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Synthesis, Characterizations and Multivariate Data Analysis of Non- and Nitrile-Functionalized *N*-Heterocyclic Carbene Complexes of Silver(I) and Palladium(II)

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ABSTRACT

*This study reports the synthesis and comprehensive characterization of asymmetrical N-heterocyclic carbene (NHC) benzimidazolium salts and their corresponding silver(I) and palladium(II) complexes. Two series of benzimidazolium salts were synthesized: N-benzyl-N'-(n-benzonitrile) benzimidazolium bromides (**1Br - 3Br**, n = 2, 3, 4) and N-benzyl-N'-(n-methylbenzene)benzimidazolium bromides (**4Br - 6Br**, n = 2, 3, 4). The salts were prepared via N-alkylation and subsequently reacted with Ag_2O to yield silver(I) NHC complexes (**Ag1 - Ag6**). Transmetallation of these silver complexes with $Pd(COD)Cl_2$ produced the corresponding palladium(II) NHC complexes (**Pd1 - Pd6**). All compounds were characterized using melting point determination, CHN elemental analysis, FTIR-ATR, and ^{1}H- and ^{13}C-NMR spectroscopy. The successful formation of benzimidazolium salts was confirmed by ^{1}H-NMR singlet peaks at δ 9.96-10.25 ppm and ^{13}C-NMR peaks at δ 114.3-143.55 ppm. The formation of metal-NHC complexes was evidenced by the disappearance of the acidic proton and the appearance of carbene peaks in the ^{13}C-NMR spectra. The Principal Component Analysis (PCA) was employed to explore relationships among*

the compounds based on their NMR data. The PCA of ^{1}H-NMR data revealed clear separation and clustering of benzimidazolium salts and silver(I)-NHC complexes, with the first two principal components explaining 95.56% of the total variance. Similarly, the PCA of ^{13}C-NMR data showed distinct clustering of benzimidazolium salts, silver(I)-NHC, and palladium(II)-NHC complexes, with 82.48% of the total variance explained by the first two principal components. These results demonstrate the ability of PCA to differentiate and classify the compounds based on their structural features and functional groups. This study showcases the potential of combining spectroscopic data with chemometric techniques for gaining insights into structural relationships in inorganic synthesis chemistry, which can be valuable for understanding the properties and potential applications of these NHC complexes.

Keywords: Silver(I)-NHC; Palladium(II)-NHC; Carbene; Nitrile-Functionalized; Principal Component Analysis

INTRODUCTION

In the past few decades, carbene has been extensively researched and has played a significant role in the field of chemical sciences. Carbenes are defined as compounds that contain a neutral divalent carbon atom with a six-electron valence shell. They have been highly transient intermediates, although they are not usually isolable due to their reactivity [1]. The covalent bond linked the carbene carbon to two adjacent groups and possess two nonbonding electrons which can either be in a singlet state or triple state [2].

The *N*-heterocyclic carbene (NHC) is classified as one of singlet carbenes that have gained the most attention in carbene chemistry. As the NHC is electron-rich nucleophilic that features a carbene centre as part of a heterocyclic ring bonded to at least one nitrogen atom [3]. This NHC was first attempted in the 1960's by Wanzlick [4] and Öfele [4,5] and later the extensive work by Lappert in the 1970s [4] which led to the discovery of complexes with ligands in organometallic chemistry. During the 1980s and 1990s, NHC has successfully synthesized and isolated stable nucleophilic carbenes which derived via deprotonation of imidazolium precursors by Bertrand [6] and Arduengo and co-workers [7]. Since the first report of stable

carbenes, the broad use of NHC in organic synthesis has been demonstrated successfully beside their role as important ligands in metal-based catalytic reactions [8].

NHCs have continued widespread as useful ligands in coordination chemistry and catalysis due to their nature of electron-rich [9]. The electronic properties of NHC are similar to those of most traditional ligands, such as phosphines, although they are more stable due to their electronic structure. NHC ligands can generate stronger bonds to the metal than phosphines due to their strong properties of σ-electron-donating [3]. They function as strong σ-donor and weak π-acceptor ligands, with nitrogen atoms donating electrons to the carbene carbon to compensate for electrons used in metal ligand (M-L) bond [10]. Thus, NHCs are viewed mainly as σ-donors that give better stability to M-L bonds.

Metal complexes of NHCs have emerged as compounds which are gaining research interest with most of all transition metals and main group metals due to their roles in catalysis and organometallic chemistry [10]. Among NHC-metal complexes, silver(I)-NHC complexes have been widely studied in organometallic chemistry because of their successful applications in catalysis, as well as in bioorganometallic chemistry [11]. The silver(I)-NHC complexes also have received much interest due to their outstanding antibacterial and anticancer activities against several pathogens [10]. The success of Ag(I)-NHC complexes and their applications is often attributed to their accessibility of synthesis, the low synthesis cost, and the high yield.

In 1995, numerous complexes have been synthesized using various ways since the earliest uses of palladium(II)-NHC complexes [12]. One of the earliest methods to synthesize palladium(II)-NHC complexes is by the direct synthesis between palladium sources and carbene precursors; however, it was less successful. Several studies have reported issues in generating palladium(II) complexes with $Pd(OAc)_2$ from NHC precursors, resulting the NHC precursor decomposition [10]. The most widely studied for palladium(II) complexes is transmetalation method such as from silver(I)-NHC to palladium(II)-NHC complexes using various palladium sources although this reactions are not always successful. Furthermore, the successful transmetalation is dependent on the choice of the palladium sources has been reported [13,14].

The palladium(II)-NHC complexes have gained great interest due to their application in some organic reactions. Particularly, this palladium(II)-NHC complexes have been demonstrated to be effective catalysts in the reactions of C-C coupling, such as Suzuki-Miyaura, Heck-Mizoroki and Kumada couplings [15]. Palladium(II)-NHC complexes are among the most efficient catalysts for a variety of C-C bond forming and coupling reactions. Various kinds of C-C coupling reactions catalyzed by palladium(II)–NHC complexes have been described, depending on the nature or orientation of the ligands of NHC, that would need sufficient alkyl or aryl substituents [11]. Besides cross coupling reactions, palladium(II)-NHC complexes have specialized in other organic transformations, including polymerization, C-H activation processes or olefin hydrogenation [15]. As a result, palladium(II) plays a special role in NHC chemistry and a variety of palladium(II)-NHC complexes have been intensively studied as catalysts in organic transformations of various Pd-catalyzed.

In this study, we synthesized the benzimidazolium salts along with its respective silver(I)-NHC complexes with Ag_2O via *in situ* deprotonation of azolium salts, whereas palladium(II)-NHC complexes was obtained by transmetalation from the silver(I)-NHC complexes. All the salts and complexes were characterized through FTIR-ATR, CHN analyzer as well as ^{1}H- and ^{13}C-NMR spectroscopy. Finally, all the compounds were undergoing multivariate data analysis of principal component analysis (PCA) as to determine the correlation and relationship between benzimidazolium salts, silver(I)- and palladium(II)-NHC complexes, respectively.

EXPERIMENTAL

Materials and Instruments

Benzimidazole (MERCK, 99%), Silver oxide (Merck, 99%), Potassium hydroxide (Merck, 99%), Potassium hexafluorophosphate (Merck, 99%), Benzyl chloride (Sigma, Aldrich, 99%), 2-(bromomethyl)benzonitrile (Sigma Aldrich, 99%), 3-(bromomethyl)benzonitrile (Sigma Aldrich, 95%), 4-(bromomethyl)benzonitrile (Sigma Aldrich, 99%), 1-(bromomethyl)-2-methylbenzene (Sigma Aldrich, 97%), 1-(bromomethyl)-3-methylbenzene

(Sigma Aldrich, 97%), 1-(bromomethyl)-4-methylbenzene (Sigma Aldrich, 97%), Dichloro(1,5-cyclooctadiene)palladium(II) (Sigma Aldrich, 99%), Dimethyl sulphoxide (QRëC, AR Grade), Acetonitrile (QRëC, AR Grade), Methanol (QRëC, AR Grade), Chloroform (R&M, AR Grade), Diethyl ether (R&M, AR Grade), Celite (Merck, particle size 0.02 – 0.1 mm) and Dimethyl sulphoxide-d_6 (with 0.03% TMS, 99.8 atom %D. For characterization of compounds, Perkin Elmer Spotlight 200 FTIR-ATR Microscopy System were used for FT-IR spectra in the range 4000 - 600 cm^{-1}. ^{1}H and ^{13}C NMR data were collected by Bruker 500 MHz Ascend spectrometer 125 MHz (^{13}C-NMR) and 500 MHz (^{1}H-NMR) in dimethyl sulfoxide-d_6 (DMSO). Melting point determination were determined by using Stuart Scientific SMP-1.

The Synthesis of Benzyl Benzimidazole

Benzimidazole (1.00 g, 8.47 mmol) and potassium hydroxide, KOH (0.95 g, 16.93 mmol) were added into 30 mL of DMSO. After 30 minutes of stirring at room temperature, dropwise additions of benzyl chloride (1.07 g, 8.47 mmol) were made to the mixture under vigorous agitation for 3 hours. The solution was then placed into a 250 mL separating funnel and extracted with chloroform (3 x 30 mL). The extract was filtered through four plies of Whatmann filter papers to get a clear solution of the desired compound. The product was air-dried in fume hood forming white solid powder of *N*-benzyl benzimidazole. Yield: 68%. M.P: 101-103 °C. FT-IR (ATR,cm^{-1}): 3032 (C-H aromatic stretching), 1612 (C=C aromatic stretching), 2223 (C=N stretching), 1187 (C-N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 5.51 (s, 1H, N-C**H**$_2$-Ar), 7.19 - 7.34 (m, 4H, arene-**H**), 7.51 - 7.69 (m, 4H, benzimi-**H**), 8.43 (s, 1H, N-C**H**-N). ^{13}C-NMR (125 MHz, d_6-DMSO, δ ppm): 48.12 (N-**C**H$_2$-Ar), 111.17, 119.96, 122.09, 122.90, 127.85, 128.21, 129.16, 134.12, 137.39 (arene-**C**/benzimi-**C**), 144.69 (N-**C**H-N). Anal. Calc. for $C_4H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45 %. Found: C, 81.02; H, 5.29; N, 13.92 %

General Procedure for the Synthesis of *N*-benzyl-*N'*-(*n*-benzonitrile/ methylbenzene) benzimidazolium bromide (1Br – 6Br) (n = 2, 3 & 4) derivatives

Benzyl benzimidazole (1.00 g, 4.80 mmol) was added dropwise in a stirring solution of 2-(bromomethyl)-benzonitrile (0.94 g, 4.80 mmol) in 30 mL of acetonitrile. The reaction mixture was left to reflux for 24 h. The product was then cooled to room temperature. The obtained precipitates formed were filtered and washed with acetonitrile (2 x 5 mL) and diethyl ether (5 mL) and were left air-dried in a fume hood.

***N*-benzyl-*N'*-(2-benzonitrile)benzimidazolium bromide, 1Br**

White solid (powder). Yield: 74 %, M.P: 145-147 °C. FTIR (ATR, cm^{-1}): 3032 (C-$H_{aromatic}$ stretching), 2222 (C≡N stretching), 1606 (C=$C_{aromatic}$ stretching), 1117 (C-N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 5.84 (2H, s, N-C**H**$_2$-Ar), 6.06 (2H, s, N-C**H**$_2$-ArCN), 7.39 - 7.63 (9H, m, arene-**H**), 7.65-8.01 (4H, m, benzimi-**H**), 10.02 (1H, s, N-C**H**-N). ^{13}C-NMR (125 MHz, d_6-DMSO, δ ppm): 49.12 (N-CH_2-Ar), 50.62 (N-**C**H_2-ArCN), 111.39, 114.28, 127.46, 127.59, 128.79, 129.27, 129.70, 130.12, 131.46, 131.84, 134.17, 134.34, 134.52, 137.32 (arene-**C**/benzimi-**C**), 114.66 (C≡N), 143.94 (N-CH-N). Anal. Calc. for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91 %. Found: C, 81.29; H, 5.72; N, 13.00 %

***N*-benzyl-*N'*-(3-benzonitrile)benzimidazolium bromide, 2Br**

White solid (powder). Yield: 69%. M.P: 150 - 152 °C. FTIR (ATR, cm^{-1}): 3031 (C-$H_{aromatic}$ stretching), 2229 (C≡N stretching), 1557 (C=$C_{aromatic}$ stretching), 1180 (C-N stretching). 1H-NMR (500 MHz, d_6 -DMSO, δ ppm): 5.86 (1H, s, N-CH_2-Ar), 5.95 (1H, s, N-CH_2-ArCN), 7.41 - 7.70 (9H, m, arene-H), 7.89 - 8.13 (4H, m, benzimi-H), 10.25 (1H, s, N-CH-N). ^{13}C-NMR (125 MHz, d_6 -DMSO, δ ppm): 49.60 (N-CH_2-Ar), 50.64 (N-CH_2-ArCN), 112.36, 114.41, 114.56, 118.88, 127.33, 127.37, 128.88, 129.24, 129.46, 130.70, 131.47, 131.56, 132.54, 132.99, 133.83, 134.30, 135.95 (arene-**C**/ benzimi-**C**), 114.56 (C≡N), 143.53 (N-CH-N). Anal. Calc. for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91 %. Found: C, 80.89; H, 5.82; N, 12.30 %

_N_-benzyl-_N'_-(4-benzonitrile)benzimidazolium bromide, 3Br

White solid (powder). Yield: 67%. M.P: 192 - 193 °C. FTIR (ATR, cm^{-1}): 3037 (C-$H_{aromatic}$ stretching), 2229 (C≡N stretching), 1557 (C=$C_{aromatic}$ stretching), 1214 (C-N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 5.85 (s, 2H, N-C**H**$_2$-Ar), 5.98 (s, 2H, N-C**H**$_2$-ArCN), 7.41 - 8.02 (m, ^{13}H, Ar-**H**), 10.21 (s, 1H, N-C**H**-N); ^{13}C-NMR (125 MHz, DMSO-d_6, δ ppm): 49.96 (N-CH_2-Ar), 50.64 (N-CH_2-ArCN), 111.95, 114.38, 118.89, 127.37, 127.42, 128.88, 129.26, 129.49, 129.62, 131.51, 131.56, 133.36, 134.26, 139.82 (arene-**C**/benzimi-**C**), 114.60 (C≡N), 143.55 (N-**C**H-N). Anal. Calc. for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91 %. Found: C, 81.42; H, 5.94; N, 12.75 %

_N_-benzyl-_N'_-(2-methylbenzene)benzimidazolium bromide, 4Br

White solid (powder). Yield: 69 %, M.P: 163-165 °C. FTIR (ATR, cm^{-1}): 2969 (C-$H_{aromatic}$ stretching), 1610 (C=$C_{aromatic}$ stretching), 1374 (CH_3 stretching), 1289 (C-N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 2.51 (3H, s, Ar-C**H**$_3$), 5.83 (2H, s, N-C**H**$_2$-Ar), 5.84 (2H, s, N-**CH**$_2$-ArCH_3), 7.19 - 7.66 (9H, m, arene-**H**), 7.93 - 8.00 (4H, m, benzimi-H), 9.96 (1H, s, N-C**H**-N). ^{13}**C NMR** (125 MHz, d_6-DMSO, δ ppm): 19.26 (Ar-CH_3), 49.06 (N-**C**H_2-Ar), 50.52 (N-CH_2-ArCH_3), 114.52, 114.55, 125.98, 127.36, 128.67, 128.93, 128.22, 29.38, 129.49, 131.35, 131.51, 131.93, 132.17, 134.46, 137.12 (arene-**C**/benzimi-**C**), 143.19 (N-CH-N). Anal. Calc. for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91 %. Found: C, 84.29; H, 7.19; N, 8.32 %

_N_-benzyl-_N'_-(3-methylbenzene)benzimidazolium bromide, 5Br

White solid (powder). Yield : 65%. M.P : 171 - 173 °C. FT-IR (ATR, cm^{-1}): 2971 (C-Haromatic stretching), 1557 (C=Caromatic stretching), 1283 (C-N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 2.51 (3H, s, Ar-CH_3), 5.78 (2H, s, N-CH_2-Ar), 5.83 (2H, s, N-CH_2-ArCH_3), 7.20 - 7.45 (9H, m, arene-H), 7.54 - 7.99 (4H, m, benzimi-H), 10.16 (1H, s, N-CH-N). ^{13}C-NMR (125 MHz, d_6-DMSO, δ ppm): 20.89 (Ar-CH_3), 50.38 (N-CH_2-Ar), 50.51 (N-CH_2-ArCH_3), 114.47, 114.54, 127.27, 127.29, 128.73, 128.85, 129.24, 129.50, 130.04, 131.29, 131.52, 131.55, 134.40, 138.75 (arene-C/benzimi-C), 143.01 (N-CH-N). Anal. Calc. for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91 %. Found: C, 83.39; H, 7.12; N, 8.82 %

***N*-benzyl-*N'*-(4-methylbenzene) benzimidazolium bromide, 6Br**

White solid (powder). Yield: 77%; M.P.: 201 - 202 °C. FTIR (ATR, cm^{-1}): 3030 (C-$H_{aromatic}$ stretching), 1557 (C=C stretching), 1372 (CH_3 stretching), 1281 (C-N stretching). 1H-NMR (500 MHz, DMSO-d_6, δ ppm): 2.30 (s, 3H, Ar-C**H**$_3$), 5.75 (s, 2H, N-C**H**$_2$-Ar), 5.80 (s, 2H, N-C**H**$_2$-ArCH_3), 7.23 - 7.98 (m, 13H, arene-**H**), 10.07 (s, 1H, N-C**H**-N); ^{13}C NMR (125 MHz, DMSO-d_6, δ ppm): 21.18 (Ar-CH_3), 50.38 (N-CH_2-Ar), 50.51 (N-C**H**$_2$-ArCH_3), 114.47, 114.54, 127.27, 127.29, 128.73,128.85, 129.24, 129.50, 130.04, 131.29, 131.52, 131.55, 134.40, 138.75 (arene-**C**/benzimi-**C**), 143.01 (N-**C**H-N). Anal. Calc. for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91 %. Found: C, 84.19; H, 7.19; N, 8.62 %

General procedure for the synthesis of *N*-benzyl-*N'*-(*n*-benzonitrile/ methylbenzene)benzimidazol-2-ylidenesilver(I) hexafluorophosphate (Ag1 – Ag6) (n = 2, 3 & 4) derivatives

A mixture of salts **1Br – 6Br** (0.50 g, 1.22 mmol) and Ag_2O (0.29 g, 1.22 mmol) in methanol (15 mL) was stirred at room temperature for 24 h and covered with aluminium foil to prevent light. The reaction mixture was filtered through pad of celite to remove unreacted silver and to the colourless filtrate, potassium hexaflourophosphate, KPF_6 (0.23 g, 1.24 mmol) was added. The reaction mixture is then stirred at room temperature for 3 h. The solvent was removed using filtration method and the resultant white powder was washed with distilled water (3 x 3 mL) to remove unreacted potassium hexaflourophosphate and evaporated in fume hood for 24 h and further recrystallized by acetonitrile (20 mL) and diethyl ether (100 mL) to give crystalline solid.

***N*-benzyl-*N'*-(2-benzonitrile)benzimidazol-2-ylidenesilver(I) hexafluorophosphate, Ag1**

White-grey crystalline solid (powder). Yield: 57 %, M.P: 243-245 °C. FTIR (ATR, cm^{-1}): 2970 (C-$H_{aromatic}$ stretching), 2223 (C=N stretching), 1612 (C=$C_{aromatic}$ stretching), 2223 (C=N stretching). 1H-NMR (500 MHz, d_6-DMSO, δ ppm): 5.71 (4H, s, N-C**H**$_2$-Ar), 5.93 (4H, s, N-C**H**$_2$-ArCN), 7.16 - 7.56 (2 x 9H, m, arene-**H**), 7.58 - 7.84 (2 x 4H, m, benzimi-H). ^{13}C-NMR (125 MHz, d_6-DMSO, δ ppm): 50.81 (N-CH_2-Ar), 52.48 (N-**C**H_2-ArCN),

110.98, 112.74, 113.10, 117.68, 125.00, 127.75, 128.51, 129.20, 129.42, 134.20, 134.23, 136.50, 139.76 (benzimi-**C**/arene-**C**), 117.68 (C≡N), 190.52, 192.10 (**C**$_{carbene}$-Ag). Anal. Calc. for $C_{44}H_{36}AgN_6PF_6$: C, 69.84; H, 4.80; N, 11.11 %. Found: C, 70.01, H, 4.35; N, 10.09%.

N-benzyl-*N'*-(3-benzonitrile)benzimidazol-2-ylidenesilver(I) hexafluorophosphate, Ag2

White-grey crystalline solid (powder). Yield: 60%. MP: 242 - 244 °C. FTIR (ATR, cm^{-1}): 2925 (C=H aromatic stretching), 2230 (C≡N stretching),1608 (C=C$_{aromatic}$ stretching), 1184 (C-N stretching). ^{1}H-NMR (500 MHz, d$_6$ -DMSO, δ ppm): 5.76 (2H, s, N-CH$_2$-Ar), 5.82 (2H, s, N-CH$_2$-ArCN), 7.24 – 7.42 (9H, m, arene-H), 7.43 – 7.78 (4H, m, benzimi-H). ^{13}C-NMR (125 MHz, d$_6$ -DMSO, δ ppm): 49.31 (N-CH$_2$-Ar), 50.24 (N-CH$_2$-ArCN), 110.13, 110.71, 110.96, 116.70, 122.88, 125.54, 125.60, 126.43, 127.15, 128.39, 128.90, 130.21, 131.69, 131.95, 134.59, 136.19 (benzimi-C/arene-C), 116.70 (C≡N), 187.58, 189.24 (Ccarbene-Ag). Anal. Calc. for $C_{44}H_{36}AgN_6PF_6$: C, 70.84; H, 4.80; N, 11.11 %. Found: C, 71.02, H, 3.95; N, 11.79%.

N-benzyl-*N'*-(4-benzonitrile)benzimidazol-2-ylidenesilver(I) hexafluorophosphate, Ag3

White-grey crystalline solid (powder). Yield: 70%M.P.: 269 - 270 °C. FTIR (ATR, cm^{-1}): 2924 (C-Haliphatic stretching), 2228 (C≡C stretching), 1609 (C=C stretching), 1183 (C-N stretching). 1H-NMR (500 MHz, d$_6$ -DMSO, δ ppm): 5.76 (s, 2 x 2H, N-CH$_2$-Ar), 5.86 (s, 2 x 2H, N-CH$_2$-ArCN), 7.27 - 7.78 (m, 2 x ^{13}H, Ar-H); ^{13}C-NMR (125 MHz, d$_6$ -DMSO, δ ppm): 49.61 (N-CH$_2$-Ar), 50.25 (N-CH$_2$-ArCN), 109.19, 110.67, 110.98, 122.82, 122.92, 125.54, 125.58, 125.61, 126.08, 126.44, 127.19, 131.04, 131.83, 131.88, 134.55, 134.61, 140.20 (benzimi-C/arene-C), 116.73 (C≡N), 187.77, 189.32 (Ccarbene-Ag). Anal. Calc. for $C_{44}H_{36}AgN_6PF_6$: C, 69.84; H, 4.80; N, 11.11 %. Found: C, 70.01, H, 4.35; N, 10.09%.

_N_-benzyl-_N'_-(2-methylbenzene)benzimidazole-2-ylidenesilver(I) hexafluorophosphate, Ag4

White-grey crystalline solid (powder). Yield: 56 %, M.P: 200-203 °C. FTIR (ATR, cm^{-1}): 2923 (C-Haromatic stretching), 1603 ($C=C_{aromatic}$ stretching), 1396 (CH_3 stretching), 1183 (C-N stretching). 1H-NMR (500 MHz, d_6 -DMSO, δ ppm): 2.14 (3H, s, Ar-CH3), 5.55 (4H, s, N-CH_2-Ar), 5.58 (4H, s, N-CH_2-ArCH_3), 6.74 - 7.18 (2 x 9H, m, arene-H), 7.21 - 7.73 (2 x 4H, m, benzimi-H). 13C-NMR (125 MHz, d_6 -DMSO, δ ppm): 19.34 (Ar-CH_3), 50.34 (N-CH_2-Ar), 52.46 (N-CH_2-ArCH_3), 112.76, 112.90, 124.84, 124.90, 126.65, 127.40, 127.63, 128.48, 128.55, 129.24, 131.10, 133.68, 134.30, 134.55, 136.39, 136.59 (benzimi-C/arene-C), 189.54, 191.14 (Ccarbene-Ag). Anal. Calc. for $C_{44}H_{42}AgN_4PF_6$: C, 71.93; H, 5.76; N, 7.63 %. Found: C, 70.01, H, 4.35; N, 8.09 %.

_N_-benzyl-_N'_-(3-methylbenzene)benzimidazole-2-ylidenesilver(I) hexafluorophosphate, Ag5

White-grey crystalline solid (powder). Yield: 60%. MP : 242 - 244 °C. FTIR (ATR, cm-1): 2925 (C-Haromatic stretching), 1608 (C=Caromatic stretching), 1184 (C-N stretching). 1H NMR (500 MHz, d_6 -DMSO, δ ppm): 5.76 (2H, s, N-CH_2-Ar), 5.82 (2H, s, N-CH_2-ArCH_3), 7.24 – 7.42 (9H, m, arene-H), 7.43 – 7.78 (4H, m, benzimi-H). ^{13}C NMR (125 MHz, d_6 -DMSO, δ ppm): 20.11 (Ar-CH3), 49.31 (N-CH2-Ar), 50.24 (N-CH_2-ArCH_3), 110.13, 110.71, 110.96, 116.70, 122.88, 125.54, 125.60, 126.43, 127.15, 128.39, 128.90, 130.21, 131.69, 131.95, 134.59, 136.19 (Benzimi-C/Arene-C), 116.70 (C≡N), 187.58, 189.24 (Ccarbene-Ag). Anal. Calc. for $C_{44}H_{42}AgN_4PF_6$: C, 71.93; H, 5.76; N, 7.63 %. Found: C, 72.01, H, 5.23; N, 7.98 %.

_N_-benzyl-_N'_-(4-methylbenzene)benzimidazole-2-ylidenesilver(I) hexafluorophosphate, Ag6

White-grey crystalline solid (powder). Yield: 68% M.P.: 266 - 267 °C. FTIR (ATR, cm^{-1}): 2975 (C-Haliphatic stretching), 1603 (C=C stretching), 1398 (CH_3 stretching), 1188 (C-N stretching). 1H-NMR (500 MHz, d_6 -DMSO, δ ppm): 2.19 (s, 2 x 3H, Ar-CH_3), 5.68 (s, 2 x 2H, N-CH_2-Ar),

5.73 (s, 2 x 2H, N-CH2-ArCH$_3$), 7.02 - 7.76 (m, 2 x 13H, Ar-H); ^{13}C-NMR (125 MHz, d$_6$ -DMSO, δ ppm): 21.06 (Ar-CH$_3$), 52.04 (N-CH$_2$-Ar), 52.31 (N-CH$_2$-ArCH$_3$), 112.91, 112.94, 124.80, 127.67, 128.51, 129.26, 129.79, 133.72, 133.95, 136.74, 137.82 (Ar-C), 189.10, 190.71 (Ccarbene-Ag). Anal. Calc. for $C_{44}H_{42}AgN_4PF_6$: C, 71.93; H, 5.76; N, 7.63 %. Found: C, 71.21, H, 5.01; N, 8.01 %.

General Procedure for the Synthesis of *N*-benzyl-*N'*-(*n*-benzonitrile/methylbenzene)benzimidazol-2-ylidenepalladium(II) dichloride (Pd1 – Pd6) (n = 2, 3 & 4) derivatives

The Pd1-Pd6 complex was prepared by transmetallation method, in which the silver(I) ion was displaced with the palladium(II) ions. The dichloro(1,5-cyclooctadiene)palladium(II), Pd(COD)Cl$_2$ (0.03 g, 0.11 mmol) and Ag1-Ag6 derivatives (0.10 g, 0.11 mmol) was combined with acetonitrile (15 ml). The mixture was stirred for 24 hours at room temperature while wrapped in a aluminium foil to avoid light. The reaction mixture, then was filtered using pad of celite. The filtrate was placed in a fume hood and allowed to evaporate, to give a pale-yellow precipitate. The pale-yellow precipitate further recrystallized by acetonitrile and then re-dissolving in diethyl ether.

***N*-benzyl-*N'*-(2-benzonitrile)benzimidazol2-ylidenepalladium(II) dichloride, Pd1**

Pale yellow solid (powder). Yield : 88%. M.P :258 - 260 °C. FT-IR (ATR, cm^{-1}): 2925 (C-Haromatic stretching), 2230 (C≡N stretching), 1478, 1353 (C-N stretching). ^{13}C NMR (125 MHz, d$_6$ -DMSO, δ ppm): 51.51 (N-CH2-Ar), 52.71 (N-CH2-ArCN), 112.04, 112.23, 112.89, 113.21, 124.91, 127.13, 127.42, 128.09, 128.38, 128.76, 128.88, 128.96, 129.19, 129.31, 129.53, 130.18, 132.38, 133.90 (benzimi-C/arene-C), 118.86 (C≡N), 176.38 (Ccarbene-Pd). Anal. Calc. for $C_{44}H_{36}PdN_6C_{12}$: C, 63.79; H, 4.39; N, 10.17 %. Found: C, 63.19; H, 4.72; N, 10.04 %.

_N_-benzyl-_N'_-(3-benzonitribenzimidazol-2-ylidenepalladium(II) dichloride, Pd2

Pale yellow solid (powder). Yield : 88%. M.P :258 - 260 °C. FT-IR (ATR, cm^{-1}): 2924 (C-$H_{aliphatic}$ stretching), 2228 (C≡N stretching), 1354, 1478, 1353 (C-N stretching). ^{13}C NMR (125 MHz, d_6 -DMSO, δ ppm): 50.68 (N-CH_2-Ar), 50.85 (N-CH_2-ArCN), 108.59, 108.71, 110.47, 110.52, 122.87, 123.01, 125.81, 125.87, 126.07, 126.21, 126.57, 126.68, 126.89, 127.03, 127.18, 127.23, 127.28, 127.41, 131.61, 131.65, 131.87, 132.29, 132.34, 132.43, 132.46, 133.25, 133.33, 136.44 (Benzimi-C/Arene-C), 120.72 (C≡N), 174.55 ($C_{carbene}$-Pd). Anal. Calc. for $C_{44}H_{36}PdN_6C_{12}$: C, 63.79; H, 4.39; N, 10.17 %. Found: C, 64.09; H, 5.06; N, 10.34 %.

_N_-benzyl-_N'_-(4-benzonitrile)benzimidazol-2-ylidenepalladium(II) dichloride, Pd3

Pale yellow solid (powder). Yield: 55%; M.P.: 257 - 259 °C. FTIR (ATR, cm^{-1}): 2924 (C-$H_{aliphatic}$ stretching), 2230 (C≡N stretching), 1478, 1342 (C-N stretching). ^1H NMR (500 MHz, d_6 -DMSO, δ ppm): 5.78 (s, 2 x 2H, N-CH_2-Ar), 5.89 (s, 2 x 2H, N-CH_2-ArCN), 7.23 - 7.69 (m, 2 x 13H, Ar-H); ^{13}C NMR (125 MHz, d_6 -DMSO, δ ppm): 52.71 (N-CH_2-Ar), 52.74 (N-CH_2-ArCN), 111.28, 113.24, 124.86, 128.11, 128.21, 128.45, 128.59, 128.69, 128.75, 128.82, 129.03, 129.16, 129.27, 129.53, 132.83, 132.95, 133.38, 141.06 (Benzimi-C/Arene-C), 122.64 (C≡N), 176.58 ($C_{carbene}$-Pd). Anal. Calc. for $C_{44}H_{36}PdN_6C_{12}$: C, 63.79; H, 4.39; N, 10.17 %. Found: C, 63.79; H, 4.30; N, 10.14 %.

_N_-benzyl-_N_'-(2-methylbenzene)benzimidazole-2-ylidenepalladium(II) dichloride, Pd4

Pale yellow solid (powder). Yield: 52 %, M.P: 254 - 256 °C. FTIR (ATR, cm^{-1}): 2926 (C-$H_{aliphatic}$ stretchng); 1478, 1352 (C-N stretching). ^{13}C-NMR (125 MHz, d_6-DMSO): δ 17.21 (Ar-CH_3) 50.61 (N-CH_2-Ar), 50.82 (N-CH_2-ArCH_3), 110.78, 110.83, 111.11, 122.47, 122.56, 124.40, 124.52, 124.67, 124.88, 125.24, 126.13, 126.20, 126.41, 126.54, 126.60, 126.81, 126.85, 127.06, 127.08, 127.38, 128.79, 129.24, 131.33, 131.44, 132.15, 132.23, 132.62, 132.72, 133.39, 133.56, 133.61, 133.72 (Benzimi-C/Arene-C), 174.39, 174.42 ($C_{carbene}$–Pd). Anal. Calc. for $C_{44}H_{42}PdN_4C_{12}$: C,

65.72; H, 5.26; N, 6.97 %. Found: C, 65.05; H, 5.79; N, 6.23 %.

N-benzyl-*N'*-(3-methylbenzene)benzimidazole-2-ylidenepalladium(II) dichloride, Pd5

Pale yellow solid (powder). Yield: 63 %. M.P: 255 - 256 °C. FT-IR (ATR, cm_{-1}): 2927 (C-$H_{aliphatic}$ stretching); 1478, 1352 (C-N stretching). ^{13}C-NMR (125 MHz, d_6 -DMSO): δ 19.24 (Ar-CH_3), 50.48 (N-CH_2-Ar), 50.63 (N-CH_2-ArCH_3), 110.70, 110.98, 116.41, 122.50, 122.71, 123.19, 123.22, 123.27, 126.18, 126.23, 126.63, 126.78, 126.98, 127.00, 127.10, 127.12, 127.23, 127.40, 132.43, 132.46, 132.52, 132.55, 133.52, 133.58, 133.62, 136.50 (Benzimi-C/Arene-C), 174.17 ($C_{carbene}$-Pd). Anal. Calc. for $C_{44}H_{42}PdN_4C_{12}$: C, 65.72; H, 5.26; N, 6.97 %. Found: C, 66.31; H, 5.87; N, 6.02 %.

N-benzyl-*N'*-(4-methylbenzene)benzimidazole-2-ylidenepalladium(II) dichloride, Pd6

Pale yellow solid (powder). Yield: 52%; M.P.: 255 - 256 °C. FTIR (ATR, cm^{-1}): 2925 (C-$H_{aliphatic}$ stretching), 1478, 1354 (C-N stretching). ^{13}C-NMR (125 MHz, DMSO-d_6, 298 K): 19.05 (Ar-CH_3), 50.35 (N-CH_2-Ar), 50.59 (N-CH_2-ArCH_3), 110.96, 111.02, 122.48, 126.05, 126.10, 126.12, 126.15, 126.61, 126.74, 127.01, 127.13, 127.42, 127.52, 127.66, 127.96, 130.51, 132.46, 133.61, 135.92 (Benzimi-C/Arene-C), 174.12 (Ccarbene-Pd). Anal. Calc. for $C_{44}H_{42}PdN_4C_{12}$: C, 65.72; H, 5.26; N, 6.97 %. Found: C, 64.55; H, 6.01; N, 5.98 %.

The Data Pre-Processing

The ^{1}H- and ^{13}C-NMR spectra were converted and transferred as .xlsx format using Microsoft Excel and imported to the dataset table in XLSTAT 2024 software [16]. Next, the Kaiser-Meyer-Olkin (KMO) test verified dataset adequacy and proceeded with the principal component analysis (PCA) to find the correlation of the ^{1}H- and ^{13}C NMR results data.

The Kaiser-Meyer-Olkin (KMO) Test

The dataset was analysed for dataset adequacy by the KMO test. An adequate dataset determines the ability to generated model to extract latent variables from the dataset. In this study, the KMO test was employed at significant level, = 0.01. The calculated KMO was ranked as KMO < 0.5 = inadequate, 0.5 < KMO < 0.7 = mediocre, 0.7 < KMO < 0.8 = good, 0.8 < KMO < 0.9 = very good and KMO > 0.9 = excellent to indicate the dataset adequacy [17].

The Dataset Transformation

To ensure that the dataset followed a normal distribution before the PCA, the dataset normality was tested using Shapiro-Wilk test at $\alpha = 0.01$. The dataset was transformed using standard deviation (n-1) method.

The principal component analysis (PCA)

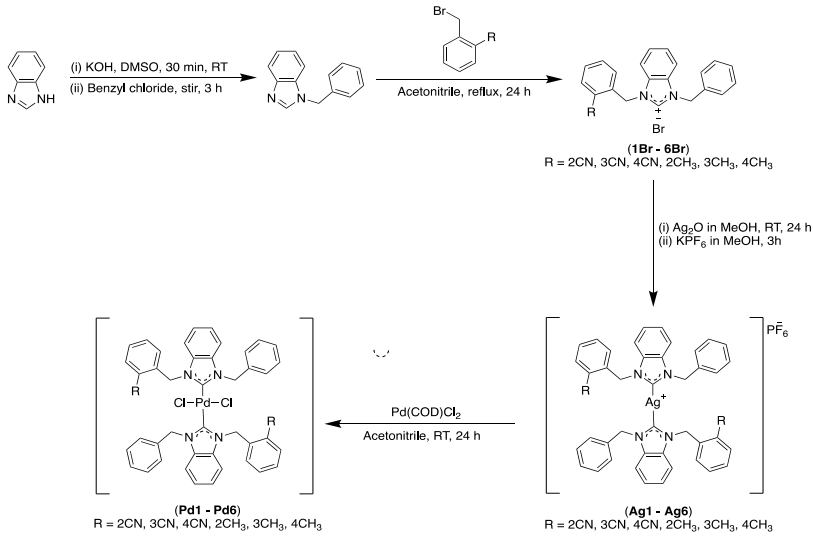
The ^{1}H- and ^{13}C-NMR spectra was extracted its ppm value to obtain dataset for PCA. The ^{1}H- and ^{13}C-NMR spectra at the baseline of δ 0 – 11 ppm for ^{1}H-NMR as well δ 0 – 200 for ^{13}C-NMR, respectively. Analysis of PCA was performed using XLSTAT software [16], and the data were scaled using Pareto scaling technique prior to PCA analysis to maximize the variation. After Pareto scaling, the variables used for PCA model were more normally distributed shown by its Gaussian curve. The number of principal components (PCs) was optimized to obtain optimum differentiation among samples. The differentiation result of samples was observed using PCA score plot. Moreover, PCA model was evaluated using its R^2 and Q^2 value to justify the good of fitness and predictivity of the PCA model, respectively.

RESULTS AND DISCUSSIONS

The Syntheses

The benzimidazolium salts were prepared via the two steps of the *N*-alkylation process as in Scheme 1. The *N*-benzylbenzimidazole salt was

obtained by reacting benzimidazole with benzyl chloride in the presence of KOH in DMSO for 3 h. Next, the resulting salt was then reacted with *n*-(bromomethyl)benzonitrile and *n*-methylbenzenebromide (where *n = 2,3,4*) in acetonitrile under reflux at 80 – 100 ºC for 24 h to obtained benzimidazolium bromide salts **1Br - 6Br,** respectively. The crystalline forms of the benzimidazolium bromide salts were obtained after recrystallization from the acetonitrile-diethyl ether.



Scheme 1: The schematic diagram formation of benzimidazolium salts (1.Br - 6.Br), silver(I)-NHC complexes (Ag1 – Ag6) and palladium(II)-NHC complexes (Pd1 – Pd6).

The corresponding silver(I)-NHC complexes **Ag1 – Ag6** are synthesized through in situ deprotonation of benzimidazolium bromide salts **1Br - 6Br**. The reaction of benzimidazolium salts with an excess amount of Ag_2O in methanol at room temperature for 24 to obtained silver bromide complexes, respectively. The reaction mixture was filtered through a pad of Celite for removal of excess unreacted Ag_2O and AgBr. The complexes were further converted to their corresponding hexafluorophosphate counterparts by metathesis reaction with KPF_6 for stability giving pure silver(I)-NHC complexes after recrystallization from the acetonitrile-diethyl ether.

The palladium(II)-NHC complexes of **Pd1 – Pd6** were synthesized via transmetallation method from corresponding silver(I)-NHC complexes of **Ag1 – Ag6** with $Pd(COD)Cl_2$, respectively. In this transmetallation reaction, the mixture was stirred in acetonitrile for 24 h at room temperature condition. After that, the reaction mixture was filtered and evaporated before recrystallization from the acetonitrile/diethyl ether. In this transmetallation reaction, the silver(I)-NHC complexes act as a transfer agent of NHC ligand to the palladium(II) ions. The benzimidazolium salts, **1Br – 6Br** and their respective silver(I)- and palladium(II)-NHC complexes, **Ag1 – Ag6** & **Ag1 – Ag6** are stable toward air and moisture, soluble in polar organic solvents such as acetonitrile, DMSO and DMF but insoluble in non-polar solvents such as diethyl ether, benzene and *n*-hexane. The detail synthetic routes for the synthesis of benzimidazolium salts, silver(I)- and palladium(II)-NHC complexes is given in **Scheme 1**, respectively.

The FTIR Analysis

The FTIR measurement was conducted in ATR (Attenuated Total Reflection) technique to detect different functional groups present in the compounds. The FTIR spectrum is recorded between 4000 and 600 cm^{-1}. Even though the FTIR spectroscopy was not fully utilized in this work due to the lack of functional groups, specific patterns were identified in these salts and their corresponding metal complexes, which could be used to confirm a successful synthesis methodology [17].

In the IR spectra of all the benzimidazolium salts **1Br - 6Br**, a broad band of medium intensity was observed at 3037 and 3030 cm^{-1}, corresponding to the C-H aromatic stretching vibrations. Noteworthy, it also shown both Figure 1 and Figure 2 that the IR peaks observable at ~3300 – 3400 cm^{-1} in the benzimidazolium salts indicative of N-H stretching vibrations as these peaks confirm the presence of protonated nitrogen atoms at the benzimidazolium core. The bands observed at 1557 cm^{-1} was attributed to the aromatic C=C stretching for both salts. Next, the FTIR spectra of salts **1Br - 6Br** also show a band of medium intensity at 1285 and 1281 cm^{-1} are assigned to the benzimidazole ring C-N stretching vibrations [18]. The FTIR spectra of 3Br salt as the representative off the nitrile-functionalized salt in Figure 1 showed a sharp peak at 2229 cm^{-1} assigned to the C≡N stretching which confirmed the present of cyano group as well as non-functionalized

benzimidazolium salt of **6Br** depicted in Figure 2.

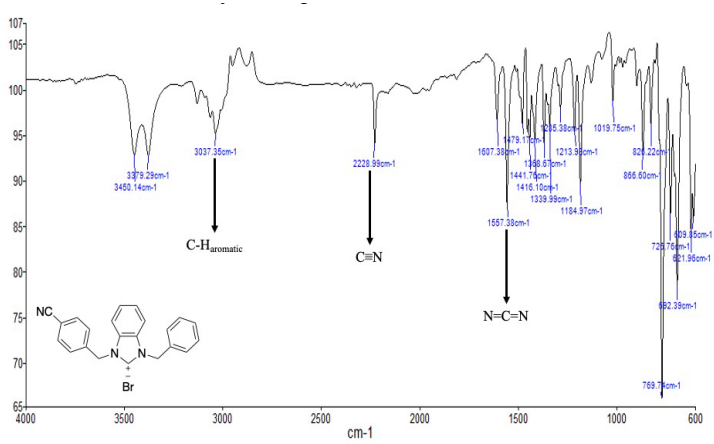


Figure 1: The representative of FTIR spectrum of the nitrile-functionalized of 3.Br benzimidazolium salt

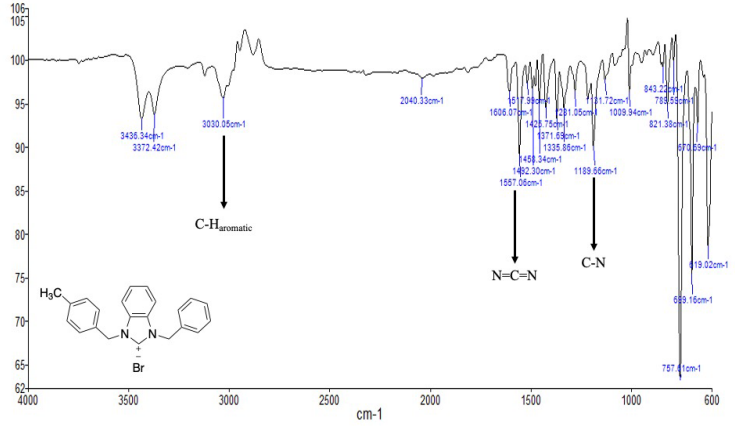


Figure 2: The representative of FTIR spectrum of the non-functionalized of 6.Br benzimidazolium salt

The Figure 3 and 4 show the representation of silver(I)- and palladium(II)-NHC complexes as it shows of shifting of correspondent peaks from the benzimidazolium moieties. The bands at 2924 – 2975 cm^{-1} are assigned to the C-H aliphatic stretching vibrations. The aromatic C=C

stretching was shifted from 1557 cm^{-1} to 1603 – 1610 cm^{-1} in the NHC complexes. Similarly, C-N stretching for the complexes was shifted to 1342 – 1478 cm^{-1}, indicating an interaction of the NHC moiety with the metal ions. The sharp peaks at 2228 – 2230 cm^{-1} are assigned to the C≡N stretching in **Ag3** and **Pd6** complexes. The nitrile vibrational band remains unchanged which indicates there is no direct interaction between the nitrile group with the metal ions [19].

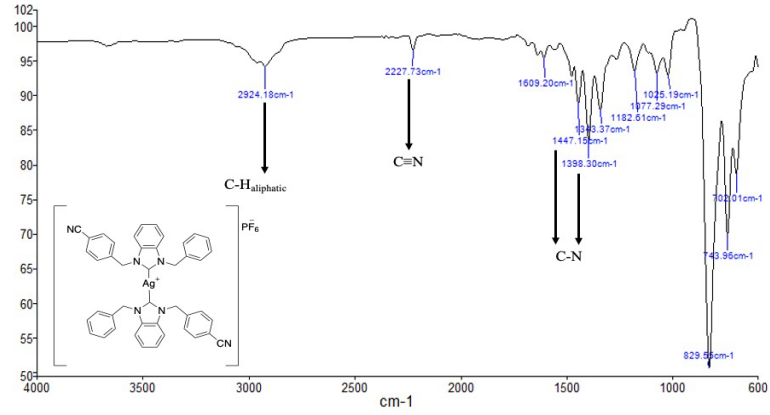


Figure 3: The representative of FTIR spectrum of the nitrile-functionalized of Ag3 silver(I)-NHC complex after the complexation reaction.

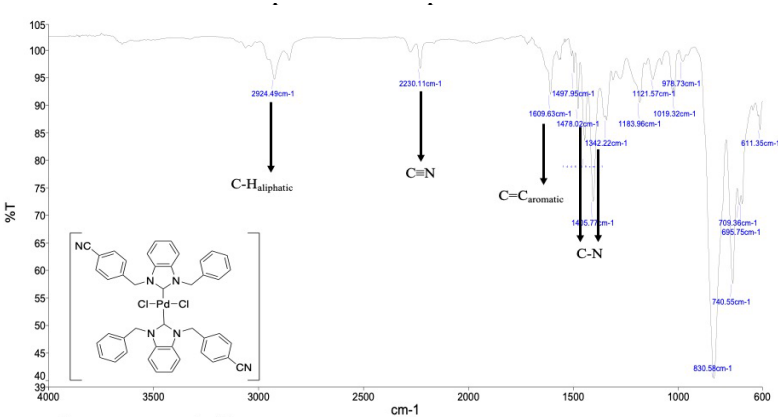


Figure 4: The representative of FTIR spectrum of the nitrile-functionalized of Pd6 palladium(II)-NHC complex after the transmetallation reaction.

The ^{1}H-NMR Spectroscopy Analysis

The ^{1}H-NMR spectra were obtained in DMSO-d_6 over a scan range of δ 0 – 11 ppm, respectively. In the ^{1}H-NMR all the benzimidazolium salt, all the salt of **1Br – 6Br** possess similar representation of the spectra, except that the additional of singlet peak at δ 2.30 – 2.51 ppm of **4Br – 6Br** indicating the presence of a methyl proton bonded to the benzene ring for the non-functionalized benzimidazolium salts. Next, the most significant observation in the all the spectra is the presence of singlet peak in the range of δ 9.96 – 10.25 ppm that corresponded to the acidic benzimidazolium C2 proton (Figure 5). This characteristic is important as this peak indicate the successfulness synthesis of the benzimidazolium salts [19].

The successful formation of the silver(I)- and palladium(II)-NHC complexes, **Ag1 – Ag6** & **Pd1 – Pd6** was confirmed by the disappearance of the characteristic acidic proton of the benzimidazolium moiety of the ^{1}H-NMR spectra of the complexes as shows in Figure 5 and 6. In the 1H NMR spectra, the complexes of **Ag1 – Ag6** & **Pd1 – Pd6,** the presence of the peaks were analogous to the spectra of their pre-carbenic benzimidazolium salts, except in the downfield region, where the peak that corresponded to the acidic proton was not observed. This evidence, hence, illustrates the formation of both silver(I)- and palladium(II)-NHC complexes.

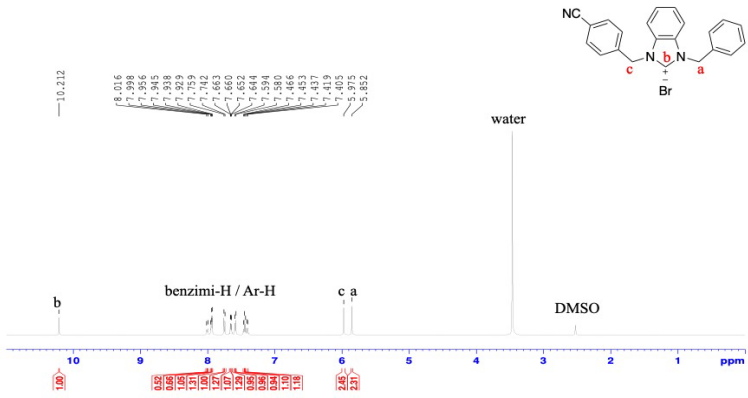


Figure 5: The representative of *^{1}H-NMR* spectrum of the nitrile-functionalized benzimidazolium salt of 3Br

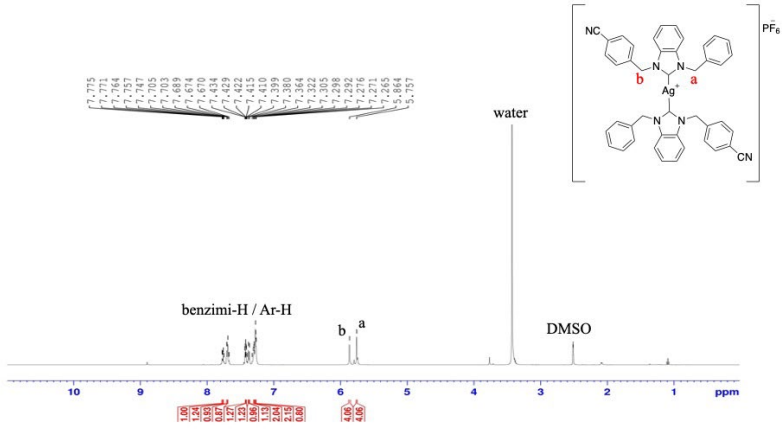


Figure 6: The representative of 1H-NMR spectrum of the nitrile-functionalized silver(I)-NHC complex of Ag3

The ^{13}C-NMR Spectroscopy Analysis

The ^{13}C-NMR spectra were obtained in DMSO-d_6 over a scan range of δ 0 – 200 ppm, respectively. The ^{13}C-NMR spectra of **1Br – 6Br** showed pre-carbenic carbon peaks of all non- and nitrile-functionalized benzimidazolium salts and were observed in the range of δ 143.01 – 143.94 ppm. The benzylic CH_2- which bears the benzonitrile moiety in the range of δ 49.12 – 49.96 ppm while the benzylic that holds the methylbenzene moiety in the range of δ 50.38 – 50.52 ppm, respectively. The indicate the successful attachment of asymmetrical benzylic moieties at the benzimidazolium nitrogen parts in the salt's establishment. Meanwhile, other peaks, such as arene carbon peak was observed at common resonances as reported previously [20].

The ^{13}C-NMR spectra of all the complexes of **Ag1 – Ag6** and **Pd1 – Pd6** showed the absence of the pre-carbenic peaks of all non- and nitrile-functionalized benzimidazolium salts and the presence of additional peaks around δ 174.12 – 190.71 ppm, which relate to the carbene carbons coordinated with the silver(I) and palladium(II) ions as shows in Figure 7 and 8 [21,22]. Besides this major change, the ^{13}C-NMR spectra of the complexes displayed resonances of aromatic, benzylic, nitrile and methyl carbon nuclei in the range of δ 174.12 – 191.14 ppm, respectively.

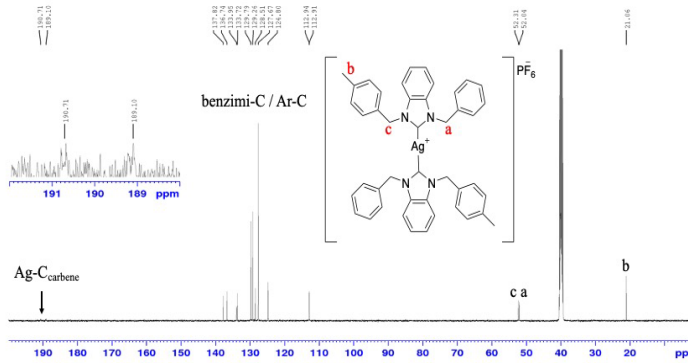


Figure 7: The representative of ^{13}C-NMR spectrum of the non-functionalized silver(I)-NHC complex of Ag6

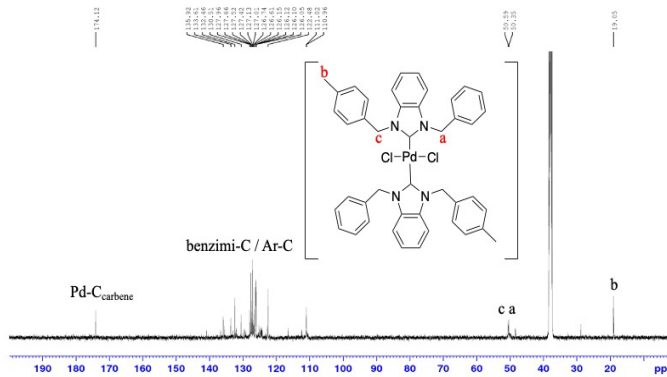


Figure 8: The representative of ^{13}C-NMR spectrum of the non-functionalized palladium(II)-NHC complex of Pd6

The Principal Component Analysis (PCA)

Moreover, we then employed the multivariate data analysis using principal component analysis (PCA) to identify correlations and relationships among the benzimidazolium salts, silver(I)-NHC complexes, and palladium(II)-NHC complexes based on their ^{1}H- and ^{13}C-NMR

spectroscopic data. The PCA is a powerful chemometric technique that reduces the dimensionality of complex datasets while retaining most of the relevant information. It achieves this by transforming the original variables into new orthogonal variables called principal components (PCs), which are linear combinations of the original variables.

In this study, the ^{1}H- and ^{13}C-NMR data were pre-processed by converting the spectra to an appropriate format (.xlsx format) and importing them into the XLSTAT software. The Kaiser-Meyer-Olkin (KMO) test was performed to assess the adequacy of the dataset for PCA, with values above 0.5 considered acceptable. The obtained KMO scores of 0.642 and 0.591 for the ^{1}H- and ^{13}C-NMR data, respectively, indicated that the datasets were suitable for PCA analysis.

We then proceeded with PCA on the scaled NMR data to maximize the variation among the samples. The number of principal components (PCs) retained was optimized to obtain the best differentiation among the samples, as visualized through score plots. The quality of the PCA models was evaluated using the R^2 and Q^2 values, which represent the goodness of fit and predictive ability, respectively. The PCA score plot for the ^{1}H-NMR data (Figure 9) showed a clear separation and clustering of the benzimidazolium salts and their corresponding silver(I)-NHC complexes along the first two principal components (PCs), which captured 64.45% and 31.11% of the total variance, respectively. The cumulative observation value of 95.56% indicated that the PCA model could explain most of the variation in the 1H-NMR data.

Similarly, the PCA score plot for the ^{13}C-NMR data (Figure 10) revealed a distinct clustering of the benzimidazolium salts, silver(I)-NHC complexes, and palladium(II)-NHC complexes based on their structural similarities and differences. The first two PCs accounted for 49.60% and 32.88% of the total variance, respectively, with an overall observation value of 82.48%, suggesting that the PCA model could capture a significant portion of the variance in the ^{13}C NMR data. We concluded that the PCA analysis was useful for correlating and classifying the benzimidazolium salts and their corresponding NHC complexes based on the NMR spectroscopic data. The clear differentiation observed in the score plots implies that the NMR data contained sufficient information to distinguish the compounds based

on their structural features and the presence/absence of specific functional groups (e.g., nitrile) [24,25].

Overall, the PCA approach demonstrated the feasibility of using spectroscopic data in combination with chemometric techniques for gaining insights into the structural relationships and correlations among a series of compounds. This multivariate data analysis strategy can be particularly valuable in the field of inorganic synthesis chemistry, where comprehensive structural characterization is crucial for understanding the properties and potential applications of the synthesized compounds.

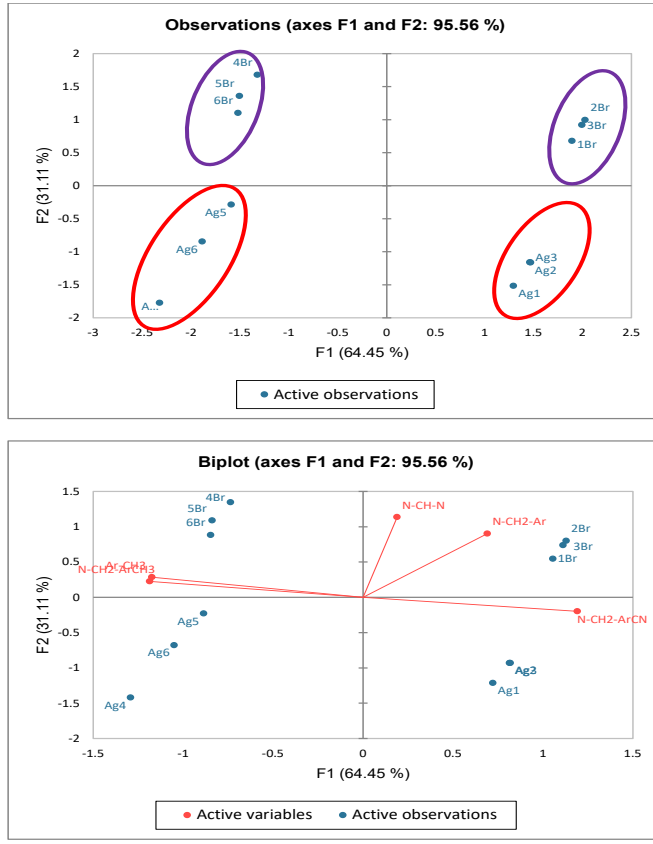


Figure 9: The principal component analysis (PCA) of the ^{1}H-NMR of benzimidazolium salts with respective silver(I)-NHC complexes with the observation/variables value of 95.56%.

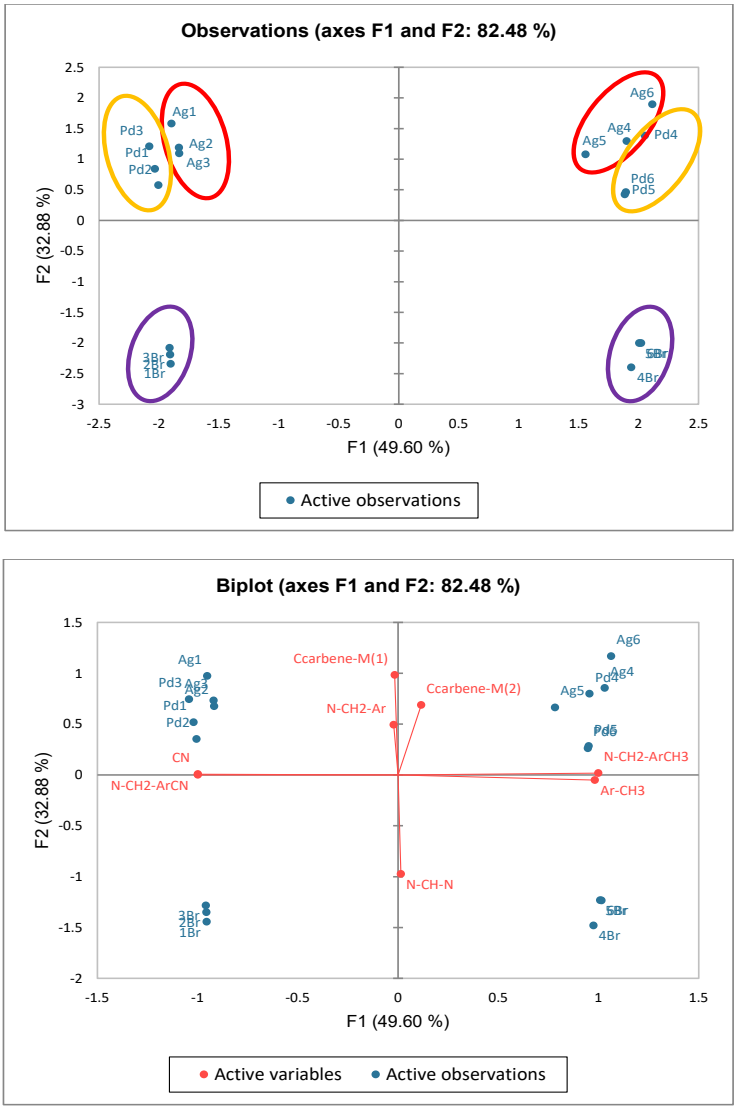


Figure 10: The principal component analysis (PCA) of the ^{13}C-NMR of benzimidazolium salts with respective silver(I)- and palladium(II)-NHC complexes with the observation/variables value of 82.48%.

CONCLUSION

In conclusion, the synthesis of benzimidazolium salt with respective silver(I)- and palladium(II)-NHC complexes and have successfully characterized by FTIR, CHN analyzer, ^{1}H- and ^{13}C-NMR spectroscopies approaches. Moreover, in this study also demonstrates the feasibility of spectroscopy instrumentations and chemometric method of principal component analysis (PCA) for insight correlation among all the compounds. Overall, the output of this research article can contribute to the deep understanding and approaches of inorganic synthesis chemistry towards the multivariate data analysis.

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AUTHOR'S CONTRIBUTION

M. Z. Nazri carried out the formal analysis, conceptualized research idea and methodology, writing original draft. N. S. M. Zaini, N. N. Kamaruddin & R. N. Rameezal carried out formal methodology and analysis. N. F. Musa carried out data validation. M. R. Razali conceptualized the central research idea, validation, supervision, funding acquisition, revisions and approved the article submission. N. Basar validation of the article.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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