

### Preliminary communication

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## CHIRAL DISCRIMINATION IN ORGANOMETALLIC SYSTEMS. REACTION BETWEEN $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]^+$ AND $(S,S)(-)_589\text{-}o\text{-PHENYLENEBIS}(1,2\text{-METHYLPHENYLPHOSPHINE})$

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### Summary

Attack on the dienyl ring of racemic  $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$  (I) by  $(S,S)(-)_589\text{-}o\text{-phenylenebis}(1,2\text{-methylphenylphosphine})$  (II) exhibits considerable kinetic diastereoselectivity in acetonitrile and acetone solvents. The corresponding reaction in dichloromethane is of lower selectivity. Recovery of unreacted dienyl salt from reactions between I and II (1/0.5 molar ratio) provides a convenient method for preparing optically active I. The CD spectrum of the latter complex is reported for the first time.

Unexpectedly, the 50/50 mixture of diastereomers obtained immediately upon reacting  $(R,S)\text{-I}$  and II in a 1/1 molar ratio, equilibrates over three days in acetonitrile to a 60/40 mixture. Thermodynamic chiral discrimination thus also operates in these systems, and the mechanism of this unexpectedly rapid inversion at the chiral iron centre is under investigation.

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There is intense current interest in the stereoselectivity of organometallic reactions and the potential of such processes in asymmetric synthesis. Recent reports [1, 2] of the preparation of optically active  $\eta^5\text{-cyclohexadienyl}$  complexes such as  $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$  (I), the chemistry of whose racemic salts has been widely explored, open up fascinating new possibilities. As part of a programme investigating the extent, mechanism,

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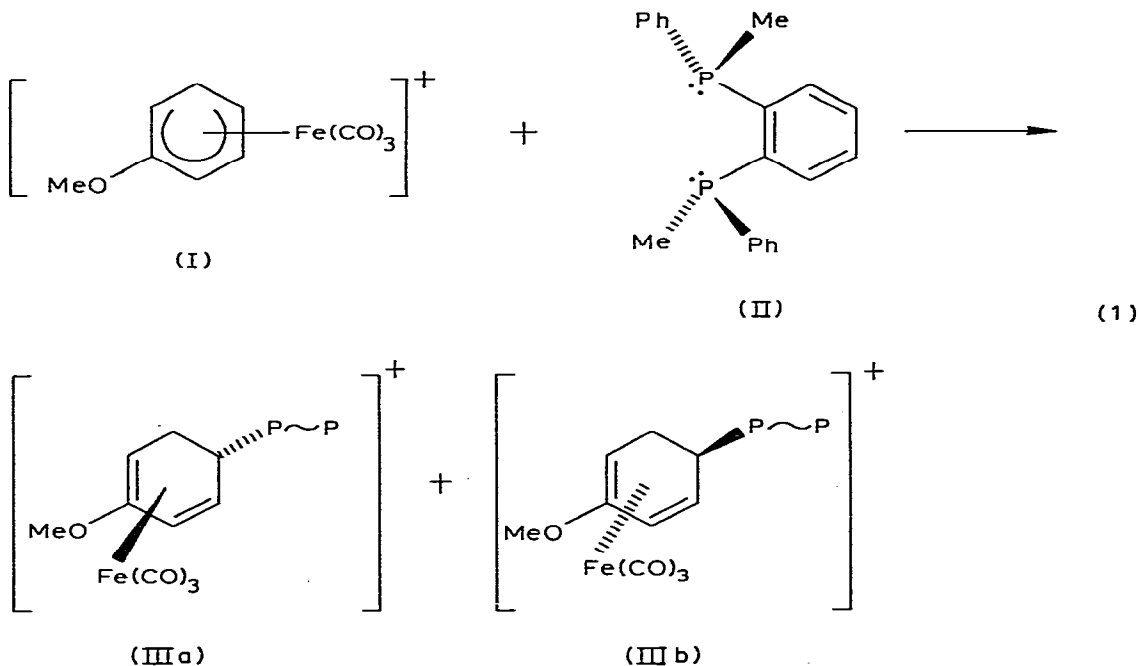
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and synthetic utility of diastereotopic discrimination between chiral  $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-dienyl})]^+$  cations and optically active nucleophiles, we report here studies of the interaction of racemic I with (*S,S*)(-)<sub>589</sub>-*O*-phenylenebis(methylphenylphosphine) (II). The synthesis and resolution of this latter optically active phosphine has been recently described [3].

Treatment of (*R,S*)-I with an equimolar amount of II at room temperature in acetone gave, upon immediate evaporation, a high yield (> 80%) of the pale yellow phosphonium salt III. This adduct was characterised by elemental analysis, the presence of two intense  $\nu(\text{CO})$  bands at 2060 and 1990  $\text{cm}^{-1}$  (acetone solution), and a  $^1\text{H}$  NMR spectrum which was fully consistent with the substituted 1,3-diene formulation shown. It was confirmed, as expected, to be a 50/50 mixture of the two diastereomers (IIIa and IIIb, eq. 1) by the presence of two distinct and equal  $\text{H}^3$  resonance at  $\tau$  4.35 and 4.60 in acetone- $d_6$ . The two diastereoisomers also exhibited distinct MeO resonances at  $\tau$  6.32 and 6.52. Similar results were achieved from in situ experiments in  $\text{CD}_3\text{CN}$ . Preliminary attempts to separate diastereomers IIIa and IIIb by crystallisation from various solvents have to date been unsuccessful.

More significantly, reaction 1 was shown to be moderately diastereoselective. Thus, in situ treatment of racemic I with II in a 1/0.5 molar ratio rapidly gave a 64/36 mixture of the diastereomers in  $\text{CD}_3\text{CN}$  (as evidenced by  $^1\text{H}$  NMR and CD spectra). Similar diastereotopic selectivity was noted in acetone solvent. This is considerably higher than that briefly reported [1] for the reaction of I with the enol trimethylsilyl ether of (+)-camphor.

In an analogous study in  $\text{CH}_2\text{Cl}_2$  treatment of (*R,S*)-I with II in a 1/0.5 molar ratio solubilized about half of the original salt I in forming a 58/42 mixture of diastereomers IIIa and IIIb (from  $^1\text{H}$  NMR).



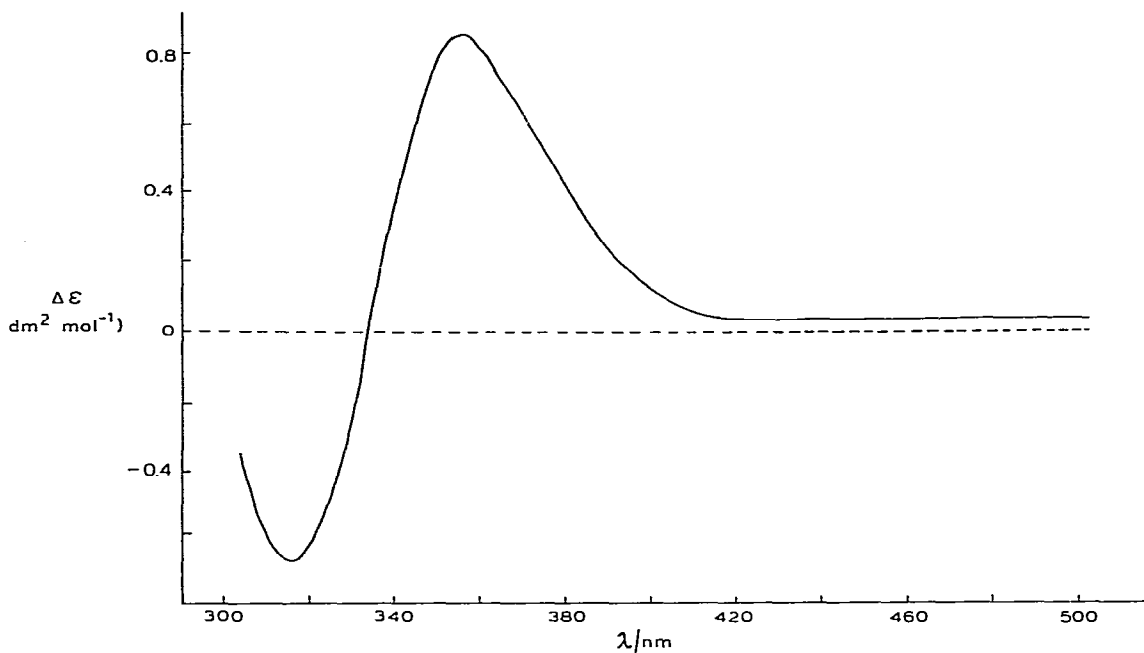
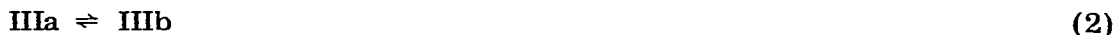


Fig. 1. CD spectrum of  $(S)(+)$ <sub>589</sub>-[Fe(CO)<sub>3</sub>(1-5-η-2-MeOC<sub>6</sub>H<sub>6</sub>)] [BF<sub>4</sub>] (ca. 6% enantiomeric excess) in water.

Recovery of unreacted dienyl salt from such reactions in acetone provides a convenient and rapid method for preparing optically active I. The CD spectrum of such a sample (calculated to be ca. 6% e.e. by comparison of its  $[\alpha]_{589}$  (+ 6.7°) with that reported [4] for optically pure  $(R)(-)$ <sub>589</sub>-I) is shown in Fig. 1. As far as we are aware, this is the first reported CD spectrum of a [Fe(CO)<sub>3</sub>(1-5-η-dienyl)]<sup>+</sup> complex. To date only rotational data have been reported [4] for optically active [Fe(CO)<sub>3</sub>(cyclo diene)] and [Fe(CO)<sub>3</sub>(cyclo dienyl)]<sup>+</sup> compounds, and strong UV absorption was reported [4] to prevent measurement below 480 nm. However, we have found no difficulty in recording CD spectra for I and the diastereomers IIIa and IIIb down to 290 nm.

A further fascinating and unexpected observation was the room temperature interconversion of diastereomers IIIa and IIIb. Thus, a 50/50 mixture of IIIa and IIIb in acetonitrile equilibrated within 3 days to a 60/40 mixture of diastereomers. This unexpectedly facile interconversion (eq. 2), involving inversion at the iron chiral centre, has considerable possible ramifications in



the use of chiral [Fe(CO)<sub>3</sub>(diene)] and [Fe(CO)<sub>3</sub>(dienyl)]<sup>+</sup> species in asymmetric syntheses, and we are currently investigating its mechanism. Exchange of the diene ligands is expected [5] to be far too slow to be implicated. Furthermore, we have been unable to trap the presumed "Fe(CO)<sub>3</sub>" intermediate. Participation by the solvent, via an intermediate such as the η<sup>2</sup>-diene species [Fe(CO)<sub>3</sub>(solvent)(η<sup>2</sup>-diene)] may be involved since, strikingly, equilibration 2 was found to occur in acetonitrile but not in chloroform.

Related studies of kinetic and thermodynamic diastereotopic discrimination in the reactions of I and similar chiral cations with a range of other optically active nucleophiles are in progress.

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