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Self-Assembly of Benzimidazole Derived Tris-NHC Ligands and Ag^I-ions to Hexanuclear Organometallic Cages and Their Unusual Transmetalation Chemistry

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Dedicated to Prof. F. E. Hahn on the occasion of his 65th birthday

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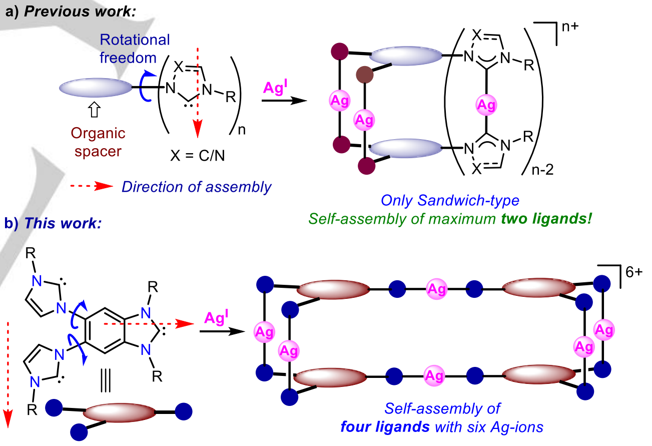
Supporting information (experimental details, characterization data, and DFT calculation details) for this article is given *via* a link at the end of the document

Abstract: Multi ligand self-assembly to attain the Ag^I-NHC built hexanuclear organometallic cages of composition $[Ag_6(\mathbf{3a},\mathbf{b})_4](PF_6)_6$ from the reaction of benzimidazole derived tris(azolium) salts $[H_3$-$\mathbf{3a},\mathbf{b}](PF_6)_3$ with Ag_2O is presented. The molecular structures of the cages are established by X-ray diffraction studies along with NMR and mass spectrometric analyses. The existence of a single assembly in solution is supported by the DOSY ^{1}H NMR spectra. Further, transmetalation reactions of these self-assembled complexes, $[Ag_6(\mathbf{3a},\mathbf{b})_4](PF_6)_6$, with Cu^I/Au^I-ions provide various coinage metal-NHC complexes having diverse molecular compositions which include the first example of a hexanuclear Cu^I-dodecacarbene complex, $[Cu_6(\mathbf{3b})_4](PF_6)_6$.

Over the last few decades, metallo-supramolecular assemblies[1] have gained much interest among the synthetic chemists because of their elegant molecular architectures, intriguing physical/chemical properties, biomedical applications, and rich host-guest chemistry.[2] Metal-controlled self-assembly of appropriate ligands is considered to be the most convenient approach to access these structures.[3] The first report of such assembly from two poly-(bipyridine) ligands and Cu^I ions by Lehn *et al*. in 1987 is recognized as the start of an era of this exciting chemistry.[4] Looking back at the library of such known assemblies, one can easily comprehend that majority of the ligand systems employed to attain such structures feature the Werner-type pyridyl-*N* or carboxylate-*O* donors.[5] Whereas the utilization of ligands featuring carbon donors to construct such structures is rather limited.[6] Nevertheless, *N*-heterocyclic carbenes (NHCs)[7] have slowly started to emerge as a new class of carbon donor ligands in this chemistry after the pioneering works by Hahn *et al*.[8] New ligand systems having diverse topologies can be designed easily which made them a potent alternative to the Werner-type ligands for the generation of metallo-supramolecular assemblies.[8c,9d-e]

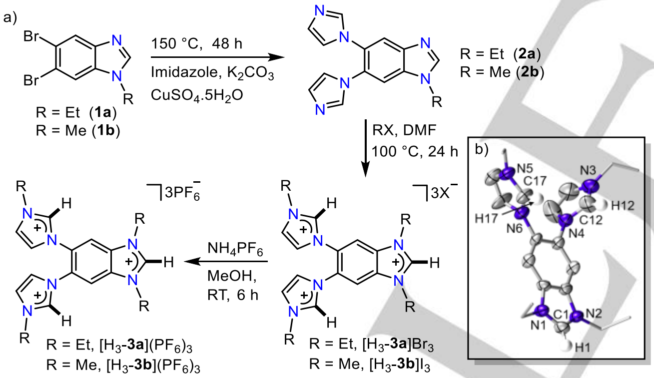
For the construction of the aforementioned NHC-based architectures, coinage metals (Ag^I and Au^I) have predominantly been utilized possibly because of their fixed linear geometry which enables the formation of predicted structures based on the employed ligand topology.[8c,9] Among coinage metals, Ag^I-based structures are, by far, the most investigated ones because of their facile synthesis *via* Ag_2O route[10] and the ability of the Ag^I-C$_{NHC}$ bond to undergo transmetalation with other transition metals.[11] A closer look at the metallo-supramolecular structures, built on exclusive Ag^I-NHC bond formations, readily reveals that they possess common structural motifs of Ag^I-ions sandwiched between two homoleptic polydentate ligands in which all the NHC donors are free to rotate (Scheme 1a).[8c,12] This restricts, by disfavouring the multidirectional self-assembly, the diversity of the molecular architectures which could be obtained by this strategy and thus limited only to the compositions $[Ag_n\mathbf{L}_2]^{n+}$ (n = 2-8, depending on the number of NHC donors in the ligand **L**).[8c,12,13] Moreover, the essentially linear geometry around the Ag^I-ions (C_{NHC}-Ag^I-C_{NHC} ≈ 180°) insists the need of diversity in the ligand topologies for the generation of diversified 3D structures.



Scheme 1. Overview of (a) the previous work on Ag^I-NHC based assemblies and (b) this work.

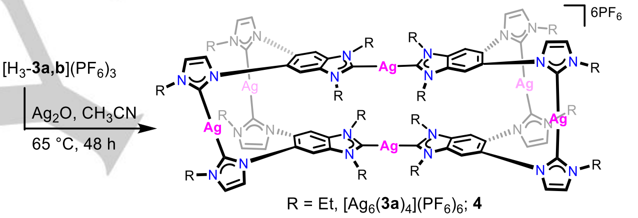
Ligands featuring mixed NHC donors with confined rotational flexibility could be one of the possible ligand types which might lead to captivating architectures *via* self-assembly of more than two NHC ligands (commonly not observed) in combination with the Ag^I-ions. However, to the extent of our knowledge, polynuclear Ag^I-NHC complexes of such ligand systems are not known till date, which motivated us to design new types of poly-NHC ligands possessing NHC donors with confined rotational freedom. Herein, we report the synthesis of Ag^I-NHC built cages of composition $[Ag_6\mathbf{L}_4]^{6+}$ *via* self-assembly of specifically designed tris-NHC ligands featuring two types of NHC donors which can lead the self-assembly in nearly two vertical directions (Scheme 1b). These hexanuclear complexes represent the unique examples of discrete polynuclear self-assemblies, obtained *via* rational design, which feature more than two poly-NHC ligands that are connected by means of exclusive Ag^I-NHC bonds. Further, transmetalation reactions of these Ag^I-NHC complexes, $[Ag_6\mathbf{L}_4]^{6+}$, with Cu^I/Au^I-ions deliver various coinage metal-NHC complexes having diverse compositions including the first example of a hexanuclear Cu^I-dodecacarbene complex.

The mixed tris(azolium) salts $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$, precursors for NHC ligands, were synthesized following the multistep procedure as shown in Scheme 2a. In the first step, the imidazole moieties were installed on the benzimidazole core *via* standard Ullmann coupling protocol[8b,14] by reacting the dibromo compounds **1a**,**b** with imidazole. Subsequent reactions with excess alkyl halides result in alkylations of the imine moieties in **2a** and **2b** to yield the tris(azolium) salts $[H_3\text{-}\mathbf{3a}]Br_3$ and $[H_3\text{-}\mathbf{3b}]I_3$, respectively. Exchange of the halide counterions in these salts with non-coordinating PF_6 anions *via* salt metathesis using NH_4PF_6 provides the $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$ as off-white solids in 84-86% yield. Poly(azolium) salt ($[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$) formations were confirmed by the NMR and ESI-mass spectral analysis. In the ^1H NMR spectra, the characteristic azolium N-CH-N proton resonances were detected at δ = 10.14 and 9.58 ppm for $[H_3\text{-}\mathbf{3a}](PF_6)_3$ and at δ = 10.01 and 9.48 ppm for $[H_3\text{-}\mathbf{3b}](PF_6)_3$. Appearance of a single resonance for both the imidazolium N-CH-N protons indicates the free rotation of the imidazolium units in solution which is imperative to attain self-assembled discrete structures rather than the polymeric structures. Further, the $^{13}C\{^1H\}$ NMR spectra display resonances for the N-CH-N azolium carbon atoms in the usual range of δ = 148.7-138.2 ppm.[15] Presence of the PF_6 ions were confirmed by ^{31}P and ^{19}F NMR analysis. Single-crystal X-ray analysis of $[H_3\text{-}\mathbf{3a}](PF_6)_3$ (Scheme 2) finally established the structures of the $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$ salts.



Scheme 2. (a) Synthesis of the benzimidazole-derived precursors for the NHC ligands **3a**,**b**. (b) Molecular structure of the trication $[H_3\text{-}\mathbf{3a}]^{3+}$ in $[H_3\text{-}\mathbf{3a}](PF_6)_3$. Hydrogen atoms except N-CH-N and counterions are omitted for clarity. The *N*-ethyl groups are shown in capped stick.

Poly-NHC ligand systems are reported to generate supramolecular architectures with coinage metals.8c,9d,11a However, in most of the known poly-NHC based Ag^I-complexes, Ag^I-ions are generally found to be sandwiched between the two homoleptic polydentate ligands.[8c,16] Polynuclear Ag^I-NHC complexes other than the typical sandwich-type where each Ag^I-ion is coordinated by only NHC donors are extremely rare. To the extent of our knowledge, only Han *et al.* have recently reported such structures *via* serendipitous alterations of the *N*-alkyl groups of a 1,2,4-triazolinylidene based poly-NHC ligand.[17] However, our present ligand system is designed in such a way that it has the potential to deliver self-assembled architectures *via* association of more than two poly-NHC ligands and Ag^I-ions. Therefore, to access new types of Ag^I-NHC based architectures, we attempted the metalation of $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$ with Ag_2O (acts as both base and metal source). Treatment of the salts $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$ with 1.5 equiv. of Ag_2O in acetonitrile generated the hexanuclear Ag^I-dodecacarbene complexes having the composition of $[Ag_6(\mathbf{3a},\mathbf{b})_4](PF_6)_6$ *via* self-assembly of four NHC ligands **3a**,**b** with six Ag^I-ions in 81-83% yields (Scheme 3). These complexes were characterized by NMR, mass, and single crystal X-ray diffraction studies. Complete absence of the azolium N-CH-N protons (δ = 9.48-10.15 ppm) of the parent salts $[H_3\text{-}\mathbf{3a},\mathbf{b}](PF_6)_3$ in the ^1H NMR spectra of the complexes $[Ag_6(\mathbf{3a},\mathbf{b})_4](PF_6)_6$ supports the formation of carbene centers. The attachment of these generated NHCs to silver ions was established by the $^{13}C\{^1H\}$ NMR spectra which exhibit the very characteristic C_{NHC}-Ag $^{13}C\{^1H\}$-NMR signals in the region of δ = 180.5-183.6 and 192.3-195.2 ppm. Notably, these $^{13}C\{^1H\}$-NMR resonances exhibit the rarely detected coupling of the NHC carbons with both the silver isotopes ($^1J(C\text{-}^{107}Ag) \approx$ 181-184 Hz and $^1J(C\text{-}^{109}Ag) \approx$ 209-213 Hz; Figure S22 and S24) and this implies that the dynamic equilibria, usually observed for the Ag^I-NHC complexes in solution, are slow in the present complexes.[8b,10b,11b] Furthermore, the presence of only three aromatic resonances with the integration ratio of 2:2:2 in the ^1H NMR spectra of the complexes (Figure S21 and S23) signifies the symmetric nature of the complexes.



R = Et, $[Ag_6(\mathbf{3a})_4](PF_6)_6$; **4**
R = Me, $[Ag_6(\mathbf{3b})_4](PF_6)_6$; **5**

Scheme 3. Synthesis of the self-assembled hexanuclear Ag^I-NHC complexes from the $[H_3\text{-}(\mathbf{3a},\mathbf{b})](PF_6)_3$ ligand precursors.

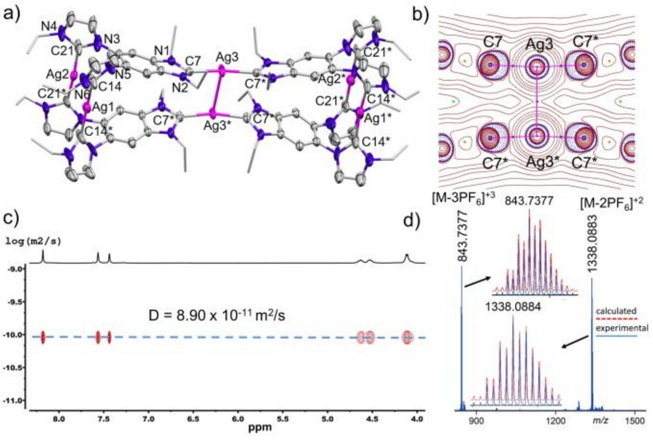


Figure 1. (a) Molecular structure of $[Ag_6(\mathbf{3a})_4]^{6+}$ cation in **4**. The hydrogen atoms are removed and the *N*-Et groups are shown in capped stick. (b) Contour line diagrams of the $\nabla^2\rho(r)$. Solid pink lines connecting the atomic nuclei represent the bond paths. Blue dots indicate the bond critical points (BCPs). (c) The ^1H DOSY NMR in CD_3CN and (d) ESI-mass spectrum of **4**.

Initial evidence for the generation of a discrete self-assembled species of composition $[Ag_6(\mathbf{3a})_4](PF_6)_6$ *via* association of four ligands and six Ag^I-ions was received from the ESI-MS analysis showing the most intense peaks at *m/z* = 1338.0883 (calcd. for $[M\text{-}2PF_6]^{2+}$ 1338.0884) and 843.7377 (calcd. for $[M\text{-}3PF_6]^{3+}$ 843.7377) with the proper

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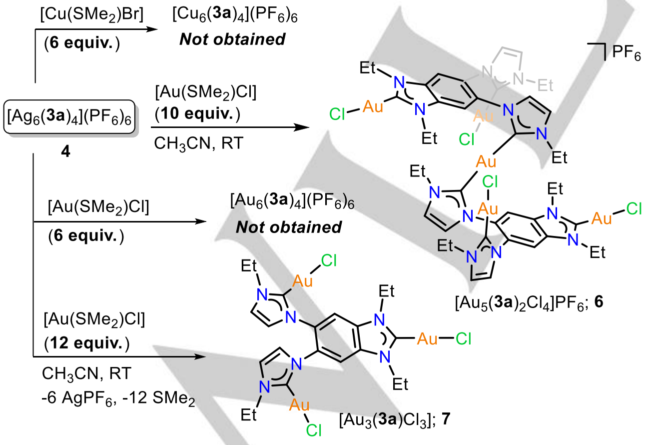
isotopic distributions (Figure 1d). Furthermore, the diffusion-ordered NMR spectroscopy (DOSY) ensures the existence of a single assembly in solution having diffusion coefficient of 8.90 x 10^{-11} m^2/s (Figure 1c). The ^1H DOSY NMR and ESI-MS data of the complex $[Ag_6(\mathbf{3b})_4](PF_6)_6$ display similar characteristics (Figure S31 and S37).

Unequivocal evidence for the formation of a hexanuclear Ag^I-dodecacarbene complex **4** was provided by single crystal X-ray diffraction analysis (Figure 1a) which shows that the structure is symmetrical in nature as indicated by the NMR analysis and each Ag^I-ion is connected to either two imidazolinylidene or benzimidazolinylidene donors. The Ag-C_{NHC} bond lengths [in the range of 2.101(16)-2.099(15) Å] fall in the range previously observed for the Ag^I-poly(NHC) complexes.[8c,11a] Notably, the observed Ag-Ag distances ($d_{Ag3\text{-}Ag3^*}$ = 3.19 Å and $d_{Ag2\text{-}Ag1}$ = 3.23 Å) indicate the existence of strong argentophilic interactions[18a-c] which have led to the significant deviation of geometry around the Ag-ions from linearity ($\angle C_{NHC}\text{-}Ag\text{-}C_{NHC}$ = 165.20-171.15°). The existence of these Ag-Ag interactions in **4** was assessed by using NBO analysis. The WBI values suggest that the interaction between the Ag3-Ag3* (WBI = 0.148) is relatively stronger than that of the Ag1-Ag2 (WBI = 0.121; Table S2), which is consistent with the crystal structure analysis as mentioned above. On contrary, the WBI between the imidazolinylidene coordinated Ag1-Ag1* ions (WBI = 0.135) in **5** was calculated to be higher than the benzimidazolinylidene coordinated Ag2-Ag2* ions (WBI = 0.113; Table S2). This is also in line with the single crystal X-ray analysis of **5** ($d_{Ag1\text{-}Ag1^*}$ = 3.14 Å and $d_{Ag2\text{-}Ag2^*}$ = 3.33 Å; Figure S34). This variation in argentophilic interactions[18d] between the complex **4** and **5** is possibly due to the subtle difference in the steric requirement of the *N*-Et and -Me moieties. Further, the topological analyses of complexes **4** (Figure 1b) and **5** (Figure S41) reveal the bond paths between the Ag^I-Ag^I ions establishing the presence of reasonably strong argentophilic interactions. Additionally, bonding analysis at the DFT level provided the optimized geometries along with the metric parameters which agree well with the experimental values (see supporting information).



Scheme 4. Synthesis of various Au^I-NHC complexes *via* transmetalation from $[Ag_6(\mathbf{3a})_4](PF_6)_6$.

Silver-NHC complexes are established to be excellent carbene transfer agents to access other metal NHC complexes.[10a,11a,19] Therefore, we initially attempted to substitute all the six Ag^I-ions in $[Ag_6(\mathbf{3a})_4](PF_6)_6$ by Cu^I to yield an analogous complex maintaining the overall structure as the Cu^I-poly(NHC) complexes having nuclearity higher than three which feature exclusive Cu^I-NHC bonds are not known.[8c,9d] In this line, complex **4** was reacted with 6 equiv. of $[Cu(SMe_2)Br]$, source for Cu^I-ion (Scheme 4). However, our efforts to isolate related hexanuclear Cu^I-NHC complex were unsuccessful. The reaction always yielded an inseparable reaction mixture; it was difficult to monitor the reaction outcome by ^1H NMR due to its complex nature and the ESI-MS analysis was found to be incompetent because of the sensitive nature of the Cu^I-NHC complex. Therefore, we shifted our attention towards the corresponding Au^I-complex and accordingly, complex **4** was treated with 6 equiv. of $[Au(SMe_2)Cl]$ (Scheme 4). Here also, we failed to obtain the related hexanuclear Au^I-NHC complex. ESI-MS analysis of the reaction mixture revealed the presence of a mixture of products having ambiguous compositions from which we could not isolate a single compound in pure form. This is in line with the transmetalation chemistry of $[Ag_6(\mathbf{3a})_4](PF_6)_6$ as observed with Cu^I-ion. Reasoning that Au^I-NHC complexes of nuclearity other than six might also be forming, the equiv. of $[Au(SMe_2)Cl]$ used for the reaction was increased periodically and the product formation was monitored *via* ESI-Mass analysis as it was found to be the best way for this system. Finally, when **4** was reacted with 10 equiv. of $[Au(SMe_2)Cl]$, ESI-mass spectrum displayed the most intense peaks at *m/z* = 1851.1502 and 908.0906 (Figure S38) which provided the preliminary indication that a pentanuclear Au^I-NHC complex of composition $[Au_5(\mathbf{3a})_2Cl_4]PF_6$ is forming (Scheme 4). The exact molecular structure of $[Au_5(\mathbf{3a})_2Cl_4]PF_6$ was established by X-ray analysis which uncovered an unusual structure featuring two different types of NHC coordination around the Au^I-ions (NHC-Au-NHC and NHC-Au-Cl; Figure 2a) which has not been observed before in a single molecule, to the best of our knowledge. The crystal structure also reveals the presence of aurophilic interaction ($d_{Au\text{-}Au}$ = 3.34 Å)[11a,20] which results in a collinear arrangement of all the three Au^I-ions coordinated by the imidazolinylidene donors ($\angle$Au1-Au2-Au1* = 180.0°). These aurophilic (Au^I-Au^I) interactions are also supported by the DFT calculations; the topological analyses clearly display the bond paths between the Au^I-Au^I ions validating the existence of such interactions (Figure S42).

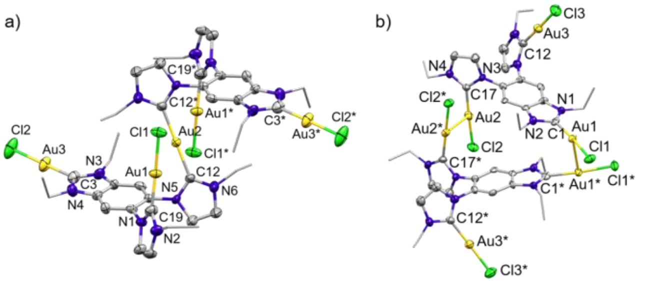
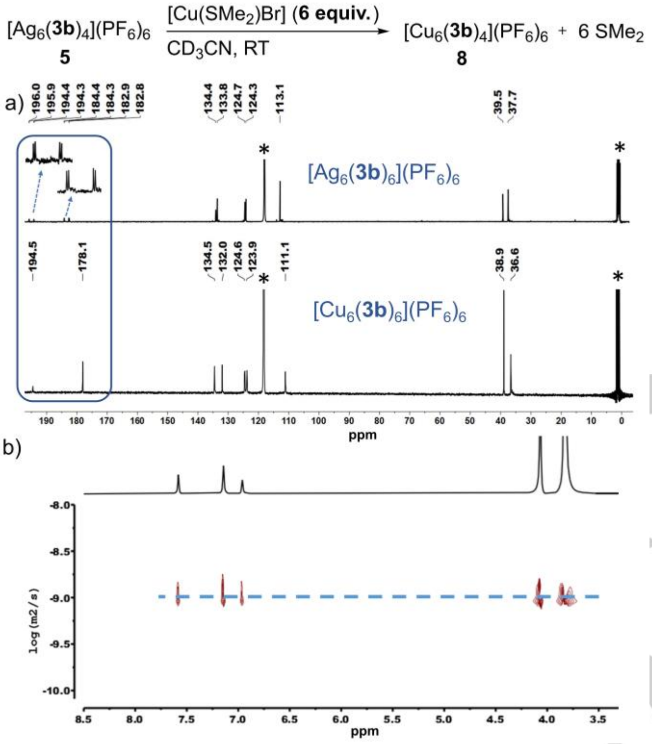


Figure 2. Crystal structures of $[Au_5(\mathbf{3a})_2Cl_4]^+$ cation in **6** (a) and **7** (b). Hydrogen atoms are removed and the *N*-Et groups are shown in capped stick.

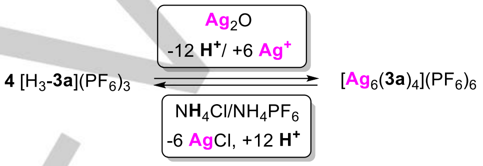
Motivated from the above results, $[Ag_6(\mathbf{3a})_4](PF_6)_6$ was eventually treated with 12 equiv. of $[Au(SMe_2)Cl]$ (one equiv. per NHC donor). To our surprise, we found that the hexanuclear structure of $[Ag_6(\mathbf{3a})_4](PF_6)_6$ was completely disintegrated and provided a trinuclear complex of composition $[Au_3(\mathbf{3a})Cl_3]$, **7** in 80% yield *via* elimination of 6 equiv. $AgPF_6$ and SMe_2 (Scheme 4). Formation of **7** was substantiated by NMR spectroscopy, ESI-Mass spectrometry, and X-ray crystallography. ^1H NMR spectrum exhibits only three resonances for the aromatic protons with the intensity ratio of 2:2:2 suggesting a symmetrical structure in solution (Figure S25) and constitution of the Au^I-NHC fragment is revealed by the $^{13}C\{^1H\}$ NMR spectrum [$\delta(C_{NHC}\text{-}Au)$ = 180.9 ppm and 183.0 ppm; Figure S26]. Further, formation of a trinuclear [Au_3(**3a**)Cl_3] complex was supported by the ESI-MS showing the highest intensity signals at *m*/*z* = 1023.0575 and 514.5578 which are readily assignable to $[M\text{-}Cl]^+$ (calcd. = 1023.0598) and $[M\text{-}2Cl+CH_3CN]^{2+}$ (calcd. = 514.5590) molecular fragments, respectively. Finally, the molecular structure was confirmed by the single crystal X-ray analysis of the complex (Figure 2b) and the complex **7** was observed to be present as a dimer in the solid-state *via* strong unsupported closed-shell $d^{10}\cdots d^{10}$ aurophilic interaction ($d_{Au\text{-}Au}$ = 2.993 and 3.234 Å; Figure S35b).[20] The Au-C_{NHC} and Au-Cl bond lengths fall within the limits observed for **6** and related Au^I-NHC complexes.[20c,21]



Scheme 5. Cu^I-NHC complex synthesis *via* transmetalation of **5**. (a) Comparison of the $^{13}C\{^1H\}$ NMR spectra of **5** (Ag-complex) and **8** (Cu-complex) in CD_3CN (*). (b) The ^1H DOSY NMR spectrum of **8** in CD_3CN.

Next, we focused on the transmetalation of the methyl variant [Ag_6(**3b**)$_4$]$(PF_6)_6$ (**5**) to learn if the wingtip group has any impact.[22] Accordingly, **5** was treated with 6 equiv. of [Cu(SMe_2)Br] (Scheme 5) at ambient temperature. To our delight, the ^1H-NMR spectrum (Figure S27) revealed the formation of a single complex and displayed similar resonances, however, slightly upfield shifted, to those of the parent Ag^I–NHC complex **5**, which probably suggests the retention of a hexanuclear structure. Further, the formation of a Cu^I-NHC complex is clearly established from the $^{13}C\{^1H\}$ NMR spectrum (Scheme 5a) of the complex showing the characteristic singlet C_{NHC} resonances at δ = 194.6 and 178.1 ppm and the released SMe_2 (2.08 ppm, ^1H NMR and 18.1 ppm, $^{13}C\{^1H\}$ NMR). Unfortunately, we could not obtain suitable single crystals for the X-ray analysis. However, the ^1H DOSY NMR spectrum of the complex **8** reveals a single diffusion coefficient value (D = 8.72 x 10^{-10} m^2/s) for all the proton signals which implies that they all belong to a single assembly (Scheme 5b) and this value is marginally higher than the corresponding Ag^I-complex **5** (D = 8.10 x 10^{-10} m^2/s; Figure S31) in line with the lower atomic weight of Cu.23 This suggests that the produced Cu^I-NHC complex **8** is also hexanuclear and having the composition of [Cu_6(**3b**)$_4$]$(PF_6)_6$ as of its parent Ag^I-NHC complex **5** which is also supported by the DFT optimization studies (Figure S43).[24] Further, it is to be noted that we could not obtain the related [Cu_6(**3a**)$_4$]$(PF_6)_6$ complex featuring the *N*-ethyl substituents as mentioned before and this could possibly be attributed to the subtle difference in the steric requirements of the ethyl and methyl groups. It is important to mention that the complex [Cu_6(**3b**)$_4$]$(PF_6)_6$ represents the first example of a hexanuclear Cu^I-dodecacarbene complex.

Interestingly, construction of the hexanuclear Ag^I-NHC cage [Ag_6(**3a**)$_4$]$(PF_6)_6$ was observed to be reversible under certain conditions (Scheme 6). The addition of NH_4Cl to [Ag_6(**3a**)$_4$]$(PF_6)_6$ completely disintegrates the assembly *via* breakage of the Ag-NHC bonds to provide the corresponding azolium salt with chloride counterion and AgCl. Anion exchange with NH_4PF_6 cleanly yields the parent azolium salt [H_3-**3a**]$(PF_6)_3$ (Figure S44).



Scheme 6. Reversible transformation of the [Ag_6(**3a**)$_4$]$(PF_6)_6$ cage.

In conclusion, we have developed a straightforward approach to access unique hexanuclear Ag^I-NHC derived organometallic cages [Ag_6(**3a**,**b**)$_4$]$(PF_6)_6$ from the tris-NHC ligands and Ag^I-ions *via* self-assembly. These complexes represent the rare examples of Ag^I-NHC based discrete self-assemblies featuring multiple NHC ligands which are obtained *via* rational design of the poly-NHC ligands. Further, the *N*-wingtip groups have been observed to influence the transmetalation reactions of these Ag^I-NHC complexes and thus, various types of homopolynuclear Cu^I/Au^I-NHC complexes including an unprecedented hexanuclear Cu^I-dodecacarbene complex were obtained *via* substitution of the Ag^I by Cu^I/Au^I-ions. Additionally, formation of the hexanuclear Ag^I-NHC cages was found to be reversible under chemical stimulus. Further studies towards the various applications of these Ag^I-NHC cages are underway in our laboratory.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

Keywords: *N*-Heterocyclic carbenes • self-assembly • DFT studies • supramolecular chemistry • transmetalation

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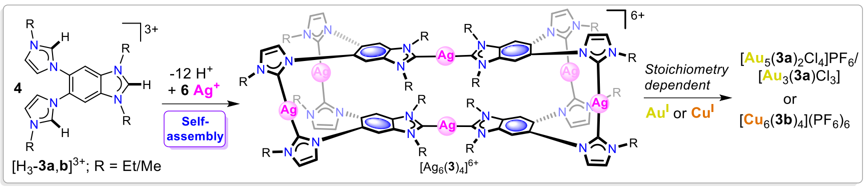

Reactions of the benzimidazole derived tris(azolium) salts [H$_3$-**3a**,**b**](PF$_6$)$_3$ with Ag$_2$O under self-assembly provide access to Ag^I-NHC based unique hexanuclear organometallic cages of composition [Ag$_6$(**3a**,**b**)$_4$](PF$_6$)$_6$ which undergo transmetalation reactions with Cu^I/Au^I-ions to produce various coinage metal-NHC complexes of diverse compositions depending on the *N*-wingtip group of the ligands **3a**,**b**.