

### Preliminary communication

---

## CHIRAL DISCRIMINATION IN ORGANOMETALLIC SYSTEMS. THE REACTIONS OF $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$ WITH OPTICALLY ACTIVE TERTIARY PHOSPHINES

DAVID J. EVANS and LEON A.P. KANE-MAGUIRE\*

*Chemistry Department, University College Cardiff, P.O. Box 78, Cardiff CF1 1XL, Wales (Great Britain)*

(Received June 25th, 1982)

### Summary

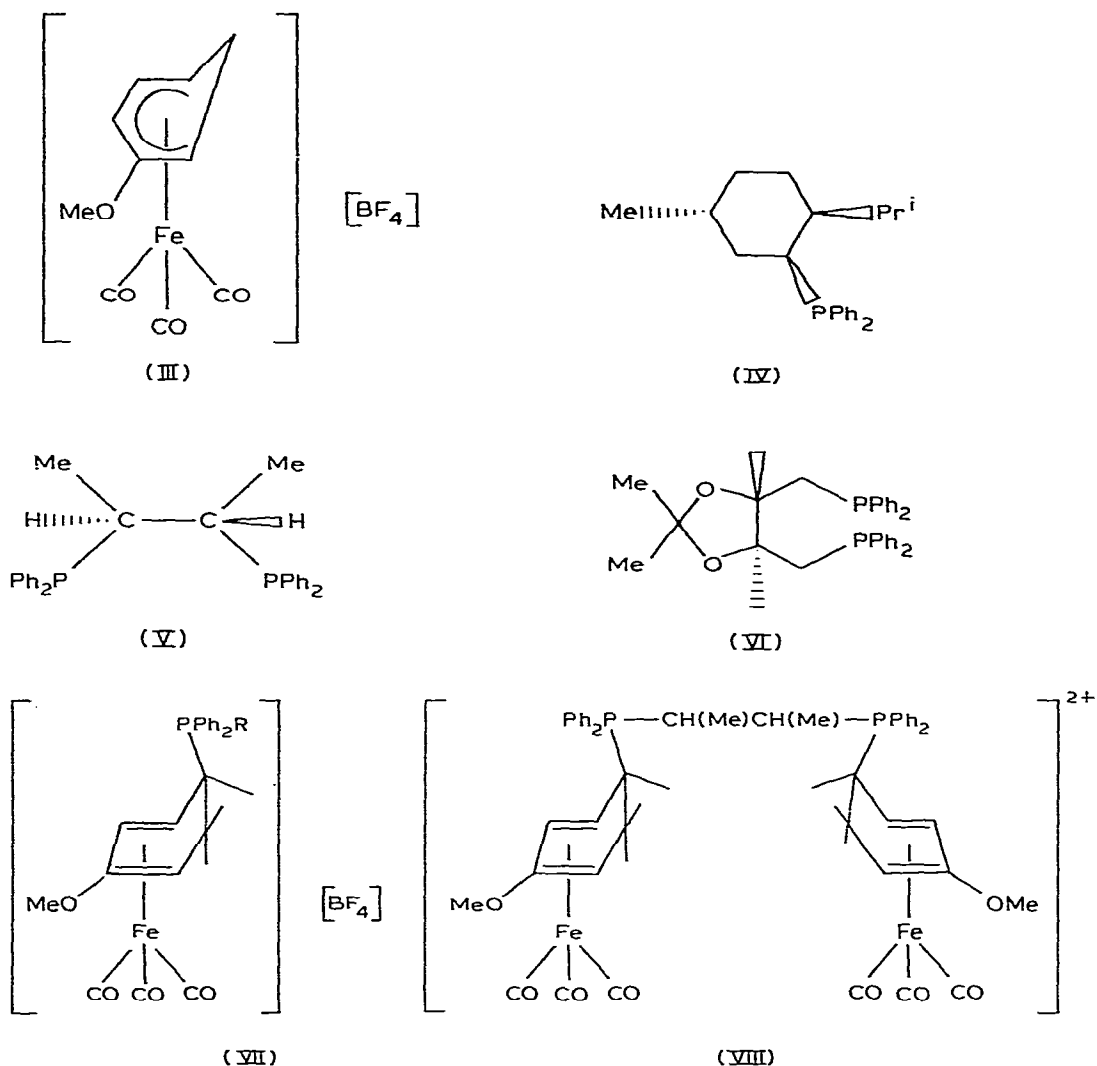
Synthetic and spectroscopic ( $^1\text{H}$  NMR, CD) studies have been made of the addition of  $(-)_589$ -neomenthylidiphenylphosphine,  $(S,S)$ - $(-)_589$ -chiraphos, and  $(+)_589$ -diop to the dienyl ring of  $(R,S)$ - $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$  (III). The chiral discrimination observed in these reactions is compared with that previously found in the related addition of  $(S,S)$ - $(-)_589$ -*o*-phenylenebis(methylphenylphosphine) to III. In contrast to the earlier study, the diastereomeric mixtures obtained with the present systems do not undergo subsequent rearrangements.

---

We recently reported [1,2] significant chiral discrimination in the additions of  $(R)$ - $(+)_589$ -1-phenylethylamine (I) and  $(S,S)$ - $(-)_589$ -*o*-phenylenebis(methylphenylphosphine) (II) to the dienyl ring of racemic  $(R,S)$ - $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)] [\text{BF}_4]$  (III). As part of a programme investigating the origins of this discrimination and its implications in asymmetric synthesis, the reactions of  $(R,S)$ -III with a range of optically active tertiary phosphines have now been investigated. The particular phosphines  $\text{PPh}_2\text{R}$  chosen, namely  $(-)_589$ -neomenthylidiphenylphosphine (IV),  $(S,S)$ - $(-)_589$ -chiraphos (V), and  $(+)_589$ -diop (VI), differ from the previously studied II in that their optical activity resides at alkyl carbon atoms rather than at the phosphorus centre itself.

Reaction of III with equimolar amounts of either IV or V in  $\text{CH}_3\text{CN}$  gave the monomeric phosphonium salts VII in high yield. These adducts were fully characterised by elemental analyses and by their  $^1\text{H}$  NMR and IR spectra which were characteristic of (substituted 1,3-diene)tricarbonyliron complexes. Each was expected to be a 50/50 mixture of diastereomers. However, unlike

\*To whom correspondence to be addressed.



earlier studies [2] with II, distinct MeO or H<sup>3</sup> proton resonances were not observed for the two diastereomers in each case, even in the presence of Eu(fod)<sub>3</sub> (CD<sub>3</sub>CN solvent, 90 MHz).

This coincidence of diastereomer proton resonances prevented quantitative in situ determination of the chiral discrimination. However, the unreacted di- enyl salt recovered from the reaction of III with IV (1/0.5 molar ratio) in acetone was found to contain an 11% enantiomeric excess 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>] (Table 1). Its CD spectrum in water revealed three bands at 354, 318, and 267 nm ( $\Delta\epsilon$  values of +1.71, -1.56, +6.43 mol<sup>-1</sup> dm<sup>2</sup>, respectively). Thus, (-)<sub>589</sub>-neomenthyldiphenylphosphine preferentially selects the (*R*)-(-)<sub>589</sub>-enantiomer of III. By analogy with earlier studies [2] using II, the actual chiral discrimination is believed to be considerably higher than that suggested by the enantiomeric excess of recovered samples of III.

TABLE 1

RECOVERY OF OPTICALLY ACTIVE  $[\text{Fe}(\text{CO})_2(1-5-\eta-2\text{-MeOC}_6\text{H}_4)][\text{BF}_4]$  (III) FROM THE REACTION OF RACEMIC III WITH OPTICALLY ACTIVE PHOSPHORUS NUCLEOPHILES

Phosphine	III/phosphine ratio	% e.e. of recovered III	Ref.
II	2/1	6–11% (S)-(+) <sub>589</sub>	2,3
IV	2/1	11% (S)-(+) <sub>589</sub>	This work
V	3/1	5% (R)-(-) <sub>589</sub>	This work
VI	3/1	1.5% (R)-(-) <sub>589</sub>	This work

In contrast, a 1/0.5 molar ratio mixture of III and (-)<sub>589</sub>-chiraphos (V) gave a quantitative yield of the dimeric phosphonium salt VIII. This was shown to be the expected mixture of four diastereomers by the presence of four distinct H<sup>3</sup> resonances (relative intensities ca. 1/1/1/1) at  $\tau$  5.03, 5.15, 5.35 and 5.41 in CD<sub>3</sub>CN. Formation of this dimer was also shown to be moderately diastereoselective from in situ <sup>1</sup>H NMR experiments in CD<sub>3</sub>CN using a 3/1 molar ratio of III to V. Accurate assessment was difficult because of the small separation of the diastereomeric H<sup>3</sup> signals and the overlap of the four MeO resonances with those of the H<sup>1,4</sup> protons. However, the relatively low enantiomeric excess of recovered (R)-(-)<sub>589</sub>-III from such a reaction in acetone (Table 1) suggests that (-)<sub>589</sub>-chiraphos (V) is less diastereoselective than either II or IV.

Finally, the only product obtained from treating racemic III with various ratios of (+)<sub>589</sub>-diop (VI) is a dimeric phosphonium salt related to VIII. This was again fully characterised by elemental analyses and its <sup>1</sup>H NMR and IR spectra. The expected four diastereomers could not be distinguished by <sup>1</sup>H NMR spectroscopy (90 MHz). This reaction appears to be the least diastereoselective of those investigated to date, since the recovered dienyl salt from a synthesis in acetone (3/1 molar ratio of III/VI) showed only a 1.5% enantiomeric excess of (R)-(-)<sub>589</sub>-III.

In contrast to earlier studies [2] using II, each of the diastereomeric mixtures obtained with the present phosphorus nucleophiles showed no significant changes in their CD or <sup>1</sup>H NMR spectra over a period of a week at room temperature. This observation, together with other evidence [3], now leads us to reinterpret the mechanism of the subsequent rearrangements observed for the diastereomeric phosphonium adducts with II.

Related studies are in progress with a range of other chiral  $[\text{Fe}(\text{CO})_2(1-5-\eta\text{-dienyl})]^+$  cations in order to determine the influence of dienyl ring substituents upon the degree of chiral discrimination.

We thank the SERC for support (DJE) and Pete Williams for helpful discussions.

## References

- 1 J.G. Atton, L.A.P. Kane-Maguire, P.A. Williams, and G.R. Stephenson, *J. Organometal Chem.*, **232** (1982) C5.
- 2 D.J. Evans, L.A.P. Kane-Maguire, and S.B. Wild, *J. Organometal Chem.*, **232** (1982) C9.
- 3 D.J. Evans, L.A.P. Kane-Maguire, P.A. Williams, and S.B. Wild, unpublished results.