Resolution of $[Fe(CO)_3(1—5\text{-}\eta\text{-Dienyl})]^+$ Cations and Assignment of Absolute Configuration by Circular Dichroism Spectroscopy

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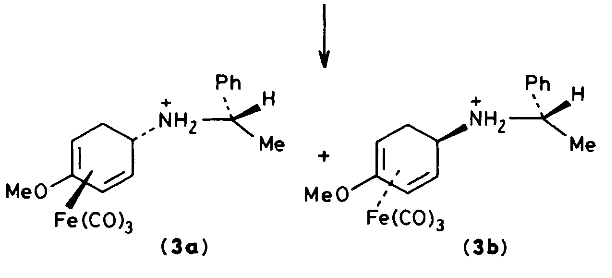
(2*R*)-$(-)_{589}$-$[Fe(CO)_3(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (**1**) and (2*S*)-(**1**) of high optical purity have been obtained by h.p.l.c. separation of the diastereoisomers from the reaction of racemic (2*R*, 2*S*)-(**1**) with (*R*)-$(+)_{589}$-1-phenylethylamine, and subsequent treatment with HBF_4; circular dichroism spectroscopy appears to provide a rapid method for the assignment of absolute configuration to chiral $[Fe(CO)_3(\pi\text{-hydrocarbon})]^{n+}$ (hydrocarbon = cyclic diene or dienyl, *n* = 0 or 1) complexes.

There has been considerable recent interest[1—6] in the preparation of optically-active $[Fe(CO)_3(\pi\text{-hydrocarbon})]^{n+}$ (hydrocarbon = cyclic diene or dienyl, *n* = 0 or 1) complexes because of their potential importance in asymmetric synthesis. However, a serious handicap to such employment is the current absence of (i) a general, simple route to fully resolved species, and (ii) a rapid method for the assignment of absolute configurations. We report here preliminary studies which appear to fulfill these requirements.

$[Fe(CO)_3(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (1)

$MeCH(Ph)NH_2$ (2)

As described previously,[4] reaction of racemic (2*R*,2*S*)-$[Fe(CO)_3(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (**1**) with an equimolar amount of (*R*)-$(+)_{589}$-1-phenylethylamine (**2**) in MeCN gives a 50/50 mixture of the diastereoisomers (**3a**) and (**3b**). We now find that these diastereoisomers can be readily separated by


(2*R*,2*S*)-(**1**) + (*R*)-(**2**)

(**3a**) (**3b**)

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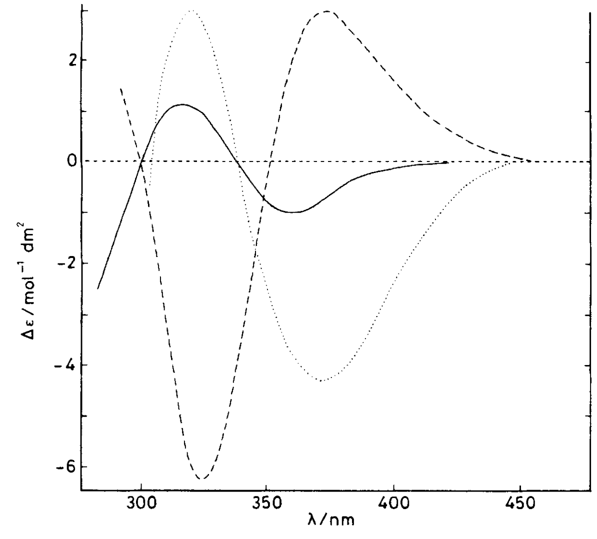
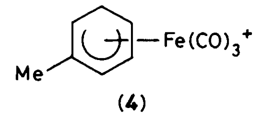


Figure 1. C.d. spectra of (a) (2*R*)-$(-)_{589}$-(**1**), 10% enantiomeric excess (e.e.) in MeCN (——); (b) (2*R*)-$(-)_{589}$-(**4**), 7% e.e. in H_2O (· · · · ·) (ordinate × 10); (c) (2*S*,5*R*)-$(+)_{589}$-(**5**), 11% e.e. in MeCN (– – –).



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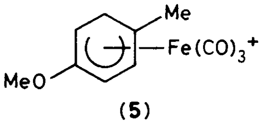

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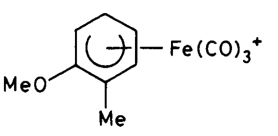

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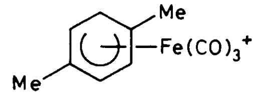

(7)

h.p.l.c. using a Hypersil silica (5—10 μm) column and tetrahydrofuran–cyclohexane (80/20) as eluant. Their i.r. ν(CO) bands showed both fractions to be neutral tricarbonyl(diene)iron species, presumably the deprotonated diastereoisomers. Addition of conc. HBF_4 to each fraction rapidly and quantitatively removed the amine substituents, generating the enantiomeric pair (2*R*)-$(-)_{589}$- and (2*S*)-$(+)_{589}$-(**1**), as confirmed by i.r. and circular dichroism (c.d.) spectroscopy. Comparison of their c.d. spectra (Figure 1) with earlier c.d. studies[4,5] of partially resolved cations established that the (2*R*)-$(-)_{589}$-cation was 90% optically pure while the (2*S*)-enantiomer was *ca.* 60% pure.

The above procedure should provide a general and rapid route to optically pure $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-cyclic dienyl})]^+$ species, and this aspect is being explored with a range of such cations.

To date the absolute configurations of only a few $[Fe(CO)_3(\pi\text{-hydrocarbon})]^{n+}$ (hydrocarbon = diene or dienyl, n = 0 or 1) complexes have been established using tedious chemical transformations to known terpenes.[2] We have been interested in establishing whether c.d. spectroscopy may provide a much more rapid and general method for the assignment of absolute configurations. To this end, partial resolution of the range of substituted dienyl cations (**1**), (**4**), (**6**), and (**7**) has been achieved using chiral discrimination in the reactions between the racemic cations and (*S*,*S*)-$(-)_{589}$-*o*-phenylenebis(methylphenylphosphine).[5,7] This is the first time that cations (**6**) and (**7**) have been reported in optically active form.

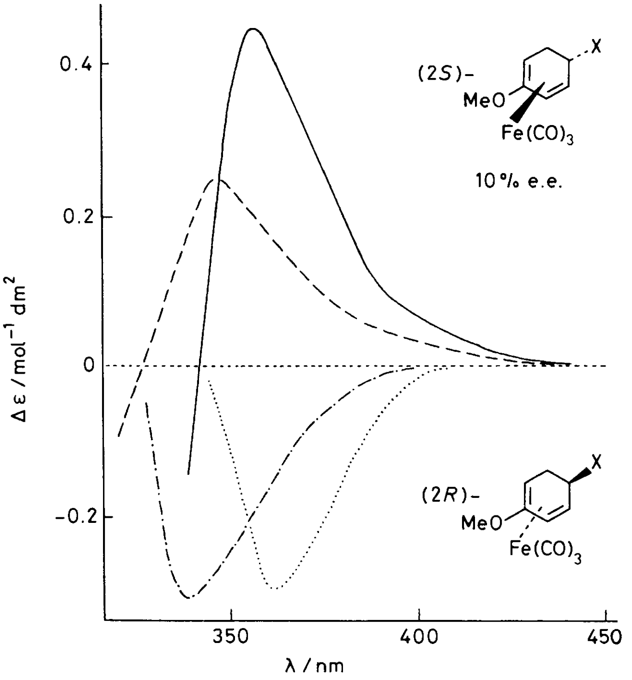

Figure 2. C.d. spectra of (2*S*)-(**8**), 10% e.e. [X = PPh_3 (——) or $4\text{-}MeOC_6H_4NH_2$ (– – –)]; and (2*R*)-(**8**), 6% e.e. [X = PBu^n_3 (– · – · –) or CN (· · · · ·)]. Solvent MeCN.

The highest wavelength c.d. band for each dienyl cation at *ca.* 350—380 nm (Figure 1) corresponds with a point of inflection at *ca.* 350 nm in the corresponding u.v. visible spectrum. The latter may arise from a metal centred d–d transition partially masked by an intense charge transfer band to lower wavelength. It therefore seems reasonable to assume that the sign of the highest wavelength c.d. band may be dominantly determined by the chirality at the iron centre. In keeping with the above hypothesis, it is seen from Figure 1 that (2*R*)-$(-)_{589}$-(**1**) and (2*R*)-$(-)_{589}$-(**4**) (whose absolute configurations have been established elsewhere[2]) both exhibit highest wavelength c.d. bands of negative sign. In contrast, for (2*S*,5*R*)-$(+)_{589}$-(**5**) of known opposite absolute configuration, the highest wavelength c.d. band has a positive sign. These preliminary findings suggest that the sign of the highest wavelength c.d. band may indeed be diagnostic of configuration for such cations. On this basis, the partially resolved $(-)_{589}$-(**6**) and $(+)_{589}$-(**7**) obtained here have been tentatively assigned (2*R*,3*S*)- and (2*S*,5*R*)-configurations, respectively.

It is probable that c.d. spectroscopy may also allow rapid assignment of absolute configurations to related $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-diene})]$ complexes. For example, the adducts (2*S*)-(**8**) (X = PPh_3, $4\text{-}MeOC_6H_4NH$) obtained by reacting (2*S*)-(**1**) with PPh_3 or $4\text{-}MeOC_6H_6NH_2$ show a positive longest wavelength c.d. band (Figure 2). In contrast, the adducts (2*R*)-(**8**) (X = PBu^n_3,CN) prepared from (2*R*)-(**1**) exhibit a negative sign for their highest wavelength c.d. bands (Figure 2).

$$[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}2\text{-}MeO\text{-}5\text{-}X\cdot C_6H_6)]^{n+}$$

(**8**) n = 0,1

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