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Electrochemical Anion Recognition By Novel Ferrocenyl Imidazole Systems

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Abstract: A novel class of anion receptors with with C-H•••X^- hydrogen bonding is introduced and demonstrated for Cl^-, Br^-, NO_3^- and HSO_4^- recognition. Cyclic voltammetry revealed that novel ferrocenylimidazolium salts, syntheses of which are briefly described, selectively complex and electrochemically recognise guest anions. Futhermore, proton NMR spectroscopy indicated the formation of 1:2 stoichiometric complexes with Cl^-, Br^- and I^- and 1:1 stoichiometric complexes with NO_3^- and HSO_4^-.

Keywords: Ferrocenylimidazolium salts; anion receptors; ^{1}H-NMR titrations, cyclo-voltammetry, recognition.

Introduction

The synthesis of receptors designed to coordinate anions is an area of intense current research activity. This is because anions are known to play ubiquitous roles in both chemical and biochemical processes. Indeed, they can act as substrates or cofactors for enzymes [1], and as nucleophiles, base, redox agents and phase transfer catalysts. During the last few years, the combination of LA and NH group as a hydrogen bond donor have been demonstrated to be essential components for anion recognition [2], but more recently the ability of 1,3-disubstituted imidazolium cations to enter into

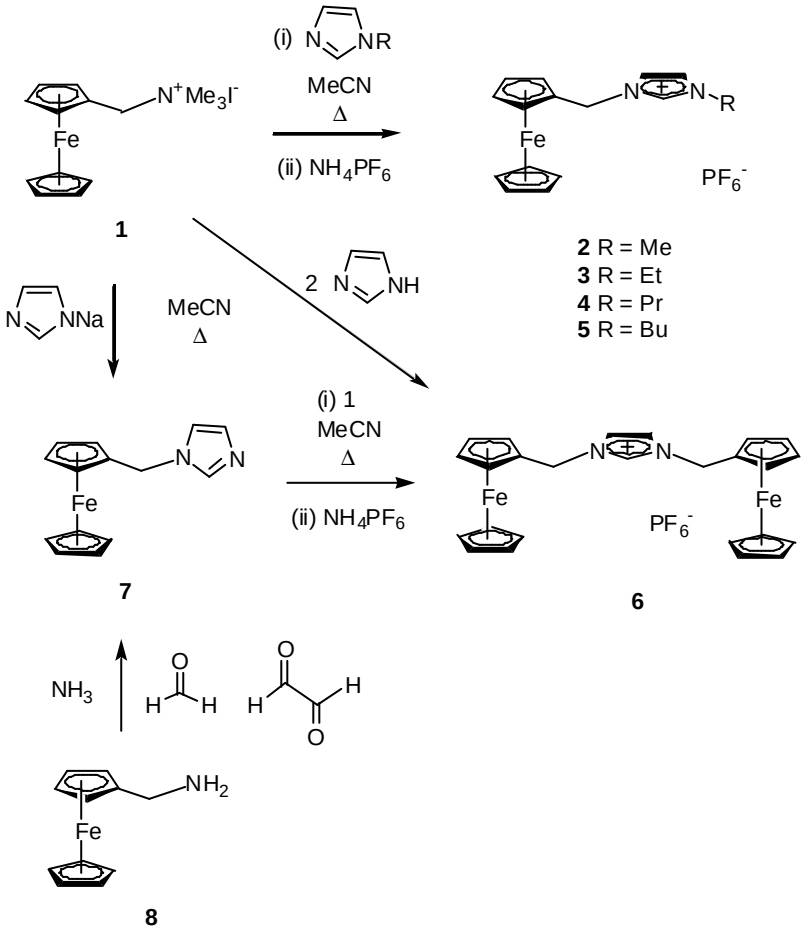
hydrogen bonds with halide ions has developed from not possible to widely accepted using solid-state X-ray crystallography and binding experiments followed by ^{1}H-NMR spectroscopy [3-8]. As part of our investigations into ionic liquids based on imidazolium salts as Lewis acid catalysts [9], and imidazolium based receptors, where we have shown that chiral tripodal systems utilizing the imidazolium moiety may distinguish between a pair of enantiomeric anions [10], we have developed efficient syntheses for several interesting ferrocenyl imidazole derivatives [11] which have shown to have properties as Lewis acids and as anion receptors.

Results and Discussion

^{1}H-NMR titrations

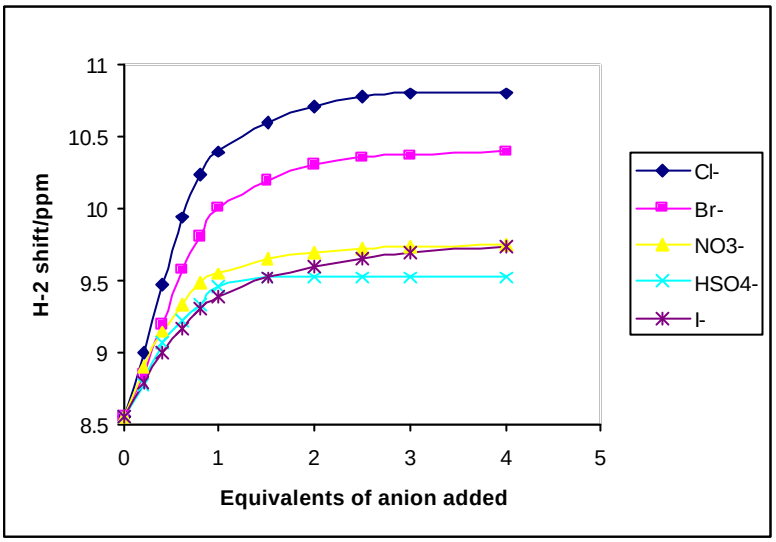
The ferrocenyl imidazolium salts 2-6, synthesised according to Scheme 1, were first tested in the Diels-Alder reaction between methacrolein and cyclopentadiene at low temperature and were shown to act as Lewis acids to produce the desired *endo* and *exo* products in yields between 30 and95% and *endo*/*exo* selectivities of between 75 and 95%. The same reaction carried out without imidazolium salt present gave no product.

Scheme 1



The anion coordination properties of 1,3-di(ferrocenylmethyl)imidazolium hexafluorophosphate (**6**) were then investigated by ^{1}H-NMR titration. Additions of $Bu_4N^+X^-$ (X = Cl, Br, I, NO_3, HSO_4) to $CDCl_3$ solutions of **6** resulted in significant downfield shift of the H-2 of the imidazole ring with concomitant broadening of the signal. The resulting titration curves, Figure 1, suggest a 1:2 imidazolium salt : anion stoichiometry in the case of X = Cl^-, Br^- and I^-, and a 1:1 imidazolium salt : anion stoichiometry in the case of X = NO_3^- and HSO_4^-. Similar results were obtained for compounds **2-5**. X-Ray crystallography, currently under investigation, will confirm the structure in the complexes between these receptors and the halide anions.

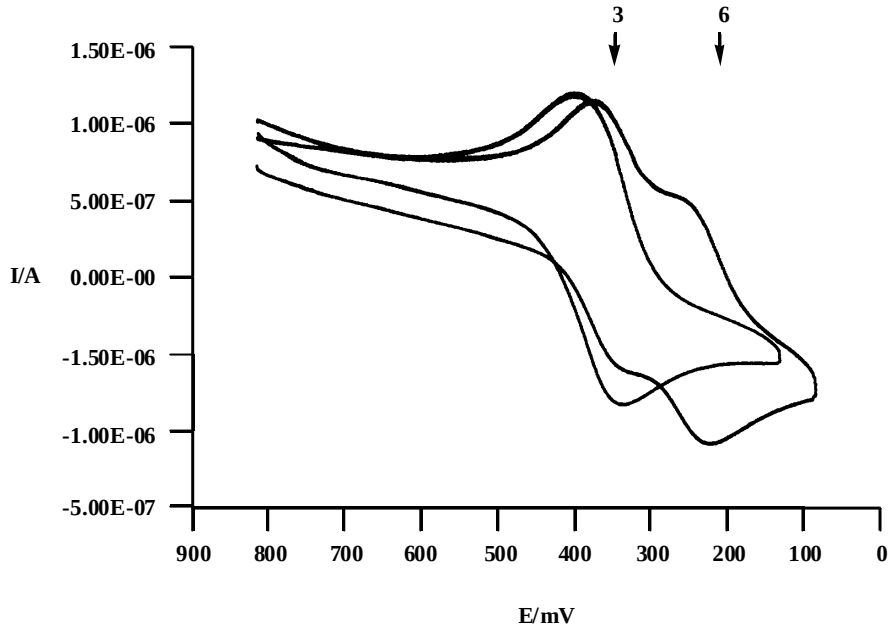
Figure 1. ^{1}H-NMR titration curves of the receptor **6** with anions.



Electrochemical anion recognition

The reversibility of the ferrocene / ferrocenium redox couple in receptors **2-5** was examined and the values obtained for $|E_{pa} - E_{pc}|$ imply good reversibility for a two electron reaction and values of i_{pa} / i_{pc} are all close to unity further supporting this claim, Table 1. The same observations were made in the case of receptor **6**, but this time two cathodic and two anodic waves are observed. Cyclic voltammograms of receptors **3** and **6** are shown in Figure 2.

Figure 2: Cyclic voltammograms of receptors **3** and **6**.



The ferrocene / ferrocenium redox couple was then examined upon addition of five equivalents of counter ion. The counter ion (Cl^-, Br^-, NO_3^-, HSO_4^-) was added in the form of its tetrabutyl ammonium salt. The results of the electrochemical analysis, Table 1, show that for the receptors **2-4** the oxidation potential is shifted anodically with increasing substituent size as would be expected.

Table 1: Electrochemical data for receptors **2**-**6**.

Compound	**2**	**3**	**4**	**5**	**6**
$E_{pa\ (free)}$ / mV	274	288	311	293	301
$E_{pc\ (free)}$ / mV	148	173	168	190	176
ΔE_{pa} (Cl^-)[a] / mV	-24	-10	-39	-3	-23
ΔE_{pa} (Br^-)[a] / mV	105	71	142	112	194
ΔE_{pa} (NO_3^-)[a] / mV	-23	-22	-35	-10	-58
ΔE_{pa} (HSO_4^-) / mV	-118	-83	-97	-82	-70
$\lvert E_{pa} - E_{pc}\rvert$[b] / mV	126	115	143	103	125
i_{pa} / i_{pc}[b]	0.986	0.981	1.021	1.002	1.267

[a]Anodic shifts upon 5 equivalents of anion added in the form of the tetrabutylammonium salt. [b]E_{pa} and E_{pc} represent the anodic and cathodic peak potentials and i_{pa} and i_{pc} represent the anodic and cathodic peak currents.

When five equivalents of a particular counter ion were added, the anodic wave was observed to shift to more negative potentials, excluding the bromide salt that gave an observed positive shift. In each case the largest negative shift was observed when five equivalents of the HSO_4^- ion were added, although this shift was always accompanied by a severe distortion of the anodic and cathodic waves. Furthermore the anodic peak current was drastically reduced and the cathodic peak current drastically increased. This phenomenon may be due to consumption of the receptor in a reduction reaction, possibly hydrogenation at the iron centre.

Conclusions

In summary, we have developed a rapid facile synthesis of ferrocenylimidazolium salts which proved to be excellent Lewis acids and act as anion receptors through C-H•••X^- hydrogen bonding forming 1:2 stoichiometric complexes with Cl^-, Br^- and I^- and 1:1 stoichiometric complexes with NO_3^- and HSO_4^-. The electrochemical data obtained for these novel receptors implies that they may be used as anion recognition molecules and possibly even as chemical or biochemical sensors. Further work will consist of the introduction of additional functionality in the ferrocenyl imidazole systems. We believe that these compounds might find uses in fields of research such as sensor materials, ligands for chiral catalysts, supramolecular photochemistry and electrochemistry, to name but a few.

Experimental

General

N-alkyl imidazoles were purchased from Aldrich and MeCN was dried over 4Å molecular sieves. The structures of all new compounds were verified on the basis of spectroscopic and analytical evidence [10]. Cyclic voltammograms were obtained at a scan of 50 mVs^{-1} in MeCN solution containing 0.1 $moldm^{-3}$ nBu_4NBF_4 as supporting electrolyte and $1x10^{-3}$ $moldm^{-3}$ receptors at room temperature. Potentials were determined with reference to a Ag/Ag^+ electrode with Pt working and auxiliary electrodes.

Syntheses of ferrocenylimidazolium salts

Monoferrocenyl substituted imidazolium salts **2-5** were prepared in very good yields by refluxing a solution of (ferrocenylmethyl)trimethylammonium iodide salt **1** [12] and the appropriate *N*-alkyl imidazole in MeCN for 16 h, followed by treatment with NH_4PF_6 (Scheme 1). Di(ferrocenylmethyl)imidazolium salt **6** was formed by heating **1** in MeCN with two equivalents of imidazole, in the presence of sodium carbonate, at reflux for one week, followed by treatment with NH_4PF_6. Compound **6** was also obtained from a 1:1 mixture of **1** and 1-ferrocenylmethylimidazole in MeCN heated under reflux for 16h followed by treatment with NH_4PF_6. Compound **7** was produced

from the reaction of imidazole sodium salt with 1 in MeCN heated under reflux for 16h. Alternatively, **7** can be formed from ferrocenylmethylamine **8** [13] using the conditions given by Arduengo et al. [14].

References

1. Lang, L. G.; Riordon, J. F.; Vallee, B. L. *Biochemistry*, **1974**, *13*, 4361.
2. (a) Beer, P. D.; Hesek, D.; Hadocova, J.; Stokes, S. E. *J. Chem. Soc., Chem. Commun*. **1992**, 270; (b) Beer, P. D.; Hazlewood, C.; Hesek, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc., Dalton Trans.* **1993**, 1327; (c) Beer, P. D.; Chen, Z.; Goulden, A. J.; Graydon, A.; Stokes, S. E.; Wear, T. *J. Chem. Soc., Chem. Commun*. **1993**, 1834; (d) Beer, P. D.; Chen, Z.; Goulden, A. J.; Grieve, A.; Hesek, D.; Szemes, F.; Wear, T. *J. Chem. Soc., Chem. Commun*. **1994**, 1269; (e) Beer, P. D.; Drew, M. G. B.; Hesek, D.; Jagessar, R. *J. Chem. Soc., Chem. Commun*. **1995**, 1187; (f) Beer, P. D.; Hesek, D.; Kingston, J. E.; Smith, D. K.; Stokes, S. E.; Drew, M. G. B. *Organometallics*, **1995**, *14*, 3288; (g) Beer, P. D.; Drew, M. G. B.; Grayton, A. R.; Smith, D. K.; Stokes, S. E. *J. Chem. Soc., Dalton Trans*. **1995**, 403; (h) Beer, P. D.; Drew, M. G. B.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc., Dalton Trans*. **1995**, 3447; (i) Beer, P. D. *Chem. Commun*. **1996**, 689.
3. Dieter, K. M.; Dymek, C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc*. **1988**, *110*, 2722.
4. Dymek, C. J.; Stewart, J. J. P. *Inorg. Chem*. **1989**, *28*, 1472.
5. Lapshin, S. A.; Yu. Chervinskii, A.;. Litvinento, L. M.; Dadali, V. A.; Kapkan, L. M.; Vdovichenko, A. N. *Zh. Org. Khim*. **1985**, *21*, 357.
6. Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans*. **1994**, 3405.
7. Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y.; Welton, T.; Zora, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3467.
8. Sato, K.; Arai, S.; Yamagishi, T. *Tetrahedron Lett*. **1999**, *40*, 5219.
9. Howarth, J.; Hanlon, K.; Fayne, D; McCormac, P. *Tetrahedron Lett.* **1997**, *17*, 3097.
10. Howarth, J.; Al-Hashimy, N. A. *Tetrahedron Lett*. **2001**, *42*, 5777.
11. Howarth, J.; Thomas, J-L.; Hanlon, K.; McGuirk, D. *Synthetic Commun*. **2000**, *30*, 1865.
12. Bublitz, D. E. *J. Organomet. Chem*. **1970**, *2*, 225.
13. Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 2*, **1991**, 751.
14. Arduengo, A. J. US Patent 5,077,414, 1991.
15. Howarth, J.; Hanlon, K. *Tetrahedron Lett.* **2001**, *42*, 751.

Samples Availability: Available from the authors. Other analogues of monoferrocenyl substituted imidazolium salts, see reference [15] for structures, are also available.