mg, 0.48 mmol). The reaction was carried out as for lactone **4**. The crude lactone was dissolved in methanol (2 mL). Palladium on carbon (10%) (43 mg) was added. The mixture was stirred for 44 h under hydrogen (1 atm), filtered through Celite, and evaporated. The residue was taken up in dichloromethane (6 mL) and treated with an excess of diazomethane swept on a stream of argon and generated by treatment of a solution of Diazald (63 mg) in ethanol (6 mL) with a solution of potassium hydroxide (18 mg) in water (100 μL). Flash chromatography (3 g of silica gel; 50%, 75% ether/hexane) gave the keto ester **7** as an oil (29 mg, 47%) contaminated with minor hydrogenolysis byproducts: ^{1}H NMR (270 MHz) δ 0.95 (m, 2 H, cyclopropyl), 1.3 (m, 2 H, cyclopropyl), 2.22 (s, 3 H, C(O)Me), 3.27 (s, 3 H, OMe), 3.84 (s, 1 H, CHN), 4.08 (dd, 1 H, J = 8.5, 4.5 Hz, CH_2O), 4.78 (t, 1 H, J = 8.5 Hz, CH_2O), 5.14 (dd, 1 H, J = 8.5, 4.5 Hz, PhC*H*N), 7.2-7.4 (m, 5 H, Ar); IR (film) 1754, 1723 cm^{-1}; MS (EI) 274 (M^+ - CH_3CO), 104 ($PhCHCH_2^+$).

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Enantioselective Cyclopropane Syntheses Using the Chiral Carbene Complexes (S_{Fe})- and (R_{Fe})-$C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$. A Mechanistic Analysis of the Carbene Transfer Reaction

Maurice Brookhart,* Yumin Liu, Emma W. Goldman, Debra A. Timmers, and Gregory D. Williams

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received June 7, 1990*

Abstract: Enantiomerically pure or enriched iron-carbene complexes of the type $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ have been prepared by three routes: (a) Diastereomeric acyl complexes $C_5H_5(CO)(PPh_2R^*)FeC(O)CH_3$ (R* = (*S*)-2-methylbutyl) have been prepared, separated by column chromatography, and converted by using standard techniques to (S_{Fe},S_P)- and (R_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$; (b) Enantiomerically enriched (76% ee) ($R_{C\alpha}$)-$C_5H_5(CO)_2FeCH(OCH_3)CH_3$ has been prepared from (*S*)-(-)-ethyl lactate and converted to enantiomerically enriched diastereomers $Cp(CO)(PR_3)$-$FeCH(OCH_3)CH_3$ (R = Me, Et). The individual diastereomers were then converted to enantiomerically enriched ethylidene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = Me, Et); (c) Racemic acyl complexes $Cp(CO)(PR_3)FeC(O)CH_3$ (R = Me, Et) have been conveniently resolved via fractional crystallization of diastereomeric hydroxy carbene salt generated by using (*S*)-(+)- or (*R*)-(-)-10-camphorsulfonic acid. The enantiomerically pure acyl complexes were converted to the corresponding enantiomerically pure carbene complexes (S_{Fe})- and (R_{Fe})-$C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ by using standard techniques. Enantioselective ethylidene transfer from these complexes to styrene, vinyl acetate, and isopropenyl acetate gave methylcyclopropanes in high optical yields. Ethylidene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = Me, Et), $C_5H_5(CO)$-$(PPh_3)Fe{=}CHCH_3^+$, and $C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$ (R* = (*S*)-2-methylbutyl) were generated in the CD_2Cl_2 solution and studied by ^{1}H and ^{13}C NMR spectroscopy. At very low temperatures (ca. -100 °C) both anticlinal (major) and synclinal (minor) isomers could be detected. Equilibrium ratios and rates of interconversion of these isomers were determined by using variable temperature ^{1}H NMR spectroscopy. A mechanistic analysis of the transfer reaction is presented by using the stereochemical results obtained coupled with deuterium labeling and relative reactivity studies. It is concluded that the most likely mechanism for carbene transfer involves reaction of the olefin with the minor but more reactive synclinal isomer of $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ followed by backside attack of the developing electrophilic center at C_γ on the Fe-C_α bond. A rationale is offered for the differing diastereoselectivities of ethylidene transfer from $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ versus $C_5H_5(CO)_2Fe{=}CHCH_3^+$ to various olefins.

Introduction

Electrophilic iron-carbene complexes, $C_5H_5(CO)(L)Fe{=}CHR^+$ (L = CO, PR_3), react with nucleophilic alkenes to form cyclopropanes[1-7] (eq 1). Derivatives of $C_5H_5(CO)(L)Fe{=}CHR^+$ which have been used for carbene transfers include R = -H,[5a6a,b,d-f,h,j,k] $-CH_3$,[2a,b,3,5b-d,7,13,14] $-C_6H_5$,[2d,g,h] *c*-C_3H_5[2c,e]

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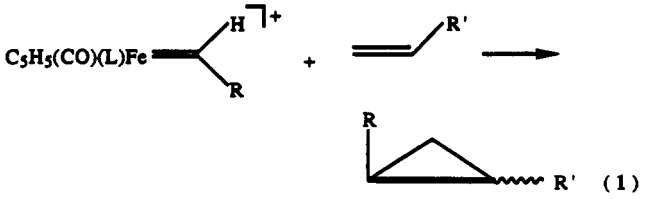
$-CH{=}C(CH_3)_2$,[4,5g] and the dimethyl derivative $C_5H_5(CO)_2Fe{=}(CH_3)_2{}^+$.[4,5d]



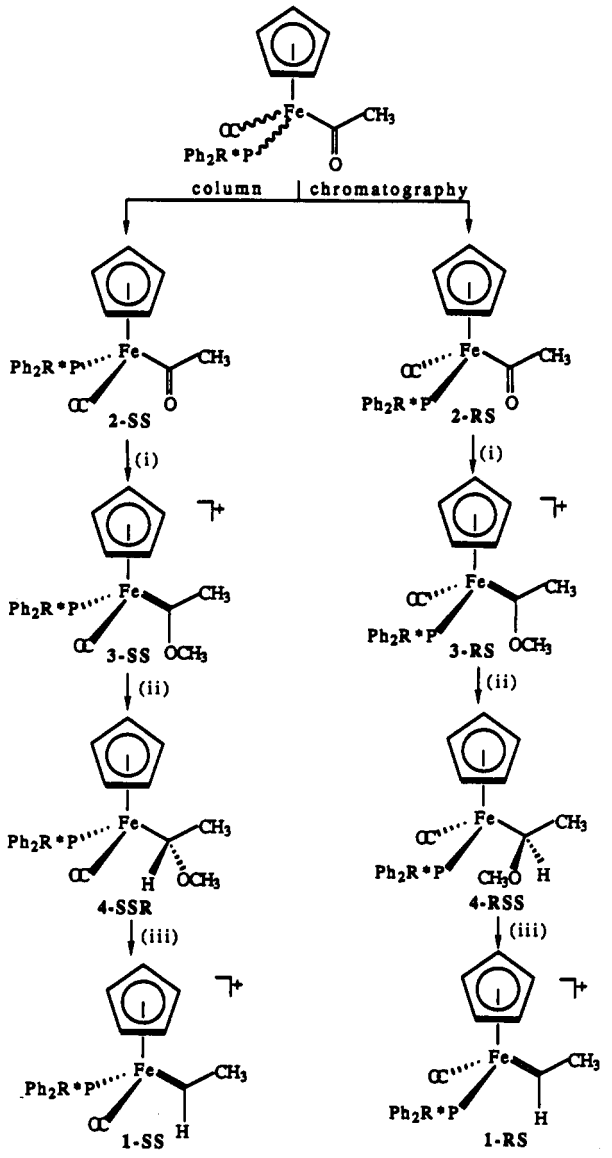
(1)

While most studies have focussed on the dicarbonyl derivatives (L = CO), the phosphine-substituted derivatives (L = PR_3) possess a chiral metal center and thus offer the possibility of enantioselective carbene transfer reactions. (The use of $Cp(NO)(PR_3)Re$–[8] and $Cp(CO)(PR_3)Fe$–[9-12] as chiral auxiliaries for diastereoselective and enantioselective transformations is well-established.) The first enantioselective carbene transfer reactions using chiral iron–carbene complexes were reported by Davison[6d] and Flood.[6f] R_{Fe} and S_{Fe} stereoisomers of $Cp(CO)(P(C_6H_5)_3)FeCH_2X$ (X = *O*-menthyl, Br) were used to transfer methylene (presumably via $Cp(CO)(P(C_6H_5)_3)Fe{=}CH_2{}^+$) to *trans*-β-methylstyrene. Enantioselectivities observed were low to moderate (10–38% ee) due most likely to the fact that C_α in the methylene complex is not a prochiral center and enantioselectivity depends solely on the selectivity of attack on the Si or Re face of the alkene.

In preliminary communications[13,14] we have described use of chiral ethylidene complexes, $Cp(CO)(PR_3)Fe{=}CHCH_3{}^+$, for enantioselective ethylidene transfers to alkenes. We report here a full account of several methods we have developed for the synthesis of enantiomerically pure or enantiomerically enriched ethylidene complexes together with results of enantioselective transfers of ethylidene to several alkenes. In addition, the ethylidene complexes have been characterized by NMR spectroscopy and equilibrium ratios, and rates of interconversion of the synclinal and anticlinal isomers have been determined. Synthetic routes to the ethylidene complexes include (a) preparation and separation of diastereomeric acyl complexes (S_{Fe},S_P)- and (R_{Fe},S_P)-$Cp(CO)(Ph_2R^*P)FeCOCH_3$ (R* = (*S*)-2-methylbutyl) and conversion to ethylidene complexes (S_{Fe},S_P)- and (R_{Fe},S_P)-$Cp(CO)Ph_2R^*P)Fe{=}CHCH_3{}^+$, (b) synthesis of enantiomerically enriched ($R_{C\alpha}$)-$Cp(CO)_2FeCH(OCH_3)CH_3$ and conversion to diastereomers (S_{Fe},$R_{C\alpha}$)- and (R_{Fe},$R_{C\alpha}$)-$Cp(CO)(PR_3)FeCH(OCH_3)CH_3$ followed by diastereomer separation and ionization to enantiomerically enriched ethylidene complexes (S_{Fe})- and (R_{Fe})-$Cp(CO)(PR_3)Fe{=}CHCH_3{}^+$ (R = $-CH_3$, $-CH_2CH_3$), and (c) resolution of (R_{Fe})- and (S_{Fe})-$Cp(CO)(PR_3)FeCOCH_3$ (R = $-CH_3$, $-CH_2CH_3$) using (*S*)-(+)- and (*R*)-(−)-10-camphorsulfonic acid followed by conversion to pure (R_{Fe})- and (S_{Fe})-$Cp(CO)(PR_3)Fe{=}CHCH_3{}^+$.

Stereochemical results reported here give substantial information regarding the mechanism of the carbene transfer reaction and in the case of (R_{Fe})- and (S_{Fe})-$Cp(CO)(PR_3)FeCOCH_3$ (R = $-CH_3$, $-CH_2CH_3$) the resolution procedure developed provides an inexpensive and convenient route to both the enantiomerically pure acyl complexes and the ethylidene complexes. This procedure can be applied generally to basic iron–acyl complexes.

Scheme I[a]



[a] (i) Me_3OBF_4 at 25 °C; (ii) $NaBH_4$/MeONa/MeOH at −78 °C; (iii) TMSOTf at −78 °C.

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Results and Discussion

Synthesis of (S_{Fe},S_P)- and (R_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)FeC(O)CH_3$, 2-*SS* and 2-*RS* ($R^*$ = (*S*)-2-Methylbutyl), and Conversion to Ethylidene Complexes (S_{Fe},S_P)- and (R_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, 1-*SS* and 1-*RS*. Scheme I summarizes the syntheses of enantiomerically pure chiral-at-iron-carbene complexes (S_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, 1-*SS*, and (R_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, 1-*RS*, and their acyl precursors 2-*SS* and 2-*RS*.[13] The chiral phosphine (*S*)-(2-methylbutyl)diphenylphosphine, PPh_2R^*, was obtained by reaction of $LiPPh_2$ with (*S*)-2-methyl-1-butylmesylate. (S_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)FeC(O)CH_3$, 2-*SS*, and (R_{Fe},S_P)-$C_5H_5(CO)PPh_2R^*)FeC(O)CH_3$, 2-*RS* (*R* = (*S*)-2-methylbutyl) (ca. 1:1 mixture), were formed in 80% yield by heating a THF solution of $C_5H_5(CO)_2FeCH_3$ with PPh_2R^* at reflux. The 1:1 mixture of 2-*SS* and 2-*RS* was separated by repeated flash chromatography with hexane/ethyl acetate (9:1).

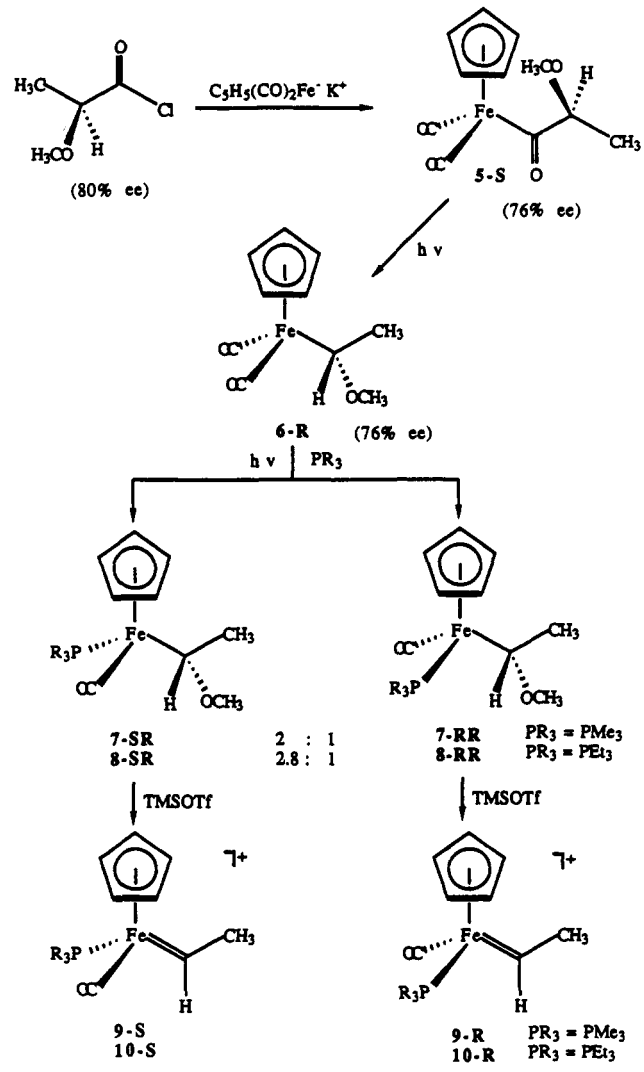
Since 2-*SS* and 2-*RS* have different chemical shifts for the C_5H_5 and CH_3 resonances; the diastereomeric purity was determined by ^1H NMR analysis. Absolute configurations at iron of the complexes 2-*SS* and 2-*RS* were determined by comparison of their CD spectra[13] with those of other iron-acyl complexes with known configurations.[15,16] The sign and magnitude of optical rotations at 436 nm, $[\alpha]^{23}_{436}$, were also used to determine the absolute configurations at the iron center. This method is consistent for a series of iron-acyl complexes:[16] $[\alpha]^{23}_{436} = -583°$ for 2-*SS* (2-*SS*:2-*RS* = 99:1) and $[\alpha]^{23}_{436} = +600°$ for 2-*RS* (2-*SS*:2-*RS* = 4:96) (see Table I for comparison).

Methylation of 2-*SS* with trimethyloxonium tetrafluoroborate in methylene chloride at 25 °C proceeds quantitatively to generate the methoxycarbene complex, $(S_{Fe}S_P)$-$C_5H_5(CO)(PPh_2R^*)Fe{=}C(OCH_3)CH_3^+$,3-*SS*.[2] The heteroatom-stabilized carbene complex 3-*SS* is reduced by quenching the methylene chloride solution of 3-*SS* with $CH_3OH/CH_3O^-Na^+/NaBH_4$ at −78 °C. Dilution with water followed by extraction with methylene chloride yields ether complex $(S_{Fe},S_P,R_{C\alpha})$-$C_5H_5(CO)(PPh_2R^*)FeCH(OCH_3)CH_3$, 4-*SSR*, as a red oil in 80% yield. In the formation of the ether complex a new chiral center at C_α is generated, and two diastereomers are expected. Only one of the diastereomers, 4-*SSR* (no 4-*SSS*), can be detected in this case. The configuration at C_α is shown in Scheme I and is assigned based on an observed "W" geometry coupling between ^{31}P and the protons of the α-CH_3 group. (This method is discussed below.) The enantiomerically pure ethylidene complex 1-*SS* was generated by abstraction of a methoxy group from the complex 4-*SSR* with TMS-OTf. By using a similar procedure, 1-*RS* was generated by converting 2-*RS* to 4-*RSS* followed by addition of TMS-OTf. When the carbene complexes are generated, the chiral centers at C_α are eliminated since Fe=C bond rotation is rapid. Spectroscopic characterization of these complexes is described below.

Synthesis of $(R_{C\alpha})$-$Cp(CO)_2FeCH(OCH_3)CH_3$ and Conversion to Enantiomerically Enriched (R_{Fe})- and (S_{Fe})-$Cp(CO)(PR_3)Fe{=}CHCH_3^+$ (R = $-CH_3$, $-C_2H_5$). Scheme II summarizes a method for using (*S*)-(−)-ethyl lactate to prepare enantiomerically enriched $(R_{C\alpha})$-$Cp(CO)_2FeCH(OCH_3)CH_3$, which can then be converted to enantiomerically enriched (R_{Fe})- and (S_{Fe})-$Cp(CO)(PR_3)Fe{=}CHCH_3^+$ (R = $-CH_3$, $-CH_2CH_3$).

Methylation of the hydroxy group of (*S*)-(−)-ethyl lactate by Ag_2O/MeI is well-known and occurs with little racemization.[17,18] In this work a sodium dispersion was used to generate the alkoxide which was methylated with MeI. This method provides an inexpensive route to (*S*)-ethyl methoxypropionate (80% ee). (*S*)-Methoxypropionyl chloride was obtained by hydrolysis of (*S*)-ethyl methoxypropionate to the acid followed by conversion to the chloride. Treatment of the (*S*)-methoxypropionyl chloride with $Cp(CO)_2Fe^-K^+$ gave the acyl complex (S_C)-$Cp(CO)_2FeC(O)CH(OCH_3)CH_3$, 5-*S*, in 80% yield. ^1H NMR shift experiments (C_6D_6, (+)-Eu(hfc)$_3$) showed the ee of 5-*S* to be 76%. (The 4% loss in ee probably occurred during formation of the acyl complex since an enolate may be formed under these basic conditions.)

Scheme II



Decarbonylation to generate the chiral α-methoxyalkyl complex $(R_{C\alpha})$-$C_5H_5(CO)_2FeCH(OCH_3)CH_3$, 6-*R*, was carried out by photolysis in a dilute acetonitrile solution at 0 °C. Since the product 6-*R* decomposes under irradiation, the maximum yield of 6-*R* was obtained after ca. 50% conversion of 5-*S*. The starting material was recovered and recycled. Overall, a 70% yield of $(R_{C\alpha})$-$Cp(CO)_2FeCH(OCH_3)CH_3$, 6-*R*, was obtained with 76% ee. Analysis of 5-*S* and 6-*R* using chiral shift reagents confirmed that no racemization occurred during decarbonylation. This result is in accord with the observation of Whitesides[19] that photolytic decarbonylation of the stereospecifically labeled complex $C_5H_5(CO)_2Fe$-$C(O)C_1HDC_2HDC(CH_3)_3$ occurs with complete retention at C_1.

The CO ligand in complex 6-*R* was substituted by PMe_3. Benzene solutions of 6-*R* in the presence of PMe_3 at 0 °C were photolyzed with a sun lamp and an ca. 2:1 mixture of diastereomers 7-*SR* and 7-*RR* were formed. Partial separation of 7-*SR* and 7-*RR* can be achieved by using low-temperature (−78 °C) column chromatography[20] and the diastereomer ratio can be in-

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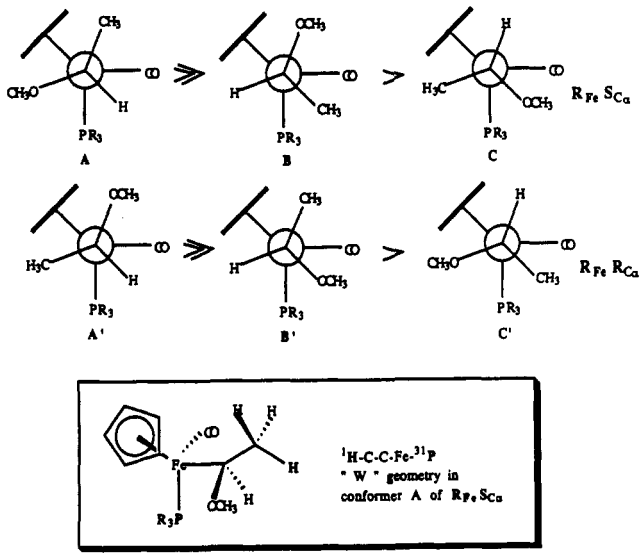
Scheme III



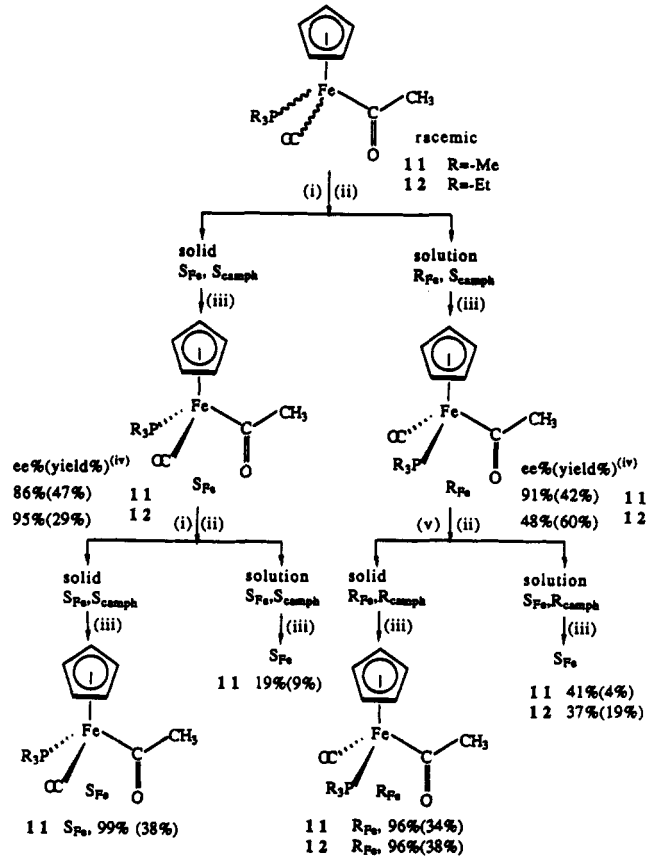
creased to 3:1. Similarly, by using PEt_3 as shown in Scheme II, a 2.8:1 ratio of **8**-*SR* and **8**-*RR* was obtained. The ratio can be enriched to 4:1 by low-temperature column chromatography.

Scheme III shows the three possible conformers for each of the two diastereomeric complexes of the type $Cp(CO)(PR_3)FeCH(OCH_3)CH_3$ based on conformational analysis studies carried out by Gladysz[8d,21] and by Davies and Seeman[22] for octahedral iron complexes $Cp(CO)(PR_3)FeCHRR'$. The energetically most favorable, sterically least crowded site for C_α substituents is between Cp and CO. The sterically least favorable site lies between CO and PR_3. Conformer A is expected to be much more stable than conformers B and C in complex (R_{Fe},$S_{C\alpha}$); similarly, conformer A′ is much more stable than conformers B′ and C′ in complex (R_{Fe},$R_{C\alpha}$) assuming that the sterically least favored position is, in these cases, occupied by H.

Spectroscopic properties of (R_{Fe},$S_{C\alpha}$) and (R_{Fe},$R_{C\alpha}$) complexes are taken to be those of the most stable conformers A and A′, respectively. In conformer A of the (R_{Fe},$S_{C\alpha}$) diastereomer the Me group lies between the CO and Cp ligands. One of the H atoms in the Me group is in a "W" geometry with respect to the phorphorus atom. In contrast, in conformer A′ of the (R_{Fe},$R_{C\alpha}$) diastereomer a similar "W" geometry relationship is not present. When one of the H atoms on the Me group is in a "W" configuration with respect to phosphorus, there exists a $^4J(CH_3\text{-}P)$ coupling of about 1.1–1.7 Hz. The relative configurations of iron and C_α can thus be assigned based on the presence or absence of this coupling. The "W" geometry coupling was also found in analogous complexes such as $Cp(CO)(PPh_3)FeCH_2CH_3$ (J_{HP} = 2.0 Hz),[23] $Cp(CO)(PMe_3)FeCH_2CH_3$ (J_{HP} = 1.9 Hz),[24] and $Cp(CO)(PR_3)FeCH(SR')CH_3$ (R = Me, Et, and Ph; R′ = Ph and $C(O)CH_3$) (J_{HP} = 1.4–1.7 Hz).[25] In the latter series of complexes, the relative Fe and C_α configurations have been confirmed by X-ray analysis of R = Me and Ph, R′ = Ph and $C(O)CH_3$.

The absolute configurations at the iron center in **7**-*SR*, **7**-*RR*, **8**-*SR*, and **8**-*RR* were formulated based on the known configuration of (*S*)-(−)-ethyl lactate at C_α, since the relative configurations of iron and C_α can be determined based on the presence or absence of a "W" geometry P–CH_3 coupling. The major diastereomers were thus assigned as S_{Fe} and the minor diastereomers as R_{Fe}. The chiral centers at C_α are eliminated when the carbene complexes are generated, and enantiomer excesses at the iron center in the carbene complexes were computed as de × ee.

Scheme IV[a]



[a] (i) (*S*)-(+)-10-Camphorsulfonic acid, CH_2Cl_2; (ii) crystallize from CH_2Cl_2/Et_2O, −25 °C; (iii) neutralization with 20% K_2CO_3; (iv) yields are based on total weight of racemic **11** and **12** used, i.e., maximum yield of a single enantiomer is 50%; (v) (*R*)-(−)-10-camphorsulfonic acid, CH_2Cl_2.

Resolution of the Acyl Complexes, $Cp(CO)(PR_3)FeC(O)CH_3$, 11, R = $-CH_3$; 12, R = $-CH_2CH_3$. Conversion of the Enantiomerically Pure Acyl Complexes $Cp(CO)(PR_3)FeC(O)CH_3$ to the Ether Complexes $Cp(CO)(PR_3)FeCH(OCH_3)CH_3$. An alternative method to generate enantiomerically pure carbene complexes involves resolution of iron–acyl complexes, followed by conversion of the acyl complexes to α-ether complexes and then to carbene complexes. The chiral reagents employed in resolutions can often be recovered, while chiral reagents used in the above two methods are either destroyed or are inconvenient to recover.

The acyl oxygen of iron–acyl complexes $C_5H_5(CO)(PR_3)FeC(O)R$ is basic and can be readily methylated or protonated to form the corresponding methoxy-or hydroxycarbene salts.[1,2,13,14,26] Protonation of **11** and **12** (shown in Scheme IV) (ν_{CO} = 1910 cm^{-1}, ν_{CO}(acyl carbonyl) = 1598 cm^{-1}) in CH_2Cl_2 with either (*S*)-(+)-10-camphorsulfonic acid or (*R*)-(−)-10-camphorsulfonic acid leads to complete conversion to a 1:1 mixture of the diasteromeric hydroxycarbene salts (ν_{CO} = 1967–1982 cm^{-1}, disappearance of ν_{CO}(acyl carbonyl) = 1598 cm^{-1}). These diastereomeric hydroxycarbene salts can be easily separated by crystallization from CH_2Cl_2/ether at −25 °C. After yellow crystalline solids separated from solution, partially resolved **11** and **12** were recovered by neutralization of the solid and solution phases, respectively, with a 20% K_2CO_3 aqueous solution. By using (*S*)-(+)-10-camphorsulfonic acid, the ee for the S_{Fe} enantiomer of **11** recovered from the solid phase was 86%, whereas the R_{Fe} enantiomer of **11** was obtained from solution phase in 91% ee.

(21) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154.
(22) (a) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1019. (b) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522.
(23) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Organomet. Chem.* **1987**, *320*, C19.
(24) Liu, Y.; Brookhart, M. Unpublished results.
(25) Brookhart, M.; Liu, Y.; Buck, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2337.
(26) Green, M. L. H.; Swanwick, M. G. *J. Chem. Soc.* (*A*) **1971**, 794.

Table I. Correlation of $[\alpha]^{23}_{436}$ and Chemical Shifts of CH_3 and C_5H_5 in ^1H NMR Shift Experiments Using (+)-Eu(hfc)$_3$ for Complexes of the Type $C_5H_5(CO)(PR_3)FeC(O)CH_3$

	$[\alpha]^{23}_{436}$	C_5H_5[a] (ppm)	C(O)CH_3[a] (ppm)
$C_5H_5(CO)(PMe_3)FeCOCH_3$, **11**-*S*	−500°	8.58	8.08
$C_5H_5(CO)(PMe_3)FeCOCH_3$, **11**-*R*	+490°	8.82	7.64
$C_5H_5(CO)(PEt_3)FeCOCH_3$, **12**-*S*	−530°	9.18	8.18
$C_5H_5(CO)(PEt_3)FeCOCH_3$, **12**-*R*	+550°	9.62	7.66
$C_5H_5(CO)(PPh_3)FeCOCH_3$, **13**-*S*	−1100°	8.36	5.86
$C_5H_5(CO)(PPh_3)FeCOCH_3$, **13**-*R*		9.28	5.32
$C_5H_5(CO)(PPh_2R^*)FeCOCH_3$, **2**-*SS*	−583°	*b*	*b*
$C_5H_5(CO)(PPh_2R^*)FeCOCH_3$, **2**-*RS*	+600°	*b*	*b*

[a] See Experimental Section for details. [b] Diastereomer ratios assayed by using standard ^1H NMR techniques (see text).

Similarly, the ee for the S_{Fe} enantiomer of **12** recovered from the solid phase was 95%, whereas the R_{Fe} enantiomer of **12** was obtained from solution phase in 48% ee. Further resolution was achieved by reprotonation of the (S_{Fe})-enriched acetyl complexes with (*S*)-(+)-10-camphorsulfonic acid, followed by crystallization and neutralization. S_{Fe} enantiomers of **11** and **12** were obtained in 95–99% ee from the solid phases recovered in this second cycle. Similarly, reprotonation of (R_{Fe})-enriched acetyl complexes with (*R*)-(−)-10-camphorsulfonic acid followed by crystallization and neutralization gives R_{Fe} enantiomers of **11** and **12** in 96% ee. A complete resolution procedure is shown in Scheme IV.

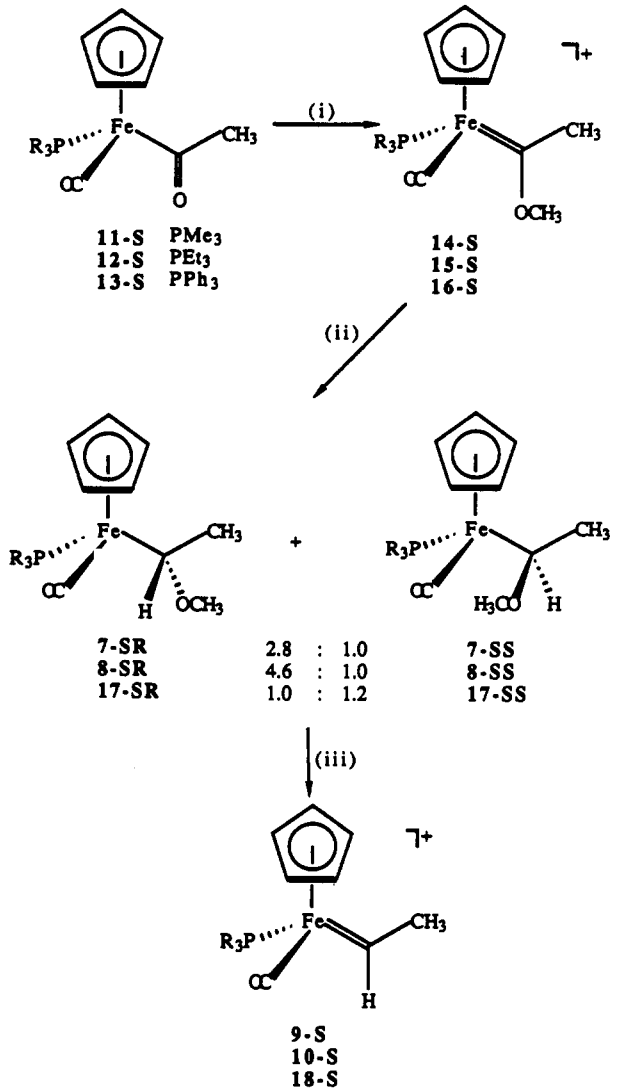
The ee's of acyl complexes were determined by ^1H NMR spectroscopy in C_6D_6 by using the chiral shift reagent (+)-Eu(hfc)$_3$. In these shift experiments, C_5H_5 and CH_3 resonances for S_{Fe} and R_{Fe} enantiomers of **11**, **12**, and **13** are widely separated upon addition of ca. 1 equiv of chiral shift reagent (+)-Eu(hfc)$_3$. For the R_{Fe} enantiomers the C_5H_5 signals shift further downfield rather than for the S_{Fe} enantiomers, while for the S_{Fe} enantiomers the $-C(O)CH_3$ signals shift further downfield than for the R_{Fe} enantiomers. This behavior[27] is consistent for acetyl complexes $Cp(CO)(L)FeC(O)CH_3$ with L = PMe_3, **11**; PEt_3, **12**, and PPh_3, **13**, as shown in Table I.

While $Cp(CO)(PR_3)FeC(O)CH_3$ (**11**, R = Me; **12**, R = Et) complexes were efficiently resolved by the above methods, we have been unable to resolve $Cp(CO)(PPh_3)FeC(O)CH_3$, **13**, by using these techniques.[28] The acyl oxygen of **13** is less basic, and complete protonation cannot be achieved by using 1 equiv of acid. By using excess acid the protonation can be driven to near completion, but crystallization results in initial recovery of the free acid and reversal of the equilibrium.

Scheme V summarizes the methods used to convert the acyl complexes to the ethylidene complexes. Methylation of **11**-*S* with methyl triflate (or trimethyloxonium tetrafluoroborate) in methylene chloride at 25 °C proceeds quantitatively to generate the methoxycarbene complex, **14**-*S* (see Scheme V). The heteroatom-stabilized carbene complex was reduced by quenching the methylene chloride solution of **14**-*S* into $CH_3OH/CH_3O^-Na^+/NaBH_4$ at −78 °C. Dilution with water followed by extraction with methylene chloride forms α-methoxyalkyl complexes **7**-*SS* and **7**-*SR* as a red oil in 80–90% yield. In the formation of these complexes a new chiral center is generated, and two diastereomers, **7**-*SR* and **7**-*SS*, are formed in an ca. 2.8:1 ratio. By similar methods compounds **12**-*S* and **13**-*S* were also converted to α-methoxyalkyl complexes as shown in Scheme V. Similar to the *S* enantiomers, **11**-*R* and **12**-*R* were converted to **7**-*RR*, **7**-*RS*, **8**-*RR*, and **8**-*RS*.

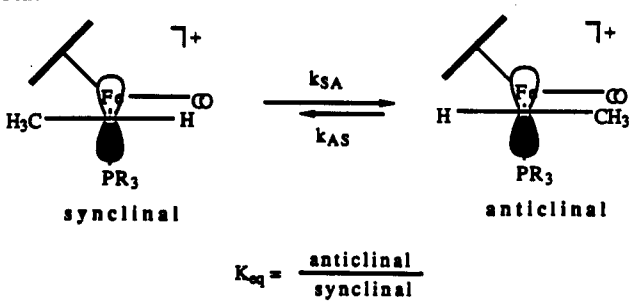
Spectroscopic Observation of the Ethylidene Complexes Cp(CO)(L)Fe=CHCH$_3^+$ (9, L = PMe$_3$; 10, L = PEt$_3$; 1-*SS*, L = PPh$_2$R* (R* = (*S*)-2-Methylbutyl), and 18, L = PPh$_3$). Rates of Interconversion and Equilibrium Ratios of Synclinal and Anticlinal Isomers. Ethylidene complexes $Cp(CO)(L)Fe{=}CHCH_3^+$,

Scheme V[a]



[a] (i) MeOTf at 25 °C; (ii) $NaBH_4$/NaOMe/MeOH at −78 °C; (iii) TMSOTf at −78 °C.

Scheme VI



9, L = PMe_3; **10**, L = PEt_3; **1**-*SS*, L = PPh$_2$R* (R* = (*S*)-2-methylbutyl) and **18**, L = PPh_3 were generated quantitatively by addition of trimethylsilyl triflate (TMS-OTf) to CD_2Cl_2 solutions of complexes $Cp(CO)(L)FeCH(OMe)CH_3$ (L = PMe_3, PEt_3, PPh$_2$R*, and PPh_3) at −78 °C. Each complex has been characterized by ^1H and ^{13}C NMR spectroscopy. As shown in Table II, the CD_2Cl_2 solutions show ^1H resonances for the H_α protons at δ 16–18 ppm and low field ^{13}C resonances of the carbene carbons at δ 360–380 ppm.[31] These characteristic shifts estab-

(27) Sullivan, G. R. *Topics in Stereochemistry*; Wiley-Interscience: New York, 1978; Vol. 10, p 287.

(28) Enantiomerically pure complexes (*S*)- and (*R*)-$C_5H_5(CO)(PPh_3)FeC(O)CH_3$ are commercially available from BP Chemicals[30] and Fluka. Procedures used for their preparation have not been published.[29]

(29) (a) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 609. (b) Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13. (c) Bechett, R. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1988**, 160. (d) Bashiardes, G.; Davies, S. G. *Tetrahedron Lett.* **1988**, *29*, 6509.

Table II. Spectroscopic and Kinetic Data for Carbene Complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$

	$^1H_\alpha$(anticlinal)[a] (ppm)	$^1H_\alpha$(synclinal)[a] (ppm)	$^{13}C_\alpha$[a] (ppm)	K_{eq} (°C)[a]	ΔG^*_{AS}[a] (kcal/mol)	ΔG^*_{SA}[a] (kcal/mol)
$C_5H_5(CO)(PMe_3)Fe{=}CHCH_3^+$, **9**	17.46	15.92	369.7	4.6 (−114)	9.3	8.8
$C_5H_5(CO)(PEt_3)Fe{=}CHCH_3^+$, **10**	17.65	15.69	366.2	10.9 (−114)	9.6	8.8
$C_5H_5(CO)(PPh_3)Fe{=}CHCH_3^+$, **18**	18.24	17.05	380	5.7 (−126)	7.8	7.3
$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, **1-*SS***	17.9	16.4		2.4 (−100)	8.6	8.3

[a] See Experimental Section for details.

Table III. Enantioselective Ethylidene Transfer Reactions to Alkenes[a]

	carbene complexes	chirality at Fe	% ee	$CH_2{=}CRR'$	% yield total cyclopropanes	trans/cis ratio	% ee product trans/cis	% optical yield trans/cis
1	$Cp(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, **1**	*S*	98	R′ = H, R = Ph	75	3.5:1.0	88, 84[b]	90, 86
2	$Cp(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, **1**	*R*	92	R′ = H, R = Ph	75	4.0:1.0	83, 77[b]	90, 84
3	$Cp(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, **1**	*S*	96	R′ = H, R = OAc	33	1.9:1.0	72, 64	75, 67
4	$Cp(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, **1**	*S*	98	R′ = OAc, R = Me	40	1.0:1.3[c]	92, 86	94, 88
5	$Cp(CO)(PPh_3)Fe{=}CHCH_3^+$, **18**	*S*	100	R′ = H, R = OAc	30	2.3:1.0	95, 83	95, 83
6	$Cp(CO)(PMe_3)Fe{=}CHCH_3^+$, **9**	*R*	77	R′ = H, R = OAc	50	1.6:1.0	70, 70	91, 91
7	$Cp(CO)(PEt_3)Fe{=}CHCH_3^+$, **10**	*R*	76	R′ = H, R = OAc	35	1.8:1.0	71, 68	93, 89
8	$Cp(CO)(PMe_3)Fe{=}CHCH_3^+$, **9**	*S*	87	R′ = H, R = OAc	59	1.6:1.0	76, 76	87, 87
9	$Cp(CO)(PEt_3)Fe{=}CHCH_3^+$, **10**	*S*	77	R′ = H, R = OAc	27	1.8:1.0	75, 73	97, 95

[a] See text and Experimental Section for reaction conditions. [b] See Scheme VII for absolute configurations of cyclopropanes. [c] 1.0:1.3 ratio of *trans*-:*cis*-1-acetoxy-1,2-dimethylcyclopropanes.

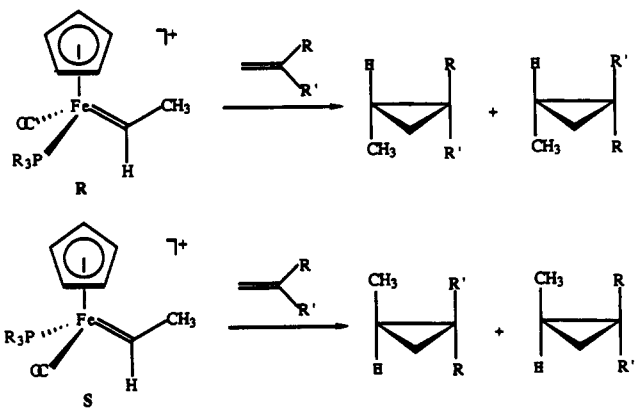
lished these species as cationic ethylidene complexes analogous to the other electrophilic carbene complexes,[2,5-8]

At −114 °C, a CD_2Cl_2 solution of **9** shows two characteristic resonances for the H_α signal at δ 17.46 and 15.92 ppm in ca. 4.6:1 ratio. The major isomer is assigned as the anticlinal isomer, and the minor isomer is assigned as the synclinal isomer as shown in Scheme VI (see below). Spin saturation transfer and variable temperature ^1H NMR experiments have established that these two isomers are in rapid equilibrium. For example, upon irradiation of the H_α (anticlinal) signal at δ 17.46 ppm of **9**, the intensity of the H_α (synclinal) signal at 15.92 ppm was reduced. Upon warming above −114 °C, these two signals broaden and coalesce into a broad singlet at δ 17.25 ppm. Upon further warming, this broad band sharpens to a quartet (J_{HH} = 7.7 Hz, −20 °C). The interconversion rates are determined by line shape analysis, and results are given in Table II. Similar to the observations for **9**, the synclinal and anticlinal isomers for **10** and **1-*SS*** were observed, and their interconversion rates were determined. Data are summarized in Table II.

For complex **18**, the interconversion barrier around the Fe=C bond is lower than for **1-*SS***, **9**, and **10**, and lower temperatures are required to reduce the rate of rotation around the Fe=C bond and allow observation of synclinal and anticlinal isomers. An equivalent volume of SO_2ClF was added to the CD_2Cl_2 solution of **18** to lower the freezing point of the solution. At −126 °C, complex **18** shows characteristic $H_{carbene}$ signals at δ 18.24 and 17.05 ppm in a 5.7:1 ratio. Upon warming, these signals broaden and coalesce into an average signal at δ 17.92 ppm.

The structures of the two carbene isomers were assigned by analogy to the work of Gladysz on the isoelectronic $Cp(NO)(PR_3)Re{=}CHR^+$ systems.[8] In these systems the structures of anticlinal isomers were established by X-ray diffraction studies. Structures of synclinal isomers were inferred from calculations on the potential energy surface for the Re=C bond rotation which showed that another stable isomer was produced by a 180° bond rotation in the anticlinal isomer. In the iron ethylidene systems we assume the more stable carbene isomers to be the anticlinal isomers by analogy to the rhenium complexes. Configurational assignments of the iron carbene isomers **9**, **10**, and **18** are definitively established by studies of the diastereoselective nucleophilic addition to equilibrating synclinal and anticlinal ethylidene isomers (L = PMe_3, PEt_3, and PPh_3).[25] Furthermore, recent X-ray analysis of complex $Cp(CO)(PPh_3)Fe{=}C(OCH_3)CH_3^+$ shows the carbene plane aligned with the Fe–CO bond as expected.[33]

Scheme VII[a]



[a] R = Ph, R′ = H; R = OAc, R′ = H; R = Me, R′ = OAc.

Enantioselective Ethylidene Transfer Reactions. Enantioselective ethylidene transfer reactions from enantiomerically pure or enriched carbene complexes **1**, **9**, **10**, and **18** to styrene, isopropenyl acetate, and vinyl acetate were carried out. In a typical procedure, trimethylsilyl triflate (1.1 equiv) was added to a methylene chloride solution (−78 °C) containing the ether complex (**4**, **7**, **8**, or **17**), olefin (10 equiv), and triethylamine (0.1 equiv). After warming to 25 °C and stirring for 3 h, the reaction solution was washed with 50 mL of saturated aqueous $NaHCO_3$ solution, and the cyclopropanes were extracted with 2-methylbutane. The *cis*- and *trans*-cyclopropane isomers were separated and purified by preparative GC, and yields were determined by use of an internal standard. Results including yields, cis/trans ratios, percent ee, and optical yields are listed in Table III and Scheme VII.

The cis or trans configuration of the methylphenylcyclopropanes can be established unambiguously by ^1H and ^{13}C NMR spectroscopy. The *cis*- and *trans*-1-methyl-2-phenylcyclopropanes exhibit spectra identical with those previously reported.[34] The splitting pattern of the proton α to the actate group established the cis or trans stereochemistry for the 1-acetoxy-2-methylcyclopropanes. The cis isomer shows a doublet of triplets with two cis vicinal coupling, J_{HH} = 6.9 Hz, and a trans vicinal coupling, J_{HH} = 3.4 Hz. The trans isomer shows a doublet of doublet of doublets, with J_{HH} = 6.7 Hz for the cis vicinal coupling and two small trans vicinal couplings.

(30) New Specialities Business, B. P. Chemical Ltd., Belgrave House, 76 Buckingham Palace Road, London, SWIW OSU, U.K.

(31) It is interesting to note that the C_α chemical shifts of $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ as well as ΔG^*_{AS} are proportional to the electronic parameters, χ_i, for the phosphine ligands as defined by Tolman.[32] These values are taken to be a quantitative measure of the electron-donating ability of the phosphine ligands.

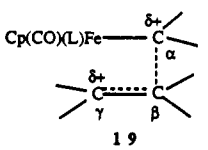
Enantiomer excesses of cyclopropanes were determined either by correlation of optical rotations with literature values (*cis*- and *trans*-2-methyl-1-phenylcyclopropanes)[34] or by shift experiments utilizing a lanthanide shift reagent (*cis*- and *trans*-1-acetoxy-2-methylcyclopropanes and *cis*- and *trans*-1-acetoxy-1,2-dimethylcyclopropanes). The ^1H NMR shift experiments were conducted by addition of (+)-Eu(hfc)$_3$ to either C_6D_6 or $CDCl_3$ solutions of the cyclopropanes. The signals for the acetate methyl groups of *trans*-1-acetoxy-2-methylcyclopropane and for the β-methyl groups of the *cis*-1-acetoxy-2-methylcyclopropane exhibited baseline separation for the two enantiomers. Absolute configurations of the major enantiomers of the *cis*- and *trans*-1-methyl-2-phenylcyclopropanes produced from ethylidene transfers to styrene are known by comparison of the optical rotations with literature values.[34] Scheme VII shows the absolute configuration of the major *cis*- and *trans*-cyclopropanes formed via ethylidene transfers from *S* and *R* carbene complexes to olefins. In the ethylidene transfers to vinyl acetate and isopropenyl acetate, absolute configurations of the products are unknown. It is assumed that these products are formed in the same manner as those from ethylidene transfer to styrene, and thus absolute configurations shown in Scheme VII are tentatively assigned on this basis.

Data in Table III demonstrate that the chiral-at-iron–carbene complexes are good reagents for enantioselective ethylidene transfers to olefins to form methylcyclopropanes with high ee's. The absolute configurations of the cyclopropanes are controlled by the configuration of the iron center. Small phosphine ligand also lead to high enantiomer excesses of cyclopropanes. The high ee's attained indicate that PMe_3 and PEt_3 effectively shield one face of the carbene moiety from attack and that such shielding does not necessarily require phosphines which can place an arene ring in a face-to-face orientation with planar carbene ligands.[9h,11,12,25]

Since the ratios of enantiomers of the product cylopropanes exceed the anticlinal/synclinal equilibrium ratios of carbene isomers, it must be concluded that the relative reactivities of the synclinal and anticlinal isomers are different. Very low ee's (<41%) in the product cyclopropanes would have been expected in the ethylidene transfers of **1**-*SS* if the reactivities of synclinal and anticlinal isomers were the same. As shown in Scheme VIII, the ethylidene transfer must proceed by either (1) reaction of the synclinal isomer with styrene followed by backside closure or (2) reaction of the anticlinal isomer with styrene followed by frontside closure. As pointed out below, the transfers must occur primarily through the (more reactive) synclinal isomers.

The Mechanism of Transfer and the Origin of Enantioselectivity. The stereochemical studies reported here coupled with earlier results allow a detailed description of the carbene transfer mechanism. It is instructive to develop a picture of the mechanism moving from general features to more specific detail.

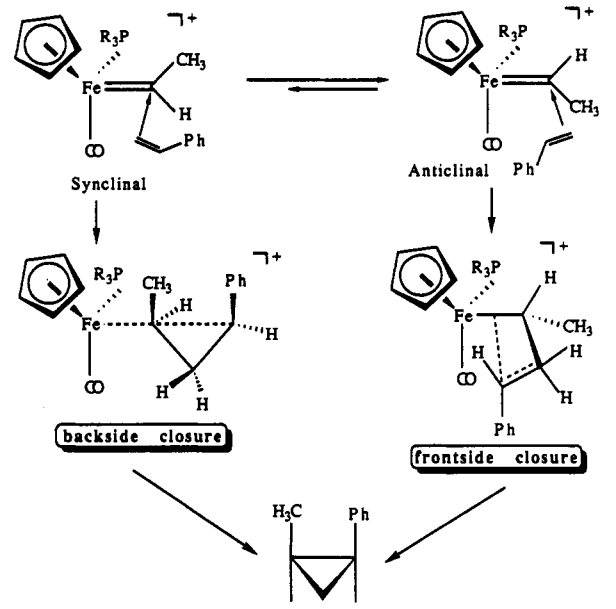
On the basis of results of several studies,[1,3,7] the electrophilic center, C_α, of the carbene complex attacks the alkene to generate partial positive at C_γ in the transition state as shown in **19** below. In certain cases where C_γ possesses a strongly electron-donating group, a stabilized carbocation intermediate is formed (after the transition state) with sufficient lifetime to allow C_γ–C_β bond rotation before product formation. This process results in loss of original alkene stereochemistry.[3]



19

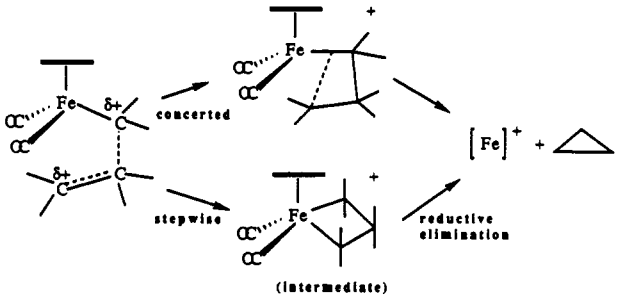
(32) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(33) Liu, Y.; Brookhart, M.; Singh, P. Unpublished results.
(34) (a) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655. (b) Aratani, T.; Nakanis, Y.; Nozaki, H. *Tetrahedron* **1970**, *26*, 1675. (b) Baldwin, J. E.; Likiger, J.; Rasttetter, W.; Neuss, N.; Huckstep, L. L.; De La Higuera, N. *J. Am. Chem. Soc.* **1973**, *95*, 3795.

Scheme VIII

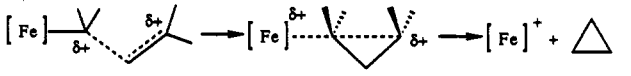


Next, the mode of ring closure must be addressed. Two stereochemically distinct pathways can be envisioned whereby the developing electrophilic center at C_γ cleaves the Fe–C_α bond and forms cyclopropane products:

(1) "Frontside" closure and electrophilic cleavage of Fe–C_α by C_γ with retention of C_α stereochemistry could happen in a concerted process or stepwise process (via a metallacycle intermediate) as shown below. Stereochemically, these pathways are indistinguishable.



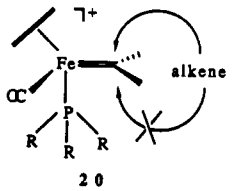
(2) "Backside" closure with electrophilic cleavage at Fe–C_α by C_γ with inversion of C_α stereochemistry are shown below.



These two possibilities are in part addressed by the stereochemical studies reported here. Starting with a phosphine-substituted ethylidene complex $Cp(CO)(PR_3)Fe{=}CHCH_3^+$ of known absolute configuration, the absolute configuration of the resultant cyclopropane will be determined by (i) the facial selectivity of alkene attack on C_α as determined by the ligands about iron, (ii) whether the synclinal and anticlinal isomer is the more reactive (the transfer rate is slow relative to the rate of isomer interconversion), and (iii) whether frontside or backside closure occurs.

On the basis of the observations of Gladysz,[8] Liebeskind,[10] and Davies[9] and on our studies[25] of nucleophilic additions to ethylidene complexes $Cp(CO)(PR_3)Fe{=}CHCH_3^+$, it is clear that PR_3 ligands very effectively shield one face of the carbene moiety and that attack can be considered to occur exclusively as shown below, **20**.

Analysis of the sterochemical results obtained for reaction of styrene with (R_{Fe},S_P)- and (S_{Fe},S_P)-Cp(CO)(PPh_2R^*)Fe=$CHCH_3^+$ (R* = (*S*)-2-methylbutyl) where both the absolute configurations of the metal center and the cyclopropane products are known suggests two possible mechanisms. These are shown in Scheme VIII and involve either reaction via the minor synclinal



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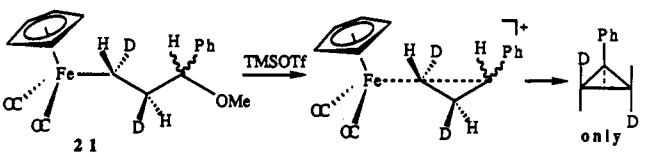
isomer followed by backside closure or reaction via the major anticlinal isomer with frontside closure. (The reaction is illustrated for production of the *cis*-(1*R*,2*S*)-1-methyl-2-phenylcyclopropane. A similar analysis is consistent with formation of the *trans*-(1*R*,2*R*)-1-methyl-2-phenylcyclopropane isomer.)

Two recent results indicate that the reaction occurs through the synclinal isomer with backside closure. First, studies involving addition of simple nucleophiles to chiral ethylidene complexes **9**, **10**, and **18** have shown that the relative reactivities of the synclinal isomers toward nucleophiles are much higher than the anticlinal isomers.[25] Furthermore, this reactivity difference increases with decreasing activity of the nucleophile. Viewing an alkene as a very weak nucleophile, attack on the synclinal isomer is expected to occur with high selectivity relative to the anticlinal isomer.[25,35] (As described in ref 25, conformational considerations provide a reasonable explanation for the relative reactivities of the synclinal and anticlinal isomers.)

A second set of experiments which suggests backside closure involves the study of deuterium-labeled γ-derivatives of the type $Cp(CO)_2FeCH_2CH_2CHRX$ which ionize to give cyclopropanes RC_3H_5.[36] A complete description of this work is contained in the following paper in this issue.[36b] The transition state for cyclopropane formation from these γ-derivatives must closely resemble the transition state for cyclopropane formation in the transfer reaction since in each case an electrophilic center at C_γ is attacking the Fe–C_α bond. Ionization of systems specifically deuterium labeled at the α and β position, for example, **21**, results in a labeling pattern in the cyclopropane product which is consistent only with cleavage of the Fe–C_α bond with inversion, a result which strongly supports the synclinal-backside closure mechanism. A similar result has recently been reported by Casey using deuterium labeled $Cp(CO)_2FeCHDCHDCH_2S(Ph)(CH_3)^+$.[37]



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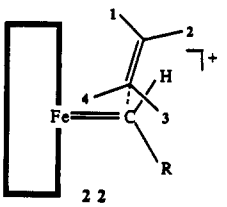
The results described above establish that (1) the transfer occurs via reaction of electrophilic C_α with the nucleophilic alkene to produce an electrophilic center at C_γ followed by cleavage of Fe–C_α by C_γ with inversion at C_α and (2) that the origin of high enantioselectivity in PR_3-substituted systems is the facial selectivity of attack of the alkene on the carbene moiety coupled with the high reactivity of the synclinal isomer relative to the anticlinal isomer. An issue yet to be addressed here is the diastereoselectivity observed in the formation of cyclopropanes. A number of transition-state models have been suggested to account for diastereoselectivities observed for reactions of electrophilic metal–carbene complexes. Most of these earlier models were based on the incorrect assumption that cleavage of Fe–C_α by C_γ occurred in a frontside mode with retention at C_α. (For a review of these earlier proposals see ref 1.)

A large number of transfers have been carried out, and a complete tabulation of these results has appeared.[1] Table IV summarizes representative results for ethylidene transfer to simple

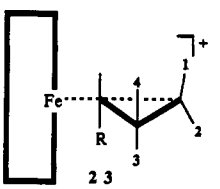
Table IV. Diastereoselectivities Observed for Ethylidene Transfers From Iron Ethylidene Complexes to Various Alkenes

	$Cp(CO)(L)Fe{=}CHCH_3$*	Substrate	Product Ratio Cis : Trans	Reference
1	L = CO		1 : 1	2a,b
2	L = CO	Ph	6 : 1	2a,b, 3
3	L = CO		> 50 : 1	2a,b
4	L = CO		> 50 : 1	2a,b
5	L = PPh_3	Ph	1 : 3	7
6	L = PPh_3	$C_6H_4(p\text{-}OCH_3)$	2 : 3	7
7	L = $PPh_2CH_2CH(CH_3)C_2H_5$	Ph	1 : 4	13

alkyl- and aryl-substituted alkenes. An interesting feature to note is that the highly reactive dicarbonyl complex $Cp(CO)_2Fe{=}CHCH_3^+$ exhibits cis (or syn) selectivity, while less reactive phosphine-substituted systems show trans selectivity. This suggests a variable transition-state model such that the structure of the transition state (and thus the diastereoselectivity) varies depending on whether the transition state is "early" or "late". For less reactive phosphine-substituted systems, transition states are late and resemble product cyclopropanes, hence trans selectivity is observed. For more reactive dicarbonyl systems the transition state is early, and the interactions present in the initial approach of the alkene determine stereochemistry. A model for an early transition state is shown in **22**. Site 2 would be sterically less crowded than site 1 resulting in cis selectivity for monosubstituted alkenes. A strong substituent preference for site 3 relative to site 4 is consistent with very high syn selectivity for ethylidene transfer to trimethylethylene (entry 3) and (*Z*)-3-hexene (entry 4). In the late transition-state model, **23**, substituents will prefer site 1 to site 2, and trans selectivity will be exhibited for monosubstituted alkenes. Pairwise comparisons support the model of a variable transition state in



22 (early transition state)



23 (late transition state)

which the later the transition state comes, the larger the trans/cis product ratio is. Reaction of $Cp(CO)_2Fe{=}CHCH_3^+$ with 1-hexene (later) gives a 1:1 cis/trans isomer ratio, while reaction with styrene (earlier) gives a 6:1 cis/trans isomer ratio. Reaction of $Cp(CO)(PPh_3)Fe{=}CHCH_3^+$ with styrene (later) gives a 1:3 cis:trans ratio while reaction with *p*-methoxystyrene (earlier) gives a 2:3 cis:trans ratio. A comparison of diastereoselectivities in benzylidene transfers yields quite similar results (see Table I, ref 1). However, cross comparison of the two systems reveals that the benzylidene complex $Cp(CO)_2Fe{=}CHC_6H_5^+$ generally gives higher cis/trans product ratios than $Cp(CO)_2Fe{=}CHCH_3^+$ which is not consistent with the expected higher selectivity of the more electrophilic ethylidene complex. The substantial steric differences of methyl and phenyl groups may result in transition states with significantly different geometries.[38] Additional experiments are

(35) Brookhart, M.; Liu, Y. *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: 1989; pp 251–270.
(36) (a) Brookhart, M.; Liu, M. *Organometallics* **1989**, *8*, 1569. (b) Brookhart, M.; Liu, Y. *J. Am. Chem. Soc.*, following paper in this issue.
(37) Casey, C. P.; Smith, L. J. *Organometallics* **1989**, *8*, 2288.

(38) A similar explanation may be invoked to explain diastereoselectivities observed in other carbene transfers using electrophilic transition-metal carbene complexes,[1] for example, the benzylidene transfer reactions of $(CO)_5W{=}C{-}HC_6H_5$ studied for Casey. For leading references, see: (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (b) Casey, C. P.; Polichnowski, S. W. Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282.

clearly required to more accurately define transition-state structures and the reasons for variation in diastereoselectivity with changes in the ligands.

Summary

Three routes were developed for synthesis of enantiomerically pure or enriched iron–ethylidene complexes $Cp(CO)(PR_3)Fe{=}CHCH_3^+$. The most convenient and practical of these involves the resolution of iron–acetyl complexes $Cp(CO)(PR_3)FeCOCH_3$ using (*S*)-(+)- and (*R*)-(−)-10-camphorsulfonic acid and conversion of the enantiomerically pure acetyl complexes to α-ether complexes $Cp(CO)(PR_3)FeCH(OCH_3)CH_3$ which are then ionized to the ethylidene complexes. The advantage of this route is that it is general and potentially applicable to any phosphine–acyl complex sufficiently basic to be protonated by camphorsulfonic acid. Ethylidene transfer from the chiral ethylidene complexes $Cp(CO)(L)Fe{=}CHCH_3^+$ (L = $P(C_6H_5)_2$((*S*)-2-methylbutyl), PMe_3, PEt_3, $P(C_6H_5)_3$) to styrene, vinyl acetate, and isopropenyl acetate gives cyclopropanes with generally high optical yields (ca 75–95%). This observation emphasizes the fact that any of these phosphines effectively shields one face of the carbene ligand from attack by the alkene. An aryl-substituted phosphine in which an aryl group may adopt a face-to-face alignment with the carbene moiety is not a necessary requirement.[9h]

Low temperature ^1H NMR observations show that the carbene complexes exist as rapidly equilibrating mixtures of synclinal and anticlinal isomers with the anticlinal isomer preferred (K_{eq} = [anticlinal]/[synclinal] ca. 3–10 at −104 °C) and barriers to isomer interconversion of ca. 8–10 kcal/mol.

A combination of the stereochemical results obtained coupled with deuterium labeling results and relative reactivity studies strongly suggest that the mechanism of carbene transfer involves reaction of the olefins with the minor but more reactive synclinal isomer of $Cp(CO)(L)Fe{=}CHCH_3^+$ followed by backside attack of the developing electrophilic center at C_γ on the Fe–C_α bond. A rationale has been offered for the differing diastereoselectivities observed in ethylidene transfer from $Cp(CO)_2Fe{=}CHCH_3^+$ versus $Cp(CO)(PR_3)Fe{=}CHCH_3^+$ to olefins. It is proposed that transition-state structures differ depending on the electrophilicity of ethylidene complex and thus how "early" or "late" the transition state occurs.

Experimental Section

General Methods. All reactions and operations were conducted under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques and a double manifold vacuum line or a Vacuum Atmospheres drybox. Nitrogen gas was purified by passage through a column of BASF catalyst and molecular sieves. Methylene chloride was distilled in an N_2 atmosphere from phosphorus pentoxide, and tetrahydrofuran, benzene, and diethyl ether were distilled in an N_2 atmosphere from sodium and benzophenone prior to use. Methanol was distilled from $Mg(OMe)_2$ and acetonitrile was distilled from CaH_2 in an N_2 atmosphere. Solvents for column chromatography were degassed by purging with N_2 for 10 min. Deuterated solvents were used as received. The (S_{Fe})-$Cp(CO)(PPh_3)FeC(O)CH_3$, **13-S**, used to carry out the enantioselective carbene transfer reactions was purchased from BP Chemicals.[30] (*S*)-(−)-Ethyl lactate (98% ee) was obtained from Aldrich. $Cp(CO)_2Fe^-K^+$ was prepared as previously described.[2c] ^1H and ^{13}C NMR spectra were recorded on either a Varian XL 400, an IBM AC200, or a Bruker WM250 spectrometer in deuterated solvents. Chemical shifts were reported by reference to the residual protio solvents ($CHCl_3$, δ 7.24 ppm, $CDHCl_2$, δ 5.32 ppm, C_6HD_5, δ 7.15 ppm). Infrared spectroscopy was conducted in solution with a calcium fluoride cell on Mattson Polaris FTIR or Beckman 4525 IR spectrometers. GC experiments were conducted on a Hewlett-Packard 5750 chromatograph with thermal detectors. A 20 ft × $^1/_4$ in. column packed with 20% QF-1 on chromasorb W was used. Elemental analysis was performed by Galbraith, Inc., Knoxville, TN.

(a) Synthesis of (*S*)-2-Methyl-1-butylmesylate. A 1-L, three-necked, round-bottomed flask equipped with a magnetic stir bar, a 50-mL additional funnel, and nitrogen inlet tube was charged with 14.0 g of (*S*)-(−)-2-methyl-1-butanol (0.16 mol), 24.2 g of triethylamine (0.24 mol), and 500 mL of methylene chloride. The reaction flask was cooled in an ice/salt water bath. Methanesulfonyl chloride (15.4 mL, 0.20 mol) was added over 25 min. The reaction mixture was stirred for an additional 20 min and then washed sequentially with 2 × 100 mL of cold water, 2 × 100 mL of a saturated aqueous solution of sodium bicarbonate, and once with 100 mL of saturated aqueous sodium chloride solution. The organic layer was separated and dried over sodium sulfate, and solvent was removed to yield 27.9 g of a yellow liquid (>98%), which was characterized as (*S*)-2-methyl-1-butylmesylate on the basis of its ^1H NMR spectrum: ^1H NMR (C_6D_6, 25 °C) δ 0.68 ppm (t, J_{HH} = 6 Hz, CH_3CH_2), 0.69 (d, J_{HH} = 6 Hz, CH_3CH), 0.90 (m, one of CH_2CH_3), 1.20 (m, one of CH_2CH_3), 1.44 (m, *CH*), 2.90 (s, CH_3O), 3.71 (m, AB quartet, OCH_2). This material was used in the subsequent step without further purification.

(b) Synthesis of PPh_2R^* (R* = (*S*)-2-Methylbutyl). A 500-mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with 300 mL of tetrahydrofuran and 37.5 g of triphenylphosphine (0.14 mol). Lithium wire (2.0 g, 0.29 mol) was cut into 1-cm long pieces, added to the reaction solution, and allowed to react for 3 h at 25 °C. The reaction solution was filtered to remove small amounts of unreacted lithium wire. The red solution was heated to reflux, and 15.8 mL of *tert*-butylchloride was added very slowly. After an additional 15 min at reflux, 27.4 g of (*S*)-2-methyl-1-butylmesylate (0.16 mol) in 50 mL of tetrahydrofuran was added slowly. The color of the solution faded. The solution was heated at reflux for 1 h. After cooling to room temperature, 100 mL of distilled water was added, the organic phase was separated and dried over sodium sulfate, and solvents were removed leaving a yellow oil. Fractional vacuum distillation yielded the two fractions of 12.3 g of a colorless liquid at 70 °C/0.1 mmHg which was determined to be starting mesylate (46%) by ^1H NMR and 16.3 g of a colorless liquid (45%) at 114 °C/0.1 mmHg which was characterized as (*S*)-(2-methylbutyl)diphenylphosphine on the basis of its ^1H and ^{13}C NMR spectra: ^1H NMR (C_6D_6, 25 °C) δ 0.94 ppm (t, J_{HH} = 6 Hz, CH_3CH_2), 1.19 (d, J_{HH} = 6 Hz, CH_3CH), 1.37 (m, one of CH_2CH_3), 1.63 (m, one of CH_2CH_3 and *CH*), 1.98 (dd, J_{H-H} = 14 Hz, J_{HH} = 7 Hz, one of PCH_2), 2.25 (ddd, J_{HH} = 14 Hz, J_{HH} = 7 Hz, J_{HP} = 1 Hz, one of PCH_2), 7.24–7.61 (m, Ar*H*); ^{13}C NMR (C_6D_6, 25 °C) δ 11.6 ppm (q, J_{CH} = 124 Hz, CH_3CH_2), 21.2 (dq, J_{PC} = 10 Hz, J_{CH} = 124 Hz, CH_3CH), 21.3 (dt, J_{PC} = 9 Hz, J_{CH} = 128 Hz, CH_2CH_3), 32.6 (dd, J_{CP} = 13 Hz, J_{CH} = 128 Hz, *CH*), 36.8 (dt, J_{CP} = 14 Hz, J_{CH} = 123 Hz, PCH_2), 128–135 (aryl carbons), 139.9 (d, J_{CP} = 14 Hz, ipso carbon), 140.3 (d, J_{PC} = 14 Hz, ipso carbon).

(c) Synthesis of (R_{Fe},S_P)- and (S_{Fe},S_P)-$Cp(CO)(PPh_2R^*)FeCOCH_3$ (R* = (*S*)-2-Methylbutyl), 2-*RS* and 2-*SS*. A 500-mL Schlenk flask equipped with a magnetic stir bar and reflux condenser with nitrogen inlet tube was charged with 7.6 g of $Cp(CO)_2FeCH_3$ (39.5 mmol), 200 mL of tetrahydrofuran, and 10.3 g of (S)-(2-methylbutyl)diphenylphosphine (39.5 mmol). The reaction solution was heated at reflux for 3 days. After allowing the reaction mixture to cool to room temperature, solvent was removed by rotary evaporation. The red solid was purified by column chromatography on alumina with 90% hexane/10% ethyl acetate. A small yellow band eluted first and was identified as the starting material $Cp(CO)_2FeCH_3$ by comparison of the ^1H NMR spectra with the authentic sample. A second orange band was collected, and solvent was removed to yield 9.9 g of a yellow-orange solid (56%). This product was characterized as a 1:1 mixture of **2-*SS*** and **2-*RS***, the title compounds, by ^1H NMR data (see below for ^1H and ^{13}C NMR data for the pure diastereomers).

(d) Separation of the Diastereomers of (R_{Fe},S_P)- and (S_{Fe},S_P)-Cp-$(CO)(PPh_2R^*)FeCOCH_3$ (R* = (*S*)-2-Methylbutyl), 2-*RS* and 2-*SS*. The 1:1 diastereomeric mixture of **2-*SS*** and **2-*RS*** were separated by using flash chromatography on silica gel 60 (230–400 mesh ASTM, purchased from EM reagents) and eluting with hexane/ethyl acetate 9:1 on a 25 cm × 9 cm column. The two diastereomers were not completely separated. Samples of the broad orange band were collected in three fractions. The first and third fractions contain ca. 80% pure diastereomers, respectively. Rechromatography of these fractions yielded the **2-*RS*** isomer as a solid with ca. 98% purity and the **2-*SS*** isomer as an oil with ca. 97% purity. The second fraction contained a 50:50 mixture of diastereomers and was rechromatographed. The **2-*RS*** and **2-*SS*** iron–acyl complexes were characterized independently by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

(S_{Fe},S_P)-$Cp(CO)(PPh_2R^*)FeCOCH_3$ (R* = (*S*)-2-methylbutyl), 2-*SS*: ^1H NMR (C_6D_6, 25 °C) δ 0.47 ppm, (d, J_{HH} = 7 Hz, $CHCH_3$), 0.87 (t, J_{HH} = 7 Hz, CH_2CH_3), 1.08–1.42 (m, CH_2CH_3), 1.74 (m, *CH*), 2.80 (s, $COCH_3$), 1.98 and 2.84 (m, diastereomeric H's of P-CH_2), 4.07 (s, C_5H_5), 7.06–7.61 (m, Ar*H*); ^{13}C NMR (CD_2Cl_2, 25 °C) δ 11.2 ppm (q, J_{CH} = 132 Hz, CH_3CH_2), 20.6 ppm (q, J_{CH} = 131 Hz, CH_3CH), 31.6 (d, J_{CH} = 137 Hz, *CH*), 32.5 (dt, J_{CP} = 11 Hz, J_{CH} = 133 Hz, CH_2), 37.2 (dt, J_{CP} = 25 Hz, J_{CH} = 143 Hz, PCH_2), 51.9 (qd, J_{CH} = 145 Hz, J_{CP} = 5 Hz, $COCH_3$), 85.2 (dd, J_{CH} = 174 Hz, J_{CP} = 18 Hz, C_5H_5), 128.1–134.7 (all aryl carbons), 136.5 (d, J_{CP} = 40 Hz, ipso carbon), 140.5 (d, J_{CP} = 37 Hz, ipso carbon), 220.9 (d, J_{CP} = 30 Hz, *CO*), 275.1

(d, J_{CP} = 22 Hz, $C(O)CH_3$); IR (THF) ν_{CO} 1915 (s), 1605 (s) cm^{-1}; optical rotations (2×10^{-3} M in hexane, **2-*SS*:2-*RS*** = 99:1) $[\alpha]^{20}_{578}$ = −340°, $[\alpha]^{20}_{546}$ = −535°, $[\alpha]^{20}_{436}$ = −583°, $[\alpha]^{20}_{365}$ = +5960. elemental Anal. Calc for $C_{25}H_{29}FeO_2P$: C, 66.97; H, 6.53; F, 12.46. Found: C, 66.86; H, 6.57; Fe, 12.49.

(R_{Fe},S_P)-Cp(CO)(PPh_2R^*)FeCOCH$_3$ (R* = (*S*)-2-methylbutyl), 2-*RS*: ^{1}H NMR (C_6D_6, 25 °C) δ 0.59 ppm (t, J_{HH} = 6.5 Hz, CH_2CH_3), 0.68 (m, one H of CH_2CH_3), 0.78 (d, J_{HH} = 7 Hz, $CHCH_3$), 0.99 (m, one H of CH_2CH_3), 1.69 (m, *CH*), 2.20 (m, one H of PCH_2), 2.55 (m, one H of PCH_2), 2.75 (s, $COCH_3$), 4.10 (s, C_5H_5), 7.06–7.61 (m, Ar*H*); ^{13}C{^{1}H off-resonance decoupled} NMR (CD_2Cl_2, 25 °C) δ 11.2 ppm (q, CH_3CH_2), 21.2 (dq, J_{CP} = 18 Hz, CH_3CH), 31.0 (dt, J_{CP} = 19 Hz, CH_2CH_3), 31.2 (d, $CHCH_2$), 37.3 (dt, J_{CP} = 24 Hz, CH_2P), 51.9 (dq, J_{PC} = 5 Hz, CH_3CO), 85.1 (d, C_5H_5), 128.1–134.0 (aryl carbons), 137.0 (d, J_{CP} = 42 Hz, ipso carbon), 139.3 (d, J_{CP} = 37 Hz, ipso carbon), 220.9 (d, J_{CP} = 31 Hz, *CO*), 274.4 (d, J_{CP} = 22 Hz, $COCH_3$); IR (THF) ν_{CO} 1915 (s), 1605 (s) cm^{-1}; optical rotations (2×10^{-3} M in hexane, **2-*SS*:2-*RS*** = 4:96) $[\alpha]^{20}_{578}$ = +260°, $[\alpha]^{20}_{546}$ = +395°, $[\alpha]^{20}_{436}$ = +600°, $[\alpha]^{20}_{365}$ = −2085.

(e) Synthesis of (S_{Fe},S_P,$R_{C\alpha}$)-Cp(CO)(PPh_2R^*)FeCH(OCH_3)CH_3, 3-*SSR*. A 50-mL Schlenk tube equipped with a magnetic stir bar and rubber septum was charged with 0.76 g of (S_{Fe},S_P)-Cp(CO)(PPh_2R^*)-FeCOCH$_3$, **2-*SS*** (1.69 mmol), 10 mL of methylene chloride, and 0.25 g of trimethyloxonium tetrafloroborate (1.69 mmol). The reaction solution was stirred for 4 h at room temperature. During this time a 500-mL Schlenk flask equipped with a magnetic stir bar and rubber septum was charged with 250 mL of dry methanol. Sodium (0.15 g, 6.96 mmol) was added. After the sodium had reacted, the reaction solution was cooled to −78 °C. Sodium borohydride (0.13 g, 3.44 mmol) was added to this mixture and stirred rapidly for at least 1 h. The red methylene chloride solution was transferred by cannula into the methanol solution at −78 °C. The reaction mixture was allowed to warm to 0 °C. Saturated aqueous sodium bicarbonate solution (200 mL) which has been flushed with nitrogen was added. The orange-red iron complex was extracted with methylene chloride. The solution was dried, and solvent was removed to yield 0.75 g of a thick red oil (95%) which was characterized as the title compound on the basis of the following data: ^{1}H NMR (C_6D_6, 25 °C) δ 0.54 ppm (d, J_{HH} = 6 Hz, $CHCH_3$), 0.86 (t, J_{HH} = 7 Hz, CH_2CH_3), 1.28 (m, CH_2CH_3), 1.9–2.1 (m, obscured, $CHCH_2$), 1.97 (dd, J_{HH} = 7 Hz, J_{HP} = 1 Hz, $FeCHCH_3$), 4.50 (m, Fe*CH*), 4.35 (s, C_5H_5), 2.52, 2.16 (m, diastereotopic CH_2P), 3.35 (s, OCH_3), 7.0–7.9 ppm (m, Ar*H*); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 11.3 ppm (s, CH_3CH_2), 20.6 (s, CH_3CH), 31.4 (s, $FeCHCH_3$), 57.9 (s, OCH_3), 77.9 (d, J_{CP} = 22 Hz, $FeCHOCH_3$), 85.3 (d, J_{CP} = 19 Hz, C_5H_5), 38.2 (d, J_{CP} = 23 Hz, CH_2P), 33.0 (d, J_{CP} = 15 Hz, CH_2CH_3), 32.7 (d, J_{CP} = 18 Hz, PCH_2CHCH_3), 222.7 (d, J_{CP} = 33 Hz, *CO*), 128.0–134.8 (aryl carbons), 137.3 (d, J_{CP} = 38 Hz, ipso carbon), 139.8 (d, J_{CP} = 37 Hz, ipso carbon); IR (CH_2Cl_2) ν_{CO} 1895 cm^{-1}. elemental Anal. Calc for $C_{26}H_{33}FeO_2P$: C, 67.25; H, 7.16. Found: C, 67.06; H, 7.21.

(f) Synthesis of (R_{Fe},S_P,$S_{C\alpha}$)-Cp(CO)(PPh_2R^*)FeCH(OCH_3)CH_3, 3-*RSS*. **3-*RSS*** was prepared in a similar manner to the **3-*SSR***. The red oil was characterized on the basis of the following data: ^{1}H NMR (C_6D_6, 25 °C) δ 0.65–0.95 ppm (m, CH_2CH_3 and one H of CH_2CH_3), 0.89 (d, J_{HH} = 6 Hz, $CHCH_3$), 1.04 (m, one H of CH_2CH_3), 1.86 (m, $CHCH_3$), 1.95 (dd, J_{HH} = 6.4 Hz, J_{HP} = 1.6 Hz, $FeCHCH_3$), 3.38 (s, OCH_3), 4.35 (s, C_5H_5), 4.47 (m, Fe*CH*), 2.33 (m, PCH_2), 7.0–7.9 (m, Ar*H*); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 10.7 ppm (s, CH_3CH_2), 21.1 (s, CH_3CH), 28.6 (s, CH_3CFe), 31.8 (m, $CH_3CH_2CH(CH_3)CH_2P$), 37.7 (d, J_{CP} = 22 Hz, PCH_2), 57.6 (s, OCH_3), 77.7 (d, J_{CP} = 21 Hz, FeCH), 85.0 (d, J_{CP} = 16 Hz, C_5H_5), 127.5–134.2 (aryl carbons), 137.9 (d, J_{CP} = 38 Hz, ipso carbon), 139.9 (d, J_{CP} = 37 Hz, ipso carbon), 222.3 (d, J_{CP} = 32 Hz, *CO*); IR (CH_2Cl_2) ν_{CO} 1895 cm^{-1}.

(g) Synthesis of (S)-Ethyl 2-Methoxypropionate, (*S*)-$CH_3(OCH_3)CHCOOCH_2CH_3$. A 500-mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet was charged with 37.3 g of sodium dispersion (40% by weight in mineral oil, 0.65 mol) and 60 mL of tetrahydrofuran and was cooled to −78 °C. A −78 °C solution of 76.9 g of (*S*)-(−)-ethyl lactate (0.65 mol) in 60 mL of tetrahydrofuran was added dropwise to the sodium dispersion at −78 °C. The reaction mixture was allowed to warm. Once the sodium was consumed, the reaction solution was rapidly cooled to −78 °C again. A solution of 99.8 g of MeI (0.70 mol) in 50 mL of tetrahydrofuran was added to the above alkoxide solution, and the mixture was allowed to warm to room temperature. The THF solvent was evaporated after the reaction mixture was stirred at room temperature for 1 h. The residue was extracted with diethyl ether and water. The ether layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, vacuum distillation gave 30.4 g (40% yield) of (*S*)-$CH_3(OCH_3)CHCOOCH_2CH_3$ at 49–51 °C/20 mmHg [^{1}H NMR ($CDCl_3$, 25 °C) δ 3.85 ppm (q, J_{HH} = 6.9 Hz, $CH(OCH_3)$), 1.36 (d, J_{HH} = 6.9 Hz, $CHCH_3$), 3.36 (s, OCH_3), 4.19 (q, J_{HH} = 7.1 Hz, OCH_2CH_3), 1.26 (t, J_{HH} = 7.1 Hz, OCH_2CH_3)]. The enantiomeric excess (80%) of (*S*)-$CH_3(OCH_3)CHCOOCH_2CH_3$ was determined by an ^{1}H NMR shift experiment using the shift reagent (+)-Eu(hfc)$_3$ in $CDCl_3$ solution. (+)-Eu(hfc)$_3$, 34 mg, was added to a 0.5-mL $CDCl_3$ solution of 15 mg of ester. ^{1}H NMR of this sample showed the OCH_3 signals to be well-separated (*S*, 6.69 ppm; *R*, 6.97 ppm). By using procedures previously described,[17,18] (*S*)-methoxypropionyl chloride was obtained by hydrolysis of (*S*)-ethyl methoxypropionate to the acid in a solution of NaOH/EtOH/H_2O followed by conversion to the chloride using oxalyl chloride.

(h) Synthesis of (S_C)-Cp(CO)$_2$FeC(O)CH(OCH_3)CH_3, 5-*S*. A solution of 3.7 g (30.1 mmol) of (*S*)-$CH_3(OCH_3)CHCOCl$ (80% ee) in 20 mL of THF at −78 °C was added dropwise to a −78 °C solution of 6.1 g (28.8 mmol) of $Cp(CO)_2Fe^-K^+$ in 150 mL of THF. The solution was allowed to warm to room temperature overnight, and the solvent was removed by rotary evaporation. (S_C)-Cp(CO)$_2$FeC(O)CH(OCH_3)CH_3, **5-*S***, was extracted into methylene chloride. The methylene chloride solution was dried over anhydrous Na_2SO_4. The yellow solid obtained after evaporation of the solvent was purified by column chromatography on alumina with hexane/ethyl acetate (10:1) as eluent. Six grams (80% yield) of pure (S_C)-Cp(CO)$_2$FeC(O)CH(OCH_3)CH_3, **5-*S***, so obtained was characterized by ^{1}H and ^{13}C NMR, IR, and elemental analysis: ^{1}H NMR (C_6D_6, 25 °C) δ 4.19 ppm (s, C_5H_5), 3.33 (q, J_{HH} = 6.6 Hz, $-CH(OMe)CH_3$), 1.13 (d, J_{HH} = 6.6 Hz, $CHCH_3$), 3.12 (s, OCH_3); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 259.4 ppm (s, Fe*C*(O)−); 215.8 (s, Fe*C*O), 215.6 (s, Fe*C*O), 93.2 (s, FeC(O)*C*H(OMe), 86.8 (s, C_5H_5), 56.7 (s, OCH_3), 16.2 (s, $CHCH_3$); ^{13}C{^{1}H gated decoupled} NMR ($CDCl_3$, 25 °C) δ 263.5 ppm (s, Fe*C*(O)−), 214.7 (s, Fe*C*O), 214.4 (s, Fe*C*O), 93.6 (d, J_{CH} = 150.2 Hz, FeC(O)*C*H(OMe)), 86.7 (d, J_{CH} = 172.4 Hz, C_5H_5), 57.1 (q, J_{CH} = 142.4, OCH_3), 16.0 (q, J_{CH} = 129.3 Hz, $CHCH_3$); IR (hexane) ν_{CO} 2012 (s), 1975 (s), and 1643 (m) cm^{-1}. elemental Anal. Calc for $C_{11}H_{12}FeO_4$ (fw = 264.06): C, 50.03; H, 4.58; Found: C, 50.14; H, 4.57. The ee of 76% was determined by a ^{1}H NMR shift experiment. Fourteen miligrams of (+)-Eu(hfc)$_3$ was added to a 0.7-mL C_6D_6 solution of 10 mg of **5-*S*** and C_5H_5 signals for **5-*S*** and **5-*R*** were observed at 5.08 and 5.40 ppm, respectively. $[\alpha]^{23}_D$ = −9.3° (ee = 76%, [M] = 0.02 mol/L in hexane).

(i) ($R_{C\alpha}$)-Cp(CO)$_2$FeCH(OCH_3)CH_3, 6-*R*, via Decarbonylation of 5-*S*. A solution of 0.20 g of **5-*S*** in 120 mL of acetonitrile at 0 °C was irradiated with a sun lamp while being purged with nitrogen. After 50% conversion, as determined by IR spectroscopy, the reaction was stopped. The solution was passed through a short column of Celite, and the solvent was removed. ($R_{C\alpha}$)-Cp(CO)$_2$FeCH(OCH_3)CH_3, **6-*R***, was obtained in the first yellow band upon column chromatography at 25 °C with hexane/ethyl acetate 8:1 on alumina. The second band containing the starting material and some $Cp_2Fe_2(CO)_4$ dimer was dissolved in acetonitrile and was photolyzed under the same conditions. After two cycles, a total of 0.12 g ($R_{C\alpha}$)-Cp(CO)$_2$FeCH(OCH_3)CH_3, **6**-R, was obtained (69% yield) [^{1}H NMR (C_6D_6, 25 °C) 4.16 ppm (s, C_5H_5), 4.85 (q, J_{HH} = 6.2 Hz, $CH(OCH_3)CH_3$), 1.76 (d, J_{HH} = 6.2 Hz, $CHCH_3$), 3.16 (s, OCH_3)]. An enantiomer excess of 76% was determined by a ^{1}H NMR shift experiment. When 10 mg of (+)-Eu(hfc)$_3$ was added to a 0.7-mL C_6D_6 solution of 1 mg of **6**-R, OCH_3 signals for **6-*R*** and **6-*S*** were shifted to 3.44 and 3.49 ppm, respectively: $[\alpha]^{23}_D$ = −47.2° (ee = 76%, [M] = 0.04 mol/L in hexane).

(j) Synthesis of (S_{Fe},$R_{C\alpha}$)- and (R_{Fe},$R_{C\alpha}$)-Cp(CO)(PMe_3)FeCH(OCH_3)CH_3, 7-*SR* and 7-*RR*. While purging with nitrogen, a solution of 0.37 g of ($R_{C\alpha}$)-Cp(CO)$_2$Fe-CH(OCH_3)CH_3, **6-*R*** (ee 76%), and 1.0 mL of PMe_3 in 30 mL of C_6H_6 was irradiated with a sun lamp for 2 h at 0 °C. The reaction solution was filtered through a short column of Celite and the solvent was removed by evaporation. The ^{1}H NMR spectrum of the crude material showed the ratio of **7-*SR*:7-*RR*** to be 2:1. The crude material was separated by column chromatography at −78 °C with 10:1 hexane/ethyl acetate on a column of basic alumina (activity II-III deactivated by addition of 10% H_2O). Three fractions were collected. The second fraction (0.12 g) exhibited a ratio of **7-*SR*:7-*RR*** = 64.5:35.5 ("enantiomeric excess" at Fe = 29% × 76% = 22% excess S_{Fe}), and the third fraction (0.07 g) (53% total yield) showed a ratio of **7-*SR*:7-*RR*** = 72.5:27.5 (enantiomeric excess at Fe = 45% × 76% = 34% excess S_{Fe}). ^{1}H NMR spectra of **7-*SR*** and **7-*RR*** are the same as those of racemic **7-*SR*,7-*RS*** and **7-*SS*,7-*RR*** (see (p) below).

(k) Synthesis of (S_{Fe},$R_{C\alpha}$)- and (R_{Fe},$R_{C\alpha}$)-Cp(CO)(PEt_3)FeCH(OCH_3)CH_3, 8-*SR* and 8-*RR*. **6-*R***, 0.37 g (1.57 mmol), and 1.5 mL of PEt_3 (10.2 mmol) in 30 mL of C_6H_6 were irradiated with a sun lamp for 2 h at 0 °C with an N_2 purge. The reaction solution was filtered through a short column of Celite, and the solvent was removed. The ^{1}H NMR spectrum of the crude material showed the ratio of **8-*SR*:8-*RR*** to be 2.8:1. The crude materials were separated by low temperature column chromatography at −78 °C with 10:1 hexane/ethyl acetate on a column of basic alumina of activity of II-III deactivated by addition of 10% H_2O.

Two fractions were collected. The first fraction contained 0.10 g with a ratio of **8-*SR*:8-*RR*** = 79:21 (enantiomer excess at Fe = 58% × 76% = 44% excess S_{Fe}). The second fraction contained 0.06 g (35% total yield) with a ratio of **8-*SR*:8-*RR*** = 64:36 (enantiomer excess at Fe = 28% × 76% = 21% excess S_{Fe}). ^1H NMR spectra of **8-*SR*** and **8-*RR*** are the same as **8-*SR*,8-*RS*** and **8-*RR*,8-*SS*** (see (q) below).

(l) Synthesis of $Cp(CO)(PR_3)FeC(O)CH_3$, 11, R = Me; 12, R = Et. $Cp(CO)_2FeCH_3$, 4–6 g, and 1.2–2 equiv of PR_3 in a minimum amount of THF solvent (5–20 mL) were heated at reflux overnight. The progress of the reaction was monitored by IR spectroscopy in the ν_{CO} stretching region. After the reaction was completed, the solvent was evaporated, and acyl complexes were separated by column chromatography on alumina. The first yellow band was eluted with hexane and contained unreacted starting material. The second band was eluted with diethyl ether. From the second fractions, red oils of **11** and **12** were obtained in 70–90% yields. Compounds **11** and **12** were characterized by ^1H, ^{13}C NMR, and IR spectroscopy and elemental analysis.

11: ^1H NMR (C_6D_6, 25 °C) δ 4.13 ppm (d, J_{HP} = 1.5 Hz, C_5H_5), 2.72 (s, $C(O)CH_3$), 0.93 (d, J_{HP} = 9.7 Hz, $P(CH_3)$); ^{13}C (C_6D_6, 25 °C) δ 83.4 ppm (s, C_5H_5), 51.9 (s, CH_3), 270.9 (d, J_{CP} = 26.9 Hz, $FeC(O)CH_3$), 18.8 (d, J_{CP} = 27.3 Hz, $P(CH_3)_3$), 220.0 (d, J_{CP} = 34.2 Hz, Fe(CO)); (CH_2Cl_2) ν_{CO} 1909, 1588 cm^{-1}. elemental Anal. Calc for $C_{11}H_{17}O_2FeP$: C, 49.28; H, 6.39. Found: C, 49.18; H, 6.42.

12: ^1H NMR (C_6D_6, 25 °C) δ 4.22 ppm (d, J_{HP} = 1.0 Hz, C_5H_5), 2.77 (s, $C(O)CH_3$), 1.2–1.6 and 0.8–0.68 (m, $P(CH_2CH_3)_3$); ^{13}C (C_6D_6, 25 °C) δ 83.3 (s, C_5H_5), 52.1 (s, CH_3), 270.5 (d, J_{CP} = 24.4 Hz, $FeC(O)CH_3$), 20.7 (d, J_{CP} = 24.7 Hz, $P(CH_2CH_3)_3$), 8.0 (s, $P(CH_2CH_3)$), 221.1 (d, J_{CP} = 31.7 Hz, Fe(CO)); IR (CH_2Cl_2) ν_{CO} 1910, 1590 cm^{-1}. Calc for $C_{13}H_{23}O_2FeP$; C, 54.21; H, 7.48. Found: C, 54.58; H, 7.75.

(m) Resolution of (S_{Fe})- and (R_{Fe})-$Cp(CO)(PMe_3)FeC(O)CH_3$, 11-*S* and 11-*R*. Racemic **11**, 0.49 g, and 0.52 g of (*S*)-(+)-10-camophorsulfonic acid were dissolved in 15 mL of methylene chloride at 25 °C and stirred for 10 min. Diethyl ether (45 mL) was added to this solution. If any solid formed, additional methylene chloride was added to dissolve this material. The saturated solution of the diastereomeric hydroxycarbene salts **19-*SS*** and **19-*RS*** was kept in the freezer (−25 °C) overnight. The crystalline solids formed were separated from the solution by simple filtration. The solid was dissolved in 30 mL of CH_2Cl_2/ether and neutralized with a 20% aqueous K_2CO_3 solution. The organic layer was dried over anhydrous K_2CO_3, and solvent was evaporated. The yellow oil was purified on a short alumina column and produced 0.23 g of **11-*S*** with ee = 86% (yield = 47%). Neutralization of the solution and purification by column chromatography produced 0.20 g of **11-*R*** with ee = 91% (yield = 42%).

A second resolution cycle carried out on enriched acyl complexes **11-*S*** and **11-*R*** gave higher enantiomeric purities of acyl complexes. Complex **11-*S*** (0.41 g, ee = 88%) and 0.47 g of (*S*)-(+)-10-camphorsulfonic acid were dissolved in 23 mL of methylene chloride and stirred at 25 °C for 10 min. Diethyl ether (64 mL) was added to the above solution. After stirring for 5 min, 12.5 mL of methylene chloride was added to dissolve the precipitated solid. The saturated solution was cooled at −25 °C overnight. By using similar separation, neutralization, and purification procedures, 0.33 g (80% yield) of **11-*S*** (ee > 99%) was obtained from the solid, and 0.08 g (20% yield) of **11-*S*** (ee = 19%) was collected from the solution.

Complex **11-*R*** (0.39 g, ee = 86%) and 0.44 g of (*R*)-(−)-10-camphorsulfonic acid were dissolved in 15 mL of methylene chloride and were stirred at 25 °C for 10 min, 45 mL of diethyl ether was added to the above solution, and the solution was cooled at −25 °C overnight. By similar separation, neutralization, and purification procedures, 0.31 g (80% yield) of **11-*R*** (ee = 96%) was obtained from the solid part and 0.03 g (9% yield) of **11-*S*** (ee = 41%) was collected from solution: $[\alpha]^{23}_{436}$ = −500° for **11-*S*** (**11-*S*:11-*R*** = >99:1, [M] = 4.8 × 10^{-4} M in hexane) and $[\alpha]^{23}_{436}$ = +493° for **11-*R*** (**11-*S*:11-*R*** = 2:98, [M] = 4.5 × 10^{-4} M in hexane).

(n) Resolution of (S_{Fe})- and (R_{Fe})-$Cp(CO)(PEt_3)FeC(O)CH_3$, 12-*S* and 12-*R*. Racemic **12** (1.0 g) and (*S*)-(+)-10-camphorsulfonic acid (1.08 g) were dissolved in 10 mL of methylene chloride at 25 °C and stirred for 10 min. Diethyl ether (20 mL) was added to this solution. After stirring at 25 °C for 10 min, yellow solid precipitated, and 8 mL of methylene chloride was added to redissolve this material. The saturated solution of the diastereomeric hydroxycarbene salts **20-*SS*** and **20-*RS*** was kept in the freezer (−25 °C) overnight, and crystalline solids were formed. The crystalline solids were separated from the solution by simple filtration. The solid was dissolved in 30 mL of CH_2Cl_2/ether and neutralized with a 20% aqueous K_2CO_3 solution. The organic layer was dried over anhydrous K_2CO_3, and the solvent was evaporated. The yellow oil was purified by using a short alumina column and 0.29 g of **12-*S*** was obtained (ee = 95%, 29% yield). Neutralization of the solution and further purification by column chromatography produced 0.60 g of **12-*R*** (ee = 48%, 60% yield).

Complex **12-*R*** (0.59 g, ee = 48%) and (*R*)-(−)-10-camphorsulfonic acid (0.59 g) were dissolved in 9 mL of methylene chloride and stirred at 25 °C for 10 min. Diethyl ether (18 mL) was added to the above solution. After stirring at room temperature for 10 min, yellow solids precipitated and 8 mL of methylene chloride was added to redissolve this material. By using a similar separation, neutralization, and purification procedure, 0.37 g (63% yield) of **12-*R*** (ee = 96%) was obtained from the solid part, and 0.19 g (32% yield) of **12-*S*** (ee = 37%) was collected from solution: $[\alpha]^{23}_{436}$ = −529° for **12-*S*** (**12-*S*:12-*R*** = 97.5:2.5, [M] = 1.0 × 10^{-3} M in hexane) and $[\alpha]^{23}_{436}$ = +545° for **12-*R*** (**12-*S*:12-*R*** = 2:98, [M] = 4.7 × 10^{-4} M in hexane).

(o) ^1H NMR Shift Experiments on Complexes $Cp(CO)(L)FeC(O)CH_3$, 11, L = PMe_3; 12, L = PEt_3; and 13, L = PPh_3. Thirteen miligrams of racemic acyl complex **11** (or enantiomerically enriched or enantiomerically pure samples) were dissolved in 0.5 mL of C_6D_6, and the ^1H NMR spectrum was recorded at room temperature (+)-$Eu(hfc)_3$ was added to the acyl complex solution, and ^1H NMR spectra were recorded. Broad Cp and CH_3 resonances were observed. These signals shifted downfield upon the addition of further quantities of (+)-$Eu(hfc)_3$. Clear separation of sharp signals for the two Cp and two CH_3 groups corresponding to the two enantiomers was achieved upon addition of a total of 34 g of (+)-$Eu(hfc)_3$ ($Eu(hfc)_3$/acyl = 0.6 mol ratio). Chemical shifts are listed in Table I, and these assignments were confirmed by shift experiments on the enantiomerically pure acyl complexes. In cases of more than 99% enantiomerically pure acyl complex, traces of the racemic acyl complex were added to verify that signals for the two enantiomers were truly separated by the shift experiment. Table I also lists the chemical shifts of C_5H_5 and $C(O)CH_3$ for **12** and **13** when 52 mg of (+)-$Eu(hfc)_3$ was added to a 0.7-mL C_6D_6 solution of 13 mg of racemic **12** and when 36 mg of (+)-$Eu(hfc)_3$ was added to a 0.5-mL C_6D_6 solution of 21 mg of racemic **13**.

(p) Synthesis of Ether Complexes $Cp(CO)(PMe_3)FeCH(OCH_3)CH_3$, 7-*SS*,7-*RR* and 7-*RS*,7-*SR*, from Acyl Complex $Cp(CO)(PMe_3)FeC(O)CH_3$, 11. Described below is a synthetic procedure for preparation of racemic diastereomers $Cp(CO)(PMe_3)FeCH(OCH_3)CH_3$, 7-*SS*,7-*RR* and 7-*RS*,7-*SR*, from racemic $Cp(CO)(PMe_3)FeC(O)CH_3$, **11**. Enantiomerically pure $(S_{Fe},S_{C\alpha})$- and $(S_{Fe},R_{C\alpha})$-$Cp(CO)(PMe_3)FeCH(OCH_3)CH_3$, 7-*SS* and 7-*SR*, can be prepared by using a similar procedure from enantiomerically pure $Cp(CO)(PMe_3)FeC(O)CH_3$, **11-*S***.

A 50-mL Schlenk tube was charged with 1.64 g (6.12 mmol) of $Cp(CO)(PMe_3)FeC(O)CH_3$, **11**, 20 mL of methylene chloride, and 1.4 mL of MeOTf (12 mmol). The solution was stirred for 1 h at 25 °C. Complete formation of methoxycarbene salt, **14**, was verified by IR spectroscopy (ν_{CO} = 1984 cm^{-1}). A 500-mL Schlenk flask was charged with 80 mL of dry methanol, and 1.2 g (52 mmol) of sodium was added. After the sodium had reacted, the solution was cooled to −78 °C. Sodium borohydride (0.95 g, 34 mmol) was added to this mixture and stirred rapidly for at least 1 h. The yellow methoxycarbene solution in methylene chloride was transferred by cannula into the methanol solution at −78 °C. The mixture was allowed to warm to 25 °C, and the orange-red iron complex was extracted into 200 mL of methylene chloride. The organic layer was dried over anhydrous Na_2SO_4, and solvent was removed to yield 1.61 g of a thick red oil (93% yield) containing the two diastereomers 7-*RS*,7-*SR* and 7-*SS*,7-*RR* in a 2.8:1.0 ratio. They were not separated.

7-*RS*,7-*SR*: ^1H NMR (C_6D_6, 25 °C) δ 4.30 ppm (d, J_{HP} = 1.1 Hz, C_5H_5), 3.98 (d of q, J_{HH} = 6.5 Hz, J_{HP} = 10.2 Hz, $FeCH(OCH_3)$), 1.84 (d of d, J_{HH} = 6.3 Hz, J_{HP} = 1.1 Hz, $FeCH(OMe)CH_3$), 3.22 (s, OCH_3), 0.97 (d, J_{HP} = 9.2 Hz, $P(CH_3)$); ^{13}C NMR (C_6D_6, 25 °C) δ 221.4 ppm (d, J_{CP} = 33.9 Hz, Fe(CO)), 83.6 (s, C_5H_5), 78.5 (d, J_{CP} = 23.8 Hz, $FeCH(OMe)CH_3$), 57.6 (s, OCH_3), 29.7 (d, J_{CP} = 2 Hz, $FeCH(OMe)CH_3$), 19.6 (d, J_{CP} = 26.6 Hz, $P(CH_3)$); IR (CH_2Cl_2) ν_{CO} = 1895 cm^{-1}.

7-*SS*,7-*RR*: ^1H NMR (C_6D_6, 25 °C) δ 4.18 ppm (d, J_{HP} = 1.2 Hz, C_5H_5), 4.38 (quintet, J_{HH} = 6.0 Hz, J_{HP} = 6.0 Hz, $FeCH(OMe)CH_3$), 1.77 (d, J_{HH} = 6.3 Hz, $FeCH(OMe)CH_3$), 3.37 (s, OCH_3), 0.88 (d, J_{HP} = 9.0 Hz, $P(CH_3)$); ^{13}C NMR (C_6D_6, 25 °C) δ 222.6 ppm (d, J_{CP} = 35.3 Hz, Fe(CO)), 83.6 (s, C_5H_5), 79.4 (d, J_{CP} = 21.2 Hz, $FeCH(OMe)CH_3$), 57.7 (s, OCH_3), 30.9 (d, J_{CP} = 2.0 Hz, $FeCH(OMe)CH_3$), 19.0 (d, J_{CP} = 27.1 Hz, $P(CH_3)_3$). IR (CH_2Cl_2) ν_{CO} = 1895 cm^{-1}. Elemental Anal. (2.8:1.0 mixture of 7-*Rs*,7-*SR* and 7-*SS*,7-*RR*) Calc for $C_{12}H_{21}O_2PFe$ (mw = 284.11): C, 50.73; H, 7.45. Found: C, 50.96; H, 7.25.

(q) Synthesis of Ether Complexes $Cp(CO)(PEt_3)FeCH(OCH_3)CH_3$, 8-*SS*,8-*RR* and 8-*RS*,-8-*SR*, from Acyl Complex $Cp(CO)(PEt_3)FeC(O)CH_3$, 12. Described below is a synthetic procedure for preparation of racemic diastereomers $Cp(CO)(PEt_3)FeCH(OCH_3)CH_3$, 8-*SS*,8-*RR* and 8-*RS*,8-*SR*, from racemic $Cp(CO)(PEt_3)FeC(O)CH_3$, **12**. Enantiomerically pure $(S_{Fe},S_{C\alpha})$- and $(S_{Fe},R_{C\alpha})$-$Cp(CO)(PEt_3)FeCH(OCH_3)CH_3$, 8-*SS* and 8-*SR*, can be prepared by the similar procedure

from enantiomerically pure $Cp(CO)(PEt_3)FeC(O)CH_3$, **12-*S***.

In a procedure similar to the synthesis of **7-*RS*,7-*SR*** and **7-*SS*,7-*RR***, acyl complex **12** was converted into the methoxycarbene salt (ν_{CO} = 1983 cm^{-1}) which was quenched into a methanol solution of $NaOMe/NaBH_4$. The diastereomers **8-*SS*,8-*RR*** and **8-*RS*,8-*SR*** were obtained as a red oil (90% yield) in a 4.6:1.0 ratio. They were not separated.

8-*RS*,8-*SR*: ^1H NMR (C_6D_6, 25 °C) δ 4.38 ppm (d, J_{HP} = 1.2 Hz, C_5H_5), 3.97 (d of q, J_{HH} = 6.4 Hz, J_{HP} = 10.0 Hz, $FeCH(OCH_3)$), 1.84 (d of d, J_{HH} = 6.3 Hz, J_{HP} = 1.4 Hz, $FeCH(OMe)CH_3$), 3.24 (s, OCH_3), 1.2–1.4 and 0.7–1.0 (m, $P(CH_2CH_3)$); ^{13}C NMR (C_6D_6, 25 °C) δ 222.6 ppm (d, J_{CP} = 31.8 Hz, Fe(*C*O)), 83.5 (s, C_5H_5), 77.3 (d, J_{CP} = 22.3 Hz, $FeCH(OMe)CH_3$), 57.5 (s, OCH_3), 29.3 (s, $FeCH(OMe)CH_3$), 21.0 (d, J_{CP} = 23.1 Hz, $P(CH_2CH_3)$), 7.9 (d, J_{HP} = 2.7 Hz, $P(CH_2CH_3)_3$); IR (C_6H_6) ν_{CO} = 1901 cm^{-1}.

8-*SS*,8-*RR*: ^1H NMR (C_6D_6, 25 °C) δ 4.26 ppm (d, J_{HP} = 1.0 Hz, C_5H_5), 4.49 (quintet, J_{HH} = 6.2 Hz, J_{HP} = 6.2 Hz, $FeCH(OMe)CH_3$), 1.79 (d, J_{HH} = 6.2 Hz, $FeCH(OMe)CH_3$), 3.38 (s, OCH_3), 0.7–0.9 and 1.1–1.4 (m, $P(CH_2CH_3)$); ^{13}C NMR (C_6D_6, 25 °C) δ 223.7 ppm (d, J_{CP} = 32.7 Hz, Fe(*C*O)), 83.2 (s, C_5H_5), 78.5 (d, J_{CP} = 20.1 Hz, $FeCH(OMe)CH_3$), 57.6 (s, OCH_3), 30.7 (s, $FeCH(OMe)CH_3$), 20.3 (d, J_{CP} = 23.0 Hz, $P(CH_2CH_3)$), 8.2 (d, J_{CP} = 2.8 Hz, $P(CH_2CH_3)_3$); IR (C_6H_6) ν_{CO} = 1901 cm^{-1}. Elemental Anal. (4.6:1.0 mixture of **8-*RS*,8-*SR*** and **8-*SS*,8-*RR***) Calc for $C_{15}H_{27}O_2PFe$ (mw = 326.19): C, 55.23; H, 8.34. Found: C, 55.12; H, 8.30.

(r) Synthesis of Ether Complexes (S_{Fe},$S_{C\alpha}$)- and (S_{Fe},$R_{C\alpha}$)-Cp(CO)(PPh_3)FeCH(OCH_3)CH_3, 17-*SS* and 17-*SR*, from Acyl Complex (S_{Fe})-Cp(CO)(PPh_3)FeC(O)CH_3, 13-*S*. By using a procedure similar to that used for the syntheses of **8-*SS*,8-*RR*** and **8-*RS*,8-*SR***, 0.95 g of **13-*S*** (ee > 99%, $[\alpha]^{23}_{436}$ = −1100°, [M] = 4.7 × 10^{-4} mol/L in hexane) in 50 mL of methylene chloride was treated with 0.5 mL of MeOTf. Methoxycarbene salt was completely formed after stirring for 1 h at 25 °C. The carbene solution was quenched into a methanol solution of NaOMe and $NaBH_4$ (0.43 g of sodium in 100 mL of MeOH and 0.36 g of $NaBH_4$) at −78 °C. By using the standard workup procedure, 0.94 g of red solid (96% yield) was obtained. The two diastereomers **17-*SR*** and **17-*SS*** were formed in a 1.0:1.2 ratio and were not separated.

17-*SR*: ^1H NMR (C_6D_6, 25 °C) δ 4.38 ppm (d, J_{HP} = 1.2 Hz, C_5H_5), 3.97 (d of q, J_{HH} = 6.4 Hz, J_{HP} = 10.0 Hz, $FeCH(OCH_3)$), 1.84 (d of d, J_{HH} = 6.3 Hz, J_{HP} = 1.4 Hz, $FeCH(OMe)CH_3$), 3.24 (s, OCH_3).

17-*SS*: ^1H NMR (C_6D_6, 25 °C) δ 4.26 ppm (d, J_{HP} = 1.0 Hz, C_5H_5), 4.49 (quintet, J_{HH} = 6.2 Hz, J_{HP} = 6.2 Hz, $FeCH(OMe)CH_3$), 1.79 (d, J_{HH} = 6.2 Hz, $FeCH(OMe)CH_3$), 3.38 (s, OCH_3).

Additional NMR data and elemental analyses have been previously reported.[2a]

(s) Generation and Spectral Characterization of Ethylidene Complexes Cp(CO)(L)Fe=$CHCH_3^+$: 9, L = PMe_3; 10, L = PEt_3; 1-*SS*, L = PPh_2R^*, and 18, L = PPh_3. Method I. A standard 5-mm (or 10-mm) NMR tube adapted for alternative high vacuum inert atmosphere use was used for generation and spectral observation of the ethylidene complexes. For example, 27 mg of the mixture of diastereomeric α-ether complexes **8-*SS*,*RR*** and **8-*SR*,*RS*** was placed in the NMR tube and dissolved in 0.5 mL of CD_2Cl_2. The solution was degassed by three freeze–pump–thaw cycles. Addition of 20 μL of trimethylsilyl triflate (TMS-OTf) (1.2 equiv) at −78 °C followed by mixing, resulted in a rapid formation of the red solution of the ethylidene complex **10**. The NMR tube was then frozen, evacuated, and sealed at liquid nitrogen temperature. The tube was warmed to −78 °C prior to introduction into the precooled NMR sample probe. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy as listed below.

Method II. The diastereomic mixture of α-ether complexes **7-*SS*,7-*RR*** and **7-*SR*,7-*RS*** (0.12 g) in 5 mL of methylene chloride was cooled to −78 °C, and 0.23 mL of $HBF_4{\cdot}(OEt)_2$ in 10 mL of diethyl ether was added to generate a deep red solution. Hexane (50 mL) was added to precipitate the carbene salt. The red solid was washed at −30 °C three times with hexane (25 mL each) and dried under vacuum. The salt was dissolved in the CD_2Cl_2 at −30 °C and transferred into the NMR tube. The NMR sample was stored at −78 °C, but ^1H NMR spectra of **9** could be recorded at 25 °C.

(t) NMR Observation of $C_5H_5(CO)(PMe_3)Fe{=}CHCH_3^+$, 9. ^1H NMR (CD_2Cl_2, 25 °C generation using method II) δ 5.37 ppm (d, J_{HP} = 1.3 Hz, C_5H_5), 17.26 (d of q, J_{HH} = 7.5 Hz, J_{HP} = 1.4 Hz, Fe=$CHCH_3$), 3.31 (d, J_{HH} = 7.6 Hz, $CHCH_3$), 1.59 (d, J_{HP} = 11.1 Hz, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2, −80 °C by method I) δ 91.6 ppm (s, C_5H_5), 369.7 (broad singlet, Fe=*C*HCH$_3$), 51.8 (s, $CHCH_3$), 213.3 (d, J_{CP} = 31.7 Hz, Fe(*C*O)), 19.6 (d, J_{CP} = 36.1 Hz, $P(CH_3)_3$). Variable temperature ^1H NMR (CD_2Cl_2, generation using method I): Signals were observed at δ 17.46 ppm (major isomer, anticlinal) and 15.92 ppm (minor isomer, synclinal) in a 4.6:1.0 ratio at −114 °C. The ΔG_{AS} = −0.5 kcal/mol was obtained from the equilibrium constant. These signals broadened when the sample is warmed. At −70 °C, the two signals coalesced into a single peak. A quartet was observed at −20 °C with J_{HH} = 7.7 Hz. Line shape analysis gives k_{AS} = 17.4 s^{-1} at −92 °C which corresponds to $\Delta G^{\ddagger}_{AS}$ = 9.3 kcal/mol. $\Delta G^{\ddagger}_{SA}$ = 8.8 kcal/mol was obtained by $\Delta G^{\ddagger}_{AS} - \Delta G_{AS}$ = 9.3 − 0.5 = 8.8 kcal/mol.

(u) NMR Observation of $C_5H_5(CO)(PEt_3)Fe{=}CHCH_3^+$, 10. ^1H NMR (CD_2Cl_2, 25 °C, method I) δ 5.41 ppm (d, J_{HP} = 1.1 Hz, C_5H_5), 16.99 (q, J_{HH} = 7.5 Hz, Fe=$CHCH_3$), 3.39 (d, J_{HH} = 7.5 Hz, Fe=$CHCH_3$), 1.8–2.2 (m, $P(CH_2CH_3)_3$); ^{13}C NMR (CD_2Cl_2, −80 °C method I) δ 91.6 ppm (s, C_5H_5), 366.2 (broad singlet, Fe=*C*HCH$_3$), 51.8 (s, Fe=$CHCH_3$), 213.8 (d, J_{CP} = 30.2 Hz, Fe(*C*O)), 18.7 (d, J_{CP} = 31.3 Hz, $P(CH_2CH_3)_3$), 6.7 (s, $P(CH_2CH_3)_3$). Variable temperature ^1H NMR (CD_2Cl_2, method I): Two signals were observed at 17.65 ppm (major isomer, anticlinal) and 15.69 ppm (minor isomer, synclinal) in a 10.9:1.0 ratio at −114 °C. The ΔG_{AS} = −0.8 kcal/mol was obtained from the equilibrium constants. Those two signals broadened when the sample was warmed. At −50 °C, these two signals coalesced into a single peak. A quartet was observed at 0 °C with J_{HH} = 7.3 Hz. Line shape analysis gives k_{AS} = 10.7 s^{-1} at −92 °C which corresponds to $\Delta G^{\ddagger}_{AS}$ = 9.6 kcal/mol. $\Delta G^{\ddagger}_{SA}$ = 8.8 kcal/mol was obtained by $\Delta G^{\ddagger}_{AS} - \Delta G_{AS}$ = 9.6 − 0.8 = 8.8 kcal/mol.

(v) NMR Observation of (S_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$, 1-*SS*. ^1H NMR (CD_2Cl_2, −30 °C generation using method I) δ 5.13 ppm (s, C_5H_5), 17.42 (broad quartet, J_{HH} = 7.0 Hz, Fe=$CHCH_3$), 3.32 (d, J_{HH} = 7.0 Hz, $CHCH_3$), 0.20–2.60 (m, alkyl protons on phosphine ligand), 7.20–7.83 (broad, phenyl region). Variable temperature ^1H NMR (CD_2Cl_2, generation using method I): Signals were observed at δ 17.9 ppm (major isomer, anticlinal) and 16.4 ppm (minor isomer, synclinal) in a 2.4:1.0 ratio at −100 °C. The ΔG_{AS} = −0.3 kcal/mol was obtained from the equilibrium constant. These signals broadened when the sample is warmed. At −80 °C, the two signals coalesced into a single peak. A quartet was observed at −30 °C with J_{HH} = 7.0 Hz. Line shape analysis gives k_{AS} = 128.3 s^{-1} at −92 °C which corresponds to $\Delta G^{\ddagger}_{AS}$ = 8.6 kcal/mol. $\Delta G^{\ddagger}_{SA}$ = 8.3 kcal/mol was obtained by $\Delta G^{\ddagger}_{AS} - \Delta G_{AS}$ = 8.6 − 0.3 = 8.3 kcal/mol.

(w) NMR Observation of $C_5H_5(CO)(PPh_3)Fe{=}CHCH_3^+$, 18. Variable temperature ^1H NMR (CD_2Cl_2, method I, 0.5 mL of SO_2ClF was added to lower the freezing point): Two signals were observed at 18.24 ppm (major isomer, anticlinal) and 17.05 ppm (minor isomer, synclinal) in a 5.7:1.0 ratio at −126 °C. The ΔG_{AS} = −0.5 kcal/mol was obtained from the equilibrium constant. Those two signals broaden when the sample was warmed. At −100 °C, the two signals coalesced into a single peak at 17.92 ppm. Line shape analysis gives k_{AS} = 65.3 s^{-1} at −114 °C which corresponds to $\Delta G^{\ddagger}_{AS}$ = 7.8 kcal/mol. $\Delta G^{\ddagger}_{SA}$ = 7.3 kcal/mol was obtained by $\Delta G^{\ddagger}_{AS} - \Delta G_{AS}$ = 7.8 − 0.5 = 7.3 kcal/mol. Additional NMR data have been previously reported.[2a]

(x) General Procedure for Transfer of Ethylidene to Olefins To Form Cyclopropanes. Method I. TMS-OTf (0.21 mL, 1.09 mmol) was added to a 10-mL methylene chloride solution at −78 °C containing 0.32 g (0.98 mmol) of **8-*SR*:8-*SS*** (derived from **12-*S***, ee = 77%), NEt_3 (10 μL, 0.07 mmol), and 1.0 mL of vinyl acetate (10.8 mmol). The reaction mixture was stirred at −78 °C for 30 min, then allowed to warm to room temperature and stirred for 3 h. The reaction mixture was quenched by addition of 50 mL of saturated aqueous sodium bicarbonate solution, and organic products were extracted into 30 mL of isopentane. The isopentane layer was dried over anhydrous K_2CO_3, filtered, and concentrated by simple distillation. The *trans*- and *cis*-1-acetoxy-2-methylcyclopropanes were isolated by preparative GC, and the yield (27%) was determined by using an internal standard (nonane). Enantiomer excesses were determined by ^1H NMR shift experiments. Results obtained by using this method are listed as entries 1–9 in Table III.

Method II. Similar to the generation of carbene complexes by method II (see (s) above), 0.17 mL of $HBF_4{\cdot}O(Me)_2$ in 5 mL of diethyl ether was added to 5 mL of methylene chloride solution at −30 °C containing 0.12 g of **8-*SR*:8-*SS*** (79:21, derived from $Cp(CO)_2FeC^*H(OCH_3)CH_3$, ee = 76%). The carbene salt was precipitated by addition of 50 mL of hexane and washed three times with 10-mL portions of hexane. The purified carbene salt and 0.5 mL of vinyl acetate were dissolved in 5 mL of methylene chloride and warmed to room temperature. Similar to method I, *trans*- and *cis*-1-acetoxy-2-methylcyclopropanes (1.9:1.0) were isolated by preparative GC, and the yield (20%) was determined by using an internal standard (nonane). Enantiomer excesses were determined by ^1H NMR shift experiments.

(y) *trans*- and *cis*-1-Acetoxy-2-methylcyclopropanes. *trans*-1-Acetoxy-2-methylcyclopropane: ^1H NMR ($CDCl_3$, 25 °C) δ 2.09 ppm (s, $COCH_3$), 3.83 (d of d of d, J_{HH} = 6.7 Hz, J_{HH} = 3.2 Hz, J_{HH} = 2.1 Hz, *H*), 1.07–1.12 ppm (m, *H*), 1.12 ppm (d, J_{HH} = 5.4 Hz, CH_3), 0.87–0.93 ppm (m, *H*), 0.57 (q, J_{HH} = 6.4 Hz, *H*).

cis-1-Acetoxy-2-methylcyclopropane: ^1H NMR (C_6D_6, 25 °C) δ 1.63 ppm (s, $OC(O)CH_3$), 4.01 (dt, J_{HH} = 3.4 Hz, J_{HH} = 6.9 Hz, $CH(OC(O)CH_3)$), 0.15 (d of t, J_{HH} = 3.4 Hz, J_{HH} = 6.0 Hz, 1 *H*), 0.5–0.7 (m,

2 H), 0.97 (d, J_{HH} = 6.1 Hz, CHCH_3).

(z) *trans*- and *cis*-1-Acetoxy-1,2-dimethylcyclopropanes. *cis*-1-Acetoxy-1,2-dimethylcyclopropane: ^{1}H NMR ($CDCl_3$, 25 °C) δ 0.20 ppm (m, 1 H), 0.90-1.10 (m, 2 H), 1.05 (d, CH_3CH), 1.43 (s, CH_3COC(O)-), 1.95 (s, COCH_3).

trans-1-Acetoxy-1,2-dimethylcyclopropane: ^{1}H NMR (C_6D_6, 25 °C) δ 0.36 ppm (m, 1 H), 0.53 (m, 1 H), 0.65 (m, 1 H), 1.05 (d, J_{HH} = 7.0 Hz, CH_3CH), 1.43 (s, 3 H, CHCOC(O)-), 1.64 (s, COCH_3).

(aa) ^{1}H NMR Shift Experiments on *trans*- and *cis*-1-Acetoxy-2-methylcyclopropanes and *trans*- and *cis*-1-Acetoxy-1,2-dimethylcyclopropanes. *trans*-1-Acetoxy-2-methylcyclopropane (5.2 mg) collected by GC was dissolved in 0.5 mL of C_6D_6. Addition of 28 mg of (+)-Eu(hfc)$_3$ resulted in baseline separation of the signals of the OC(O)CH_3 group for each enantiomer. The OC(O)CH_3 signal for (1*S*,2*R*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 8.27 ppm (major), and the OC(O)CH_3 signal for (1*R*,2*S*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 8.12 ppm.

cis-1-Acetoxy-2-methylcyclopropane (2.9 mg) collected by GC was dissolved in 0.5 mL of $CDCl_3$. Addition of 36mg of (+)-Eu(hfc)$_3$ resulted in baseline separation of the signals of the CH_3 groups for each enantiomer. The CH_3 signal for (1*R*,2*R*)-*cis*-1-acetoxy-2-methylcyclopropane shifted to 3.53 ppm (doublet), and the CH_3 signal for (1*S*,2*S*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 3.46 ppm (doublet).

Similar results were obtained on the *trans*- and *cis*-1-acetoxy-1,2-dimethylcyclopropanes by using the shift reagent (+)-Eu(hfc)$_3$.

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Investigation of the Stereochemistry of Fe-C_α Bond Cleavage When Phenylcyclopropane Is Generated by γ-Ionization of Stereospecifically Deuterated $C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$ Complexes. A Transition-State Model for Transfer of the Carbene Ligand from $C_5H_5(CO)_2Fe{=}CHR^+$ to Alkenes

Maurice Brookhart* and Yumin Liu

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received June 7, 1990*

Abstract: $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, and stereospecifically deuterium labeled *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **7a,b** and *erythro*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **8a,b** were synthesized. Treatment of compound **4** with trimethylsilyl triflate results in ionization of the γ-methoxy group and formation of phenylcyclopropane in good yields. Ionization of **7a,b** gives a 1:1 mixture of *cis*-2,*cis*-3-dideuterio- and *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane, while ionization of **8a,b** gives *cis*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane. These results established that the cyclopropane ring is formed by backside attack of electrophilic C_γ on C_α with net inversion of stereochemistry at C_α. These reactions serve as models for the reactions of carbene complexes $C_5H_5(CO)_2Fe{=}CHR^+$ with alkenes to give cyclopropanes and suggest that in the transfer reactions Fe-C_α is cleaved with inversion.

Introduction

The carbene ligands of electrophilic iron-carbene complexes of the general type $C_5H_5(CO)(L)Fe{=}CRR'^+$ can be transferred to alkenes to generate cyclopropanes.[1] The initial stage of the transfer reaction involves attack of electrophilic C_α of the iron complex on the alkene to generate positive charge at C_γ. Several studies support this contention,[1a,2-4] the most compelling of which is the demonstration that the reaction of $C_5H_5(CO)_2Fe{=}CHCH_3^+$ with *p*-methoxystyrene generates a γ-benzyl carbocation intermediate, $C_5H_5(CO)_2FeCH(CH_3)CH_2C^+(H)(C_6H_4OCH_3)$, prior to formation of cyclopropane products.[3]

Shown in Scheme I are two mechanisms for attack of electrophilic C_γ on C_α which result in generation of the cyclopropane through C_γ-C_α bond formation and Fe-C_α bond cleavage. One involves frontside attack of the electrophilic C_γ at the Fe-C_α bond and cleavage with retention of C_α stereochemistry.[5] The second involves backside attack of C_γ on Fe-C_α and cleavage with inversion of C_α stereochemistry. The plausibility of the inversion mechanism was initially noted by us[6] based on analogy with solvolysis of γ-Sn derivatives in which the Sn-C_α bond is cleaved with inversion at C_α.[7] This mode of cleavage is suggested by a combination of stereochemical and relative reactivity studies on

(1) For a complete tabulation of references concerning carbene transfer reactions of iron-carbene complexes, see: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) References 1-5 in the preceding paper in this issue.

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