Base-free synthesis of benchtop stable Ru(III)-NHC complexes from RuCl₂·3H₂O and their use as precursors for Ru(II)-NHC complexes

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A series of Ru(III)-NHC complexes, identified as [Ru(II)(PyNHC)₂][Cl₂](H₂O)] (1a-c), have been prepared, starting from RuCl₂·3H₂O following a base-free route. The Lewis acidic Ru(III) centre operates via a halide-assisted, electrophilic C-H activation for carbene generation. Best results were obtained with azolium salts having a single anion while ligand precursors with Cl⁻, BF₄⁻, and PF₆⁻ gave no complex formation and those with Br⁻ gave a product with mixed halides. The structurally simple, air and moisture-stable complexes represent rare examples of paramagnetic Ru(III)-NHC complexes. Further, these benchtop stable Ru(III)-NHC complexes were shown to be excellent metal precursors for the synthesis of new Ru(II)-NHC complexes (2a-c) and [Ru(II)(PyNHC)₂(CNC)]PF₆ (3a-c) complexes. All the complexes have been characterised using spectroscopic methods, and structures of 1a, 1b, 2c and 3a have been determined using the single-crystal X-ray diffraction technique. This work allows easy access to new Ru-NHC complexes for the study of new properties and novel applications.

Introduction

Ru complexes with NHC ligands have become increasingly popular in recent years due to improved catalytic efficiency and tuneable stereoelectronic properties, which help in catalyst designing. These Ru-NHC complexes have found applications from homogeneous catalysis to therapeutic drugs, olefin metathesis reactions and solar cells (DSSCs). In general, the synthesis of Ru-NHC complexes involves one of the common Ru metal precursors Ru(Cl)₂(PPh₃)₃, [Ru(Cl)₂(p-cymene)]₂, [Ru(Cl)₂(CO)]₂, Ru⁴Cl₂(DMSO)₂, [Ru(Cl)₂(COD)]₄, etc., where one or more of the ligands are replaced with the in situ generated NHC ligands. Ru-precursor complexes play a significant role in the development of new Ru-complexes. Depending on the design of Ru based catalyst, selection of suitable Ru precursor is the most critical step. Generally, the synthesis of Ru-NHC complexes requires a base for the generation of NHCs from their azolium ligand precursors. Involvement of base in such reactions has its shortcomings, namely, the limited or no use of aerobic conditions, less scope to employ green solvents, and possibility of forming undesired side products. Nolan and coworkers have recently developed a “weak base” route for generating NHC-metal complexes. The simple “weak base” route has been described as a cost-effective and environmentally benign approach which can be extended further with various metals for NHC-based complexes. Among the various synthetic routes reported for the generation of NHCs and their corresponding metal complexes, namely, base-assisted deprotonation of azolium salts followed by metatation, transmetallation of preformed Ag(I)/Cu(I) carbenes, and C-H activation of azolium salts in the presence of metal precursors, C-H activation is considered as one of the simplest routes for the generation of carbene due to the less probability of formation of side product.

We have recently started the investigation of Ru(II)-NHC (CNC = pyridine-dicarbene pincer ligands) complexes with smaller N-alkyl wingtips on carbenes for transfer hydrogenation and related catalysis and compared their activity with the molecular catalysts with similar catalyst design. During our investigation, we noticed that even after a few decades of investigation of Ru(II)-NHC complexes, the formation so far and complexes (1a–c) reported in this paper.

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Figure 1. Ru(III)-NHC complexes known so far and complexes (1a–c) reported in this paper.
research in this field, a suitable Ru complex with an NHC ligand, which can be used as a precursor for the synthesis of new complexes with other co-ligands, is still unavailable. Further, it is surprising to note that till now, only four examples of Ru(III)-NHC complexes have been reported (Fig. 1.), all of which were obtained upon oxidation of their Ru(II)-NHC analogues.

Herein, we report a “base-free” synthesis of a series of Ru(III)-NHC complexes [RuIII(PyNHC)(Cl)2(H2O)] (1a-c) (PyNHC = 3-methyl-1-(pyridine-2-yl)imidazol-2-ylidene (1a), 3-isopropyl-1-(pyridine-2-yl)imidazol-2-ylidene (1b) and 3-methyl-1-(pyridine-2-yl)benzimidazol-2-ylidene (1c)) derived from pyridine functionalised N-alkylated azolium salts, and RuCl3·3H2O. Further, we have utilised these Ru(III)-PyNHC complexes as metal precursors for the synthesis of a series of the corresponding Ru(II)-PyNHC-(PPh3) complexes (2a-c) and Ru(II)-PyNHC- CNCMe (CNCMe2·2HBr = 2,6-Bis[3-(methyl)imidazolium] pyridine dibromide)pincer complexes (3a-c).

Results and Discussion

Synthesis and characterisation of 1a-c

The reaction of ligand precursors with RuCl3·3H2O in a 1:1 ratio in THF at reflux temperature afforded the new Ru(III)-PyNHC complexes 1a-c (Scheme 1) depending on the counterion of the azolium salt. Initial attempts with azolium salts having BF4 or PF6 counterions (to prevent the formation of mixed-halide complexes) gave no reaction with or without a base. In the presence of weak or strong bases, such as 

Scheme 1. Synthesis of Ru(III)-PyNHC complexes (1a-c).

with iodide counterion improved the yield for 1b, and, again, the LC-MS of crude product indicated no formation of mixed-halide complexes. It is reasonable to believe that the Lewis acidic Ru(III) metal centre operates via a halide-assisted electrophilic C-H activation for the generation of carbene, where the C-H activation is also affected by the halide ions of the azolium ion pairs. The synthesis of 1a-c has been scaled up to the gram scale starting from 1 g of RuCl3·3H2O. All three complexes were obtained in excellent yields (75–82%) from iodide salts of their corresponding azolium precursors.

Complexes 1a-c have been characterised by IR, UV-Vis spectroscopy, and ESI mass spectrometry. The paramagnetic nature (low spin d) of the Ru centre in these complexes was confirmed by measurement of their magnetic moment using the Evans method. The values for magnetic moments were found within the range of 1.70–1.72 BM establishing the presence of one unpaired electron. To determine the thermal stability of complexes 1a-c, thermogravimetric analysis was performed under a nitrogen atmosphere. The plots showed no weight loss in complexes up to 150 °C. The loss of H2O molecule from complexes was observed at 250 °C (1a), 230 °C (1b), and 175 °C (1c), and the gradual decrease in weight can be attributed to the loss of chloride ligands present in the system. Stretching frequencies for C=N and C-C bonds obtained using IR spectroscopy were compared with the ligand precursors and found to lie within the expected range 1500-1200 cm⁻¹ (ImCN), and 1600-1400 cm⁻¹ (PyNHC) and C-H stretch lie in a range 3100-3000 cm⁻¹. The characteristic MLCT absorption maxima in UV-vis spectra for the Ru-NHC bond in the three complexes were observed at 384 nm (5337 M⁻¹cm⁻¹) (1a), 385 nm (3181 M⁻¹cm⁻¹) (1b) and 392 nm (5132 M⁻¹cm⁻¹) (1c) (Fig. 3.). ESI+ mass spectrometry showed peaks for the fragments [M-Cl]⁺, [M-Cl₂H₂O]⁺, and [M-Cl₂H₂O(S)]⁻ (where S=Solvent, i.e., MeCN or MeOH), in complexes 1a-c. HRMS spectrogram of the molecular ion peak at m/z assignable to [M-Cl]⁺, i.e., 348.9315 (1a), 376.9613 (1b), and 398.9501 (1c) confirmed the elemental...
composition (See S1). Complexes 1a and 1b have also been characterised by Powder XRD, and their structures have been determined by the single-crystal X-ray diffraction technique.

**Description of crystal structures of 1a-b**

Molecular structures of 1a and 1b were determined using the single-crystal X-ray diffraction technique. Complexes 1a and 1b crystallised in orthorhombic (Pna2₁) and monoclinic (I2/a) crystal systems, respectively. The structures exhibited a pseudo-octahedral geometry around the Ru(III) centre. The bidentate ligand forms a five-membered metallacycle with a bite angle of 79.7(7)° and 78.34(19)° in 1a and 1b, respectively. In both the structures, the coordinated H₂O ligand was replaced by the solvent of crystallisation, i.e., MeCN in 1a (Fig. 3) and MeOH in 1b (Fig. 4). Therefore, the structure obtained for complex 1a is denoted as 1a-MeCN, and that of 1b is denoted as 1b-MeOH. Acetonitrile was observed trans to pyridine N-atom in 1a-MeCN, whereas in 1b-MeOH, π-donor methanol was found trans to the NHC. In another complex [Ru(IILPyNHC)Cl₂(NO)],⁴⁶,⁴⁷ reported earlier, the π-acid ligand NO has also been found trans to the pyridine N-atom. The Ru-C₅₂tetraene bond distance in 1b-MeOH (1.972(2)Å) is shorter than the corresponding distance in 1a-MeCN (1.998(6)Å) and the previously reported Ru(II)-NO (2.049(5)Å).⁴⁸ The shortening of bond length in 1b-MeOH could be due to the increased π-back donation from the Ru(III) centre with a π-donor MeOH ligand at the trans position. Selected bond parameters have been listed in Table S2 (See S1). DFT calculations of isomeric cis/trans-forms w.r.t position of solvent molecule from pyridine N-atom confirm that in the case of π-acid MeCN ligand, isomer with the

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![Figure 3](image3.png)

**Figure 3.** ORTEP diagrams for complex 1a-MeCN obtained from X-ray diffraction. Hydrogen atoms and solvent molecule are excluded for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances(Å) and bond angles(°) are Ru1-C1 1.998(6); Ru1-N1 2.042(5); Ru1-N4 2.038(6); C1-Ru1-N1 77.9(2); and N1-Ru1-N4 176.6(2).

![Figure 4](image4.png)

**Figure 4.** ORTEP diagrams for complex 1b-MeOH obtained from X-ray diffraction. Hydrogen atoms and solvent molecule are excluded for clarity. Ellipsoids are shown at the 50% probability level. Selected bond distances(Å) and bond angles(°) are Ru1-C1 1.972(2); Ru1-N1 2.073(2); Ru1-O1 2.2259(18); C1-Ru1-N1 78.32(9); and C1-Ru1-O1 169.35(9).

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![Figure 5](image5.png)

**Figure 5.** Optimised cis/trans isomeric forms of 1a w.r.t solvent molecule (H₂O and MeCN) and relative Gibbs free energies (at 298.15 K) and 1M solution.
no sign of decay. Further, these complexes enrich the list of very rare Ru(III)-NHC complexes, which have, so far, been obtained by oxidising a Ru(II)-NHC complex as Ru(II) precursor. To check the usefulness of 1a-c as starting material for the preparation of Ru(II)-NHC complexes with different ancillary ligands, complexes 1a-c have been used to prepare the phosphine complexes 2a-c following the same procedure as preparation of RuCl(Cl)(PPh3) from RuCl3·3H2O. Further, to demonstrate the thermal stability of these complexes as metal precursors, Ru-PyNHC-CNC pincer complexes 3a-c have been prepared under ethylene glycol reflux conditions (190 °C).

Synthesis of phosphine complexes 2a-c from 1a-c
The reaction of complexes 1a-c with a 6-fold excess of triphenylphosphine in methanol at reflux temperature gave the corresponding Ru(II)-PyNHC-(PPh3) complexes formulated as [Ru(II)(PyNHC)2(C2Cl2)(PPh3)3] 2a-c in 60–80% yield (Scheme 2). The air-stable, yellow complexes were characterised by ESI+ -MS, 1H and 31P NMR, and the molecular structure of 2c was determined by single-crystal X-ray diffraction technique. HRMS spectroscopy exhibited a molecular ion peak at m/z fragment 820.1361 (2a), 848.1688 (2b), and 870.1545 (2c) assignable to [M-Cl]+. The poor solubility of 2a–c in common organic solvents and phosphine dissociation in solution makes it difficult to obtain good quality 1H NMR data. However, for 2b in CD2CN and 2c in DMSO-d6, 1H NMR could be obtained with a sufficient S/N ratio for the identification of relevant peaks. Compound 2a was not soluble in CD2CN, and PPh3 dissociation in DMSO-d6 resulted in poor-quality 1H NMR data. The 31P NMR spectrum of 2b in CD2CN shows a singlet at 25.9 ppm with very small signals for one phosphine-dissociated species at 49.3 ppm and the free PPh3 at -6 ppm. The corresponding signals for complex 2a were observed at 26.7 ppm and 35.4 ppm and for 2c at 24.2 ppm, and 33.3 ppm, respectively, with significant PPh3 dissociation.

Description of crystal structure 2c
The structure of complex 2c has been determined by X-ray crystallography (Fig. 6). It crystallised in a monoclinic (P21/c) space group and displayed a pseudo-octahedral geometry around the Ru(II) centre with a solvent (MeCN) bound to the metal and a Cl- counterion in the lattice (hence denoted as 2c-MeCN). The Ru1-C1 bond length in 2c-MeCN is 1.964(4) Å, whereas in Ru(III)-PyNHC analogues, the values for these bond distances in 1a-MeCN and 1b-MeOH are 2.052(16) Å and 2.007(5) Å respectively. The short Ru-C carbene bond in 2c-MeCN can be attributed to the increased π-back-donation from the Ru(II) compared to Ru(III) metal centre. In an example reported by Siemeling et al., the lengthening of bond distance was also observed upon oxidation from Ru(II)-NHC (1.972(2) Å) to Ru(III)-NHC (2.032(8) Å). Other relevant bond parameters are listed in Table S2 (See S5).

Synthesis of CNC-pincer complexes 3a-c from 1a-c
In another example for the preparation of derivatives of 1a-c, we have synthesised a series of [Ru(l)(PyNHC)(CNCBu)(Cl)PF6] pincer complexes 3a-c starting from 1a-c (Scheme 3). This approach involves the reaction of CNC ligand precursor with our precursor complexes 1a-c in ethylene glycol at reflux temperature (190 °C) to yield complexes 3a-c. A complex, [Ru(II)(PyNHC)(CNCBu)Cl]PF6, structurally similar to 3a-c has been reported in the literature, where the synthetic strategy involves the preparation of Ru-CNC-Bu pincer complex from [Ru(COD)Cl2], polymer followed by reaction with PyNHC-BuHBr in the presence of Ag2O as a base.

The successful synthesis of 3a-c indicates the thermal stability of Ru(III)-PyNHC precursors 1a-c. NaI was added to reduce the possibility of mixed halide complexes. Complexes 3a-c were characterised by ESI+ mass spectrometry and NMR spectroscopy. HR-MS spectroscopy exhibited a molecular ion...
peak at m/z fragment 627.0079 \( (3a) \), 655.0365 \( (3b) \), and 677.0242 \( (3c) \) assignable to \([\text{M-PF}_6]\)\(^{+}\). The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of complexes \(3a-c\) in DMSO-\(d_6\) show two distinct sets of signals, indicating the existence of two isomeric structures. In \(^1\text{H}\) NMR, in addition to the expected, downfield shifted signal (d, 10.27 \((3a)\), 10.29 \((3b)\), and 10.44 ppm \((3c)\) doublet) for the proton at the ortho position of the pyridine unit in the bidentate ligand PyNHC\(^8\) (similar to the reported complex \([\text{Ru}^\text{II}(\text{PyNHC}^\text{a})](\text{CNC}^\text{a}))\text{Br}[\text{PF}_6]_2\), another doublet at \(\delta 9.81\) \((3a)\), 9.81 \((3b)\) and 9.90 ppm \((3c)\) are also observed. Similarly, in the alkyl region, two sets of peaks, double the number of expected signals, are obtained. This could be due to cis/trans-isomers with respect to the two pyridine units, as has been reported earlier for structurally similar Ru-tpy complexes (tpy = terpyridine).\(^{40}\) Another possibility for the existence of two signals could arise due to iodide substitution by a dmso-\(d_6\) molecule resulting in an equilibrium between iodide coordinated and dissociated forms. Therefore, the trans-isomer or the iodide coordinated form show a downfield shifted signal, but the cis-isomer or the iodide dissociated form do not show such a shift. The \(^{13}\text{C}\) NMR spectra also show two sets of peaks for the two types of carbene for CNC\(^\text{Me}\) ligand and the bidentate (PyNHC\(^8\)) ligand. The exact reason, out of the two possibilities, for the existence of two sets of peaks, is uncertain at this time and is currently being investigated.

The solid-state structure and geometry around the Ru centre in \(3a\) have been confirmed by the single-crystal X-ray diffraction technique. It crystallised in a monoclinic (\(P2_1/c\)) space group, and the structure revealed the three five-membered metallacycles, two of which are formed by pincer ligand, and one is due to the bidentate ligand framework. The crystal structure of \(3a\) shows an octahedral geometry around the Ru(II) centre and confirms the structure as depicted in Scheme 3; however, due to poor diffraction, the data quality is not sufficient to discuss bond parameters.

Conclusions

In summary, we report a base-free, scalable synthesis of a series of new, benchtop stable Ru(III)-NHC complexes \(1a-c\) based on a bidentate PyNHC\(^8\) ligand framework bearing \(R = \text{Me}\) and \(\text{tPr}\) alkyl wingtips. Alkyl wingtips. These Ru(III) complexes serve as metal precursors for the preparation of phosphine complexes, \(2a-c\) and CNC pincer complexes \(3a-c\). The synthesis of complexes \(3a-c\) indicates the thermal stability as well as the usability of complexes \(1a-c\) in harsh reaction conditions. All new compounds have been characterised by usual characterisation techniques, and the structures of \(1a, 1b, 2c\), and \(3a\) have been confirmed by single-crystal X-ray diffraction technique. The results reported here present a straightforward route to prepare Ru(III)-NHC complexes from simple starting materials. Further studies on the synthesis of analogues Ru(III)-NHC complexes with different alkyl wingtips of the NHC units, variation of azole rings and their use as metal precursors for the synthesis of Ru(II)-NHC complexes with different ligands are currently undergoing.

Experimental Section

Materials

All reactions were performed in oven dried glassware under an inert atmosphere using Schlenk line technique. Azoles (1-H-imidazole and 1-H-benzimidazole) were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL)-India. Solvents: dichloromethane (DCM), hexane, ethyl acetate (EtOAc), tetrahydrofuran (THF), methanol (MeOH), and ethylene glycol (\(\text{CH}_2\text{OH}\)) were purchased from S. D. Fine-Chem Limited and used after purification. Methanol has been degassed before using as a solvent in a reaction. Deuterated NMR solvents, DMSO-\(d_6\) and CD\(_3\)CN, were purchased from Euromerica and Sisco Research Laboratories Pvt. Ltd. (SRL) respectively and distilled from Ca\(_2\)H\(_2\) before use. 2-Bromopyridine was purchased from Spectrochem (India). Alkyl halides and RuCl\(_3\)3\(\text{H}_2\)O were purchased from Spectrochem (India) and Sigma-Aldrich respectively.

Characterisation methods

ESI+-MS chromatograms were recorded using Bruker-Daltonics-MicroTOF-QII mass spectrometer for exact mass and true isotopic measurement. Electronic absorption spectra were recorded in a quartz cuvette using a Varian UV-vis spectrophotometer. A Bruker Avance (III) spectrometer operating at 400 MHz (\(^1\text{H}\)), 162 MHz (\(^13\text{C}\)), and 100 MHz (\(^{15}\text{N}\)) and Bruker Avance NEO spectrometer operating at 500 MHz (\(^1\text{H}\), 202 (\(^13\text{C}\)), and 126 MHz (\(^{15}\text{C}\)) were used to record the NMR spectra. Magnetic susceptibilities (\(\chi\)) were evaluated using NMR Evans method\(^{45}\) by taking the chemical shift difference in residual solvent peak DMF, in the mixture of DMF:DMSO-\(d_6\) :: 2:3 in 0.5 ml, in \(^1\text{H}\) NMR spectra, recorded at 400 MHz spectrometer at room temperature, which was further used to calculate magnetic moment (\(\mu_\text{B}\)). The mixture of solvents was taken to suppress the coordination of DMSO-\(d_6\) to Ru(III) centre. Powder XRD patterns were recorded on Rigaku SmartLab X-ray diffractometer using Cu-K\(\alpha\) radiation. Thermogravimetric analyses were carried out on a TGA-50 series thermal analyser within the temperature range from 25 to 800 \(^\circ\text{C}\) under inert atmosphere. ATR (attenuated total reflectance) spectra were recorded using Bruker Alpha II spectrophotometer in solid state in the wavenumber range 4000-500 cm\(^{-1}\). Elemental analyses were carried out on Thermo Scientific FLASH 2000 (formerly the FLASH EA1112) CHNS-O elemental analyser.
X-ray data collection and refinement

The single crystal X-ray diffraction data of complexes were obtained using dual-core Agilent technologies (Oxford Diffraction) Super Nova CCD System equipped with micro focus Mo and Cu sources. Data was recorded at 293(2) K using graphite-mono chromated Mo Kα radiation source. Data for complexes 1b and 2c, and Cu Kα radiation source for complexes 1a and 3a. Data were collected using CrystAlisPro CCD and reduced using CrystAlisPro RED software. The SHELXT program was used to solve the structure with intrinsic phasing, and refinement by the full matrix least-squares on F² was carried out using SHELXL within Olex2 program for graphical interface. For 2c, a solvent mask was calculated, and 168 electrons were found in a volume of 1262 Å³ in one void per unit cell. This is consistent with the presence of 2(CH₃CN) per asymmetric unit which account for 176 electrons per unit cell. All non-hydrogen atoms were refined anisotropically. ORTEP-3 was used to create the images. All crystallographic and bond parameters of complexes and a larger basis set def2-TZVP on all other atoms (BS2).

DFT calculations

All DFT calculations were performed using the ORCA 5.0.3 program package developed by Neese and coworkers. The geometry optimisations and frequency calculations in gaseous phase were carried out starting from X-ray geometry using M06L meta-generalised gradient approximation (m-GGA) functional along with “DEGRID3” integration grids and Ahlrichs’s def2-TZVP with def2-ECP on Ru, and def2-SVP basis set on all other atoms (BS1).

Synthesis of complexes

Synthesis of 1a: Under an inert atmosphere, a 50 ml Schlenk tube was charged with L¹-HI (1.74 mmol, 0.500 g), RuCl₃·3H₂O (1.74 mmol, 0.455 g) and THF (7–8 ml). The reaction mixture was stirred for 12 hours at reflux temperature resulting in brown precipitate and a dark brown solution. Subsequently, the brown solid product was filtered and washed several times with THF and dried under vacuum. Yield = 0.591 g (1.54 mmol, 78%). Liquid chromatography mass spectrometry mass spectrometry (LCMS) : 330.92 [M-CI-H₃O]⁺, 348.93 [M-CI]⁺, 366.94 [M-CI-H⁺]⁺, 698.81 [2M-CI-2HCl]⁺. High resolution mass spectrometry (HRMS) for [M-CI]⁺ (CH₃CN)_2N(O)Ru in CH₃CN: Calculated: 348.9313; Found: 348.9315. Magnetic moment, μB = 1.72 BM. UV-vis λmax(CH₃CN), nm (ε, M⁻¹ cm⁻¹): 343 (1944), 384 (5337). The X-ray quality crystals were obtained by slow diffusion of diethyl ether in acetonitrile solution of 1a at 4 °C. Anal. Calcd. for C₂₁H₂₁Cl₄N₂Ru (M = 407.66 g/mol): C 32.41, H 2.97, N 13.74, Found: C 32.03, H 2.94, N 13.39.

Synthesis of 1b: Following the synthetic procedure described for 1a, L¹-HBr (1.85 mmol, 500 mg) and RuCl₃·3H₂O (1.85 mmol, 0.485 g) were added in THF (7-8 ml). The reaction mixture was stirred for 12 hours at reflux temperature. The precipitate obtained was filtered and washed several times with THF and dried under vacuum. The product was collected as red brown solid. Yield = 0.226 g (1.017 mmol, 55%). LCMS: 358.96 [M-CI-H₃O⁺]⁻, 376.96 [M-CI]⁻, 397.99 [M-CI-H⁺]⁻, 798.81 [2M-CI-2HCl]⁻. HRMS for [M-CI]⁻ (CH₃CN)_2N(O)Ru in CH₃CN: Calculated: 376.9636; Found: 376.9613. Magnetic moment, μB = 1.72 BM. UV-vis λmax(CH₃CN), nm (ε, M⁻¹ cm⁻¹): 343 (3492), 381 (4558). The X-ray quality crystals were obtained by slow diffusion of diethyl ether in methanol solution of 1b at 4 °C.

1b: synthesized from L¹-HI, LCMS (ESI⁺): 358.96 [M-CI-H₂O⁺]⁺, 376.96 [M-CI]⁺, 399.97 [M-CI-H⁺]⁺, 754.88 [2M-CI]⁺. HRMS for [M-CI]⁺ (CH₃CN)_2N(O)Ru in CH₃CN: Calculated: 376.9636; Found: 376.9613. Magnetic moment, μB = 1.72 BM. UV-vis λmax(CH₃CN), nm (ε, M⁻¹ cm⁻¹): 342 (3492), 385 (3181). The X-ray quality crystals were obtained by slow diffusion of diethyl ether in methanol solution of 1b at 4 °C. Attempts at elemental analyses failed to give the acceptable nitrogen content, while carbon and hydrogen are in the acceptable range. We suspect an instrumental error in the N-content determination. Anal. Calcd. for C₂₁H₂₁Cl₄N₂Ru (M = 425.94 g/mol): C 33.78, H 4.02, N 9.85, Found: C 33.53, H 4.38, N 7.44.

Synthesis of ligand precursors

Ligand precursors L¹-HI, L¹-HBr, and L¹-HI were prepared following the synthetic procedure reported in literature. To eliminate the possibility for the formation of mixed halide complexes observed in synthesis of 1b from L¹-HBr, different analogues of ligand L²-HX (X = Cl, I, Br, and PF₅) were prepared accordingly. L²-HCl was synthesised using 2-Chloropyridine and 1-methyl-1H-imidazole, L²-HI was prepared by anion exchange of L²-HBr with NaI in acetone at room temperature, the precipitate of NaBr was crashed out from the solution and filtrate was reduced under rotary evaporator and triturated with hexane to obtain the desired compound in good yield. Similarly, L¹-HBF₄ and L¹-HPF₆ were obtained by ion exchange with NaBF₄ and NH₄PF₆ respectively in aqueous medium.
Synthesis of 1c: Following the synthetic procedure described for 1a, L3-HI (1.48 mmol), 500 mg and RuCl3·3H2O (1.48 mmol, 0.387 g) were added in THF (7-8 ml). The reaction mixture was stirred for 12 hours at reflux temperature resulting in dark brown solid and dark brown solution. Subsequently, the brown solid product was filtered and washed several times with THF and dried under vacuum. Yield = 0.530 g (1.22 mmol, 82%). LCMS: 377.95 [M-2Cl-H2O+CH3OH], 418.98 [M-2Cl-H2O+2CH3OH+CH3CN]. HRMS for [M-Cl]+: C13H12Cl3N2O1Ru in CH3CN: Calculated: 398.9511, found: 398.9501. Magnetic moment, µB = 1.73 BM. UV-vis λmax/CH3CN, nm (ε, M-1·cm-1): 446 (3228), 392 (5132). Attempts at elemental analyses failed to give the acceptable nitrogen content, while carbon and hydrogen are in the acceptable range. We suspect an instrumental error in the N-content determination. Anal. Calcd. for C13H12Cl3N2O1Ru·1CH3OH: C 31.40, H 4.68, N 4.50%. The reaction was again heated to reflux at 65 °C for 6 hours. The light brown solid was collected and washed with methanol and diethyl ether and dried under vacuum. Yield = 0.907g (1.001 mmol, 87%). M.P. 160 °C. LCMS: 689.05 [M-Cl-PPh3]+, 870.15 [M-Cl]+, 911.18 [M-Cl2CH3CN]+. HRMS for [M-Cl]+: C43H31Cl2N3P2Ru in CH2CN: Calculated: 870.1512, found: 8701545. UV-vis λmax/CH3CN, nm (ε, M-1·cm-1): 306 (8145). 1H NMR (500 MHz, DMSO) δ 9.37 (d, J = 5.7 Hz, 1H), 8.97 (d, J = 5.9 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.74 (dd, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.25 – 7.18 (m, 12H), 7.02 (td, J = 7.9, 2.1 Hz, 6H), 6.97 (t, J = 7.5, 6.8 Hz, 12H), 6.38 (t, J = 6.6 Hz, 1H), 3.71 (s, 3H). 31P NMR (202 MHz, DMSO) δ 33.28, 24.22. The X-ray quality crystals were obtained by slow diffusion of diethyl ether in acetonitrile solution of 2c at -18 °C. Attempts at elemental analyses failed to give the acceptable nitrogen content, while carbon and hydrogen are in the acceptable range. We suspect an instrumental error in the N-content determination. Anal. Calcd. for C45H33Cl2N3P2Ru·1CH3OH (M = 937.84 g/mol): C 64.03, H 4.84, N 4.48, Found: C 64.16, H 4.55, N 3.81%.

**Synthesis of 2a:** Following the synthetic procedure described for 1b, complex 2b was prepared from 1b. The bench top methanol was degassed under N2 atmosphere and cooled to room temperature and added 1b (1.211 mmol, 0.500 g) and triphenylphosphine in an equivalent ratio of 1 to 6 respectively. The reaction was again heated to reflux at 65 °C for 6 hours. The pale-yellow solid was collected and washed with methanol and diethyl ether and dried under vacuum. Yield = 0.865g (0.979 mmol, 81%). M.P. 175 °C. LCMS: 586.07 [M-Cl-PPh3]+, 627.10 [M-Cl-PPh3+CH3CN], 848.17 [M-Cl]+, 889.18 [M-Cl2CH3CN]+. HRMS for [M-Cl]+: C43H31Cl2N3P2Ru in CH2CN: Calculated: 848.1668; Found: 848.1688. UV-vis λmax/CH3CN, nm (ε, M-1·cm-1): 323 (5983). 1H NMR (500 MHz, CD3CN) δ 8.50 (dd, J = 5.8 Hz, 1H), 7.91 (d, J = 2.5 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.50 (dd, J = 7.6, 2.8 Hz, 1H), 7.33 (t, J = 7.4 Hz, 6H), 7.22 (t, J = 7.6 Hz, 12H), 7.19 – 7.14 (m, 12H), 7.09 (d, J = 2.2 Hz, 1H), 6.55 (t, J = 6.6 Hz, 1H), 4.01 – 3.92 (m, 1H), 0.62 (d, J = 6.7 Hz, 6H). 31P NMR (202 MHz, CD3CN) δ 49.94, 25.88. Attempts at elemental analyses failed to give the acceptable nitrogen content, while carbon and hydrogen are in the acceptable range. We suspect an instrumental error in the N-content determination. Anal. Calcd. for C45H33Cl2N3P2Ru·2H2O·0.1CH3OH (M = 951.87 g/mol): C 60.57, H 5.40, N 4.41, Found: C 60.80, H 5.20, N 5.00%.

Synthesis of 2c: Following the synthetic procedure described for 2a, complex 2c was prepared from 1c. The bench top methanol was degassed under N2 atmosphere and cooled to room temperature and added 1c (1.152 mmol, 0.500 g) and triphenylphosphine in an equivalent ratio of 1 to 6 respectively. The reaction was again heated to reflux at 65 °C for 6 hours. The light brown solid was collected and washed with methanol and diethyl ether and dried under vacuum. Yield = 0.907g (1.001 mmol, 87%). M.P. 160 °C. LCMS: 689.05 [M-Cl-PPh3]+, 870.15 [M-Cl]+, 911.18 [M-Cl2CH3CN]+. HRMS for [M-Cl]+: C43H31Cl2N3P2Ru in CH2CN: Calculated: 870.1512, found: 8701545. UV-vis λmax/CH3CN, nm (ε, M-1·cm-1): 306 (8145). 1H NMR (500 MHz, DMSO) δ 9.37 (d, J = 5.7 Hz, 1H), 8.97 (d, J = 5.9 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.74 (dd, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.25 – 7.18 (m, 12H), 7.02 (td, J = 7.9, 2.1 Hz, 6H), 6.97 (t, J = 7.5, 6.8 Hz, 12H), 6.38 (t, J = 6.6 Hz, 1H), 3.71 (s, 3H). 31P NMR (202 MHz, DMSO) δ 33.28, 24.22. The X-ray quality crystals were obtained by slow diffusion of diethyl ether in acetonitrile solution of 2c at -18 °C. Attempts at elemental analyses failed to give the acceptable nitrogen content, while carbon and hydrogen are in the acceptable range. We suspect an instrumental error in the N-content determination. Anal. Calcd. for C45H33Cl2N3P2Ru·1CH3OH (M = 937.84 g/mol): C 64.03, H 4.84, N 4.48, Found: C 64.16, H 4.55, N 3.81%.

**General procedure of the synthesis of CNC-pincer complexes:** An oven dried Schlenk tube with magnetic stirring bar was charged with ligand precursor (1 equiv.), bidentate metal precursor (1 equiv.), and NaI (0.149 g, 1 mmol) in ethylene glycol (10 ml), the resulting mixture was refluxed under N2 atmosphere for 4 h. On completion of the reaction, cooled it to room temperature, add aqueous solution of KPF6 (0.184 g, 1 mmol, 10 ml water), then stirred for 2 min at room temperature. A desired complex was precipitated out, filtered the precipitate, washed with H2O and dried under vacuum.

**Synthesis of 3a:** This complex was prepared by general procedure, using 2,6-Bis-[3-(methyl)midaizoliumpyridine dibromide (0.100 g, 0.25 mmol) and 1a (0.096 g, 0.25 mmol) to give the desired complex as a yellowish orange solid. The X-ray quality crystals of 3a were obtained by slow diffusion of diethyl ether in methanol solution at 4 °C. Yield = 0.129 g (67%). M.P. 278 °C. HRMS for [M-PF6]+: C29H24N3P2Ru in CH2CN: Calculated: 627.056, Found: 627.0579. 1H NMR (400 MHz, DMSO, Component a:b ratio 45:55) δ 10.27 (d, J = 5.7 Hz, 1H) (a), 9.81 (d, J = 5.8 Hz, 1H) (b), 8.51 (d, J = 1.9 Hz, 2H), 8.45 – 8.40 (m, 4H),...
Conflicts of interest

There are no conflicts of interest to declare.

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