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Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]acridine (tpac): a new extended polycyclic bis-phenanthroline ligand

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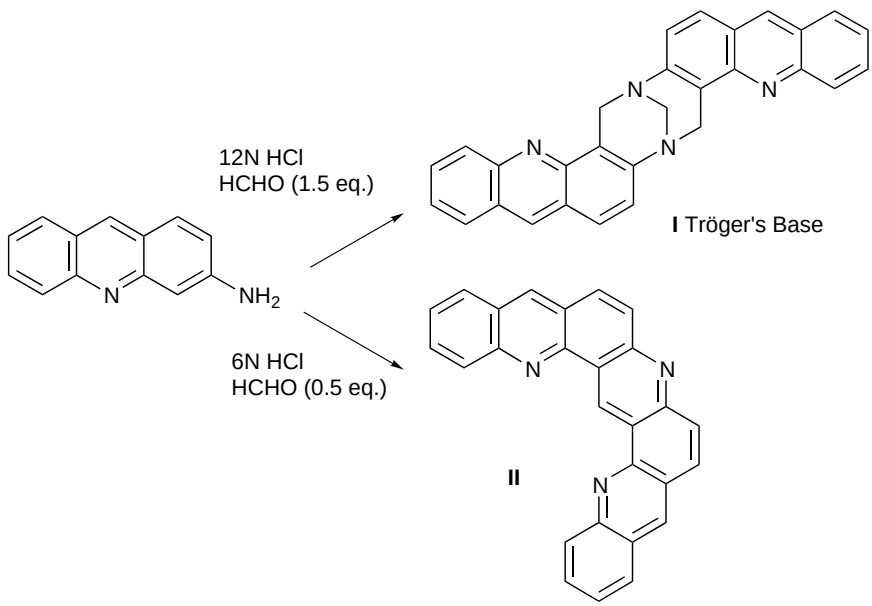
Abstract—A new heptacyclic planar molecule has been synthesized in a very efficient one-pot reaction from 5-aminophenanthroline. Ru(II) mono- and dinuclear complexes based on this new bridging ligand, Tpac, have been prepared.

We have developed a chemistry based on modifications of the acridine nucleus to design new polycyclic heterocycles. In particular, the reaction of 3-aminoacridine with formaldehyde in acidic medium was studied in detail.[1] The nature of the reaction products strongly depends on the acid concentration, and on the stoichiometry in formaldehyde. In strong acids, and in the presence of 1.5 equiv. of formaldehyde, the heterocyclic analogue of Tröger's base **I** is produced quantitatively, but in 6N HCl and in the presence of 0.5 equiv. of formaldehyde, a very slow reaction leads to the thermodynamic product of the reaction, the triaza-heptacycle **II** (Scheme 1).

The postulated pathway for these reactions, shown in Scheme 2, is based on that suggested by Wagner in 1954 to explain the products formed from the reaction of aromatic amines with formaldehyde.[2] In Scheme 2,



Scheme 1.

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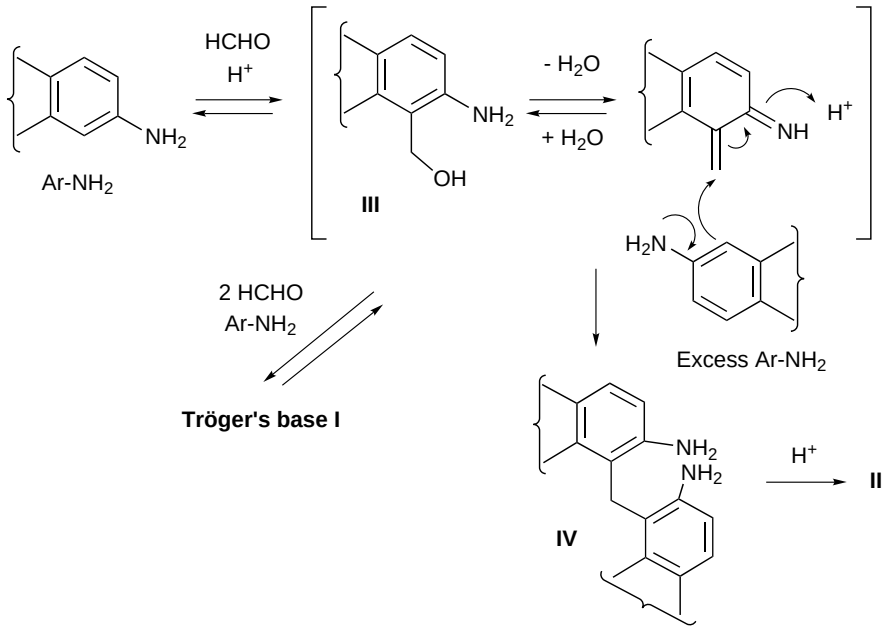
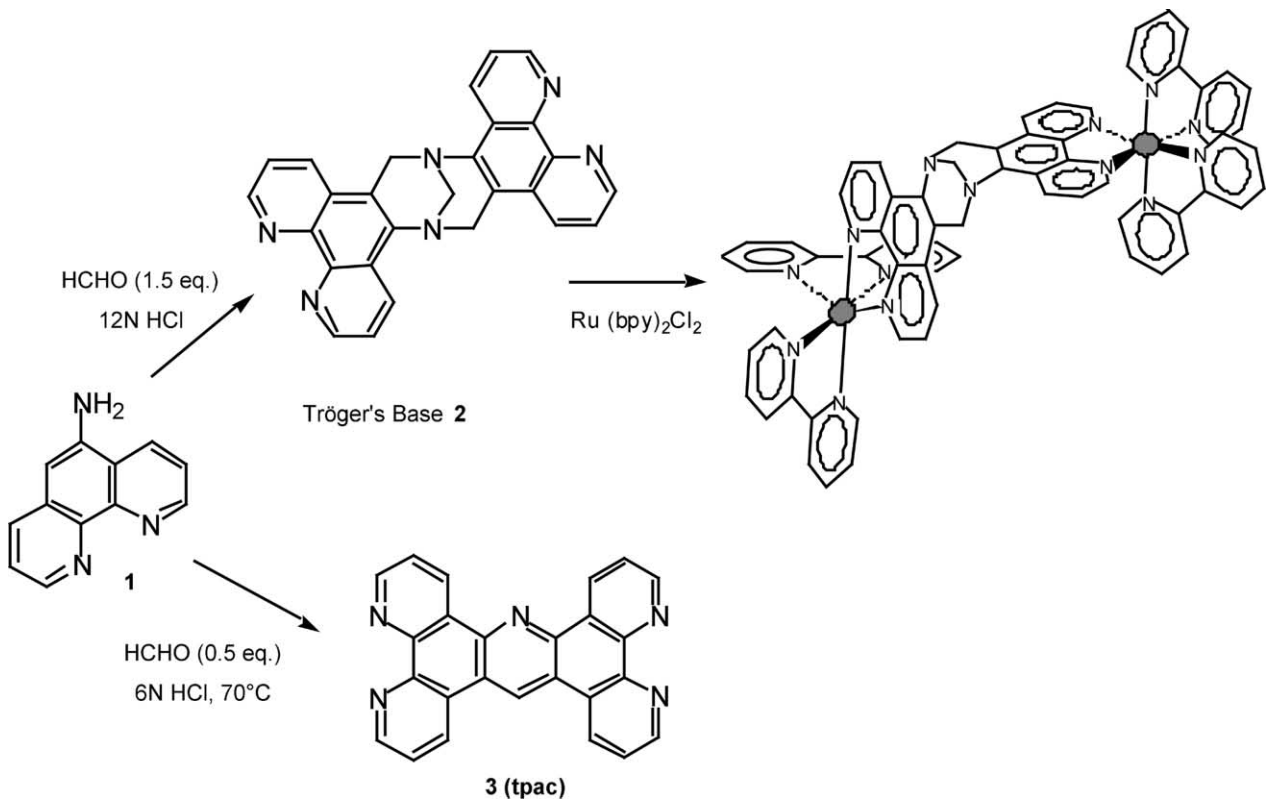


Scheme 2.

electrophilic substitution on the aromatic amine with formaldehyde gives 3-amino-4-hydroxymethyl compound **III**. In the presence of a large amount of formaldehyde, the reaction yields the Tröger's base **I**, but in the presence of excess aromatic amine, methylene-bis(arylamine) intermediate **IV** is produced. The formation of the aza-heptacycle **II** results from cyclization and oxidation of this intermediate. Considering the importance of phenanthroline derivatives in the field of mono and polymetallic complexes, we have applied the same methodology to the synthesis of new phenanthroline-type ligands. The first step was the optimization of the synthesis of the phenanthroline type Tröger's base analogue (BT) **2** described earlier by Yashima.[3] Reacting the 5-amino-[1,10]phenanthroline (**1**) with an excess of paraformaldehyde (1.5 equiv.) in 12N hydrochloric acid, afforded **2** in 81% yield. The corresponding bimetallic complex $[Ru(bpy)_2]_2BT^{4+}$ was successfully prepared (Scheme 3).[4]

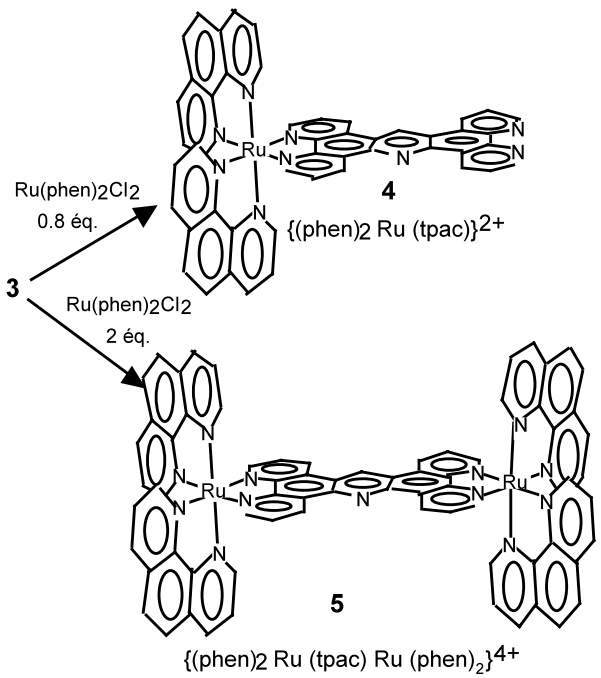


Scheme 3.

The interest of polyazaaromatic ligands with extended conjugation as building blocks for multicomponent systems (including molecular wires, metallodendrimers or luminescent DNA probes[5–7]) prompted us to develop novel synthetic strategies to obtain planar heterocycles containing the phenanthroline skeleton. In this work we report the synthesis and characterization of a new fully conjugated bridging ligand tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]acridine **3** (or tpac) along with the first Ru(II) mono- and dinuclear complexes based on this ligand.

Following the mechanism shown in Scheme 2, tpac **3** was prepared in one-step by reacting 2 equiv. of 5-amino[1,10]phenanthroline with formaldehyde in 6N HCl. The reaction proceeded very slowly (8 days at 70°C); it was followed by HPLC. Different intermediates were successively observed. Compound **3** was isolated as a beige solid (yield >85%, 95% purity).[8] Unexpectedly as compared to other extended ligands which display very low solubility in most organic solvents, **3** was found soluble in alcohols (methanol or ethanol) and was therefore easily purified by crystallization in ethanol.

Syntheses of the mono- and dinuclear complexes $[Ru(phen)_2(tpac)]^{2+}[PF_6^-]_2$ **4** and $[(phen)_2Ru(tpac)\text{-}Ru(phen)_2]^{4+}[PF_6^-]_4$ **5** are shown in Scheme 4. Complex **4** was prepared by reacting 1 equiv. of $Ru(phen)_2Cl_2$ with 1.2 equiv. of tpac in a mixture of $EtOH/H_2O$ under reflux. The desired product was isolated by precipitation with NH_4PF_6 and purified by HPLC. The ^1H NMR spectrum[9] is consistent with the structure of the complex. The chloride salt of complex **4** was further characterized by electrospray mass spectrometry in H_2O.[9] Complex **5** was prepared by using the same experimental procedure but reacting 2 equiv. of $Ru(phen)_2Cl_2$ with 1 equiv. of tpac. The ^1H NMR spectrum assigned with the aid of a COSY spectrum is in perfect agreement with the structure of the dinuclear complex. The chloride salt of complex **5** was also characterized by electrospray mass spectrometry.[10]



Scheme 4.

The absorption spectra of both complexes exhibit intense bands in the UV region and less intense bands in the visible. The λ_{max} are very similar (448 nm for **4** and 450 nm for **5** in CH_3CN). Only the ε differs from **4** to **5** (1.6×10^4 and 2.8×10^4 M^{-1} cm^{-1}, respectively, at λ_{max} in CH_3CN). A monochromatic excitation at 450 nm in acetonitrile produced a luminescence for **4** and **5** at 608 and 614 nm, respectively. Interestingly, in water, both complexes were luminescent (613 nm for **4** and 620 nm for **5**). This is quite different from the data obtained with mononuclear complexes whose extended ligand contains a pyrazine central moiety such as in $Ru(phen)_2(dppz)^{2+}$, $Ru(bpy)_2(tpphz)^{2+}$ or $Ru(phen)_2(phehat)^{2+}$ that do not luminesce in water.[7,11] Another striking result is the similarity of the spectroscopic properties between **4** and **5**. Compound **5** exhibits a slight red-shift of luminescence relatively to **4** (<10 nm), either in acetonitrile or in water, whereas the shifts for the tpphz complexes (70 nm) are more important.[11,12] The two metallic centres in **5** seem thus to behave rather independently as the λ_{max} in absorption and emission do not change importantly from the mononuclear to the dinuclear complex in contrast to the ε.

This work demonstrates the efficiency of the synthesis of the new heptacycle tpac, and the interest to use it as ligand to gain more information on the particular behaviours of complexes based on similar extended planar ligands.

Acknowledgements

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8. Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]acridine (tpac) **3**: A mixture of 5-aminophenanthroline **1** (345 mg, 1.7 mmol) and paraformaldehyde (27 mg, 0.9 mmol) in 6N HCl was stirred for 8 days at 70°C. The solution was then diluted with water and basified by adding aqueous ammonium hydroxide. The solid that deposited was filtered, washed with water and dried. Purification was achieved by crystallization in ethanol. Compound **3** was thus obtained in 59% yield (200 mg, 0.52 mmol); mp >300°C; ^{1}H NMR (CD_3OD, 200 MHz) δ (ppm): 8.33–8.39 (m, 4H), 7.61–7.73 (m, 5H), 6.86–7.03 (m, 4H); MS (EI) m/z 383 $(M)^+$. Anal. calcd for $C_{25}H_{13}N_5{\cdot}0.5H_2O$: C, 76.62; H, 3.47; N, 17.87. Found: C, 76.78; H, 3.27; N, 17.94.
9. $[Ru(phen)_2(tpac)]^{2+}[PF_6^-]_2$ **4**: 59 mg (0.11 mmol) of $Ru(phen)_2Cl_2$ dissolved in hot ethanol/water (1/1) was added dropwise to a boiling solution of **3** (59 mg, 0.15 mmol) in ethanol/water 1/1 (10 mL). The solution was then maintained under reflux for 4 h. The suspension formed after cooling to room temperature was filtered off. A saturated aqueous NH_4PF_6 solution was added to the filtrate to precipitate the crude complex. The solid was filtered, washed with water, ethanol and diethyl ether. The desired mononuclear complex was separated from the dinuclear impurity by HPLC; ^{1}H NMR (CD_3CN, 300 MHz) δ (ppm): 10.58 (m, 1H), 9.72–9.88 (m, 4H), 8.89–8.96 (m, 2H), 8.70 (dd, 4H), 8.31 (s, 4H), 7.98–8.12 (m, 8H), 7.81–7.89 (m, 2H), 7.69–7.75 (m, 4H); MS (EI) m/z 880.0 ($[M-Cl^-]^+$), 421.9 ($[M-2Cl^-]^{2+}$).
10. $[(Phen)_2Ru(tpac)Ru(phen)_2]^{4+}[PF_6^-]_4$ **5**: A mixture of 46 mg (0.12 mmol) of tpac and 125 mg (0.23 mmol) of $Ru(phen)_2Cl_2$ in 17 mL ethanol/water (1/1) was refluxed for 7 h. After the mixture was cooled to room temperature, the formed suspension was filtered off and an excess of NH_4PF_6 was added to the filtrate to precipitate complex **5**. The orange powder was filtered, washed with water, ethanol and diethylether and dried. The desired complex **5** was further purified by HPLC; ^{1}H NMR (CD_3CN, 300 MHz) δ (ppm): 10.57 (s, 1H), 10.01 (d, 2H), 9.65 (d, 2H), 8.65 (dd, 8H), 8.30 (2s, 8H), 8.24 (m, 4H), 8.18 (d, 4H), 8.06 (d, 4H), 7.88 (m, 4H), 7.67 (m, 8H); MS (EI) m/z 688.9 ($[M-2Cl^-]^{2+}$), 446.9 ($[M-3Cl^-]^{3+}$) and 326.0 ($[M-4Cl^-]^{4+}$).
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