4′-Nitro-2,2′:6′,2′′-terpyridine, 4′-Amino-2,2′:6′,2′′-terpyridine and Their Homo- and Heteroleptic Iron(II) and Ruthenium(II) Complexes

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The new ligands 4′-nitro-2,2′:6′,2′′-terpyridine and 4′-amino-2,2′:6′,2′′-terpyridine and their homoleptic and heteroleptic iron(II) and ruthenium(II) complexes have been prepared and the electrochemistry of the complexes has been investigated.

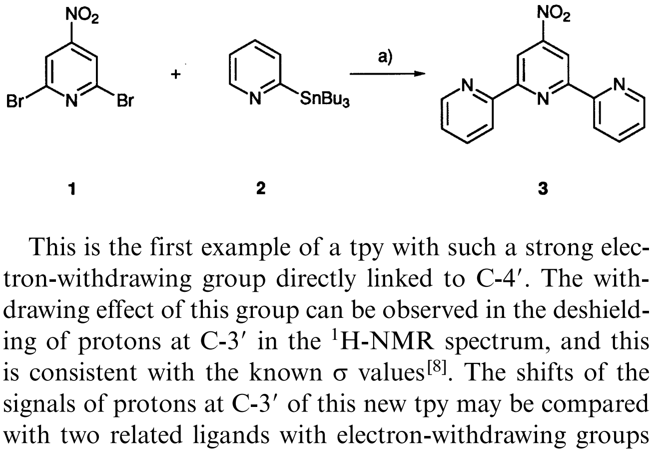
2,2′:6′,2′′-Terpyridine (tpy) is a versatile ligand for complex formation with transition metals. Particular interest rests in 4′-substituted tpy ligands and many substituents can be directly inserted by the Kröhnke methodology[1]. Some of these substituents may then be further derivatised. Some functionalised 2,2′:6′,2′′-terpyridines, such as 5,5′′-dimethyl-4′-hydroxy-2,2′:6′,2′′-terpyridine (Me_2-HO-tpy)[2], 4′-hydroxy-2,2′:6′,2′′-terpyridine (HO-tpy)[3] and 4′-chloro-2,2′:6′,2′′-terpyridine (Cl-tpy),[3] in which the functional groups are directly linked to C-4′, have also been reported. The placing of electron-withdrawing or electron-donating substituents in the 4′-position of 2,2′:6′,2′′-terpyridine alters the electronic properties of the whole ligand. A nitro substituent is electron-withdrawing with respect to hydrogen, whilst the amino group is electron-donating.

To the best of my knowledge, only one synthesis of a nitrogen substituent directly attached to C-4′ of tpy, 4′-dimethylamino-2,2′:6′,2′′-terpyridine (Me_2N-tpy), has been reported[4]. Dimethylamine and Cl-tpy were allowed to react in the presence of iron(II) salts to give the iron(II) complex of Me_2N-tpy, which was then oxidised with hydrogen peroxide under basic conditions to yield the free ligand Me_2N-tpy. In this communication the synthesis of 4′-nitro-2,2′:6′,2′′-terpyridine (O_2N-tpy) and 4′-amino-2,2′:6′,2′′-terpyridine (H_2N-tpy) is reported. These compounds are precursors for new ligands and complexes.

Although electrophilic reactions on pyridine rings do not normally occur, oxidation of the ring nitrogen atom to form pyridine *N*-oxide facilitates electrophilic attack at C-4 of the pyridine ring. By utilising standard methods, commercially available 2,6-dibromopyridine was converted to 2,6-dibromopyridine *N*-oxide, which was then treated with nitric acid in sulphuric acid to give 2,6-dibromo-4-nitropyridine *N*-oxide[5]. Subsequent deoxygenation with phosphorus trichloride in chloroform produced 2,6-dibromo-4-nitropyridine (**1**) in 43% overall yield.

Compound **1** was then used in a Stille coupling reaction[6] with 2 equivalents of tributyl(pyridin-2-yl)stannane (**2**)[7] in the presence of 1 mol-% of $Pd(PPh_3)_4$ to give O_2N-tpy (**3**) in 50% yield as a pale yellow microcrystalline solid (Scheme 1).

Scheme 1. a) 1 mol-% of $Pd(PPh_3)_4$, toluene, 110°C, 16 h, 50%



This is the first example of a tpy with such a strong electron-withdrawing group directly linked to C-4′. The withdrawing effect of this group can be observed in the deshielding of protons at C-3′ in the ^{1}H-NMR spectrum, and this is consistent with the known σ values[8]. The shifts of the signals of protons at C-3′ of this new tpy may be compared with two related ligands with electron-withdrawing groups at C-4′ (Table 1).

Table 1. Shifts of protons at C-3′ of tpy in $CDCl_3$ solution

tpy	σ	δ	ref.
Cl-tpy	0.24	8.48	[3]
$MeSO_2$-tpy	0.73	8.97	[9]
O_2N-tpy	0.81	9.16	

The homoleptic complex $[Fe(O_2N\text{-tpy})_2][PF_6]_2$ (**4**) (95%) was obtained as a blue microcrystalline solid from the reaction of **3** with $FeCl_2 \cdot 4\ H_2O$ in ethanol, followed by precipitation with $[NH_4][PF_6]$ (Scheme 2).

All spectroscopic data (^{1}H NMR, IR, UV, MS), as well as elemental analysis, confirmed the formation of this homoleptic iron(II) complex. Complex **4** exhibits the expected MLCT absorption at 605 nm in the electronic spectrum and, as a consequence of the strong electron-withdrawing effect of the nitro group, the compound appears blue.

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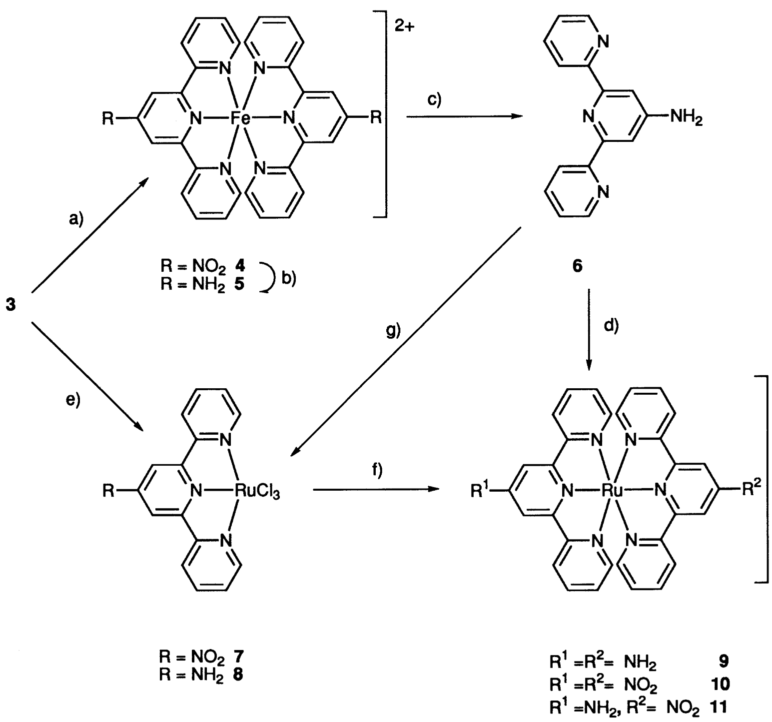
Scheme 2. a) $FeCl_2 \cdot 4\ H_2O$, ethanol, 25°C, 30 min, 95%. – b) Fe/HCl, ethanol, 78°C, 30 min, 96%. – c) **5**, NaOH, H_2O_2, 25°C, 70%. – d) $RuCl_3 \cdot 3\ H_2O$, ethylene glycol, microwave, 30 min, 95%. – e) $RuCl_3 \cdot 3\ H_2O$, ethanol, 78°C, 1 h, 95%. – f) ethanol, *N*-ethylmorpholine, 1 h; **7** → **10** (10%); **8** → **11** (20%). – g) as (e), 95%



When coordinated, ligand **3** may be reduced with metallic iron and hydrochloric acid in ethanol. Reduction of the blue iron(II) complex **4** gave the purple amino complex **5** in 96% yield. All data are consistent with the assigned structure. This complex exhibits an MLCT absorption at 566 nm in the electronic spectrum due to the presence of the electron-releasing group.

The iron(II) complex **5** was cleaved with hydrogen peroxide under basic conditions to give H_2N-tpy (**6**) as yellow monoclinic crystals in 70% yield. All data are consistent with the proposed structure of this free tpy ligand. Ligand **6** was also prepared directly, in 90% yield, by selective reduction of the nitro group of **3** in refluxing ethanol over palladium on charcoal in the presence of hydrazine hydrate[10].

Ruthenium(II) complexes of tpy ligands have always been of interest to chemists due to their photochemical and photophysical properties[11][12]. The formation of kinetically inert ruthenium(II) complexes of these ligands, i.e. $[Ru(H_2N\text{-}tpy)_2][PF_6]_2$ (**9**), $[Ru(O_2N\text{-}tpy)_2][PF_6]_2$ (**10**), and $[(H_2N\text{-}tpy)Ru(O_2N\text{-}tpy)][PF_6]_2$ (**11**), was also investigated. The synthesis of the three ruthenium(II) complexes was carried out in two stages to allow for the synthesis of heteroleptic species[4].

Alternatively, the homoleptic complexes **9** and **10** could also be obtained by direct reaction of the ligands **3** and **6** with $RuCl_3 \cdot 3\ H_2O$ in ethylene glycol in a microwave oven for 10 min. The resulting ruthenium(II) complexes were precipitated as their hexafluorophosphate salts. While the amino complex **9** can be prepared without any side reactions, some reduction of the nitro groups of **3** was observed in this protic solvent.

In the ^{1}H-NMR spectra of ruthenium(II) complexes **9**, **10**, and **11** in CD_3CN solution, the chemical shifts of the 3′-H protons are of interest. These protons were observed as a singlet [$\delta = 7.91$ (**9**), $\delta = 9.47$ (**10**)] in the homoleptic complexes. The protons of the amino groups in **9** were observed as broad singlets at $\delta = 5.84$. The situation, however, changed in the heteroleptic complex **11**. While the signals of the 3′-H protons of the nitro-substituted ligand were shifted to higher field and observed at $\delta = 9.40$, those of the 3′-H protons of the amino-substituted ligand were shifted to lower field, appearing at $\delta = 7.97$. More dramatically, the signals of the amino protons were shifted to lower field in this electron-donating/accepting complex and were observed at $\delta = 6.06$.

All five complexes are electrochemically active in acetonitrile solution, exhibiting waves corresponding to the iron(II)/iron(III) or ruthenium(II)/ruthenium(III) processes. As expected, the introduction of the electron-releasing amino and the strongly electron-withdrawing nitro substituents has a dramatic influence on these redox processes. The iron(II) complex **5** has a potential of 0.356 V (versus ferrocene/ferrocenium) while **4** exhibits a potential of 0.963 V, shifted by about 60 mV with respect to $[Fe(MeSO_2\text{-}tpy)_2][PF_6]_2$ ($E^0 = 0.904$ V). This effect is in accord with the strength of the electron-withdrawing nitro group (cf.

Table 1). This means that this ligand is the strongest electron-withdrawing tpy ligand yet synthesised. The potential difference between the electron-acceptor and electron-donor iron complexes **4** and **5**, respectively, is 0.607 V.

The homoleptic ruthenium(II) complex **9** showed a potential of 0.474 V, which is shifted by 32 mV with respect to $[\mathrm{Ru(Me_2N\text{-}tpy)_2}][\mathrm{PF_6}]_2$[4]. This is consistent with the electron-donating effect of the two methyl groups in the latter complex. The potential of the homoleptic complex **10** was 1.114 V in comparison to $[\mathrm{Ru(MeSO_2\text{-}tpy)_2}][\mathrm{PF_6}]_2$ (E^0 = 1.10 V)[4]. In the donor/acceptor complex **11** the potential was shifted by 266 mV and 374 mV with respect to the ruthenium(II) complexes **9** and **10**, respectively, and was observed at 0.740 V. The potential difference between the electron-donor and electron-acceptor complexes **9** and **10** is 0.640 V.

In conclusion, a new method has been established for the synthesis of novel 4′-nitro-2,2′:6′,2′′-terpyridine and 4′-amino-2,2′:6′,2′′-terpyridine, which are precursors for new heterocycles and oligopyridines. These new tpy ligands may be incorporated in metal complexes, which are under current investigation.

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Experimental Section

Palladium-Catalysed Coupling Reaction. − General Procedure: Compound **1** (1 mol) or **2** (2 mol) and $\mathrm{Pd(PPh_3)_4}$ (1 mol-%) were heated under nitrogen in 50 ml of toluene for 16 h. Upon cooling to room temperature 10 ml of 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 ($\mathrm{MgSO_4}$) and the solvent was removed. Concentrated hydrochloric acid (30 ml) was added to the residue and this was extracted with dichloromethane (3 × 30 ml). The aqueous phase was cautiously neutralised by the addition of solid sodium hydroxide. The ligand **3** was then filtered off and purified by chromatography on silica gel with dichloromethane to give 50% yield.

3: m.p. 177°C. − IR (KBr): $\tilde{\nu}$ = 1531, 1359 $\mathrm{cm^{-1}}$. − UV ($\mathrm{CH_3CN}$): λ_{max} = 279, 345 nm; λ_{min} = 305 nm. − ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 9.16 (s, 3′-H, 2 H), 8.76 (d, 6-H, J = 7.80 Hz, 2 H), 8.64 (d, 3-H, J = 7.80 Hz, 2 H), 7.91 (ddd, 4-H, J = 8.30, 7.80, 1.95 Hz, 2 H), 7.42 (ddd, 5-H, J = 8.30, 7.80, 1.95 Hz, 2 H). − ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 158.44, 156.33, 154.05, 149.47, 136.97, 124.77, 121.33, 113.33. − MS (Maldi-TOF); *m/z*: 278. − $\mathrm{C_{11}H_{10}N_4O_2}$ (278.273): calcd. C 64.74, H 3.62, N 20.13; found C 64.51, H 3.58, N 20.09.

6: m.p. 179−180°C. − IR (KBr): $\tilde{\nu}$ = 3226 $\mathrm{cm^{-1}}$. − ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 8.67 (d, 6-H, J = 7.80 Hz, 2 H), 8.60 (d, 3-H, J = 7.80 Hz, 2 H), 7.84 (ddd, 4-H, J = 8.30, 7.80, 1.95 Hz, 2 H), 7.75 (s, 3′-H, 2 H), 7.32 (ddd, 5-H, J = 8.30, 7.80, 1.95 Hz, 2 H), 4.33 (br. s, $\mathrm{NH_2}$, 2 H). − ^{13}C NMR ($\mathrm{CDCl_3}$): δ = 156.52, 156.23, 154.55, 148.89, 136.76, 123.61, 121.30, 106.77. − MS (Maldi-TOF); *m/z*: 248. − $\mathrm{C_{15}H_{12}N_4}$ (248.21): calcd. C 72.56, H 4.87, N 22.57; found C 72.01, H 4.93, N 22.55.

Synthesis of the Homoleptic Ruthenium(II) Complexes in a Microwave Oven. − General Procedure: A suspension of tpy **3** or **6** (1 mol) and $\mathrm{RuCl_3 \cdot 3\,H_2O}$ (0.5 mol) in ethylene glycol (5 ml) was heated in a microwave oven at 600 W during 10 min. In each case the red solution was then poured into water (40 ml). Upon adding $[\mathrm{NH_4}][\mathrm{PF_6}]$ the desired complexes were isolated and purified by chromatography on silica gel followed by recrystallisation by diffusion of diethyl ether into the acetonitrile solution.

9: ^{1}H NMR ($\mathrm{CD_3CN}$): δ = 9.47 (s, 3′-H, 4 H), 8.73 (d, 3-H, J = 7.80 Hz, 4 H), 7.98 (ddd, 4-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 7.37 (d, 6-H, J = 7.80 Hz, 4 H), 7.24 (ddd, 5-H, J = 8.30, 7.80, 1.95 Hz, 4 H). − MS (Maldi-TOF); *m/z*: 657.

10: ^{1}H NMR ($\mathrm{CD_3CN}$): δ = 8.24 (d, 3-H, J = 7.80 Hz, 4 H), 7.91 (s, 3′-H, 4 H), 7.83 (ddd, 4-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 7.40 (d, 6-H, J = 7.80 Hz, 4 H), 7.11 (ddd, 5-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 5.84 (br. s, $\mathrm{NH_2}$, 4 H). − MS (Maldi-TOF); *m/z*: 627.

Synthesis of the Heteroleptic Ruthenium(II) Complex: Compounds **3** and **6** (1 mol) were hated separately with $\mathrm{RuCl_3 \cdot 3\,H_2O}$ (1 mol) in ethanol at reflux during 1 h. The insoluble dark solids **7** and **8** were filtered off in yields of 95%. These salts (1 mol) were treated with 1 mol of tpy **6** and **3**, respectively, in ethanol for 1 h to yield complex **11**. This compound was purified by the addition of water (50 ml) as described above.

Alternatively, the reaction of the salts **7** and **8** with tpy ligands **3** and **6**, respectively, gave the homoleptic complexes **9** and **10** under the same conditions.

11: − ^{1}H NMR ($\mathrm{CD_3CN}$): δ = 9.40 (s, 3′′′-H, 4 H), 8.70 (d, 3′′-H, J = 7.80 Hz, 4 H), 8.27 (d, 3-H, J = 7.80 Hz, 4 H), 7.99 (ddd, 4′′-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 7.96 (s, 3′-H, 4 H), 7.86 (ddd, 4-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 7.60 (d, 6-H, J = 7.80 Hz, 4 H), 7.33 (ddd, 5′′-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 7.13 (d, 6′′-H, J = 7.80 Hz, 4 H), 7.03 (ddd, 5-H, J = 8.30, 7.80, 1.95 Hz, 4 H), 6.06 (br. s, $\mathrm{NH_2}$, 2 H). − MS (Maldi-TOF); *m/z*: 597.

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