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Application of three-legged piano-stool cyclopentadienyl-N-heterocyclic carbene iron(II) complexes as *in situ* catalysts for the transfer hydrogenation of ketones

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ABSTRACT

A one pot system has been developed based on nine related 1,3-dialkylated imidazolium salts for the *in situ* generation of *N*-heterocyclic carbene iron(II) complexes in which the complexes were directly tested as catalysts for the transfer hydrogenation of ketones. This is a simplified reproducible process that aims to eliminate unnecessary purification steps for the isolation of such catalysts prior to application. Complexes **10**–**12** have been prepared under similar conditions, isolated and structurally characterized by spectroscopic and crystallographic methods. Solid state structures of the three complexes were similar and showed distorted octahedral three-legged piano stool geometry around each iron center similar to reported complexes bearing related ligands. As a basis for comparison with the *in situ* catalyzed systems, the isolated complexes were also tested as catalysts for the transfer hydrogenation of ketones. As a result, under optimized reaction conditions, all the *in situ* generated catalysts were found to provide excellent activities similar to those based on the isolated complexes with moderate to excellent conversions to the desired alcohol products. Turn over numbers up to 200 at a conversion of 100% was recorded for a wide range of aliphatic, aromatic and cyclic ketones.

1. Introduction

The selective reduction of carbonyl groups for the production of alcohols is a vital process for the pharmaceutical and fine chemicals industries. Comparatively, it is best achieved by transfer hydrogenation (TH) instead of direct hydrogenation using molecular hydrogen since TH is cheaper and safer both because no free hydrogen is used and it does not require special reactor, stirring, or gas handling auxiliaries. Removal of the need for hydrogen storage, monitoring and dispensing equipment in principle means that ordinary glassware will suffice for most processes. It also implies that process scale up to industrial levels of production is easily achievable due to the elimination of mass transfer limitations associated with the poor solubility of hydrogen gas [1].

Thus far, because of their exceptional activities, the most studied catalysts for TH are based on platinum group metals (PGMs). However the PGMs suffer from limited availability, high cost and toxicity issues not particularly suited to pharmaceuticals and food processing applications [2]. Iron is a much suited metal for these and related applications, thus it is not surprising that the chemistry of iron based N-heterocyclic carbene (NHC) complexes has been a very active topic in recent literature, especially in homogeneous catalysis [3] where catalyst recovery and contamination is a major concern. Ingleson and Layfield [4] have recently reviewed and contextualized the current state of iron-NHC chemistry which revealed that one of the reasons for the lesser development of iron-NHC complexes is the difficulty encountered in their synthesis and isolation [5]. However, three-legged piano-stool cyclopentadienyl (Cp)-Fe(II) complexes are well known to offer the advantage of ease of reaction monitoring by spectroscopy: infrared (carbonyl shifts are easily monitored) or NMR (shifts in Cp region) and can be prepared from a relatively inexpensive precursor $[CpFe(CO)_2]_2$ [6]. Recent interest in Fe-NHC chemistry includes a report on the direct activation of the NHC ligand in low coordinate Fe-NHC complexes to yield new complexes with unusual coordination [7]. It has been shown that iron-NHC complexes are usually prepared *via* the free carbene route which is a limited route due to well documented difficulties associated with the handling of reactive free carbenes [8]. To mitigate the handling of free carbenes, transmetallation of NHCs from a silver complex [9] is widely applied for the synthesis of NHC-metal complexes, but thus far no reported cases on adaptation for the preparation of iron based NHC complexes has been recorded. However, iron-NHC complexes can be prepared by the reaction of moisture sensitive and unstable basic

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metal acetates, alkoxides, or amides with imidazolium salts [10]. Hence, a few successful cases of iron-NHC complexes have been recorded as reviewed by Ingleson and Layfield [4]. More specifically, by combining the advantages of $[CpFe(CO)_2]_2$ as a precursor and the strong σ-donor properties of NHC ligands, Buchgraber et al. [11] and Mercs et al. [12] have studied the coordination chemistry of piano-stool Cp-iron-NHC complexes similar to those isolated in this study.

It is important to note that iron is not new to catalysis especially heterogeneously and as a component of biological systems. Prominent amongst its use are in Harber-Bosch ammonia synthesis [13] and Fischer-Tropsch process [14]. Examples of well-defined NHC or Cp containing homogeneous systems include work by Tatsumi and co-workers who utilized unsaturated half-sandwich NHC iron complexes to activate C—H bonds of thiophenes, furans and pyridine [15]. The application of organometallic and coordination complexes of iron as catalysts for the reduction of carbonyl groups has been explored by several groups. For example, the group of Morris and co-workers has developed very efficient systems for asymmetric TH of ketones based on tetradentate PNNP ligands [16]. Casey and co-workers, inspired by bifunctional, ionic hydrogenation catalysis established for ruthenium, have disclosed catalytic activity of related Cp-iron counterparts [17]. Their catalysts showed high activity in hydrogenation of several ketones, aldehydes, and imines using molecular H_2 as a reducing agent and also displayed activity in transfer hydrogenation reaction by use of 2-propanol as source of hydrogen. In addition, Kandepi and co-workers have developed new Fe(II) complexes containing functionalized-Cp NHC ligands that showed good catalytic activity in hydrosilylation of aldehydes and transfer hydrogenation of ketones [18].

The examples mentioned above reveal a reemergence in the last decade of interest in well-defined iron complexes as credible alternatives to PGMs in some homogeneous catalysis projects. Hence, in continuation with our interest in the study of imidazolium family of compounds as ionic liquids and ligands in organometallic chemistry [19], the current work was aimed at the evaluation of NHC-Fe systems as simple, active, *in situ* generated one pot catalysts. The study reports combination of the simplicity of TH, *in situ* one pot catalyst generation and use of abundant, cheap and environmentally friendlier iron catalyst in one process.

2. Experimental

2.1. General procedures

All manipulations were performed using 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 done using a 400 MHz Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform. Infrared spectra for the ligands were recorded neat using a Perkin Elmer universal ATR Spectrum 100 FT-IR spectrophotometer, while the solution IR data for the complexes were recorded in CH_2Cl_2 on a Perkin Elmer FT-IR spectrophotometer; model RX 1. Low resolution MS samples were run on a Thermo Finnigan Linear ion trap mass spectrometer using electrospray ionization in positive mode. Accurate mass data was obtained on a Thermo Electron DFS Dual focusing magnetic sector instrument using ESI in positive mode; polyethylenimine was used as reference solution. Ligand 3 was purchased from Aldrich, while other ligands were synthesized according to a literature method [20]. Preparation of $CpFe(CO)_2I$ was based on our published procedure [21]. Transfer hydrogenation reaction was monitored by gas chromatography (GC) with an Agilent capillary GC model 6820 fitted with a DB wax polyethylene column (0.25 mm in diameter, 30 m in length), a flame ionization detector and nitrogen gas was used as carrier gas at a flow rate of 2 mL/min. Reagents were purchased from Aldrich or Merck and were used as received.

2.2. General procedure for the synthesis of ligands **1**–**9**

The ligands (except 3) were all synthesized by adaptation of the methods of Starikova et al. [20]. A typical and generic procedure is described. Spectroscopic and analyses data are presented. *N*-monosubstituted azole (0.1 mmol) and dry toluene were placed in a two-neck flask and stirred until a homogeneous solution was formed; then alkyl halide (0.3 mmol) was added drop wise with continuous stirring. After addition of the alkyl halide, the mixture was stirred while heating at 40 °C for 24 h. The solvent was removed and the ligand was dried under vacuum.

2.2.1. 1,3-Dimethylimidazolium iodide (**1**)

Brown solid. Yield (4.80 g, 98%) IR (ATR cm^{-1}): 3433, 3152, 3094, 2953, 1619, 1572, 1341, 1170, 1084, 1020, 826, 748, 617; δ_H (400 MHz, $CDCl_3$): 4.07 (6H, s, NCH_3), 7.35 (2H, s, NCH) and 9.97 ppm (1H, s, CH); δ_C (100 MHz, $CDCl_3$): 37.12 (NCH_3),123.36 (NCH) and 137.76 ppm.; *m*/*z* (ESI) 96.7 (M^+-I^-). HRMS (ESI) calcd for $C_5H_9IN_2$, 97.07657 (M^+-I^-); found, 97.07628 (M^+-I^-).

2.2.2. 1-Methyl-3-ethylimidazolium bromide (**2**)

White solid. Yield (4.70 g, 98%). IR (ATR cm^{-1}): 3065, 2975, 1670, 1571, 1467, 1172, 1101, 856, 789, 649, 789, 621, 417; δ_H (400 MHz, $CDCl_3$): 1.47 (3H, t, *J* 7.3 Hz, CH_3), 3.97 (3H, s, NCH_3), 4.32 (2H, q, NCH_2), 7.54 (2H, s, NCH) and 10.07 ppm (1H, s, CH); δ_C (100 MHz, $CDCl_3$): 15.64 (CH_3), 36.63 (NCH_3), 45.18 (NCH_2), 122.01 (NCH), 123.71 (NCH) and 136.73 ppm.; *m*/*z* (ESI) 111.5 (M^+-Br^-). HRMS (ESI) calcd for $C_6H_{11}BrN_2$, 111.09222 (M^+-Br^-); found, 111.09196 (M^+-Br^-).

2.2.3. 1-Methyl-3-butylimidazolium bromide (**4**)

Colorless oil. Yield (1.98 g, 91%). IR (ATR cm^{-1}): 3077, 2959, 1626, 1570, 1463, 1166, 1109, 752, 619, 460; δ_H (400 MHz, $CDCl_3$): 0.74 (3H, t, *J* 7.4 Hz, CH_3), 1.18 (2H, m, CH_2), 1.70 (2H, m, CH_2), 3.92 (3H, s, NCH_3), 4.14 (2H, t, *J* 6.7 Hz, NCH_2), 7.42 (1H, s, NCH), 7.53 (1H, s, NCH) and 10.03 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.41 (CH_3), 19.37 (CH_2), 32.11 (CH_2), 36.65 (NCH_3), 49.72 (NCH_2), 122.29, 123.83, 136.99 ppm; *m*/*z* (ESI) 139.4 (M^+-Br^-) HRMS (ESI) calcd for $C_6H_{11}BrN_2$, 139.12352 (M^+-Br^-); found, 139.12327 (M^+-Br^-).

2.2.4. 1-Methyl-3-pentylimidazolium chloride (**5**)

Light yellowish oil. Yield (1.62 g, 86%). IR (ATR cm^{-1}): 2929, 2859, 1520, 1466, 1123, 1108, 731, 662; δ_H (400 MHz, $CDCl_3$): 0.82 (3H, t, *J* 7.4 Hz, CH_3), 1.24 (4H, m, CH_2), 1.48 (2H, q, CH_2), 3.52 (2H, t, *J* 6.7 Hz, NCH_2), 3.58 (3H, s, NCH_3), 6.78 (1H, s, NCH), 6.93 (1H, s, NCH) and 7.33 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 14.05 (CH_3), 22.52 (CH_2), 28.04, 32.51, 33.29, 62.36, 125.29, 128.21, 137.73 ppm; *m*/*z* (ESI) 153.0 (M^+-Cl^-) HRMS (ESI) calcd for $C_9H_{17}ClN_2$, 153.13917 (M^+-Cl^-); found, 153.13877 (M^+-Cl^-).

2.2.5. 1,3-Diethylimidazolium bromide (**6**)

Colorless oil. Yield (1.34 g, 94%). IR (ATR cm^{-1}): 3426, 3066, 2977, 1562, 1448, 1350, 1229, 1164, 1083, 1032, 956, 908, 803, 753, 643; δ_H (400 MHz, $CDCl_3$): 1.40 (6H, t, *J* 7.4 Hz, CH_3), 4.38 (4H, q, NCH_2), 7.45 (2H, s, NCH) and 10.38 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 16.48 (CH_3), 41.96 (NCH_2), 129.46 (NCH), 136.72 ppm; *m*/*z* (ESI) 124 (M^+-Br^-) HRMS (ESI) calcd for $C_7H_{13}BrN_2$, 125.10787 (M^+-Br^-), found, 125.10700 (M^+-Br^-).

2.2.6. 1,3-Dibutylimidazolium bromide (**7**)

Colorless oil. Yield (1.45 g, 80%). IR (ATR cm^{-1}): 3401, 2959, 2874, 1649, 1510, 1462, 1280, 1107, 1080, 1025, 951, 734, 664; δ_H

(400 MHz, $CDCl_3$): 0.86 (6H, t, *J* 7.4 Hz, CH_3), 1.27 (4H, m, CH_2), 1.81 (4H, m, CH_2), 4.27 (4H, m, NCH_2), 7.48 (2H, s, NCH) and 10.20 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.42 (CH_3), 19.40 (CH_2), 32.13 (CH_2), 49.74 (NCH_2), 122.22 (NCH), 136.87 ppm; *m/z* (ESI) 180.8 (M^+-Br^-) HRMS (ESI) calcd for $C_{11}H_{21}BrN_2$, 181.17047 (M^+-Br^-), found, 181.17000 (M^+-Br^-).

2.2.7. 1,3-Dipentylimidazolium chloride (**8**)

Light yellowish oil. Yield (1.50 g, 72%). IR (ATR cm^{-1}): 3291, 3113, 2956, 2929, 2860, 1509, 1465, 1457, 1377, 1284, 1229, 1108, 1078, 1056, 917, 812, 730, 695, 663, 624; δ_H (400 MHz, $CDCl_3$): 0.83 (6H, t, *J* 7.4 Hz, CH_3), 1.70 (4H, m, CH_2), 3.10 (4H, m, CH_2), 3.54 (4H, m, CH_2), 3.85 (4H, t, *J* 6.8 Hz, NCH_2), 6.83 (1H, s, NCH), 6.97 (1H, s, NCH) and 7.45 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.78 (CH_3), 22.05 (CH_2), 28.54 (CH_2), 47.07 (CH_2), 62.37 (NCH_2), 125.20 (CH), 136.88 ppm; *m/z* (ESI) 208.8 (M^+-Cl^-) HRMS (ESI) calcd for $C_{13}H_{25}ClN_2$, 209.20177 (M^+-Cl^-), found, 209.20175 (M^+-Cl^-).

2.2.8. 1,3-Dihexylimidazolium bromide (**9**)

Light yellowish oil. Yield (2.32 g, 99%). IR (ATR cm^{-1}): 3416, 2928, 2859, 1563, 1508, 1459, 1378, 1231, 1162, 1108, 1078, 1056, 917, 812, 728, 642, 562; δ_H (400 MHz, $CDCl_3$): 0.83 (6H, t, *J* 6.8 Hz, CH_3), 1.34 (4H, m, CH_2), 1.73 (4H, m, CH_2), 1.86 (4H, m, CH_2), 2.26 (4H, m, CH_2), 4.28 (4H, t, *J* 7.1 Hz, NCH_2), 7.48 (2H, s, NCH) and 10.36 ppm (1H, s, CH), δ_C (100 MHz, $CDCl_3$): 13.90 (CH_3), 22.37 (CH_2), 31.07 (CH_2), 32.78 (CH_2), 41.02 (CH_2), 50.04 (NCH_2), 128.19 (NCH), 129.01 (NCH), 137.83 ppm; *m/z* (ESI) 236.8 (M^+-Br^-) HRMS (ESI) calcd for $C_{15}H_{29}BrN_2$, 237.23307 (M^+-Br^-), found, 237.23309 (M^+-Br^-).

2.3. General procedure for the synthesis of iron(II) NHC complexes 10–12

To a suspension of the imidazolium salt (1.0 molar equiv.) in dry THF (15 ml) was added KOtBu (1.2 molar equiv.). After 1 h, the solution was added to a solution of the metal precursor [FeI(Cp)$(CO)_2$] (0.9 molar equiv.) in dry toluene (40 ml). After stirring for 20 h, the formed precipitate was separated by centrifugation, washed once with dry toluene (30 ml), and then extracted with dry dichloromethane (2 × 30 ml). Evaporation of the solvent gave the crude product, which was recrystallized by slow diffusion of hexane into dichloromethane solution to yield single crystals suitable for X-ray diffraction.

2.3.1. (η^5-C_5H_5)Fe$(CO)_2$(ImMe)I (**10**)

Complex **10** was prepared from dimethylimidazolium iodide (0.21 g, 0.90 mmol), KOtBu (0.12 g, 1 mmol), and [CpFe$(CO)_2$I] (0.24 g, 0.8 mmol). The crude product was obtained as a brownish paste. Yield (0.12 g, 53%). IR (CH_2Cl_2, cm^{-1}): 2048, 2000. υ(CO); δ_H (400 MHz, $CDCl_3$): 3.92 (6H, s, CH_3), 5.50 (5H, s, Cp) and 7.27 ppm (2H, s, NCH), δ_C (100 MHz, $CDCl_3$): 40.65 (NCH_3), 87.30 (Cp), 127.04 (NCH), 163.62 (C—Fe), 211.37 ppm (CO); *m/z* (ESI) 273.3 (M^+-I^-). HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2Fe^+$, 237.03264 (M^+-I^-), found, 237.03256 (M^+-I^-).

2.3.2. (η^5-C_5H_5)Fe$(CO)_2$(ImMeEt)I (**11**)

Complex **11** was prepared from 1-methyl-3-ethylimidazolium bromide (0.2 g, 1.04 mmol), KOtBu (0.14 g, 1.25 mmol) and [CpFe$(CO)_2$I] (0.28 g, 0.94 mmol) to give a greenish-brown paste which was passed through a column of silica gel. The product was obtained by elution with ethyl acetate/methanol (90:10) to give a green paste. Yield (0.22 g, 57%). IR (CH_2Cl_2, cm^{-1}): 2047, 2000 υ(CO); δ_H (400 MHz, $CDCl_3$):1.50 (3H, t, *J* 7.3 Hz, CH_3); 3.94 (3H, s, NCH_3), 4.29 (2H, t, NCH_2), 5.49 (5H, s, Cp), 7.27(1H, s, NCH) and 7.29 ppm (1H, s, NCH), δ_C (100 MHz, $CDCl_3$): 16.08 (CH_3), 40.71 (NCH_3), 47.32 (NCH_2), 87.34 (Cp), 124.16 (NCH), 127.68 (NCH), 163.17 (C-Fe), 211.25 ppm (CO), *m/z* (ESI) 287.0 (M^+-I^-). HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2Fe^+$, 287.04829 (M^+-I^-), found, 287.04815 (M^+-I^-).

Table 1
Summary of crystal data and refinement parameters of compounds **10**, **11** and **12**.

Compound	**10**	**11**	**12**
Formula	$C_{12}H_{13}FeIN_2O_2$	$C_{13}H_{15}FeIN_2O_2$	$C_{16}H_{21}FeIN_2O_2$
Formula weight	399.99	414.02	456.10
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pmn2_1$	$P2_1/c$	*P*-1
a, Å	15.1440(7)	10.0123(6)	9.0524(3)
b, Å	6.6844(3)	9.8060(6)	10.2842(3)
c, Å	14.0118(6)	15.4172(8)	10.2882(3)
α,°	90	90	89.086(2)
β,°	90	92.1350(10)	75.128(2)
γ,°	90	90	79.328(2)
Cell volume, Å^3	1418.39(11)	1512.62(15)	909.20(5)
Z	4	4	2
D_{calcd}, Mg/m^3	1.873	1.818	1.666
Final *R* indices	0.0287, 0.0635	0.0235, 0.0495	0.0713, 0.1989
R indices (all data)	0.0328, 0.0650	0.0341, 0.0537	0.1252, 0.2281

2.3.3. (η^5-C_5H_5)Fe$(CO)_2$(I^iPr)I (**12**)

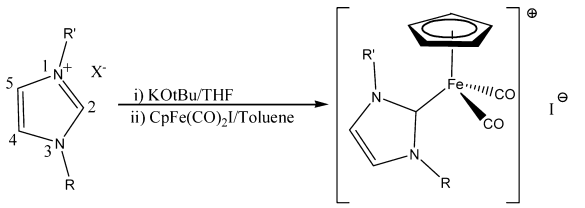
Complex **12** was prepared from 1,3-diisopropylimidazolium tetrafluoroborate (0.30 g, 1.00 mmol), KOtBu (0.14 g, 1.25 mmol) and [CpFe$(CO)_2$I] (0.37 g,1.00 mmol) to give a yellow-powder. Yield (0.31 g, 57%). IR (CH_2Cl_2, cm^{-1}): 2049, 2001 υ(CO); δ_H (400 MHz, $CDCl_3$):1.54 (12H, d, *J* 6.4 Hz, CH_3); 4.95 (2H, m, CH), 5.45 (5H, s, Cp) and 7.35 ppm (2H, s, NCH), δ_C (100 MHz, $CDCl_3$): 23.2 (CH_3), 53.5 (CH), 87.4 (Cp), 122.4 (NCH), 161.4 (C—Fe), 210.8 ppm (CO); *m/z* (ESI) 328.7(M^+-I^-). HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2Fe^+$, 329.09525 (M^+-I^-), found, 329.09476 (M^+-I^-).

2.4. X-ray crystal determination of complexes **10**, **11** and **12**

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 the APEX 2 [22] 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+ [22] and face indexed absorption corrections were made using XPREP [22]. 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 [23] and ORTEP-3 [24]. The crystal data and experimental data for **10**, **11** and **12** are summarized in Table 1.

2.5. General procedure for the transfer hydrogenation of ketones

The samples were typically prepared as follows: The ketone (2.1 mmol), iron(II) metal precursor (0.5 mol%), imidazolium salt (**1**–**9**, 0.5 mol%) and KOH (0.112 g, 0.2 M) in 10 ml 2-propanol were introduced into a Schlenk tube fitted with a reflux condenser and heated at 82 °C in an inert atmosphere. The reaction was then monitored at various time intervals by the use of GC. This was achieved by taking an aliquot which was first passed through a pad of silica and then injected (0.1 μl) into the GC with a DB wax polyethylene column (see details above). The corresponding alcohol and acetone were the only products detected in all cases. The identity of the alcohol was assessed by comparison with commercially available (Aldrich Chemical Co.) pure samples. Conversion to the product was



1 R = R' = CH_3, X = I
2 R = CH_3, R' = C_2H_5, X = Br
3 R = R' = $CH(CH_3)_2$, X = BF_4
4 R = CH_3, R' = C_4H_9, X = Br
5 R = CH_3, R' = C_6H_{11}, X = Cl
6 R = R' = C_2H_5, X = Br
7 R = R' = C_4H_9, X = Br
8 R = R' = C_5H_{11}, X = Cl
9 R = R' = C_6H_{13}, X = Br

10 R = R' = CH_3 - (ImMe)
11 R = CH_3, R' = CH_2CH_3 (ImMeEt)
12 R = R' = $CH(CH_3)_2$, (I'Pr)

Scheme 1. Synthetic route to the formation of the three-legged piano stool NHC-iron(II) complexes.

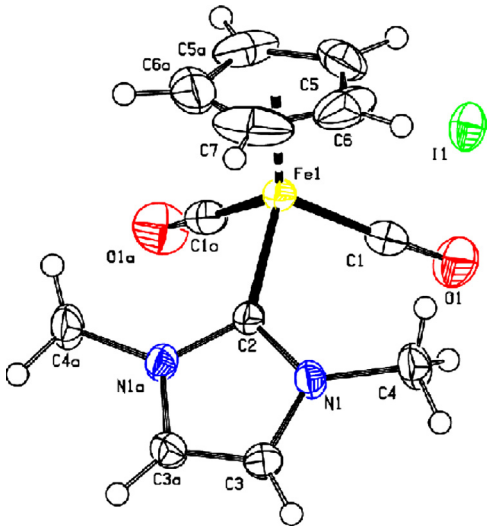


Fig. 1. ORTEP diagram of compound **10** shown at 50% probability thermal ellipsoids.

calculated from integration of its GC peak relative to that of residual unreacted ketone.

3. Results and discussion

3.1. Synthesis and characterization

This study involves the synthesis of a series of symmetrical and unsymmetrical imidazolium based ionic salts (**1**–**9**) and *in situ* generation of their piano-stool type iron(II) complexes. The ligands were prepared by methods adopted from literature [20], which involved the addition of an alkyl halide to monoalkylated imidazoles to obtain the imidazolium salts in high yields (72–99%). Formation of imidazolium salts **1**–**9** was confirmed by ^{1}H and ^{13}C NMR spectroscopy due to appearance of a characteristic proton peak at *circa* 10.5 ppm linked to the corresponding carbon at *circa* 137 ppm (position 2, Scheme 1) respectively. All the mass spectra exhibited peaks for the parent [M^+–X^-] ion, which is an additional evidence indicating formation of imidazolium salts **1**–**9**.

Piano-stool NHC-iron(II) complexes **10**–**12** were synthesized *in situ* by the reaction of metal precursor ($CpFe(CO)_2I$) with the corresponding NHC ligands generated from the imidazolium salts as shown in Scheme 1. The reaction was easily monitored by infrared spectroscopy. Observance of a shift toward higher energy (*circa* 2048 and 2000 cm^{-1}) for CO vibration in the product due to coordination of the nucleophilic NHC ligand when compared to respective peaks (2001 and 1996 cm^{-1}) for the iron(II) precursor ($CpFe(CO)_2I$) was indicative of NHC coordination and complex formation. In essence, complexation is inferred by the complete disappearance of the low energy peak at 1996 cm^{-1} which was accompanied by the appearance of a new peak at *circa* 2048 cm^{-1}. Compounds **10** and **12** were directly isolated as brown and yellow crystals respectively, while compound **11** required further purification. This was achieved by elution with a mixed solvent system (ethyl acetate/methanol; 9:1) that yielded a brownish-green paste which was later recrystallized as brown crystals from a saturated solution of dichloromethane. At room temperature, all the compounds showed good stability in solution and they can be handled and stored in air without decomposition. Determination of molecular structure of the new compounds was achieved by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction analyses. As expected the ^{1}H and ^{13}C NMR signals of the Cp ring were observed at δ 5.45–5.51 ppm and δ 87.1–87.5 ppm respectively which agree with reported data for related compounds [10]. Appearance of a resonance peak at around 161.5–164.2 ppm in ^{13}C NMR spectra, confirmed coordination of the NHC ligand and Fe—$C_{(carbene)}$ bond formation [10]. The positive mode ESI spectra showed intense molecular ion peaks corresponding to [M^+–I^-] which served as further confirmation of complex formation.

3.2. Molecular structures of compounds *10*, *11* and *12*

Crystals suitable for X-ray analysis for compounds **10** and **12** were obtained by slow diffusion of hexane into a saturated solution of dichloromethane at room temperature, while crystals of compound **11** were obtained from a saturated solution in dichloromethane as described above. The solid state structures of **10**–**12** are shown in Figs. 1–3, respectively. A summary of the crystal data and refinement parameters are presented in Table 1, while selected bond lengths and angles are presented in Table 2. The molecular structure revealed ionic complexes with iodide as the counter anion. Solid state structures of the three complexes were similar and showed distorted octahedral three-legged piano stool geometry around each iron center. The two CO and the NHC ligand form the equatorial legs of the complex with the Cp ligand occupying three apical positions. It should be noted that a piano stool iron complex similar to compound **12** bearing a different counter ion (BF_4^-) has been reported by Mercs et al. [11]. The size of the counterion has been reported [19d] to affect the ability of ionic salts to pack in a regular pattern and hence influence important physical properties like melting point which determines suitability as ionic liquids and solvents. The key crystallographic parameters are quite similar between **12** and the complex of Mercs et al. suggesting similarity between the different counterions.

3.3. Catalytic transfer hydrogenation

In situ generated complexes of all the nine imidazolium salts were tested as potential catalysts for transfer hydrogenation of a variety of ketones in 2-propanol acting both as hydrogen source and solvent for the reaction. The initial exploratory study presented in Table 3 was based on the isolated and characterized complexes **10**, **11** and **12**. It was conducted to establish if there will be any catalytic activity with cyclohexanone as the model substrate. The idea was hinged on the assumption that any catalytic activity using the iron complexes will be highest in their pure isolated form. Positive results will then be transferred to the study of one pot *in situ* generated systems. In this instance, the three complexes were all

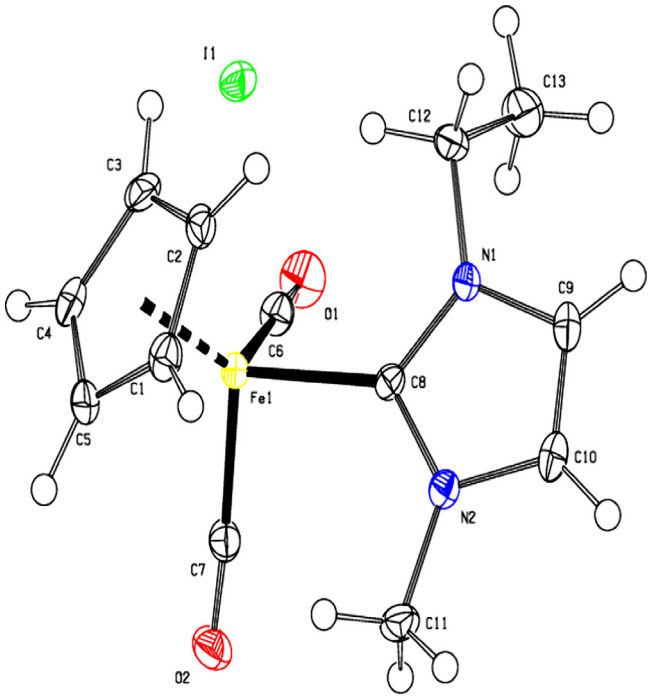


Fig. 2. ORTEP diagram of compound **11** shown at 50% probability thermal ellipsoids.

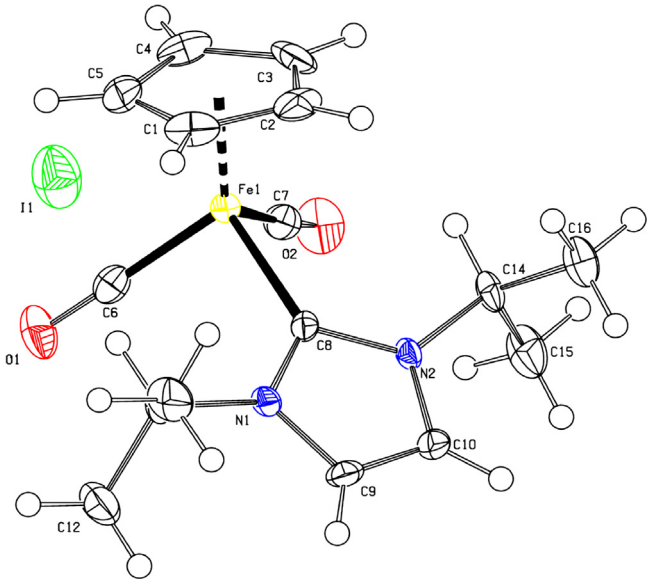


Fig. 3. ORTEP diagram of compound **12** shown at 50% probability thermal ellipsoids.

found to show activity, with highest conversion of 100% and turn over number (TON) of 200 obtained for complex **11** (Table 3).

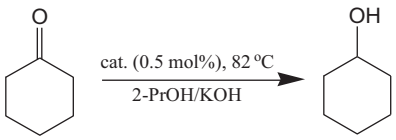
This was an encouraging result that compared favorably (and in fact showed better TON values) with results for iron [18] and ruthenium [25] NHC complexes published earlier. It should be noted that catalytic transfer hydrogenation of ketones to alcohols has been reported to occur through sole activation by ionizable inorganic salts MOH (M = Li, Na, K) [26,27], hence we carried out a series of experiments to establish and isolate the role of the various components in the catalytic process and to establish optimum conditions for a comprehensive *in situ* study. Under similar conditions, a blank test run was monitored over a 48 h period with only KOH as additive 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. The next test was based on the metal precursor $CpFe(CO)_2I$ as catalyst (without the imidazolium salt) with the result that 46% conversion to cyclohexanol was recorded after 12 h. In the absence of base (KOH), there was no reaction for this system. Hence, at this stage it can safely be concluded that the catalytic process is only feasible under a basic environment similar to the conditions required for the de-protonation of imidazolium salts for the generation of active NHC ligands.

Having established that the catalysts were active for the model systems, we then moved toward our main objective of simplifying the catalytic testing process *via* a one pot *in situ* catalyst generation and testing thereby alleviating the laborious isolation and purification steps described for **10**–**12**. This was achieved by using a methodology that presents significant practical advantages for homogeneous catalysis especially given the fact that the active specie may be quite reactive and relatively unstable when isolated. In order to optimize the reaction, the following parameters were investigated and the result is presented in Fig. 4:

Table 2
Selected bond length (Å) and angle (°) for compounds **10**, **11** and **12**.

	10	**11**	**12**
Bond lengths			
Fe-Centroid	1.940(5)	2.108(2)	2.106(9)
Fe-C6	1.777(5) (Fe-C1a)	1.777(2)	1.779(9)
Fe-C7	1.777(5) (Fe-C1)	1.773(2)	1.787(9)
Fe-C8	1.969(6) (Fe-C2)	1.972(2)	1.972(8)
C6-O1	1.144(5) (C1a-O1a)	1.380(3)	1.133(10)
C7-O2	1.144(5) (C1-O1)	1.145(3)	1.132(11)
Bond angles			
C6-Fe-C7	93.4(3) (C1a-Fe-C1)	92.20(11)	92.70(2)
C6-Fe-C8	95.05(19) (C1a-Fe-C2)	91.33(10)	94.30(3)
C7-Fe-C8	95.05(19) (C1-Fe-C2)	96.30(10)	94.90(4)
N1-C8-N2	104.2(5) (N1a-C2-N1)	104.38(19)	104.0(6)

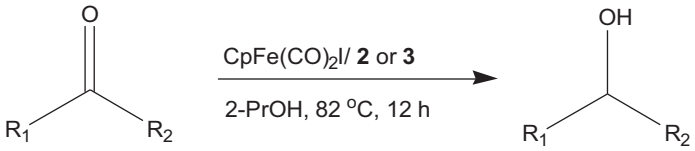
Table 3
Catalytic transfer hydrogenation catalyzed by complex **10**, **11** and **12**.



Catalyst	Substrate	Conversion (%)[a]	Time (h)	TOF[b]	TON[c]
10	Cyclohexanone	82	11	15	164
11	Cyclohexanone	100	9	22	200
12	Cyclohexanone	91	9	20	182

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

Table 4
One pot Fe-catalyzed reduction of ketones based on imidazolium salts **2** and **3**.



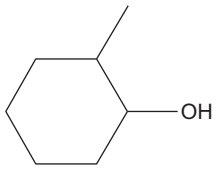
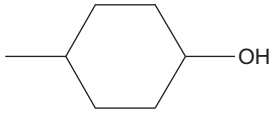
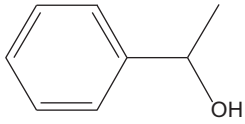
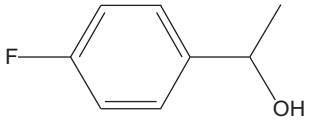
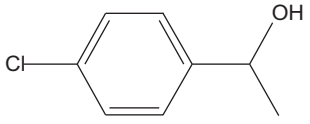
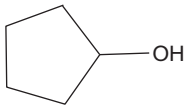
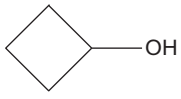
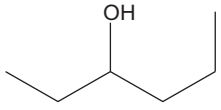
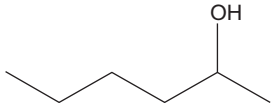
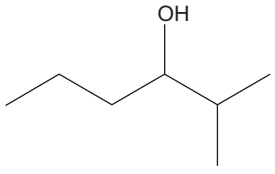
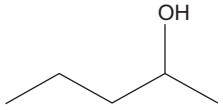
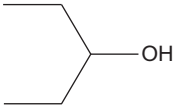
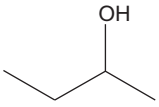
Entry	Product	Compound **2**		Compound **3**	
		Conversion	(%) TON	Conversion	(%) TON
1		28	56	45	90
2		87	174	92	184
3		55	110	68	136
4		49	98	33	66
5		83	166	89	178
6		32	64	50	100
7		17	34	100	200
8		10	20	No reaction	–
9		21	42	27	54
10		3	6	2	4
11		39	78	60	120

Table 4 (*Continued*)

Entry	Product	Compound **2**		Compound **3**	
		Conversion	(%) TON	Conversion	(%) TON
12		29	58	12	24
13		84	168	46	92

- *Concentration*: best results were obtained with solutions of 0.5 M concentration of catalyst.
- *Temperature*: optimum result was obtained at 82 °C, at room temperature no reaction occurred, and at temperatures above 100 °C, the reaction rate declined due to decomposition of the catalyst system.
- *Time*: 12 h was established as the optimum; beyond which the conversion saturates and tails off.

Thus, in a typical experiment, a solution of the metal precursor and imidazolium salt (0.5 mol%) was made in freshly distilled isopropanol. After the mixture was thoroughly stirred and mixed, a base (typically, KOH) and the ketone to be reduced were added and the reaction mixture was heated to 82 °C and left stirring for 12 h. Progress was monitored by gas chromatography.

The imidazolium salts (**1**–**9**, Scheme 1) were tested as described above for *in situ* catalyst generation and application in transfer hydrogenation under the optimized conditions and the result is presented in Fig. 5. All the catalysts except compounds **4** and **5** gave good conversions and turn overs to cyclohexanol at the end of the 12 h reaction time.

The structurally unsymmetrical catalysts **4** and **5** with one long *N*-alkyl carbon chain substituent showed decline in catalytic activity as compared to the control reaction at any given temperature while compounds **2** and **3** exhibited comparatively higher catalytic activities. It seems from these results that a large dissimilarity between *N*-alkyl substituents of imidazolium compounds resulted in catalyst deactivation. Catalyst stability and activity seems to depend on the symmetry of the imidazolium salt, highly symmetrical salts (where R=R□) resulted in high catalyst activity and those of low symmetry (R ≠ R□) showed only modest activity or are completely inactive if the dissimilarity is large as observed for **4** and **5**. Recently we have proposed a mechanism on the transfer hydrogenation of ketones using NHC ligands [19b].

As a result of the better catalytic activities of compounds **2** and **3**, they were used to test the scope and limitations of the catalytic transfer hydrogenation of thirteen aromatic, cyclic and aliphatic ketones as a range of substrates that differ electronically and have a variety of steric demands relative to the ketone C=O bond. Best activity (TON up to 184) was achieved with γ-substituted aromatic ketones. In general, catalytic activity of compounds **2** and **3** show similar trends except for a few obvious differences (Table 4, entries 7 and 13). In addition, alkyl ketones which are usually difficult to reduce were also converted to the corresponding alcohols by this system. In general, compound **3** which also contain symmetrical *N*-alkyl substituents also gave better results in comparison to compound **2** with slightly dissimilar *N*-alkyl substituents.

By introduction of an electron-donating group to the *alpha* position of cyclohexanone, the recorded conversion was drastically reduced (Table 4, entry 1). However, a better conversion was obtained when the same electron-donating group was at the *gamma* position. This may be attributed to steric interference that resulted in limited access to the reactive site in the α-substituted substrate. But, the introduction of electron-withdrawing halogen groups to the γ position of acetophenone (entries 4 and 5) showed no identifiable trend probably due to the high electronegativity of fluorine which although in the same halogen group as chlorine, tends to be chemically unique resulting in decreased activity as compared to chlorine that increased the ease of conversion of the ketone.

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

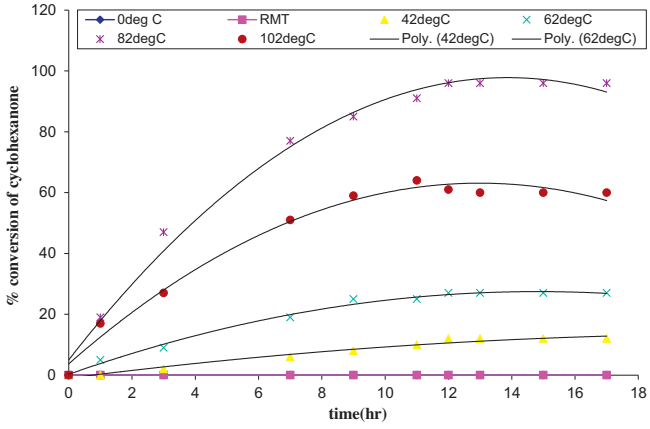


Fig. 4. Effect of reaction variables on conversion of cyclohexanone in a one pot process based on ligand **3**.

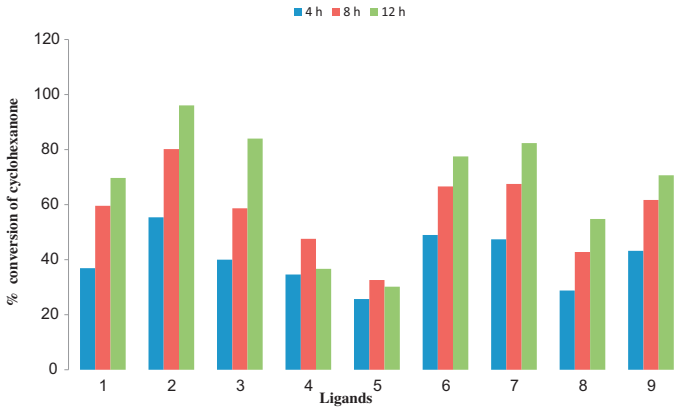


Fig. 5. One pot conversion of cyclohexanone based on imidazolium salts **1**–**9**.

compounds as compared to the more sterically hindered reactive site in the straight-chain ketones that led to diminished conversions to the alcohols. This trend is further observed when 2-ketones are compared with 3-ketones, hence it can safely be concluded that steric access to the C=O bond is a key determinant of reactivity. Also, symmetrical imidazolium salts where the *N*-alkyl substituents are the same (R=R′, Scheme 1) or very close showed better catalytic results than low symmetry salts with widely dissimilar substituents.

4. Conclusions

Both symmetrical and unsymmetrical 1,3-dialkylimidazolium salts have been successfully synthesized. Similarly, iron(II) complexes of the general type $[CpFe(CO)_2(NHC)]I^-$ were also successfully synthesized and characterized spectroscopically and by crystallography. The activity of the new complexes as catalysts generated *in situ* in a one pot reaction was tested in hydrogen transfer reactions. The results have revealed that catalytic activities comparable to those obtained for well-defined isolated complexes was obtainable for the *in situ* generated catalysts and the method is wide in scope tolerating a variety of ketones (aromatic, aliphatic and cyclic) in 2-propanol as the hydrogen source and solvent.

Supplementary material

Crystallographic data in cif format for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, with numbers CCDC 844526–844528 for compounds **10**–**12**, 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, deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk.

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