



Synthesis, Characterization and Structure Report of Silver(I) N-heterocyclic Carbene Complex Derived from 1-Methyl-3-(4-picolyl) Imidazolium Salt

Siraj, I. T.

Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Bayero University, P.M.B 3011,
Kano - Nigeria

Email: itsirajo.chm@buk.edu.ng

ABSTRACT

1-Methyl-3-(4-picolyl) imidazolium chloride was synthesized by the reaction of 4-picolyl chloride hydrochloride with 1-methyl imidazole. Treatment of the synthesized 1-methyl-3-(4-picolyl) imidazolium chloride with silver (I) oxide resulted in the formation of bis N-heterocyclic carbene (NHC) silver (I) complex. The compound was characterized spectroscopically using proton and carbon-13 nuclear magnetic resonance (NMR), and mass spectrometry. Its molecular structure was analyzed using single crystal X-ray crystallographic analysis. The bis-N-heterocyclic carbene silver(I) complex synthesized shows approximately linear geometry around each of the silver atom of the type $[\text{Ag}(\text{NHC})_2]^+$.

Keywords: N-heterocyclic Carbene, synthesis, characterization, X-ray crystallography, silver (I)

INTRODUCTION

N-heterocyclic carbenes (NHCs) have continued to received sizeable part of attention (Ren *et al.*, 2017) since the isolation of the first free crystalline N-heterocyclic carbene and its subsequent complexation (Arduengo, 1991). This important development opened up the area of NHC to the world of chemistry, which attracted a huge interest and advancement in the field of carbene chemistry. Immediately their use as ligands in organometallic chemistry hugely increased and several other free NHCs based on saturated heterocycles, the imidazolin-2-ylidenes, were isolated and reported by Arduengo (Arduengo, 1999).

The use of NHC complexes in homogenous catalysis has received a huge interest from different research groups and has been a major driving force in the development of NHC chemistry which has contributed immensely in organic processes (Mathew *et al.*, 2014). The extensive work of Hermann on their use in various catalytic processes (Hermann, 2002) and other reviews (Nolan *et al.*, 2009, Johnson and Albrecht, 2017) has been particularly important in this field. The catalytic potentials of the NHCs was explored because of their perceived similarities to phosphine ligands. Quite a number of examples in which a known phosphine based catalyst has been modified by replacing one or more of the phosphine ligands with an NHC have been reported (Grubbs *et al.*, 1996). The catalytic activities of the NHC incorporated catalysts were almost always found to

be more suited for many catalytic reactions than the original phosphine catalyst. Part of the possible reasons for the enhanced performance of these new catalyst may be that the non-labile, bulky NHC ligand provides the metal centre with considerable steric protection, and as a good σ -donor, stabilises the pre-catalyst and coordinatively unsaturated, catalytically relevant, intermediate. In addition to their use as catalyst, their wide range of medicinal applications have been reviewed (Hindi *et al.*, 2009, Johnson *et al.*, 2017)

Wanzlick and Öfele in their first report of NHC complexes (Wanzlick and Schönherr, 1968, Öfele, 1968) have shown that NHC complexes can be prepared by *in situ* deprotonation of imidazolium salts in the presence of a suitable metal complex, without the necessity of isolating a free carbene. In both cases a ligand in the metal precursors acted as a base, deprotonating the imidazolium salt which then complexed the metal *in situ*.

Our interest is to develop a series of pyridine functionalised imidazolium salts and convert them into N-heterocyclic carbene complexes. In this paper a synthesis of pyridine functionalized imidazolium salt and their conversion into the silver NHC complexes through the *in situ* method is reported.

MATERIALS AND METHODS

Unless otherwise stated all reactions were performed under nitrogen atmosphere using standard Schlenk line techniques. All reagents,

unless otherwise stated were purchase from Aldrich and were used without further purification. Mass spectra were recorded on a thermo Finnigan LCQDUO mass spectrometer using ESI. The data were given in mass unit per charge and the intensities of the signal were indicated in percent of the base ion. ¹H NMR spectra were recorded on Bruker AVANCE/DPX 400(400 MHz) and or AVANCE/DRX 500 (500 MHz) in CDCl₃ and DMSO-d₆ with tetramethyl silane as external standard.

Single crystal measurements were made at 123K with graphite monochromated MoK α 1 radiation (wavelength 0.71073 Å) on an Oxford Diffraction Gemini S diffractometer equipped with a CCD detector and a variable temperature device. Initial atomic sites were located using direct methods. Remaining non-hydrogen atom sites were calculated using difference Fourier maps. Refinement of atomic co-ordinates and thermal parameters was to convergence and by full-least squares methods on F² within SHELX-97 (Sheldrick, 1998). Where the quality of the data allowed, H-atoms bound to O or N were refined isotropically, all other H-atoms were placed in calculated positions and in a riding mode. Reported wR2 values are based on F² and all reflections, whilst reported R1 values are based on F and on observed reflections with I>2 σ (I).

Synthesis of 1-Methyl-3-(4-picolyl) Imidazolium Chloride (1)

4-Picolyl chloride hydrochloride (1.30g, 7.93 mmol) was neutralized using a saturated solution of sodium carbonate. The liberated 4-picolyl chloride was extracted into diethyl ether (3 x 40 mL) at 0°C, dried with anhydrous sodium sulphate and filtered. The filtrate was concentrated to 80 mL, 1-Methyl imidazole (0.656g, 8 mmol) in methanol (80 mL) at 0°C was added. Diethyl ether was removed under pressure and the solution stirred at room temperature overnight. The solvent was taken off under reduce pressure. An oily

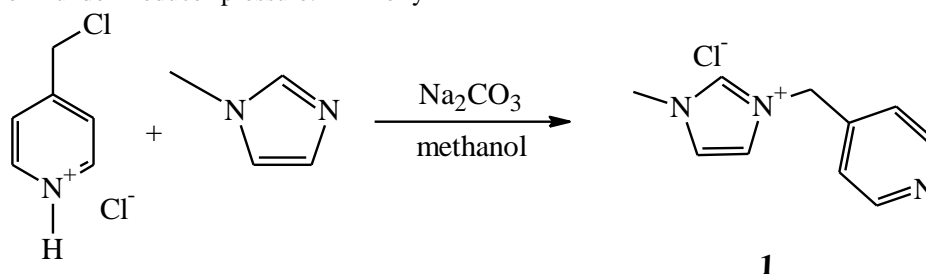
product was obtained. ¹H NMR (400 MHz, Solvent CDCl₃) δ ppm: 4.41 (s, -CH₂- 2H), 7.18 (d, -CH- of Py 2H), 8.23 (d, -CH- of Py 2H), 7.37 (s, -NCHN- of imid. 1H) 6.79 (s, -CH- of imid. 1H), 6.85 (s, -CH- of imid. 1H). MS (ESI, methanol; m/z) = 174[M]⁺.

Synthesis of [Ag (3-methyl-1-picolylimidazol-2-ylidene)₂]Cl. (2)

A mixture of **1** (1.03g, 4.93 mmol) and silver (I) oxide (0.395g, 1.70 mmol) was taken up in 50 mL DCM and the mixture was covered with aluminum foil and stirred at room temperature for 5hrs. The solution was filtered through celite to give a dark brown solution. The solvent was removed under vacuum and was recrystallised from DCM – diethyl ether by vapour diffusion which gave white crystalline product. ¹H NMR (400 MHz, Solvent CDCl₃) δ ppm: 5.34 (s, -CH₂- 4H), 7.85 (d, -CH- of Py 4H), 8.63 (d, -CH- of Py 4H), 6.88 (s, -CH- of imid. 2H), 7.45 (s, -CH- of imid. 4H). MS (ESI, methanol; m/z): 489 [M]⁺

RESULTS AND DISCUSSION

1-Methyl-3-(4-picolyl) imidazolium chloride, **1**, was successfully prepared in good yield (73%) according to Scheme 1. The initial method used, involved refluxing 1-methyl imidazole with 4-picolyl bromide hydrobromide at reflux temperature in the presence of NaHCO₃ as a base. It gave the intended product but with other side reactions which make the isolation and purification of the desired product very difficult. Therefore, a new procedure was developed, the picolyl chloride hydrochloride was neutralized with a base to liberate the deprotonated picolyl chloride which was reacted with 1-methyl imidazole in methanol at 0°C using ice full beaker. This procedure avoids using an elevated temperature which may be responsible for the side reaction of the pyridine, and the desired product was obtained in pure form as an oil.



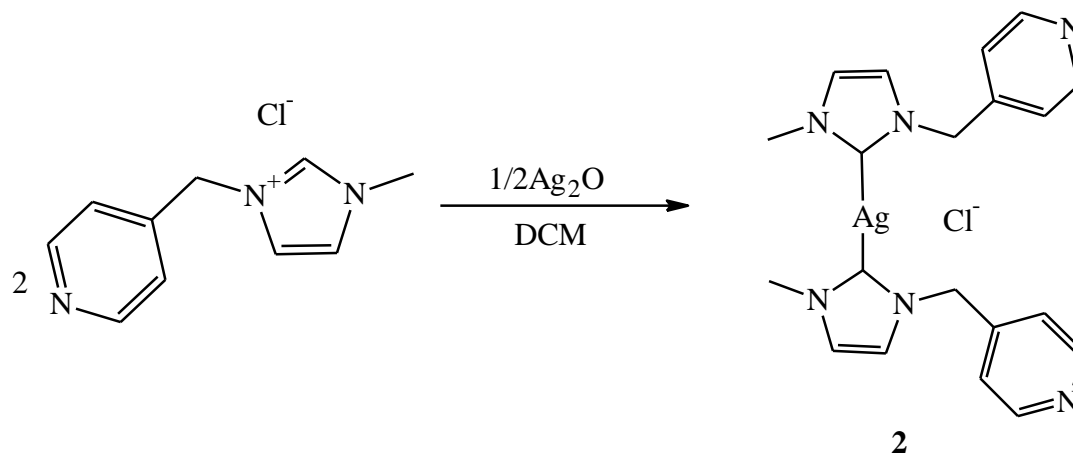
Scheme 1: Synthesis of 1-methyl - 3- (4-picolyl) imidazolium chloride, **1**

The oil formed was found to be the desired compound using ¹H NMR and mass spectral analysis. The ¹H NMR spectrum revealed doublets at 7.19 ppm and 8.23 ppm which may be assigned to the pyridine ring protons. Singlets at 6.79 ppm, 6.85 ppm and 7.37 ppm assigned to the imidazole ring protons while a peak at 4.40 ppm was assigned

to the methylene spacer between the imidazole and pyridine ring. Furthermore, the terminal methyl protons on the imidazole were observed to resonate at 3.46 ppm. The mass spectrometry reveals a positive ion peak at m/z = 174 as the only major peak which is consistent with the expected value of the desired product (**1**).

A mixture of the synthesized 1-methyl-3-(4-picolyl) imidazolium chloride and silver (I) oxide was stirred at room temperature with a total exclusion of light according to Scheme 2, the product was filtered through celite to remove any unreacted silver (I) oxide, and the solvent was removed in vacuum which afforded the desired complex, **2**, as a stable white precipitate. The product was identified to be the silver complex **2**, initially by using ^1H NMR and mass spectral analysis. The NMR peaks were found to be similar to that of the imidazolium salt **1**, the only notable difference was the disappearance of the carbenic proton (NCHN) at 7.37 ppm in the spectra of the

complex. This indicated that carbenic proton has been abstracted and silver (I) has subsequently bonded instead, forming the NHC complex similar observation was reported by Ibrahim, (2013). This was further boosted by the mass spectrometry peaks. It was observed that the molecular ion peak at 489 is in good agreement with the molecular formula of the proposed product. The mass spectra further indicated that the silver was linked to two carbene ligands to give a complex of the type $[\text{Ag}(\text{L})_2]\text{Cl}$, rather than $[\text{Ag}(\text{L})\text{Cl}]$ which are also observed from these type of reactions (Lin and Vasam 2007, Danopoulos *et al* 2001).



Scheme 2: Synthesis of 1-methyl-3-(4-picolyl) silver NHC complex

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into DCM solution of the silver compound at room temperature. The crystallographic information is given in Table 1.

The complex crystallizes in the triclinic space group P-1. The asymmetric unit consists of one Ag(I) attached to two NHC ligands, a chloride counter ion and one water molecule (Figure 1). The structure shows an almost linear geometry about silver (I) center with C(2) – Ag(1) – C(12) bond angle of $175.6(2)^\circ$ which is consistent with the typical $[\text{Ag}(\text{NHC})_2]^+$ complexes (between 174° and

177°) (Garrison and Young 2005). The silver – carbene carbon distances were observed to be identical (Ag(1) – C(2) = $2.088(4)$ Å and Ag(1) – C(12) = $2.085(4)$ Å) which are also within the expected range of typical $[\text{Ag}(\text{NHC})_2]^+$ complexes. It is thought that the two pyridyl rings on the carbene ligand should be directed towards the methyl group to avoid steric hindrance, but instead they are arranged adjacent to one another as shown in Figure 1. Furthermore, the pyridyl rings are twisted with respect to imidazole ring, with N(2) – C(5) – C(6) bond angle of 112° which may facilitate the stacking of pyridyl and imidazole ring in the crystal lattice.

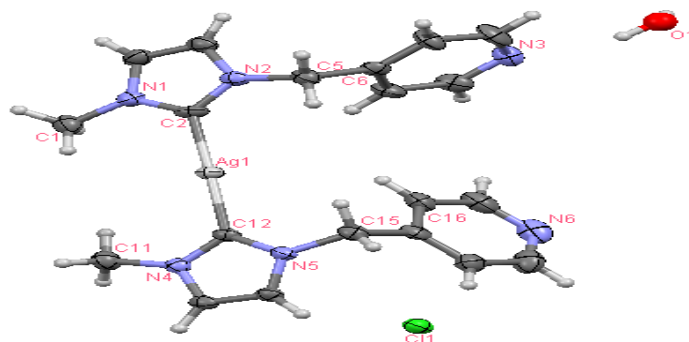


Figure 1: Crystal Structure of **2**, thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles ($^\circ$). Ag(1) – C(12) $2.085(4)$, Ag(1) – C(2) $2.088(4)$, N(1) – C(1) = $1.463(9)$, N(2) – C(5) = $1.449(9)$, C(2) – Ag(1) – C(12) = $175.6(2)$, C(2) – N(2) – C(5) = $125.7(5)$, N(2) – C(5) – C(6) = $112.0(5)$, C(11) – N(4) – C(12) $124.6(5)$.

Table 1. Selected Crystal Data, Data collection, and Refinement Parameters for 2

Chemical Formula	C ₂₀ H ₂₄ AgClN ₆ O
Formula weight	507.77
Colour	Colourless
Lattice Type	Triclinic
Space group	P-1
a/Å	10.0958(15)
b/Å	10.624(2)
c/Å	10.9551(14)
α/°	81.716(13)
β/°	89.005(12)
γ/°	66.893(16)
V/Å ³	1068.5(3)
Z	2
T/K	123(2)
ρ/gcm ⁻³	1.578
μ/mm ⁻¹	1.092
F000	516
No of reflection collected	4710
No of independent reflections/R _{int}	3163/0.045
No of observed Reflection (>2δ(I))	2270
R1 (obsd/all)	0.0391/0.0634
wR2 (obsd/all)	0.0769/0.0832
Largest difference in peak and hole	1.121, -0.613
eÅ ⁻³	

CONCLUSION

An imidazolium salt (1-methyl-3-(4-picolyl) imidazolium chloride) was successfully prepared from the reaction of imidazole and picolyl chloride hydrochloride. It was converted into NHC complexes by its reaction with silver (I) oxide. Both, imidazolium salt and the complex were characterized spectroscopically (using mass spectrometry and NMR) and single crystal X-ray diffraction analysis, the data revealed that two carbenic ligand are joined by silver atom giving [Ag(L)₂]Cl formulation.

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