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Ferrocenyl imidazolium salts as a new class of anion receptors with C–H···X[−] hydrogen bonding

Jean-Luc Thomas, Joshua Howarth,* Keith Hanlon and Damien McGuirk

School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland

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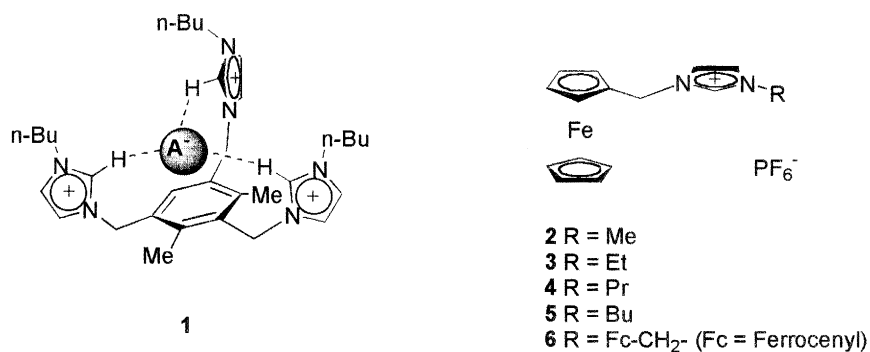
Abstract

Ferrocenylimidazolium salts have been synthesised as novel anion receptors. ¹H NMR studies showed that these compounds bind Cl[−], Br[−], I[−], NO₃[−] and HSO₄[−] anions strongly in CDCl₃ through C–H···X[−] hydrogen bonding. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: ferrocenylimidazolium salts; anion receptors; hydrogen bonding.

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 a metal unit as a Lewis acid together with an amide N–H group as a hydrogen bond donor have been demonstrated to be essential components for anion recognition.² However, over the past decade, 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 ¹H NMR spectroscopy.^{3–7} Recently, the imidazolium derivative **1** has been described as a new anion receptor with C–H···X[−] hydrogen bonding between the hydrogen on the electron-deficient C-2 carbon atom of the imidazolium ring and guest anions such as Cl[−], Br[−] and I[−].⁸ Following the same aim, as part of our investigation into ionic liquids based on imidazolium salts as Lewis acid catalysts,⁹ we have developed efficient syntheses for several interesting ferrocenyl imidazole derivatives **2–6**¹⁰ which proved to act as both Lewis acids and anion receptors.

* Corresponding author. Tel: 353 1 7045312; fax: 353 1 704 5503; e-mail: howarthj@ccmail.dcu.ie (J. Howarth)

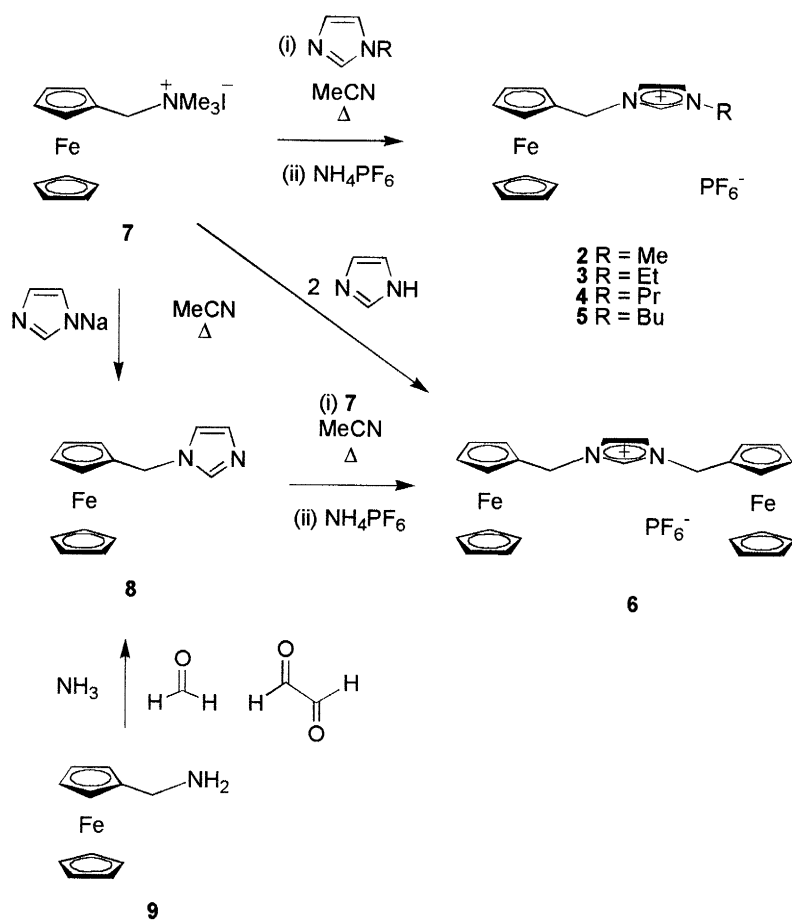


Monoferrocenyl substituted imidazolium salts **2–5** were prepared in very good yields by refluxing a solution of (ferrocenylmethyl)trimethylammonium iodide salt **7**¹¹ and the appropriate *N*-alkyl imidazole in MeCN for 16 h, followed by treatment with NH₄PF₆ (Scheme 1). Di(ferrocenylmethyl)imidazolium salt **6** was formed by heating **7** in MeCN with two equivalents of imidazole, in the presence of sodium carbonate, at reflux for one week, followed by treatment with NH₄PF₆. Compound **6** was also obtained from a 1:1 mixture of **7** and 1-ferrocenylmethylimidazole **8** in MeCN heated under reflux for 16 h followed by treatment with NH₄PF₆. Compound **8** was produced from the reaction of imidazole sodium salt with **7** in MeCN heated under reflux for 16 h. Alternatively **8** can be formed from ferrocenylmethylamine **9**¹² using the conditions given by Arduengo et al.¹³

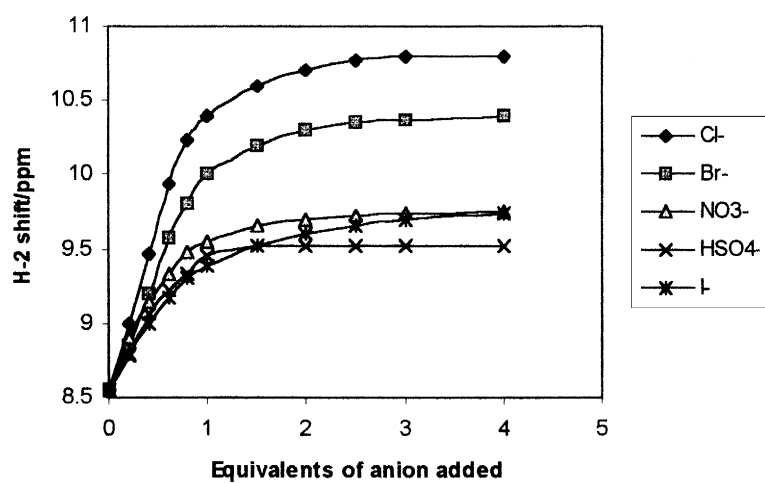
The ferrocenyl imidazolium salts **2–6** were first tested in the Diels–Alder reaction between methacrolein and cyclopentadiene at low temperature and proved to act as Lewis acids to produce the desired *endo* and *exo* products in yields between 30 and 95% and *endo/exo* selectivities of between 75 and 95%. The same reaction carried out without imidazolium salt gave no product. The anion coordination properties of 1,3-di(ferrocenylmethyl)imidazolium hexafluorophosphate **6** were then investigated by ¹H NMR titration. Additions of Bu₄NX (X=Cl, Br, I, NO₃, HSO₄) to CDCl₃ 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 (Fig. 1) suggest a stoichiometry of 1:2 imidazolium salt:halide anion in the case of X=Cl, Br and I, and a stoichiometry of 1:1 imidazolium salt:halide anion in the case of X=NO₃ and HSO₄. 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.

The ferrocene/ferrocenium redox couple is currently being examined upon addition of 5 equivalents of counter ion Cl⁻, Br⁻, NO₃⁻ and HSO₄⁻. The first results of the electrochemical analysis show that for the receptors **2–6**, the oxidation potential is shifted anodically with increasing substituent size. This increasing oxidation potential implies that it is increasingly more difficult to oxidise the receptor as the substituent size increases. In each case the largest negative shift was observed when 5 equivalents of the HSO₄⁻ 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, or possibly hydrogenation at the iron centre. These results and more electrochemical studies of these receptors will be submitted for publications in the near future.

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 NO₃⁻ and HSO₄⁻. 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



Scheme 1.

Fig. 1. ^1H NMR titration curves of the receptor **6** with halide anions

materials, ligands for chiral catalysts, supramolecular photochemistry and electrochemistry, to name but a few.

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