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# Enantioselective benzylidene transfer reactions using the chiral-at-iron benzylidene complexes ($S_{Fe}S_c$)- and ($R_{Fe}S_c$)-$Cp(CO)(Ph_2R^*P)Fe{=}CHC_6H_5^+$ ($R^*$ = (*S*)-2-methylbutyl) and ($S_{Fe}$)- and ($R_{Fe}$)-$Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+$

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## Abstract

Diastereomeric benzoyl complexes ($S_{Fe}S_c$)- and ($R_{Fe}S_c$)-$Cp(CO)(Ph_2R^*P)Fe{-}COC_6H_5$ ($R^*$ = (*S*)-2-methylbutyl) have been prepared, separated and converted to the benzylidene complexes ($S_{Fe}S_c$)- and ($R_{Fe}S_c$)-$Cp(CO)(Ph_2R^*P)Fe{=}CHC_6H_5^+$. These complexes transfer benzylidene to styrene and vinyl acetate to give phenylcyclopropane derivatives with moderate to high enantioselectivity. The stereochemistry observed is consistent with a mechanism involving reaction of the *synclinal* benzylidene isomer with the alkene followed by backside attack of the developing electrophilic center at $C_\gamma$ on the Fe–$C_\alpha$ bond. Benzylidene complexes ($S_{Fe}$)- and ($R_{Fe}$)-$Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+$ have been prepared in unknown but likely high enantiomeric purity from (*S*)-mandelic acid. Benzylidene transfer from these complexes to vinyl acetate gives phenylcyclopropane derivatives with moderate enantioselectivity.

## Introduction

Electrophilic iron carbene complexes of the general type $Cp(CO)(L)Fe{=}CHR^+$ (L = CO, $PR_3$) transfer the carbene moiety to alkenes to form cyclopropanes. Numerous carbene derivatives have been studied and include R = H [1–6], $CH_3$ [7–10], $C_6H_5$ [11], c-$C_3H_5$ [12], and $CH{=}C(CH_3)_2$ [13]. Transfer reactions of such complexes have been recently reviewed [14].

In $Cp(CO)(PR_3)Fe{=}CHR^+$ systems the metal center is chiral and provides the opportunity for enantioselective carbene transfer reactions. The first studies of this type were carried out by Davison [5] and Flood [6] who transferred methylene from optically active $Cp(CO)(PPh_3)FeCH_2X$ (X = O-menthyl, Br) to *trans*-β-methylstyrene. In these systems the methylene carbon is not a prochiral center and

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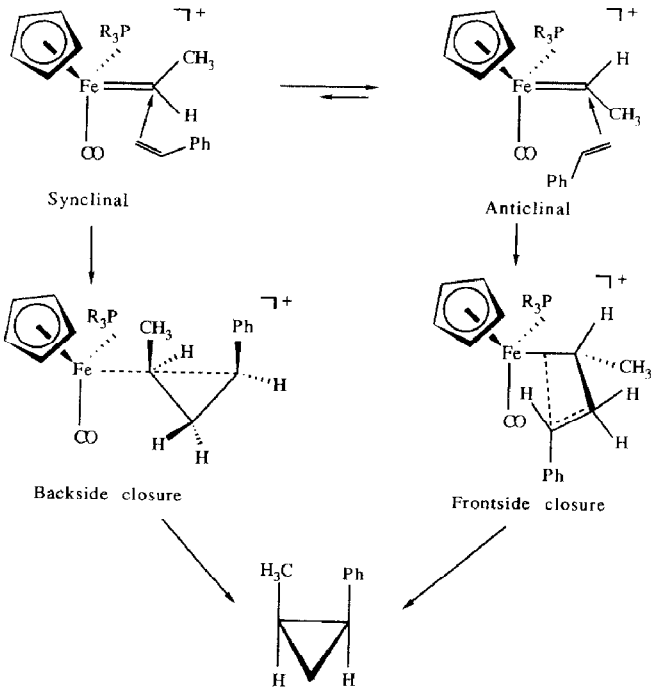



Scheme 1

enantioselectivity depends solely on the selectivity of attack on the *Si* versus *Re* face of the *β*-methylstyrene. Enantioselectivity in these systems is moderate and ranged from 10–38%.

We have examined enantioselective ethylidene transfer from complexes of the type $Cp(CO)(L)Fe{=}CHCH_3^+$ where the ethylidene carbon, $C_\alpha$, is a prochiral center [10,15]. In these systems quite high enantioselectivity can be obtained. For example, transfer of ethylidene from $(S_{Fe})$-$Cp(CO)(R^*Ph_2P)Fe{=}CHCH_3^+$ ($R^* = (S)$-2-methylbutyl), **1**-$S_{Fe}S_c$ (or **1**-*SS*) *, to styrene yields *cis*- and *trans*-1-phenyl-2-methyl-cyclopropanes in 86% and 90% ee, respectively.

Substantial mechanistic information has been deduced from these studies. As shown in Scheme 1, ethylidene complexes exist as rapidly equilibrating mixtures of *anticlinal* and *synclinal* isomers, with the *anticlinal* isomers being favored over the synclinal isomers ca. 3/1 to 10/1 [14–16]. Results of Gladysz [17], Davies [18], and Liebeskind [19] establish that the phosphine sterically shields one face of the carbene moiety and thus alkene attack will occur on the opposite face. Thus, the stereochemistry observed is consistent with either styrene attack on the major *anticlinal* isomer with "frontside" closure or attack on the minor *synclinal* isomer with "backside" closure. These mechanisms are illustrated in Scheme 1 using an iron ethylidene complex with $S_{Fe}$ absolute configuration. We have established that the *synclinal* isomers are much more reactive toward nucleophiles than *anticlinal*

* In the remainder of the paper the first letter designates the chirality of the iron center and the second letter the chirality of the carbon center.

isomers [16]. This fact strongly suggests that the mechanism of transfer involves attack of the alkene (a weak nucleophile) on the *synclinal* isomer with backside closure [20*].

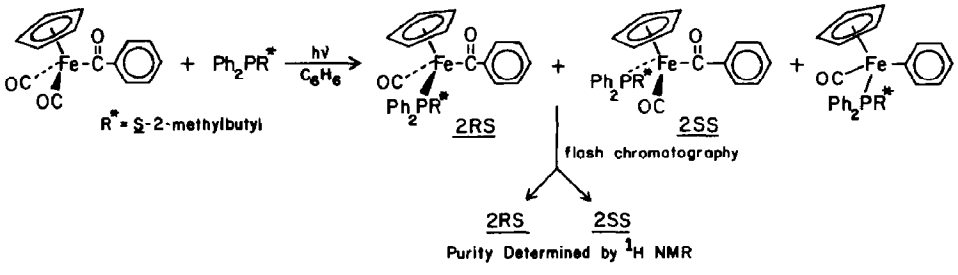
To further probe the utility and mechanistic features of enantioselective carbene transfer reactions, we have examined benzylidene transfers using chiral-at-iron benzylidene complexes $Cp(CO)(PR_3)Fe{=}CHC_6H_5^+$. The systems differ from the ethylidene systems in that the *anticlinal/synclinal* isomer ratios are substantially higher (> 30/1) [21] than their ethylidene analogs. We report here the synthesis and enantioselective benzylidene transfer reactions of $Cp(CO)(PPh_2R^*)Fe{=}CHC_6H_5^+$, *2-SS* and *2-RS*, to styrene and vinyl acetate and of (*S*)- and (*R*)-$Cp(CO)(PEt_3)$-$Fe{=}CHC_6H_5^+$ to vinyl acetate.

## Results and discussion

*A. Synthesis and enantioselective benzylidene transfer reactions of $Cp(CO)(Ph_2PR^*)$-$Fe{=}CHC_6H_5^+$ complexes [$R^*$ = (S)-2-methylbutyl]*

Photolysis of a benzene solution of the benzoyl complex $Cp(CO)_2FeCOC_6H_5$ in the presence of $Ph_2PR^*$ results in CO substitution to form a 50/50 mixture of the diastereomeric benzoyl complexes *2SS* and *2RS* (See Scheme 2) in 58% yield. Also isolated in 38% yield is a 50/50 diastereomeric mixture of the corresponding decarbonylated phenyl complexes $Cp(CO)(Ph_2PR^*)FeC_6H_5$. These phenyl and benzoyl products are readily separated by flash chromatography with 10/1 hexanes/ethyl acetate. Under these conditions, *2SS* and *2RS* are also separated with the *2SS* diastereomer eluting first. Complex *2SS* was isolated as a 98/2 *2SS/2RS* mixture and *2RS* was isolated as a 92/8 *2RS/2SS* mixture. The diastereomeric purities of the benzoyl complexes are established by $^1H$ NMR. The *2SS* diastereomer has a distinct well-separated multiplet for two phenyl hydrogens at $\delta$ 8.15 while *2RS* has a similar distinct multiplet at $\delta$ 8.07. The absolute configuration of *2SS* and *2RS* was established by correlation of their CD spectra (Fig. 1) with the CD spectra of iron acetyl complexes of similar structure and known absolute configuration [10,22].

Alkylation of a clear orange solution of *2SS* in $CH_2Cl_2$ with methyl triflate at room temperature generated a dark red solution of the heterocarbene complex *3SS* (Scheme 3). Subsequent reduction of *3SS* with borohydride in basic methanol yielded the diastereomeric pair of $\alpha$-ether complexes *4SSS/4SSR* **. Similar




Scheme 2

* Reference number with asterisk indicates a note in the list of references.

** The third letter designates the chirality of $C_\alpha$.

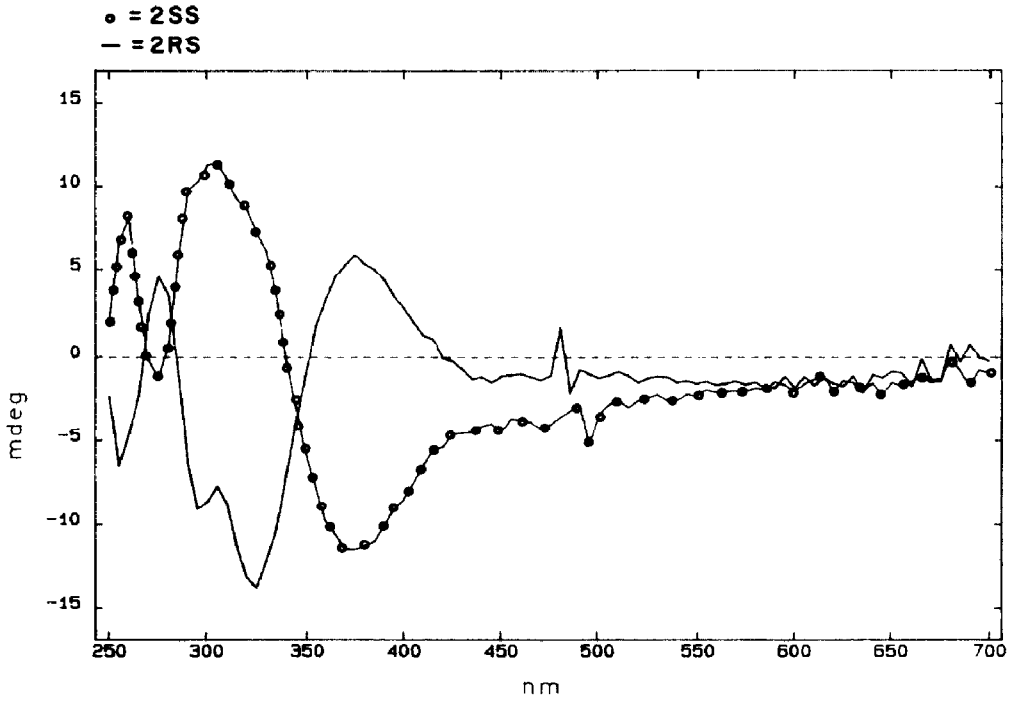
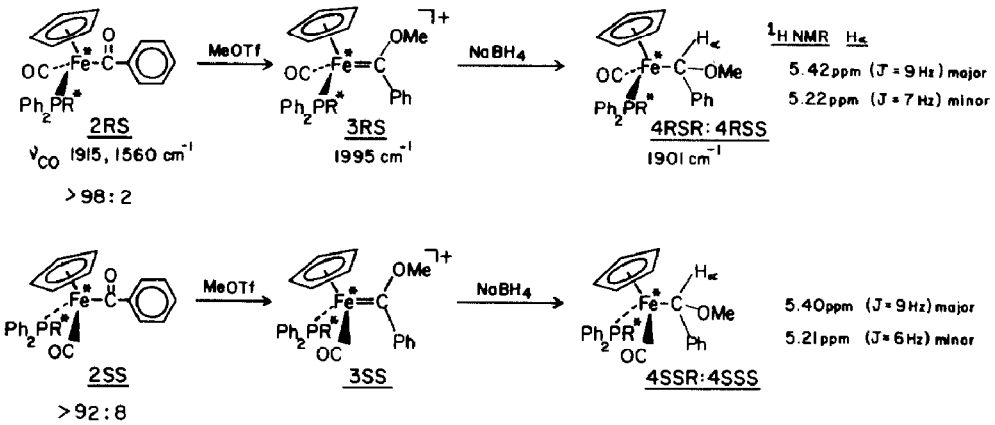



Fig. 1. CD spectra of *2SS* and *2RS* $6\times10^{-5}$ *M* solutions in n-hexane.

treatment of *2RS* led to *4RSS/4RSR*. The $^1$H NMR data for $\alpha$-ethers **4** are summarized in Table 1.

However, as was previously observed for $\alpha$-ether complexes $Cp(CO)(PPh_3)Fe\text{-}CH(OCH_3)Ph$ (**7**) [21] *4SSS/4SSR* and *4RSS/4RSR* undergo facile phosphine dissociation–reassociation in solution at 25 °C resulting in epimerization of the chiral iron center (Scheme 4). The equilibrium ratio of the four diastereomers is 3 *4SSR*/3 *4RSS*/1 *4SSS*/1 *4RSR*. As discussed previously [21], the diastereomers with the $Fe_SC\alpha_R/Fe_RC\alpha_S$ configuration are the thermodynamically more stable. The rate of $Ph_2PR^*$ dissociation from the equilibrated diastereomer mixture of




Scheme 3

Table 1

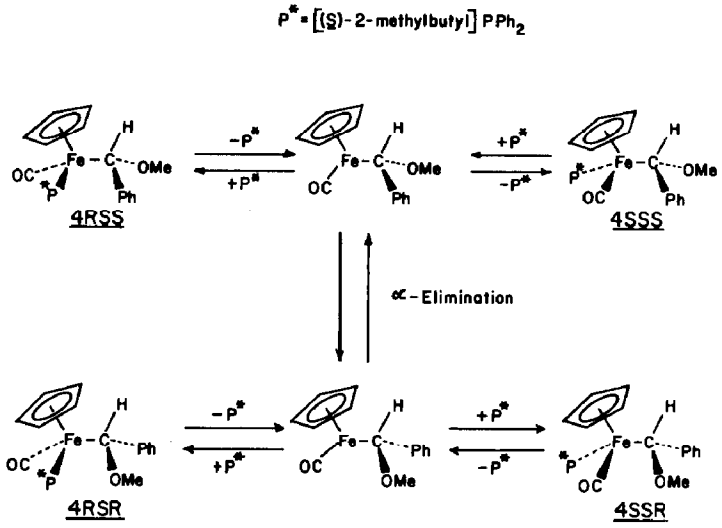
$^1$H NMR data for α-ether complexes Cp(CO)($Ph_2PR^*$)FeCH($OCH_3$)$C_6H_5$ [a,b]

| Diastereomer | $\delta(H_\alpha)$ | $\delta(C_5H_5)$ | $\delta(OCH_3)$ |
|---|---|---|---|
| *4SSS* | d 5.22<br>$^3J$(PH) = 6.6 Hz | s 3.85 | s 2.94 |
| *4RSR* | d 5.21<br>$^3J$(PH) = 6.4 Hz | d 3.85<br>$^3J$(PH) = 1.0 Hz | s 2.94 |
| *4SSR* | d 5.42<br>$^3J$(PH) = 8.9 Hz | s 4.02 | s 3.29 |
| *4RSS* | d 5.40<br>$^3J$(PH) = 8.8 Hz | d 4.02<br>$^3J$(PH) = 1.1 Hz | s 3.20 |

[a] Chemical shifts are in ppm relative to 7.15 for $C_6D_5H$. [b] Due to diastereomer mixtures, definitive assignments of the resonances for the phenyl and 2-methylbutyl protons could not be made.

α-ethers **4** is $1.8 \times 10^{-4}$ $s^{-1}$ ($t_{1/2}$ = 63 min, $T$ = 293 K). The rate was measured by adding 8 equivalents of $PEt_3$ to an equilibrated solution of diastereomers **4** and monitoring by $^1$H NMR the disappearance of diastereomers **4** and appearance of a 3/2 mixture of *10RS/10SR* and *10SS/10RR*, Cp(CO)($PEt_3$)FeCH($OCH_3$)Ph.

Phosphine dissociation–reassociation account for loss of configuration at iron but $C_\alpha$ epimerization must also occur. When a 6/1 mixture of *4SSR/4SSS* was monitored by $^1$H NMR over time, it equilibrated to the thermodynamic 3 *4SSR*/3 *4RSS*/1 *4SSS*/1 *4RSR* mixture. If *only* loss of configuration at iron were taking place via phosphine dissociation–reassociation, *4SSS* would give only *4RSS* and *4SSR* would give only *4RSR* ultimately yielding a 6 *4SSR*/6 *4RSR*/1 *4SSR*/1 *4RSR* mixture. The fact that this is not the case and that the equilibrium 3/3/1/1 ratio is obtained demonstrates that epimerization of $C_\alpha$ must also occur along with phosphine dissociation–reassociation in solution at 25 °C resulting in loss of configuration at *both* iron and $C_\alpha$ in α-ethers **4**. A mechanism for epimerization at $C_\alpha$ has

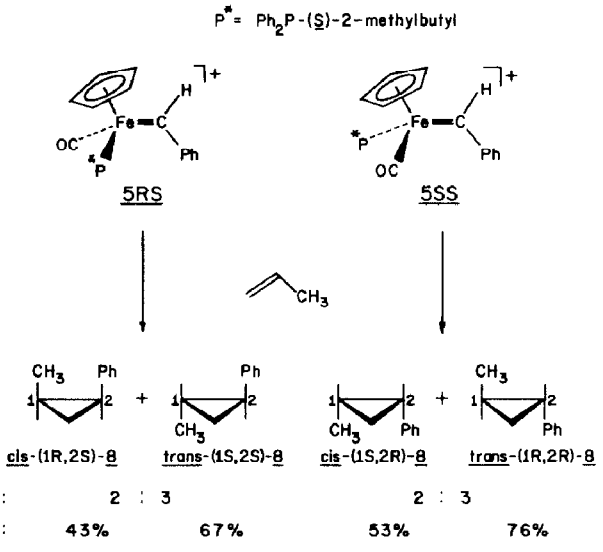



Scheme 4

been previously advanced which involves α-hydrogen elimination to the carbene hydride $Cp(CO)(PR_3)Fe(H)=C(OCH_3)Ph$ followed by carbene rotation and hydrogen migration back to $C_\alpha$ [21].

*Benzylidene transfer reactions.* To minimize racemization of α-ethers **4** prior to benzylidene generation and transfer, all manipulations of these complexes were performed at −20 °C where the rate of phosphine dissociation is expected to be very slow. Benzoyl complexes *2SS* and *2RS* were, separately, alkylated at room temperature with methyl triflate. The solutions of heterocarbene complexes *3SS* and *3RS* were then added to rapidly stirring −78 °C $NaBH_4/NaOCH_3/CH_3OH$ solutions. Work-up at −20 °C gave orange powders of *4SSS/4SSR* and *4RSS/4RSR* which were immediately dissolved in $CH_2Cl_2$, cooled to −78 °C and treated with 1.1 equivalents of trimethylsilyl triflate to generate the diastereomeric cationic iron benzylidene complexes *5SS* and *5RS* which differ only in configuration at iron. The benzylidene complexes *5SS* and *5RS* are both characterized by a low field doublet at 16.9 ppm ($^3J$(PH) 9.9 Hz) for $H_\alpha$ in the $^1$H NMR spectrum.

Benzylidene transfer from *5SS* and *5RS* to propene afforded *cis*- and *trans*-1-methyl-2-phenylcyclopropanes **8** in 21% yield (Scheme 5). The absolute configurations and enantiomeric purity of the *cis*- and *trans*-1-methyl-2-phenylcyclopropanes (Table 2) were established by comparing their optical rotations to the known rotations of enantiomerically pure 1-methyl-2-phenylcyclopropanes [23*–25*]. Correcting for diastereomeric impurities, the optical yields of *cis*-(1*S*,2*R*)-**8** and *trans*-(1*R*,2*R*)-**8** from *5SS* are ca. 53 and 76% (±8%). Similarly, *5RS* yields *cis*-(1*R*,2*S*)-**8** and *trans*-(1*S*,2*S*)-**8** in ca. 48 and 76% (±8%) optical yield. The difference between the enantiomeric purity (approximately 20–25%) of the *cis*- and *trans*-cyclopropanes **8** formed from the reaction of *5SS* or *5RS* with propene is a result of the fact that the transition states leading to the four possible *cis*- and *trans*-1-methyl-2-phenylcyclopropane products are all diastereomeric. Although all four transition states leading to products are also diastereomeric for ethylidene complexes *1SS* and *1RS*




Scheme 5

Table 2

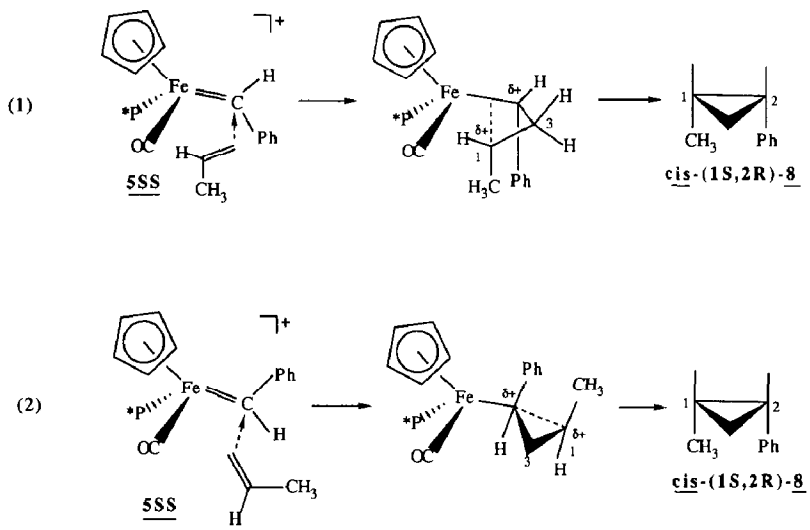
Optical rotations, % ee's, and optical yields of *cis*- and *trans*-1-methyl-2-phenylcyclopropanes **8**

| Acyl precursor *2SS/2RS* | *Trans*-**8**/*cis*-**8** ratio | Major enantiomers produced | Optical [b] rotation $[\alpha]_D^{23}$ (°) | Concentration [a] | ee (%) [c] | Optical yield (%) |
|---|---|---|---|---|---|---|
| 98/2 | 3/2 | *Trans*-(1*R*,2*R*) | −83.3 | 0.45 | 73±8 | 76±8 |
| | | *Cis*-(1*S*,2*R*) | +32.5 | 0.27 | 51±8 | 53±8 |
| 8/92 | 3/2 | *Trans*-(1*S*,2*S*) | +73.5 | 0.52 | 64±8 | 76±8 |
| | | *Cis*-(1*R*,2*S*) | −26.3 | 0.21 | 41±8 | 48±8 |

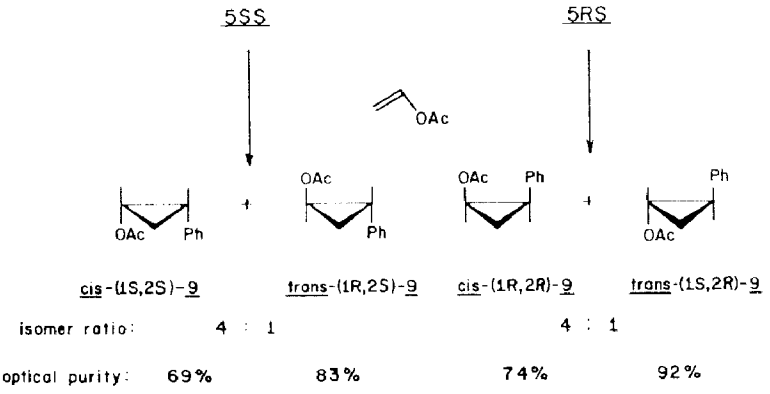
[a] Concentrations are in g/100 ml GLC-purified cyclopropanes. [b] Optical rotations were recorded in absolute ethanol. [c] See Refs. 9 and 11.

it appears coincidental that they gave similar enantiomeric purities for both *cis*- and *trans*-1-methyl-2-phenylcyclopropane products [10].

The stereochemical results of benzylidene transfer from *5SS* and *5SR* can be rationalized by either of two mechanisms discussed in the introduction and illustrated in Scheme 1: (a) reaction of propene with the *anticlinal* isomer followed by frontside closure or (b) reaction of the *synclinal* isomer followed by backside closure. These mechanisms are specifically illustrated in Scheme 6 for reaction of *5SS* with propene and production of the *cis*-1-(*S*)-methyl-2-(*R*)-phenylcyclopropane isomer. In view of the observation that *synclinal* benzylidene isomers are much more reactive than *anticlinal* benzylidene isomers towards nucleophiles and that selectivity *increases* with decreasing nucleophilicity, we favor the mechanism involving reaction of the *synclinal* benzylidene isomer with the weakly nucleophilic propene followed by backside closure. In this regard it is interesting to note that the enantioselectivity observed for the formation of 1-methyl-2-phenylcyclopropanes **8** from reaction of *5SS* or *5RS* with propene is not as high as previously observed for ethylidene transfer to styrene from the analogous ethylidene complexes *1SS* and




Scheme 6




Scheme 7

*1RS*. A reasonable explanation for this observation consistent with the proposed mechanism is that since the *anticlinal/synclinal* ratio for *5SS* and *5RS* is much greater than in the case of the ethylidene complexes *1SS* and *1RS*, significant reaction occurs via the major *anticlinal* isomers of *5SS*, *5RS* with the same "backside" closure. Operation of this pathway leads to production of the "minor" enantiomers and reduction of the ee's.

Since $PEt_3$ and $PPh_2R^*$ can adopt conformations such that the face of the carbene moiety is not directly shielded by a face-to-face arrangement with an arene ring, it could be suggested that the minor enantiomers come from alkene attack on the *synclinal* isomers over these "less shielding" phosphines followed by backside closure. Several observations suggest this route to the minor enantiomers is unlikely: (a) deuteride addition to $Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+$ using $Et_3BD^-$ occurs exclusively over CO [21b], (b) attack of weak nucleophiles in dilute solution on $Cp(CO)(PEt_3)F{=}CHCH_3^+$ exhibit very high facial selectivity [16], (c) ethylidene transfers to alkenes using optically pure $Cp(CO)(PEt_3)Fe{=}CHCH_3^+$ and $Cp(CO)(PPh_2R^*)Fe{=}CHCH_3^+$ exhibit ee's greater than 90% [10,21c], and (d) *5RS* upon reaction with vinyl acetate yields *trans*-(1*S*,2*R*)-**9** in greater than 90% ee (see below).

Benzylidene transfer from *5SS* and *5RS* to vinyl acetate (with work up of *4SSS/4SSR* and *4RSS/4RSR* at $-20\,^{\circ}C$) gave *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes **9** in approximately 30% yield (Scheme 7).

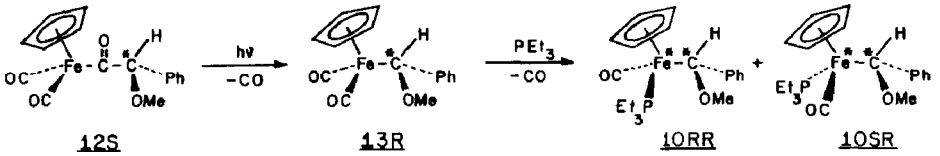
Although the absolute configurations of the 1-acetoxy-2-phenylcyclopropanes could not be established, *5SS* and *5RS* did obviously yield *cis*- and *trans*-cyclopropanes which were enantiomers of one another. Assuming that the backside closure mechanism outlined in Scheme 6 applies, the product *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes arising form *5SS* and *5RS* would be those shown in Scheme 7. Correcting for diastereomeric impurities, *5SS* yielded *cis*-(1*S*,2*S*)-**9** and *trans*-(1*R*,2*S*)-**9** in optical yields of 69 and 83% ($\pm 2\%$). Similarly, *5RS* yields *cis*-(1*R*,2*R*)-**9** and *trans*-(1*S*,2*R*)-**9** in optical yields of 74 and 92% ($\pm 2\%$). (The enantiomeric purities of the 1-acetoxy-2-phenylcyclopropanes were determined using $Eu(hfc)_3$. (See Experimental section for details.) The fact that the enantiomeric excess is in one case as high as 92% suggests that *5SS* and *5RS* have high optical purities.

*B. Synthesis and benzylidene transfer reactions of optically active $Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+$ complexes*

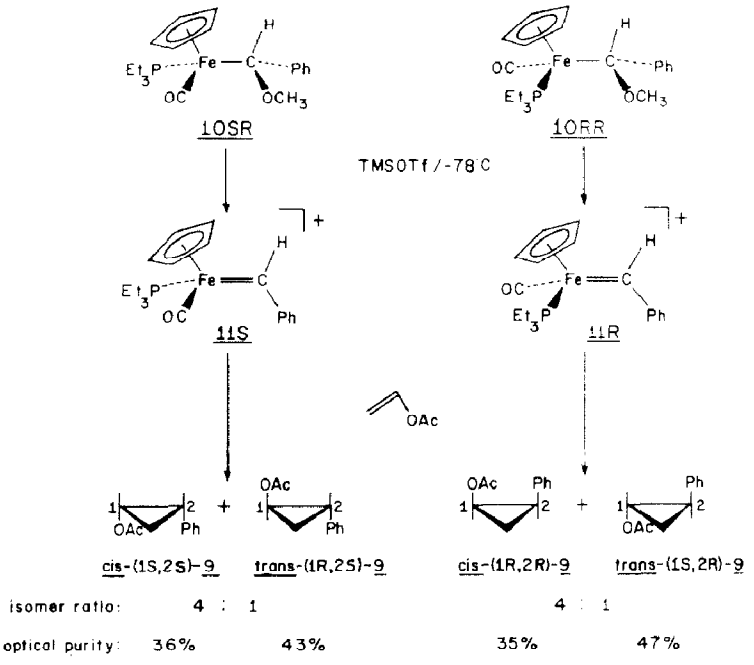
Optically pure (*S*)-$Cp(CO)_2FeCOCH(OCH_3)C_6H_5$ (*12S*) has been prepared from naturally occurring *S*-mandelic acid. Photolysis of a benzene solution of *12S* results in decarbonylation followed by migration of the alkyl group with retention of configuration to form (*R*)-$Cp(CO)_2FeCH(OCH_3)C_6H_5$ (*13R*) [21]. Photolysis of *12S* in the presence of excess $PEt_3$ results in loss of two equivalents of CO and formation of a 3/2 mixture of $\alpha$-ether complexes *10RR* and *10SR* (Scheme 8). Diastereomers *10RR* and *10SR* were separated by column chromatography on basic alumina at $-52°$C with 25/1 hexanes/$Et_2O$. Their diastereomeric purity was determined by $^1$H NMR integration of resonances for $H_\alpha$ at 4.93 ppm for *10SR* and 5.19 ppm for *10RR*. Both complexes were isolated in > 98% diastereomeric purity. The optical rotations ($[\alpha]_{436}^{23}$ in n-hexane) for *10RR* and *10SR* were +740 and $-720°$, respectively and are in the range expected for enantiomerically pure materials. (Since the absolute rotations of enantiomerically pure *10RR* and *10SR* are not known, we have assumed for purposes of calculating ee's and optical yields that complexes with these rotations are enantiomerically pure. For most of the transfers, less enantiomerically pure materials were used: *10RR*, $[\alpha]_{436} = +650°$, assumed ee = 87%; *10SR*, $[\alpha]_{436} = -620°$, assumed ee = 86%. Determination of ee's using chiral shift reagents were not successful for *10RR*, *10SR*).

Treatment of clear orange $-78°$C $CH_2Cl_2$ solutions of *10RR* and *10SR* with TMSOTf generates the enantiomeric benzylidene complexes *11R* and *11S* which differ only in configuration at iron. The benzylidene complex is characterized by its low field $^1$H NMR resonance at 17.04 ppm for $H_\alpha$ and $^{13}$C NMR resonance at 333.5 ppm (d, $^2J$(PC) = 23.1 Hz) for the carbene carbon $C_\alpha$. Subsequent transfer of benzylidene to vinyl acetate from *11R* and *11S* forms 1-acetoxy-2-phenylcyclopropanes **9** in 24 and 21% isolated yields respectively (Scheme 9). The cyclopropanes **9** formed from both *11R* and *11S* are a 4/1 mixture of *cis* and *trans* isomers. The *cis* and *trans* isomers **9** were separated by preparative gas chromatography and enantiomeric purities were determined by a chiral shift experiments using $Eu(hfc)_3$. Correcting for enantiomeric impurities, *11R* yielded *cis*-(1*R*,2*R*)-**9** and *trans*-(1*S*,1*R*)-**9** in 35 and 47% (±5%) optical yields. Similarly, *11S* yielded *cis*-(1*S*,2*S*)-**9** and *trans*-(1*R*,2*S*)-**9** in 36 and 43% (±5%) optical yields. Complex *11R* yielded the same *cis*-**9** and *trans*-**9** enantiomers as those obtained from *5RS* while *11S* yielded identical enantiomers to those obtained from *5SS*. Since it is the chirality at iron which dictates the stereochemistry of the product cyclopropanes, these results confirm the absolute configuration assigned to the metal centers.

The enantioselectivites observed for benzylidene transfer from *11R* and *11S* to vinyl acetate are lower than those obtained for *5RS* and *5SS*. There are two plausible explanations. First, the optical purities of *11S* and *11R* may be lower than




Scheme 8




Scheme 9

estimated (see above). Secondly, a greater fraction of the benzylidene transfer may occur via reaction of vinyl acetate with the *anticlinal* isomer of *11S* or *11R* relative to the *anticlinal* isomer of *5RS* or *5SS*.

## Summary

(1) Benzylidene complexes $Cp(R^{\star}PPh_2)Fe{=}CHC_6H_5^+$, *5RS* and *5SS*, of high optical purity and $Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+$, *11R* and *11S*, of unknown but likely high optical purity have been prepared.

(2) Complexes *5RS*, *5SS*, *11S* and *11R* transfer benzylidene to styrene and vinyl acetate to form cyclopropanes with moderate to high optical yields (35–92% ee).

(3) The stereochemical results obtained are consistent with alkene attack on the *synclinal* isomer with backside closure as the major reaction pathway.

(4) Optical yields for benzylidene transfer from *5RS* and *5SS* to propene to give 1-methyl-2-phenylcyclopropanes are lower than those obtained for reaction of the analogous iron ethylidene complexes with styrene. The probable explanation for this observation lies in the lower *synclinal/anticlinal* isomer ratios observed for the benzylidene complexes relative to the ethylidene complexes. We are currently testing this hypothesis by examining ethylidene transfers from chiral ethylidene complexes with very high *anticlinal/synclinal* ratios.

## Experimental section

All manipulations were performed under a nitrogen atmosphere using standard or modified Schlenk techniques unless otherwise noted. Solvents were dried and rendered oxygen-free by distillation under a nitrogen atmosphere from sodium

benzophenone (THF, hexanes, benzene, toluene, $Et_2O$), $P_2O_5$ ($CH_2Cl_2$), or magnesium methoxide ($CH_3OH$). All other solvents were degassed with nitrogen prior to use. NMR spectra were recorded on either an IBM AC-200, Bruker WM-250 or Varian XL-400 using residual solvent peaks as references. (ie. $CDHCl_2$ $\delta$ 5.32; $C_6D_5H$, $\delta$ 7.15; $C_6D_5CD_2H$, $\delta$ 2.09 ). IR spectra were recorded on a Beckmann 4250 Spectrophotometer.

Photolyses were performed using a sunlamp (GE H100PFL44-4 Reflector Flood Lamp). Preparative GLC was performed on either a Varian Aerograph 90-P or Hewlett-Packard HP-5750 equipped with a Hewlett-Packard HP-3390A Integrator using a thermal conductivity detector. Optical rotations were performed on a Perkin–Elmer 241 polarimeter using 1 ml polarimetry cells. CD spectra were recorded on a AVIV Model 40DS Spectrophotometer. (*S*)-2-Methylbutyldiphenylphosphine [10], $Cp(CO)_2FeCOC_6H_5$ [26] and *10SS* and *10RR* [21] were prepared according to published methods. All other reagents were used as received.

*Synthesis of benzoyl diastereomers ($\eta^5$-$C_5H_5$)(CO)[$Ph_2$P-(S)-2-methylbutyl]Fe-$COC_6H_5$ 2SS and 2SR*

3.20 g (10.7 mmol) $Cp(CO)_2FeCOC_6H_5$ were dissolved in 75 ml dry benzene in a pyrex photolysis tube fitted with an ice-water cooled cold finger. 5.85 g (22.8 mmol) (*S*)-2-methylbutyldiphenylphosphine were dissolved in 25 ml of benzene and the solution added to the photolysis tube. The reaction mixture was stirred rapidly, purged with nitrogen and photolyzed with a sunlamp for 2.5 h. The progress of the reaction was monitored by IR by noting the disappearance of absorption bands at 2010, 1965, and 1620 $cm^{-1}$ for starting material and appearance of absorption bands at 1920, 1595, 1580, 1560 $cm^{-1}$ for product. Solvent removal gave a crude dark red oil as product. The crude product was flash chromatographed with 10/1 hexanes/ethyl acetate. The first band to elute was orange side product $Cp(CO)(Ph_2PR^*)FeC_6H_5$ (a 50/50 *SS/RS* diastereomer mixture). Thereafter the desired benzoyl complexes eluted as a broad orange band. Several fractions of the band were collected with diastereomer *2SS* eluting first. Solvent removal gave orange powder as product. The diastereomeric purity of the fractions was determined by $^1H$ NMR. The purity of the *2SS* diastereomer was best determined by a phenyl hydrogen multiplet at $\delta$ 8.15 while a corresponding multiplet at $\delta$ 8.07 was used to assess the purity of diastereomer *2RS*. Pure materials were combined while mixtures were rechromatographed. Yield: 3.10 g (58%) *2SS* (98 : 2 *2SS/2RS*) + *2SR* (92/8 *2RS/2SS*) and 1.92 g (38%) phenyl complex.

*2SS*: IR ($C_6H_6$): 1920, 1595, 1580, 1560 $cm^{-1}$. $^1H$ NMR ($C_6D_6$): $\delta$ 0.33 (d, 3H, $J = 6.5$ Hz) -CH-C$H_3$; 0.63 (t, 3H, $J = 7.4$ Hz) $CH_2$-C$H_3$; 0.8–1.8 (m 3H) -C$H$, -C$H_2$; 1.97 (ddd, 1H, $J = 9.5$, 14, 14 Hz) P-C$H$H′; 2.81 (ddd, 1H, $J = 2.7$, 8.5, 14 Hz) P-CH$H'$; 4.15 (d, 5H, $^3J$(PH) = 1.2 Hz) $\eta^5$-$C_5H_5$; 7.01–7.35 (m, 9H), 7.63 (m, 2H), 7.83 (m, 2H), 8.15 (m, 2H): $C_6H_5$'s. $^{13}C$ NMR ($C_6D_6$): $\delta$ 11.01, -$CH_2$-$CH_3$; 20.13, -$CH_2CH_3$; 31.26, -$CH_2$; 32.59 (d, $^2J$(PC) = 13.5 Hz) -$CH$; 37.33, (d, $^1J$(PC) = 24.4 Hz) P-$CH_2$; 85.25, $\eta^5$-$C_5H_5$; 127.4, 128.1, 129.1, 129.9, 130.2, 132.2, 132.3, 134.8, 134.9, 136.1, 136.8, 150.9: $C_6H_5$'s; 221.8 (d, $^2J$(PC) = 32.4 Hz) $CO$. Elemental Analysis Found: C, 70.84; H, 6.37; O, 6.03; P, 5.80; Fe, 10.96. $C_{30}H_{31}O_2PFe$ calc: C, 70.60; H, 6.12; O, 6.27; P, 6.07; Fe, 10.94%. Optical rotation ($2.4 \times 10^{-4}$ g/ml 98/2 *2SS/2RS* n-hexane) 365 nm: +2040°; 436 nm: −640°; 546 nm: −320°;

578 nm: −240°. A CD spectrum was recorded on a $6 \times 10^{-5}$ *M* solution of 98/2 *2SS/2RS* and is shown in Fig. 1.

*2RS*: IR ($C_6H_6$): 1920, 1595, 1580, 1560 $cm^{-1}$. $^1H$ NMR ($C_6D_6$): δ 0.48 (t, 3H, $J = 7.5$ Hz) -$CH_2$-$CH_3$; 0.69 (d, 3H, $J = 6.6$ Hz) -CH-$CH_3$; 0.80–1.75 (m, 3H) -CH, -$CH_2$; 2.18 (ddd, 1H, $J = 7.5, 14, 14$) P-CHH′); 2.57 (ddd, 1H, $J = 3.8, 8.5, 14$ Hz) P-CHH′; 4.16 (d, 5H, $^3J$(PH) = 1.4 Hz) $\eta^5$-$C_5H_5$; 7.0–7.15 (m, 7H), 7.32 (m, 2H), 7.61 (m, 2H), 7.80 (m, 2H), 8.07 (m, 2H): $C_6H_5$'s. $^{13}C$ NMR ($C_6D_6$): δ 10.77, -$CH_2$-$CH_3$; 21.37 (d, $^3J$(PC) = 9.8 Hz) -CH-$CH_3$; 30.20 (d, $^2J$(PC) = 13.4 Hz) -CH; 31.02, -$CH_2$; 37.43 (d, $^1J$(PC) = 23.9 Hz) P-$CH_2$; 85.30, $\eta^5$-$C_5H_5$; 127.06, 127.56, 128.16, 128.47, 129.21, 129.81, 132.6, 134.2, 137.2, 139.8, 151.3 $C_6H_5$'s; 221.7 (d, $^2J$(PC) = 31.4 Hz) -CO. Elemental Analysis Found: C, 70.72; H, 6.32; O, 6.22; P, 5.60; Fe, 11.50. $C_{30}H_{31}O_2PFe$ calc: C, 70.60; H, 6.12; O, 6.27; P, 6.07; Fe, 10.94%. Optical rotation ($2.4 \times 10^{-4}$ g/ml 92/8 *2RS/2SS* in n-hexane) 365 nm: −464°; 436 nm: +764°; 546 nm: +321°; 578 nm: +232°. A CD spectrum was recorded on a $6 \times 10^{-5}$ *M* solution of 92/8 *2RS/2SS* and is shown in Fig. 1.

*Heterocarbene complexes Cp(CO)($Ph_2PR^*$)Fe=C($OCH_3$)$C_6H_5^+$ $OTf^-$ 3SS and 3RS*

30 mg *2SS* or *2RS* was dissolved in 500 μl $CD_2Cl_2$ in a 5 mm NMR tube and 2 equivalents MeOTf were added at room temperature. The solution turned from clear orange to deep red upon mixing. *3SS*: IR ($CH_2Cl_2$): 1995 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): δ 0.61 (t, 3H, $J = 7.5$ Hz) -$CH_2$-$CH_3$; 0.63 (d, 3H, $J = 7.5$ Hz) -CH$CH_3$; 0.8–1.0 (m, 2H) $CH_2$; 1.4–1.6 (br m, 1H) -CH; 2.26–2.33 (m, 2H) P-CHH′; 4.01 (s, 3H) -$OCH_3$; 4.81, (d, 5H, $^3J$(PH) = 1.2 Hz) $\eta^5$-$C_5H_5$; 6.43–6.48 (m, 2H), 7.35–7.56 (m, 13H): $C_6H_5$'s. $^{13}C$ NMR ($CD_2Cl_2$): δ 11.06, $CH_2$-$CH_3$; 20.98, CH-$CH_3$; 31.55 (d, $J$(PC) = 7.5 Hz), -CH; 37.96 (d, $^1J$(PC) = 28.7 Hz) P-$CH_2$; 31.62, $CH_2$; 62.5, -$OCH_3$; 89.7, $\eta^5$-$C_5H_5$; 122.3, 129.0, 129.6, 130.1, 131.1, 131.8, 132.1, 132.6, 132.9, 152.0: -$C_6H_5$'s.

*3RS*: IR ($CH_2Cl_2$): 1995 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): δ 0.43 (d, 3H, $J = 6.6$ Hz) -$CH_2$-$CH_3$; 0.68 (d, 3H, $J = 7$ Hz) -CH-$CH_3$; 1.08 (dq, 2H, $J = 6.4$ Hz) -$CH_2$; 1.54 (br m, 1H) -CH; 2.17 (ddd, 1H, $J = 6.3, 6.3, 15.7$ Hz) P-CHH′; 2.43 (ddd, 1H, $J = 4.3, 8.5, 15.9$ Hz) P-CHH′; 3.99 (s, 3H) -$OCH_3$; 4.80 (d, 5H, $^2J$(PH) = 1.3 Hz) $\eta^5$-$C_5H_5$; 6.43 (m, 2H), 7.29–7.70 (m, 13H): $C_6H_5$'s. $^{13}C$ NMR ($CD_2Cl_2$): δ 11.10, -$CH_2$-$CH_3$; 20.45 (d, $^3J$(PC) = 5.5 Hz) -CH-$CH_3$; 30.09, -$CH_2$; 31.62 (d, $^2J$(PC) = 6.5 Hz) -CH; 38.13 (d, $^1J$(PC) 27.7 Hz) P-$CH_2$; 62.6, -$OCH_3$; 89.7, $\eta^5$-$C_5H_5$; 122.4, 129.0, 129.7, 129.9, 130.1, 131.1, 132.1, 132.2, 132.5, 132.7, 133.4, 150.8: -$C_6H_5$'s; 215.6 (d, $^2J$(PC) = 27.5 Hz) -CO; 332.0 (d, $^2J$(PC) = 24.5 Hz) =C.

*α-Ether complexes Cp(CO)($Ph_2PR^*$)Fe–CH($OCH_3$)$C_6H_5$ (4)*

1.00 g (2 mmol) **2** was dissolved in 50 ml $CH_2Cl_2$ and 700 μl (6.2 mmol) MeOTf added. The mixture was stirred overnight at room temperature and turned from clear orange to dark red to form heterocarbene **3**. The progress of the reaction was monitored by IR with the disappearance of absorption bands for **2** and appearance of absorption bands for **3** at 1920, 1595, 1580, 1560 $cm^{-1}$ and appearance of a single absorption band at 1990 $cm^{-1}$ for **3**. The heterocarbene solution was added to a rapidly stirring −78°C $NaBH_4$/$NaOCH_3$/$CH_3OH$ (500 mg Na, 470 mg $NaBH_4$ in 50 ml $CH_3OH$) solution. The dark red color of **3** immediately discharged to clear orange.The mixture was stirred at −78°C for 10 min then warmed to 0°C

and stirred for 10 min. 50 ml $CH_2Cl_2$ and 50 ml of a saturated aqueous bicarbonate solution were added and the mixture vigorously mixed. The orange $CH_2Cl_2$ layer was filtered through a plug of anhydrous $K_2CO_3$. The water layer was extracted two times with 30 ml $CH_2Cl_2$, the $CH_2Cl_2$ extracts combined and solvent removed in vacuo to give an orange oily product. The oil was dissolved in a minimum amount of 2-methylbutane and cooled to $-40\,^\circ C$ to yield 1.0 g (95%) pure orange powder as product. IR ($CH_2Cl_2$): $\nu$(CO) 1905 $cm^{-1}$. $^1H$ NMR for the four possible diastereomers is given in Table 1. $^{13}C$ NMR ($C_6D_6$): *4SSR*: $\delta$ 86.00, Cp; 80.26 (d, $J = 20.1$ Hz), $CH_\alpha$; 58.20, $OCH_3$; 38.26 (d, $J = 21.4$ Hz) P-$CH_2$; 31.45, $CH$; 5.78, $CH_2CH_3$; 11.30, $CH_2CH_3$; 21.69, $CHCH_3$. *4RSS*: $\delta$ 85.91, Cp; 86.05 (d, $J = 16.4$ Hz), $CH_\alpha$; 58.20, $OCH_3$; 37.82 (d, $J = 20.8$ Hz), P-$CH_2$; 31.20, $CH$; 5.78, $CH_2CH_3$; 11.30, $CH_2CH_3$; 21.56, $CHCH_3$. *4SSS*: $\delta$ 85.36, Cp; 82.60 (d, $J$ 23.9 Hz), $CH_\alpha$; 58.20, $OCH_3$; 32.86 (d, $J$ 10.7 Hz), P-$CH_2$; 31.08, $CH$; 6.06, $CH_2CH_3$; 11.03, $CH_2CH_3$; 20.69, $CHCH_3$. *4RSR*: $\delta$ 85.27, Cp; 86.28 (d, $J = 16.4$ Hz), $CH_\alpha$; 58.20, $OCH_3$; 30.74 (d, $J = 10.7$ Hz), P-$CH_2$; 30.88, $CH$; 6.06, $CH_2CH_3$; 11.03, $CH_2CH_3$, 20.43, $CHCH_3$. Elemental analysis Found: C, 70.69; H, 6.71. for racemic mixture $C_{31}H_{35}O_2PFe$ Calc: C, 70.74; H, 6.66%.

*Spectral characterization of benzylidene complexes 5RS / 5SS*

8 mg of racemic **4** was dissolved in 500 $\mu$l $CD_2Cl_2$ in a 5 mm NMR tube, cooled to $-78\,^\circ C$ and one equivalent of TMSOTf added to generate a deep red solution of *5RS / 5SS* which was characterized by NMR. $^1H$ NMR ($CD_2Cl_2$, $T = 202$ K): $\delta$ 16.67 (br s, 1H) $H_\alpha$; 6.8–8.0 (m, 15H) $C_6H_5$'s; 5.20 (s, 5H) Cp; 0.8–2.5 (m, 11H) 2-methylbutyl. $^{13}C$ NMR ($CD_2Cl_2$, $T = 202$ K): $\delta$ 341.0 (d, $^2J$(PH) = 24 Hz) =*C*.

*In-situ synthesis of α-ether complexes 4SSS / 4SSR and 4RSS / 4RSR Cp(CO)($Ph_2$-PR*)FeCH($OCH_3$)$C_6H_5$ and benzylidene complexes 5SR and 5SS. Benzylidene transfers to propene and vinyl acetate*

*A. Reactions with propene.* General procedure: 260 mg (0.49 mmol) of either benzoyl *2SS* or *2RS* was dissolved in 10 ml $CH_2Cl_2$ and 160 $\mu$l (0.97 mmol) MeOTf was added. The solution was stirred overnight at room temperature and turned from clear orange to dark red over the course of the reaction. Complete formation of heterocarbene **3** was evidenced by the disappearance of the IR absorption bands at 1920, 1595, 1580, and 1560 $cm^{-1}$ for **2** and appearance of a single absorption band at 1990 $cm^{-1}$ for **3**. The solution of **3** was then added slowly to a rapidly stirring $-78\,^\circ C$ $NaBH_4/NaOCH_3/CH_3OH$ solution (4.3 mmol Na, 2.1 mmol $NaBH_4$ in 25 ml $CH_3OH$). The dark red color immediately discharged to clear orange upon addition. After allowing the reaction mixture to stir at $-78\,^\circ C$ for 15–20 min the solution was warmed to $-20\,^\circ C$ and 20 ml of $CH_2Cl_2$ and 20 ml of a saturated aqueous bicarbonate solution were added and the mixture stirred. The bottom $CH_2Cl_2$ layer was transferred via a cannula needle through a plug of celite/anhydrous $K_2CO_3$ into a $-30\,^\circ C$ cooled Schlenk tube. Solvent was slowly removed at $-20--30\,^\circ C$ to give orange powdery **4** as product. This product was immediately redissolved in 8 ml $CH_2Cl_2$ to form a clear orange solution which was cooled to $-78\,^\circ C$. 3 $\mu$l $Et_3N$ were added and an equal volume of propene (ca. 8 ml) condensed into the reaction tube. Addition of 150 $\mu$l (0.78 mmol) TMSOTf immediately generated a deep red solution of benzylidene **5**. The reaction mixture was allowed to warm to room temperature over the course of 4 h then stirred at

room temperature for 1 h with a constant purge through the reaction solution. 30 ml $Et_2O$ and 30 ml saturated aqueous bicarbonate solution were added and the solution stirred. The top reddish-brown ether layer was filtered through a plug of degassed neutral alumina. Solvent volume was reduced under vacuum to approximately 1 ml and this solution gas chromatographed. (A 12 foot stainless steel column of 20% QF-1 on 80-100 HP Chromosorb W was used with an oven temperature of 110°C and helium flow of 35 ml/min. The retention times of the *cis*-**8** and *trans*-**8** 1-methyl-2-phenylcyclopropanes were 23.5 and 26 min respectively.) Pure materials were collected by GC. The total isolated yield of cyclopropanes **8** was 13.4 mg (21% based on starting benzoyl) for *2SS* and 13.6 mg (22% based on starting benzoyl) for *2RS*. The ratio of *cis* and *trans* products was 2/3 and their $^1H$ NMR spectra matched those reported in the literature. The enantiomeric purity of the 1-methyl-2 phenyl cyclopropanes was determined by measuring their optical rotations in absolute ethanol and comparing them to the known absolute rotations of enantiomerically pure materials (optical purities are ±8%, See Table 1 for details).

*B. Reactions with vinyl acetate.* General procedure: 410 mg (0.8 mmol) of either benzoyl *2SS* or *2RS* was dissolved in 20 ml $CH_2Cl_2$ forming a clear orange solution. 120 μl MeOTf (1.1 mmol) were added and the solution stirred overnight at room temperature. As the reaction proceeded the solution turned dark red. Complete formation of heterocarbene **3** was evidenced by the disappearance of absorption bands for **2** in the IR and appearance of a single absorption band at 1990 $cm^{-1}$ for **3**. The heterocarbene solution was slowly added to a rapidly stirring −78°C $NaBH_4/NaOCH_3/CH_3OH$ solution (6.09 mmol, $Na^0$; 3.04 mmol $NaBH_4$ in 30 ml $CH_3OH$). The dark red color immediately discharged to clear orange upon addition. The reaction mixture was stirred at −78°C for 15–20 min and then warmed to −20°C. 30 ml $CH_2Cl_2$ and 30 ml saturated aqueous bicarbonate were added and the mixture stirred. The bottom orange $CH_2Cl_2$ layer was transferred via cannula needle through a plug of celite/anhydrous $K_2CO_3$ into a −30°C cooled Schlenk tube. Solvent was removed in vacuo at −20–−30°C to give **4** as an orange powder. To **4** was added 15 ml $CH_2Cl_2$ to form a clear orange solution. 3 μl $Et_3N$ was added and 310 μl (1.58 mmol) TMSOTf to generate a deep red solution of benzylidene **5**. Vinyl acetate (1 ml, 10.8 mmol) was added and the reaction mixture allowed to warm to room temperature over the course of 4 h. Then, 30 ml $Et_2O$ and 30 ml aqueous bicarbonate were added to the solution and the mixture stirred. The top red-brown ether layer was filtered through a plug of degassed neutral alumina. The solvent volume was reduced to approximately 1 ml in vacuo and the remaining solution gas chromatographed. (GC conditions: 20 foot stainless steel column of 20% QF-1 on 80-100 HP Chromosorb W was used with an oven temperature of 170°C and helium flow of 60 ml/min. The retention times of the *cis*-**9** and *trans*-**9** 1-acetoxy-2-phenylcyclopropanes were 40 and 45 min, respectively.) The total isolated yield of cyclopropanes **8** was 42.2 mg (30% based on starting benzoyl) for *2SS* and 40.8 mg (29% based on starting benzoyl) for *2SR*. The *cis*/*trans* isomer ratio was 4/1. The enantiomeric purity of the *cis*-**9** and *trans*-**9** 1-acetoxy-2-phenylcyclopropanes was determined by a $^1H$ NMR chiral shift experiment. Samples of the products were dissolved in $C_6D_6$ and $Eu(hfc)_3$ added incrementally. For the *cis*-1-acetoxy-2-phenylcyclopropanes the $H_A$ proton resonance was monitored as it moved downfield and eventually split out to give distinct resonances for the

enantiomeric *cis*-cyclopropanes. For the *trans*-1-acetoxy-2-phenylcyclopropanes the methyl peak was monitored. *2SS* and *2RS* gave *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes which were enantiomers of one another. The enantiomeric purity of the *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes obtained from *2SS* were 69 and 83% (±2%) and the enantiomeric purity of the *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes obtained from *2RS* were 74% and 92% (±2%). Assignments of the proton NMR signals of the cyclopropanes were established be decoupling experiments and comparison to known values of analogous *cis* and *trans* coupling constants.

*Cis-1-acetoxy-2-phenylcyclopropane.* $^1$H NMR ($C_6D_6$): δ 4.17 (ddd, 1H, $J_{AC}$ = 3.8, $J_{AB}$ = 6.8, $J_{AD}$ = 6.8 Hz) $H_A$; 1.84 (ddd, 1H, $J_{AB}$ = 6.8, $J_{BC}$ = 7, $J_{BD}$ = 9.7 Hz) $H_B$; 1.02 (ddd, 1H, $J_{AC}$ = 3.8, $J_{BC}$ = 7, $J_{CD}$ = 7 Hz) $H_C$; 0.76 (ddd, 1H, $J_{AD}$ = 6.8, $J_{BD}$ = 9.7, $J_{CD}$ = 7 Hz) $H_D$; 1.39 (s, 3H) C$H_3$; 7.19–7.34 (m, 5H), C$_6H_5$. $^{13}$C NMR ($CDCl_3$): δ 10.5 (t, $J$(CH) = 162 Hz) $C_3$; 20.5 (q, $J$(CH) = 129 Hz) $CH_3$; 21.9 (d, $J$(CH) = 160 Hz) $C$(2); 53.2 (d, $J$(CH) = 193 Hz) $CH$(1); 126.2 (d, $J$(CH) = 167 Hz); 127.9 (d, $J$(CH) = 160 Hz); 128.5 (d, $J$(CH) = 161 Hz): $C_6H_5$; 136.2, $C_{ipso}$; 171.2, $C$=O. Elemental analysis. Found: C, 75.03; H, 6.91. $C_{11}H_{12}O_2$ calc: C, 75.00; H, 6.82%.

*Trans-1-ethoxy-2-phenyl-cyclopropane.* $^1$H NMR ($C_6D_6$): δ 4.19 (ddd, 1H, $J_{AB}$ = 3.3, $J_{AC}$ = 3.6, $J_{AD}$ = 6.6 Hz) $H_A$; 2.03 (ddd, 1H, $J_{AB}$ = 3.3, $J_{BC}$ = 10, $J_{BD}$ = 7 Hz) $H_B$; 1.05 (ddd, 1H, $J_{AC}$ = 3.6, $J_{BC}$ = 10, $J_{CD}$ = 6.7 Hz) $H_C$; 0.86 (ddd, 1H, $J_{AD}$ = 6.6, $J_{BD}$ = 7, $J_{CD}$ = 6.7 Hz) $H_D$; 1.61 (s, 3H) C$H_3$; 7.14–7.34 (m, 5H) C$_6H_5$. $^{13}$C NMR ($CDCl_3$): δ 14.3 (t, $J$(CH) = 162 Hz) $C$(3); 20.4 (q, $J$(CH) = 129 Hz) $CH_3$; 22.9 (t, $J$(CH) = 160 Hz) $C$(2); 55.8 (t, $J$(CH) = 188 Hz) $C$(1); 126.1–128.3, $C_6H_5$; 139.5, $C_{ipso}$; 170.7, $C$=O. Elemental analysis. Found: C, 74.85; H, 6.94. $C_{11}H_{12}O_2$ calc: C, 75.00; H, 6.82%.

*Synthesis of 10SR and 10RR Cp(CO)(PEt$_3$)FeCH(OCH$_3$)C$_6$H$_5$*

This preparation was done as previously described by photolysis of (*S*)-$Cp(CO)_2FeCOC^*H(OCH_3)C_6H_5$ in the presence of $PEt_3$ yielding a 3/2 mixture of *10SR* and *10RR* [21]. The diastereomers were separated by column chromatography on Act. II–III basic alumina at −52°C using 25/1 hexanes/$Et_2O$. Diastereomer *10RR* eluted first. The diastereomeric purity was determined by $^1$H NMR integration of resonances for $H_\alpha$ at 4.93 ppm for *10SR* and 5.19 ppm for *10RR*. For the benzylidene transfer reactions described here *10RR* was > 98% diastereomerically pure and *10SR* was > 90% diastereomerically pure. Full spectroscopic data for these complexes have been published. The optical rotations for the diastereomers used in this study were (in n-hexane) $[\alpha]_{436}^{23} = +650°$ for *10RR* and $[\alpha]_{436}^{23} = -620°$ for *10RR*. The maximum rotations of *10RR* and *10SR* were +740° and −720°. If it is assumed that these values represent materials of 100% enantiomeric purity, complexes *10RR* and *10SR* used here are 87 and 86% enantiomerically pure. These purities were used in calculating optical purities of cyclopropanes from benzylidene transfer from *10RR* and *10SR* to vinyl acetate.

*Benzylidene transfer from 10RR and 10SR to vinyl acetate*

*General procedure*: 220 mg (0.57 mmol) **10** was dissolved in 7 ml $CH_2Cl_2$ and cooled to −78°C. Then 3 μl $Et_3N$ and 90 μl (0.98 mmol, 2 equivalents) TMSOTf added to generate a deep red solution of benzylidene **11**. 523 μl (5.7 mmol, 10

equivalents) vinyl acetate was added and the reaction mixture slowly warmed to room temperature over 4 h. $Et_2O$ (30 ml) and a saturated aqueous bicarbonate solution (30 ml) were added and the solution mixed. The top $Et_2O$ layer was filtered through a plug of neutral alumina. The water layer was extracted two times with 10 ml $Et_2O$, the $Et_2O$ extracts combined and solvent volume reduced to 1 ml. This solution was gas chromatographed as described earlier herein. The products *cis*- and *trans*-1-acetoxy-2-phenylcyclopropanes **9** were isolated in a 4/1 *cis*/*trans* ratio. Yields of cyclopropanes **9** were 24% (24.1 mg) from *10RR* and 21% (21 mg) from *10SR*. A $^1H$ NMR chiral shift experiment was performed as described earlier to determine the enantiomeric purity of the cyclopropanes. *10RR* gave identical *cis*- and *trans*-cyclopropane enantiomers to those obtained from *2RS* in 30% and 40% enantiomeric excess, respectively. *10RS* gave identical *cis*- and *trans*-cyclopropane enantiomers to those obtained from *2SS* in 31% and 37% enantiomeric excess respectively.

*Synthesis of* $Cp(CO)(PEt_3)Fe{=}CHC_6H_5^+ OTf^-$ *11*

8 mg ($2.3 \times 10^{-3}$ mmol) racemic **10** was dissolved in 500 μl $CD_2Cl_2$ in a 5 mm NMR tube, cooled to −78°C and one equivalent TMSOTf added to generate a deep red solution of **11**. The samples was characterized by NMR. $^1H$ NMR ($CD_2Cl_2$, $T = 202$ K): δ 0.85 (dt, 9H, $J = 7.7$, 18 Hz) $CH_3$; 1.67 (dq, 6H, $J = 7.7$, 38 Hz) P-$CH_2$; 5.48 (s, 5H) Cp; 7.56 (dd, 2H, $J = 7.5$, 7.5 Hz) $H_{meta}$; 7.74 (t, 1H, $J = 7.5$ Hz) $H_{para}$; 7.88 (d, 2H, $J = 7.5$ Hz) $H_{ortho}$; 17.04 (br s, 1H) $H_\alpha$. $^{13}C$ NMR ($CD_2Cl_2$, $T = 202$ K): δ 6.72, $CH_3$; 19.18 (d, $J = 31.3$ Hz) P-$CH_2$; 92.3, Cp; 136.0, 130.9, 129.6 $C_{ortho}$, $C_{meta}$, $C_{para}$; 152.1, $C_{ipso}$; 216.0 (d, $J = 30.1$ Hz) $CO$; 333.5 (d, $J = 23.1$ Hz) $=C$.

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