Table II. Important Distances (Å) and Angles (deg) for Molecule 1[a]

Bond Distances			
Sn1–Cl1	2.624 (2)	Sn2–Cl1	2.607 (2)
Sn1–Cl2	2.627 (2)	Sn2–Cl2	2.633 (2)
Sn1–Cl12	2.890 (3)	Sn2–Cl11	2.891 (2)
Sn1–Cl22	2.986 (3)	Sn2–Cl24	2.880 (3)
Sn1–D1	3.24	Sn2–D3	3.26
Sn1–D2	3.11	Sn2–D4	3.20
Al1–Cl11	2.177 (4)	Al2–Cl24	2.164 (4)
Al1–Cl12	2.167 (4)	Al2–Cl22	2.169 (4)
Al1–Cl13	2.098 (4)	Al2–Cl21	2.104 (4)
Al1–Cl14	2.100 (4)	Al2–Cl23	2.116 (4)
Bond Angles			
Sn1–Cl1–Sn2	101.9 (1)	Sn1–Cl2–Sn2	101.1 (1)
Cl1–Sn1–Cl2	78.4 (1)	Cl1–Sn2–Cl2	78.6 (1)
Cl12–Sn1–Cl22	169.1 (1)	Cl11–Sn2–Cl24	166.5 (1)
D1–Sn1–D2	101.9	D3–Sn2–D4	99.7
Sn1–Cl12–Al1	120.7 (1)	Sn2–Cl11–Al1	117.8 (1)
Sn1–Cl22–Al2	115.6 (1)	Sn2–Cl24–Al2	122.3 (1)
interplane angles		C10–C15/C20–C25	66.3
		C30–C35/C40–C45	65.3
angle Sn–D/ring plane normal		C10–C15	8.8
		C20–C25	5.0
		C30–C35	10.4
		C40–C45	6.9

[a] D1–D4 are centroids of the respective benzene rings.

phosphate).[6] All these compounds have in common that only *one* arene molecule is attached to the group 14 metal center. In an attempt to obtain a first example of bis(arene) complexes, the reaction of $Sn(AlCl_4)_2$ with aromatic hydrocarbons was reinvestigated, and the results are presented in this communication.

Treatment of the freshly prepared molten salt $Sn(AlCl_4)_2$ with benzene under reflux conditions, followed by cooling the resulting solution, affords a benzene-containing colorless crystalline product, mp 110 °C, which is stable at room temperature. The crystal structure analysis[7] of this compound revealed the presence of a dimeric species of the composition $[(\eta^6\text{-}C_6H_6)_2SnCl(AlCl_4)]_2\cdot C_6H_6$ (1) with two η^6-coordinated benzene rings at each tin atom and one molecule of crystal benzene with no specific metal contacts (Figure 1). Two $(\eta^6\text{-}C_6H_6)_2Sn$ dications are bridged by two 1,3-bidentate tetrahedral $AlCl_4^-$ anions and by two two-coordinate Cl^- anions. The Sn(II) centers adopt a distorted octahedral coordination geometry. The structure can also be described as an eight-membered ring in an elongated chair form composed of Sn(1)–Cl(12)–Al(1)–Cl(11)–Sn(2)–Cl(24)–Al(2)–Cl(22) (Figure 2). The tin and the chlorine atoms of this ring are almost coplanar (maximum deviation from planarity 0.11 Å for Sn2), and the Al atoms lie above and below this plane, respectively (inclination angles of 116.17 and 112.43° with the planes Cl11–Al1–Cl12 and Cl22–Al2–Cl24, respectively). Although the molecule has no crystallographic symmetry, its structure approaches C_{2h} symmetry. Each tin atom is situated nearly centroid above its two arene rings, which are inclined with respect to each other, forming angles of 101.9° (Sn1) and 99.7° (Sn2), respectively. The angles between the normals to the arene planes and the Sn–D (see Table II) lines in the range between 5.0 and 10.4° are evidence for η^6-coordination. The observed very long distances of the Sn atoms from the ring centers (3.11 and 3.24 Å for Sn(1) and 3.26 and 3.20 Å for Sn(2)) indicate only very weak attractive forces between the two components. The Sn–Cl distances vary between 2.607 (2) and 2.633 (2) Å (Cl^- bridge) and 2.880 (3) and 2.986 (3) Å ($AlCl_4^-$ bridge). The packing of the molecules in the unit cell is such that there are no specific contacts between the individual dimers.

We note that there is an interesting parallel for the structure of 1 in one of the ylide complexes reported previously from this laboratory.[8] In $[(CH_3O)_3Ti(CH_2)_2P(CH_3)_2]_2$, the Ti(IV) are the centers of a similar pair of edge-sharing, doubly-chelated octahedra.

It is also noteworthy that the analogous reactions between freshly prepared $Sn(AlCl_4)_2$ melts and arenes of higher donor capability like hexamethylbenzene, xylene, or mesitylene do not lead to the formation of bis(arene) complexes. In the case of hexamethylbenzene, the tetrameric species $[(\eta^6\text{-}C_6Me_6)SnCl(AlCl_4)]_4$ was isolated (when chlorobenzene was used as a solvent),[5] whereas no crystalline arene complexes were obtained with xylene and mesitylene.[9] With lead as the central atom and benzene as the donor component, the monoarene complex $(\eta^6\text{-}C_6H_6)Pb(AlCl_4)_2\cdot C_6H_6$ was isolated.[4b] In the case of the corresponding $Pb(AlBr_4)_2$ system, benzene-containing crystals were formed, which were shown to be composed of cross-linked $Pb(AlBr_4)_2$ units without any metal–arene contacts.[5]

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages); a listing of structural factors (31 pages). Ordering information is given on any current masthead page.

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When Phenylcyclopropanes Are Generated by γ-Ionization of *erythro*- and *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, Cleavage of the Fe–$C_\alpha$ Bond Occurs with Inversion of Configuration of C_α

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Summary: 2,3-Dideuterio-r-1-phenylcyclopropanes are stereospecifically generated by abstraction of the γ-methoxide groups from *erythro*- and *threo*-d_2-C_5H_5-$(CO)_2Fe$–CHD–$CHDCH(OCH_3)C_6H_5$ using TMSOTf. 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.

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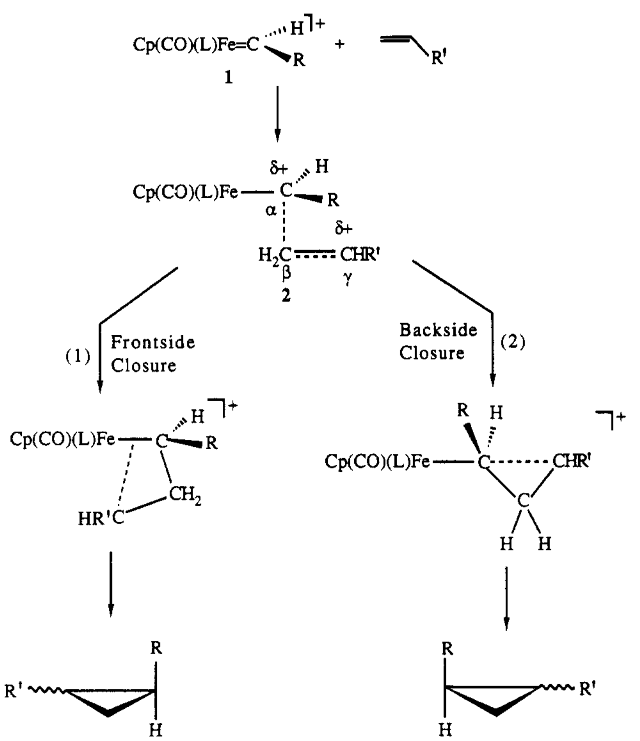
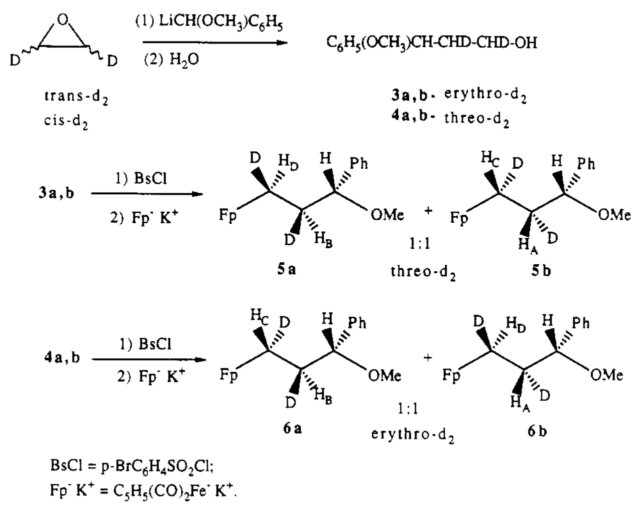
Scheme I

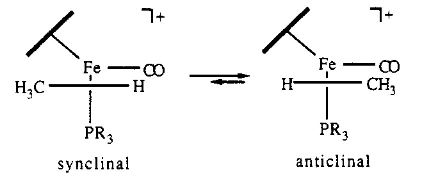


Scheme II



Electrophilic iron carbene complexes, $C_5H_5(CO)(L)$-$Fe{=}CHR^+$, react with alkenes to give cyclopropanes.[1-8] The initial stage of the transfer mechanism involves attack of the iron carbene on the alkenes to generate positive charge at C_γ.[1,2,4,8] For example, in the reaction of C_5H_5-$(CO)_2Fe{=}CHCH_3^+$ with $CH_2{=}CHC_6H_4(\text{-}p\text{-}OCH_3)$ we have demonstrated that a true γ-benzyl carbocation intermediate, $C_5H_5(CO)_2FeCH(CH_3)CH_2C^+(H)(C_6H_4OCH_3)$, is generated.[4] Two mechanisms for attack of electrophilic C_γ on C_α which result in C_γ–C_α bond formation and Fe–C_α bond cleavage are shown in Scheme I. One involves frontside attack of electrophilic C_γ at the Fe–C_α bond and retention of C_α stereochemistry while the other involves backside attack of C_γ and inversion of C_α stereochemistry.

The latter possibility was first suggested by us[2a] based on the close analogy with cyclopropane formation from solvolysis of γ-tin derivatives in which the Sn–C_α bond is cleaved with inversion at C_α.[9,10] Mechanism 2 is further supported by stereochemical[3,11] and relative reactivity studies[11,12] which strongly suggest that $C_5H_5(CO)(L)Fe{=}CHR^+$ systems react with alkenes via the minor *synclinal* isomers (eq 1) with backside attack of electrophilic C_γ on C_α.



(1)

To further probe the stereochemistry of Fe–C_α cleavage, we have examined ionization of γ-iron derivatives stereospecifically deuterium labeled at C_α and C_β. As noted above, this method for generating cyclopropanes is well established for γ-tin,[9,13] γ-silicon,[14] and γ-boron[15] deriva-

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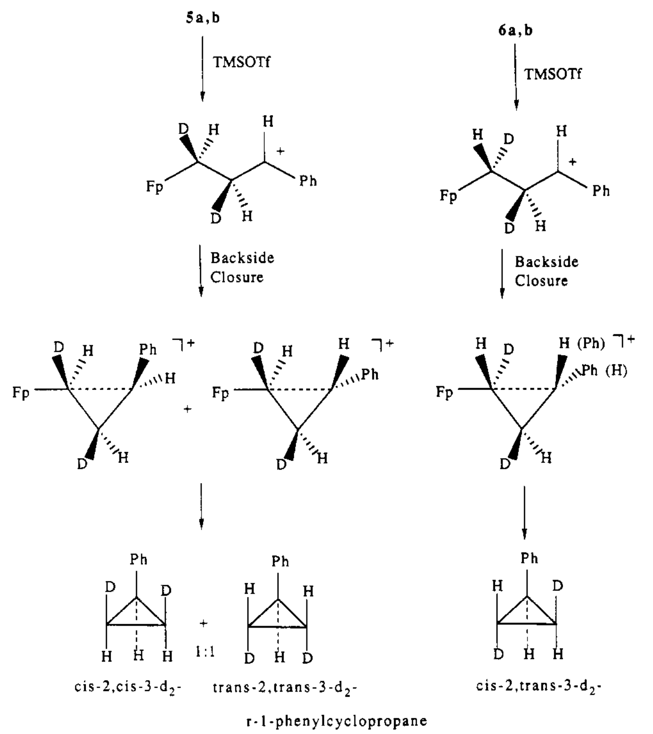
Scheme III



tives and recently Casey[16] has demonstrated that cyclopropane itself can be generated from reaction of $C_5H_5(CO)_2Fe$–$CH_2CH_2CH_2Br$ with Ag^+. As an extension of our earlier work on the intermediacy of γ-benzyl carbocations in transfer reactions,[4] we report here stereospecific formation of 2,3-dideuterio-*r*-1-phenylcyclopropanes by abstraction of the γ-methoxide group from *erythro*- and *threo*-d_2-$C_5H_5(CO)_2Fe$–CHD–CHD–$CH(OCH_3)C_6H_5$ using trimethylsilyl triflate (TMSOTf). These results establish Fe–C_α bond cleavage with inversion of configuration at C_α.

As shown in Scheme II, the stereospecifically labeled γ-methoxy iron complexes *threo*(*syn*)- and *erythro*-(*anti*)-d_2-$C_5H_5(CO)_2Fe$–CHD–CHD–$CH(OCH_3)C_6H_5$, **5a,b**[17] and **6a,b**,[17] respectively, were synthesized from *trans*- and *cis*-ethylene-d_2 oxides.[18] Treatment of *trans*-ethylene-d_2 oxide with $LiCH(OCH_3)C_6H_5$[19] gives *erythro*(*anti*)-d_2 alcohols **3a,b**[17,21] (75–80%). Similarly, *cis*-ethylene-d_2 oxide leads to *threo*(*syn*)-d_2 alcohols **4a,b**.[17,21] Conversion of **3a,b** and **4a,b** to brosylates followed by S_N2 displacement using $C_5H_5(CO)_2Fe^-$ yields **5a,b** and **6a,b**, respectively (60%). The stereochemistry of each step has literature precedent,[22] and the expected configurations of **5a,b** and **6a,b** were verified by determination of vicinal $^3J_{HH}$ coupling constants and $\{^1H, {}^1H\}$ COSY 2D NMR experiments.[23]

Formation of d_2-phenylcyclopropanes by ionization of **5a,b** and **6a,b** were carried out by addition of TMSOTf (1.0 equiv) to CH_2Cl_2 solutions of **5a,b** or **6a,b** at −78 °C containing triethylamine (0.1 equiv) followed by warming to 25 °C overnight. The crude d_2-phenylcyclopropanes were purified by GC; yields were determined to be 70–75% by use of an internal standard.

As illustrated in Scheme III, the *threo*-d_2 isomers **5a,b** give a 1:1 mixture of *cis*-2,*cis*-3-d_2- and *trans*-2,*trans*-3-d_2-*r*-1-phenylcyclopropanes while the *erythro*-d_2 isomers **6a,b** yield a single product, *cis*-2,*trans*-3-d_2-*r*-1-phenylcyclopropane. The configurations of labeled cyclopropanes are readily assigned by ^1H NMR analysis. For example, upon decoupling H_1, the H_2 and H_3 signals of the *cis*-2,*trans*-3-d_2 isomer appear as doublets ($^3J_{H2H3}$ = 6.4 Hz) while similar decoupling of H_1 applied to the 1:1 mixture of *cis*-2,*cis*-3-d_2 and *trans*-2,*trans*-3-d_2 isomers results in simplification of H_2 and H_3 to sharp singlets.[17]

The deuterium-labeling patterns observed are consistent only with cyclopropane ring formation by backside attack of electrophilic C_γ on C_α with net inversion of stereochemistry at C_α (mechanism 2 in Scheme I). Frontside attack of C_γ on the Fe–C_α bond and cleavage with retention of configuration lead to the converse labeling results. While a discrete benzyl carbocation is shown in Scheme III, it is also possible that γ-ionization is synchronous with C_α–C_γ bond formation and Fe–C_α bond cleavage.

These observations coupled with earlier results[1–4,11,12] lead to a detailed mechanistic description of the carbene transfer reaction: The electrophilic iron carbene, 1, attacks the alkene to generate an electrophilic center at C_γ. In cases where C_γ possesses a strongly electron-donating group, a stabilized carbocation intermediate is formed with sufficient lifetime to allow C_γ–C_β bond rotation.[4] The developing (or full)[24] γ-carbocation then attacks the Fe–C_α bond at the backside such that C_α stereochemistry is inverted. When substituted carbene complexes of the type $C_5H_5(CO)(L)Fe{=}CHR^+$ are employed, the transfers proceed primarily via the less stable but more reactive *synclinal* isomers as opposed to the major *anticlinal* isomers (eq 1). In the case of enantiomerically pure systems $C_5H_5(CO)(L)Fe^*{=}CHR^+$, the absolute stereochemistry and high enantiomeric excesses of the cyclopropane products are completely consistent with reaction through the *synclinal* isomers via mechanism 2.[3]

Acknowledgment is made to the National Institute of Health (GM28938) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank E. L. Eliel for helpful discussions.

Supplementary Material Available: ^1H and ^{13}C NMR and elemental analysis data for $(n\text{-}Bu)_3SnCH(OCH_3)C_6H_5$ and $C_6H_5CH(OCH_3)CH_2CH_2OH$, ^1H and ^{13}C NMR, IR, and elemental analysis data for $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, ^1H NMR data for phenylcyclopropane, $\{^1H, {}^1H\}$ COSY 2D NMR spectra for $C_6H_5CH(OCH_3)CH_2CH_2OH$, $C_5H_5(CO)_2FeCH_2CH_2CH(OC-$

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(19) $LiCH(OCH_3)C_6H_5$ were generated by lithium–tin exchange reaction between *n*-BuLi and $(n\text{-}Bu)_3SnCH(OCH_3)C_6H_5$.[17,20]

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(23) The β- and α-hydrogens H_A, H_B, H_C, and H_D in $Cp(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$[17] appear at δ 2.15 (H_A), 1.95 (H_B), 1.74 (H_C), and 1.36 ppm (H_D). Decoupling experiments establish $J(H_AH_C)$ = 4.2 Hz, $J(H_AH_D)$ = 13.2 Hz, $J(H_BH_D)$ = 4.7 Hz, and $J(H_BH_C)$ = 13.1 Hz. In **5a,b**, $\{^1H, {}^1H\}$ COSY 2D NMR experiments show that H_A correlates with H_C and H_B with H_D. H_A and H_C appear as doublets with J = 4.2 Hz and H_B and H_D as doublets with J = 4.7 Hz verifying structures **5b** and **5a**, respectively. In **6a,b**, $\{^1H, {}^1H\}$ COSY 2D NMR experiments show that H_A correlate with H_D and H_B with H_C. H_A and H_D appear as doublets with J = 13.2 Hz and H_B and H_C as doublets with J = 13.1 Hz, establishing structures **6b** and **6a**, respectively.

(24) A concerted process can not be distinguished from a mechanism involving a discrete γ-carbocation with insufficient lifetime to allow C_γ–C_β bond rotation prior to C_α–C_γ bond formation.

$H_3)C_6H_5$, *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.

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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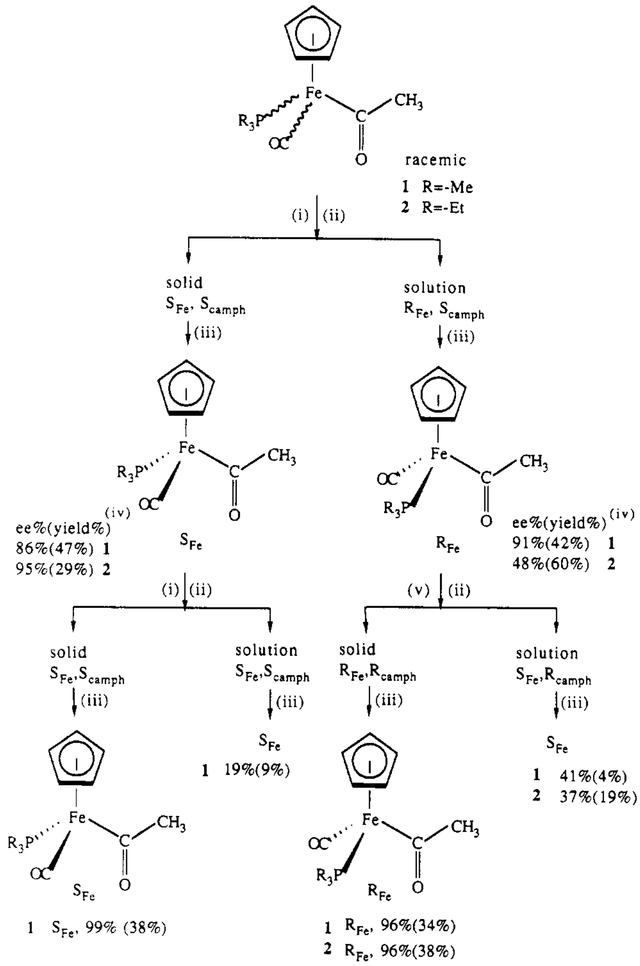
Summary: A simple and efficient method for resolving acetyl complexes $C_5H_5(CO)(PR_3)Fe{-}C(O)CH_3$ (R = CH_3, CH_2CH_3) has been developed. These acyl complexes were converted to optically pure carbene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = CH_3, CH_2CH_3) which transfer ethylidene to vinyl 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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(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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(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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