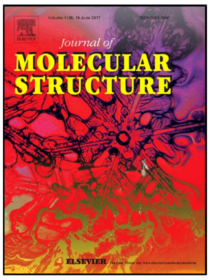

A New Strategy Towards Tridentate *N*-Heterocyclic Carbene Ligands Derived From Benzimidazolium and Mixed-azolium Salt

Tabinda Fatima, Rosenani A. Haque, Mohd. R. Razali

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A New Strategy Towards Tridentate *N*-Heterocyclic Carbene Ligands Derived From Benzimidazolium and Mixed-azolium Salt

Tabinda Fatima, Rosenani A. Haque and Mohd. R. Razali‡
School of Chemical Sciences, Universiti Sains Malaysia, Penang, 11800, Malaysia

‡Corresponding email: mohd.rizal@usm.my

ABSTRACT

The tridentate *N*-heterocyclic carbenes (NHC) ligands derived from tris azolium salts by a new synthetic approach are described. The tris azolium salts have been obtained by reacting the initially synthesized precursor 3-(2-bromoethyl)-1-methylbenzimidazolium bromide (**I**) with benzimidazole/imidazole resulting in the tris azolium salts namely, **1** and **2**. The ligand potential of the salts **1** and **2** was investigated by the formation of NHC-Ag(I) complexes **3** and **4,** using Ag_2O. The most downfield resonances in ^{13}C NMR around 180-190 ppm indicates the successful coordination of carbene with Ag(I).

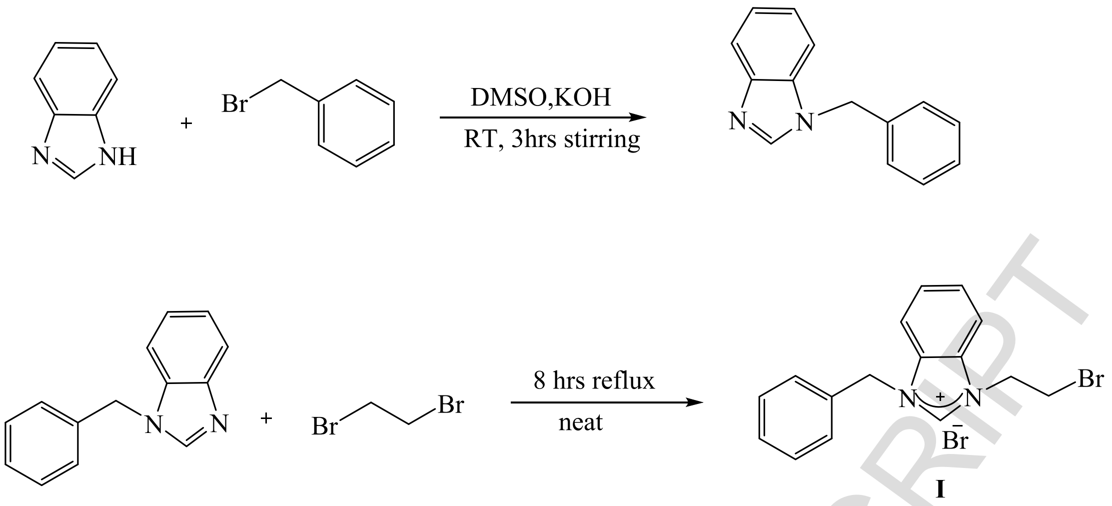
Keywords: Tri-*N*-heterocyclic carbene, Ag(I) complexes, Crystal structure, Azolium.

The *N*-heterocyclic carbenes ever since their discovery **[1]** are the intensively studied ligands in organometallic chemistry owing to their ability to form complexes with virtually all the elements of the periodic table in addition to their easy accessibility and structural diversity **[2]**. Started with the mono NHC complexes with a variety structural motifs, this area has been extended by the introduction of numerous complexes containing poly NHCs ligands that include the bis-, tri-, tetra- and hexa-NHCs **[3]**.

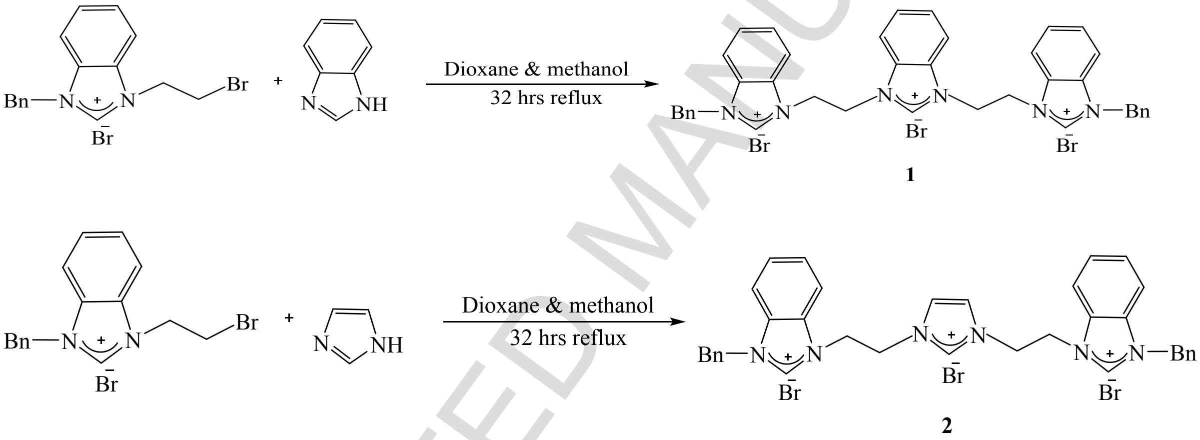
Among the different types of poly *N*-heterocyclic carbene systems featuring metal complexes, the tri-NHC systems are relatively scarce. The first known tri-NHC ligand and respective metal complexes were reported by Hu et al., that was synthesized by a simple synthetic approach involving the quaternization of *N*-methylimidazole with 1,1,1-tris(bromomethyl) ethane **[4]**. Meanwhile, Rit et al., have reported the preparation of tricarbene ligand by the reaction of imidazole with 1,3,5-tribromobenzene followed by the alkylation of the free imine **[5]**. Both strategies in obtaining these tri-NHC ligands involves the uses of a tridentate linker that connects the three imidazolium units in a single step.

In our attempt to obtain tri-NHC compound, the benzimidazole was firstly *N*-substituted and then followed by quaternized with 1,2-dibromoethane that facilitate the formation of 3-(2-bromoethyl)-1-methylbenzimidazolium bromide (**I**) (Scheme 1) **[6].** The synthesis of the key reactant (**I**) was carried out by different strategy which involves the neat reaction of *N*-substituted benzimidazole with 1,2-dibromoethane on a reflux at 80°C for 8 hours. This then resulted the formation of white precipitates that were collected and washed with DCM, somewhat different with reported synthesis procedure that involves this type of reaction however using diethy ether as solvent and several days of stirring at room temperature **[7**,**8]**. Subsequently the salt (**I**) was reacted with unsubstituted benzimidazole in a solvent mixture of 1,4-dioxane and methanol, in which after 32 hrs of reflux the tri-NHC precursor was precipitated out (Scheme 2) **[9]**. The reaction of salt (**I**) with benzimidazole without the uses of any strong base required for deprotonation of 1H proton indicates that this synthetic route is unique compared to the reported single step methods of substitution and addition on the nitrogens (N1 & N3) of imidazole which involve the use of strong bases **[10]**. This direct alkylation has been carried out taking advantage of the reactivity of benzimidazole/imidazole with alkyl halides which under vigorous conditions resulted in the formation of 1,3-dialkylbenzimidazolium halides **[11]**.

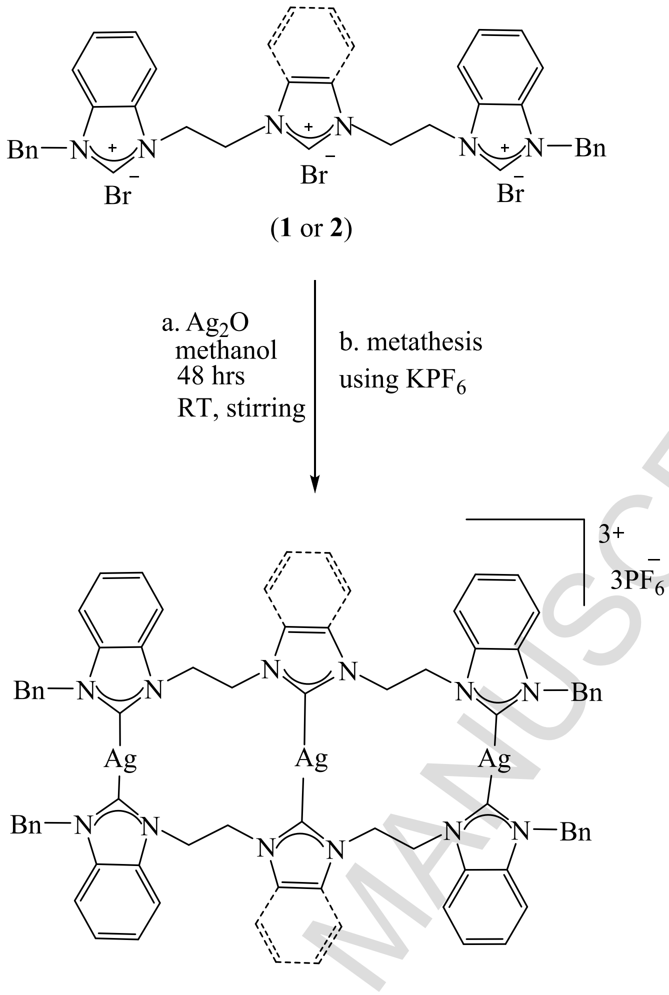
We thereafter extended our approach to synthesize the tri-NHC ligand precursor of mixed azolium salts. This was achieved by the introduction of the benzimidazolium and imidazolium units in one tri-NHC system, by following the aforementioned strategy **[12]** (Scheme 2). To the best of our knowledge such NHC systems are unprecedented and can serve as a new class of NHC ligands. Further the potential of the salts **1** and **2** as ligands was investigated by the formation of respective Ag(I) complexes (Scheme 3) **[13]**. The complexation with Ag(I) was preferred as NHC-Ag(I) complexes are most suitable candidates for transmetallation **[14]** and biological studies **[15]** in addition to catalysis **[16]** for the purpose of future studies.



Scheme 1: Synthesis of 3-(2-bromoethyl)-1-benzylbenzimidazolium bromide salt **I**.



Scheme 2: Synthesis of tris benzimidazolium bromide salts **1** and **2**, respectively.



(**3** or **4**)

Scheme 3: Synthesis of tri NHC-Ag(I) complexes **3** and **4**, respectively.

Spectroscopic investigation at each step of synthesis supported the formation of desired salts along with the confirmation of the designed structures (**I**, **1** and **2**) through single crystal X-ray diffraction data. The *N*, *N'*-substitution and addition of benzimidazole with precursor **I** in a single step without the use of any base was evidenced by the disappearance of the absorption band of medium intensity for N-H vibrations of benzimidazole/ imidazole around 3400 cm^{-1}. This was further supported by the disappearance of the 1-H acidic proton resonance at *ca.* 12.6 ppm. In these tris azolium salts, there are three pre-carbenic centres under two different chemical environments. Hence as expected, two resonance signals appeared in the form of two singlets in the most downfield region at 10.1-10.3 ppm in the salts **1**, which is a characteristic feature for the two types of acidic protons (NC*H*N) of benzimidazolium salts **[17].** For salt **2**, these acidic protons show resonances in the region of

9.3-9.9 ppm **[18]**. All the bridging dimethylene protons in salt **1** appear as singlet at around 5.2 ppm, whereas in salt **2** as the two methylene are similar, thus show two triplets in the region of 4.8-5.1 ppm. The benzylic protons present in the salts **1** and **2** appear as singlets around 5.8 ppm implying the conformational flexibility of these salts in the solution, as in case of rigid molecules, the benzylic protons have been reported to appear as sharp doublets **[19]**.

In the ^{13}C NMR spectra, the pre-carbenic carbons (N*C*HN) exhibit resonances at *ca.* 143 and 144 ppm for salt **1**, while for salt **2** are around 134 and 143 ppm, respectively. The formation of tri-NHC-Ag(I) complexes demonstrated by disappearance of resonance signals for the two sets of acidic protons around 10 ppm which supports the generation of carbene. The resonances for the other protons underwent broadening of signals, somewhat similar to that reported for poly NHC-Ag(I) complexes which indicates that the complexes have a highly flexible structure **[20]**. The signals remain the same even by undertaking low temperature NMR studies. The successful complexation was further supported by the appearance of two sets of doublets attributed to two types of carbenoid centres coordinating with Ag^{107} and Ag^{109} as clearly observed in complex **3 (**Figure 1). For the doublets of doublets set, the carbene-silver coupling could be observed with the coupling constants of 180.6 Hz for C-^{107}Ag and 209.0 Hz for C-^{109}Ag. This splitting pattern is consistent with the literature reports on the carbene-Ag(I) coupling constants **[21]**. The other set of doublets remained unresolved appearing at 188 ppm **[22]**. For complex **4** two unresolved doublets were observed at 188.5 and 190.1 ppm.

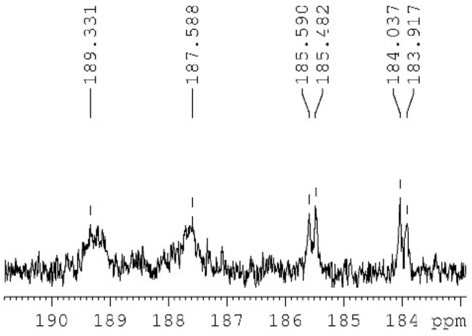


Figure 1: Selected part of ^{13}C NMR spectrum of NHC-Ag(I) complex **3** (*d_3*-acetonitrile) highlighting the appearance of the resonance signal for the two types of carbene-Ag bonds which is an indication of a successful synthesis of the tri NHC-Ag(I) complex.

Single crystal X-ray crystallography studies of the precursor shows that the compound **I** crystallizes in triclinic space group *P*-1 with two anion units (Figure 2), two bromide cations and one water molecule in the asymmetric unit **[23]**. The water molecule behaves as hydrogen bonds donor to two independence bromide ions in the lattice.

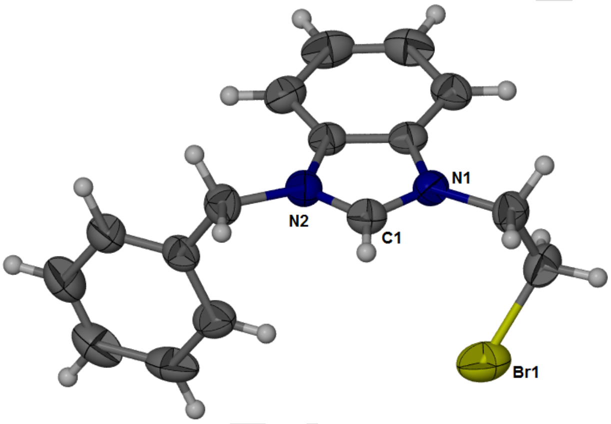


Figure 2: Structure of anion unit in **I** with an ellipsoids shown at 50% probability. Molecules in the lattice omitted for clarity.

Both of the salts **1** and **2** crystallise in monoclinic space group C2/*c* with one and the half of the molecule in the asymmetric unit **[24]**. The presences of the bromide cations in the lattice thus balance the entire charge of the molecule. The crystal of **2** contains as well three water molecules in the lattice. The crystal structure clearly depicts the three azolium units connected *via* dimethylene linker having their planes parallel to each other, while the benzyl rings are projecting perpendicular to the planes of benzimidazolium rings (Figure 3). The nitrogen to the precarbene carbon bond distance of benzimidazolium unit ranges from 1.328(6)-1.333(6) Å, while for imidazole ring it ranges from 1.296(10)-1.314(10) Å. The internal ring angles at the precarbenic centre (N-C-N) of benzimidazole and imidazole are in the range of 109.5°-110.4°, both in salts **1** and **2**. The face-to-face π-π stacking of the aromatic rings being a dominance supramolecular interaction in **1** while hydrogen bonds interactions between water molecule and bromide ions in the lattice being the main supramolecular interactions in stabilizing compound **2**.

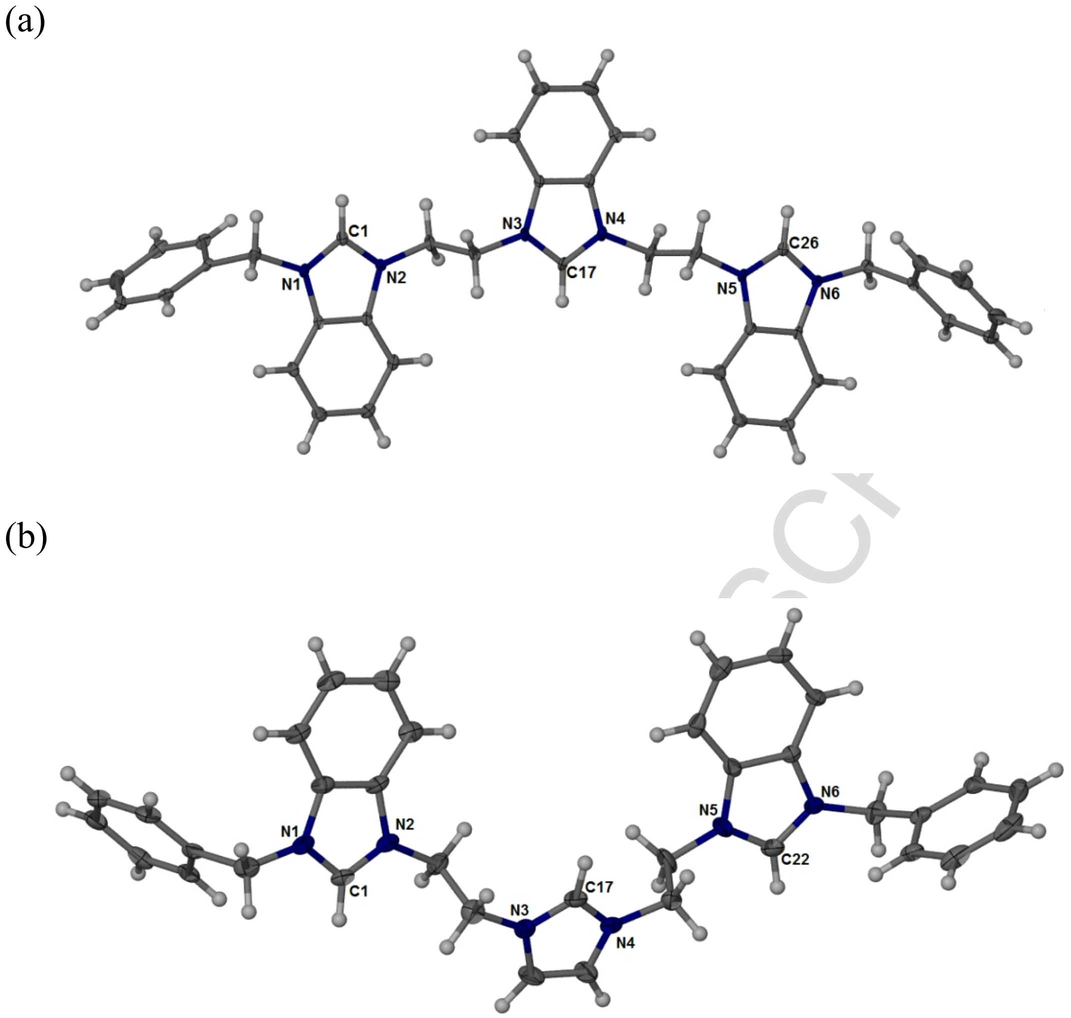


Figure 3: Structure of **1** and **2** with an ellipsoids shown at 50% probability. Molecules in the lattice omitted for clarity.

The structures of tri NHC-Ag(I) complexes **3** and **4** could not be further supported by single crystal X-ray diffraction data as all the efforts to obtain single crystals remain unsuccessful. However, the evidence of successful complexation with Ag(I) by ^{13}C-NMR studies along with elemental analysis supported the formation of tri-NHC trinuclear Ag(I) complexes with the stoichiometry of $[Ag_3L_2]\cdot 3PF_6$ (where L = **1** or **2**) which signifies the formation of the expected complexes.

In conclusion, a new approach for the synthesis of tris azolium salts has been explored that represents a new class of NHC ligands. The transmetallation and anticancer study of such compounds are underway.

Acknowledgments

This work was supported by RUI grant 1001/PKIMIA/811346.

Appendix A. Supplementary material

Spectroscopic data are presented as supporting information and CCDC 1520347-1520349 contains the crystallographic data for **I**, **1** and **2**, respectively. Copy of this material can be obtained from the Director, CCDC, 12 union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk/deposit).

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[6] *3-(2-bromoethyl)-1-benzyl benzimidazolium bromide (**I**):* *N*-benzyl benzimidazole was synthesized according to the literature procedure. The *N*-benzyl benzimidazole (1.00 g, 4.80 mmol) was reacted with 1,2-dibromoethane (4 ml, 46 mmol) in neat. The reaction mixture was refluxed at 80°C for 8 hours. After completion of reaction time the product appeared as white crystalline salt. The excess 1,2-dibromoethane was rotary evaporated, dichloromethane was added to the solid residue and was filtered. The filtrate was left to evaporate in the fume cupboard and after evaporation of solvent the product was collected in crystalline form. Salt **I** was collected as colorless

crystals. Yield: 1.05 g (53%). M.p.: 205-207°C. Anal.Calc.for $C_{16}H_{16}Br_2N_2$: C, 48.48; H, 4.04; N, 7.07. Found: C, 48.24; H, 3.94; N, 6.77. FTIR (KBr) υ (cm^{-1}): 3136, 3025 (C_{arom}-H); 2966, 2884 (C_{aliph}-H), 1610, 1492, 1458 (C_{arom}=C_{arom}), 1561 (C_{arom}-N), 1263 (C_{aliph}-N). ^1H NMR (500 MHz, DMSO-*d*$_6$) δ ppm: 3.85 (2H, $-CH_2-Br$, t, *J* = 5.0 Hz), 4.62 (2H, N-CH_2-, t, *J* = 5.0 Hz), 5.85 (2H, N-CH_2-Ar, s), 7.35-8.13 (9H, Ar-H, m), 10.01 (1H, NCHN, s). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ ppm: 49.6 (CH_2-Br), 49.7 (N-CH_2), 58.5 (Ar-CH_2); 114.1, 126.5, 128.2, 128.9, 130.7, 131.5, 134.0 (Ar-C); 142.8 (NCHN).

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[9] *Benzyl substituted tris benzimidazolium bromide salt (**1**):* The synthesis was carried out by reacting (I) (1.00 g, 2.50 mmol) with benzimidazole (0.15 g, 1.26 mmol) in a solvent mixture of 1,4-dioxane (20ml) and methanol (2 ml). The reaction was carried out on reflux for 32 hours. The tris benzimidazolium bromide salt appeared in the form of white precipitates which was filtered, washed with fresh 1,4-dioxane and dichloromethane and left to dry in the fume cupboard. Salt **1** was collected as white powder. Yield: 0.63 g (60%). M.p.: 263-267°C. Anal.Calc.for $C_{39}H_{37}Br_3N_6$: C, 56.45; H, 4.46; N, 10.13. Found: C, 56.74; H, 4.63; N, 10.41. FTIR (KBr) υ (cm^{-1}): 3124 (C_{arom}-H); 2995 (C_{aliph}-H), 1614, 1485, 1435 (C_{arom}=C_{arom}), 1557 (C_{arom}-N), 1286 (C_{aliph}-N). ^1H NMR (500 MHz, DMSO-*d*$_6$) δ ppm: 5.23 (8H, 2 × $-CH_2-CH_2-$, s), 5.77 (4H, 2 × $-CH_2-$Ar, s), 7.38-7.45 (14H, Ar-H, m), 7.46-7.65 (4H, Ar-H, m), 7.78-8.18 (4H, Ar-H, m), 10.13 (2H, NCHN, s), 10.27 (1H, NCHN, s). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ ppm: 44.8, 45.6, 49.9, 50.1 (CH_2), 111.7, 113.2, 116.2, 125.3, 126.9, 128.2, 130.7, 131.5, 133.6 (Ar-C); 143.0, 144.2 (NCHN).

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[12] Salt **2** was prepared following the same procedure as that for salt **1** except that and benzimidazole was replaced by imidazole (0.12 g, 1.8 mmol). Salt **23** was collected as white powder. Yield: 0.71 g (51%). M.p.: 173-177°C. Anal.Calc.for $C_{35}H_{35}Br_3N_6$: C, 53.93; H, 4.49; N, 10.78. Found: C, 54.28; H, 4.21; N, 10.45. FTIR (KBr) υ (cm^{-1}): 3127 (C_{arom}-H); 2964 (C_{aliph}-H), 1620, 1465 (C_{arom}=C_{arom}), 1557 (C_{arom}-N), 1260 (C_{aliph}-N). ^{1}H NMR (500 MHz, DMSO-*d$_6$*) δ ppm: 5.23 (8H, 2 × -CH_2-CH_2-, s), 5.80 (4H, 2 × -CH_2-Ar, s), 7.38-7.75 (16H, Ar-H, m), 7.97-8.08 (4H, Ar-H, m), 9.37 (1H, NCHN, s), 9.97 (2H, NCHN, s). ^{13}C NMR (125 MHz, DMSO-*d$_6$*) δ ppm: 46.7, 48.2, 50.5 (CH_2), 113.9, 114.5, 123.4, 127.4, 128.8, 131.3 (Ar-C); 134.1, 143.2 (NCHN).

[13] *Tri NHC-Ag(I) complex (3):* Salt **1** (0.27 g, 0.34 mmol) was dissolved in 50 ml of methanol and silver oxide (0.24 g, 1.00 mmol) was added to it. The reaction mixture was stirred at room temperature for 2 days. The reaction was carried out in a round bottom flask wrapped with aluminium foil in order to exclude light. After completion of reaction time the product was separated from the insolubles like AgBr and unreacted Ag_2O by filtering through a column of celite. The resulted silver complex in bromide form was subjected to metathesis using potassium hexafluorophosphate (0.18 g, 1 mmol). The mixture was stirred for 2 hours and the resulting precipitates were filtered, washed with distilled water and left to dry at room temperature. The silver complex **3** was collected as white powder. Yield: 0.37 g (57%). M.p.: 246-250°C. Anal.Calc.for $C_{78}H_{68}Ag_3F_{18}N_{12}P_3$: C, 48.49; H, 3.52; N, 8.70. Found: C, 48.79; H, 3.87; N, 8.57. FTIR (KBr) υ (cm^{-1}): 3110, 3062 (C_{arom}-H), 2949 (C_{aliph}-H), 1607, 1477, 1446 (C_{arom}=C_{arom}), 1267 (C_{aliph}-N). ^{13}C NMR (125 MHz, Acetonitrile-*d$_3$*) δ ppm: 43.6, 46.2, 50.6(CH_2); 111.5, 123.6, 124.3, 126.5, 128.2, 129.1, 132.6, 133.3, 134.8(Ar-C); 183.9 & 185.6 [d, $^1J_{(C\text{-}107Ag)}$ = 180.6 Hz & $^1J_{(C\text{-}109Ag)}$ = 209 Hz), 187.6 (C-Ag, br d), 189.3 (C-Ag, br d).

Tri NHC-Ag(I) complex (4): Complex **4** was prepared following the same procedure as that for complex **3** except that salt **1** was replaced by salt **2** (0.23 g, 0.30 mmol). The silver complex **4** was collected as white powder. Yield: 0.37 g (57%). M.p.: 251-255°C. Anal.Calc.for $C_{70}H_{64}Ag_3F_{18}N_{12}P_3$: C, 45.88; H, 3.49; N, 9.17. Found: C, 45.62; H, 3.58; N, 9.03. FTIR (KBr) υ (cm^{-1}): 3129 (C_{arom}-H), 2948 (C_{aliph}-H), 1615, 1452, 1476 (C_{arom}=C_{arom}), 1240 (C_{aliph}-N). ^{13}C NMR (125 MHz, Acetonitrile-*d$_3$*) δ ppm: 46.4, 50.2, 51.5(CH_2); 112.5, 124.3, 126.2, 128.6, 132.9, 136.3, 138.9(Ar-C); 188.5 & 190.1 (C-Ag, br d).

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[23] *Crystal structure details of* ***I****:* Formula $C_{32}H_{32}N_4Br_2\cdot 2Br\cdot H_2O$. Fw = 810.23, Triclinic, space group *P*-1 , a = 9.1159(7) Å , b = 10.3486(8) Å, c = 18.0330(13) Å, α = 90.499(1)°, β = 97.554(1)°, γ = 98.025(1)°, V = 1669.3(2) $Å^3$, Z = 2, $D_{(calc)}$ = 1.612 g cm^{-3}, $F_{(000)}$ = 804, Crystal size 0.12 x 0.24 x 0.27 , T = 100 K, θ_{min} = 1.1°, θ_{max} = 30.0°, Tot = 67209, Uniq. Data = 9750, $R_{(int)}$ = 0.052, R = 0.0591, wR_2 = 0.1175, S = 1.06.

[24] *Crystal structure details of* ***1****:* Formula $C_{39}H_{37}N_6\cdot 3Br$. Fw = 829.45, Monoclinic, space group *C2/c*, a = 45.472(3) Å, b = 11.4437(7) Å, c = 21.6836(14) Å, α = γ = 90°, β = 99.8532(14)°, V = 11117.0(12) $Å^3$, Z = 12, $D_{(calc)}$ = 1.487 g cm^{-3}, $F_{(000)}$ = 5016, Crystal size 0.14 x 0.14 x 0.34 , T = 100 K, θ_{min} = 1.8°, θ_{max} = 28.0°, Tot = 83757, Uniq. Data = 13427, $R_{(int)}$ = 0.050, R = 0.0637, wR_2 = 0.2011, S = 1.04. The crystal contained significant pores (556 $Å^3$) containing disordered solvent that could not be satisfactorily refined. The data was therefore treated with the SQUEEZE routine of PLATON and accounted for 88 electrons per unit cell. $R1_{(obs)}$ and $wR2_{(obs)}$ before SQUEEZE = 0.1305 and 0.2489 respectively.

Crystal structure details of ***2****:* Formula $C_{35}H_{35}N_6\cdot 3Br\cdot 3H_2O$. Fw = 833.44, Monoclinic, space group *C2/c*, a = 45.5050(17) Å, b = 11.5567(4) Å, c = 22.0400(8) Å, α = γ = 90°, β =113.6650(13)°, V = 1616.6(7) $Å^3$, Z = 12, $D_{(calc)}$ = 1.564 g cm^{-3}, $F_{(000)}$ = 5064, Crystal size 0.09 x 0.17 x 0.26 , T = 100 K, θ_{min} = 1.0°, θ_{max} = 25.5°, Tot = 133318, Uniq. Data = 9890, $R_{(int)}$ = 0.102, R = 0.0634, wR_2 = 0.1868, S = 1.12. Two of the bromide anions in the lattice are disordered over two positions and were refined with half occupancies.