SYNTHESIS, X-RAY STRUCTURAL DETERMINATION AND COORDINATION CHEMISTRY OF 4'-FERROCENYL- 2,2' : 6',2''-TERPYRIDINE

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Abstract:

4'-Ferrocenyl-2,2' : 6',2''-terpyridine(Fctrpy) has been prepared from ferrocene carboxaldehyde and 2-acetylpyridine. A single crystal X-ray structure analysis indicates typical bond distances and angles with nearly coplanar aromatic rings. The angle between the cyclopentadienyl ring of the ferrocene moiety and the central pyridyl ring of the terpyridine is 19.2° Ruthenium complexes, Ru(Fctrpy)$_2^{2+}$ and Ru(trpy) (Fctrpy)$^{2+}$ (trpy = 2,2' : 6',2''-terpyridine) have been prepared and characterized electrochemically and spectrophotometrically.

Article:

The synthesis of substituted 2,2' : 6',2''-terpyridines is an area of great current interest." The properties of transition metal complexes can be fine tuned by the use of substituents on the terpyridine ligands. We have synthesized a terpyridine ligand that contains a ferrocenyl moiety at the 4' position. The ligand is unique in that the substituent itself can be modified *in situ* by oxidation of the ferrocenyl moiety to ferrocenium. We report here the synthesis and X-ray structural characterization of 4'-ferrocenyl-2,2' : 6',2''-terpyridine, Fctrpy, (1), its coordination to a ruthenium centre, and the properties of ruthenium complexes containing the Fctrpy ligand.

The ligand 1 was synthesized in two steps from ferrocenecarboxaldehyde using the elegant method reported by Constable, *et al.* who synthesized 4'phenyl-2,2' : 6'2''-terpyridine, 4'-Phtrpy, (2), from benzaldehyde.[3] Ferrocenecarboxaldehyde was reacted with two equivalents of 2-acetylpyridine, in the presence of base, to yield orange crystals of 2-ferrocenyl-1,5-bis(2-pyridyl)-1,5-pentanedione (3), in reasonable yield, eq. 1.
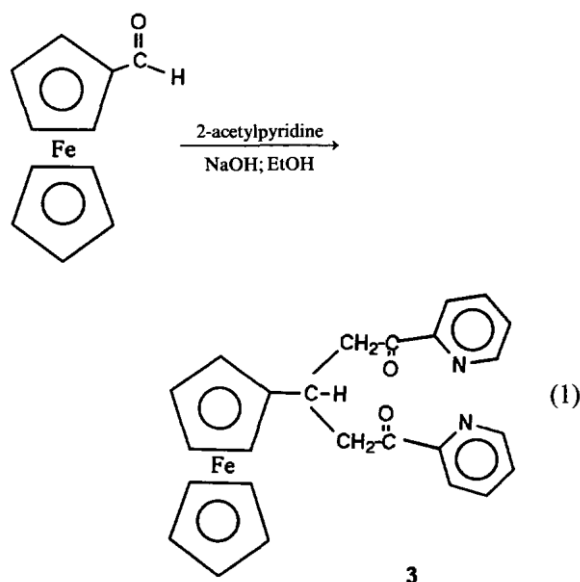
Table 1. UV-visible data[a]

| Compound	λ_{MAX} ($\varepsilon \times 10^{-3}$)				
Ferrocene	—	438	322	—	—
trpy	—	—	—	278	—
Fctrpy	—	454 (2.5)	363 (6.1)	280 (107)	248 (107)
Ru(trpy)$_2$$^{2+}$	—	478 (14)	306 (61)	—	269 (39)
Ru(trpy)-(Fctrpy)$^{2+}$	515 (sh)	478 (15)	306 (61)	—	270 (41)
Ru(Fctrpy)$_2$$^{2+}$	526 (15)	482 (15)	310 (60)	284 (44)	275 (49)

[a]Acetonitrile solvent.

The pentanedione was converted to **1** in good yield by reaction with ammonium acetate in refluxing ethanol in the air, eq. 2. Both new compounds were characterized by 'H NMR and microanalysis.*

The structure of 1 was confirmed by a single crystal X-ray structural determination.† An ORTEP view of 1 is shown in Fig. 1. As in the structure of 2[3] the three pyridyl rings are in a *transoid* arrangement and are approximately co-planar : the angles between the central and the outer pyridyl rings average 7.3°, which is comparable to a value of 8.2° in 2. The average C-C and C-N bond distances are 1.384 ± 0.010 Å and 1.342 ± 0.003 Å, respectively. These compare with values of 1.370 ± 0.013 Å and 1.342 ± 0.002 Å for 2.[3] The terpyridine moiety is not co-planar with the ferrocenyl cyclopentadienyl ring, the dihedral angle between the two rings being 19.2°. For a series of closely related species 1, 2 and 4-biphenylferrocene[5] (4), there is a correlation between the interannular bond distance and the twist angle. For 4, 2 and 1, the bond distances are 1.55 Å, 1.492 Å, and 1.471 Å, respectively, and the twist angles are 5.9°, 10.9°, and 19.2°. The larger twist angle occurs because of greater steric interactions between nonbonded hydrogen atoms as the interannular distance decreases. The ferrocene moiety has C-C bond distances of 1.416 ± 0.008 Å, compared to 1.42 ± 0.07 Å for 4.

The properties of 1 are a combination of those of the constituent parts. The UV-visible spectrum of 1 essentially consists of π to π* (trpy) bands[6] at 248 and 280 nm and ferrocene charge transfer bands at 351 and 452 nm[7] (Table 1). The red shift of the ferrocenyl bands of 1 relative to the 322 and 439 nm of ferrocene, and the reduction potential of the ferrocenyl moiety (0.57 V vs 0.41 V for ferrocene), reflect the electron withdrawing character of the trpy substituent.

Ruthenium complexes [Ru(trpy) (Fctrpy)]$^{2+}$ (5), and [Ru(Fctrpy)$_2$]$^{2+}$ (6), were prepared from Fctrpy and RuCl$_3$ · xH$_2$O or Ru(DMSO)$_4$Cl$_2$,[8] respectively. In the first case, a two step synthetic route through the intermediate Ru(Fctrpy)Cl$_3$ was used.[9] In each case, alcoholic solvents were used because use of DMSO or dimethylformamide lead to decomposition of Fctrpy to generate Fe(trpy)$_2$-type byproducts. Both 5 and 6 were characterized by ^{1}H NMR and microanalysis.‡

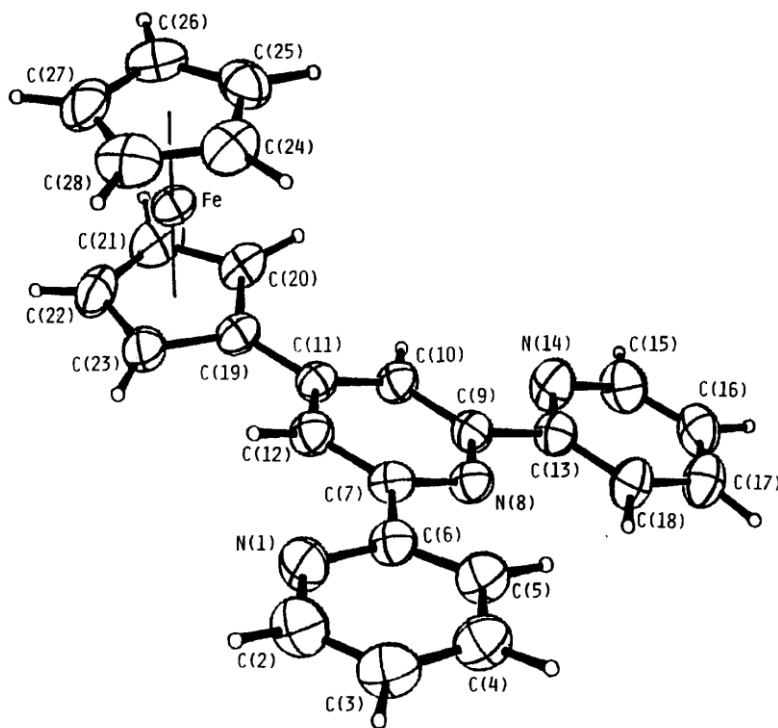$$3 \xrightarrow[O_2, \text{ EtOH}]{NH_4OAc} 1$$

(2)
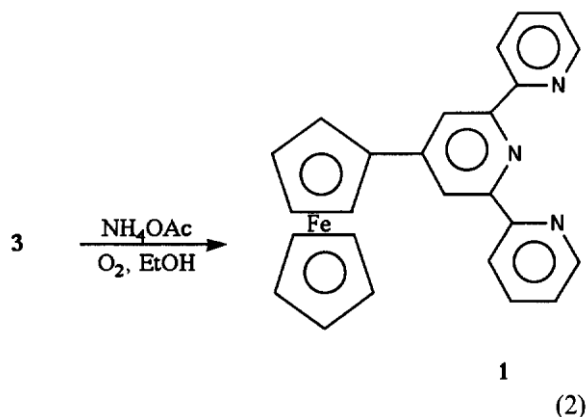
Fig. 1. ORTEP diagram (50% probability ellipsoids) of **1** showing the atom numbering scheme and solid-state conformation; small circles represent hydrogen atoms. Representative bond lengths and angles are included in the text.

The intensely red ruthenium complexes exhibit typical $d(Ru) \cdots \pi^*(trpy)$ transitions around 480 nm and $\pi(trpy) \cdots \pi^*(trpy)$ transitions in the UV region[4] (Table 1). Surprisingly, an additional absorption band is observed around 530 nm with an intensity proportional to the number of Fctrpy ligands. Other than $Ru(tro)_2^{2+}$ (tro = 4'-phenyl2,2' : 6',2"-terpyridyl), for which absorption maxima at 490 nm ($\varepsilon = 24,200$) and 560 nm ($\varepsilon = 8,000$) are reported, substituted terpyridyl complexes of ruthenium(II) tend to exhibit a single maximum in the visible region.[4,6] The absence of a 530 nm band in free Fctrpy and its disappearance upon oxidation of the ferrocene site suggests that the 530 nm band may be a ruthenium-to-ferrocene charge transfer band and is presently under further investigation.

Table 2. Cyclic voltammetry data

Compound	$E_{1/2}$, volts vs Ag/AgCl			
	$Ru^{III/II}$	Fc^+/Fc	trpy Reductions	
Ferrocene	——	0.41	—	a
trpy	—	—	< −1.7	a
Fctrpy	—	0.57	< −1.7	a
$Ru(trpy)_2^{2+}$	1.19	—	−1.19, −1.52	b
$Ru(trpy)(Fctrpy)^{2+}$	1.42	0.59	−1.21, −1.52	b
$Ru(Fctrpy)_2^{2+}$	1.39	0.58	−1.22, −1.52	b

[a] $CH_3CN/TEAP$.
[b] $CH_2Cl_2/TBAH$.

Results of cyclic voltammetric studies on Fctrpy, $[Ru(trpy)(Fctrpy)^{2+}$, and $[Ru(Fctrpy)_2]^{2+}$ are listed in Table 2. The ferrocene moieties of each exhibit a reversible oxidation to ferrocenium at about 0.6 V and ruthenium(III/II) waves are observed at about 1.4 V (vs Ag/AgC1 reference). The ruthenium(III/II) waves are irreversible due to deposition on the electrode and/or decomposition of the complex. Coulometric studies show that oxidation of $[Ru(trpy)(Fctrpy)\}^{2+}$ at 0.8 V results in the loss of one electron whereas oxidation of $[Ru(Fctrpy)_2]^{2+}$ at the same voltage results in the loss of two electrons. This oxidation of the ferrocenyl moiety of $[Ru(trpy)(Fctrpy)]^{2+}$ or $[Ru(Fctrpy)_2]^{2+}$ leads to the loss of the 530 nm shoulder or maximum, respectively, in the visible spectrum and the $d(Ru) \cdots \pi^*(trpy)$ band shifts to 501 nm. Oxidation of the ferrocenyl moiety

apparently stabilizes the trpy π* orbital, leading to a lower energy d(Ru) $\cdots$ π*(trpy) transition. Comparison to ruthenium complexes of other substituted trpy ligands' suggests that the effect of the ferrocene or the ferricinium substituent is similar to that observed for other substituents. A weak absorption band is observed above 900 nm in [Ru(Fctrpy),]$^{4+}$, presumably a ruthenium(II)-ferrocenium intervalence transfer transition.

Attachment of a terpyridyl moiety to the ferrocene increases the ferrocenium/ferrocene reduction potential by about 0.17 V, independent of whether or not the terpyridyl is bound to a ruthenium(II) centre. This increase is similar to that observed for 3- or 4-ferrocenylpyridine[10] and considerably larger than the increase observed for phenylferrocene.[11]

Notes:
* Characterization Data for 1: Found : C, 72.2 ; H, 4.6 ; N, 9.9. Calc. for $C_{25}H_{19}FeN_3$: C, 72.2 ; H, 4.6 ; N, 10.0%. ^{1}H NMR [(CD$_3$)$_2$CO] : δ 4.12 (s, 5H); 4.54 (t, J= 2.0, 2H) ; 5.04 (t, J = 2.0, 2H) ; 7.45 (m, 2H) ; 7.98 (td, J = 7.9, 1.8, 2H); 8.62 (s, 2H) ; 8.71 (m, 4H). Characterization Data for 3 : Found : C, 68.4 ; H, 5.1; N, 6.3. Calc. for $C_{25}H_{22}O_2FeN_2$: C, 68.5 ; H, 5.1 ; N, 6.4%. ^{1}H NMR (CDCl$_3$): δ 3.51-3.71 (b, 4H); 4.05 (b, 1H) ; 4.18 (b, 9H); 7.49 (d, J = 8Hz, 2H); 7.80 (t, J = 8Hz, 2H) ; 7.97 (t, J = 8Hz, 2H) ; 8.67 (d, J = 8Hz, 2H).
† Crystal Data for 1 using Cu-K$_\alpha$ at T = 298K : Monoclinic, space group P2$_1$ /C(C$_{2h}^5$)-No. 14, a = 7.898(2), b = 22.062(3), c = 11.405(2) Å, β = 107.21(1)°, V = 1898(1) Å^3, Z = 4, M_r = 417.30, D_{calc} = 1.460g cm^{-3}, 4084 reflections collected, R = 0.037 (R$_w$ = 0.050) for 2406 $[I > 3.0\,\sigma\,(I)]$ unique reflections.
‡ Characterization Data for 5 : Found : C, 45.9 ; H, 3.1; N, 7.7. Calc. for $C_{50}H_{38}F_{12}FeN_6P_2Ru$ C, 46.1; H, 2.9 ; N, 8.1%. ^{1}H NMR [(CD$_3$)$_2$CO]: δ 4.37 (s, 5H); 4.78 (t, J = 2.0, 2H); 5.51 (t, J = 2.0, 2H); 7.3 (m, 4H); 7.76 (m, 4H); 8.06 (t, J = 4, 4H); 8.5-9.1 (m, 7H); 9.18 (s, 2H).
Characterization Data for 6 : Found : C, 48.6 ; H, 3.4 ; N, 6.2. Calc. for $C_{40}H_{30}F_{12}FeN_6P_2Ru$ C, 49.0; H, 3.1 ; N, 6.8% ^{1}H NMR [(CD$_3$)$_2$CO]: δ 4.36 (s, 5H); 4.77 (t, J = 1.8, 2H); 5.35 (t, J = 1.9, 2H); 7.18 (ddd, J = 5.7, 5.5, 1.7, 2H); 7.42 (d, J = 4.7, 2H); 7.94 (td, J = 7.9, 1.5, 21-11: 8.64 (d = 7.2. 2H); 8.74 (s, 2H).

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