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FERROCENYLPYRIDINES: A NEW SYNTHESIS OF 4′-FERROCENYLTERPYRIDINE AND THE SINGLE CRYSTAL STRUCTURE OF A C_3-FERROCENOPHANE, $[(\eta\text{-}C_5H_4CHCH_2C(O)2\text{-}C_5H_4N)_2CHC(O)2\text{-}C_5H_4N]Fe$

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Abstract—The synthesis and characterization of the new ligand 4′-ferrocenylterpyridine is reported together with the synthesis and characterization of a new C_3-ferrocenophane containing three acylpyridine units. The terpyridine ligand was prepared in a two-step synthesis from ferrocenecarbaldehyde by aldol condensation and subsequent cyclization. Attempts to prepare the analogous 1,1′-bis-terpyridylferrocene derivative resulted in the formation of a new ferrocenophane: a consequence of inter-annular attack of an anion generated on the side chain of one cyclopentadienyl ring on a carbonyl centre on the side chain of the other cyclopentadienyl ring. The single crystal X-ray structure of this ferrocenophane, $[(\eta\text{-}C_5H_4CHCH_2C(O)2\text{-}C_5H_4N)_2CHC(O)2\text{-}C_5H_4N]Fe$, as its dichloromethane solvate, $[Fe(C_{33}H_{27}N_3O_3)]\cdot CH_2Cl_2$, has been determined.

In a series of recent publications we have dealt with the synthesis of metallocenylbipyridines[1,2] because such compounds have potential applications in molecular sensing and redox active self-assembly devices. We have also reported the synthesis of mixed phosphine–bipyridyl ferrocenes to extend the coordination possibilities of these compounds.[3,4] In addition we have shown previously that 6-ferrocenyl-2,2′ : 6′,2″-terpyridine (**1**) and 3′-ferrocenyl-2,2′ : 6′,2″-terpyridine (**2**) can be prepared from the direct reaction of lithioferrocene with 2,2′ : 6′,2″-terpyridine.[5] When the coordination chemistry of compound **1** was examined using a range of transition metals it was observed that in some cases there was a high propensity towards metallation of the ferrocenyl ring caused by the directing influence of the adjacent nitrogen group. While this phenomenon is of interest in its own right it can be an inconvenience, adding an unwanted complication in the designed synthesis of new multifunctional complexes for molecular sensors. The poor yields of compound **2** (where the complication does not exist on coordination) in the direct synthesis has meant this is not a viable alternative. This

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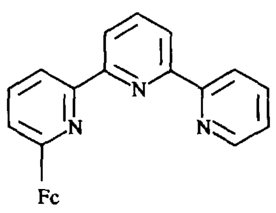

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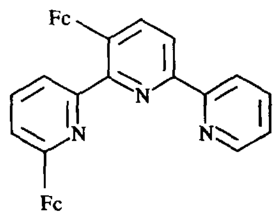

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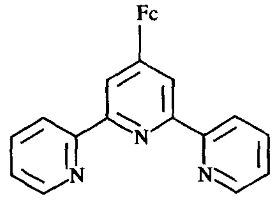


3

meant that we required an alternative preparation of either compound **2** or **3**, with **3** the ideal choice because its higher degree of symmetry should facilitate metal complex characterization. This paper describes the new synthesis and full characterization of compound **3** in high yields, together with the synthesis and characterization of important synthetic intermediates.

EXPERIMENTAL

All reaction solvents were dried and freshly distilled. ^{1}H NMR spectra were recorded using either a Bruker WH-250 or a WH-400 instrument using $CDCl_3$ as the solvent unless otherwise indicated (abbreviations used: bd, broad doublet; dt, doublet of triplets; ad, asymmetric doublet). Mass spectra were obtained by chemical ionization or FAB in the case of higher molecular weight (>600 amu) compounds.

Ferrocenylcarbaldehyde and 1,1′-ferrocenyl-bis-carbaldehyde were prepared from the reaction of lithio- or dilithio-ferrocene with DMF using known techniques.[6–8] The former aldehyde was obtained pure by sublimation while the latter was purified by crystallization. Acetylpyridines were used as supplied from the commercial suppliers.

Reaction of dilithioferrocene with 2,2′:6′,2″-terpyridine

The reaction of an isolated sample of dilithioferrocene with 2,2′:6′,2″-terpyridine (1.0 g) in diethyl ether followed by an aerobic work-up gave an orange oil which on column chromatography on basic alumina gave mixtures which contained compounds **1**–**3** and lesser quantities of disubstituted compounds such as **1a**. Identification of the isomers was made on the basis of NMR spectroscopy, particularly correlation spectra. The ^{1}H NMR spectra of **1** and **2** are identical to those reported previously.[5] The ^{1}H NMR spectrum of **3** is reported later in this text.

1-[6-(2,2′:6′,2″-terpyridinyl)]-1′-[3′-(2,2′:6′,2″-terpyridinyl)] ferrocene (**1a**). ^{1}H NMR: 3.95 (t, 2H), 4.14 (t, 2H), 4.33 (t, 2H), 4.84 (t, 2H), 7.19–7.39 (4m, 4H), 7.58–7.73 (4m, 4H), 7.87 (td, 1H), 7.92 (t, 1H), 8.10 (d, 1H), 8.20 (d, 1H), 8.31 (dd, 1H), 8.33 (dd, 1H), 8.42 (dd, 1H), 8.47 (dd, 1H), 8.52 (ddd, 1H), 8.58 (dt, 1H), 8.62 (ddd, 1H), 8.73 (ddd, 1H). MS: parent ion *m/z* 648. Found: C, 74.5; H, 3.9; N, 12.9. Calc. for $C_{40}H_{28}FeN_6$: C, 74.5; H, 3.8; N, 13.0%.

Preparation of 1,5-bis-(2-pyridyl)-3-(ferrocenyl)pentane-1,5-dione (**4**)

Ferrocenecarbaldehyde (10.0 g, 0.047 mol) in ethanol (100 cm^3) was added to a mixture of sodium hydroxide (15 g) in water (60 cm^3) and 2-acetylpyridine (24.4 cm^3, 0.22 mol). A bright red solid precipitated. A further quantity of ethanol and water (100 cm^3) in the same ratio as before was added to make a homogeneous solution. The mixture was then stirred for 8 h. Water (200 cm^3) was added followed by dichloromethane (300 cm^3), which was used to extract the reaction products. After drying the organic layer with $MgSO_4$, the dichloromethane was removed *in vacuo* to leave a red solid. This was washed with a little cold dichloromethane until a yellow solid remained. This yellow powder was vacuum dried to give a 16.06 g, 77% yield of **4**. The wash solution was evaporated to give an oil which was chromatographed to give a red product, identified as compound **5** eluted with petroleum ether–diethyl ether (50:50 v/v) and further quantities of **4**.

Compound **4**. Melting point 190°C. IR: ν(CO) 1697 cm^{-1}. ^{1}H NMR: 3.52 (add, 2H, CH_2), 3.78 (add, 2H, CH_2), 3.96 (m, 1H, CH), 4.09 (t, 2H), 4.41 (m, 2H), 4.42 (s, 5H, cyclopentadienyl protons), 7.46 [ddd, 2H, H(5)], 7.82 [td, 2H, H(4)], 8.04 [dd, 2H, H(3)], 8.16 [dd, 2H, H(6)]. ^{13}C NMR: 30.37 (CH), 44.40 (CH_2, aliphatic proton resonances), 67.73, 67.33 (overlapping resonances) and 94.12 (ferrocenyl C resonances), 122.00, 127.09, 136.93, 148.97, 153.73 (pyridinyl C resonances), 156.49 (CO). MS *m/z* (rel. int.): 438 (85), M$^{+\bullet}$; 373 (12), M$^{+\bullet}$−Cp; 317 (100), M$^{+\bullet}$−FeCp; 252 (82), M$^{+\bullet}$−FeCp$_2$; 241 (26); 224 (84); 199 (72); 168 (28); 121 (50). Found C, 68.3; H, 5.1; N, 6.5. Calc. for C$_{25}$H$_{22}$FeN$_2$O$_2$: C, 68.5; H, 5.1; N, 6.4%.

Compound **5**. Melting point 118–119°C. IR: ν(CO) 1658 cm^{-1}. ^{1}H NMR: 4.17 (s, 5H, C$_5$H$_5$), 4.49 (t, 2H, β-C$_5$H$_4$), 4.67 (t, 2H, α-C$_5$H$_4$), 7.46 [ddd, 1H, H(3)], 7.75 [dt, 1H, H(4)], 8.16 [d, 1H, H(5)], 8.70 [ddd, 1H, H(6), pyridinyl proton], 7.84 (d, 2H, vinylic protons). ^{13}C NMR: 67.35, 70.00, 71.66, 80.59 (q, ferrocenyl); 117.95, 123.05, 126.68, 137.12, 147.34, 148.91, 156.61 (q, pyridinyl+vinylic); 188.85 (q); q = quaternary. MS *m/z* (rel. int.): 317 (100), M$^{+\bullet}$; 252 (51); M$^{+\bullet}$−Cp; 225 (22); 224 (29); 168 (18); 167 (24); 121 (20). Found: C, 67.1; H, 4.5; N, 4.1. Calc. for C$_{18}$H$_{15}$FeNO: C, 68.2; H, 4.8; N, 4.4%.

Preparation of 1,5-bis-(3-pyridyl)-3-(ferrocenyl)-pentane-1,5-dione (**6**)

An identical reaction to that above using 3-acetylpyridine instead of 2-acetylpyridine gives 1,5-bis-(3-pyridyl)-3-(4′-ferrocenyl)pentane-1,5-dione (**6**) in 83% yield.

Compound **6**. Melting point 132–134°C; IR: ν(CO) 1687 cm^{-1}. ^{1}H NMR: 3.48 (m, 4H), 3.86 (m, 1H), 4.21 (2t, 4H), 4.22 (s, 5H), 7.50 (dd, 2H), 8.28 (d, 2H), 8.85 (bm, 2H), 9.25 (bm, 2H). ^{13}C NMR: 30.73, 44.88 (alkyl); 67.00, 67.69, 68, 56, 92.31 (ferrocenyl); 123.64, 132.33, 135.45, 149.67, 153.52, 156.38 (pyridinyl); 197.94 (CO). MS *m/z* (rel. int.): 439(13); 438(72), M$^{+\bullet}$, 317 (52); 266 (22); 252 (87); M$^{+\bullet}$−FeCp$_2$; 241 (26); 224 (84), 199 (72); 212 (73); 121 (68); 106 (100). Found C, 67.8; H, 4.9; N, 6.2. Calc. for C$_{25}$H$_{22}$FeN$_2$O$_2$: C, 68.5; H, 5.1; N, 6.4%.

Preparation of 4′-ferrocenyl-2,2′:6′,2″-terpyridine (**3**) *from compound* **4**

A mixture of 1,5-bis(2-pyridyl)-3-(4′-ferrocenyl)pentane-1,5-dione (0.99 g, 2.25 mmol) and ammonium acetate (9.23 g) was suspended in ethanol (100 cm^3). The mixture was then heated gently in air until the temperature reached 70°C when the solution changed colour to blue–black. The mixture was then refluxed for 1 h. After cooling water (100 cm^3) was added, an orange precipitate formed, which was subsequently filtered off by suction and water washed. The precipitate was found to be pure by ^{1}H NMR and further crystallization was not required. Yield: 0.74 g, 78%. Melting point 119–120°C. ^{1}H NMR: 4.10 (s, 5H, Cp), 4.50 (t, 2H, β-C$_5$H$_4$), 5.06 (2t, 2H, α-C$_5$H$_4$), 7.37 [ddd, 2H, H(5), H(5″)], 7.86 [td, 2H, H(4), H(4″)], 8.53 [s, 2H, H(3′), H(5′)], 8.66 [d, 2H, H(3), H(3′)], 8.75 [ddd, 2H, H(6), H(6″)]. ^{13}C NMR: 67.54, 70.31, 81.74 (substituted Cp); 70.12 (unsubstituted Cp); 117.83, 121.48; 123.79, 136.93, 149.19, 150.89, 155.45, 156.63 (pyridinyl C). MS *m/z* (rel. int): 417 (82), M$^{+\bullet}$; 352 (100), M$^{+\bullet}$−Cp; 208 (18); 207 (18); 206 (28); 175 (17). Found: C, 72.2; H, 4.6; N, 10.3. Calc. for C$_{25}$H$_{19}$FeN$_3$: C, 72.0; H, 4.6; N, 10.1%.

Preparation of 4′-ferrocenyl-3,2′:6,3″-terpyridine (**7**) *from compound* **6**

Cyclization of compound **6** in the presence of ammonium acetate yielded **7** in a 90% yield as orange crystals following extraction into dichloromethane, washing with sodium bicarbonate solution, drying over MgSO$_4$, filtration and crystallization.

Compound **7**. Melting point 219–220°C, with decomposition from 160°C. ^{1}H NMR: 4.03 (s, 5H), 4.45 (t, 2H), 4.80 (t, 2H), 7.40 (bm, 2H), 7.66 (s, 2H), 8.43 (bm, 2H), 8.64 (bm, 2H), 9.30 (bm, 2H). ^{13}C NMR: 67.55, 70.64, 70.09, 80.69, (ferrocenyl); 116.55, 124.08, 135.57, 147.02, 148.71, 151.63, 154.25, 156.36. MS *m/z* (rel. int.): 418 (24); 417 (100) M$^+$; 350 (18); 208 (34); 121 (42); 56 (24). Found: C, 71.8; H, 4.5; N, 10.0. Calc. for C$_{25}$H$_{19}$FeN$_3$: C, 72.0; H, 4.6; N, 10.1%.

Preparation of 1,1′-{[C$_3$]-1,3-(2-acetoxylpyridinyl)-2-carbonylpyridinyl} ferrocene (**9**)

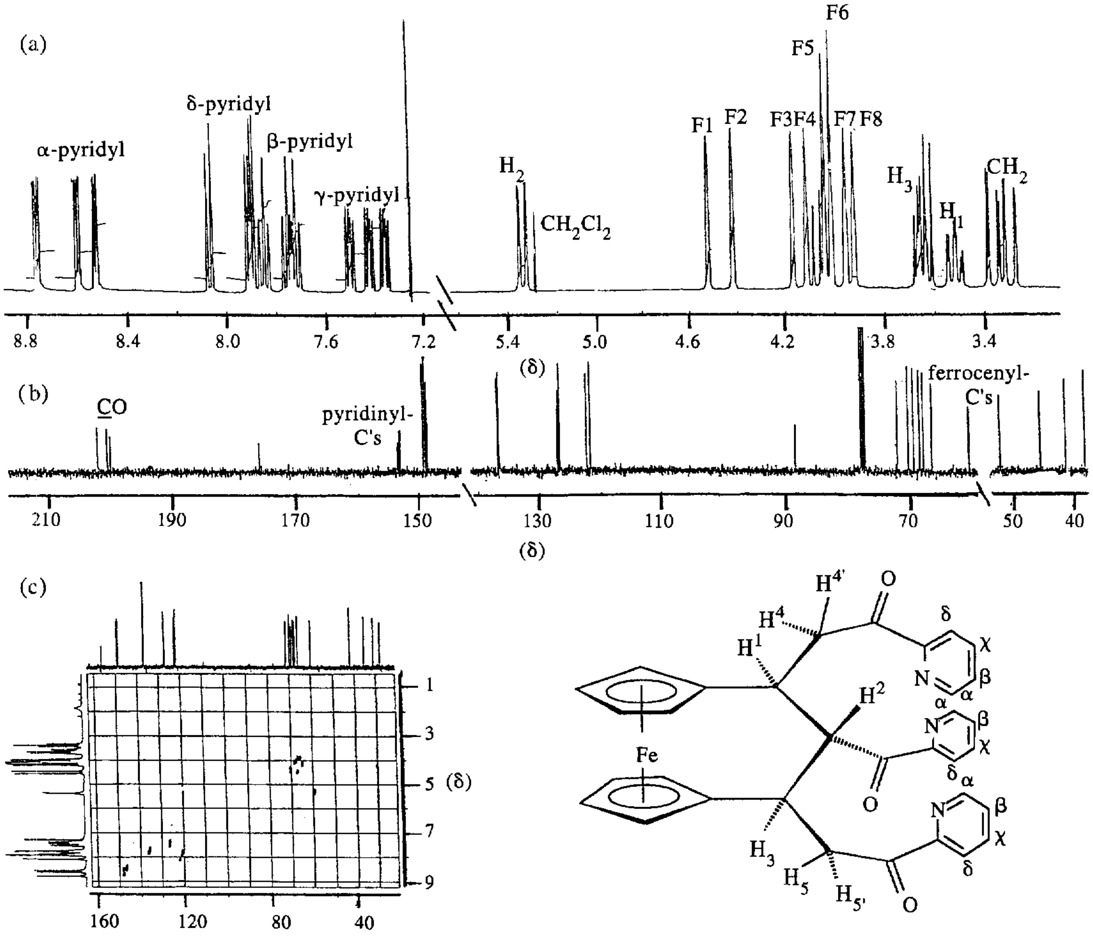
A solution of 2-acetylpyridine (4.2 cm^3, 0.03 mol), ferrocene bis-carbaldehyde (1.9 g, 0.008 mol) and sodium hydroxide (1.5 g) in water (12.5 cm^3) and ethanol (17.5 cm^3) was stirred for 1 h at room temperature under an N$_2$ atmosphere. Water (10 cm^3) was then added to give a brown precipitate. The precipitate was filtered *in vacuo* and was subsequently redissolved in dichloromethane (minimum vol.) and washed through a medium porosity sinter into a Schlenk tube. The solvent was then reduced in volume to approximately 15 cm^3 and a layer of approximately the same volume of petroleum ether (b.p. 60–80°C) was added. The solvents were allowed to slowly diffuse over a 2–3 day period to give a layer of well formed yellow crystals. The residual solution was decanted and concentrated while the crystals were isolated and dried. Chromatography of the supernatant solution gave two fractions, one red and one yellow. The yellow crystals were characterized as follows. Yield: 3.4 g, 75%. IR: ν(CO) 1697; 1695 cm^{-1}. Melting point 189–190°C. ^{1}H NMR$^{\neq}$: 3.28 (dd, 1H), 3.36 (dd, 1H), 3.52 (td, 1H), 3.62 (d, 1H), 3.66 (m, 1H), 3.92

(m, 1H), 3.95 (m, 1H), 4.01 (bs, 1H), 4.04 (bs, 1H), 4.04 (dd, 1H), 4.11 (m, 1H), 4.16 (bd, 1H), 4.41 (bd, 1H), 4.51 (bd, 1H), 5.34 (dd, 1H), 7.35 (ddd, 1H), 7.42 (ddd, 1H), 7.50 (ddd, 1H), 7.72 (ddd, 1H), 7.72 (dd, 1H), 7.84 (td, 1H), 7.89 (bd, 1H), 7.91 (bd, 1H), 8.06 (d, 1H), 8.53 (ddd, 1H), 8.60 (ddd, 1H), 8.77 (ddd, 1H). The spectrum is shown in Fig. 1. ^{13}C NMR: 27.59, 30.79, 35.17, 41.89 ($CH+CH_2$); 59.79 (CH); 65.81, 67.18, 67.73, 67.81, 68.81, 68.73, 69.54, 69.59, 71.31, 76.54, 76.85, 77.17 (ferrocenyl CH); 87.66, 87.74 (substituted ferrocenyl C); 121.63, 121.67, 122.27, 126.68, 126.87, 127.08, 136.53, 148.39, 148.71, 149.06, 152.92, 152.95, 153.02; 176.00, pyridinyl C's; 200.01, 200.49, 202.02 (CO). Found: C, 69.8; H, 5.0; N, 7.6. Calc. for $C_{33}H_{27}FeN_3O_3$: C, 69.6; H, 4.8; N, 7.4%. MS *m/z* (rel. int.): 569 (100), $M^{+\bullet}$; 463 (27); $M^{+\bullet}-[C(O)pyr]$; 449 (75), $M^{+\bullet}-[CH_2C(O)pyr]$; 373 (79); 343 (17); 342 (19); 328 (23); 266 (31), 252 (85); 224 (87), peak match on high resolution accurate mass FAB identical within experimental error. FAB-MS showed traces of $M^{+\bullet}+Na$ in crystallized material. The identity of the yellow crystals was unambiguously determined by an X-ray structure determination.

Crystal data

$[C_{33}H_{27}FeN_3O_3]\cdot CH_2Cl_2$, Table 1; $M_r = 654.37$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.469(3)$, $b = 10.713(3)$, $c = 18.608(7)$ Å, $\alpha = 91.02(1)$, $\beta = 92.61(1)$, $\gamma = 93.28(2)°$, $V = 1484.6$ Å^3, $Z = 2$, $D_c = 1.464$ g cm^{-3}, $F(000) = 676$, μ(Mo-K_α) = 7.3 cm^{-1}, $T = 150$ K, crystal size $0.45 \times 0.40 \times 0.35$ mm.

All crystallographic measurements were made as described previously,[9] using a Delft Instruments FAST TV area dectector diffractometer positioned at the window of a rotating anode generator operating at 50 kV, 50 mA with Mo-K_α radiation ($\lambda = 0.71069$ Å). 10,731 intensities corresponding to slightly more than a hemisphere of data ($2.2 < \theta < 29.8°$; $-9 < h < 10$, $-11 < k < 14$, $-10 < l < 25$) were recorded and processed to



F1-F8 = ferrocenyl resonances

Fig. 1. NMR spectra of compound **9**. (a) ^{1}H NMR. (b) ^{13}C NMR. (c) ^{1}H–^{13}C COSY.

Table 1. Crystal data and details of data collection and refinement for $[Fe(C_{33}H_{27}N_3O_3)] \cdot CH_2Cl_2$

Formula	$[Fe(C_{33}H_{27}N_3O_3)] \cdot CH_2Cl_2$
Formula weight	654.37
Crystal system	Triclinic
a (Å)	7.469(3)
b (Å)	10.713(3)
c (Å)	18.608(7)
α (°)	91.02(1)
β (°)	92.61(1)
γ (°)	93.28(2)
V (Å^3)	1484.64
θ range for cell (°)	1–25
Space group	$P\bar{1}$
Z	2
D_c (g cm^{-3})	1.464
F(000)	676
μ(Mo-K_α) (cm^{-1})	7.3
T (K)	150
Crystal size (mm^3)	0.45 × 0.40 × 0.35
θ range for data (°)	2.2–29.8
h_{min}, h_{max}	−9,10
k_{min}, k_{max}	−11,14
l_{min}, l_{max}	−10,25
Total data measured	10,731
Total unique	6844
R_{int}	0.0399
Total observed	5232
Significance test	$F_0 > 3\sigma(F_0)$
Absorption correction factors, min, max	1.128, 1.256
No. of parameters	622
ρ_{min}, ρ_{max} (e Å^{-3})	−0.55, +0.43
$(\Delta/\sigma)_{max}$	0.53
Weighting scheme	unit weight
R^a	0.0319
$R_w{}^a$	0.0370

$^a R = \Sigma[\Delta F/\Sigma(F_0)]$; $R_w = [\Sigma\{w(\Delta F)^2\}/\Sigma\{w(F_0)^2\}]^{1/2}$.

yield 6844 unique data (merging $R = 0.0399$), of which 5232 were considered observed $[F_0 > 3\sigma(F_0)]$ and used in the refinement. The data were corrected for absorption effects (DIFFABS)[10] (min. and max. absorption correction factors 1.128 and 1.256).

The structure was solved by direct methods (SHELX-S)[11] and refined by full-matrix least-squares on F (SHELX-80).[12] The non-hydrogen atoms were anisotropic and the hydrogen atoms isotropic. Final R and R_w values (both based on F) were 0.0319 and 0.0370, respectively, for 522 parameters and 5232 observed data. Unit weights were used and this gave satisfactory agreement analyses. Maximum excursions in the final difference map were −0.55 and +0.43 e Å^{-3}. Important bond lengths and angles are given in Table 2. The atomic coordinates, anisotropic displacement factor coefficients, hydrogen atom parameters, full lists of bond lengths and angles, and tables of structure factors have been deposited with the Editor, from whom copies are available on request. Atom coordinates have also been deposited with the Cambridge Crystallographic Data Centre. All calculations were done on a 486DX2/66 personal computer. The diagram was drawn by the programme SNOOPI.[13] Sources of scattering factor data are given in ref. 12.

A similar reaction using an excess of the acyl anion led to the formation of a second unidentified yellow product in high yield. IR: ν(CO) 1665 cm^{-1}. MS m/z: 955 (100), M$^{+\bullet}$; 856 (13); 834 (8); 780 (15); 779 (14); 759 (14); 735 (19).

Reaction of ruthenium trichloride with **3**

A mixture of ruthenium trichloride trihydrate (120 mg, 0.46 mmol) and compound **3** (420 mg, 1.0 mmol) was refluxed in ethanol under N_2 for 2 h. TLC in ethanol indicated the formation of four new violet complexes. Addition of diethyl ether precipitated the violet product mixture, which was washed free of unreacted ligand with ether. Dissolution of a portion of the violet powder in dichloromethane and addition of a top layer of equal volume of diethyl ether resulted in the formation of violet microcrystals, which contained two compounds, one major (80%) and one minor (20%). Yield 72%.

^{1}H NMR (CD_2Cl_2): 3.88 (s, 5H), 4.10 (s, 5H), 4.47 (t, 2H), 4.56 (t, 2H), 4.69 (t, 2H), 4.87 (t, 2H), ferrocenyl resonances, 7.14–8.56 (overlapping m, 20H), major compound; 3.90, 4.13, 4.48, 4.57, 4.70, 4.88, minor compound, ferrocenyl resonances only. MS: ion clusters at m/z 815, 890, 935, 1035 and 1081.

RESULTS AND DISCUSSION

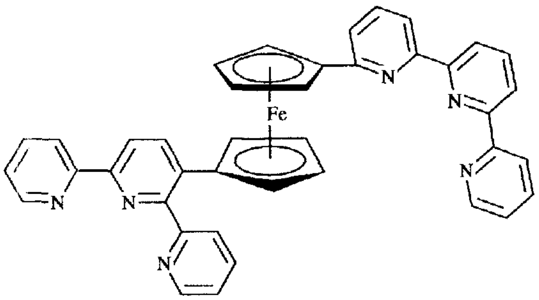
Our recent interest in the synthesis of metallapolypyridyls for use in molecular sensing triggered the desire for an improved synthesis of ferrocenyl terpyridines. In an earlier publication we reported the synthesis of compounds **1** and **2** from the direct reaction of lithioferrocene with the appropriate terpyridine.[4] Since that time we have been able to refine the separation methodology and thus in the initial part of the work we decided to re-examine this simple reaction to observe if compound **3** was indeed present in the reaction mixture. By careful product separation of the mixture obtained from dilithioferrocene and terpyridine on a basic alumina support followed by crystallization, we were indeed able to identify and isolate

Table 2. Important bond lengths (Å) and angles (°) for [Fe($C_{33}H_{27}N_3O_3$)]·CH_2Cl_2

C(24)—Fe	2.022(4)	C(25)—Fe	2.030(4)
C(26)—Fe	2.049(4)	C(27)—Fe	2.046(4)
C(28)—Fe	2.026(4)	C(29)—Fe	2.006(4)
C(30)—Fe	2.029(4)	C(31)—Fe	2.049(4)
C(32)—Fe	2.049(4)	C(33)—Fe	2.035(4)
C(6)—O(1)	1.213(4)	C(12)—O(2)	1.218(4)
C(18)—O(3)	1.215(3)	C(1)—N(1)	1.332(4)
C(5)—N(1)	1.343(4)	C(13)—N(2)	1.342(4)
C(17)—N(2)	1.326(4)	C(19)—N(3)	1.340(4)
C(23)—N(3)	1.334(4)	C(2)—C(1)	1.389(4)
C(6)—C(1)	1.511(5)	C(3)—C(2)	1.395(4)
C(4)—C(3)	1.363(5)	C(5)—C(4)	1.382(5)
C(7)—C(6)	1.511(5)	C(8)—C(7)	1.539(5)
C(9)—C(8)	1.549(5)	C(24)—C(8)	1.516(5)
C(10)—C(9)	1.576(5)	C(18)—C(9)	1.523(5)
C(11)—C(10)	1.528(5)	C(29)—C(10)	1.512(5)
C(12)—C(11)	1.520(5)	C(13)—C(12)	1.500(5)
C(14)—C(13)	1.393(4)	C(15)—C(14)	1.382(4)
C(16)—C(15)	1.380(4)	C(17)—C(16)	1.392(4)
C(19)—C(18)	1.510(5)	C(20)—C(19)	1.391(4)
C(21)—C(20)	1.384(4)	C(22)—C(21)	1.376(5)
C(23)—C(22)	1.387(5)	C(25)—C(24)	1.429(4)
C(28)—C(24)	1.440(4)	C(26)—C(25)	1.430(4)
C(27)—C(26)	1.421(4)	C(28)—C(27)	1.428(4)
C(30)—C(29)	1.436(4)	C(33)—C(29)	1.442(4)
C(31)—C(30)	1.429(4)	C(32)—C(31)	1.419(4)
C(33)—C(32)	1.428(4)		

C(5)—N(1)—C(1)	117.2(3)	C(17)—N(2)—C(13)	117.1(3)
C(23)—N(3)—C(19)	117.4(3)	C(2)—C(1)—N(1)	123.2(3)
C(6)—C(1)—N(1)	117.6(3)	C(6)—C(1)—C(2)	119.2(3)
C(3)—C(2)—C(1)	118.3(3)	C(4)—C(3)—C(2)	119.1(3)
C(5)—C(4)—C(3)	118.7(3)	C(4)—C(5)—N(1)	123.6(4)
C(1)—C(6)—O(1)	119.9(3)	C(7)—C(6)—O(1)	122.3(3)
C(7)—C(6)—C(1)	117.9(3)	C(8)—C(7)—C(6)	112.8(3)
C(9)—C(8)—C(7)	111.1(3)	C(24)—C(8)—C(7)	108.6(3)
C(24)—C(8)—C(9)	110.6(2)	C(10)—C(9)—C(8)	114.7(2)
C(18)—C(9)—C(8)	114.3(2)	C(18)—C(9)—C(10)	104.9(2)
C(11)—C(10)—C(9)	111.4(2)	C(29)—C(10)—C(9)	112.3(3)
C(29)—C(10)—C(11)	111.0(3)	C(12)—C(11)—C(10)	112.2(3)
C(11)—C(12)—O(2)	122.2(3)	C(13)—C(12)—O(2)	120.3(3)
C(13)—C(12)—C(11)	117.5(3)	C(12)—C(13)—N(2)	116.9(3)
C(14)—C(13)—N(2)	123.1(3)	C(14)—C(13)—C(12)	120.0(3)
C(15)—C(14)—C(13)	118.5(3)	C(16)—C(15)—C(14)	119.2(3)
C(17)—C(16)—C(15)	118.0(3)	C(16)—C(17)—N(2)	124.1(3)
C(9)—C(18)—O(3)	123.0(3)	C(19)—C(18)—O(3)	120.4(3)
C(19)—C(18)—C(9)	116.5(3)	C(18)—C(19)—N(3)	117.1(3)
C(20)—C(19)—N(3)	123.3(3)	C(20)—C(19)—C(18)	119.6(3)
C(21)—C(20)—C(19)	118.3(3)	C(22)—C(21)—C(20)	118.8(3)
C(23)—C(22)—C(21)	119.1(3)	C(22)—C(23)—N(3)	123.1(3)
C(25)—C(24)—C(8)	128.1(3)	C(28)—C(24)—C(8)	125.1(3)
C(28)—C(24)—C(25)	106.7(3)	C(26)—C(25)—C(24)	108.9(3)
C(27)—C(26)—C(25)	107.8(3)	C(28)—C(27)—C(26)	108.1(3)
C(27)—C(28)—C(24)	108.5(3)	C(30)—C(29)—C(10)	127.2(3)
C(33)—C(29)—C(10)	125.7(3)	C(33)—C(29)—C(30)	107.0(3)
C(31)—C(30)—C(29)	108.5(3)	C(32)—C(31)—C(30)	108.0(3)
C(33)—C(32)—C(31)	108.5(3)	C(32)—C(33)—C(29)	108.0(3)

samples of 4′-ferrocenyl-2,2′ : 6′,2″-terpyridine (**3**); however, yields were very low indeed. In addition, we were able to identify a number of disubstituted ferrocenes also present in minor concentrations by NMR, for example the bis-terpyridylferrocene **1a**. In compound **3** the complication of ferrocene metallation is less likely in its derived complexes; however, access to larger quantities of this symmetrical 4′-ferrocenyl derivative is required.

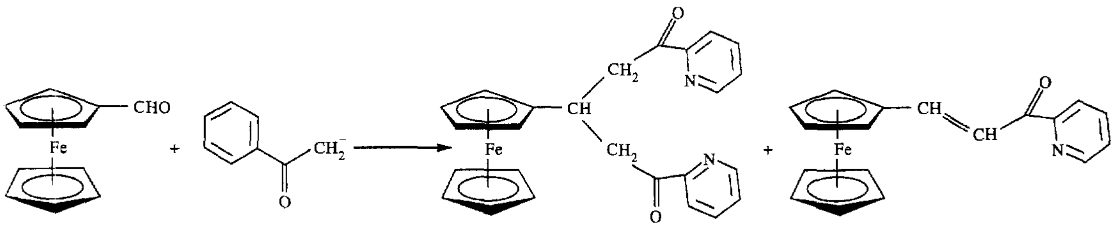


1a

Sauvage and co-workers have recently described the synthesis and coordination chemistry of ferrocenyl-4-phenyl-4′-(2,2′ : 6′,2″-terpyridine), i.e. a ferrocenyl terpyridine with a phenyl spacer between the ferrocene and the terpyridyl units.[14] For our purposes, having the ferrocene directly linked to the terpyridine is more appropriate since we wish to simplify the π-interactions between the coordinating site and the redox centre. To achieve this objective the synthetic procedure we chose was via the preparation of an appropriately substituted ferrocenylpentane-1,5-dione. In one literature report, Thumnel[15] has reported the synthesis of an unusual fused ferrocenylterpyridine system by the condensation of ferrocenecarbaldehyde with the morpholine enamine of an appropriate pyridocycloalkane. In addition, a modified approach using an aldol condensation–Michael addition strategy has proved effective for the synthesis of 4′-pyridylterpyridine in some recently published work by Constable and co-workers,[16] related to the work of Potts.[17]

When ferrocenecarbaldehyde was treated with two molar equivalents of the carbanion derived from 2-acetylpyridine, the desired dienone derivative **4** was indeed obtained in high yield. It was isolated as a yellow powder from the synthesis. A small quantity of the red elimination product from the aldol condensation, **5**, was also obtained. Both **4** and **5** were unambiguously characterized by ^{1}H NMR, mass spectroscopy and elemental analysis. The vinylic proton resonances in **5** are observed at extremely low field (7.84) as an apparent doublet at 250 MHz. Large quantities of **5** (90%) can of course be prepared by alteration of the reaction stoichiometry, since it is an extremely important synthetic intermediate in its own right and is a desirable starting material for a range of Kroncke synthesis products.[18] The phenyl analogue of this compound was reported by Hauser and Lindsay as early as 1957.[19] In the case of **4**, the ^{1}H NMR spectrum shows no irregularities, with the substituted ferrocenyl cyclopentadienyl proton resonance upfield of that of the unsubstituted cyclopentadienyl resonance, as would be expected. A similar reaction with 3-acetylpyridine gave the analogous 3-pyridyl derivative **6** as a yellow orange solid.

Treatment of **4** with ammonium acetate resulted in the clean preparation of the desired 4′-ferrocenyl-2,2′ : 6′,2″-terpyridine (**3**) in high yield. The product precipitates from the reaction mixture as an orange–brown powder which is isolated simply by filtration. Again, full characterization of the product was made by a range of spectroscopies and the product was identical to that obtained previously from the reaction of lithioferrocene with terpyridine. Surprisingly, compound **3** is more air- and light-sensitive in solution than the other ferrocenylterpyridine derivatives and darkens in air rapidly on exposure to light and also on attempted chromatography forms a violet compound on contact with silica gel. This violet colour is indicative of protonation of the pyridyl residues. Cyclization of compound **6** similarly results in the formation

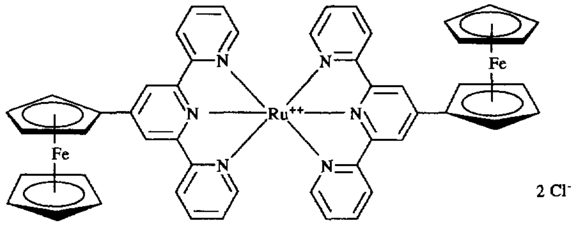


Scheme 1.

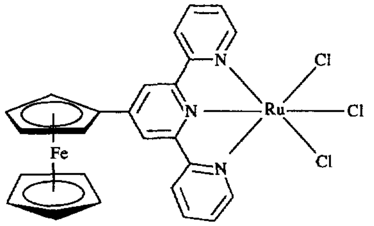
of the terpyridylferrocene, 4′-ferrocenyl-3,2′ : 6′,3″-terpyridine (**7**), in high (90%) yield.

This derivative does not exhibit the same high sensitivity towards silica gel. Interestingly, on attempted synthesis of the intermediate dione required for the cyclization to 4′-ferrocenyl-4,2′ : 6′,4″-terpyridine, it was observed that only traces of the desired product were obtained (the major product isolated contained three pyridinyl residues) ; therefore, no attempt was made to prepare the latter isomer.

One preliminary experiment to evaluate the coordination properties of **3** was carried out : the reaction of two equivalents of compound **3** with ruthenium trichloride in ethanol gave rise to four new violet complexes as witnessed by TLC. On attempted crystallization, it was observed that two of these complexes predominated (^{1}H NMR), both of which contained two ferrocenyl terpyridine ligands. The major compound present could be identified by accurate mass FAB spectroscopy as being the $[(\text{Fc-4}'\text{-terpy})_2\text{Ru}]^{2+}2\text{Cl}^-$ complex, (Ru(L3)_2). NMR of the major compound present in the mixture indicates no symmetry in the complex with respect to two ferrocenyl ligands, as would be expected for the dicationic bis-ferrocenyl complex. The minor products presumably derive from related ruthenium di- and trichlorides, e.g. Ru(L3)Cl_3, in accordance with related results reported previously for unsubstituted terpyridine ligands.[16]

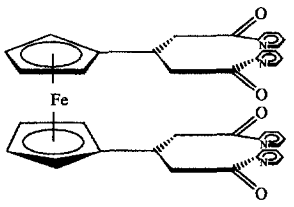


Ru(L3)$_2$



Ru(L3)Cl$_3$

In the initial attempts at the synthesis of compound **8**, the precursor to the bis-terpyridine derivative, large quantities of an unknown yellow compound, **9**, were obtained. This was subsequently identified following a detailed spectroscopic study and this was later confirmed by single crystal X-ray diffraction. NMR spectral data are shown in Fig. 1.



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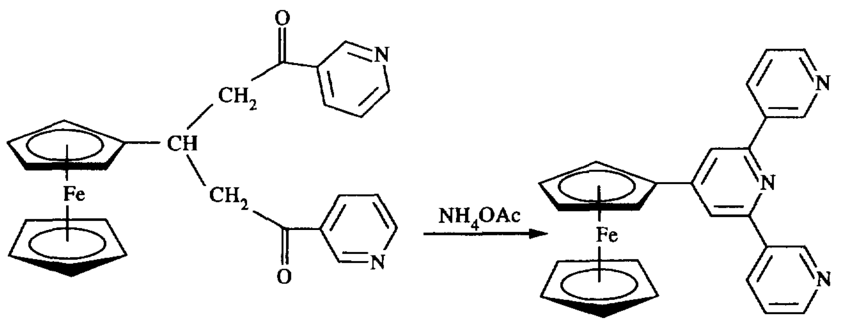
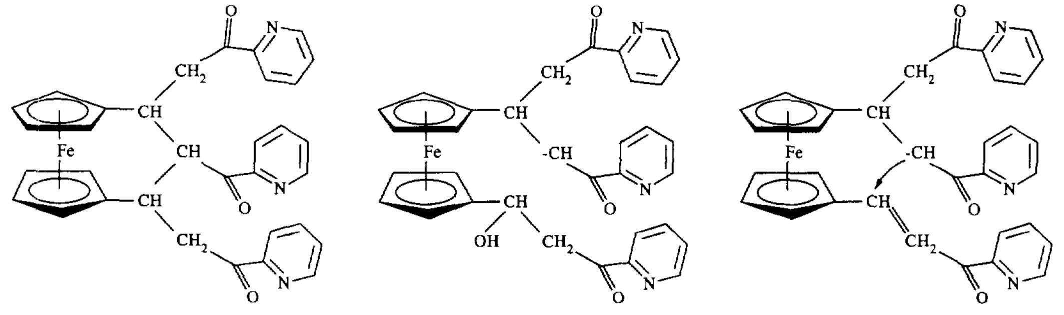
It was immediately evident that the product was a ferrocenophane, with the characteristic low field proton resonance at δ5.33 due to the proton on the middle carbon in the three-carbon bridge. This proton resonance is a doublet of doublets with one



6 **7**

Scheme 2.



9 **10** **11**

Scheme 3.

^1H–^1H vicinal coupling constant much larger than the other (11.5 Hz vs 2.3 Hz) because of the significant differences in their dihedral angles, with respect to protons on the α-carbon atoms. All ferrocene protons are inequivalent because of the asymmetric substituents. It is clear that compound **9** is formed as a consequence of intramolecular attack of a stabilized intermediate anion onto an α-carbon centre on the other cyclopentadienyl ring, as shown in **10**, or the Michael addition of the anion to the vinylketone, as shown in **11**. In related work we have established that the Michael addition of the anion derived from 2-acetylpyridine occurs on the isolated compound **5** to give the dione **4**. The formation of C_3-ferrocenophanes in particular is well known to be a facile process because a three-carbon bridge is favoured by the ferrocenyl ring spacing. In compound **9** there are two chiral centres, which is verified by ^1H NMR in that only one pair of diastereomers is observed. There is no evidence for the formation of another diastereomeric pair. This is a consequence of the precise geometry of the attacking anion onto the lower ring substituents. An X-ray study of compound **9** showed that it crystallized as a dichloromethane solvate (1 : 1) and has the structure shown in Fig. 2. The Fe—C(Cp) distances are slightly asymmetric and range from 2.006(4) to 2.049(4) Å, average 2.034 Å. The dimensions of the two CP rings are almost eclipsed, as expected [C—C = 1.421(4)–1.442(4) Å, average 1.430 Å ; C—C—C = 106.7(3)–108.9(3)°, average 108.0°] ; the two rings are almost eclipsed and are nearly parallel (dihedral angle between the two Cp planes = 9.1°). It is interesting to note that the two acylpyridyl moieties bonded to the carbons [C(8) and C(10)] are oriented differently with respect to the respective Cp rings, probably to minimize interligand steric interactions and for better packing in the crystal. Thus, C(7) lies in a direction nearly perpendicular to the ring through C(24)–C(28) [dihedral angle C(7)—C(8)—C(24)—C(25) = 61.4°], whilst C(11) is nearly

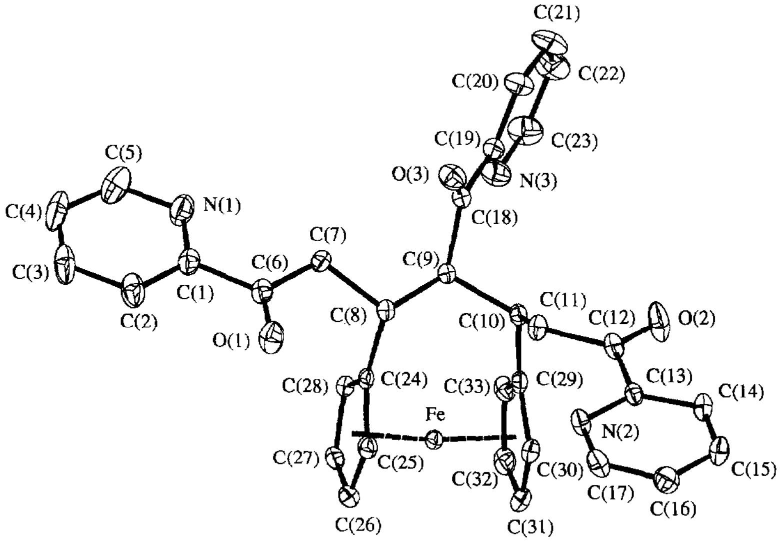


Fig. 2. The SNOOPI drawing of compound **9**, with the hydrogen atoms omitted for clarity.

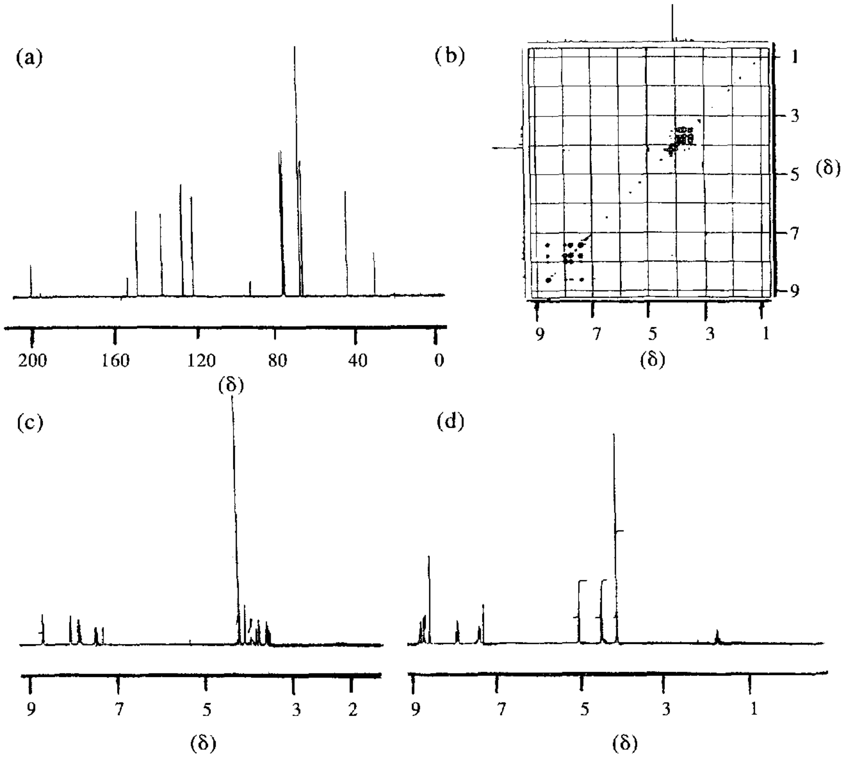
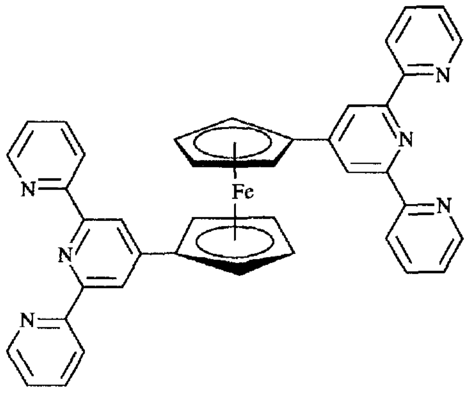


Fig. 3. Spectra of compound **4a**. (a) ^{13}C NMR. (b) ^{1}H–^{1}H COSY. (c) ^{1}H NMR. (d) ^{1}H NMR of compound **3**.

parallel to the ring through C(29)–C(33) [C(11)—C(10)—C(29)—C(30) = 5.4°]. The pyridyl moieties are all planar and the corresponding bond lengths and angles are equal within experimental error. The acyl groups are slightly out of the respective pyridyl planes as indicated by the torsion angles, N(1)/C(2)—C(1)—C(6)—O(1)/C(7) = 1.5/2.3°, N(2)/C(11)—C(13)—C(12)—O(3)/C(14) = 3.6/6.6° and N(3)/C(9)—C(19)—C(18)—O(3)/C(20) = 5.9/10.8°. Other geometry parameters are as expected. It is noted that molecule **9** is of interest in its own right since reduction of the carbonyls would lead to a ligand having three bidentate three-electron donor coordination sites. The ^{13}C–^{1}H correlation spectrum of **9** is shown in Fig. 1 with the important structural assignments indicated. Further attempts at the preparation of compound **12** using higher ratios of the anion vs ferrocenyldialdehyde led only to the formation of a second, much higher molecular weight, as yet unidentified compound (m/z = 955 by FAB mass spectrometry), derived from the reaction of six acylpyridine units with the dialdehyde. A full description of this latter work and the reaction chemistry of the 4-acetylpyridine derivative reactions will appear elsewhere. Current studies are aimed at the preparation of coordination complexes of compound **3** and the development of an alternative synthetic route to compound **12**.



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Note added in proof—Since the original submission of this article two papers have appeared on the same topic.[20,21]

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