

Novel Synthesis of a Doubly Cyclometallated Diruthenium Complex with Strongly Coupled Metal Centres

Edwin C. Constable,^a Alexander M. W. Cargill Thompson^a and Stefan Greulich^b

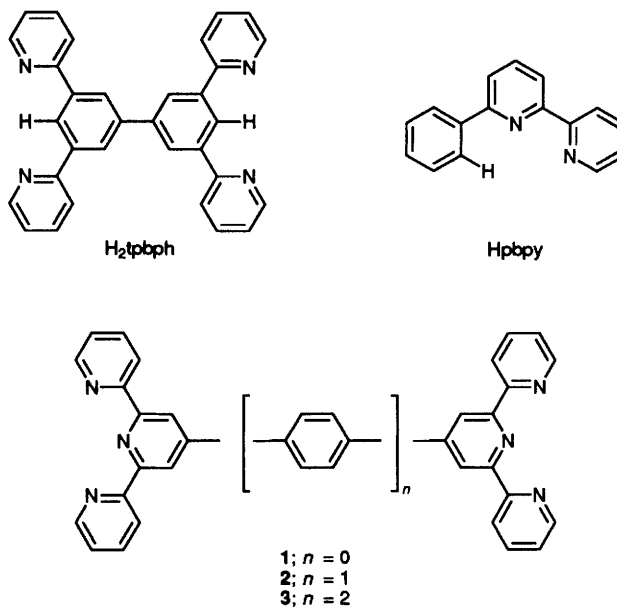
^a Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

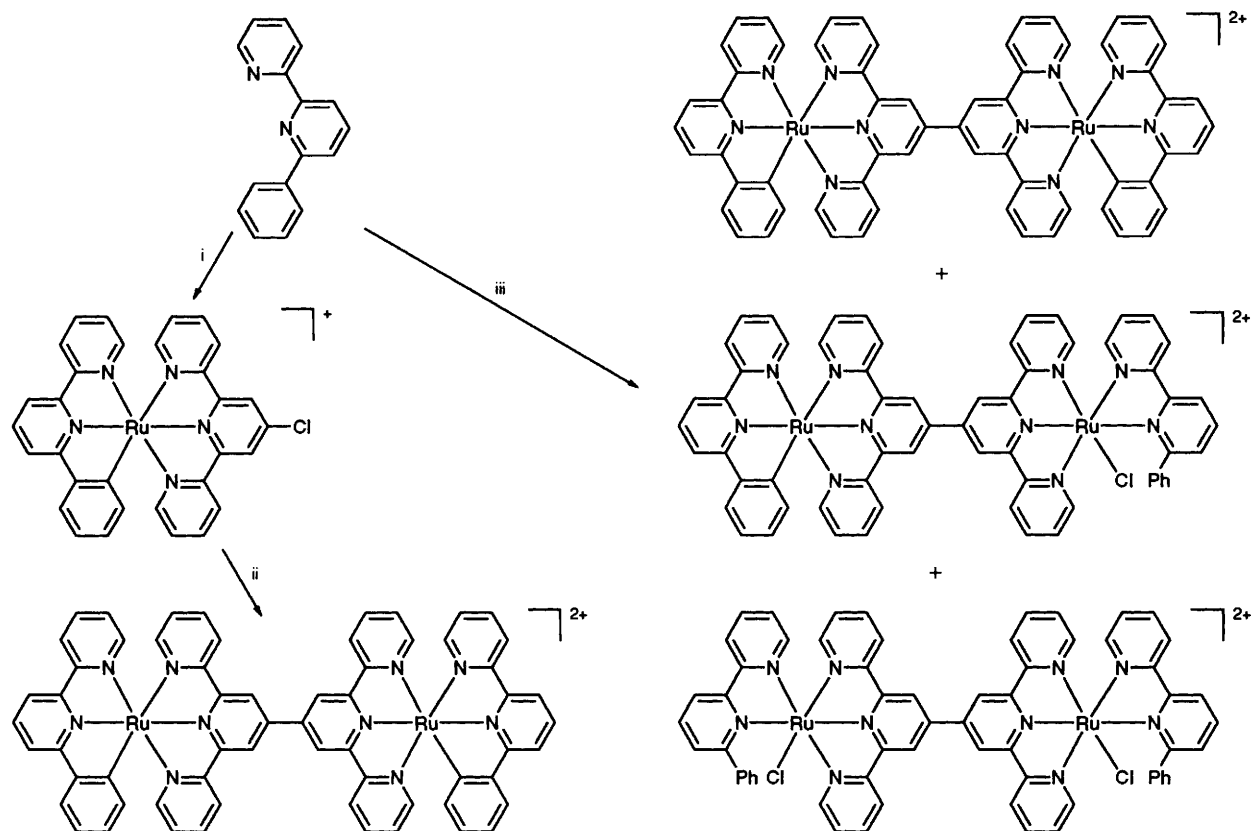
^b Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg (EHICS), 1 rue Blaise Pascal, BP 296 F, 67008 Strasbourg Cedex, France

A novel coupling method by which a ruthenium(II) complex of a 4'-chloro-substituted 2,2':6',2''-terpyridine is converted to a dinuclear doubly cyclometallated complex is reported; the dinuclear complex can be oxidized to give a strongly coupled mixed-oxidation state Ru^{III}Ru^{II} species.

There is considerable interest in polynuclear supramolecular systems incorporating photo- and redox-active ruthenium or osmium oligopyridine centres.¹ Cyclometallated ruthenium(II) complexes have been investigated as potential photocatalysts,² but few examples are known of multiply cyclometallated polynuclear systems.^{3,4} In this note we describe a novel synthesis of such a compound and demonstrate that the site of metallation does not critically determine the metal-metal interactions.

The ligand H₂tpbph [H₂tpbph = 3,3',5,5'-tetra(2-pyridyl)-biphenyl] gives rise to doubly cyclometallated complexes such as [(tpty)Ru(tpbph)Ru(tpty)]ⁿ⁺ [tpty = 4'-(4-methylphenyl)-2,2':6',2''-terpyridine; n = 2,3,4] which exhibits very strongly coupled ruthenium centres in the mixed valence (Ru^{II}, Ru^{III}; n = 3) state.⁴ This coupling was thought to be associated with the bridging tpbph²⁻ ligand,⁴ and is in contrast to that previously reported for complexes such as [LRuL'RuL]⁴⁺ (L = tpy or tpty; L' = 1, 2 or 3).⁵ In order to distinguish between the necessity for the tpbph²⁻ ligand, as opposed to a more general requirement for an N₅C donor set at the ruthenium centres, we decided to prepare the related complexes [(pbpy)RuL'Ru(pbpy)]²⁺ (L' = 1, 2 or 3; Hpbpy = 6-phenyl-2,2'-bipyridine).





Scheme 1 Reagents and conditions: i, $[Cl_3Ru(Citpy)]$, $HOCH_2-CH_2OH$; ii, $[Ni(PPh_3)_2Cl_2]$, PPh_3 , Zn, N_2 , dmf; iii, $[Cl_3Ru(1)RuCl_3]$, $HOCH_2CH_2OH$

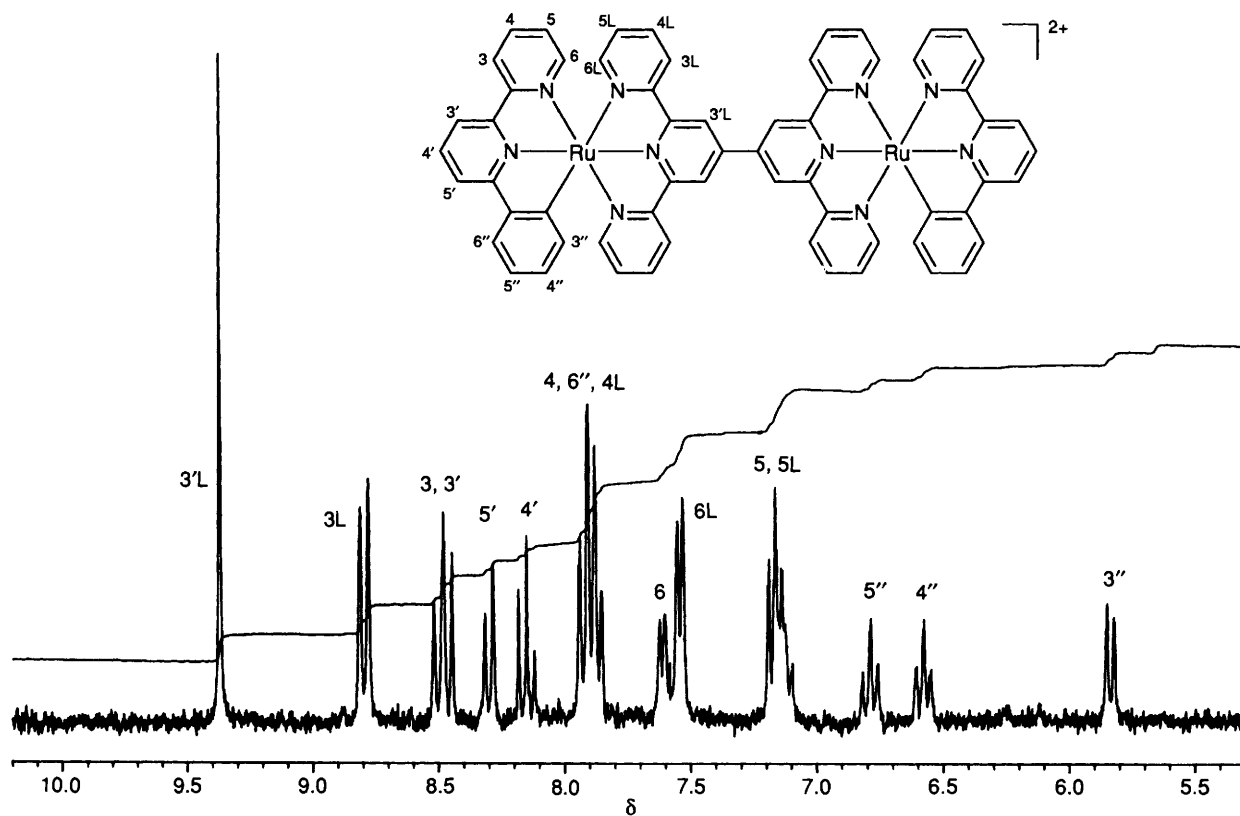


Fig. 1 250 MHz 1H NMR spectrum of a CD_3CN solution of $[(pbpy)Ru(1)Ru(pbpy)][PF_6]_2$ showing the assignments

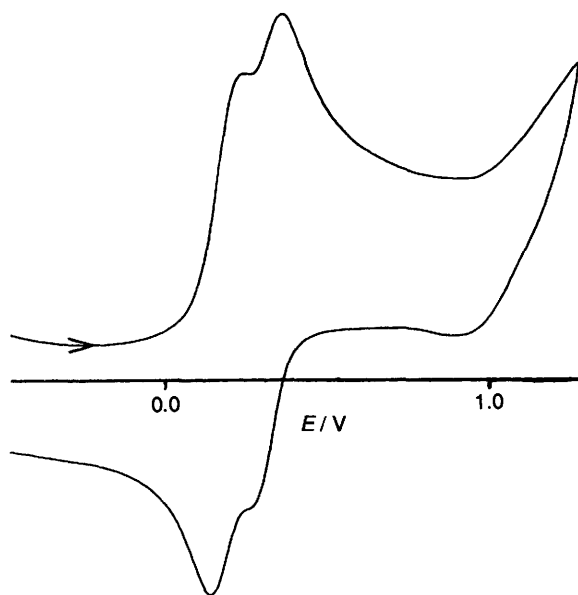


Fig. 2 Cyclic voltammogram of a MeCN solution of $[(\text{pbpy})\text{Ru}(\mathbf{1})\text{Ru}(\text{pbpy})][\text{PF}_6]_2$ (E/V vs. Fc/Fc^+ internal reference; $[\text{Bu}_4\text{N}][\text{BF}_4]$ supporting electrolyte)

The reaction of excess of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with $\mathbf{1}$ gave $[\text{Cl}_3\text{Ru}(\mathbf{1})\text{RuCl}_3]$ as an insoluble brown material. However, reaction of this with Hpbpy under a variety of conditions yielded mixtures of metallated and non-metallated complexes which were not fully separable by chromatography (Scheme 1). We, therefore, decided to extend the methodology that we have developed for the synthesis of symmetrical ligands such as $\mathbf{1}$ and $\mathbf{3}^{5,6}$ to the direct formation of complexes of these species. The reaction of Hpbpy with $[\text{Cl}_3\text{Ru}(\text{Cltpy})]^7$ ($\text{Cltpy} = 4'$ -chloro-2,2':6',2''-terpyridine) in ethane-1,2-diol resulted in the formation of the cyclometallated complex $[(\text{pbpy})\text{Ru}(\text{Cltpy})][\text{PF}_6]$ in 40% yield. We have previously defined the conditions leading to the formation of metallated or non-metallated complexes of Hpbpy .⁸ Treatment of a solution of $[(\text{pbpy})\text{Ru}(\text{Cltpy})][\text{PF}_6]$ in dmf ($\text{dmf} = N,N$ -dimethylformamide) with $[\text{Ni}(\text{PPh}_3)_n]$ ($n = 3,4$; prepared *in situ* by the reaction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ with an excess of PPh_3 and zinc dust) gave a dark-coloured solution. The dmf was removed *in vacuo*, the residue extracted with CHCl_3 and the solid dissolved in methanol to give a blue solution which was treated with $[\text{NH}_4][\text{PF}_6]$ and concentrated to give pure $[(\text{pbpy})\text{Ru}(\mathbf{1})\text{Ru}(\text{pbpy})][\text{PF}_6]_2$ as a blue solid in 80% yield. If the starting complex $[(\text{pbpy})\text{Ru}(\text{Cltpy})][\text{PF}_6]$ is free from non-metallated impurities, the blue complex is obtained analytically pure; otherwise, it is necessary to chromatograph the mixture of salts resulting from the coupling reaction (silica, 8:1 MeCN-saturated aqueous KNO_3).

The ^1H NMR spectrum of a solution of this salt in CD_3CN is presented in Fig. 1. This unambiguously establishes the formation of the symmetrical double cyclometallated species. The upfield shift of the proton adjacent to the site of metallation is characteristic.⁸ Although the complex is stable in the solid state, solutions in acetonitrile are oxidised slowly in air to generate paramagnetic species. The cyclic voltammogram of an acetonitrile solution of the complex is presented in Fig. 2. The complex exhibits oxidation processes at +0.17 and +0.30 V (vs. Fc/Fc^+) which are comparable to those at +0.34 and +0.50 V (vs. Fc/Fc^+) previously reported for $[(\text{ttpy})\text{Ru}(\text{tpbph})\text{Ru}(\text{ttpy})]^{n+}$.⁴ The formation of a stable mixed-oxidation state complex with the non-metallating bridging ligand $\mathbf{1}$ clearly indicates that the anionic tpbph^{2-} ligand is not a prerequisite for the strong electronic coupling of

the two metal centres. The differences in redox potentials for the two Ru^{II} , Ru^{III} processes in the complex of $\mathbf{1}$ ($\Delta E_{1/2} = 0.13$ V) is similar to that previously described for the tpbph^{2-} complex ($\Delta E_{1/2} = 0.16$ V).

In the same way that the near-IR spectrum of the mixed oxidation state complex cation $[(\text{ttpy})\text{Ru}(\text{tpbph})\text{Ru}(\text{ttpy})]^{3+}$ exhibits an intense intervalence transfer band ($\lambda_{\text{max}} = 1820$ nm, 5494 cm^{-1} ; $\epsilon = 27000$) so does that of the cation $[(\text{pbpy})\text{Ru}(\mathbf{1})\text{Ru}(\text{pbpy})]^{3+}$ ($\lambda_{\text{max}} = 1657$ nm, 6035 cm^{-1} ; $\epsilon = 25000$ – 30000).

In conclusion, we have demonstrated that the nickel(0) coupling of metal-complexes of halogenoarenes provides a highly efficient method for the direct formation of metal complexes of higher oligopyridines. We have also shown that the strong electronic interactions between the metal centres reported in complexes of tpbph^{2-} are a consequence of the presence of the N_5C donor sets and not of the presence of the specific tpbph^{2-} ligand.

We thank the SERC and Ciba-Geigy plc for support, and Michael J. Hannon for considerable assistance with some aspects of this work.

Received, 14th June 1993; Com. 3/03412G

References

- G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano and V. Balzani, in *Perspectives in Coordination Chemistry*, ed. A. F. Williams, C. Floriani and A. E. Merbach, VHC, Basel, 1992, p. 153; G. Denti, S. Serroni, S. Campagna, V. Ricevuto and V. Balzani, *Coord. Chem. Rev.*, 1991, **111**, 227; C. Steel and F. Vögtle, in *Perspectives in Coordination Chemistry*, ed. A. F. Williams, C. Floriani and A. E. Merbach, VHC, Basel, 1992, p. 31; L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. Von Zelewsky, C. Seel, M. Frank and F. Vögtle, *Coord. Chem. Rev.*, 1991, **111**, 255; M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 1321; G. R. Newkome, F. Cardullo, E. C. Constable, C. N. Moorefield and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1993, 925; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1992, 617; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, in *Supramolecular Chemistry*, ed. V. Balzani and L. de Cola, Kluwer, Dordrecht, 1992, p. 319; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, *Supramolecular Chem.*, accepted for publication.
- J.-P. Collin, M. Beley, J.-P. Sauvage and F. Barigelletti, *Inorg. Chim. Acta*, 1991, **186**, 91; P. Revco, J. H. Medley, A. R. Garber, N. S. Bhacca and J. Selbin, *Inorg. Chem.*, 1985, **24**, 1096; P. Revco, R. H. Schmehl, W. R. Cherry and F. R. Fronczek, *Inorg. Chem.*, 1985, **24**, 4078; P. Revco, W. R. Cherry, J. H. Medley, A. R. Garber, R. J. Gale and J. Selbin, *Inorg. Chem.*, 1986, **25**, 1842.
- M. Beley, S. Chodorowski, J.-P. Collin and J.-P. Sauvage, *Tetrahedron Lett.*, 1993, **34**, 2933.
- M. Beley, J.-P. Collin, R. Louis, B. Metz, and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1991, **113**, 8521.
- J.-P. Collin, P. Lainé, J.-P. Launay, J.-P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434; F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1993, 942.
- E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 3467; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, *Polymer Prepr. Am. Chem. Soc., Div. Polym. Chem.*, 1993, **34**, 110.
- E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher and M. A. M. Daniels, *New J. Chem.*, 1992, **16**, 855.
- E. C. Constable and M. J. Hannon, *Inorg. Chim. Acta*, in the press.