Transfer hydrogenation of ketones in the presence of half sandwich ruthenium (II) complexes bearing imidazoline and benzimidazole ligand

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Dedicated to Prof. Jürgen Martens in appreciation of his outstanding contributions to synthetic organic chemistry

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Abstract
This article explores the possibility of using imidazoline and benzimidazole derivatives as interesting ligands due to the fact that they are structurally simple, readily available, inexpensive, and they allow easy introduction of various substituents into their structure. Therefore, *N*-substituted imidazoline and benzimidazole ligands and their new ruthenium complexes [$RuCl_2(\eta^6$-*p*-cymene)(L)] (L = *N*-substituted imidazoline/benzimidazole) were synthesized and characterized. The catalytic performances of new complexes are investigated for the transfer hydrogenation of ketones. Furthermore, corresponding secondary alcohols were also obtained in good yields.

Keywords: Azole ligands, ruthenium, transfer hydrogenation, ketones

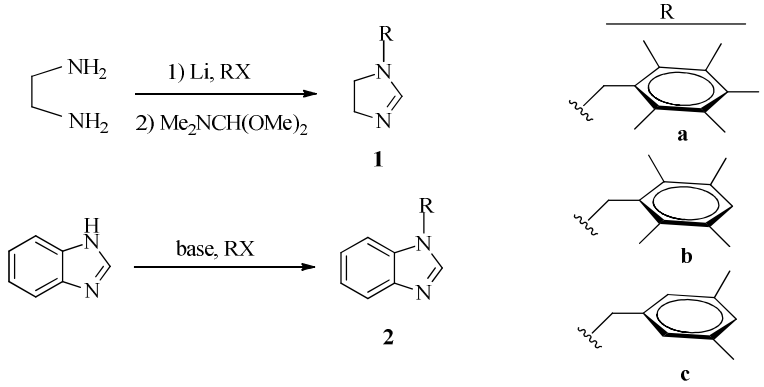
Introduction

Transfer hydrogenation is a potentially useful protocol for the reduction of carbonyl compounds to their corresponding alcohols, which are key intermediates in pharmaceuticals, perfumes, agrochemicals, materials and fine chemicals.[1-3] In transfer hydrogenation, 2-propanol, glycerol, formic acid, and its salts have been employed as the hydrogen source.[4-8] 2-propanol is a popular reactive solvent for the transfer hydrogenation reactions since it is easy to handle and is relatively non-toxic, environmentally benign and inexpensive.[9-11] Transition metal catalyzed transfer hydrogenation of ketones and aldehydes have attracted attention for the relatively benign nature of the reagents and mild reaction conditions employed.[12-16]Among the different metal

catalyzed hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation of ketones[17] and imines.[18] The ability of ruthenium to exist in a variety of oxidation states as well as to assume wide range of coordination geometry are the main reasons behind ruthenium compounds being effective catalysts for a variety of organic reactions. Heterocyclic ligands containing nitrogen atoms are drawing a great deal of attention in coordination chemistry and homogeneous catalysis[19] because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate substituents.[20]
Herein we report the synthesis and characterization of novel half sandwich ruthenium complexes with *N*-substituted imidazoline and benzimidazole ligand and then investigated their catalytic performances for the transfer hydrogenation of ketones.

Results and Discussion

Nitrogen containing heterocyclic ligands have received great deal of attention in the fields of coordination chemistry, homogeneous catalysis and organic synthesis because organometallic complexes bearing nitrogen donor ligands usually exhibit high reactivities. The strategies employed in the synthesis of the *N*-substituted imidazoline and benzimidazole ligands are summarized in Scheme 1.

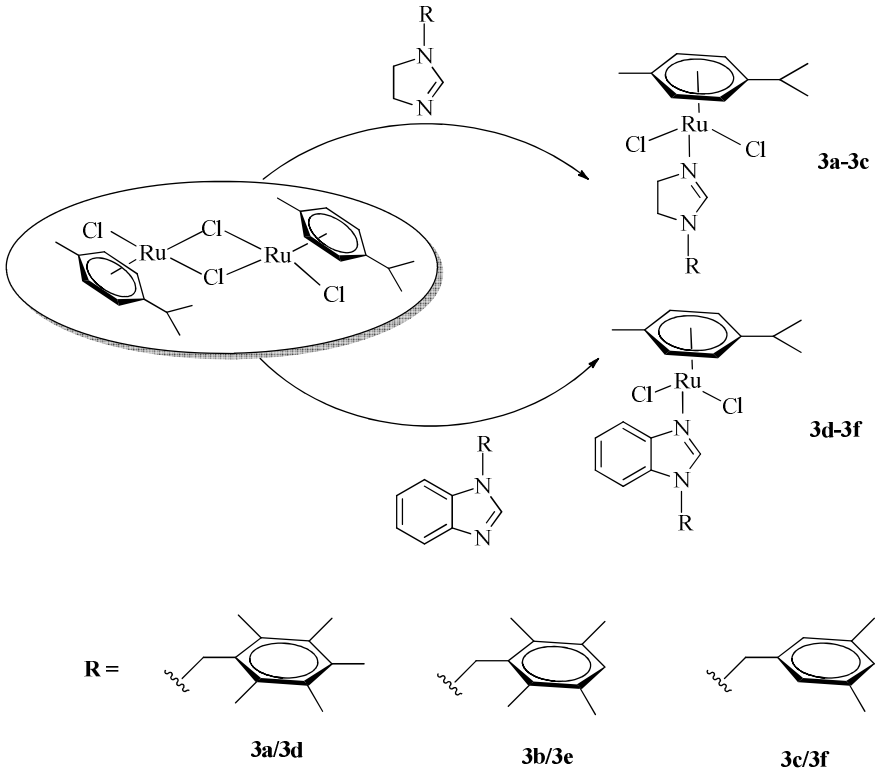


Scheme 1. Synthesis of *N*-substituted imidazoline and benzimidazole ligands.

All new ligands were isolated as colourless and air stable solids. They were characterized by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis techniques which support the proposed structures. The ^{1}H NMR spectra of the N-substituted imidazoline (**1a–1c)** and benzimidazole (**2a-2c**) in $CDCl_3$ exhibit as a singlet in the range δ 6.66-6.97 ppm (**1a-1c**) and δ 7.43-8.01 ppm (**2a-2c**) characteristic of the NCH=N proton. In ^{13}C NMR, the chemical shift of the corresponding C(2) atom was detected in the region 156.4-157.5 ppm (**1a-1c**) and 140.6-143.5 ppm (**2a-2c**). These new N-substituted imidazoline and benzimidazoles show typical spectroscopic signatures which are in line with recently reported findings for this type ligands.[21,22]

The low toxicity and stability of nitrogen based ligands, such as imidazole derivatives, have attracted the attention of synthetic organic chemists. Togni and Venanzi[19] have exhaustively discussed the relevance of N-donors in organometallic chemistry. There are reports of highly catalytic reactive complexes bearing nitrogen ligands.[23-26] We are particularly interested in the possibility of using imidazole and benzimidazole derivatives as ligands since they are structurally simple, readily available, and inexpensive, and they allow for easy introduction of various substituents into their structure.

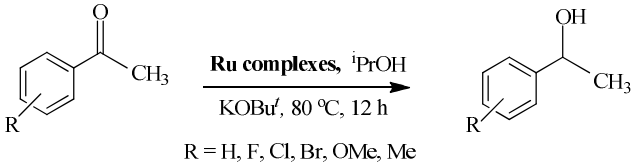
Half sandwich ruthenium (II) complexes bearing azole ligand were synthesized and characterized by ^{1}H NMR and ^{13}C NMR. η^6-arene ruthenium complexes (**3a-3f**) bearing N-substituted imidazoline and benzimidazole (L) were obtained from treatment of the [Ru(*p*-cymene)Cl_2]$_2$ with L in 1:2 stoichiometric ratio in toluene at 110 ºC for 5 h. (Scheme 2).



Scheme 2. Synthesis of η^6-arene ruthenium complexes with N-substituted imidazoline and benzimidazole ligand.

All the complexes were isolated as air-stable, non-hygroscopic solids, soluble in dimethyl-formamide, dimethylsulfoxide and halogenated solvents such as chloroform, dichloromethane but insoluble in petroleum ether, diethyl ether, and *n*-hexane and do not show any signs of decomposition in solution upon exposure to air for days.

Noyori *et al.* discovered a ruthenium(II) complexes that proved to be excellent catalysts for the transfer hydrogenation of ketones under mild conditions.[27,28] Ruthenium complexes of the type [$RuCl_2(\eta^6$-arene)(**P**)] with **P** as a monodentate phosphorus ligand,[29] despite being stable and easy to prepare, have seldom been used in transfer hydrogenation. Rossell and coworkers[30] reported the use of [$RuCl_2(\eta^6$-*p*-cymene)(PPh_3)] and [$RuCl_2(\eta^6$-*p*-cymene)($PMePh_2$)] in the reduction of cyclohexanone, Li and coworkers[31] have recently reported very good activities of [$RuCl_2(\eta^6$-benzene)(PAr_3)] complexes (Ar = Ph, *p*-$CF_3C_6H_4$) in the reduction of the same substrate. Catalytic hydrogen transfer reactions of ruthenium complexes of N-coordinated imidazoline and benzimidazole ligand are very limited for this reaction. Due to the encouraging application of half sandwich ruthenium compounds in transfer hydrogenation catalysis, we have also examined the catalytic activity of the complexes **3a-3f** toward reduction of carbonyl group of ketones. The classical transfer hydrogenation of acetophenone by 2-propanol was chosen as a model reaction. The results depicted in Table 1 indicates that complexes **3a-3f** are active catalysts, leading to nearly quantitative conversions (yield 98%) of acetophenone into 1-phenylethanol after 12 h. The results of the catalytic transfer hydrogenation (Scheme 3) of acetophenone, *p*-fluoroacetophenone, *p*-chloroacetophenone, *p*-bromoacetophenone, *p*-methoxyacetophenone, *p*-methylacetophenone and *o*-methylacetophenone are summarized in Table 1.



Scheme 3. Transfer hydrogenation of acetophenones.

Table 1. Transfer hydrogenation of ketones with 2-propanol catalyzed by ruthenium imidazoline and benzimidazole complex

Entry	Substrate: R in $RC_6H_4COCH_3$	catalyst	Yield (%)[a]	TON	TOF(h^{-1})
1		**3a**	79	790	66
2		**3b**	83	830	69
3	H	**3c**	98	980	82
4		**3d**	98	980	82
5		**3e**	96	960	80
6		**3f**	96	960	80
7		**3a**	78	780	65
8		**3b**	82	820	68
9	*p*-F	**3c**	73	730	61
10		**3d**	90	900	75

Table 1 (continued)

11		**3e**	91	910	76
12		**3f**	86	860	72
13		**3a**	57	570	47
14		**3b**	80	800	67
15		**3c**	86	860	72
16	*p*-Cl	**3d**	97	970	81
17		**3e**	90	900	75
18		**3f**	92	920	77
19		**3a**	65	650	54
20		**3b**	92	920	77
21		**3c**	77	770	64
22	*p*-Br	**3d**	95	950	79
23		**3e**	88	880	73
24		**3f**	93	930	78
25		**3a**	74	740	62
26		**3b**	71	710	59
27		**3c**	82	820	68
28	*p*-OMe	**3d**	84	840	70
29		**3e**	79	790	66
30		**3f**	76	760	63
31		**3a**	65	650	54
32		**3b**	58	580	48
33		**3c**	53	530	44
34	*p*-Me	**3d**	67	670	56
35		**3e**	59	590	49
36		**3f**	61	610	51
37		**3a**	77	770	64
38		**3b**	63	630	52
39		**3c**	67	670	56
40	*o*-Me	**3d**	89	890	74
41		**3e**	74	740	62
42		**3f**	83	830	69

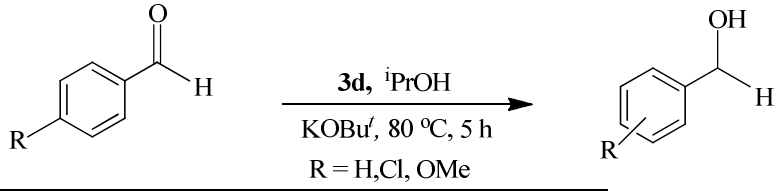
[a] Reaction conditions: Catalyst (1.0 mol %), ketone (1mmol), iPrOH (10 mL), $KOBu^t$ (5mmol%), 80 ºC, 12 h. Purity of compounds is checked by NMR and GC, and yields are based on the product alcohols. TON: moles of product per moles of catalyst; TOF: moles of product per moles of catalyst per hour, in h^{-1}

Table 2. Effect of the amount of catalyst and temperature on the transfer hydrogenation using **3d**

Entry	Substrate: R in $RC_6H_4COCH_3$	Catalyst (3d) (mol%)	Temp. (^oC)	Yield (%)[a]	TON	TOF(h^{-1})
1		0.5	80	68	340	28
2	H	0.1	80	47	47	4
3		1.0	50	32	320	27
4		0.5	80	58	290	24
5	*p*-Cl	0.1	80	42	42	3
6		1.0	50	39	390	32

[a] Reaction conditions: ketone (1mmol), iPrOH (10 mL), $KOBu^t$ (5mmol%), 12 h. Purity of compounds is checked by NMR and GC, and yields are based on the product alcohols. TON: moles of product per moles of catalyst; TOF: moles of product per moles of catalyst per hour, in h^{-1}.

Table 3. Transfer hydrogenation of benzaldehydes with 2-propanol catalyzed by **3d** complex



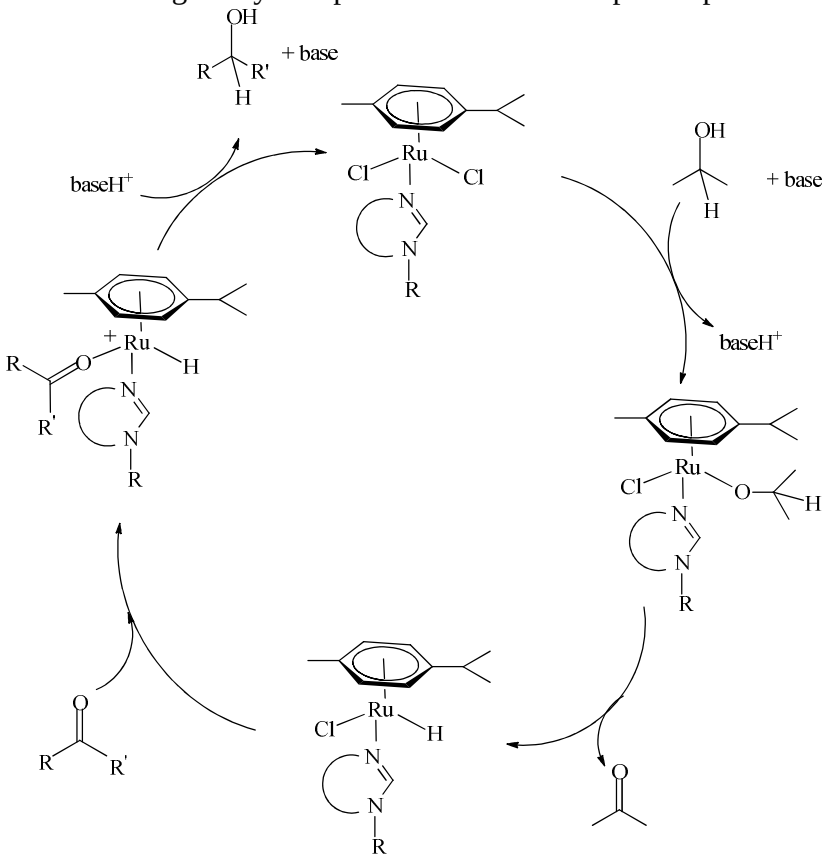
Entry	Substrate: R in RC_6H_4COH	Yield (%)[a]	TON	TOF(h^{-1})
1	H	89	890	178
2	Cl	91	910	182
3	OMe	81	810	162

[a] Reaction conditions: benzaldehyde (1mmol), iPrOH (10 mL), $KOBu^t$ (5mmol%), 5 h. Purity of compounds is checked by NMR and GC, and yields are based on the product alcohols. TON: moles of product per moles of catalyst; TOF: moles of product per moles of catalyst per hour, in h^{-1}

The nature and position of substituents in the aromatic ketones result in significant effects on the catalyst activity. The *p*-substituted acetophenone with the electron donor substituent *p*-methoxy is reduced more slowly than acetophenone. Notably, with an electron-donating methyl group in the *o*-position the reaction is accelerated, but when the *p*-position of substrate is substituted the rate is lowered. The activities of complexes have been explained on the basis of electron releasing groups present on aromatic ring and electronic effects about the metal centre. It has been observed that the presence of electron releasing groups on the aromatic ring increases electron density on metal centre and the rate of transfer hydrogenation. It is noteworthy that the *N*-substituted imidazoline ruthenium complexes (**3a-3c**) display differences from *N*-substituted benzimidazole ruthenium complexes (**3d-3f**) in reactivity (Table 1). As substituent, pentamethyl benzyl group on the aromatic ring is the more effective than other substitents. Consequently,

complex **3d** was observed the most active complex. In order to test the effect of temperature on catalyst (**3d**) performance, the catalytic reaction was performed at 50 °C and the lower yield was obtained (Table 2, entries 3, 6). The effect of catalyst loading on the product yield in transfer hydrogenation of acetophenone and *p*-chloroacetophenone was examined under the same reaction conditions. The most efficient complex **3d** was used to investigate the effect of catalyst loading. The lower yield was obtained when the load of catalyst from 1.0 mol% to 0.5 mol% and 0.1 mol% was decreased (Table 2, entries 1,4 and 2,5). When the examined to transfer hydrogenation of Ru(II) arene complexes in the literature, it is seen that catalysts used in this study have been an passable efficiency in the transfer hydrogenation.[32] Interestingly, the complex **3d** also efficiently catalyzes the reduction of benzaldehyde derivatives to benzylalcohol derivatives with 81-91 % yields (Table 3).

Although no mechanistic studies have been performed, the catalytic transformation of ketones most probably follows the classical pathway in which ketones coordinate to hydride ruthenium metal intermediate.[33,34] Formation of the compounds containing Ru-H from Ru-Cl precursors are well-documented[35] such as in situ generated Ru-H species can act as the active catalysts for transfer hydrogenation of ketones.[36-38] The proposed mechanism of transfer hydrogenation of ketone using catalysts reported in the manuscript is depicted in Scheme 4.



Scheme 4. The proposed mechanism of transfer hydrogenation of ketone with half sandwich ruthenium (II) complexes.

In order to generate the catalytic active species, ruthenium complex and potassium tert-butoxide were dissolved in 2-propanol. A base such as potassium tert-butoxide is necessary to formation of the compounds containing Ru-H from Ru-Cl.

Conclusions

In summary, this report describes the preparation and characterization of new *N*-substituted imidazoline (**1a-1c**) and benzimidazole (**2b**) ligands, and the transfer hydrogenation activity of novel half sandwich ruthenium (II) complexes (**3a-3f**). The catalytic reaction results demonstrated that all complexes are highly efficient in transfer hydrogenation of ketones. We are currently investigating the scope and application of these complexes as catalysts for various organic reactions.

Experimental Section

General. All synthesis were carried out under an inert atmosphere using Schlenk line techniques. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK). Solvents were dried with standard methods and freshly distilled prior to use. Elemental analyses were performed by LECO CHNS-932 elemental analyzer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. FT-IR spectra was recorded as KBr pellets in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum 100. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J* values) are given in Hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. All catalytic reactions were monitored on a Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70-230 mesh). Solvent ratios are given as v/v.

General procedure for the preparation of the 1-alkylimidazoline. A solution of *N*-alkylethane-1,2-diamine (10 mmol) and $Me_2NCH(OMe)_2$ (11 mmol) was slowly heated. When the oil-bath temperature reached 75–80 ^{o}C, NMe_2H and MeOH began to distil off. The pale yellow residue was distilled at 90–100 ^{o}C (0.1mmHg) to obtain a colorless liquid.

***N*-(2,3,4,5,6-Pentamethylbenzyl)imidazoline** (**1a**). Yield: 1.61 g (70%). FT-IR ν_{CN}: 1598 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 6.66 (s, 1H, NC*H*N), 4.28 (s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6), 3.83 and 3.27 (t, 4H, *J* 9.9 Hz, NCH_2CH_2N), 2.30, 2.28, and 2.26 (s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 156.4 (N*C*HN), 134.9,

133.0, 132.9 and 129.8 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6), 55.0 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 49.3 and 46.8 (NCH_2CH_2N), 17.1, 16.8, and 16.6 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6). Anal. Calc. for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.25; H, 9.60; N: 12.15 %.

***N*-(2,3,5,6-Tetramethylbenzyl)imidazoline** (**1b**). Yield: 1.66 g (77%). FT-IR ν_{CN}: 1595 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 6.66 (s, 1H, NC*H*N), 6.97 (s, 1H, $NCH_2C_6H(CH_3)_4$-2,3,5,6), 4.27 (s, 2H, $NCH_2C_6H(CH_3)_4$-2,3,5,6), 3.28 and 3.24 (t, 4H, *J* 9.9 Hz, NCH_2CH_2N), 2.26 and 2.24 (s, 12H, $NCH_2C_6H(CH_3)_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 156.4 (N*C*HN), 134.1, 133.4, 132.3, and 131.5 ($NCH_2C_6H(CH_3)_4$-2,3,5,6), 54.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 49.2 and 46.3 (NCH_2CH_2N), 20.5 and 15.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6). Anal. Calc. for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.71; H, 9.34; N: 12.90 %.

***N*-(3,5-Dimethylbenzyl)imidazoline** (**1c**). Yield: 1.41 g (75%). FT-IR ν_{CN}: 1601 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 6.96 (s, 1H, NC*H*N), 6.94 (s, 1H, $NCH_2C_6H_3(CH_3)_2$-3,5), 6.87 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 4.22 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 3.84 and 3.14 (t, 4H, *J* 9.9 Hz, NCH_2CH_2N), 2.33 (s, 6H, $NCH_2C_6H_3(CH_3)_2$-3,5). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 157.5 (N*C*HN), 138.3, 136.9, 129.4, and 125.6 ($NCH_2C_6H_3(CH_3)_2$-3,5), 55.2 ($NCH_2C_6H_3(CH_3)_2$-3,5), 51.6 and 46.2 (NCH_2CH_2N), 21.3 ($NCH_2C_6H_3(CH_3)_2$-3,5). Anal. Calc. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.57; H, 8.55; N: 14.90 %.

General procedure for the preparation of the N-substituted benzimidazoles. The synthesis and characterization of **2a** and **2c** ligands have been indicated by R.W. Hartmann in 2011.[39]

Synthesis of *N*-(2,3,5,6-tetramethylbenzyl)benzimidazole (**2b**). Benzimidazole (10 mol) was added to a solution of NaH (10 mol) in dry THF (30 mL), the mixture was stirred for 1 h at room temperature, and the 2,3,5,6-tetramethylbenzyl chloride (10.1 mol) was added dropwise and heated for 8 h. The solvent was removed in vacuum, after that dichloromethane (50 mL) was added in the Schlenk tube. The mixture was filtered and then the salt was separated from solution. The solution was concentrated and diethyl ether was added. The colorless product was obtained as a crystalline material.

N-(2,3,5,6-tetramethylbenzyl)benzimidazole (2b). Yield: 2.43 g (92%). Mp170-171 ^oC. FT-IR $\nu_{(CN)}$: 1473 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.45 (s, 1H, NC*H*N), 7.88-7.84 (m, 1H, NC_6H_4N), 7.58-7.55 (m, 1H, NC_6H_4N), 7.43-7.33 (m, 2H, NC_6H_4N), 7.11 (s, 1H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 5.33 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 2.31 and 2.18 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 143.2 (N*C*HN), 141.5, 133.9, 122.6, 120.1, 113.7, and 109.7 (NC_6H_4N), 134.7, 132.7, 129.6 and 123.1 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 43.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 20.5 and 15.5 ($CH_2C_6H(CH_3)_4$-2,3,5,6). Anal. Calc. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.75; H, 7.67; N: 10.57 %.

Synthesis and characterization of the ruthenium imidazoline/benzimidazole complexes 3a-3f

A solution of the N-substituted imidazoline and benzimidazole (1.05 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) in toluene (20 mL) were heated under reflux for 5 h. Upon cooling to room temperature, orange crystals of **3a–f** were obtained. The crystals were filtered off, washed with diethyl ether (3 × 15 mL) and dried under vacuum.

[$RuCl_2$(*p*-cymene)(*N*-(2,3,4,5,6-pentamethylbenzyl)imidazoline)] (**3a**). Yield: 0.47 g (88%). Mp 220-221 °C. IR: ν_{CN} 1612 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.21 (s, 1H, NC*H*N), 5.37 and 5.19 (d, 4H, *J* 5.4 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 4.40 (s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6), 4.07 and 3.41 (t, 4H, *J* 10.5 Hz, NCH_2CH_2N), 2.97 (hept., 1H, *J* 6.6 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.25 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.28, 2.24 and 2.23 (s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6), 1.26 (d, 6H, *J* 6.6 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 160.6 (N*C*HN), 135.5, 133.1, 133.0 and 128.0 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6), 101.8, 96.9, 81.9, and 80.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 57.0 and 48.3 (N*C*$H_2C$$H_2$N), 46.4 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 30.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 22.2 $(CH_3)_2CHC_6H_4CH_3$-*p*), 18.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 17.1, 16.9, and 16.7 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6). Anal: Calc. for $C_{25}H_{36}Cl_2N_2Ru$: C, 55.91; H, 6.76; N, 5.22. Found: C, 55.94; H, 6.79; N, 5.26 %.

[**$RuCl_2$(*p*-cymene)(*N*-(2,3,5,6-tetramethylbenzyl)imidazoline)**] (**3b**). Yield: 0.42 g (81%). Mp 217-218 °C. IR: ν_{CN} 1614 cm^{-1}.^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.23 (s, 1H, NC*H*N), 7.97 (s, 1H, $NCH_2C_6H(CH_3)_4$-2,3,5,6), 5.37, and 5.19 (d, 4H, *J* 5.7 Hz, $(CH_3)_2CHC_6H_4CH_3$-p), 4.39 (s, 2H, $NCH_2C_6H(CH_3)_4$-2,3,5,6), 4.07, and 3.38 (t, 4H, *J* 10.2 Hz, NCH_2CH_2N), 2.96 (hept., 1H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.23 and 2.19 (s, 12H, $NCH_2C_6H(CH_3)_4$-2,3,5,6), 2.22 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.27 (d, 6H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 160.8 (N*C*HN), 134.3, 133.4, 131.9, and 130.7 ($NCH_2C_6H(CH_3)_4$-2,3,5,6), 101.8, 96.9, 81.9, and 80.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 57.0, and 48.2 (N*C*$H_2C$$H_2$N), 45.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 30.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 22.2 $(CH_3)_2CHC_6H_4CH_3$-*p*), 20.5 and 15.7 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 18.7 $(CH_3)_2CHC_6H_4CH_3$-*p*). Anal: Calc. for $C_{24}H_{34}Cl_2N_2Ru$: C, 55.17; H, 6.56; N, 5.32. Found: C, 55.14; H, 6.51; N, 5.40 %.

[**$RuCl_2$(*p*-cymene)(*N*-(3,5-dimethylbenzyl)imidazoline)**] (**3c**). Yield: 0.43 g (87%). Mp 155-156 °C. IR: ν_{CN} 1598 cm^{-1}.^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.38 (s, 1H, NC*H*N), 6.92 (s, 1H, $NCH_2C_6H_3(CH_3)_2$-3,5), 6.79 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 5.40 and 5.22 (d, 4H, *J* 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 4.20 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 4.11 and 3.35 (t, 4H, *J* 10.2 Hz, NCH_2CH_2N), 3.00 (hept., 1H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.29 (s, 6H, $NCH_2C_6H_3(CH_3)_2$-3,5), 2.23 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.29 (d, 6H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 161.3 (N*C*HN), 138.5, 135.1, 129.0, and 125.8 ($NCH_2C_6H_3(CH_3)_2$-3,5), 102.0, 96.8, 81.8, and 80.9 $(CH_3)_2CHC_6H_4CH_3$-*p*), 57.3 and 48.1 (N*C*$H_2C$$H_2$N), 51.8 (N*C*$H_2C_6H_3(CH_3)_2$-3,5), 30.7 $(CH_3)_2CHC_6H_4CH_3$-*p*), 22.3 $(CH_3)_2CHC_6H_4CH_3$-*p*), 21.3 ($NCH_2C_6H_3(CH_3)_2$-3,5), 18.7 $(CH_3)_2CHC_6H_4CH_3$-*p*). Anal: Calc. for $C_{22}H_{30}Cl_2N_2Ru$: C, 53.44; H, 6.12; N, 5.67. Found: C, 53.47; H, 6.09; N, 5.70 %.

[**$RuCl_2$(*p*-cymene)(*N*-(2,3,4,5,6-pentamethylbenzyl)benzimidazole)]** (**3d**). Yield: 0.53 g (91%). Mp 228-229 °C. IR: ν_{CN} 1463 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.97 (s, 1H, NC*H*N), 8.13-8.10 (m, 1H, NC_6H_4N), 7.53-7.51 (m, 1H, NC_6H_4N), 7.42-7.39 (m, 2H, NC_6H_4N), 5.40 and 5.31 (d, 4H, *J* 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.34 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 2.66 (hept., 1H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.26, 2.20 and 2.18 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 2.12 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.10 (d, 6H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 144.2 (N*C*HN), 142.9, 136.7, 124.0, 123.7, 120.9, and

110.5 (NC_6H_4N), 134.0, 133.6, 133.3, and 126.4 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 101.9, 98.0, 83.0, and 80.9 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 45.1 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 30.5 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 17.2, 16.9, and 16.7 ($CH_2C_6(CH_3)_5$-2,3,4,5,6). Anal: Calc. for $C_{29}H_{36}Cl_2N_2Ru$: C, 59.58; H, 6.21; N, 4.79. Found: C, 59.55; H, 6.18; N, 4.82 %.

[**$RuCl_2$(p-cymene)(N-(2,3,5,6-tetramethylbenzyl)benzimidazole)**] (**3e**): Yield. 0.48 g (85%). Mp 231-232 °C. IR: ν_{CN} 1460 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.97 (s, 1H, NC*H*N), 8.13-8.08 (m, 1H, NC_6H_4N), 7.51-7.47 (m, 1H, NC_6H_4N), 7.43-7.36 (m, 2H, NC_6H_4N), 7.09 (s, 1H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 5.39 and 5.31 (d, 4H, *J* 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.33 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 2.63 (hept., 1H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.28 and 2.16 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 2.14 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.09 (d, 6H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 144.2 (N*C*HN), 142.8, 134.0, 124.1, 123.7, 120.8, and 110.5 (NC_6H_4N), 134.8, 133.8, 133.0, and 129.3 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 101.8, 98.1, 82.9, and 80.9 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 44.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 30.5 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 20.5 and 15.7 ($CH_2C_6H(CH_3)_4$-2,3,5,6). Anal: Calc. for $C_{28}H_{34}Cl_2N_2Ru$: C, 58.94; H, 6.01; N, 4.91. Found: C, 58.97; H, 6.05; N, 4.87 %.

[$RuCl_2$(*p*-cymene)(N-(3,5-dimethylbenzyl)benzimidazole)] (**3f**). Yield: 0.43 g (80%). Mp 256-257 °C. IR: ν_{CN} 1465 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 1H, NC*H*N), 8.11-8.03 (m, 1H, NC_6H_4N), 7.59-7.41 (m, 1H, NC_6H_4N), 7.38-7.31 (m, 2H, NC_6H_4N), 7.00 (s, 1H, $NCH_2C_6H_3(CH_3)_2$-3,5), 6.80 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 5.53 and 5.40 (d, 4H, *J* 5.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.13 (s, 2H, $NCH_2C_6H_3(CH_3)_2$-3,5), 2.80 (hept., 1H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.26 (s, 6H, $NCH_2C_6H_3(CH_3)_2$-3,5), 2.14 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.21 (d, 6H, *J* 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm): 144.9 (N*C*HN), 142.6, 134.6, 132.3, 124.2, 118.8, and 112.7 (NC_6H_4N), 138.7, 133.8, 130.1, and 125.2 ($NCH_2C_6H_3(CH_3)_2$-3,5), 102.6, 97.9, 83.0, and 81.2 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 49.6 ($NCH_2C_6H_3(CH_3)_2$-3,5), 30.6 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 21.3 ($NCH_2C_6H_3(CH_3)_2$-3,5), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-*p*). Anal: Calc. for $C_{26}H_{30}Cl_2N_2Ru$: C, 57.56; H, 5.57; N, 5.16. Found: C, 57.51; H, 5.60; N, 5.20 %.

General procedure for the transfer hydrogenation of ketones

Under an inert atmosphere, a mixture containing the complexes [$RuCl_2$(1-alkylimidazoline)(*p*-cymene)]/[$RuCl_2$(1-alkylbenzimidazole)(*p*-cymene)] (**3a-f**) (0.01mmol), $KOBu^t$ (5 mmol%), ketone (1 mmol) was heated at 80 ºC in *i*-PrOH (10 mL) for 12 h. The solvent was removed under reduced pressure and product distribution was determined by ^1H NMR spectroscopy and GC.

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