Ni(0) catalysed homo-coupling reactions: a novel route towards the synthesis of multinuclear ruthenium polypyridine complexes featuring made-to-order properties.

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Abstract

A new synthetic procedure for the efficient preparation of dinuclear ruthenium(II) polypyridyl complexes is reported. The compounds synthesized are $[(bpy)_2Ru(BPBT)Ru(bpy)_2](PF_6)_2$ and $[(bpy)_2Ru(BPZBT)Ru(bpy)_2](PF_6)_2$. (bpy = 2,2'-bipyridine; H_2BPBT = 5,5'-bis(pyridin-2-yl)-3,3'-bis(1,2,4-triazole); H_2BPZBT = 5,5'-bis(pyrazin-2-yl)-3,3'-bis(1,2,4-triazole). Electrochemical experiments show that the two dinuclear systems investigated exhibit pH switchable intercomponent interactions.

Keywords;

Ruthenium complexes, coupling reactions, electrochemistry, dinuclear complexes.

1. Introduction

The investigation of multinuclear metal complexes has gained a central place in the search for supramolecular structures as potential building blocks for photochemically and electrochemically driven molecular devices. Several different approaches have been taken and many multinuclear compounds containing two or more metal centres have been reported. [1] However, it is now clear that in order to be able to produce more efficient supramolecular devices, based on multinuclear, luminescent and redox active complexes, larger assemblies will be required. [2]

Most of the reported synthetic procedures, including the so-called "complexes as ligands/complexes as metals" strategy used to build up the larger assemblies reported up to now [3] are based on a stepwise metal coordination of multidentate ligands and iterative protection/deprotection methods Such synthetic approaches require a considerable amount of time and effort both in the development of synthetic and separation techniques. For example, recently a series of ruthenium bis(bpy) complexes (bpy = 2,2'-bipyridyl), based on the ligand 5,5'-bis(pyridin-2-yl)-3,3'-bis(1,2,4-triazole) (H_2BPBT, see Figure 1) were reported. [4] In this study it was observed that during the synthesis of complexes containing H_2BPBT, mixtures of mononuclear, dinuclear and trinuclear compounds were obtained. Our earlier work on pyridine-triazoles has shown that for these ligands coordination can occur through either the N2 or the N4 atom of the triazole ring yielding complexes with different physical properties in addition deprotonation of the triazole rings also has to be considered. [5] These observations clearly indicate that obtaining pure well defined products with multidentate ligands is often far from straightforward.

Figure 1 Ligand structures

In this contribution, we wish to report a new method for the synthesis of unambiguously defined multinuclear complexes based upon Ni(0) catalysed homo-coupling reactions of suitable mononuclear precursors. The method has been employed to investigate the previously reported dinuclear metal complexes containing H_2BPBT and a new pyrazine analogue containing 5,5'-bis(pyrazin-2-yl)-3,3'-bis(1.2.4-triazole) (H_2BPZBT, see Figure 1) has also been prepared. The compounds synthesized have the molecular formulae $[(bpy)_2Ru(BPBT)Ru(bpy)_2](PF_6)_2$ and $[(bpy)_2Ru(BPZBT)Ru(bpy)_2](PF_6)_2$ respectively. To the best of our knowledge, this is the first example of a Ni(0)-catalysed homo-coupling reaction applied to ruthenium polypyridyl complexes.[6] The electronic interactions between the two redox active metal centres in the dinuclear compounds obtained have also been studied and are found to be strongly pH dependent.

2. Results and Discussion.

The synthetic pathway used is outlined in scheme 1. The brominated triazoles **2a** and **2b** were obtained adapting conditions previously reported for the bromination of triazoles [7], while the coupling reaction involving complexes **3a** and **3b** was carried out using standard conditions similar to those reported for the coupling of heteroaromatic compounds.[8] NMR and HPLC analysis of **3a** and **3b** clearly indicate that only one isomer, N2 bound, is obtained in both cases. **4a** and **4b** are obtained as the sole product of the respective coupling reaction and they can be precipitated by the addition of diethyl ether. Analytical pure samples can be obtained by re-crystallisation from a water/acetone mixture.[9] None of the steps of this synthesis require the use of chromatography for purification purposes and no mixture of counter ions was obtained as reported in the earlier study on the H_2BPT compound. [4] In addition, in the compounds obtained the triazole rings are clearly deprotonated and coordinated to the N2 atom of the triazole ring. Detailed synthetic procedures and a detailed characterization of the compounds will be reported elsewhere.

Scheme 1

It should be noted that the assembly of kinetically inert metal compounds (such as Ru(II) and Os(II) complexes) *via* classical Pd(0) or Ni(0) catalysed coupling reactions is a relatively new approach to the fabrication of multicomponent molecular systems. For instance, palladium catalysed hetero-coupling reactions such as the Heck, [10] the Suzuki [11]and the Stille reaction [12] have recently been successfully applied for this purpose. The homo-coupling reaction reported here represents a simplified route to the synthesis of symmetric multinuclear complexes, since it involves the use of only one substrate (i.e. the bromide derivative) as the starting material.[13]

The interest in multinuclear metal complexes arises from the possibility of electronic interactions between the metal centres.[1] Such interaction allows intercomponent processes such as photoinduced energy and electron transfer to occur. To obtain information about the electronic interactions in the compounds, electrochemical studies were carried out. In acetonitrile solution, both **4a** and **4b** undergo two successive, reversible one-electron oxidation processes that can be attributed to the sequential oxidation of the two ruthenium centres. $E_{1/2}$ values of + 0.80 V and + 0.98 V *vs* SCE and of + 0.92 V and + 1.09 V *vs* SCE were found for complexes **4a** and **4b**, respectively.[14,15] The extent of electronic coupling between the two metal centres can be estimated from the relationship:

$$K_c = e^{\Delta E / 25.69}$$

where K_c is the comproportionation constant and ΔE is the difference (in mV) between the first and the second oxidation potential [16]. K_c values of 1100 and 750 were found for **4a** and **4b**, respectively, indicating that in both complexes the bridging ligand mediates noticeable electronic interactions between the two redox centres.

Interestingly, protonation of the triazolate rings of the bridge has dramatic consequences on the electronic coupling between the two metal subunits. Upon addition of triflic acid [17], complex **4b** exhibited only one reversible oxidation process, with $E_{1/2}$ at +1.13 V. The comparison of the area of the differential voltammetry peaks associated to the metal based oxidation processes in both protonated and non protonated **4b** suggests that the protonated species undergoes a two-electron oxidation. This process has been assigned to the simultaneous oxidation of the two metal centres. In the absence of electrochemical evidence for electronic interaction, only an upper limit of 20 can be given for the K_c value. For **4a** two one-electron processes were still observed after protonation of the bridge, with $E_{1/2}$ at +1.06 V and +1.17 V, figures that correspond to a K_c value of 70.

The above experimental data clearly show that the electronic interaction between the metal sites in both **4a** and **4b** is significantly reduced upon protonation of the bridge. This behaviour can be explained by considering that metal-metal interaction in such dinuclear Ru(II) complexes mainly occurs via superexchange-assisted interaction based on a hole-transfer mechanism [5c, 15, 18, 19]. Under this condition, the extent of the interaction depends on the energy-gap between the higher-energy $d\pi$ metal orbitals (metal-based HOMO) and the lower-energy, filled, σ bridging ligands orbitals (bridge-based HOMO). The σ bridging ligand orbitals are stabilized upon protonation, so that the energy gap between relevant orbitals *increases*, leading to *decreased* superexchange-assisted electronic interactions. Therefore **4a** and **4b** exhibit pH control of metal-metal interaction. This result resembles that reported in somewhat similar tetranuclear ruthenium complexes containing protonable imidazole containing ligands. [20]

3. Conclusions

In conclusion, we have illustrated the efficiency of the Ni(0)-catalized coupling as a novel route for obtaining multinuclear metal complexes with made-to-order properties. The results obtained are promising for the efficient and unambiguous preparation of larger multicomponent ruthenium(II) complexes, including assemblies featuring pH switchable electrochemically driven molecular devices

4. Acknowledgements.

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$Ru_2C_{52}H_{38}N_{18}P_2F_{12}\cdot 4H_2O$: C, 42.26; H, 3.10; N, 17.12; found: C, 42.80; H, 2.75; N, 16.80; *m/z* 1117.2, 559 (M^+ calc for $Ru_2C_{52}H_{38}N_{18}$: 1117.2).

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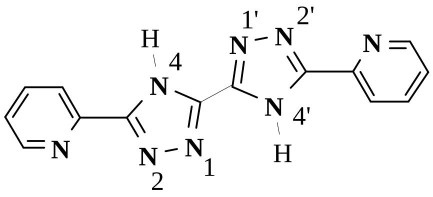
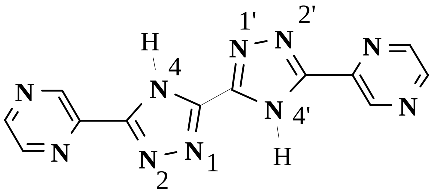


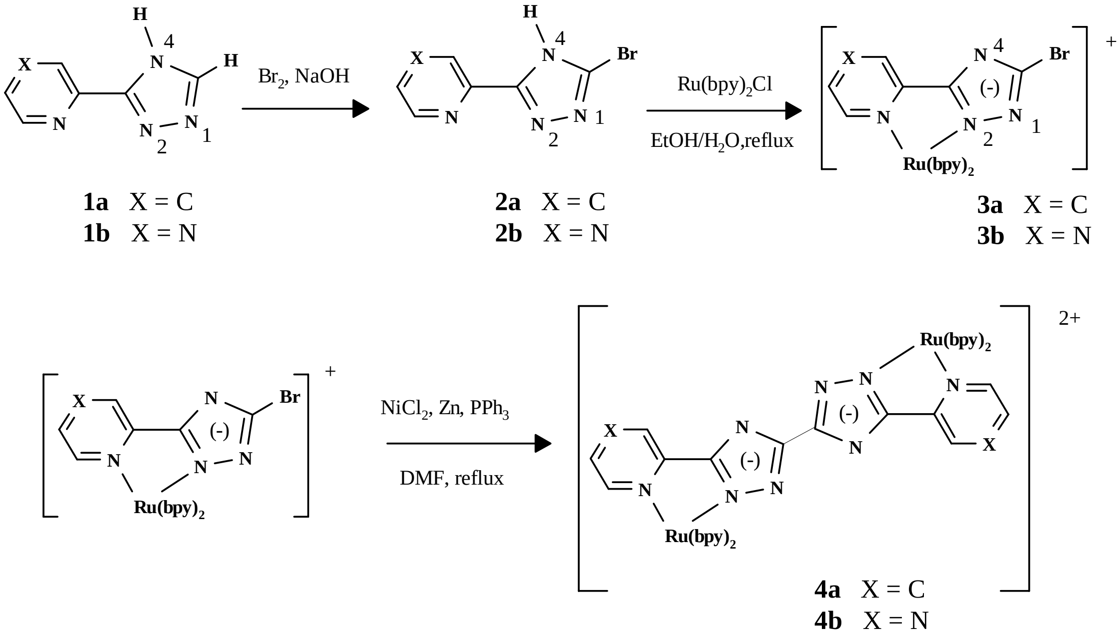
H_2BPBT



H_2BPZBT

Figure 1 Ligand structures

Scheme



1a X = C
1b X = N

2a X = C
2b X = N

3a X = C
3b X = N

4a X = C
4b X = N

Captions for Supplementary Material

S1: Electrochemistry of complex **4b** in acetonitrile before (a) and after addition of two equivalents of triflic acid (b). Ferrocene was used as internal standard.

S2: ^{1}HNMR spectra of complex **3a**, 400 MHz, DMSO.

S3: ^{1}HNMR spectra of complex **3b**, 400 MHz, DMSO.

S4: ^{1}HNMR spectra of complex **4a**, 400 MHz, DMSO.

S5: ^{1}HNMR spectra of complex **4b**, 400 MHz, DMSO.

Justification for Publication.

In the search for molecular devices capable of carrying out particular functions driven by either photonic or electrochemical stimuli, there is a continuing interest in the synthesis of multinuclear supramolecular compounds. Particular interest is paid in these studies to the design of antenna systems and molecular switches. In this contribution we wish to report a new molecular switch. In the dinuclear compounds reported the electronic coupling between the two metal centres can be modulated by pH and the magnitude of the interaction can be read by electrochemical means.

In the synthesis of such compounds the complexity of both the bridging ligands and the presence of various metal centres has lead to increasing difficulties in obtaining pure complexes. Often various coordination isomers are obtained and sometimes the presence of protonation equilibria complicates a definite assignment of the materials obtained. In this contribution we also report an alternative approach to assemble mononuclear components into well defined dinuclear systems based on a Ni(0) based coupling reaction. An approach that leads to very pure compounds and avoids the formation of side products. In a more general way it is an interesting example of how general organic chemistry techniques can be used effectively in the preparation of inorganic coordination complexes. So far there are not many examples of other similar reactions. We therefore feel that publication of our results as a Chem. Commun. is justified.