

Ruthenium complexes of chelating amido-functionalized N-heterocyclic carbene ligands: Synthesis, structure and DFT studies

SACHIN KUMAR^a, ANANTHA NARAYANAN^a, MITTA NAGESWAR RAO^a,
MOBIN M SHAIKH^b and PRASENJIT GHOSH^{a,*}

^aDepartment of Chemistry and ^bNational Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
e-mail: pghosh@chem.iitb.ac.in

Abstract. Synthesis, structure and density functional theory (DFT) studies of a series of new ruthenium complexes, [1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidene]RuCl(*p*-cymene) [R = Me (**1c**), *i*-Pr (**2c**), CH₂Ph (**3c**); *p*-cymene = 4-*i*-propyltoluene] supported over *N/O*-functionalized N-heterocyclic carbene (NHC) ligands are reported. In particular, the ruthenium (**1–3c**) complexes were synthesized from the respective silver complexes, [1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidene]₂Ag⁺Cl[−] [R = Me (**1b**), *i*-Pr (**2b**), CH₂Ph (**3b**)] by the treatment with [Ru(*p*-cymene)Cl₂]₂ in 65–76% yields. The molecular structures of (**1–3c**) revealed the chelation of the N-heterocyclic carbene ligand through the carbene center and an amido sidearm of the ligand in all of the three complexes. The density functional theory studies on the ruthenium (**1–3c**) complexes indicated strong binding of the NHC ligand to the metal center as was observed from the deeply buried NHC-Ru σ -bonding molecular orbitals.

Keywords. Carbenes; ruthenium; DFT; amido-functionalized NHC.

1. Introduction

Ruthenium adds several new and interesting options to the ever-growing world of transition metal mediated organic methodologies, in constant demand for meeting the everyday challenges of organic synthesis.¹ For instance, the ruthenium complexes display selective C–H activation reactions of particular relevance to synthesizing biaryl and heterocyclic frameworks,² and thereby providing useful alternatives to the already overstretched palladium mediated carbon–carbon cross-coupling reactions.³ As such, the C–H activations, and more so the selective C–H activation ones, fall among the difficult but much desired challenges, currently confronting the world of synthesis today.⁴ Apart from the elegant selective C–H activation reactions, the ruthenium engages in a variety of other synthetically important transformations namely, asymmetric transfer hydrogenation reactions,⁵ metathesis,⁶ olefin epoxidation reactions,⁷ hydroformylation reactions,⁸ electrooxidation reactions,⁹ facial cycloaddition of azides with terminal alkynes regioselectively¹⁰ etc. to name a few.

The phenomenal success of the N-heterocyclic carbenes in homogeneous catalysis, has also made them

increasingly popular as ligands for stabilizing transition metal complexes.¹¹ Easy tunability of the sterics and the electronic environments through constant variation of the substituents on the nitrogen atom of the imidazole ring, make these ligands versatile in stabilizing a variety of transition metal complexes in varied oxidation states. With our interests being in biomedical¹² and catalytic applications¹³ of transition metal complexes of N-heterocyclic carbene ligands,¹⁴ we became involved in synthesizing its ruthenium complexes for their potential utility in chemical catalysis.

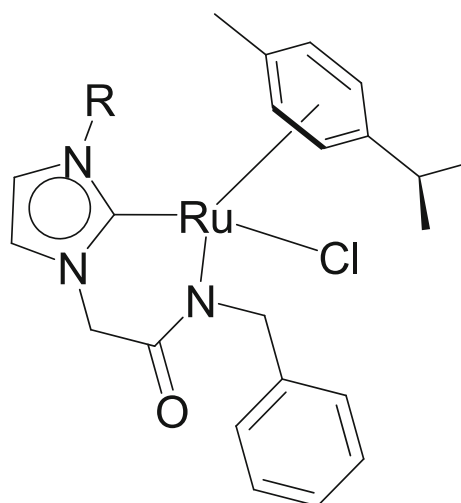
In this contribution, we report a series of ruthenium complexes, [1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidene]RuCl(*p*-cymene) [R = Me (**1c**), *i*-Pr (**2c**), CH₂Ph (**3c**); *p*-cymene = 4-*i*-propyltoluene], supported over *N/O*-functionalized N-heterocyclic carbene ligands (figure 1). The Ru–NHC interaction in the (**1–3c**) complexes have been investigated using density functional theory (DFT) studies.

2. Experimental

2.1 General procedures

All manipulations were carried out using a combination of a glove box and standard Schlenk techniques.

*For correspondence



R = Me (**1c**), *i*-Pr (**2c**), CH₂Ph (**3c**)

Figure 1. Ruthenium (**1–3c**) complexes of chelating amido-functionalized N-heterocyclic carbene ligands.

Solvents were purified and degassed by standard procedures. RuCl₃•xH₂O was purchased from SD-fine Chemicals (India) and used without any further purification. The **1a**,¹⁵ (**2–3b**)¹⁶ and [Ru(*p*-cymene)Cl₂]₂¹⁷ were synthesized according to reported literature procedures. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. ¹H NMR peaks are labelled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-ToF spectrometer. The electronic spectra were recorded in acetonitrile by using Jasco V-570 UV/VIS/NIR Spectrophotometer. Cyclic voltammetric measurements were carried out using a BAS Epsilon electrochemistry system. Elemental Analyses were carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data for (**1–3c**) were collected on an Oxford Diffraction Excalibur-S diffractometer and crystal data collection and refinement parameters are summarized in Supporting Information table S1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on *F*² with SHELXTL (Version 6.10).¹⁸

2.2 Synthesis of {[1-(methyl)-3-N-(benzylacetamido)imidazol-2-ylidene]₂Ag⁺Cl⁻ (**1b**)}

A mixture of 1-(methyl)-3-N-(benzylacetamido)imidazolium chloride (**1a**) (4.37 g, 16.4 mmol) and

Ag₂O (2.02 g, 8.72 mmol) in dichloromethane (*ca.* 40 mL) was stirred at room temperature for 4 h. The reaction mixture was then filtered and the solvent was removed under vacuum to give the product **1b** as off-white solid (2.31 g, 47%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 9.36 (br, 1H, NH), 7.36 (br, 1H, NCHCHN), 7.29 (br, 2H, C₆H₅), 7.11 (m, 3H, C₆H₅), 6.94 (br, 1H, NCHCHN), 5.29 (br, CH₂), 4.36 (s, 2H, CH₂), 3.77 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25°C): δ 182.3 (NCN-Ag), 167.2 (CO), 138.5 (*ipso*-C₆H₅), 128.4 (*m*-C₆H₅), 128.1 (*o*-C₆H₅), 126.9 (*p*-C₆H₅), 123.4 (NCHCHN), 121.6 (NCHCHN), 53.9 (COCH₂), 43.2 (CH₂NH), 38.8 (CH₃). IR (KBr Pellet): 1676 (ν_{CO}) cm⁻¹. Anal. calcd. for C₂₆H₃₀AgN₆O₂Cl•CH₂Cl₂: C, 47.22; H, 4.70; N, 12.24. Found: C, 47.46; H, 5.03, N, 11.84.

2.3 Synthesis of [1-(methyl)-3-N-(benzylacetamido)imidazol-2-ylidene]Ru(*p*-cymene)Cl (**1c**)

A mixture of {[1-(methyl)-3-{N-(benzylacetamido)imidazol-2-ylidene}]₂Ag⁺Cl⁻ (**1b**) (0.302 g, 0.502 mmol) and [Ru(*p*-cymene)Cl₂]₂ (0.307 g, 0.502 mmol) was dissolved in dichloromethane (*ca.* 40 mL) and was stirred at room temperature for 6 h, when the formation of an off-white AgCl precipitate was observed. The reaction mixture was then filtered and the solvent was removed under vacuum to yield the crude product as a brown solid. The crude product **1c** was purified by column chromatography on a silica gel by elution with a CHCl₃/CH₃OH (v/v 10:1) mixed medium to give the product **1c** as brown solid (0.181 g, 72%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 7.50 (d, 2H, ³J_{HH} = 8 Hz, *o*-C₆H₅), 7.35 (m, 3H, *m/p*-C₆H₅), 7.00 (d, 1H, ³J_{HH} = 2 Hz, NCHCHN), 6.97 (d, 1H, ³J_{HH} = 2 Hz, NCHCHN), 5.31 (d, 1H, ²J_{HH} = 15 Hz, CH₂), 5.13 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.89 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.83 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.82 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.46 (s, 2H, CH₂), 4.45 (d, 1H, ²J_{HH} = 15 Hz, CH₂), 3.99 (s, 3H, CH₃), 2.45 (sept, 1H, ³J_{HH} = 7 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 1.98 (s, 3H, *p*-CH₃C₆H₄CH(CH₃)₂), 1.11 (d, 3H, ³J_{HH} = 7 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 0.88 (d, 3H, ³J_{HH} = 7 Hz, *p*-CH₃C₆H₄CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25°C): δ 175.2 (NCN-Ru), 169.7 (CO), 143.6 (*ipso*-C₆H₅), 128.7 (*m*-C₆H₅), 128.0 (*o*-C₆H₅), 126.1 (*p*-C₆H₅), 122.8 (NCHCHN), 122.0 (NCHCHN), 107.4 (*ipso-p*-CH₃C₆H₄CH(CH₃)₂), 100.1 (*ipso-p*-CH₃C₆H₄CH(CH₃)₂), 88.6 (*p*-CH₃C₆H₄CH(CH₃)₂), 85.2 (*p*-CH₃C₆H₄CH(CH₃)₂),

83.0 (*p*-CH₃C₆H₄CH(CH₃)₂), 81.9 (*p*-CH₃C₆H₄CH(CH₃)₂), 55.5 (COCH₂), 55.4 (CH₂NH), 37.8 (CH₃), 31.5 (*p*-CH₃C₆H₄CH(CH₃)₂), 24.9 (*p*-CH₃C₆H₄CH(CH₃)₂), 20.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 18.7 (*p*-CH₃C₆H₄CH(CH₃)₂). IR (KBr Pellet): 1686 (ν_{CO}) cm⁻¹. Anal. calcd. for C₂₃H₂₈RuN₃OCl: C, 55.36; H, 5.66; N, 8.42. Found: C, 55.35; H, 6.02; N, 8.34.

2.4 Synthesis of [1-(*i*-propyl)-3-*N*-(benzylacetamido)imidazol-2-ylidene]Ru(*p*-cymene)Cl (**2c**)

A mixture of {[1-(*i*-propyl)-3-{*N*-(benzylacetamido)imidazol-2-ylidene}]₂Ag⁺Cl⁻ (**2b**) (0.331 g, 0.505 mmol) and [Ru(*p*-cymene)Cl₂]₂ (0.308 g, 0.505 mmol) was dissolved in dichloromethane (*ca.* 40 mL) and was stirred at room temperature for 6 h, when the formation of an off-white AgCl precipitate was observed. The reaction mixture was then filtered and the solvent was removed under vacuum to yield the product **2c** as a brown solid. The crude product **2c** was purified by column chromatography on a silica gel by elution with a CHCl₃/CH₃OH (v/v 10:1) mixed medium to give the product **2c** as brown solid (0.202 g, 76%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 7.47 (d, 2H, ³J_{HH} = 7 Hz, *o*-C₆H₅), 7.32 (br, 2H, *m*-C₆H₅), 7.29 (br, 1H, NCHCHN), 7.21 (t, 1H, ³J_{HH} = 7 Hz, *p*-C₆H₅), 6.95 (s, 1H, NCHCHN), 5.23 (d, 1H, ²J_{HH} = 15 Hz, CH₂), 5.10 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 5.10 (sept, 1H, ³J_{HH} = 7 Hz, CH(CH₃)₂), 4.84 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.81 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.70 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.43 (s, 2H, CH₂), 4.37 (d, 1H, ²J_{HH} = 15 Hz, CH₂), 2.45 (sept, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 1.97 (s, 3H, *p*-CH₃C₆H₄CH(CH₃)₂), 1.55 (d, 3H, ³J_{HH} = 7 Hz, CH(CH₃)₂), 1.50 (d, 3H, ³J_{HH} = 7 Hz, CH(CH₃)₂), 1.11 (d, 3H, ³J_{HH} = 7 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 0.86 (d, 3H, ³J_{HH} = 7 Hz, *p*-CH₃C₆H₄CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25°C): δ 175.4 (NCN-Ru), 169.9 (CO), 143.8 (*ipso*-C₆H₅), 128.8 (*m*-C₆H₅), 128.2 (*o*-C₆H₅), 126.3 (*p*-C₆H₅), 122.9 (NCHCHN), 122.2 (NCHCHN), 107.6 (*ipso*-*p*-CH₃C₆H₄CH(CH₃)₂), 100.3 (*ipso*-*p*-CH₃C₆H₄CH(CH₃)₂), 88.8 (*p*-CH₃C₆H₄CH(CH₃)₂), 85.4 (*p*-CH₃C₆H₄CH(CH₃)₂), 83.2 (*p*-CH₃C₆H₄CH(CH₃)₂), 82.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 56.7 (COCH₂), 55.6 (CH₂NH), 52.8 (CH(CH₃)₂), 52.5 (CH(CH₃)₂), 31.6 (*p*-CH₃C₆H₄CH(CH₃)₂), 25.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 23.4 (CH(CH₃)₂), 23.2 (CH(CH₃)₂), 20.3 (*p*-CH₃C₆H₄CH(CH₃)₂). IR (KBr Pellet): 1686 (ν_{CO})

cm⁻¹. Anal. calcd. for C₂₅H₃₂RuN₃OCl•0.5CH₂Cl₂: C, 53.78; H, 5.84; N, 7.38. Found: C, 53.54; H, 6.23; N, 6.87.

2.5 Synthesis of [1-(benzyl)-3-*N*-(benzylacetamido)imidazol-2-ylidene]Ru(*p*-cymene)Cl (**3c**)

A mixture of {[1-(benzyl)-3-{*N*-(benzylacetamido)imidazol-2-ylidene}]₂Ag⁺Cl⁻ (**3b**) (0.421 g, 0.557 mmol) and [Ru(*p*-cymene)Cl₂]₂ (0.170 g, 0.278 mmol) was dissolved in dichloromethane (*ca.* 40 mL) and was stirred at room temperature for 6 h, when the formation of an off-white AgCl precipitate was observed. The reaction mixture was then filtered and the solvent was removed under vacuum to yield the crude product as a brown solid. The crude product **3c** was purified by column chromatography on a silica gel by elution with a CHCl₃/CH₃OH (v/v 10:1) mixed medium to give the product **3c** as brown solid (0.208 g, 65%). ¹H NMR (CDCl₃, 400 MHz, 25°C): δ 7.50 (br, 1H, C₆H₅), 7.48 (br, 1H, C₆H₅), 7.41–7.39 (br, 2H, C₆H₅), 7.36–7.34 (br, 3H, C₆H₅), 7.32 (br, 2H, C₆H₅), 7.29 (br, 1H, C₆H₅), 7.03 (br, 1H, NCHCHN), 6.91 (br, 1H, NCHCHN), 5.67 (d, 1H, ²J_{HH} = 16 Hz, CH₂), 5.55 (d, 1H, ²J_{HH} = 16 Hz, CH₂), 5.29 (d, 1H, ³J_{HH} = 16 Hz, CH₂), 4.91 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.75 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.67 (d, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 4.48 (s, 2H, CH₂), 4.44 (br, 1H, *p*-CH₃C₆H₄CH(CH₃)₂), 4.33 (d, 1H, ³J_{HH} = 16 Hz, CH₂), 2.46 (sept, 1H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 1.98 (s, 3H, *p*-CH₃C₆H₄CH(CH₃)₂), 1.11 (d, 3H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂), 0.88 (d, 3H, ³J_{HH} = 6 Hz, *p*-CH₃C₆H₄CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25°C): δ 175.9 (NCN-Ru), 169.8 (CO), 143.0 (*ipso*-C₆H₅), 136.90 (*ipso*-C₆H₅), 128.9 (*m*-C₆H₅), 128.2 (*m*-C₆H₅), 128.1 (*o*-C₆H₅), 128.0 (*o*-C₆H₅), 127.9 (*p*-C₆H₅), 127.1 (*p*-C₆H₅), 122.1 (NCHCHN), 121.9 (NCHCHN), 107.8 (*ipso*-*p*-CH₃C₆H₄CH(CH₃)₂), 99.4 (*ipso*-*p*-CH₃C₆H₄CH(CH₃)₂), 87.6 (*p*-CH₃C₆H₄CH(CH₃)₂), 84.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 83.5 (*p*-CH₃C₆H₄CH(CH₃)₂), 82.3 (*p*-CH₃C₆H₄CH(CH₃)₂), 55.2 (COCH₂), 53.5 (CH₂NH), 51.6 (CH₂Ph), 31.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 24.4 (*p*-CH₃C₆H₄CH(CH₃)₂), 20.1 (*p*-CH₃C₆H₄CH(CH₃)₂), 18.5 (*p*-CH₃C₆H₄CH(CH₃)₂). Anal. calcd. for C₂₉H₃₂RuN₃OCl: C, 60.56; H, 5.61; N, 7.31. Found: C, 60.35; H, 5.85; N, 7.60.

3. Computational methods

Density functional theory calculations were performed on the ruthenium (**1–3**)**c** complexes using GAUSSIAN 03¹⁹ suit of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) has been employed in the study.²⁰ The SDD valence basis set was used for ruthenium atom,²¹ while all other atoms are treated at the 6-31G(d) basis set.²² All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. A tight SCF convergence criteria (10^{-8} a.u.) was used for all calculations. Natural Bond Orbital (NBO) analysis was performed using the NBO 3.1²³ program implemented in the GAUSSIAN 03 package.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the Charge Decomposition Analysis (CDA)²⁴ which is a valuable tool in analysing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.²⁵ The orbital contributions in the ruthenium (**1–3**)**c** complexes can be divided into three parts:

- (i) σ -donation from the $[\text{NHC}]^- \rightarrow [\text{Ru}(p\text{-cymene})\text{Cl}]^+$ fragments,

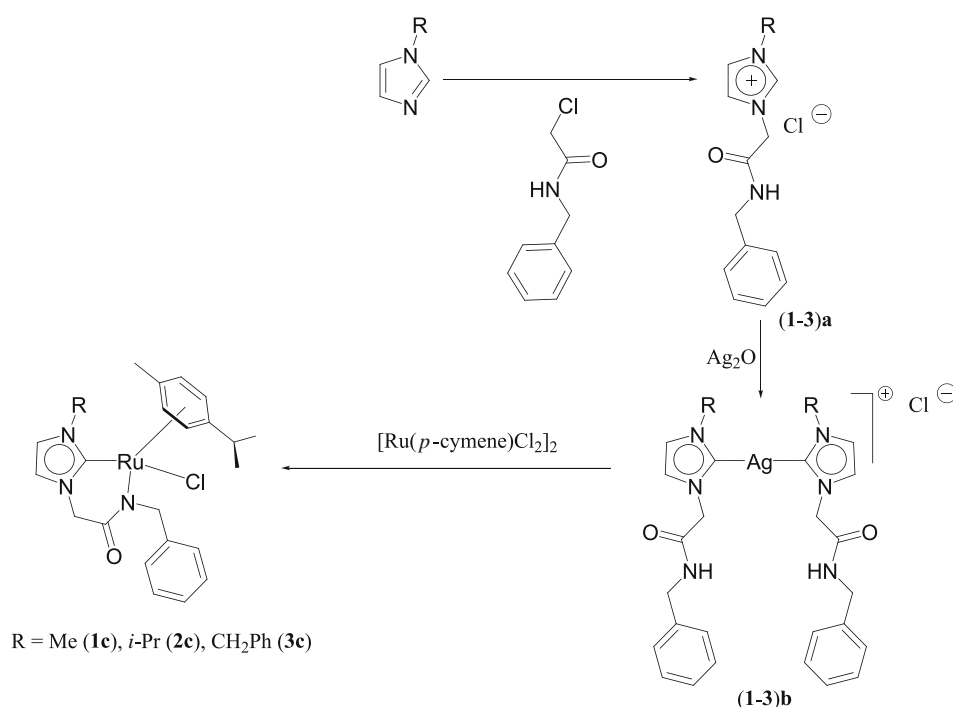
- (ii) π -back donation from $[\text{NHC}]^- \leftarrow [\text{Ru}(p\text{-cymene})\text{Cl}]^+$ fragments and
- (iii) repulsive polarization (r).

The CDA calculations were performed using the program *AOMix*,²⁶ using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the *AOMix* program. The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs respectively), construction of orbital interaction diagrams, the CDA were performed using the *AOMix*-CDA.²⁷

4. Results and discussion

A series of ruthenium (**1–3**)**c** complexes was stabilized over amido-functionalized N-heterocyclic carbene ligands namely, [1-(*R*)-3-*N*-(benzylacetamido)imidazol-2-ylidene] [*R* = Me, *i*-Pr and CH_2Ph]. Specifically, the ruthenium (**1–3**)**c** complexes were synthesized by a commonly used carbene transfer route from their respective silver (**1–3**)**b** complexes by treatment with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ in 65–76% yield (scheme 1).

As expected, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the (**1–3**)**c** complexes showed the appearance of a slightly



Scheme 1. Synthesis of Ru–NHC (**1–3**)**c** complexes

upfield shifted (NCN-Ru) resonance at *ca.* 175.2–175.9 ppm. In the ^1H NMR spectrum, the amido (CONH) resonance was conspicuous by its absence, unlike in the silver (**1–3**)**b** complexes, for which it appeared at *ca.* 9.12–9.36 ppm and thus suggestive of ligand chelation to the metal center after deprotonation of the amido sidearm moiety. It is worth noting that the deprotonation of the amido-sidearm resulting in the chelation to the ruthenium center occurred in the absence of any additional base. Interestingly, the (CH_2) moieties in the (**1–3**)**c** complexes were found to be diastereotopic in nature as it appeared as two set of doublets exhibiting two-bond geminal coupling ($^2J_{\text{HH}}$) of 14–16 Hz in the ^1H NMR spectra.

The molecular structures of the ruthenium (**1–3**)**c** complexes showed chelation of the N-heterocyclic carbene through an N-amido functionalized sidearm and a carbene moiety to the metal center (figure 2 and see Supporting Information figures S1–S2 and table S1). The aryl group of the cymene moiety was seen bound in a η^6 -fashion to the metal center in these complexes. The (**1–3**)**c** complexes, having chelated amido-functionalized N-heterocyclic carbene ligands, closely resemble their non-chelated counterparts.²⁸

The Ru–C_{carbene} bond distances in (**1c**) [2.0172(19) Å], (**2c**) [2.033(5) Å] and (**3c**) [2.019(3) Å], were

in close agreement with the sum of individual covalent radii of Ru and C atoms (2.018 Å)²⁹ and with other reported ruthenium N-heterocyclic carbene complexes, namely, $[\text{RuCl}\{2-(4,4\text{-dimethyl-4,5-dihydrooxazol-2-yl})-(3\text{-mesityl})\text{imidazolidene}\}(p\text{-cymene})\text{PF}_6]$ [2.038(3) Å],²⁹ $[\text{RuCl}\{2-(4(\text{S})\text{-}t\text{-butyl-4,5-dihydrooxazol-2-yl})-(3\text{-mesityl})\text{imidazolidene}\}(p\text{-cymene})\text{PF}_6]$ [2.03(2) Å],²⁹ and $[\text{ethylene-bis}(\text{N-methylimidazolidene})\text{RuCl}(\text{PF}_6)]$ [2.033(15) Å].³⁰ Additionally, the Ru–Cl bond and Ru–C_{centroid} bond distances in (**1c**) [2.4256(14) Å and 1.706 Å], (**2c**) [2.4325(8) Å and 1.712 Å] and (**3c**) [2.4404(7) Å and 1.719 Å] were comparable to the $[\text{RuCl}\{2-(4,4\text{-dimethyl-4,5-dihydrooxazol-2-yl})-(3\text{-mesityl})\text{imidazolidene}\}(p\text{-cymene})\text{PF}_6]$ [2.420(1) Å and 1.708 Å].²⁹ Along the same line, the Ru–N_{amido} bond distances in (**1c**) [2.125(5) Å], (**2c**) [2.126(2) Å] and (**3c**) [2.1074(16) Å] also match well with the other ruthenium complexes namely, $[\text{hydridotris}(\text{pyrazolyl})\text{borate}]\text{Ru}[\text{P}(\text{OMe})_3]_2(\text{NHPh})$ [2.1012(15) Å]³¹ and $[2-(\text{benzimidazol-2-yl})-6-(3,5\text{-dimethylpyrazol-1-yl})\text{pyridine}]\text{RuCl}(\text{PPh}_3)_2$ [2.088(17) Å].³²

The electronic spectra of the complexes (**1–3**)**c** in acetonitrile showed a strong absorption at 242–249 nm (2223–2371 $\text{M}^{-1}\text{cm}^{-1}$) attributed to a ligand based transition along with two shoulders appear at

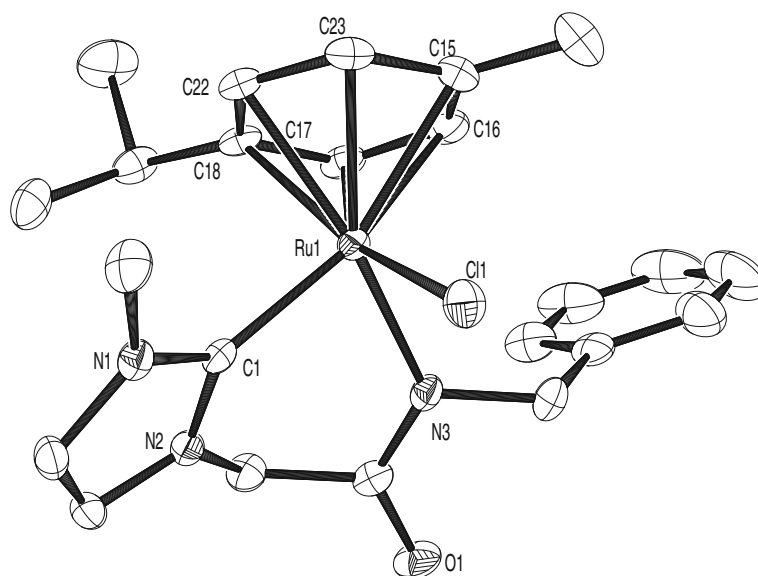


Figure 2. ORTEP diagram of **1c** with thermal ellipsoids drawn at 50% probability level. Selected bond length (Å) and bond angles (°): Ru1–C1 2.0172(19), Ru1–N3 2.1074(16), Ru1–Cl1 2.4404(7), C1–Ru1–N3 84.31(7), C1–Ru1–Cl1 87.31(6), N1–C1–N2 104.02(16).

392–395 nm ($314\text{--}373\text{ M}^{-1}\text{ cm}^{-1}$) and 459–463 nm ($249\text{--}286\text{ M}^{-1}\text{ cm}^{-1}$) (see Supporting Information figures S3–S5 and table S2). Furthermore, the electrochemical behaviour of (1–3)c complexes as analysed by cyclic voltammetry studies showed two quasi-reversible oxidation responses on the positive side of SCE at 0.93–0.94 V, attributable to a Ru(II)–Ru(III) oxidation process,³³ and at 1.41–1.44 V, attributable to a Ru(III)–Ru(IV) oxidation process³⁴ (see Supporting Information figures S6–S8 and table S3).

The NHC–Ru interaction in the (1–3)c complexes has been investigated using density functional theory (DFT) studies by computing the minimum energy structure at the B3LYP level of theory using 6-31G(d)/SDD basis set through geometry optimization using atomic coordinates adopted from the X-ray analysis and subsequently undertaking the single point calculation. The carbene–Ru interaction was probed by performing the post-wave function analysis using the Natural Bond Orbital (NBO) calculations on the (1–3)c complexes as well as on the corresponding N-heterocyclic carbene ligand and the metal ion fragments (see Supporting Information tables S4–S12).

Both the natural and Mulliken charge analysis showed significant increase of electron density at the metal center in the (1–3)c complexes with subsequent reduction of the same on the free NHC ligand fragment (see Supporting Information tables S4–S6). The Ru–NHC bond in (1–3)c involved an interaction of the sp^2

hybridized carbene carbon orbital with a sd hybridized ruthenium orbital as observed from NBO analysis studies (see Supporting Information tables S7–S8).

The Charge Decomposition Analysis (CDA) performed on the (1–3)c complexes provided insight about the relative extent of NHC ligand to metal σ -donation denoted by d and the metal to NHC ligand π -back donation denoted by b , occurring in these complexes (see Supporting Information table S9). The high d/b ratio observed for the 1c (5.63), 2c (5.96) and 3c (5.28) complexes suggested the predominance of the σ -interaction in the carbene–Ru bond, and which is in agreement with the as such good σ -donation ability of the N-heterocyclic carbene ligands. It is worth noting that the σ -donation (d) and π -back donation (b) values obtained for (1–3)c represent the donation occurring between a metal center of the $[\text{Ru}(p\text{-cymene})\text{Cl}]^+$ and a functionalized NHC-ligand fragment. This particular interaction is a composite of two interactions namely a $\text{Ru}\text{--}\text{C}_{\text{carbene}}$ interaction and a $\text{Ru}\text{--}\text{N}_{\text{amido}}$ interaction that arise out of chelation of the NHC ligand to the metal center through an N-amido sidearm and a carbene moiety.

The molecular orbital (MO) correlation diagram, constructed from the individual fragment molecular orbitals (FMOs) of the free NHC ligand and the $[\text{Ru}(p\text{-cymene})\text{Cl}]^+$ fragments using AOMix program,³⁵ provided useful insights on the nature of the Ru–NHC interaction in the (1–3)c complexes (figure 3 and see

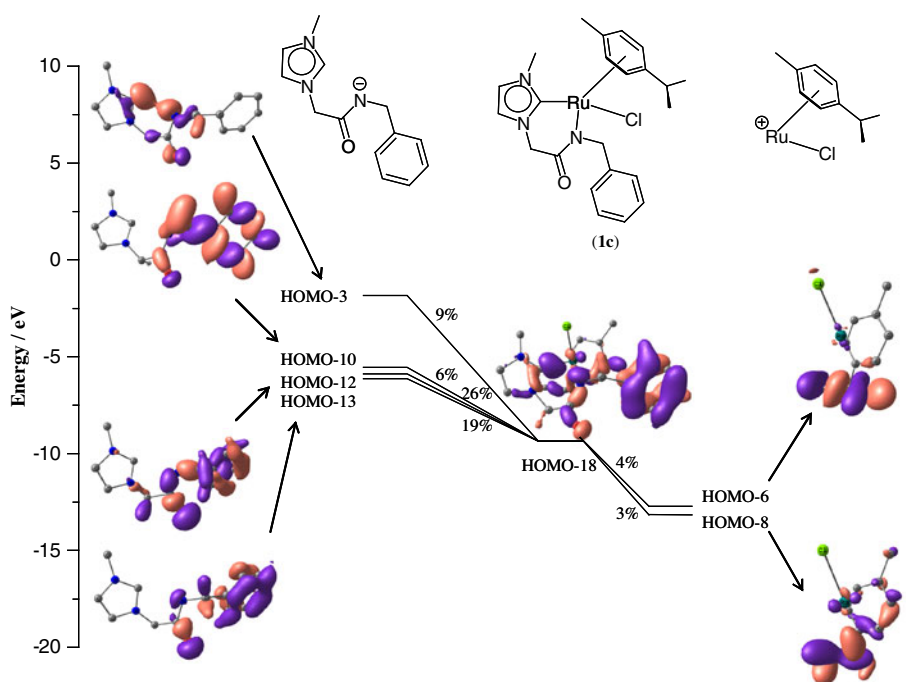


Figure 3. Simplified orbital interaction diagram showing the major contribution of NHC–ruthenium bond in 1c.

Supporting Information figures S9–S10). Of particular interest are the molecular orbitals representing the Ru–NHC σ -interaction that comprised of the interaction of the carbene lone pair with the ruthenium based orbital namely, **1c** (HOMO-18), **2c** (HOMO-18) and **3c** (HOMO-20). In this regard, it is worth noting that these Ru–NHC σ -bonding molecular orbitals, by virtue of being low lying, remain unaffected by the incoming electrophiles or nucleophiles and thereby contribute toward the stability of the ruthenium (**1–3c**) complexes.

5. Conclusion

In summary, a series of new ruthenium (**1–3c**) complexes was synthesized employing the transmetallation route from its silver (**1–3b**) complexes. The molecular structures of the (**1–3c**) complexes revealed chelation of the N-heterocyclic carbene ligand to the metal center through an N-amido sidearm moiety and a carbene moiety. The density functional theory studies carried out on these ruthenium complexes reflected strong σ -donating nature of the N-heterocyclic carbene ligands. Further computational studies suggested that the low lying and deeply seated molecular orbitals corresponding to the NHC–Ru σ -interaction pointed towards a greater stability of the NHC–Ru bond in these complexes.

Electronic supplementary information

CCDC-676785 (**1c**), CCDC-697327 (**2c**) and CCDC-685445 (**3c**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk. Complete reference [19], CIF files giving X-ray crystallographic data of (**1–3c**), UV-vis and CV data, the B3LYP coordinates of the optimized geometries of (**1–3c**), computational data and the control experiment data are available free of charge via the internet at <http://www.ias.ac.in/chemsci>.

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