



2-Ferrocenyl-substituted pyrylium ions from coupling of ethynylferrocene with cyclomanganated chalcones

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ABSTRACT

2-Ferrocenyl-substituted pyrylium salts are produced when orthomanganated chalcones are reacted with ethynylferrocene in CCl₄. When the reaction is carried out in benzene, intermediate ferrocenyl-substituted (η^5 -pyranil)Mn(CO)₃ species can be isolated which give the pyrylium cations on oxidation. The electrochemistry of the 2-ferrocenyl-pyrylium cations shows both oxidation (of the ferrocenyl) and reduction (of the pyrylium) processes, and the UV–visible spectra show a broad band at ca 680 nm which can be assigned to an intramolecular charge transfer transition.

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1. Introduction

Pyrylium cations are aromatic species formally related to benzene by replacement of a CH by an O⁺ ion. They are less aromatic than benzene or pyridine, so are more reactive and find wide application in organic synthesis [1]. They have uses ranging from dyes and photosensitisers to corrosion-inhibitors and have a well developed oxidation-reduction chemistry [2]. Balaban et al. have reviewed the many syntheses of pyrylium salts containing different organic substituents [1]. However there appear to be relatively few pyrylium cations incorporating organometallic substituents. Russian workers have briefly reported examples of ferrocenyl-substituted pyrylium perchlorates, and showed these were readily transformed into the corresponding pyridines, but gave few physical data [3]. Caro's group have investigated the synthesis, structures and some reactions of pyrylium cations substituted by an acetylenic-CO₂(CO)₆ moiety, or by (η^5 -C₅H₄)M(CO)₃ (M = Mn, Re), (η^6 -C₆H₅)Cr(CO)₃ or 4-ferrocenyl groups [4], as well as bispyrylium salts incorporating ferrocenyl methylene substituents [5]. Shaw et al. have reported pyrylium cations directly σ -bonded to Mn(CO)₅ or Fe(CO)₂Cp groups, and investigated their electrochemistry [6].

We have previously established a new synthesis of pyrylium cations, via the reaction of cyclomanganated chalcones with

alkynes [7]. The present report uses this method to provide 2-ferrocenyl-pyrylium compounds and describes spectroscopic and electrochemical properties.

2. Results and discussion

2.1. Reaction of ferrocenylethyne with cyclomanganated chalcones

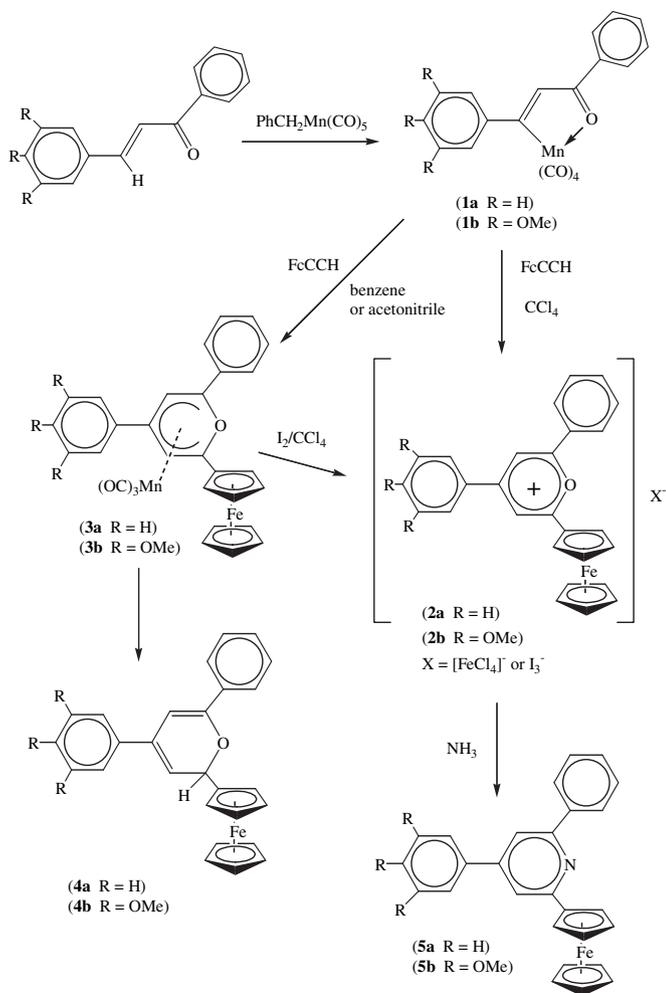
Reactions carried out with the parent chalcone and the trimethoxy-substituted analogue are summarized in Scheme 1.

When FcCCH (Fc = ferrocenyl) was reacted with the cyclomanganated chalcone **1a** in refluxing CCl₄ a green powder precipitated. This was identified as being the ferrocenyl-substituted pyrylium cation **2a** with [FeCl₄][−] as the counterion, this assignment supported by microanalytical data and by high resolution ESI-MS peaks found for the cation and anion in the +ve and −ve ion modes respectively. NMR spectra were not obtainable because of the paramagnetism of the [FeCl₄][−] anion. The green colour is also strongly indicative of a ferrocenyl-pyrylium species by comparison with the colour reported for analogues isolated as ClO₄[−] salts in earlier work [3]. The positioning of the ferrocenyl group on the ring adjacent to the oxygen atom has precedent from earlier studies where the bulky group of the alkyne ends up in this position [7].

In contrast, when the reaction between **1a** and FcCCH was carried out in refluxing benzene (or acetonitrile) the resulting solution was intensely red. Chromatography separated two main products. The first of these was an η^5 -(ferrocenyl)pyranil-

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manganese tricarbonyl, **3a**, corresponding to the major product reported from reactions of other alkynes with cyclomanganated chalcones [7,8]. This was fully characterized by elemental analysis, and by an X-ray crystal structure determination (see below), with further validation provided by ^1H and ^{13}C NMR spectra. The ESI-MS gave a single peak assignable to $[\text{M}-\text{Mn}(\text{CO})_3]^+$ suggesting very ready oxidation and loss of the manganese carbonyl group to generate the very stable pyrylium cation in the source of the mass spectrometer. As expected [7], oxidation of **3a** also cleaved the manganese carbonyl group to generate the pyrylium cation **2a**, isolated as the I_3^- salt, a reaction distinguished by a dramatic colour change from deep red to intense green. Interestingly, during the chromatographic separation the red band from which **3a** was isolated was tailed by a faint green streak which suggests oxidation of the pyranyl-manganese to form the pyrylium salt was taking place on the silica.

The second product from the reaction in benzene was orange and was characterized as the substituted pyran **4a**, arising presumably from protio-demetalation of the pyranyl-manganese species **3a**. This was identified by elemental analysis and by ^1H and ^{13}C NMR spectra. In particular a distinctive doublet proton resonance at δ 6.20 was assigned to the additional hydrogen on the pyran C2. For this example ESI-MS gave a main peak assignable to $[\text{M}]^+$, presumably through oxidation of the ferrocene to ferricenium in the source, a process that has precedent [9].

The formation of the various products can be accounted for by analogy with our earlier proposals for reactions between alkynes

and orthomanganated chalcones [7]. In the first step, the alkyne inserts into the Mn–C bond of the cyclomanganated chalcone with the bulkier substituent adjacent to the manganese. This seven-membered ring extrudes the $\text{Mn}(\text{CO})_n$ group as the C–O bond forms to give a six-membered ring, with the Mn retained on the face of the ring by coordination in an η^5 -fashion, giving the isolated species **3a**. In benzene this compound is essentially stable under the reaction conditions, although a small amount of protio-demetalation to generate **4a** occurs, presumably induced by small amounts of adventitious water. In CCl_4 the same initial processes take place, but now the species **3a** undergoes oxidation *in situ* to eliminate the manganese and generate the pyrylium cation **2a**. Decomposition of some of the ferrocenyl groups by the CCl_4 must provide the counterion $[\text{FeCl}_4]^-$. It is well-established [10] that solutions of ferrocene in CCl_4 undergo an efficient photolytic/radical conversion to $[\text{Cp}_2\text{Fe}]^+[\text{FeCl}_4]^-$, so presumably this is occurring in our system, with the ferricenium cation providing the oxidizing agent for converting **3a** to **2a**. The yields of **2a**· $[\text{FeCl}_4]^-$ are reasonable so formation is obviously efficient even with thermal conditions under normal laboratory lighting.

Exactly the same types of products were characterized in the corresponding reactions of the substituted cyclomanganated chalcone **1b**, giving **2b**, **3b**, **4b** with similar yields.

For further characterization, the pyrylium cations **2a** or **2b** were converted in to the corresponding pyridines **5a** or **5b** using the known reaction with aqueous NH_3 [3,4]. Ferrocenyl-substituted pyridines have been used recently to prepare ruthenium complexes with anticancer activities [11].

2.2. Crystal structure of (4,6-diphenylpyranyl)tricarbonyl manganese, **3a**

The X-ray crystal structure of the η^5 -pyranyl-manganese complex **3a** was determined. Fig. 1 shows the overall geometry. The structure has a $\text{Mn}(\text{CO})_3$ group attached to the five carbon atoms of the pyran ring with the oxygen displaced from the plane of the ring, away from the side attached to the manganese. The C(1)–C(5) atoms are coplanar to within ± 0.03 Å, with the Mn 1.696(1) Å from the plane. The individual Mn–C distances vary from 2.095(2) [to C(3)] to 2.275(2) Å [to C(1)]. The ferrocenyl group is attached to C(1) and is orientated so that the Fe is on the opposite side of the rings to the Mn, no doubt for steric reasons. The two phenyl rings are attached at C(3) and C(5), with their planes twisted by 22.5° and

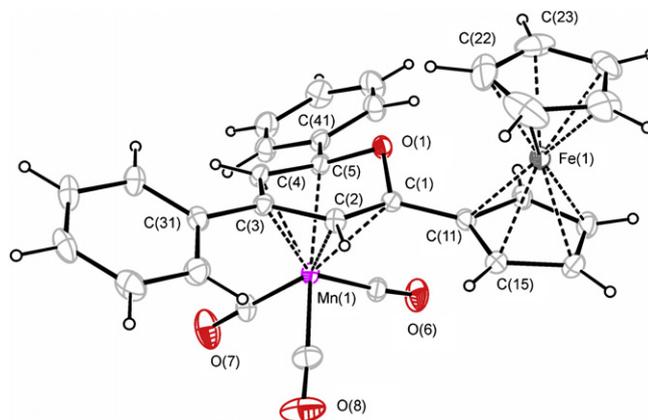


Fig. 1. The structure of (2-ferrocenyl-4,6-diphenylpyranyl- η^5)tricarbonylmanganese (**3a**). Selected distances (Å) Mn(1)–C(1) 2.275(2), Mn(1)–C(2) 2.124(2), Mn(1)–C(3) 2.095(2), Mn(1)–C(4) 2.098(2), Mn(1)–C(5) 2.190(2), C(1)–O(1) 1.397(2), C(5)–O(1) 1.411(2), C(1)–C(2) 1.365(2), C(2)–C(3) 1.410(2), C(3)–C(4) 1.411(2), C(4)–C(5) 1.381(2), Mn(1)–plane of [C(1)–C(5)] 1.696(1), Fe(1)–plane of [C(11)–C(15)] 1.636(1), Fe(1)–plane of [C(21)–C(25)] 1.635(1).

24.8° respectively from being coplanar with the C(1)–C(5) plane. The Cp rings of the ferrocenyl group are 8° from the eclipsed conformation, with equal Fe⋯ring-plane distances [1.635(1) Å]. The plane of the C(11)–C(15) ring is only 10.3° from the C(1)–C(5) one which should allow some π -electron communication between the two rings, perhaps explaining why the C(11)–C(1) distance [1.431(2) Å] is significantly shorter than the C(3)–C(31) and C(5)–C(51) ones [av. 1.464(2) Å] even though they are all formally sp^2 – sp^2 C–C bonds. There are two previous structures reported for η^5 -pyranyl-manganese compounds, with 1-methyl-3,5-diphenyl or with 1-styryl-3,5-diphenyl substituents; these have slightly longer Mn⋯ring distances (1.715 and 1.742 Å respectively), but are otherwise very similar [7].

2.3. Electrochemistry of the pyrylium salts

Electrochemical data for pyrylium cations are given in Table 1 and the cyclic voltammogram of **2a** is shown in Fig. 2. Electrochemistry of triarylpyrylium salts (**P**) has been well-studied and generally shows two cathodic processes associated with reduction first to the radical **P**[•] then the anion **P**^{•−} [2,6]. Pyrylium salts can also be oxidised [13]. For triphenylpyrylium the reduction processes occur at −0.22 and −1.40 V (CH_2Cl_2 , $[\text{Fc}^*]^{+/0} = 0.0$ V). In MeCN the radical formed from the first reduction can undergo a dimerisation reaction, the bipyrene product generating an anodic feature (~0.7 V) on the reverse scan [2]. This signal was not observed in dichloromethane.

For **2a** the first pyrylium reduction occurs at −0.40 V, the observed cathodic shift is as predicted due to the electron donating ability of the attached ferrocenyl group. An i_a/i_c of 0.7 for this process and new broad feature occurring at ~0.6 V on the anodic sweep is consistent with a chemical reaction of the radical species that may be dimerisation of the radical to the bipyrene. The effect of the trimethoxybenzene group in **2b** on the redox potentials is minor. It would appear however that this group stabilises the radical species formed at −0.41 V with respect to the chemical reaction that generates the feature at 0.7 V. The second pyrylium reduction of both **2a** and **2b** is electrochemically irreversible and cathodically shifted to a similar extent from that of triphenylpyrylium to ca. −1.5 V. The ferrocenyl $[\text{Fc}]^{+/0}$ redox couple occurs at 0.92 and 0.89 V for **2a** and **2b** respectively, consistent with the attachment of a strongly electron withdrawing group to the Fc unit [12].

Both of the ferrocenyl-pyrylium salts contain the electrochemically non-innocent tetrachloroferrate counter anion. This ion undergoes a reversible $[\text{FeCl}_4]^{-/2-}$ reduction at 0.08 V. A sample of tetrabutylammonium tetrachloroferrate displayed the same reduction feature at 0.08 V (cf. [15]).

2.4. UV–visible spectra of the pyrylium salts

The UV–visible spectra of the pyrylium salts **2a** and **2b** show strong bands in the 200–300 nm range which can be attributed mainly to the ferrocenyl moiety, and in the 350–450 nm region

Table 1
Half wave potentials for pyrylium salts in dichloromethane solution.

	E^0/V^a			
	$\text{P}^{0/-}$	$\text{P}^{0\cdot}$	$\text{FeCl}_4^{-/2-}$	$\text{Fc}^{+/0}$
Triphenylpyrylium. BF_4^- [cf 2,6]	−1.40	−0.22		
2a · FeCl_4^-	−1.52 (E _{p,c})	−0.40	0.08	0.92
2b · FeCl_4^-	−1.59 (E _{p,c})	−0.41	0.07	0.89
Bu_4N^+ · FeCl_4^-			0.08	

^a 1×10^{-3} M in CH_2Cl_2 , 0.1 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, GCE, referenced to $[\text{Fc}^*]^{+/0} = 0.0$ V [14].

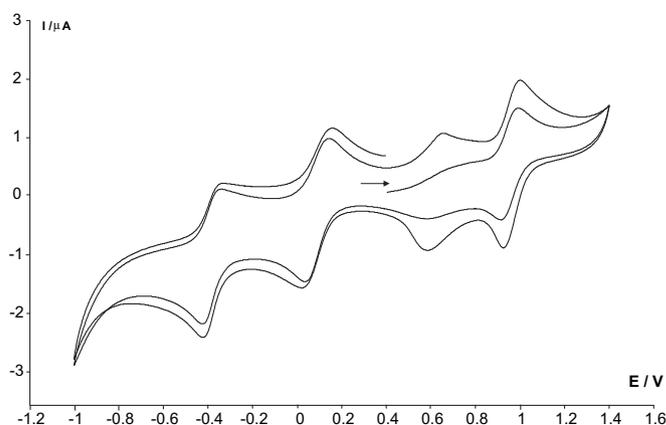


Fig. 2. Cyclic voltammogram of **2a**· $[\text{FeCl}_4]$ (CH_2Cl_2 , $[\text{Bu}_4\text{N}][\text{BF}_4]$, GCE, 100 mV s^{-1}).

from the pyrylium group. These are readily assigned from published data [1, 2, 16]. More interesting is a weak, broad band at around 694 nm in benzene, with small shifts to 669 and 692 nm in acetone and dichloromethane respectively. This absorption can be attributed to an intramolecular charge transfer transition from the ferrocenyl centre to the pyrylium ring, promoted by the combination of a readily-oxidised and a readily-reduced group in the same species. The counter anion in **2a** and **2b**, tetrachloroferrate containing the d^5 Fe(III) ion, is pale yellow and does not contribute to any significant UV–visible absorption. There is no sign of the low energy band in the η^5 -pyranyl nor the pyran species **3** or **4**, as expected.

Triphenylpyrylium tetrafluoroborate in dichloromethane displays strong fluorescent emission at 461 nm, but this is quenched for the **2a/2b** salts.

2.5. Conclusion

A new synthesis of 2-ferrocenyl-substituted pyrylium salts has been established, which allows more ready variation of substituents than the previous routes [3]. It also avoids the strongly acid conditions used in the usual syntheses [1] which may be an advantage for some substituents. By varying the solvent, intermediate species can be isolated. The 2-ferrocenyl-pyrylium cations incorporate both a reducible and an oxidisable centre and both redox processes are clearly seen in the electrochemical measurements. The UV–visible spectra show a broad band at ca 680 nm which arises from an internal charge transfer from the ferrocenyl moiety to the pyrylium ring.

3. Experimental

3.1. General

Petroleum spirit (b.p. 60–80 °C) and all other solvents in preparative and chromatographic work were of analytical grade. Other commercial reagents were used without purification. Coupling reactions with the alkyne were carried out under a nitrogen atmosphere, other reactions required no precautions. P.l.c refers to preparative layer chromatography on silica (Merck Kieselgel 60PF₂₅₄: 200 × 200 × 2 mm). Infrared spectra were recorded on a Digilab FTS-45 FTIR instrument, NMR spectra on a Bruker AC300 instrument in CDCl_3 , and UV–visible spectra on a Varian Cary 100 instrument. Low resolution electrospray mass spectrometry (ESI-MS) was carried out on VG Platform II and high resolution ESI-MS on a Bruker MicroTOF, with MeOH as mobile phase.

Electrochemical measurements of the pyrylium salts were carried out in a standard cell with glassy carbon (working), Pt (auxiliary) and Ag/AgCl (reference) electrodes on 1×10^{-3} M solutions of the analyte with 0.1 M $\text{Bu}_4\text{N}^+\text{BF}_4^-$ supporting electrolyte in CH_2Cl_2 . Potentials were referenced to $[\text{Fc}^*]^{+/0} = 0.0$ V [14]. The sample of tetrabutylammonium tetrachloroferrate was prepared by a literature method [17]. Cyclomanganated chalcones were synthesised as reported by Tully et al. [18] using $\text{PhCH}_2\text{Mn}(\text{CO})_5$ prepared by the standard method [19]. Ferrocenylethyne was generously provided by Professor M. I. Bruce, University of Adelaide.

3.1.1. Reaction of cyclomanganated chalcone **1a** with FcCCH in CCl_4

The manganese complex **1a** (106 mg, 0.28 mmol) and FcCCH (119 mg, 0.56 mmol) were dissolved in CCl_4 (20 mL), and heated under reflux for 1 h. The mixture turned from yellow to green, and IR monitoring showed all ν_{CO} bands of **1** had disappeared. On cooling, a green powder formed which was collected by filtration and shown to be 2-ferrocenyl-4,6-diphenylpyrylium tetrachloroferrate (**2a**· $[\text{FeCl}_4]$) (82 mg, 47%). Found: C 51.34 H 3.93%; calc for $\text{C}_{27}\text{H}_{21}\text{Fe}_2\text{OCl}_4$: C 52.73; H 3.44%. ESI-MS positive ion: m/z 417.096, calc for $[\text{C}_{27}\text{H}_{21}\text{FeO}]^+$ 417.094; negative ion: m/z 195.807, calc for $[\text{FeCl}_4]^-$ 195.809.

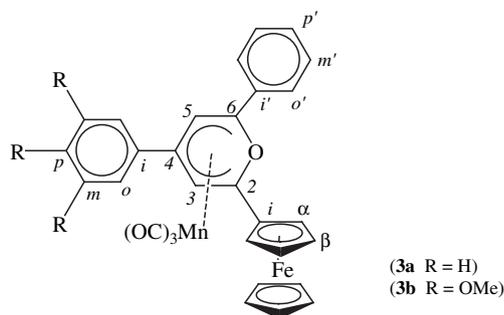
3.1.2. Reaction of cyclomanganated chalcone **1b** with FcCCH in CCl_4

In exactly the same fashion 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium tetrachloroferrate (**2b**· $[\text{FeCl}_4]$) was prepared in 58% yield from **1b** (106 mg, 0.28 mmol) and FcCCH (119 mg, 0.57 mmol) as a green powder, identified spectroscopically. ESI-MS positive ion: m/z 507.129, calc for $[\text{C}_{30}\text{H}_{27}\text{FeO}_4]^+$ 507.129; negative ion: m/z 195.813, calc for $[\text{FeCl}_4]^-$ 195.809.

3.1.3. Reaction of cyclomanganated chalcone **1a** with FcCCH in benzene

Cyclomanganated chalcone **1a** (106 mg, 0.28 mmol) and ferrocenylethyne (119 mg, 0.32 mmol) were heated under reflux in benzene (20 mL) for 2.5 h. The reaction mixture turned from yellow to red, and ν_{CO} bands of **1a** were absent. The solvent was removed under vacuum, and the residue chromatographed [p.l.c., $\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:1] to give two major bands.

Band 1, red, R_f 0.8 was (2-ferrocenyl-4,6-diphenylpyrylium- η^5) tricarbonylmanganese, **3a**, (47 mg, 26%) as red crystals after crystallisation from ether/pentane. Found: C, 64.80; H, 3.81%, calc for $\text{C}_{30}\text{H}_{21}\text{FeMnO}_4$: C, 64.78; H, 3.81%. IR: (ν_{CO} , cm^{-1}) 2012vs, 1951m, 1931m.



Numbering system for NMR of **3a/b**. The numbering of other compounds follows the same convention.

^1H NMR (CDCl_3) δ 7.50 (d, $J = 8.6$ Hz, 2H, Ph o'), 7.28–7.58 (m, 8H, Ph-H), 5.72 (s, 1H, pyr H3), 5.71 (s, 1H, pyr H5), 4.80 (dd, $J = 1.6$ Hz, 2H, Fc α), 4.43 (dd, $J = 1.6$ Hz, 2H, Fc β), 4.19 (s, 5H, Fc C_5H_5). ^{13}C NMR

(CDCl_3) δ 137.4 (Ph i), 137.0 (Ph i'), 129.2 (Ph m), 128.7 (Ph m'), 128.5 (Ph p), 128.5 (Ph p'), 127.5 (Ph o), 122.7 (Ph o'), 111.1 (pyr C2), 96.8 (pyr C4), 93.4 (pyr C6), 85.0 (pyr C3), 80.6 (pyr C5), 78.3 (Fc i), 69.9 (Fc C_5H_5), 67.4 (Fc α), 64.7 (Fc β).

ESI-MS m/z 417 $[\text{M}-\text{Mn}(\text{CO})_3]^+$. This compound was further characterized by an X-ray crystal structure determination, see below.

Band 2, orange, R_f 0.2 was 2-ferrocenyl-4,6-diphenylpyran, **4a**, (10 mg, 8%), as orange crystals from ether/pentane. Found: C, 77.52; H, 5.30%, calc for $\text{C}_{27}\text{H}_{22}\text{OFe}$: C, 76.83; H, 5.32%.

^1H NMR (CDCl_3) δ 7.86 (d, $J = 21.0$ Hz, 1H, pyr H3), 7.32 (m, 10H, Ph-H), 6.78 (s, 1H, pyr H5), 6.20 (d, $J = 21.0$ Hz, 1H, pyr H2), 4.75 (dd, $J = 1.6$ Hz, 2H, Fc α), 4.71 (dd, $J = 1.6$ Hz, 2H, Fc β), 4.11 (s, 5H, Fc C_5H_5). ^{13}C NMR (CDCl_3), δ 151.3 (pyr C6), 148.3 (Ph i), 142.3 (pyr C4), 123.6 (pyr C3), 120.5 (pyr C5), 120.0–128.0 (Ph-C), 77.0 (pyr C2), 69.6 (Fc C_5H_5), 69.2, 66.9, 66.7 (Fc C_5H_4). ESI-MS m/z 418.125 $[\text{M}]^+$, calc for $\text{C}_{27}\text{H}_{22}\text{OFe}$ 418.122.

3.1.4. Reaction of cyclomanganated chalcone **1b** with FcCCH in benzene

Similarly, **1b** (120 mg, 0.23 mmol) and FcCCH (65 mg, 0.31 mmol) were refluxed in benzene for 2.5 h to give a red solution. Chromatography (1:1 $\text{CH}_2\text{Cl}_2/\text{hexane}$) gave two major products.

The first was [2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium- η^5]tricarbonylmanganese, **3b**, (56 mg, 40%) as red crystals after crystallisation from ether/pentane. Found: C, 60.41; H, 4.20%, calc for $\text{C}_{33}\text{H}_{27}\text{FeMnO}_7$: C, 60.39; H, 4.15%. IR: (ν_{CO} , cm^{-1}) 2012vs, 1951m, 1931m. ESMS: (MeOH), (positive ion) m/z 507 (100%, $[\text{M} - \text{Mn}(\text{CO})_3]^+$).

^1H NMR (CDCl_3) δ 7.50 (d, 2H, $J = 8.6$ Hz, Ph o'), 7.28–7.58 (m, 3H, Ph-H), 7.13 (s, 2H, Ph o), 5.63 (s, 1H, pyr H3), 5.32 (s, 1H, pyr H5), 4.80 (dd, $J = 1.6$ Hz, 2H, Fc α), 4.43 (dd, $J = 1.6$ Hz, 2H, Fc β), 4.19 (s, 5H, Fc C_5H_5), 4.03 (s, 3H, p OMe), 3.97 (s, 6H, m OMe). ^{13}C NMR (CDCl_3) δ 142.3 (Ph i), 137.0 (Ph i'), 131.3 (Ph m), 128.9 (Ph m'), 128.6 (Ph p), 126.5 (Ph o), 123.0 (Ph o'), 110.7 (pyr C2), 96.8 (pyr C4), 93.4 (pyr C6), 85.0 (pyr C3), 80.9 (pyr C5), 78.2 (Fc i), 69.9 (Fc C_5H_5), 67.4, 64.7 (C_5H_4), 60.4 (m OMe), 56.5 (p OMe).

The second product was (2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyran, **4b**, (31 mg, 24%) as orange crystals from ether/pentane. Found: C, 70.29; H 6.81%, calc for $\text{C}_{30}\text{H}_{28}\text{O}_4\text{Fe}$: C, 70.88; H, 5.55%. ESI-MS m/z 508.137 $[\text{M}]^+$, calc 508.133.

^1H NMR (CDCl_3) δ 7.32 (m, 5H, Ph-H), 7.12 (d, $J = 21.0$ Hz, 1H, pyr H3), 6.74 (s, 1H, pyr H5), 6.68 (s, 2H, Ph o), 6.10 (d, $J = 21.0$ Hz, 1H, pyr H2), 4.80 (dd, $J = 1.6$ Hz, 2H, Fc α), 4.45 (dd, $J = 1.6$ Hz, 2H, Fc β), 4.27 (s, 5H, C_5H_5), 3.94 (s, 3H, p OMe), 3.85 (s, 6H, m OMe). ^{13}C NMR (CDCl_3) δ 153.7 (pyr C6), 151.3 (Ph i), 148.4 (pyr C4), 123.6 (pyr C3), 120.6 (pyr C5), 77.4 (pyr C2), 120.0–128.0 (Ph-C), 69.6, (Fc C_5H_5), 66.9, 66.7, 66.2, (Fc C_5H_4), 56.2 (p OMe), 60.9 (m OMe).

3.1.5. Preparation of 2-ferrocenyl-4,6-diphenylpyrylium triiodide, (**2a**· I_3)

The pyrylium complex **3a** (50 mg, 0.09 mmol) and iodine (46 mg, 0.36 mmol) were stirred in CCl_4 for 1 h. The solution changed from yellow to green and all of **4** had been consumed (IR). Solvent was removed under vacuum to leave a green oil, which solidified to a green solid when mixed with diethyl ether, tentatively identified as **2a**· I_3 , (40 mg, 51%) from ESI-MS measurements. Attempts to purify the solid by recrystallisation were unsuccessful. Further characterisation was by conversion to the corresponding pyridine derivative **5a** (see below).

3.1.6. Reaction of 2-ferrocenyl-4,6-diphenylpyrylium tetrachloroferrate with ammonia

The solid pyrylium salt **2a**· $[\text{FeCl}_4]$ (40 mg, 0.05 mmol) was treated with a few drops of 30% aqueous ammonia. The resulting

mixture was chromatographed (p.l.c., ethyl acetate/hexane 1:2) to afford one major yellow band, R_f 0.8. Removal gave a yellow oil of 2-ferrocenyl-4,6-diphenylpyridine (12 mg, 57%), **5a**, which did not crystallize. ESI-MS: m/z 415.105 $[M]^+$, calc for $C_{27}H_{21}NFe$ 415.102; m/z 416.110 $[M + H]^+$, calc for $C_{27}H_{22}NFe$ 416.110; m/z 438.095 $[M + Na]^+$, calc for $C_{27}H_{21}NFeNa$ 438.092.

1H NMR ($CDCl_3$) δ 7.28–8.21 (m, 10H, Ph-H), 6.91 (s, 2 \times 1H, pyr H3, H5), 5.10 (dd, $J = 2.4$ Hz, 2H, Fc α), 4.45 (dd, 2H, $J = 2.4$ Hz, Fc β), 4.11 (s, 5H, Fc C_5H_5). ^{13}C NMR ($CDCl_3$) δ 127.0–130.0 (Ph-C), 159.5 (pyr C6), 149.2 (pyr C4), 139.8 (Ph i), 139.3 (pyr C2), 139.1 (Ph i'), 116.5 (pyr C3), 115.6 (pyr C5), 84.0 (Fc i), 69.9 (Fc α), 69.7 (Fc C_5H_5), 67.1 (Fc β).

3.1.7. Reaction of 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyrylium tetrachloroferrate with ammonia

Similarly the pyrylium salt **2b** [$FeCl_4$] (40 mg, 0.05 mmol) treated with a few drops of 30% ammonia afforded a yellow band, R_f 0.8. Removal and crystallisation from CH_2Cl_2 /pentane gave yellow crystals of 2-ferrocenyl-4-(3,4,5-trimethoxyphenyl)-6-phenylpyridine (19 mg, 56%), **5b**. Found: C, 70.79; H, 5.71; N, 2.77%. Calc for $C_{30}H_{27}NFeO_3$: C, 71.30; H, 5.38; N, 2.77%. ESI-MS: m/z 506 $[M + H]^+$.

1H NMR ($CDCl_3$) δ 7.28–8.21 (m, 10H, Ph-H), 6.91 (s, 2 \times 1H, pyr H3, H5), 5.10 (dd, $J = 2.4$ Hz, 2H, Fc α), 4.45 (dd, 2H, $J = 2.4$ Hz, Fc β), 4.11 (s, 5H, Fc C_5H_5), 4.00 (s, 3H, p OMe), 3.97 (s, 6H, m OMe). ^{13}C NMR ($CDCl_3$) δ 127.0–130.0 (Ph-C), 157.0 (pyr C6), 153.8 (pyr C4), 139.8 (Ph i), 139.6 (pyr C2), 139.1 (Ph i'), 116.5 (pyr C3), 115.6 (pyr C5), 84.0 (Fc i), 69.9 (Fc α), 69.7 (Fc C_5H_5), 67.1 (Fc β), 56.5 (p OMe), 60.4 (m OMe).

3.2. X-ray crystal structure determination of (2-ferrocenyl-4,6-diphenylpyranyl- η^5)-tricarbonylmanganese (**3a**)

Crystal data: $C_{30}H_{21}FeMnO_4$, M_r 556.26, monoclinic, space group $P2_1/c$, $a = 7.417(2)$, $b = 14.716(4)$, $c = 21.750(6)$ Å, $\beta = 94.39(2)^\circ$, $V = 2366.8(12)$ Å³, $D_{calc} = 1.56$ g cm⁻³, $Z = 4$, $\mu(Mo K\alpha) = 1.183$ mm⁻¹, red crystals from CH_2Cl_2 /pentane, size $1.08 \times 0.32 \times 0.20$ mm³, $F(000) = 1136$, $T = 93(2)$ K. Total data 34245, unique data 5435 ($R_{int} 0.029$), $2^\circ < \theta < 27.5^\circ$, $T_{max,min} 1.00$, 0.671 , $R_1 = 0.0254$, [4871 data with $I > 2\sigma(I)$], wR_2 (all data) 0.0653, GoF 1.069, residual $\Delta e \leq |0.38| e \text{ \AA}^{-3}$. The structure was solved by direct methods and developed and refined routinely using the SHELX-97 programmes [20] running under WinGX [21] with hydrogen atoms included in calculated positions.

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Appendix A. Supplementary material

Full details of the structure determination of **2b** have been deposited with the Cambridge Crystallographic Data Centre as CCDC 767138, which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] A.T. Balaban, A. Dinculescu, G.N. Dorofeenko, G.W. Fischer, A.V. Koblik, V.V. Mezheritskii, W. Schroth, Pyrylium salts: synthesis, reactions and physical properties. Academic Press, New York, 1982.
- [2] F. Pragst, R. Ziebig, U. Seydewitz, G. Driesel, *Electrochem. Acta* 23 (1980) 341; R. Beddoes, D. Heyes, R.S. Menon, C.I. F Watt, *J. Chem. Soc., Perkin Trans(II)* (1996) 307; D. Heyes, R.S. Menon, C.I.F. Watt, J. Wiseman, P. Kubinski, *J. Phys. Org. Chem.* 15 (2002) 689.
- [3] V.V. Krasnikov, Y.P. Andreichikov, N.V. Kholodiva, G.N. Dorofeenko, *Zh. Org. Khim* 13 (1977) 1566; G.N. Dorofeenko, V.V. Krasnikov, *Zh. Org. Khim.* 8 (1972) 2620.
- [4] K.L. Malisza, S. Top, J. Vaissermann, B. Caro, M.C. Sénéchal-Tocquer, D. Sénéchal, J.Y. Saillard, C. Triuki, S. Kahlal, J.F. Britten, M.J. McGlinchey, G. Jaouen, *Organometallics* 14 (1995) 5273; B. Caro, F.R. Guen, M.C. Sénéchal-Tocquer, V. Prat, J. Vaissermann, *J. Organomet. Chem.* 543 (1997) 87; M. Salmain, K.L. Malisza, S. Top, G. Jaouen, M.C. Sénéchal-Tocquer, D. Sénéchal, B. Caro, *Bioconjugate Chem.* 5 (1994) 655; B. Caro, M.C. Sénéchal-Tocquer, D. Sénéchal, P. Marrec, J.Y. Saillard, C. Triuki, S. Kahlal, *Tetrahedron Lett.* 34 (1993) 7259; M. Salmain, B. Caro, F. Le Guen-Robin, J.C. Blais, G. Jaouen, *ChemBioChem* 5 (2004) 99.
- [5] F. Ba, N. Cabon, F. Robin-Le Guen, P. Le Poul, N. Le Poul, Y. Le Mest, S. Golhen, B. Caro, *Organometallics* 27 (2008) 6396.
- [6] M.J. Shaw, J. Mertz, *Organometallics* 21 (2002) 3434; M.J. Shaw, S.J. Afridi, S.L. Light, J.N. Mertz, S.E. Ripperda, *Organometallics*, 23 (2004) 2778.
- [7] W. Tully, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 507 (1996) 103; W. Tully, L. Main, B.K. Nicholson, *J. Organomet. Chem.*, 633 (2001) 162.
- [8] W.J. Mace, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 690 (2005) 3340.
- [9] W. Henderson, J.S. McIndoe, *Mass spectrometry of inorganic, coordination and organometallic compounds; tools, techniques, tips*. Wiley, Chichester, 2005.
- [10] L.A. Pena, A.J. Seidl, L.R. Cohen, P.E. Hoggard, *Transition Met. Chem.* 34 (2009) 135; S.L. Phan, P.E. Hoggard, *Inorg. React. Mech.* 1 (1998) 17; O. Traverso, R. Rossi, V. Carassiti, *Synth. React. Inorg. Met-Org. Chem.* 4 (1974) 309; D.M. Papsun, J.K. Thomas, J.A. Labinger, *J. Organomet. Chem.* 208 (1981) C36.
- [11] M. Auzias, B. Therrien, G. Süß-Fink, P. Štěpnička, W.H. Ang, P.J. Dyson, *Inorg. Chem.* 47 (2008) 578.
- [12] C.J. McAdam, B.H. Robinson, J. Simpson, *Acta Cryst E59* (2003) m687.
- [13] M.R. Detty, J.M. McKelvey, H.R. Luss, *Organometallics* 7 (1988) 1131.
- [14] F. Barrière, W.E. Geiger, *J. Am. Chem. Soc.* 128 (2006) 3980.
- [15] M. Yamagata, N. Tachikawa, Y. Katayama, T. Miura, *Electrochim. Acta* 52 (2007) 3317; L.J. Sacks, *Anal. Chem.* 35 (1963) 1299.
- [16] Y.S. Sohn, D.N. Hendrickson, H.B. Gray, *J. Am. Chem. Soc.* 93 (1971) 3603.
- [17] M.T. Hay, S.J. Geib, *Acta Cryst. E61* (2005) m190.
- [18] W. Tully, L. Main, B.K. Nicholson, *J. Organomet. Chem.* 503 (1995) 75.
- [19] L. Main, B.K. Nicholson, *Adv. Metal-Org. Chem.* 3 (1994) 1.
- [20] G.M. Sheldrick, SHELX97 Programs for the solution and refinement of crystal structures. University of Göttingen, Germany, 1997.
- [21] L.J. Farrugia, WinGX, Version 1.70.01, University of Glasgow, UK. L.J. Farrugia, *J. Appl. Cryst.* 32 (1999) 837.