

## New Classes of Anion Receptor containing Charged and Neutral Transition Metal Lewis Acidic Recognition Sites

Paul D. Beer,<sup>a</sup> Christian A. P. Dickson,<sup>a</sup> Nicholas Fletcher,<sup>a</sup> Alistair J. Goulden,<sup>a</sup> Alan Grieve,<sup>a</sup> Jana Hodacova<sup>a</sup> and Trevor Wear<sup>b</sup>

<sup>a</sup> *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*

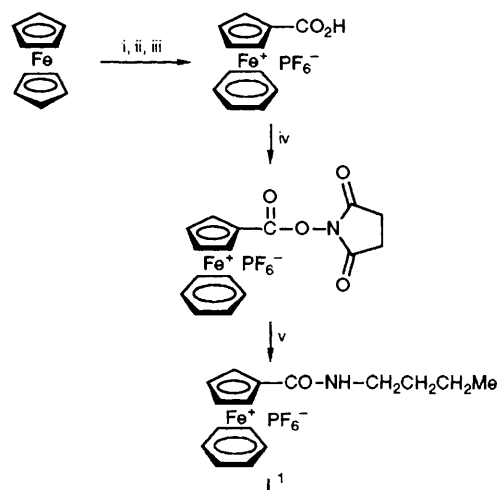
<sup>b</sup> *Kodak Limited, Headstone Drive, Harrow, Middlesex, UK HA1 4TY*

A variety of new classes of anion receptor containing positively charged or neutral organometallic and coordination transition metal Lewis acidic binding sites in combination with amide N–H groups have been prepared and shown to complex halide anionic guest species.

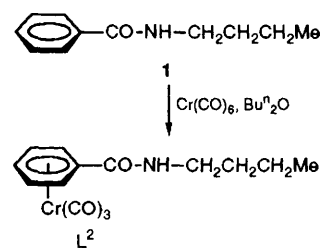
Stimulated by the indispensable role anionic guest substrates are known to play in chemical and biochemical processes the subject area of anion coordination chemistry is of intense current interest.<sup>1</sup> We recently reported two new classes of acyclic anion receptor based on positively charged cobalticinium<sup>2</sup> and polybipyridinium moieties.<sup>3</sup> In the former case anion recognition is greatly enhanced if a closely structurally integrated amide N–H group can form a favourable hydrogen bond with the coordinated anion guest. As an extension to this experimental observation we reasoned that in principle any Lewis acidic binding site in close proximity to one or more amide N–H groups may lead to the successful molecular recognition of an anionic guest species. This communication provides substantial evidence in support of this simple concept through the design, synthesis and preliminary anion coordination chemistry of a variety of new classes of anion receptor incorporating positively charged or neutral organometallic and coordination transition metal Lewis acidic binding sites in combination with amide N–H groups.

The new amide arene cyclopentadienyl iron cation hexafluorophosphate salt L<sup>1</sup> and neutral amide arene tricarbonyl chromium compound L<sup>2</sup> were prepared according to Schemes 1 and 2.†

The addition of tetrabutylammonium chloride or bromide salts to deuteriated acetonitrile <sup>1</sup>H NMR solutions of L<sup>1</sup> and L<sup>2</sup> resulted in remarkable shifts of the respective protons of both receptors. Of particular note are the substantial downfield shifts of the amide protons, Δδ = 2.5 ppm for L<sup>1</sup>, and 0.9 ppm for L<sup>2</sup> with chloride. Interestingly negligible shifts were

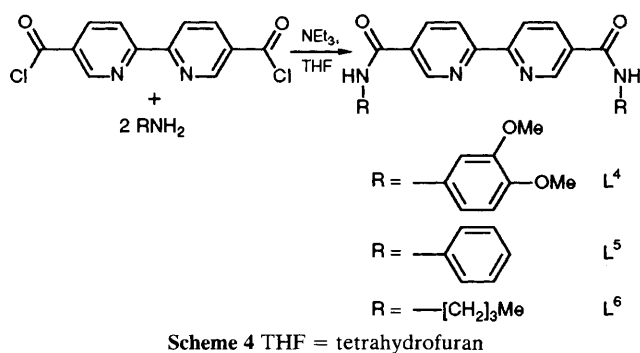
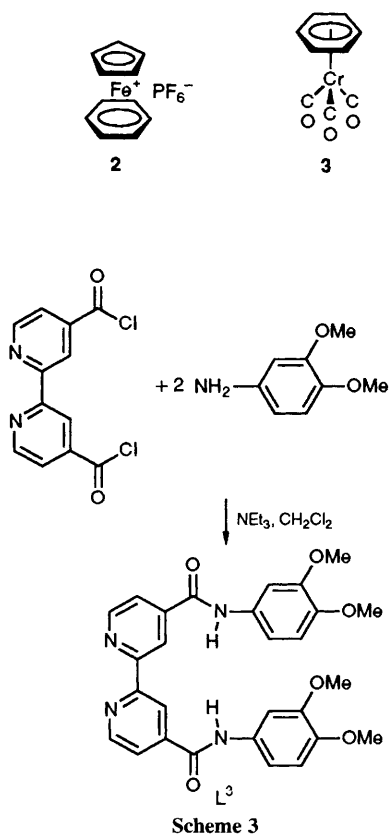


**Scheme 1** Reagents and conditions: i, CO<sub>2</sub>, Al, AlCl<sub>3</sub>, benzene; ii, H<sub>2</sub>O; iii, NH<sub>4</sub>PF<sub>6</sub>; iv, *N*-hydroxysuccinimide, *N,N'*-dicyclohexylcarbodiimide, acetone, room temp.; v, Bu<sup>n</sup>NH<sub>2</sub>, Et<sub>3</sub>N, acetone



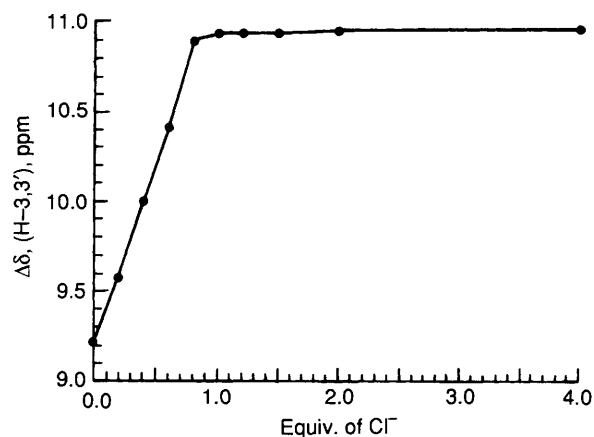
**Scheme 2**

† All new compounds gave spectroscopic and analytical data in accordance with assigned structures.

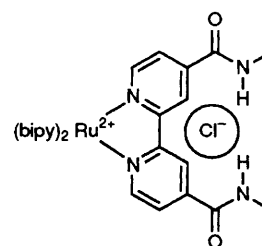


observed under identical experimental conditions with aryl amide **1** and the corresponding benzene organometallic derivatives **2** and **3** suggesting the Lewis acidic organometallic fragment and a significant  $\text{CO}\cdots\text{NH}\cdots\text{halide}$  anion hydrogen bonding interaction is the vital combination for the overall anion recognition process.

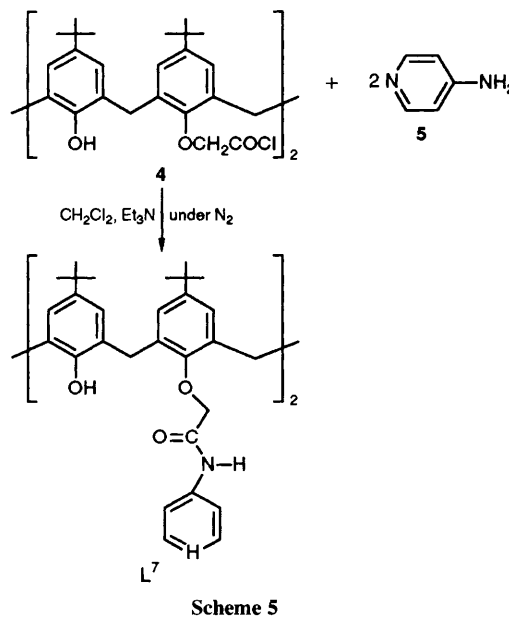
The new 4,4'- and 5,5'-amide disubstituted bipyridine ligands  $\text{L}^3$ – $\text{L}^6$  were synthesised in high yields *via* condensation reactions of respective 4,4'- and 5,5'-bis(chloro)carbonyl-2,2'-bipyridines<sup>4</sup> with appropriate primary aryl and alkyl amines (Schemes 3 and 4). The ruthenium(II) complexes  $[\text{RuL}^3\text{--}6(\text{bipy})_2][\text{PF}_6]_2$  were obtained by refluxing the appropriate ligand with  $[\text{RuCl}_2(\text{bipy})_2]\cdot 2\text{H}_2\text{O}$ <sup>5</sup> in ethylene glycol, followed by purification on Sephadex LH-20 and precipitation of the complexes on addition of ammonium hexafluorophosphate. Neutral platinum(II) complexes  $[\text{PtCl}_2\text{L}]$  were prepared from aqueous ethanolic solutions of ligand and  $\text{K}_2\text{PtCl}_4$ . Evidence for chloride and bromide anion recognition came from <sup>1</sup>H NMR titration studies in acetonitrile with tetrabutylammonium halide salts. Noteworthy perturbations of the amide and bipyridyl-H-3,3' protons were observed; for example with  $[\text{RuL}^3(\text{bipy})_2][\text{PF}_6]_2$ ,  $\Delta\delta = 1.72$  ppm ( $-\text{CONH}-$ ) and 1.41



**Fig. 1** <sup>1</sup>H NMR titration curve of  $[\text{RuL}^3(\text{bipy})_2][\text{PF}_6]_2$  and  $\text{Cl}^-$  in  $\text{CD}_3\text{CN}$  solution; shift of bipy H-3,3'

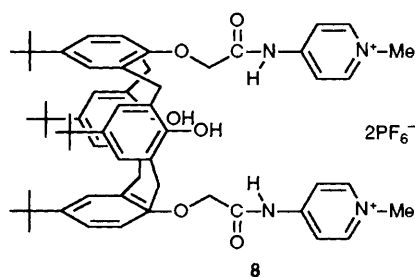
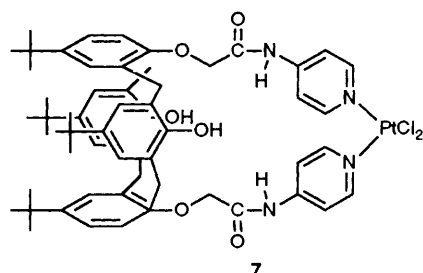
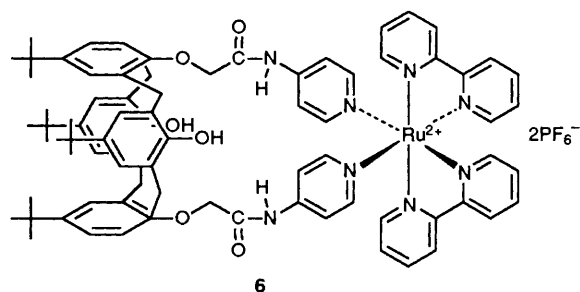


**Fig. 2** Proposed solution complex of  $[\text{RuL}^3(\text{bipy})_2][\text{PF}_6]_2$  and  $\text{Cl}^-$



ppm ( $-\text{H}-3,3'$ ) on addition of one equivalent of chloride. In all cases the titration curves suggested 1:1 solution complexes (Fig. 1) in which the halide guest anion is coordinating in a chelate fashion in close proximity to the two amide N-H groups and nearby Lewis acidic transition metal (Fig. 2).<sup>‡</sup> In addition cyclic voltammetric electrochemical investigations in acetonitrile revealed the respective ligand-centred reduction waves of  $[\text{RuL}^3\text{--}6(\text{bipy})_2][\text{PF}_6]_2$  to undergo cathodic shifts of up to 50 mV in the presence of chloride. No halide interactions with  $[\text{Ru}(\text{bipy})_3][\text{PF}_6]_2$  itself or the  $[\text{PtCl}_2(\text{bipy})]$  complex were observed under analogous proton NMR and electrochemical experimental conditions.

<sup>‡</sup> No halide induced proton shifts were observed with the free ligands.



To illustrate further how to incorporate and convert host structural frameworks into potential anion receptors the new calix[4]arene receptor molecule **L**<sup>7</sup> was prepared *via* the condensation reaction of **4**<sup>6</sup> and two moles of 4-aminopyridine **5** (Scheme 5). Although <sup>1</sup>H NMR titration investigations in acetonitrile revealed **L**<sup>7</sup> itself not to coordinate halide anions the corresponding [RuL<sup>7</sup>(bipy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **6**, [PtL<sup>7</sup>Cl<sub>2</sub>] **7** and quaternised **8** derivatives all formed 1:1 solution complexes with chloride and bromide anionic guests in which pyridyl, amide and methylene -OCH<sub>2</sub>- proton shifts of up to 0.9 ppm were observed. Thus, whilst calix[4]arenes and crown ether-

modified calix[4]arene<sup>8</sup> host molecules are known to form solution complexes with organic and metal cationic guest species, **6-8** represent the first examples of calix[4]arene anion receptors.

In conclusion we have demonstrated that a variety of new receptors containing charged or neutral organometallic and coordinated transition metal Lewis acidic centres combined with amide N-H groups can recognise halide anionic guest species *via* mutual electrostatic attraction and favourable amide N-H...anion hydrogen bonding interactions. This simple concept of Lewis acid centre and amide N-H hydrogen bond donor, by appropriate host cavity design, paves the way for the future development of new anion-selective reagents.

We thank the SERC for a CASE studentship to N. F., Kodak for a studentship to A. J. G. and the SERC for use of the Mass Spectrometry Service of University College Swansea, the AFRC for a studentship to A. G. and Serpentix for a postdoctoral research fellowship to J. H.

Received, 29th October 1992; Com. 2/05791C§

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§ Delayed at authors' request.