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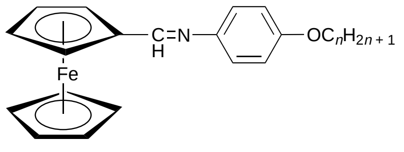
Syntheses of Ferrocene Derivatives with Potentially Mesogenic Functional Substituents

W. Edward Lindsell* and Lin Xinxin

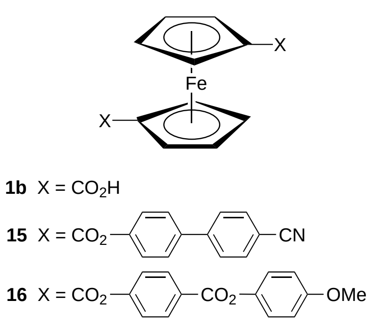
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

Ferrocenyl imines, $Fe\{\eta^5\text{-}C_5H_4CH{=}NC_6H_4OC_nH_{2n+1}\text{-}4)\}(\eta^5\text{-}C_5H_5)$ and $Fe\{\eta^5\text{-}C_5H_3\text{-}1\text{-}(CO_2Et)\text{-}3\text{-}(CH{=}NC_6H_4OC_nH_{2n+1}\text{-}4)\}(\eta^5\text{-}C_5H_5)$ (n = 5–9) produced from formylferrocene and 1-(ethoxycarbonyl)-3-(formyl)ferrocene, respectively, and some diaryl esters of ferrocenedicarboxlic acids have been synthesised and characterised by analysis and spectroscopy.

There is considerable interest in metal-containing liquid crystalline materials[1] and a number of mesogenic compounds containing the ferrocene moiety has been made in recent years, including monofunctionalised, 1,3- and 1,1′-difuntionalised and trifunctionalised systems.[3] We are interested in developing mesogenic ferrocene entities with suitable substituents for inclusion as side-chains in polymers. In this paper we report syntheses and characterisation of some precursor compounds.



5–9 n = 5–9, respectively

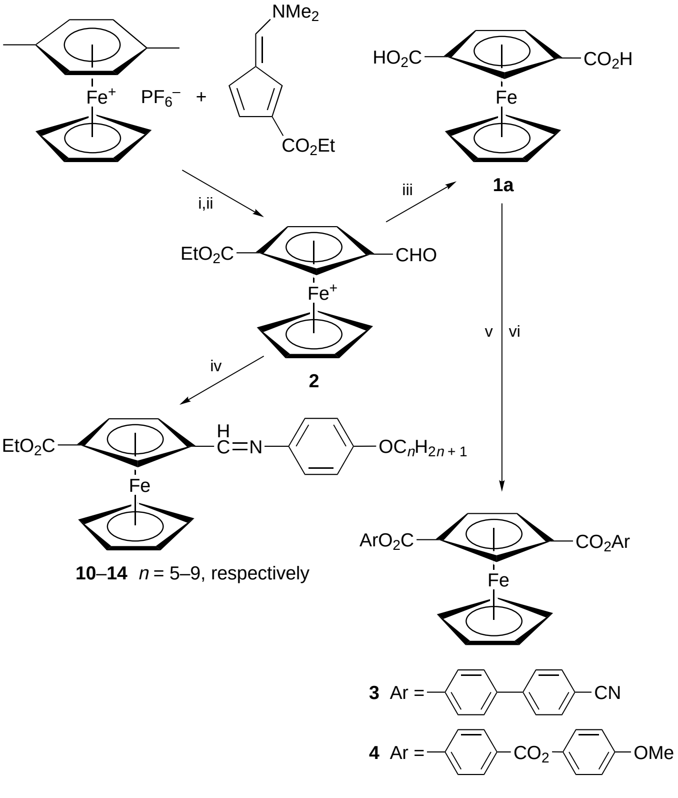


1b X = CO_2H

15 X = CO_2–

16 X = CO_2–

Various 1,3-ferrocene diesters with enantiotropic mesophases have previously been prepared from ferrocene-1,3-dicarboxylic acid (**1a**), but the only reported route to the precursor diacid involves a lengthy set of sequential reactions from ethylferrocene.[3,15] We have used a simpler, more versatile route to 1,3-disubstituted ferrocenes from (η^5-cyclopentadienyl)(η^6-*p*-xylene)iron(II) hexafluorophosphate, easily prepared from unsubstituted ferrocene, and 2-(ethoxycarbonyl)-6-(dimethylamino)pentafulvene, see Scheme 1.[16] The initial product, following work-up by hydrolysis, is 1-(ethoxycarbonyl)-3-(formyl)ferrocene (**2**) and this can be used directly to form other 1,3-substituted derivatives by reactions at the aldehydic and/or ester functions. Alternatively, **2** is readily oxidised by silver(I) to ferrocene-1,3-dicarboxylic acid (**1a**) from which 1,3-diesters and related ferrocenes are preparable.



Scheme 1 *Reagents*: i, $h\nu$, ii, $NaOH_{aq}$–EtOH; iii, Ag_2O–NaOH; iv, $H_2NC_6H_4OC_nH_{2n+1}\text{-}4$; v, $(COCl)_2$; vi, HOAr

Using **2** as a precursor, the new derivatives **10–14** were prepared. Also, for synthetic and spectroscopic comparisons, the imines **5–9** were obtained from formyl ferrocene. Moreover, we produced diester derivatives from **1a**, including the previous uncharacterised species **3** and **4**, and the related 1,1′-isomers **15** and **16** from ferrocene-1,1′-dicarboxylic acid.

The new compounds were characterised by analytical measurements and by IR, ^1H and, in some cases, ^{13}C NMR spectra. NMR resonances were assigned and include typical signals for the aromatic, imine and ester nuclei; *e.g.* $[Fe\{\eta^5\text{-}1,3\text{-}C_5H_3(CO_2Et)(CH{=}NC_6H_4OC_5H_{11}\text{-}4)\}(\eta^5\text{-}C_5H_5)]$ (**10**) δ_H ($CDCl_3$) 0.9 (br, 3 H, CH_3), 1.4 (complex, 7 H, CH_2 and CH_3), 1.8 (m, 2 H, CH_2), 3.95 (~t, 2 H, OCH_2), 4.98, 5.07 and 5.40 (br, 3 H, H-2, -4, -5 of C_5H_3), 6.9 and 7.1 (AA′BB′ m, 4, H, C_6H_4), 8.30 (s, 1 H, CH=N); δ_C ($^{13}C\{^1H\}$; $CDCl_3$) 14.0 and 14.5 (CH_3), 22.4, 28.2 and 29.0 (CH_2), 60.4 and 68.3 (OCH_2), 70.9 (C_5H_5), 70.7, 71.1 and 72.5 (CH, C-2, -4, -5 of C_5H_3), 74.0 (*quat.*-C, CCO_2Et of C_5H_4), 83.8 (*quat.*-C, CCH=N of C_5H_4), 115.1 and 121.7 (*arom.*-CH), 145.2 (*quat. arom.*-C), 157.3 (CH=N), 157.6 (*quat. arom.*-C), 170.6 (CO). Visual observations of the thermal properties of the isolated compounds, using a hot-stage microscope, do not indicate well defined thermotropic mesogenic properties for most of the products, but attachment of an array of these entities as side chains to a functionalised polymer backbone by linking to the second substituent of a di-substituted ferrocene may generate liquid crystalline polymers.

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*To receive any correspondence (*e-mail:* W.E.Lindsell@hw.ac.uk).

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Techniques used: IR, ^{1}H and ^{13}C NMR, thermal polarising optical microscopy

Tables: 1 (yields, melting points and analytical data for ferrocene derivatives)

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