^{-1} $\nu_{C\equiv O}$	Nmr,[b] τ		
		CH_3	C_5H_5	C_6H_5
CH_3	*c*	10.16 d (6.5)	5.78 s, br	2.70 m,c (B)
$OS(O)CH_3$	1957	8.43 s, 8.22 s[d]	5.31 s, br	2.49 m,c, 2.59 m,c (A)
$S(O)_2CH_3$	1969	7.44 s	5.38 s, br	2.58 m,c (B)
		7.62 s	5.31 d (1.2)	2.52 m,c (A)
$OS(O)CH_2C_6H_5$	1957		*c*	
$S(O)_2CH_2C_6H_5$	1965		*c*	

[a] Measured in liquid SO_2 at −30° on a Beckman IR-9 spectrophotometer. [b] Measured in liquid SO_2 at −37° (A) or in $CDCl_3$ at 40° (B); coupling constants (Hz) in parentheses. Abbreviations: s, singlet; d, doublet; m,c, center of a complex multiplet; br, broad. [c] Not measured. [d] Intensity ratio 63:37.

Determination of Ratios of Diastereomers in Mixtures. The ratios of **3a-3b** and **4a-4b** (as well as **3Aa-3Ab** and **4Aa-4Ab**) were determined by measuring the heights of the respective C_5H_5 proton resonances on a Varian A60 instrument using a sweep width of 500 Hz and a sweep time of 250 sec. The values so obtained agreed to within ±1% with those obtained by multiple integration of the C_5H_5 signals at a sweep width of 250 Hz. The ratios of **5a-5b** and **5Aa-5Ab** were measured by comparison of the areas under the respective CH_3 peaks, recorded at a sweep width of 100 Hz.

Reactions of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ (R = CH_3 and $CH_2C_6H_5$) with Neat SO_2. Solutions of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ (R = CH_3 and $CH_2C_6H_5$) in neat SO_2 were examined by infrared and nmr spectroscopy with a view to detecting and characterizing the intermediates in the insertion. Procedures employed were analogous to those described earlier[26] for several metal-alkyl complexes. Spectroscopic data are summarized in Table V.

Physical Measurements. Infrared spectra were recorded either on a Perkin-Elmer Model 337 spectrophotometer or on a Beckman Model IR-9 spectrophotometer as indicated in the appropriate tables. Hydrogen-1 nmr spectra were obtained on a Varian A-60 or A60-A spectrometer using tetramethylsilane as an internal standard. Specific rotations, [α]D, were measured on a Perkin-Elmer Model 141 polarimeter using a 1-dcm cell.

Results

Preparation, Characterization, and Properties of Complexes. The reactions of organoiron complexes which were conducted in this investigation are set out in Scheme I.[27,28]

The acyl **1** resulted upon treatment of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ with $ClCOCH_2CH(CH_3)C_6H_5$ and was characterized through elemental analyses and its infrared and nmr spectra (Table I). It was also obtained in an optically active form as (*R*)-**1** (designated as **1A**) by using (*R*)-$ClCOCH_2CH(CH_3)C_6H_5$ in the above reaction.

The decarbonylation of **1** either under photochemical conditions or chemically with $Rh[P(C_6H_5)_3]_3Cl$[29] afforded the corresponding alkyl, **2**. This alkyl may be also synthesized by treatment of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ with $BrCH_2CH(CH_3)C_6H_5$. The latter reaction gives a better yield and is preferred for synthesis of larger quantities of **2**. However, the decarbonylation provided a convenient route to the optically active alkyl (*S*)-**2** (designated as **2A**) because of the ready availability of **1A**. Analytical data and spectroscopic properties of **2** are furnished in Table I.

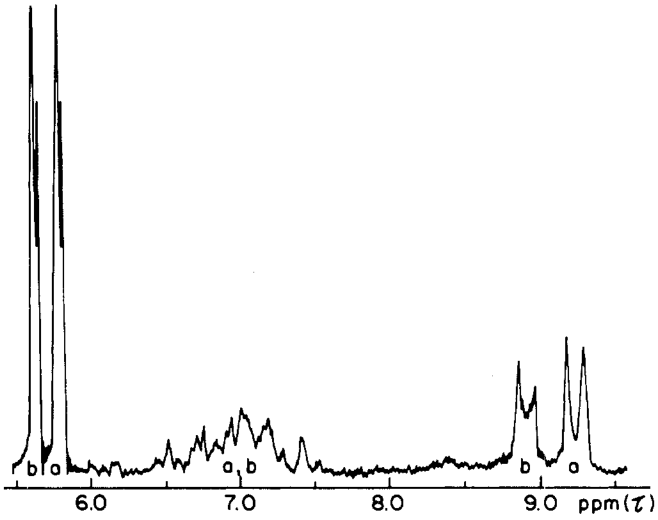

Figure 1. The ^1H nmr spectrum of a 50:50 mixture of **3a** (a) and **3b** (b) in $CDCl_3$.

Treatment of **2** or **2A** with triphenylphosphine in acetonitrile or THF at *ca.* 65° afforded **3** and **3A**, respectively. The acyl **3** possesses two chiral centers, the metal and the γ carbon of the acyl fragment, and hence is present as a mixture of two diastereomerically related pairs of enantiomers, (*R*,*R*)-**3**-(*S*,*S*)-**3** and (*R*,*S*)-**3**-(*S*,*R*)-**3**, designated as **3a** and **3b**. The nmr spectrum in the τ 5.5-9.5 range of a 50:50 mixture of **3a** and **3b** is shown in Figure 1. The two pairs of enantiomers were generally obtained in an approximate ratio 53:47 owing to an incomplete elution of the slower moving pair during column chromatography. A similar ratio of the diastereomers (*R*,*R*)-**3** and (*S*,*R*)-**3**, designated as **3Aa** and **3Ab**, was obtained upon chromatographic purification of optically active **3A**. **3a** and **3b** are separable by a combination of chromatography on alumina and crystallization from benzene-pentane; this is described in detail in the Experimental Section. Progress of the separation may be followed by nmr spectroscopy since the C_5H_5 group protons are diastereotopic by external comparison (separation 0.16 ppm, *cf.* Table I). Although complete separation of **3a** and **3b** was not attempted in this study, it certainly appears to be feasible through a sufficient number of chromatographies and crystallizations. Highly enriched **3a-3b** mixtures of 90:10 and 9:91 were entirely adequate for stereochemical investigations. In contrast to **3a** and **3b**, the diastereomers **3Aa** and **3Ab** crystallize as a 50:50 mixture. Accordingly, a slightly different procedure of chromatography and crystallization had to be employed for their separation; it is detailed in the Experimental Section. Samples of **3Aa-3Ab** were isolated as 94:6 and 8:92 mixtures.

3b was found to be configurationally stable in $CDCl_3$ solution over 10 days at 25°. Both **3a** and **3b** which were re-

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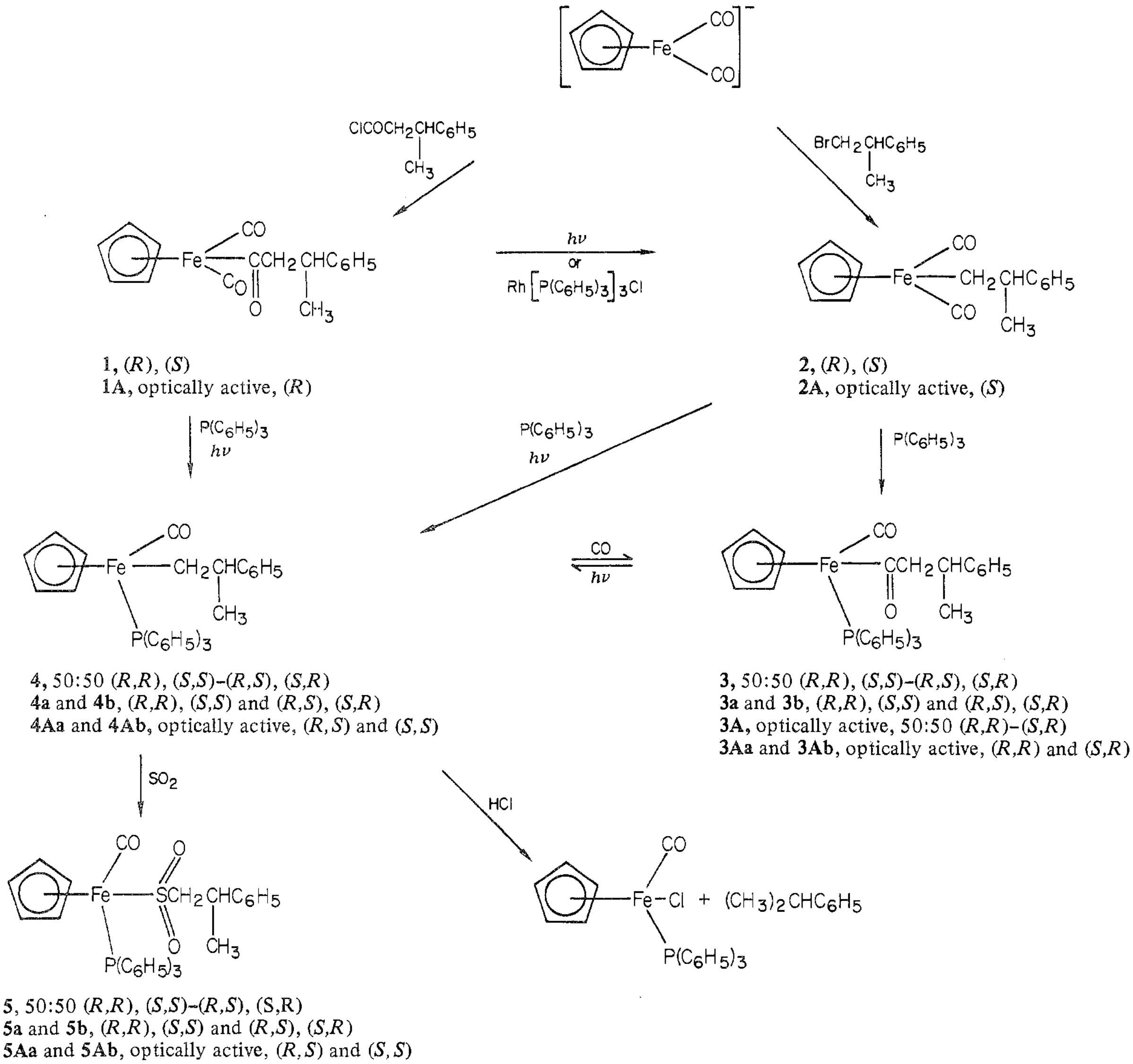
(26) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, 12, 717 (1973).

(27) The absolute configuration of the iron precedes that of the carbon in all of the designations employed in this paper; *e.g.*, (*R*,*S*) means (Fe-*R*, C-*S*). For assignment of the absolute configuration to optically active $C_6H_5CH(CH_3)CH_2COOH$, see J. S. Birtwistle, K. Lee, J. D. Morrison, W. A. Sanders, and H. S. Mosher, *J. Org. Chem.*, 29, 37 (1964).

(28) **3a**, **3b**, **4a**, **4b**, **5a**, and **5b** are related as follows. **4a** is the dominant pair of enantiomers obtained from the decarbonylation of **3a**, and **4b** from **3b**. **5a** and **5b** are derived from **4a** and **4b**, respectively. A similar relationship exists among **3Aa**, **3Ab**, **4Aa**, **4Ab**, **5Aa**, and **5Ab**. **3a** (and **3Aa**) and **3b** (and **3Ab**), respectively, stand for the chromatographically faster and slower eluting isomers of **3**, as indicated in the text.

(29) J. J. Alexander and A. Wojcicki, *Inorg. Chem.*, 12, 74 (1973).

Scheme I



1, (*R*), (*S*)
1A, optically active, (*R*)

2, (*R*), (*S*)
2A, optically active, (*S*)

4, 50:50 (*R*,*R*), (*S*,*S*)-(*R*,*S*), (*S*,*R*)
4a and **4b**, (*R*,*R*), (*S*,*S*) and (*R*,*S*), (*S*,*R*)
4Aa and **4Ab**, optically active, (*R*,*S*) and (*S*,*S*)

3, 50:50 (*R*,*R*), (*S*,*S*)-(*R*,*S*), (*S*,*R*)
3a and **3b**, (*R*,*R*), (*S*,*S*) and (*R*,*S*), (*S*,*R*)
3A, optically active, 50:50 (*R*,*R*)-(*S*,*R*)
3Aa and **3Ab**, optically active, (*R*,*R*) and (*S*,*R*)

5, 50:50 (*R*,*R*), (*S*,*S*)-(*R*,*S*), (S,R)
5a and **5b**, (*R*,*R*), (*S*,*S*) and (*R*,*S*), (*S*,*R*)
5Aa and **5Ab**, optically active, (*R*,*S*) and (*S*,*S*)

covered after a 1-hr irradiation in benzene showed virtually no epimerization at the metal (Table II). However, prolonged (163 hr) thermal treatments of various **3a**-**3b** mixtures in acetonitrile at 80° led to the isolation of approximately 58:42 **3a**-**3b** (Table IV). Optically active **3Aa** and **3Ab** show specific rotations, $[\alpha]^{23}$D, which differ both in sign and in magnitude (−127.0 and +48.5°, Table I), indicative of the presence of more than one chiral center.

Photolysis of a mixture of **1** or **2** and triphenylphosphine or of **3** alone affords the alkyl **4**. Of the three photochemical reactions, the decarbonylation of **3** is the recommended synthetic route because of the good yield and high purity of the iron alkyl produced. Complex **4**, like **3**, contains two chiral centers and therefore exists as a mixture of two diastereomerically related pairs of enantiomers, (*R*,*R*)-**4**-(*S*,*S*)-**4** and (*R*,*S*)-**4**-(*S*,*R*)-**4**, referred to as **4a** and **4b**. The two pairs are usually obtained in a ratio 54:46 because of a discard of the last part of the chromatographic band upon purification. They can be separated by a combination of chromatography on alumina and crystallization from benzene-pentane; in this fashion **4a**-**4b** mixtures of 98:2 and 9:91 were isolated. Each pair of enantiomers was characterized by elemental analyses and infrared and nmr spectroscopy, as shown in Table I. Optically active **4A**, synthesized photochemically from **1A** and triphenylphosphine, can be similarly separated into the diastereomers (*R*,*S*)-**4** and (*S*,*S*)-**4**, designated as **4Aa** and **4Ab**. In each case, the nmr signals of the diastereotopic (by external comparison) C_5H_5 protons (separation 0.23 ppm, *cf.* Table I) were used to follow progress of the separation and to determine composition of the mixtures.

In constrast to **3a** and **3b**, **4a** and **4b** undergo epimerization when stored in $CDCl_3$ solution at 25° for 48 hr. The extent of this epimerization is higher for **4b** (36%) than for **4a** (27%). **4a** epimerizes also when irradiated in benzene solution (17% epimerization in 25 min). The latter process is accompanied by considerable decomposition to an unidentified material. The Fe-C σ bond in **4** is readily cleaved by HCl to give η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ and cumene, thus confirming the identity of R in the alkyl complex.

Chloroform solutions of optically active **4Aa** and **4Ab** darkened too rapidly to permit measurement of their specific rotations.

Reaction between **4** and neat SO_2 at reflux afforded the corresponding isolable *S*-sulfinate, **5**. The nmr spectrum of **5** showed the presence of diastereotopic (by external comparison) CH_3 protons; however, the C_5H_5 group protons gave only one resonance, a doublet (J_{H-P} = 1.3 Hz). Complex **5**, like **3** and **4**, possesses two chiral centers and therefore also exists as a mixture of two diastereomerically related pairs of enantiomers, designated as **5a** and **5b**. Although no attempt was made to separate **5** into **5a** and **5b**, mixtures enriched in **5a** and **5b** (95:5 and 16:84, respectively) were isolated from the respective reactions of **4a** and **4b** with SO_2 (Table III). Similarly, the SO_2 insertion into **4Aa** and **4Ab** yielded **5Aa** and **5Ab**, respectively, which also displayed some optical activity. **5a** was shown to be configurationally stable in $CDCl_3$ solution at 25° over a period of 10 days.

Stereochemistry of Reactions. Three reactions were examined with a view to ascertaining stereochemical outcome at the iron center. They were (a) **3** → **4** photochemical decarbonylation, (b) **4** → **3** carbonylation, and (c) **4** → **5** SO_2 insertion.

Data on the decarbonylation are presented in Table II. This conversion proceeds with high but unequal stereospecificities of 78 and 51%, respectively, for **3a** and **3b**. The following observations need to be taken into consideration in evaluating partial epimerization at iron in this reaction.

First, the unreacted **3** is slightly richer in **3a** than is the starting **3**; this might be due to incomplete elution of the slower moving band of **3b** on chromatography. Assuming, however, that this difference is due to a faster decarbonylation of **3b** than of **3a**, one can readily calculate the ratios **4a-4b** which would have resulted from the completely stereospecific conversion of the reacted **3**. Thus a 90:10 mixture of **3a-3b** would have given *ca.* 90:10 **4a-4b**, and a 12:88 mixture of **3a-3b** would have given 11:89 **4a-4b**. It is readily seen that these changes in the ratios are too small to contribute significantly to the observed difference in per cent stereospecificity for the decarbonylation.

Second, it has been noted that **4a** (and presumably also **4b**) undergoes some epimerization (17%) when irradiated in benzene solution for 25 min. Considerable decomposition of **4** occurs under these conditions. This decomposition precluded running control experiments with a view to ascertaining how much of the observed epimerization of **4** in the decarbonylation of **3** occurs subsequent to the extrusion of CO. From qualitative considerations, however, the amount of such epimerization must be substantial considering that the decarbonylation experiments were run for a period of 1 hr.

Third, as may be seen in Table II, **4** becomes richer in **4a** upon chromatography on alumina. This enrichment is most likely due to some decomposition of the slower moving **4b** during the elution. It has been further observed that solutions of **4a** and **4b** in $CDCl_3$ epimerize on storage at 25° (*vide supra*), with the latter pair of enantiomers equilibrating more rapidly than the former. Both of the aforementioned processes will tend to increase the ratio **4a-4b** in mixtures, as is in fact observed experimentally. Unfortunately, their contributions cannot be readily evaluated quantitatively for the decarbonylation.

Because of the foregoing complications it was not possible to obtain per cent stereospecificity for the conversion of **3** to **4**. However, a lower limit for this reaction may be set as the average of the values obtained using **4a** and **4b** in separate experiments, *viz.*, 64%; in all probability the actual per cent stereospecificity is much higher, possibly even 100%.

The carbonylation of **4** in CH_3CN at 25° and under 4 atm of CO proceeds relatively slowly and after 25 hr affords a 25% yield of **3**. Starting with a 37:63 mixture of **4a-4b**, one obtains **3a-3b** in a ratio 49:51. The unreacted **4**, recovered in a 60% yield, analyzes as a 52:48 mixture of **4a-4b**.

Since **4** is found to be configurationally unstable under the conditions of the carbonylation, no conclusion can be drawn regarding stereospecificity of this reaction. The 52:48 ratio of recovered **4a-4b** may be a result of the faster epimerization of **4b** than of **4a** which has already been mentioned (*vide supra*). Epimerization of **4** prior to the carbonylation receives further support from the isolation of **3a-3b** in a ratio 49:51. The acyl **3b** is configurationally stable in $CDCl_3$ at 25° and might be expected to possess some configurational stability also in CH_3CN under CO at 25°.

The reaction between **4** and SO_2 was carried out both in neat SO_2 at reflux and in *ca.* 2 *M* solution of SO_2 in CH_2Cl_2 at 20°. Results of these experiments, presented in Table III, are very similar and reflect high stereospecificity at iron of the insertion.

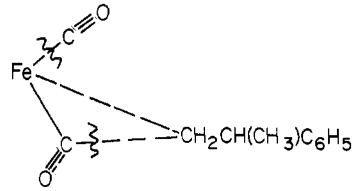
The insertion in **4a** proceeds with >95% stereospecificity, whereas that in **4b** occurs with a lower, *ca.* 82%, stereospecificity. It is unlikely that the observed difference results from epimerization of **5** either during the reaction or upon work-up, since **5a** was shown to possess high configurational stability. Instead, the lower stereospecificity for the conversion of **4b** to **5b** than of **4a** to **5a** is best attributed to partial epimerization of **4b** prior to the insertion.

Discussion

Stereochemical Implications to Mechanism. Of the three reactions examined, the photochemical decarbonylation of **3** and the SO_2 insertion in **4** were found to proceed with high stereospecificity at iron. By contrast, the carbonylation of **4** did not provide any meaningful stereochemical information. We shall now consider the implications of our stereochemical results to the mechanism of the former two reactions.

(a) Photochemical Decarbonylation. There are two stereochemical facets of the photochemical decarbonylation of metal-acyl complexes which must be considered together with the present results in discussing the mechanistic implications of the latter. First, photochemical decarbonylation proceeds through the elimination of a terminal rather than the acetyl CO; this has been demonstrated for η^5-$C_5H_5Fe(CO)_2{}^{13}C(O)CH_3$.[30] Second, photochemical decarbonylation occurs with retention of configuration at the α carbon of the alkyl fragment, as shown for η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C(O)CHDCHDC(CH_3)_3$.[11] These results indicate that the alkyl part of the acyl moiety migrates onto the metal in a very stereospecific, presumably concerted,[31] fashion.

The observation of high stereospecificity at iron in this study may be rationalized in one of the following ways. The reaction may proceed in a concerted fashion, with the photochemically excited CO being replaced by the migrating $CH_2CH(CH_3)C_6H_5$ group as shown in I. This pathway would lead to inversion of configuration at iron.[32] Alternatively,



I

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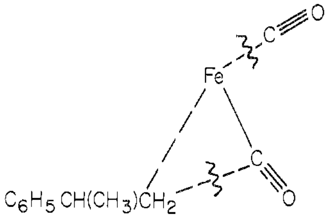
(30) J. J. Alexander, private communication, quoted in ref 29.

(31) An intramolecular radical pair mechanism has also been proposed for the decarbonylation; see H. M. Walborsky and L. E. Allen, *J. Amer. Chem. Soc.*, **93**, 5465 (1971).

however, the Fe–CO bond may break prior to the migration of the $CH_2CH(CH_3)C_6H_5$. This latter process would lead to the formation of a genuine intermediate with reduced coordination number of iron, *viz.*, η^5-$C_5H_5Fe[P(C_6H_5)_3]C(O)CH_2CH(CH_3)C_6H_5$. If this second pathway is realized, then the present stereochemical result at iron demonstrates that such an intermediate possesses substantial configurational stability and does not readily adopt a planar geometry around the metal. We cannot, obviously, differentiate between the above two mechanistic possibilities from the data on hand.

In addition to the foregoing, there is one other type of mechanism which we feel deserves consideration. It is depicted schematically below (II). In this concerted pathway the migrating alkyl group displaces the CO from the back side; alternatively, the carbonyl group becomes detached before the migration of the $CH_2CH(CH_3)C_6H_5$ occurs. In either case, the outcome is retention at iron.[32]



II

Knowledge of the absolute configuration of iron in **3Aa** (or **3Ab**) and **4Aa** (or **4Ab**) is necessary to resolve between a mechanism of type I and type II. We considered using circular dichroism spectroscopy in an attempt to correlate the absolute configurations of the metal in **3Aa** and **4Aa**. However, our plans were thwarted by the relative instability of **4** in solution which precluded measurement of specific rotations of **4Aa** and **4Ab**. Plans are now underway to resolve this problem crystallographically using an iron acyl and the corresponding iron alkyl which are similar to those investigated herein.[19]

(b) Sulfur Dioxide Insertion. Kinetic and stereochemical studies concerned with the sulfur dioxide insertion have been carried out mainly on complexes of the formula η^5-$C_5H_5Fe(CO)_2R$. Cleavage of the Fe–R bond therein is an electrophilic process which proceeds with a large and negative entropy of activation[7] and with inversion of configuration at the α carbon, as demonstrated for η^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$.[11] Spectroscopic studies have shown the intermediacy of O-bonded sulfinates for the insertion in several complexes.[26] Based on these and other reported results, a mechanism has been proposed whose salient features are depicted schematically in eq 1.

$$\begin{tikzcd}
\mathrm{Fe{-}R} \arrow[rr, dashed, "SO_2"] & & \mathrm{Fe^+O_2SR^-} \arrow[dl, shift left] \arrow[dr] & \\
& \mathrm{Fe{-}OS(O)R} \arrow[ur, shift left] \arrow[rr] & & \mathrm{Fe{-}S(O)_2R}
\end{tikzcd} \qquad (1)$$

In order to ascertain whether a similar reaction scheme likely holds for the monocarbonyls η^5-$C_5H_5Fe(CO)(PR_3')R$, we examined spectroscopically (*cf.* Table V) solutions of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ ($R = CH_3$ and $CH_2C_6H_5$) in neat SO_2. These complexes are structurally similar to, but simpler and more stable than, the alkyl **4**.

Dissolution of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ ($R = CH_3$ or $CH_2C_6H_5$) in liquid SO_2 affords a monocarbonyl whose infrared $\nu_{C\equiv O}$ band differs from that of the parent alkyl complex (1905 cm^{-1} [23,24]) and from the final *S*-sulfinato product. The observed species is converted to the *S*-sulfinate on storage. The ^1H nmr spectrum of this intermediate with $R = CH_3$ shows two CH_3 signals at higher fields than the corresponding resonance for the *S*-sulfinate. Significantly, in all cases investigated, $M{-}OS(O)CH_x$ protons have been found to absorb at higher fields than those of the isomeric $M{-}S(O)_2CH_x$.[26] The appearance of two CH_3 signals in the nmr spectrum of the reaction intermediate derived from η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and SO_2 most likely arises from the presence of diastereomers, as would be expected for η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]OS(O)CH_3$ (chiral metal and sulfur). Thus, combined spectroscopic evidence points to the formation of the *O*-sulfinates in the SO_2 insertion in η^5-$C_5H_5Fe(CO)(PR_3')R$ and suggests a mechanism similar to that proposed for the dicarbonyls η^5-$C_5H_5Fe(CO)_2R$.

The observed high stereospecificity at iron of the conversion of **4** (Fe–R) to **5** ($Fe{-}S(O)_2R$) means that each step of the reaction scheme in eq 1 is highly stereospecific. Intramolecular isomerization of Fe–OS(O)R to $Fe{-}S(O)_2R$ (**5**) may be analogous to the isomerization of $[(NH_3)_5Co{-}ONO]^{2+}$ to $[(NH_3)_5Co{-}NO_2]^{2+}$,[33] and its high stereospecificity does not appear unusual. However, the high configurational stability of the proposed contact ion pair, $Fe^+O_2SR^-$, is definitely surprising. Here the iron is bonded to only three ligands and might be expected to adopt a planar configuration. Such a configuration would lead to epimerization at the metal, provided that the sulfinate ion is capable of traversing the two faces of this plane. It is possible that the low dielectric constant of the medium[34] restricts mobility of the sulfinate ion and thus confers configurational stability on the cation.

Although the SO_2 insertion in **4** is a highly stereospecific process, we do not know whether it proceeds with retention or inversion at iron. This is an important point because the mechanism in eq 1 requires that the configuration at iron be retained. We hope to settle this question by X-ray crystallography. It is very relevant, however, that the SO_2 insertion in a related complex, η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C(O)OC_{10}H_{19}$ ($C_{10}H_{19}O$ = (−)-mentholate), has been recently reported to take place with retention at iron.[16]

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Registry No. **1**, 51552-92-2; **1A**, 51607-99-9; **2**, 51552-93-3; **2A**, 51608-00-5; **3a**, 41529-61-7; **3b**, 41572-74-1; **3A**, 51608-01-6; **3Aa**, 51608-02-7; **3Ab**, 51608-03-8; **4a**, 51552-94-4; **4b**, 51608-04-9; **4Aa**, 51608-05-0; **4Ab**, 51608-06-1; **5a**, 51552-95-5; **5b**, 51608-07-2; **5Aa**, 51608-08-3; **5Ab**, 51608-09-4; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, 12100-51-5; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]OS(O)CH_3$, 51552-96-6; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_3$, 31811-87-7; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]OS(O)CH_2C_6H_5$, 51552-97-7; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]S(O)_2CH_2C_6H_5$, 31811-66-2; $Na[\eta^5$-$C_5H_5Fe(CO)_2]$, 12152-20-4; $C_6H_5CH(CH_3)CH_2COCl$, 51552-98-8; $C_6H_5CH(CH_3)CH_2Br$, 2114-39-8; $P(C_6H_5)_3$, 603-35-0; SO_2, 7446-09-5; HCl, 7647-01-0.

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(32) Although spatial arrangement of the η^5-C_5H_5, $P(C_6H_5)_3$, and CO (of the original acyl moiety) ligands remains unaltered in this transformation, the reaction is said to proceed with *inversion* at iron. This is because the *R,S* stereochemical designation follows the priority sequence $CO > C(O)CH_2CH(CH_3)C_6H_5 > CH_2CH(CH_3)C_6H_5$. A strictly analogous argument holds for *retention* at iron. We thank Professor H. Brunner for a helpful comment.

(33) R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, 78, 4886 (1956).

(34) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, 60, 160 (1956).