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Synthesis and Characterization of Pyridine Functionalized Imidazolium Salt and its Silver(I) N-heterocyclic Carbene Complex

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ABSTRACT

Reaction of imidazole with two equivalent of 2-picolyl chloride afforded bis (2-picolyl) imidazolium salts (**1**). Treatment of the synthesized imidazolium salt with silver(I) oxide resulted in the formation of bis NHC silver(I) complex (**2**). The compound was characterized spectroscopically (NMR, mass spectrometry), by elemental analysis and 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 $[Ag(NHC)_2]^+$. The metal to ligand ratio was found to be 1:2.

Keywords: Imidazolium salt, N-heterocyclic carbene, picolyl, silver

Introduction

N-heterocyclic carbenes (NHCs) are cyclic carbenes that have at least one α-amino substituent. An interest on this class of carbenes started after a separate report of Ofele and Wanzlick *et al.* all in 1968. Their chemistry blossomed only after the report of the synthesis and characterization of first crystalline carbene in 1991 by Arduengu *et al.* obtained from adamantyl substituted imidazolium salts. NHCs were found to be similar to the well known phosphine ligand (Hermann and Kocher 1997) but more electron rich, as such more firmly bound to the metal ion therefore forming a more stable complex. Due to this qualities they replaced phosphine in homogenous catalysis and lots of research on the use of the NHCs and their complexes in homogenous catalysis have been reported, these include olefin metathesis (Colacino *et al*., 2007), C-C coupling reaction (Hermann, 2002), polymerization reaction (Nolan *et al*., 2009), hydrosilation and hydroformylation (Nolan *et al*., 2009) etc.

The first structurally characterised silver NHC complex was obtained from the reaction of free carbene and silver salt (Young and Garrison, 2005). But the free carbenes are difficult to obtain, this problem of generating free carbene was solved by synthesising the silver NHC complex *in situ* from the reaction of imidazolium salt and the silver source. Example, Wang and Lin in 1998 reported the synthesis of silver NHC complex *in situ* from the reaction of silver(I) oxide and imidazolium salt. Also in 2000 Tulloch *et al*. reported the *in situ* synthesis of another silver NHC complex from reaction of imidazolium salt and silver(I) carbonate same year they also reported the *in situ* formation of pyridine functionalized NHC complexes of palladium ((C-N)PdMeBr, C-N = 3-R-1 (2-methylpyridine)-imidazolin-2-ylidene (R = ^{t}Bu or mes)). They were found to be excellent catalysts for Heck arylation and also have good activity towards amination reactions. Danopoulos *et al*. in 2002 also reported the synthesis and isolation of free pyridine functionalized NHC ligand from the reaction of 1-(2,6-diisopropylphenyl)imidazole and 2-bromo-6-trimethylsilyl pyridine and subsequent deprotonation of the formed imidazolium salt with $KN(SiMe_3)_2$ in THF at -10 to 0°C. Although air sensitive, it was stable enough for its crystal to be isolated at room temperature and be analyzed by single crystal X-ray crystallography. Motherwell *et al*. in 2002 reported the isolation and crystal structure of first free pyridine functionalized bis NHC ligand, reacting the free ligand with $RuCl_2(PPh_3)_3$ produced a catalytically active Ruthenium bis carbene complex which catalyzed hydrogenation of C=O and C=N.

The *in situ* procedure of forming silver NHC complexes lead to the synthesis of many other silver NHC complexes (Young and Garrison, 2005 and Lin and Vasam, 2007) and they were widely used to synthesise many other transition metal NHC complexes through transmetalation reaction. In this paper a synthesis of pyridine functionalized imidazolium salt and its conversion into the silver NHC complexes through this in situ method is reported.

Materials and Methods

General Considerations: Unless otherwise stated all reactions were performed under nitrogen 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 change and the intensities of the signal were indicated in percent of the basis ion. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE/DPX 400(400 MHz) and or AVANCE/DRX 500 (500 MHz) in $CDCl_3$ and DMSO with tetramethyl silane as standard. Elemental analyses were carried out at the micro analytical laboratory at the University of Strathclyde, Glasgow.

Single crystal measurements were made at 123K with graphite monochromated MoKα1 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 were to convergence and by full-least squares methods on F2 within SHELX-97 (Sheldrick, 1997). 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 $I>2\sigma(I)$.

Synthesis of Bis - (2-Methylpyridine) Imidazolium Chloride (1)

2-Chloromethyl pyridine hydrochloride (2.03g, 12.38mmol), imidazole (0.27g, 4.03mmol) and $NaHCO_3$ (1.01g) were taken up in 20mL ethanol. The mixture was reflux for 2 days under nitrogen atmosphere. The solution was cooled and the solvent removed under vacuum. The residue was taken up in DCM and dried over sodium sulphate, it was filtered and the DCM was removed to give dark oil. The oil was triturated with THF to give a white precipitate. Yield 1.36g, (76.70%) (Siraj, 2012).

^{1}H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 5.69 (4H, s, $-CH_2-$), 7.29 (m, CH of Py, 2H), 7.56 (d, -CH- of imid. 2H), 7.77 (m, -CH- of Py, 4H), 8.85 (d, -CH- of Py, 2H), 11.09 (s, -NCHN- of imid. 1H). ^{13}C{^{1}H} NMR (400 MHz, Solvent $CDCl_3$) δ ppm : 151.90 (C_{Py}), 149.38 (C_{Py}), 137.95 (NCN), 137.34 (C_{Py}), 123.87 (C_{Py}), 123.64 (C_{Py}), 121.65 ppm (C_{imid}), 53.75 (C of CH_2). MS (ESI, methanol; m/z): 251 $[M]^+$. Anal. Calculated for $C_{15}H_{14}N_4Cl_1.H_2O$: C, 59.10; H, 5.62; N, 18.39. Found: C, 59.27; H, 5.86; N, 18.52.

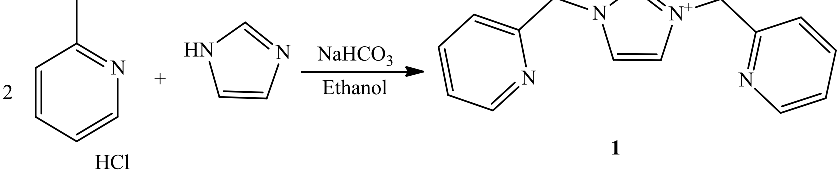
Synthesis of [Ag-((2–picolyl)$_2$ imidazol-2-yledene)$_2$ Chloride (2)

A mixture of **1** (1.255g, 4.35mmol) and silver(I) oxide (0.505g, 2.19mmol) was taken up in 25mL DCM and the mixture was completely wrapped in aluminium foil and stirred for 5 hrs at room temperature. The solution filtered through celite, reduced in volume and precipitated by diethyl ether to give white crystals (0.66g, 46% yield) (Wang and Lin, 1998).

^{1}H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 5.39 (s, $-CH_2-$ 4H), 7.22 (s, -CH- of imid 2H), 7.30 (m, -CH- of Py, 4H), 7.73 (m, -CH- of Py 2H), 8.61 (m, -CH- of Py 2H). ^{13}C{^{1}H} NMR (400 MHz, Solvent $CDCl_3$) δ ppm : 154.32 (C_{Py}), 149.47 (C_{Py}), 138.98 (C_{Py}), 123.05 (C_{Py}), 123.12 (C_{Py}), 121.63 (C_{imid}), 56.83 (C of CH_2). MS (ESI, methanol; m/z): 609 $[M]^+$. Anal. Calculated for $Ag_2C_{30}H_{28}N_8Cl_5$: C, 40.30; H, 3.16; N, 12.54. Found: C, 40.30; H, 2.73; N, 12.55.

Results and Discussion

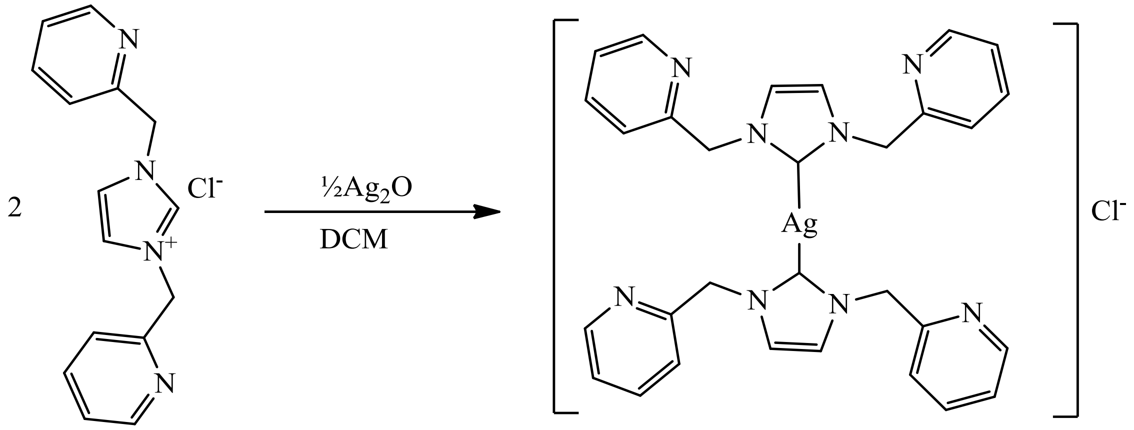
The ligand, bis-(2-picolyl) imidazolium chloride, was successfully synthesized by refluxing imidazole, two equivalents of 2-picolyl chloride hydrochloride and a base ($NaHCO_3$) in ethanol according to scheme 1. The $NaHCO_3$ was used to deprotonate both the 2-picolyl chloride hydrochloride and the imidazole. Filtering the product and removing the solvent under vacuum afforded a dark brown oil. The oil was triturated with THF which resulted in a brownish precipitate of the target product in good yield.



Scheme 1: Synthesis of bis- (2-methyl pyridine) imidazole

The compound was confirmed spectroscopically to be the intended bis 2-picoly imidazolium chloride (**1**)**.** In the ^{1}H NMR spectrum the appearance of resonances downfield at 11.09ppm which was assigned to the most acidic imidazolium proton (-NCHN-) is in keeping with most of the similar imidazolium salts peaks reported in the literature (Muehlhofer *et al*., 2002). The methylene spacers linked to the imidazole shows a resonance at 5.45ppm**.** Furthermore, the appearance of positive ion peak at m/z = 251 as the major peak in the mass spectra further indicates the formation of the ligand**.** This was confirmed by good agreement between the expected and observed values in the microanalysis.

In accordance with the general reaction for the generation of silver-NHC complexes, the ligand, was reacted with slight excess of silver(I) oxide in dichloromethane according to scheme 2, in the absence of light. The product was filtered through celite to remove any unreacted silver(I) oxide and the solvent removed under vacuum to give white solid product which was assumed to be compound **2**.



2

Scheme 2: Synthesis of bis-(2-picolyl) NHC silver (I) complex

The ^{1}H NMR spectrum has multiplet peaks at 7.29, 7.72 and 8.58ppm which may be assigned to the 2-pyridyl protons, while the peak at 5.38ppm can be attributed to the methylene spacer between the pyridyl and imidazole ring. The downfield signal observed in the imidazolium salt (**1**) at 8.94ppm was absent in the new complex, which indicates the deprotonation of the imidazolium salt and consequently the formation of the carbene. Also, the ^{13}C NMR spectral signals are of the expected compound **2**. The Positive ion peak in the mass spectrometry at m/z = 609 further suggest the formation of the silver bis carbene complex **2**.

The complex was crystallised in the triclinic space group P-1, the crystallographic information are given in Table 1. The asymmetric unit reveals a twin identical species having two NHC ligand molecules, one silver atom, one chloride ion and a H_2O molecule in each specie as shown Figure 1. The silver ion is bridging the two NHC ligands in near linear geometry arrangement about the silver centre, with bond angle C1 – Ag1 – C2 of 174.4(4) and the C1 – Ag1 –C2 (171.2(4)) slightly less, and falls short of the typical $[Ag(NHC)_2]^+$ bond angle. The Ag-C1 bond distance was observed to be 2.08(9) Å which is similar to the other Ag-C distances in the molecule and also similar to the Ag-C distances reported in other silver NHC complexes (Muehlhofer 2002 and Ahrens *et al*., 2006).

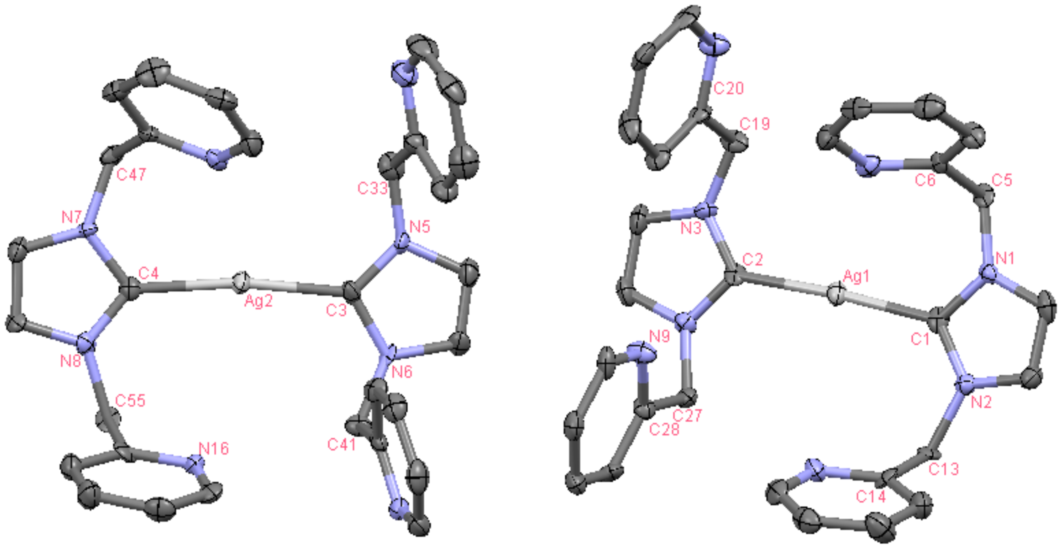


Figure 1: Crystal Structure of **2,** thermal ellipsoids drawn at 30% probability level. Some selected bond length (Å) and bond angles (°). Hydrogen, Cl^- and H_2O omitted for clarity. Ag(1) – C(1) 2.08(9), Ag(1) – C(2) 2.088(9), Ag(2) – C(3) 2.080(9), Ag(2) – C(4) 2.077(9), C(1) – Ag(1) – C(2) 175.4(4), C(3) – Ag(2) – C(4) 171.2(4), N(1) – C(5) – C(6) 110.6(8), N(2) – C(13) – C(14) 112.6(8),

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

Compound	**2**
Chemical Formula	$C_{30}H_{28}AgClN_8$
Formula weight	356.57
Colour	Colourless
Lattice Type	Triclinic
Spacegroup	P-1
a/Å	10.738(5)
b/ Å	10.988(5)
c/ Å	25.655(5)
α/°	102.186(5)
β/°	95.527(5)
γ/°	99.735(5)
V/ Å	2889(2)
Z	2
T/K	298(2)
ρ/gcm-3	1.173
μ/mm^{-1}	0.721
F000	1040
No of reflection collected	24617
No of independent reflections/R	12587
No of observed Reflection (I>2δ(I)	8068
No of parameters Refined	748
R1 (obsd/all)	0.105/0.161
wR2 (obsd/all)	0.218/0.248
Largest difference in peak and hole eÅ^{-3}	3.975, -1.403

Conclusion

Bis (2-picolyl) imidazolium chloride has been synthesized from alkylation of imidazole, and subsequently it was converted into silver(I) NHC complexes by the use of Ag_2O. Both imidazolium chloride and its silver(I) complex has been characterized spectroscopically and by single crystal X-ray structure. Although not reported in this work but it has the potentials to be use as a gate way to obtaining many more corresponding transition metal complexes through transmetalation reaction.

Acknowledgement

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