$H_3)C_6H_5$, *erythro*-$d_2$-**3a,b**, *threo*-$d_2$-**4a,b**, *threo*-$d_2$-**5a,b**, and *erythro*-$d_2$-**6a,b**, $^{13}C$ NMR data for *threo*-$d_2$-**5a,b** and *erythro*-$d_2$-**6a,b**, and $^1H$ NMR data and decoupling results for *cis*-2,*cis*-3-$d_2$-*r*-1-phenylcyclopropane, *trans*-2,*trans*-3-$d_2$-*r*-1-phenylcyclopropane, and *cis*-2,*trans*-3-$d_2$-*r*-1-phenylcyclopropane (13 pages). Ordering information is given on any current masthead page.

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# Resolution of the Chiral-at-Iron Acetyl Complexes $C_5H_5(CO)(PR_3)FeC(O)CH_3$ (R = $CH_3$, $CH_2CH_3$). Enantioselective Cyclopropane Synthesis Using the Chiral Carbene Complexes ($S_{Fe}$)- and ($R_{Fe}$)-$C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = $CH_3$, $CH_2CH_3$)

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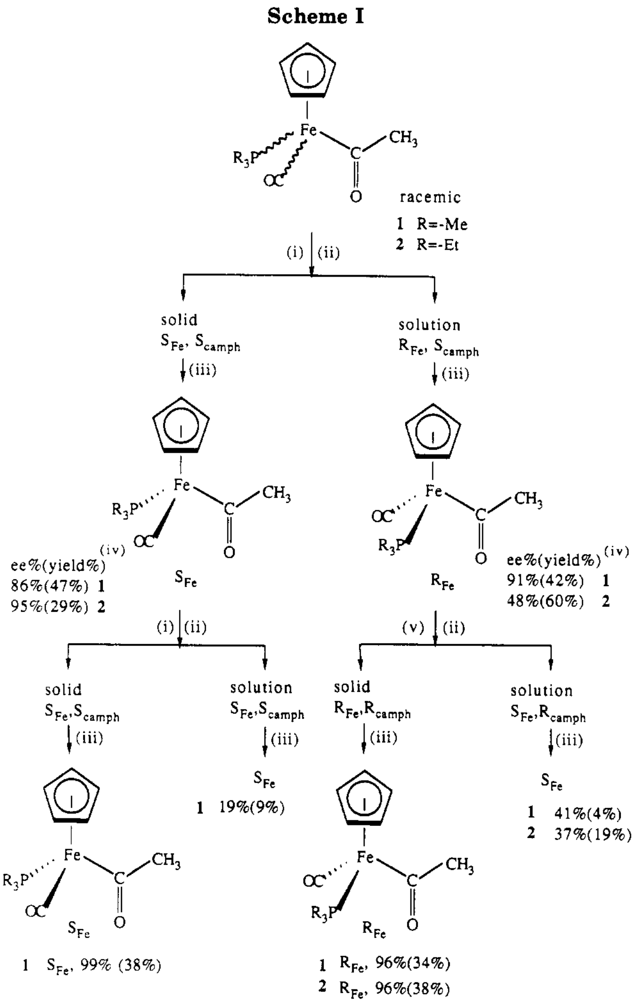
*Summary:* A simple and efficient method for resolving acetyl complexes $C_5H_5(CO)(PR_3)Fe{-}C(O)CH_3$ (R = $CH_3$, $CH_2CH_3$) has been developed. These acyl complexes were converted to optically pure carbene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = $CH_3$, $CH_2CH_3$) which transfer ethylidene to vinyl acetate with high enantioselectivity. The potential utility of $C_5H_5(CO)(PMe_3)Fe$ and $C_5H_5(CO)(PEt_3)Fe$ as chiral auxillaries is illustrated by the transfer reactions.

$C_5H_5(NO)(PPh_3)Re$ and $C_5H_5(CO)(PR_3)Fe$ have been extensively used as chiral auxillaries to carry out diastereoselective reactions[1–6] and, when the auxillary is optically pure, enantioselective reactions.[7–10] Of particular synthetic interest are iron acyl complexes of the type $C_5H_5(CO)(PR_3)FeC(O)R'$, since these species can be elaborated in many useful ways.[1–7,9,10] Brunner has prepared several optically pure acyl complexes.[11,12] For example, (*R*)- and (*S*)-$C_5H_5(CO)(PPh_3)Fe{-}C(O)CH_3$ were resolved via separation of the diastereomers of $C_5H_5(CO)(PPh_3)$-$Fe{-}C(O){-}O$–menthyl followed by reaction with $CH_3Li$.[11,13] We have achieved chromatographic separation of the diastereomers of $C_5H_5(CO)(PPh_2R^*)FeC(O)CH_3$ ($R^*$ =

Scheme I



(i) (1S)-(+)-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 1 and 2 used, i.e., maximum yield of a single enantiomer is 50%.
(v) (1R)-(-)-10-camphorsulfonic acid, $CH_2Cl_2$.

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(1) For examples from the Gladysz lab, see: (a) Constable, A. G.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, C21. (b) Kiel, W. A.; Lin, G.-H.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisentein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4862. (c) Kiel, W. A.; Lin, G.-H.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (d) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103.

(2) For examples from the Davies lab, see: (a) Baird, G. J.; Davies, S. G. *J. Organomet. Chem.* **1983**, *248*, C1. (b) Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* **1985**, *26*, 2129. (c) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764. (d) Ayscough, A. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1648. (e) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *J. Organomet. Chem.* **1985**, *285*, 213. (f) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *Tetrahedron Lett.* **1985**, *26*, 2125. (g) Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1446. (h) Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, *25*, 1845.

(3) For examples from the Liebeskind lab, see: (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Liebeskind, L. S.; Fengl, R.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3075, 3079. (c) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (d) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

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(5) Ojima, I.; Kwan, *J. Am. Chem. Soc.* **1988**, *110*, 5617.

(6) Herndon and co-workers have demonstrated that Michael addition reactions of $C_5H_5(CO)(PBu_3)FeCOCH{=}CHR$ exhibit high diastereoselectivity. Thus, $PBu_3$ serves to effectively shield one face of the double bond from nucleophilic attack. Herndon, J. W.; Wu, C.; Ammon, H. L. *J. Org. Chem.* **1988**, *53*, 3875.

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(12) Diastereomers of $Cp'(CO)Fe(COR)P(C_6H_5)_2NR'R^*$ ($Cp'$ = $C_5H_5$, $C_9H_7$(indenyl); R = $CH_3$, $C_2H_5$, $CH(CH_3)_2$, $CH_2C_6H_5$; $R'$ = H, $CH_3$, $C_2H_5$, $CH_2C_6H_5$; $R^*$ = (*S*)-$CH(CH_3)C_6H_5$) have been separated by liquid chromatography and fractional crystallization: Brunner, H.; Vogt, H. *J. Organomet. Chem.* **1980**, *191*, 181.

(13) Optically pure complexes (*S*)- and (*R*)-$C_5H_5(CO)(PPh_3)FeC(O)$-$CH_3$ are commercially available from BP Chemicals[10] and Fluka. Procedures used for their preparation have not been published.

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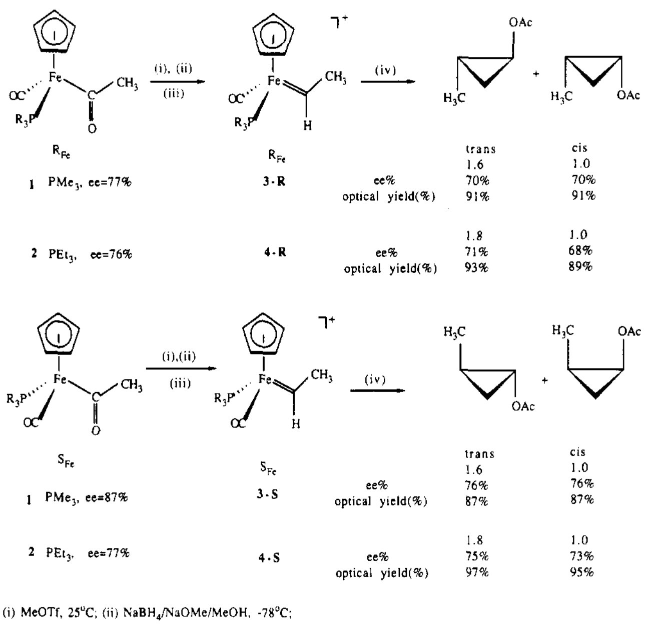
### Scheme II



(i) MeOTf, 25°C; (ii) NaBH$_4$/NaOMe/MeOH, -78°C;
(iii) TMSOTf, -78°C; (iv) -78°C to 25°C, 0.1 equiv. NEt$_3$ and 10 equiv. vinyl acetate.

(*S*)-2-methylbutyl).[7] No convenient procedures are available for resolution of simple trialkylphosphine acyl complexes. Described here is an easy and inexpensive procedure for resolution of $C_5H_5(CO)(PR_3)FeC(O)CH_3$ (**1**, R = $CH_3$; **2**, $CH_2CH_3$) which should prove to be a general method for resolution of chiral metal acyl complexes. The utility of optically pure **1** and **2** is illustrated by conversion to the corresponding optically pure iron ethylidene complexes followed by ethylidene transfer to vinyl acetate to form cyclopropanes with high enantioselectivity.

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 give the corresponding methoxy- or hydroxycarbene salts.[4,7,14] Protonation of **1**[15] and **2**[15] ($\nu_{CO}$ = 1910 cm$^{-1}$) in $CH_2Cl_2$ with either (1*S*)-(+)- or (1*R*)-(−)-10-camphorsulfonic acid leads to complete conversion to 1:1 mixtures of diastereomeric hydroxycarbene salts ($\nu_{CO}$ = 1967–1977 cm$^{-1}$). These diastereomeric carbene salts can be readily separated by successive crystallizations in $CH_2Cl_2/Et_2O$ at −25 °C, and optically pure **1** or **2** can be recovered by simple neutralization. Results are summarized in Scheme I, and a typical resolution procedure is described.[16] The enantiomeric excesses of the acetyl complexes **1** and **2** were determined by $^1H$ NMR spectroscopy using the chiral shift reagent (+)-Eu(hfc)$_3$.[15] Absolute configurations were assigned by using the sign and magnitude[17] of $[\alpha]^{23}_{436}$ in analogy with similar acyl complexes of known configuration.[7,12,13]

Optically pure **1** and **2** are readily converted to optically pure ethylidene complexes $C_5H_5(CO)(PMe_3)Fe{=}CHCH_3^+$ (**3**) and $C_5H_5(CO)(PEt_3)Fe{=}CHCH_3^+$ (**4**) using standard procedures.[4] Methylation of **1** and **2** with methyl triflate ($CH_2Cl_2$) followed by hydride reduction using $NaBH_4/CH_3OH/CH_3ONa$ yields $C_5H_5(CO)(PMe_3)FeCH(OCH_3)CH_3$ (**5**)[15] and $C_5H_5(CO)(PEt_3)FeCH(OCH_3)CH_3$ (**6**).[15] Treatment of either **5** or **6** with TMSOTf ($CH_2Cl_2$, −78 °C) yields carbene salts **3** and **4**. Both *anticlinal* and *synclinal* isomers are observed at −104 °C (**3**-anticlinal:**3**-synclinal = ca. 4.6:1.0, **4**-anticlinal:**4**-synclinal = ca. 10.9:1.0), and rates of interconversion have been determined by using variable-temperature $^1H$ NMR data.[4a]

Enantioselective ethylidene transfers from **3** and **4** to vinyl acetate were performed, and results are summarized in Scheme II. Reactions were conducted by adding TMSOTf (1.1 equiv) to the ether complexes (**5** or **6**) in $CH_2Cl_2$ (−78 °C) containing vinyl acetate (10 equiv) and triethyl amine (0.1 equiv). Reaction mixtures were warmed to 25 °C and stirred for 2 h prior to workup. The product *cis*- and *trans*-cyclopropanes[15] were separated and purified by GC; yields of 50–60% for **3** and 27–35% for **4** were determined by using nonane as an internal standard. Enantiomeric excesses were determined by $^1H$ NMR spectroscopy using the chiral shift reagent (+)-Eu(hfc)$_3$. Optical yields for all products are high and fall in the range of 89–97%. Absolute configurations are unknown. Configurations shown in Scheme II are based on analogy with ethylidene transfers to styrene[7] and are consistent with the most likely mechanism for transfer that involves alkene attack on the more reactive synclinal isomers followed by $C_\gamma$–$C_\alpha$ bond formation via inversion of the configuration at $C_\alpha$.[4a,18,19] The high ee's obtained 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 may place an arene ring in a face-to-face orientation with the planar carbene ligand.[2h,5,6]

In summary, a simple and efficient method for resolving acyl complexes $C_5H_5(CO)(PR_3)FeC(O)CH_3$ (R = $CH_3$, $CH_2CH_3$) has been developed and is potentially applicable to any chiral acyl complex sufficiently basic to be protonated by alkyl sulfonic acids. Optically pure carbene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = $CH_3$, $CH_2CH_3$) were used to carry out ethylidene transfer with high enantioselectivity that illustrates the potential utility of $C_5H_5(CO)(PMe_3)Fe$ and $C_5H_5(CO)(PEt_3)Fe$ as chiral auxillaries.

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**Supplementary Material Available:** $^1H$, $^{13}C$ NMR, IR, and elemental analysis data for **1**, **2**, **5**, and **6** and $^1H$ NMR data for *cis*-1-acetoxy-2-methylcyclopropane and *trans*-1-acetoxy-2-methylcyclopropane and $^1H$ NMR shift experiments on **1-S** using (+)-Eu(hfc)$_3$ (4 pages). Ordering information is given on any current masthead page.

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[14] Green, M. L. H.; Swanwick, M. G. *J. Chem. Soc. A* 1971, 794.

[15] See supplementary material for $^1H$ and $^{13}C$ NMR spectral data, and elemental analyses and $^1H$ NMR shift experiments.

[16] A 0.49-g sample of **1** (1.83 mmol) in 15 mL of $CH_2Cl_2$ was treated with 0.52 g (2.24 mmol) of (1*S*)-(+)-10-camphorsulfonic acid. Ether (45 mL) was added, and the solution was stirred at room temperature for 10 min. A small additional quantity of $CH_2Cl_2$ was added if any precipitation was evident. The homogeneous solution was then cooled to −25 °C overnight. Crystalline solid was isolated by filtration and (S)-**1** (47% yield and 86% ee) was regenerated by neutralization with aqueous $K_2CO_3$. Neutralization of the solution phase results in (*R*)-**1** (42% yield and 91% ee). Recycling (*S*)-**1** in analogous fashion results in 80% yield (overall yield 38%) of (*S*)-**1** (>99% ee). Similarly, treatment of (*R*)-**1** with (1*R*)-(−)-10-camphorsulfonic acid and neutralization of the solid fraction following crystallization results in 80% yield (overall yield 34%) of (*R*)-**1** (96% ee).

[17] $[\alpha]^{23}_{436}$ = −500° for (*S*)-**1** (>99% ee) and $[\alpha]^{23}_{436}$ = +493° for (*R*)-**1** (96% ee); $[\alpha]^{23}_{436}$ = −529° for (*S*)-**2** (95% ee) and $[\alpha]^{23}_{436}$ = +545° for (*R*)-**2** (96% ee).

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