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Toward high nuclearity ruthenium complexes: creating new binding sites in metal complexes

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The nickel-catalyzed coupling of a ruthenium *ortho*-chloroimine complex creates a new vacant bidentate binding site suitable for generating higher nuclearity ruthenium complexes.

Current interest in ruthenium dendrimers stems from their light-harvesting properties.[1] Enhanced ruthenium content is vital to ascertain an increased probability of light absorption, however, there are inherent difficulties in synthesizing large metallodendrimers.[2] One synthetically powerfully approach (complexes-as-metals/complexes-as-ligands) calls for an iterative protection/deprotection sequence, which consumes both time and material.[3] Another drawback to most systems is the slow increase in metal ion content, which necessitates several more steps to obtain dendrimers with high (>20) metal ion content.[2a,b] In this work, we propose to create new binding sites in metal complexes in order to rapidly increase ion content in metallodendrimers. Previous work has demonstrated that ruthenium complexes containing anionic ligands may be homocoupled,[4] however, new chelating sites have never been created and utilized for further metal complexation.

In our synthetic approach, a ligand (Fig. 1, **a**) containing a bidentate binding site and an *ortho*-chloroimine site forms a ruthenium complex by selectively complexing a metal ion with octahedral coordination geometry in the free bidentate site of the ligand (Fig. 1, **b**). The *ortho*-chloroimine site in **b** is then coupled to create a new bidentate binding site (Fig. 1, **c**), which may in turn bind to another metal ion (Fig. 1, **d**), form a 'complex-metal' [Fig. 1, **e**; *cf.*, $Ru(bpy)_2Cl_2$], or give a closed dendrimer (Fig. 1, **f**). Repeating the steps that lead to **b** and **c** on the 'complex-metal' **e** will afford a new 'complex-ligand', capable of forming large metallodendrimers. The total metal ion content will grow more rapidly than with current approaches.[3] Although many stereoisomers may exist, the differences in their electrochemical and spectroscopic properties are not expected to be great.[5]

Our first goal was to outline the conditions for the nickel-catalyzed coupling reaction. Allowing 4-chloro-2,2′-bipyridine (Clbpy) to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ gave monometallic complex **1a** in 92% yield.† Mixing 2 equivalents of **1a** in DMF with an *in situ* generated nickel catalyst[6] gave dimetallic complex **2a** in 57% yield,† in which the newly formed 2,2′:4′,4″:2″,2‴-quaterpyridine (qpy) ligand bridges two metal centres.[7]

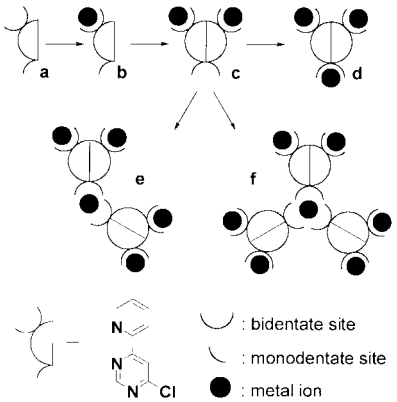
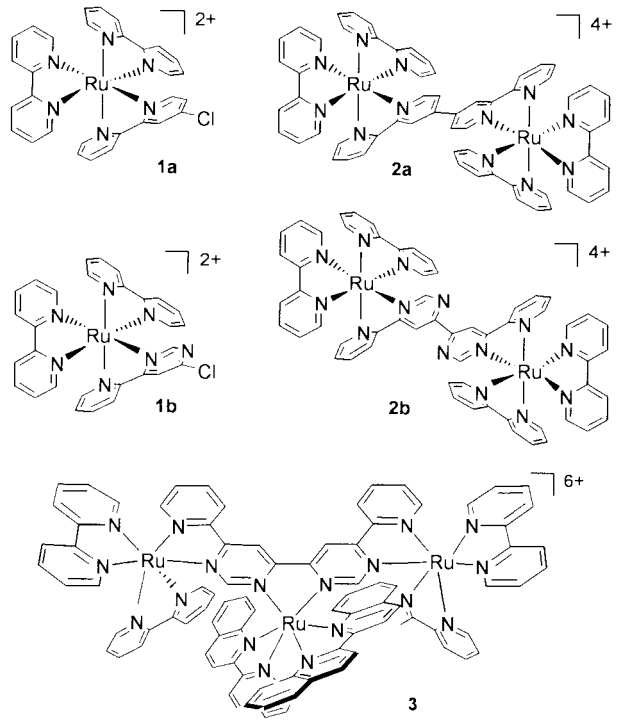


Fig. 1 Ligand **a** [*e.g.* 4-chloro-6-(2′-pyridyl)pyrimidine] contains a bidentate and a monodentate binding site, and reacts with a metal ion to give complex **b**. Homocoupling complex **b** creates a new bidentate binding site in **c**, which may then form a trinuclear complex **d**, a 'complex-metal' **e** (*cf.*, $Ru(bpy)_2Cl_2$), or a closed dendrimer **f**.



The absorption spectra (acetonitrile solution) of **1a** and **2a** are dominated by ligand-centred (LC) transitions in the UV region and metal-to-ligand charge-transfer (CT) transitions in the visible region.‡ A small red shift is noted in the metal-to-ligand CT band in **2a** (465 nm) compared to **1a** (448 nm) owing to the greater extent of electron delocalization in the qpy bridging (BL) compared to bpy. However, little electronic interaction between the metal centres is revealed by cyclic voltammetry (acetonitrile solution *vs.* SCE). Two chemically reversible coincidental one-electron oxidations are centred at +1.24 V. A reversible one-electron reduction at −1.12 V is followed by three further reductions at −1.42, −1.56 and −1.65 V.

With the proper reaction conditions now available, our next target ligand was 4-chloro-6-(2′-pyridyl)pyrimidine (ClPpy), as metal complexation is favoured at the bidentate pyridylpyrimidine site rather than the *ortho*-chloropyrimidine site. Thus, ClPpy was allowed to react with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in ethanol–water to afford red monometallic complex **1b** in 79% yield.† It is important to note that no protection/deprotection sequence was required; the bidentate pyridylpyrimidine moiety is a better binding site than the monodentate, sterically encumbered *ortho*-chloropyrimidine site.

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In complex **1b**, the Ru-to-BL CT band (480 nm) is lower in energy than the Ru-to-bpy CT band (433 nm), as expected based on earlier work with pyridylpyrimidines.[8] The higher energy UV region is dominated by LC π–π* transitions.[9] The first one-electron reduction is ascribed to the pyridylpyrimidine ligand (−0.92 V) and is followed by coincidental reductions of the two bpy units (−1.52 V).[8] The metal-based oxidation (+1.38 V) is at a slightly higher potential than that of $Ru(bpy)_3$ (+1.26 V), which is consistent with stabilized metal d_π orbitals owing to the presence of the electron deficient pyridylpyrimidine BL.

The addition of **1b** to the Ni-catalyst in DMF[6] gave the purple binuclear complex **2b** in 80% yield.†‡§ Thus, the sterically hindered *ortho*-chloropyrimidine site in **1b** has undergone C–C coupling to give a bidentate diimine site. The Ru-to-BL CT band undergoes a red shift to 554 nm as well as a slight blue shift to 431 nm for the Ru-to-bpy CT band. The latter is expected owing to the stabilization of the metal orbital due to better π-backbonding with the extended BL. The former usually occurs only on binucleation of the same heterocycle.[8] In this case, the electronic conjugation between the two heterocycles is enhanced owing to the *trans*-conformation of the pyridimine nitrogen lone pairs (N_{1p}), which minimize N_{1p}–N_{1p} and C–H···C–H repulsion, leading to a co-planar arrangement.[10]

The first two reductions (−0.57 and −0.99 V) are ascribed to the BL as the reduction of the bridging qpy in **2a** occurs at −1.12 V. Subsequent reductions at bpy (−1.49 and −1.78 V) are in accord with reductions of bpy in diruthenium complexes of diazine heterocycles.[11] The metal-centred oxidations occur at +1.42 V, with an anodic and cathodic separation of 120 mV, indicative of metal–metal interaction rather than irreversibility.[12]

The effectiveness of our approach was confirmed by the reaction of $Ru(biq)_2Cl_2$ (biq = 2,2′-biquinoline) with **2b**, which gave the green trinuclear complex **3** in 55% yield.† The effect of binding the $Ru(biq)_2$ unit into the central chelating site was threefold: it introduced biq LC bands at 271, 360 and 380 nm, a Ru-to-biq CT band at 567 nm and caused a red shift in the Ru-to-BL CT out to 616 nm. These effects are similar to those reported for the polynucleation of Ru(II)(2,3-dipyridylpyrazine)$_3$ with three $Ru(biq)_2$ units.[13] The oxidation potential is as expected for a linear trimetallic system; the external Ru centres oxidize first (+1.58 V), followed by the central Ru centre. However, the latter oxidation occurs outside of the solvent potential window (> +2.00 V) owing to the proximity of two Ru(III) ions and the stabilization of the metal d_π orbital by enhanced back-donation to biq.

The first reduction (+0.04 V) is ascribed to the bridging ligand and is induced by the electron-accepting $Ru(biq)_2$ unit. The next BL reduction (−0.38 V) occurs at a more positive value than the first reduction potential of **2b**. The next two one-electron reductions (−0.83 and −1.20 V) occur on the $Ru(biq)_2$ unit as biq has a lower reduction potential than bpy.[9] The next two waves are two simultaneous one-electron reductions of the external bpy units at −1.50 and −1.80 V. They are fully reversible and follow what one would expect in a heteroligand complex.[9]

Interestingly, the separation between the first and second reduction potential of the bridging ligand in both **2b** and **3** is approximately the same. This suggests that the delocalized BL orbital stays approximately the same 'size' in both **2b** and **3**. Electron delocalisation appears to be as complete with or without a metal ion, restricting rotation about the pyrimidine–pyrimidine C–C bond.

In conclusion, we have introduced a powerful new method for creating new binding sites for metal ions in polynuclear complexes. This methodology is extendable to other types of binding sites and metal ions. We are currently investigating the formation of dendrimeric complexes by using **2b** and analogues as 'complex-ligands' as well as the photophysical properties of these complexes.

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Notes and references

† All new complexes were isolated as their PF_6 salts, recrystallized from acetonitrile–toluene, and characterized by ^1H and ^{13}C NMR, MS, IR, UV-VIS and electrochemistry. Yields are unoptimized.

‡ λ_{max}/nm(MeCN) (ε/L mol^{-1} cm^{-1}); **1a**: 245 (21 500), 287 (61 400), 448 (11 000); **2a**, 244 (45 100), 285 (68 300), 465 (19 100); **1b**: 245 (25 900), 282 (56 100), 433 (11 400), 480 (8300); **2b**: 247 (57 000), 285 (122 000), 431 (24 700), 554 (31 700); **3**: 271 (99 000), 283 (104 000), 358 (37 400), 382 (31 000), 435 (27 000), 567 (20 000), 616 (19 000).

§ To $NiBr_2(PPh_3)_2$ (25 mg, 3.4×10^{-5} mol), Zn-dust (10 mg, 1.5×10^{-4} mol) and NEt_4I (29 mg, 1.1×10^{-4} mmol) was added DMF (3.4 mL).[6] The mixture was stirred under nitrogen at 50 °C for 1 h before adding **1b** (100 mg, 1.1×10^{-4} mol). After 1 h, the mixture was cooled to room temp. and and KPF_6 (0.1 g, 5.4×10^{-4} mol) in water (10 mL) added. The mixture was filtered and the remaining solid was recrystallized twice from acetonitrile–toluene giving **2b** as a purple solid (78 mg, 79%).

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