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The coordination chemistry of 4′-(4-*tert*-butylphenyl)-2,2′:6′,2″-terpyridine—a solubilising oligopyridine

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Abstract—The preparation of a solubilised 2,2′:6′,2″-terpyridine ligand is described together with the characterisation of an unexpected intermediate. Homoleptic complexes of the solubilised ligand 4′-(4-*tert*-butylphenyl)-2,2′:6′,2″-terpyridine, **1**, with cobalt(II), cobalt(III), ruthenium(II), iron(II) and nickel(II) have been prepared. The ligand is slightly electron releasing and solubilises the complexes in organic media. © 1997 Elsevier Science Ltd

Oligopyridines provide versatile and robust metal binding domains for metallosupramolecular chemistry [1–3]. One of the difficulties associated with the study of the coordination behaviour of the higher oligopyridines is the insolubility of the ligands themselves in most common solvents. In order to overcome such solubility problems we recently introduced the 4-*tert*-butyphenyl substituent as a solubilising group for oligopyridines [4,5] and have shown its utility in the preparation and characterisation of 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine [6] and 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′:6⁗′,2⁗″:6⁗″,2⁗‴-septipyridine [7] complexes. In this paper we describe our detailed studies of the solubilised ligand 4′-(4-*tert*-butylphenyl)-2,2′:6′,2″-terpyridine **1** and report coordination complexes with a number of transition metals.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 300 or Bruker AC250 spectrometers; electron impact (EI) mass spectra were recorded on a VG 70-250 spectrometer, with 3-nitrobenzyl alcohol as the matrix for the FAB experiments. Laser desorption time-of-flight mass spectra were recorded on a PerSeptive Biosystems Voyager-RP Biospectrometry Workstation using 2,5-dihydroxybenzoic acid as a matrix. IR spectra were recorded on a Genesis Series FTIR spectrophotometer with the samples in compressed KBr disks. Electrochemical measurements were performed with an Amel model 553 potentiostat connected to an Amel model 567 function generator and an Amel model 560A interface or an Eco Chemie Autolab PGSTAT 20 system using platinum bead or glassy carbon working and auxiliary electrodes with an Ag/AgCl electrode as reference. The experiments were conducted using purified acetonitrile as solvent and freshly recrystallised 0.1 M $[Bu^n_4N][BF_4]$ or $[Bu^n_4N][PF_6]$ as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. The compounds 4-*tert*-butylbenzaldehyde and 2-acetylpyridine were used as supplied by Avocado Chemicals.

Preparations

1,6-Bis(2-pyridyl)-4-(4-tert-butylphenyl)-pentane-1,5-dione (**3**). 4-*tert*-Butylbenzaldehyde (460 mg, 2.84 mmol) was suspended in aqueous NaOH (2 cm^3, 2 M) at 0°C and 2-acetylpyridine (0.3 cm^3, 2.5 mmol) was added with constant stirring over 10 min. The resulting yellow solution was left stirring at room temperature for 12 h, and then extracted twice with dichloromethane (2 × 50 cm^3). The dichloromethane was removed *in vacuo* to give a yellow oil, which was chromatographed over silica (dichloromethane eluant). The major product band was collected, and the solvent removed *in vacuo* to give **3** as a white solid (193 mg, 40%). Mp 129–130°C. Found: C, 77.7; H, 6.9; N, 7.0. Calc. for $C_{25}H_{26}N_2O_2$: C, 77.7; H, 6.8; N, 7.2%. IR: 1697 s, 1583 m, 1435 m, 1363 m, 993 s, 774

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m, 582 m cm^{-1}. EIMS: *m/z* 386 $\{M\}^+$. ^1H NMR ($CDCl_3$, δ): 8.64, (2H, d, H^6), 7.93 (2H, d, H^{ortho}), 7.78 (2H, qd, H^5), 7.28 (4H, m, H^3, H^{meta}), 4.11 (1H, quin, CH), 3.55 (4H, qd, CH_2), 1.26 (9H, s, $C(CH_3)_3$).

4′-(4-tert-*Butylphenyl*)-2,2′:6′,2″-*terpyridine* (**1**). *Method* 1—*from* **3**. A solution of **3** (170 mg, 0.44 mmol) and ammonium acetate (3 g, excess) in glacial acetic acid (10 cm^3) was heated to reflux for 2 h. The green solution was cooled, neutralised with aqueous sodium carbonate and extracted with dichloromethane (2×50 cm^3). The solvent was removed *in vacuo* to afford a green oil from which a light green solid was obtained by addition of water (20 cm^3). This was collected by filtration to give **3** as a light green solid (0.117 g, 73%). Mp 174–175°C. Found: C, 82.9; H, 6.3; N, 11.6. Calc. for $C_{23}H_{23}N_3$: C, 82.2; H, 6.3; N, 11.5%. IR: 1582 s, 1566 m, 1466 m, 1387 m, 833 m, 794 s cm^{-1}. EIMS: *m/z* 365 $\{M\}^+$, 350 $\{M\text{-}CH_3\}$.

Method 2—*from* **7**. A mixture of **7** (0.8 g), and ammonium acetate (10 g, excess) was heated at reflux in glacial acetic acid (50 cm^3) for 3 h. After this time, the reaction mixture was worked-up as described above to afford **1** as a light green solid (0.47 g, 81%).

3-(4-tert-*Butylphenyl*)-1,5-*bis*(2-*pyridyl*)-2-(2-*pyridylcarbonyl*)*cyclohexane*-1,5-*diol* (**7**). 4-*tert*-Butylbenzaldehyde (1.97 g, 12.2 mmol) was dissolved in ethanol (75 cm^3) and a solution of sodium hydroxide (2.5 g in water (20 cm^3) was added followed by 2-acetylpyridine (4.77 cm^3, 42.5 mmol) added drop-wise over 10 min. The mixture was then stirred at room temperature for 12 h after which time the white precipitate was collected by filtration. The solid was washed with water and a little cold methanol and dried *in vacuo* to give **7** (4.6 g, 74%). M.p. 203–205 (dec). Found: C, 75.5; H, 6.6; N, 8.2. Calc. for $C_{32}H_{33}N_3O_3$: C, 75.7; H, 6.6; N, 8.3%. IR: 1693 s, 1590 s, 1569 m, 1471 m, 1445 m, 1437 m, 1413 m, 1361 m, 1270 m, 1135 s, 1114 m, 1086 m, 994 m, 770 m, 745 s, 668 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1.10 (9H, s, Me), 2.04 (1H, d, *J* 14.4 Hz, H^{6eq}), 2.10 (1H, dd, *J* 13.2, 3.3 Hz, H^{4eq}), 2.73 (1H, dd, *J* 13.0, 13.2 Hz, H^{4ax}), 3.08 (1H, d, *J* 14.4 Hz, H^{6ax}), 4.03 (1H, ddd, *J* 12.0, 3.3, 13.0 Hz, H^3), 5.45 (1H, d, *J* 12.0 Hz, H^2), 6.22 (1H, br s, OH), 6.53 (1H, br s, OH), 6.89 (1H, dd, $P(3)^5$), 6.99 (2H, d, *J* 8.5 Hz, H^{ortho}), 7.12 (1H, dd, $P(1)^5$), 7.14 (1H, dd, $P(2)^5$), 7.20 (2H, d, *J* 8.5 Hz, H^{meta}), 7.37 (1H, d, $P(2)^3$), 7.40 (1H, dd, $P(2)^4$), 7.44 (1H, dd, $P(3)^4$), 7.62 (1H, d $P(3)^3$), 7.67 (1H, dd, $P(1)^4$), 7.77 (1H, d $P(1)^3$), 8.29 (1H, d, $P(3)^6$), 8.45 (1H, d, $P(2)^6$), 8.51 (1H, d, $P(1)^6$). ^{13}C NMR ($CDCl_3$, δ): 31.7 (CH_3), 34.7 (CMe_3), 40.5 (C^3), 47.0 (C^4), 47.1 (C^6), 54.5 (C^2), 76.5 (C^5), 79.8 (C^1), 119.0 (C^{B3}), 120.7 ($C^{A5/C5}$), 122.3 ($C^{A3/C3}$), 122.4 ($C^{A3/C3}+C^{A5/C5}$), 125.3 (C^{Ar3}), 126.5 (C^{B5}), 128.5 (C^{Ar2}), 136.5 ($C^{A4/B4/C4}$), 136.9 ($C^{A4/B4/C4}$), 137.2 ($C^{A4/B4/C4}$), 139.5 (C^{Ar1}), 148.3 ($C^{A6/B6/C6}$), 148.5 ($C^{A6/B6/C6}$), 148.6 ($C^{A6/B6/C6}$), 149.5 (C^{Ar4}), 154.4 (C^{B2}), 163.7 ($C^{A2/C2}$), 165.8 ($C^{A2/C2}$), 206.2 (C=O).

$[Ru(\mathbf{1})Cl_3]$. **1** (150 mg, 0.41 mmol) was added to a solution of $RuCl_3 \cdot 3H_2O$ (107 mg, 0.41 mmol) in ethanol (10 cm^3), and the suspension was heated to reflux for 90 min. The reaction mixture was then cooled and the dark brown solid was collected by filtration, washed with a small volume of cold methanol, and dried *in vacuo* to yield $[Ru(\mathbf{1})Cl_3]$ (158 mg, 67%).

$[Ru(\mathbf{1})_2][PF_6]_2$. **1** (32 mg, 0.09 mmol) was added to $[Ru(\mathbf{1})Cl_3]$ (50 mg, 0.09 mmol) in methanol (10 cm^3); *N*-ethylmorpholine (3 drops) was then added and the mixture heated to reflux for 1 h. After cooling, the resulting dark red solution was filtered through celite to remove any solids and excess methanolic ammonium hexafluorophosphate added to precipitate $[Ru(\mathbf{1})_2][PF_6]_2$. This was collected by filtration, washed with a small volume of cold aqueous methanol, and ether, and dried *in vacuo* to yield a red/brown powder (36 mg, 37%). This was recrystallised by reducing a 1:1 acetone–water solution in volume to yield red microcrystals. Found: C, 52.6; H, 4.2; N, 7.5. Calc. for $RuC_{50}H_{46}N_6P_2F_{12} \cdot H_2O$: C, 52.7; H, 4.2; N, 7.4%. MALDI-TOF MS: *m/z* 978 $\{[Ru(\mathbf{1})_2][PF_6]\}^+$, 833 $\{[Ru(\mathbf{1})_2]\}^+$.

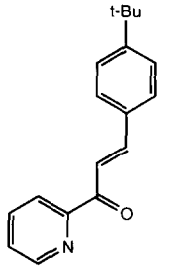
$[Fe(\mathbf{1})_2][PF_6]_2$. A solution of $[Fe(H_2O)_6][SO_4]$ (71 mg, 0.273 mmol) in methanol (50 cm^3) and a solution of **1** (200 mg, 0.547 mmol) in warm methanol (50 cm^3) were mixed and the resulting deep purple solution stirred at room temperature for 30 min. Excess methanolic ammonium hexafluorophosphate was added and the volume reduced *in vacuo* to precipitate $[Fe(\mathbf{1})_2][PF_6]_2$. This was collected by filtration and washed with ether to give the complex as a fine purple solid (148 mg, 50%). This could be recrystallised by reducing a 1:1 acetone–water solution in volume to yield dark purple microcrystals. Found: C, 55.4; H, 4.8; N, 7.1%. Calc. for $FeC_{50}H_{46}N_6P_2F_{12} \cdot 0.5\ H_2O$: C, 55.3; H, 4.4; N, 7.7%. MALDI-TOF MS: *m/z* 787 $\{[Fe(\mathbf{1})_2]\}^+$.

$[Co(\mathbf{1})_2][PF_6]_2$. A solution of $Co(OAc)_2 \cdot 4H_2O$ (14 mg, 0.055 mmol) in methanol (10 cm^3) was added to a solution of **1** (40 mg, 0.110 mmol) in methanol (10 cm^3) and the resulting mixture was stirred at ambient temperature for 30 min. Excess methanolic ammonium hexafluorophosphate was added to the deep red solution, and precipitation was induced by reduction in volume *in vacuo*. The precipitate was collected by filtration, washed with aqueous methanol, and ether, and dried *in vacuo* to yield $[Co(\mathbf{1})_2][PF_6]_2$ as a dark red microcrystalline solid (26 mg, 44%). Found: C, 55.5; H, 4.6; N, 7.7. Calc. for $CoC_{50}H_{46}N_6P_2F_{12}$: C, 55.6; H, 4.3; N, 7.8%. MALDI-TOF MS: *m/z* 789 $\{[Co(\mathbf{1})_2]\}^+$, 423 $\{[Co(\mathbf{1})]\}^+$.

$[Co(\mathbf{1})_2][PF_6]_3$. A solution of $Co(OAc)_2 \cdot 4H_2O$ (14 mg, 0.055 mmol) in methanol (10 cm^3) was added to a solution of **1** (40 mg, 0.110 mmol) in methanol (10 cm^3). Activated charcoal (15 mg) and hydrogen peroxide (10 drops) were added to the resulting red solution and the reaction mixture was stirred at ambient temperature for 48 hours while air was gently bubbled through it. The solution was then filtered through celite to remove solids and excess methanolic ammonium hexafluorophosphate added. The volume

was reduced *in vacuo* to precipitate $[Co(\mathbf{1})_2][PF_6]_3$ which was collected by filtration, washed with aqueous methanol and ether, and dried *in vacuo* to give a fine red powder (25 mg, 37%). Analysis found: C, 49.7; H, 3.9; N, 7.2. Calculated for $CoC_{50}H_{46}N_6P_3F_{18}$: C, 49.1; H, 3.8; N, 6.9%. MALDI TOF MS: *m/z* 789 $\{[Co(\mathbf{1})_2]\}^+$, 424 $\{[Co(\mathbf{1})]\}^+$.

$[Ni(\mathbf{1})_2][PF_6]_2$. A solution of $Ni(OAc)_2 \cdot 4H_2O$ (14 mg, 0.055 mmol) in warm methanol (10 cm^3) was added to a solution of **1** (40 mg, 0.110 mmol) in warm methanol (10 cm^3) and the mixture heated to reflux for 3 h. After cooling, excess methanolic ammonium hexafluorophosphate was added, and the volume reduced *in vacuo* to precipitate a fine brown solid. This was isolated by filtration, washed with aqueous methanol and then ether to yield $[Ni(\mathbf{1})_2][PF_6]_2$ as a pale brown microcrystalline solid (25 mg, 42%). Found: C, 56.8; H, 4.8; N, 7.8. Calc. for $NiC_{50}H_{46}N_6P_2F_{12}$: C, 55.6; H, 4.3; N, 7.8%. MALDI-TOF: *m/z* 790 $\{[Ni(\mathbf{1})_2]\}^+$, 424 $\{[Ni(\mathbf{1})]\}^+$.



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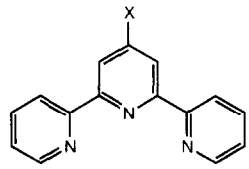


1 X = 4-*tert*-BuC_6H_4

4 X = H

5 X = Ph

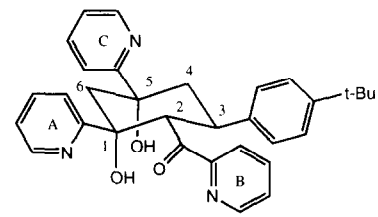
6 X = 4-BrC_6H_4

RESULTS AND DISCUSSION

Ligand synthesis

Our initial approach to the synthesis of **1** relied upon a classical route analogous to that which we previously reported for 4′-phenyl-2,2′ : 6′,2″-terpyridine **5** [8]. The reaction of one equivalent of 4-*tert*-butylbenzaldehyde with 0.9 equiv. of 2-acetylpyridine in aqueous ethanolic sodium hydroxide solution yielded a number of products instead of the expected enone **2**. Chromatographic purification of the mixture of organic products over silica using dichloromethane as eluant gave the diketone **3** as the major product in 40% isolated yield as a white solid. Compound **3** exhibited the expected parent ion at *m/z* 386 in its mass spectrum and carbonyl stretching mode in its infrared spectrum at ν1697 cm^{-1}, characteristic of the saturated diketone **3** rather than the enone **2**. The reaction of **3** with an excess of ammonium acetate in glacial acetic acid yielded the desired ligand **1** as a pale green solid in 73% yield.

Ligand **1** exhibited a parent ion at *m/z* 365 in its mass spectrum together with a ^1H NMR spectrum fully consistent with the molecular symmetry. ^1H NMR spectroscopic data for **1** and a series of related ligands are presented in Table 1. A number of features are evident from these data, all of which indicate that the introduction of the hydrophobic group onto the periphery of the ligand has no major effects upon the metal binding domain. Firstly, the chemical shifts for the terminal pyridine rings are almost independent of the substituent on the central ring; the greatest variation is seen in H^3 in which a variation of 0.05 ppm is observed. The introduction of the aryl substituent into the 4′-position has a significant downfield shifting effect upon $H^{3'}$ ($\approx$0.3 ppm) although the chemical shift of $H^{3'}$ is almost independent of the



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Structure 1.

nature of any substituents introduced into the *para* position of the phenyl ring. This result accords well with previous studies of metal complexes of 4′-aryl-2,2′ : 6′,2″-terpyridines in which the nature of the aryl group was found only to have very small effects upon metal-centred redox and spectroscopic properties [9] and contrasts markedly with the dramatic variations in such properties that result from the introduction of electron-releasing or -withdrawing substituents directly into the 4′-position of the 2,2′ : 6′,2″-terpyridine [10].

The formation of the diketone **3** in the 1 : 1 reaction of 2-acetylpyridine with 4-*tert*-butylbenzaldehyde was rather unexpected and we investigated the reaction with an excess of 2-acetylpyridine in an attempt to optimise the formation of **3**. After reaction for 12 h in aqueous ethanolic sodium hydroxide solution, a single white product was obtained in 74% yield. However, this product had a different melting point to **3** and exhibited a carbonyl stretching frequency at 1693 cm^{-1}; furthermore, the parent ion in the mass spectrum was observed at *m/z* 508. We have previously noted the formation of 3 : 2 and 3 : 1 condensation

Table 1. ^{1}H NMR spectroscopic data for 2,2′:6′,2″-terpyridines and for homoleptic metal complexes of **1**

Compound	H^6	H^5	H^4	H^3	$H^{3'}$	H^o	H^m	Other
1[a]	8.72	7.34	7.87	8.66	8.74	7.86	7.52	^{t}Bu 1.38
4[a]	8.70	7.34	7.86	8.63	8.46			$H^{4'}$ 7.97
5[a]	8.71	7.35	7.89	8.68	8.75	7.91	7.48	H^p 7.48
6[a]	8.73	7.36	7.89	8.67	8.70	7.78	7.64	
$[Ru(\mathbf{1})_2][PF_6]_2$[b]	7.43	7.18	7.94	8.65	9.01	8.16	7.81	^{t}Bu 1.47
$[Fe(\mathbf{1})_2][PF_6]_2$[b]	7.19	7.08	7.91	8.61	9.18	8.27	7.86	^{t}Bu 1.49
$[Co(\mathbf{1})_2][PF_6]_3$[b]	7.43	7.42	8.26	8.71	9.26	8.29	7.91	^{t}Bu 1.49

[a] $CDCl_3$
[b] CD_3CN

Table 2. Cyclic voltammetric data for homoleptic metal complexes of **1** and **4** in CH_3CN solution (all potentials quoted against $Fc/Fc^+ = 0.0$ V)

	E°/V M(II/III)	E°/V 1st redn	E°/V 2nd redn
$[Ru(\mathbf{4})_2][PF_6]_2$	0.92	−1.67	−1.92
$[Fe(\mathbf{4})_2][PF_6]_2$	0.73	−1.66	−1.82
$[Co(\mathbf{4})_2][PF_6]_2$	−0.09	−1.13	−2.05
$[Ru(\mathbf{1})_2][PF_6]_2$	0.89	−1.61	−1.89
$[Fe(\mathbf{1})_2][PF_6]_2$	0.72	−1.60	−1.78
$[Co(\mathbf{1})_2][PF_6]_2$	−0.18	−1.17	−2.03
$[Ni(\mathbf{1})_2][PF_6]_2$		−1.29	−1.53

products from the reaction of 2-acetylpyridine with a variety of substituted benzaldehydes[11] and the observed mass of 505 suggests the formation of the 3:1 adduct **7**. The ^{13}C NMR spectrum of a $CDCl_3$ solution of **7** exhibits a total of 28 resonances in accord with the proposed structure (data are presented in the experimental section). An APT spectrum confirmed the assignment of the various types of carbon atom. The ^{1}H NMR spectrum of a $CDCl_3$ solution of **7** is presented in Fig. 1, together with the assignments which follow from a COSY experiment and is fully in accord with the proposed structure. The COSY spectrum of the aliphatic region is presented in Fig. 2. A crucial observation is that the coupling constants are all similar to those observed in the structurally characterised 3:1 adduct of 2-acetylpyridine and 3,4-dimethoxybenzaldehyde [11] and on this basis **7** is assigned the 1R*, 2S*, 3R*, 5R* conformation. The resonances at δ 6.53 and 6.22 disappear upon shaking with D_2O and are unambiguously assigned to the hydroxyl protons.

Interestingly, when **7** and ammonium acetate were heated in glacial acetic acid for 3 h, the desired ligand **1** was obtained in 81% yield. Thus, although the preparation of **1** through the intermediate **7** sacrifices one equivalent of 2-acetylpyridine, an overall yield of 60% (with respect to the more expensive component, *tert*-butylbenzaldehyde) is obtained. This contrasts with the overall yield of 30% when the 'logical' intermediate **3** is utilised. These synthetic transformations are summarised in Scheme 1.

Coordination chemistry of **1**

We have investigated the formation of homoleptic $[M(\mathbf{1})_2]^{n+}$ with labile metal centres and with kinetically inert ruthenium(II) centres.

The homoleptic complex $[Ru(\mathbf{1})_2][PF_6]_2$ was prepared in a two step route which involved the intermediacy of $[Ru(\mathbf{1})Cl_3]$, which would also be required for the preparation of heteroleptic species in the future. The reaction of one equivalent of **1** with a boiling ethanolic solution of commercial ruthenium trichloride trihydrate resulted in the precipitation of a dark brown powder of stoichiometry $\{Ru(\mathbf{1})Cl_3\}$ in 67% yield. These ill-characterised and insoluble species are usually used without further purification or characterisation, and this approach was adopted with this compound. The reaction of $[Ru(\mathbf{1})Cl_3]$ with one equiv. of **1** in refluxing methanol in the presence of *N*-ethylmorpholine gave a deep red solution from which the red salt $[Ru(\mathbf{1})_2][PF_6]_2$ was precipitated in 37% yield upon the addition of ammonium hexafluorophosphate. The low yield of this complex reflects the solubilising effect of ligand **1** and additional material may be obtained from the mother liquor by chromatographic separation.

The reaction of 2 equivalents of **1** with methanolic solutions containing one equivalent of iron(II) sulfate, cobalt(II) acetate or nickel(II) acetate resulted in the formation of coloured solutions from which the complexes $[M(\mathbf{1})_2][PF_6]_2$ could be isolated by the addition of ammonium hexafluorophosphate. The purple complex $[Fe(\mathbf{1})_2][PF_6]_2$ was obtained in 50% yield whilst red $[Co(\mathbf{1})_2][PF_6]_2$ and golden brown $[Ni(\mathbf{1})_2][PF_6]_2$

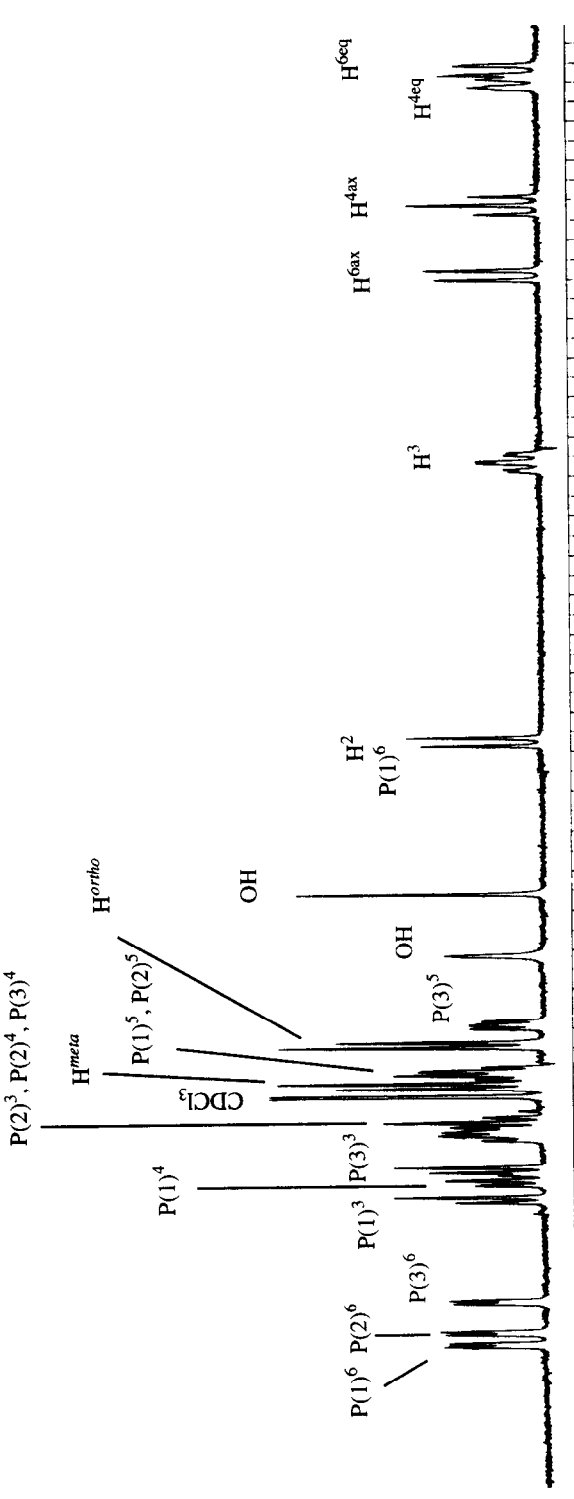
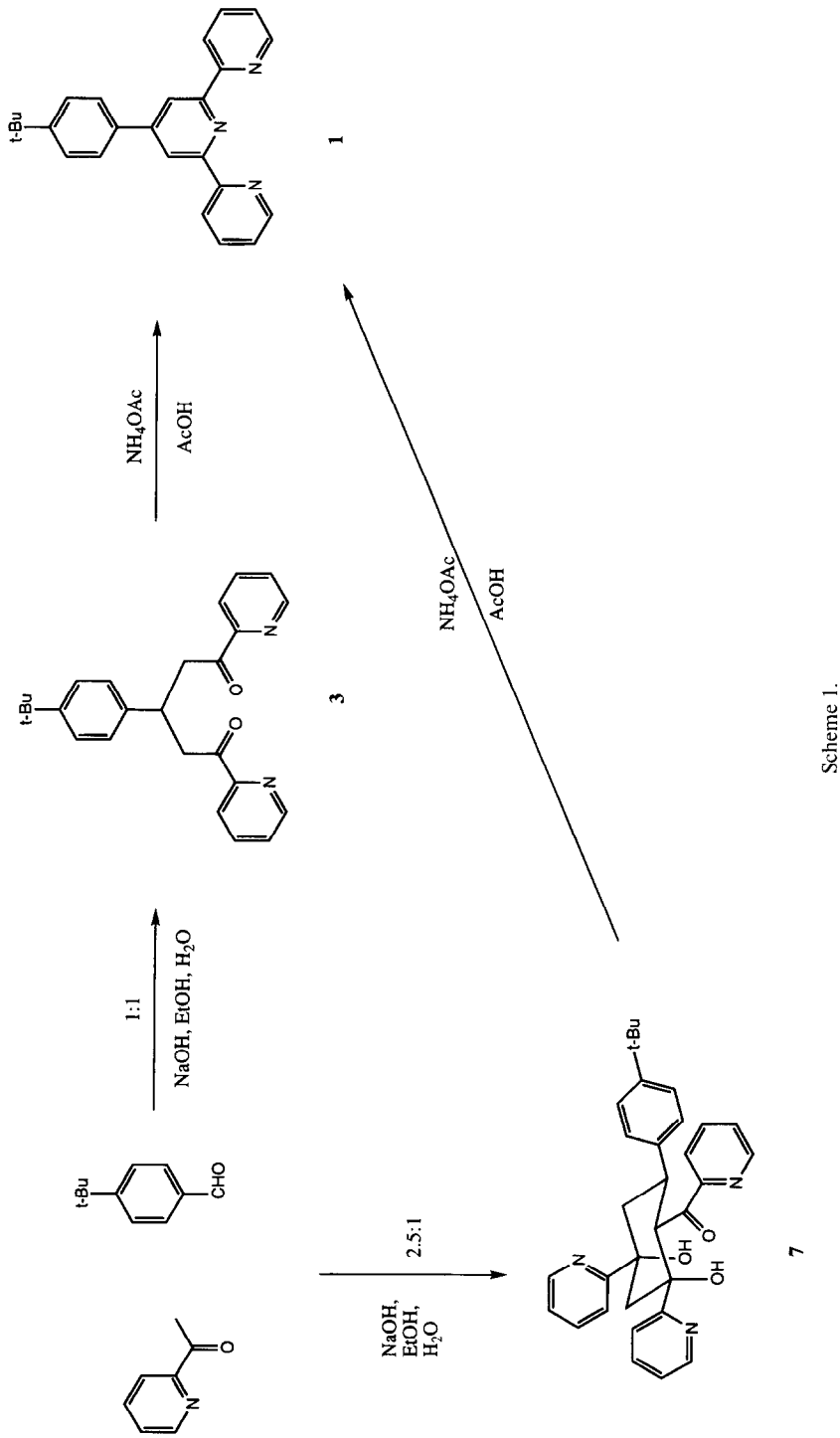


Fig. 1. 300 MHz ^{1}H NMR spectrum of a $CDCl_3$ solution of **7** showing the assignments following from the COSY spectrum. The *tert*-butyl resonance at δ 1.10 has been omitted. P(1), P(2) and P(3) refer to the three pyridyl rings—the connectivities follow from the COSY experiment, but assignment of the individual rings has not been possible.


t-Bu
CHO
1:1
NaOH, EtOH, H2O
3
NH4OAc
AcOH
1
NaOH,
EtOH,
H2O
2.5:1
7
NH4OAc
AcOH

Scheme 1.

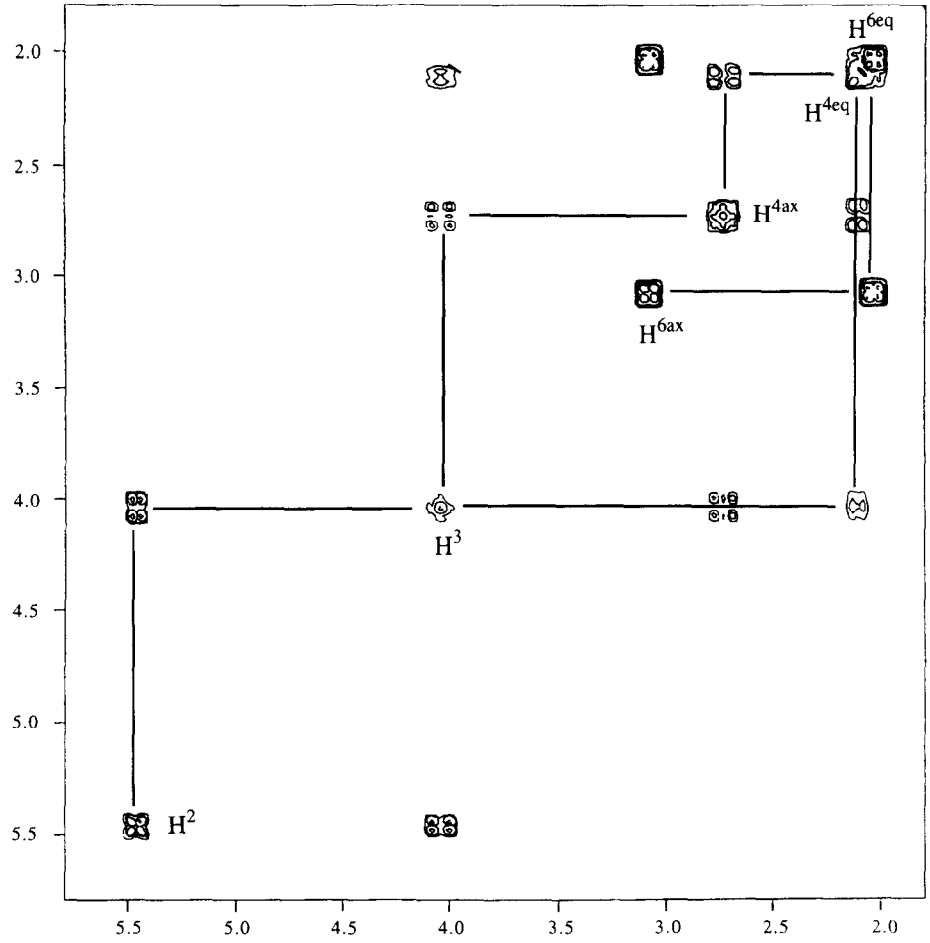


Fig. 2. 300 MHz ^{1}H NMR COSY spectrum of a $CDCl_3$ solution of **7** showing the aliphatic region.

were obtained in 44% and 42% yield, respectively. The cobalt(II) complex could be oxidised to the corresponding cobalt(III) species by oxidation with hydrogen peroxide and dioxygen in the presence of activated charcoal which is isolated as the red salt $[Co(\mathbf{1})_2][PF_6]_3$ in 37% yield. Once again, the solubilising effect of the substituent is notable and we have determined that 10.6 mg of $[Fe(\mathbf{1})_2][PF_6]_2$ may be dissolved in 1 cm^3 of CH_2Cl_2. In contrast, $[Fe(tpy)_2][PF_6]_2$ is almost insoluble in this solvent.

In each case, the matrix assisted laser desorption time-of-flight (MALDI-TOF) mass spectrum exhibited the expected $[M(\mathbf{1})_2]$ ions. All of the complexes are soluble in acetonitrile or acetone. Of the five complexes, the ruthenium(II), iron(II) and cobalt(III) species are diamagnetic whilst the cobalt(II) and nickel(II) complexes are paramagnetic. ^{1}H NMR spectroscopic data for the various complexes are presented in Table 1. In the case of the diamagnetic complexes, the aromatic region contains only five resonances in the sequence $H^{3'}$, H^3, H^4, H^6 and H^5 with $H^{3'}$ lying to lowest field. The major change upon coordination is the upfield coordination shifting of H^6 ($\Delta\delta$ +1.29 (Ru), +1.53 (Fe), +1.29 (Co); $\Delta\delta = \delta(\mathbf{1}) - \delta[M(\mathbf{1})_2][PF_6]_2$) and the downfield shifting of $H^{3'}$ ($\Delta\delta$ −0.30 (Ru), −0.44 (Fe), −0.52 (Co)). Both of these effects are due to the conformational change from *trans*, *trans* in the free ligands to *cis*, *cis* in the metal complexes [12], in the complexes $H^{3'}$ is deshielded by the proximity of H^3 and H^6 lies in the shielding region above the central pyridine ring of the other ligand.

The cobalt(II) complex is paramagnetic and the ^{1}H NMR spectrum exhibits seven shifted resonances (δ 94, 53, 42, 31, 12.0, 9.5 and 9.2; Fig. 3) together with the *tert*-butyl resonance at δ 1.94. The resonances are broadened and no coupling is discernible. This is a typical pattern for a low-spin $[Co(Xtpy)_2]^{2+}$ solution species as typified by $[Co(typ)_2][PF_6]_2$ [13]. The ^{1}H NMR spectrum of $[Co(tpy)_2][PF_6]_2$ in CD_3CN solution exhibits a total of six resonances at δ 99.2, 57.1, 47.7, 34.5, 22.0 and 9.0. Comparison of the two spectra allow the assignment of the δ 9.5 and 9.2 res-

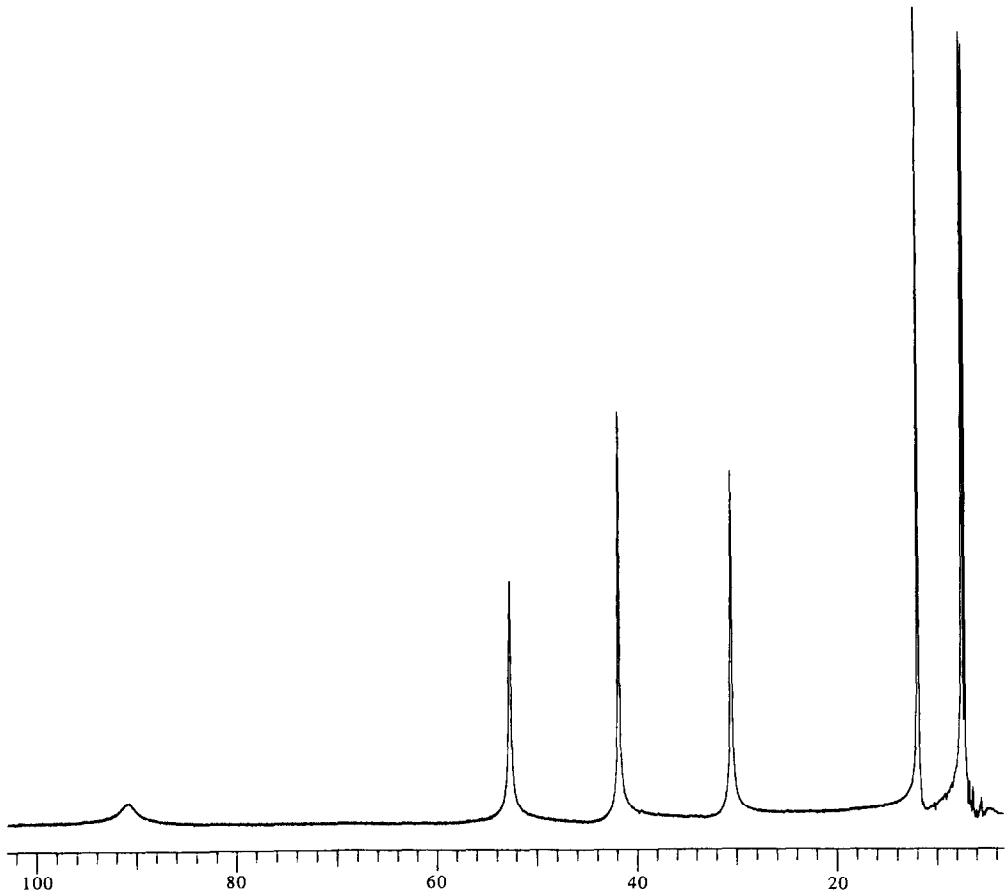


Fig. 3. 300 MHz ^{1}H NMR spectrum of a CD_3CN solution of the paramagnetic complex $[Co(\mathbf{1})_2][PF_6]_2$ showing the shifted resonances of the aromatic protons.

onances to the *ortho* and *meta* protons of the aryl substituent.

All of the complexes are redox active and their behaviour has been studied by cyclic voltammetry in acetonitrile solution. With the exception of the nickel complex, each of the $[M(\mathbf{1})_2][PF_6]_2$ compounds exhibited a single reversible metal(II)/(III) process and all of the complexes showed two quasi-reversible ligand-centred reduction processes. In each case, the metal(II)/(III) potential is found to lower potential than observed in the appropriate $[M(\mathbf{4})_2][PF_6]_2$ compounds suggesting that the *tert*-butylphenyl substituent is electron-releasing. We have shown previously that the behaviour of the reductive processes in such compounds is complex and may not be simply related to the electron-withdrawing or-releasing nature of the substituents [14]. The electron-releasing character of the *tert*-butylphenyl substituent may be quantified by use of a Hammett σ^+ parameter and we have previously established correlations between the metal(II)/(III) redox processes in $[M(Xtpy)(Ytpy)]^{n+}$ complexes and σ^+ [10]. In this case it allows us to define a σ^+ parameter for the *tert*-butylphenyl substituent. A plot of the observed redox potential for a variety of $[Ru(Xtpy)_2]^{2+}$ complexes (Xtpy = 4′-substituted tpy ligand) [10] against $\sigma^+(X)$ gives a straight line (Fig. 4a) of formula:

$$E^\circ(Ru) = 0.245\sigma^+ + 0.944.$$

Inserting the observed redox potential for $[Ru(\mathbf{1})_2][PF_6]_2$ into this equation a σ^+ parameter of -0.22 is found for the *tert*-butylphenyl substituent. This value may be verified by making a similar analysis of the redox potentials of a series of $[Fe(Xtpy)_2][PF_6]_2$ complexes. In this case, a plot of E° against σ^+ for the iron complexes gives a straight line of formula:

$$E^\circ(Fe) = 0.212\sigma^+ + 0.755.$$

Using this formula and a value for σ^+(*tert*-butylphenyl) of -0.22, the calculated potential of $[Fe(\mathbf{1})_2][PF_6]_2$ is 0.71 V which corresponds well to the observed potential of 0.72 V.

In conclusion, we have shown that the solubilised

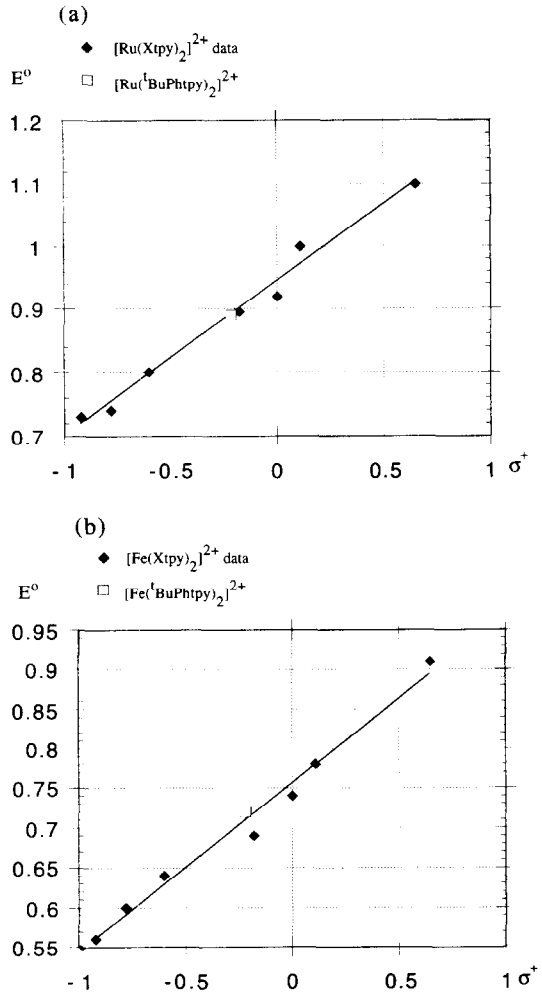


Fig. 4. Plots of (a) the ruthenium(II)/(III) potential (*vs* Fc/Fc^+) against σ^+ for the X substituent in a series of $[Ru(Xtpy)_2]^{2+}$ complexes (Xtpy = 4′-substituted 2,2′ : 6′,2″-terpyridine) and (b) the iron(II)/(III) potential (*vs* Fc/Fc^+) against σ^+ for the X substituent in a series of $[Fe(Xtpy)_2]^{2+}$ complexes (Xtpy = 4′-substituted 2,2′ 6′,2″-terpyridine). In each case the redox potentials for the complexes with **1** are also shown.

ligand **1** behaves as a 'normal' 2,2 : 6′,2″-terpyridine and that the coordination behaviour is not drastically altered by the introduction of the hydrophobic substituent. The *tert*-butylphenyl substituent is slightly electron-releasing. Having established that **1** introduces no unexpected properties to the metal complexes, we are currently investigating the use of such solubilising oligopyridines in the surface generation functionalisation of metallodendrimers.

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