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Synthesis and Characterization of Ag(I) Complexes Derived from New *N*-Heterocyclic Carbenes

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Two new unsymmetrical imidazolium salts *viz*., [1-(4-ethylphenyl)-3-propyl-1*H*-imidazole-3-ium bromide] (**3**) and [1-(2,6-dimethylphenyl)-3-propyl-1*H*-imidazole-3-ium bromide] (**4**) have been synthesized *via* the reaction of propyl bromide with imidazole derivatives, [1-(4-ethylphenyl)-1*H*-imidazole] (**1**) and [1-(2,6-dimethylphenyl)-1*H*-imidazole] (**2**) in absence of solvent. Then two new *N*-heterocyclic carbene silver complexes (**5** and **6**) were prepared through the reaction of imidazoluim salts (**3** and **4**) as a source of *N*-heterocyclic carbene with Ag_2O by *in situ* method. These complexes can be used in the future as a transfer agent for preparing other transitional metal carbine complexes (NHCs) *via* transmetallation method. The formation of these compounds was confirmed by spectral analysis.

Keywords: Imidazolium salts, Heterocyclic carbene, Silver(I) carbene complexes.

INTRODUCTION

Imidazolium salts have great attention as a precursor of *N*-heterocyclic carbene compounds due to its easy synthesis, where several methodologies have been achieved for its preparation [1-7]. By modifying the substituents on N-atoms of imidazole compound,variety of imidazole salts can be obtained and used to prepare many transition metals complexes type *N*-heterocyclic carbene complexes (NHCs) under appropriate conditions [8-11]. The strong donor of σ-bond for these compounds (*N*-heterocyclic carbene) make their complexes more stable as compared to phosphine in addition of its variety applications depending on the transition element [12-15].

The spark of interest began for these compounds when crystals were obtained for the first free carbene by Arduengo *et al*. [16]. Due to the sensitivity of free carbene compounds toward air, moisture and heat, as well as the difficulty of syntheis and stability for a long time [17,18], *in situ* method as an alternative method was utilized to generate carbene by using metal bases such as silver oxide (Ag_2O) for the generation of carbene through deprotonation of imidazolium and to avoid the isolation of free carbene which results in the direct use in the process of complexity [19,20]. By this method, silver complexes (*N*-heterocyclic carbene) can be obtained under ambient conditions and does not require harsh conditions. Several silver carbene complexes were synthesized by this method [21,22]. The most important application of Ag(NHC)carbene complexes to use as a metal transferring agents for synthesis of several other complexes that are faced difficulties to synthesize *via* normal methods [23,24].

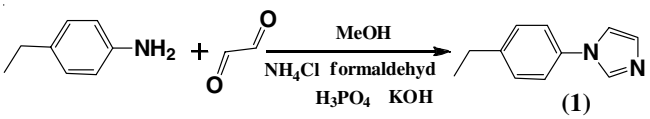
EXPERIMENTAL

All the chemical reagents used as received without further purification. Bruker Avance AMX 250, 400 spectrometer has been used to obtain NMR spectra. Mass spectra have been recorded in electrospray (ES) mode. FTIR spectra were obtained by using Jasco FT-IR-660 plus Spectrometer. Elemental analysis of the complexes were estimated at Elemental Analysis Service Science Centre, London Metropolitan University. Stuart melting point (digital) SMP30 apparatus has been used to measure melting points.

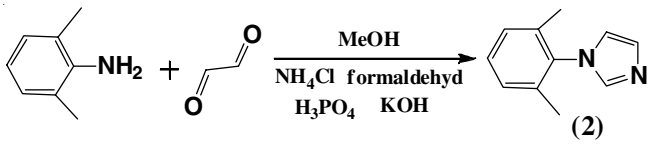
Synthesis of precursors (1 and 2): Both aryl imidazole derivatives (**1** and **2**) have been synthesized according to reported methods [25-27].

4-Ethylaniline (6.05 g, 0.05 mol) or 2,6-dimethylaniline (6.05 g, 0.05 mol) and aqueous glyoxal (30 %, 8.1 mL, 0.05 mol) were dissolved in 25 mL of methanol and the mixture stirred for 16 h at room temperature, until a thick yellow mixture was obtained. After that NH_4Cl (5.4 g, 0.1 mol) and aqueous formaldehyde (37 %, 8 mL, 0.1 mol) were added.

The reaction mixture was refluxed for 1 h after addition of 200 mL of methanol. Then added H_3PO_4 (7 mL, 85 %) in the mixture while stirring for 10 min and refluxed for 12 h. After removing the solvent, the obtained residue has been poured into 100 g of ice and neutralized by aqueous solution of KOH (40 %), until residue reached pH 9. The product was obtained by extraction using ethyl acteate (2 × 100 mL) then the organic layer washed with brine and finally dried by using $MgSO_4$. The residue was purified by distillation under vacuum on a Kugelrohr to obtain white powder (**Schemes I and II**).



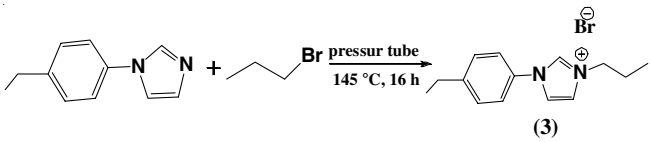
Scheme-I: Synthesis reaction of [1-(4-ethylphenyl)-1*H*-imidazole] (**1**)



Scheme-II: Synthesis reaction of 1-(2,6-dimethylphenyl)-1*H*-imidazole (**2**)

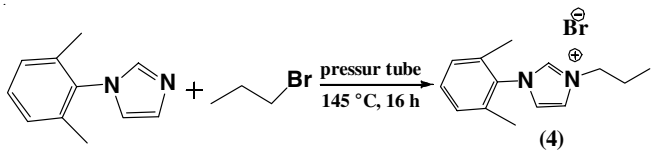
Synthesis of ligands: Unsymmetrically substituted imidazolium salts (**3** and **4**) have been synthesized according to reported method by using free solvent method [28]. These two salts have been characterized by ^{1}H NMR, ^{13}C NMR and mass analysis.

Synthesis of [1-(4-ethylphenyl)-3-propyl-1*H*-imidazole-3-ium bromide] (3): In a pressure tube with stirring bar, a mixture of precuror **1** (0.688 g, 4 mmol) and propyl bromide (0.49 g, 4 mmol) was stirred at 140 ºC for 16 h and then the mixture was left overnight at room temperature. The product was purified by CH_2Cl_2-Et_2O using diffusion purification method to gain a white precipitate (**Scheme-III**).



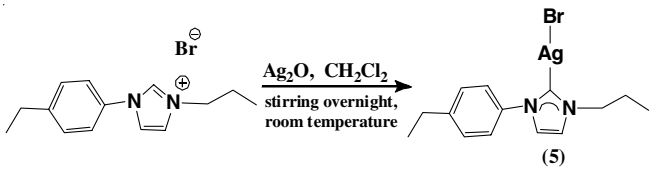
Scheme-III: Synthesis reaction of imidazolium salt (**3**)

Synthesis of [1-(2,6-dimethylphenyl)-3-propyl-1*H*-imidazole-3-ium bromide] (4): In a pressure tube with stirring bar a mixture of precuror **2** (0.86 g, 5 mmol) and propyl bromide (0.61 g, 5 mmol) was stirred at 145 ºC for 16 h After that the mixture was left to cool at room temperature and then the product was purified by CH_2Cl_2-Et_2O using diffusion purification method to gain a white precipitate (**Scheme-IV**).

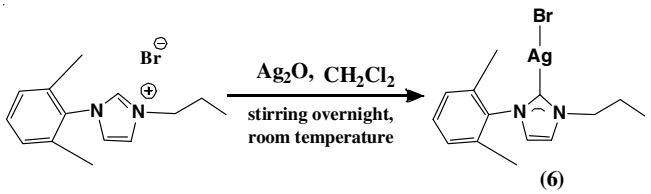


Scheme-IV: Synthesis reaction of imidazolium salt (**4**)

Synthesis of silver complexes: The silver complexes (**5** and **6**) were obtained from the reaction of imidazoluim salts and Ag_2O by *in situ* method [19,29,30]. Imidazolium salts were mixed with Ag_2O in a 1:1 molar ratio in dichloromethane and stirred for overnight at room temperature. Crude product was filtered through celite and recrystallized using CH_2Cl_2-Et_2O to obtain a white solids in high yield (90 and 88 %), respectively (**Schemes V and VI**).



Scheme-V: Synthesis of silver complex [Ag(NHC)Br] (**5**)



Scheme-VI: Synthesis of silver complex [Ag(NHC)Br] (**6**)

RESULTS AND DISCUSSION

Table-1 represents the physico-chemical properties and elemental analysis of imidazoluim salts and their silver(I) complexes.

^{1}H NMR analysis: ^{1}H NMR spectrum of precursor **1** in $CDCl_3$ showed three singlet signals at δ (8.3 ppm, 1H), (7.7 ppm, 1H) and (7.1, ppm, 1H) ppm related to imidazole protons. Doublet signals were noticed at δ (7.3, 2H) and (7.5, 2H) ppm assigned to protons of benzene ring. The spectrum also revealed two signals with integration of 2H and 3H assigned, respectively to (CH_2) and (CH_3) of *para*-substituted ethyl group.

^{1}H NMR spectrum of precursor **2** in DMSO-d_6 showed a singlet signal at (1.9, 6H) ppm, related to two methyl groups. The signals of imidazole ring were also noticed at (7.1 ppm, 2H) and (7.7 ppm, 1H). Multiplet signals within range (7.2-7.4 ppm, 3H) assigned to three aromatic protons.

^{1}H NMR spectrum of imidazolium salt (**3**) in $CDCl_3$ in comparison to precursor **1** exhibited new signals at (0.95 ppm,

TABLE-1
PHYSICAL PROPERTIES OF IMIDAZOLUIM SALTS AND SILVER COMPLEXES

Compd.	m.f.	Colour	Yield (%)	m.p. (°C)	Elemental analysis (%): Found (calcd.)		
					C	H	N
3	$C_{14}H_{19}N_2Br$	White	80	220-222	57.23 (56.96)	6.98 (6.49)	9.85 (9.49)
4	$C_{14}H_{19}N_2Br$	White	85	230-235	57.57 (56.96)	6.89 (6.49)	9.65 (9.49)
5	$C_{14}H_{18}N_2AgBr$	White	90	148-150	41.95 (41.82)	4.85 (4.51)	7.24 (6.97)
6	$C_{14}H_{18}N_2AgBr$	White	88	155-158	41.90 (41.82)	4.60 (4.51)	7.10 (6.97)

TABLE-2
SELECTED FTIR DATA (cm^{-1}) OF IMIDAZOLUIM SALTS AND SILVER COMPLEXES

Compound	ν(C=N)	ν(C-N)	ν(C=C)	ν(C-H) ar.	ν(C-H) aliph.
$[C_{14}H_{19}BrN_2]$ (**3**)	1465	1375	1512	3117	2985
$[C_{14}H_{19}BrN_2]$ (**4**)	1470	1365	1500	3070	2980
[Ag(NHC)Br] (**5**)	1480	1380	1550	3180	2970
[Ag(NHC)Br] (**6**)	1488	1390	1558	3190	2966

t, 3H), (1.95 ppm, m, 2H) and (4.3 ppm, t, 2H) attributed to (CH_2), (CH_2) and (CH_3) of propyl group, respectivelu. As well as a downfield shift of the imidazole signals from (8.3, 7.7 and 7.1 ppm to 10.9, 8.4 and 8.27 ppm resulted in the formation of imidazolium salt (**3**) formation.

^{1}H NMR analysis confirmed the formation of imidazolium salt (**4**) in DMSO-d_6 through the appearance of three peaks at (0.95 ppm, t, 3H), (1.98 ppm, m, 2H) and (4.35 ppm, d, 2H), with integration 7H, attributed respectively to (CH_2), (CH_2) and (CH_3) of propyl group. The signals of imidazole ring were shifted to downfield from (7.4 ppm, s, 1H), (6.9 ppm, d, 2H) to (9.7ppm, s, 1H), (8.3 ppm, d, 1H) and (8.1 ppm, d, 1H). The spectrum also showed an additional singlet signal at (2.1 ppm, s, 6H) related to methyl groups.

^{13}C NMR analysis: ^{13}C NMR spectrum of imidazolium salt (**3**) in $CDCl_3$ exhibited chemical shifts at δ 135.0, 123.56 and 120.89 ppm assigned to carbon atoms of imidazole ring. The chemical shift at 121.48, 129.65,?=132 and 146.41) ppm, assigned to the carbon atoms of benzene ring. In addition the spectrumshowed chemical shiftsrelated to the propyl and ethyl groups at (10.6, 23.68, 51.46) ppm and (15.12, 28.24) ppm, respectively.

Three chemical shifts observed in ^{13}C NMR spectrum of imidazolium salt (**4**) in DMSO-d_6 at 10.26, 22.64 and 50.65 ppm assigned to propyl carbon atoms. The chemical shift of two methyl groups appeared at 17.02 ppm, while the chemical shifts of carbon atoms related to imidazole ring showed at 123.24, 130.51 and 137.28 ppm. Similarly, the chemical shifts related to benzene ring carbon atoms appeared at 123.69, 128.79, 133.54 and 134.64 ppm.

^{1}H NMR analysis of silver(I) complexes (5 and 6): ^{1}H NMR spectra of silver(I) complexes (**5** and **6**) confirmed the disappearance of (NCHN) signals, which was appeared in the spectra of two imidazolium salts at 10.9 and 9.7 ppm, respectively, as a result of generation of carbene (NCN) upon coordination with silver ion. The signals of imidazole ring for complex **5** were shifted from 8.4 and 8.27 ppm to 7.3 and 7.2 ppm due to the resonance loss of imidazole which resulted in the formation of complex **5**.

The same observation was observed in the spectrum of complex **6**, where the signals of imidazole ring were shifted from 8.3 and 8.1 ppm to 7.8 and 7.6 ppm for the same reason.

^{13}C NMR analysis of silver complexes (5 and 6): The chemical shifts related to *N*-heterocyclic carbenes appeared in spectra of imidazolium salts (**3** and **4**) at (135.0 and 137.24 ppm), respectively. However, the same was found to be disappeared in spectra of silver(I) complexes (**5** and **6**), which confirmed the formation of both silver complexes. In addition, new chemical shifts were emerged in spectra of both silver(I) complexes at 179.48 and 180 ppm, which was assigned to (Ag-C).

Mass analysis: Mass spectrum of both imidazolium salts (**3** and **4**) gave base peak at *m/z* = 215.15, 100% attributed to the molecular weight of $[C_{14}H_{19}N_2]^+$, $[M\text{-}Br]^+$.

Mass spectra of silver(I) complexes: Mass spectrum silver complex (**5**) showed a mother ion peak at *m/z* 573.14, 100 %) for *bis*-carbene silver fragment $[Ag(NHC)_2{}^+H]^+$ which was formed in gas state [31]. While mass spectrum of another silver complex (**6**) gave a mother ion peak at *m/z* = 401.97, 100 %) can be attributed to molecular weight of $[C_{14}H_{18}AgBrN_2]^+$, $[M\text{-}H]^+$.

FTIR analysis: FTIR spectra of both imidazolium salts (**3** and **4**), showed absorption bands within frequencies ranges 3100-3070 and 2995-2885 cm^{-1}, related to ν(C-H) of aromatic and aliphatic groups, respectively. The peaks at 1555-1550 and 1390 cm^{-1} can be assigned to ν(C=C) and ν(C-N), respectively. Also the spectra revealed absorption peak in 1470-1465 cm^{-1} region, which is attributed to the stretching vibrations of ν(C=N), which slightly shifting in spectra of both silver complexes upon formation of Ag(I) complexes and generation of carbene compounds through deprotonation of imidazolium salts. Table-2 shows the frequencies of key characteristic bands related to imidazolium salts and their two silver complexes.

Conclusion

We have synthesized new imidazolium salts (**3** and **4**) as a precursors of *N*-heterocyclic carbenes by reaction of *N*-aryl-imidazole derivatives (**1** and **2**) with propyl bromide in absence of any solvent. Two silver complexes (**5** and **6**) were synthesized *via* the reaction of imidazolium salts with silver oxide by *in situ* method under convenient condition. The formation of all synthesized compounds has been characterized.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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