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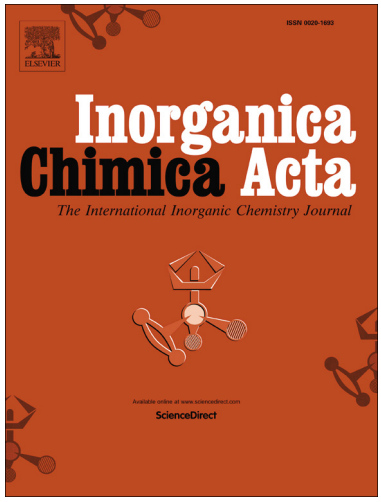

Research paper

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Ruthenium(II) complexes bearing *N*-heterocyclic carbene ligands with wingtip groups and their catalytic activity in the transfer hydrogenation of ketones

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Abstract

A series of new silver(I) complexes bearing *N*-heterocyclic carbene (NHC) ligands with wingtip groups were synthesized by the reaction of 1,3-dialkylimidazolinium salts with silver(I) oxide in dichloromethane. The silver complexes were used as carbene-transfer agents to synthesize ruthenium(II) complexes with the general formula $[RuCl_2(NHC)(\eta^6\text{-}p\text{-cymene})]$. All the synthesized complexes were characterized by elemental analysis, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and the molecular and crystal structure of **3d** was determined by single-crystal X-ray diffraction. These ruthenium complexes were tested as catalysts in the transfer hydrogenation of ketones using ^{i}PrOH as a hydrogen source. All compounds tested showed good catalytic activity in these reactions.

Keywords: *N*-Heterocyclic carbene; ruthenium complexes; silver complexes; transfer hydrogenation.

1. Introduction

Functional group transformation is one of the most fundamental reactions in organic synthesis, and considerable research efforts have been devoted to the development of new methods in this area. Hydrogenation and transfer hydrogenation of unsaturated compounds are the most commonly used organic transformation catalyzed by metal complexes [1], and a broad variety of substrates include aldehydes, ketones, esters, nitriles, imines, alkenes, alkynes, nitroarenes, azobenzene, and carbon dioxide can be reduced by these methods [2].

Transfer hydrogenation is the transfer of hydrogen from a reagent other than molecular hydrogen to an unsaturated molecule via a metal catalyst. In this process, the metal catalyst is able to abstract a hydride and a proton from the hydrogen donor and deliver them to the hydrogen acceptor [3]. As a hydrogen donor, a wide number of alcohols such as ^{i}PrOH, 2-butanol, glycerol, ethanol or other hydrogen donors such as formic acid, aqueous sodium formate, formic acid/triethylamine mixture are used for transfer hydrogenation [4]. Among them, ^{i}PrOH and formic acid have been widely used as a hydrogen donor. Transfer hydrogenation is the operationally simple, safe and environmentally friendly method when compared with the conventional hydrogenation reaction using the highly flammable and potentially explosive hydrogen gas [5]. The most common application of this process is the formation of secondary alcohols by transfer hydrogenation of ketones. Transfer hydrogenation of ketones catalyzed by metal complexes is an environmentally benign procedure to produce alcohols, and a broad range of alcohols are accessible by transfer hydrogenation of ketones using ^{i}PrOH under mild reaction conditions in the presence of various metal catalysts including Ru, Ir, Rh and others [6]. Particularly, asymmetric transfer hydrogenation of ketones provides an efficient method for the preparation of enantiopure chiral secondary alcohols, which are useful intermediates for the synthesis of pharmaceuticals, agrochemicals and fine chemicals [7]. To date, numerous catalytic systems using *NN*, *PP*, *PN*, *CN*, *NNN*, *NNC*, *CNC*, *SNS* etc., type of ligands for transfer hydrogenation of ketones have been developed [8]. A base is generally required for transfer hydrogenation. However, some complexes are reported to catalyze the transfer hydrogenation under base-free conditions [9]. For example, Corberan and Peris have reported the catalytic transfer hydrogenation of ketones, aldehydes and imines in ^{i}PrOH under base-free conditions at room temperature using $CpIr^{III}$(NHC) complexes as the catalyst [9b]. Recently, *N*-heterocyclic carbenes (NHC) have attracted much attention due to their numerous applications in catalysis [10], material [11] and medicinal sciences [12]. NHCs are neutral, two-electron donor ligands, which have strong σ-donating and weak π-accepting ability and they can form the more stable metal-ligand bond with a range of transition metals than phosphine ligands [13]. This strong metal-carbon bond prevents the decomposition of NHC complexes during catalytic reactions. The first examples of *N*-heterocyclic carbenes as ligands for transition metals were independently reported by Öfele [14] and Wanzlick in 1968 [15]. Since then, a variety of NHC complexes have been successfully synthesized, and extensively used as catalysts in C-C bond formation and functional group transformation reactions [16]. The first use of NHC complexes for the transfer hydrogenation was reported by Nolan in 2001 [17]. After that, many metal-NHC

complexes have been used as the catalyst in transfer hydrogenation [18]. Among them, NHC complexes of Ru, Ir, and Rh have demonstrated good activity for transfer hydrogenation reactions [19]. Ruthenium(II) complexes are very efficient catalyst precursors in the transfer hydrogenation of ketones [20] and offer a cost advantage over common used iridium and rhodium for transfer hydrogenation. Various arene-Ru-NHC complexes have been reported as effective catalysts for the transfer hydrogenation of ketones, aldehydes, imines, nitriles, and alkenes [21].

In this study, the new [$RuCl_2$(NHC)(*p*-cymene)] (NHC = imidazolidin-2-ylidene) complexes were readily synthesized by treating the [$RuCl_2$(*p*-cymene)]$_2$ dimers directly with the corresponding Ag(I)-NHC complexes, which were prepared by reaction of Ag_2O with symmetrical 1,3-dialkylimidazolinium salts in dichloromethane. The catalytic activity of ruthenium complexes was evaluated in the reduction of ketones by transfer hydrogenation using ^{i}PrOH as a hydrogen donor.

2. Experimental

2.1. Materials and methods

All reactions for the preparation of the ruthenium(II)-NHC complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich, Merck and Fluka. [$RuCl_2$(*p*-cymene)]$_2$ was synthesized according to published procedures [22]. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with 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. Coupling constants (*J* values) are given in Hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, q = quartet and m = multiplet signal. FT-IR spectra were recorded on the ATR unit in the range 400-4000 cm^{-1} on Perkin Elmer Spectrum 100. GC was measured by GC-FID on an Agilent 6890N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with Stuart SMP 40 melting point apparatus and uncorrected. Elemental analyses were performed at the Inönü University research center.

2.2. Synthesis of imidazolinium salts, 1

A mixture of *N*,*N*'-dialkylethylenediamines (6.2 mmol), NH_4Cl (6.2 mmol) and triethyl orthoformate (10 mL) was heated for 12 h at 110 ˚C. Upon cooling to room temperature,

colorless crystals were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 mL) and dried under vacuum. The crude product was recrystallized from ethanol/diethyl ether.

2.3. Synthesis of silver(I)-NHC complexes, 2

A solution of the appropriate imidazolinium chloride (1.12 mmol), Ag_2O (0.56 mmol) and activated molecular sieves 4Å in dichloromethane (25 mL) was stirred for 24 h at room temperature in the dark conditions, covered with aluminum foil under argon. The reaction mixture was filtered through celite, and the solvent was removed under vacuum to afford the product. The crude product was recrystallized from dichloromethane: hexane (1:2) at room temperature. The resulting white solid was isolated by filtration and dried in vacuum.

2.3.1. Chloro-[1,3-di(1-phenylethyl)imidazolidin-2-ylidene]silver(I), 2a

Yield: 0.38 g, 81%, m.p. 285-287 ^oC. IR, υ: 1656 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.63 (d, 6H, J = 4.0 Hz, CH(CH_3)C_6H_5), 5.42 (q, 2H, J = 8.0 Hz, CH(CH_3)C_6H_5), 3.20 and 3.48 (t, 4H, J = 8.0 Hz, NCH_2CH_2N), 7.27-7.44 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$) δ: 17.6 (CH(*C*H_3)C_6H_5), 43.7 (N*C*H_2*C*H_2N), 59.2 (*C*H(CH_3)C_6H_5), 126.5, 126.7, 126.8, 127.1, 128.2, 128.3, 128.7, 129.3, 138.7 (Ar-*C*). Anal. Calc. for $C_{19}H_{22}N_2AgCl$: C, 54.09; H, 5.22; N, 6.64. Found: C, 54.12; H, 5.23; N, 6.66%.

2.3.2. Chloro-[1,3-di(1-(4-methyphenyl)ethyl)imidazolidin-2-ylidene]silver(I), 2b

Yield: 0.40 g, 80%, m.p. 161-163 ^oC. IR, υ: 1663 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.62 and 1.80 (d, 6H, J = 8.0 Hz, CH(CH_3)C_6H_4-CH_3), 5.27 and 5.38 (q, 2H, J = 8.0 Hz, CH(CH_3)C_6H_4-CH_3), 2.34 and 2.35 (s, 6H, CH(CH_3)C_6H_4-CH_3), 3.08-3.71 (m, 4H, NCH_2CH_2N), 7.10-7.33 (m, 8H, Ar-H). ^{13}C NMR ($CDCl_3$) δ: 17.7 and 19.0 (CH(*C*H_3)C_6H_4-CH_3), 21.0 and 21.1 (CH(CH_3)C_6H_4-*C*H_3), 43.6 and 45.3 (N*C*H_2*C*H_2N), 57.5 and 58.9 (*C*H(CH_3)C_6H_4-CH_3), 126.7, 127.0, 129.5, 129.9, 134.4, 135.7, 138.0, 138.8 (Ar-*C*). Anal. Calc. for $C_{21}H_{26}N_2AgCl$: C, 56.06; H, 5.78; N, 6.23. Found: C, 56.09; H, 5.76; N, 6.21%.

2.3.3. Chloro-[1,3-di(1-(3,4-dimethylphenyl)ethyl)imidazolidin-2-ylidene]silver(I), 2c

Yield: 0.41 g, 77%, m.p. 148-150 ^oC. IR, υ: 1632 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.79 (d, 6H, J = 8.0 Hz, CH(CH_3)C_6H_3-(CH_3)-3,4), 5.23 (q, 2H, J = 4.0 Hz, CH(CH_3)C_6H_3-(CH_3)$_2$-3,4), 2.24 and 2.26 (s, 12H, CH(CH_3)C_6H_3-(CH_3)$_2$-3,4), 3.53-3.73 (m, 4H, NCH_2CH_2N), 7.11-7.16 (m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) δ: 19.1 (CH(*C*H_3)C_6H_3-(CH_3)$_2$-3,4), 19.5 and 19.9 (CH(CH_3)C_6H_3-(*C*H_3)$_2$-3,4), 45.4 (N*C*H_2*C*H_2N), 57.5 (*C*H(CH_3)C_6H_3-(CH_3)$_2$-3,4), 124.4, 128.2, 128.3, 130.3, 130.4, 134.8, 134.9, 137.5, 137.6 (Ar-*C*). Anal. Calc. for $C_{23}H_{30}N_2AgCl$: C, 57.80; H, 6.28; N, 5.86. Found: C, 57.84; H, 6.26; N, 5.87%.

2.3.4. Chloro-[1,3-di(benzhydrylimidazolidin-2-ylidene)]silver(I), 2d

Yield: 0.53 g, 87%, m.p. 286-288 °C. IR, υ: 1644 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 4.06 (s, 4H, NCH_2CH_2N), 6.38 (s, 2H, C*H*-Ar), 7.12-7.40 (m, 20H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 48.8 (N*C*H_2*C*H_2N), 66.4 (*C*H-Ar), 126.8, 127.2, 128.3, 128.4, 128.5, 128.7, 128.9, 129.0, 129.3, 135.5 (Ar-*C*). Anal. Calc. for $C_{29}H_{26}N_2AgCl$: C, 63.79; H, 4.77; N, 5.13. Found: C, 63,75; H, 4.78; N, 5.14%.

2.3.5. Chloro-[1,3-di(1-phenyl-1-(4-methylphenyl)methyl)imidazolidin-2-ylidene]silver(I), 2e

Yield: 0.56 g, 88%, m.p. 160-162 °C. IR, υ: 1637 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 4.04 (s, 4H, NCH_2CH_2N), 6.32 (s, 2H, C*H*-Ar), 7.03-7.37 (m, 18H, Ar-*H*), 2.32 (s, 6H, C_6H_4-CH_3). ^{13}C NMR ($CDCl_3$) δ: 48.8 (N*C*H_2*C*H_2N), 66.2 (*C*H-Ar), 21.1 (C_6H_4-*C*H_3), 127.1, 128.2, 128.3, 128.4, 128.7, 128.8, 128.9, 129.2, 129.9, 132.5, 135.7, 138.9 (Ar-*C*). Anal. Calc. for $C_{31}H_{30}N_2AgCl$: C, 64.86; H, 5.23; N, 4.88. Found: C, 64.89; H, 5.21; N, 4.89%.

2.4. Synthesis of ruthenium(II)-NHC complexes, 3

A solution of required silver(I)-NHC complex (0.33 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.16 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark. Afterwards, the resulting mixture was filtered through celite, and the solvent was removed under vacuum to afford the product. The crude product was recrystallized from dichloromethane: diethyl ether (1:2) at room temperature. The orange-brown crystals were filtered off, washed with diethyl ether (3 x 10 mL) and dried under vacuum.

2.4.1. Dichloro-[1,3-di(1-phenylethyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 3a

Yield: 0.15 g, 79%, m.p. 194-196 °C. IR, υ: 1512 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.74 (d, 6H, J = 4.0 Hz, CH(CH_3)C_6H_5), 6.13 (q, 2H, J = 8.0 Hz, C*H*(CH_3)C_6H_5), 3.66-3.77 (m, 4H, NCH_2CH_2N), 7.36-7.55 (m, 10H, CH(CH_3)C_6H_5), 1.03 (d, 6H, J = 8.0 Hz, *p*-$CH_3C_6H_4$CH(CH_3)$_2$), 1.70 (s, 3H, *p*-C$H_3C_6H_4$CH(CH_3)$_2$), 2.31 (sept, 1H, J = 8.0 Hz, *p*-$CH_3C_6H_4$C*H*(CH_3)$_2$), 5.15 and 5.22 (d, 4H, J = 8.0 Hz, *p*-$CH_3C_6H_4$CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ: 19.8 (CH(*C*H_3)C_6H_5), 43.4 (N*C*H_2*C*H_2N), 57.5 (*C*H(CH_3)C_6H_5), 125.6, 127.0, 129.0, 142.7 (CH(CH_3)*C*$_6H_5$), 17.2 (*p*-$CH_3C_6H_4$CH(*C*H_3)$_2$), 22.4 (*p*-*C*$H_3C_6H_4$CH(CH_3)$_2$), 30.3 (*p*-$CH_3C_6H_4$*C*H(CH_3)$_2$), 83.1, 87.2, 93.7, 105.4 (*p*-CH_3*C*$_6H_4$CH(CH_3)$_2$), 209.2 (Ru-C_{carb}). Anal. Calc. for $C_{29}H_{36}N_2RuCl_2$: C, 59.58; H, 6.16; N, 4.79. Found: C, 59.55; H, 6.17; N, 4.80%.

2.4.2. Dichloro-[1,3-di(1-(4-methylphenyl)ethyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 3b

Yield: 0.17 g, 85%, m.p. 165-167 °C. IR, υ: 1511 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.62-1.68 and 1.76-1.82 (m, 6H, CH(C*H*$_3$)C_6H_4-CH_3), 6.05-6.26 (m, 2H, C*H*(CH_3)C_6H_4-CH_3), 2.30 and 2.39 (s, 6H, CH(CH_3)C_6H_4-C*H*$_3$), 3.28-3.67 (m, 4H, NC*H*$_2$C*H*$_2$N), 7.10-7.47 (m, 8H, CH(CH_3)C_6*H*$_4$-CH_3), 1.14 and 1.27 (d, 6H, *J* = 4.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$), 1.93 (s, 3H, *p*-C*H*$_3$$C_6H_4CH(CH_3)_2$), 2.64 (sept, 1H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4$C*H*(CH_3)$_2$), 5.13, 5.30, 5.34 and 5.45 (d, 4H, *J* = 4.0 Hz, *p*-CH_3C_6*H*$_4$CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ: 20.9 (CH(*C*H$_3$)C_6H_4-CH_3), 22.8 (CH(CH_3)C_6H_4-*C*H$_3$), 43.6 and 43.9 (N*C*H$_2$*C*H$_2$N), 55.4 and 57.7 (*C*H(CH_3)C_6H_4-CH_3), 125.1, 127.7, 128.6, 129.7, 136.6, 140.1 (CH(CH_3)*C*$_6H_4$-CH_3), 17.6 (*p*-$CH_3C_6H_4CH(CH_3)_2$), 22.6 (*p*-*C*H$_3$$C_6H_4CH(CH_3)_2$), 30.6 (*p*-$CH_3C_6H_4$*C*H($CH_3$)$_2$), 83.2, 84.4, 86.2, 87.3, 94.2, 105.9 (*p*-CH_3*C*$_6H_4$CH(CH_3)$_2$), 207.6 (Ru-C_{carb}). Anal. Calc. for $C_{31}H_{40}N_2RuCl_2$: C, 60.78; H, 6.53; N, 4.57. Found: C, 60.80; H, 6.52; N, 4.58%.

2.4.3. Dichloro-[1,3-di(1-(3,4-dimethylphenyl)ethyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 3c

Yield: 0.17 g, 81%, m.p. 186-188 °C. IR, υ: 1504 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 1.71 (d, 6H, *J* = 4.0 Hz, CH(C*H*$_3$)C_6H_3-(CH_3)-3,4), 6.02 (q, 2H, *J* = 4.0 Hz, C*H*(CH_3)C_6H_3-(CH_3)$_2$-3,4), 2.34 and 2.41 (s, 12H, CH(CH_3)C_6H_3-(C*H*$_3$)$_2$-3,4), 3.61-3.73 (m, 4H, NC*H*$_2$C*H*$_2$N), 7.17-7.27 (m, 6H, CH(CH_3)C_6*H*$_3$-(CH_3)$_2$-3,4), 1.04 (d, 6H, *J* = 4.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$), 1.69 (s, 3H, *p*-C*H*$_3$$C_6H_4CH(CH_3)_2$), 2.36-2.39 (m, 1H, *p*-$CH_3C_6H_4$C*H*(CH_3)$_2$), 5.19 and 5.22 (d, 4H, *J* = 8.0 Hz, *p*-CH_3C_6*H*$_4$CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ: 19.3 (CH(*C*H$_3$)C_6H_3-(CH_3)$_2$-3,4), 19.8 and 20.3 (CH(CH_3)C_6H_3-(*C*H$_3$)$_2$-3,4), 43.4 (N*C*H$_2$*C*H$_2$N), 57.2 (*C*H(CH_3)C_6H_3-(CH_3)$_2$-3,4), 122.9, 127.1, 130.0, 135.2, 137.1, 140.2 (CH(CH_3)*C*$_6H_3$-(CH_3)$_2$-3,4), 17.2 (*p*-$CH_3C_6H_4CH(CH_3)_2$), 22.4 (*p*-*C*H$_3$$C_6H_4CH(CH_3)_2$), 30.3 (*p*-$CH_3C_6H_4$*C*H($CH_3$)$_2$), 82.8, 87.4, 93.3, 105.6 (*p*-CH_3*C*$_6H_4$CH(CH_3)$_2$), 208.6 (Ru-C_{carb}). Anal. Calc. for $C_{33}H_{44}N_2RuCl_2$: C, 61.87; H, 6.87; N, 4.37. Found: C, 61.84; H, 6.89; N, 4.38%.

2.4.4. Dichloro-[1,3-dibenzhydrylimidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 3d

Yield: 0.20 g, 87%, m.p. 227-229 °C. IR, υ: 1495 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 2.95 and 3.82 (t, 4H, *J* = 12.0 Hz, NC*H*$_2$C*H*$_2$N), 7.75 (s, 2H, C*H*(C_6H_5)$_2$), 7.20-7.66 (m, 20H, CH(C_6*H*$_5$)$_2$), 1.03 (d, 6H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$), 1.59 (s, 3H, *p*-C*H*$_3$$C_6H_4CH(CH_3)_2$), 1.98 (sept, 1H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4$C*H*(CH_3)$_2$), 4.81 and 5.11 (d, 4H, *J* = 8.0 Hz, *p*-CH_3C_6*H*$_4$CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ: 46.6 (N*C*H$_2$*C*H$_2$N), 64.1 (*C*H-Ar), 127.4, 127.5, 127.7, 127.9, 128.6, 130.9, 139.6, 141.8 (CH(*C*$_6H_5$)$_2$), 17.2 (*p*-$CH_3C_6H_4CH(CH_3)_2$), 22.9 (*p*-*C*H$_3$$C_6H_4CH(CH_3)_2$), 30.1 (*p*-$CH_3C_6H_4$*C*H($CH_3$)$_2$), 84.6, 85.6, 95.9, 104.1 (*p*-CH_3*C*$_6H_4$CH(CH_3)$_2$), 208.5 (Ru-C_{carb}). Anal. Calc. for $C_{39}H_{40}N_2RuCl_2$: C, 66.10; H, 5.65; N, 3.95. Found: C, 66.12; H, 5.64; N, 3.95%.

2.4.5. Dichloro-[1,3-di(1-phenyl-1-(4-methylphenyl)methyl)imidazolidin-2-ylidene](*p*-cymene)ruthenium(II), 3e

Yield: 0.20 g, 83%, m.p. 181-183 ^{o}C. IR, υ: 1511 cm^{-1} (NCN). ^{1}H NMR ($CDCl_3$) δ: 3.80 (t, 4H, *J* = 8.0 Hz, NC*H*$_2$C*H*$_2$N), 7.00 and 7.02 (s, 2H, C*H*-Ar), 7.19-7.69 (m, 18H, C_6H_4-CH_3, C_6H_5), 2.27 and 2.46 (s, 6H, C_6H_4-C*H*$_3$), 1.01 and 1.04 (d, 6H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$), 1.60 (s, 3H, *p*-C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 1.99 (sept, 1H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$), 4.79, 4.84, 5.07 and 5.14 (d, 4H, *J* = 8.0 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ: 46.6 (N*C*H$_2$*C*H$_2$N), 63.9 and 64.0 (*C*H-Ar), 22.7 and 23.1 (C_6H_4-*C*H$_3$), 127.3, 127.4, 127.6, 127.9, 128.5, 128.6, 129.2, 130.6, 130.9, 136.6, 137.1, 137.3, 138.6, 139.8, 142.1 (CH(Ar-*C*)$_2$), 17.2 (*p*-CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$), 21.1 (*p*-*C*H$_3$C$_6$H$_4$CH(CH$_3$)$_2$), 30.0 (*p*-CH$_3$C$_6$H$_4$*C*H(CH$_3$)$_2$), 84.3, 84.8, 85.3, 86.0, 95.8, 103.9 (*p*-CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$), 208.2 (Ru-C_{carb}). Anal. Calc. for $C_{41}H_{44}N_2RuCl_2$: C, 66.84; H, 5.97; N, 3.80. Found: C, 66.87; H, 5.96; N, 3.81%.

2.5. General procedure for the transfer hydrogenation of ketones

Ketone (1 mmol) was added to a mixture of ruthenium catalyst **3a-e** (0.01 mmol) and KOH (2 mmol) in ^{i}PrOH (3 mL). The mixture was heated at 80 °C for 2-6 h. At the end of the reaction, the mixture was cooled to room temperature and filtrated through to short silica gel column. Afterwards, volatiles were removed under reduced pressure and product distribution was determined by GC using dodecane used as an internal standard. Conversions are based on ketone derivatives.

2.6. Mercury poisoning experiment

Ketone (1 mmol) was added to a mixture of ruthenium catalyst **3a**/**3d** (0.01 mmol) and KOH (2 mmol) in ^{i}PrOH (3 mL). One drop of Hg was added with a syringe to the reaction mixture. The mixture was heated at 80 °C for 6 h. At the end of the reaction, the mixture was cooled to room temperature and aliquots were withdrawn from the reaction vessel to filtrate through to short silica gel column. Afterwards, volatiles were removed under reduced pressure and product distribution was determined by GC using dodecane used as an internal standard. Conversions are based on ketone derivatives.

2.7. X-ray crystallographic data

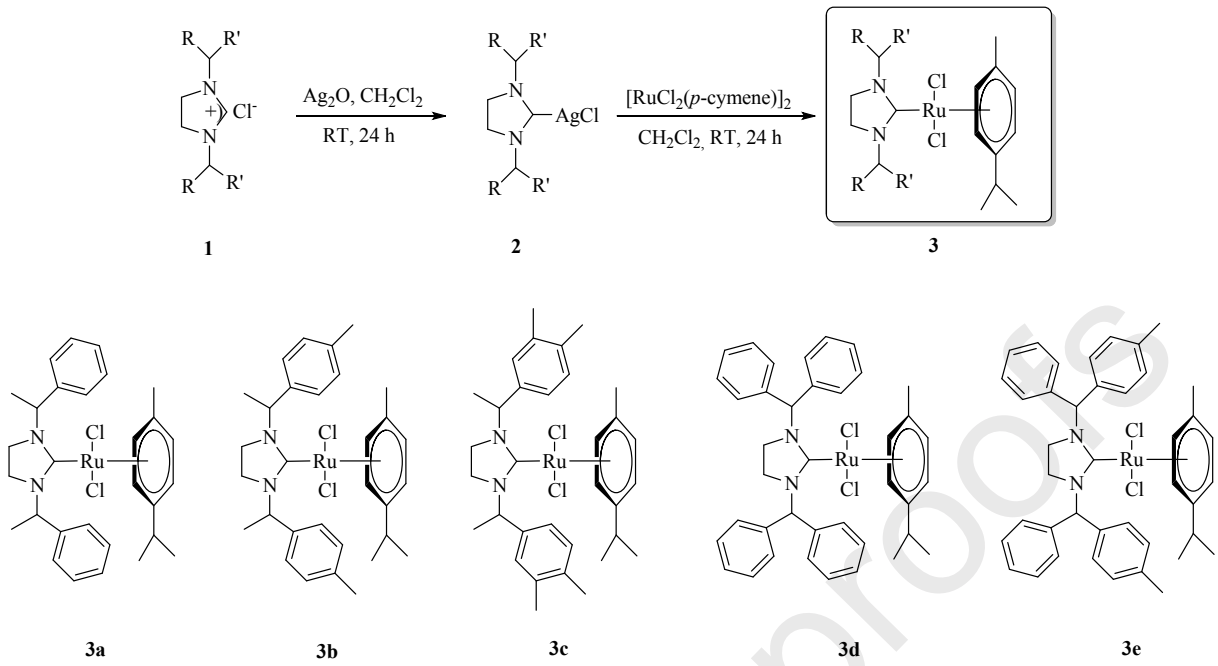
The crystallographic data collection of the complex **3d** was conducted at 293(2) K on a Rigaku Oxford Xcalibur diffractometer with an Eos-CCD detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Data collection, cell refinement and data reduction along with absorption correction were performed using the CrysAlis^{Pro} software package [23]. The

crystal structure was solved with the SHELXT structure solution program using *Intrinsic Phasing* method [24] embedded in the Olex2 [25]. The refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method in SHELXL [26]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the complex were placed at idealized positions and refined using the riding model. A summary of crystal data, experimental details, and refinement results for the complex are given in Table 1.

3. Results and discussion

3.1. Synthesis of Ag(I)-NHC and Ru(II)-NHC complexes

In this study, a series of new Ag(I)-NHC and Ru(II)-NHC complexes were synthesized and characterized (Scheme 1). The symmetrical imidazolinium chloride salts **1** used as the precursors of NHC ligands were synthesized by cyclization reactions of *N*,*N*'-dialkylalkanediamines with triethyl orthoformate in the presence of ammonium chloride as reported previously [27]. The Ag(I)-NHC complexes **2a-e** were prepared via the *in situ* deprotonation of imidazolinium salts by Ag_2O according to the general method described by Wang and Lin [28]. Treatment of the imidazolinium salts with Ag_2O in dichloromethane at room temperature in the dark afforded the expected silver complexes Ag(I)-NHC **2a-e** (Scheme 1). The silver-NHC complexes **2a-e** was obtained in high yields as white solids, soluble in halogenated solvents. These complexes are stable in air but are light sensitive. In the ^{1}H NMR and ^{13}C NMR spectra of **2a-e**, the disappearance of the downfield resonance signals of imidazolinium (NC*H*N) proton and imidazolinium (N*C*N) carbon signal suggests the formation of the Ag(I)-NHC complexes. In the ^{1}H NMR spectrum of **2a-e**, C*H* proton signals bonded with the nitrogen of imidazolidine ring appear as a quartet at 5.42 ppm for **2a** and 5.23 ppm for **2c**, two quartet at 5.27 and 5.38 ppm for **2b**, a singlet 6.38 and 6.32 ppm respectively for **2d** and **2e**. The methylene protons of imidazolidine ring give two triplet at 3.20 and 3.48 ppm for **2a** and two multiplet in range of 3.20-3.73 ppm for **2b** and **2c**, whereas the same signals were observed as a singlet at 4.06 and 4.04 ppm for **2d** and **2e**, respectively. The aromatic protons of NHC ligand were observed as multiplet in range of 7.03-7.44 ppm in the ^{1}H NMR of **2a-e**. In the **2a-e** complexes, the resonances for carbene carbon were not detected, which has also been mentioned in the literature and given as a reason for the fluxional behavior of the NHC complexes [29]. Silver-NHC complexes **2a-e** exhibit a characteristic υ(C=N) bond vibrations typically at 1656, 1663, 1632, 1644 and 1637 cm^{-1}, respectively for **2a-e.**



Scheme 1. The synthesis of (*p*-cymene)-ruthenium(II)-NHC complexes.

The ruthenium(II)-NHC complexes **3a-e** were prepared via transmetalation method from the corresponding silver(I)-NHC complexes and $[RuCl_2(p\text{-cymene})]_2$ (Scheme 1). The reaction of $[RuCl_2(p\text{-cymene})]_2$ with 2 equivalents of **2a-e** in dichloromethane at room temperature afforded the corresponding (*p*-cymene)-ruthenium(II)-NHC complexes **3a-e**, which were isolated as orange-brown crystals in moderate to good yields after purification. A single crystal of complex **3d** for X-ray diffraction analysis was obtained from slow vapor diffusion of diethyl ether into a dichloromethane solution at room temperature. These complexes are very stable against air and moisture in the solid-state. The new ruthenium complexes were characterized using ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis techniques, which support the proposed structures. The ruthenium complexes exhibit characteristic υ(C=N) bands in the range of 1495-1512 cm^{-1} for **3a-e**. NMR analyses of the complexes showed that the *N*-heterocyclic carbene ligands had been transferred from the silver complexes to ruthenium. In the ^{1}H NMR spectrum of **3a-e**, aromatic protons signals of *p*-cymene ligands appear as two doublet in range of 4.79-5.22 ppm with the same coupling constants for **3a** and **3c-e**, whereas aromatic protons of *p*-cymene ligand were observed as four doublets in range of 5.13-5.45 ppm in the ^{1}H NMR of **3b**. The methyl signals of isopropyl group on *p*-cymene ligands appear as two doublets in range of 1.01-1.27 ppm for **3b** and **3e**, a singlet in range of 1.03-1.04 ppm for **3a**, **3c,** and **3d**. The methyl signals of *p*-cymene ligands were observed as a singlet in range of 1.59-1.93 ppm in the ^{1}H NMR of **3a-e**.

The ^{13}C NMR chemical shifts provide a useful diagnostic tool for this type of metal carbene complexes. The characteristic resonance of the carbene carbon was observed at 209.2, 207.6, 208.6, 208.5 and 208.2 ppm respectively for **3a-e**. The resonances of aromatic carbons of NHC ligands appear between 122.9 and 142.7 ppm, whereas resonances for aromatic carbons of *p*-cymene ligands were found in the range 83.1-105.9 ppm for **3a-e**, these values were similar to those found for other (*p*-cymene)-ruthenium(II)-NHC complexes [19d, 21d]. The elemental analysis data of the complexes 3**a-e** agrees closely with the theoretical requirements of their structures.

3.2. Description of the crystal structure of complex 3d

The complex **3d** crystallizes in the monoclinic space group $P2_1/c$; its molecular and crystal structure is depicted in Fig. 1. In the complex, coordination geometry around the Ru(II) atom can be described as a *pseudo*-octahedral piano-stool geometry, with three sites occupied by the η^6-*p*-cymene ligand and the remaining three by the two chlorides and an NHC ligand. The NHC moiety makes coordination with two benzhydryl imidazolidin wingtip substituents. The ruthenium atom is situated 1.7076(5) Å from the centroid of the *p*-cymene ring, which is consistent with the values reported in similar complexes [30]. In the *p*–cymene ligand, the arene ring (C5–C10) has a planar configuration with the rmsd at 0.026 Å. In the crystal packing of **3d**, intra- and intermolecular C–H···Cl type weak interactions play a role for the stabilization of the complex. Fig. S1 displays the crystal packing fashion of the complex with these intra- and intermolecular interactions.

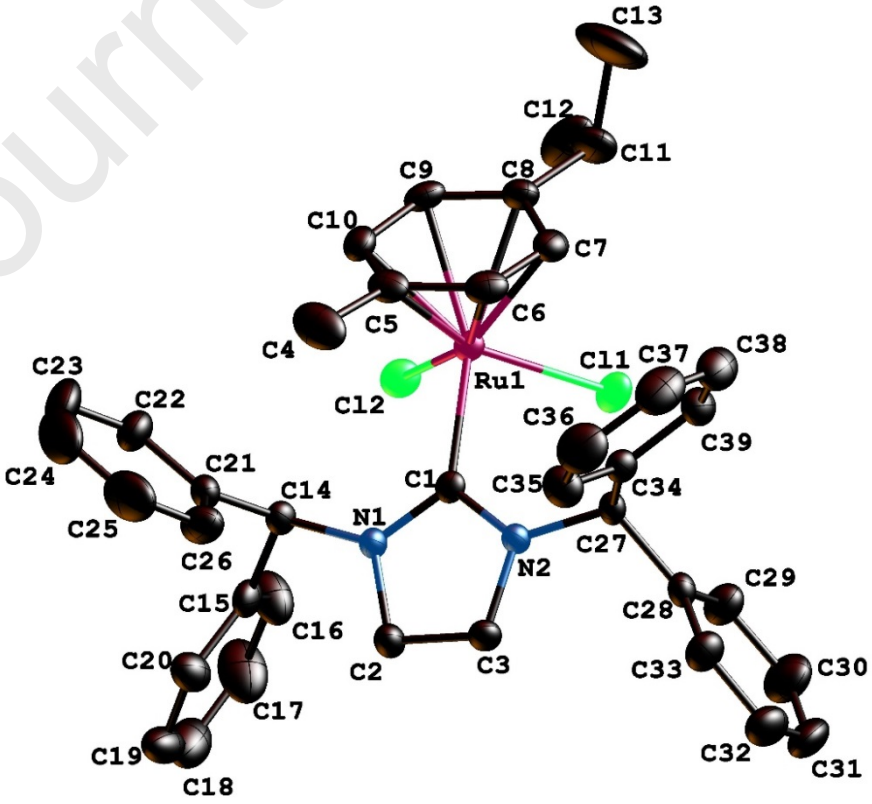
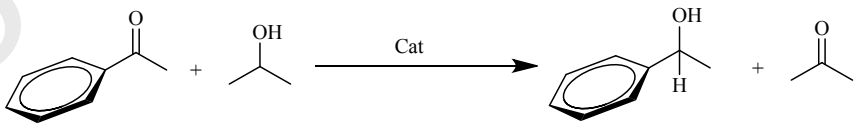


Fig. 1. Crystal structure of [$RuCl_2$(NHC)(η^6-*p*-cymene)] complex (**3d)**. Thermal ellipsoids are depicted at the 30% probability level. Selected bond distances (Å) and angles (°): Ru1–Cl1 2.4336(9), Ru1–Cl2 2.4300(8), Ru1–C1 2.108(3), Ru1–C5 2.243(3), Ru1–C6 2.189(3), Ru1–C7 2.154(3), Ru1–C8 2.263(3), Ru1–C9 2.229(3), Ru1–C10 2.186(3), C1–N1 1.356(3), C1–N2 1.354(3); Cl1–Ru1–Cl2 82.21(3), C1–Ru1–Cl1 89.81(8), C1–Ru1–Cl2 92.80(8), Cl1–Ru1–C^{arene} 124.127(2), Cl2–Ru1–C^{arene} 124.208(2), C1–Ru1–C^{arene} 130.042(3), C1–N1–C14 127.6(3), C1–N2–C27 127.0(2). For the sake of clarity, hydrogen atoms are omitted.

3.3. Transfer hydrogenation of ketones

The catalytic activities of new ruthenium complexes **3a-e** were investigated in the transfer hydrogenation of ketones using ^{i}PrOH as a hydrogen source. Initially, the reduction of acetophenone to 1-phenyl ethanol was used as a model reaction to determine the optimal catalytic conditions with **3a** as a catalyst (Table 1). Although the the some reports under base-free conditions have been known [9], the addition of base is frequently crucial to the efficiency of transfer hydrogenation reaction. Seven different bases were tested and among them, KOH displayed the highest reactivity (entry 5). It is noteworthy that, in the absence of base, no conversion was detected and only 9% conversion was observed without catalyst (entry 13). When the [$RuCl_2$(*p*-cymene)]$_2$ was used as catalyst, phenyl ethanol was obtained in 59% conversion. Lower catalyst ratio was caused the by the drop of conversions (entries 10, 11). The catalytic system was used in transfer hydrogenation of acetophenone at room temperature, the formation of phenyl ethanol was not appreciable. When this catalytic system was used at 50 ^{o}C for 6h, phenyl ethanol was observed only 15% conversion (entry 9), whereas good conversion was observed at 80 °C for 6h.

Table 1. Screening of transfer hydrogenation reaction conditions



Entry	**Cat.**	**Cat. (% mol)**	**Base**	Conversion **(%)**
1	**3a**	1	NEt_3	15
2	**3a**	1	Cs_2CO_3	75
3	**3a**	1	K_2CO_3	61
4	**3a**	1	NaOH	92

5	**3a**	1	KOH	96
6	**3a**	1	*t*-BuOK	69
7	**3a**	1	NaOAc	39
9	**3a**	1	KOH	15[b]
10	**3a**	0.5	KOH	65
11	**3a**	0.25	KOH	42
12	$[RuCl_2(p\text{-cymene})]_2$	1	KOH	59
13	-	-	KOH	9

[a]*Reaction conditions*: KOH (2 mmol), ^{i}PrOH (10 mL), acetophenone (1.0 mmol), 80 ^{o}C, 6 h. The purity of compounds is checked by GC using dodecane as an internal standard and conversions are based on ketones. [b]KOH (2 mmol), ^{i}PrOH (10 mL), acetophenone (1.0 mmol), 50 ^{o}C, 6 h.

Also, the time-dependent reaction profile at different catalyst loadings was followed with complex **3a** (Figure 2). When 1 mol% of complex **3a** was used, the only trace amount of the product was identified after 60 min period, but no induction period was observed for 0.5 mol% catalyst loading in the same time. The 1 mol% of complex **3a** gave the 87% conversion within 2h gradually and no remarkable change was observed in the conversion after 4h as represented Figure 2. As demonstrated by TEP (Tolman Electronic Parameter) data, NHC ligands with bulky substituents generally exhibit better donor properties [31]. Also, the carbene ligand of the compound is seemingly bulky enough to slow down the approach of substrates, while the compound with the sterically least demanding ligands on the NHC-N-atoms might be unable to stabilize either the active species and/or the transition states. In here, the high induction time might be the consequence of steric and electronic effects of the wingtip groups in the ruthenium *N*-heterocyclic carbene complexes.

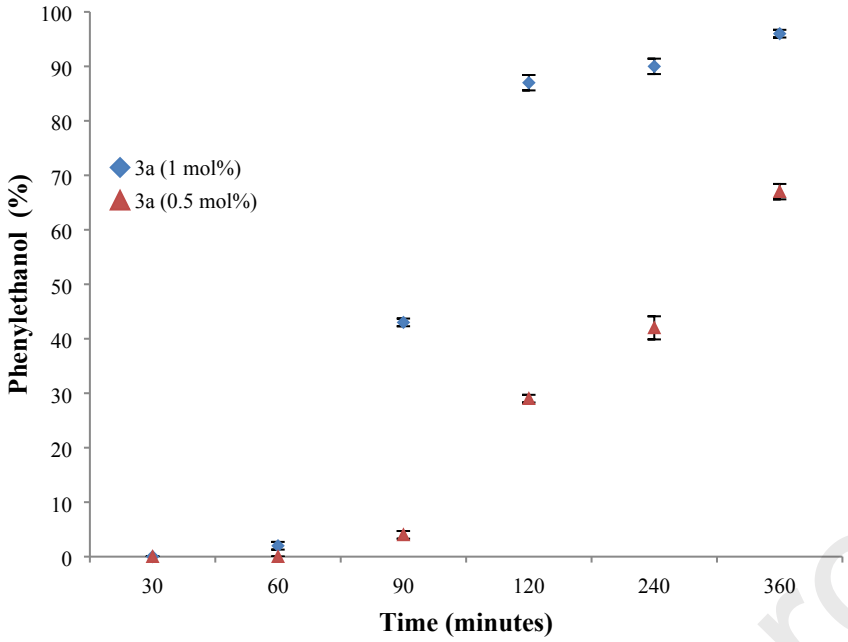


Fig. 2. Time dependence of the transfer hydrogenation. Reaction conditions: Catalyst (0.01 mmol or 0.005 mmol), substrate (1 mmol), ^{i}PrOH (3 mL), KOH (2 mmol), 80 ^{o}C.

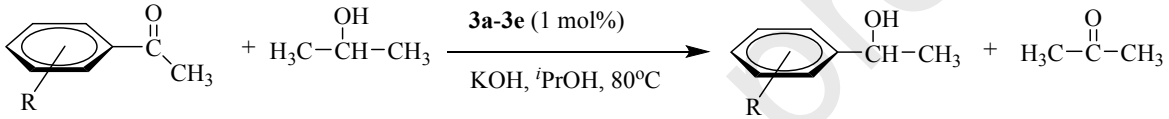
The catalytic experiments were carried out using 1 mmol ketone, 0.01 mmol **3a-e**, 2 mmol KOH and 3 mL ^{i}PrOH at 80 ^{o}C for 2-6 h. Under these reaction conditions, complex **3d** proved to be the most effective catalyst relative to **3a**, **3c, 3b,** and **3e** for transfer hydrogenation of acetophenone. The reduction of acetophenone with **3d** was completed within 6 h in 98% (Table 2, entry 4). In contrast, acetophenone was reduced within 6h using 3**a**, **3b, 3c** and **3e** in 96, 94, 96 and 89% conversion, respectively (Table 2, entries 1-5).

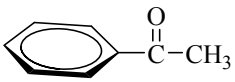
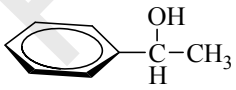
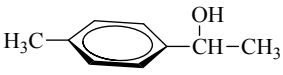
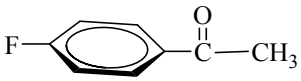
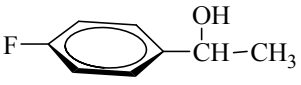
We next extended our investigations to include transfer hydrogenation of substituted acetophenone derivatives. A variety of ketones were transformed into the corresponding secondary alcohols. The results are shown in Table 2. Under those conditions, *p*-methylacetophenone, *p*-methoxyacetophenone, *p*-floroacetophenone, *p*-nitroacetophenone react very cleanly and in good conversions with ^{i}PrOH (Table 2, entries 9, 14, 19 and 21). The presence of electron withdrawing (NO_2) or electron donating (CH_3 or OCH_3) substituent on acetophenone (Table 2, entries 8, 14 and 21) has a significant effect on the reduction of ketones to their corresponding alcohols. For example, when **3d** was used as the catalyst, the *p*-tolylethanol products was observed in 72% yield (Table 2, entry 9), whereas in the case of 3**a**, **3b, 3c** and **3e** *p*-methylacetophenone was reduced in 38, 33, 52 and 55% conversion, respectively (Table 2, entries 6-10). *p*-Methoxyacetophenone was reduced using **3a-e** in 33, 23, 43, 45 and 35% conversion, respectively (Table 2, entries 11-15). When *p*-

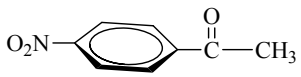
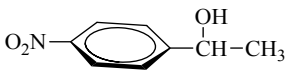
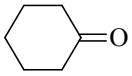
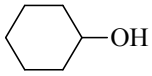
floroacetophenone was used as the substrate, yields were increased slightly (Table 2, entries 16-20). The maximum conversion of 4-nitroacetophenone to corresponding alcohol was achieved over a period of 2h (Table 2, entries 21-25).

The ruthenium complexes also catalyzed the transfer hydrogenation of cyclohexanone very effectively (Table 2 entries 26-30). The conversion of cyclohexanone to corresponding alcohol was achieved over a period of 3h, the products were obtained with 98-99% conversion. Among the tested complexes, the complex **3d** is highly efficient in the transfer hydrogenation of ketone to a secondary alcohol. When the obtained results compared with similar previously Ru-NHC complexes, new Ru-NHC complexes (**3a-e)** have similar catalytic activity [19c,d and 21].

Table 2. Hydrogen transfer from ^{i}PrOH to ketones in the presence of **3a-e** and KOH.[a]



Entry	Substrate	Product	Time (h)	Cat.	Conversion (%)
1			6	**3a**	96
2			6	**3b**	94
3			6	**3c**	96
4			6	**3d**	98
5			6	**3e**	89
6			6	**3a**	38
7			6	**3b**	33
8			6	**3c**	52
9			6	**3d**	72
10			6	**3e**	55
11			6	**3a**	33
12			6	**3b**	23
13			6	**3c**	43
14			6	**3d**	45
15			6	**3e**	35
16			6	**3a**	80
17			6	**3b**	73

18			6	**3c**	75
19			6	**3d**	85
20			6	**3e**	74
21			2	**3a**	98
22			2	**3b**	96
23			2	**3c**	94
24			2	**3d**	95
25			2	**3e**	96
26			3	**3a**	99
27			3	**3b**	98
28			3	**3c**	98
29			3	**3d**	99
30			3	**3e**	98

[a]*Reaction conditions*: Cat. (0.01 mmol), substrate (1 mmol), [i]PrOH (3 mL), KOH (2 mmol), 80 [o]C. The purity of compounds is checked by GC using dodecane as an internal standard, conversions are based on ketone derivatives.

The ability of Hg(0) to poison metal-particle heterogeneous catalysts, by amalgamating the metal or adsorbing on the metal surface, has been known for more than 90 years and is a widely used test [32]. This experiment is performed by adding Hg(0) to the reaction solution. The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst; if Hg(0) does not suppress catalysis, that is evidence for a homogeneous catalyst. We also carried out the mercury poisoning experiment to assess whether the reaction system is homogeneous or heterogeneous. The Hg(0)-poisoning experiments were performed with catalysts **3a** and **3d** in the presence of excess Hg. The results showed no significant inhibition of conversion to products when the complex **3a** was used as a catalyst at different times (Table 3, entries 1-3). Thus, the present catalysis appears to be homogeneous in nature. We could mention that influence of nanoparticles on the performance of the catalysts was excluded by such an experiment and that this is not the reason for the long induction period.

Table 3. Mercury poisoning test of Ru catalysts in transfer hydrogenation of acetophenone.[a]

Entry	Cat.	Time	Conversion	Conversion with Hg

		(h)	(%)	(%)[b]
1	**3a**	1	2	<2
2	**3a**	3	87	87
3	**3a**	6	96	94
4	**3d**	6	98	97

[a]*Reaction conditions*: Cat. (0.01 mmol), substrate (1 mmol), ^{i}PrOH (3 mL), KOH (2 mmol), 80 ^{o}C. The purity of compounds is checked by GC using dodecane as an internal standard, conversions are based on ketone derivatives. [b]One drop of Hg was added with a syringe.

4. Conclusion

From readily available starting materials, such as 1,3-dialkyl-imidazolidin-2-ylidene, five [$RuCl_2$(*p*-cymene)(1,3-dialkyl-imidazolidin-2-ylidene)] complexes **3a-e** have been prepared by transmetallation from Ag-NHC complexes. The silver(I) and ruthenium(II) NHC complexes were characterized by elemental analysis and spectroscopic methods. Also, the molecular and crystal structure of one of the [$RuCl_2$(NHC)(η^6-*p*-cymene)] complexes **3d,** was determined by the single-crystal X-ray diffraction technique. Structural studies indicate that the half-sandwich Ru atom completes its coordination sphere with two chlorido ligands, the η^6-*p*-cymene ligand and a carbon atom of NHC, presenting a *pseudo*-octahedral piano-stool geometry. The chlorido ligands are responsible for the stabilization of the crystal structure of the complex, with C–H···Cl type intra- and intermolecular interactions. The ruthenium complexes were applied to transfer hydrogenation of ketones. Transfer hydrogenation reactions were carried out using ^{i}PrOH as the hydrogen donor with **3a-e** as the catalysts and KOH as the base at 80 ^{o}C for 2-6 h. High yields were obtained. These ruthenium complexes demonstrated good catalytic activity in the transfer hydrogenation of ketones. The ruthenium complex **3d** containing an NHC ligand with benzhydryl substituents showed better catalytic performance than the other complexes. Also, the fact that no catalyst poisoning was observed in the presence of mercury indicates the participation of a homogeneous catalyst.

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Supplementary

Crystallographic data as .cif files for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1890673 for the complex **3d**. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. fax: (+44) 1223-336-033, email: deposit@ccdc.cam.ac.uk.

Conflicts of interest

The authors declare that they have no conflict of interest.

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Highlights

*Silver and ruthenium-*N*-heterocyclic carbene complexes were synthesized and characterized.

*The silver complexes were used as carbene-transfer agents to synthesize ruthenium(II) complexes.

*These ruthenium complexes were tested as catalysts in the transfer hydrogenation of ketones.

Conflicts of interest

The authors declare that they have no conflict of interest.

Ruthenium(II) complexes bearing N-heterocyclic carbene ligands with wingtip groups and their catalytic activity in the transfer hydrogenation of ketones

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