Regioselective Functionalization of Tetrabromophenanthroline−Ruthenium Complexes

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Structural, photophysical and photochemical characterization and reactivity of a novel polypyridyl ruthenium complex based on 3,5,6,8-tetrabromophenanthroline are discussed.

Signal storage at a molecular level is a great challenge for chemistry.[1] The possibility of connecting different functionalities selectively to one ligand of a metal complex may open the route towards higher integrated molecular units capable of processing various external stimuli in a predesignated order. The implementation of this concept demands ligands with a multitude of potential connecting groups which can selectively be transformed.[2] 3-bromo- and 3,8-dibromophenanthrolines have proved useful for the preparation of mononuclear[3] and multiheteronuclear complexes.[4] These systems have found applications ranging from DNA photoprobes,[5] to metalloligands in catalysis.[6] A very useful and well-established feature of these bromophenanthroline−ruthenium complexes is their susceptibility towards nucleophilic aromatic substitution.[7]

We have improved the bromination reaction of phenanthroline first published by Dénes and Chira,[8] which allows for the selective formation of 3,5,6,8,-tetrabromophenanthroline (Br_4phen) in a one-step multigram reaction, Figure 1.[8]

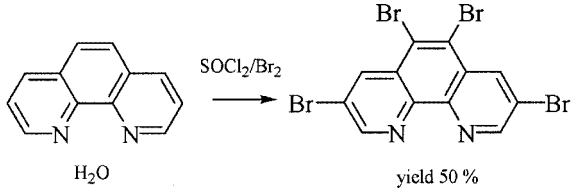

Figure 1. Improved preparation of 3,5,6,8-tetrabromophenanthroline (Br_4phen)

Br_4phen readily forms a complex with $[tbbpy]_2RuCl_2$ resulting in $[(tbbpy)_2Ru(Br_4phen)]^{2+}$, **1**. The structural characterization using two-dimensional NMR spectroscopy suggests that a symmetrical complex is formed as indicated by the presence of only two signals for the four phenanthroline-based protons. ^{13}C, HSQC, and HMBC spectroscopy allows the complete assignment of all signals in the ^1H- and ^{13}C NMR spectra, which together with mass spectroscopy suggests that Br_4phen coordinates in a similar fashion as the unsubstituted phenanthroline. The X-ray crystallographic characterization confirms this assumption, and as seen from Table 1 shows no significant differences compared with the parent complex $[(tbbpy)_2Ru(phen)]^{2+}$, **2** (see Supporting Information). The molecular structure is depicted in Figure 2.

Table 1. Bond lengths (Å) and angles (°)

	1	**2**
Ru−N1	2.046(5)	2.055(4)
Ru−N2	2.060(5)	2.056(5)
Ru−N3	2.064(5)	2.053(4)
Ru−N4	2.052(5)	2.055(4)
Ru−N5	2.047(5)	2.060(4)
Ru−N6	2.071(5)	2.074(4)
C2−Br1	1.891(6)	–
C5−Br2	1.883(6)	–
N1−Ru−N2	79.27(19)	79.9(2)
N3−Ru−N4	78.21(19)	77.88(16)
N5−Ru−N6	78.25(19)	78.99(16)

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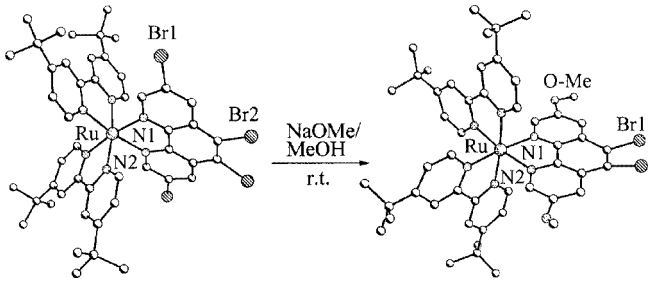

Figure 2. Regioselective nucleophilic substitution of **1** with NaOMe leading to **3**; molecular structure of **1**; anions and hydrogen atoms omitted, and the structural motif of **3** confirming the regioselective substitution

Reaction of **1** with NaOMe at room temperature in methanol leads to the selective formation of one product that contains two bromine and two new methoxy functions, as confirmed by ESI-MS. The fact that the positions of all the bipyridine-based signals in the ^{1}H NMR spectra did not change, together with the presence of only one new signal at $\delta = 4.15$ ppm for the methoxy function, suggests the formation of a symmetrical species where substitution at the phenanthroline moiety has taken place. The regioselective formation of the 5,6-dibromo-3,8-dimethoxyphenanthroline ruthenium complex **3** could be confirmed by a structural motive depicted in Figure 2.

Photophysical investigation of compounds **1** to **3** suggests that tetrabromo substitution lowers the electron density of the phenanthroline ligand considerably. The absorption and emission wavelength of **1** are red-shifted relative to **2**, see Table 2. This finding correlates well with the data obtained for the oxidation potential of $Ru^{II/III}$, which clearly shows that the four bromine substituents significantly decrease the electron density at the metal center (difference of 137 mV). Introduction of the methoxy groups increases the electron density, as expected.[9] The introduction of two methoxy groups has a pronounced influence on the photophysical properties, and this is in agreement with an electron-donating substituent.

Table 2. Photophysical and electrochemical properties of complexes **1**−**3** in acetonitrile

Compound	$E_{1/2}$ ox in V (vs. Fc/Fc$^+$)	λ_{max} in nm	λ_{em} in nm
1	0.92	470	680
2	0.783	444	610
3	0.845	450	615

In conclusion, rutheniumpolypyridyl complexes based on the ligand Br_4phen are readily obtainable. Most importantly a regioselective nucleophilic substitution with NaOMe at the 3,8-position is possible. It is evident from the conventional reactivity of bromine-substituted aromatics that **1** and **3** are potentially very interesting synthons in itself, opening the possibility to derivatise the previously not easily accessible 5,6-position. Initial investigations on the photochemical reactivity of **3** using ion exchange HPLC suggest that Br_2OMe_2phen is very photolabile.

Experimental Section

All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. All other reagents were of HPLC grade. *cis*-[Ru(tbbpy)$_2$Cl$_2$]·2H$_2$O,[10] was prepared by standard procedures. All reagents for synthesis, $RuCl_3 \cdot 3H_2O$ (Chempur), 1,10-phenanthroline (Aldrich) and all other materials were commercially available and of reagent grade.

3,5,6,8-tetrabromophenanthroline (Br_4phen): 1,10-phenanthroline monohydrate (4.0 g, 20 mmol) was dissolved in $SOCl_2$ (200 mL). Freshly distilled Br_2 (9.3 g, 120 mmol) was carefully added. This mixture was refluxed for 31 h and cooled to room temperature, and the bright yellow precipitate was filtered off (3,5,6,8,-tetrabromophenanthroline). The precipitate was washed with aqueous NH_3 until a colorless solution was obtained. The white solid was recrystallized from toluene. ^{1}H NMR ($CDCl_3$): $\delta = 9.16$ (2 H, d), 8.91 (2 H, d) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 122.0$, 125.1, 129.6, 139.0, 143.6, 152.4 ppm. MS (DCI with H_2O): 497 [M + H$^+$] 417 (M − Br + H$^+$), 338 (M − Br_2 + H$^+$), 257 (M$^+$ − Br_3). Yield 5.22 g (52% based on phen).

Synthesis of [(tbbpy)$_2$Ru(Br_4phen)](PF$_6$)$_2$ (1): 3,5,6,8-Tetrabromo-1,10-phenanthroline (1.15 g, 2.32 mmol) and [(tbbpy)$_2$RuCl$_2$] (1.5 g, 2.11 mmol) were refluxed in a mixture of ethanol (80 mL) and H_2O (20 mL) for 8 hours. The crude reaction mixture was filtered, washed twice with ethanol/H_2O (80:20), and the combined filtrate was concentrated to the half volume. On addition of NH_4PF_6 and stirring at room temperature for 1 hour, the crude product precipitated. Recrystallization from acetone/water gave the desired product. Crystals suitable for X-ray analysis were obtained from acetone/water. ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.997$ [4,7, 2 H, s (lc)], 8.792 [3′′, 2 H, s (lc)], 8.788 [3′, 2 H, s (lc)], 8.055 [2,9, 2 H, s (lc)], 7.599 [5′′, 2 H, d (lc)], 7.527 (6′,6′′, 4 H, m), 7.310 [5′, 2 H, d (lc)], 1.391 [CH$_3$(*tert*-butyl), 18 H, s], 1.362 [CH$_3$(*tert*-butyl), 18 H, s] ppm. MS (Micro-ESI in $CHCl_3$ + methanol); *m*/*z* (relative intensity) with matching isotope pattern: 1279 (100) (**1** + PF_6), 1201 (34) (**1** − Br + PF_6), 567 (51) (**1**$^{2+}$). Crystal data for **1**: $[C_{48}H_{52}Br_4N_6Ru]^{2+} \cdot 2\,[PF_6]^-$, $M = 1423.61$ g mol^{-1}, bordeaux-red prism, size 0.02 × 0.02 × 0.01 mm, tetragonal, space group $I4_1/a$, $a = b = 32.5281(3)$, $c = 20.5151(4)$ Å, $V = 21706.6(5)$ Å^3, $T = -90$ °C, $Z = 16$, $\rho_{calcd.} = 1.742$ g cm^{-3}, μ (Mo-K_α) = 33.74 cm^{-1}, psi-scan, trans(min): 0.5565, trans(max): 0.7367, $F(000) = 11264$, 20023 reflections in $h(-42/42)$, $k(-29/29)$, $l(-19/26)$, measured in the range $2.66° \le \Theta \le 27.49°$, completeness $\Theta_{max} = 99.8\%$, 12423 independent reflections.

Synthesis of [(tbbpy)$_2$Ru(phen)](PF$_6$)$_2$ (2): 1,10-phenanthroline (0.018 g, 0.09 mmol) and [(tbbpy)$_2$RuCl$_2$] (0.06 g, 0.085 mmol) were reacted and purified according to **1**. Yield 96 mg (95%). Crystals suitable for X-ray analysis were obtained from acetone/water. ^{1}H NMR ([D$_3$]acetonitrile): $\delta = 8.613$ [4,7, 2 H, s (lc)], 8.504 [3′, 2 H, s (lc)], 8.456 [3′′, 2 H, s (lc)], 8.299 (5,6, 2 H, s), 8.058 [2,9, 2 H, s (lc)] 7.753 (3,8, 2 H, m), 7.705 (6′, 2 H, d), 7.463 [5′, 2 H, d (lc)], 7.405 (6′′, 2 H, d), 7.200 [5′′, 2 H, d (lc)], 1.437 [CH$_3$(*tert*-butyl), 18 H, s], 1.322 [CH$_3$(*tert*-butyl), 18 H, s] ppm. MS FAB in nba *m*/*z* (relative intensity) with matching isotope pattern: 980 (22) (**2** + PF_6); 834 (15) (**2**). Crystal data for **2**: $[C_{48}H_{56}N_6Ru]^{2+} \cdot 2\,[PF_6]^- \cdot 2\,C_3H_6O$, $M = 1224.15$ g mol^{-1}, red-brown prism, size 0.12 × 0.10 × 0.09 mm, triclinic, space group $P\bar{1}$, $a = 12.1999(7)$, $b =$

13.3243(7), c = 18.989(1) Å, α = 76.854(2), β = 74.819(3), γ = 78.206(3)°, V = 2866.3(3) Å^3, T = −90 °C, Z = 2, $\rho_{calcd.}$ = 1.418 g cm^{-3}, μ (Mo-K_α) = 4.13 cm^{-1}, psi-scan, trans(min): 0.9521, trans(max): 0.9637, F(000) = 1264, 19624 reflections in h(−15/15), k(−17/14), l(−24/24), measured in the range 2.11° ≤ Θ ≤ 27.44°, completeness Θ_{max} = 97.4%, 12753 independent reflections.

Synthesis of [(tbbpy)$_2$Ru(OMe$_2$Br$_2$phen)](PF$_6$)$_2$ (3): 1 (200 mg, 0.14 mmol), was dissolved in a solution of freshly prepared NaOMe (1 M) in MeOH (100 mL). The solution was stirred for 6 h and H_2O (200 mL) was added. The pH of the solution was slowly adjusted to 7 by adding dilute HCl. The resulting opaque orange solution was extracted with CH_2Cl_2 until colorless, and the solvent was removed from the combined organic phases. The precipitate was dissolved in a minimal amount of EtOH and concentrated aqueous NH_4PF_6 added. The precipitate was recrystallized from acetone/water. Yield 170 mg (90%). ^{1}H NMR ([D$_6$]acetone): δ = 8.879 [3′, 2 H, s (lc)], 8.844 [3′′, 2 H, s (lc)], 8.174 [4,7, 2 H, s (lc)], 7.939 (6′, 2 H, d), 7.845 [2,9, 2 H, s (lc)], 7.828 (6′′, 2 H, d), 7.618 [5′, 2 H, d (lc)], 7.397 [5′′, 2 H, d (lc)], 4.156 [CH$_3$(OMe), 6 H, s], 1.428 [CH$_3$(*tert*-butyl), 18 H, s], 1.367 [CH$_3$(*tert*-butyl), 18 H, s] ppm . MS FAB in nba *m*/*z* (relative intensity) with matching isotope pattern: 1181 (5) (**3** + PF$_6$); 1035 (5) (**3**). Crystal data for **3**: $C_{52}H_{61}Br_2F_{12}N_6O_2P_2Ru$, M = 1304.72 g mol^{-1}, red prism, size 0.02 × 0.02 × 0.01 mm, monoclinic, space group $P2_1/n$, a = 13.983(3), b = 39.063(5), c = 10.4711(15) Å, β = 100.945(13)°, V = 5615.4(17) Å^3, T = −153 °C, Z = 4, $\rho_{calcd.}$ = 1.543 g cm^{-3}, μ(Mo-K_α) = 6.22 cm^{-1}, F(000) = 2654, 21731 reflections in h(−15/13), k(−45/45), l(−12/12), measured in the range 1.52° ≤ Θ ≤ 14.56°, completeness Θ_{max} = 72.1%, 6903 independent reflections.

CCDC-216455 and -216456 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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