Anion binding in (arene)ruthenium(II)-based hosts†

Sara Jane Dickson,[a] Stefano C. G. Biagini[b] and Jonathan W. Steed*[a]

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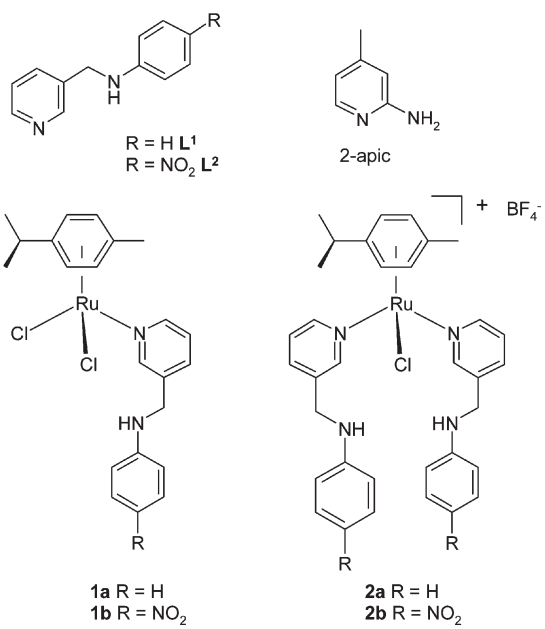
Asymmetric ruthenium(II) complexes of a flexible aminomethylpyridine derivative exhibit diastereotopic ligand methylene protons, as measured by NMR spectroscopy; binding of external anions renders these protons equivalent possibly by increasing dynamically averaged symmetry; the amount of anion needed to raise average symmetry correlates to the anion binding constant.

There is currently a great deal of interest in the use of transition metal ions as sensing and structural elements in the design of supramolecular hosts for anions.[1–4] An early report by Hamilton *et al.* concerning Ru(II) terpyridyl-thiourea derivatives[5] has been followed by recent results on monodentate pyridylurea complexes[6–11] and anion binding by coordinated, chelating biimidazole complexes.[12,13] Anion templation has also been used to guide self-assembly of coordination complexes, as in the elegant helicates reported by Rice and co-workers.[14] We have previously reported anion binding and sensing by 3-aminopyridine ruthenium(II) derivatives, in which the semi-labile Ru(II) centre acts as a structural 'core', organising the two anion-binding aminopyridine ligands.[15] We now report the extension of this chemistry to extended 3-aminomethylpyridine derivatives and the consequences on the compounds' anion-binding behaviour and symmetry.

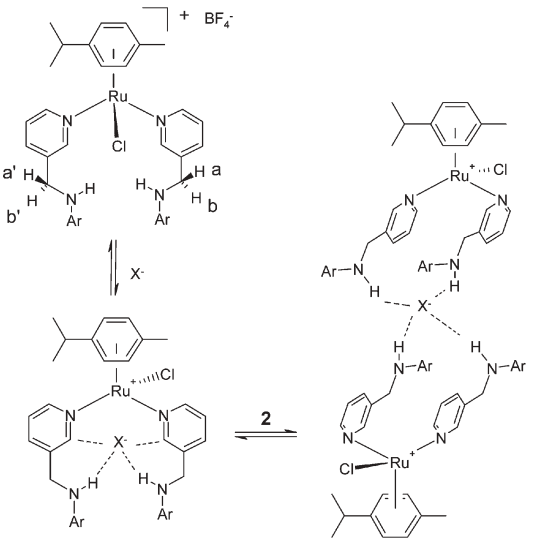
Ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ are readily prepared from the reaction of pyridine 3-carboxaldehyde with aniline and *p*-nitroaniline, respectively, followed by reduction with sodium borohydride. Reaction of these ligands with the chloro-bridged dimer $[\{Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mu\text{-}Cl)\}_2]$[16] in toluene solution results initially in the adducts $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl_2(\mathbf{L^1})]$ (**1a**) and $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl_2(\mathbf{L^2})]$ (**1b**). Treatment of complexes of type **1** with one equivalent of $AgBF_4$ and additional $\mathbf{L^1}$ or $\mathbf{L^2}$ in methanol–acetone (1 : 1 v/v) solution gives the monocationic Ru(II) complexes $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mathbf{L^1})_2]BF_4$ (**2a**) and $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mathbf{L^2})_2]BF_4$ (**2b**). The new complexes were fully characterised by elemental analysis, ESI-MS, IR spectroscopy (nujol) and ^1H and $\{^1H\}$-^{13}C NMR spectroscopy (see ESI†). The ^1H NMR spectrum of complex **2a** shows a broad AB quartet resonance assigned to the methylene protons, $H^{a,a'}$ and $H^{b,b'}$ (Scheme 1) at 4.40 and 4.32 ppm, with ^2J = 17.2 Hz, consistent with geminal coupling. In contrast, in the ^1H NMR spectrum of the free ligand and in complex **1a** this resonance occurs as a singlet at 4.36 and 4.58 ppm, respectively. The inequivalence of protons H^a and H^b must arise from the fact that the molecule is point group C_s and H^a and H^b (Scheme 1) are not related by the mirror symmetry of the molecule. Instead, the mirror plane relates H^a to $H^{a'}$ and H^b to $H^{b'}$. These protons remain diastereotopic even without invoking any restricted rotation or effects such as intramolecular hydrogen bonding of the amine protons to the coordinated chloride ligand.[8,17,18] The resonance assigned to the NH protons in **2a** occurs at 5.37 ppm, the downfield chemical shift suggests enhanced hydrogen bonding compared to the free ligand and **1a** (δ 4.19 and 4.40 ppm, respectively) and presumably arises from hydrogen bonding to the BF_4^- anion. Examination of X-ray crystal structures of related 2-aminopyridine derivatives[19] including the 2-amino-4-picoline (2-apic) complex $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl_2(2\text{-apic})]$ (**3**) (see ESI†) shows that intramolecular hydrogen bonding to halides in these types of complexes is possible for *ortho* aminopyridines. However, examination of molecular models and the structure of the related nicotinamide (nic) complex $[Tl_2Cl_4(\mu\text{-}Cl)_2(nic)_4]\cdot 2nic$[20] shows that it is impossible for complexes of type **2**. The intrinsic asymmetry of **2a** is supported by a dilution study. The chemical shift of the NH resonance remains essentially unchanged across the concentration range 1.9–31.0 mol dm^{-3}. Any intermolecular association would be expected to exhibit concentration dependence.



Compound **2b** behaves similarly to **2a**, with the presence of the nitro group designed to enhance the hydrogen bond acidity of the

[a]*Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: jon.steed@durham.ac.uk; Fax: +44 (0)191 384 4737; Tel: +44 (0)191 334 2085*
[b]*School of Physical Sciences, University of Kent Canterbury, Kent, UK CT2 7NH*

† Electronic supplementary information (ESI) available: Experimental details and crystal structure information for compound **3** (CCDC 657924) in CIF or other electronic format. See DOI: 10.1039/b712699a



Scheme 1 Anion binding by complex **2** forms both 1 : 1 and 2 : 1 host : guest complexes.

secondary amine. The NH resonance occurs at 6.67, 5.94 and 4.92 ppm for **2b**, **1b** and **L**[2], respectively. The strongly hydrogen bonded nature of the NH proton is evident from the observation of coupling to the methylene resonances H^a and H^b, while this coupling is barely resolved for **2a**. Similarly, in the IR spectrum of **2b** the *ν*(NH) stretch occurs at lower wavenumber than in **2a**.

Complexes **2** were designed as hosts for binding anions external to the complex. Their anion complexation ability was determined from ^{1}H NMR spectroscopic titrations with a variety of anions as their tetrabutylammonium salts in $CDCl_3$ solution. Anion binding constants for the formation of 1 : 1 and 2 : 1 host : guest complexes are given in Table 1. The use of both 1 : 1 and 2 : 1 stoichiometry models for complexes **2** is consistent with previous work on 3-aminopyridine derivatives that suggests the formation of compounds in which a single anion is sandwiched between two hosts[15] and resulted in a much improved fit to the titration data than a 1 : 1 model alone. The stoichiometry was confirmed by Job plot analysis for **2a** binding Br^- which gave a maximum of 0.66 (Fig. 1). Furthermore, an ESI-mass spectrum of **2a** in the presence of 0.5 equivalents of NBu_4Br gave a peak at *m*/*z* 1357, corresponding to $\{(\mathbf{2a})_2Br\}^+$. Job plot analysis of the corresponding chloride complex suggests only 1 : 1 binding, however, and the

Table 1 Anion binding constants (M^{-1}) for complexes **1** and **2** in $CDCl_3$ at 20 °C. Errors are <10%, anions added as NBu_4^+ salts, host concentration 0.006 mol dm^{-3} (dash indicates not measured)

	K_{11} and K_{21}/M^{-1}			
Anion	**1a**	**1b**	**2a**	**2b**
Cl^-	~0	102	K_{11} 4325 K_{21} 209[a]	K_{11} 11 020 K_{21} 357
Br^-	—	—	K_{11} 1870 K_{21} 102	K_{11} 4630 K_{21} 432
NO_3^-	~0	—	K_{11} 115 K_{21} 72	K_{11} 2770 K_{21} 468
$CF_3SO_3^-$	~0	—	K_{11} 87[a] K_{21} 69	K_{11} 198 K_{21} 175
$MeCO_2^-$	—	—	K_{11} 3390 K_{21} 174[a]	K_{11} 13 240 K_{21} 962

[a] Large error.

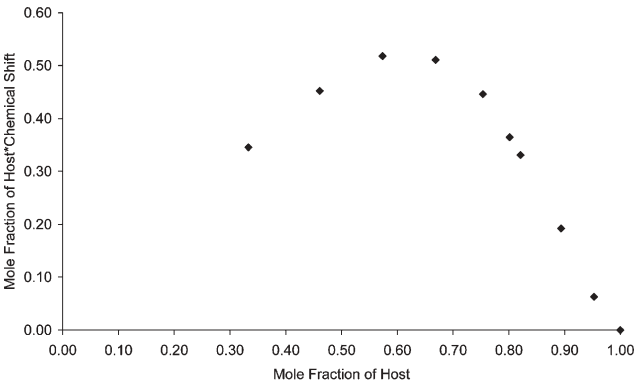


Fig. 1 Job plot for **2a** binding Br^-.

second binding constant is presumably much smaller than the first. The single formal charge on the host presumably allows two hosts to fit around a single anion without severe electrostatic repulsion. Interestingly, virtually no displacement of the unidentate pyridyl ligands was observed during the titrations even in the presence of nucleophilic anions such as Cl^-, in contrast to previous work on 3-aminopyridine derivatives.[15] However, leaving a sample of **2a** overnight in the presence of one equivalent of Cl^- led to the formation of *ca.* 20% **1a**.

The titration results reveal that control compound **1a** does not bind anions, while a very small affinity is noted for the more acidic hydrogen bond donor **1b**. Compounds **2a** and **2b** are both effective anion hosts, however, with the nitro-substituted **2b** consistently binding more strongly than **2a**. The hosts are moderately selective for chloride and acetate, consistent with anion basicity. Titrations with HSO_4^- and $H_2PO_4^-$ resulted in precipitation in the case of **2b** and small chemical shift changes for **2a**. Surprisingly, monitoring the appearance of the ^{1}H NMR resonance assigned to the methylene protons H^a and H^b as a function of added anion showed that addition of strongly bound anions that are good hydrogen bond acceptors rapidly results in the collapse of this resonance to a singlet. In contrast, weakly interacting anions such as $CF_3SO_3^-$ do not affect the appearance of the resonance even after the addition of a fivefold excess, Fig. 2. In all cases, more equivalents of anion are required to collapse the AB quartet to a singlet for **2a** than for **2b** and the number of equivalents required approximately inversely correlates with the anion binding affinity, thus a singlet methylene resonance is observed for **2a** upon addition of only 0.4 equivalents of Cl^-, while 0.8 equivalents of acetate and two equivalents of nitrate are required. The anion binding equilibria observed for complexes **2** are summarised in Scheme 1. In order to remove the inequivalence of protons H^a and H^b in complexes **2**, anion binding must induce a time-averaged plane of symmetry running along the N–Ru–N axis or involve temporary dissociation of the pyridyl ligand. The latter explanation seems relatively unlikely because we have shown that the displacement of ligand to form **1a** in the presence of chloride takes hours to days (*vide supra*). The magnetic equivalence is also unlikely to occur by anion association to form a transient 20-electron complex since this would not result in increased symmetry in any case other than Cl^- binding. Chloride loss to form a transient 16-electron species is, however, possible and would result in the required symmetry. Thus we tentatively suggest that the evidence is consistent with strong anion association in hosts **2**

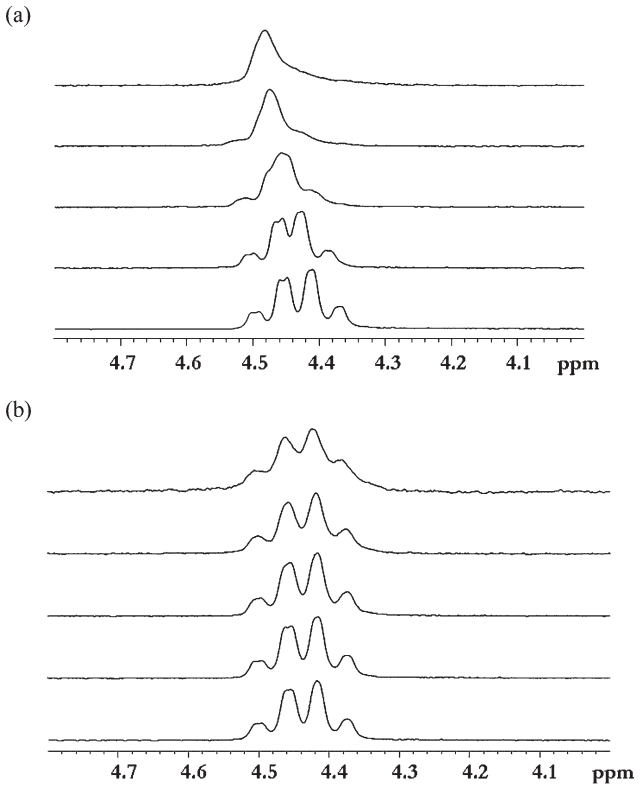


Fig. 2 ^{1}H NMR spectra of the methylene region of host **2a** as a function of (a) added $NBu_4^+Br^-$ and (b) added $NBu_4^+CF_3SO_3^-$ (bottom to top 0, 0.2, 0.5, 1.0 and 5.0 equivalents of anion). In the absence of added anion, the methylenic protons H^a and H^b are inequivalent and appear as a geminal AB quartet with added coupling to the NH proton just visible. Addition of strongly bound anions such as Br^- results in the collapse of the resonance to a singlet after *ca.* one equivalent. Analogous titration with weakly bound anions such as $CF_3SO_3^-$ results in the persistence of the AB quartet to at least 5 equivalents of added anion.

leading to increased lability of the coordinated chloride ligand as a result of electrostatic repulsion, such that in the presence of tightly bound anions X^- the complex is rapidly interconverting between the 18-electron $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)Cl(\mathbf{L^{1/2}})_2]^+\cdot X^-$ and the transient 16-electron $[Ru(\eta^6\text{-}C_6H_4MeCHMe_2)(\mathbf{L^{1/2}})_2]^{2+}\cdot X^-\cdot Cl^-$. Sixteen-electron Ru(II) compounds such as $[RuCl_2(PPh_3)_3]$ are well known in the literature.[21] At present this mechanism remains unproven and is the subject of further study.

In conclusion, we have prepared two robust coordination compound hosts able to bind a range of anions forming both 1 : 1 and 2 : 1 host : guest complexes. These compounds exhibit a novel equilibrium in which anion binding promotes time-averaged equivalence of H^a and H^b. This synergic situation offers a new and, to our knowledge, hitherto unrecognised and unutilised way to fine-tune and monitor anion binding and selectivity. Work is currently in progress on fluorescent sensing analogues of these compounds.

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