NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: D. Ramaiah, M. Viji, N. Tyagi and N. Naithani, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ02822A.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/njc

View Article Online
DOI: 10.1039/C7NJ02822A

Journal Name

ARTICLE

Aryl Appended Neutral and Cationic Half-sandwich Ruthenium(II)-*NHC* Complexes: Synthesis, Characterisation and Catalytic Applications

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mambattakkara Viji,[a,b] Nidhi Tyagi,[a] Neeraj Naithani[c] and Danaboyina Ramaiah*[d]

Half-sandwich ruthenium(II) complexes **1**-**6** bearing imidazolylidene and pyridyl-imidazolylidene ligands have been synthesised in good yields and were characterised on the basis of spectral and analytical evidence. In addition, the structures of the complexes **1**-**4** were unambiguously established through single crystal X-ray analysis. Transmetalation of the ligands followed by the complexation with ruthenium precursors yielded the air and moisture stable complexes. The crystal structures of these complexes exhibited piano-stool geometries with η^6-coordination of the *p*-cymene or hexamethylbenzene moieties. These complexes exhibited catalytic activity in the transfer hydrogenation of carbonyls in alkaline medium using 2-propanol as the hydrogen source. The effect of variations in the catalyst structure on the transfer hydrogenation and stability was investigated in detail as well as theoretical calculations were employed to understand the mechanism of the catalytic activity. The neutral ruthenium-*NHC* complexes **1** and **2** showed the efficiency of *ca.* 100% at a catalyst loading of *ca.* 2 mol% within 2 h of reaction in 2-propanol, whereas quantitative yields were obtained in presence of the cationic ruthenium-*NHC* complexes **3**-**6** within 1 h at a low catalyst loading of *ca.* 0.5 mol%, thereby demonstrating their robustness for the transfer hydrogenation of the aromatic ketones.

Introduction

During the past decade, the development of ligands bearing donors other than phosphorus has been an active area of interest in homogeneous catalysis, and organic synthesis. Of the various ligands reported, *N*-heterocyclic carbenes (*NHCs*) have emerged as a flexible class when compared to phosphorous containing ligands.[1] Furthermore, *NHCs* bearing transition metal complexes have been well studied for their use as catalysts in C=O, C=C and C=N reduction reactions and also in olefin metathesis.[2-4] Of the reported examples, the metal complexes based on iridium, rhodium, and ruthenium complexes having various ligands especially *NHC* ligands have been found to be excellent catalysts for the reactions like hydrogenation, dehydrogenation, transfer hydrogenation (TH), and hydrosilylation.[5,6] Among these examples, the ruthenium complexes bearing *NHCs* have exhibited high catalytic efficacy for the reduction of ketones, aldehydes, imines, nitro aromatics, alkenes, and carbon dioxide.[7,8]

Of the various reduction reactions, the transfer hydrogenation is preferred in the large-scale industry due to the advantages such as the reduced waste generation and energy consumption.[9] In this context, Noyori and Baratta and co-workers have developed Ru(II) and Os(II) complexes as efficient catalysts for the transfer hydrogenation of the ketones and imines.[10,11] Though, a good number of examples of the metal-*NHC*-complexes have been reported for the transfer hydrogenation reactions,[12] the development of new catalysts with high stability is quite challenging in recent years. Herein, we report the synthesis and catalytic activity of a novel series of neutral and cationic ruthenium(II)-*NHC* complexes **1**-**6** appended with anthracene and phenyl moieties. Uniquely, these systems showed significantly increased air and moisture stability due to the coordination of Ru(II) with *NHC* ligands. These systems acted as efficient and better catalysts for the reduction of the aromatic ketones, substituted with electron donor and acceptor functional groups, when compared to the literature known complexes under similar conditions.

Results and discussion

Synthesis and characterisation of the complexes

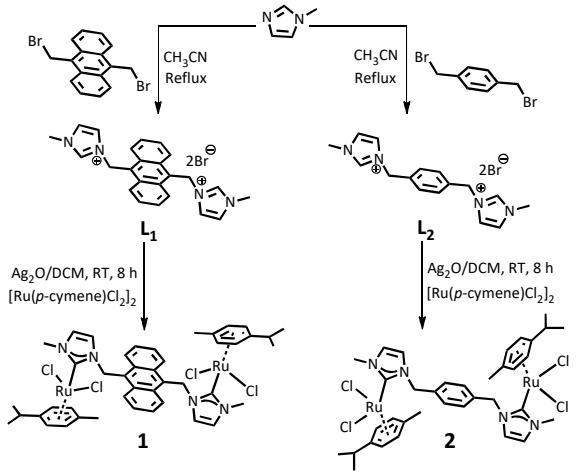
The ligands L_1 and L_2, substituted anthracene and phenyl were prepared as per the reported procedure.[13,14] The

[a] Photosciences and Photonics, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, India.
[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST Campus, Trivandrum 695 019, India.
[c] Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Trivandrum 695 022, India
[d] CSIR-North East Institute of Science and Technology, Jorhat 785 006, India
E-mail: rama@neist.res.in or d.ramaiah@gmail.com

Electronic Supplementary Information (ESI) available: Figures S1-S24, Tables S1-S4 and Scheme S1 shows the characterization data and catalytic studies of the complexes. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7NJ02822A

subsequent reactions of L_1 and L_2 with Ag_2O followed by complexation with $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ resulted in the synthesis of dinuclear ruthenium complexes **1** and **2** in *ca.* 39 and 40% yields, respectively (Scheme 1). The cationic complexes **3**-**6**, on the other hand, were synthesised in a three-step route starting from the imidazole derivative[15] as shown in Scheme 2. In the first step, the synthesis of the imidazolium salts L_3, L_4 and L_5 was achieved by the reaction of 2-(1H-imidazol-1-yl)pyridine with the corresponding aryl halide. Subsequently, the complexes **3**-**6** were synthesised by the deprotonation of the ligand precursors with Ag_2O followed by complexation with the ruthenium precursors, such as $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and $[Ru(hexamethylbenzene)Cl_2]_2$. These complexes were isolated in moderate yields as their hexafluorophosphate salts after treatment with ammonium hexafluorophosphate.



Scheme 1. Synthesis of the neutral ruthenium-*NHC* complexes **1** and **2**.

All the ligands and their metal complexes were characterised on the basis of analytical and spectral evidence (Figs. S1-S12, ESI). For example, the singlet at δ 8.87 ppm and 9.26 ppm corresponding to the imidazolium proton in L_1 and L_2 was disappeared upon the formation of complexes **1** and **2**, respectively. In their ^{13}C NMR spectrum, a new signal due to the C_2 (carbene carbon) of the imidazol-2-ylidene units appeared at δ 173.16 and 173.97 ppm, respectively for **1** and **2.** Similarly, the ligands were characterised having downfield signals for the strongly de-shielded C_2 protons of the imidazolium moiety, which appeared at δ 9.37, 10.32 and 10.08 ppm for L_3, L_4 and L_5, respectively. The ruthenium complexes **3-6** were furthermore characterised by the disappearance of carbenic protons followed by the appearance of downfield shift for the carbenic carbons at δ 186.14, 190.56, 186.22 and 185.88 ppm, respectively. In addition, the structures of the representative complexes **1**-**4** have been unambiguously established through single crystal X-ray structure analysis (Fig 1).

To understand the redox and thermal stability properties of the complexes **1**-**6**, we have carried out cyclic voltammetry, square wave measurements and thermogravimetric analysis (TGA) under different conditions. The oxidation potentials *vs* Ag/Ag^+ measured for all complexes, which showed one electron oxidation of the redox couple Ru(II)/Ru(III) as reported in the literature for the similar systems.[16] These complexes exhibited quasi-reversible electrochemical wave and the potentials are found to be +1.13, +1.14, +1.48, +1.28, +1.47, and +1.49 V, respectively, for the complexes **1**-**6** (Fig. S13, ESI). In the thermogravimetric analysis of the complexes **1** and **2**, we observed a two step decomposition pattern in the temperature range *ca.* 20-900 ^oC, and the weight loss was found to be *ca.* 66 and 59%, respectively (Fig. S14, ESI). Similarly, the thermograms of the complexes **3**-**6** under similar conditions showed a weight loss of *ca.* 62, 72, 70, and 85%, respectively. These observations can be attributed to the loss of chloride ions first followed by the decomposition of the aromatic moieties present in these complexes.

Single crystal X-ray analysis of the complexes 1-4

X-ray quality crystals of the complexes were grown in triclinic and monoclinic fashion through slow evaporation of a mixture (9:1) of chloroform and methanol. For example, in the case of complexes **1** and **2**, the coordination geometry around both the Ru(II) centres is best described as pseudo-octahedral with arene ring having three coordination sites in a η^6-fashion, carbene and two chloride ions occupying the remaining coordination sites. Fig. 1 shows the ORTEP diagrams of the complexes **1**-**4** along with the atom numbering scheme and their selected crystallographic data, bond lengths and bond angles are summarised in Tables S1-S2 (ESI).

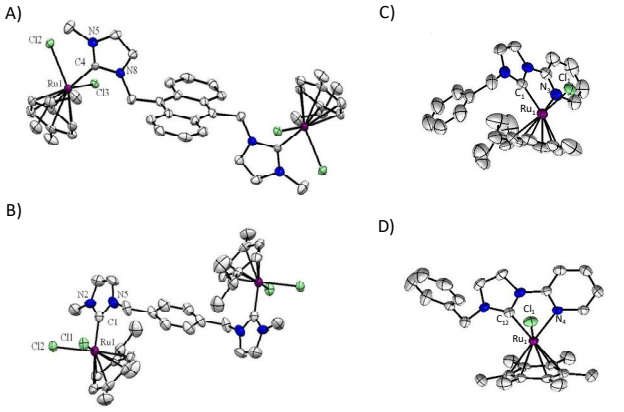


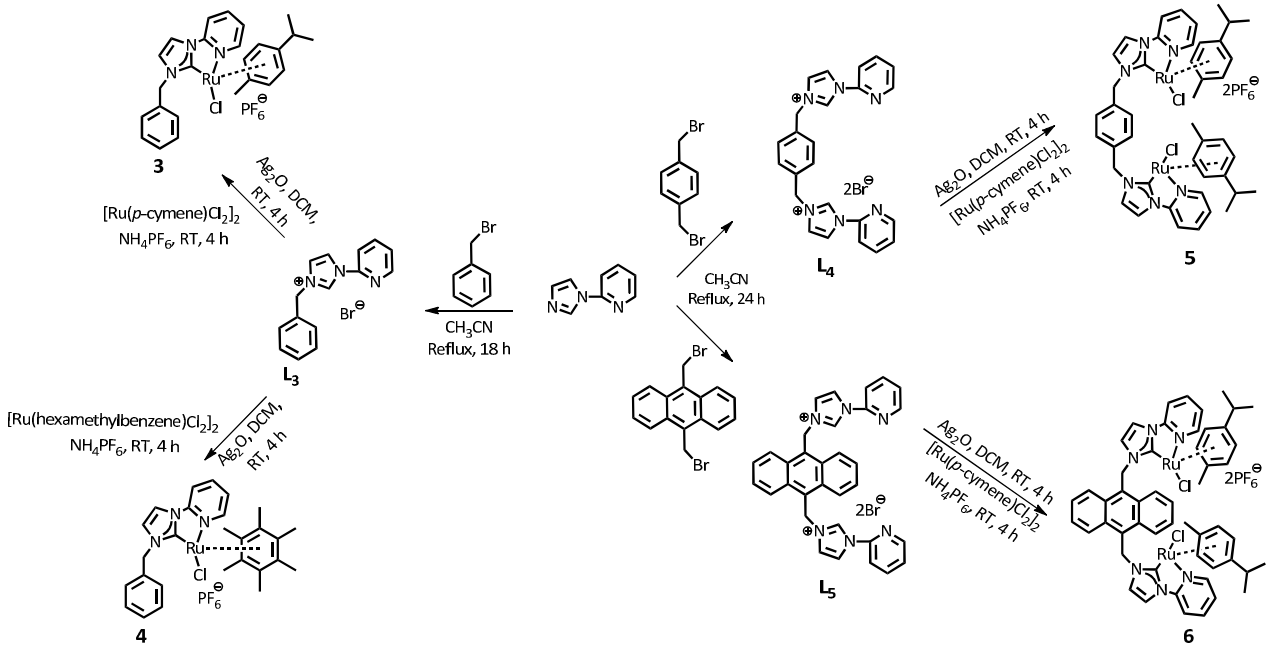
Fig. 1. ORTEP diagrams of the complexes **1-4** at 50% probability level. A) **1**: $[Ru_2(L_1)(\eta^6\text{-}p\text{-cymene})_2Cl_4]$, B) **2**: $[Ru_2(L_2)(\eta^6\text{-}p\text{-cymene})_2Cl_4]$, C) **3**: $[Ru(L_3)(\eta^6\text{-p-cymene})Cl]^+$, and D) **4**: $[Ru(L_3)(\eta^6\text{-hexamethylbenzene})Cl]^+$. (Hydrogen atoms, solvents and counter ions were omitted for clarity.

Both the complexes **1** and **2** showed coordinatively saturated ($18e^-$) "three-legged piano-stool" geometry with the π-bonded η^6-arene ring forming the seat and a carbene donor atom of L_1/L_2 and two Cl^- ions constituting the legs of the stool.

View Article Online
DOI: 10.1039/C7NJ02822A

The Ru-C (carbene) distances of 2.074(7) Å in **1** and 2.056 Å in **2** are comparable to those in the low-spin Ru(II)-carbene complexes.[17] The *p*-cymene ring in the both these complexes is almost planar, and ruthenium is displaced by 1.719 Å (for **1**) and 1.693 Å (for **2**) from the centroid of *p*-cymene ring, which is similar to the reported Ru(II) arene complexes.[18,19] In both these complexes, the coordination of two imidazolyl carbene units to Ru(II) centres produces a twist for these moieties. The Ru(II) centres adopt a *trans*-position to each other in such a way that each Ru(II) centre is 0.462 Å away from the anthracene plane in **1**, while in case of the complex **2**, we observed Ru(II) centre is 3.297 Å away from the benzene ring.

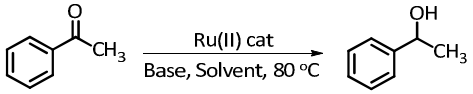
Similarly, the ruthenium atom in the cationic complexes **3** and **4** is surrounded by the η^6-bonded arene (*p*-cymene ring in **3** and hexamethylbenzene in **4**), *NHC* ligand (L_3), and chloride ion and thus attains a "three legged piano-stool" geometry; which is archetypical of $[(\eta^6\text{-arene})Ru(L_3)Cl]^+$ half-sandwich arene complexes. The arene ring constitutes a seat, while chloride, pyridine nitrogen (Npy) and carbene carbon of the *NHC* ligand (L_3), constitutes three legs of the piano-stool. In these complexes (**3** and **4**), Ru-Cl and Ru-Npy bond lengths are of approximately identical 2.4 and 2.1 Å, respectively and analogous to the literature reports.[20] The Ru–*NHC* bond lengths are 2.017 (for **3**) and 2.024 Å (for **4**), typical of Ru-*NHC* σ-bonds, indicating that the back-donation is negligible for these complexes.[21] In particular, Ru-Ar distances are found to be 1.714(3) (for **3**) and 1.740(2) (for **4**) from the centroid of the arene, which is comparable to reported literature values for similar "three legged piano-stool" ruthenium complexes.[22] In both these complexes, the ligand (L_3) binds to the ruthenium metal centre via *NHC*, Npy atom forming one five-membered chelate ring having the bite angles of C(1)-Ru(1)-N(3) = 76.63° and C(12)-Ru(1)-N(4) = 76.05°, for **3** and **4**, respectively. Interestingly, the phenyl arm attached to imidazolyl nitrogen showed a flip, when a plane is drawn through *NHC* ligand (L_3), towards the leg of the piano-stool geometry in the complex **3**. In contrast, reverse to the leg of the piano-stool geometry was observed in the case of the complex **4**, which could be attributed due to the steric factors of the hexamethylbenzene moiety in the latter case.



Scheme 2. Synthesis of the cationic ruthenium-*NHC* complexes **3**-**6**.

Catalytic activity of the complexes

To understand potential use of the Ru-*NHC* complexes **1**-**6**, in transfer hydrogenation of carbonyl compounds, we employed acetophenone as the model substrate (Scheme 3). The catalytic reactions were carried out under different conditions using 0.1 mmol of the substrate in presence of different solvents, base promoters, 0.5-2 mol% of the catalysts at 80 ± 2 °C. The catalysts in different solvents and bases were pre-heated at 40 °C and then acetophenone was added slowly. The reaction mixture was then refluxed at 80 °C for a specified time period. The transfer hydrogenation products obtained were analysed through GC-MS and NMR techniques (Figs. S15-S24, ESI). Table 1, summarises transfer hydrogenation results



Scheme 3. Transfer hydrogenation of acetophenone in presence of the complexes **1**-**6**.

View Article Online
DOI: 10.1039/C7NJ02822A

using acetophenone as the substrate in presence of the Ru-*NHC* complexes **1-6** under different conditions. For example, the complexes **1**-**2** in t-butanol in the presence of both NaOH and KOH as promoters showed negligible reaction for 2 h (entries 1-2). In contrast, when we employed glycerol as the hydrogen source under similar reaction conditions and NaOH as the base promoter, we observed good substrate conversion yields in the range *ca.* 48-65% (entry 3). We observed a non-negligible conversion of the substrate in presence of the complexes **1-6**, when we used Cs_2CO_3 (entry 4) and Na_2CO_3 (entry 5) as the base promoter. Upon changing the base to KO^tBu, we obtained an increase in the reaction yields to the tune of *ca.* 55-60% (entry 6) for the complexes **1** and **2**, and *ca.* 40-75% for **3-6**. Interestingly, the complexes **1** and **2** in the presence of both NaOH and KOH have been proven to catalyse the efficient reduction of acetophenone at a loading of 2 mol% in 2-propanol, affording 1-phenylethanol about *ca.* 95-100% (entries 7-8) and achieving a TOF (turn over frequency) of *ca.* 50 h^{-1} at 50% formation of the product. The investigation of transfer hydrogenation reactions with the complexes **3-6** (0.5 mol%) in presence of both NaOH and KOH in 2-propanol exhibited excellent catalytic efficiencies, affording *ca.* 99-100% (entries 7-8) conversion for the substrate and a TOF of *ca.* 200 h^{-1} at 50% formation of the product. When the catalyst loading was decreased by *ca.* 50%, the complexes **1** and **2** at 1 mol%, showed lower efficiency for the conversion of the substrate (*ca.* 62 and 58%) (entry 9), respectively. Similarly reduced conversion yields of *ca.* 45-60% were observed with the complexes **3-6** at a loading of 0.25 mol% (entry 9). These results demonstrate that we require a minimum of 0.5 and 2 mol% loading of the catalysts **3-6** and **1-2**, respectively, to achieve *ca.* 100% transfer hydrogenation of acetophenone under moderate reaction conditions.

Table 1. Optimization of reaction conditions for transfer hydrogenation of acetophenone in presence of the complexes **1**-**6**.[a]

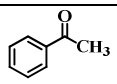
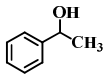
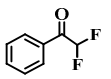
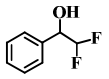
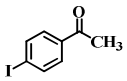
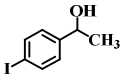
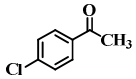
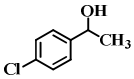
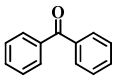
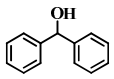
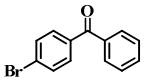
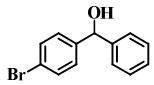
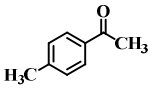
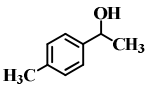
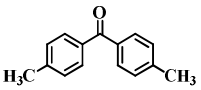
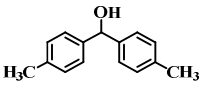
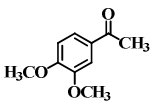
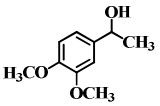
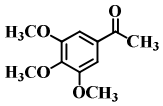
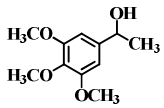
Entry	Solvent	Base	Conversion (%)					
			Complex **1**	Complex **2**	Complex **3**	Complex **4**	Complex **5**	Complex **6**
1	t-Butanol	NaOH	nc	nc	nc	nc	nc	nc
2	t-Butanol	KOH	nc	nc	nc	nc	nc	nc
3	Glycerol	NaOH	50	48	52	60	62	65
4	2-propanol	Cs_2CO_3	<10	<10	10	15	10	12
5	2-propanol	Na_2CO_3	21	15	6	3	15	18
6	2-propanol	KO^tBu	60	55	40	46	64	75
7	2-propanol	KOH	>99	95	>99	>99	100	100
8	2-propanol	NaOH	100	>99	100	100	100	100
9	2-propanol	NaOH	[b]62	[b]58	[c]45	[c]48	[c]58	[c]60

[a] Average of three independent experiments and S.D ± 1% and experimental conditions: acetophenone (0.1 mmol), complexes **1-2** (2 mol%) and **3-6** (0.5 mol%), base (0.1 mmol), solvent (2 mL), temperature (80 ± 2 °C), reaction time 2 h. Yields determined by GC-MS analyses. [b] Complexes **1-2** (1 mol%). [c] Complexes **3-6** (0.25 mol%). nc: no conversion.

To explore the substrate scope of the reaction, the neutral and cationic Ru(II)-*NHC* complexes **1-6** were tested as pre-catalysts for the transfer hydrogenation of various aromatic ketones (Tables 2 and 3). For example, the substrates bearing electronegative groups like 2,2-difluoro-1-phenylethanone (entry 2) exhibited *ca.* 100% conversion to the reduced product using the catalysts **1** and **2** in the presence of both NaOH and KOH as the base promoters in 2-propanol. Similar observations were also made with the chloro- and iodo-substituted acetophenone (entries 3-4), which have resulted in *ca.* 95-100%. When we employed benzophenone (entry 5) and (4-bromophenyl)(phenyl)methanone (entry 6) as the substrates, we observed quantitative conversion (*ca.* 90-100%) under similar reaction conditions. Similarly, in the case of the reactions with electron rich aromatic ketones such as tolylethanone (entry 7), di-tolylmethanone (entry 8), 1-(3,4-dimethoxyphenyl)-ethanone (entry 9), and 1-(3,4,5-trimethoxy-phenyl)ethanone (entry 10), we observed excellent conversion to their corresponding alcohols in the range *ca.* 90-99%, and NaOH used as the base promoter. Interestingly, upon changing the base promoter to KOH, we observed *ca.* 92-99% conversion of the substrate to the product within 3 h of reaction under identical conditions. The substrate scope of the reaction was investigated through employing aliphatic ketones and aliphatic/aromatic aldehydes. Surprisingly, we observed negligible conversion of these substrates to the reduced products in presence of both the complexes **1** and **2** under similar conditions (entries 11-12). These experiments confirm that, both the neutral complexes **1** and **2** were found to be quite efficient and selective only for transfer hydrogenation of the aromatic ketones, while the aliphatic ketones/aldehydes showed negligible reaction under identical conditions.

View Article Online
DOI: 10.1039/C7NJ02822A

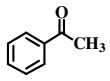
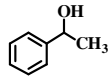
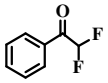
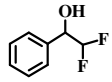
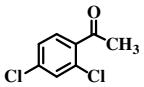
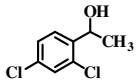
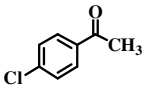
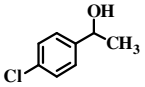
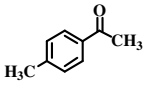
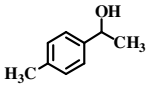
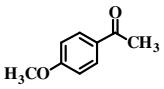
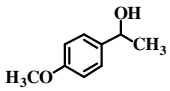
Table 2. Transfer Hydrogenation of the aromatic ketones catalyzed by the complexes **1** and **2**.[a]

Entry	Substrate	Product	Complex **1** Conversion % (TOF, h^{-1})		Complex **2** Conversion % (TOF, h^{-1})	
			NaOH	KOH	NaOH	KOH
1			100, 96[c] (50.00)	>99, 94[c] (49.75)	>99, 95[c] (49.95)	95, 93[c] (47.60)
2			100, 98[c] (50.00)	100, 97[c] (50.00)	100, 99[c] (50.00)	100, 96[c] (50.00)
3			>99, 97[c] (49.98)	98, 95[c] (49.00)	100, 97[c] (50.00)	96, 92[c] (48.00)
4			>99, 98[c] (49.90)	99, 94[c] (49.90)	>99,96[c] (49.95)	95, 91[c] (47.50)
5			97, 94[c] (48.50)	96, 90[c] (48.00)	100, 94[c] (50.00)	>99, 96[c] (49.55)
6			91, 89[c] (45.50)	>99, 95[c] (49.95)	95, 90[c] (47.50)	98, 93[c] (49.00)
7			>99, 92[c] (49.60)	>99[b],91[c] (33.30)	98, 90[c] (49.00)	>99[b], 88[c] (33.30)
8			98, 91[c] (49.00)	95[b], 89[c] (31.00)	97, 92[c] (48.50)	96[b], 91[c] (32.00)
9			93, 90[c] (46.50)	97[b], 93[c] (32.30)	98 , 94[c] (49.00)	96[b], 91[c] (32.00)
10			96, 92[c] (48.00)	96[b],90[c] (32.00)	90, 85[c] (45.00)	92[b],88[c] (30.00)
11			nc	nc	nc	nc
12			nc	nc	nc	nc

[a] Average of three independent experiments and S.D ± 1% and experimental conditions: substrate (0.1 mmol), complexes **1** or **2** (2 mol%, 0.002 mmol), base (NaOH/KOH, 0.1 mmol), 2-propanol (2 mL), temperature (80 ± 2 °C), reaction time 2 h. [b] Reaction time 3 h. [c] Isolated yield. nc: negligible or no conversion. TON (turn over number) = (moles of substrate/moles of catalyst); TOF (turn over frequency), h^{-1} = TON/time of reaction (h) at 50% product formation.

View Article Online
DOI: 10.1039/C7NJ02822A

Table 3. Transfer hydrogenation of the aromatic ketones catalyzed by the complexes **3**-**6**.[a]

Entry	Substrate	Product	Conversion (%), (Time, h) (TOF, h^{-1})			
			Complex **3**	Complex **4**	Complex **5**	Complex **6**
1			> 99 (2) (199)	99 (2) (198)	100 (2) (200)	100 (2) (200)
2			100 (1) (400)	100 (1) (400)	100 (1) (400)	100 (1) (400)
3			100 (2) (200)	100 (2) (200)	100 (1) (400)	100 (1) (400)
4			100 (2) (200)	100 (2) (200)	100 (2) (200)	100 (1) (200)
5			100 (4) (100)	> 99 (4) (99)	97 (3) (129)	100 (3) (133)
6			> 99 (5) (80)	98 (5) (78)	100 (3) (133)	> 99 (3) (132)

[a] Average of three independent experiments and S.D ± 1% and experimental conditions: Substrate (0.1 mmol), complexes **3-6** (0.5 mol%, 0.0005 mmol), base (NaOH, 0.1 mmol), 2-propanol (2 mL) at 80 ± 2 °C. TON (turn over number) = (moles of substrate/moles of catalyst); TOF (turn over frequency), h^{-1} = TON/time of reaction (h) at 50% product formation.

To understand the potential of the cationic complexes **3**-**6**, we have expanded the transfer hydrogenation reactions towards some of the electron rich and deficient aromatic ketones as shown in Table 3. The reactions were performed by following the optimized conditions at different time scales. With a catalyst loading of *ca.* 0.5 mol%, the complexes **3**-**6** exhibited excellent catalytic efficiency for the transfer hydrogenation of 2,2-difluoro-1-phenylethanone (entry 2) within 1 h of reaction time, affording a highest TOF value of *ca.* 400 h^{-1}. Likewise the reactions with 1-(2,4-dichlorophenyl)ethanone (entry 3) and 1-(4-chlorophenyl-ethanone (entry 4) yielded quantitative conversion (*ca.* 100%) of the substrates. To achieve the quantitative yields of *ca.* 100% conversion, we required nearly 2 h for the mononuclear complexes **3** and **4**, while only *ca.* 1 h is required for the dinuclear complexes **5** and **6**. Susequently, we have carried out the reactions using substrates such as 1-(*p*-tolyl)ethanone (entry 5) and 1-(4-methoxyphenyl)ethanone (entry 6) under similar conditions, wherein we observed quantitative substrate conversion (*ca.* 97-100%) at a catalyst loading of only 0.5 mol%. The observed conversion efficiency and afforded TOF values for these reactions clearly confirm the stability and recyclability of the catalysts.

To determine the specificity and efficacy of the complexes, we have carried out the transfer hydrogenation by employing ligand precursors (L_1-L_5) and also compared with the literature known ruthenium based catalysts under similar conditions (Table S3, ESI). Interestingly, we observed negligible conversion of acetophenone to the desired product in presence of the ligand precursors (entry 3). In contrast, the reactions with the commercially available ruthenium catalysts such as $[Ru(p\text{-cymene})Cl_2]_2$ (entry 4) and the second generation "Hoveyda-Grubbs" catalyst[23] (entry 5) furnished moderate yields of the product under identical conditions. When compared to the catalytic activity of the complexes **3-6** (TOF = *ca.* 200 h^{-1}) with the literature reported Ru(II) pincer complexes such as $Ru(CNC)(CO)Br_2$,[24] Ru(2,6-bis(arylimidazol-2-ylidene)-pyridine)-$(PPh_3)Cl_2$,[25] and Ru(II)-NNC[26], the latter examples showed the TOF values of *ca.* 117 h^{-1}, 333 h^{-1} and 245 h^{-1}, respectively, employing acetophenone as the substrate. The high catalytic activity of the complexes can be attributed to the strong sigma binding affinity of *N*-heterocyclic carbene (*NHC*) ligand, which facilitates the formation of strong metal-carbon bond and prevents the decomposition of the catalysts under reaction conditions. In comparison to the neutral ruthenium complexes **1** and **2**, the cationic ruthenium complexes **3-6** showed better catalytic

View Article Online
DOI: 10.1039/C7NJ02822A

activity. This observation can be ascribed to the strong binding of both *NHC* and pyridine substituents to the metal centre in the latter cases.

The mechanism of transfer hydrogenation of the aromatic ketones to the corresponding aromatic alcohols using the ruthenium complexes **1-6** is shown in Scheme S1 (ESI), based on experimental evidence and literature reports.[27] The loss of chloride molecule followed by the addition of 2-propoxide gives an active ruthenium catalyst species A, which can further undergo β-hydride migration and loss of acetone molecule to give the ruthenium hydride complex B. The subsequent formation of the coordinated complex C can be rationalized through the interaction of the intermediate complex B with the substrate, which in turn can undergo hydride transfer to form the intermediate D. The desired aromatic alcohol formation can be postulated through the reaction of the intermediate D with the solvent 2-propanol in the presence of the base promoter and thereby generating the activated ruthenium catalyst species A. The chelating capability of the *NHC* ligands as well as availability of two *cis* labile chloride ions provided the stability and reactivity to the ruthenium complexes synthesised.

The proposed mechanism was furthermore rationalized through theoretical calculations employing density function theory method using B3LYP level and double ξ basis sets.[28-30] All calculations were done by Gaussion 09 software suite. Solvent molecules (acetone, isopropanol), acetophenone, 1-phenylethanol and the intermediate species A, B and D were optimised at the same level of calculations (Table S4, ESI). In the first step, conversion of the species A to B (Ru-H, 1.74 Å) via β-hydride elimination, we observed a value of *ca.* 40.75 kcal/mol for the heat of reaction (energy required to break Ru-O bond) with the release of acetone molecule. Furthermore, the interaction of the intermediate B with acetophenone gives the intermediate D for which we obtained the heat of reaction value of *ca.* -40.71 kcal/mol (energy released during Ru-O bond formation). Finally, for the hydrogen transfer step in the transformation of the intermediates D to A, we observed a value of *ca.* 0.28 kcal/mol. These studies have demonstrated that the intermediates postulated were energetically favorable, thereby confirming that this reaction proceeds through a thermodynamically stable pathway.

Conclusions

In summary, we designed and synthesized a novel series of mono- and dinuclear "piano-stool" structured ruthenium(II)-*NHC* complexes **1-6** and evaluated their catalytic efficiency for the transfer hydrogenation of the aromatic ketones under different conditions. A high catalytic activity was observed with all the complexes with a low catalyst loading. Our investigations have revealed the important role of the *N*-heterocyclic carbene (*NHC*) in the catalytic transfer hydrogenation reactions. These complexes exhibited high selectivity and specificity for the aromatic ketones bearing both electron rich and deficient groups, whereas aliphatic ketones and aldehydes showed negligible reaction under identical conditions. Importantly, the neutral ruthenium-*NHC* complexes **1** and **2** at 2 mol% showed catalytic efficiency of *ca.* 100% within 2 h, whereas only *ca.* 0.5 mol% loading of catalyst and 1 h required to achieve *ca.* 100% conversion with the cationic ruthenium-*NHC* complexes **3-6**. The detailed investigations on the mechanistic aspects of the transfer hydrogenation reactions through theoretical studies have furthermore confirmed that the reaction to proceed through a thermodynamically stable pathway. These complexes showed superior activity and stability when compared to the reported catalysts, thereby demonstrating their use as efficient catalysts for the transfer hydrogenation of the aromatic ketones.

Experimental section

Materials and methods

General experiments and spectroscopic techniques for the characterization of the compounds have been described in the literature.[14,31-32] Cyclic voltammetry measurements were carried out using a CV-50W elctroanalyzer in dichloromethane and acetonitrile solutions using platinum wire as auxiliary electrode and glassy-carbon as working electrode. The oxidation potentials of the complexes were referenced Ag/AgCl electrode and ferrocene (0.45 V, $E_{1/2}$) was used as an external standard. Thermogravimetric analysis was performed at a heating rate of 10 °C/min in N_2 atmosphere using Schimadzu, DTG-60 equipment. Anthracene, Ag_2O, methylimidazole, benzyl bromide, $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and $[Ru(\text{hexamethyl-benzene})Cl_2]_2$ were purchased from S. D. Fine Chemicals and Aldrich India, and used without further purification. All the substrates used (aromatic/aliphatic ketones and aldehydes) for the catalytic reactions were purchased from Sigma and used without further purification. All solvents were purified and dried prior to use.

X-ray crystallography

Single crystals of **1**.3$CHCl_3$ and **2**·2$CHCl_3$ were obtained from a $CHCl_3$–CH_3OH (9:1) mixture. The data sets for the single-crystal X-ray studies for **1**.3$CHCl_3$ and **2**.2$CHCl_3$ were collected with Mo Kα (λ = 0.71073 Å) radiation on a RIGAKU diffractometer. The data set for the complexes **3** and **4** were collected with Mo Kα (λ = 0.71073 Å) on a Bruker APEX-II diffractometer. All calculations were performed using SHELXTL.

DFT calculations

DFT calculations of the complexes **1** and **2** were carried out using Gaussian 09 program package.[28] The Becke's three parameters hybrid exchange functional with the Lee–Yang–Parr (LYP) non-local correlation functional was used throughout the computational study.[29,30] A LANL2DZ basis set was used in the calculations.

Synthesis of the ligands and the complexes

***Synthesis of the complex 1*:** To a solution of L_1 (50 mg, 0.09 mmol) in dry CH_2Cl_2 (20 mL) was added Ag_2O (22 mg, 0.09 mmol). The reaction mixture was stirred for 4 h at 25 °C

View Article Online
DOI: 10.1039/C7NJ02822A

followed by the addition of *p*-cymene dimer precursor [Ru(η^6-*p*-cymene)Cl_2]$_2$ (55 mg, 0.09) and further stirred for 4 h. The reaction mixture was then passed through celite column and the solvent was evaporated to dryness. Orange solid was obtained by precipitation in diethyl ether, yielded the complex **1** in 39%. The single crystals were obtained by recrystallisation from a mixture (9:1) of CH_3Cl and CH_3OH. Mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.36-1.37 (d, 12H), 1.58 (s, 6H), 2.31 (s, 6H), 3.04-3.10 (quint, 2H), 4.10 (s, 4H), 5.43 (s, 4H), 5.63 (s, 4H),6.13 (s, 2H), 6.74(s, 2H), 7.59 (m, 4H), 8.38 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6); δ 20.9, 23.9, 30.6, 32.9, 47.1, 117.7, 123.9, 125.5, 126.0, 126.6, 127.9, 128.7, 131.2, 163.9, 173.1 ppm; Elemental Anal. Calcd for $C_{44}H_{50}Cl_4N_4Ru_2$ (%): C, 53.88; H, 5.34; N, 5.71. Found: C, 53.65; H, 5.54; N, 5.88.

***Synthesis of the complex 2*:** To a solution of L_2 (50 mg, 0.11 mmol) in dry CH_2Cl_2 (20 mL) was added Ag_2O (27 mg, 0.11 mmol). The reaction mixture was stirred for 4 h at 25 °C followed by the addition of *p*-cymene dimer precursor [Ru(η^6-*p*-cymene)Cl_2]$_2$ (67 mg, 0.11 mmol) and further stirred for 4 h. The reaction mixture was then passed through celite column and the solvent was evaporated to dryness. Orange solid was obtained by precipitation in diethyl ether, yielded the complex **2** in 40%. The single crystals were obtained by recrystallisation from a mixture (9:1) of CH_3Cl and CH_3OH. Mp > 300 °C ; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.26-1.27 (d, 12H), 1.58 (s, 6H), 2.07 (s, 6H), 2.91-2.97 (quint, 2H), 4.05 (s, 4H), 5.08 (s, 4H), 5.39 (s, 4H), 6.78 (s, 2H), 6.98 (s, 2H), 7.32 (s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 21.4, 23.9, 30.3, 31.5, 117.2, 125.0, 126.1, 127.4, 127.7, 128.4, 137.1, 165.4, 173.9 ppm; Elemental Anal. Calcd for $C_{36}H_{46}Cl_4N_4Ru_2$ (%): C, 49.09; H, 5.49; N, 6.36. Found: C, 48.99; H, 5.42; N, 6.30.

***Synthesis of the complex 3*:** To a solution of L_3 (50 mg, 0.15 mmol) in dry CH_2Cl_2 (15 mL) was added Ag_2O (19 mg, 0.079 mmol). The reaction mixture was stirred for 4 h at 25 °C followed by addition of metal precursor [Ru(η^6-*p*-cymene)Cl_2]$_2$ (48 mg, 0.079 mmol) and further stirred for next 4 h. The reaction mixture was then passed through celite column and the solvent was evaporated to dryness. The solid obtained was again dissolved in water and 1.5 equivalent of ammonium hexafluorophosphate in water was added. The solid obtained by precipitation was dried and further recrystallised from diethyl ether, to give the complex **3** in 50%. The single crystals were obtained by recrystallisation from a mixture (9:1) of CH_3Cl and CH_3OH. Mp > 300 °C; ^{1}H NMR (500 MHz, CD_3CN, TMS) δ 0.88-0.91 (d, 6H), 2.14 (s, 3H), 2.35-2.41 (quint, 1H), 5.49-5.50 (dd, 1H), 5.54-5.57 (d, 1H), 5.72-5.75 (d, 1H), 5.86-5.88 (t, 1H), 5.97-5.98 (t, 1H), 6.09-6.11 (d, 1H), 7.25 (s, 1H), 7.26 (s, 1H), 7.45 (s, 5H), 7.78-7.80 (d, 1H), 7.88-7.89 (d, 1H), 8.11-8.15 (m, 1H), 9.16-9.17 (t, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 19.2, 22.3, 24.3, 31.8, 55.8, 83.2, 87.9, 91.0, 92.1, 101.0, 106.3, 109.6, 113.6, 124.2, 125.5, 127.2, 129.3, 130.1, 136.5, 142.5, 152.7, 156.5, 186.1 ppm; ESI-MS: m/z Calcd for $C_{25}H_{27}N_3ClRu$, 506.0937; Found, 506.0949 (M+); Elemental Anal. Calcd for $C_{25}H_{27}N_3ClPF_6Ru$ (%): C, 46.05; H, 4.33; N, 6.44. Found: C, 46.26; H, 4.28; N, 6.46.

***Synthesis of the complex 4*:** To a solution of L_3 (50 mg, 0.15 mmol) in dry CH_2Cl_2 (15 mL) was added Ag_2O (19 mg, 0.079 mmol). The reaction mixture was stirred for 4 h at 25 °C followed by addition of metal precursor [Ru(hexamethyl-benzene)Cl_2]$_2$ (53 mg, 0.079 mmol) and further stirred for 4 h. The reaction mixture was then passed through celite column and the solvent was evaporated to dryness. The solid obtained was again dissolved in water and 1.5 equivalent of ammonium hexafluorophosphate in water was added. The solid obtained by precipitation was dried and further recrystallised from diethyl ether, to yield **4** in 60%. The single crystals were obtained by recrystallisation from a mixture (9:1) of CH_3Cl and CH_3OH. Mp > 300 °C; ^{1}H NMR (500 MHz, CD_3CN, TMS) δ 2.19 (s, 18H), 544-5.52 (q, 2H), 7.09-7.10 (d, 1H), 7.35-7.38 (m, 3H), 7.46-7.50 (m, 3H), 7.71-7.73 (d, 1H), 7.80-7.81 (d, 1H), 8.06-8.09 (m, 1H), 8.70-8.71 (m, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 16.5, 55.6, 99.9, 113.0, 124.1, 125.2, 130.3, 136.3, 141.9, 153.1, 153.7, 190.6 ppm; ESI-MS: m/z Calcd for $C_{27}H_{31}ClN_3Ru$, 534.1250; Found, 534.1263 (M+); Elemental Anal. Calcd for $C_{27}H_{31}ClN_3PF_6Ru$ (%): C, 47.69; H, 4.74; N 6.18. Found: C, 47.65; H, 4.79; N, 6.14.

***Synthesis of the ligand L_4*:** To a mixture of 2-(1H-imidazol-1-yl)pyridine (200 mg, 1.37 mmol) in dry CH_3CN (10 mL) was added 1,4-bis(bromomethyl)benzene (182 mg, 0.69 mmol). The reaction mixture was refluxed for 24 h at 100 °C in a pressure tube and the product obtained was then filtered and washed thoroughly with acetonitrile and dried under vacuum. The product was further purified by recrystallisation from acetonitrile to give precursor L_4 in 80%. Mp > 200 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 5.58 (s, 4H), 7.62 (s, 4H), 7.64-7.67 (m, 2H), 8.03-8.05 (m, 4H), 8.20-8.24 (m, 2H), 8.55-8.56 (t, 2H), 8.65-8.66 (m, 2H), 10.32 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 52.0, 114.2, 119.7, 123.4, 125.2, 129.1, 135.1, 140.5, 146.3, 149.1 ppm; ESI-MS: Calcd for $C_{24}H_{22}N_6$, 394.1895; Found, 393.1836 (M^+-1).

***Synthesis of the complex 5*:** To a solution of L_4 (50 mg, 0.09 mmol) in dry CH_2Cl_2 (20 mL) was added Ag_2O (21 mg, 0.09 mmol). The reaction mixture was stirred for 4 h at 25 °C followed by the addition of metal precursor [Ru(η^6-*p*-cymene)Cl_2]$_2$ (55 mg, 0.09 mmol) and further stirred for 4 h. The reaction mixture was then passed through celite column and the solvents were evaporated to dryness. The solid obtained was again dissolved in water and 2.5 equivalent of ammonium hexafluorophosphate in water was added. The solid obtained by precipitation was dried and further recrystallised from diethyl ether, yielded the complex **5** in 40%. Mp > 300 °C; ^{1}H NMR (500 MHz, CD_3CN, TMS) δ 0.86-0.91 (m, 12H), 2.25 (s, 6H), 2.3-2.4 (quint, 2H), 5.48-5.49 (d, 2H), 5.55-5.58 (d, 2H), 5.74-5.77 (d, 2H), 5.85-5.88 (t, 2H), 5.99-6.02 (m, 2H), 6.10-6.12 (m, 2H), 7.25-7.26 (d, 2H), 7.43-7.48 (m, 6H), 7.77-7.86 (m, 2H), 7.87-7.88 (t, 2H), 8.11-8.12 (d, 2H),

View Article Online
DOI: 10.1039/C7NJ02822A

9.15-9.16 (d, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 19.2, 22.5, 24.3, 31.8, 55.4, 83.3, 88.0, 91.0, 92.1, 100.9, 106.4, 109.8, 113.6, 124.2, 125.4, 127.2, 130.0, 137.0, 142.5, 152.6, 156.5, 186.2 ppm; Elemental Anal. Calcd for $C_{44}H_{48}Cl_2N_6P_2F_{12}Ru_2$ (%): C, 43.11; H, 4.11; N, 6.86. Found: C, 43.09; H, 4.23; N, 6.79.

***Synthesis of the ligand L_5*:** To a solution of 2-(1H-imidazol-1-yl)pyridine (200 mg, 1.37 mmol) in dry CH_3CN (10 mL) was added 9,10-dibromomethylanthracene (251 mg, 0.69 mmol). The reaction mixture was refluxed for 24 h at 100 °C in a pressure tube and the product obtained was then filtered and washed thoroughly with acetonitrile and dried under vacuum. The product was further purified by recrystallisation from acetonitrile to give ligand L_5 in 75%. Mp > 240 °C; ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 6.72 (s, 4H), 7.59-7.60 (t, 2H), 7.63-7.66 (m, 2H), 7.79-7.81 (m, 4H), 8.00-8.02 (d, 2H), 8.17-8.20 (m, 2H), 8.48-8.49 (d, 2H), 8.63-8.69 (d, 6H), 10.08 (s, 2H); 13C NMR (125 MHz, DMSO-d_6) *δ* 45.6, 114.5, 119.4, 123.2, 124.6, 125.3, 126.3, 127.7, 130.8, 134.6, 140.5, 146.2, 149.2 ppm; ESI-MS: Calcd for $C_{32}H_{26}N_6$, 494.2208; Found, 493.2213 (M^+-1).

***Synthesis of the complex 6*:** To a solution of L_5 (50 mg, 0.076 mmol) in dry CH_2Cl_2 (20 mL) was added Ag_2O (18 mg, 0.076 mmol). The reaction mixture was stirred for 4 h at 25 °C followed by the addition of metal precursor [Ru(η^6-*p*-cymene)Cl_2]$_2$ (47 mg, 0.076 mmol) and further stirred for 4 h. The reaction mixture was then passed through celite column and the solvent was evaporated to dryness. The solid obtained was again dissolved in water and 2.5 equivalent of ammonium hexafluorophosphate in water was added. The solid obtained by precipitation was dried and further recrystallised from diethyl ether, to yield the complex **6** in 45%. Mp > 300 °C; ^{1}H NMR (500 MHz, CD_3CN, TMS) *δ* 1.01-1.06 (m, 12H), 2.27 (s, 6H) 2.57-2.65 (q, 2H), 5.89-5.90 (d, 2H), 6.13-6.14 (d, 2H), 6.34-6.35 (d, 2H), 6.44-6.45 (d, 2H), 6.61-6.68 (m, 4H), 6.77-6.81 (m, 2H), 7.48-7.51 (m, 2H), 7.68-7.69 (d, 2H), 7.73-7.76 (m, 8H), 8.12-8.16 (m, 2H), 8.66 (s, 2H), 9.25-9.27 (d, 2H); ^{13}C NMR (125 MHz, CD_3CN); *δ* 19.3, 22.5, 32.1, 49.3, 84.3, 87.7, 91.7, 92.8, 100.9, 107.1, 108.7, 113.6, 117.8, 124.3, 126.1, 128.7, 129.9, 132.1, 142.6, 152.5, 156.6, 185.8 ppm; Elemental Anal. Calcd for $C_{52}H_{52}Cl_2N_6P_2F_{12}Ru_2$ (%): C, 47.10; H, 4.10; N, 6.34. Found: C, 47.32; H, 4.13; N, 6.28.

General procedure for the transfer hydrogenation reaction: Solvent (2 mL) was degassed by purging with N_2. The desired quantity of the catalyst was added and dissolved by sonicating for 10 min at 25°C. The base (0.1 mmol) was added and the mixture then preheated at 40 °C for 10 min. Then substrate (0.1 mmol) was then added and the temperature was raised to 80 °C and allowed the reaction to continue for the specified time. Aliquots were taken at different intervals and analyzed by GC-MS. After the reaction time, the mixture was passed through a pad of silica in hexane and the reaction mixture collected was evaporated to dryness. The products were further analyzed by various spectral and analytical techniques. The catalytic reactions were carried out in triplicates to confirm the reproducibility of the results.

Acknowledgements

We acknowledge the financial support from Department of Biotechnology (BMB/2015/53) and Council of Scientific and Industrial Research. This is contribution No. PPG-367 from CSIR-NIIST, Trivandrum. We are grateful to Dr. Sunil Varughese (CSIR-NIIST, Trivandrum) and Mr. P. Alex Andrews (IISER, Trivandrum) for single crystal X-ray structures analysis.

Notes and references

1 (a) S. Diez-Gonzalez and S. P. Nolan, *Coord. Chem. Rev.,* 2007, **251**, 874-883; (b) A. G. Nair, R. T. McBurney, D. B. Walker, M. J. Page, M. R. D. Gatus, M. Bhadbhade and B. A. Messerle, *Dalton Trans.,* 2016, **45**, 14335-14342; (c) O. Prakash, K. N. Sharma, H. Joshi, P. L. Gupta and A. K. Singh, *Dalton Trans.,* 2013, **42**, 8736-8747; (d) J. M. Farrell, R. T. Posaratnanathan and D. W. Stephan, *Chem. Sci.,* 2015, **6**, 2010-2015; (e) L. Agnes, D. C. Jean, L. J. Nicholas, W. J. P. Andrew and P. Rinaldo, *New J. Chem.,* 2011, **35**, 2162-2168; (f) A. K. Sharma, H. Joshi, K. N. Sharma, P. L. Gupta and A. K. Singh, *Organometallics*, 2014, **33**, 3629-3639; (g) J. A. Mataa, M. Poyatos, and E. Peris, *Coord. Chem. Rev.,* 2007, **251**, 841-859; (h) C. Cesari, A. Cingolani, C. Parise, S. Zacchini, V. Zanotti, M. C. Cassani and R. Mazzoni, *RSC Adv.,* 2015, **5**, 94707- 94718.

2 (a) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.,* 2006, **128**, 4101-4111; (b) S. Ganesamoorthy, P. Jerome, K. Shanmugasundaram and R. Karvembu, *RSC Adv.,* 2014, **4**, 27955-27962; (c) A. Y. Khalimon, E. M. Leitao, and W. E. Piers, *Organometallics*, 2012, **31**, 5634-5637; (d) D. Wang, Q. Bi, G. Yin, W. Zhao, F. Huang, X. Xieac and M. Jiang, *Chem. Commun.,* 2016, **52**, 14226-14229.

3 (a) G. Amenuvor, C. Obuah, E. Nordlander and J. Darkwa, *Dalton Trans.*, 2016, **45**, 13514-13524; (b) Y. Baoyi, X. Yu,H. B. Fatma, L. Karen, L. A. Alex, H. V. Kristof and V. Francis, *New J. Chem.,* 2015, **39**, 1858-1867; (c) T. Jin, D. He, W. Li, C. J. Stanton, S. A. Pantovich, G. F. Majetich, H. F. Schaefer, J. Agarwal, D. Wang and G. Li, *Chem. Commun.,* 2016, **52**, 14258-14261.

4 (a) D. Gülcemal, A. G. Gökçe, S. Gülcemal and B. Çetinkaya, *RSC Adv.,* 2014, **4**, 26222-26230; (b) C. Ricardo, A. A. Inaam, S. David, M. Bouchaib, G. Salaheddine and D. H. Pierre, *New J. Chem.,* 2003, **27**, 6-8; (c) G. C. Vougioukalakis and R. H. Grubbs, *J. Am. Chem. Soc.,* 2008, **130**, 2234-2245; (d) J. R. Chen, C. F. Li, X. L. An, J. J. Zhang, X. Y. Zhu and W. J. Xiao, *Angew. Chem. Int. Ed.,* 2008, **47**, 2489-2492; (e) O. Debleds, and J.-M. Campagne, *J. Am. Chem. Soc.,* 2008, **130**, 1562-1563.

5 (a) Y. H. Chang, W. J. Leu, A. Datta, H. C. Hsiao, C. H. Lin, J. H. Guh and J. H. Huang, *Dalton Trans.,* 2015, **44**, 16107-16118; (b) S. Sergio, B. Miriam and E. Peris, *Organometallics,* 2010, **29**, 275-277; (c) O. Prakash, K. N. Sharma, H. Joshi, P. L. Gupta and A. K. Singh, *Organometallics*, 2014, **33**, 983-993; (d) W. H. Wan, M. T. James, F. Etsuko and H. Yuichiro, *New J. Chem.,* 2013, **37**, 1860-1866; (e) Z. Mingshuo, L. Le and B. H. Seth, *J. Am. Chem. Soc.,* 2014, **136**, 7058-7067; (f) F. Saleem, G. K. Rao, A. Kumar, G. Mukherjee and A. K. Singh, *Organometallics*, 2014, **33**, 2341-2351.

View Article Online
DOI: 10.1039/C7NJ02822A

6 (a) W. Baratta, D. R. Paolo, D. Z. Alessandro, S. Alessandra, Z. Ennio and R. Pierluigi, *Angew. Chem. Int. Ed.,* 2004, **43**, 3584-3588; (b) O. Prakash, H. Joshi, K. N. Sharma, P. L. Gupta and A. K. Singh, *Organometallics,* 2014, **33**, 3804-3812; (c) C. Shujie, L. Guoping and C. Chun, *New J. Chem.,* 2015, **39**, 5360-5365; (d) A. M. Alexandre, H. M. Robert, *Inorg. Chem.,* 2010, **49**, 11039-11044; (e) O. Prakash, K. N. Sharma, H. Joshi, P. L. Gupta and A. K. Singh, *Organometallics*, 2014, **33**, 2535-2543.

7 (a) M. Yigit, B. Yigit, I. Ozdemir, E. Cetinkaya and B Cetinkaya, *Appl. Organomet. Chem.,* 2006, **20**, 322-327; (b) D. Chatterjee, and P. Sarkar, *J. Coord. Chem.,* 2016, **69**, 650-655; (c) F. Saleem, G. K. Rao, S. Kumar, M. P. Singh and A. K. Singh, *Dalton Trans.,* 2015, **44**, 19141-19152; (d) S. Horn and M. Albrecht, *Chem. Commun.,* 2011, **47**, 8802-8804; (e) M. Poyatos, A. Maisse-Francois, S. Bellemin-Laponnaz, E. Peris and L. H. Gade, *J. Organomet. Chem.,* 2006, **691**, 2713-2720.

8 (a) W. Chao-Yu, F. Ching-Feng, L. Yi-Hong, P. Shei-Ming and L. Shiuh-Tzung, *Inorg. Chem.,* 2007, **46**, 5779-5786; (b) F. Saleem, G. K. Rao, A. Kumar, G. Mukherjee and A. K. Singh, *Organometallics*, 2013, **32**, 3595-3603; (c) L. Yanyun, Y. Shenluan, W. Xiaofeng, X. Jianliang, S. Weiyi, D. Zhenrong and G. Jingxing, *J. Am. Chem. Soc.,* 2014, **136**, 4031-4039; (d) S. Kumar, F. Saleem and A. K. Singh, *Dalton Trans.,* 2016, **45**, 11445-11458.

9 (a) A. Arturo, A. M Jose, E. Peris, L. Frederic, M. Jean and C. Evelina, *Organometallics,* 2012, **31**, 3911-3919; (b) W. Yawen, X. Dong, L. Qian, W. Chao and X. Jianliang, *Green Chem.,* 2013, **15**, 629-634; (c) P. Om, N. S. Kamal, J. Hemant, L. G. Pancham and K. S. Ajai, *Organometallics,* 2014, **33**, 2535-2543.

10 O. Takeshi, U. Noriyuki, T. Kunihiko, M. Kunihiko, S. Christian and R. Noyori, *J. Am. Chem. Soc.,* 2006, **128**, 8724-8725.

11 W. Baratta, G. Chelucci, E. Herdtweck, S. Magnolia, K. Siega and P. Rigo, *Angew. Chem. Int. Ed.,* 2007, **46**, 7651-7654.

12 S. Dıez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676.

13 K. Ganesan and Y. Alias, *Int. J. Mol. Sci.,* 2008, **9**, 1207-1213.

14 (a) M. Viji, A. K. Nair, P. C. Nandajan and D. Ramaiah, *RSC Adv.,* 2014, **4**, 47982-47986; (b) D. Ramaiah, P. P. Neelakandan, A. K. Nair and R. R. Avirah, *Chem. Soc. Rev.,* 2010, **39**, 4158-4168; (c) A. K. Nair, P. P. Neelakandan and D. Ramaiah, *Chem. Commun.*, 2009, 6352-6354.

15 (a) A. K. Verma, J. Singh, V. Kasi Sankar, R. Chaudhary and R. Chandra, *Tetrahedron Lett.,* 2007, **48**, 4207-4210; (b) G. J. Barbante, P. S. Francis, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson and P. J. Barnard, *Inorg. Chem.,* 2013, **52**, 7448-7459.

16 (a) R. Ramasamy, K. Christian and S. Fritz, *Electrochem. Commun.,* 2000, **2**, 190-194; (b) K. Mahn-Jong, K. Rama, Y. Hongwei, M. M. Frederick, P. Fausto, S. Scolastica, C. Sebastiano, H. Tina, K. Gary and R. Krishnan, *Inorg. Chem.,* 2002, **41**, 2471-2476.

17 (a) D. Joseph, K. Mukesh, Z. Matthias and T. P. Elizabeth, *Organometallics,* 2013, **32**, 966-979; (b) W. Julia, P. Alexander, E. K. Fritz and W. Baratta, *Organometallics,* 2013, **32**, 4042-4045.

18 E. M. Robert, E. A. Rhona, M. P. del Socorro, C. Haimei, C. Jeff, D. H. Nathan, P. Simon, P. Andrew, B. Gary, I. J. Duncan and J. S. Peter, *J. Med. Chem.,* 2001, **44**, 3616-3621.

19 G. Mani, L. Rangasamy, E. Suresh, R. Anvarbatcha, A. A. Mohammad and P. Mallayan, *Dalton Trans.,* 2014, **43**, 1203-1219.

20 M. Zirngast, E. Pump, A. Leitgeb, J. H. Albering and C. Slugovc, *Chem. Commun.,* 2011, **47**, 2261-2263.

21 D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics,* 2009, **28**, 321-325.

22 D. Pandiarajan and R. Ramesh, *J. Organomet. Chem.,* 2013, **723**, 26-35.

23 J. Louie, C. W. Bielawski and R. H. Grubbs, *J. Am. Chem. Soc.,* 2001, **123**, 11312-11313.

24 M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree and E. Peris, *Organometallics*, 2003, **22**, 1110-1114.

25 A. A. Danopoulos, S. Winston and W. B. Motherwell, *Chem. Commun.,* 2002, 1376-1377.

26 F. Zeng and Z. Yu, *Organometallics*, 2008, **27**, 6025-6028.

27 D. A. Alonso, P. Brandt, S. J. M. Nordin and P. G. Andersson, *J. Am. Chem. Soc.,* 1999, **121**, 9580-9588.

28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al*., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

29 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785-789.

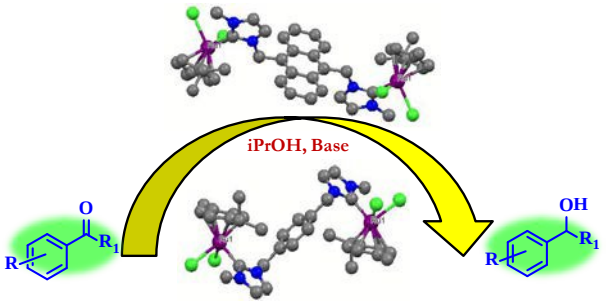
30 A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098-3100.

31 (a) K. Bhattacharyya, D. Ramaiah, P. K. Das and M. V. George, *J. Phys. Chem.,* 1986, **90**, 5984-5988; (b) J. Joseph, N. V. Eldho and D. Ramaiah, *J. Phys. Chem. B,* 2003, **107**, 4444-4450; (c) M. Hariharan, S. C. Karunakaran and D. Ramaiah, *Org. Lett.,* 2007, **9**, 417; (d) E. Kuruvilla, P. C. Nandajan, G. B. Schuster and D. Ramaiah, *Org. Lett.,* 2008, **10**, 4295-4298.

32 (a) N. Tyagi, M. Viji, S. C. Karunakaran, S. Varughese, S. Ganesan, S. Priya, P. S. Saneesh Babu, A. S. Nair and D. Ramaiah, *Dalton Trans.,* 2015, **44**, 15591-15601; (b) D. Ramaiah, I. Eckert, K. T. Arun, L. Weidenfeller and B. Epe, *Photochem. Photobiol.,* 2004, **79**, 99-104; (c) V. S. Jisha, A. J. Thomas and D. Ramaiah, *J. Org. Chem.,* 2009, **74**, 6667-6673.

TABLE OF CONTENTS

View Article Online
DOI: 10.1039/C7NJ02822A



Synthesized aryl appended half-sandwich Ru(II)-*NHC* complexes and demonstrated their use as selective catalysts for transfer hydrogenation of the aromatic ketones.