Reversible cyclometallation at a ruthenium(II) centre

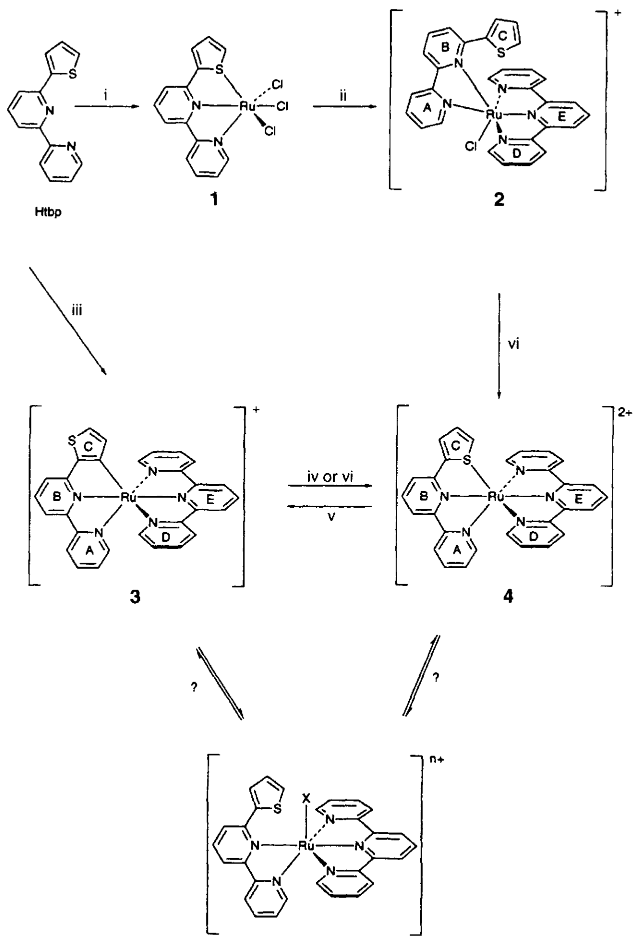
Edwin C. Constable,* Simon J. Dunne, David G. F. Rees and Chantal X. Schmitt

Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland

The metallated complex [Ru(tbp)(tpy)][PF$_6$] [Htbp = 6-(2-thienyl)-2,2′-bipyridine, tpy = 2,2′:6′,2″-terpyridine] is converted to the non-metallated species [Ru(Htbp)(tpy)][PF$_6$] containing an N,N,S-bonded Htbp ligand upon treatment with acid; this process is reversed upon reaction of [Ru(Htbp)(tpy)][PF$_6$] with aqueous sodium hydroxide solution.

Cyclometallation represents a facile method for the activation of aromatic rings[1] and we are interested in defining the structural features which delineate such bonding modes when heteroaromatic compounds are involved.[2,3] Although various mechanistic details relating to cyclometallation at square-planar d^8 centres are known, little is known about the course of reaction at octahedral d^6 centres. In this communication, we report the pH dependent reversible cyclometallation of 6-(2-thienyl)-2,2′-bipyridine (Htbp) at a ruthenium(II) centre.

The ligand Htbp was prepared as previously described.[4] The reaction of Htbp with 'ruthenium trichloride' in ethanol yields [Ru(Htbp)Cl$_3$] **1** containing an S,N,N-bonded ligand (Scheme 1). This reacts in turn with tpy (tpy = 2,2′:6′,2″-terpyridine) to yield a crimson solution from which the salt [Ru(Htbp)(tpy)Cl][PF$_6$] (*m/z* 608, {Ru(Htbp)(tpy)Cl}) is readily isolated.†[5] This product is entirely analogous to the non-metallated complex [Ru(Hpbp)(tpy)Cl][PF$_6$] obtained from the reaction of Hpbp (Hpbp = 6-phenyl-2,2′-bipyridine) with [Ru(tpy)Cl$_3$]. The conformation **2** of the non-metallated complex is confirmed by the observation of a resonance at δ 10.25 assigned to H^{6A} in the ^{1}H NMR spectrum [Fig. 1(*a*)] which is characteristic of H^6 of a pyridine ring *cis* to a chloro ligand.[6] We have previously rationalised the formation of complexes with conformation **2** in terms of their kinetic stability with respect to conversion to the cyclometallated species.[6] The



Scheme 1 *Reagents and conditions*: i, RuCl$_3$, EtOH; ii, tpy; iii, [Ru(tpy)Cl$_3$]; iv, dilute HCl; v, aqueous NaOH; vi, MeCO$_2$H, reflux

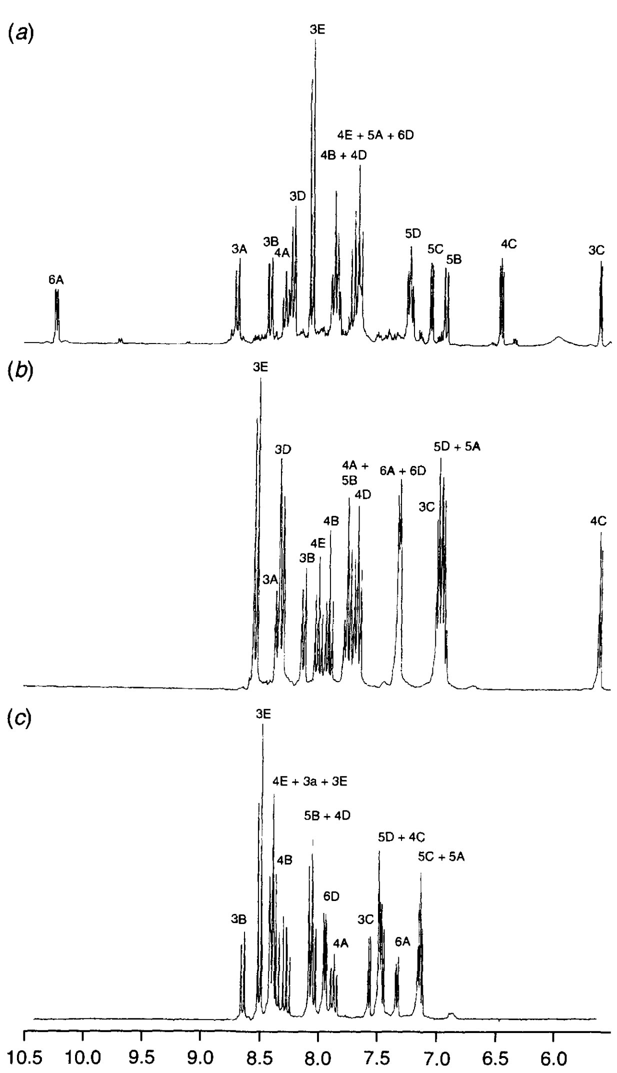


Fig. 1 Partial 300 MHz ^{1}H NMR spectra of CD$_3$CN solutions of (*a*) [Ru(Htbp)(tpy)Cl][PF$_6$] **2**, (*b*) [Ru(tbp)(tpy)[PF$_6$] and (*c*) [Ru(Htbp)-(tpy)[PF$_6$]$_2$. All assignments made by COSY spectroscopy and numbering scheme as indicated in the reaction scheme.

presence of the non-coordinated thiophene ring is confirmed by an AMX pattern (δ 5.69, 6.55 and 7.07) assigned to H^{3C}, H^{4C} and H^{5C} ($J_{3,4}$ 3.4 Hz, $J_{4,5}$ 5.1 Hz) respectively. The ruthenium(II)/(III) couple of this complex (+0.43 V *vs.* ferrocene) is typical of ruthenium in an N_5Cl environment {*cf.* [Ru(tpy)(bpy)Cl]$^+$ (bpy = 2,2′-bipyridine), +0.42 V[6]}.

In contrast, the reaction of Htbp with [Ru(tpy)Cl_3] in water-rich conditions (methanol–water, 90:10) resulted in the near-exclusive formation of a cyclometallated species **3** which was isolated as the purple salt [Ru(tbp)(tpy)][PF_6] (*m/z* 572, [Ru(tbp)(tpy)]) in 75% yield. The ^1H NMR spectrum of a CD_3CN solution of this complex is presented in Fig. 1(*b*), and the cyclometallated formulation is confirmed by the observation of two doublets (δ 5.74, H^{4C} and 7.01, H^{5C}; $J_{4,5}$ 4.65 Hz) for the metallated thiophene ring. The complex is redox active and the ruthenium(II)/(III) couple of +0.16 V is typical of an N_5C donor set about the metal centre {*cf.* [Ru(tpy)(pbp)]$^+$, +0.12 V [6]}.

Although solutions of [Ru(tbp)(tpy)][PF_6] are thermally stable, we noted that an orange compound (**4**) was formed upon standing in light. Irradiation resulted in the complete conversion to this orange compound. The same orange species was obtained when either [Ru(tbp)(tpy)][PF_6] or [Ru(Htbp)(tpy)Cl][PF_6] were heated in glacial acetic acid, or when [Ru(tbp)(tpy)][PF_6] was treated with dilute hydrochloric acid. The mass spectrum of this species exhibits only three clusters of peaks above *m/z* 400; *m/z* 718 [Ru(Htbp)(tpy)][PF_6], 592 [Ru(Htbp)(tpy)F] and 572 [Ru(Htbp)(tpy)]. The ruthenium(II)/(III) potential of +0.665 V is indicative of an N_5X donor set, in which X is an electron rich donor. These data suggest that the orange compound might contain an S-bonded thiophene ligand. The ^1H NMR spectrum of a CD_3CN solution is presented in Fig. 1(*c*). No resonances associated with coordinated solvent were observed. The most characteristic feature is the observation of an AMX pattern for the coordinated but non-metallated thiophene ring (δ H^{3C}, 7.53; H^{4C}, 7.43; H^{5C}, 7.01). These values correlate well with those for the coordinated ring in [Ru(Htbp)$_2$Cl]$^+$ (δ H^{3C}, 7.66; H^{4C}, 7.30; H^{5C}, 7.18). We therefore formulate the product as [Ru(Htbp)(tpy)][PF_6]$_2$ containing an N,N,S-bonded Htbp ligand.

Formally, the interconversion of the cyclometallated ring to the (coordinated) non-metallated ring is a protonation and the conversion of **3** and **4** was achieved by treatment with acid. We were intrigued by this observation, because in related reactions at square-planar palladium(II) centres, reactions in glacial acetic acid lead to the cyclometallated species.[2] The reactivity at the octahedral centre was clearly different and we decided to investigate the reaction of [Ru(Htbp)(tpy)][PF_6]$_2$ with base. Treatment of an orange aqueous acetonitrile solution of [Ru(Htbp)(tpy)][PF_6]$_2$ with aqueous sodium hydroxide resulted in the formation of a purple solution from which the cyclometallated compound [Ru(tbp)(tpy)][PF_6] could be isolated in quantitative yield. This compound was identical in all respects with **3** prepared directly from Htbp and could be subsequently converted back to **4** upon treatment with acid.

To the best of our knowledge, the above observations represent the first example of a fully reversible cyclometallation system. We believe that the introduction of the donor atom into the ring which is capable of metallation is responsible for this behaviour. The putative intermediate leading to cyclometallation is of the form **5**. Unlike the Hpbp ligand, it is now possible for such an intermediate to lead to *either* **3** *or* **4**. We are currently investigating other systems which are expected to show such behaviour.

We should like to thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant numbers: 21-37325.93 and 20-043359.95), and the University of Basel and Ciba-Geigy for support.

Footnote

† All new compounds were fully characterised.

References

1 I. Omae, *Organometallic Intramolecular Coordination Compounds*, Elsevier, Amsterdam, 1986; M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567.

2 E. C. Constable, *Polyhedron*, 1984, **8**, 1037.

3 See for example: A. M. W. Cargill Thompson, E. C. Constable, J. Cherryman and T. Liddiment, *Inorg. Chim. Acta*, 1955, **235**, 165; E. C. Constable and A. M. W. Cargill Thompson, *Supramol. Chem.*, 1994, **4**, 95 and references therein.

4 E. C. Constable, R. P. G. Henney and T. A. Leese, *J. Organomet. Chem.*, 1989, **361**, 277.

5 E. C. Constable, R. P. G. Henney and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 2335; *J. Chem. Soc., Chem. Commun.*, 1989, 913.

6 E. C. Constable and M. J. Hannon, *Inorg. Chim. Acta*, 1993, **211**, 101.

7 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

Received, 21st February 1996; Com. 6/01271J