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An assessment of second harmonic generation by donor acceptor molecules containing stilbenyl or diarylazo bridges between ferrocenyl donor and nitro acceptor groups

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Abstract

The compounds [Fe(η^5-C_5H_5)(η^5-C_5H_4–Ar) (Ar = 4,4′-$C_6H_4N_2C_6H_4NO_2$ (**1**), 4,4′-$C_6H_4N_2C_6H_3$(2′-Me)NO_2 (**2**), 4,4′-C_6H_3(3-Me)$N_2C_6H_3$(2′-Me)NO_2 (**3**) and *trans*-4,4′-C_6H_4(CH=CH)$C_6H_4NO_2$ (**4**) have been synthesized and their second order non-linear optical properties assessed by use of the Kurtz powder test for second harmonic generation on irradiation at 1907 nm. The stilbenyl compound, **4**, gave a signal of similar intensity to that of a urea standard but the others gave no detectable signal.

Key words: Ferrocene; Second harmonic generation; Non-linear optics; Diarylazo; Stilbenyl

1. Introduction

The continuing development of optical data transmission and processing technologies is generating a need for new materials which exhibit non-linear optical (NLO) properties. Although materials having third order NLO properties are of greater importance for optical data processing, there is continuing interest in molecular materials that exhibit second order NLO properties [1]. For large second order effects to be observed, it is necessary for the material to be composed of acentric molecules in which there is a large difference between the ground and excited state dipole moments of the molecule, as well as a large transition moment for the electronic excitation. The synthetic chemist can address these requirements by producing polarizable dipolar molecules. More difficult to meet is the further requirement that the molecules should pack in a non-centrosymmetric arrangement to produce a polar material. Although careful molecular design can be used to exercise some control over packing, chance still plays a major role in the discovery of new NLO materials. Thus the synthesis and evaluation of families of compounds, in order to determine which molecular features lead to NLO active materials, remains an important aspect of current research.

Research on organic NLO materials is now quite well developed [1], but work on organometallic NLO materials containing d-block metals is still in its infancy. Since their first report of a metallocene derivative exhibiting substantial second order NLO properties appeared in 1987 [2], Green and co-workers have continued to investigate compounds that contain ferrocenyl groups as the donor functionality and have now found a number of materials that show substantial second harmonic generation (SHG) on irradiation at 1907 nm [3].

In our laboratory, we have been investigating the use of d-block metal centres as the acceptor functionality in metal-organic materials which have the potential to exhibit second order NLO properties. In particular, we have found high SHG in materials where molybdenum or tungsten mononitrosyl acceptor groups are

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linked by polarizable bridges to ferrocenyl donor groups [4]. The synthesis routes to some of these complexes involve, as intermediates, compounds in which a ferrocenyl substituent is linked by a polarizable [5] diarylazo or stilbenyl bridge to a nitro group. The ability of these dipolar ferrocenyl derivatives to produce SHG has been evaluated by use of the Kurtz powder test, and the results provide data that complement those obtained by Green and co-workers.

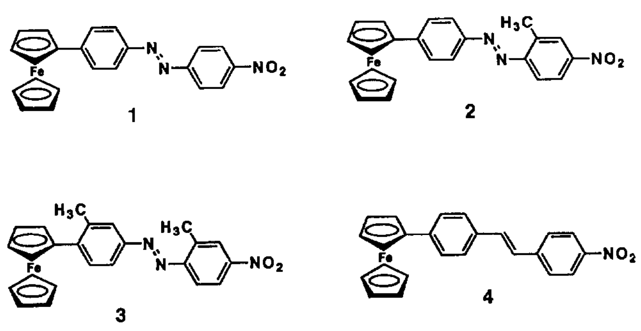


Fig. 1.

2. Discussion

2.1. Synthetic studies

The compound 4-nitro-4′-ferrocenylazobenzene (1) (Fig. 1) can be prepared from ferrocene *via* a diazonium coupling reaction using the commercial dye Disperse Orange 3 (4-nitro-4′-aminoazobenzene). However, this reaction gives a very poor yield, and a much better method for obtaining compounds such as **1** involves use of a condensation, the Mills Reaction, which is shown in Scheme 1. This approach has previously been used to prepare a number of ferrocenylazobenzenes including **1** [6]. However, in the present work it was necessary to use an alternative route to **1** because of the unavailability of one of the precursors for the Mills reactions, 4-nitrosonitrobenzene. The new compounds **2** and **3** were prepared in fairly high yield by condensing 4-ferrocenylaniline [7] or 4-ferrocenyl-3-methylaniline with 2-nitroso-5-nitrotoluene. The latter was prepared by the partial oxidation of 2-methyl-4-nitroaniline with Caro's acid [8].

The stilbene derivative, 4-ferrocenyl-4′-nitro-*trans*-stilbene (**4**), was obtained by using a classical base-catalysed condensation reaction between 4-nitrophenylacetic acid and 4-ferrocenylbenzaldehyde. The latter is a known compound [9] but for this study, it was prepared by a new method involving the DIBAL reduction of 4-ferrocenylbenzonitrile [10].

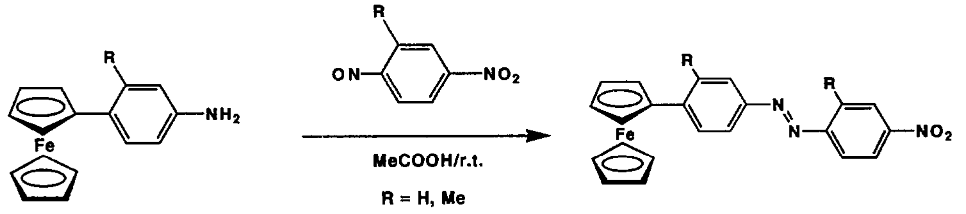
The ferrocenyl derivatives were characterized by IR and ^{1}H NMR spectroscopy. EI mass spectrometry and elemental analyses. These techniques all gave results in accord with the proposed molecular formulations. In addition to the usual aromatic absorptions around 1600 cm^{-1}, mono-arylferrocenes exhibit a medium intensity band at *ca.* 890 cm^{-1} that can be observed in the spectra of all the compounds discussed here. This band is quite characteristic of such substances, and may be associated with a C–H bending mode of the ferrocene ring [11]. The characteristic absorptions for the NO_2 group were also observed in the nitro derivatives.

All of the compounds exhibit ^{1}H NMR signals associated with the aryl protons, and in the stilbene derivative, **4**, the ethylene bridge signals appear as doublets with a coupling constant of ≃ 16 Hz, in accord with the expected *trans* stereochemistry. The ferrocenyl groups give rise to the expected pattern of signals, with the unsubstituted C_5H_5 ring giving a singlet at essentially the same shift as ferrocene itself. The monosubstituted C_5H_4 ring exhibits an unsymmetrical pair of triplets corresponding to the spectrum of an A_2B_2 system. These signals appear to low field of the C_5H_5 singlet, showing that all four ring protons are deshielded by the aryl ring. In some cases, these triplets are not resolved at the NMR frequency used (270 MHz).

All of the compounds provide intense molecular ion peaks in their mass spectra and fragmentation patterns are as expected for simple aryl compounds. The nitro compounds show loss of NO_2 (M − 46) and in some cases loss of NO (M − 30).

2.2. Electrochemical studies

The electrochemical properties of the nitro ferrocenyl compounds were investigated in dichloromethane solution by cyclic voltammetry and the results obtained



Scheme 1.

TABLE 1. Cyclic voltammetry data for ferrocenyl compounds 4-Fc-Z [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$]

Z (compound no.)	E_f (V) [a]	ΔE_p (mV)	Other waves	
			E_f (V)	ΔE_p (mV)
$-C_6H_4-NH_2$	+0.49	420		
H (ferrocene)	+0.57	70		
$-C_6H_4CH{=}CHC_6H_4NO_2$ (**4**)	+0.59	115	−0.93	185
$-C_6H_3\text{-}2\text{-}(CH_3)N{=}NC_6H_3\text{-}2\text{-}(CH_3)-NO_2$ (**3**)	+0.62	90	−0.77	90
			−1.03	85
$-C_6H_4N{=}NC_6H_4NO_2$ (**1**)	+0.64	145	−0.73	160
			−1.02	170
$-C_6H_4-N{=}N-C_6H_3\text{-}2\text{-}(CH_3)-NO_2$ (**2**)	+0.64	185	−0.76	195
			−1.03	170
$-C_6H_4-CHO$	+0.65	130		
$-C_6H_4-CN$	+0.67	180		
$-C_6H_3\text{-}2\text{-}(CH_3)-NO_2$	+0.67	100	−1.04	115
$-C_6H_4-NO_2$	+0.71	170	−0.98	470

[a] All potentials measured relative to SCE in dry CH_2Cl_2 using a platinum-bead working electrode; 0.2 M $[NBu_4][BF_4]$ as supporting electrolyte; scan rate 200 mV s^{-1}.

are presented in Table 1 along with data for some other monoaryl compounds used in this study.

The oxidation potentials are in accord with earlier reports of electrochemical studies on ferrocenyl derivatives [10,12] in that they demonstrate that the E_f value for oxidation is highly sensitive to substitution on the aryl ring directly attached to ferrocene. Thus, in 4-$FcC_6H_4NO_2$, the strongly electron withdrawing nitro group causes a 140 mV anodic shift in oxidation potential relative to that for FcH. Comparison of the oxidation potentials of 4-$FcC_6H_4NO_2$ and FcC_6H_4-2-(CH_3)-4-NO_2 reveals a 40 mV cathodic shift as an *ortho* methyl group is added to the benzene ring. A comparison of **1** and **4** shows that the change from the diarylazo substituent to stilbenyl produces a 50 mV cathodic shift, which is in keeping with the superior electron withdrawing nature of the azo function. An additional irreversible wave at highly cathodic potential is observed in compounds with nitro groups, and a pair of such waves are seen for the nitro-azo compounds. These may be attributed to reduction processes of these groups. A comparison of the ΔE_p values with that of the ferrocene standard indicates that none of the compounds show truly reversible one-electron oxidation waves attributable to the ferrocenyl moiety, but several have quasi-reversible oxidation waves.

2.3. *Electronic spectral studies*

There are two important reasons for studying the solution electronic absorption spectra of molecular species designed to exhibit NLO properties. Firstly, it is necessary to know at which wavelengths transparency can be expected. Transparency at the fundamental frequency (usually 1907 or 1064 nm) used in the Kurtz powder test for SHG is desirable, and any absorption at the second harmonic frequencies (usually 953 or 532 nm) will reduce the amount of SHG observed from a solid sample. For the purposes of SHG in the visible region, the onset of absorption closer to the UV region is desirable, but this is not essential for other second order NLO properties such as the linear electro-optic effect.

The second aspect of importance is the phenomenon of solvatochromism, *i.e.* solvent-induced shifts in absorption spectra. These arise from dipolar interactions between solvent and solute molecules, so that the greatest changes in absorption spectra are observed between solvents of largely differing polarity (*e.g.* n-hexane and DMF). Previous reports have noted that the occurrence of significant solvatochromism is often an indicator of high molecular hyperpolarisability, β, and hence of potential bulk NLO properties [13]. As regards metal-organic compounds, relationships have been drawn between solvatochromism and MLCT excitations [14]. The compound (*cis*)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] provides an example of a species which displays marked solvatochromism and also a high powder SHG [2]. The electronic absorption spectra of some dipolar ferrocenyl compounds have already been investigated in detail by others. 4-Ferrocenylnitrobenzene shows three bands of which two are in the UV region. The visible band in particular shows marked bathochromic shifts as more electron-withdrawing aryl substituents are introduced, and is thought to be due to an MLCT excitation [15]. For the ferrocenylazobenzenes [6a], two bands are again present and similar shifts are observed, implying large resonance interactions between 4-ferrocenyl and 4′-substituents occurring *via* the azobenzene bridge. Electronic spectra were recorded in dichloromethane

TABLE 2. UV-visible excitation maxima for ferrocenyl compounds 4-Fc-Z [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$]

Z (compound no.)	λ_{max} (nm) [a]	ϵ (mol^{-1} dm^3 cm^{-1})
$C_6H_4NO_2$	324	8600
	396	2600
	500	2800
$-C_6H_4N{=}NC_6H_4NO_2$ (1)	372	26500
	540	6300
$-C_6H_4N{=}NC_6H_3\text{-}2\text{-}(CH_3)\text{-}4\text{-}NO_2$ (2)	374	24200
	536	5900
Ferrocene [b]	326	50
	440	87
Azobenzene [c]	316	21200
	441	519
4-Ferrocenylazobenzene [c]	350	25100
	488	4640

[a] All spectra recorded in dichloromethane at ambient temperature; concentrations of *ca.* 10^{-5} M for UV spectra and *ca.* 10^{-4} M for visible spectra were used. [b] In absolute ethanol [18]. [c] In absolute ethanol [6b].

for the ferrocenyl compounds **1** and **2**, and data are presented in Table 2 along with data for several reference compounds. A solvatochromism study, involving eight solvents of differing dielectric properties, was carried out on **2**, but only modest shifts of up to 24 nm were observed, as shown in Table 3.

2.4. *Kurtz powder tests and structural investigations*

Compounds containing both nitro and ferrocenyl groups have molecular structures which could be expected to give rise to large second order hyperpolarizabilities (β values) [16–18]. Calculations indicate that, for $(\eta^5\text{-}C_5R_5)Fe(\eta^5\text{-}C_5H_4CH{=}CR'C_6H_4NO_2\text{-}4)$ ($R = R' = H$; $R = H$, $R' = CN$; $R = Me$, $R' = H$, CN) the, ferrocenyl group acts as a π-donor, comparable with *p*-methoxyphenyl, and that substituents which enhance the donor character of the ferrocenyl moiety increase β. However, iron d–d transitions contribute little to β although the lower ionization potential of Fe leads to higher β values than were observed for the corresponding Ru complexes [17,18]. If such molecules also crystallize in a non-centrosymmetric array, then this could produce materials which possess high bulk second order NLO coefficients, $\chi^{(2)}$. Thus compounds **1** to **4**, together with 4-ferrocenylnitrobenzene and 4-ferrocenyl-3-methylnitrobenzene, were tested for powder SHG using a 1907 nm laser fundamental. However, of these, only the stilbenyl compound, **4**, gave a detectable signal, and this was about equal to that from a urea standard (under the same conditions, DAN gave a signal 5.0 times that from urea). Although these findings reveal little about the molecular hyperpolarizabilities of these systems, they do emphasize the importance of crystal packing in determining the ability of a material to exhibit SHG. In the case of M(NO)$\{HB(Me_2C_3HN_2)_3\}Cl\{NHC_6H_4N{=}NC_6H_4(\eta^5\text{-}C_5H_4)\text{-}Fe(\eta^5\text{-}C_5H_5)\}$ ($M = Mo$, W), for which there is a favourable crystal packing, a high SHG intensity was obtained in the Kurtz powder test [4].

TABLE 3. Solvatochromism study for 4-nitro-2-methyl-4′-ferrocenyl-azobenzene (**2**)

Solvent	λ_{max} (vis.) [a]	λ_{max} (UV) [b]
n-Pentane	518	368
Ethyl acetate	526	371
Methanol	528	370
Acetone	529	370
Ethanol	531	373
Chloroform	536	372
Dichloromethane	536	374
DMF	542	379

[a] Spectra recorded at ambient temperature using concentrations of *ca.* 10^{-4} M. [b] Spectra recorded at ambient temperature using concentrations of *ca.* 10^{-5} M.

Single crystals suitable for X-ray study could not be obtained from **1**, **3** or **4**, but a single crystal X-ray diffraction study of **2** was possible [17]. This showed that the space group adopted is centrosymmetric (monoclinic $P2_1/c$). The unit cell contains four molecules which align antiparallel to give a complete cancellation of dipoles, precluding a bulk non-zero $\chi^{(2)}$. This explains why, despite its favourable molecular structure, **2** exhibits no powder SHG. It seems likely that similar centrosymmetric packing arrays may occur in the other ferrocenyl compounds that show no SHG activity. In an attempt to investigate this further, powder X-ray diffraction studies were undertaken. The results suggest that the derivatives **1** and **2** adopt different crystal packing arrangements but, since compound **1** exhibits no SHG, it seems likely that it too adopts a centrosymmetric packing arrangement, albeit different from that adopted by **2**. Clearly, the SHG-active stilbene compound **4** must have a non-centrosymmetric crystal structure which is different from either of those found with the azo compounds. This is perhaps a surprising result in view of the structural similarity to its azo-analogue, **1**. However, powder X-ray diffraction traces for **4** and **1** confirm that these two compounds do indeed adopt different packing arrangements. These findings indicate that in these dipolar ferrocenyl systems, quite small changes in molecular structure can result in differences in crystal packing which have a major effect on second order NLO properties.

3. Experimental details

The known compounds 4-ferrocenylnitrobenzene [7], 4-ferrocenyl-3-methylnitrobenzene [10] and 4-ferrocenylbenzonitrile [10] were prepared by a modified version of the standard diazonium reaction. The procedure used is described below for 4-ferrocenyl-3-methylnitrobenzene and data are provided for 4-ferrocenylnitrobenzene prepared in this fashion. The known compound 4-ferrocenylaniline [7] and the new compound 4-ferrocenyl-3-methylaniline were prepared by a modified version of the tin/HCl reduction of their nitro precursors. This procedure is described below for 4-ferrocenyl-3-methylaniline and data are also given for 4-ferrocenylaniline prepared by this method, 2-Nitroso-5-nitrotoluene was prepared from 2-methyl-4-nitroaniline by oxidation with Caro's acid [8]. A pure sample of 4-nitro-4′-aminoazobenzene was obtained by an overnight Soxhlet extraction of the commercial dye Disperse Orange 3 using dichloromethane. All other reagents were used as supplied. Silica gel 60 (70–230 mesh) was used for all column chromatography, which was carried out on a column of dimensions 50 × 3.5 cm^2. Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham.

Infrared spectra were recorded using a PE 297 spectrometer with samples as KBr discs. ^1H NMR (270 MHz) spectra were obtained from solutions in $CDCl_3$ using a Jeol GX 270 spectrometer. Cyclic voltammetric measurements were made using a PAR 174A polarograph. Solutions in CH_2Cl_2 were *ca.* 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in $[N^nBu][BF_4]$ as base electrolyte. A Pt bead test electrode was used with a scan rate of 200 mV s^{-1}. An SCE reference electrode was used with ferrocene as an internal standard. Potentials are quoted relative to the SCE. The determination of the second harmonic intensity of powder samples was made relative to that of powdered urea. Pulses (width 4 ns, repetition rate 1 Hz) of 0.2 mJ energy at a wavelength of 1.907 μm were weakly focused on to sample cells containing finely ground (ungraded) material and the second harmonic light at 950 nm measured on an S1 photomultiplier tube. Boxcar gate sampling was used to provide data points averaged over 10 pulses and the mean of these points provided the values of relative harmonic intensity for SHG quoted.

3.1. 4-Ferrocenyl-3-methylnitrobenzene

Ferrocene (3.80 g, 20.4 mmol) was added to sulphuric acid (spec. grav. 1.84, 25 cm^3) and the resulting deep blue ferrocenium solution was stirred at room temperature for 2 h. The solution was then poured into ice/water (100 cm^3) and allowed to warm to room temperature. A solution of sodium nitrite (0.91 g, 13.2 mmol) in water (5 cm^3) at 0°C was added dropwise to a stirred solution of 2-methyl-4-nitroaniline (1.83 g, 12.0 mmol) in 1:1 water/hydrochloric acid (spec. grav. 1.18) (10 cm^3) kept at 0°C by an ice/water bath and the mixture was stirred for 30 min to ensure full diazotization. Copper powder (1.0 g) was added to the ferrocenium solution and the diazonium solution was added dropwise with the vigorous stirring.

After 24 h stirring at room temperature, effervescence due to liberated nitrogen had ceased and ascorbic acid (5 g) was added to the dark mixture to reduce any remaining ferrocenium to ferrocene. Dichloromethane (100 cm^3) was added and the organic layer separated. The aqueous layer was extracted with further dichloromethane (4 × 50 cm^3), and the combined organic extracts were filtered through Celite before removal of the solvent *in vacuo* to give a dark solid. This was subjected to column chromatography using gradient elution with an increasing proportion of dichloromethane in n-hexane. The first yellow fraction, eluted with pure n-hexane, yielded unchanged ferrocene, and the second, eluted with 50% dichloromethane/n-hexane, gave upon evaporation deep red-purple microcrystalline 4-ferrocenyl-3-methylnitrobenzene (1.31 g, 34%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}C_6H_3\text{-}2\text{-}(CH_3)\text{-}4\text{-}NO_2$, m.p. 122–125°C (lit. [10] 127–129°C). Anal. Found: C, 63.6; H, 4.9; N, 4.1%; M^+, 321. $C_{17}H_{15}FeNO_2$ calc.: C, 63.6; H, 4.7; N, 4.4%; M, 321. ν_{max} (NO_2) 1505s and 1340s cm^{-1}. $\delta_H(CDCl_3)$ 8.01 and 7.98 ($1\frac{1}{2}$H, br s, C_6H_3; $\frac{1}{2}$H, s, C_6H_3]; 7.78 [1H, d, $J(HH) = 9$ Hz, C_6H_3); 4.58 and 4.42 (2H, d, $J(HH) = 2$ Hz; 2H, d, $J(HH) = 2$ Hz, C_5H_4); 4.13 (5H, s, C_5H_5); 2.51 (3H, s, CH_3). m/z 321 (M^+), 291 $(M - NO)$, 275 $(M - NO_2)$, 121 $(M - C_{12}H_{10}NO_2)$.

3.2. 4-Ferrocenylnitrobenzene

This was prepared similarly but starting from 4-nitroaniline (1.66 g, 12.0 mmol). The second major fraction from column chromatography, eluted with 40% dichloromethane/n-hexane, yielded the product as a deep red-purple microcrystalline solid (1.33 g, 36%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}C_6H_4\text{-}4\text{-}NO_2$, m.p. 166–169°C (lit. [7] 169–170°C). Anal Found: C, 62.4; H, 4.3; N, 4.5%; M^+, 307. $C_{16}H_{13}FeNO_2$ calc.: C, 62.6; H, 4.3; N, 4.6%; M, 307. ν_{max} (NO_2) 1505s and 1340s cm^{-1}. $\delta_H(CDCl_3)$ 8.14 and 7.56 (2H, d, $J(HH) = 9$ Hz; 2H, d, $J(HH) = 9$ Hz. C_6H_4); 4.74 and 4.47 (2H, d, $J(HH) = 2$ Hz; 2H, d, $J(HH) = 2$ Hz, C_5H_4); 4.06 [5H, s, C_5H_5). m/z 307 (M^+), 261 $(M - NO_2)$, 121 $(M - C_{11}H_8NO_2)$.

3.3. 4-Ferrocenylbenzonitrile

This was prepared similarly but starting from 4-aminobenzonitrile (1.42 g, 12.0 mmol). The second major fraction from column chromatography, eluted with 60% dichloromethane/n-hexane, yielded the product as an orange-red microcrystalline solid (1.34 g, 39%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}C_6H_4\text{-}4\text{-}CN$, m.p. 139–142°C (lit. [10] 145–146°C). Anal. Found: C, 70.8; H, 4.7; N, 5.0%; M^+, 287. $C_{17}H_{13}FeN$ calc.: C, 71.1; H, 4.6; N, 4.9%; M, 287. ν_{max} (CN) 2220s cm^{-1}. $\delta_H(CDCl_3)$ 7.56 and 7.51 (2H, d, J(HH) = 9 Hz; 2H, d, J(HH) = 9 Hz, C_6H_4); 4.69 and 4.42 (2H, t, J(HH) = 2 Hz; 2H, d, J(HH) = 2 Hz, C_5H_4); 4.4 [5H, s, C_5H_5]. m/z 287 (M^+), 222 ($M - C_5H_5$), 166 ($M - C_5H_5Fe$), 121 ($M - C_{12}H_8N$)

3.4. 4-Ferrocenyl-3-methylaniline

A mixture of granulated tin (2.0 g) and 4-ferrocenyl-3-methylnitrobenzene (1.89 g, 6.5 mmol) in 1 : 1 hydrochloric acid (spec. grav. 1.18)/ethanol (50 cm^3) was stirred under reflux for 2 h. The resulting orange solution was then cooled to room temperature and neutralized with 40% aqueous sodium hydroxide. Water (100 cm^3) and dichloromethane (100 cm^3) were added, and the mixture filtered through dichloromethane/silica gel to remove inorganic salts. The orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 × 30 cm^3). The combined organic extracts were evaporated to dryness to yield 4-ferrocenyl-3-methylaniline (1.70 g, 90%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}C_6H_3\text{-}2\text{-}(CH_3)\text{-}4\text{-}NH_2$, m.p. 87–91°C. Anal. Found: C, 70.5; H, 6.2; N, 5.0%; M^+, 291. $C_{17}H_{17}FeN$ calc.: C, 70.1; H, 5.9; N, 4.8%; M, 291. ν_{max} (NH_2) 3410m and 3340m cm^{-1}. $\delta_H(CDCl_3)$ 7.50, 6.54 and 6.48 (1H, d, J(HH) = 8 Hz; 1H, dd, J(HH) = 2 and 8 Hz; 1H, d, J(HH) = 2 Hz, C_6H_3); 4.39 and 4.22 (2H, t, J(HH) = 2 Hz; 2H, t, J(HH) = 2 Hz, C_5H_4); 4.11 (5H, s, C_5H_5); 3.57 (2H, br s, NH_2); 2.30 (3H, s, CH_3). m/z 291 (M^+), 121 ($M - C_{12}H_{12}N$).

3.5. 4-Ferrocenylaniline

This compound was prepared in the way described for 4-ferrocenyl-3-methylaniline but starting from 4-ferrocenylnitrobenzene (1.89 g, 6.5 mmol). This afforded the product as an orange powder (1.71 g, 95%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}C_6H_4\text{-}4\text{-}NH_2$, m.p. 157–159°C (lit. [7] 159–160.5°C). Anal. Found: C, 69.3; H, 5.7; N, 5.1%; M^+, 277. $C_{16}H_{15}FeN$ calc.: C, 69.3; H, 5.5; N, 5.1%; M, 277. ν_{max} (NH_2) 3445m and 3355m cm^{-1}. $\delta_H(CDCl_3)$ 7.29 and 6.63 (2H, d, J(HH) = 9 Hz; 2H, d, J(HH) = 9 Hz, C_6H_4); 4.53 and 4.23 (2H, t, J(HH) = 2 Hz; 2H, t, J(HH) = 2 Hz, C_5H_4); 4.03 [5H, s, C_5H_5); 3.62 (1H, br s, NH_2). m/z 277 (M^+), 156 ($M - C_5H_5Fe$), 121 ($M - C_{11}H_{10}N$).

3.6. 4-Ferrocenylbenzaldehyde

A solution of DIBAL (diisobutylaluminiumhydride; 1.0 M in dry dichloromethane, 3.5 cm^3) was added dropwise to a stirred solution of 4-ferrocenylbenzonitrile (1.0 g, 3.5 mmol) in dry toluene (20 cm^3) at room temperature under a dry nitrogen. Addition was complete after 15 min, during which a 3°C in temperature was detected. The solution was stirred for a further 2 h, then methanol (5 cm^3) was added to destroy any residual DIBAL. Aqueous sulphuric acid (sulphuric acid, spec. grav. 1.84, in water 1 : 3, 20 cm^3) was added to hydrolyse the intermediate imine complex and the solution was then extracted with dichloromethane (5 × 10 cm^3). The organic extracts were combined and evaporated to yield the crude product. This was purified by column chromatography with an 80% dichloromethane/n-hexane solution as eluent. The first major fraction (red-orange) was 4-ferrocenylbenzonitrile (0.10 g, 10% recovery), and the second major fraction (orange) yielded 4-ferrocenylbenzaldehyde (0.85 g, 84%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}C_6H_4\text{-}4\text{-}CHO$, m.p. 133–136°C (lit. [9] 136.5–137°C. Anal. Found: C, 70.1; H, 5.2%; M^+, 290. $C_{17}H_{14}FeO$ calc.: C, 70.4; H, 4.9%; M, 290. ν_{max}(OC–H) 2810w, 2790w and 2730w; ν_{max}(CO) 1695s cm^{-1}. $\delta_H(CDCl_3)$ 9.97 (1H, s, OCH); 7.79 and 7.59 (2H, d, J(HH) = 8 Hz; 2H, d, J(HH) = 8 Hz, C_6H_4); 4.74 and 4.43 (2H, t, J(HH) = 2 Hz; 2H, t, J(HH) = 2 Hz, C_5H_4); 4.04 (5H, s, C_5H_5). m/z 290 (M^+), 121 ($M - C_{11}H_8CHO$).

3.7. 4-Nitro-4′-ferrocenylazobenzene (1)

This compound was prepared in the way described for ferrocenyl-3-methylnitrobenzene but starting from 4-nitro-4-′-aminoazobenzene (2.91 g, 12.0 mmol). Again column chromatography using gradient elution was used to separate the products. The second major fraction (purple-red) was eluted with 100% dichloromethane to give 4-nitro-4′-ferrocenylazobenzene as dark green microcrystals (0.35 g, 7%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{–}C_6H_4N{=}NC_6H_4\text{-}4\text{-}NO_2$, m.p. 246–249°C (lit. [6a] 260°C dec.). Anal. Found: C, 64.4; H, 4.3; N, 10.4%; M^+, 411. $C_{22}H_{17}FeN_3O_2$ calc.: C, 64.3; H, 4.2; N, 10.2%; M, 411. ν_{max} (NO_2) 1520s and 1345s cm^{-1}. $\delta_H(CDCl_3)$ 8.39 and 8.03 (2H, d, J(HH) = 9 Hz; 2H, d, J(HH) = 9 Hz, $C_6H_4\text{–}NO_2$); 7.91 and 7.63 (2H, d, J(HH) = 9 Hz; 2H, d, J(HH) = 9 Hz, C_6H_4–Fc); 4.77 and 4.45 (2H, s; 2H, s, C_5H_4); 4.08 (5H, s, C_5H_5). m/z 411 (M^+), 365 ($M - NO_2$), 261 ($M - N_2C_6H_4NO_2$).

3.8. 4-Nitro-2-methyl-4′-ferrocenylazobenzene (2)

A mixture of 2-nitroso-5-nitrotoluene (3.6 g, 22 mmol) and 4-ferrocenylaniline (5.0 g, 18 mmol) in glacial acetic acid (spec. grav. 1.05, 400 cm^3) was stirred at room temperature for 5 days. Water (1 dm^3) and dichloromethane (100 cm^3) were added, the mixture shaken and the organic layer separated. The aqueous layer was extracted with further dichloromethane (3 × 50 cm^3), and the combined organic extracts were evaporated to dryness to yield the crude product. This was purified by column chromatography using gradient elution from 50% dichloromethane/n-hexane to 100% dichloromethane. The major purple band, eluted with 70% dichloromethane/n-hexane, afforded upon evaporation deep purple microcrystalline **2** (4.5 g, 59%)

(η^5-C_5H_5)Fe(η^5-C_5H_4)–C_6H_4N=NC_6H_3-2-(CH_3)-4-NO_2, m.p. 156–160°C. Anal. Found: C, 64.7; H, 4.8; N, 9.8%; M$^+$, 425. $C_{23}H_{19}FeN_3O_2$ calc.: C, 65.0; H, 4.5; N, 9.9%; M, 425. ν_{max} (NO_2) 1520s and 1345s cm^{-1}. δ_H($CDCl_3$) 8.23, 8.14 and 7.71 (1H, s; 1H, d, J(HH) = 9 Hz; 1H, d, J(HH) = 9 Hz, C_6H_3); 7.91 and 7.63 (2H, d, J(HH) = 8 Hz; 2H, d, J(HH) = 8 Hz, C_6H_4-Fc); 4.77 and 4.45 (2H, s; 2H, s, C_5H_4); 4.08 (5H, s, C_5H_5); 2.80 (3H, s, CH_3). *m/z* 425 (M$^+$, 261 (M – $N_2C_6H_4CH_3NO_2$).

3.9. 4-Nitro-2-methyl-3′-methyl-4′-ferrocenylazobenzene (3)

This compound was prepared a similar way 2 but starting from 4-ferrocenyl-3-methylaniline (5.24 g, 18 mmol). Upon evaporation, the major purple fraction from the column yielded deep green-black microcrystalline **3** (5.14 g, 65%)

(η^5-C_5H_5)Fe(η^5-C_5H_4)–C_6H_3-2-(CH_3)-4-N=NC_6H_3-2-(CH_3)-4-NO_2, m.p. 142–145°C. Anal. Found: C, 65.3; H, 4.9; N, 9.6%; M$^+$, 439. $C_{24}H_{21}FeN_3O_2$ calc.: C, 65.6; H, 4.8; N, 9.6%; M, 439. ν_{max} (NO_2) 1520s and 1345s cm^{-1}. δ_H($CDCl_3$) 8.23, 8.14 and 7.84 (1H, s; 1H, dd, J(HH) = 2, 9Hz; 1H, d, J(HH)9 Hz, C_6H_3); 7.78–7.75 and 7.70 (2H, m; 1H, d, J(HH) = 9 Hz, C_6H_3); 4.62 and 4.41 (2H, t, J(HH) = 2 Hz; 2H, t, J(HH) = 2 Hz, C_5H_4); 4.16 (5H, s, C_5H_5); 2.80 (3H, s, CH_3); 2.55 (3H, s, CH_3). *m/z* 439 (M$^+$), 271 (M – $N_2C_6H_3CH_3NO_2$).

3.10. 4-Nitro-4′-ferrocenylstilbene (4)

A solution of 4-ferrocenylbenzaldehyde (0.5 g, 1.72 mmol), 4-nitrophenylacetic acid (1.0 g, 5.52 mmol) and piperidine (1 cm^3) was stirred at reflux in pyridine (5 cm^3) under nitrogen for 13 h. The mixture was cooled and the solvent removed *in vacuo*. The residue was subjected to column chromatography using gradient elution starting from a 70% dichloromethane/n-hexane solution with increasing dichloromethane concentration. The first major band (red) yielded upon evaporation dark brick-red **4** (0.47 g, 66%), the second major fraction (orange) was unchanged 4-ferrocenylbenzaldehyde (0.12 g, 23% recovery).

(η^5-C_5H_5)Fe(η^5-C_5H_4)–C_6H_4CH=CHC_6H_4-4-NO_2, m.p. 270°C (dec.). Anal. Found: C, 70.0; H, 4.7; N, 3.0%; M$^+$, 409. $C_{24}H_{19}FeNO_2$ calc.: C, 70.4; H, 4.7; N, 3.4%; M, 409. ν_{max} (NO_2) 1510s and 1330s cm^{-1}. δ_H($CDCl_3$) 8.22 and 7.64 (2H, d, J(HH) = 9 Hz; 2H, d, J(HH) = 8 Hz, C_6H_4–NO_2); 7.48 (4H, s, C_6H_4–Fc); 7.26 and 7.13 (1H, d, $J(HH)_{trans}$ = 16 Hz; 1H, d, $J(HH)_{trans}$ = 16 Hz, CH=CH); 4.69 and 4.37 (2H, t, J(HH) = 2 Hz; 2H, t, J(HH) = 2 Hz, C_5H_4); 4.05 (5H, s, C_5H_5). *m/z* 409 (M$^+$), 379 (M – NO), 362 (M – 1 – NO_2).

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