



# Rhodium (I) Complexes of Quinoline Functionalised Heterocyclic Carbene Ligands

Aminu Ahmed<sup>1</sup> and Abdullahi Mustapha<sup>2\*</sup>

<sup>1</sup>Kano University of Science and Technology, Wudil, Kano, Nigeria.

<sup>2</sup>Department of Chemistry, Federal University Dutse PMB 7156, Jigawa State, Nigeria.

## Authors' contributions

*This work was carried out in collaboration between both authors. Author AA designed the study and carried out the Experimental work and wrote the protocol. Author AM managed the literature searches and provided the Ortep drawing for the crystal structures. Both authors read and approved the final manuscript.*

Original Research Article

Received 8<sup>th</sup> February 2014

Accepted 10<sup>th</sup> April 2014

Published 26<sup>th</sup> April 2014

## ABSTRACT

In this paper, two types of quinoline functionalized rhodium complexes were synthesized by stirring imidazolium salts with silver oxide to obtain silver carbenes. According to the method, the corresponding non chelated rhodium complexes were access by transmetallation of silver carbenes. Reaction of the non chelated rhodium complexes gave the chelated analogue that was insoluble in most solvents. All the non chelated complexes were structurally characterized by 1H NMR, 13 NMR, microanalysis and X-ray crystallography. The crystal geometry of the complexes adopted square planar structures. All the rhodium complexes were stable enough in air and with moisture.

*Keywords: NHC; Imidazolium salt; ligand; chelation.*

## 1. INTRODUCTION

Prior to the isolation of the first stable crystalline Nucleophilic Heterocyclic Carbenes (NHC) by Arduengo et al. [1], complexes of NHCs were reported in 1968 by Ofele, Wanzlick and Shonherr were prepared directly from imidazolium salts [2,3]. In his contribution Lampert prepared a wide range of transition metal- NHC compounds from electron rich olefins in 1970 and the complexes were found to be active catalysts for hydrosilylation [4].

\*Corresponding author: Email: [abmustapha2004@yahoo.com](mailto:abmustapha2004@yahoo.com);

Encouraged by the promise of these early applications utilizing Rh(I) complexes of simple monodentate NHC ligands, there was a natural evolution to expand the catalytic applications of Rh and Ir NHC complexes systems through modification of the NHC ligands. The desired qualities of modified NHC ligands include the incorporation of functional groups leading to easily recoverable catalyst, water or methanol soluble catalyst, and catalyst containing flexible steric bulk as well as chiral and bidentate pincer ligands [5] and combination of the strongly bound NHC moiety with more weakly nucleophilic functional groups to furnish ligands with hemi labile donor groups as these can increase catalytic activities by stabilizing the low valent centers formed during catalysis. These functional groups may be incorporated at one or both of the ring nitrogens to give access to bidentate or tridentate NHC ligands.

Functionalized Rh(I) (NHC) complexes have been reported in the literature with picolyl [6], an ether, ester, amide and ketone [7], amino and pyridyl [8]. Other Rh(I) and Ir(I) NHC complexes have also been reported: Crabtree and Chianese reported the effect of linker length and counter ion on the formation of chelated complexes of rhodium(I) NHC complexes where they observed that short linker length and non coordinating counter ion favored chelated rhodium(I) NHC complexes while long linker length and coordinating counter ion disfavored the formation of chelated complexes [9].

Different approaches are normally employed to prepare Rh and Ir NHC complexes. In many coordination strategies available, three of them are more prominent: oxidative addition of the imidazolium ring, deprotonation of the imidazolium salts with suitable base and transmetalation of the previously obtained silver carbene.

One of the potentially very mild ways to make transition metal NHC complexes is by oxidative addition of the azolium C-H bond to an appropriate low-valent metal centre. Theoretical and experimental work by McGuinness et al. in 2001 [10] indicates that this is an efficient synthetic route. However, this method gives rhodium (III) or iridium (III) NHC complexes, without formation of the desired low valent NHC complexes.

The best synthetic method of obtaining the low valent Rh(I) and Ir(I) NHC complexes is via deprotonation of the imidazolium precursor with suitable base. However, a strong base such as potassium tert-butoxide or potassium hydride is usually employed to prepare the free carbene. This sometimes causes problems because the acidic protons or electrophilic sites may be attacked by the base.

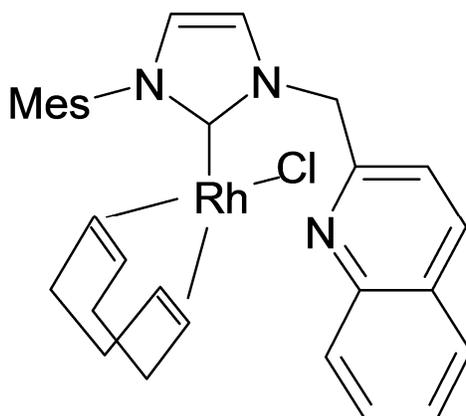
Gratifyingly, the important work of Wang and Lin demonstrated that silver complexes of NHCs could be synthesized directly from imidazolium salts and  $\text{Ag}_2\text{O}$  or  $\text{Ag}_2\text{CO}_3$  and silver(I) NHC complexes are easy to transfer the carbene ligands to other metals such as Pd, Au, including Rh and Ir [11]. By using this simple way, our desired Rh(I) complexes were prepared by transmetalation of silver carbene protocol. However it is worth to note that the reaction yield via silver carbene is just depended on the imidazolium salt/ metal ratio and the starting metal complex used. Mas-Marza et al. reported that Rh(III) and Ir(III) NHC can also be prepared by the transmetalation, as the silver carbene can play dual role: (i) in NHC transfer and (ii) as oxidizing agent [12].

In this paper, the synthesis and characterization of a series of  $[\text{Rh}(\text{COD})\text{Cl}]$  NHC complexes of quinoline functionalized via  $\text{Ag}^{\text{I}}(\text{NHC})$  is outlined. Several chelated complexes are also described, and only a  $[\text{Rh}(\text{COD})\text{Cl}]$  NHC complex was obtained by treatment of the neutral complexes with  $\text{AgBF}_4$  and characterized perfectly.

## 2. MATERIALS AND METHODS

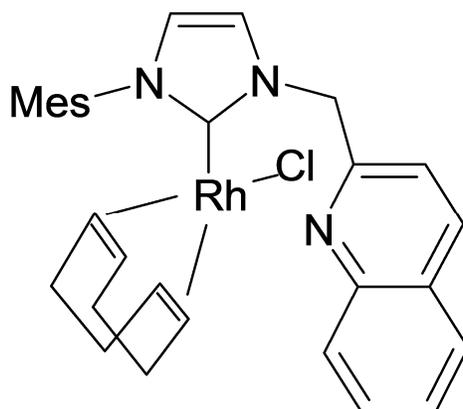
All reactions were performed under the atmosphere of dry dinitrogen or argon using standard Schlenk techniques, and solvents were purified and dried by usual means [13], unless otherwise indicated. Silver (I) NHC complexes were prepared as detailed by Wang and Lin [14] and all other reagents were used as received. All NMR data are quoted  $\delta$ /ppm.  $^1\text{H}$  and  $^{13}\text{C}$  (proton decoupled) spectra NMR were recorded on a Bruker DPX Advance 400 at 400MHz,  $^{13}\text{C}$  at 100.61 MHz) respectively at ambient temperature, unless otherwise stated, and referenced to  $\text{SiMe}_4$ . Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the department of Chemistry, Cardiff University. Micro analysis was performed by Warwick Analytical Service. All reactions involving silver compounds were performed with the exclusion of light.

Synthesis of [1-methyl-3-(2-methylquinoline) imidazolin-2-ylidene] (1, 5-cyclooctadiene) rhodium (I) Chloride 2a



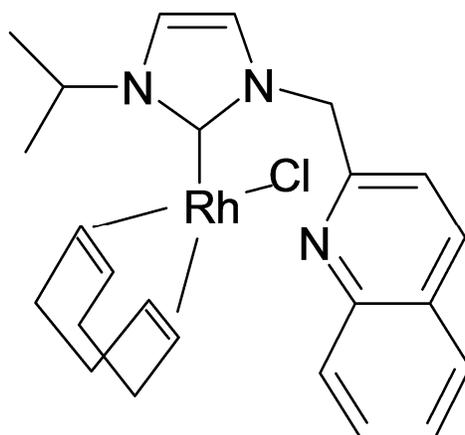
$[\text{RhCl}(\text{cod})]_2$  (99mg, 0.2 mmol) in 10ml of DCM was added to 20 ml of DCM solution of  $[\text{Ag}(1\text{-methyl-3-(2-methylquinoline) imidazolin-2-ylidene})_2][\text{AgCl}_2]$  1a (147mg, 0.40mmol). The reaction mixture was stirred over night and filtered through celite to remove silver chloride and any insoluble residue. The filtrate was concentrated and hexane was added to precipitate out the desired carbene complex as a yellow powder (152mg, 80.42%). Crystals suitable for X- ray crystallography were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for  $\text{C}_{22}\text{H}_{25}\text{N}_3\text{RhCl}$ : C, 56.20; H, 5.33; N, 8.95%. Found: C, 54.80; H, 5.23; N, 8.66%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz, 298K):  $\delta$  8.10(d, 1H,  $J = 8.5 \text{ Hz}$ , quin-H), 8.00(d, 1H,  $J = 8.5 \text{ Hz}$ , quin-H), 7.75(d, 1H,  $J = 8.0 \text{ Hz}$ , quin-H), 7.70(t, 2H,  $J = 6.7 \text{ Hz}$ , quin-H), 7.45(t, 1H, 7.5  $\text{ Hz}$ , quin-H), 6.80(s, 2H, CHHC), 6.50(d, 1H,  $J = 14.8 \text{ Hz}$ ,  $\text{CH}_{2\text{linker}}$ ), 5.60(d, 1H,  $J = 14.8 \text{ Hz}$ ,  $\text{CH}_{2\text{linker}}$ ), 5.00(broad, 2H, COD), 4.10(s, 3H,  $\text{CH}_3$ ), 3.40(broad, 1H, COD), 3.20(broad, 1H, COD), 2.30(m, 4H,  $j = 4.4 \text{ Hz}$ , COD), 1.90(m, 4H,  $J = 4.2 \text{ Hz}$ , COD).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz, 298K): 181.60 (C-Rh), 154.88, 145.53, 135.57, 127.82, 127.05, 125.86, 125.73, 124.78, 120.78, 118.99, 118.87, 96.93(N- $\text{CH}_3$ ), 66.32, 54.96, 35.83, 31.33, 30.65, 27.20, 26.66.

[1-mesityl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 2b



Following the procedure for the synthesis of complex 2a, 2b was obtained from 1b (110 mg, 0.23mmol) and  $[\text{RhCl}(\text{cod})_2]$  (58 mg, 0.12mmol). Yield = 95 mg (71.00%). Crystals suitable for X- ray crystallography were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for  $\text{C}_{30}\text{H}_{33}\text{N}_3\text{RhCl}$ : C, 62.78; H, 5.76; N, 7.32%. Found: C, 61.44; H, 5.48; N, 7.06%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHZ, 298K):  $\delta$  8.15(m, 1H,  $J = 8.4 \text{ Hz}$ , quin-H), 8.00(d, 1H,  $J = 8.1 \text{ Hz}$ , quin-H), 7.80(d, 1H,  $J = 5.7 \text{ Hz}$ , quin-H), 7.70(s, 1H, Ar-H), 7.50(t, 2H,  $J = 7.0 \text{ Hz}$ , quin-H), 7.05(t, 2H, quin-H, Ar-H), 6.90(s, 1H, CHHC), 6.70(s, 1H, CHHC), 6.50(d, 1H,  $J = 15.4 \text{ Hz}$ ,  $\text{CH}_{2\text{linker}}$ ), 6.10(d, 1H,  $J = 15.4 \text{ Hz}$ ,  $\text{CH}_{2\text{linker}}$ ), 4.80(broad, 2H, COD), 3.30(broad, 1H, COD), 3.00(broad, 1H, COD), 2.40(broad, 3H, COD), 2.30(s, 3H, p- $\text{CH}_3$ ), 1.80(s, 6H, o- $\text{CH}_3$ ), 1.50(broad, 4H, COD).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHZ, 298K): 155.03, 145.70, 136.61, 135.05, 134.97, 134.01, 132.36, 127.68, 127.52, 126.16, 125.69, 125.48, 124.62, 121.19, 119.73, 118.75, 95.44( $\text{NCH}_2$ ), 55.14, 31.56, 29.58, 26.93, 25.95(p- $\text{CH}_3$ ), 19.06(o- $\text{CH}_3$ ), 17.06, 15.75. HR-MS for  $[\text{M} - \text{Cl}]^+ = 538.18(100\%)$ : calculated, 538.1730( $\text{C}_{30}\text{H}_{33}\text{N}_3\text{Rh}$ ), found, 538.1751.

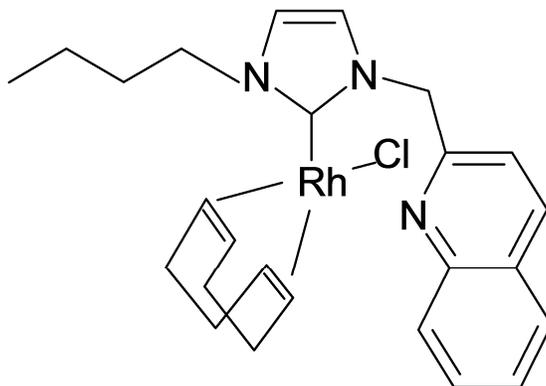
[1-isopropyl-3-(2-methylquinoline)imidazolin-2-ylidene] (1, 5-cyclooctadiene) rhodium(I) Chloride 2c



Following the procedure for the synthesis of complex 2a, 2c was obtained from 1c (134mg, 0.276mmol) and  $[\text{RhCl}(\text{cod})_2]$  (68 mg, 0.14mmol) . Yield = 110 mg (80.29%). Crystals

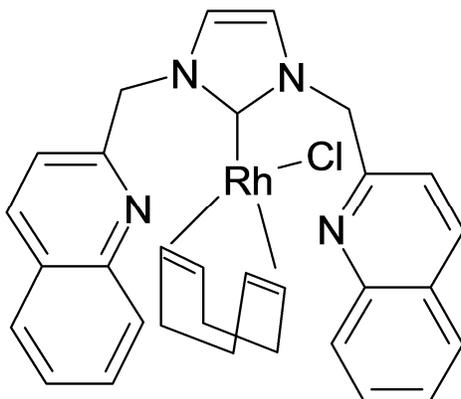
suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for  $C_{24}H_{29}N_3RhCl$ : C, 57.90; H, 5.83; N, 8.4%. Found: C, 53.85; H, 5.59; N, 7.47%.  $^1H$  NMR ( $CDCl_3$ , 400MHZ, 298K):  $\delta$  8.10(m, 1H, J = 8.5 Hz, quin-H), 8.00(d, 1H, J = 8.4 Hz, quin-H), 7.70(d, 1H, J = 8.1 Hz, quin-H), 7.65(t, 2H, J = 4.1 Hz, quin-H), 7.45( t, 1H, J = 7.0 Hz, quin-H), 6.80( s, 2H, CHHC), 6.50(d, 1H, J = 14.8 Hz,  $CH_{2linker}$ ), 5.75(m, 1H, J = 6.8 Hz, iPr-H), 5.60(d, 1H, J = 14.8 Hz  $CH_{2linker}$ ), 5.00(m, 1H, J = 7.6 Hz, COD), 4.90(m, 1H, J = 5.2 Hz, COD), 3.35(m, 1H, J = 2.6 Hz, COD), 2.1-2.40(m, 4H, J = 4.5 Hz COD), 1.7-2.00(m, 4H, J = 6.6 Hz, COD), 1,5(d, 6H, J = 4.2 Hz  $CH_3$ ).  $^{13}C$  NMR ( $CDCl_3$ , 100MHZ, 298K): 180.38(C-Rh), 155.00, 145.53, 135.60, 127.80, 127.04, 126.74, 125.87, 125.73, 124.76, 119.22, 115.25, 97.17,66.24, 55.19, 50.17, 31.50, 30.46, 27,38, 26.45, 22.19, 21.36, 20.72. HR-MS for  $[M - Cl]^+$  = 462.1415(100%): calculated, 462.1417( $C_{24}H_{29}N_3Rh$ ), found, 462.1415.

[1-n-butyl-3-(2-methylquinoline) imidazolin-2-ylidene] (1, 5-cyclooctadiene) rhodium (I) Chloride 2d



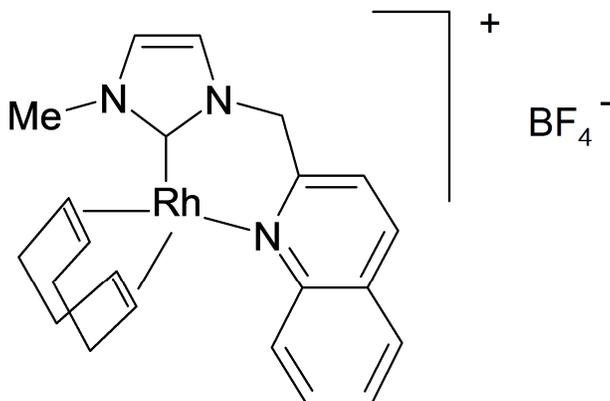
Following the procedure for the synthesis of complex 2a, 2d was obtained from 1d (150mg, 0.300mmol) and  $[RhCl(cod)]_2$  (74 mg, 0.15mmol). Yield = 121 mg (79.08%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for  $C_{25}H_{31}N_3RhCl$ : C, 58.66; H, 6.06; N, 8.21%. Found: C, 58.44; H, 6.48; N, 7.37%.  $^1H$  NMR ( $CDCl_3$ , 400MHZ, 298K):  $\delta$  8.10(m, 1H, J = 9.5 Hz, quin-H), 8.00(d, 1H, J = 8.4 Hz, quin-H), 7.75(d, 1H, J = 7.9 Hz, quin-H), 7.65(t, 2H, J = 4.8 Hz, quin-H), 7.45( t, 1H, quin-H), 6.75( s, 2H, CHHC), 6.50(d, 1H, J = 14.8 Hz,  $CH_{2linker}$ ), 5.60(d, 1H, J = 14.8 Hz,  $CH_{2linker}$ ), 5.00(broad, 2H, COD), 4.50(m, 2H, J = 6.1 Hz,  $CH_2$ ), 3.30(m, 2H, J = 2.3 Hz, COD), 2.40(m, 2H, J = 3.3 Hz  $CH_2$ ), 1.8(m, 4H, J = 2.4 Hz, COD) 1.40(m 2H, J = 7.4,  $CH_2$ ), 1.0(t, 3H, J = 7.4 Hz,  $CH_3$ ).  $^{13}C$  NMR ( $CDCl_3$ , 100MHZ, 298K): 178.66(C-Rh), 155.72, 146.45, 136.45, 128.73, 127.97, 126.76, 126.62, 125.67, 119.86, 119.73, 115.80, 84.35, 83.04, 55.73, 52.42, 50.97, 33.20, 31.87, 29.14, 28.03, 22.97, 22.08. HR-MS for  $[M - Cl]^+$  = 476.1578(100%): calculated, 476.1573( $C_{24}H_{29}N_3Rh$ ), found, 476.1578.

[bis-1, 3-(2-methylquinoline) imidazolin-2-ylidene] (1, 5-cyclooctadiene) rhodium (I) Chloride 2e.



Following the procedure for the synthesis of complex 2a, 2e was obtained from 1e (300mg, 0.600mmol) and  $[\text{RhCl}(\text{cod})]_2$  (150 mg, 0.30mmol). Yield = 250 mg (68.87%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for  $\text{C}_{31}\text{H}_{30}\text{N}_4\text{RhCl}$ : C, 62.37; H, 5.03; N, 9.39%. Found: C, 61.59; H, 5.13; N, 8.967%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz, 298K):  $\delta$  8.10(m, 2H, J = 8.5 Hz quin-H), 8.00(d, 2H, J = 8.4 Hz quin-H), 7.75(d, 2H, J = 8.1 Hz quin-H), 7.65(m, 4H, J = 4.8 Hz quin-H), 7.50( t, 2H, J = 7.0 Hz quin-H), 6.85( s, 2H, CHHC), 6.50(d, 1H, J = 14.9 Hz  $\text{CH}_{2\text{linker}}$ ), 5.80(d, 1H, J = 14.8 Hz  $\text{CH}_{2\text{linker}}$ ), 5.00(broad, 2H, COD), 4.50(broad, 2H,  $\text{CH}_2$ ), 3.30(m, 2H, J = 2.7 Hz, COD), 2.30(m, 4H, J = 4.0 Hz, COD), 1.90(m, 4H, J = 8.5 Hz, COD).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100MHz, R.T): 183.45(C-Rh), 155.64, 146.52, 136.52, 128.78, 128.03, 126.75, 126.61, 125.74, 120.58, 119.78, 98.38( $\text{CH}_2$ ) 67.93, 55.92, 32.84, 30.56, 27.81, 26.98, 21.63. HR-MS for  $[\text{M}-\text{Cl}]^+$  = 561.1548(100%): calculated, 561.1526( $\text{C}_{31}\text{H}_{30}\text{N}_4\text{Rh}$ ), found, 561.1548.

[1-methyl-3-(2-methylquinoline) imidazolin-2-ylidene] (1, 5-cyclooctadiene) rhodium(I) tetrafluoroborate 2e



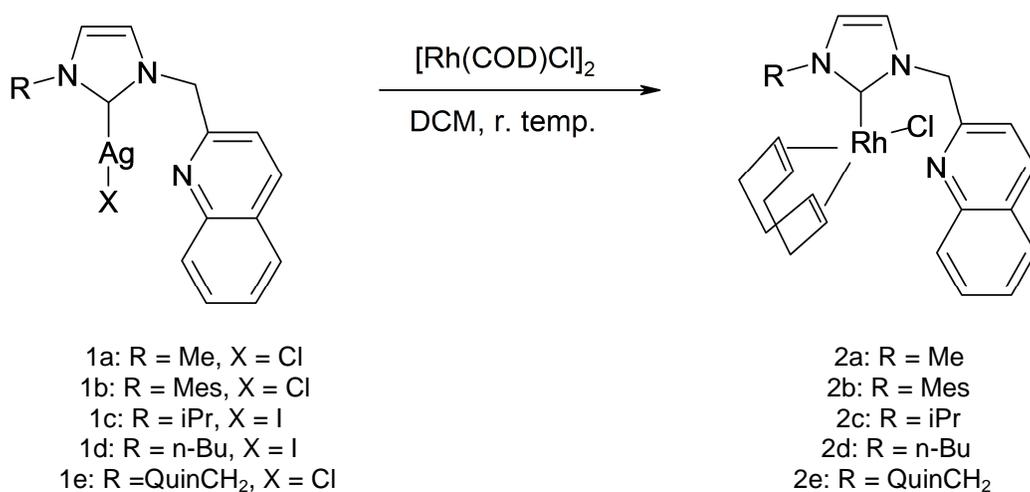
$\text{AgBF}_4$  (26 mg, 0.132mmol) was added to a stirred solution of complex 2a (62 mg, 0.132mmol) in 10 ml of DCM. The reaction mixture was stirred for 1 hour and reaction filtered through celite to remove silver chloride and any insoluble residue. The filtrates was then added drop by drop to a stirring solution of hexane to precipitate the compound which was then dried in vacuum to afford the desired compound as a deep yellow powder(42 mg,

60.87%). Anal. Calcd for  $C_{22}H_{25}N_3RhBF_4$ : C, 50.70; H, 4.80; N, 8.07%. Found: C, 42.18; H, 4.26; N,  $CDCl_3$ , 100MHz, 298K):

### 3. RESULTS AND DISCUSSION

The use of free carbene route by deprotonation of the imidazolium salts with strong base, which was expected to produce the corresponding free carbene, was not successful presumably because of interference from deprotonation of benzylic methylene protons [14]. Therefore, all the Rh(I) NHC complexes presented in this work were prepared from the  $Ag^I(NHC)$  complexes prepared from their corresponding imidazolium salts. Treatment of  $[Rh(COD)Cl]_2$  with the methylene bridged quinoline functionalized  $Ag^I(NHC)$  complexes in dichloromethane at ambient temperature gave the desired rhodium carbene complexes as yellow solids in good yield after work up as shown in Scheme 1 below. All the prepared rhodium complexes were characterised by  $^1H$  NMR,  $^{13}C$  NMR and mass spectroscopy, elemental analysis and X-ray crystallography. The  $^{13}C$  NMR data for the coordinating carbene carbons for complexes 2a, 2b, 2c and 2e appear at  $\delta$  values of 181.60, 180.38, 178.66 and 183.45ppm respectively, suggesting the formation of the Rh-C bond which are in the usual range for other Rh(I)-NHC complexes [12]. The carbenic carbon in complex 2b was not observed in the  $^{13}C$  NMR spectrum. The  $^1H$  NMR shifts corresponding to the protons of the quinoline ring are essentially similar to those of the silver complexes from which they were made, indicating that the quinoline nitrogen donor remains uncoordinated. Furthermore,  $^1H$  NMR spectra show diastereotopic protons for the  $CH_2$  linker ( $\delta = 6.5$  and  $5.6$  for complex 2a, 6.5 and 6.1 for complex 2b, 6.5 and 5.75 for complex 2c, 6.5 and 5.6 for complex 2d and 6.5 and 5.8 for complex 2e) which suggests that this group is out of the coordination plane of the molecule thus reducing its symmetry.

Elemental analysis results for complex 2a were satisfactory but no reasonable data could be obtained from the mass spectrum. Suitable crystals for X-ray single crystal diffraction were obtained from a DCM/ n-pentane solution at ambient temperature. The detailed solid state coordination sphere around the rhodium centre of complex 2a is confirmed by the X-ray crystal structural analysis. The complete molecular structure of complex 2a is depicted in Fig. 1 below with selected bond distances and bond angles shown in Table 1 below.



**Scheme 1. Synthesis of quinoline functionalised Rh(I) NHC complexes**

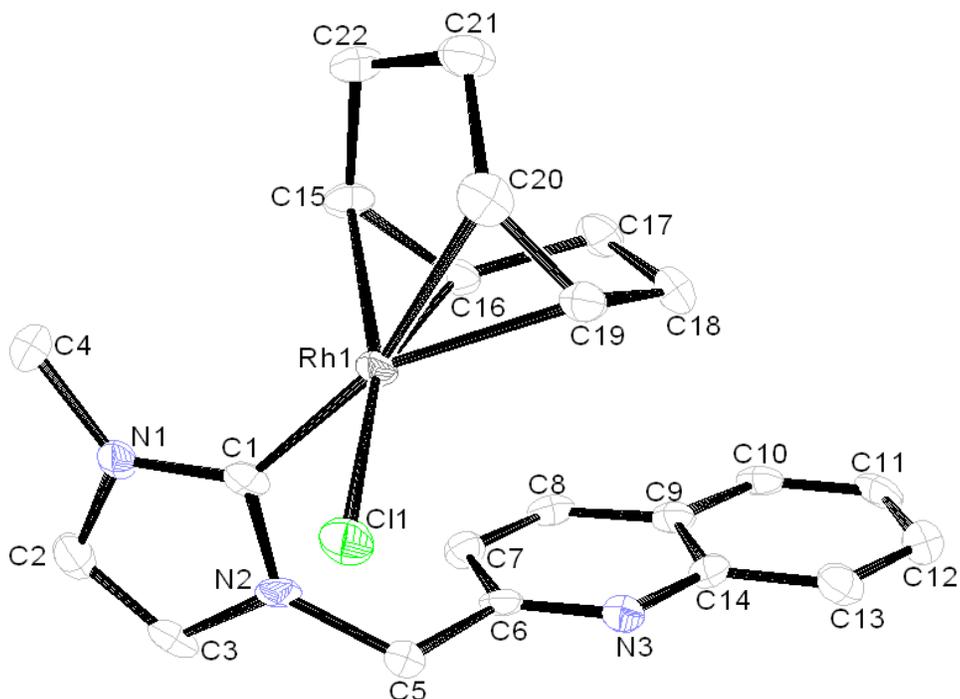


Fig. 1. ORTEP projection of complex 2a excluding hydrogen atoms for clarity, showing atom labeling scheme

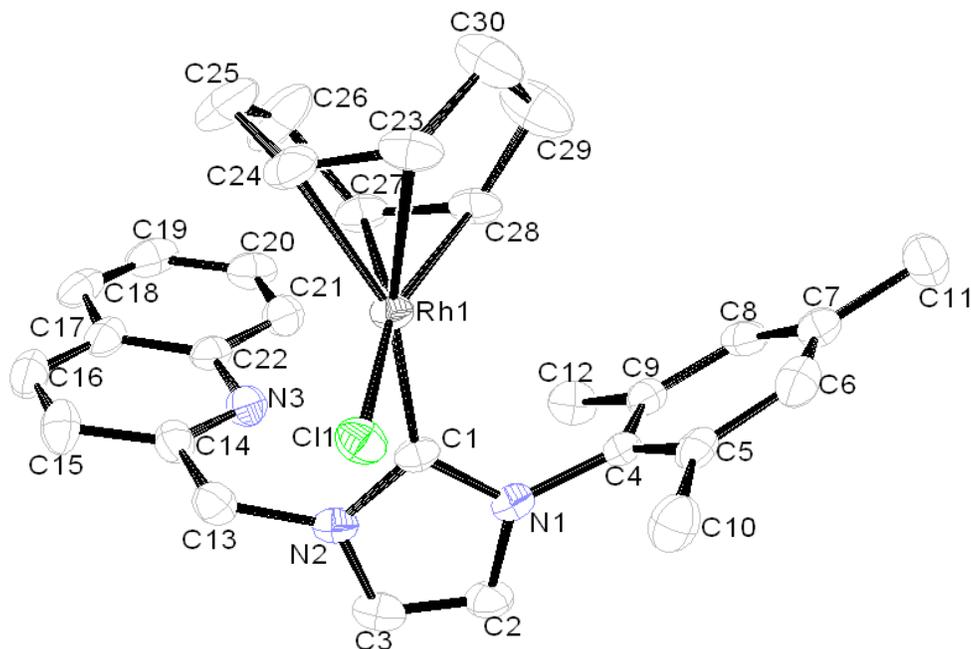
Table 1. Selected bond lengths (Å) and bond angles (°) of 2a

C1 - N1	1.356(6)	C16 - Rh1	2.126(5)	N1- C1- Rh1	131.4 (4)
C1 - Rh1	2.028(5)	C19 - Rh1	2.206(5)	C1- Rh1-Cl1	87.99(14)
C1 - N2	1.362(7)	Rh1- Cl1	2.386(13)	N2- C5- C6	113.90(4)
N2 - C3	1.394(9)	C20- Rh1	2.233(6)	C1-Rh1-C15	92.00(2)
C15 -Rh1	2.123(5)	N1- C1- N2	103.8(4)	C1-N2- C3	111.00(4)

The structural arrangement of complex 2a shows that the molecular geometry around the rhodium ion is a square planar arrangement with two coordination sites occupied by carbene and chloride in a *cis* fashion. The distances of Rh-C(COD) trans to the carbene donor appear to be longer than those in the *cis* arrangement, suggesting that the  $\sigma$ -donor nature of the diaminocarbene is stronger than that of the chloride. No major deviations were observed in the bond lengths and bond angles of complex 2a compared with those reported in the literature [7,15].

The  $^1\text{H}$  NMR shifts for complex 2b corresponding to the protons of the quinoline ring are essentially similar to those of the silver complexes from which they were made, indicating that the quinoline nitrogen donor remains uncoordinated with the carbenic carbon not observed in the  $^{13}\text{C}$  NMR spectrum. The high resolution MS measurement were consistent with the proposed formulation with  $[\text{M} - \text{Cl}]^+$  observed at  $M/z = 538.18$  Da (100% intensity). Crystals suitable for X-ray crystallography were obtained for complex 2b by diffusion of n-

pentane into the DCM solution of the compound enabling elucidation of the solid state structure as depicted in Fig. 2.



**Fig. 2. ORTEP projection of complex 2b excluding hydrogen atoms for clarity showing atom labelling scheme**

Selected bond lengths (Å) and bond angles (°) of 2b: C1 - N1=1.355(5), C1 - Rh1= 2.045(5), C1- N2=1.355(5), N2 - C3=1.379(9), C23 -Rh1= 2.202(4), N1- C1-N2=103.7(3), N1-C1-Rh1 130.8 (4), C1-Rh1- Cl1= 87.67(11), C1- N1- C4=124.3(3).

Elemental analysis of complex 2b returned satisfactory results. There are no significant deviations in terms of the bond lengths and bond angles of complex 2b with complex 2a and all are within the range reported in the literature [3,4,11].

Complex 2c was characterized by spectroscopic analysis, elemental analysis and X- ray crystallography. The  $^1\text{H}$  NMR spectrum for complex 2c displays similar pattern with that of complexes 2a and 2b. The synthesis of complex was confirmed by  $^{13}\text{C}$  NMR, which reveals Rh-C resonance at a  $\sigma$  value of 180.38 ppm. The high resolution MS measurement was consistent with the proposed formulation with  $[\text{M}-\text{Cl}]^+$  observed at  $M/z = 462.14$  Da (100% intensity) and elemental analysis results were in agreement with the proposed formulation. Crystals suitable for X-ray structural determination were obtained by diffusion of n-pentane into the saturated DCM solution of the compound and the geometry as well as bond distances and bond angles are similar to those obtained in 2a and 2b.

The geometry of rhodium in complex 2c is square planar and the parameters in terms of bond distances and internal angles in the complex are consistent the reported values [15,16]. High resolution MS of complex 2d displays a cluster of peak  $M/z = 476.16$  Da (100% intensity) assignable to the  $[\text{M}-\text{Cl}]^+$  and the elemental analysis gave results consistent with the formulation of the complex.



## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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