Full Paper

Applied Organometallic Chemistry

Received: 21 August 2012 Revised: 25 September 2012 Accepted: 16 October 2012 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/aoc.2947

Application of ferrocenylimidazolium salts as catalysts for the transfer hydrogenation of ketones

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Ferrocenylimidazolium salts with methylene and phenyl groups bridging the ferrocenyl and alkylimidazolium moieties were synthesized and characterized by spectroscopic and analytical methods. Crystal structures of two new compounds are also reported. Cyclic voltammetry was used to analyze the influence of the two bridging groups or spacers on electrochemical properties of the salts relative to the shifts in the formal electrode or peak potentials (E^0 or $E_{1/2}$) of the ferrocene/ferrocenium redox couple. Results from this study showed that all the salts exhibited higher electrode potentials relative to ferrocene, which is due to the electron-withdrawing effect of the imidazolium ion on the ferrocenyl moiety. Application of the salts as catalysts in transfer hydrogenation of ketones resulted in high conversion of saturated ketones to corresponding alcohols and turnover numbers as high as 1880. The catalysts were chemoselective towards reduction of the C=C bonds of conjugated 3-penten-2-one and 4-hexen-3-one to yield saturated ketones, while unconjugated 5-hexen-2-one was hydrogenated to an unsaturated alcohol. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: ferrocenylimidazolium salts; hydrogen transfer catalysis; cyclic voltammetry; X-ray diffraction

Introduction

Transfer hydrogenation of ketones to the corresponding alcohols has become an important transformation in organometallic chemistry, especially as applied to the pharmaceutical[1] and fine chemical industries.[2] Much of the work conducted to date on catalytic transfer hydrogenation of ketones has utilized effective but expensive and sometimes toxic transition metals such as iridium,[3] platinum,[4] rhodium,[5] gold[6] and ruthenium.[7] Therefore, the search for inexpensive, mild and environmentally friendly catalysts is important in order to expand the scope of available routes to achieving this important reaction. Iron and its compounds such as ferrocene satisfy these requirements.

The synthesis of compounds based on ferrocene such as ferrocenylimidazolium salts has thus attracted interest because of the rich chemistry and applications associated with it.[8] In addition, the functionalization of ferrocene with imidazolium salts gives them unique electronic properties, such as the ability to stabilize reactive carbocations.[9] Also, the powerful donor capacity of ferrocene is in principle advantageous to additional stabilization of electron-deficient carbene moieties and metal centres in high oxidation states.[10,11] This has led to numerous industrial applications in medicine,[12,13] catalysis,[14–21] as sensors[22] and as components of immunoassay reagents.[21,23–28]

Most importantly, applications of these salts in electrochemical processes and as ligand precursors have been noted and, due to the presence of two electro-active groups, i.e. ferrocene and imidazole, ferrocenylimidazolium salts have also found use as molecular recognition species.[29] The presence of ferrocene in ferrocenylimidazolium salts gives rise to a ferrocene/ferrocenium redox couple, the redox potential of which depends on the imidazolium ring *N*-substituents (R in Schemes 1 & 2).[18] Also, the interaction between the ferrocene and the imidazolium ring depends on the nature of the bridge between the two moieties.[29] Thomas *et al.*[30] have synthesized novel ferrocenyl compounds for use as anion recognition molecules, where they investigated the electrochemical properties of the salts by the technique of cyclic voltammetry (CV). Bai *et al.*[31] have also synthesized ferrocenylbenzimidazolium salts and investigated the binding constants of halide (Cl^-, Br^- and I^-) ions to the cation. Studies by Bildstein *et al.*[32] on the electrochemical properties of ferrocenylbenzimidazolium salts, using CV, showed significant electronic communication between the imidazolium moiety and the *N*-ferrocenyl substituent. The CV of iron(II) *N*-heterocyclic carbene (NHC) complexes[33,34] has also been conducted in order to establish the influence of the NHC ligand on the catalytic activity of the iron centre. Hence numerous examples exist in the literature that have established the popularity and wide application of ferrocenylimidazolium salts.[10,35–39]

Furthermore, due to their ability to stabilize various metal centres, their application as ligand precursors in the synthesis of ferrocenyl

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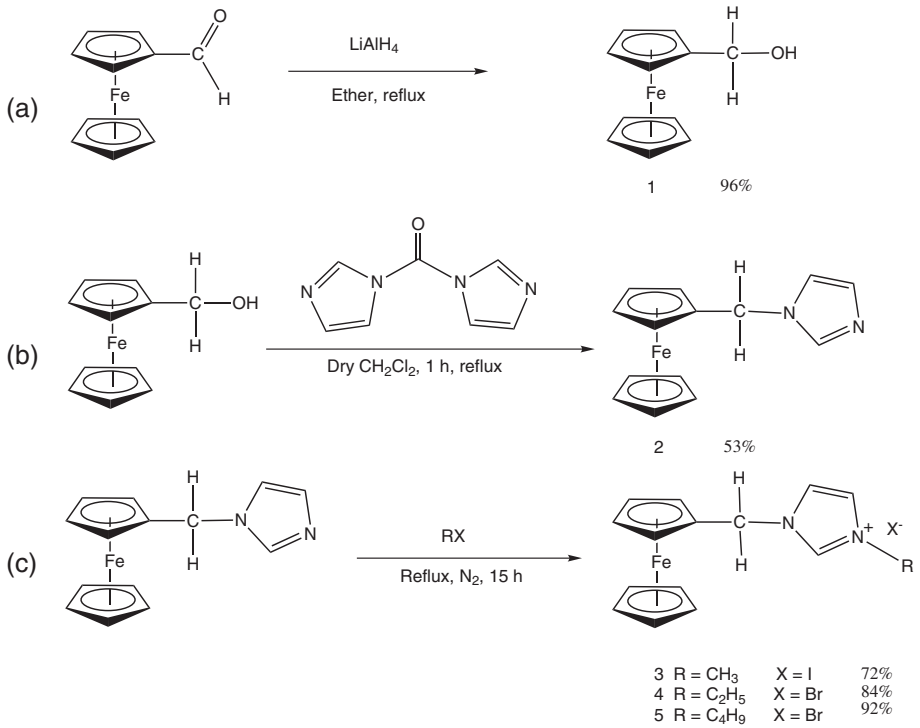
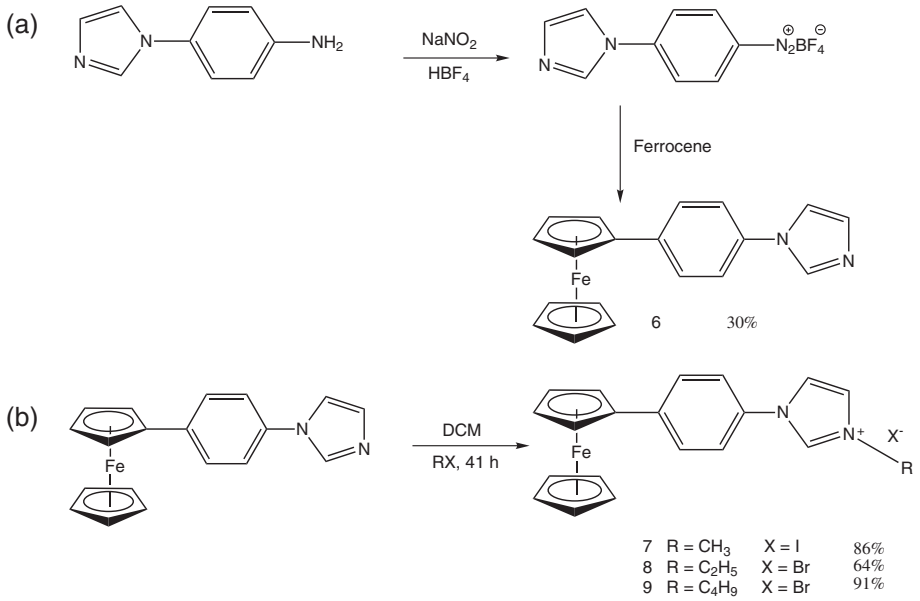


Scheme 1. Synthesis of ferrocenylmethyleneimidazolium salts.



Scheme 2. Synthesis of ferrocenylphenylimidazolium salts.

NHC complexes has been shown to be of great importance. For instance, Bildstein *et al.*[40] have synthesized metal complexes of W(0), Pd(II) and Hg(II) with ferrocenylimidazolium salts. Coleman *et al.*[8] have also synthesized and structurally characterized a palladium(II) ferrocenyl NHC complex. In addition, Seo *et al.*[41] have successfully obtained chiral ferrocenylimidazolium salts and used them as precursors in the synthesis of rhodium and iridium complexes. When applied as catalysts in transfer hydrogenation of ketones, these complexes have shown moderate enantioselectivities. In 2009, Jiang *et al.*[42] reported good enantioselectivities for the transfer hydrogenation of ketones, catalysed by Rh(I) complexes of planar ferrocene-based chiral NHC ligands. To the best of our knowledge, this report presents the first direct use of ferrocenylimidazolium salts as catalysts for the transfer hydrogenation of a wide variety of ketones under relatively mild reaction conditions.

Results and Discussion

Synthesis

Syntheses of the two classes of salts reported herein, one containing a methylene and the other a phenyl group linking

ferrocenyl to imidazolium moieties, were conducted via two different routes. The ferrocenylmethyleneimidazolium salts were synthesized following adaptation of our earlier reported procedure.[43a] In this procedure (Scheme 1), ferrocenylmethyleneimidazole (**2**) was prepared from ferrocenylmethanol (**1**), which in turn was prepared by the reduction of ferrocenecarboxaldehyde with lithium aluminum hydride. The target salts (**3–5**) were obtained through alkylation of **2** with corresponding alkyl halides and subsequent solvent washing with diethyl ether to ensure complete removal of any unreacted **2**. Compounds **3–5** were isolated in relatively high yields (72–92%). Salts **3** and **4** were obtained as yellow powders, while **5** was isolated as a dark-brown powder.

On the other hand, the synthesis of the ferrocenylphenylimidazolium salts was achieved by employing a Gomberg–Bachmann reaction involving diazotisation of 4-(1*H*-imidazol-1-yl)aniline followed by coupling of ferrocene to afford **6** in an improved yield as compared to previously reported results for related reactions (Scheme 2).[39] Alkylation of **6** with the corresponding alkylhalides (RX) generated the target molecules **7–9** in moderate to high yields. Salt metathesis (Scheme 3) with sources of counter-anions yielded compounds **10–12** in high yields (81–96%). The metathesis was conducted in order to widen the variety of counter-anions and investigate in more detail their effects on the physical properties of isolated salts.

It is worth noting that the chemical nature of the spacer (aliphatic or aromatic) that linked the ferrocenyl to the imidazolium moiety had an effect on the physical properties of the salts. As a general trend, the melting points of the ferrocenylmethyleneimidazolium compounds **3–5** and **10–11** were lower than those of the corresponding ferrocenylphenylimidazolium salts **8**, **9** and **12**, the only exceptions being compounds **3** and **7** (see Table 1). The observed trend is attributed to larger molecular sizes of the phenyl-linked salts and extensive network of cooperative pi-pi stacking interactions due to the phenyl linker in **8**, **9** and **12** which provided additional intermolecular attractive forces and stabilization in the solid state. Thus compounds **8, 9** and **12** have higher melting points than the corresponding methylene-linked compounds **3–5** and **10–11**. Compound **10** was isolated as oil, which could be due to a change in the size of the counter-anion. It is well established that a good match in relative ionic size (cation-to-anion) is required for solidification and crystallization of ionic salts.[43,44] Increasing the length of the alkyl chain on the imidazole from methyl to ethyl (**12** and **8**), did not significantly affect the melting point of the ferrocenylphenylimidazolium salts, but when the alkyl length was further lengthened to butyl a decrease in the melting point was observed, which is in agreement with reported literature data where it was attributed to increased degrees of freedom of the alkyl side chain R.[12]

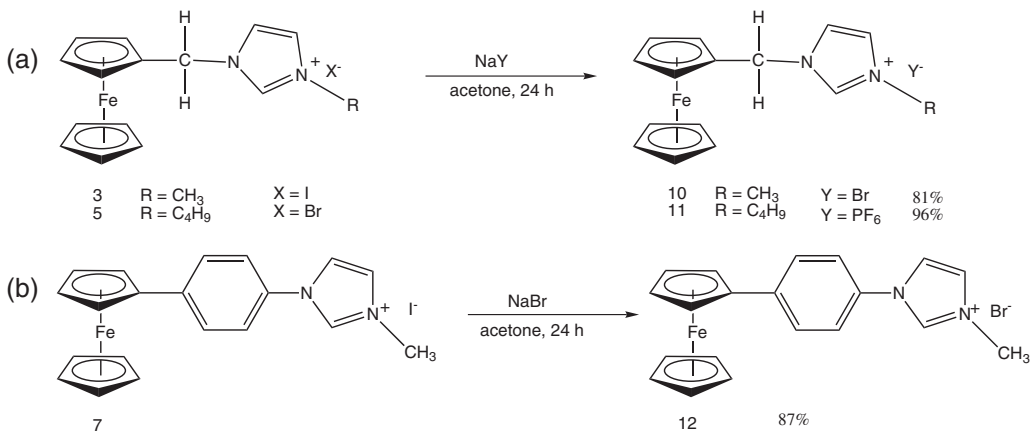
Spectroscopic Characterization

The NMR data give some indication of the level of electronic interaction between the cationic centres and the various anions. A measure of the degree of deshielding of the counter-anions was observed by monitoring the shifts to higher resonances (^{1}H NMR) of the imidazole protons in the salts as compared to the starting neutral compounds **2** and **6**. This, as expected, is proportional to electronegativity of counter-anions (Table 1). Generally, the deshielding effect was more pronounced for ferrocenylphenylimidazolium salts, which highlighted the effect of unsaturation in the phenyl group. The effect of the alkyl chain length (R) was studied in the two sets of salts by varying its size from ethyl (**4** and **8**) to butyl (**5** and **9**). A similar trend was observed for both sets of salts, where a shielding effect was observed with a slight shift to lower frequency from 10.62 and 11.27 ppm to 10.56 and 11.23 ppm respectively, due to the increased electron density from the alkyl groups.

The compounds were also analysed by infrared spectroscopy and mass spectrometry (MS). They all exhibited similar infrared spectral patterns. The band observed around 1528–1573 cm^{-1} corresponds to the N-C-N stretch in neutral imidazole.[11] The C-H and N-H stretching frequencies were observed between 2934–3079 and 3300–3639 cm^{-1} respectively. The bands that are characteristic of the presence of ferrocene in a molecule[11] were observed around 820–1150 cm^{-1}. All the salts exhibited characteristic molecular ion peaks ($m/z = M^+ - X^-$) in MS.

Molecular Structures of Compounds 4 and 11

Compounds **4** and **11** were structurally analysed by X-ray diffraction studies. Crystals suitable for analysis were obtained by slow diffusion of hexane into saturated dichloromethane (DCM) solutions of the respective compounds. ORTEP diagrams of compounds **4** and **11** are shown in Figs 1 and 2 respectively. Crystal and experimental refinement data are summarized in Table 2.



Scheme 3. Anion exchange of ferrocenylimidazolium salts.

Table 1. Structural variations of the ferrocenylimidazolium salts **2–12**

Compounds	–R	X^-	m.p. (°C)	^{1}H NMR (ppm)[a]
2	None	None	80	7.45
3	CH_3	I	145.5	9.96
4	C_2H_5	Br	92.3	10.62
5	C_4H_9	Br	85.5	10.56
6	None	None	161.5	7.84
7	CH_3	I	140.5	10.65
8	C_2H_5	Br	184.5	11.27
9	C_4H_9	Br	158.5	11.23
10	CH_3	Br	Oil	9.97
11	C_4H_9	PF_6	Paste	8.62
12	CH_3	Br	179.5	10.64

[a] chemical shift of imidazole proton

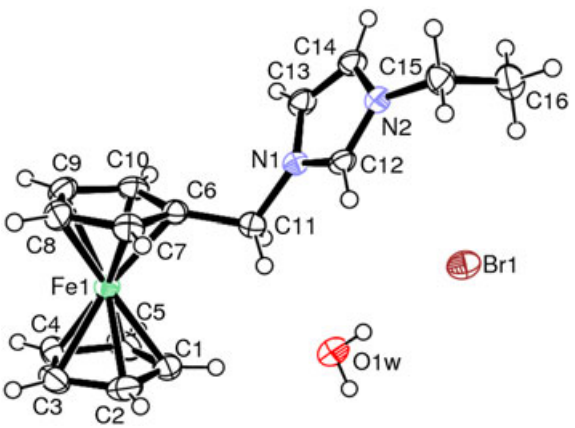


Figure 1. ORTEP representation of compound **4**. Thermal ellipsoids are represented at the 50% probability level. Selected bond lengths (Å): N1-C11 = 1.477(3); Fe1-C10 = 2.032(2); N2-C15 = 1.473(3); N2-C12 = 1.329(3); Fe1-C6 = 2.016(2). Selected bond angles (°): N1-C12-N2 = 108.4(2); C12-N1-C11 = 124.2(2); C12-N2-C15 = 124.5(2); C10-Fe1-C6 = 121.12(16).

Compound **4** crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The structure consists of ferrocenyl moiety with methylene linker to ethylimidazolium bromide and a molecule of water of crystallization.

Compound **11** crystallised in the monoclinic space group $P2_1$ with two molecules in the asymmetric unit. The structure consists of methylene-linked ferrocenyl and butylimidazolium moieties counterbalanced by a hexafluorophosphate anion.

Cyclic Voltammetry

The ferrocenylimidazolium salts were analysed by cyclic voltammetry. The voltammograms are presented in Figs 3 and 4, where the potentials were scanned in the anodic forward direction, denoted by the arrow (→), from −1.00 to +1.00 V. A reversible redox wave similar to unsubstituted ferrocene was observed for all compounds **2–12**. The influence of the imidazolium

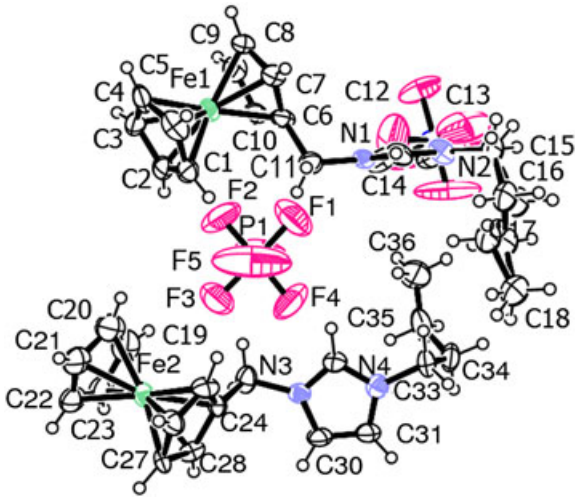


Figure 2. ORTEP representation of compound **11**. Thermal ellipsoids are represented at the 50% probability level. Selected bond lengths (Å): N1-C11 = 1.484(15); Fe1-C10 = 2.005(13); N2-C15 = 1.481(17); N2-C14 = 1.335 (16); Fe1-C6 = 2.041(13). Selected bond angles (°): N1-C14-N2 = 107.5(12); C14-N1-C12 = 110.9(12); C14-N2-C15 = 125.4(12); C10-Fe1-C1 = 120.4(6).

Table 2. Summary of crystal and experimental refinement data for compounds **4** and **11**

Compound	**4**	**11**
Formula	$C_{16}H_{21}BrFeN_2O$	$C_{18}H_{23}F_6FeN_2P$
Formula weight	393.11	468.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a (Å)	12.8696(9)	9.7739(13)
b (Å)	7.5858(5)	16.4278(19)
c (Å)	16.8379(11)	12.6114(18)
α (°)	90	90
β (°)	94.021(2)	93.755(5)
γ (°)	90	90
Cell volume (Å^3)	1639.77(19)	2020.6(5)
Z	4	4
D_{calcd} (Mg m^{-3})	1.592	1.539
Crystal size (mm^3)	0.33 × 0.31 × 0.06	0.73 × 0.07 × 0.02
Final R indices	$R_1 = 0.0318$	$R_1 = 0.0721$
	$wR_2 = 0.0748$	$wR_2 = 0.1442$
R indices (all data)	$R_1 = 0.0462$	$R_1 = 0.1815$
	$wR_2 = 0.0791$	$wR_2 = 0.1839$

substituent on the ferrocenyl moiety was easily evaluated by comparison of the half-wave potentials ($E_{1/2}$) of the salts relative to ferrocene. The data presented in Table 3 show that all the $E_{1/2}$ values (for compounds **2–12**) shifted to more positive potentials (0.482 to 0.595 V) when compared to ferrocene (0.436 V). This is attributed to the electron-withdrawing ability of the imidazolium moiety, which, by draining electron density away from the ferrocenyl centre, made oxidation relatively more difficult. The neutral ferrocenylimidazoles (**2** and **6**) have lower $E_{1/2}$ values in comparison to the corresponding salts. The cyclic voltammograms of some of the salts containing halide counter-anions (e.g. **4**, **5** and **12**) displayed second redox peaks, which were attributed to the presence of iodide or bromide counter-ions in the molecular sphere of the salts. The presence of iodide or

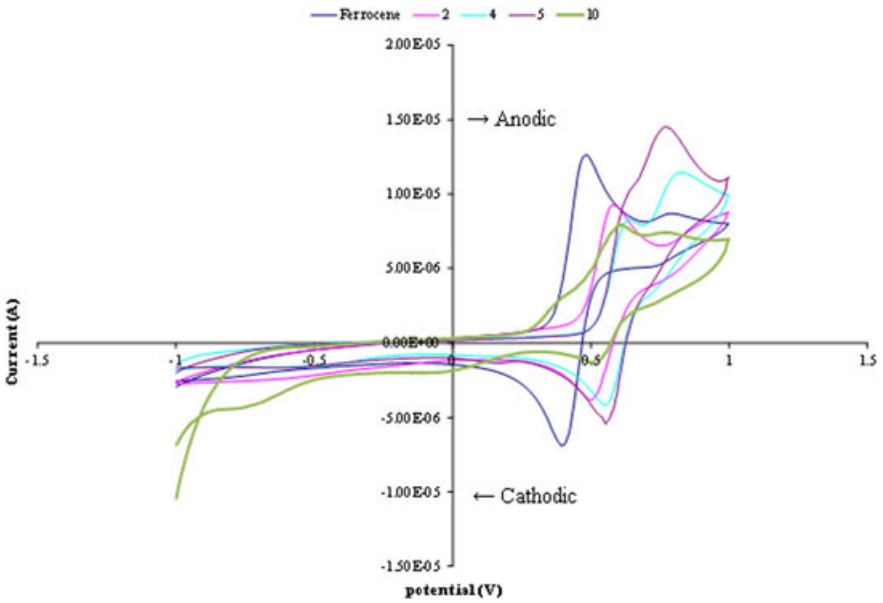


Figure 3. Comparison of the cyclic voltammograms of compounds **2**, **4**, **5** and **10** with that of ferrocene. Arrows (→ or ←) indicate scan direction.

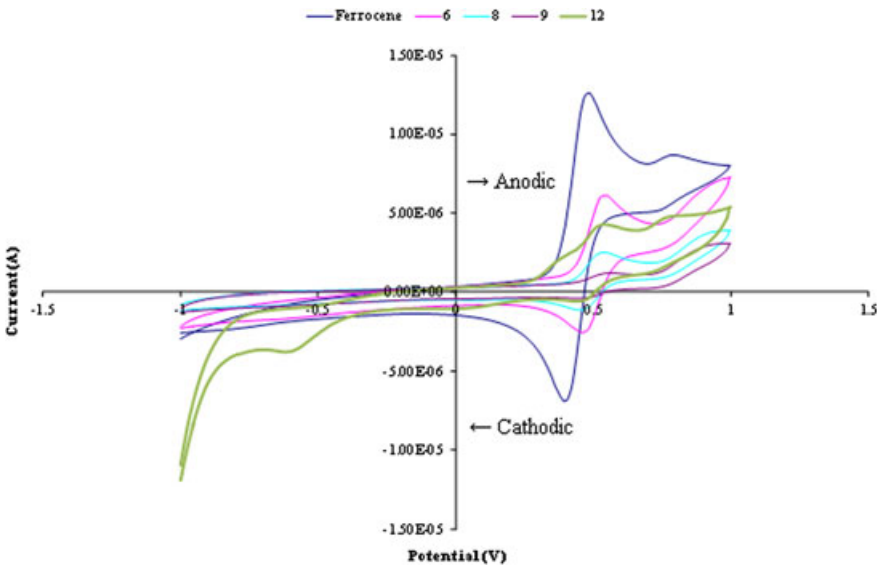


Figure 4. Comparison of cyclic voltammograms of ferrocenyl compounds **6**, **8**, **9** and **12** with that of ferrocene. Arrows (→ or ←) indicate scan direction.

bromide counter-ions in ferrocenylimidazolium salts has been reported to show an additional redox peak due to increased electro-activity of the imidazolium centre in conjunction with the halides that are in close proximity.[32,40] It is worth noting that an increase in the chain length of the imidazolium alkyl substituent had a direct positive effect on the $E_{1/2}$ values of the salts, due to an increase in the positive inductive effect of relatively longer alkyl chains.

In addition, data in Table 3 clearly showed the difference between the two sets of salts, i.e. between those with methylene (**2–5** and **10**) and those with phenyl (**6–9** and **12**) linkers. Generally, the methylene-linked salts exhibited higher formal electrode potentials than corresponding phenyl-linked ones. This is due to delocalization of electrons in the phenyl ring, which decreases the electron-withdrawing effect of the imidazolium moiety that is responsible for the general shift to more positive potentials for all the salts as compared to ferrocene (see above). This renders the $E_{1/2}$ value in compounds **6–9** and **12** less positive than those of compounds **2–5** and **10**. Batterjee *et al.* have reported a similar effect in which the electrode potentials shifted to lower positive values as a result of the introduction of a double bond in their compounds.[45]

Furthermore, oxidation became more difficult, which led to a shift to higher positive potentials as the size of anion increased. This trend was observed for both methylene-linked (**3** and **10**) and phenyl-linked (**7** and **12**) salts on changing counter-ions from bromide to iodide. A possible explanation could be that, as the anion size increases, there is a relatively larger charge distribution and the electron-withdrawing ability of the imidazolium moiety increases. As a result, a lower electron density is experienced

Table 3. Cyclic voltammetry data for ferrocenylimidazolium salts, showing oxidation (anodic) and reduction (cathodic) peak potentials (E_{pa} and E_{pc}, respectively) and peak currents (i_{pa} and i_{pc}, respectively)

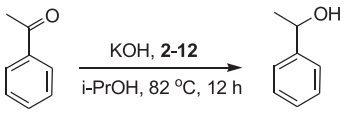
Compound	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	$E(E_{pc} - E_{pa})$ (V)	i_{pc} (μA)	i_{pa} (μA)	i_{pc}/i_{pa}
Ferrocene	0.479	0.393	0.436	0.086	10.7	8.88	1.20
2	0.577	0.506	0.542	0.071	6.53	5.77	1.13
3	0.631	0.553	0.592	0.078	8.93	10.5	0.85
4	0.621	0.540	0.581	0.081	4.39	2.68	1.64
5	0.637	0.553	0.595	0.084	8.90	8.10	1.10
6	0.518	0.446	0.482	0.072	4.33	3.74	1.16
7	0.565	0.494	0.529	0.071	6.86	7.93	0.87
8	0.536	0.458	0.497	0.078	0.79	0.80	0.99
9	0.547	0.458	0.503	0.089	0.39	0.37	1.06
10	0.601	0.512	0.557	0.089	2.47	2.29	1.08
11	0.619	0.547	0.583	0.072	5.59	3.63	1.54
12	0.524	0.458	0.491	0.066	0.94	1.55	0.61

by the ferrocenyl centre, which makes oxidation relatively difficult. By using ^{1}H NMR chemical shifts, we have in the past probed the effect of increasing the size of the anion on the acidity of imidazole protons and found that, as the anionic size decreased, the chemical shifts of resonances in the ^{1}H NMR spectra shifted downfield.[43a] This confirmed that the size of the anion had an influence on electrostatic interactions between the imidazolium moiety and the ferrocenyl centre.

Catalytic Transfer Hydrogenation

Application of the salts as potential catalysts was investigated in transfer hydrogenation of both saturated and unsaturated ketones. Catalytic transfer hydrogenation of ketones to alcohols by the use of simple ionizable inorganic salts MOH (M = Li, Na, K) is well established.[46,47] In this study we have used transfer hydrogenation as a benchmark for testing structure–activity relationships. The study began with a set of exploratory experiments that utilized acetophenone as substrate and 0.05 mol% of the ferrocenylimidazolium salts as catalysts. The solvent, propan-2-ol, was the H-transfer agent and the reaction was conducted at 82 °C for 12 h in a basic KOH environment. The result of this study is presented in Table 4. All compounds **2–12** showed high activities toward conversion of acetophenone to the desired alcohol. Turnover numbers (TON) up to 1880 were observed, which are comparable to some of the precious metal-catalyzed reactions highlighted in this report.[3] Further exploratory work was conducted in order to establish the roles of the various components in the catalysis and to clarify the identity of the active species, since it has been well established that inorganic salts are capable of independent activation in this type of reactions. Hence a blank test run was conducted in which only the catalyst salt was added and, as expected, no catalytic activity was observed. The next test run involved only KOH base monitored over a 48 h period and the result showed a maximum conversion of 20% to the desired alcohol product after 12 h, with little or no improvement with time. Variation in the relative concentration of the base showed insignificant change in the catalytic result. These observations support our proposed mechanism[48] involving the formation of a K-NHC intermediate (formed via coordination of potassium from KOH to the reactive carbene moiety from deprotonation of the catalyst salt) as the active species for this set of catalytic reactions. Moreover, in order to clarify whether the K-NHC complex was the only active species or it was just catalyzed by the base, potassium *tert*-butoxide (^{t}BuO$^-$K$^+$) and an organic base, triethylamine, were screened under similar conditions. In the absence of the catalyst salt, 30% conversion of acetophenone to 1-phenylethanol was observed for ^{t}BuO$^-$K$^+$ and no reaction was observed with triethylamine. Addition of compound **11** improved the activity of the ^{t}BuO$^-$K$^+$-initiated reaction to 65%, still with no sign of activity in the triethylamine-catalyzed reaction, indicating that the organic base was unsuitable for this reaction. Further evidence is provided (see supporting information) from ^{1}H and ^{13}C NMR spectroscopic monitoring of a solution of KOH and compound **11**. ^{1}H NMR results showed deprotonation of the salt due to the disappearance of the imidazolium proton signal at 8.59 ppm. Coordination of potassium to the deprotonated reactive carbene species was confirmed by the appearance of a downfield signal at 152.46 ppm which corresponded to a carbene–K bond. This is similar to values recorded

Table 4. Transfer hydrogenation of acetophenone catalysed by compounds **2–12**

Compound	Conversion (%)[a]	TOF[b]	TON[c]
			
2	63	105	1260
3	72	120	1440
4	70	117	1400
5	80	133	1600
6	57	95	1140
7	68	113	1356
8	69	115	1380
9	94	157	1880
10	66	110	1320
11	74	123	1480
12	61	102	1220

[a]Conversion was determined by gas chromatographic analysis.
[b]Turnover frequency (TOF) = mol product/(mol catalyst × time), determined after time *t*.
[c]Turnover number (TON) = mol product/mol catalyst.

for related metal–NHC bonds.[33,34,49] An important work by Arnold *et al.*[50] has provided clear evidence on the isolation and structural characterisation of K-NHC compounds.

Having established optimum conditions for the reaction and roles of major components, the study was extended to other ketones, aimed at establishing its scope and limitations. For the extended study, the more active compounds (**5** and **9)** were used since they gave highest catalytic TON for their respective series. It is interesting to note that **5** and **9** had potentials that shifted the most to positive values in the CV study and are structurally similar except for difference in linker, i.e. methylene vs. phenyl, respectively. Table 5 presents results of this study. By introduction of an electron-donating group to the *ortho* position of cyclohexanone, the recorded conversion was drastically reduced (Table 5, entry 2). However, a better conversion was obtained when the same electron-donating group was at the *para* position. This may be attributed to steric interference that resulted in limited access to the reactive site in the *o*-substituted substrate. Likewise, the introduction of electron-withdrawing groups to acetophenone brought about significant drops in conversion (entries 8 and 9). In general, the cyclic aliphatic ketones gave better conversions than their straight-chain counterparts, which may be attributed to accessibility of the C=O bond in the relatively rigid cyclic compounds as compared to the more sterically hindered reactive site in the straight-chain ketones that led to diminished conversions to the alcohols.

The study was further extended to the investigation of three aliphatic α,β-unsaturated ketones. Contrary to expectation, two of the substrates were not converted to the corresponding alcohols; instead they were reduced to saturated ketones at moderate to high yields (entries 10 and 11). In two of the cases investigated, chemoselectivity of the catalyst towards hydrogenation of the C=C bond over the C=O bond was facilitated by conjugated keto-ene resonance stabilization. Examples of this selectivity abound; for example, Bond[51] earlier reported on the relative selectivity of hydrogen addition to a conjugated C=C bond over the C=O bond. Recently, Ide *et al.*[52] reported the preferred hydrogenation of C=C bond over C=O bond in their catalytic system, which was attributed to higher activation barriers for the C=O bond. However, unconjugated 5-hexen-2-one (entry 12) was selectively reduced to an unsaturated alcohol. This can be attributed to the ethyl spacer between the C=C and C=O bonds of the 5-hexen-2-one which disrupted the keto-ene conjugation and resonance stabilization.

Overall, compound **9** gave the best conversion and better catalytic activity as compared to **5**. The high activity exhibited by **9** was due to its molecular structure, which also contributed to its high melting point, shift to higher resonance of the imidazole proton in ^{1}H NMR analysis and also a shift to more positive potentials in the CV study.

Conclusions

In this study, two series of ferrocenylimidazolium salts comprising 12 compounds were synthesized and fully characterized. Application of the salts as catalysts in the transfer hydrogenation of ketones resulted in high efficiencies and turnover numbers as high as 1880. Electrochemical studies by cyclic voltammetry showed that all the salts exhibited positive electrode potentials relative to ferrocene, which is due to the electron-withdrawing effect of the imidazolium ion on the ferrocenyl moiety. A comparative analysis of the catalytic and CV data revealed a direct correlation between the observed high catalytic activities and the tendency of the formal electrode potentials ($E_{1/2}$) towards higher positive values. Hence this set of results may serve as a benchmark in future catalyst design for NHC complexes derived from ferrocenylimidazolium salts.

Experimental

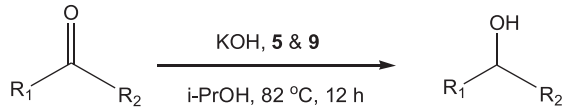
General Procedure

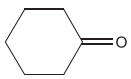
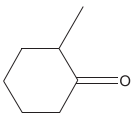
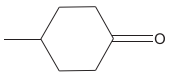
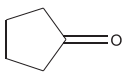
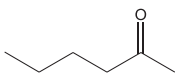
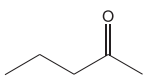
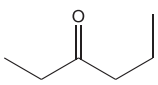
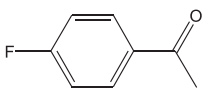
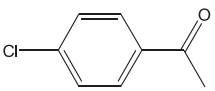
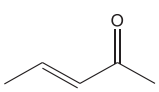
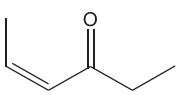
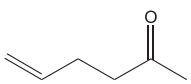
All manipulations involving air and moisture sensitive compounds were performed through the use of standard Schlenk techniques under an atmosphere of dry nitrogen. All solvents were dried and purified by standard procedures prior to use. Glassware was oven dried at 110 °C. All NMR experiments were conducted on a 400 MHz Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform. Infrared spectra were recorded with a PerkinElmer Universal ATR Spectrum 100 FT-IR spectrometer. All low-resolution mass data were run on a Thermo Finnigan linear ion trap mass spectrometer using electrospray ionisation in positive mode. Accurate mass data were obtained on a Thermo Electron DFS dual-focusing magnetic sector instrument using electrospray ionization (ESI) in positive mode. Polyethylenimine was used as reference solution. Cyclic voltammograms were obtained with a METROHM 797 VA Computrace at a scan rate of 0.05 V s^{-1} in acetonitrile solution containing 0.1 mol L^{-1} of tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) as the supporting electrolyte. An Ag/AgCl couple was used as the reference electrode to determine the potential with Pt working and auxiliary electrodes. All reagents and solvents were purchased from Aldrich or Merck. Reagents were used as received without further purification. Compounds **1**,[43d] **2**,[43a–c] **3**,[43a] **6**[39] and **7**[53] were characterized by comparing their analytical and spectroscopic data with those of related compounds found in the literature.

*Synthesis of 1-(ferrocenyl)methanol (**1**)*

Ferrocenecarboxaldehyde (10 g, 0.047 mol) was dissolved in mimimal anhydrous diethyl ether and transferred to a pressure-equalizing dropping funnel. An ethereal solution of lithium aluminium hydride, (LAH, 1.80 g, 0.047 mol) was prepared in a three-necked round-bottomed flask. The aldehyde solution was added to the ethereal solution dropwise while stirring under nitrogen atmosphere. The solution was maintained at reflux for 2 h (45 °C), while being monitored by thin-layer chromatography (TLC). After completion it was allowed to cool, followed by the addition of 60 ml diethyl ether. Excess LAH was destroyed by dropwise addition of cold ethyl acetate, followed by addition of ice-water slurry. The organic layer was separated, washed with water (3 × 100 ml) and then dried over anhydrous magnesium sulfate before concentration using a rotary evaporator, after which it was dried under vacuum to give a yellow powder. Yield 7.2 g, 96%; m.p. 76–78 °C; IR (attenuated total reflectance (ATR) cm^{-1}) 3920, 3219, 2932, 1656, 1379, 1350, 1235, 1189, 987, 807, 498, 476; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.29 (s, 2H, CH_2), 4.25 (s, 2H, C_5H_4), 4.19 (s, 7H, C_5H_4, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.58, 68.51, 68.48, 68.08 (ferrocenyl moiety), 60.97 (CH_2OH); *m/z* (ESI): 199 ($M^+ - OH$, 92%), 216 (M^+, 42%). Anal. calcd for $C_{11}H_{12}FeO$ 216.02538. (M^+); found 216.02375 (M^+).

Table 5. Transfer hydrogenation of saturated and unsaturated ketones catalysed by compounds **5** and **9**



Entry	Ketones	% Conversion[a] (**5**)	% Conversion[a] (**9**)	TON[b] (**5**)	TON[b] (**9**)
1		76	83	1520	1660
2		50	20	1000	400
3		62	93	1240	1860
4		9	6	180	120
5		9	24	180	480
6		13	11	269	220
7		10	5	200	100
8		21	58	420	1160
9		31	62	620	1240
10[c]		68	57	1360	1140
11[c]		89	85	1780	1700
12		30	48	600	960

[a]Conversion was determined by gas chromatographic analysis.
[b]Turnover number (TON) = mol product/mol catalyst.
[c]Converted to saturated ketone.

*Synthesis of 1-(ferrocenylmethylene)imidazole (**2**)*

Ferrocenylmethanol, **1** (0.5 g, 2.3 mmol) and an excess of *N,N′*-carbonyldiimidazole (0.52 g, 3.2 mmol) were dissolved in a minimum of amount DCM (10 ml). The mixture was brought to reflux and the temperature maintained at 45 °C. TLC was used to monitor the reaction, which was completed after 1 h. The reaction was quenched and allowed to cool to room temperature. Diethyl ether (30 ml) was then added to the product mixture, which was stirred for 5 min at room temperature. Solvent was removed *in vacuo* and the resulting product was subjected to column chromatography on silica gel. Diethyl ether was used to flash down any unreacted starting material. Ethyl acetate (100%) was later used to obtain the product, as yellow powder. Yield 0.32 g, 53%; m.p. 80 °C; IR (ATR cm^{-1}) 3392, 3117, 1638, 1509, 1437, 1237, 1218, 1102, 1077, 809, 740, 658, 479; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H, CH), 7.00 (s, 1H, NCH), 6.89 (s, 1H, NCH), 4.84 (s, 2H, CH_2), 4.16 (m, 9H, C_5H_4, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.47 (imd-C), 129.00 (NCH), 118.60 (NCH), 82.51, 68.58, 68.31 (ferrocenyl moiety), 46.52 (CH_2); *m/z* (ESI): 199 (M^+ − imd [imd = imidazole], 6%), 267 (M^+, 100%), 268 (M^+ + 1, 18%). Anal. calcd for $C_{14}H_{14}N_2Fe$ 267.05847 (M^+); found 267.05748 (M^+).

*Synthesis of 1-(ferrocenylmethylene)-3-methylimidazolium iodide (**3**)*

In a two-necked flask, methyl iodide (0.3 ml, 8.1 mmol) was added to ferrocenylmethylene imidazole (0.05 g, 0.19 mmol) and was allowed to reflux gently at 50 °C under an atmosphere of nitrogen for 15 h. The mixture was then allowed to cool to room temperature, washed with anhydrous diethyl ether (5 × 3 ml) until diethyl ether remained clear after washing. A yellow powder was obtained. Yield 0.056 g, 72%; m.p. 145.5 °C; IR (ATR cm^{-1}) 3173, 1566, 1331, 1243, 1331, 1174, 1150, 811, 754, 710, 619, 553, 480; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H, CH), 7.28 (s, 1H, NCH), 7.26 (s, 1H, NCH), 5.34 (s, 2H, CH_2), 4.47 (s, 2H, C_5H_4), 4.26 (m, 7H, C_5H_4, C_5H_5), 4.04 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.96 (imd-C), 123.27 (NCH), 121.55 (NCH), 78.46, 77.30, 69.86, 69.70, 69.24 (ferrocenyl moiety), 50.05 (NCH_3); *m/z* (ESI): 199 ($M^+ - imd - I^-$, 6%), 281 ($M^+ - I^-$, 100%), 282 ($M^+ - I^- + 1$, 18%). Anal. calcd for $C_{15}H_{17}N_2FeI$ 281.07412 ($M^+ - I^-$); found 281.07350 ($M^+ - I^-$).

*Synthesis of 1-(ferrocenylmethylene)-3-ethylimidazolium bromide (**4**)*

Synthesis similar to **3** using ethyl bromide (0.6 ml, 8.1 mmol), to give a yellow powder. Yield 0.06 g, 84%; m.p. 92.3 °C; IR (ATR cm^{-1}) 3432, 3386, 3138, 3065, 2065, 1626, 1565, 1558, 1463, 1412, 1347, 1319, 1236, 1157, 1027, 1007, 848, 807, 774, 708, 554, 506, 485, 447; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.62 (s, 1H, CH), 7.16 (s, 1H, NCH), 7.11 (s, 1H, NCH), 5.34 (s, 2H, CH_2), 4.42 (s, 2H, C_5H_4), 4.36 (q, *J* 7.3, 2H, NCH_2,), 4.23 (s, 7H, C_5H_4, C_5H_5), 1.56 (t, *J* 7.3, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.94 (imd-C), 120.18 (NCH), 120.99 (NCH), 77.58, 70.09, 69.85, 69.54, 50.16 (ferrocenyl moiety), 45.56 (NCH_2), 15.76 (CH_3); *m/z* (ESI): 199 ($M^+ - imd - Br^-$, 6%), 295 ($M^+ - Br^-$, 100%), 296 ($M^+ - Br^- + 1$, 18%). Anal. calcd for $C_{16}H_{19}N_2FeBr$ 295.08977 ($M^+ - Br^-$); found 295.08962 ($M^+ - Br^-$).

*Synthesis of 1-(ferrocenylmethylene)-3-butylimidazolium bromide (**5**)*

Synthesis similar to **3** using butyl bromide (2.6 ml, 8.1 mmol). A dark-brown powder was obtained. Yield 0.07 g, 92%; m.p. 85.5 °C; IR (ATR cm^{-1}) 3571, 3393, 3168, 2965, 1563, 1448, 1155, 1105, 812, 656, 631, 553, 478; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H, CH), 7.03 (m, 2H, NCH, NCH), 5.36 (s, 2H, NCH_2), 4.41 (s, 2H, C_5H_4), 4.26 (m, 9H, C_5H_4, C_5H_5, NCH_2), 1.87 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 0.95 (t, *J* 7.2, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), 136.42 (imd-C), 120.80 (NCH), 120.66 (NCH), 78.83, 77.33, 69.84, 69.56, 69.30 (ferrocenyl moiety), 49.98 (NCH_2), 32.12 (CH_2), 19.53 (CH_2), 13.44 (CH_3); *m/z* (ESI): 199 ($M^+ - imd - Br^-$, 6%), 323 ($M^+ - Br^-$, 100%), 324 ($M^+ - Br^- + 1$, 22%); Anal. calcd for $C_{18}H_{23}N_2FeBr$ 323.12107 ($M^+ - Br^-$); found 323.12104 ($M^+ - Br^-$).

*Synthesis of 1-(4-ferrocenylphenyl)imidazole (**6**)*

A solution of sodium nitrite (0.088 g, 1.26 mmol) in water (2 ml) was added dropwise to an ice-cold solution of 4-(1*H*-imidazol-1-yl) aniline (0.2 g, 1.26 mmol) and aqueous tetrafluoroboric acid (50%, 0.4 ml, 6.2 mmol) in water (4 ml), whereupon a yellowish precipitate was observed. After complete addition of the sodium nitrite solution, the mixture was stirred for another 5 min, followed by the dropwise addition of a solution of ferrocene (0.24 g, 1.26 mmol) prepared from a mixture of CH_3CN and CH_2Cl_2 (1:2) 3 ml, resulting in a greenish-brown suspension. The cooling bath was removed and the mixture was further stirred for 1 h. Subsequently, H_2O (40 cm^3) was added and the reaction mixture extracted with CH_2Cl_2 (2 × 14 ml). The red organic layer was washed with dilute Na_2SO_4; the solvent was removed *in vacuo*, resulting in a brown residue, which was washed with *n*-hexane (3 × 6 cm^3) to remove residual ferrocene. A brownish-orange powder was obtained. Yield 0.12 g, 30%; m.p. 161.5 °C; IR (ATR cm^{-1}) 3096, 1660, 1531, 1488, 1302, 1249, 1103, 1055, 1031, 1002, 885, 813, 725, 655, 531, 509, 482, 456; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H, CH), 7.54 (d, *J* 8.4, 2H, C_6H_4), 7.29 (m, 3H, C_6H_4, NCH), 7.19 (s, 1H, NCH), 4.64 (t, *J* 1.6, 2H, C_5H_4), 4.35 (t, *J* 1.6, 2H, C_5H_4), 4.04 (s, 5H, C_5H_5), ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.24 (imd-C), 135.57 (Ar-C), 135.10 (Ar-C), 130.35 (Ar-CH), 127.24 (Ar-CH), 121.57 (NCH), 118.24 (NCH), 83.88, 69.73, 69.38, 66.95 (ferrocenyl moiety); *m/z* (ESI): 262 ($M^+ - imd$, 17%), 329 (M^+, 100%), 330 (M^+ + 1, 22%); Anal. calcd for $C_{19}H_{16}N_2Fe$ 329.07412 (M^+); found 329.07411 (M^+).

General Procedure for the Preparation of Compounds 7–9

In a two-neck flask, 1-(4-ferrocenylphenyl) imidazole (1 molar equiv.) was reacted with the respective alkylhalide (5 molar equiv.) in CH_2Cl_2 (15 ml). The mixture was stirred for 41 h at room temperature. After solvent removal, the mixture was treated with Et_2O (10 cm^3), filtered, washed with Et_2O (3 × 15 ml) and dried *in vacuo*. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution.

*Synthesis of 1-(4-ferrocenylphenyl)-3-methylimidazolium iodide (**7**)*

This compound was prepared from 1-(4-ferrocenylphenyl)imidazole (0.1 g, 0.3 mmol) and methyl iodide (0.1 ml, 1.5 mmol). The crude product was obtained as an orange powder. Yield 0.12 g, 86%; m.p. 140.5 °C; IR (ATR cm^{-1}) 3396, 3079, 1552, 1528, 1220, 1071, 820, 749, 620, 542, 504, 459; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H, CH), 7.64 (m, 4H, C_6H_4), 7.52 (s, 1H, NCH), 7.40 (s, 1H, NCH), 4.66 (t, *J* 1.7, 2H, C_5H_4), 4.39 (t, *J* 1.7, 2H, C_5H_4), 4.27 (s, 3H, NCH_3), 4.04 (s, 5H, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.15 (imd-C), 135.93 (Ar-C), 131.59 (Ar-C), 127.67 (Ar-CH), 123.99 (Ar-CH), 122.04 (NCH), 120.37 (NCH), 82.37, 69.88, 67.89, 66.79 (ferrocenyl moiety), 37.63 (NCH_3); *m/z* (ESI): 262 ($M^+ - imd - I^-$, 7%), 343 ($M^+ - I^-$, 100%), 344 ($M^+ - I^- + 1$, 22%); Anal. calcd for $C_{20}H_{19}N_2FeI$ 343.08977 ($M^+ - I^-$); found 343.08906 ($M^+ - I^-$).

*Synthesis of 1-(4-ferrocenylphenyl)-3-ethylimidazolium bromide (**8**)*

This compound was prepared from 1-(4-ferrocenylphenyl)imidazole (0.056 g, 0.17 mmol) and ethyl bromide (0.06 ml, 0.85 mmol). The crude product was obtained as an orange powder. Yield 0.025 g, 64%; m.p. 184.5 °C; IR (ATR cm^{-1}) 3378, 3096, 1608, 1530, 1492, 1300, 1249, 1058, 885, 815, 741, 658, 531, 501, 455; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 1H, CH), 7.64 (m, 4H, C_6H_4), 7.53 (s, 1H, NCH), 7.19 (s, 1H, NCH), 4.66 (q, *J* 7.3, 2H, NCH_2), 4.65 (t, *J* 1.6, 2H, C_5H_4), 4.38 (t, *J* 1.6, 2H, C_5H_4), 4.04 (s, 5H, C_5H_5), 1.67 (t, *J* 7.3, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.92 (imd-C), 135.56 (Ar-C), 130.36 (Ar-C), 127.70 (Ar-CH), 121.50 (Ar-CH), 121.55 (NCH), 120.05 (NCH), 83.87, 69.72, 66.82, 66.58 (ferrocenyl moiety), 45.84 (NCH_2), 15.73 (CH_3); *m/z* (ESI): 262 ($M^+ - imd - Br^-$, 8%), 329 ($M^+ - C_2H_5 - Br^-$, 100%), 357 ($M^+ - Br^-$, 80%), 358 ($M^+ - Br^- + 1$, 18%); Anal. calcd for $C_{21}H_{21}N_2FeBr$ 357.10542 ($M^+ - Br^-$); found 357.10388 ($M^+ - Br^-$).

*Synthesis of 1-(4-ferrocenylphenyl)-3-butylimidazolium bromide (**9**)*

This compound was prepared from 1-(4-ferrocenylphenyl)imidazole (0.024 g, 0.0732 mmol) and butyl bromide (0.04 ml, 0.366 mmol). The crude product was obtained as a brownish-orange powder. Yield 0.03 g, 91%; m.p. 158.5 °C; IR (ATR cm^{-1}) 3076, 1527, 1304, 1057, 962, 887, 820, 885, 729, 656, 536, 507, 458; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H, CH), 7.64 (d, *J* 8.4, 2H, C_6H_4), 7.53 (m, 3H, C_6H_4, NCH), 7.34 (s, 1H, NCH), 4.66 (m, 4H, C_5H_4, NCH_2), 4.38 (t, *J* 1.7, 2H, C_5H_4), 4.04 (s, 5H, C_5H_5), 1.98 (m, 2H, CH_2), 1.23 (m, 2H, CH_2), 1.01 (t, *J* 7.4, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.84 (imd-C), 135.84 (Ar-C), 131.70 (Ar-C), 127.68 (Ar-CH), 127.19 (Ar-CH), 121.65 (NCH), 119.76 (NCH), 82.46, 69.84, 66.77, 65.53 (ferrocenyl moiety), 42.71 (NCH_2), 32.27 (CH_2), 19.54 (CH_2), 13.51 (CH_3); *m/z* (ESI): 262 ($M^+ - imd - Br^-$, 8%), 329 ($M^+ - C_4H_9 - Br^-$, 100%), 385 ($M^+ - Br^-$, 78%), 386 ($M^+ - Br^- + 1$, 22%); Anal. calcd for $C_{23}H_{25}N_2FeBr$ 385.13672 ($M^+ - Br^-$); found 385.13641 ($M^+ - Br^-$).

*Synthesis of 1-(ferrocenylmethylene)-3-methylimidazolium bromide (**10**)*

In a two-necked flask was added sodium bromide (0.043 g, 0.42 mmol) to an acetone solution of 1-(ferrocenylmethylene)-3-methylimidazolium iodide (**3**) (0.1 g, 0.25 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was then filtered through a plug of celite and concentrated *in vacuo* to give an orange oil. Yield 0.073 g, 81%; IR (ATR cm^{-1}) 3438, 3080, 1614, 1572, 1557, 1454, 1425, 1221, 1153, 1105, 1037, 1003, 822, 749, 673, 621, 543, 503, 462; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H, CH), 7.17 (s, 1H, NCH), 7.15 (s, 1H, NCH), 5.33 (s, 2H, CH_2), 4.43 (s, 2H, C_5H_4), 4.24 (s, 7H, C_5H_4, C_5H_5), 4.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.64 (imd-C), 122.83 (NCH), 121.18 (NCH), 78.46, 77.34, 69.87, 69.63, 69.25 (ferrocenyl moiety), 50.15 (CH_3); *m/z* (ESI): 199 ($M^+ - imd - Br^-$, 6%), 281 ($M^+ - Br^-$, 100%), 282 ($M^+ - Br^- + 1$, 22%); Anal. calcd for $C_{15}H_{17}N_2FeBr$ 281.07412 ($M^+ - Br^-$); found 281.07381 ($M^+ - Br^-$).

*Synthesis of 1-(ferrocenylmethylene)-3-butylimidazolium hexafluorophosphate (**11**)*

In a two-necked flask, sodium hexafluorophosphate (0.035 g, 0.21 mmol) was added to an acetone solution of (ferrocenylmethylene)-3-butylimidazolium bromide (**5**) (0.05 g, 0.13 mmol). The mixture was stirred under a nitrogen atmosphere for 24 h at room temperature. The reaction mixture was then filtered through a plug of celite, concentrated *in vacuo* to afford an orange-brown paste. Yield 0.1 g, 96%. IR (ATR cm^{-1}): 3639, 3167, 2934, 1562, 1448, 1154, 820, 775, 555, 501, 478; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H, CH), 7.18 (s, 1H, NCH), 7.17 (s, 1H, NCH), 5.15 (s, 2H, NCH_2), 4.38 (t, *J* 1.6, 2H, C_5H_4), 4.23 (t, *J* 1.6, 2H, C_5H_4), 4.20 (s, 5H, C_5H_5), 4.08 (t, *J* 5.7, 2H, NCH_2), 1.82 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.93 (t, *J* 7.2, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 134.49 (imd-C), 121.86 (NCH), 121.72 (NCH), 78.38, 77.35, 69.89, 69.54, 69.23 (ferrocenyl moiety), 49.97 (NCH_2), 31.79 (CH_2), 19.39 (CH_2), 13.30 (CH_3); *m/z* (ESI): 199 ($M^+ - imd - PF_6^-$, 7%), 323 ($M^+ - PF_6^-$, 100%), 324 ($M^+ - PF_6^- + 1$, 22%). Anal. Calcd for $C_{18}H_{23}N_2FeBr$ 323.12107 ($M^+ - PF_6^-$); found 323.12105 ($M^+ - PF_6^-$).

*Synthesis of 1-(4-ferrocenylphenyl)-3-methylimidazolium bromide (**12**)*

In a two-necked flask was added sodium bromide (0.019 g, 0.18 mmol) to an acetone solution of 1-(3-methyl-(4-ferrocenylphenyl)imidazolium iodide, **7** (0.05 g, 0.11 mmol). The mixture was stirred at room temperature for 24 h. The resultant mixture was then filtered through a plug of celite and concentrated *in vacuo* to give a yellowish-brown powder. Yield 0.035 g, 87%; m.p. 179.5 °C; IR (ATR cm^{-1}) 3452, 3397, 3079, 1706, 1553, 1423, 1220, 1003, 821, 749, 621, 519. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H, CH), 7.64 (m, 4H, C_6H_4), 7.54 (s, 1H, NCH), 7.45 (s, 1H, NCH), 4.65 (t, *J* 1.6, 2H, C_5H_4), 4.38 (t, *J* 1.6, 2H, C_5H_4), 4.26 (s, 3H, NCH_3), 4.04 (s, 5H, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.26 (imd-C), 136.27 (Ar-C), 131.73 (Ar-C), 127.81 (Ar-CH), 124.07 (Ar-CH), 122.15 (NCH), 120.45 (NCH), 82.54, 70.07, 70.01, 66.95 (ferrocenyl moiety), 37.70 (NCH_3); *m/z* (ESI): 262 ($M^+ - imd$ Br^-, 8%), 343 ($M^+ - Br^-$, 100%), 344 ($M^+ - Br^- + 1$, 22%). Anal. calcd for $C_{20}H_{19}N_2FeBr$ 343.08977 ($M^+ - Br^-$); found 343.08885 ($M^+ - Br^-$).

General Procedure for Transfer Hydrogenation

Ferrocenylimidazolium salts as catalysts, 0.05 mol%, ketones (2.1 mmol) and KOH (0.112 g, 10 ml, 2 mmol, 0.2 M in propan-2-ol) were introduced into a round-bottomed flask fitted with a condenser and refluxed at 82 °C. The transfer hydrogenation reaction was monitored with an Agilent capillary gas chromatograph, model 6820, fitted with a DB wax polyethylene column (0.25 mm diameter, 30 m length) and a flame ionization detector. Nitrogen gas was used as carrier gas at a flow rate of 2 mL min^{-1}. The oven temperature for the aromatic (except 4-fluoroacetophenone) and the cyclic (except cyclobutanone) ketones was 70 °C, while for the remaining ketones the oven temperature was 50 °C. Samples (0.1 µl) were injected at 260 °C front inlet temperature for the aromatic (except 4-fluoroacetophenone) and the cyclic ketones (except cyclobutanone). For the remaining ketones the front inlet temperature was 180 °C. The identity of the alcohols was assessed by comparing their retention times with commercially available (Aldrich Chemical Co.) pure samples. Conversions obtained were calculated from the integration values of the gas chromatographic peaks, which were related to residual unreacted ketone.

X-ray crystal determination

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50 kV, 30 mA) using APEX 2[54] data collection software. The collection method involved ω-scans of width 0.5 ° and 512 × 512-bit data frames. Data reduction was carried out using the program SAINT+[54] and face-indexed absorption corrections were made using XPREP.[54] The crystal structure was solved by direct methods using SHELXTL. Non-hydrogen atoms were first refined isotropically, followed by anisotropic refinement by full matrix

least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL, PLATON[55] and ORTEP-3.[56]

Supporting Information

Supporting information may be found in the online version of this article. Crystallographic data in cif format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 876270 and 844511 for compounds **4** and **11**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or http:// www.ccdc.cam.ac.uk.

Acknowledgements

The authors wish to thank the University of KwaZulu-Natal and the National Research Foundation (NRF) for financial support. Dr Manuel Fernandes is also thanked for crystallographic data collection and solution.

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