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Preliminary communication

THE USE OF CHIRAL IRON COMPLEXES IN ASYMMETRIC SYNTHESIS: THE PREPARATION OF OPTICALLY ACTIVE *trans*-1-METHYL-2-PHENYLCYCLOPROPANES

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Summary

The preparation, resolution and use in asymmetric synthesis of the diastereomeric (+)- and (—)-(h^5-C_5H_5)Fe(CO)(Ph_3P)(h^1-$CH_2OC_{10}H_{19}$), the first example of a characterized optically active transition metal organometallic carbene transfer reagent is described. The (+)-isomer gave (—)-*trans*-(1*R*,2*R*)-1-methyl-2-phenylcyclopropane in 26% e.e., while the (—)-isomer gave (+)-*trans*-(1*S*,2*S*)-1-methyl-2-phenylcyclopropane in 38.5% e.e.

The diastereomeric complexes (+)- and (—)-(*pentahapto*-cyclopentadienyl)(*monohapto*-methyl menthyl ether)carbonyltriphenylphosphineiron (IVa and IVb) were prepared from (*pentahapto*-cyclopentadienyl)(*monohapto*-methyl methyl ether)dicarbonyliron [1] (I) by the reaction sequence outlined in Scheme 1*. The diastereomers IVa and IVb were separated by fractional recrystallization from pentane.

Insofar as the circular dichroism (CD) spectra, in the range 300—500 nm, of a variety of resolved (h^5-C_5H_5)Fe(CO)(Ph_3P)X compounds are very similar, and are thought [2] to depend only on the absolute configuration at the iron center, we have assigned the absolute stereochemistries of the isomers IVa and IVb, as shown below, on the basis of the comparison of their CD spectra (Fig. 1) to those of [(h^5-C_5H_5)Fe(CO)(Ph_3P) {C(=NHCHCH$_3$Ph)-CH$_3$}]BF_4 (V) [3]. The absolute configuration of (V) has been determined by X-ray crystallography [4].

Cleavage of IVa** with HBF_4, in a neat solution of *trans*-1-phenyl-

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[*] Satisfactory analyses, IR, NMR and mass spectra have been obtained for the new compounds.

[**] The (+)-isomer IVa used in the reaction was ca. 87% optically pure, based on comparison of its ORD to three times recrystallized material.

Scheme 1

$(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}CH_2OCH_3) + Ph_3P$

(I)

$\xrightarrow[\text{Petrol}]{h\nu}$ $(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)(h^1\text{-}CH_2OCH_3)$

(II)

$\downarrow$ HCl, CH_2Cl_2

$(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)(h^1\text{-}CH_2Cl)$

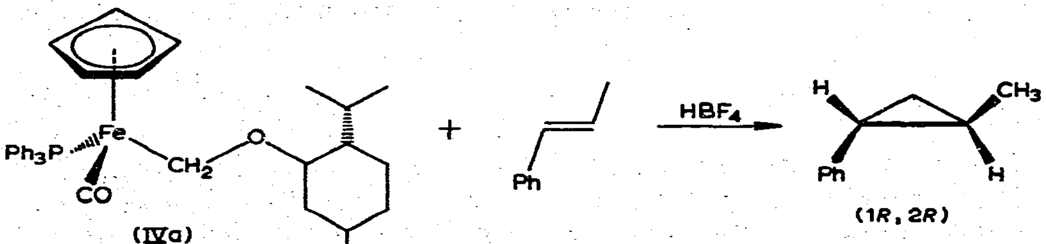
(III) (Thermally unstable yellow solid)

$\xrightarrow[\text{Ether}]{NaOC_{10}H_{19}}$

$(h^5\text{-}C_5H_5)Fe(CO)(Ph_3P)(h^1\text{-}CH_2OC_{10}H_{19})$

(IVa, IVb)

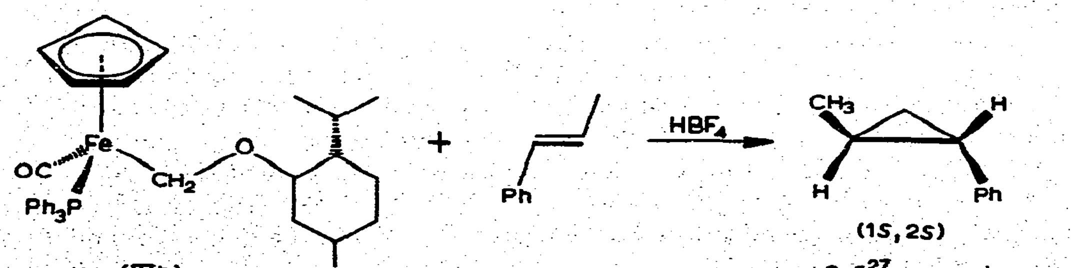
propene gave as the only cyclopropane *trans*-1-methyl-2-phenylcyclopropane, whose optical rotation indicated that the major component was the (1*R*,2*R*)-isomer (26% e.e.). Conversely, IVb gave mainly the *trans*-(1*S*,2*S*)-1-methyl-2-phenylcyclopropane (38.5% e.e.)*.



(IVa)

(1*R*,2*R*)

$[\alpha]^{27}_{589}$ − 25 ± 3°



(IVb)

(1*S*,2*S*)

$[\alpha]^{27}_{589}$ + 37 ± 3°

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[*] The configurations and the optical purity of the cyclopropanes were made by comparison of the rotations at 589 nm to 100% optically pure (+)-*trans*-(1*S*,2*S*)-([1-^{13}C]methyl)-2-phenylcyclopropane [5]. The yields were ca. 9% for the optically-active cyclopropanes.

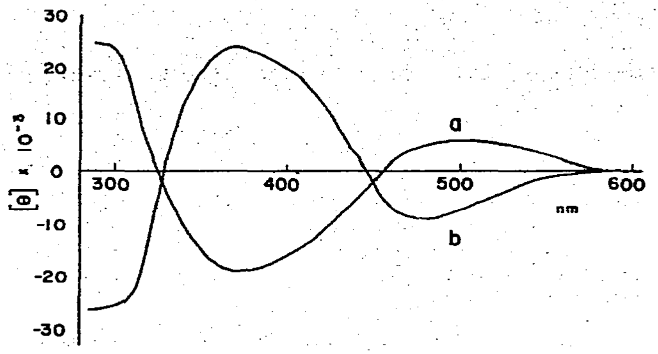


Fig.1. The CD spectra of IVa and IVb, ca. 10^{-3} *M* in benzene.

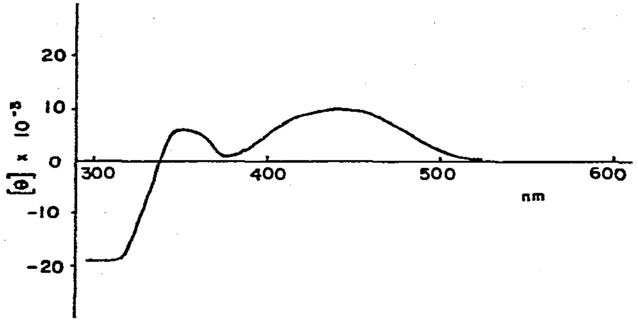
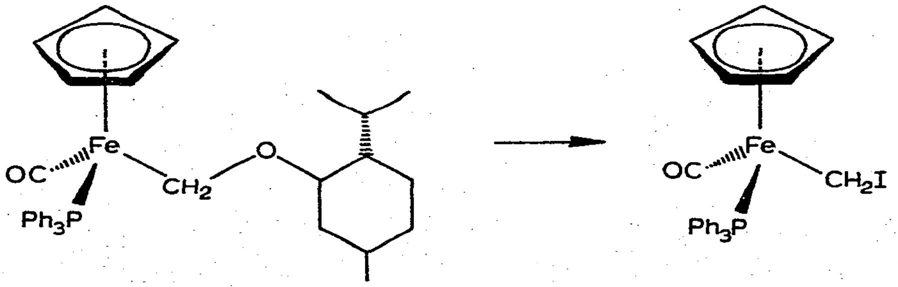


Fig.2. The CD spectra of VIb, ca. 10^{-3} *M* in DMSO.

The cyclopropanes prepared above were separated from *trans*-1-phenylpropene, and (—)-menthol and were compared by GC to an authentic sample of enantiomeric *trans*-1-methyl-2-phenylcyclopropane [6] which was prepared by the method of Seyferth and Haas [7].

Cleavage of IVb with HI yielded the red compound VIb whose CD spectrum is displayed in Fig. 2. This complex is somewhat more stable than the enantiomeric chloro derivative (III).



(IVb) (VIb)

Acknowledgements

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