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Silver (I) complexes of methylene bridged quinoline functionalised Heterocyclic Carbene Ligands

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Abstract

This paper describes the synthesis of Silver (I) complexes of methylene bridged quinoline functionalized Heterocyclic Carbene Ligands, by stirring imidazolium salts with silver oxide to obtain the complexes in good yield. The complexes were structurally characterized by ^{1}H NMR, ^{13} NMR, microanalysis and X-ray crystallography. The geometry of the complexes as revealed by the crystal structure showed that the complexes have linear structures. All reactions involving silver were conducted under the exclusion of light.

Keywords: NHC, Imidazolium salt, ligand, silver

Introduction

The synthesis of Ag^1 N-heterocyclic carbene (NHC) was first reported by Arduengo in 1993 using the free carbene route (Arduengo, 1993). This was accomplished by deprotonation of the imidazolium salt to make the free carbene (1, 3-dimesitylimidazolin-2-ylidene) and subsequent reaction of with silver triflate to yield the desired homoleptic Ag^1(NHC). Several other Ag^1 (NHCs) have been synthesised using this method (Arduengo, 1993; Caballero, 2003). However, this method has been applied to the synthesis of only a limited number Ag^1(NHC) due to the difficulty of generating most free carbenes, which have other acidic protons especially azolium salts with methylene linkers(Lin and Vasam, 2004). Ag^1(NHC) can also be synthesized by transmetallation, as in the use of NHC ligands on $AgPF_6$ yielding homoleptic imidazolindin-2-ylidene complex (Ku *at al.,* 1999).

The *in situ* deprotonation of imidazolium salts with basic silver precursors is the most commonly used method to synthesise Ag^1(NHC) complexes. In their reaction Guerret *et al.,*(2000) demonstrated that Ag(OAc) reacts with 1,2,4-triazolium salts producing polymeric Ag^1(1,2,4-triazolin-3,5-diylidene) complexes with alternating Ag^1 and 1,2,4-triazolin-3,5-diylidene units. The use of Ag(OAc) protocol has not been widely utilised with the reports of Ag^1(NHC) complexes being restricted to a few examples with symmetrically alkyl substituted NHCs.

The most commonly used base is silver (I) oxide, pioneered by Lin and Wang (1998). These workers reported that stirring 1, 3-diethylbenzimidazolium bromide with Ag_2O in Dichloromethane (DCM), or with AgBr and NaOH under phase transfer conditions gave the Ag^1(benzimidazollin-2-ylidene)$_2$ complexes in high yield.

The principle advantage of the Ag_2O protocol is its tolerance to oxygen and moisture, indeed water is the by-product of the reaction. There are in fact reports of the reactions being carried out at ambient temperature, in a variety of solvents including water (Garrison *at al.,* 2003). The formation of silver complexes in water suggests that the deprotonation of the imidazolium salt and coordination to metal centre is a concerted process because free carbenes are water sensitive (Garrison and Youngs, 2005). Several groups have successfully prepared a variety Ag^1(NHC) complexes through the application of the Ag_2O method of Wang and Lin with different kinds of imidazolium salts (Lee *et al.,* 1999 and Bildstein *et al.,* 1999). Modification of Wang and Lin's original method used dichloromethane as solvent (McGuinness and Cavell, 2000; Tulloch *et al*., 2000), thereby allowing the reaction to be carried out at elevated temperatures for less reactive imidazolium salts.

In the cases where the imidazolium salts are insoluble in DCM, the use of solvent mixtures such as DCM-MeCN (Samantaray *et al.,* 2006) and DCM – EtOH (Wang *et al.,* 1999) has been found to be useful. The reaction can also be performed in DMSO at 55°C as reported recently (Garrison *et al.,* 2001). Furthermore, addition of molecular sieves to the reaction has also been reported to facilitate the formation of Ag^1(NHC) complexes by removing the water generated in the reaction (Nielsen *et al.,* 2002). Silver (I) carbonate was also reported to have been used in the synthesis of Ag^1(NHC), though less effective than the Ag_2O protocol as a longer reaction time is required for the reaction to reach completion (Tulloch *et al*., 2000). McGuinness and Cavell reported the synthesis of a series of mono donor-functionalised Pd^{II}(NHC) by the use of Ag_2O protocol via transmetallation of Ag^1(NHC) complexes with appropriate palladium precursors (McGuinness and Cavell, 2000). In another report, the application of the Ag_2O protocol to synthesise phenoxy- functionalised (Nielsen *et al.,* 2001), pyridyl-functionalised, (Nielsen *et al.,* 2002) thiophene and furan-functionalised Ag^1(NHC) complexes were demonstrated. Other Ag^1(NHC) prepared were not isolated but used directly as transmetallation reagents (Nielsen *et al.,* 2003).

The wide applicability and ease of preparation of stable Ag^1(NHC) complexes via the Ag_2O route and the good transmetallation properties of these complexes promised ready access to donor-functionalised NHC complexes of catalytically interesting transition metals (Nielsen *et al.,* 2004). The ability to obtain Ag^1(NHC) complexes from the reaction of Ag_2O with imidazolium, saturated imidazolidinium and benzimidazolium salts indicates that their formation is relatively unaffected by the electronics of the heterocyclic ring (Nielsen *et al.,* 2004). The reaction is also tolerant of steric group and wide range functional groups on the NHC N-substituents.

The use of Ag^1(NHC) in homogenous catalysis has recently appeared in the literature: such as in the preparation of 1,2-bis(borane) esters (Corberan *et al.,* 2006), ring opening polymerization of lactides (Sentman *et al.,* 2005; Samantaray *et al.,* 2006) and olefin polymerization (Wang, *et al.,* 2006). However, the increased interest in the chemistry of Ag^1(NHC) complexes has been mainly due to their role as transfer agents in the development of many important metal-NHCs. The fact that active hydrogen atoms other than C_2-H can be protected effectively by this method it solved difficulties encountered in the synthesis of metal- NHCs by other methods (McGuinness and Cavell, 2000).

Experimental

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 (Armarego and Perrin 1996), unless otherwise indicated, all other reagents were used as received. All NMR data are quoted δ/ppm. ^{1}H and ^{13}C (proton decoupled) spectra NMR were recorded on a Bruker DPX Advance 400 (^{1}H at 400MHz, ^{13}C at 100.61 MHz) at ambient temperature, unless otherwise stated, and referenced to $SiMe_4$. 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 Ag (1-methy-3-(-2-methylquinoline) imidazolin-2-ylidine) $_2$][$AgCl_2$] 2a

A mixture of 1-methyl-3-(2-methylquinoline) imidazolium chloride (0.30g, 1.16mmol) and Ag_2O (0.14g, 0.59mmol) in dichloromethane was stirred for 12 hours. The solution was filtered through celite and the filtrate concentrated. Diethyl ether was added to precipitate the carbene complex which was repeatedly washed with diethyl ether and dried under vacuum to give the desired silver carbene complex. Crystals suitable for X- ray structure were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{14}H_{13}N_3AgCl$: C, 45.86; H, 3.55; N, 11.46; Cl, 9.67%. Found: C, 45.71; H, 3.45; N, 11.33; Cl, 9.60%. ^{1}H NMR ($CDCl_3$. 400MH$_Z$, 298K): 8.10 (d, 2H, J = 8.5 H$_{Z,}$ Quin-H), 8.00 (d,2H, J = 8.4 H$_{Z,}$ Quin-H), 7.80 (d, 2H, J = 8.1 H$_{Z,}$ CHHC), 7.5 (d, 2H, J = 8.4 H$_{Z,}$ Quin-H), 7.35 (d, 2H, J = 1.7 H$_{Z,}$ Quin-H) 7.15 (d, 2H, J = 1.8 H$_{Z,}$ Quin-H), 6.95 (s,1H, Quin-H), 5.50 (s, 4H CH_2), 3,85 (s, 6H, CH_3). ^{13}C NMR ($CDCl_{3,}$ 100MH$_Z$, 298K): 181.18 (C-Ag), 155. 45, 148.09, 138. 12, 130.55, 129.62, 128.11, 127.92, 127.50, 123.01, 122.31, 120.20, 58.14, 39.27. MS (HRMS, Da): M/z (224.09) [(NHC)+H]$^+$ (100%).

Synthesis of [Ag (1-mesityl-3-(-2-methylquinoline) imidazolin-2-ylidine)Cl] 2b

A mixture of 1-mesityl 3-(2-methylquinoline) imidazolium chloride (0.50g, 1.38mmol) and Ag_2O in dichloromethane was stirred at room temperature for 12 hours. The solution was filtered through celite and the filtrate concentrated. Diethyl ether was added to precipitate the carbene complex which was repeatedly washed with diethyl ether and dried under vacuum to give the desired silver carbene complex. Crystals suitable for X-ray structure were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{22}H_{21}N_3AgCl$: C, 56.13; H, 4.46; N, 8.93; Cl, 7.55%. Found: C, 56.23; H, 4.53; N, 8.77; Cl, 7.55%. ^{1}H NMR ($CDCl_3$. 400MHZ, 298K) : 8.10 (d, 1H, J = 8.4 H$_{Z,}$ Quin-H), 8.00 (d, 1H, J = 8.5 H$_{Z,}$ Quin-H), 7.80 (d, 2H, J = 8.1 H$_{Z,}$ CHHC), 7.70 (t, 1H, J = 1.4 H$_{Z,}$ Quin-H), 7.50 (t, 1H, J = 7.0 H$_{Z,}$ Quin-H), 7.35 (t, 2H, J = 8.7 H$_{Z,}$ Quin-H), 6.90 (s, 3H, Aromatic-H), 5.60 (s, 2H, CH_2), 2.25 (s, 3H,m-CH_3), 1.95 (s, 6H, O-CH_3). ^{13}C NMR ($CDCL_3$, 100 MHZ, R.T.): 155.40, 148.0, 139.20, 138.18, 135.08, 130.59, 129.84, 129.64, 128.16, 127.95, 127.50, 123.57, 122.29, 119.74, 58.16, 21.47, 18.11. MS(HRMS, Da): M/z (328.15) [(NHC)+H]$^+$ (100%).

Synthesis of [Ag (1-isopropyl- 3-(2-methylquinolin) imidazolin-2-ylidine)I] 2c

Following the method for the synthesis of **2b**, compound **2c** was synthesized from 1-isopropyl-3-(2-methylquinoline) imidazolium iodide (0.10g, 0.26mmol) and Ag_2O(32mg, 0.14mmol) in dichloromethane.(Yield =0.12g, 73 %). Calcd. for $C_{16}H_{17}N_3AgI$: C, 39.52; H, 3.50; N, 8.65; I, 7.55%. Found: C, 39.70; H, 3.42; N, 8.57; I, 25.92%. ^{1}H NMR ($CDCl_3$. 400MH$_Z$, 298K): 8.05(d, 2H, J = 8.5 H$_{Z,}$ quin-H), 7.65(t, 2H, J = 7.0 H$_{Z,}$ quin-H), 7.50(d, 2H, J =5.2 H$_{Z,}$ quin-H), 7.10(s, 1H, CHHC), 6.90(s, 1H, CHHC), 5.60(s, 2H, NCH_2C), 4.85(m, 1H, NCHC), 1.35(d, 6H, J = 6.8 $H_{Z,}$ CH_3). ^{13}C NMR ($CDCL_3$, 100 MH_Z, R.T.): 184.10(C-Ag), 156.55, 137.91, 130.18, 129.47, 128.12, 127.91, 121.71, 121. MS (HRMS, Da): M/z = 609.1886 $[Ag(NHC)_2]^+$ (100%).

Synthesis of [Ag(1-n-butyl-3-(-2-methylquinolin)imidazolin-2-ylidine)I] 2d

Following the method for the synthesis of **2c**, compound **2d** was synthesized from 1-nbutyl-3-(2-methylquinoline)imidazoliumiodide (0.50g, 1.27mmol) and Ag_2O(0.15g, 0.64mmol) in dichloromethane.(Yield = 0.40g, 62.50%). Calcd. for $C_{17}H_{19}N_3AgI$: C, 40.82; H, 3.80; N, 8.40%. Found: C, 39.90; H, 3.67; N, 7.79%.^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d, 1H, J = 8.5 $H_{Z,}$ quin-H), 7.90(d, 1H, J = 8.5 $H_{Z,}$ quin-H), 7.60(m, 2H, J = 8.1 $H_{Z,}$ quin-H), 7.55(d, 1H, J = 8.5 $H_{Z,}$ quin-H), 7.40(t, 1H, J = 7.2 $H_{Z,}$ quin-H), 7.00(s, 1H, CHHC), 6.80(s, 1H, CHHC), 5.60(s, 2H, methylene linker-H), 4.10(t, 2H, NCH_2), 1.70(m, 2H, J = 7.5 $H_{Z,}$ CH_2), 1.20(m, 2H, J = 7.0 $H_{Z,}$ CH_2), 0.80(t, 3H, J = 7.3 $H_{Z,}$ CH_3). ^{13}C NMR ($CDCL_3$, 100 MH_Z, R.T.): 183.23(C-Ag), 155.02, 146.52, 136.50, 128.80,128.07, 126.70, 126.50, 126.14, 125.76, 120.30, 119.96, 64.84, 56.56, 50.68, 32.50, 18.75. MS(HRMS, Da): M/z (637.2189) $[Ag(NHC)_2]^+$ (100%)

Synthesis of [Ag (1-(-2-methylpropiophenone)-3-(-2-methylquinolin) imidazolin-2-ylidine) Cl]

Following the method for the synthesis of **2d**, compound **2e** was synthesized from 1-(2-methylpropiophenone)-3-(-2-methylquinolin) imidazolium chloride (0.30g, 0.77mmol) and Ag_2O (90mg, 0.39mmol) in dichloromethane. (Yield = 0.32g, 90.00%). Anal. Calcd. for $C_{23}H_{21}N_3OAgCl$: C, 55.38; H, 4.14; N, 8.43%. Found: C, 55.78; H, 4.18; N, 8.22%. ^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d,2H, J = 10.7 $H_{Z,}$ quin-H), 7.75(d, 1H, J = 7.1 $H_{Z,}$ quin-H), 7.60(d,1H, J = 7.5 $H_{Z,}$ arom-H), 7.50(t, 1H, J = 7.3 $H_{Z,}$ arom-H), 7.35(s,2H, arom-H), 7.25(s, 2H, CHHC), 7.20(d, IH, J = 6.8 $H_{Z,}$ quin-H), 7.10(t, 2H, J = 8.4 $H_{Z,}$ quin-H), 6.90(d, 1H, J = 11.8 $H_{Z,}$ arom-H), 5.50(s,2H,NCH_2qiun), 2.00(s, 6H, CH_3). ^{13}C NMR ($CDCL_{3,}$ 100MH_Z, 298K):196.71(PhCOC), 153.72, 146.53, 136.77, 136.59, 131.72, 129.18, 129.12, 128.17, 127.94, 127.60, 126.72, 126.66, 126.46, 126.12, 120.91, 118.72, 118.43, 118.38, 66.99, 57.61, 27.56. MS(HRMS, Da): M/z (356.1642) $[(NHC)+H]^+$ (100%), 817.2445 $[Ag(NHC)_2]$+ (36%).

Synthesis of [Ag (bis-1, 3(2-methylquinolin) imidazolin-2-ylidine) Cl] 2f

Following the method for the synthesis of **2e**, compound **2f** was synthesized from bis-1, 3-(2-methylquinoline) imidazolium chloride (0.30g, .78mmol) and Ag_2O (93mg, 0.40mmol) in 20 ml of dichloromethane. (Yield =.0.12g, 40%). Anal. Calcd. for $C_{23}H_{18}N_4AgCl$: C, 55.94; H, 3.65; N, 11.35%. Found: C, 56.39; H, 3.61; N, 11.21%. ^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): 8.10(d, 2H, J = 8.4 $H_{Z,}$ quin-H), 8.00(d, 2H, J = 8.5 $H_{Z,}$ quin-H), 7.75(d,2H, J =8.1 $H_{Z,}$ quin-H), 7.65(t, 2H, J = 5.6 $H_{Z,}$ quin-H), 7.5(t, 2H, J = 7.1 $H_{Z,}$ quin-H), 7.35(d, 2H, J = 8.5 $H_{Z,}$ quin-H), 7.15(s, 2H, HHC), 5.5(s, 4H, NCH_2C). ^{13}C NMR ($CDCL_3$, 100 MHZ, 298K): 180.37(C-Ag), 154.09, 146.58, 136.71, 129.08, 128.09, 126.70, 126.47, 126.01, 121.31, 118.75, 56.74. MS (HRMS, Da): M/z (351.16) $[(NHC)+H]^+$ (100%).

Results and discussion

The methylene-bridged quinoline functionalised Ag^1(NHC) complexes were prepared following the method reported by Wang and Lin (1998), i.e. by interaction of the imidazolium salts with Ag_2O as shown in scheme 1.

1a : R = Me, X = Cl
1b : R = Mes, X = Cl
1c : R = ipp, X = I
1d : R = n-Bu, X = I
1e : R = PhCOC(Me)$_2$, X = Cl
ff : R = QuinCH$_2$, X = Cl

2a: R = Me, X = Cl
2b: R = Mes, X = Cl
3c: R = ipp, X
2d R = n-Bu, X = I
2e : R = PhCOC(Me$_2$)X = Cl
2f: R = QuinCH$_2$ X = Cl

Scheme 1: Synthesis of methylene bridged quinoline functionalised Ag^1(NHC) complexes

It was found that: (i) with the relatively unreactive sterically hindered imidazolium salts (**2e** and **2f**) the reaction was carried out in refluxing dichloromethane, whereas for all other imidazolium salts the reaction occurred at room temperature ; (ii) synthesis in refluxing dichloromethane increases the formation of by-product (iii) the purity of the product is improved by addition of activated molecular sieves to the reaction medium.

Compound **2a** was characterised by ^{1}H NMR, ^{13} NMR, microanalysis and X- ray crystallography. The room temperature ^{1}H NMR of Complex **2a** was consistent with the proposed structure showing complete disappearance of imC$_2$-H resonance and the protons of the methylene linker was observed to move up field. In the ^{13}C NMR there was sharp singlet peak at 181.18 ppm which is assignable to the carbene carbon of the Ag^1(NHC) complex. Microanalysis returned satisfactory results for complex **2a.** Crystals suitable for X- ray structural determination were obtained by diffusing Et$_2$O into a DCM solution of the complex, figure 1.

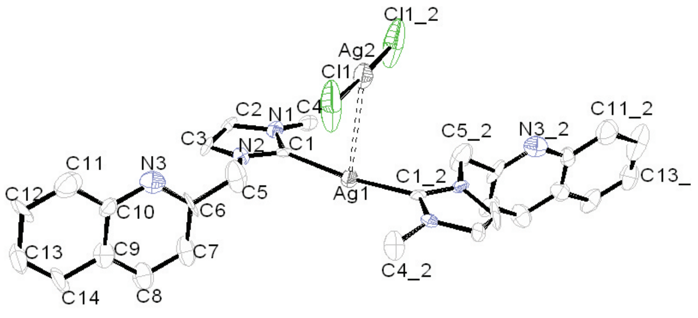

Figure 1: ORTEP projection of complex **2a** excluding hydrogen atoms for clarity showing atom labelling scheme.

Complex **2a** as shown in the above figure consists of a linear $[Ag(NHC)_2]^+$ cation and a linear $[AgCl_2]^-$ with the two ions associating through Ag^1- Ag^1 interaction. The Ag-C bond distance (Ag(1)-C(1) = 2.106(12) are comparable to those reported by Wang and Lin (2.073 Ǻ) (Guerret *et al.,* 2000). The geometry of C(1)-Ag(1)-C(1_2) is close to linear (170.8°(8) though it is lower than what was obtained by Wang and Lin (175.6°) [6]. The Ag(1)-Ag(2) separation of 3.201 Ǻ is smaller than the contact van de Waals distance of 3.44Ǻ and is at upper range of the ligand-unsupported Ag-Ag bond lengths (range 2.80-3.30 Ǻ) [54]. The Cl(1)-Ag-Cl(1) angle of

176.6° deviates only slightly from that of the coordinated linear species. Some selected bond lengths (A) and angles (o) are presented in table 1 below.

Table 1: Selected bond lengths (Ǻ) and bond angles (°) of **2a**

Ag1- Ag2 3.201(4)	N2-C5 1.48(2)	C1-Ag1-Ag2 94.6(4)
Ag2-Cl1 2.290(5)	N2-C1-N1 104.0(10)	C1-Ag1-Ag2 85.4(4)
Ag1-C1 2.106(12)	N2-C1-Ag1 130.6(8)	Cl1-Ag1-Cl1 176.6(11)
C1-N1 1.353(16)	N1-C1-Ag1 125.2(9)	C3-C2-N1 107.8(11)
C1-N2 1.351(14)	C1-Ag1-C1 170.8(8)	C1-N2-C5 119.3(10)

The ^1H NMR spectrum of complex **2b** shows the disappearance of C_2-H signal with other signals consistent with the proposed structure. The ^{13}C NMR spectrum reveals the absence of $C_{carbene}$ resonance and the elemental analysis returned satisfactory results. A ES-MS showed a peak corresponding to cation [M^+-Cl =328.15] with intensity of 100% similar to that of the corresponding imidazolium salt indicating that under these conditions the silver complex undergoes decomposition .This decomposition of silver(NHC) complexes and the observation of the corresponding salts has been reported using ES-MS (Bonnet *et al.,* 2004). Crystals suitable for X-ray crystallography were obtained by diffusion of Et_2O into a saturated DCM solution of the complex and the crystal structure is depicted in Figure 2 below. The geometry of the silver in the carbene complex is that of distorted linear with C13- Ag1-Cl2 bond angle of 169.03° (10) which is similar to the silver carbene complex reported by Cesar and Gade (169.4° (1)) (Cesar *et al.,* 2002) and lower than those reported by Danopoulos et al (176.1°(2)) (Nielsen *et al.,* 2002), Pytkowicz etal (175.2°(5)) (Pytkowicz *et al.,* 2001) and (173.5°(2)) (Paas *et al*., 2006). All other bond lengths and bond angles are consistent with the reported values (Nielsen *et al.,* 2002; Pytkowicz *et al.,* 2001; Paas *et al.,* 2006; Pytkowicz *et al.,* 2001). Some selected bond length and bond angles are presented in table 2 below.

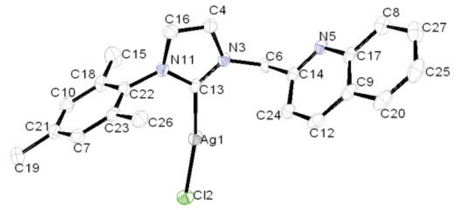

Figure 2: ORTEP projection of complex **2b** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 2: Selected bond lengths (Ǻ) and bond angles (°) of **2b**

Ag1-Cl2 2.350(9)	N5-C14 1.320(5)	Ag1-C13-N11 123.7(3)
Ag1-Cl3 2.090(3)	C4-C16 1.344(5)	N3-C13-N11 104.9(3)
N3-C13 1.342(5)	C4-N3 1.384(4)	N3-C6-C14 111.6(3)
N11-C13 1.354(4)	C13-Ag1-Cl2 169.03(10)	C13-N11-C22 122.6(3)
N3-C6 1.474(4)	Ag1-C13-N3 131.4(2)	C6-C14-N5 116.2(3)

The formation of complexes **2c**, **2d, 2e** and **2f** were confirmed by ^1H NMR and ^{13}C NMR spectroscopy. The ^1H NMR revealed complete disappearance of the C_2-H protons while the $C_{carbene}$ of complexes **2c, 2d** and **2f** appeared at 184, 183 and 180 ppm respectively, and that of complex **2e** was not observed. High resolution mass spectroscopy of complex **2f** indicated only the decomposition of the complexes as only the its corresponding imidazolium salt ions was observed at M/z = 351 (100% intensity) equivalent to $[(NHC)+H]^+$. ^1H NMR and ^{13}C NMR spectra of complex **2c** are consistent with the bis carbene formulation with the $C_{carbene}$ of the complex appearing at 184.10 ppm. HRMS showed cluster at M/z = 609 (100% intensity) attributable to $[Ag(NHC)_2]^+$ of the bis carbene. A look at the spectra of the complexes indicate that there is no significant difference between complexes 2a-2f in terms of the chemical shift of quinoline protons and that of the methylene linkers and the C-Ag carbene resonances were observed between 180.37 -184.10 which are within the range reported in the literature (180-243 ppm) (Garrison *et al.,* 2005). Elemental analysis of complex **2c** returned a satisfactory results consistent with the proposed structure as suitable crystal for X-ray crystallography could not be obtained. Complex **2d** revealed a cluster at M/z = 637 Da (100% intensity) attributable to the cation of biscarbene $[Ag(NHC)_2]^+$. The ^{1}H NMR and ^{13}C NMR spectra as well as the elemental analysis of complex **2e** are consistent with the proposed silver carbene complex. MS analysis revealed a cluster at M/z = 356 Da (100% intensity) and 817 Da (36%) attributable to the cation of the corresponding salt $[(NHC)+H]^+$ and biscarbene ion $[Ag(NHC)_2]^+$ respectively. The observation of the peak attributable to the bis carbene ion may not necessarily indicate that the complex is indeed a biscarbene. Danopoulos and colleagues reported that silver NHCs with solid-state motifs of C-Ag-X and C-Ag-X_2 formed biscarbenes (C_2-Ag) in the gas phase (Tulloch *et al.,* 2000).

Compounds **2a** and **2b** are the first examples of quinoline functionalised Ag1(NHC) complexes and were structurally characterised by X-ray crystallography and formulated as $[Ag(NHC)_2]^+[AgCl_2]^-$ and [Ag(NHC)Cl] respectively. Results of MS data indicated that complexes **2c**, **2d** and **2d** may have a similar formulation to that of **2a** because of the presence of cluster attributable to $[Ag(NHC)_2]$. However the MS is not enough to formulate the formula of Ag^1(NHC) complexes as Nielson and colleagues reported that silver NHCs with solid-state motifs of C-Ag-X and C-Ag-X_2 formed biscarbenes (C_2-Ag) in the gas phase (Nielsen *et al.,* 2002). All the Ag^1(NHC) complexes showed stability to air and moisture and were not exposed to light.

Conclusions

Ag^1(NHC) complexes have been valuable intermediates in the preparation of functionalised Pd^{II}(NHC) complexes that are difficult to be accessed via other methodologies. Thus a range of imidazolium salts was reacted with Ag_2O to form the corresponding silver (I) carbene complexes. The syntheses of the silver complexes were confirmed by the absence of C_2-H in the ^{1}H NMR spectrum, and other analytical techniques.

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