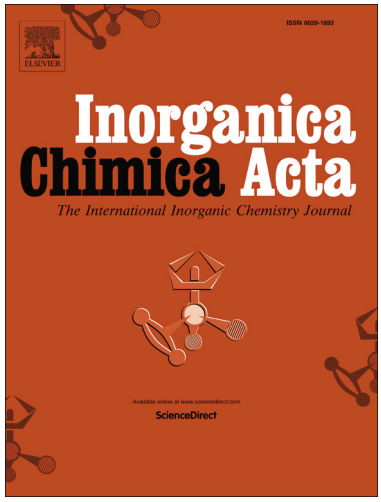

Research paper

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Muthukumaran Nirmala, Kaliyappan Murugan, Subbarayan Vijayapritha, Periasamy Viswanathamurthi, Roberta Bertani, Jan Grzegorz Malecki

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Olefin-tethered organoruthenium carbene complexes: Synthesis, X-ray structure and catalytic insights on hydrogenation of esters

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Abstract

A series of Ru(II) complexes encompassing imidazolylidene olefin arm have been designed. The newly synthesized ligands and complexes were fully characterized by ^{1}H, ^{13}C NMR, and elemental analyses. Structural geometry for one of the envoy Ru(II) carbene complexes **3a** was confirmed by single-crystal X-ray diffraction studies. The complexes acquired a distorted octahedral geometry. The highly active [Ru(II)-NHC] complex **3b**, showed excellent catalytic performance for the hydrogenation of esters in 1,4-dioxane medium. The effects of solvent, base, wingtip substituents, time and catalyst loading were also investigated. The reported catalyst performed exceptionally well for a range of esters and furnishes very good yield of hydrogenated products.

Key words:

imidazolylidene olefin arm

N-heterocyclic carbene

Ruthenium(II) complexes

X-ray diffraction

Hydrogenation of esters

1. Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has experienced swift expansion over the past decade [1], mainly after the report of the first stable NHC [2]. To date, a number of NHCs with various backbones and topologies have been investigated. Besides, the N-functional group in NHC provides the additional donor site like σ and π-bonding, which offers control over the coordination environment of the metal as well as unusual behaviors. In recent years, the olefin group attached N-heterocyclic carbenes have gained escalating attention due to their essential role in homogeneous catalysis as a π-electron reservoir to stabilize the metal center in the catalytic cycle [3-5]. In this circumstance, olefin tagged NHC ligands are fairly promising architectures, due to their coordination and dissociation, which is a key feature in many catalytic systems [6, 7]. When these two steps are in dynamic equilibrium, or when they operate in tandem in a catalytic cycle, the hemilability effect [8, 9] may be exploited to improve catalytic efficacy, even though the life span of some synchronized olefins may be too short for the system to be detected or excluded [10]. The first olefin functionalized carbene was isolated in 2001, but its potential in catalysis was not reported [3]. Afterwards, the iridium complexes of N-allyl-substituted benzimidazol-2-ylidene compounds were synthesized and deliberated its catalytic activity towards the hydrogenation of carbonyl compounds [11]. Followed by the above, use of NHC–olefin ligands (NHC = N-heterocyclic carbene) in transition metal systems such as Pd(II), Ru(II), Ir(I)) [4, 5,11, 18] and NSHC–olefin (NSHC = N,S-heterocyclic carbene) in Pd(II), Cu(I), Au(III), Rh(I), Ir(I) [12, 13] have been investigated in copious catalytic reactions in which, the olefin functionalized ruthenium carbene complexes have shown excellent catalytic efficiencies in catalytic hydrogenation reactions [4]. The combinative use of a robust (carbene) and flimsy (olefin) M–C bond is anticipated to facilitate the metal to be more flexible to coordinative changes. Moreover, the η^2 σ-donor olefin side arm performs a vital role in the catalytic cycle to offer the adequate stability to the catalytic transition state.

The reduction of esters to the corresponding alcohols is an important reaction in organic synthesis as it is often used in natural product synthesis, for the preparation of organic building blocks and in industry for the manufacture of pharmaceuticals, agrochemicals, flavors, and fragrances [14a]. Usually, the classical procedures for the reduction of esters was carried out by

using stoichiometric amounts of metal hydride reagents (e.g. lithium aluminum hydride, dibutyl aluminum hydride, or boron hydride), [14b-e] low atom economy and under anhydrous laborious workup procedures etc. While transition metal based homogeneous systems capable of hydrogenation of esters are very scarce [14b-e]. In these systems, large amounts of additives, such as an organic base, [14b] inorganic acids, [14b] salts, [14c, d] zinc, [14e] and fluorinated alcoholic solvents [14b] were needed to obtain high conversion of esters into alcohols. Moreover, the catalytic hydrogenations might serve as a relatively green and environmentally benign substitute since no side products are formed compared to the classic stoichiometric reduction processes. Therefore, there is a growth of more active well defined homogeneous catalysts for ester hydrogenation is noteworthy. Recently, ruthenium, iridium, and osmium complexes have gained a reputed position in the homogeneous hydrogenation of esters under milder reaction conditions. Among them, the ruthenium catalyzed hydrogenation of esters into alcohols have been scarcely explored [15, 16].

Based on the above facts, and in continuance of our current research in the utility of transition metal NHC complexes for diverse organic transformations [17], in this paper, we account the synthesis and characterization of ruthenium(II) complexes bearing olefin N-heterocyclic carbene (NHC) ligands with different wingtip substituents in the imidazole ring, together with their catalytic properties with regard to hydrogenation of esters using KO*t*Bu as the base. The striking features of these reactions embrace the use of low toxicity organic materials, admirable atom economy, water is the only by-product, and high selectivity towards the products.

2. Experimental methods

2.1. General considerations

All experiments were performed using standard Schlenk technique or in a glovebox under nitrogen atmosphere. All reagents were purchased from Aldrich chemical Co. and used as received without further purification. The microanalysis of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000-400 cm^{-1} using a Bruker FT-IR spectrophotometer.^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were taken in DMSO-

d_6 or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane. Thin-layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by Merck silica gel 60 (0.063-0.200 mm). Melting points were determined in open capillary tubes on a Technico micro heating table and are uncorrected.

2.2. Synthesis of NHC ligands

The NHC ligands were prepared according to previous literature report [18]. To a solution of 1-substituted imidazole (18.2 mmol) in 30 mL of acetonitrile, allyl bromide (2.2 g, 18.2 mmol) was added in a Schlenk tube. The mixture was stirred overnight, and then the solvent was removed under vacuum to give brown oil. The product has been washed with diethyl ether (2 X 3 mL) and dried under *vacuum*.

*Synthesis of 1-methyl-3-allylimidazolium chloride (**1a**)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-methylimidazole to give brown oil **1a**. Yield: 91%. Anal. Calcd. for $C_7H_{11}N_2Br$ (203.07): C,41.40; H,5.46; N,13.79 %. Found: C,41.35; H,5.40; N, 13.84 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 9.32 (s, 1H, NCHN), 7.37 (d, 1H, Imi-H), 6.93 (d, 1H, Imi-H), 6.0-4.51 (allyl group protons), 3.50 (s, 3H, NCH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 137.1 (N*C*N), 131.8 (NCH_2-*C*H= CH_2), 124.4 (NCHCHN), 122.7 (NCH*C*HN), 120.8 (NCH_2-CH=*C*H_2), 51.3 (N*C*H_2-CH=CH_2), 36.2 (N*C*H_3).

*Synthesis of 1-^{i}propyl-3-allylimidazolium chloride (**1b**)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-*i*-propyl imidazole to give brown oil **1b**. Yield: 87%. Anal. Calcd. for $C_9H_{15}N_2Br$ (231.13): C, 46.77; H, 6.54; N, 12.12 %. Found: C, 46.69; H,6.62; N, 12.20 %. ^{1}H NMR (300.13 MHZ, $CDCl_3$, δ): 8.75 (s, 1H, NC*H*N), 7.11-7.10 (d,*J* = 1.5 Hz, 1H, Imi-*H*), 7.007-7.005 (d, *J* = 1.2 Hz, 1H, Imi-*H*), 5.65 (dd, J = 6.2 Hz, J = 2.4 Hz, 1H, -*CH*=CH_2), 5.62 (dd, *J* = 6.7 Hz, *J* = 4 Hz, 1H, -*C*H=CHH_{cis}), 5.58 (dd, *J* = 4 Hz, *J* = 6.1 Hz, 1H, -*C*H=CHH_{trans}), 4.99-4.98 (d, *J* = 4 Hz, 2H, CH_2).^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 137.1 (N*C*N), 132.3 (NCH_2-*C*H=CH_2), 124.2

(N*C*HCHN), 122.8 (NCH*C*HN), 120.6 (NCH_2-CH=*C*H_2), 51.1 (N*C*H_2-CH=CH_2), 58.9 *C*H(CH_3)$_2$), 28.1 CH(*C*H_3)$_2$).

*Synthesis of 1-^{t}butyl-3-allylimidazolium chloride (**1c**)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-*t*-butyl imidazole to give brown oil **1c**. Yield: 85%. Anal. Calcd. for $C_{10}H_{17}N_2Br$ (245.15): C, 48.99; H, 6.99; N, 11.43 %. Found: C, 48.81; H, 6.65; N, 11.35 %. ^{1}H NMR (300.13 MHZ, $CDCl_3$, δ): 9.56 (s, 1H, NC*H*N), 7.33 (d, 1H, Imi-*H*), 7.13(d, 1H, Imi-H), 5.5-4.2 (allyl group protons), 1.03 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 133.5 (NCN), 128.3 (NCH_2-*C*H=CH_2), 120.9 (N*C*HCHN), 119.5 (NCH*C*HN), 117.3 (NCH_2-CH=*C*H_2), 51.1 (N*C*H_2-CH=CH_2), 50.2 N-C(CH_3)$_3$), 21.62 C(CH_3)$_3$).

2.3. Synthetic procedure for ruthenium(II) NHC complexes

1-substituted 3-allylimidazolium chloride (2 mmol) was dissolved in 25 mL of dichloromethane and transferred into a Schlenk vessel. Excess Silver(I) oxide (1.5 mmol) was added, and the mixture was stirred for 24 h at room temperature under argon atmosphere [19]. Then the unreacted Ag_2O was filtered through a plug of Celite. The resulting solution was filtered through celite, solvent was evaporated in *vaccuo*, washed with diethylether (2 ml x 2) and dried in vacuo. [$RuBr_2(PPh_3)_3$] (1 g, 1 mmol) was taken up in 5 mL of dichloromethane and added to a solution of Ag complex in 10 mL of CH_2Cl_2. The mixture was stirred overnight at room temperature. After filtration in air, the solvent was removed in vacuum to give the product. The final compound is stable in air. Single crystals of the compound **3a** were achieved by slow evaporation of a concentrated solution in a mixture of dichloromethane and acetone.

*Compound **3a** (R = Me)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-methyl-3-allylimidazolium chloride to give complex **3a**. Yield: 79%. M.pt.: 243-245 °C. Anal. Calcd. for $C_{14}H_{20}N_4Br_2Ru$ (505.21): C, 33.28; H, 3.99; N, 11.09 %. Found: C, 33.33; H 3.93; N, 11.02 %.^{1}H NMR (300.13 MHZ, $CDCl_3$, δ): 6.9 (d, 1H Imi-H); 6.8 (d, 1H Imi-H); 5.8-3.9 (allyl group protons), 3.7 (s, 3H, NCH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 198.04

(N*C*N), 124.18 (Imi-*C*), 122.95 (Imi-*C*), 108.98 (NCH_2-*C*H=CH_2), 102.59 (NCH_2-CH=*C*H_2), 48.25 (N*C*H_2-CH=CH_2), 36.08 (N*C*H_3).

*Compound **3b** (R = ^{i}propyl)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-(i-propyl-3-allylimidazolium chloride to give complex **3b**. Yield: 82 %. M.pt.: 237-240 °C. Anal. Calcd. for $C_{18}H_{28}N_4Br_2Ru$ (561.31): C, 38.52; H, 5.03; N, 9.98 %. Found: C, 38.46; H, 5.10; N, 9.90 %. ^{1}H NMR (300.13 MHZ, $CDCl_3$, δ): 6.95 (d, 1H, Imi-H), 6.8 (d, 1H, Imi-H), 5.6-4.2 (allyl group protons), 3.7 (m, 1H, $CH(CH_3)_2$), 1.21 (d, 6H, $CH(CH_3)_2$). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 198.73 (NCN), 126.39 (N*C*HCHN), 119.21 (NCH*C*HN), 109.29 (NCH_2-*C*H=CH_2), 102.47 (NCH_2-CH=*C*H_2), 63.87 (N*C*H_2-CH=CH_2), 56.3 $NCH(CH_3)_2$), 26.2 $CH(CH_3)_2$).

*Compound **3c** (R = ^{t}butyl)*

The synthetic procedure of this compound is same as that of above representative procedure, using 1-(*t*-butyl)-3-allylimidazolium chloride to give complex **3c**. Yield: 81 %. M.pt.: 223-225 °C. Anal. Calcd. for $C_{20}H_{32}N_4Br_2Ru$ (589.37): C, 40.76; H, 5.47; N, 9.51 %. Found: C, 40.69; H, 5.40; N, 9.42 %.^{1}H NMR (300.13 MHZ, $CDCl_3$, δ): 6.9 (d, 1H, Imi-H), 6.8 (d, 1H, Imi-H), 5.9-3.5 (allyl group protons), 1.14 (s, 9H, $NC(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ): 198.9 (N*C*N), 125.47 (N*C*HCHN), 124.37 (NCH*C*HN), 109.29 (NCH_2-*C*H=CH_2), 102.47 (NCH_2-CH=*C*H_2), 66.3 (NCH_2-CH=CH_2), 49.1 $NC(CH_3)_3$), 23.5 $C(CH_3)_3$).

2.4. Typical procedure for the catalytic hydrogenation

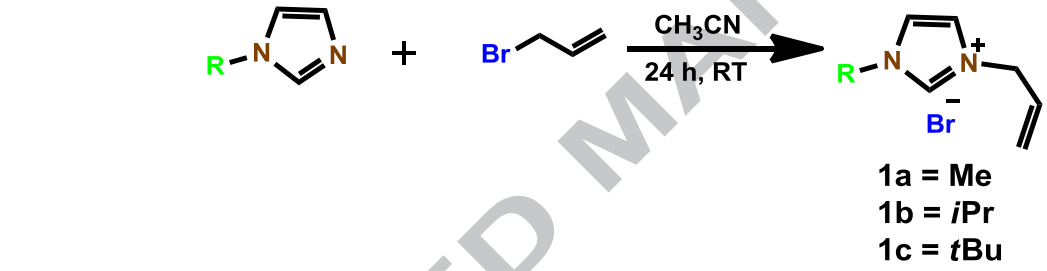
To a mixture of catalyst (0.01 mmol), KO*t*Bu (10 mol %), and 1,4-dioxane (4.0 mL) in a Parr high-pressure reactor was added the ester (1.0 mmol). The dark red solution was purged with H_2 and stirred under 400 psi of H_2 at 105 °C for 8 h. Products isolation were performed *via* column chromatography using silica gel as stationary phase and *n*-pentane/ethylacetate or *n*-pentane/isopropanol mixture as eluent. The products were confirmed by ^{1}H NMR.

2.5. X-ray crystallography

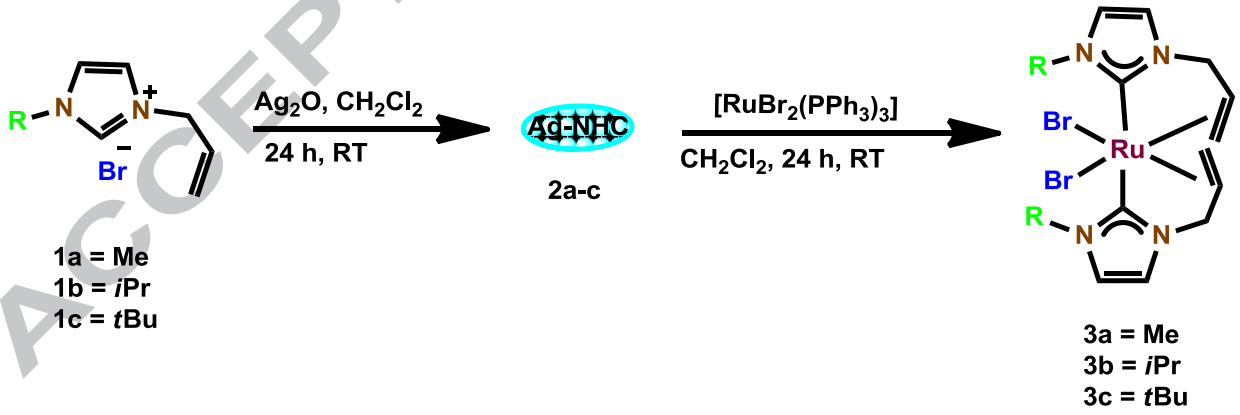
Crystal of complex **3a** was mounted on glass fibers used for data collection. Crystal data were collected at 295 K using a Gemini Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Ka radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS [20]. Refinement and all further calculations were carried out using SHELXL [20]. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares on F2. Atomic scattering factors were incorporated into the computer programs.

3. Results and discussion

3.1. Synthesis



Scheme 1. General preparation of olefin-tethered NHC ligands (**1a-c**)



Scheme 2. General synthesis of [Ru-NHC] complexes (**3a-c**)

Olefin-tethered NHC ligands (**1a-c**) were prepared by the reaction of allyl bromide with various 1-substituted imidazoles in presence of acetonitrile medium under stirring at overnight

(**Scheme 1**). After evaporation of the solvent under *vacuum*, the oily products were washed with diethyl ether and with dichloromethane to provide the target compounds as brown oils in very good yield. The synthetic route for the preparation of Ag(I)–NHC complexes **2a-c** illustrated in this work is shown in **Scheme 2**. The Schlenk tube used for the synthesis of silver complexes was draped with aluminum foil to prohibit the light. Silver complexes **2a-c** were prepared by the reaction of excess silver(I) oxide with the corresponding imidazolium salts **1a-c** in dichloromethane overnight [19]. The resultant black suspension was filtered through a pad of Celite and the solvent was evaporated to dryness under reduced pressure. The residue was washed with diethyl ether and afforded the corresponding silver complexes as thick yellow oils in very good yields. The synthesis of ruthenium NHC complexes was attained by transmetallation process. The corresponding Ag(I)–NHC complexes **2a-c** were reacted with dichloromethane solution of $[RuBr_2(PPh_3)_3]$ for 24 h. This reaction yielded a black AgBr precipitate, which was filtered off using a pad of Celite, followed by the solvent was reduced under *vaccum*. Diethyl ether was added to precipitate the complexes as pale yellow solids, which were washed with an additional amount of diethyl ether and crystallized from dichloromethane/acetone solvent mixture to render the complexes (**3a-c**) in good yields. They are greatly soluble in CH_2Cl_2, $CHCl_3$, THF and DMSO. Nonetheless, they are sparingly soluble in acetonitrile, but insoluble in hexane, pentane and Et_2O. All the complexes (**3a-c**) were completely characterized by ^1H, ^{13}C NMR and elemental analyses. The CHN data of the ruthenium-NHC complexes are in good concord with the proposed molecular formulae.

3.2. Spectroscopic description

The ^1H NMR spectra of the ligands (**1a-c**) and complexes (**3a-c**) have shown the signals in the expected region (Fig. S1-S5, ESI). As estimated the NHC hydrogen atom of the imidazolium salts gives rise to a singlet at 9.5-8.7 ppm in the ligands. The generation of free carbene and subsequent formation of the [Ru-NHC] complexes were unequivocally confirmed by the nonappearance of the ^1H NMR resonances of imidazolium (NCHN) protons. The allyl protons of imidazolium ligands resonated at the region 6.0-4.0 ppm whereas in the ruthenium complexes the allylic protons shifted to high field region. The significant high field shift of the resonances of the allyl protons particularly for the $CH{=}CH_2$ protons indicates the coordination of the allylic double bond with the ruthenium metal. The shift in resonance is similar to an

observation previously described for N-allyl double bond coordination to metal centers [21, 11, 22]. In addition, a singlet appeared around 3.5-3.7 ppm for compounds **1a** and **3a** corresponding to NCH_3 group protons. Furthermore, the spectra of compounds **1b** and **3b** showed peaks in the region ~1.2 ppm region for isopropyl group. Moreover, a clear singlet appeared around 1.1 ppm for the compounds (**1c** & **3c**) corresponding to tertiary butyl protons.

The ^{13}C NMR spectra have shown the expected signals in the appropriate regions (Fig. S6-S11, ESI). The spectra of complexes have shown the carbenic carbon signal in the region 198.04-198.90 ppm. For the ligand and complexes the imi-C appeared in the region 126.3-119.2 ppm. The disappearance of the ^1H NMR signals of NCHC and the downfield shift of ^{13}C NMR signals of NCN carbene carbon at ca. 198.04-198.90 ppm in the ^1H and ^{13}C NMR spectra of [Ru-NHC] complexes are indicative of the Ru-$C_{carbene}$ bond formation [23]. The downfield shift of the resonances for the Ru-$C_{carbene}$ carbon is due to the coordination of the allylic C=C double bond with metal as a σ donor/π acceptor, which weakens the ruthenium carbene interactions [21]. The high field shift of resonances of allylic carbon of the complexes when compared to ligands further supports the coordination of the allylic C=C bond with ruthenium metal. Moreover, the signal for methyl, isopropyl and tertiary butyl groups are also appeared in the expected region in the spectra of ligands and complexes.

*3.3. X-ray crystal structure description of complex **3a***

Even though the analytical and spectral data gives some idea about the molecular formulae of the complexes, they do not indicate the exact coordination of bis(carbene) units in them. To gain additional insight into the coordination chemistry and the structural parameters of the complexes, single crystals of one of the complexes (**3a**) were grown and characterized by X-ray diffraction analysis. Single crystals of **3a** apt for X-ray diffraction studies were acquired by slow evaporation of a concentrated solution in a mixture of dichloromethane and acetone. No single crystals could be obtained for the other complexes, but the resemblance in their spectroscopic uniqueness implies that **3a** is a good structural replica for all three complexes. They invariably have shown a common octahedral Ru(II) structure with the NHC-olefin ligand with the anticipated bis-η^2 coordinated olefin for **3a**. In **3a**, one carbene ligand was *trans* to bromide (Ru(1)-C(8) = 2.045(4)). The Ru-C_{NHC} bond lengths (2.033(4)- 2.045(4) Å) are inconspicuous for ruthenium-carbene bonds [24, 25]. Chelation is inveterate for all donor groups,

including the η^2-coordination mode of the olefin in **3a** as construed from NMR spectroscopy. The crystal data and structure refinement parameters for complex **3a** were collected in Table 1 and the selected bond lengths and bond angels are depicted in table 2. The ORTEP view, packing arrangement of atoms in unit cell and space fill model of the complex **3a** are given in Fig. **1**-**3**. The average olefine–ruthenium bond distances of Ru(1)-C(12) and Ru(1)-C(13) is 2.308(5) Å was slightly higher than Ru(1)- C(5) and Ru(1)- C(6) (average) (2.176 Å) bond distances and the Ru(1)- Br(1) and Ru(1)- Br(2) bond distance are 2.5915(6) Å and 2.6404(6) Å respectively [4].

3.4. Catalytic hydrogenation of esters

For our initial catalytic exploration, we chose the reduction of methyl benzoate in the presence of 1 mol % of catalyst **3a-3c** at 30 bar H_2 and 105°C (Table 3). Catalyst **3b** was attested to be the most efficient complex for the hydrogenation of methyl benzoate in terms of yield and selectivity. To our pleasure, the preferred reaction was completed after 8 h giving a very high yield (96%) of benzyl alcohol (Table 3, entry 8). Optimization of key reaction parameters such as temperature, solvent, base and reaction time showed the better optimization condition for hydrogenation of esters. In order to assess the crucial role of base in promoting the generation of metal intermediates all along the catalytic cycle, various bases such as K_2CO_3, $NaHCO_3$, $KHCO_3$, NaOH, KOH and KO*t*Bu were screened. Among the bases employed, KO*t*Bu was found to be the best and led to higher yield for this reaction (Table 4, entry 6). At this point it is important to note that for most active ruthenium catalysts a substantial amount of base is required to form the catalytically active species.

It is well known that the solvent can have thoughtful effect on the hydrogenation reaction. We are paying attention in exploring the solvent-dependent differences in the behavior of catalysts on carrying out the model reaction in the most recurrently used solvents such as, toluene, 1,4-dioxane, xylene, acetonitrile, DMF, DMSO, EtOH and H_2O (Table 4). Aromatic hydrocarbon solvents such as toluene and *p*-xylene (Table 4, entries 7, 12) were afford moderately good yield than polar aprotic (DMF, DMSO; Table 4, entries 11, 13), whereas 1,4-dioxane endow with excellent yield in 8 h (Table 4, entry 6), while water were unsuccessful (Table 4, entries 14). Delightfully, decreasing the pressure from 30 bar H_2 (Table 1, entry 8, yield 96%) to10 bar H_2 a good yield (79%) of the desired product (Table 1, entry 9) has been achieved. The dihydrogen solubility of the solvents has been taken in to account [26]. However,

nature of solvents, their polarity and their ability to dissolve reactants and catalyst have also played a vital role in the efficiency of the catalytic system and in some cases, which overcome their solubility of dihydrogen. As expected, protic solvents except water, have shown to form a good catalytic system. This may due to the poor solubility of catalyst in aqueous medium.

To prove the general applicability of the new catalyst system, diverse esters were reduced to the corresponding alcohols using 1 mol % **3b** in 4 mL 1,4-dioxane at 30 bar H_2 (Table 5). Excellent yield and conversion was obtained for ethyl benzoate, giving benzyl alcohol (Table 5, entry 1). The model substrate with its fruity flavor was hydrogenated gives the benzyl alcohol with an excellent yield of 96% (Table 5, entry 2). Short- chain, aliphatic linear compound ethyl acetate reduced towards the corresponding alcohol with outstanding yield of 99 % (Table 5, entry 4). The recent catalysts explored for the hydrogenation of benzyl benzoate (benzyl alcohol, isolated yield 86 %) and propyl propionate (propan-1-ol, isolated yield 68 %) shows moderately lesser yield when compared to our present catalytic system (benzyl alcohol, isolated yield 92 % and propan-1-ol, isolated yield 77 %) [27]. However, the hydrogenation of butyl benzoate gave a good yield of 89 % (Table 5, entry 3). Hydrogenation of benzyl benzoate led to high yield of benzyl alcohol (Table 5, entry 5). The catalyst **3b** hydrogenate bromo-substituted methyl benzoate, affording the (4-bromophenyl)methanol in 96 % yield without dehalogenation (Table 5, entry 6). Even the γ-butyrolactone hydrogenated competitively offers the desired 1,4-diol was obtained in 86 % yield (Table 5, entry 7). Interestingly, the isolated yield of butane-1,4-diol under the present synthetic methodology is more convenient and most efficient catalytic route (isolated 86 %) than the catalytic route demonstrated for the preparation of butane-1,4-diol (isolated 73 %) by Osamu *et. al*. [16]. Methyl nicotinate was transformed into the corresponding pyridin-3-ylmethanol in excellent yield (Table 5, entry 8). However, the methyl cyclohexane carboxylate hydrogenated well and gives the cyclohexylmethanol in 93 % (Table 5, entry 9). The aliphatic linear compound propyl propionate was reduced to the corresponding propan-1-ol in 77 % yield under optimized reaction condition (Table 5, entry 10). After the catalytic reaction, the catalyst was recovered by the addition of CH_2Cl_2/diethylether mixture. Then, the catalyst was thoroughly washed with diethyl ether and its NMR spectrum was recorded (Figure S12, see supporting information). The NMR spectrum shows that, the resonance corresponding to the coordinated olefin was disappeared in a very short period of time (within five minutes). On the other hand, new peaks corresponding to $–CH_2$ and $–CH_3$ protons were appeared in the NMR

spectrum of recovered catalyst. Hence, complex **3b**, comprising an olefin-tethered NHC ligand, is not stable under hydrogenation conditions, and the olefin wingtip group is hydrogenated at an early stage of the reaction. While this intramolecular olefin hydrogenation may generate coordinatively unsaturated species as active catalyst, it also transforms the NHC into a monodentate ligand. [4a]. The synthetic upshot of this finding and the detailed mechanism of the reaction are being explored.

4. Conclusions

Efforts to provoke imidazolin-2-ylidenes and their ruthenium(II) complexes by transmetallation method was demonstrated. The resultant complexes exhibit high catalytic activity in the hydrogenation of esters. The complex **3a** was characterized by single crystal X-ray diffraction analysis, and all complexes were completely characterized by ^{1}H and ^{13}C NMR spectroscopy. Under optimized conditions, diverse esters converted into their corresponding alcohols in good to outstanding yields. All over, this study expounds that ruthenium complexes of olefin-functionalized NHCs are active catalysts for the hydrogenation of ester reaction. The dilatation to other donor functionalities, conspicuously olefin-tethered ruthenium(II) complexes are a possible avenue for further catalyst optimization. Research efforts at such more decisive ruthenium(II) NHC complexes are under evolution in our laboratory.

Acknowledgment

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Appendix A. Supplementary data

^{1}H and ^{13}C NMR spectra of NHC ligands and their ruthenium complexes. CCDC reference number 1469200 for complex **3a**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://

5. References

1. For selected reviews on N-heterocyclic carbenes, see: (a) F. E. Hahn, M. C. Jahnke, Angew. Chem., Int. Ed. 47 (2008) 3122;
   (b) S. Gu, C. Chen, W. Chen, Curr. Org. Chem. 15 (2011) 3291;
   (c) S. Díez-González, N. Marion, S. P. Nolan, Chem. Rev. 109 (2009) 3612;
   (d) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, Chem. Rev. 109 (2009) 3561;
   (e) S. Bellemin- Laponnaz, S. Dagorne, Chem. Rev. 114(2014) 8747;
   (f) A. T. Normand, K. J. Cavell, Eur. J. Inorg. Chem. (2008) 2781;
   (g) L.-A. Schaper, S. J. Hock, W. A. Herrmann, F. E. Kühn, Angew. Chem., Int. Ed. 52 (2013) 270;
   (h) E. Peris, Chem. Rev. (2017), DOI: 10.1021/acs. chemrev.6b00695.
2. A. J. Arduengo III, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
3. A. Furstner, H. Krause, L. Ackermann, C.H. Lehmann, Chem. Commun. 19 (2001) 2240.
4. (a) C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy, M. Albrecht, Organometallics, 28 (2009) 5112;
   (b) S. Horn, C. Gandolfi, M. Albrecht, Eur. J. Inorg. Chem. (2011), 2863;
   (c) S. Horn, M. Albrecht, Chem. Commun. 47 (2011) 8802.
5. L. Benhamou, J. Wolf, V. Cesar, A. Labande, R. Poli, N. Lugan, G. Lavigne, Organometallics, 28 (2009) 6981.
6. (a) J. A. Reingold, S. U. Son, S. B. Kim, C. A. Dullaghan, M. Oh, P. C. Frake, G. B. Carpenter, D. A. Sweigart, Dalton Trans. (2006) 2385;
   (b) N. Marion, S. P. Nolan, Acc. Chem. Res. 41 (2008) 1440;
   (c) M. Jeganmohan, C. H. Cheng, Chem.–Eur. J. 14 (2008) 10876;
   (d) S. Diez-Gonzalez, S. P. Nolan, Acc. Chem. Res. 41 (2008) 349;
   (e) G. C. Vougioukalakis, R. H. Grubbs, Chem. Rev. 110 (2009) 174.

7. (a) B. Marciniec, Coord. Chem. Rev. 249(2005) 2374;
(b) E. Colacino, J. Martinez, F. Lamaty, Coord. Chem. Rev. 251 (2007) 726;
(c) E. Jiménez-Núñez, A. M. Echavarren, Chem. Rev. 108 (2008) 3326;
(d) A. Fürstner, Chem. Soc. Rev. 38 (2009) 3208;
(e) A. Sivaramakrishna, H. S. Clayton, M. M. Mogorosi, J. R. Moss, Coord. Chem. Rev. 254 (2010) 2904;
(f) W. H. Zhang, S. W. Chien, T. S. A. Hor, Coord. Chem. Rev. 255(2011) 1991.
8. (a) Z. Q. Weng, S. H. Teo, T. S. A. Hor, Acc. Chem. Res. 40 (2007) 676;
(b) K. E. Neo, H. V. Huynh, L. L. Koh, W. Henderson, T. S. A. Hor, Dalton Trans. (2007) 5701;
(c) J. Zhang, A. F. Li, T. S. A. Hor, Dalton Trans. (2009) 9327;
(d) F. Li, T. S. A. Hor, Adv. Synth. Catal. 350 (2008) 2391.
9. (a) A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27;
(b) C. Muller, D. Vos, P. Jutzi, J. Organomet. Chem. 600 (2000) 127;
(c) P. Braunstein, F. Naud, Angew. Chem., Int. Ed. 40 (2001) 680;
(d) P. Y. Shi, Y. H. Liu, S. M. Peng, S. T. Liu, Organometallics, 21 (2002) 3203;
(e) C. Foltz, B. Stecker, G. Marconi, S. Bellemin-Laponnaz, H. Wadepohi, L. H. Gade, Chem. Commun. (2005) 5115;
(f) D. B. Grotjahn, Y. Gong, L. Zakharov, J. A. Golen, A. L. Rheingold, J. Am. Chem. Soc. 128 (2006) 438;
(g) H. M. Lee, C. C. Lee, P. Y. Cheng, Curr. Org. Chem. 11 (2007) 1491;
(h) S. Wurtz, F. Glorius, Acc. Chem. Res. 41 (2008) 1523.
10. (a) M. S. Sanford, J. A. Love, R. H. Grubbs, J. Am. Chem. Soc. 123 (2001) 6543;
(b) S. F. Vyboishchikov, M. Bühl, W. Thiel, Chem.–Eur. J. 8 (2002) 3962;
(c) D. Karshtedt, J. H. Koh, M. R. Gagné, Org. Lett. 6 (2004) 3013;
(d) P. E. Romero, W. E. Piers, J. Am. Chem. Soc. 127 (2005) 5032;
(e) G. L. J. Bar, G. C. Lloyd-Jones, K. I. Booker-Milburn, J. Am. Chem. Soc. 127 (2005) 7308;
(f) S. H. Hong, A. G. Wenzel, T. T. Salguero, M. W. Day, R. H. Grubbs, J. Am. Chem. Soc. 129 (2007) 7961;

(g) L. Canovese, F. Visentin, C. Santo, G. Chessa, V. Bertolasi, Organometallics, 29 (2010) 3027.

11. F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, Organometallics, 24 (2005) 2203.
12. D. R. Anderson, D. D. Hickstein, D. J. O'Leary and R. H. Grubbs, J. Am. Chem. Soc. 128 (2006) 8386;
13. (a) F. E. Hahn, N. Meier, T. Pape, Z. Naturforsch. 61b (2006) 820;
    (b) H. V. Huynh, N. Meier, T. Pape, F. E. Hahn, Organometallics, 25 (2006) 3012;
    (c) X. Han, L. L. Koh, Z. Weng, T. S. A. Hor, Dalton Trans. (2009) 7248;
    (d) X. Han, L. L. Koh, Z. Weng, T. S. A. Hor, Organometallics, 29 (2010) 2403.
14. (a) S. Werkmeister, K. Junge, M. Beller, Org. Process Res. Dev. 18 (2014) 289.
    (b) H. T. Teunissen, C. J. Elsevier, Chem. Commun. (1998) 1367;
    (c) U. Matteoi, G. Menchi, M. Bianchi, P. Frediani, F. Piacenti, J. Organomet. Chem. 498 (1995) 177;
    (d) H. T. Teunissen, C. J. Elsevier, Chem. Commun. (1997) 667;
    (e) K. Nomura, H. Ogura, Y. Imanishi, J. Mol. Catal. A, 178 (2002) 105.
15. G. A. Filonenko, M. J. B. Aguila, E. N. Schulpen, R. van Putten, J. Wiecko, C. Muller, L. Lefort, E. J. M. Hensen, E. A. Pidko, J. Am. Chem. Soc. 137 (2015) 7620.
16. O. Ogata, Y. Nakayama, H. Nara, M. Fujiwhara, Y. Kayaki, Org. Lett. 18 (2016) 3894.
17. (a) M. Nirmala, G. Prakash, P. Viswanathamurthi, J. G. Malecki,J. Mol. Catal. A: Chem. 403 (2015) 15;
    (b) M. Nirmala, G. Prakash, R. Ramachandran, P. Viswanathamurthi, J. G. Malecki, W. Linert, J. Mol. Catal. A: Chem. 397 (2015) 56;
    (c) M. Nirmala, G. Saranya, P. Viswanathamurthi, Inorg. Chim. Acta, 442 (2016) 134;
    (d) M. Nirmala, P. Viswanathamurthi, J. Chem. Sci. 128 (2016) 9;
    (e) M. Nirmala, P. Viswanathamurthi, J. Chem. Sci. 128 (2016) 1725;
    (f) M. Nirmala, G. Saranya, P. Viswanathamurthi, R. Bertani, P. Sgarbossa, J. G. Malecki, J. Organomet. Chem. 831 (2017) 1.
18. R. A. Haque, A. W. Salman, S. Budagumpi, A. Al-Ashraf Abdullahb, A. M. S. Abdul Majid, Metallomics, 5 (2013) 760.
19. C. del Pozo, M. Iglesias, F. Sánchez, Organometallics, 30 (2011) 2180.

20. G. M. Sheldrick, Acta Crystallogr. Sect. A. 64 (2008) 112.

21. E.F. Hahn, B. Heidrich, A. Hepp, T. Pape, J. Organomet. Chem. 692 (2007) 4630.

22. (a) F.E. Hahn, B. Heidrich, T. Pape, A. Hepp, M. Martin, E. Sola, L.A. Oro, Inorg. Chim. Acta, 359 (2006) 4840;

(b) H.V. Huynh, N. Meier, T. Pape, F.E. Hahn, Organometallics, 25 (2006) 3012;

(c) M. Tamm, F.E. Hahn, Inorg. Chim. Acta 288 (1999) 47.

23. (a) M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, Organometallics,22 (2003) 1110.

(b) X. Cheng, Y. Lu, H. J. Xu, Y. Z. Li, X. T. Chen, Z. L. Xue, Inorg. Chim. Acta 363 (2010) 430-437.

(c) F. L. Zeng, Z. K. Yu, Organometallics,27 (2008) 6025-6028.

24. (a) H. M. J. Wang, Lin, I. J. B, Organometallics,17 (1998) 972.

(b) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, Organometallics,22 (2003) 1663.

(c) P. L. Arnold, A. C. Scarisbrick, Organometallics, 23 (2004) 2519.

(d) M. Poyatos, A. Maisse-Franc-ois, S. Bellemin-Laponnaz, E. Peris, L. H. Gade, J. Organomet. Chem. 691 (2006) 2713.

(e) P. Mathew, A. Neels, M. Albrecht, J. Am. Chem. Soc. 130 (2008) 13534.

25. R. Cariou, C. Fischmeister, L. Toupet, P. H. Dixneuf, Organometallics, 25 (2006) 2126.

26. E. Brunner, J. Chem. Eng. Data, 30 (1985) 269.

27. S. Werkmeister, K. Junge, B. Wendt, E. Alberico, H. Jiao, W. Baumann, H. Junge, F. Gallou, M. Beller, Angew. Chem. Int. Ed. 53 (2014) 8722.

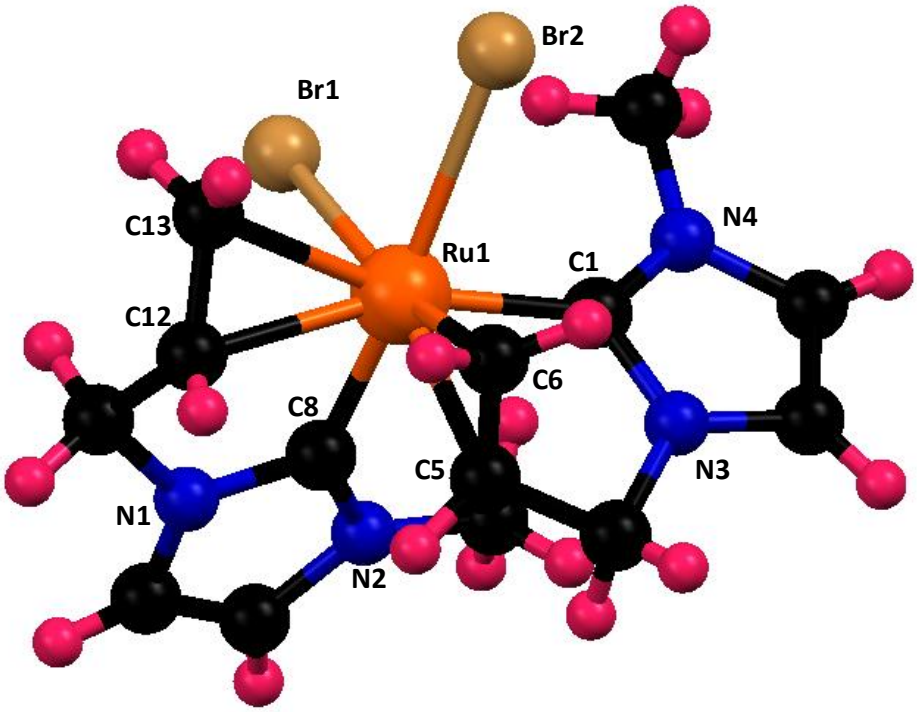


Figure 1. ORTEP representation of the X-ray crystal structure of [Ru-NHC] complex **3a**.

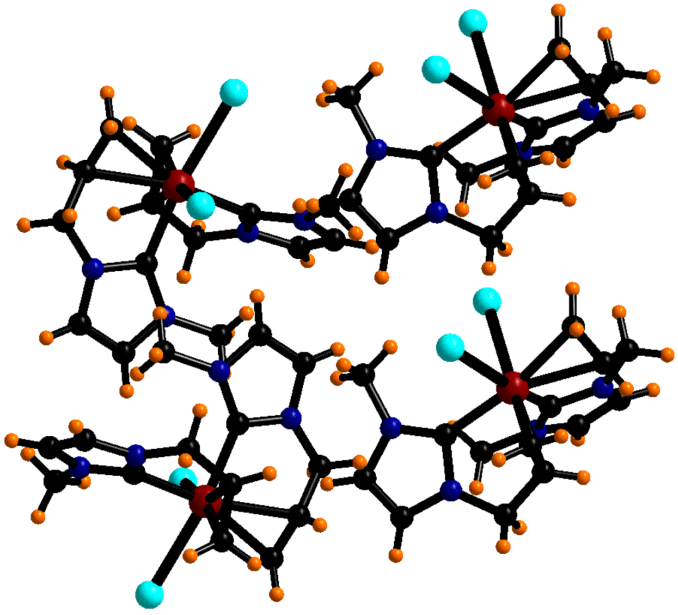


Figure 2. Packing diagram of [Ru-NHC] complex **3a**.

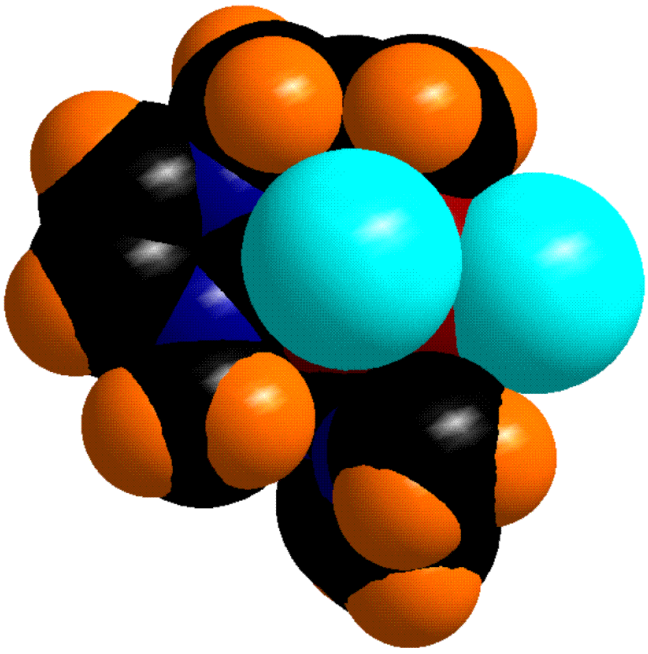


Figure 3. Space fill modeling of [Ru-NHC] complex **3a**.

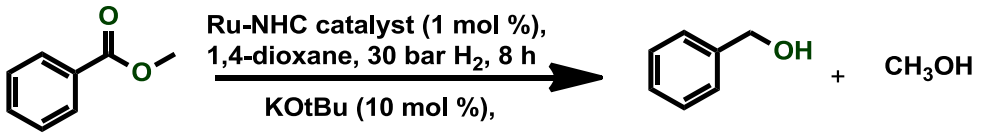
Table 1. Crystal data and structure refinement parameters of **3a**

Parameters	**3a**
Empirical formula	C_{14} H_{20} Br_2 N_4 Ru
Formula weight	505.23
Temperature (K)	295
Crystal system	Monoclinic
Space group	*P 21/c*
a/Å	11.7563(4)
b/Å	8.1471(3)
c/Å	17.5324(7)
α/°	90
β/°	90.671(4)
γ/°	90
Volume (Å^3)	1679.12(4)
Z	4
ρ_{calc}/mg mm^{-3}	1.999
Absorption coefficient (mm^{-1})	5.692
F(000)	984
Data collected	8485
Unique data	2959
R_{int}	0.0417
GOF on F^2	1.046
R_1 ($I>2\sigma(I)$)	0.0358
wR_2 ($I>2\sigma(I)$)	0.0847
R_1 values (all data)	0.0470
wR_2 values (all data)	0.0847

Table 2. Selected structural parameters of **3a**

Interatomic distances (Å)	
Ru(1)- Br(1)	2.5915(6)
Ru(1)- Br(2)	2.6404(6)
Ru(1)- C(1)	2.033(4)
Ru(1)- C(5)	2.193(4)
Ru(1)-C(6)	2.159(4)
Ru(1)-C(8)	2.045(4)
Ru(1)-C(12)	2.305(5)
Ru(1)-C(13)	2.313(5)
Bond angles(°)	
Br(1)-Ru(1)-Br(2)	87.43(2)
C(1)-Ru(1)-Br(1)	98.52(12)
C(1)-Ru(1)-Br(2)	84.08(12)
C(1)-Ru(1)-C(5)	78.08(17)
C(1)-Ru(1)-C(6)	87.09(19)
C(1)-Ru(1)-C(8)	93.18(17)
C(1)-Ru(1)-C(13)	162.66(19)
C(5)-Ru(1)- Br(1)	158.12(13)
C(5)-Ru(1)-Br(2)	113.41(13)
C(5)-Ru(1)-C(12)	84.05(19)
C(5)-Ru(1)-C(1)	107.2(2)
C(6)-Ru(1)-Br(1)	164.73(16)
C(6)-Ru(1)-Br(2)	78.99(16)
C(6)-Ru(1)-C(5)	37.01(19)
C(6)-Ru(1)-C(12)	83.5(2)
C(6)-Ru(1)-C(13)	87.9(2)
C(8)-Ru(1)-Br(1)	79.12(12)
C(8)-Ru(1)-Br(2)	165.74(12)
C(8)-Ru(1)-C(5)	79.50(17)
C(8)-Ru(1)-C(6)	114.9(2)
C(8)-Ru(1)-C(12)	75.36(18)
C(8)-Ru(1)-C(13)	103.97(19)
C(12)-Ru(1)-Br(1)	95.00(14)
C(12)-Ru(1)-Br(2)	110.86(13)
C(12)-Ru(1)-C(13)	34.12(19)
C(13)-Ru(1)-Br(1)	82.52(15)
C(13)-Ru(1)-Br(2)	78.66(14)
N(3)-C(1)-Ru(1)	117.3(3)

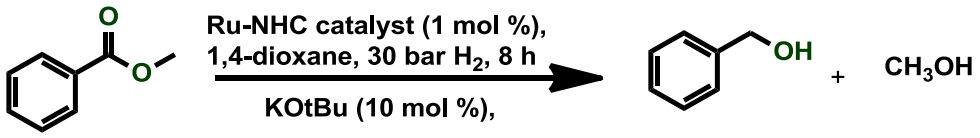
Table 3. Influence of wingtip substituent and catalyst loading on the catalytic activity of [Ru-NHC] complexes



Entry	Catalyst	Amount of catalyst (mol%)	Wingtip (R)	Time(h)	p [bar]	Yield(%)[a]
1	3a	0.5	Me	8	50	75
2	3b	0.5	^{i}Pr	8	50	86
3	3c	0.5	*t*Bu	8	50	79
4	3a	1	Me	8	50	83
5	3b	1	^{i}Pr	8	50	98
6	3c	1	*t*Bu	8	50	88
7	3a	1	Me	8	30	82
8[c]	**3b**	**1**	**^{i}Pr**	**8**	**30**	**96**
9	3b	1	^{i}Pr	8	10	79
10	3c	1	*t*Bu	8	30	86
11	-	-	-	24	30	n.r

[a] Reaction conditions: catalyst (0.5-1 mol %), KO*t*Bu (10 mol %), and 1,4-dioxane (4.0 mL), ester (1.0 mmol)
[b] Isolated yield after column chromatography.
[e] Better optimization condition.

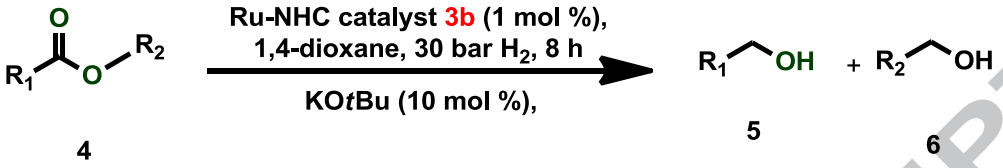
Table 4. Evaluation of conditions for hydrogenation of ester reaction using **3b**[a]

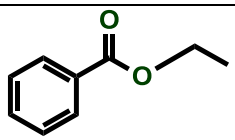
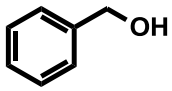
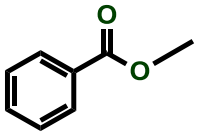
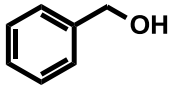
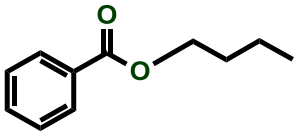
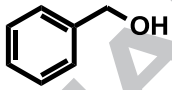
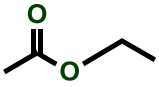
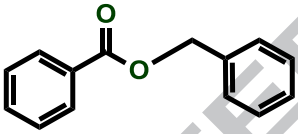
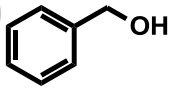
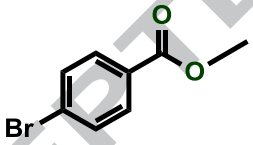
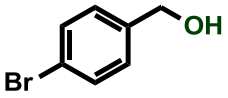
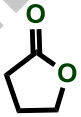
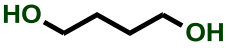
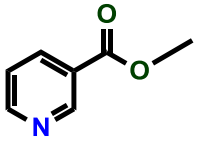
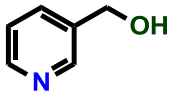
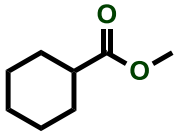
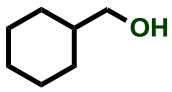
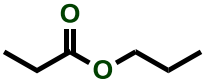


Entry	Base	Solvent	Temp (˚C)	Time (h)	Yield (%)[b]
1	K_2CO_3	1,4-dioxane	105	8	43
2	$NaHCO_3$	1,4-dioxane	105	8	28
3	$KHCO_3$	1,4-dioxane	105	8	39
4	NaOH	1,4-dioxane	105	8	61
5	KOH	1,4-dioxane	105	8	69
6[e]	**KO*t*Bu**	**1,4-dioxane**	**105**	**8**	**96**
7	KO*t*Bu	Toluene	110	12	78
8	KO*t*Bu	Acetonitrile	82	16	69
9	KO*t*Bu	1,4-dioxane	101	18	95
10	KO*t*Bu	C_2H_5OH	78	12	54
11	KO*t*Bu	DMF	150	12	52
12	KO*t*Bu	*p*-xylene	138	12	69
13	KO*t*Bu	DMSO	140	12	45
14	KO*t*Bu	H_2O	100	12	n.r
15[c]	-	1,4-dioxane	105	24	n.r
16[d]	KO*t*Bu	1,4-dioxane	105	24	n.r

[a] Reaction conditions: catalyst (0.01 mmol), KO*t*Bu (10 mol %), and solvent (4.0 mL) , ester (1.0 mmol)
[b] Isolated yield after column chromatography.
[c] The reaction was carried out without base
[d] The reaction was carried out without catalyst.
[e] Better optimization condition.

Table 5. Catalytic hydrogenation of esters[a]



S. No	Reactant	Product		Yield (5)[b] %
1[c]				94
2[c]			CH_3OH	96
3[c]				89
4			-	>99
5			-	92
6			-	96
7			-	86
8			-	95
9			-	93
10			-	77

[a] Reaction conditions: Substrate (1 mol %), catalyst (1 mol %), KO*t*Bu (10 mol %), in 1,4-dioxane were heated to 105ºC for 8 h under 30 bar H_2.

[b] Isolated yield after column chromatography.
[c] Yields of methanol and ethanol are not reported.

Graphical abstract

Olefin-tethered organoruthenium carbene complexes: Synthesis, X-ray structure and catalytic insights on hydrogenation of esters

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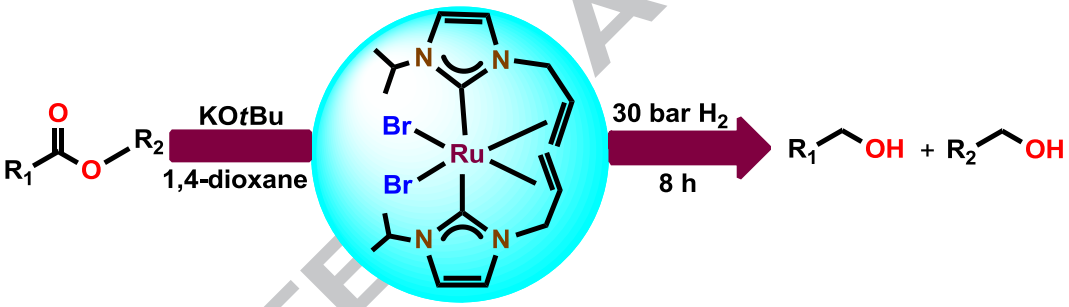

Research Highlights

- New olefin-tethered organoruthenium carbene complexes have been synthesized and epitomized.
- X-ray studies confirmed an octahedral geometry of the new complexes.
- The newly synthesized complexes catalyze the hydrogenation of esters efficiently.