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N-Heterocyclic Carbenes

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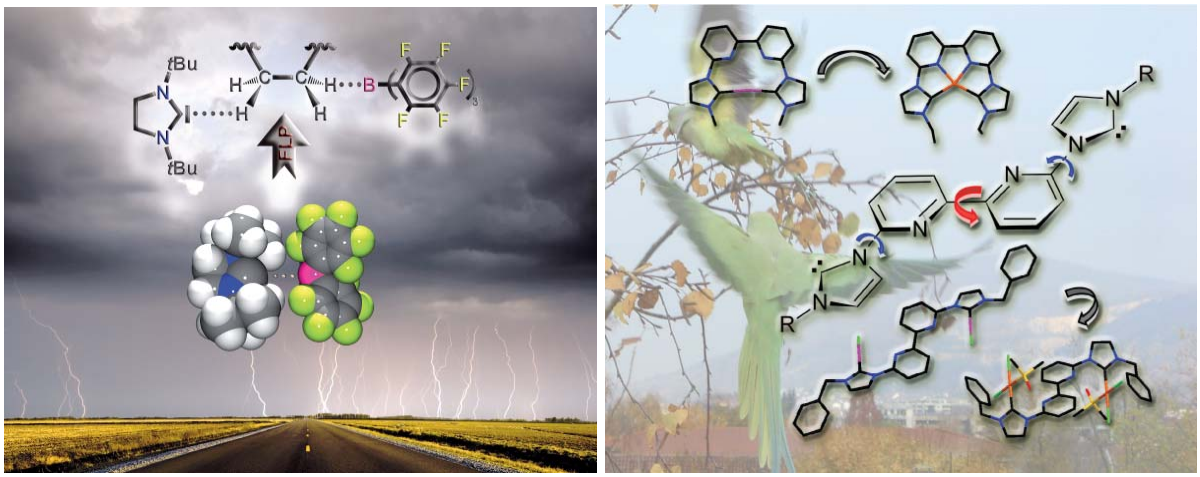

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Synthesis, structures and catalytic activities of ruthenium(II) carbonyl chloride complexes containing pyridine-functionalised *N*-heterocyclic carbenes†

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A series of ruthenium(II) carbonyl chloride complexes with pyridine-functionalised *N*-heterocyclic carbenes, *trans*(Cl)- and *cis*(Cl)-[Ru(Py–NHC)$(CO)_2Cl_2$] [Py–NHC = 3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene, **1a** and **1b**; 3-*n*-butyl-1-(2-pyridyl)imidazol-2-ylidene, **2a** and **2b**; 3-*tert*-butyl-1-picolylimidazol-2-ylidene, **3a** and **3b**; 3-*n*-butyl-1-picolylimidazol-2-ylidene, **4a** and **4b**; 3-benzyl-1-picolylimidazol-2-ylidene, **5a** and **5b**] have been prepared by transmetallation from the corresponding silver carbene complexes and characterised by elemental analyses, infrared and ^{1}H and ^{13}C NMR spectroscopies. The yields of *trans*(Cl)- and *cis*(Cl)-isomers could be controlled by altering the reaction conditions: the *trans*-isomers were kinetically formed as the main products in 60–70% yield in CH_2Cl_2 at ambient temperature while the thermodynamic *cis*-isomers were obtained as the major products in 70–80% yield in toluene at refluxing temperature. The *trans*-isomer was transformed into the thermodynamic *cis*-isomer by heating in CH_2Cl_2 in a Teflon-lined stainless autoclave for 24 h at 120 °C. The molecular structures of **1a**, **1b**, **2b**, and **4b** have been determined by single-crystal X-ray diffraction. These complexes showed catalytic activities in hydrogen transfer reactions of ketones.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted increasing attention as they have been proven to act as efficient spectator ligands in coordination chemistry and homogeneous catalysis.[1–6] In many cases NHC complexes show higher thermal stability and catalytic activities than their phosphine counterparts partially owing to the strong metal–NHC bonds and the high σ-donating ability of NHC ligands.[7] The incorporation of the carbene functionality into ligand systems containing other "classical" donor groups offers vast opportunities for ligand design and the discovery of new efficient catalysts.[8–10]

Pyridine-functionalised bidentate carbene ligands (Py–NHCs) have been frequently used as versatile ancillary ligands in organometallic complexes in recent years.[8] Bidentate pyridine-functionalised NHC complexes including those containing Rh,[11–15] Ir,[12–18] Ni,[19,20] Pd,[21–28] Cu,[29] and Ag[11,19,30] have been prepared, some of which showed catalytic activities in hydrosilylation of acetylenes,[15] cyclization of acetylenic carboxylic acids,[15] hydrogen transfer to ketones,[15] reduction of nitroarenes,[17] C–C coupling reactions,[22,23] and olefin polymerization.[19,28] However, few reports have been published on Ru[31–35,14] and Os[36] complexes containing bidentate pyridine-functionalised NHC ligands. We recently reported the synthesis and characterisation of pyridine-functionalised NHC Ru(II) nitrosyl complexes and their catalytic activity in hydrogen transfer of ketones.[35]

The Ru(II) carbonyl chloride complexes [Ru(L)$(CO)_2Cl_2$] containing bpy, bipy, dmbpy, or PR_3 ligands have been intensively studied for nearly twenty years,[37–45] but their catalytic activities in hydrogen transfer of ketones have not been investigated. In addition, Ru(II) carbonyl chloride complexes with a Py–NHC ligand have not yet been reported. Herein, we report the preparation and characterisation of stereoisomers of [Ru(Py–NHC)$(CO)_2Cl_2$] with pyridine-functionalised bidentate carbenes (Py–NHCs, Chart 1). Their catalytic activities in hydrogen transfer of ketones have also been presented.

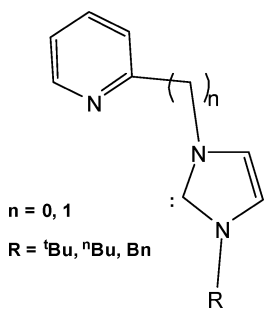

Chart 1

Results and discussion

Synthesis and characterisation of [Ru(Py–NHC)$(CO)_2Cl_2$]

Among the reported strategies, the transmetallation route has proved to be one of the most useful methods in the preparation of metal–NHC complexes.[46] A silver *N*-heterocyclic carbene complex, prepared from the reaction of an imidazolium precursor

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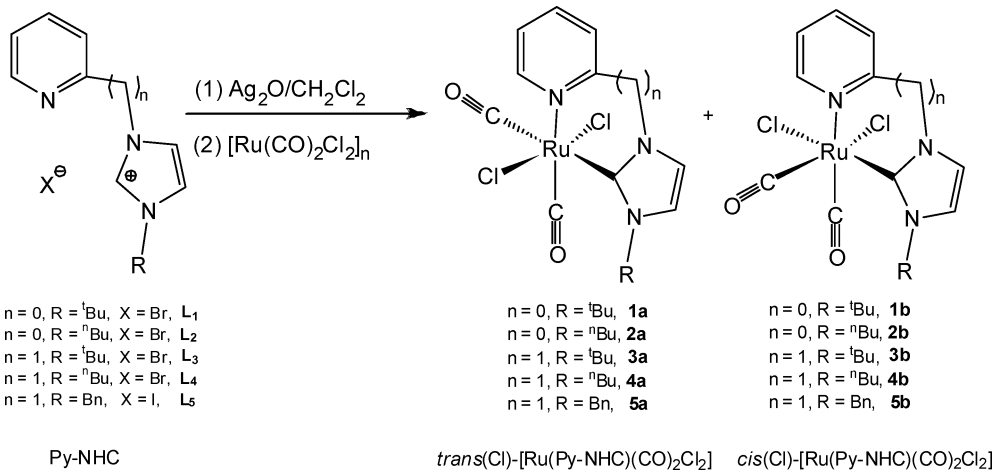
† Electronic supplementary information (ESI) available: ^{1}H NMR spectra (DMSO-d_6, 500 MHz) of **2b**, **4b**, and **5b**. CCDC reference numbers 714989–714992. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904882k



Scheme 1 Synthesis of ruthenium(II) carbonyl chloride complexes **1a–5a** and **1b–5b**.

and Ag_2O, reacts with the metal precursor to give the desired product. We have employed this route in the current work to prepare Ru(II) carbonyl chloride complexes **1a–5a** and **1b–5b** (Scheme 1). Reacting imidazolium salts $\mathbf{L_1}$–$\mathbf{L_5}$ with an excess of Ag_2O in CH_2Cl_2 afforded the corresponding silver *N*-heterocyclic carbene complexes.[30] The mixture was filtered through Celite to remove unreacted silver oxide and insoluble residues. The filtrate was treated with $[Ru(CO)_2Cl_2]_n$ to gave a mixture of the complexes with *trans*(Cl)–*cis*(CO) (*trans* for short) and *cis*(Cl)–*cis*(CO) (*cis* for short) configurations, which were separated by column chromatography. It was found that the yields of the products depend on the solvent and the reaction temperature. The reactions in CH_2Cl_2 at room temperature gave the *trans*-isomers as the main products (yield 60–70%) and the *cis*-isomers as the minor products (yield 10–20%), while the reactions in toluene at refluxing temperature afforded the *trans*-isomers (5–10% yield) and *cis*-isomers (70–80% yield), respectively.

It has been known that the reaction of $[Ru(CO)_2Cl_2]_n$ with an unsymmetric bidentate ligand leads in principle to the formation of three stereoisomers: *trans*(Cl)–*cis*(CO), *cis*(Cl)–*cis*(CO) and *trans*(CO)–*cis*(Cl),[38] as depicted in Chart 2. Few *trans*(CO)–*cis*(Cl) isomers have been reported,[39] which was suggested to be due to the thermodynamically unfavourable *trans* positions of both carbonyl ligands.[38] With the *N*,*C* bidentate ligands Py–NHCs in the current work, two diastereoisomeric forms of the *cis*(Cl)–*cis*(CO) isomer are possible. NMR data revealed that only one diastereomer *cis*(Cl)–*cis*(CO) is present, as only one set of resonances was observed for the pyridine moiety of the Py–NHC ligand. Crystal structure determination indicated that this is diastereomer *cis*(Cl)–*cis*(CO)–2 (*cis*-isomer for short), in which one carbonyl ligand coordinates *trans* to the pyridine group and one chloride is *trans* to the NHC carbene carbon atom.

Complexes **1a–5a** and **1b–5b** are very soluble in CH_3OH and CH_2Cl_2, but insoluble in Et_2O and hydrocarbon solvents. These complexes are stable in air and in the solid state. However, the yellow methanol solution of the *trans*-isomers **1a–5a** turned dark green after a few days while the *cis* compounds **1b–5b** are stable in air in methanol.

The ^{1}H NMR spectra of **1a–5a** and **1b–5b** do not exhibit the signals at 10–12 ppm, the imidazolium C_2–H proton signals of the precursors, suggesting the coordination of the carbene carbon in Py–NHCs ligand to the Ru atoms.[11,12] There is a singlet signal at 5.6–6.0 ppm in *trans*-isomers **3a**, **4a**, and **5a**, indicating that the two H atoms of the CH_2 linker between the py and NHC rings are identical. However, two doublet signals of AM pattern are observed in the *cis*-isomers **3b** (6.15, 5.40 ppm), **4b** (5.83, 5.25 ppm), and **5b** (5.90, 5.34 ppm), indicating that the two proton atoms of the CH_2 linker are diastereotopic. Furthermore, a clear AB pattern signal centered at 5.63 ppm is observed for the CH_2 group of Bn in **5b**, indicating that the two protons of the CH_2 group of Bn are also diastereotopic (Fig. 1S, ESI†). This suggests that there is restricted rotation around the N–C(Bn) bond as a result of the crowded environment around the ruthenium(II) centre. ^{1}H NMR spectra of **2b** and **4b** also implies the same inequivalence of the two proton atoms of the CH_2 group of *n*-Bu, which directly connects with the imdazolyl ring. Two sextet signals at 4.39 and

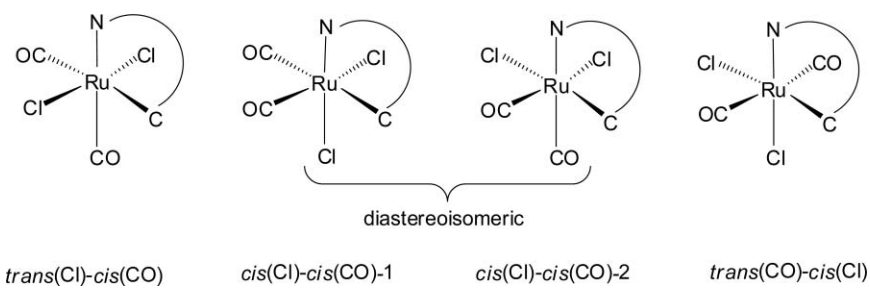


Chart 2

4.13 ppm are found for this CH_2 group in **4b**. One multiplet signal centered at 4.21 ppm, which can be regarded as the overlapping of the two sextet signals, is observed for the same CH_2 group in **2b** (Fig. 1S, ESI†). The other difference between the ^{1}H NMR spectra of *trans*- and *cis*-isomers is that the frequency of the H6 atom in the Py ring is observed at 9.0–9.1 ppm for the *trans*-isomers, but is found at 9.2–9.4 ppm for the *cis*-isomers. The ^{13}C NMR signals for the carbene carbon atoms of **1a–5a** and **1b–5b** appear at 150–180 ppm, locating in the characteristic range reported for metal complexes bearing Py–NHCs.[11–36] The ^{13}C NMR spectra of the carbonyl carbon atoms in these complexes show two slightly different resonances at 201–192, and 196–187 ppm, similar to those of $[Ru(L)(CO)_2Cl_2]$ (L = bpy, bipy, dmbpy and PR_3).[38–41]

The IR spectra of complexes **1a–5a** and **1b–5b** show two absorptions of terminal CO groups in the range of 2050–2064 and 1990–2008 cm^{-1}. These absorptions do not allow a differentiation between the *trans* and *cis* conformations.

It was found that heating the kinetic *trans*-isomers **1a–5a** in CH_2Cl_2 for 24 h at 120 °C in a Teflon-lined stainless autoclave quantitatively gave the thermodynamic *cis*-isomers **1b–5b**. The isomerization is very clean, as no side product was observed by ^{1}H NMR spectroscopy.

Molecular structures of 1a, 1b, 2b and 4b

Crystals of **1a**·$2H_2O$ for X-ray diffraction structure determination were obtained by recrystallization from a saturated methanol solution of **1a** at −10 °C, while those of **1b**, **2b**, and **4b** were obtained by evaporation of a methanol solution of **1b**, **2b**, and **4b** in air. The details of the molecular structures of complexes **1a**, **1b**, **2b**, and **4b** are displayed in Fig. 1–4, respectively. The crystallographic data for **1a**·$2H_2O$, **1b**, **2b**, and **4b** are given in Table 1. Selected bond distances and angles are shown in Table 2.

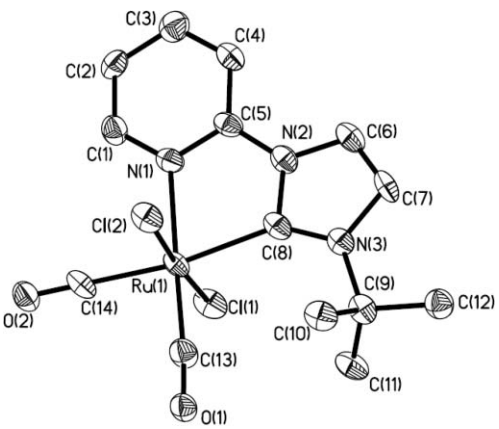


Fig. 1 ORTEP representation of the structure of **1a** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The ORTEP drawings of **1a**, **1b**, **2b**, and **4b** shown in Fig. 1–4 confirm that the coordination geometry around the ruthenium atom can be rationalised as a slightly distorted octahedron. The unit cell of **1a**·$2H_2O$ contains two co-crystallized water molecules. The structure of **1a** shows that two chloride atoms occupy mutually *trans* positions and two CO groups are located *trans* to the pyridine nitrogen and the carbene carbon, respectively. The structures of **1b**, **2b** and **4b** are similar, with two chloride atoms

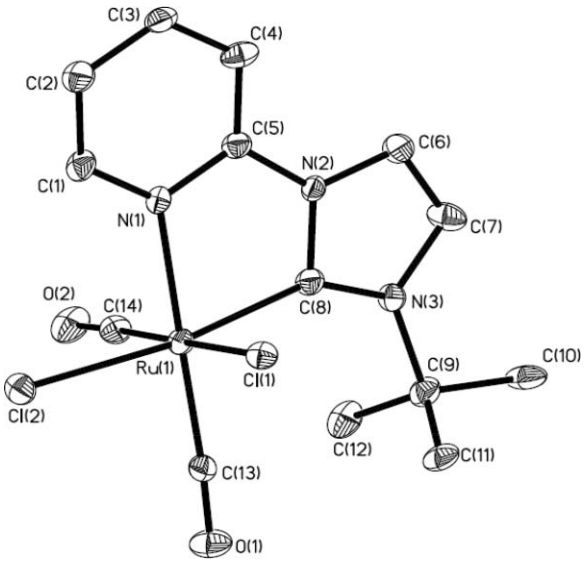


Fig. 2 ORTEP representation of the structure of **1b** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

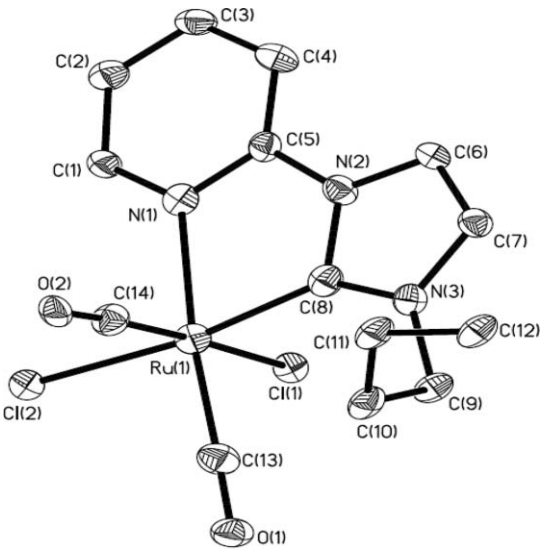


Fig. 3 ORTEP representation of the structure of **2b** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

occupying mutually *cis* positions, one of the CO group *trans* to the pyridine nitrogen and the other one *trans* to the chloride atom.

The Ru–$C_{carbene}$ distances of 2.116(4) Å (**1a**), 2.052(4) Å (**1b**), 2.014(4) Å (**2b**), 2.027(4) Å (**4b**) are in the range reported for Ru–NHC complexes.[47–49] It is noteworthy that the Ru–$C_{carbene}$ distances in *trans*-isomer **1a** [2.116(4) Å] is longer than in *cis*-isomers **1b** [2.052(4) Å], **2b** [2.014(4) Å], and **4b** [2.027(4) Å]. The Ru–$C_{carbene}$ bond of **1a** is located *trans* to CO, while it is *trans* to Cl in *cis*-isomers **1b**, **2b**, and **4b**, confirming that CO exerts a strong *trans*-influence. The Ru–C_{CO} bond lengths in **1a**, **1b**, **2b**, and **4b** are in the range of 1.852(4)–1.917(5) Å, typical for Ru–CO distances of the reported Ru(II) carbonyl complexes.[38–41] The Ru–C_{CO} bond (Ru1–C14) of complex **1a**, *trans* to *N*-heterocyclic carbene carbon [1.917(5) Å], is longer than that *trans* to pyridine nitrogen (Ru1–C13) [1.859(5) Å]. It is the longest Ru–C_{CO} bond in all of these complexes due to the strong σ-donation of the *trans* carbene

Table 1 Summary of crystallographic aata for **1a**·2H_2O, **1b**, **2b**, and **4b**

Compound	**1a**·2H_2O	**1b**	**2b**	**4b**
Formula	$C_{14}H_{15}Cl_2N_3O_2Ru·2H_2O$	$C_{14}H_{15}Cl_2N_3O_2Ru$	$C_{14}H_{15}Cl_2N_3O_2Ru$	$C_{15}H_{17}Cl_2N_3O_2Ru$
Formula weight	465.29	429.26	429.26	443.29
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a/Å	11.732(2)	14.312(12)	14.7065(12)	7.7333(16)
b/Å	8.9321(16)	6.517(6)	9.6796(7)	17.937(4)
c/Å	18.799(3)	17.998(15)	12.6558(11)	12.653(3)
β/°	97.904(2)	106.647(11)	115.0470(10)	93.690(3)
V/Å^3	1951.3(6)	1608(2)	1632.2(2)	1751.5(7)
D_{calc}/g cm^{-3}	1.584	1.773	1.747	1.681
Z	4	4	4	4
T/K	291(2)	291(2)	291(2)	291(2)
Radiation Mo Kα	0.71073	0.71073	0.71073	0.71073
F (000)	936	856	856	888
Absorption coefficient/mm^{-1}	1.098	1.316	1.296	1.211
θ range for data collection/°	2.19 to 25.99	2.40 to 26.00	2.60 to 26.00	2.00 to 26.00
Data/restr./paras	3821/0/220	3140/0/202	3198/0/200	3436/0/209
Reflections collected	10 192	7795	8525	9321
Reflections unique	3821	3140	3198	3436
Completeness to θ/° (%)	25.99 (99.9)	26.00 (99.6)	26.00 (99.7)	26.00 (99.8)
R_{int}	0.0398	0.0399	0.0361	0.0404
Max. and min. transmission	0.79 and 0.74	0.77 and 0.72	0.75 and 0.70	0.79 and 0.76
Goodness-of-fit on F^2	1.001	1.04	1.090	1.033
R_1/wR_2 [$I > 2\sigma(I)$]	0.0482/0.0995	0.0399/0.0819	0.0467/0.1018	0.0434/0.0885
R_1/wR_2 (all data)[a]	0.0681/0.1039	0.0513/1.039	0.0580/0.1041	0.0567/0.0903
Larg. peak and hole/e Å^{-1}	0.383/−0.896	0.456/−1.024	0.482/−0.883	0.378/−0.837

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

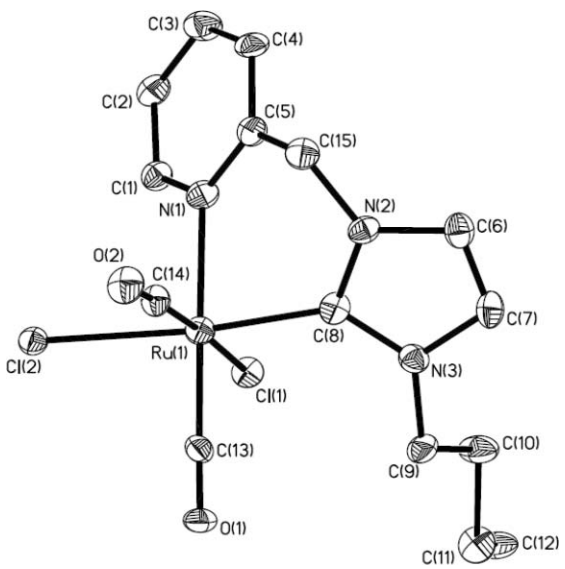


Fig. 4 ORTEP representation of the structure of **4b** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for **1a**, **1b**, **2b**, and **4b**

	1a	**1b**	**2b**	**4b**
Bond length				
Ru1–C8	2.116(4)	2.052(4)	2.014(4)	2.027(4)
Ru1–N1	2.159(4)	2.131(3)	2.156(3)	2.172(3)
Ru1–Cl1	2.3968(12)	2.436(2)	2.4388(11)	2.4344(10)
Ru1–Cl2	2.3891(12)	2.431(2)	2.4458(11)	2.4861(11)
Ru1–C13	1.859(5)	1.879(4)	1.863(5)	1.868(4)
Ru1–C14	1.917(5)	1.852(4)	1.866(5)	1.876(4)
C13–O1	1.138(5)	1.113(5)	1.132(5)	1.129(5)
C14–O2	1.116(5)	1.126(5)	1.141(5)	1.109(5)
Bond angle				
N1–Ru1–C8	77.01(16)	78.72(13)	77.49(15)	84.59(15)
C13–Ru1–C14	87.5(2)	90.09(18)	90.1(2)	88.48(18)
C14–Ru1–C8	170.7(2)	91.47(17)	93.70(19)	93.59(16)
C13–Ru1–C8	101.8(2)	102.41(16)	98.5(2)	95.51(16)
C14–Ru1–N1	93.65(18)	93.82(15)	94.72(16)	94.09(15)
C13–Ru1–N1	178.82(18)	175.90(16)	173.92(18)	177.41(15)
C14–Ru1–Cl2	91.25(15)	88.23(13)	87.61(15)	85.68(12)
C13–Ru1–Cl2	91.97(16)	86.12(12)	90.84(16)	90.36(12)
C8–Ru1–Cl2	88.75(12)	171.46(11)	170.55(13)	174.07(12)
N1–Ru1–Cl2	87.97(10)	92.78(9)	93.08(9)	89.59(10)
C14–Ru1–Cl1	91.40(15)	178.12(12)	176.52(15)	176.39(13)
C13–Ru1–Cl1	91.20(16)	90.94(14)	89.58(16)	90.69(12)
C8–Ru1–Cl1	88.14(12)	89.84(12)	89.78(13)	89.99(10)
N1–Ru1–Cl1	88.81(10)	85.12(10)	85.86(9)	86.73(9)
Cl2–Ru1–Cl1	175.95(4)	90.27(4)	88.93(4)	90.81(3)

carbon. Ru–$N_{pyridine}$ bond lengths of 2.159(4) Å (**1a**), 2.131(3) Å (**1b**), 2.156(3) Å (**2b**), and 2.172(3) Å (**4b**) are similar to those observed in [Ru(L)$(CO)_2Cl_2$] (L = bpy, bipy, dmbpy, PR_3).[38–41] The lengths of the Ru1–Cl bonds in *cis*-isomers **1b**, **2b**, and **4b** (2.436(2)–2.4861(11) Å) are longer than those of in *trans*-isomer **1a** (2.3968(12) Å and 2.3891(12) Å), which can be explained by the *trans* influences of carbonyl and carbene carbon groups since the chlorine atoms Cl1 and Cl2 are located *trans* to the carbonyl (C14O2) and carbene carbon (C8), respectively, in **1b**, **2b**, and **4b**.

The $C_{carbene}$–Ru–$N_{pyridine}$ bond angle in the six-membered chelating ring of **4b** [84.59(15)°] is larger than those in the five-membered chelating rings of **1a** [77.01(16)°], **1b** [78.72(13)°],

and **2b** [77.49(15)°]. The *N*-heterocyclic carbene ring and the pyridine ring are almost co-planar in **1a**, **1b** and **2b**. They form an obtuse dihedral angle in **4b** [110.3(3)°].

Catalytic transfer hydrogenation of ketones

Ruthenium complexes have been used as active catalysts for transfer hydrogenation reactions.[50–53] However, only a very limited number of Ru–NHC complexes have been reported as catalysts for this transformation.[54–55] Thus **1a–5a** and **1b–5b** were tested as catalysts for transfer hydrogenation of ketones.

The reduction of acetophenone to 1-phenylethanol by 2-propanol was chosen as a model reaction to explore the catalytic behaviours of complexes **1a–5a** and **1b–5b**, using 2-propanol as the hydrogen donor in the presence of base, see eqn (1). The catalytic trials were carried out using substrate ketone (4.0 mmol), a Ru catalyst precursor (8 μmol), KOH (0.2 mmol), and ^{i}PrOH (10 mL), with a catalyst : base : substrate ratio of 2 : 50 : 1000. An ^{i}PrOH solution of the base was added to an ^{i}PrOH solution containing the catalyst and the substrate. The reaction mixture was kept at 82 °C. The conversion was monitored by GC. In order to evaluate the difference between the various carbene complexes, the time-dependent conversions were followed (Fig. 5).

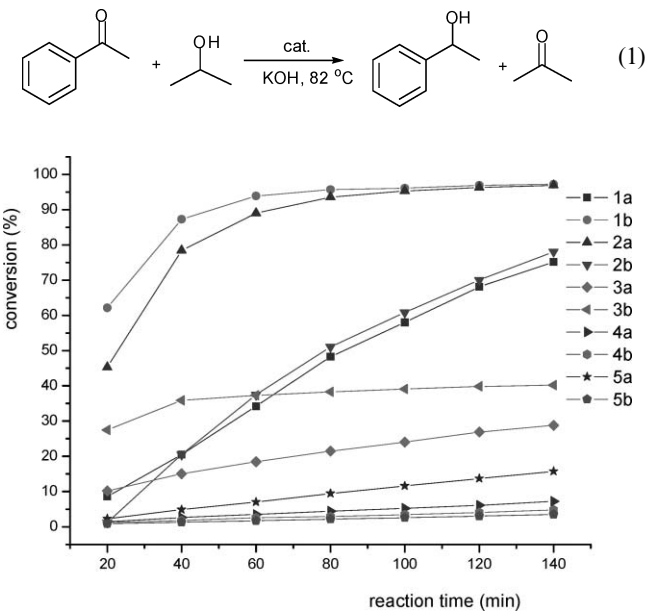


Fig. 5 Conversion *vs.* reaction time of the catalytic transfer hydrogenation of acetophenone; 8 μmol catalyst; 0.2 mmol KOH; 4 mmol acetophenone; solvent ^{i}PrOH 10 ml, $T = 355$ K.

It was found that complexes **1a**, **1b**, **2a**, and **2b** are more active than **3a**, **3b**, **4a**, **4b**, **5a**, and **5b**, suggesting that the presence of the five-membered ring between the pyridine and imidazole group is beneficial for the transfer hydrogenation of acetophenone compared with the six-membered ring. **1b** is the most active catalyst among these complexes. It should be mentioned that **1b** bears a *t*-butyl group at the nitrogen atom of the imidazole moiety. Noyori and co-workers have shown that the true catalyst in transfer hydrogenation reactions is formally a 16-electron intermediate species.[56] It is assumed that the bulky ligand favours the formation of the stable 16-electron intermediate, which shows high activity in the transfer hydrogenation process.

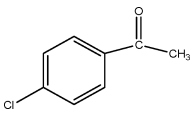
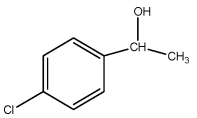
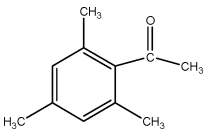
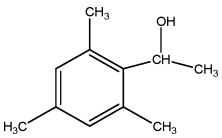
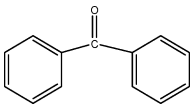
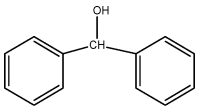
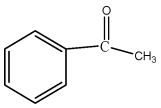
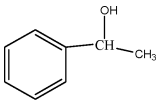
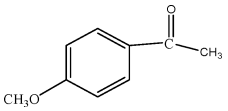
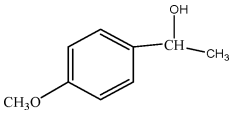
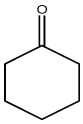
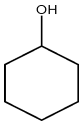
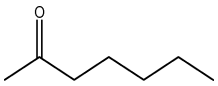
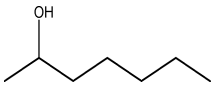
In order to determine the fate of carbonyl ligands in the catalytic reaction, we have attempted to probe if the carbonyl ligand still existed in the coordination sphere of ruthenium for the catalytic reduction of acetophenone with **1b**. After the catalytic reaction, the reaction mixture was evaporated to give a solid. The IR spectrum of the isolated solid showed the absence of the carbonyl ligand around the ruthenium atom, indicating that the carbonyl group did not survive under the reaction conditions. To further explore the fate of complex **1b** before the catalytic reaction starts, complex **1b** was added to the solution of 0.1 mol L^{-1} KOH in ^{i}PrOH (10 mL) and refluxed for several hours under nitrogen, then the reaction mixture was evaporated to give a black solid. The IR spectra of the isolated solids showed the absence of carbonyl ligands, indicating that the carbonyl group did not survive in the basic solution, which probably results in a vacant site on the ruthenium for the catalytic reaction. It is thus reasonable to assume that these ruthenium complexes just act as precursors to the active catalysts and the carbonyl ligands probably play no important role in transfer hydrogenation reactions. It should be noted that other reported ruthenium carbonyl complexes supported by Cp analogous ligands are involved in the mechanism of metal hydride intermediates in which the CO groups still survive in the coordination sphere of ruthenium for the hydrogenation transfer reactions.[57]

Since complex **1b** was found to be the most efficient catalyst in transfer hydrogenation of acetophenone, we further explored its catalytic potentials in the reduction of other aryl and alkyl ketones with the reaction conditions identical to those used in the transfer hydrogenation of acetophenone (Table 3). It was found that **1b** is efficient in transfer hydrogenation of 4-methoxyacetophenone to 4-methoxyphenylethanol (85% conversion after 6 h, entry 5) and 4-chloroacetophenone to 4-chloroacetophenol (76% conversion after 6 h, entry 1), moderate active in the case of diphenylketone (47% after 6 h, entry 3) and 2-heptanone (38% after 6 h, entry 7), but shows a poor activity in the reduction of cyclohexanone (14% after 6 h, entry 6) and 2,4,6-trimethylacetophenone (10% after 6 h, entry 2). These different activities in these substrates may be attributed to the electron and steric effects of the substituents on the ketones.

Conclusion

We have described the preparation, molecular structures and catalytic activities of *trans* and *cis*-isomers of Ru(II) carbonyl complexes bearing pyridine-functionalised *N*-heterocarbene ligands. Using the Ag carbene transmetallation route, these new complexes were readily accessible and were fully characterised. The yields of the *trans*- and *cis*-complexes were controlled by altering the reaction conditions. *Trans*-isomers were found to be transformed into *cis*-isomers in dichloromethane in a Teflon-lined stainless autoclave. Their potential as catalyst precursors for transfer hydrogenation of ketones has also been tested. The presence of the five-membered ring between the pyridine and imidazole group is found to be beneficial for the transfer hydrogenation of acetophenone.

Table 3 Catalytic transfer hydrogenation of ketones with **1b**[a]

Entry	Ketone	Alcohol	Conversion% (6 h)[b]
1			76
2			10
3			47
4			91
5			85
6			14
7			38

[a] Experimental condition: reactions were carried out at 82 °C; acetophenone (4 mmol), complex **1b** (8 μmol), KOH (0.2 mmol) in 2-propanol (10 mL); ketone : Ru : KOH = 1000 : 2 : 50. [b] The conversion was determined by GC analysis.

Experimental section

Materials and physical methods

Unless otherwise noted, all reactions and manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. The solvents were purified using standard methods and degassed before use. Methanol and CH_2Cl_2 were dried over Mg/I_2 and P_2O_5, respectively, and then distilled under nitrogen. Other chemicals were purchased from commercial sources and used without further purification.

The following starting materials were prepared according to the literature methods: $[Ru(CO)_2Cl_2]_n$,[40] 1-*tert*-butyl imidazole,[58] 3-*tert*-butyl-1-(2-pyridyl)imidazolium bromide (**L$_1$**),[30] 3-*n*-*butyl*-1-(2-pyridyl)imidazolium bromide (**L$_2$**),[23] 3-*tert*-butyl-1-(2-picoly)imidazolium bromide (**L$_3$**),[30] 3-*n*-butyl-1-(2-picoly)-imidazolium bromide (**L$_4$**),[30] 3-benzyl-1-(2-picoly)imidazolium iodide (**L$_5$**).[19]

Elemental analyses were performed in an Elementar Vario ELIII elemental analyzer. NMR measurements were carried out in DMSO-d_6 on a Bruker AM-500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are referenced to the solvent. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The GC analyses of the catalytic mixtures were performed on a Shimadzu GC-2010 equipment.

Syntheses

trans(Cl)-[Ru(Py–NHC)(CO)$_2$Cl$_2$] (1a–5a) and *cis*(Cl)-[Ru(Py–NHC)(CO)$_2$Cl$_2$] (1b–5b)

Route 1. A mixture of **L$_1$–L$_5$** (1.0 mmol), silver oxide (1.0 mmol) and CH_2Cl_2 (30 mL) was stirred at room temperature for 12 h, and was then filtered through Celite to remove unreacted silver oxide and insoluble residues. $[Ru(CO)_2Cl_2]_n$ (1.0 mmol) was added to the pale yellow solution, stirred for 12 h at room temperature and then filtered through Celite to remove the silver halide. The products were chromatographed using silica gel. Elution with CH_2Cl_2 : MeOH (40 : 1) afforded a pale yellow band that contained the desired *trans*-product, and then elution with CH_2Cl_2 : MeOH (20 : 1) yielded a yellow band, which is the *cis*-product. Removal of the volatiles under vacuum gave the *trans*-products **1a–5a** as pale yellow powders (60–70%) and the *cis* complexes **1b–5b** as yellow powders (10–20%).

Route 2. A mixture of **L$_1$–L$_5$** (1.0 mmol), silver oxide (1.0 mmol) and CH_2Cl_2 (30 mL) was stirred at room temperature for 12 h. The mixture was filtered through Celite to remove unreacted silver oxide and insoluble residues. CH_2Cl_2 was removed from the reaction mixture under vacuum. $[Ru(CO)_2Cl_2]_n$ (1.0 mmol) in toluene (30 mL) was added to the remaining pale yellow solid, and refluxed for another 12 h. The products were purified by column chromatography using CH_2Cl_2 : CH_3OH = 40 : 1 to give *trans*-isomers with a yield of 5–10%; and then with CH_2Cl_2 : CH_3OH (20 : 1) to give *cis*-isomers in 70–80% yield.

trans(Cl)-{[3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} (1a)

Yield, 0.26 g (60%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.08 (d, 1H, $^3J_{H-H}$ = 5.0 Hz, 6-*H* of Py), 8.56 (s, 1H, 4,5-imidazol-2-ylidene *H*), 8.40–8.36 (m, 2H, 3,5-*H* of Py), 7.85 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.67 (t, 1H, $^3J_{H-H}$ = 5.5 Hz, 4-*H* of Py), 1.88 (s, 9H, [C(C*H*$_3$)$_3$]). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.7, 194.9 (*C*O), δ 185.8 (2-imidazol-2-ylidene C), 153.5, 151.9, 143.6 (Py C), 125.1, 123.1, 116.9, 113.9 (Py and 4,5-imidazol-2-ylidene C), 60.2 [*C*(CH$_3$)$_3$], 32.1 [C(*C*H$_3$)$_3$]. Anal. Calcd for $C_{14}H_{15}Cl_2N_3O_2Ru$: C, 39.17; H, 3.52; N, 9.79; Found: C, 39.23; H, 3.66; N, 10.04. IR (KBr): ν (CO) 2055 and 1990 cm^{-1}.

trans(Cl)-{[3-*n*-butyl-1-(2-pyridyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} (2a)

Yield, 0.25 g (60%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.06 (d, 1H, $^3J_{H-H}$ = 5.2 Hz, 6-*H* of Py), 8.54 (s, 1H, 4, 5-imidazol-2-ylidene *H*), 8.37 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, 5-*H* of Py), 8.31 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, 3-*H* of Py), 7.82 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.64 (t, 1H, $^3J_{H-H}$ = 6.4 Hz, 4-*H* of Py), 4.39 (t, 2H,

$^{3}J_{H-H}$ = 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 1.95 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.42 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.95 (t, 3H, $^{3}J_{H-H}$ = 7.3 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 201.1, 194.4 (*C*O), δ 187.6 (2-imidazol-2-ylidene C), 153.9, 152.3, 143.5 (Py C), 125.8, 125.40, 118.3, 112.6 (Py and 4,5-imidazol-2-ylidene C), 51.6 ($NCH_2CH_2CH_2CH_3$), 33.9 ($NCH_2CH_2CH_2CH_3$), 20.2 ($NCH_2CH_2CH_2CH_3$), 14.8 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{15}Cl_2N_3O_2Ru$: C, 39.17; H, 3.52; N, 9.79; Found: C, 38.93; H, 3.66; N, 9.88. IR (KBr): ν (CO) 2063 and 2002 cm^{-1}.

trans(Cl)-[(3-*tert*-butyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (3a)

Yield, 0.31 g (70%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.14 (d, 1H, $^{3}J_{H-H}$ = 5.4 Hz, 6-*H* of Py), 8.16 (t, 1H, $^{3}J_{H-H}$ = 7.6 Hz, 5-*H* of Py), 7.77 (d, 1H, $^{3}J_{H-H}$ = 7.7 Hz, 3-*H* of Py), 7.73 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.69 (t, 1H, $^{3}J_{H-H}$ = 6.2 Hz, 4-*H* of Py), 7.65 (s, 1H, 4,5-imidazol-2-ylidene *H*), 6.00 (s, 2H, CH_2 linker) 1.83 (s, 9H, [C(CH_3)$_3$]). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.5, 193.8 (*C*O), δ 173.7 (2-imidazol-2-ylidene C), 157.1, 156.9, 141.4 (py C), 126.1, 125.8, 123.6, 122.2 (Py and 4,5-imidazol-2-ylidene C), 61.3 [*C*(CH_3)$_3$], 54.7 (PyCH_2N), 32.9 [C(*C*H$_3$)$_3$]. Anal. Calcd for $C_{15}H_{17}Cl_2N_3O_2Ru$: C, 40.64; H, 3.87; N, 9.48; Found: C, 40.33; H, 3.69; N, 9.64. IR (KBr): ν (CO) 2051 and 1980 cm^{-1}.

trans(Cl)-[(3-*n*-butyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (4a)

Yield, 0.30 g (68%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.09 (d, 1H, $^{3}J_{H-H}$ = 5.0 Hz, 6-*H* of Py), 8.17 (t, 1H, $^{3}J_{H-H}$ = 7.3 Hz, 5-*H* of Py), 7.79 (d, 1H, $^{3}J_{H-H}$ = 7.7 Hz, 3-*H* of Py), 7.68 (t, 1H, $^{3}J_{H-H}$ = 6.4 Hz, 4-*H* of Py), 7.63 and 7.60 (s, 2 × 1H, 4,5-imidazol-2-ylidene *H*), 5.88 (s, 2H, CH_2 linker), 4.34 (t, 2H, $^{3}J_{H-H}$ = 7.8 Hz, $NCH_2CH_2CH_2CH_3$), 1.89 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.43 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.96 (t, 3H, $^{3}J_{H-H}$ = 7.3 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.5, 193.4 (*C*O), δ 175.5 (2-imidazol-2-ylidene C), 157.7, 156.6, 141.3 (Py C), 126.7, 125.9, 123.7, 122.3 (py and 4,5-imidazol-2-ylidene C), 54.1 (PyCH_2N), 50.5 ($NCH_2CH_2CH_2CH_3$), 33.9 ($NCH_2CH_2CH_2CH_3$), 20.3 ($NCH_2CH_2CH_2CH_3$), 14.5 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{15}H_{17}Cl_2N_3O_2Ru$: C, 40.64; H, 3.87; N, 9.48; Found: C, 40.52; H, 4.03; N, 9.48. IR (KBr): ν (CO) 2054 and 1994 cm^{-1}.

trans(Cl)-[(3-benzyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (5a)

Yield, 0.31 g (65%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.13 (d, 1H, $^{3}J_{H-H}$ = 5.4 Hz, 6-*H* of Py), 8.19 (t, 1H, $^{3}J_{H-H}$ = 7.7 Hz, 5-*H* of Py), 7.81 (d, 1H, $^{3}J_{H-H}$ = 7.6 Hz, 3-*H* of Py), 7.69 (t, 1H, $^{3}J_{H-H}$ = 6.2 Hz, 4-*H* of Py), 7.65 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.41 (t, 2H, $^{3}J_{H-H}$ = 7.3 Hz, 3,5-*H* of Ph), 7.35 (t, 1H, $^{3}J_{H-H}$ = 7.1 Hz, 4-*H* of Ph), 7.27 (d, 2H, $^{3}J_{H-H}$ = 8.7 Hz, 2,6-*H* of Ph); 7.10 (s, 1H, 4,5-imidazol-2-ylidene *H*), 6.00 (br, 2H, CH_2 of Bn), 5.66 (s, 2H, CH_2 linker). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 199.6, 193.5 (*C*O), 176.9 (2-imidazol-2-ylidene C), 157.9, 156.6, 141.4 (Py C), 137.6, 129.6, 128.7, 128.1 (Py and 4,5-imidazol-2-ylidene C), 126.8, 126.1, 124.2, 122.7 (Ph, C), 53.8, 53.7 (PyCH_2N and PhCH_2N). Anal. Calcd for $C_{18}H_{15}Cl_2N_3O_2Ru$: C, 45.29; H, 3.17; N, 8.80; Found: C, 45.22; H, 3.39; N, 8.51. IR (KBr): ν (CO) 2053 and 1988 cm^{-1}.

cis(Cl)-{[3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} (1b)

Yield, 0.33 g (80%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.34 (d, 1H, $^{3}J_{H-H}$ = 4.9 Hz, 6-*H* of Py), 8.59 (s, 1H, 4,5-imidazol-2-ylidene *H*), 8.39 (t, 1H, $^{3}J_{H-H}$ = 7.7 Hz, 5-*H* of Py), 8.34 (d, 1H, $^{3}J_{H-H}$ = 8.1 Hz, 3-*H* of Py), 7.85 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.73 (t, 1H, $^{3}J_{H-H}$ = 6.1 Hz, 4-*H* of Py), 1.84 (s, 9H, [C(CH_3)$_3$]). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 199.3, 191.5 (*C*O), δ 175.0 (2-imidazol-2-ylidene C), 152.1, 148.9, 143.5 (Py C), 123.7, 117.6, 113.6 (Py and 4,5-imidazol-2-ylidene C), 59.9 [*C*(CH_3)$_3$], 31.4 [C(*C*H$_3$)$_3$]. Anal. Calcd for $C_{14}H_{15}Cl_2N_3O_2Ru$: C, 39.17; H, 3.52; N, 9.79; Found: C, 39.33; H, 3.76; N, 9.94. IR (KBr): ν (CO) 2074 and 2008 cm^{-1}.

cis(Cl)-{[3-*n*-butyl-1-(2-pyridyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} (2b)

Yield, 0.34 g (80%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.25 (d, 1H, $^{3}J_{H-H}$ = 5.0 Hz, 6-*H* of Py), 8.53 (s, 1H, 4,5-imidazol-2-ylidene *H*), 8.37 (t, 1H, $^{3}J_{H-H}$ = 7.5 Hz, 5-*H* of Py), 8.26 (d, 1H, $^{3}J_{H-H}$ = 8.5 Hz, 3-*H* of Py), 7.80 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.70 (t, 1H, $^{3}J_{H-H}$ = 6.5 Hz, 4-*H* of Py), 4.27–4.15 (m, 2H, J_1 = 7.5 Hz, J_2 = 8 Hz, $NCH_2CH_2CH_2CH_3$), 1.85 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.37 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.93 (t, 3H,$^{3}J_{H-H}$ = 7.5 Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 198.5, 190.7 (*C*O), δ 178.1 (2-imidazol-2-ylidene C), 152.3, 148.9, 143.2 (Py C), 125.6, 123.4, 118.4, 113.2 (Py and 4,5-imidazol-2-ylidene C), 51.1 ($NCH_2CH_2CH_2CH_3$), 32.9 ($NCH_2CH_2CH_2CH_3$), 19.74 ($NCH_2CH_2CH_2CH_3$), 14.2 ($NCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{15}Cl_2N_3O_2Ru$: C, 39.17; H, 3.52; N, 9.79; Found: C, 39.09; H, 3.36; N, 9.58. IR (KBr): ν (CO) 2062 and 1991 cm^{-1}.

cis(Cl)-[(3-*tert*-butyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (3b)

Yield, 0.35 g (75%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.37 (d, 1H, $^{3}J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.15 (t, 1H, $^{3}J_{H-H}$ = 7.5 Hz, 5-*H* of Py), 7.75 (d, 1H, J_{H-H} = 7.5 Hz, 3-*H* of Py), 7.69 (s, 2 × 1H, 4,5-imidazol-2-ylidene *H*), 7.68 (t, 1H, $^{3}J_{H-H}$ = 9.0 Hz, 4-*H* of Py), 6.15 (d, 1H, $^{2}J_{H-H}$ = 15.5 Hz, C*H*H linker), 5.40 (d, 1H, $^{2}J_{H-H}$ = 15.5 Hz, CH*H* linker), 1.80 (s, 9H, [C(CH_3)$_3$]). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 201.2, 196.5 (*C*O), δ 165.1 (2-imidazol-2-ylidene C), 157.3, 156.7, 142.9 (Py C), 127.1, 126.8, 125.8 (Py and 4,5-imidazol-2-ylidene C), 63.1[*C*(CH_3)$_3$], 57.8 (PyCH_2, C), 34.3 [C(*C*H$_3$)$_3$]. Anal. Calcd for $C_{15}H_{17}Cl_2N_3O_2Ru$: C, 40.64; H, 3.87; N, 9.48; Found: C, 40.33; H, 3.54; N, 9.14. IR (KBr): ν (CO) 2057 and 1988 cm^{-1}.

cis(Cl)-[(3-*n*-butyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (4b)

Yield, 0.33 g (70%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.36 (d, 1H, $^{3}J_{H-H}$ = 4.5 Hz, 6-*H* of Py), 8.14 (t, 1H, $^{3}J_{H-H}$ = 3.0 Hz, 5-*H* of Py), 7.76 (d, 1H, $^{3}J_{H-H}$ = 7.5 Hz, 3-*H* of Py), 7.68 (t, 1H, $^{3}J_{H-H}$ = 5.0 Hz, 4-*H* of Py), 7.64 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.55 (s, 1H, 4,5-imidazol-2-ylidene *H*), 5.83 (d, 1H, $^{2}J_{H-H}$ = 16.0 Hz, C*H*H linker), 5.25 (d, 1H, $^{2}J_{H-H}$ = 16.0 Hz, CH*H* linker), 4.39, 4.13 (two sextet, 2H, $NCH_2CH_2CH_2CH_3$), 1.80 (m,

2H, $NCH_2CH_2CH_2CH_3$), 1.41 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, 3H, $^3J_{H-H} = 7.0$ Hz, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 192.2, 187.4 (CO, C), δ 160.9 (2-imidazol-2-ylidene C), 149.4, 148.4, 134.9 (Py C), 119.2, 119.1, 117.9, 116.8 (Py and 4,5-imidazol-2-ylidene C), 48.9 ($PyCH_2$, C), 44.2, 27.2, 13.9, 8.2 ($NCH_2CH_2CH_2CH_3$, C). Anal. Calcd for $C_{15}H_{17}Cl_2N_3O_2Ru$: C, 40.64; H, 3.87; N, 9.48; Found: C, 40.32; H, 4.11; N, 9.31. IR (KBr): ν (CO) 2063 and 1992 cm^{-1}.

cis(Cl)-[(3-benzyl-1-picolylimidazol-2-ylidene)Ru(CO)$_2$Cl$_2$] (5b)

Yield, 0.30 g (65%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.39 (d, 1H, $^3J_{H-H} = 5.6$ Hz, 6-*H* of Py), 8.16 (t, 1H, $^3J_{H-H} = 7.3$ Hz, 5-*H* of Py), 7.78 (d, 1H, $^3J_{H-H} = 7.6$ Hz, 3-*H* of Py), 7.72 (t, 1H, $^3J_{H-H} = 6.6$ Hz, 4-*H* of Py), 7.69 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.41 (t, 2H, $^3J_{H-H} = 7.4$ Hz, 3,5-*H* of Ph), 7.35 (t, 1H, $^3J_{H-H} = 7.2$ Hz, 4-*H* of Ph), 7.27 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.17 (d, 2H, $^3J_{H-H} = 7.4$ Hz, 2,6-*H* of Ph), 5.90 (d, 2H, $^2J_{H-H} = 16.2$ Hz, C*H*H linker), 5.63 (dd, 2H, $^2J_{H-H} = 15.9$ Hz, CH_2 of Bn), 5.34 (d, 2H, $^2J_{H-H} = 16.2$ Hz, CH*H* linker). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 197.6, 193.6 (*C*O), 173.2 (2-imidazol-2-ylidene C), 155.8, 141.2, 137.4 (Py C), 129.7, 129.1, 128.7, 128.1 (Py and 4,5-imidazol-2-ylidene C), 127.7, 125.5, 124.5, 123.5 (Ph, C), 55.7, 55.5 ($PyCH_2N$ and $PhCH_2N$). Anal. Calcd for $C_{18}H_{17}Cl_2N_3O_2Ru$: C, 45.29; H, 3.17; N, 8.80; Found: C, 45.47; H, 3.21; N, 8.55. IR (KBr): ν (CO) 2060 and 1987 cm^{-1}.

Conversion of *trans*-isomers (1a–5a) to *cis*-isomers (1b–5b)

A solution of **1a–5a** in 10 mL of dichloromethane was transferred to a Teflon-lined stainless autoclave and heated at 120 °C for 24 h. After evaporation of the solvent, a yellow solid **1b–5b** was obtained quantitatively as revealed by ^{1}H NMR spectrum. No other product was observed.

General procedure for the catalytic hydrogen transfer

The procedure used follows standard literature methods.[50–53] The hydrogen transfer reactions are carried out using standard Schlenk glassware.

Organic substrate ketone (4.0 mmol) and a Ru complex (8 μmol) were dissolved in ^{i}PrOH (8 mL) in a Schlenk tube. The solution was freeze–pump–thaw degassed before the reaction started. Then, the solution was allowed to warm to 82 °C for 30 min under nitrogen. By addition of 2 mL of a 0.1 mol L^{-1} KOH in ^{i}PrOH, the reaction starts immediately. The reaction progress was monitored by GC analysis.

X-Ray crystal structure determinations of 1a·2H$_2$O, 1b, 2b, and 4b†

The single crystals was mounted on a glass fibre with silicon grease. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and collected for absorption using SADABS program.[59] The structures were solved by direct methods and refined on F^2 against all reflections by full-matrix least-squares methods with SHELXTL (version 6.10) program.[60] The hydrogen atoms in these compounds were positioned geometrically and refined in the riding-model approximation. All non-hydrogen atoms were refined with anisotropic thermal parameters.

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