

COMMUNICATION

Synthesis of a novel ferrocene derivative having flame-retardant and smoke-suppressant properties

P Carty,*† J Grant* and A Simpson‡

* Department of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Coach Lane, Newcastle upon Tyne NE7 7XA, and ‡ Procter and Gamble Technical Centre, Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS, UK

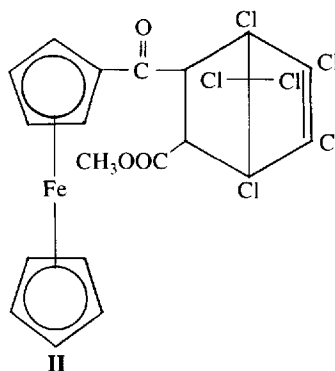
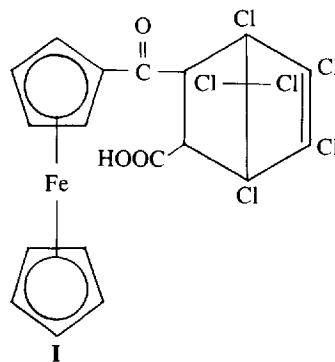
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Reaction of ferrocene with chlorendic anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid anhydride) under Friedel-Crafts reaction conditions affords a new monosubstituted derivative of ferrocene which has significant flame-retardant and smoke-suppressant properties when incorporated into poly(vinyl chloride) (PVC). The monocarboxylic acid from the above reaction undergoes smooth methylation with diazomethane to give the corresponding methyl ester. ^1H and ^{13}C NMR spectra of these compounds have been compared with those obtained from similar compounds, namely β -ferrocenoylpropanoic acid and its methyl ester. Distant asymmetric centres in the chlorendic anhydride substituent markedly affect the proton spectra of the ferrocene derivative.

Keywords: Ferrocene, chlorendic anhydride, flame retardant, smoke suppressant, flexible PVC, ^1H NMR spectra

In connection with other investigations concerning the synthesis of novel organometallic additives for polymers,¹ chlorendic anhydride was examined with respect to its behaviour in electrophilic substitution reactions with ferrocene. (Chlorendic anhydride is the trivial name widely used for the reactive flame-retardant 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride. The parent acid is also known as HET acid.) Careful addition of anhydrous aluminium chloride to a stirred solution of ferrocene and freshly prepared chlorendic anhydride in dichloromethane affords, in good yield, the monosubstituted ferrocene derivative $\eta\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CORCO}_2\text{H}$, where R represents the chlorendic

residue (I). Recrystallisation from benzene/petroleum ether gives dark red, air-stable crystals which are soluble in ether, dichloromethane and acetone and are insoluble in water.



Compound I has flame-retarding and smoke-suppressant activity in flexible PVC. A solution of I in dry ether reacts smoothly with ethereal diazomethane over a period of 12 h to give red crystals of the corresponding methyl ester (II). Infrared spectra of both

† Author to whom correspondence should be sent.

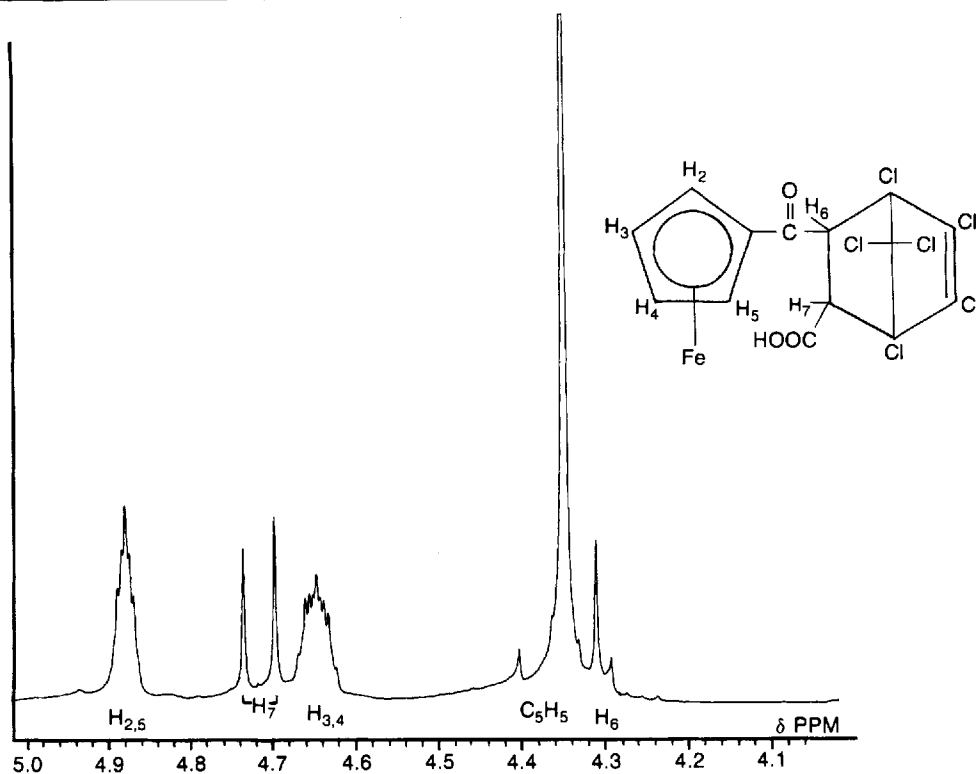


Figure 1 ^1H NMR spectrum of the ferrocene/chlorendic anhydride derivative I.

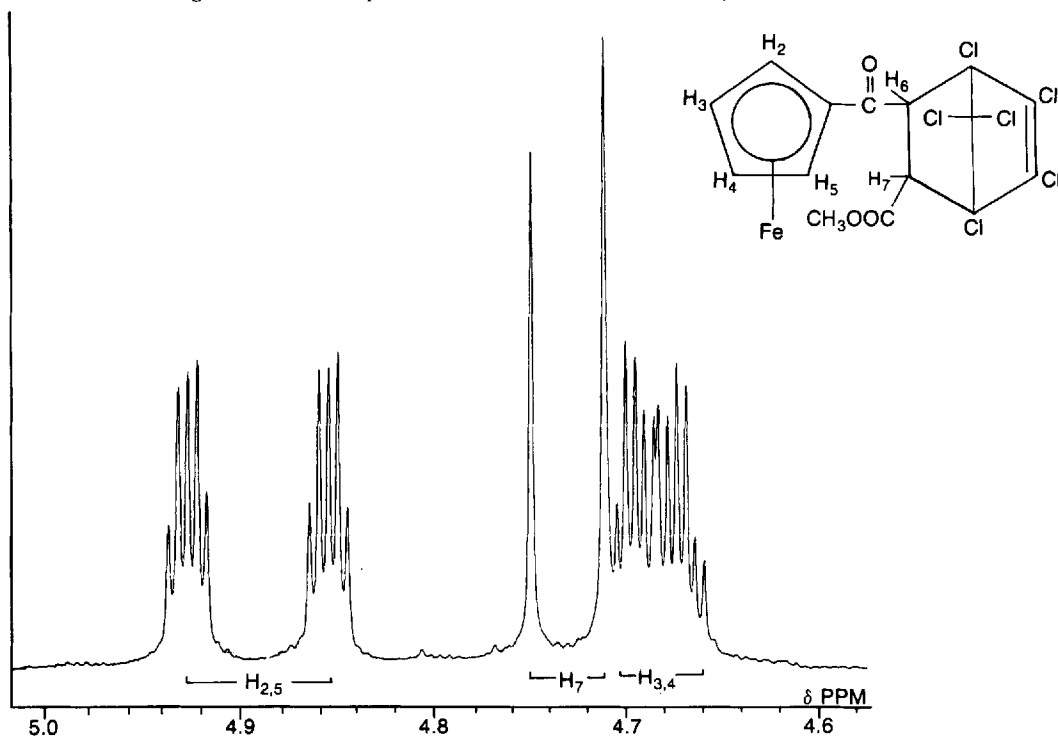


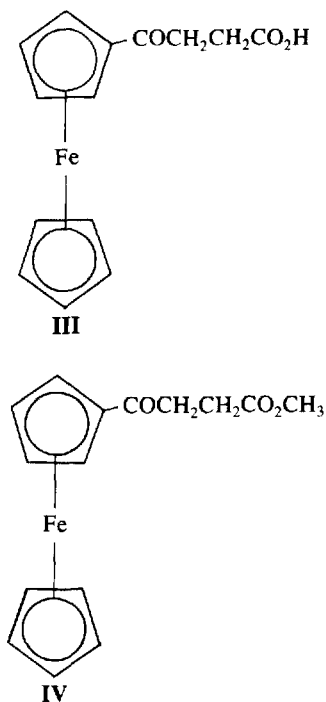
Figure 2 ^1H NMR spectrum of the methyl ester of the ferrocene/chlorendic anhydride derivative II.

compounds confirmed the presence of the important structural features in these compounds, i.e. $\nu(\text{C}=\text{O}$, ketone) 1660 cm^{-1} , $\nu(\text{C}=\text{C})$ 1600 cm^{-1} , $\nu(\text{C}=\text{O}$, acid) 1720 cm^{-1} , $\nu(\text{C}=\text{O}$, ester) 1760 cm^{-1} , and bands at 1100 cm^{-1} and 1000 cm^{-1} indicated monosubstituted ferrocene derivatives. Both compounds gave elemental analysis in good agreement with the proposed structures. ^1H and ^{13}C NMR spectra in deuteriochloroform using a 270 MHz instrument were determined and important parts of the ^1H spectra are shown in Figs 1 and 2.

Both compounds show a very unusual splitting pattern of the substituted ring protons. The expected A_2B_2 system typical of a monosubstituted ferrocene² was not apparent: in an attempt to resolve these unusual ^1H NMR spectra we synthesized two model ferrocene compounds for comparison, namely β -ferrocenylpropanoic acid (**III**) and its methyl ester (**IV**).³

Part of the ^1H NMR spectrum of compound **III** is shown in Fig. 3.

The ^1H NMR spectra for compounds **III** and **IV** show a splitting pattern typical of a monosubstituted ferrocene. For cyclopentadienyl rings which are singly substituted by electron-withdrawing groups, protons $\text{H}_{2,5}$ and $\text{H}_{3,4}$ generally give rise to unsymmetrical pairs of triplets corresponding to the spectrum of an A_2B_2 case. The ^1H NMR spectra of the chlondic anhydride derivatives of ferrocene show distinctive non-equivalence of the substituted ring protons, the effect being even more pronounced in the case of the



methyl ester. This unusual splitting pattern cannot be a result of interaction between the iron atom in the ferrocene nucleus and the carboxylic acid group in the substituent as shown in **V** as we would expect no such interaction to occur in the case of the methyl ester.

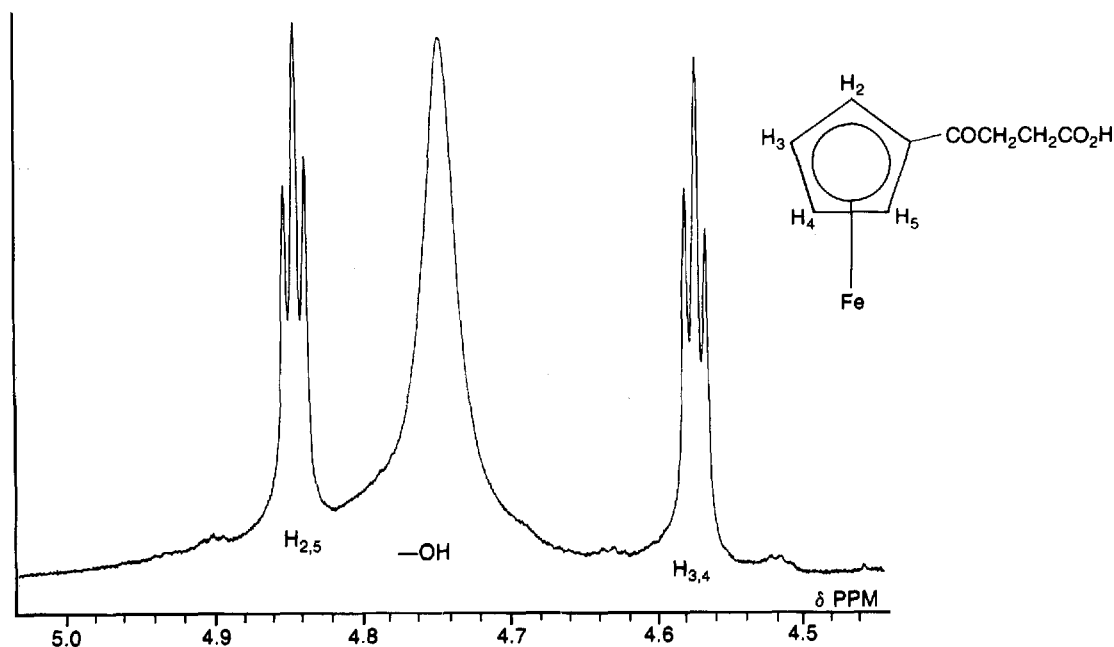
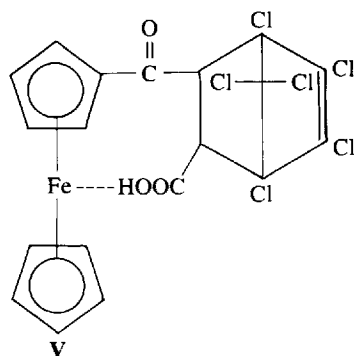


Figure 3 ^1H NMR spectrum (substituted cyclopentadienyl ring protons and carboxyl group only) of β -ferrocenylpropanoic acid **III**.



We have concluded that the unusual splitting pattern of the protons in the substituted ferrocene ring is probably a result of chirality in the chlorendic substituent. There are asymmetric carbon atoms present in the

chlorendic group and we believe the asymmetry is essentially the source of the non-equivalence of the pairs of protons in the substituted ring of the chlorendic derivatives.

We are currently examining the chemistry of these chlorendic compounds in more detail and intend to carry out an X-ray structure determination on the chlorendic methylester derivative.

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