

## Preliminary communication

# CHIRAL DISCRIMINATION IN ORGANOMETALLIC SYSTEMS. REACTION OF $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]^+$ WITH $(R)-(+)_{\text{s89}}-1$ -PHENYLETHYLAMINE

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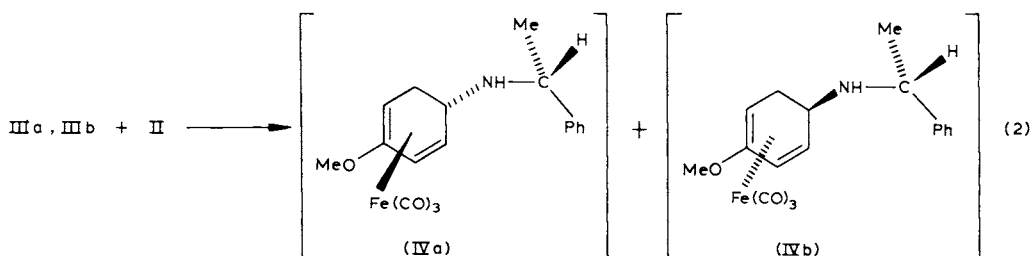
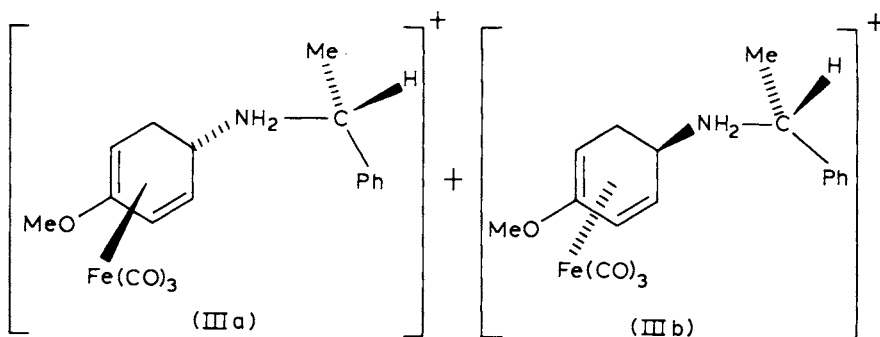
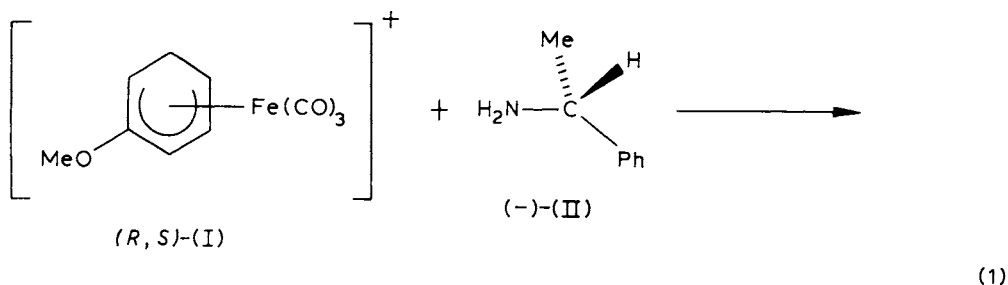
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## Summary

CD spectral studies show that kinetic diastereotopic discrimination occurs in the reaction of  $(R,S)-[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]^+$  (I) with  $(R)-(+)_{\text{s89}}-1$ -phenylethylamine (II) in  $\text{CH}_3\text{CN}$ . This process involves initial attack by the amine at the C(5) position of the dienyl ring to give diastereometric cations of formula  $[\text{Fe}(\text{CO})_3\{\text{PhCH}(\text{Me})\text{NH}_2 \cdot \text{C}_6\text{H}_6\text{OMe}\}]^+$  (IIIa, IIIb). Subsequent room temperature epimerization of an equimolar mixture of these two diastereomers is excluded by CD and  $^1\text{H}$  NMR experiments. Addition of further amine (I/II molar ratio of 1/2) causes deprotonation of the amine substituents in (IIIa, IIIb) to give the corresponding neutral diastereomers (IVa, IVb).

There has been considerable recent interest in the preparation of optically active  $[\text{Fe}(\text{CO})_3(\pi\text{-hydrocarbon})]^{n+}$  (hydrocarbon = diene or dienyl,  $n = 0$  or 1) complexes and their potential use in asymmetric synthesis [1–3]. As part of a programme investigating the extent and mechanism of diastereotopic discriminations in the reactions of chiral  $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-dienyl})]^+$  cations with optically active nucleophiles, we report here studies of the addition of  $(R)-(+)_{\text{s89}}-1$ -phenylethylamine (II) to the dienyl ring of  $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$  (I).

This reaction proceeds in two stages as shown in eq. 1 and 2. Analogous cationic and neutral adducts have been previously reported [4] from the reaction of II with the acyclic dienyl cation  $[\text{Fe}(\text{CO})_3(\text{syn,syn-1,5-dimethyl-pentadienyl})]^+$ .



Treatment of racemic I with excess ( $> 2$  molar) (*R*)-(+)<sub>589</sub>-1-phenylethylamine in CH<sub>3</sub>CN at room temperature gave the neutral final products IV quantitatively, as shown by <sup>1</sup>H NMR and IR spectra. Alternatively, IV can be isolated as a yellow gum in 66% yield from a synthesis in THF. The neutral (diene) iron tricarbonyl nature of this final product was confirmed by its characteristic <sup>1</sup>H NMR spectrum [5] and the presence of two intense  $\nu(\text{CO})$  bands at 2050 and 1980 cm<sup>-1</sup> in CH<sub>3</sub>CN solution. The compound gave satisfactory elemental analyses and showed a weak peak for the expected parent ion at *m/z* 369 in its electron impact mass spectrum. The <sup>1</sup>H NMR spectrum (in CD<sub>3</sub>CN) also established exclusive addition at the C(5) ring position, and showed (IV) to be a 50/50 mixture of diastereomers IVa and IVb. Addition of Eu(fod)<sub>3</sub> contact-shift reagent was necessary to distinguish the separate MeO resonances for the two diastereomers. The equimolar mixture of these isomers was also clearly revealed by a <sup>13</sup>C NMR spectrum in CD<sub>3</sub>CN.

On the other hand, reaction of I and II in a 1/1 ratio in CH<sub>3</sub>CN gave III quantitatively. The [BF<sub>4</sub>]<sup>-</sup> salt could be isolated as a cream solid in 76% yield. As expected, its <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN:  $\tau$  2.60 (m, 5H, aromatic), 4.65 (m, 1H, H(3)), 5.24 (s, 2H, NH<sub>2</sub>), 5.62 (m, 1H, H(1)), 6.33 (s, 3H, OMe),

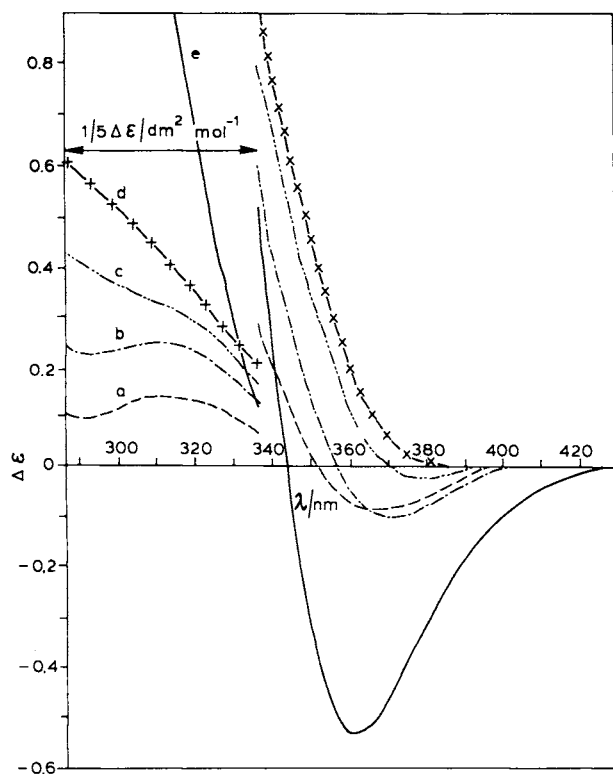


Fig. 1. CD spectra of mixtures of  $(R,S)\text{-}[\text{Fe}(\text{CO})_3(1-5-\eta\text{-}2\text{-MeOC}_6\text{H}_6)][\text{BF}_4]$  and  $(R)\text{-}(+)\text{-}1\text{-phenylethylamine}$  in  $\text{CH}_3\text{CN}$ . Curves (a)–(e) refer to the following molar ratios: (a) 1/0.25, - - - -; (b) 1/0.5 - · - · -; (c) 1/0.75, · · · · ·; (d) 1/1, -X-X-; (e) 1/2, —.

6.68 (m, 1H, H(4)), 6.83 (m, 1H, H(5')), 7.36 (m, 1H, CH), 7.50 (m, 1H, H(6')), 7.75 (m, 1H, H(6)), 8.42, 8.49 (dd, 3H,  $\text{CH}_3$ ) was shifted to lower field compared with IV, while it exhibited  $\nu(\text{CO})$  bands at somewhat higher frequency (2065 and 2000  $\text{cm}^{-1}$  in  $\text{CH}_3\text{CN}$ ). It could alternatively be generated in situ by protonation of IV with  $\text{CF}_3\text{COOD}$  in  $\text{CD}_3\text{CN}$ .

The series of CD spectra in Fig. 1 clearly establishes that chiral discrimination occurs in reaction 1. The spectra were recorded immediately upon mixing I and II in  $\text{CH}_3\text{CN}$  in the molar ratios (a) 1/0.25, (b) 1/0.5, (c) 1/0.75, (d) 1/1, and (e) 1/2, respectively. Spectra (d) and (e) thus represent the vicinal CD arising from the 50/50 mixtures of diastereomers IIIa/IIIb and IVa/IVb, respectively. If no chiral discrimination occurs in process 1, spectra (a)–(c) would be expected to have exactly the same form as (d) with appropriate isodichroic points, but with intensities decreased by factors of 4, 2, and 1.33, respectively. This is clearly not the case, and is especially noticeable at longer wavelengths where there is in fact a change in sign on proceeding down the series (a) to (d). Unfortunately, the ratio of diastereomers IIIa and IIIb in such mixtures, and hence an estimation of the chiral discrimination energy involved, could not be established by  $^1\text{H}$  NMR spectroscopy. Only one MeO signal for III was observed in all cases investigated, even in the presence of  $\text{Eu}(\text{fod})_3$  or  $\text{Eu}(\text{fmcam})_3$ .

Addition of diethyl ether to mixtures such as (b) in  $\text{CH}_3\text{CN}$  conveniently recovered the unreacted dienyl salt I in optically active form. Comparison of its CD spectrum with that previously reported [6] for  $(S)\text{-(+)}_{589}\text{-[Fe(CO)}_3\text{-(1-5-}\eta\text{-2-MeOC}_6\text{H}_6\text{)]}^+$  shows that  $(R)\text{-(+)}_{589}\text{-1-phenylethylamine}$  preferentially selects the  $(S)\text{-(+)}_{589}$ -enantiomer of I. However, for reasons which will be elaborated upon in a subsequent communication, the enantiomeric excess of such recovered samples of I is believed to be considerably less than that present *in situ*.

The CD spectrum of (d), containing initially a 50/50 mixture of IIIa and IIIb, does not change significantly over a period of 6 days at room temperature. Subsequent addition of concentrated  $\text{HBF}_4$  regenerates racemic  $(R,S)\text{-I}$ . The possibility of *exo-endo*-rearrangement of the amine ring substituent could be excluded by the constancy of the  $^1\text{H}$  NMR chemical shifts over this period, and in particular the failure to observe any shift in the signal for the ring  $\text{H}(5')$  proton.

However, kinetic chiral discrimination and subsequent rearrangement have been recently observed [6] in the related addition of  $(S,S)\text{-(+)}_{589}\text{-o-phenylene-bis(methylphenylphosphine)}$  to the dienyl ring of I. This latter phosphine nucleophile preferentially selects the  $(R)\text{-(+)}_{589}$ -enantiomer of I. Similar studies are in progress with other optically active nucleophiles and various organometallic cations such as I.

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