

Synthesis and Characterization of N-Heterocyclic Carbene and their Complexes with Pd(II)

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Abstract— N-heterocyclic carbenes (NHCs) are a significant and powerful class of ligands, New imidazolium salts (DII, DTI) and N-heterocyclic carbene complexes were designed (Pd-NHC), synthesized and structurally characterized by NMR (¹H,¹³C), IR, and other methods.

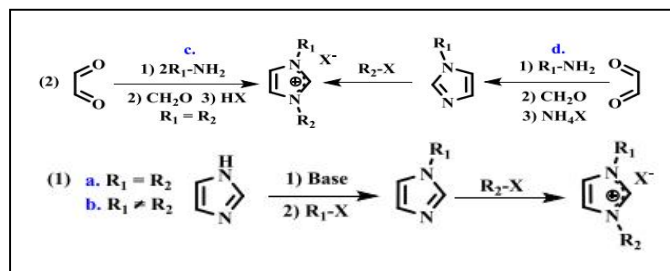
Index Terms— N-Heterocyclic carbene; Pd-NHC complexes; imidazole.

1 Introduction

Although known for many decades, it is only in the last ten years that N-heterocyclic carbenes (NHCs) have come to occupy a central position in the armory of organometallic chemists[1]–[5]. For a long time, Chemists have been fascinated by the surprising versatility of NHCs that play an important role in all fields of chemistry today, especially in organometallic you can explore the enormous possibility of obtaining different metal complexes[6]–[8]. The unusual stability of NHC is in part a result of shielding by sterically demanding substituents on the ring.

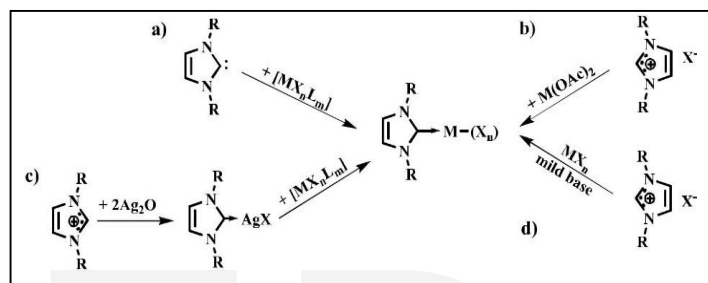
However, much more important is the electronic stabilization by mesomeric interaction of the lone pairs of electrons on the nitrogen atoms with the empty p orbital of the sp² hybridized carbenic carbon atom[9]–[15]. This latter feature, the importance of resonance structures, also nicely explains why NHCs are electron-rich nucleophilic species, whereas other carbenes. The sp²-hybrid orbital is normally described as orbital and NHC in fact behave like typical donor ligands that can substitute classical 2e⁻ donor ligands such as amines[16]–[21].

NHCs are usually prepared by the deprotonation of imidazolium salts, therefore first of all it is necessary to synthesize the appropriate substituted pro-ligands. An NHC precursor can be prepared using several methods. (see Scheme 1)



Scheme 1. Different ways to synthesis an imidazolium salt

Today, transition metal complexes of NHCs are mainly formed using four methods (see Scheme 2):



Scheme 2. Four general methods to synthesize NHC-M complexes

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2 MATERIALS AND METHODS

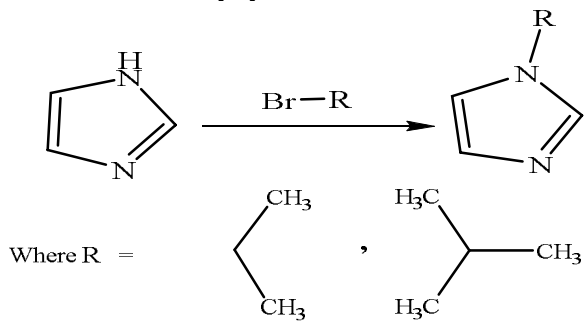
2.1 Experimental

All reactions for the preparation of imidazolium salts and NHC-palladium complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Nuclear magnetic resonance spectra were recorded on Bruker 400 MHz spectrometers at ambient temperature. ¹H and ¹³C NMR peaks are labelled as singlet (s), doublet (d), triplet (t), and multiplet (m), chemical shifts were referenced with respect to solvent signals. FT-IR spectra were recorded on shimadzu.

2.2 General methods for Synthesis of Alkyl-imidazole:

Alkyl-imidazole was prepared by added bromo alkane (1mmol), imidazole (1 mmol), 30 ml methanol, K₂CO₃ (1 mmol), and anhydrous CuSO₄ (0.001 g) were mixed and heated at 90 °C under argon for 5 h. After cooling to RT, the resultant solid was extracted with a mixture of MeOH/CHCl₃ (2x40

mL). The white solid was filtered and washed with water and a mixture of THF/Et₂O [17].

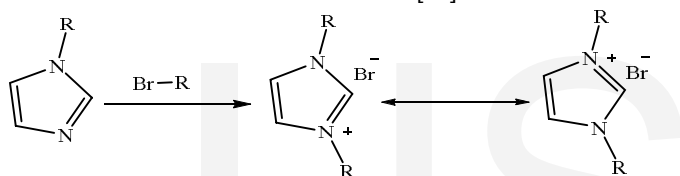


II R = propane, TI R = isobutane

Scheme 3. Preparation of Alkyl-imidazole

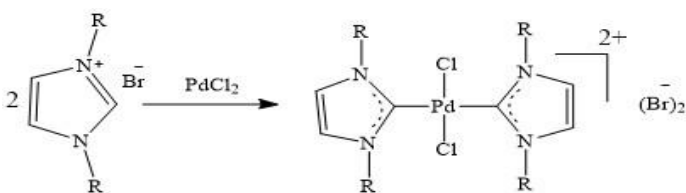
2.3 General Procedure for Synthesis of 1,3-dialkylimidazole salts:

Alkyl-imidazole (1.5 mmol) and bromo alkane (1.5 mmol) were stirred in dioxane (40 mL) at 85 °C for 24 h. After cooling to RT, the desired white/yellow precipitate was filtered off and dried under vacuum[15].



Scheme 4. Preparation of 1,3-dialkylimidazole salts

2.4 General method for the preparation of the NHC-palladium complexes:



Scheme 5. Preparation of NHC-palladium complexes

2.5 1-isopropyl-1H-imidazole (II):

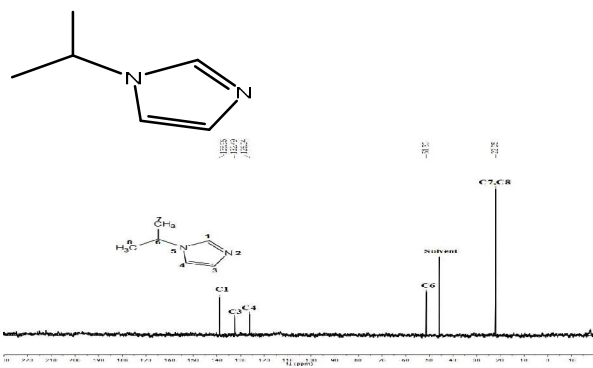


Fig 1. ¹³C NMR spectrum for II

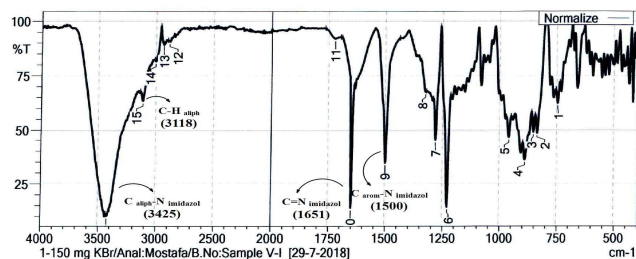


Fig 2 .IR spectrum for II

Yield 0.17 g (77.27%). FT-IR(KBr): ν (cm⁻¹); 3425(C aliph-N imidazol),3118(C-H aliph),1651(C=N imidazol),1500(C arom-N imidazol), 1327(C aliph-N imidazol) 13C NMR (400MHZ, DMSO-d₆) δ 138.96 , 132.49 , 126.24 , 51.30 , 22.05 .

2.6 1,3-diisopropyl-1H-imidazolium (DII):

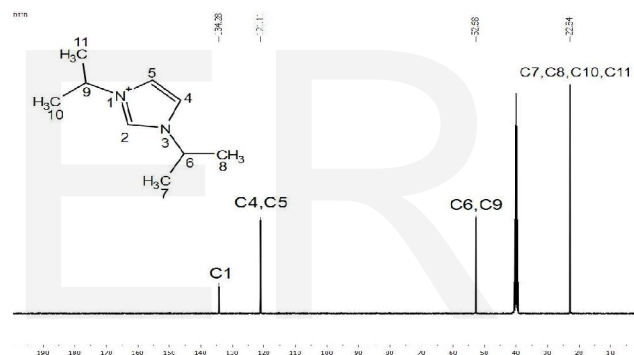
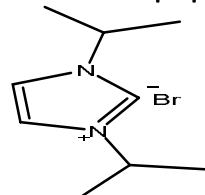


Fig 3 .¹³C NMR spectrum for DII

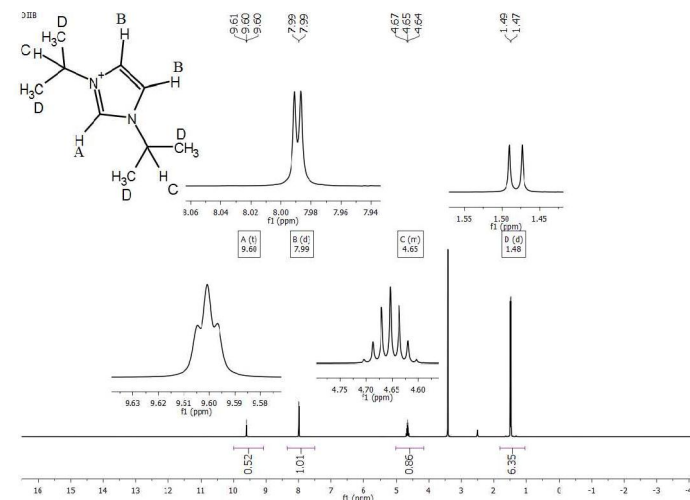


Fig 4 .¹H NMR spectrum for DII

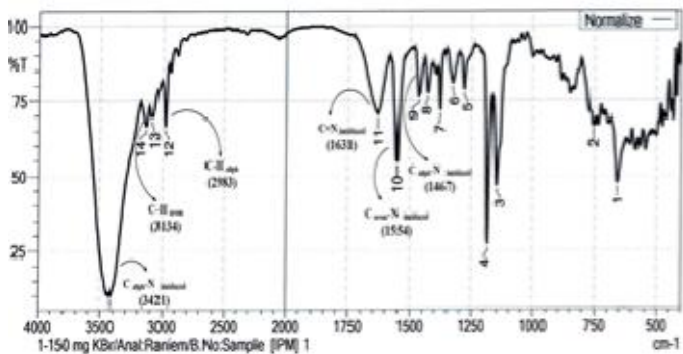


Fig 5 .IR spectrum for DII

White powder. Yield 0.399 g (69.08%), mp: 185-187°C. FT-IR(KBr): $\nu(\text{cm}^{-1})$; 3421(C aliph -N imidazol), 3134(C-H arom), 2983(C-H aliph), 1631(C=N imidazol), 1554(C arom -N imidazol), 1467(C aliph-N imidazol). ¹H NMR (400 MHz, DMSO-d₆) δ 9.60 (t, J = 1.8 Hz, 1H), 7.99 (d, J = 1.6 Hz, 1H), 5.02 – 4.15 (m, 1H), 1.48 (d, J = 6.7 Hz, 6H). ¹³C NMR (400 MHz, DMSO-d₆) δ 134.28 , 121.11 , 52.68 , 22.84 .

2.7 1-(tert-butyl)-1H-imidazole(TI):

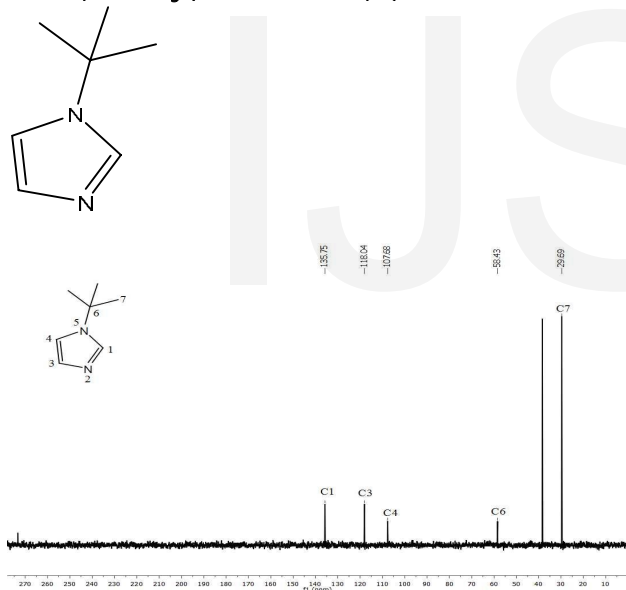


Fig 6 .¹³C NMR spectrum for TI

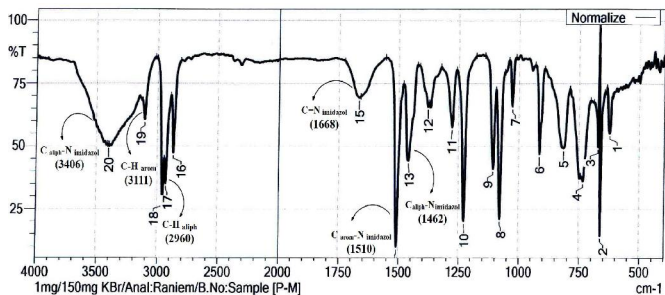


Fig 7 .IR spectrum for TI

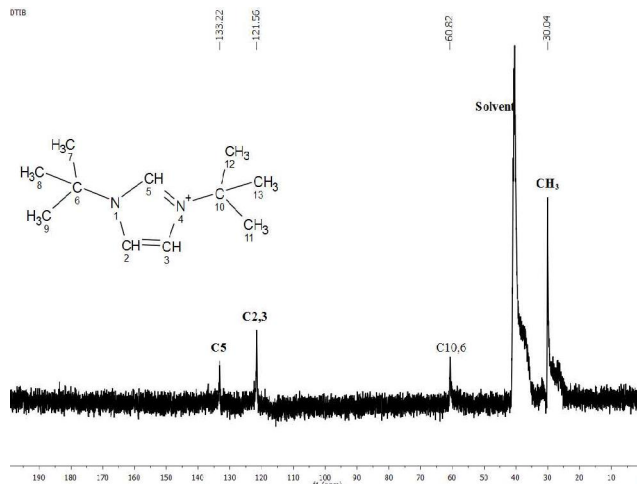


Fig 8 .¹³C NMR spectrum for DTI

Yield 0.200 g (70.21%), FT-IR(KBr): $\nu(\text{cm}^{-1})$; 3406(C aliph -N imidazol), 3111(C-H arom), 2960(C-H aliph), 1668(C=N imidazol), 1510(C arom-N imidazol), 1462(C aliph-N imidazol). ¹³C NMR (400 MHz, DMSO-d₆) δ 135.75 , 118.04 , 107.68 , 58.43 , 29.69.

2.7 1,3-di-tert-butyl-1H-imidazolium(DTI):

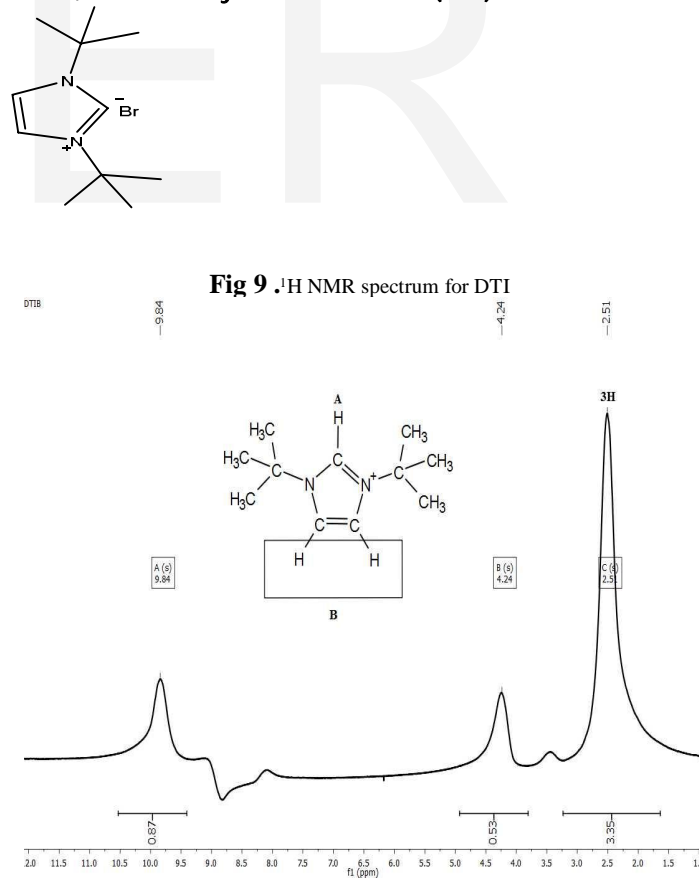


Fig 9 .¹H NMR spectrum for DTI

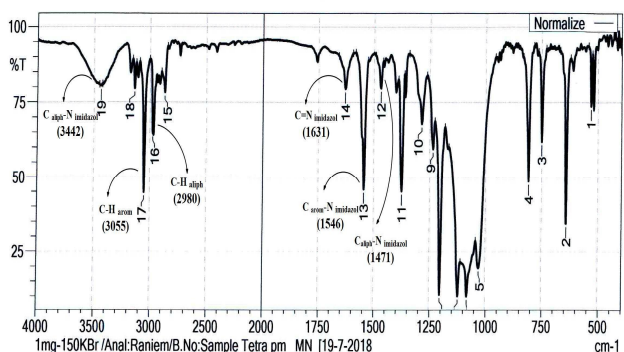


Fig 10 .IR spectrum for DTI

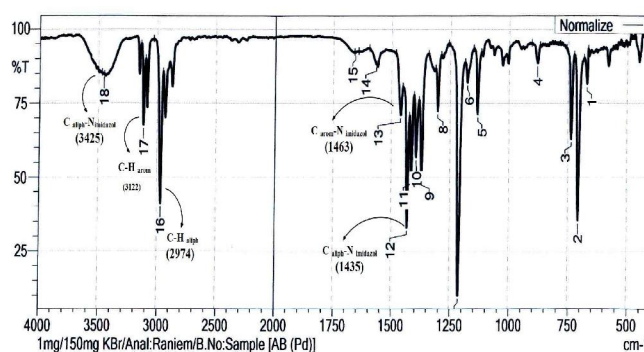


Fig 12 .IR spectrum for [Pd(DII)₂Cl₂]Br₂

White powder. Yield 0.310 g (51.62%), mp: 199-200°C FT-IR(KBr): $\nu(\text{cm}^{-1})$; 3442(C aliph -N imidazol), 3055(C-H arom), 2980(C-H aliph), 1631(C=N imidazol), 1546(C arom-N imidazol), 1471(C aliph-N imidazol). ¹H NMR (400 MHz, DMSO-d₆) δ 9.84 (s, 1H), 4.24 (s, 1H), 2.51 (s, 3H). ¹³C NMR (400 MHz, DMSO-d₆) δ 133.22 , 121.56 , 60.82 , 30.04 .

Brouwn powder. Yield 0.0711g (55.54%), mp: 270-272°C. FT-IR(KBr): $\nu(\text{cm}^{-1})$; 3425(C aliph -N imidazol), 3122(C-H arom), 2974(C-H aliph), 1463(C arom -N imidazol), 1435(C aliph-N imidazol). ¹H NMR (400 MHz, DMSO-d₆) δ 4.84 (s, 1H), 2.80-2.86 (m, 1H), 1.22-128 (dd, J = 6.7 Hz, 6H).

2.8 Bromide bis(1,3- diisopropyl imidazolium)palladium(II) chloride[Pd(DII)2Cl2]Br⁻2:

2.9 Bromide bis(1,3- di-tert-butyl imidazolium)palladium(II) chloride[Pd(DTI)2Cl2]Br⁻2:

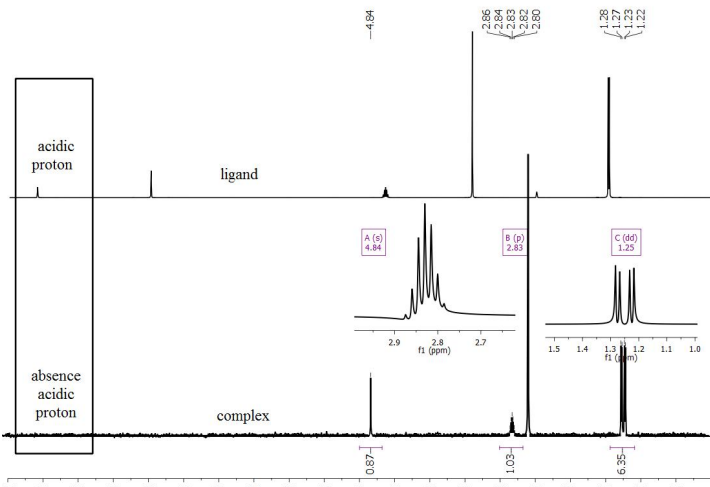
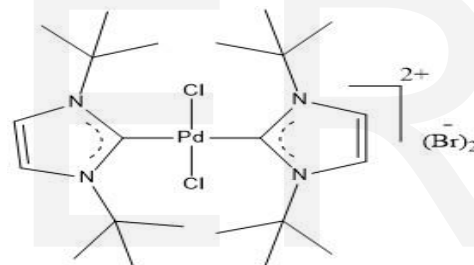
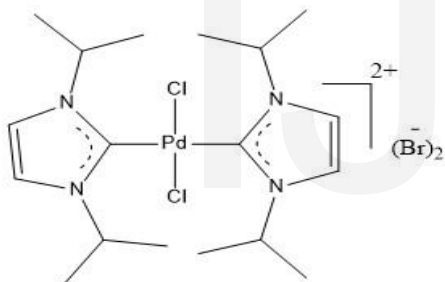


Fig 11 .¹H NMR for (DII & [Pd(DII)₂Cl₂]Br⁻₂

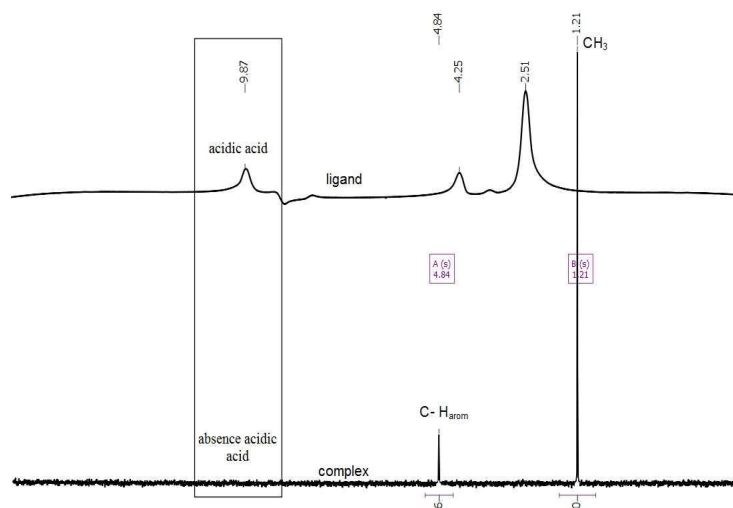


Fig 13 .¹H NMR for (DTI & [Pd(DTI)₂Cl₂]Br⁻₂

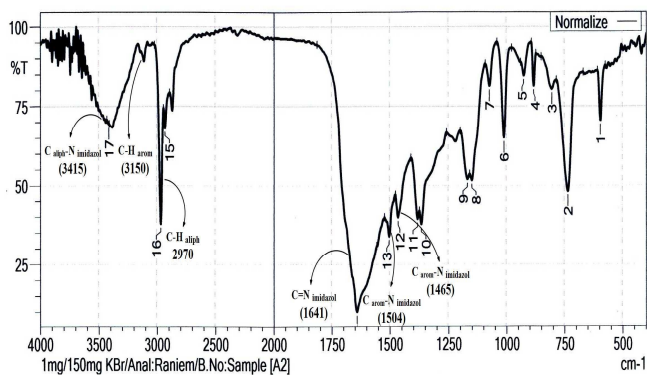


Fig 14 .IR spectrum for $[Pd(DTI)_2Cl_2]Br^-_2$

Brouwn powder. Yield 0.0699 (50.21%) ,mp: 310-312°C. FT-IR(KBr): $\nu(cm^{-1})$; 3415(C aliph -N imidazol), 3150(C-H arom), 2970 (C-H aliph), 1504 (C arom -N imidazol), 1465(C aliph-N imidazol). 1H NMR (400 MHz, DMSO- d_6) δ 4.84 (s, 1H), 1.21 (s, 9H).

3 Determine the metal content of the complexes:

$[Pd(DII)_2Cl_2]Br^-_2$:



$X = 0.0069g$ ($PdSO_4$ calculated)

The actual rate is determined by taking 0.022g of the complex in a melting-pot and diluting the compound with concentrated sulfuric acid and put it in the cauldron at 500 ° C for three hours, The weight of the output was 0.0065g, which is the actual rate of the palladium sulfate in the complex.

In a similar way, we determined the metal content of the complex $[Pd(DTI)_2Cl_2]Br^-_2$ where we obtained the results:

Table 1. The metal content of the complexes $[Pd(DII)_2Cl_2]Br^-_2$ & $[Pd(DTI)_2Cl_2]Br^-_2$

complex	PdSO ₄ %		Pd%	
	(found)	(cal)	(found)	(cal)
$[Pd(DII)_2Cl_2]Br^-_2$	29.54	31.36	15.45	16.36
$[Pd(DTI)_2Cl_2]Br^-_2$	27.27	28.63	14.43	15.05

4 RESULTS AND DISCUSSION

Imidazolium salts can be obtained from Alkyl-imidazole by stepwise aryl-/alkylation. Firstly, we prepared Alkyl-imidazole by reaction of bromo alkane with imidazole(Scheme 3), in the presence of K_2CO_3 and anhydrous $CuSO_4$. The imidazolium salt can be obtained by refluxing Alkyl-imidazole with bromo alkane (Scheme 4). Both compounds were characterized by IR, 1H NMR, ^{13}C NMR.

For Alkyl-imidazole and imidazolium salts (II, TI, DII,DTI) strong and sharp stretching vibrations (3425, 3406, 3421, 3442, cm^{-1}) (Fig 2,5,6,10) appeared for tertiary nitrogens of imidazolium ring (C aliph -N imidazol) [7].

NMR spectra of all the compounds were analyzed in DMSO - d_6 over the scan range 0 to 15 δ ppm for 1H NMR and 0 to 210 δ ppm for ^{13}C NMR studies. In the 1H NMR spectra, acharacteristic sharp singlet (Ha) for imidazolium salts for acidic proton (NCHN) indicated the successful formation of target ligands (DII,DTI) (Fig 4,9) [10]. Similarly, the structural features of the salts were further confirmed by the ^{13}C NMR data. In ^{13}C NMR spectra, the chemical shift values of (NCN) were observed within the range δ 133.22 -134.28 ppm (Fig 3,8), which is also in agreement with reported data for similar azolium salts [2], [6]. Synthesis of Pd-NHC complexes was confirmed by the disappearance of acidic proton peak (Ha) in 1H NMR spectrum for $[Pd(DII)_2Cl_2]Br^-_2$ & $[Pd(DTI)_2Cl_2]Br^-_2$ (Fig 11,13) [10].

5 Conclusion

Four new compounds (NHC precursors, Pd-NHC complexes) based on imidazole were synthesized and fully characterized by NMR($^1H,^{13}C$), IR. By means of imidazole ring, N-Heterocyclic Carbene and ionic liquid were synthesized. Through these compounds, organometallic complexes of palladium were synthesized, Carbon is associated with a sigma bond with the metal.

6 References:

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