Induction of metal-centered chirality by planar chirality in [Fe{η-C$_5$H$_2$Me(R^1)(CO$_2$R^2)}(COR)(CO)(PR$_3$)] complexes

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The reaction of planar-chiral (alkyl)(cyclopentadienyl)dicarbonyliron complexes with triphenylphosphine gives [Fe{η-C$_5$H$_2$Me(R^1)(CO$_2$R^2)}(CO)(COR)(PPh$_3$)] with a high diastereoselectivity (> 90%) for the induction of metal-centered chirality.

Optically active organometallic complexes have increasingly become useful in application to organic syntheses and mechanistic studies. Among the complexes, optically active cyclopentadienyl–metal complexes such as planar-chiral and chiral-at-metal cyclopentadienyl complexes have received recent interest.[1] Several asymmetric reactions using the latter complexes including [Fe(η-C$_5$H$_5$)(COR)(CO)(PR$_3$)],[2] [Re(η-C$_5$H$_5$)(NO)(PPh$_3$)(ArCHO)][PF$_6$][3] and [Rh(η-C$_9$H$_6$-1-(CH$_2$)$_m$PR$_2$)(COR)I][4] have appeared in the literature, whereas successful examples, in which a stereocontrol reaction occurring at a metal center is effectively governed by a planar chirality, are scarce. Information about the stereochemistry controlled by a certain chirality source is of prime importance in new applications to asymmetric reactions.

We previously showed a new method for the synthesis of planar chiral cyclopentadienyl–cobalt,[5] –rhodium[6] and –ruthenium[7] complexes using a chiral trisubstituted cyclopentadiene and isolated them in an enantiomerically pure form. Here we have applied this method to the preparation of planar chiral (alkyl)(cyclopentadienyl)dicarbonyliron complexes and found that they undergo asymmetric induction of metal-centered chirality controlled by the planar chirality [eqn. (1)].
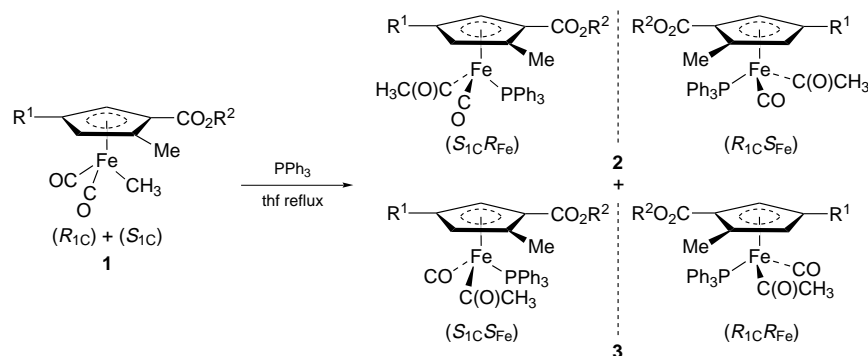
[Fe{η-C$_5$H$_2$Me(R^1)(CO$_2$R^2)}(CO)$_2$R] + L →
  [Fe*{η-C$_5$H$_2$Me(R^1)(CO$_2$R^2)}(COR)(CO)L]   (1)

It is well known that cyclopentadienyliron–alkyl complexes, [Fe(η-C$_5$H$_5$)(CO)$_2$R], undergo a migratory insertion of carbon monoxide on treatment with phosphorus compounds such as phosphines and phosphites, and afford three-legged piano-stool iron-acyl complexes, [Fe(η-C$_5$H$_5$)(CO)(PR$_3$)(COR)], which show chirality at the metal center.[8] Several reports have appeared on the induction of iron-centered chirality,[9] however only a modest diastereoselectivity of the asymmetric induction has been attained using chiral cyclopentadienyl ligands.[9b] Here we report the effective induction of metal-centered chirality in

the reaction of planar-chiral (alkyl)(trisubstitutedcyclopentadienyl)dicarbonyliron complexes with phosphines.

We synthesized the planar-chiral iron–alkyl complexes **1** by a literature method starting from trisubstituted cyclopentadienes.[10]
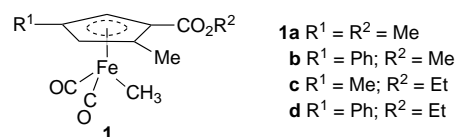
We investigated the influence of the planar chirality on the stereochemistry of a reaction occurring at the iron center in the reaction with phosphines giving acetyl iron complexes. Thus racemic iron–methyl complexes **1** ($R_{1c} + S_{1c}$) were heated with 5 equiv. of triphenylphosphine in thf for 48 h and acetyl complexes were obtained as a stereoisomeric mixture (Scheme 1), which were purified by column chromatography on alumina and identified by ^{1}H and ^{31}P NMR and IR spectroscopy. The resulting acetyl complexes possess two chiral centers, *i.e.* metal-centered chirality and planar chirality, and hence may exist as a mixture of two diastereomerically related pairs of enantiomers **2**(SR,RS) and **3**(SS,RR). The ratio of **2** to **3** has been determined by ^{1}H NMR† and HPLC‡ using a chiral column. The diastereoselectivities found in the above reactions are summarized in Table 1 along with chemical yields. The planar chirality effectively induces iron-centered chirality, and the size of a range of substituents R^1 on the cyclopentadienyl ligand strongly affects the diastereoselectivity of the reaction. A methyl group on the cyclopentadienyl ring gives a modest diastereoselectivity of *ca.* 75:25 while a larger phenyl group results in an increased diastereoselectivity up to *ca.* 95:5. It has already been reported that planar-chiral [Fe(η-C$_5$H$_3$Me-1-Ph-3)(CO)$_2$Me] did not exhibit any diastereoselectivities upon reaction with triphenylphosphine[9a] and even a diastereomeric analog bearing a chiral (S)-binaphthyl group on the cylopentadienyl ring showed only a modest diastereoselectivity of 40%.[9b] The high diastereoselectivity (*ca.* 90% de) observed in the

Scheme 1

Table 1 Asymmetric induction of planar-chiral [Fe{η-C$_5$H$_2$Me(R^1)-(CO$_2$R^2)}(CO)$_2$Me] complexes on treatment with PPh$_3$

Product	R^1	R^2	Yield (%)	2:3^a
2a, 3a	Me	Me	80	74:26
2b, 3b	Ph	Me	58^b	96:4
2c, 3c	Me	Et	85	75:25
2d, 3d	Ph	Et	52^b	95:5

^{a} Determined by HPLC using Chiralcel OD and ^{1}H NMR analyses. ^{b} Some decomposition of **1** was observed during the reaction, but the crude and purified products showed the same ratio of **2** to **3**.

present work may be attributed to an effective asymmetrical environment constructed by three suitable substituents, *i.e.* small, moderate and large groups, on the cyclopentadienyl ring.

A diastereomeric mixture of acetyl complexes was separated into two diastereomerically related pairs of enantiomers, **2** and **3**, by fractional crystallization from hexane–benzene. X-Ray crystallographic analysis has been performed for the major isomer **2c** (Fig. 1) and revealed that the absolute configuration is a pair of (*SR*) and (*RS*) configurational isomers, indicating that planar chirality S_{1c} induces metal-centered chirality R_{Fe} in the reaction of **2** with PPh$_3$.§,¶ In addition, the diastereo-selectivity in the present reaction has been found to be thermodynamically controlled since a separate experiment showed that pure diastereomer **2c** was converted to a mixture of
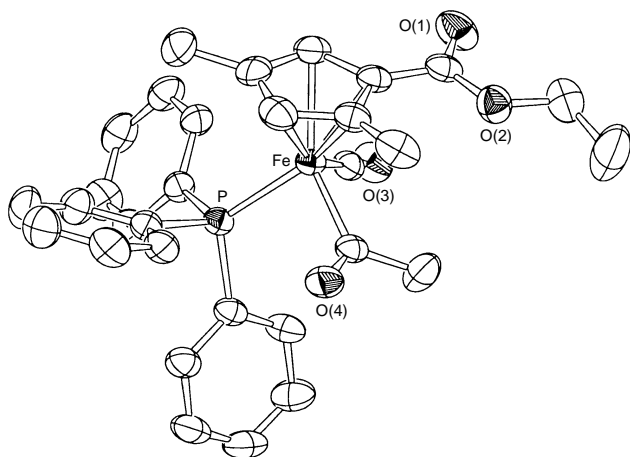

Fig. 1 Molecular structure of **2c** with hydrogen atoms omitted for clarity

2c and **3c** with a diastereoisomer ratio of 75:25 when heated in thf for 48 h which is the same diastereoisomeric ratio as observed in the reaction of **1c** with triphenylphosphine under the same reaction conditions.

Footnotes and References

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† *Selected data*: **2c**: reddish orange crystal. IR(Nujol) 1930, 1720, 1610 cm^{-1}. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 4.86 (d, 1 H), 4.42–4.35 (q, 2 H), 3.98 (t, 1 H), 2.40 (s, 3 H), 1.62 (s, 3 H), 1.51 (s, 3 H), 1.21 (t, 3 H). ^{31}P NMR (C$_6$D$_6$, PPh$_3$): δ 73.12. **3c**: yellow orange crystal. IR(Nujol) 1930, 1720, 1610 cm^{-1}. ^{1}H NMR (270 MHz, C$_6$D$_6$): δ 4.60 (d, 1 H), 4.16–4.03 (q, 2 H), 3.86 (t, 1 H), 2.60 (s, 3 H), 2.37 (s, 3 H), 1.33 (s, 3 H), 0.94 (t, 3 H). ^{31}P NMR (C$_6$D$_6$, PPh$_3$): δ 71.55.

‡ The HPLC analyses were carried on a chiral stationary phase HPLC (Daicel Chiralcel OD).

§ *Crystal data* for **2c**: C$_{31}$H$_{31}$FeO$_4$P, M = 554.40, triclinic, space group $P\bar{1}$, a = 10.651(2), b = 13.604(2), c = 9.611(2) Å, α = 95.10(1), β = 103.51(1), γ = 83.01(1)°, U = 1341.3(4) Å^3, Z = 2, D_c = 1.37 g cm^{-3}, μ = 6.53 cm^{-1}, T = 293 K. 8276 measured reflections, 7883 unique reflections, R = 0.051, R_w = 0.063. The data were collected on a Rigaku AFC5R four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) by the ω–2θ scan method to 2θ_{max} = 60.1°.

The structure was solved by heavy-atom Patterson methods. Hydrogen atoms were placed in appropriate trigonal or tetrahedral positions. All calculations were performed using the teXan crystallographic software package from the Molecular Structure Corporation. CCDC 182/554.

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