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Research Article

Synthesis and Characterization of New Silver (I) N-Heterocyclic Carbene Complex Derived from Imidazol-2-ylidene salt

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Abstract

A new *N*, *N'*-imidazolium salt 1-(2,6-diisopropylphenyl)-3- (4,6-dimorpholino -1,3,5-traizine-2-yl)-1H-imidazol-3-ium chloride) as a precursor of N - heterocyclic carbene ligand was prepared via the reaction of 1 - (2, 6 - diisopropyl phenyl - 1*H* - imidazole) with 1, 3, 5 - triazine derivative bearing morpholine substituent (2, 6 -dimorpholine - 6- chloro-1, 3, 5-triaziazine). Linear coordinated Ag (I) NHC complex was synthesised via deprotonation of the imidazolium salt and reaction with Ag_2O in darkness at room temperature by in situ method. The complex was synthesised for using as transfer agent to prepare another transition metals complexes by transmetallation method in the future. The imidazolium salt and their silver complex have been characterized by ^{1}H and ^{13}C NMR spectroscopy as well as mass spectrometry.

Keywords: Heterocyclic carbene, Silver complexes.

الخلاصة

تم في هذا البحث تحضير ملح جديد من املاح الاميدازول 1- (2،6- ثنائي ايزوبروبيل فنيل)-3- (4،6- ثنائي مورفولين - 1،3،5 – ترايزين -2- يل) -*H*1 – اميدازو -3- ليوم كلورايد. (1- (2,6-diisopropylphenyl) - 3 - (4,6 - dimorpholino -1, 3,5-traizine-2-yl) - 1H-imidazol-3-ium chloride) من خلال مفاعل الايميدازول احادي التعويض 1- (2،6- ثنائي ايزوبروبيل فنيل-1 H اميدازول (2,6 - diisopropyl phenyl -1*H*- imidazole) - 1مع مركب الترايزين ثنائي التعويض 2 و6- ثنائي المورفولين-6 - كلورو-1،3،5 - ترايزين (2 ,6 - dimorpholine – 6 - chloro-1,3,5-triaziazine). تم استخدام ملح الاميدازول كمصدر لتحضير ليكاند نوع كربين الحلقات الغير متجانسة - N Heterocyclic carbene (NHC) من خلال نزع البروتون من حلقة الاميدازول باستخدام اوكسيد الفضة الاحادية Ag_2O المستخدم كقاعدة لتوليد الكربين و كمصدرللفضة لتحضير معقد الفضة باستخدام الطريقة المباشرة. الغرض من تحضير هذا المعقد هو امكانية استخدامه كناقل لليكند transfer agent في تحضير بعض العناصر الانتقالية الاخرى باستخدام طريقة transmetalation مستقبلا. تم تشخيص الملح المحضر ومعقد الفضة باستخدام مطيافية الرنين المغناطيسي وكذلك تقنية طيف الكتلة.

Introduction

N - Heterocyclic carbene (NHC) compounds have got much attention especially when Arduengo synthesized the first free carbene in 1991 [1]. NHC ligands derived from imidazolium salts have received a lot of attention due to the ease of their synthesis. Through modification of the substituents on the nitrogen atoms many imidazolium salts were achieved with a variety of steric properties and asymmetric environment [2], [3], [4], [5], [6], [7], [8], [9].

1, 3, 5 - triazine compound was widely used as a core in synthesis of many compounds due to their reactivity toward nucleophilic substitution reaction and their ring stability (82.5 K cal/mole) [10] as well as their application in different fields like herbicide production, [11] polymers photostabilizers, [12] and biological properties for example morpholine – s - triazine is used to treat lung and ovarian cancer [13].

Silver N- heterocyclic carbene complexes were synthesized first time in 1993 by Arduengo and his workers. [14]. Due to sensitivity of free carbene toward moisture air and heat. A few number of silver heterocyclic carbene have been prepared by this method as a result of decompose of free carbene ligands [15] [16]. To overcome this obstruction, in situe method was used in synthesis these complexes by using basic silver sources like Ag_2O in the deprotonation of imidazolium salts. A lot of silver heterocyclic carbene complexes were synthesized by this method due to their easiness of preparation, ambient conditions, and high yield [17] [18]

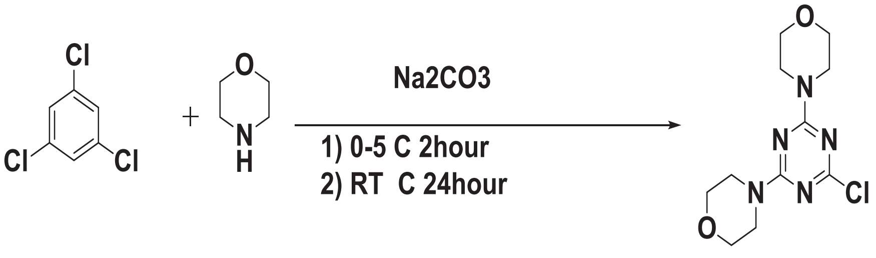
Silver N-heterocyclic carbene complexes were used as transfer agent for synthesis other transition metals carbene complexes in addition their applications in different fields. [19] [20]

Materials and Methods

Chemical reagents (morpholine C_4H_9NO, cyanuric chloride $C_3N_3Cl_3$, Ammonium chloride NH_4Cl, 2, 6-diisopropyl aniline $(CH_3)_2CH]_2C_6H_3NH_2$, glyoxal $C_2H_2O_2$, formaldehyde CH_2O, and silver oxide Ag_2O were used as received. NMR spectra were obtained using Bruker Avance AMX 250, 400 and JEOL Eclipse 300 spectrometer, mass spectra were obtained in electrospray (ES) mode. The analysis is performed in the laboratories of School of Chemistry of Cardiff University United Kingdom.

1. Synthesis of 2, 4-di morpholine-6-chloro-1, 3, 5-triazin. [21]

In a round bottom flask cyanuric chloride (9.22 g, 50 mmol) was dissolved in acetone (200 mL) and ice water (200 mL). Morpholine (8.7 g, 100 mmol) was added to the reaction gradually with Na_2CO_3 (10.69 g, 100 mmol). The mixture was stirred ice bath for 2 hours at 0-5 ^{o}C, followed by stirring at room temperature for 24 hours. The white precipitate formed was isolated by filtration and recrystallized from hot ethanol. Yield: 8.8 g (72 %).

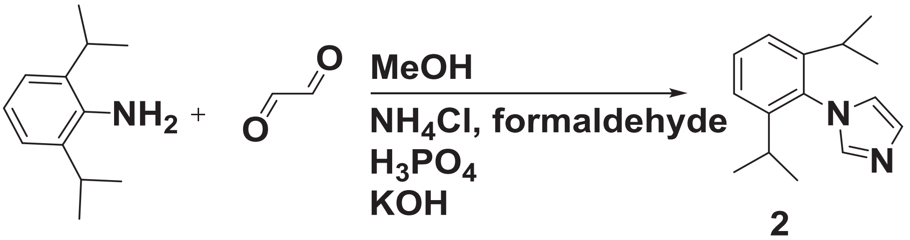


1

Scheme 1 synthesis of 2,4-dimorpholine-6-chloro-1,3,5-triazine

2. Synthesis of 1-(2,6-diisopropylphenyl)-1*H*-Imidazole. [22] [23]

2, 6-diisopropylaniline (8.8g, 0.05 mol) in MeOH (25 mL) was stirred with 30% aqueous glyoxal (8.1mL, 0.05mol) for 16 h at room temperature. A bright yellow mixture was formed. NH_4Cl (5.4 g, 0.1 mol) was added followed by 37% aqueous formaldehyde (8 mL ,0.1 mol). The mixture was diluted with MeOH (200 mL) and refluxed for 1 h. H_3PO_4 (7 mL, 85% soln) was added over a period of 10 min. The resulting mixture was then stirred overnight. After removal of solvent, the dark residue was poured onto ice (200 g) and treated with aqueous 40% KOH solution until pH = 9. The resulting mixture was extracted with EtOAc (2 × 200mL) and the organic phases were combined and washed sequentially with H_2O and brine solution before drying with anhydrous $MgSO_4$. After filtration, the solvent was removed and residue was purified by distillation on a Kugelrohr under vacuum at 240 ° C.

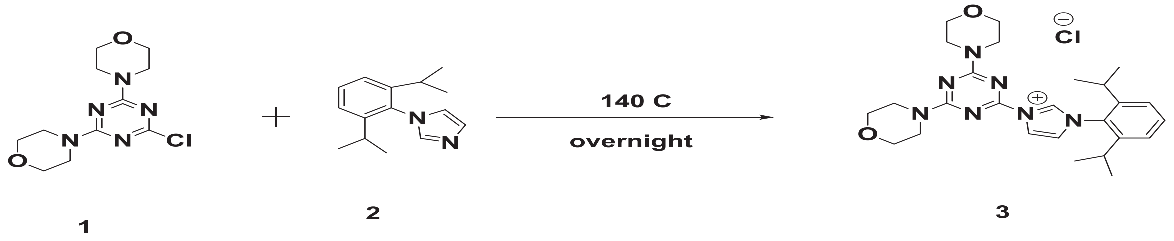


2

Scheme 2 synthesis of 1-(2,6-diisopropylphenyl) - 1H Imidazole

3. Synthesis of 1-(2,6-diisopropylphenyl)-3-(2, 4 - dimorpholine- 1, 3, 5 triaz – 6 - yl) imidazolium chloride.

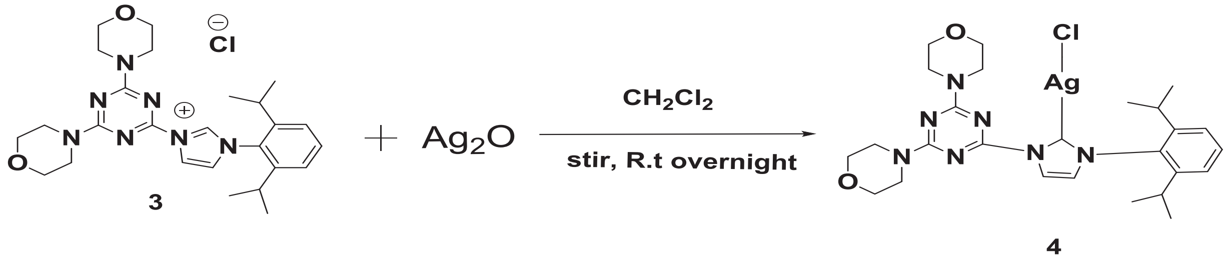
In a tub pressure a mixture of the 1-(2,6-diisopropylphenyl)-1*H*-Imidazole (0.5 g, 2.1 mmol) (**2**) and 2,6-dimorpholine-chloro- 1,3,5-triazine (**1**) (0.62 g, 2.1 mmol) was stirred at 140 ^{0}C overnight. Crud product was dissolved in CH_2Cl_2 (20 mL) and diethyl ether (100 mL) to obtain a white precipitate, yield= 0.89 g (80%).



Scheme 3 synthesis of 1- (2,6-diisopropyl) -3-(2,4-dimorpholine-1,3,5 triaz-6-yl) imidazolium chloride

4. Synthesis of [Ag(NHC)Cl]

Imidazolium salt (3) (0.41 g, 0.8 mmol) was dissolved in 20mL of CH_2Cl_2 and Ag_2O (0.09 g, 0.4 mmol) was added to the solution, the reaction was stirred under nitrogen for overnight at room temperature before filtration through celite. The reaction was protected from light by an aluminum foil. The solvent was removed in vacuo and the resulting solid recrystallised (CH_2Cl_2/Et_2O) to produce a whit precipitate



Scheme 4 synthesis of Ag (I) NHC complex

Results and Discussion

Triazine derivative (**1**) (Scheme 1) was prepared according to Dudley method [21] by reaction of 2 equivalent of morpholine with 1 equivalent cyanuric chloride in basic condition to neutralize the hydrogen chloride formed as a side product during the reaction. The recrystallization of crude product was conducted by hot ethanol to produce a white product with 72% yield.1H NMR spectrum confirmed the conversion of cyanuric chloride to secondary amin triazine (2, 4- dimorpholine -6-chloro 1, 3, 5-triazine) by appearance a multiplet at 3.74-3.5 ppm with integration of 16H corresponding to the methylene groups of the morpholine moieties consistent with previous literatures Figure 1 [24].

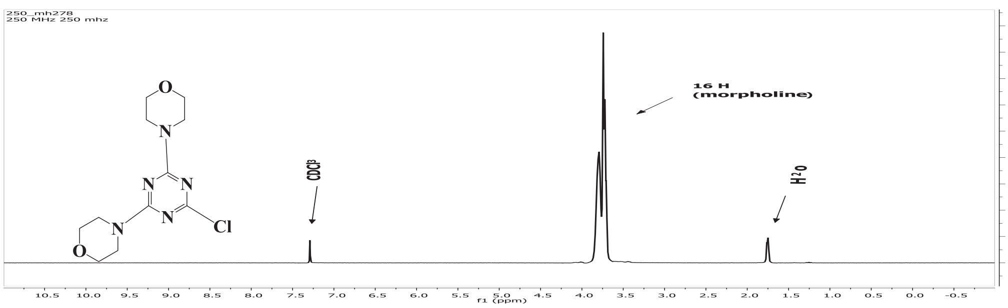


Figure 1: ^{1} H NMR spectrum of 2,4-dimorpholine -6-chloro- 1,3,5-triazine, **1**.

^{13}C NMR spectra showed two peaks for morpholine in 66.6 and 43.8 ppm in addition two signals in range in 169.7and 164.4 ppm consistent with carbon atoms of triazine Figure 2. Low resolution mass spectrometry (ES+) was confirmed the formation of compound by appearance of peak at 286 (100%) which can be attributed to the molecular weight of compound $[C_{11}H_{16}O_2N_5Cl]^+$ $[M+H]^+$. $[M+H]^+$.

1-(2,6-diisopropylphenyl)-1*H*-Imidazole (2) was synthesis by reaction of glyoxal, ammonium chloride, 1 eq of 2, 6-diisopropylaniline and phosphoric acid in methanol according to previous method (Scheme1) [9,21].1H NMR shows duplet peaks at 1.17 ppm with integration of t 12 H, triplet peak at 2.42 ppm with integration 2H and three singlet peaks at 6.99, 7.31 and 7.52 ppm for imidazole protons as well as doublet peak at 7.29 ppm for *meta*- 2H and multiplet peak at 7.48 ppm for *para*- 1H proton Figure 3.

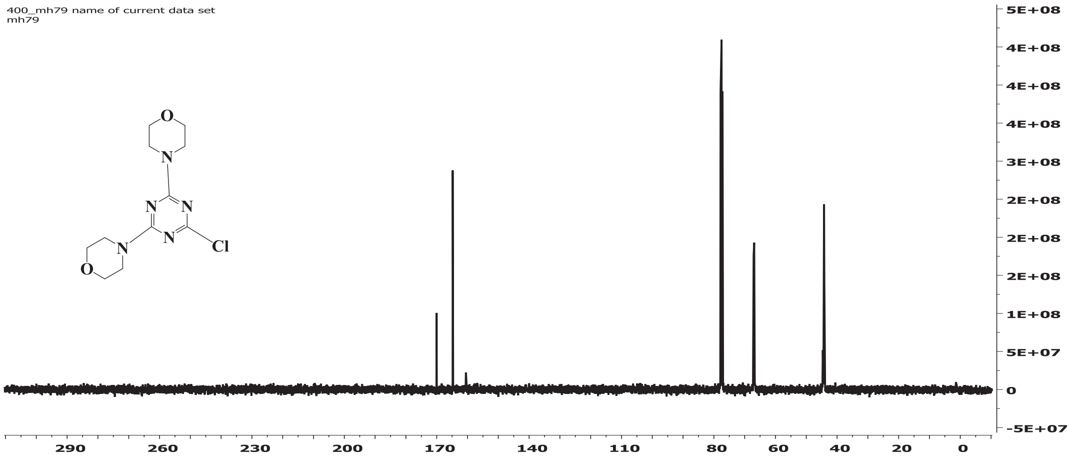


Figure 2: ^{13} C NMR specrtum of 2,4-dimorpholine-6- chloro- 1,3,5-triazine,**1**

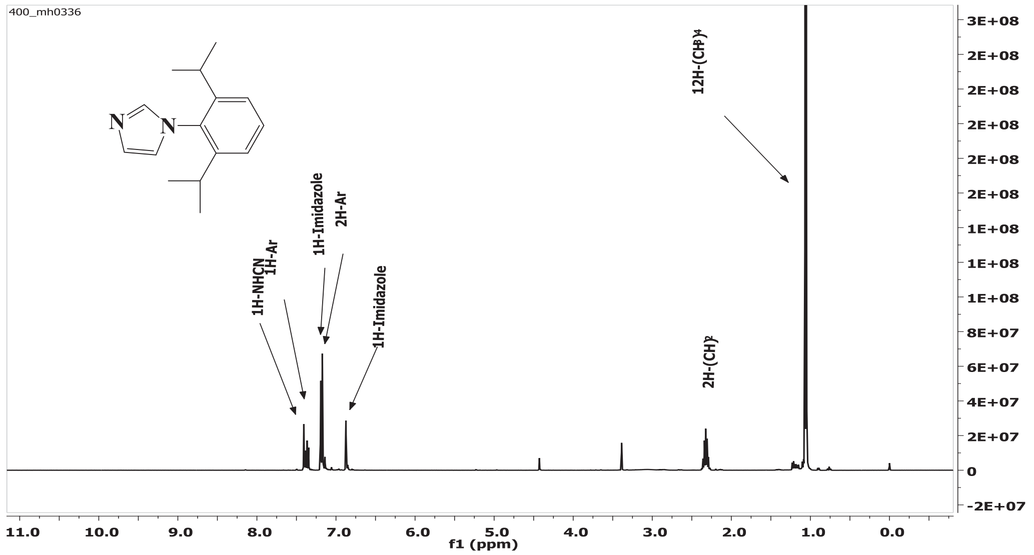


Figure 3: ^{1}H NMR of 1-(2,6-diisopropylphenyl)- 1H- imidazole, **2**

In order to synthesis the imidazolium salt (3), the corresponding of N-Heterocyclic carbene ligand was synthesised by mixing of 1-(2,6-diisopropylphenyl) imidazole and 2,4-dimorpholine-6-chloro1,3,5-triazinine in pressure tube in absence of solvent at 140 ^{0}C for overnight, the product was dissolved in dichloromethane and diethyl ether to produce clean powder in yield 70%.1H NMR observed two doublet peaks at 1.19 and 1.15 ppm for four methyl group, multiplet peak at 2.34 ppm with integration 2H for $(CH)_2$, multiplet peaks in ranges 3.6-3.9 ppm with integration of 16H corresponding to the methylene groups of the morpholine substituents, singlet peaks at 7.78, 8.82 and 10.53 ppm integration to 1H for each peak for imidazole protons, doublet peak and multiplet peak at 7.6 and 7.5 corresponding to 2H in position meta and 1H in Para respectively Figure 4.

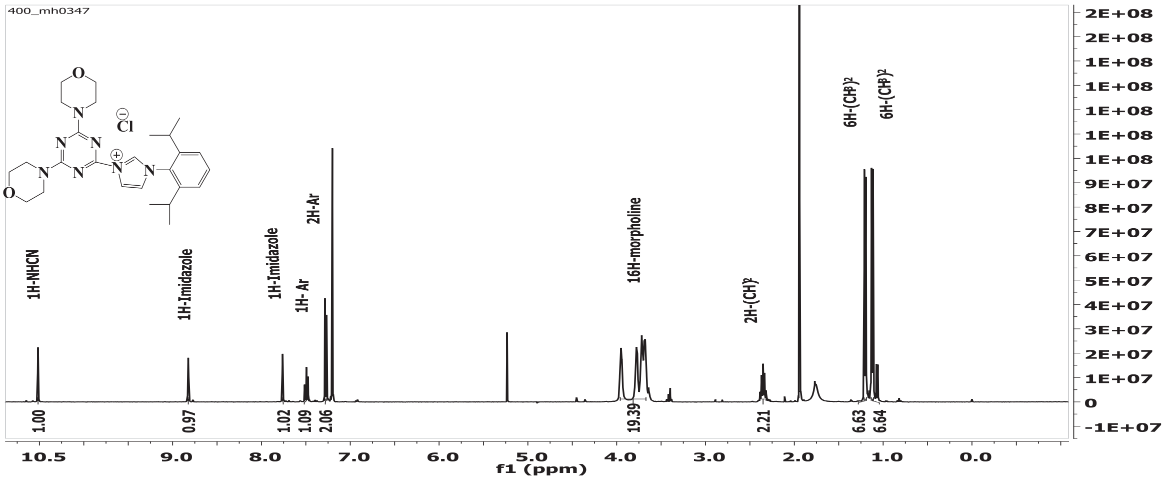


Figure 4: ^{1} H NMR spectrum of imidazolium salt, **3**

^{13} C NMR also confirmed the formation of imidazolium salt. peaks were emerged in ranges 120-145 ppm consistent with imidazole ring and aryl carbon atoms, two doublet peaks were emerged at 44.2, 44.6, 66.0, 66.6 ppm corresponding with morpholine carbon atoms, in addition two peaks at 24.4, 24.6 and 28.7 for methyl groups as well as two peaks in 158.9 and 164.6 observed can be attributed to triazine carbon atoms Figure 5 Mass ES spectrometry gave peak at 478.32 corresponding to [M-Cl]+, Figure 6.

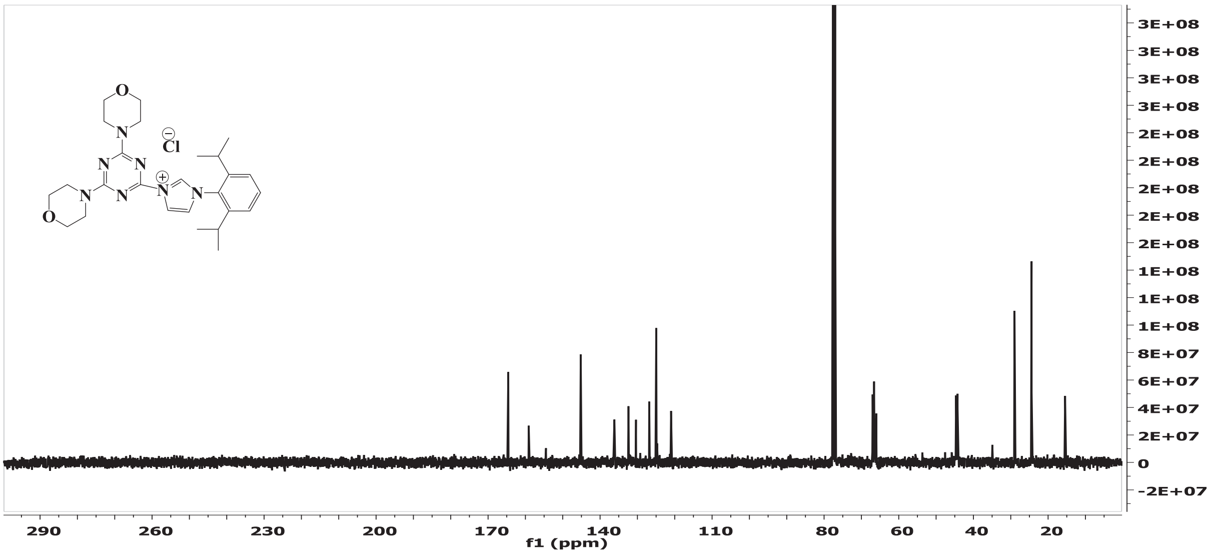


Figure 5: ^{13} C NMR spectrum of imidazolium salt, **3**

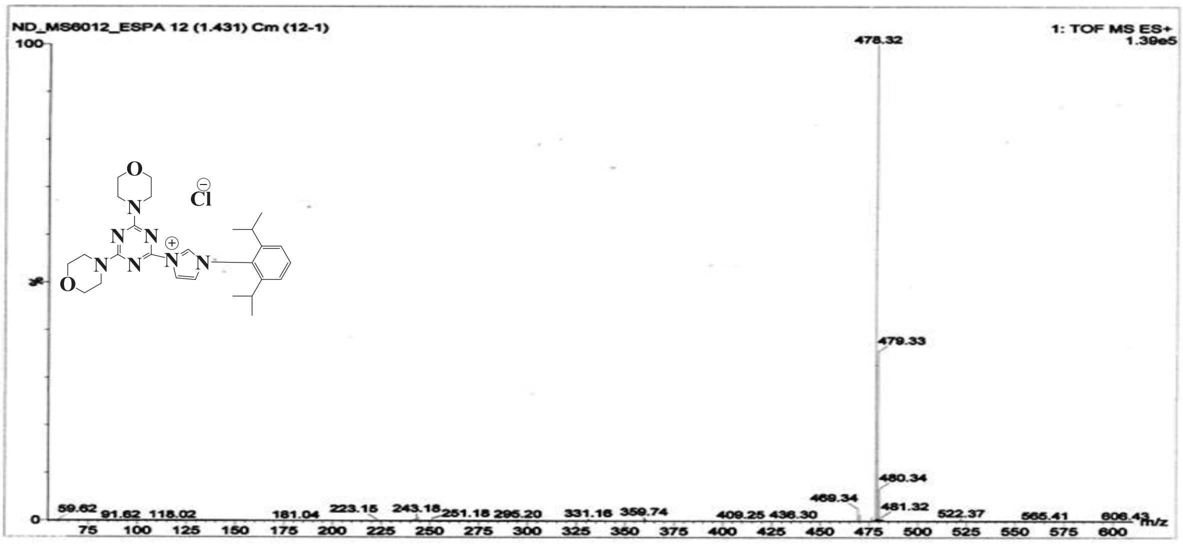


Figure 6: mass spectrum of imidazolium salt, **3**

Silver N-heterocyclic carbene complex [Ag(NHC)Br] was synthesised via in situ method [17] [25]by reaction of the imidazolium salt with of Ag_2O under ration 2:1% in dry dichloromethane under nitrogen at room temperature overnight, the reaction was protected from light by aluminum foil to avoid the photodecomposition of silver complex.

The reaction was set up by filtration through a pad of celite. The product of crud has been recrystallized by diffusion of diethyl ether in concentrated dichloromethane solution of the crude product. The imidazolium salt Deprotonation was confirmed by peak disappearance at 10.53 ppm which attributed to (NCHN) in addition peaks attributed to imidazole ring in position C4and C5 were moved up field at 6.95 and 8.15 ppm Comparison with the ligand precursors in the ranges 7.8, 8.8 ppm as coordination result with Ag and formation of complex ,Figure 7.

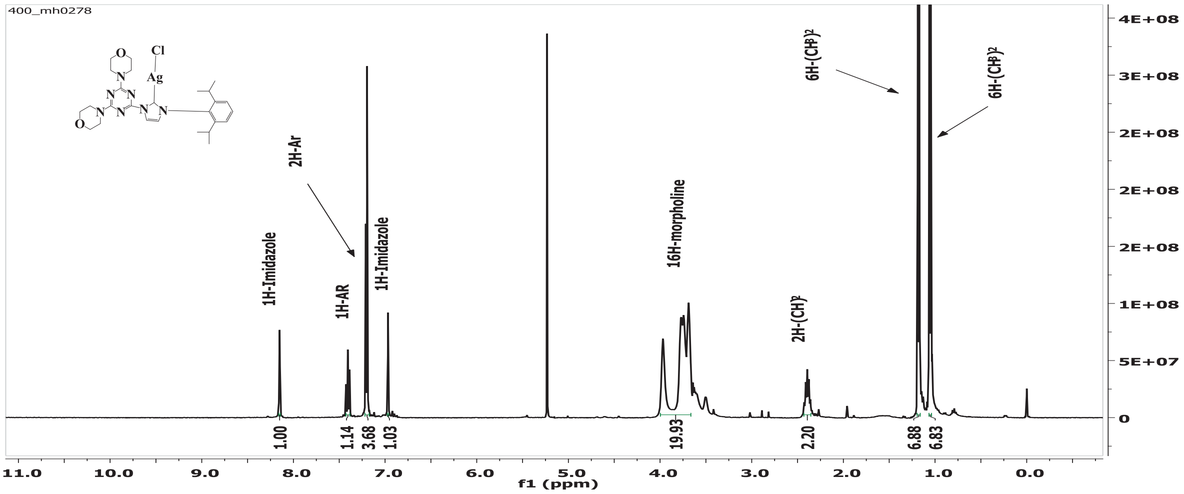


Figure 7: 1H NMR of [Ag (NHC) Cl], **4**

The formation of the silver complex was confirmed by the ^{13} C NMR spectrum by disappearance of NHCN peak and the emergence of a weak peak at 187 ppm for Ag-C carbene which consistent with previous literatures .1^{3} C NMR spectrum was observed singl peak for Ag-C instead of two due to fluxional changes between the ionic and neutral complex; for example Internal change between the mono- and bis-carbene species.

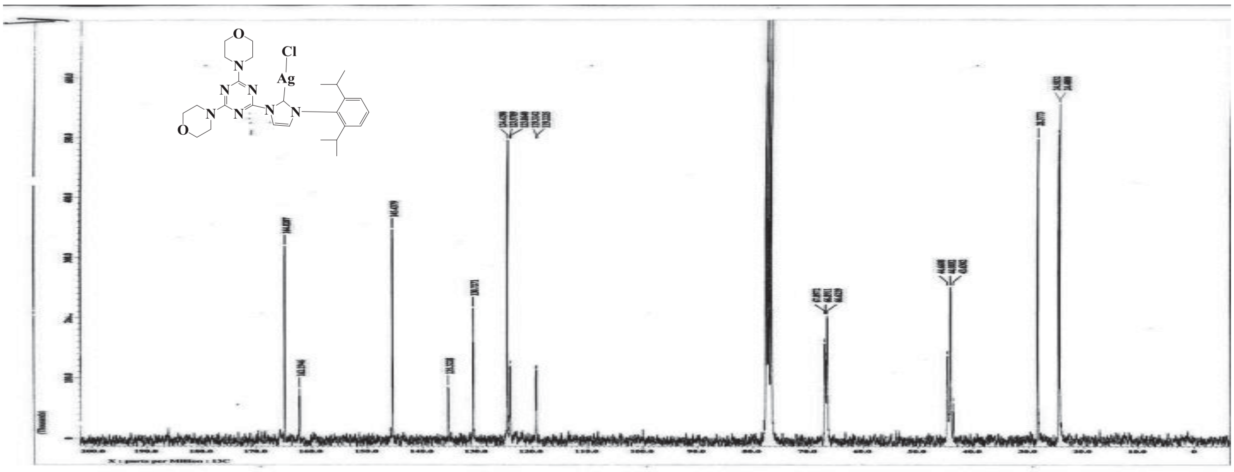


Figure 8: ^{13} C NMR of [Ag(NHC) Cl] complex, **4**

Mass spectrum of the silver complex has been found that the complex formed biscarbene structures in gas state with the formula, [Ag (NHC)$_2$]+, which is combatable with previous reports in the literature ,Figure 9 [26].

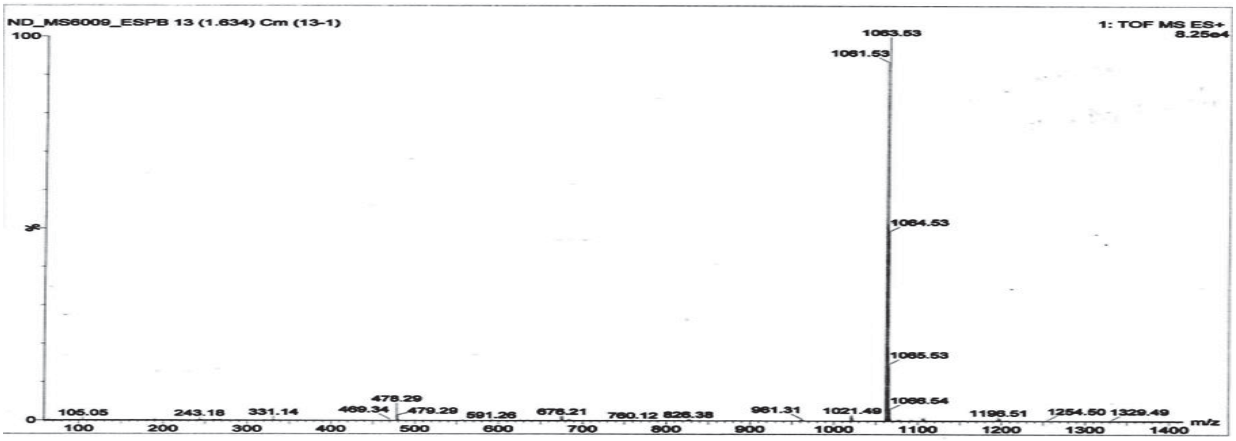


Figure 9: mass spectrum of [Ag (NHC) Cl] complex**, 4**

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