Homoleptic and heteroleptic iron(II) and ruthenium(II) complexes of novel 4′-nitro-2,2′ : 6′,2″-terpyridines and 4′-amino-2,2′ : 6′,2″-terpyridines

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Several series of 4-nitro-6-bromo-2,2′-bipyridines and of symmetrical and unsymmetrical 4′-nitro- and 4′-amino-2,2′ : 6′,2″-terpyridines have been prepared. The structure of 4′-amino-2,2′ : 6′,2″-terpyridine has been determined by X-ray structure analysis. The unusual internal angles of the two terminal rings with respect to the central one have been rationalized in terms of hydrogen bonding between the amino protons and nitrogen atoms of the terminal pyridine rings. The new ligands have been used in the preparation of homo- and heteroleptic ruthenium(II) and iron(II) complexes and their chemical and electrochemical properties have been investigated. The synthesis and properties of a heteroleptic iron(II) complex with both 4′-nitro- and 4′-amino-2,2′ : 6′,2″-terpyridines are reported for the first time.

Since the metal-bonded 2,2′ : 6′,2″-terpyridines (tpy) with spacers at C(4′) provide a means of directionality, and thus a means of linear communication, the functionalization of tpy at this position has been of interest to chemists. A number of substituents can be directly inserted by the Kröhnke methodology.[1] Some 2,2′ : 6′,2″-terpyridines with functionalities directly attached to C(4′) such as 4′-hydroxy-2,2′ : 6′,2″-terpyridine,[2] 4′-chloro-2,2′ : 6′,2″-terpyridine,[2] 4′-bromo-2,2′ : 6′,2″-terpyridine,[3] 4′-methylthio-2,2′ : 6′,2″-terpyridine[4] and 4′-methanesulfonyl-2,2′ : 6′,2″-terpyridine[4] have been reported and have been used in the development of the chemistry of multinucleated complexes.[5] The only reported example of a nitrogen-containing 2,2′ : 6′,2″-terpyridine is 4′-dimethylamino-2,2′ : 6′,2″-terpyridine.[6] The literature methods have not permitted the simultaneous introduction of functionalities (substituents) at C(4′) and at the terminal pyridine rings.

We have already published the synthesis of dimethyl-substituted 4′-ethoxy- and 4′-hydroxy-2,2′ : 6′,2″-terpyridines.[7] Now we report the synthesis of such 2,2′ : 6′,2″-terpyridines bearing nitro and amino groups at C(4′), as well as methyl groups at the terminal pyridine rings, which are precursors to new ligands and heterocycles.[8]

Results and discussion

In studies of functionalized 2,2′ : 6′,2″-terpyridines, we have become interested in 2,2′ : 6′,2″-terpyridines with amino and nitro groups that are directly linked to C(4′) of 2,2′ : 6′,2″-terpyridine, motivated by the electron-donating and -withdrawing properties, respectively, of these groups. Here we report the syntheses of both ligands and of the homo- and heteroleptic iron(II) and ruthenium(II) complexes, whose electronic and electrochemical properties were then compared.

Synthesis of tpy ligands

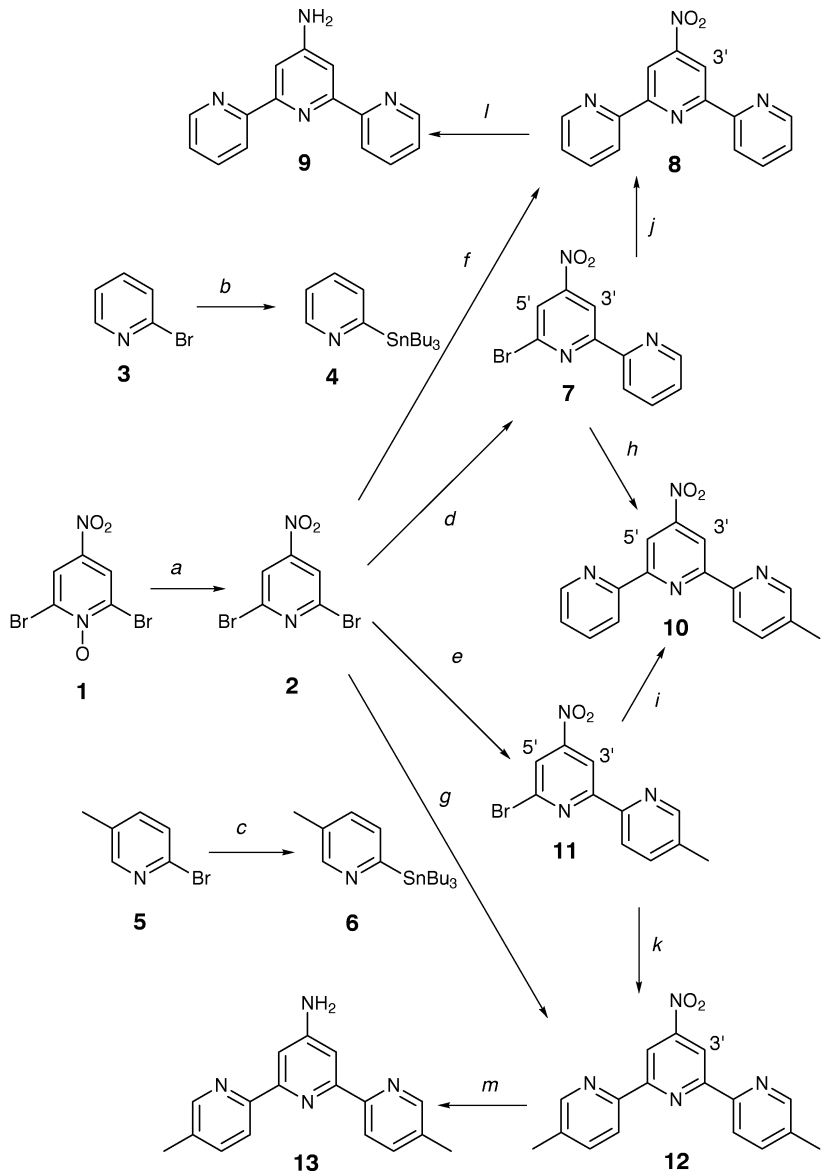
The Stille reaction,[9] which consists of the reaction of stannyl and bromo compounds in the presence of a catalytic amount of palladium(0), has found wide application in the synthesis of aromatic and heterocyclic compounds. The advantage of this method is that many functionalities, such as nitro groups, do not react under the reaction conditions.

The key compound of the Stille coupling here was 2,6-dibromo-4-nitropyridine, **2** (Scheme 1). Commercially available 2,6-dibromopyridine was converted to 2,6-dibromopyridine-*N*-oxide, which was then reacted with nitric acid in sulfuric acid to give 2,6-dibromo-4-nitropyridine-*N*-oxide.[10] Subsequent deoxygenation with phosphorus trichloride in chloroform[11] produced **2** as a yellow microcrystalline compound in 43% overall yield.

2-Bromopyridine, **3**, was converted to tributyl(pyridin-2-yl) stannane, **4**, upon reaction with butyllithium and tributyltin chloride in tetrahydrofuran.[12] Compound **2** was reacted with 1 equiv. of **4** in the presence of 0.01 equiv. of $Pd(PPh_3)_4$ for 16 h at reflux in toluene to give 4-nitro-6-bromo-2,2′-bipyridine, **7**, in 60% yield as yellow crystals. 2-Bromo-5-methylpyridine, **5**,[13] was converted to tributyl(5-methylpyridin-2-yl) stannane, **6**, in the same manner as in the synthesis of **4**. When **2** was reacted under the same conditions with 1 mole equiv. of **6** we obtained 4-nitro-6-bromo-5′-methyl-2,2′-bipyridine, **11**, in 65% yield as a pale yellow crystalline solid. However, if **2** was reacted with two equivalents of **4** in the presence of the catalyst under the same conditions, ligand **8** was directly obtained in 68% yield. Alternatively, **2** was reacted with two equivalents of **6** under the same conditions to give **12** in 64% yield. The unsymmetrical tpy ligand **10** was obtained in good yield upon reaction in toluene of bipyridines **7** or **11** with the stannanes **4** or **6**, respectively, in the presence of 0.01 equivalent of $Pd(PPh_3)_4$.

A doublet in the ^{1}H NMR spectra of bipyridines **7** and **11** was observed at δ 9.10 and 9.08, respectively, due to protons H^3 and an additional doublet due to the protons H^5 was observed at δ 8.05 and 8.16 at similar shift to protons H^3 of **2** (Table 1).

The two symmetrical unsubstituted and substituted terpyridines **8** and **12**, respectively, and the unsymmetrical terpyridine **10** are interesting target molecules. In the ^{1}H NMR spectra of **8**, **10** and **12** we observed a singlet due to protons $H^{3'}$ at δ 9.16, 9.12 and 9.08, respectively, which is fully consistent with the inductive effect of the methyl groups. In the unsymmetrical terpyridine **10**, while each proton was observed as a separate signal, the proton $H^{5'}$ was also observed at δ 9.12, in other words, the protons $H^{3'}$ and $H^{5'}$ are identical



Scheme 1 (*a*) PCl_3, $CHCl_3$, 61 °C, 20 h, 73%; (*b*) THF, −78 °C, *n*-BuLi, Bu_3SnCl, 1 h, 95%; (*c*) as (*b*), 97%; (*d*) **4** (1 equiv.), $Pd(PPh_3)_4$ (0.01 equiv.), toluene, 110 °C, 16 h, 60%; (*e*) **6** (1 equiv.), as (*d*), 65%; (*f*) **4** (2 equiv.), as (*d*), 68%; (*g*) **6** (2 equiv.), as (*d*), 64%; (*h*) **6** (1 equiv.), as (*d*), 96%; (*i*) **4** (1 equiv.), as (*d*), 96%; (*j*) as (*d*), 81%; (*k*) with **6**, as (*d*), 70%; (*l*) Pd/C (10%), EtOH, 78 °C, $H_2NNH_2 \cdot H_2O$, 1 h, 76%; (*m*) as (*l*), 69%.

(Table 1). All the data of elemental analysis and mass spectra are consistent with the proposed structures.

The two nitroterpyridines **8** and **12** had been readily reduced with hydrazine hydrate in the presence of palladium on charcoal in ethanol.[14] In the IR spectra of **9** and **13**, no bands assigned to nitro groups were observed, but bands attributed to amino groups were observed at about 3400 cm^{-1}. All the data are in accord with the proposed structures.

In conclusion, this method permits the synthesis of the functionalised 2,2′-bipyridines **7** and **11**, as well as the novel nitroterpyridines **8**, **10** and **12** and the aminoterpyridines **9** and **13**, which are precursors to new heterocycles and oligopyridines that are under current investigation.

Crystal structure of 4′-amino-2,2′ : 6′,2″-terpyridine

The X-ray crystal structure of 4′-amino-2,2′ : 6′,2″-terpyridine, **9**, confirms the proposed structure and is presented in Fig. 1. The three pyridine rings exhibit *transoid* configurations about the interannular C—C bonds, as it had previously been reported in 4′-dimethylamino-2,2′ : 6′,2″-terpyridine.[6] This configuration minimizes electrostatic interactions between the nitrogen lone pairs and also the van der Waals interactions between the *meta* protons. The interannular C—C bonds [C(5)—C(6), 1.490(3) Å] are comparable with those of 4′-dimethylamino-2,2′ : 6′,2″-terpyridine [1.492(4) Å].[6] In other terpyridine derivatives, the three pyridine rings are not coplanar and the interplanar angles of the two terminal rings with

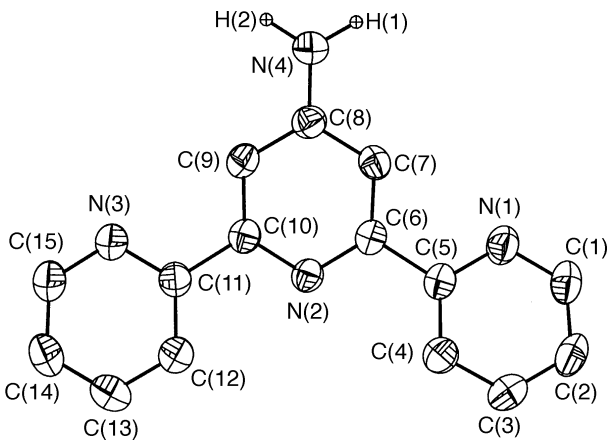


Fig. 1 Crystal structure of the terpyridine ligand **9**.

Table 1 ^{1}H NMR spectroscopic data for 2,2′-bipyridines and 4′-substituted- 2,2′ : 6′,2″-terpyridines in $CDCl_3$ solutions

	H^3	H^4	H^5	H^6	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	$H^{3''}$	$H^{4''}$	$H^{5''}$	$H^{6''}$	Others
7	9.10		8.05		8.45	8.76	8.76	8.73					
	d		d		d	ddd	ddd	d					
J	1.45		1.50		8.30	8.30	8.30	7.80					
						7.80	7.80						
						1.95	1.95						
8	8.64	7.91	7.42	8.76	9.16								
	d	ddd	ddd	d	s								
J	7.80	8.30	8.30	7.80									
		7.80	7.80										
		1.95	1.95										
9	8.60	7.84	7.32	8.67	7.75								4.33
	d	ddd	ddd	d	s								s
J	7.80	8.30	8.30	7.80									NH_2
		7.80	7.80										
		1.95	1.95										
10	8.52	7.71		8.58	9.12		9.12		8.76	7.91	7.42	8.63	2.46
	d	dd		d	s		s		d	ddd	ddd	d	s
J	7.80	7.80		1.45					7.80	8.30	8.30	7.80	CH_3
		1.95								7.80	7.80		
										1.95	1.95		
11	9.08		8.16		8.34	8.67		8.55					2.44
	d		d		d	dd		d					s
J	1.45		1.50		7.80	7.80		1.50					CH_3
						1.95							
12	8.51	7.70		8.57	9.08								2.45
	d	dd		d	s								s
J	8.30	8.30		1.50									CH_3
		1.50											
13	8.07	7.72		8.58	7.94								8.75
	d	dd		bs	s								s
J	8.30	8.30											NH_2
		1.45											

the central ring are similar and vary from 5.7° (4′-phenyl-2,2′ : 6′,2″-terpyridine),[15] 7.4° (4′-dimethylamino-2,2′ : 6′,2″-terpyridine)[6] to 10.9° (6,6″-dibromo-4′-phenyl-2,2′ : 6′,2″-terpyridine).[16] In the aminoterpyridine **9**, however, the interplanar angles of the two terminal rings with the central ring are 11.23° and 20.68°, respectively. This deviation from the expected angles is due to intermolecular hydrogen bond formation. Fig. 2 illustrates that a hydrogen-bonded network extends through the lattice involving amino protons and nitrogen atoms of the terminal pyridine rings. The distances N(1)—H(1) of 2.271 Å and N(3)—H(2) of 2.333 Å are in accord with the known values.[17,18]

The N(4)—C(8) distance of 1.364(3) Å strongly suggests an sp^2 character for the nitrogen atom and a high degree of π-conjugation of the amino group with the aromatic ring (Table 2).

Preparation and characterization of homo- and heteroleptic iron(II) complexes

2,2′ : 6′,2″-Terpyridines react readily with iron(II) salts at room temperature to yield purple metal complexes; however, 6,6″-disubstituted-2,2′ : 6′,2″-terpyridines react with iron(II) salts only at elevated temperature to give the metal complexes.

Nitroterpyridines **8**, **10** and **12** were reacted with excess $FeCl_2 \cdot 4H_2O$ in ethanol at room temperature to give the blue mononucleated iron complexes **14**–**16** (Scheme 2). In the ^{1}H NMR spectra of complexes **14**–**16**, the $H^{3'}$ resonance was observed as a singlet at δ 9.64 (**14**), 9.57 (**15**) and 9.53 (**16**), which exactly correlates with the electron-releasing methyl groups. Interestingly, in the unsymmetrical complex **15**, the signal due to the two protons adjacent to the nitro group were split and were observed at δ 9.57 ($H^{3'}$) and 9.59 ($H^{5'}$) (Table 3).

The nitroterpyridine iron(II) complexes **14** and **16** were easily reduced to the aminoterpyridine iron(II) complexes **17** and **18**, respectively, in ethanol in the presence of iron and hydrochloric acid. This reaction is easy to follow due to the colour change from blue to purple. Alternatively, the isolated aminoterpyridines were reacted directly with $FeCl_2 . 4H_2O$ to give **17** and **18**. In the ^{1}H NMR spectra of the complexes the $H^{3'}$ signal was observed as a singlet at δ 8.07 (**17**), or 7.97 (**18**), which also correlates with the electron-releasing methyl groups.

Our attempt to synthesize the heteroleptic iron(II) complex **19** was successful. Ten milligrams of each ligand **8** and **9** were dissolved in 3 ml ethanol and $FeCl_2 . 4H_2O$ was added in excess (Scheme 3). The statistical distribution of the two homoleptic complexes **14**, **17** and the heteroleptic complex **19** should be 1 : 1 : 2. The three complexes (with chloride as counter ion) were successfully separated by chromatography on aluminium oxide with an eluting solution of acetonitrile–water–ammonia (9 : 1 : 0.2). The purple complex **14** was isolated as the first fraction followed by the dark blue complex **19**. The blue complex **17** was isolated as the last fraction. This is the first example of a heteroleptic iron(II) complex that has been separated from the two homoleptic ones by chromatography.

In the electronic spectrum the metal-to-ligand charge transfer (MLCT) absorption of **19** was shifted by about 18 nm to lower energy and was observed at 623 nm, compared to the MLCT absorption of **14** at 605 nm (Fig. 3).

The ^{1}H NMR spectrum of the heteroleptic complex **19** shows significant shifts of some signals (Table 3) when compared to the homoleptic complexes **14** and **17**. The proton $H^{3'}$ of the aminoterpyridine moiety of **19** was shifted to low field and observed at δ 8.23 ($\Delta\delta = 0.22$) while proton $H^{3'}$ of the nitroterpyridine moiety was shifted to high field and observed at δ 9.54 ($\Delta\delta = 0.10$). More dramatically, the amino protons were shifted to low field at δ 6.55 ($\Delta\delta = 0.42$). All other signals belonging to the aminoterpyridine moiety were shifted to low field while the protons of the nitroterpyridine moiety were shifted to high field.

All iron(II) complexes are electrochemically active in acetonitrile solution, each exhibiting a wave corresponding to the

Table 2 Selected bond lengths (Å) and angles (°) for **9**

N(1)—C(1)	1.332(3)	N(2)—C(10)	1.349(3)
N(1)—C(5)	1.348(3)	C(6)—C(7)	1.374(3)
C(1)—C(2)	1.370(4)	C(7)—C(8)	1.395(3)
C(2)—C(3)	1.370(4)	C(8)—C(9)	1.393(3)
C(3)—C(4)	1.381(3)	C(8)—N(4)	1.364(3)
C(4)—C(5)	1.380(3)	N(3)—C(11)	1.345(3)
C(5)—C(6)	1.490(3)	N(3)—C(15)	1.334(4)
N(2)—C(6)	1.347(3)		
C(1)—N(1)—C(5)	117.2(2)	C(5)—C(6)—C(7)	120.0(2)
N(1)—C(1)—C(2)	124.2(3)	N(2)—C(6)—C(7)	123.9(2)
C(1)—C(2)—C(3)	118.3(2)	C(7)—C(8)—N(4)	120.9(2)
C(2)—C(3)—C(4)	119.0(2)	C(9)—C(8)—N(4)	121.8(2)
C(3)—C(4)—C(5)	119.3(2)	N(2)—C(10)—C(9)	123.5(2)
N(1)—C(5)—C(4)	122.0(2)	N(2)—C(10)—C(11)	115.5(2)
N(1)—C(5)—C(6)	116.4(2)	C(11)—N(3)—C(15)	116.7(3)
C(4)—C(5)—C(6)	121.6(2)	C(10)—C(11)—N(3)	117.0(2)
C(6)—N(2)—C(10)	116.3(2)	N(3)—C(11)—C(12)	121.8(2)
C(5)—C(6)—N(2)	116.0(2)	N(3)—C(15)—C(14)	124.5(3)

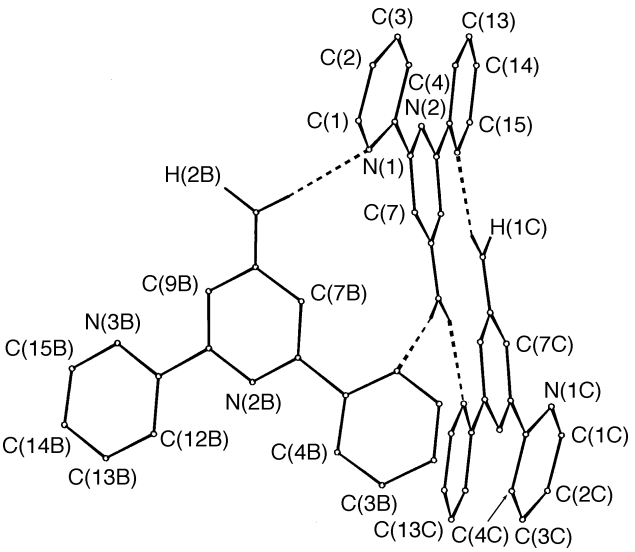
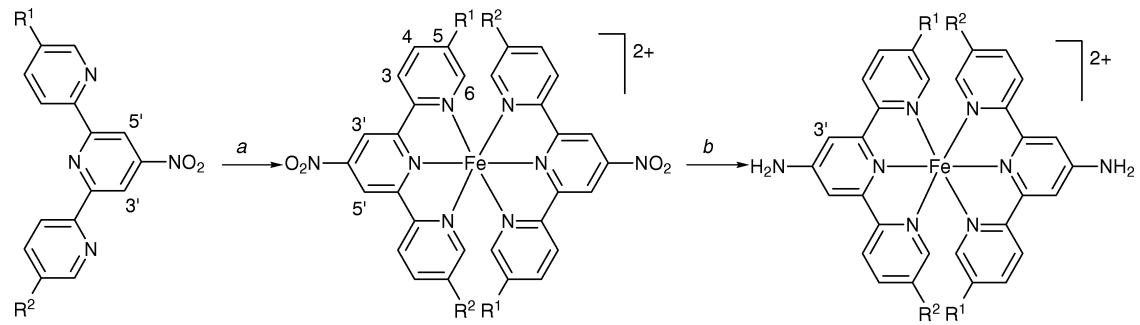


Fig. 2 Hydrogen bonds among the terpyridine ligand **9** in the crystal lattice. The distances are: N(1)—H(1), 2.27 Å and N(3)—H(2), 2.333 Å.

Fe^{II}/Fe^{III} process. As expected, the introduction of the electron-releasing amino and the strong electron-withdrawing nitro substituents has a dramatic effect upon the redox couple (Table 4). The redox potential of the aminoterpyridine iron(II) complexes **17** and **18** ranges between 0.308–0.356 V (*vs.* ferrocene/ferrocenium internal reference). However, the potential of the nitropyridine iron(II) complexes **14**–**16** ranges between 0.900–0.963 V. This increase is due to the electron-withdrawing nitro group and is finetuned by the methyl groups: the redox potential decreases in the series **14** (unsubstituted) > **15** (one methyl group) > **16** (two methyl groups). This means that, among a series of substituted tpy ligands, we have synthesized the strongest electron-withdrawing ligand **8** and the corresponding metal complex **14** ($E^\circ = 0.963$ V) with respect to $[Fe(MeSO_2\text{-tpy})_2][PF_6]_2$ ($E^\circ = 0.904$ V). The potential difference between these electron-donor and electron-acceptor complexes ranges between 0.600–0.650 V. The heteroleptic iron(II) complex **19** exhibits a potential of 0.654 V, which is about the average of the potentials of the homoleptic iron(II) complexes **14** and **17**.

Preparation and characterization of homo- and heteroleptic ruthenium(II) complexes

Ruthenium(II) complexes of terpyridines are of interest because of their photochemical and photophysical properties.[19,20] We chose the formation of kinetically inert ruthenium(II) complexes to exemplify the application of these new ligands. The advantage of ruthenium(II) complexes is that not only the homoleptic but also the heteroleptic ones can be formed in good yields (Scheme 4).[6]



$R^1 = R^2 = H$ **8**
$R^1 = H, R^2 = Me$ **10**
$R^1 = R^2 = Me$ **12**

$R^1 = R^2 = H$ **14**
$R^1 = H, R^2 = Me$ **15**
$R^1 = R^2 = Me$ **16**

$R^1 = R^2 = H$ **17**
$R^1 = R^2 = Me$ **18**

3' and 5' differ only in the case of unsymmetrical terpyridine **10**

Scheme 2 (*a*) $FeCl_2 \cdot 4H_2O$, EtOH, 25 °C, 5 min, **14** (98%), **15** (96%), **16** (94%); (*b*) EtOH–H_2O, Fe powder, conc. HCl, 78 °C, 15 min, **17** (88%), **18** (82%).

Table 3 ^{1}H NMR spectroscopic data for acetonitrile solutions of metal(II) complexes

	X-tpy					Y-typ					
	3	4	5	6	3′	3″	4″	5″	6″	3‴	Others
14	8.72 d	7.97 ddd	7.15 ddd	7.12 d	9.64 s						
15[a]	8.59 d	7.04 d		6.89 bs	9.57 s	8.69 d	7.95 ddd	7.12 ddd	7.77 d	9.59 s	2.16 s CH_3
16	8.57 d	7.76 d		6.81 s	9.53 s						2.13 s CH_3
17	8.23 d	7.80 ddd	7.05 ddd	7.24 d	8.07 s						6.13 s NH_2
18	8.10 d	7.80 ddd		6.96 s	7.97 s						6.01 bs NH_2 2.16 s CH_3
19	8.29 d	7.83 ddd	6.97 ddd	7.26 d	8.23 s	8.64 d	7.92 ddd	7.20 ddd	6.99 d	9.54 s	6.55 s NH_2
22	8.73 d	7.98 ddd	7.24 ddd	7.37 d	9.47 s						
23	8.24 d	7.83 ddd	7.11 ddd	7.40 d	7.91 s						5.84 bs NH_2
24	8.27 d	7.86 ddd	7.33 ddd	7.60 d	7.96 s	8.70 d	7.99 ddd	7.03 ddd	7.13 d	9.40 s	6.06 bs NH_2
25	8.46 d	7.85 ddd	7.17 ddd	7.43 d	7.91 s	8.46 d	7.88 ddd	7.08 ddd	7.30 d	8.26 s	3.45 s NMe_2
26	8.25 d	7.84 ddd	7.17 ddd	7.48 d	7.93 s	8.45 d	7.88 ddd	7.08 ddd	7.31 d	8.30 s	5.95 bs NH_2

[a] $H^{5'}$ appears at δ 9.59 and the coupling constants are as follows: J = 7.80 (d); J = 8.30, 7.80, 1.95 (ddd).

Table 4 Electrode potentials ($E°$/V) in acetonitrile solutions (*vs.* ferrocene/ferrocenium)

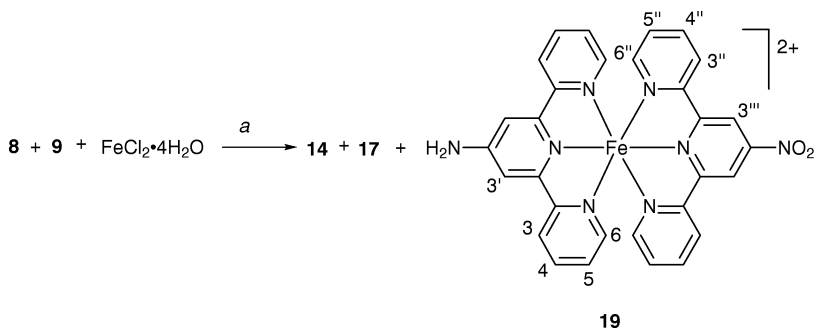
	M^{2+}/M^{3+}	1st reduction	2nd reduction	3rd reduction
14	0.963	−0.825	−0.990[a]	−1.490
15	0.931	−0.861[a]	−1.299	
16	0.900	−1.011	−1.566	
17	0.356	−1.271	−2.284	
18	0.308	−2.008		
19	0.654	−0.939	−2.114	
22	1.114	−0.861	−1.289	
23	0.474	−1.266		
24	0.740	−0.997[a]	−1.305	
25	0.485	−1.270	−1.825[a]	−2.047[a]
26	0.564			

[a] Irreversible.

Initially, hydrated $RuCl_3$ was reacted with one equivalent of the free ligands **8** or **9** at reflux in ethanol or methanol to obtain the insoluble dark blue or brown ruthenium(III) complexes **20** and **21**, respectively. The ruthenium(III) salts **20** and **21** were then reacted at reflux with one equivalent of the corresponding ligand, **8** or **9**, respectively, in Methanol in the presence of the reducing agent *N*-ethylmorpholine, to obtain the homoleptic ruthenium(II) complexes **22** and **23**, respectively.

Alternatively, a mixture of hydrated ruthenium trichloride (1 equiv.) and either **8** (2 equiv.) or **9** (2 equiv.) in 5 ml ethylene glycol was heated in a microwave oven for 10 min to yield the homoleptic ruthenium(II) complexes **22** and **23**, respectively, as red-orange solutions.

The heteroleptic ruthenium(II) complex **24** was obtained by reaction of ruthenium(III) salts **20** and **21** with one equivalent



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Scheme 3 (*a*) EtOH, 25 °C, 5 min, **19** (29%).

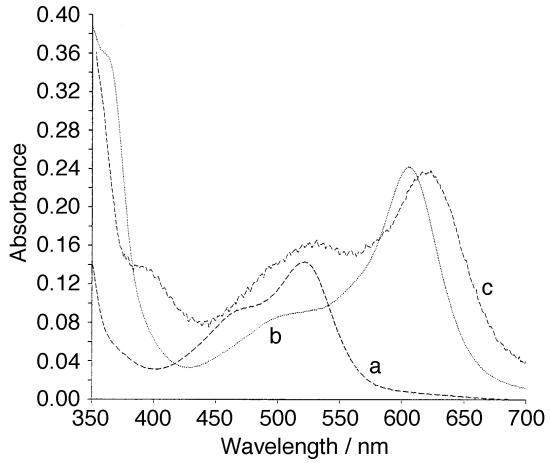

Fig. 3 UV/VIS spectra of the homoleptic iron(II) complexes **17** (*a*), **14** (*b*) and the heteroleptic Fe(II) complex **19** (*c*) in acetonitrile solutions.

of the complementary ligands **9** or **8**, respectively, in methanol in the presence of *N*-ethylmorpholine. The ruthenium(II) complexes **22**–**24** were precipitated as their red-orange hexafluorophosphate salts and were purified by chromatography followed by recrystallization.

In the reactions to obtain the heteroleptic ruthenium(II) complex, a byproduct was identified in which the nitro group was reduced to a hydroxylamine. In order to confirm this, we synthesized [(Me_2N-tpy)Ru(HOHN-tpy)] **25** by reaction of **20** with 4′-dimethylamino-2,2′ : 6′,2″-terpyridine[6] in methanol at reflux. In this series, when ruthenium(III) salt **20** and **9** or ruthenium(III) salt **21** and **8** were reacted in refluxing methanol or in ethylene glycol under microwave irradiation we obtained the ruthenium(II) complex **26** in good yields. We believe that some trace of metallic ruthenium in the protic solvents is involved in the reduction of the nitro group to the hydroxylamine.[21]

The homo- and heteroleptic ruthenium(II) complexes **22**–**26** exhibit analogous NMR (Table 3) and electrochemical (Table 4) properties as the iron(II) complexes.

In conclusion, the Stille coupling reaction has been used for the synthesis of novel 4-nitro-6-bromo-2,2′-bipyridines, 4′-nitro-2,2′ : 6′,2″-terpyridines and 4′-amino-2,2′ : 6′,2″-terpyridines that are precursors for new heterocycles and oligopyridines. The homoleptic and heteroleptic iron(II) and ruthenium(II) complexes have been investigated. In particular, the heteroleptic iron(II) complex is of interest as it can be incorporated into multinucleated metal complexes that are under current investigation.

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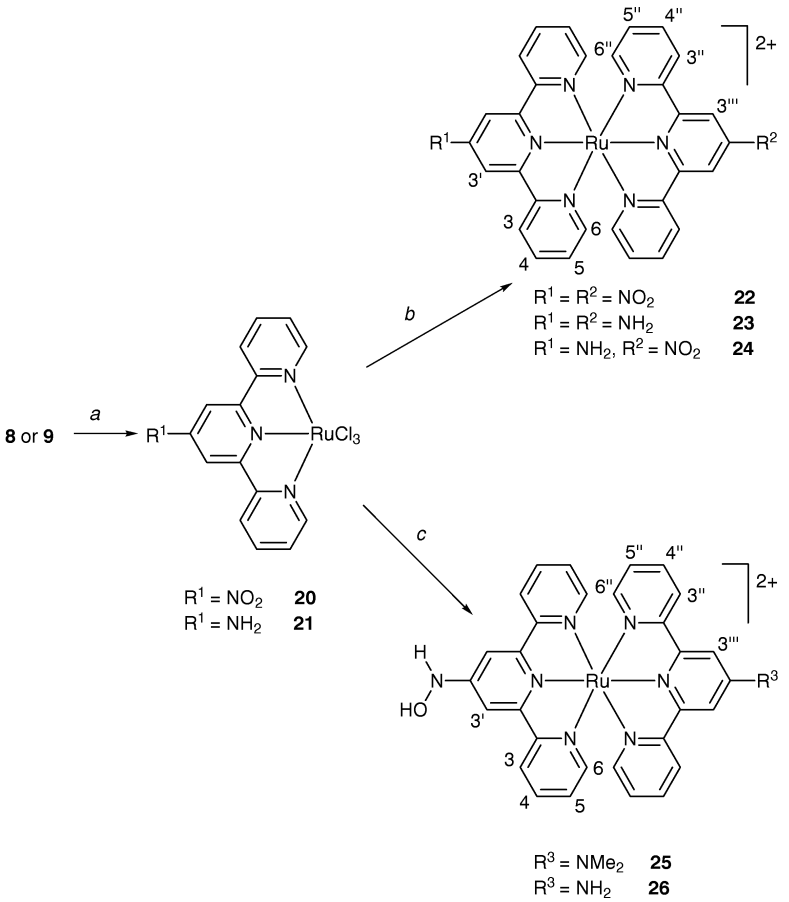
Experimental

All reagents were used as supplied. Silica gel (0.060–0.200 mm) was obtained from Chemie Uetikon and aluminium oxide (type 507 C neutral; 100–125 mesh) from Fluka. Melting points were measured on a Büchi 535 apparatus and are not corrected. IR spectra were recorded on a Mattson Genesis Fourier transform spectrophotometer with samples in compressed KBr discs. UV/VIS spectra were measured on a Perkin Elmer Lambda 19. Proton and carbon NMR spectra



Scheme 4 (*a*) $RuCl_3 \cdot 3H_2O$, EtOH, 78 °C, 2 h, 70%; (*b*) *N*-ethylmorpholine, EtOH, 78 °C, 2 h, **22** (33%), **23** (92%), **24** (80%); (*c*) as (*b*), **20**, Me_2N-tpy → **25** (77%), **20**, **9** or **21**, **8** → **26** (48%).

were recorded on a Bruker AM 250 spectrometer and referenced against Me_4Si. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were recorded using a PerPespective Biosystems Voyagers-RP Biospectrometry Workstation. Electrochemical measurements were performed with an Ecochemie Autolab PGSTAT 20 potentiostat.

Crystal structure determination of 9

Data collection was carried out on a four-circle Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å); $T = 293$ K. Details of the crystal parameters, data collection and refinement are listed in Table 5. The structure was solved by direct methods using the program SIR92.[22] Anisotropic least squares refinement was carried out on all non-hydrogen atoms using the program CRYSTALS.[23] Scattering factors were taken from the International Tables for X-Ray Crystallography.[24]

CCDC reference number 440/072.

Syntheses

2,6-Dibromo-4-nitropyridine, 2. 2,6-Dibromo-4-nitropyridine-*N*-oxide, **1** (5.41 g, 0.018 mol), was suspended in 25 ml chloroform and then cooled to 0 °C. Phosphorus trichloride (7.45 g, 4.74 mol) was gradually added and then heated for 20 h at 100 °C. Upon cooling to room temperature the yellow solution was poured into ice water and the crystals were filtered. The pale yellow crystals were purified by chromatography on aluminium oxide using dichloromethane as solvent. The yield was 3.74 g (73%). mp 125 °C. IR (KBr): 3090w, 1544s, 1348s, 1297m, 1169m, 1141m, 1036m, 881m, 735s. ^{1}H NMR ($CDCl_3$): δ 8.20 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 142.37, 120.50, 116.80. (Found: C, 21.03; H, 0.78; N, 9.72; Br, 57.60%. Calcd for $C_5H_2Br_2N_2O_2$: C, 21.30; H, 0.72; N, 9.94; Br, 56.69%).

General procedure for Stille coupling reactions. Bromo compound (1 mol), stannanyl compound (1 or 2 mole equiv.) and $Pd(PPh_3)_4$ (0.01 or 0.02 mole equiv.) were heated under nitrogen in 50 ml toluene for 16 h. After cooling to room temperature, 20 ml saturated ammonium chloride was added and the organic phase separated. The aqueous phase was extracted with toluene (3 × 20 ml). The combined organic phases were dried ($MgSO_4$) and the solvent was removed. Concentrated hydrochloric acid (30 ml) was added to the residue, followed by extraction with dichloromethane (3 × 30 ml). The aqueous phase was cautiously neutralized by solid sodium hydroxide. The oligopyridines were then extracted with dichloromethane (3 × 30 ml) and dried ($MgSO_4$). The solvent was removed followed by purification on silica gel with dichloromethane.

Table 5 Crystal data and data collction parameters for tepyridine ligand **9**

Formula	$C_{15}H_{12}N_4$
M	248.29
Crystal	Monoclinic
Space group	*C*2/*c*
a/Å	13.807(1)
b/Å	11.784(1)
c/Å	16.444(2)
α/°	90
β/°	109.818(7)
γ/°	90
U/Å^3	2517.0(4)
Z	8
F(000)	1040
D_c/g cm^{-3}	1.31
μ/mm^{-1}	0.08
Crystal size/mm	0.08 × 0.18 × 0.32
T/K	293
Radiation	Mo Kα (λ = 0.710 69)
Scan type	ω/2ϑ
ϑ_{max}/°	26.32
Reflections collected	3736
Independent reflections	2179
Reflections in refinement	1404
Number of variables	180
Final *R*	0.0545
Final *Rw*	0.0610

4-Nitro-6-bromo-2,2′-bipyridine, 7. **2** (0.40 g, 1.42 mmol), tributyl(pyridin-2-yl)stannane, **4** (0.542 g, 1.42 mmol), and $Pd(PPh_3)_4$ (0.020 g, 0.01 mole equiv.) gave **7** (0.240 g, 60%) as yellow crystals. mp 78 °C. IR (KBr): 1531s, 1380m, 1347s, 1282m, 1145m, 797m, 748s, 736m. UV/VIS (CH_3CN): λ_{max} 280, 326; λ_{min} 302 nm. ^{13}C NMR ($CDCl_3$): δ 159.56, 156.22, 155.66, 149.57, 142.33, 138.18, 125.37, 121.66, 116.91, 112.55. MS (MALDI-TOF): *m*/*z* 280. (Found: C, 43.02; H, 2.37; N, 14.83%. Calcd for $C_{11}H_8BrN_3O_2$: C, 42.88; H, 2.16; N, 15.00%).

4′-Nitro-2,2′ : 6′,2″-terpyridine, 8. **2** (1.17 g, 4.15 mmol), **4** (3.18 g, 8.30 mmol, 2 equiv.) and $Pd(PPh_3)_4$ (0.100 g, 0.02 mole equiv.) gave **8** (0.907 g, 68%) as pale yellow needles. mp 177 °C. IR (KBr): 1561m, 1531s, 1467w, 1400m, 1358s, 1338m, 1268w, 1058w, 797w, 748s. UV/VIS (CH_3CN): λ_{max} 279, 345; λ_{min} 305 nm. ^{13}C NMR ($CDCl_3$): δ 158.44, 156.33, 154.05, 149.47, 136.97, 124.77, 121.33, 113.33. MS (MALDI-TOF): *m*/*z* 278. (Found: C, 64.51; H, 3.58; N, 20.09%. Calcd for $C_{15}H_{10}N_4O_2$: C, 64.74; H, 3.62; N, 20.13%).

4′-Amino-2,2′ : 6′,2″-terpyridine, 9. Under nitrogen, **8** (0.100 g, 0.36 mmol) was heated under reflux for 1 h in 30 ml ethanol in the presence of 0.100 g of 10% palladium on charcoal. Hydrazine hydrate (4 ml, 95%) was gradually added. TLC control of the solution after 2 min showed only a purple colour upon reaction with an iron(II) solution and no trace of a blue colour, which would indicate the nitropyridine. The resulting solution was filtered and washed with 30 ml dichloromethane. The solvents were removed, 20 ml water was added and extracted with dichloromethane (3 × 30 ml). The combined organic phases were then dried ($MgSO_4$), filtered and dichloromethane was removed. Chromatographic separation on aluminium oxide with dichloromethane–ethyl acetate (1 : 2) followed by recrystallization from ethanol–ethyl acetate (4 : 1) gave **9** (0.070 g, 76%) as colourless crystals. mp 179–180 °C. IR (KBr): 3226m, 1652s, 1611m, 1586s, 1564s, 1474m, 1458m, 1416m, 987m, 790m. ^{13}C NMR ($CDCl_3$): δ 156.52, 156.26, 154.55, 148.89, 136.76, 123.61, 121.30, 106.77. MS (MALDI-TOF): *m*/*z* 248. (Found: C, 72.01; H, 4.93; N, 22.55%. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57%).

5-Methyl-4′-nitro-2,2′ : 6′,2″-terpyridine, 10. From 4-nitro-6-bromo-5′-methyl-2,2′-bipyridine, **11** (0.150 g, 0.508 mmol), **4** (0.195 g, 0.508 mmol) and $Pd(PPh_3)_4$ (0.010 g, 0.01 mole equiv.), we obtained **10** (0.120 g, 81%) as yellow crystals. Upon reaction of **7** (0.100 g, 0.357 mmol), tributyl(5-methylpyridin-2-yl)stannane, **6** (0.150 g, 0.357 mmol), and $Pd(PPh_3)_4$ (0.010 g, 0.01 mole equiv.), **10** (0.100 g, 96%) was obtained as yellow crystals. mp 222–3 °C. IR (KBr): 1559m, 1536s, 1407m, 1360s, 1265m, 745m. UV/VIS (CH_3CN): λ_{max} 280, 345; λ_{min} 311 nm. ^{13}C NMR ($CDCl_3$): δ 158.68, 158.44, 156.43, 154.27, 151.68, 150.03, 149.54, 137.58, 137.08, 134.91, 124.82, 121.45, 120.99, 113.16, 113.11. MS (MALDI-TOF): *m*/*z* 292. (Found: C, 66.06; H, 3.99; N, 19.73%. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.17%).

4-Nitro-6-bromo-5′-methyl-2,2′-bipyridine, 11. **2** (0.500 g, 1.77 mmol), **6** (0.710 g, 1.77 mmol) and $Pd(PPh_3)_4$ (0.020 g,

0.01 mole equiv.) gave **11** (0.340 g, 65%) as pale yellow crystals. mp 120 °C. IR (KBr): 1530s, 1482m, 1403m, 1349s, 1140m, 734m. UV/VIS (CH_3CN): λ_{max} 285, 333; λ_{min} 308 nm. ^{13}C NMR ($CDCl_3$): δ 155.69, 150.14, 150.09, 150.01, 142.28, 137.61, 135.62, 121.33, 120.12, 112.53, 18.49. MS (MALDI-TOF): *m/z* 294. (Found: C, 45.29; H, 2.87; N, 14.83%. Calcd for $C_{11}H_8BrN_3O_2$: C, 44.92; H, 2.74; N, 14.29%).

4′-Nitro-5,5″-dimethyl-2,2′ : 6′,2″-terpyridine, 12. **2** (1.15 g, 4.08 mmol), **6** (3.26 g, 8.16 mmol, 2 mole equiv.) and $Pd(PPh_3)_4$ (0.100 g, 0.02 mole equiv.) gave **12** (0.800 g, 64%) as a pale yellow solid. mp 104 °C. IR (KBr): 1530s, 1384s, 1369s, 1358s, 1294m, 1260m, 739m. UV/VIS (CH_3CN): λ_{max} 285, 330; λ_{min} 310 nm. ^{13}C NMR ($CDCl_3$): δ 158.53, 150.37, 149.98, 137.46, 134.76, 124.58, 120.91, 112.70, 18.54. MS (MALDI-TOF): *m/z* 306. (Found: C, 66.76; H, 3.59; N, 18.97%. Calcd for $C_{17}H_{14}N_4O_2$: C, 66.66; H, 4.61; N, 18.29%).

4′-Amino-5,5″-dimethyl-2,2′ : 6′,2″-terpyridine, 13. Under the same conditions as for the reduction of **9** we obtained **13** (0.075 g, 69%) from **12** (0.120 g, 0.392 mmol) as colourless crystals. mp 203 °C. IR (KBr): 3318m, 1655s, 1638m, 1600s, 1574m, 1509m, 1473m, 1071m, 1033m, 1011m, 553m. UV/VIS (CH_3CN): λ_{max} 269 nm. ^{13}C NMR ($CDCl_3$): δ 150.10, 150.02, 145.03, 144.02, 138.49, 136.77, 121.29, 105.45. MS (MALDI-TOF): *m/z* 276. (Found: C, 74.02; H, 5.93; N, 20.75%. Calcd for $C_{17}H_{16}N_4$: C, 73.89; H, 5.85; N, 20.27%).

Alternatively, both 4′-aminoterpyridines **9** and **13** were prepared by the cleavage of the corresponding iron(II) complexes. The iron(II) complexes **17** and **18** (0.100 g of each were dissolved in 1 : 1 water–acetonitrile (30 ml) to which potassium hydroxide (0.20 g) has been added. Hydrogen peroxide solution (30%) was added dropwise, while the mixture was stirred at room temperature, until all of the complex had been oxidatively cleaved, giving a brown suspension with no residual purple colour. This suspension was collected on Celite and washed with dichloromethane (30 ml) and methanol (20 ml) to dissolve any precipitated ligands. The solvents were removed and separation by chromatography was carried out as described above. **9** (0.040 g, 66%) and **13** (0.042 g, 67%) were obtained in good yields.

General procedure for the synthesis of iron(II) complexes of nitroterpyridines. Nitroterpyridines **8**, **10** or **12** were dissolved in 5 ml ethanol and excess iron(II) chloride tetrahydrate was added to yield the blue complexes. The complexes were filtered over Celite and washed with 50 ml water. The resulting iron(II) complexes were precipitated as their hexafluorophosphate salts by the addition of methanolic ammonium hexafluorophosphate. The complexes were filtered over Celite, washed with 30 ml water, followed by diethyl ether and then dried. The complexes were then dissolved in acetonitrile and solvent was removed. The blue compounds have been purified on a silica gel column utilizing acetonitrile–ammonia (10 : 0.5) as eluent, followed by recrystallization by diffusion of diethyl ether into the acetonitrile solution. The yields of these reactions are about 95%.

Data of **14**. Compound **8** (0.050 g, 0.18 mmol) gave **14** (0.080 g, 98%). IR (KBr): 1534s, 1356s, 1357m, 836s, 559m. UV/VIS (CH_3CN): λ_{max} 339, 355, 505sh, 605; λ_{min} 345, 421 nm. ^{13}C NMR (CD_3CN): δ 162.86, 157.37, 154.16, 154.08, 140.48, 129.30, 126.40, 117.42. MS (MALDI-TOF): *m/z* 612. (Found: C, 39.49; H, 2.33; N, 12.26%. Calcd for $C_{30}H_{20}F_{12}FeN_8O_4P_2$: C, 39.93; H, 2.23; N, 12.42%).

Data of **15**. Compound **10** (0.050 g, 0.16 mmol) gave **15** (0.075 g, 96%). IR (KBr): 1536s, 1437m, 1349s, 1338m, 835s, 558m. UV/VIS (CH_3CN): λ_{max} 281, 286, 363, 607; λ_{min} 284, 311, 427 nm. MS (MALDI-TOF): *m/z* 668. (Found: C, 41.99; H, 3.10; N, 11.47%. Calcd for $C_{34}H_{28}F_{12}FeN_8O_4P_2$: C, 42.61; H, 2.94; N, 11.69%).

Data of **16**. Compound **12** (0.050 g, 0.17 mmol) gave **16** (0.075 g, 94%). IR (KBr): 1536s, 1434m, 1353s, 1340s, 835s, 558. UV/VIS (CH_3CN): λ_{max} 280, 359, 606; λ_{min} 306, 417, 427 nm. MS (MALDI-TOF): *m/z* 640. (Found: C, 40.53; H, 2.76; N, 12.07%. Calcd for $C_{32}H_{24}F_{12}FeN_8O_4P_2$: C, 41.31; H, 2.60; N, 12.07%).

General procedure for the synthesis of iron(II) complexes of aminoterpyridines. To a mixture of 0.050 g each of nitroterpyridines **8** and **12** in 25 ml ethanol–water (4 : 1) and 0.090 g powdered metallic iron was added 0.5 ml concentrated hydrochloric acid and the mixture was heated for 15 min at 100 °C. The colour of the blue complexes formed changed immediately to purple. Ethanol was removed and the residue was dissolved in 30 ml water. The complexes were filtered over Celite and worked up as described for complexes **17** and **18**. The yields of these reactions are about 85%.

Data of **17**. Compound **8** (0.060 g, 0.216 mmol) gave **17** (0.080 g, 88%). IR (KBr): 3398m, 1638m, 1621m, 1484m, 1450m, 842s, 558m. UV/VIS (CH_3CN): λ_{max} 372, 525sh, 566; λ_{min} 423 nm. ^{13}C NMR (CD_3CN): δ 160.24, 159.49, 157.65, 154.43, 138.98, 127.80, 123.63, 109.98. MS (MALDI-TOF): *m/z* 552. (Found: C, 42.46; H, 3.14; N, 13.48%. Calcd for $C_{30}H_{24}F_{12}FeN_8P_2$: C, 42.78; H, 2.87; N, 13.30%).

Data of **18**. Compound **12** (0.050 g, 0.163 mmol) gave **18** (0.060 g, 82%). IR (KBr): 3401m, 1638s, 1621s, 1490m, 1458m, 842s, 558m. UV/VIS (CH_3CN): λ_{max} 283, 320s 368s, 558; λ_{min} 430 nm. MS (MALDI-TOF): *m/z* 608. (Found: C, 45.54; H, 3.62; N, 12.11%. Calcd for $C_{34}H_{32}F_{12}FeN_8P_2$: C, 45.45; H, 3.59; N, 12.47%).

Synthesis of the heteroleptic iron(II) complex 19. Compounds **8** (0.010 g, 0.040 mmol) and **9** (0.011 g, 0.040 mmol) were dissolved in 3 ml ethanol; $FeCl_2 \cdot 4H_2O$ was added in excess and a blue mixture was obtained. The three complexes were separated on an aluminium oxide column utilizing acetonitrile–ammonia (10 : 0.5) as eluent. As first fraction we obtained purple complex **17** and as second fraction the dark blue heteroleptic complex **19**. The blue complex **14** was obtained as the last fraction. The solvent mixture with **19** was removed, water was added followed by ammonium hexafluorophosphate. The complex was filtered over celite, washed with 30 ml water, followed by diethyl ether and dried. The complex was then dissolved in acetonitrile and solvent was removed. Upon recrystallization by diffusion of diethyl ether into the acetonitrile solution, **19** (0.010 g, 29%) was obtained.

Data of **19**. IR (KBr): 3405m, 1638m, 1526m, 1349m, 1092m, 1066s, 1040m, 980m, 559s. UV/VIS (CH_3CN): λ_{max} 271, 391sh, 525, 623; λ_{min} 444, 562 nm. ^{13}C NMR (CD_3CN): δ 159.21, 158.35, 158.06, 154.35, 153.60, 140.15, 139.60, 129.128, 127.86, 125.56, 124.28, 117.15, 110.47. MS (MALDI-TOF): *m/z* 582. (Found: C, 41.84; H, 2.42; N, 12.99%. Calcd for $C_{30}H_{22}F_{12}FeN_8P_2$: C, 41.31; H, 2.54; N, 12.85%).

Synthesis of terpyridine ruthenium trichlorides 20 and 21. A mixture of 0.050 g each of terpyridines **8** and **9** and 1 equiv. of ruthenium trichloride trihydrate were heated at reflux for 2 h in 20 ml methanol. The dark blue **20** and brown **21** insoluble salts were collected by filtration and washed with methanol (5 ml), diethyl ether (5 ml) and dried. The yield was about 70%.

Data of **20**. IR (KBr): 1600m, 1538s, 1423m, 1344s, 1279m, 798m, 755m.

General procedure for the synthesis of ruthenium(II) complexes. A mixture of 1 mole equiv. of **20** or **21** with 1 mole equiv. terpyridine **8** or **9**, respectively, in 20 ml ethanol in the

presence of 0.3 ml *N*-ethylmorpholine was heated under reflux for 2 h. The solution was then filtered over Celite and washed with 50 ml water. The resulting ruthenium(II) complexes (**22** or **23**) were precipitated as their hexafluorophosphate salts by the addition of methanolic ammonium hexaflurophosphate and worked up as described for iron(II) complexes.

Alternatively, the homoleptic complexes **22** and **23** have also been prepared in a microwave oven. A suspension of terpyridines **8** or **9** (1 mol) and $RuCl_3 \cdot 3H_2O$ (0.5 mol) in ethylene glycol (5 ml) was heated in a microwave oven at 600 W for 10 min. The red solution was then poured into water (40 ml). After filtration upon adding $[NH_4][PF_6]$ the desired complex was isolated and purified as above. The yields were 20% (**22**) and 90% (**23**).

Data of **22**. Compounds **20** (0.030 g, 0.064 mmol) and **8** (0.020 g, 0.064 mmol) gave **22** (0.020 g, 33%). IR (KBr): 1530s, 1349s, 842s, 558m. UV/VIS (CH_3CN): λ_{max} 274, 519; λ_{min} 403 nm. MS (MALDI-TOF): *m/z* 657. (Found: C, 38.66; H, 2.41; N, 12.16%. Calcd for $C_{30}H_{20}F_{12}N_8O_4P_2Ru$: C, 38.03; H, 2.13; N, 11.83%).

Data of **23**. Compounds **21** (0.040 g, 0.091 mmol) and **9** (0.025 g, 0.091 mmol) gave **23** (0.074 g, 92%). IR (KBr): 3395m, 1634s, 1619m, 1477m, 1430m, 844s, 787m, 558m. UV/VIS (CH_3CN): λ_{max} 274, 299sh, 350sh, 492; λ_{min} 395 nm. MS (MALDI-TOF): *m/z* 597. (Found: C, 40.05; H, 3.12; N, 12.13%. Calcd for $C_{30}H_{24}F_{12}FeN_8P_2 \cdot H_2O$: C, 39.97; H, 2.91; N, 12.43%).

Data of **24**. Compounds **21** (0.040 g, 0.091 mmol) or **20** (0.030 g, 0.064 mmol) with **8** (0.025 g, 0.091 mmol) or **9** (0.018 g, 0.064 mmol), respectively, gave **24** (0.067 g, 80%) and (0.050 g, 85%). IR (KBr): 3401m, 1636m, 1528m, 1479m, 1430m, 1346s, 836s, 558s. UV/VIS (CH_3CN): λ_{max} 273, 348sh, 465sh, 523; λ_{min} 402 nm. MS (MALDI-TOF): *m/z* 627. (Found: C, 40.05; H, 2.19; N, 12.13%. Calcd for $C_{30}H_{22}F_{12}FeN_8O_2P_2$: C, 39.27; H, 2.42; N, 12.21%).

Data of **25**. Compounds **20** (0.020 g, 0.043 mmol) and 4′-dimethylamino-2,2′ : 6′,2″-terpyridine (0.011 g, 0.043 mmol) gave **25** (0.030 g, 77%). IR (KBr): 3400m, 1618m, 1524m, 1426m, 840s, 558m. UV/VIS (CH_3CN): λ_{max} 272, 302, 496; λ_{min} 289, 390 nm. MS (MALDI-TOF): *m/z* 641. (Found: C, 40.57; H, 2.83; N, 12.26%. Calcd for $C_{32}H_{28}F_{12}N_8OP_2Ru$: C, 41.26; H, 3.03; N, 12.03%).

Data of **26**. Compounds **21** (0.030 g, 0.069 mmol) and **8** (0.020 g, 0.069 mmol) gave **26** (0.030 g, 48%). IR (KBr): 3405m, 3333m, 2925m, 1655m, 1637m, 1619m, 1474m, 1432m, 832s, 789m, 559s. UV/VIS (CH_3CN): λ_{max} 271, 304, 492; λ_{min} 289, 390 nm. MS (MALDI-TOF): *m/z* 613. (Found: C, 39.27; H, 2.33; N, 12.26%. Calcd for $C_{30}H_{24}F_{12}N_8OP_2Ru$: C, 39.88; H, 2.68; N, 12.40%).

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