# Synthesis, characterization and applications of vinyl functionalized N-heterocyclic carbene supported ruthenium(II) derivatives

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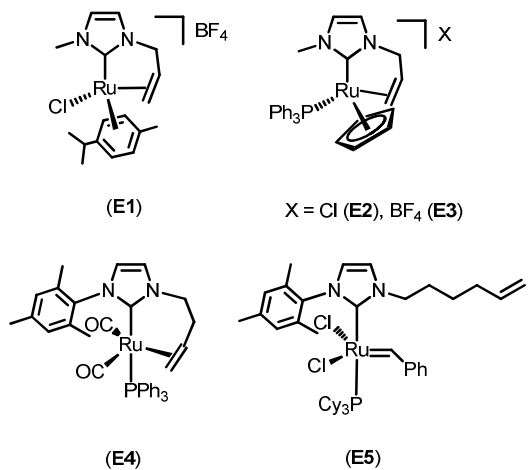
New ruthenium(II) N-heterocyclic carbene complexes of the general formula $[ArCH_2(VIm)RuCl_2(p\text{-cymene})]$ (VIm = vinylimidazole; Ar = mesitylene (**5**) or napthalene (**6**)) are obtained from the transmetallation reaction between $[MesCH_2(VIm)AgBr]$ (Mes = mesitylene (**3**)) or $[NpCH_2(VIm)AgCl]$ (Np = napthalene (**4**)) and $[(p\text{-cymene})RuCl_2]_2$. The silver carbene complexes (**3**) and (**4**) are synthesized from the direct reaction between the corresponding π-functionalized imidazolium salts, $[MesCH_2(VIm)Br]$ (**1**) or $[NpCH_2(VIm)Cl]$ (**2**), with silver oxide in good yield. The compounds (**1**), (**2**), (**5**) and (**6**) are characterized by elemental analysis, FT-IR and multinuclear ($^1H$ and $^{13}C$) NMR spectroscopy. Furthermore, ligand (**1**) is characterized by single crystal X-ray diffraction technique. The coordination mode and possible olefin-Ru π-interaction in (**5**) and (**6**) are investigated. The complexes (**5**) and (**6**) are stable and soluble in dichloromethane and chloroform.Compounds (**5**) and (**6**) are catalytically active towards the hydrogen transfer reactions.

**Keywords:** Coordination chemistry, Metal-olefin interactions, Transmetallation, Hydrogenation, Heterocyclic compounds, Carbenes, N-Heterocyclic carbenes, Carbonyls, Silver, Ruthenium

Functionalized N-heterocyclic carbenes (NHCs) with excellent opportunities for electronic and steric ligand tuning properties have provided an impetus for development of transition metal catalysts. Besides, the N-functional groups in NHC render the additional donor site like σ- and π-bonding, softness and size, which provide control over the coordination environment of the metal as well as unusual catalytic activities. Apart from this, the functional groups are introduced in NHC for hemilability, chirality and bite angles modification.[1]

Among a wide range of functional group choice, hemilabile functional group such as olefin donor functionalized NHCs were synthesized and tested for their importance in catalysis.[2-16] In particular, the hemilabile nature of olefin group attached to NHC plays a crucial role in homogeneous catalysis as a π-electron reservoir to stabilize the metal center during the catalytic cycle. The first olefin functionalized carbene was isolated in 2001. However, its potential application in catalysis was not reported.[2] Later the iridium complexes of N-allyl-substituted benzimidazol-2-ylidene compounds were synthesized and tested for their catalytic activity in catalytic transfer hydrogenation of carbonyl compounds.[3] Other similar catalysts were developed and their catalytic efficiencies were tested.[4-16] In particular, the terminal olefin

functionalized NHC supported metal derivatives were known only with ruthenium, iridium, rhodium and nickel, in which the olefin functionalized ruthenium NHC showed excellent catalytic efficiency in catalytic transfer hydrogenation reactions.[15,16] Moreover, the π-donor olefin side arm plays an important role in the catalytic cycle to provide enough stability to the transition state. The terminal olefin functionalized NHCs $[N\text{-}(CH_2)_nCH=CH_2]$ with chain length of $n = 1$ and 2 showing ruthenium-olefin interaction[2,10,11] where ruthenium coordination number is four or five (**E1-E4**) are shown below. Notably such a type of interaction was absent in **E5**. Besides, the role of rigid/short olefin



(E1)

X = Cl (E2), BF₄ (E3)

(E4)

(E5)

moieties attached to NHC-Ru compounds, for example, vinyl substituted NHCs and their ruthenium derivatives are not known. Herein, we report the first N-vinyl-N′-methylaryl heterocyclic carbene precursors and their ruthenium(II) *p*-cymene derivatives, (**5**) and (**6**).

## Materials and Methods

All manipulations were carried out under nitrogen using Schlenk-vacuum line techniques and argon filled glove box. The solvents were purified according to standard procedures.[17] 2-(Bromomethyl)-1,3,5-trimethylbenzene[18] and [(*p*-cymene)RuCl$_2$]$_2$[19] were prepared accordingly to previously reported methods. Silver oxide (Avra), vinylimidazol (Aldrich), DMSO-$d_6$ (Acros), D$_2$O (Aldrich), CDCl$_3$ (Aldrich) and 1-(chloromethyl)naphthalene (Aldrich) were purchased from commercial sources. FT-IR measurements (neat) were made on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometer at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and referenced to the solvent resonances as internal standards. Elemental analyses were carried out by the Euro EA Elemental Analysis instrument. The crystal structure of (**1**) was recorded on an Oxford Supernova diffractometer. Single crystals were mounted on a Goniometer KM4/Xcalibur equipped with Sapphire2 (large Be window) detector (MoK radiation source, = 0.71073 Å). Crystals of (**1**) were obtained from mixtures of dichloroethane/hexane solution) of (**1**) at room temperature over a period of seven days. Data were collected at 293 K. The structure was solved by direct methods using the SIR-97 program[20] and refined with a full matrix least-squares method on F$^2$ using the SHELXL-97 program.[21,22]

**(1):** To a solution of 2-(bromomethyl)-trimethylbenzene (1.0 g, 4.69 mmol ) in 1,4-dioxane (10 mL), was slowly added vinylimidazole (0.463 g, 4.92 mmol) and the reaction mixture was stirred at 60 °C for one day. The white compound was collected by cannula filtration, washed with acetone, diethyl ether, and dried *in vacuo*. Yield: 1.33 g (92% based on 2-(bromomethyl)-1,3,5-trimethylbenzene). M.pt.:181-183 °C. Anal. (%): Calcd. : for C$_{15}$H$_{19}$N$_2$Br (306.07): C, 58.8; H, 6.3; N, 9.2; found: C, 58.4; H, 6.4; N, 9.0. FT-IR (neat, cm$^{-1}$): ν = 3056, 2989, 2961, 2155, 1572, 1542, 1455, 1339, 1163, 1143, 1114, 1087, 1049, 1030, 976, 949. $^1$H NMR (400 MHz, CDCl$_3$): δ = 10.78 (s, 1H, 2-Im*H*), 8.07 and 6.91 (s, 2×1H, 4,5 Im*H*), 7.40-7.46 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, Vinyl*H*), 6.87 (s, 2H,

Ar*H*), 5.98-6.03 (dd, $^2J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 15.7 Hz, 1H, Vinyl*H*), 5.57 (s, 2H, ArC*H$_2$*N), 5.30-5.33 (dd, $^2J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, Vinyl*H*), 2.23 (s, 9H, ArC*H$_3$*) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 139.96, 137.91 (Ar*C*), 135.21 (2-Im*C*), 129.84 (Ar*C*), 128.17 (vinyl *C*H), 124.71 (Ar*C*), 121.01, 119.78 (4,5-Im*C*), 109.95 (vinyl *C*H$_2$), 47.99 (ArC*H$_2$*N), 20.88 (Ar *C*H$_3$), 19.73 (2×Ar *C*H$_3$) ppm.

**(2)**: To a solution of 1-(chloromethyl)naphthalene (1.0 g, 5.66 mmol) in 1,4-dioxane (10 mL), was slowly added vinylimidazole (0.559 g, 5.94 mmol) and the reaction mixture was stirred at 60 °C for 36 h. The phase separation occurred during this process. The reddish brown viscous phase was separated and washed with 1,4-dioxane (2 mL), acetone (5 mL) and hexane (5 mL). The reddish brown viscous oil was dried under high vacuum for 4 h to yield brownish yellow solid. Yield: 1.150 g (75% based on 1-(chloromethyl)naphthalene). M.pt.: 68-70 °C. Anal. (%): Calcd. : for C$_{16}$H$_{15}$N$_2$Cl (270.76): C, 71.0; H, 5.6; N, 10.3; found: C, 70.8; H, 5.7; N, 10.1. FT-IR (neat, cm$^{-1}$): ν = 3041, 1650, 1547, 1511, 1368, 1156, 958, 914 cm$^{-1}$. $^1$H NMR (400 MHz, D$_2$O and DMSO-d$_6$): δ = 9.01 (s, 1H, 2-Im*H*), 7.93-7.99 (m, 3H, Ar*H*), 7.72 and 7.51 (s, 2×1H, 4,5 Im*H*), 7.54-7.62 (m, 4H, Ar*H*), 6.98-7.04 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, Vinyl*H*), 5.81 (s, 2H, ArC*H$_2$*N), 5.69-5.73 (dd, $^2J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, Vinyl*H*), 5.35-5.38 (dd, $^2J_{HH}$ = 2.7 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, Vinyl*H*) ppm. $^{13}$C NMR (100 MHz, D$_2$O and DMSO-d$_6$): δ = 135.82, 135.11 (2-Im*C*), 132.04, 131.94, 130.69, 130.66, 129.50, 129.42, 129.18, 127.28, 124.32, (Ar*C*), 128.23 (Vinyl *C*H), 123.74, 120.88 (4,5-Im*C*), 111.03 (Vinyl *C*H$_2$), 52.34 (ArC*H$_2$*N) ppm.

**(3):** A mixture of (**1**) (0.500 g, 1.63 mmol) and Ag$_2$O (0.207 g, 0.89 mmol) was taken up in dichloromethane (30 mL) and the suspension was stirred for 16 h at RT in dark. The resulting solution was filtered through celite, solvent was evaporated *in vacuo*, washed with diethyl ether (2 mL×2), hexane (2 mL×2) and dried *in vacuo*. Yield: 0.430 g (63% based on **1**). Product formation was confirmed by $^1$H NMR and then used for the transmetallation reaction without further characterization due to light sensitive and hygroscopic nature of (**3**). $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.31-7.36 (dd, $^3J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 11.2 Hz, 1H, Vinyl*H*), 7.30 and 6.65 (s, 2×1H, 4,5 Im*H* ), 6.91 (s, 2H, Ar*H*), 5.39 (d, $^2J_{HH}$ = 1.1 Hz, 1H, Vinyl*H*), 5.34 (s, 2H, ArC*H$_2$*N), 5.05 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Vinyl*H*), 2.28 (s, 3H, Ar *C*H$_3$), 2.25 (s, 6H, 2×Ar *C*H$_3$) ppm.

**(4):** A mixture of (**2**) (0.568 g, 2.09 mmol) and Ag$_2$O (0.267 g, 1.15 mmol) was taken up in MeOH (10 mL) and dichloromethane (10 mL) and the suspension was stirred for 16 h at RT in dark. The resulting solution was filtered through celite, solvent was evaporated *in vacuo*, washed with diethyl ether (2 mL×2), hexane (2 mL×2) and dried *in vacuo* to yield (**4**). Yield: 0.633 g (79% based on **2**). Product formation was confirmed by ^{1}H NMR then used for the transmetallation reaction without further characterization due to light sensitive and hygroscopic nature of (**4**). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.91-7.94 (m, 1H, Ar*H*), 7.76-7.82 (m, 2H,Ar*H* and Im*H* ), 7.41-7.51 (m, 3H, Ar*H* and Im*H*), 7.33-7.36 (t, *J* = 8.0 Hz, *J* = 7.2 Hz, 1H, Ar*H*), 7.27-7.28 (d, *J* = 2.2 Hz, 2H, Ar*H*), 6.92 (d, *J* = 1.6 Hz, 1H, Vinyl*H*), 5.80 (s, 2H, ArC*H$_2$*N), 5.26-5.30 (dd, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 15.8 Hz, 1H, Vinyl*H*), 4.89-4.91 (dd, $^2J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 8.9 Hz, 1H, Vinyl*H*) ppm.

**(5):** A mixture of compound (**3**) (0.2 g, 0.48 mmol) and [(*p*-cymene)RuCl$_2$]$_2$ (0.147 g, 0.24 mmol) was taken up in dichloromethane (10 mL) and stirred for 24 h at RT. The resulting solution was filtered through celite, solvent was evaporated *in vacuo*, washed with diethyl ether (2 mL×2), hexane (2 mL×2) and dried *in vacuo*. Yield: 0.195 g (74% based on **3**). M.pt.: 140 $^o$C (decomp.). Anal. (%): Calcd. : for C$_{25}$H$_{32}$Cl$_2$N$_2$Ru (532.1): C, 56.4; H, 6.1; N, 5.3; found: C, 56.2; H, 6.0; N, 5.2. FT-IR (neat, cm$^{-1}$): $\nu$ = 3107, 2960, 2913, 2865, 1639, 1612, 1465, 1444, 1415, 1383, 1311, 1259, 1220, 1193, 1155, 1087, 1021 cm$^{-1}$. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.27-8.33 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 15.9 Hz, 1H,Vinyl*H*), 7.22 (d, *J* = 1.9 Hz, Im*H* ), 6.91 ( s, 2H, Ar*H*), 6.39-6.40 (d, *J* = 1.68 Hz, 1H, Im*H* ), 5.51 (d, *J* = 5.6 Hz, 2H, *p*-cyAr*H*), 5.23 (s, 2H, ArC*H$_2$*N), 5.17 (d, $^3J_{HH}$ = 15.9 Hz, 1H, Vinyl*H*), 4.92 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Vinyl*H*), 2.99 (sept, 1H, *p*-cy C*H*(CH$_3$)$_2$), 2.30 (s, 3H, Ar C*H$_3$*), 2.24 (s, 6H, 2×Ar C*H$_3$*), 2.11 (s, 3H, *p*-cy C*H$_3$*), 1.27 (d, *J* = 6.9, 6H, *p*-cy CH(C*H$_3$*)$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): $\delta$ = 175.54 (Ru-*C*), 138.62, 136.61, 129.44 (Ar*C*), 128.16 (Vinyl *C*H), 121.07, 117.48 (4,5-Im*C*), 108.29 (Vinyl *C*H$_2$), 101.75, 99.94, 85.49 (*p*-cy-*C*), 57.24 (*p*-cy-*C*H(CH$_3$)$_2$), 49.65 (Ar*C*H$_2$N), 30.76 (*p*-cy-*C*H$_3$), 20.96 (Ar-*C*H$_3$), 20.05 (2×Ar-*C*H$_3$), 18.68 (*p*-cy-CH(C*H$_3$*)$_2$) ppm.

**(6):** A mixture of compound (**4**) (0.200 g, 0.53 mmol) and [(*p*-cymene)RuCl$_2$]$_2$ (0.161 g, 0.26 mmol) was taken up in dichloromethane (10 mL) and stirred for 24 h at RT. The resulting solution was filtered through celite, solvent was evaporated *in vacuo*, residue was washed with diethyl ether (2 mL×2), hexane (2 mL×2), acetone (10 mL) and dried *in vacuo* to yield (**6**). Yield: 0.182 g (61% based on **4**). M.pt.: 326-328 $^o$C. Anal. (%): Calcd.: for C$_{26}$H$_{28}$Cl$_2$N$_2$Ru (540.07): C, 57.8; H, 5.2; N, 5.2; found: C, 57.6; H, 5.1; N, 5.2. FT-IR (neat cm$^{-1}$): $\nu$ = 2962, 2905, 1636, 1446, 1413, 1258, 1078, 1009 cm$^{-1}$. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.25-8.31 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 16.0 Hz, 1H, Vinyl*H*), 8.12 (d, *J* = 8.1 Hz, 1H, im*H* ), 7.91 (d, *J* = 7.84, 1H, Ar*H*), 7.84 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.55-7.63 (m, 2H, Ar*H*), 7.42-7.45 (m, 2H, Ar*H*) 7.08 (d, *J* = 6.96 Hz, 1H, Im*H*), 7.00 (s, 1H, Ar*H*), 5.29 (s, 2H, *p*-cyAr*H*), 5.24 (s, 1H, Vinyl*H*), 4.94-4.96 (d, *J* = 8.68 Hz, 1H, Vinyl*H*), 4.86 (s, 2H, ArC*H$_2$*N), 2.84 (sept, 1H, *p*-cy C*H*(CH$_3$)$_2$), 1.94 (s, 3H, *p*-cyC*H$_3$*), 1.16 (s, 6H, *p*-cyCH(C*H$_3$*)$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): $\delta$ = 177.86 (Ru-*C*), 136.38, 133.70, 133.63, 130.60, 127.15, 126.52, 125.13, 124.47 (Ar*C*), 128.78, 128.59 (Vinyl *C*H),123.80, 123.18, 118.68 (4,5-Im*C*), 108.26 (Vinyl *C*H$_2$), 101.64, 99.10 (*p*-cy-*C*), 53.39 (*p*-cy-*C*H(CH$_3$)$_2$), 52.58 (Ar*C*H$_2$N), 30.54 (*p*-cy-*C*H$_3$), 18.54 (*p*-cy-CH(C*H$_3$*)$_2$) ppm.

## Results and Discussion

### Synthesis and characterization of (1)-(6)

The methyl aryl substituted vinylimidazolium salts (**1**) or (**2**) were isolated in very good yield as shown in Scheme 1. (**1**) was obtained from acetone and diethyl ether wash of crude sample. Similarly, (**2**) was isolated as a reddish brown viscous oil from the crude reaction mixture, washed with 1,4-dioxane, acetone and hexane. Under high vacuum, the reddish brown oil of (**2**) became brownish yellow solid. (**2**) is hygroscopic and turns liquid under ambient condition while it remaining solid under inert atmosphere, which melts at 68–70 °C. Compound (**1**) is stable and high melting white solid (M. pt.: 181–183 °C). Solubility of (**1**) in halogenated solvents like dichloromethane and chloroform is much better than (**2**).

Crystals of (**1**) were grown by vapor diffusion of hexane into CH$_2$Cl$_2$ solution. The structure indeed confirmed the formation of the imidazolium salt (**1**) and revealed the presence of the "Mes-CH$_2$-" unit, which is attached to the N-vinyl imidazolium platform (Fig. 1). (**1**) crystallized in the monoclinic space group *P2(1)/n*.[23] N-vinyl-N′-CH$_2$ imidazolium unit is almost in the same plane while the Mes group is
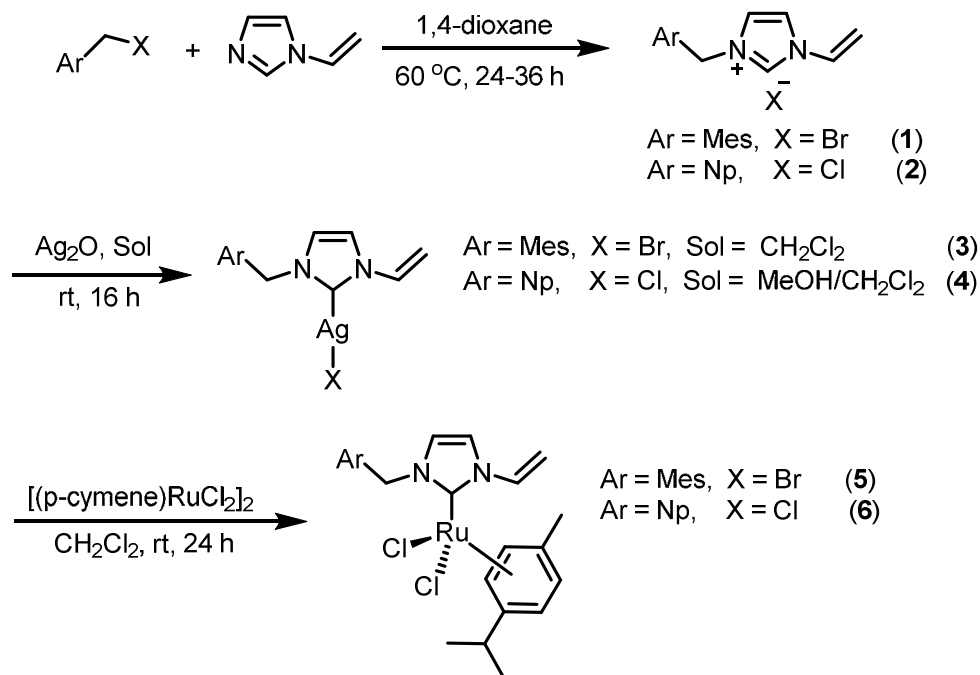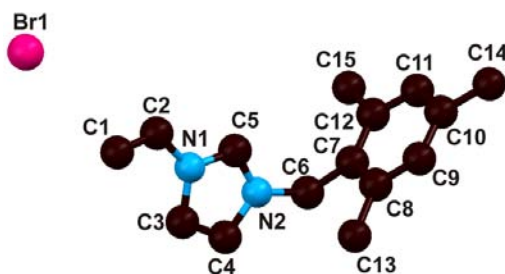
**Scheme 1**



Fig. 1 – Soild state structure of (**1**). [Important bond lengths (Å) and angles (deg.): N(1)-C(5) 1.342(5), N(1)-C(3) 1.394(5), N(1)-C(2) 1.424(4), N(2)-C(5) 1.323(4), N(2)-C(4) 1.376(4), N(2)-C(6) 1.479(4), C(2)-C(1) 1.328(6), C(5)-N(1)-C(3) 108.8(3), C(5)-N(1)-C(2) 123.4(3), C(3)-N(1)-C(2) 127.8(3), C(5)-N(2)-C(4) 109.2(3), C(5)-N(2)-C(6) 127.1(3), C(4)-N(2)-C(6) 123.8(3), C(3)-C(4)-N(2) 107.6(3), C(1)-C(2)-N(1) 122.2(4), N(2)-C(5)-N(1) 108.5(3), N(2)-C(6)-C(7) 112.8(3)].

projecting away from this plane. The torsion angle for C(3)-N(1)-C(2)-C(1) is 10.6°. The torsion angle for C(5)-N(2)-C(6)-C(7) is 44.21°. The C(5)-N(2)-C(6) angle (127.1(3)°) is slightly wider than the C(5)-N(1)-C(2) angle (123.4(3)°). The N(1)-C(5) and N(2)-C(5) bond distances are not equal; N(1)-C(5) is slightly longer (1.342(5) Å) than N(2)-C(5) 1.323(4) Å. The C(1)-C(2) bond distance (1.328(6) Å) is typical for the carbon-carbon double bond. The bond distance of N(1)-C(2) is (1.424(4) Å) considerably shorter than N(2)-C(6) (1.479(4) Å).

The 1:1 reaction between (**1**) or (**2**) and silver oxide resulted the formation of corresponding N-heterocyclic carbene derivatives of (**3**) and (**4**) respectively, in very good yield (Scheme 1). (**3**) and (**4**) were obtained from diethyl ether and hexane wash of the corresponding crude reaction mixtures. (**3**) and (**4**) became black in the presence of light and oxygen, and were soluble in selected polar organic solvents like chloroform, dichloromethane, acetone and DMSO. Therefore, the formation of (**3**) and (**4**) were confirmed by ^{1}H NMR after the reaction work-up, Then the crude products of (**3**) and (**4**) were used as precursors for transmetallation reactions with [(*p*-cymene)RuCl$_2$]$_2$.

(**5**) and (**6**) were obtained in very good yield from the reaction between [(*p*-cymene)RuCl$_2$]$_2$ and corresponding silver salts of N-heterocyclic carbene derivatives, (**3**) or (**4**) respectively (Scheme 1). (**5**) and (**6**) were isolated from the corresponding crude reaction mixtures by washing with diethyl ether/hexane or diethyl ether/hexane/acetone, respectively. (**5**) and (**6**) are stable under anaerobic condition. (**5**) is a free flowing orange yellow solid, while (**6**) is a red orange sticky solid.

Formation of (**1**), (**2**) (**5**) and (**6**) was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis. The purity and molecular composition of (**1**), (**2**), (**5**) and (**6**) were verified by elemental analysis.

The ^{1}H and ^{13}C NMR spectra of (**1**) and (**2**) in CDCl$_3$ or D$_2$O and DMSO-$d_6$ display the expected resonances. Comparison of the ^{1}H NMR spectra of (**3**)-(**6**) with those of the corresponding ligands (**1**) and (**2**) revealed that the C–H signals (single resonance at $\delta$ = 10.78 ppm for **1** and $\delta$ = 9.01 ppm for **2**) of the free ligands disappeared, which confirmed the formation of the M–carbene bond (Fig. 2). In ^{1}H NMR, the chemical shift values of N-C$H$=C$H_2$ protons in (**5**) and (**6**) are sligtly upfield shifted compared to corresponding free ligands, which clearly indicates the absence of vinyl-Ru interaction in (**5**) and (**6**),[6-8] However, the vinyl group showed some sort of   overlap with five membered NHC ring.

In ^{13}C NMR additional resonances appearing for (**5**) and (**6**) in the downfield region ($\delta$ = 175.54 ppm for **5** and 177.86 ppm for **6**) are attributed to the carbene carbon attached to the ruthenium center, while the N$C$HN signals (single resonance around $\delta$ = 124.71 ppm for **1** and $\delta$ = 124.32 ppm for **2**) of (**1**) and (**2**) disappeared (Fig. 3).[24] The ^{1}H NMR spectra of
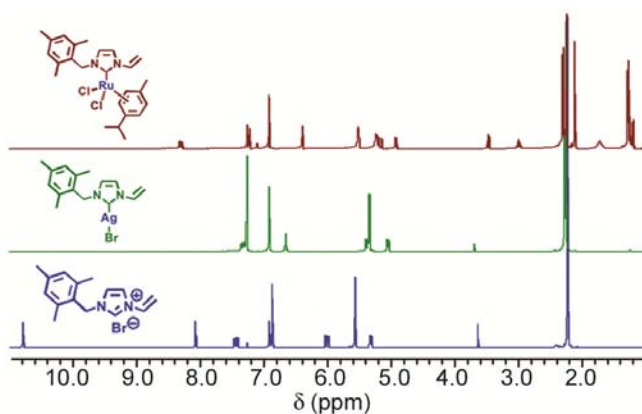


Fig. 2 – ^{1}H NMR spectrum of (**1**), (**3**) and (**5**) in CDCl$_3$ at RT.
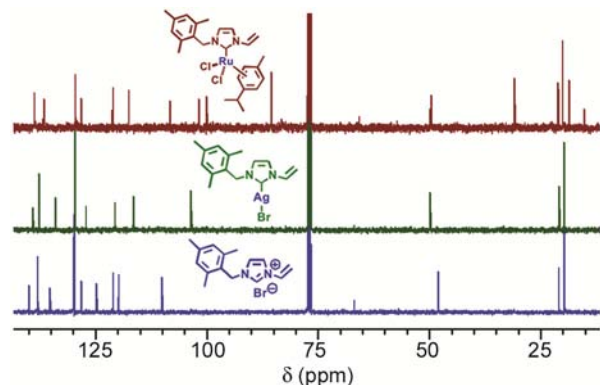


Fig. 3 – ^{13}C NMR spectrum of (**1**), (**3**) and (**5**) in CDCl$_3$ at RT.

(**1**)-(**6**) showed three sets of signals for the protons of vinyl [NC$H_a$C(H$_b$)(H$_c$)] group. In general, the shielding of vinyl H$_a$ decreased in (**5**) and (**6**) compared to the corresponding free ligands (**1** and **2**) or even its silver carbene derivarives (**3** and **4**). Therefore metallation causes strong downfield shift of H$_a$ chemical shift value while the chemical shift value of H$_b$ and H$_c$ were gradually moved towars upfield region. Several attempts were made to obtain single crystals of the complexes (**5**) and (**6**). However, we could not grow suitable crystals, probably due to the choice of N-substituent.

### UV-visible spectra of (**5**) and (**6**)

UV-visible absorption spectra of (**5**) and (**6**) were measured in chloroform at room temperature and displayed nearly similar absorption patterns (Fig. 4). Molecule (**5**) showed strong absorptions at 245 and 271 nm, in addition to a weak absorption at 406 nm. The substitution of mesitylene by naphthalene moiety in (**6**) triggered the absorption enhancement at 278 nm, while the absorption peak at 243 and 404 nm decreased. The strong and sharp absorptions around 240 and 270 can be attributed to the  -to- * transition of ligand. The broad peak around 400 nm with less intensity can be assigned to the ligand-to-metal charge transition.

### Nature of ruthenium-carbene bond in (**5**) and (**6**)

The basic level molecular optimization (RB3LYP/ 6-311+G level) was carried out for the model carbenes, [(MesCH$_2$N)(CH)$_2$C(N′CHCH$_2$)] (**1L**) and [(NpCH$_2$N)(CH)$_2$C(N′CHCH$_2$)] (**2L**) to elucidate the bonding situations (Table 1).[25] The optimized
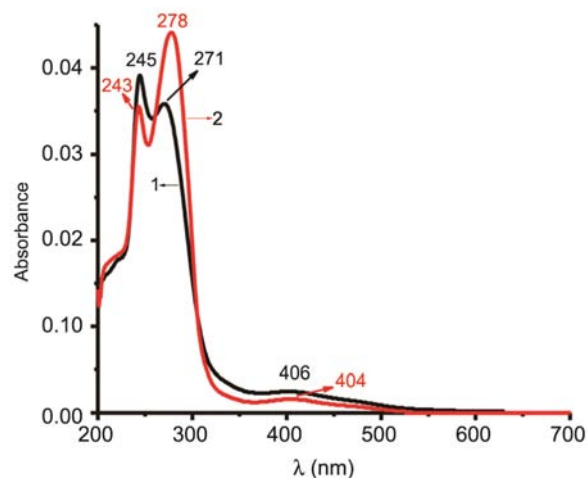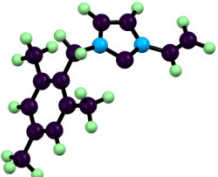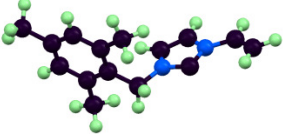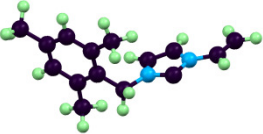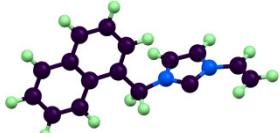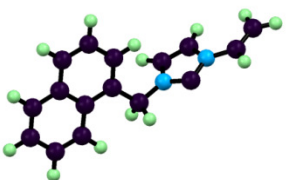


Fig. 4 – The UV-vis spectra of (**5**) (curve 1) and (**6**)(curve 2) in CHCl$_3$ at RT.

Table 1 – Molecular optimization (rb3lyp/6-311+g level) of [(MesCH$_2$N)(CH)$_2$C(N′CHCH$_2$)] (**1L**) and [(NpCH$_2$N)(CH)$_2$C(N′CHCH$_2$)] (**2L**)

| No. | Conformer | Energy, HF (Hartree) | ZPE (Hartree) | Energy (ZPE corr.) | Relative energy | |
|---|---|---|---|---|---|---|
| | | | | | Hartree | kcal mol$^{-1}$ |
| 1 | | -691.8580257 | 0.2967905 | -692.1548162 | 0.002558 | 1.60517058 |
| 2 | | -691.8583761 | 0.2966259 | -692.155002 | 0. 0023722 | 1.488579222 |
| 3 | | -691.860622 | 0.2967522 | -692.1573742 | 0 | 0 |
| 4 | | -727.5510356 | 0.2604657 | -727.8115013 | 0.0023641 | 1.483496391 |
| 5 | | -727.5532569 | 0.2606085 | -727.8138654 | 0 | 0 |

geometries are shown in Fig. 5 and the full sets of calculated data are given in Table 1. The most stable geometrical orientations of **1L** and **2L** are comparable and are also similar to (**1**). As shown in fig. 5, in **III** and **IV**, the vinyl π electron is detached from the ring and not delocalized. However as discussed above in $^1$H NMR study, the vinyl π electron showed significant delocalization with ring in (**5**) and (**6**) when (**1**) and (**2**) bind with ruthenium center. Unlike CH$_2$=CH-(CH$_2$)$_n$-N ($n$ = 1, 2, 3, 4), in the case of **1L** and **2L**, the vinyl electrons are readily available for the delocalization when metal binds with carbene centre.[2-16]

**Hydrogenation of benzophenone by (5) and (6)**

The hydrogenation of ketone is one of the important areas of research in organic synthesis.[26-30] The overall quest in this area is to produce the economically viable and efficient catalysts by tuning the steric and electronic properties of Rh, Ru, Ir, Pt,

Ni and Fe based catalysts. Of course, NHC based ligands do show considerable contribution in this field.[31,32] Most recently Albrecht and his co-workers have reported the catalytic transfer hydrogenation of benzophenone and other functional groups using chelating NHC ruthenium complexes, where different functional groups exhibited a distinct hydrogenation efficiency on benzophenone. Notably, [(*p*-cymene)Ru(Cl){C(NMe)(NCH$_2$CH=CH$_2$)-(CH$_2$)$_2$}]$^+$BF$_4^-$ was the most efficient catalyst, with conversion of above 90% after 5 h as compared to other chelating NHC ruthenium complexes.[16] This may be due to the labile coordinating nature of allyl group in [(*p*-cymene)Ru(Cl){C(NMe)(NCH$_2$CH=CH$_2$)(CH$_2$)$_2$}]$^+$BF$_4^-$. Therefore, we believe that further studies on catalytic transfer hydrogenation of benzophenone using newly developed vinyl functionalized NHC supported catalysts (**5**) and (**6**) can give preliminary insights about similar catalytic processes.
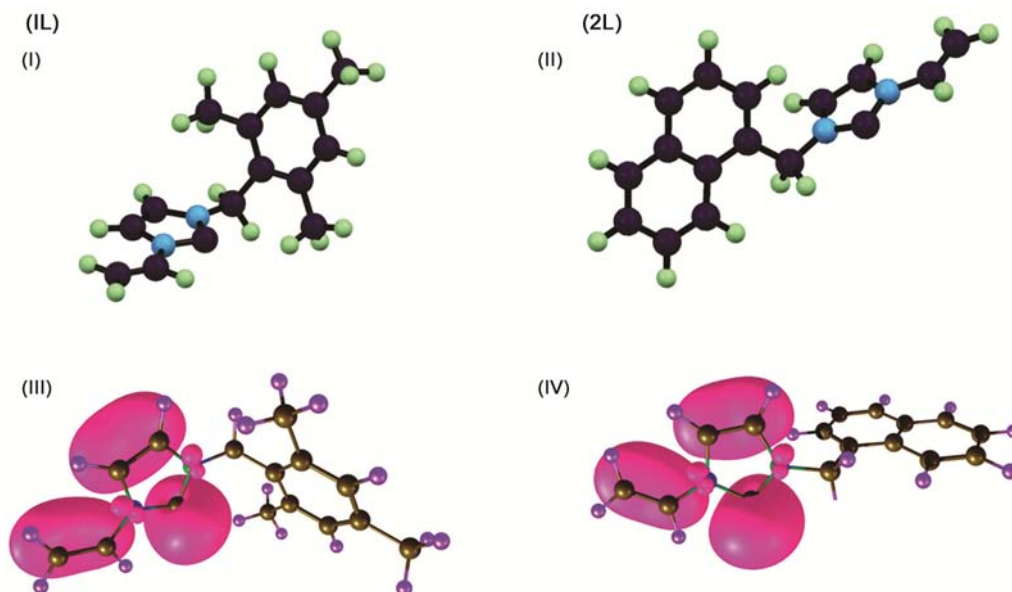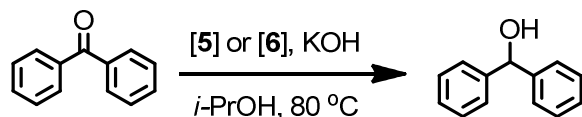
Fig. 5 – Geometry optimizations (rb3lyp/6-311+g level) [(MesCH₂N)(CH)₂C(N′CHCH₂)] (**1L**) and [(NpCH₂N)(CH)₂C(N′CHCH₂)] (**2L**) where the vinyl π electron is detached from ring and not delocalized.



Catalytic hydrogenation of benzophenone using catalysts (**5**) or (**6**) in the presence of KOH in isopropanol at 80 °C. benzophenone:KOH:catalyst ratio is 100:50:1

**Scheme 2**

**Catalytic activity**

The catalytic behavior of (**5**) and (**6**) toward the hydrogenation of benzophenone was studied. The benzophenone, KOH and catalyst were loaded (100:50:1 ratio) in dry isopropanol and the reaction mixture was heated at 80 °C (Scheme 2). Dry isopropanol was used as a solvent and proton source for the reaction. Two different sets of experiments were carried out under inert atmosphere in a Schlenk tube without degassing the solvent. The reactions were carried out for 30 minutes in one set of experiment, while in the other set it was for 5 h. The reaction progress was continuously monitored by TLC, FT-IR, ¹H and ¹³C NMR. From the analysis, we observed as follows: (i) as expected, diphenylmethanol is the only product isolated in the conversion, (ii) (**5**) is a better catalyst (69% yield within 30 minutes and 81% yield within 5 h) than (**6**) (19% yield within 30 minutes and 66% yield within 5 h) and (iii) benzophenone was not completely consumed within 30 minutes or 5 h.

**Conclusions**

In summary, the new pre-NHC precursors featuring a short π donor functional group attached with carbene and new vinyl functionalized NHC supported ruthenium derivatives, (**5**) and (**6**) were synthesized from the corresponding silver carbene precursors, (**3**) and (**4**) respectively. NHC metal derivatives (**5**) and (**6**) were characterized by FT-IR, UV-vis and multinuclear NMR techniques. The spectral studies on (**5**) and (**6**), show the presence of vinyl π electron delocalization with five membered NHC ring in (**5**) and (**6**), and, the absence of π coordination towards ruthenium center. The reduction of benzophenone using ruthenium(II) N-heterocyclic carbene derivatives (**5**) and (**6**) was studied. Synthesis of polymer supported catalysts using (**5**) and (**6**) is in progress and will be reported in due course.

**Supplementary Data**

CCDC 887546 contains the supplementary crystallographic data for compound (**1**) in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk. Other supplementary data associated with this article, viz., ^{1}H NMR and ^{13}C NMR are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(05)588 -595_SupplData.pdf

## Acknowledgement

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