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Introduction

The first Ag(I)-NHC complex was prepared by deprotonation of the imidazolium salt and reaction with a Ag(I) source.¹ The disclosure of the Ag₂O synthetic methodology by Lin and Wang led to numerous reports of Ag(1)-NHC complexes.²⁻⁴ Ag(1)-NHC complexes are mostly unreactive with air and water which simplifies their synthesis, isolation, and characterization. This persistence in the presence of air and water permits unique applications in the biomedical field.⁴ Ag(I)-NHC complexes of a caffeine derivative were recently shown to be effective against a variety of respiratory pathogens.⁵ A recent report illustrated the use of Ag(1)-NHC complexes against fungi, gram-positive and gram-negative bacteria.⁶ Anticancer activity of Ag(1)-NHC complexes against ovarian (OVCAR-3) and breast (MB157) cancers has also been reported.⁷ They were also reported to be precursors to Ag nanoparticles, which have been shown to inhibit HIV-1 replication.8 In addition to their biomedical applications, Ag(1)-NHC complexes have shown promise in the

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Toward molecular rotors: tetra-*N*-heterocyclic carbene Ag(ı)-halide cubane-type clusters†

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1,3-Bis(3'-butylimidazol-1'-yl)benzene diiodide (**2a**), 1,3-bis(3'-but-3''-enyl-imidazolium-3'-yl)benzene diiodide (**2b**), 1,3-bis(3'-pent-4''-enyl-imidazolium-3'-yl)benzene diiodide (**2c**), 1,3-bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene diiodide (**2d**), or 1,3-bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene dibromide (**2e**) was reacted with Ag₂O yielding unprecedented tetra-*N*-heterocyclic carbene-Ag(*i*)-X cubane-type clusters. These were characterized by ¹H and ¹³C NMR spectroscopy, ESI-TOF MS, elemental analysis, and X-ray crystallography. Results from VT ¹³C NMR spectroscopy and cross-over experiments are consistent with intramolecular exchange suggesting that the Ag(*i*) complexes are molecular rotors.

synthesis of liquid crystals,⁹ and as catalytic reagents for the preparation of 1,2-bis(borate) esters¹⁰ and for the ring-opening polymerization (ROP) of L-lactides.¹¹ Furthermore, they have been proven useful in transmetallation to many late transition metals such as Cu,^{12,13} Ni,¹⁴ Pd,¹⁵ Pt,¹⁶ Au,¹⁷ and Rh.¹²

The same properties that gave Ag(i)–NHC complexes unique applications in the biomedical field, catalysis and transmetallation made them good candidates for incorporation into supramolecular architectures.¹⁸ However, Ag(i)–NHC complexes have received little attention in this field.^{18,19} Only a few Ag(i) complexes are known to form supramolecular architectures, demonstrating coordination polymers in the solid state.^{18,20,21} Additionally, while organic and inorganic examples of molecular rotors are known, to our knowledge no molecular rotors with NHC ligands have been reported.²² We report the synthesis and characterization of the first series of tetra-NHC-Ag(i)-X cubane clusters, which contain a distorted cubical core in the solid state. VT ¹³C NMR and cross-over experiments are consistent with intramolecular Ag–C exchange.

Results and discussion

Synthesis and characterization

1,3-Bis(imidazol-1'-yl)benzene $(1a)^{23}$ and 1,3-bis(1',2',4'-triazol-1'-yl)benzene (1b) were synthesized in good yields using copper-catalyzed coupling of the desired heterocycle and 1,3dibromobenzene. The isolation procedure was improved with filtration through basic alumina, which eliminated the need for silica-gel chromatography. Compounds 1a and 1b were treated with haloalkanes to produce various salts (2a-2e) in good to excellent yields. The salts were reacted with Ag₂O

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[†]Electronic supplementary information (ESI) available: CIF files, tables, VT ¹³C NMR spectra, NMR spectra, ESI-TOF MS data, and figures giving crystallographic data for complexes **3a–3e**. CCDC 912930 (**3e**), 912931 (**3d**), 921155 (**3b**), 912933 (**3c**) and 868624 (**3a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt32862g



yielding free-flowing, white powders (**3a–3e**, Scheme 1) in good to excellent yields. The loss of the imidazolium proton signals at δ 11–12 in the ¹H NMR spectra, and the appearance of NHC signals at δ 180–188 in the ¹³C NMR spectra were consistent with the formation of Ag(i)–NHC complexes.

The ESI-TOF MS of the white powders provided more evidence that a Ag(i)–NHC complex had been formed. The $[M + H]^+$ ion for compound **2a** was observed within 7 ppm of the calculated value. Many fragments of complexes **3a–3e** were observed, all of which had excellent correlation between the experimental values and the predicted values. This confirmed the presence of the Ag(i)–NHC complexes **3a–3e** in solution.

Supramolecular building blocks

Although the $[M + H]^+$ peak for complex 3a was observed in ESI-TOF MS it represents only a small fraction of the ions observed. Other complexes observed in ESI-TOF MS of complex 3a are shown in Scheme 2. The $[M - I]^+$ fragment for all complexes was observed with excellent correlation between the calculated and observed isotopic distributions. The complexes observed included the monomeric complex 4, biscarbene complex 5, and the supramolecular complex 6. Complex 4 was observed *via* two fragments: $[4 - I]^+$ and $[4 - AgI + H]^+$. Complex 5 is of the "bis-carbene salt" type and these types of fragments are found in the MS of most Ag(I)-NHC complexes.²⁰

Three fragments of complex 5 were observed: $[5 + H]^+$, $[5 - I]^+$, and $[5 - 2I]^{2+}$. Five fragments of complex 6 were observed by losses of AgI and I. This phenomenon is not limited to complex 3a. Complexes 3b-3d also exhibit this occurrence. This data confirms that complexes 3a-3d are precursors to supramolecular building blocks. Supramolecular complexes, like complex 6, were not observed for AgBr complex 3e. Expansions of each individual fragment along with its calculated spectra are given in the ESI.[†]



Scheme 2 Ions observed in HR ESI-MS.

X-ray crystallography

Crystals suitable for X-ray diffraction were grown for complexes **3a–3e**. ORTEP illustrations of the X-ray structures of complexes **3a–3e** are illustrated in Fig. 1–5. An alternative perspective on the "Ag-X-cubane structure" is as a tetra-capped Ag-tetrahedron. The ORTEP illustrations in Fig. 1–5 are drawn in this manner for clarity. The Ag–C_{carbene} bond distances vary slightly (≤ 0.040 Å). The Ag–I bond lengths are similar to other Ag–I cubanes.²⁴ The Ag–Ag distances vary significantly. Ag–Ag distances shorter than the sum of the van der Waals radii (3.44 Å) are considered evidence for "argentophilic" interactions.²⁵ Complexes **3a**, **3d**, and **3e** may have argentophilic interactions between Ag1–Ag2 and Ag3–Ag4 as their distances are short enough for Ag–Ag interactions to occur (Table 1).²⁵ Complex



Fig. 1 ORTEP diagram of imidazolyl-Agl complex **3a** with hydrogens omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths are given in Table 1. Selected bond angles (°): Ag1–I1–Ag2 61.047(5), Ag1–I2–Ag2 63.318(5), Ag1–I1–Ag3 81.227(5), Ag1–I2–Ag4 71.522(6), I1–Ag2–I2 118.866(7).



Fig. 2 ORTEP diagram of imidazolyl-AgI complex **3b** with hydrogens omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths are given in Table 1. Selected bond angles (°): Ag1–I1–Ag2 62.769(13), Ag1–I2–Ag2 58.653(12), I1–Ag2–I2 121.188(15).



Fig. 3 ORTEP diagram of imidazolyl-Agl complex **3c** with hydrogens omitted for clarity. Both occupations of the pentenyl chain are shown. Thermal ellipsoids are shown at 50% probability. Selected bond lengths are given in Table 1. Selected bond angles (°): Ag1ⁱ–I1–Ag2 79.61(3), Ag1ⁱ–I1–Ag1 79.53(3), I1–Ag2–I2ⁱ 93.31(3).



Fig. 4 ORTEP diagram of triazolyl-Agl complex **3d** with hydrogens omitted for clarity. Thermal ellipsoids are shown at 25% probability. Selected bond lengths are given in Table 1. Selected bond angles (°): Ag1–I1–Ag2 63.45(2), Ag1–I2–Ag2 61.86(2), I1–Ag2–I2 118.95(3).



Fig. 5 ORTEP diagram of triazolyl-AgBr complex **3e** with hydrogens omitted for clarity. Thermal ellipsoids are shown at 20% probability. Selected bond lengths are given in Table 1. Selected bond angles (°): Ag1–Br1–Ag2 65.86(4), Ag1–Br2–Ag2 65.86(4), Ag1–Br1–Ag3 83.35(4), Ag1–Br2–Ag4 87.64(4), Br1–Ag2–Br2 108.33(4).

3b and **3c** may also have argentophilic interactions between Ag1–Ag2 and Ag1ⁱ–Ag2ⁱ. The Ag–I–Ag bond angles are acute whereas the I–Ag–I angles are obtuse, which is in agreement with other Ag–I cubanes.²⁴

¹³C NMR studies

Ag has two spin 1/2 NMR active isotopes of roughly equal proportions (107 Ag 51.8% and 109 Ag 49.2%). Consequently, the predicted 13 C_{carbene} resonance would be two doublets as was recently reported at low temperatures.²⁶ However, like many other Ag(ı)–NHC complexes, the 13 C_{carbene} peaks were singlets for complexes **3a–3e**.²⁰ This phenomenon in the past has been attributed to the rapid metal exchange at the Ag(ı)–NHC bond.²

Since the possibility of intermolecular and intramolecular ¹³C-^{107/109}Ag exchange for complexes **3a-3e** exists, several experiments were performed to examine the 13C-107/109Ag exchange. The concentration dependence of the ¹³C_{carbene} signal for imidazolyl complex 3a was found to be negligible in DMSO-d₆. In an attempt to generate the mixed triazolyl/imidazolyl cluster in a statistical fashion, the Ag metallation was carried out with an equimolar mixture of 2a and 2d (see Experimental section). The spectral data were consistent with the formation of the homoleptic complexes only. No signals assignable to the mixed triazolyl/imidazolyl complex were observed. Additionally crossover experiments were used to test for intermolecular exchange. Imidazolyl complex 3a and triazolyl complex 3d were combined in DMSO-d₆ in varying proportions. The ¹³C_{carbene} shifts for triazolyl complex 3d were very small (\leq 0.14 ppm). The ${}^{13}C_{carbene}$ signal for imidazolyl complex 3a shifted slightly when exposed to complex 3d. The largest shift ($\Delta \delta = 0.45$ ppm) occurred when the two were mixed in equal amounts, yet the triazolyl ¹³C_{carbene} chemical shift remained unchanged (see ESI⁺). These data are not consistent with intermolecular exchange.

Table 1 Selected interatomic distances

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	3 a , X = I	3 b , X = I	3c, X = I	3d , X = I	3e, X = Br
Ag1-Ag2	3.0566(2)	3.0341(6)	3.088(2)	3.0882(10)	3.1379(12)
Ag1-Ag3(Ag1 ⁱ)	3.7790(2)	3.2985(8)	3.836(3)	3.5737(10)	3.75674(15)
$Ag1 - Ag4(Ag2^{i})$	3.4248(2)	3.5177(6)	3.724(2)	3.5845(10)	3.7635(14)
$Ag2 - Ag3(Ag1^{i})$	3.7978(2)	3.5177(6)	3.724(2)	3.5352(10)	3.7520(13)
$Ag3(Ag1^{i}) - Ag4(Ag2^{i})$	3.1275(2)	3.0341(6)	3.088(2)	3.0883(10)	3.1564(12)
Ag1-X1	2.9552(2)	2.8846(5)	3.073(2)	2.9400(9)	2.9475(16)
Ag1-X2	2.9259(2)	3.1789(5)	2.890(2)	3.0575(9)	2.6543(15)
Ag2-X2	2.8976(2)	3.0084(5)	2.948(2)	2.9479(9)	2.8697(16)
$Ag2-X4(X2^{i})$	2.8332(2)	3.3254(8)	2.926(2)	2.9001(9)	2.7032(11)
C–Ag1	2.164(2)	2.185(5)	2.192(8)	2.185(7)	2.122(9)

Table 2	VT 13C	NMR	data
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balescence temp (°C)	$k (s^{-1})$	ΔG^{\ddagger}	
40	478	10.7	
40	478	10.7	
40	478	10.7	
30	362	11.3	
30	441	11.2	
	40 40 40 30 30	40 478 40 478 40 478 40 478 30 362 30 441	

^{*a*} In 2 : 1 DMF : CD_2Cl_2 . ^{*b*} In DMF.

VT ¹³C NMR studies

The ¹³C_{carbene} singlet for complexes 3a-3e decoalesced at low temperature (see ESI[†]) into two broad signals. The coalescence temperatures, and subsequently, the ΔG^{\ddagger} were determined for each complex (Table 2). The imidazolyl complexes 3a-3c, which differ only by the alkyl chain-butyl vs. butenyl vs. pentenyl, had identical coalescence temperatures and activation barriers, thus the side chain did not impact the exchange rate. The triazolyl complexes 3d and 3e had a slightly higher barrier than imidazolyl complexes 3a-3c. The halogen had a small effect on the exchange rate of complexes 3d and 3e, and almost no impact on the ΔG^{\ddagger} . This result is in contrast to other reports where the halogen had large impacts on the intermolecular exchange rate.²⁶ The results from crossover and VT ¹³C NMR experiments are consistent with intramolecular ^{107/109}Ag-¹³C exchange in complexes 3a-3e rather than intermolecular exchange. Such an intramolecular process may be viewed as a molecular rotor-type mechanism for Ag-C interchange.

Conclusion

In summary, we report the synthesis and characterization of five examples of tetra-NHC-Ag(I)-X cubane clusters. The complexes were characterized with ¹H and ¹³C NMR spectroscopy, ESI-TOF MS, and X-ray crystallography. Complexes **3a–3d** are precursors to supramolecular building blocks observed in the mass spectra. The results from VT ¹³C NMR, crossover experiments and a mixed synthesis are consistent with intramolecular Ag–C exchange, which can be conceptualized as a molecular rotor-type mechanism.

Experimental

General methods

Molecular sieves, Celite®, K_2CO_3 , and Al_2O_3 (basic, 50–200 µm) were stored in an oven at 130 °C prior to use. Ag₂O (99%) was purchased from Sigma-Aldrich and used as received. NMR spectra were recorded on 300 or 500 MHz Bruker instruments. Chemical shifts (δ) were expressed in ppm downfield to TMS at $\delta = 0$ and referenced to the residual solvent peak.²⁷ CD₂Cl₂, CH₂Cl₂, DMSO-d₆ and CD₃CN were dried by passing through activated alumina.²⁸ ESI-TOF MS data was collected using a Synapt G2 HDMS instrument. 1,3-Bis(3'-butylimidazol-1'-yl)-benzene diiodide (**2a**) was synthesized and isolated according to a literature procedure (Scheme 1).²⁹

Synthesis and characterization

1,3-Bis(imidazol-1'-yl)benzene (1a). 1,3-Dibromobenzene (69.0 mL, 0.571 mol), imidazole (97.2 g, 1.43 mol), K₂CO₃ (235.9 g, 1.43 mol), CuO (11.4 g, 0.143 mol), and DMSO (540 mL) were combined and heated at 150 °C for 48 h.²³ The reaction was cooled, CH_2Cl_2 (2.7 L) was added, and the reaction mixture was filtered through a column of basic alumina. The filter was washed with 10:1 CH_2Cl_2 :isopropanol (2 L). The resulting filtrate was concentrated under reduced pressure yielding a yellow oil that was left overnight *in vacuo*. The oil became a free-flowing, bright yellow solid, which was washed with EtOAc (30 mL), sonicated for 1 min, cooled in an ice bath and collected as an off-white solid (83.4 g, 70%). Spectroscopic data of **1a** was identical to previously reported data.²³

1,3-Bis(1',2',4'-triazol-1'-yl)benzene (1b). 1,3-Dibromobenzene (13.7 mL, 113 mmol), 1,2,4-triazole (19.5 g, 283 mmol), CuO (2.19 g, 28.3 mmol), K₂CO₃ (39.1 g, 283 mmol), and DMSO (150 mL) were combined and heated at 150 °C for 48 h. After cooling, CH₂Cl₂ (1.5 L) was added. The mixture was filtered through a column of basic alumina, and the filter was washed with CH₂Cl₂ (500 mL). The filtrate was concentrated, washed with EtOAc (100 mL) and dried to yield an off-white solid (20 g, 83%). ¹H NMR (DMSO-d₆, 300 MHz): δ 9.43 (s, 2H), 8.39 (s, 1H), 8.31 (s, 2H), 7.93 (d, *J* = 8 Hz, 2H), 7.76 (t, *J* = 8 Hz, 1H). ¹³C{¹H} NMR (DMSO-d₆, 125.8 MHz): δ 153.1, 143.2, 138.2, 131.7, 118.6, 110.7. [M + H]⁺ found, 212, calc., 212.

1,3-Bis(3'-but-3"-enyl-imidazolium-3'-yl)benzene diiodide (2b). 1,3-Bis(imidazol-1'-yl)benzene (1a) (0.75 g, 3.57 mmol),

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4-iodo-1-butene (1.96 g, 10.7 mmol) and CH₃CN (5 mL) were combined, protected from light, and heated at 120 °C. After 1 h, the reaction was allowed to cool yielding yellow needles, which were collected and washed with cold CH₃CN (4 mL) and with Et₂O (2 × 4 mL). The resulting white solid (1.22 g, 60%) was dried *in vacuo*. ¹H NMR (CD₃OD, 300 MHz): δ 9.99 (s, 2H), 8.52 (s, 1H), 8.39 (s, 2H), 8.09 (m, 5H), 6.02 (m, 2H), 5.26 (m, 4H), 4.58 (t, *J* = 7.0 Hz, 4H), 2.89 (m, 4H). ¹³C{¹H} NMR (CD₃OD, 75.5 MHz): δ 137.6, 137.2, 134.3, 133.7, 125.1, 124.9, 123.1, 119.9, 118.3, 51.0, 35.2. Anal. Calc. for C₂₀H₂₄N₄I₂: C, 41.83; H, 4.21; N, 9.76. Found: C, 41.80; H, 4.08; N, 9.84.

1,3-Bis(3'-pent-4"-enyl-imidazolium-3'-yl)benzene diiodide (2c). 1,3-Bis(imidazol-1'-yl)benzene (1a) (1.75 g, 8.30 mmol), 5-iodo-1-pentene (4.88 g, 24.9 mmol), and CH₃CN (15 mL) were combined, purged with Ar and heated at 120 °C. After 1 h, the reaction was cooled and the volatiles were removed in vacuo. The resulting pale orange solid was dissolved in a minimal amount of CH₃CN. Et₂O (45 mL) was added to the solution producing an off-white precipitate, which was collected yielding 3.87 g, 77%. Crystals for elemental analysis were obtained by slow evaporation of a saturated solution of complex 2c in CH₂Cl₂. ¹H NMR (CD₃CN, 500 MHz): δ 10.17 (s, 2H), 8.50 (s, 1H), 8.18 (s, 2H), 7.90 (m, 2H) 7.68 (s, 2H), 5.89 (m, 2H), 5.06 (dd, J = 13.7 Hz, 4H), 4.33 (t, J = 7.1 Hz, 4H), 2.16 (m, 9H). ${}^{13}C{}^{1}H$ NMR (DMSO-d₆, 125.8 MHz): δ 136.9, 135.7, 135.7, 135.6, 131.9, 123.6, 122.6, 121.1, 115.8, 49.1, 29.6, 28.0. Calculated for C₂₂H₂₈N₄I₂: C, 43.87; H, 4.69; N, 9.30. Found: C, 43.90; H, 4.55; N, 9.33.

1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene diiodide (2d). 1,3-Bis(1',2',4'-triazol-1'-yl)benzene (**1b**) (2.2 g, 4.7 mmol), 1-iodobutane (11 mL, 94 mmol), and CH₃CN (40 mL) were combined and heated at 140 °C for 18 h. After cooling, the volatiles were removed under reduced pressure. The crude solid was washed with CH₂Cl₂ (20 mL) yielding a pale yellow solid (4.9 g, 82%). ¹H NMR (DMSO-d₆, 500 MHz): δ 11.12 (s, 2H), 9.57 (s, 2H), 8.52 (t, *J* = 2.2 Hz, 1H), 8.21 (dd, *J*¹ = 2.0 Hz, *J*² = 7.5 Hz, 2H), 8.07 (t, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 8.2 Hz, 4H), 1.95 (m, 4H), 1.42 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). ¹³C{¹H} NMR (DMSO-d₆, 125.8 MHz): δ 145.0, 142.4, 135.9, 131.9, 122.0, 113.0, 47.9, 30.3, 18.7, 13.2.

1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene dibromide (2e). 1,3-Bis(1',2',4'-triazol-1'-yl)benzene (1b)(1.0)g, 4.70 mmol), 1-bromobutane (5.0 mL, 47 mmol), and CH₃CN (30 mL) were combined and heated at 140 °C for 18 h. After cooling, the volatiles were removed under reduced pressure. The crude solid was washed with CH₂Cl₂ (20 mL) yielding a light-brown solid (1.6 g, 70%). ¹H NMR (DMSO-d₆): δ 11.23 (s, 2H), 9.59 (s, 2H), 8.56 (s, 1H), 8.22 (d, J = 8.3 Hz, 2H), 8.05 (t, J = 8.2 Hz, 1H), 4.36 (t, J = 7.2 Hz, 1H), 1.97 (m, 4H), 1.42 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H). ¹³C{¹H} NMR (DMSO-d₆, 75.5 MHz): δ 145.2, 142.5, 136.1, 132.0, 122.0, 112.9, 47.9, 30.5, 18.8, 13.3.

Bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra- μ^3 iodotetrasilver(i) (3a). 1,3-Bis(3'-butylimidazol-1'-yl)benzene diiodide (2a) (0.40 g, 0.69 mmol), Ag₂O (0.18 g, 0.76 mmol), molecular sieves (0.3 g, 4 Å beads), and CH₂Cl₂ (40 mL) were

combined, protected from light and stirred for 12 h under Ar. The solution was filtered through celite, concentrated to dryness, and CH₂Cl₂ (20 mL) was added. The resulting solution was filtered through celite, concentrated under reduced pressure, and washed with Et_2O (3 × 4 mL). The free-flowing, white powder was dried overnight under reduced pressure yielding 0.37 g, 67%. Crystals suitable for X-ray and elemental analysis were grown by slow vapor diffusion of Et₂O into a saturated solution of complex 3a in CH₂Cl₂. ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.38 (t, J = 1.8 Hz, 2H), 7.53 (dd, J = 6.6 Hz, 4H), 7.43 (t, J = 2.1 Hz, 2H), 7.31 (d, J = 1.7 Hz, 4H), 7.12 (d, J = 1.7 Hz, 4H), 4.32 (t, J = 7.4 Hz, 8H), 1.89 (m, J = 7.5 Hz, 8H), 1.42 (m, J = 7.5 Hz, 8H), 0.96 (t, J = 7.3 Hz, 12H). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 187.0, 141.8, 130.5, 123.4, 122.5, 121.9, 121.4, 52.5, 34.1, 20.4, 14.2. Anal. Calc. for C₄₀H₅₂N₈Ag₄I₄: C, 30.33; H, 3.31; N, 7.07. Found: C, 30.46; H, 3.59; N, 6.89.

Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-µ³-iodotetrasilver(1) (3b). 1,3-Bis(3'-but-3"-enyl-imidazolium-1'-yl)benzene diiodide (2b) (0.40 g, 0.70 mmol), Ag₂O (0.18 g, 0.77 mmol), molecular sieves (0.3 g, 4 Å beads), and CH₂Cl₂ (50 mL) were combined, protected from light and stirred for 12 h under Ar. The solution was filtered through celite, concentrated to dryness, and CH₂Cl₂ (30 mL) was added. The solution was filtered through celite, concentrated under reduced pressure, and washed onto a filter with Et₂O (5 mL), and washed with additional Et_2O (3 × 4 mL). The freeflowing, white powder was dried overnight under reduced pressure yielding 0.39 g, 71%. Crystals suitable for X-ray analysis were grown by slow evaporation of a saturated solution of complex 3b in CH₂Cl₂. ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.48 (s, 1H), 7.53 (m, 1H), 7.43 (m, 2H), 7.29 (d, J = 1.8 Hz, 2H), 7.12 $(d, J = 1.8 \text{ Hz}, 2\text{H}), 5.90 \text{ (m, 2H)}, 5.09 \text{ (dd}, J^1 = 17.2 \text{ Hz}, J^2 = 10.3$ Hz, 4H), 4.39 (t, J = 7.3 Hz, 4H), 2.70 (m, 4H). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 187.8, 141.9, 135.2, 130.5, 123.3, 122.8, 121.1, 118.0, 52.0, 36.4.

Bis(µ-1,3-bis(3'-pent-4"-enyl-imidazol-2'-ylidene)benzene-к-С)tetra- μ^3 -iodotetrasilver(1) (3c). 1,3-Bis(3'-pent-4"-enyl-imidazolium-1'-yl)benzene diiodide (2c) (0.51 g, 0.85 mmol), Ag₂O (0.22 g, 0.93 mmol), molecular sieves (0.3 g, 4 Å beads) and CH₂Cl₂ (43 mL) were protected from light and stirred at room temperature for 16 h. The reaction mixture was filtered through celite to produce a pale yellow filtrate, and was concentrated under reduced pressure, yielding a yellow crystalline solid. The solid was dissolved in CH2Cl2 (20 mL) and filtered through celite. The volatiles were removed in vacuo, and the resulting solid was washed with $Et_2O(3 \times 4 \text{ mL})$ to yield an offwhite, free-flowing solid (0.53 g, 39%). Crystals suitable for X-ray were obtained through slow vapor diffusion of Et₂O into a saturated solution of complex **3c** in CH₂Cl₂. ¹H NMR $(CD_2Cl_2, 300 \text{ MHz}): \delta 8.41 \text{ (s, 2H)}, 7.54 \text{ (t, } J = 7.2 \text{ Hz, 2H}), 7.42 \text{ (cd})$ (d, J = 7.2 Hz, 4H), 7.32 (s, 4H), 7.12 (s, 4H), 5.85 (m, 4H), 5.01 $(dd, J^1 = 17.2 \text{ Hz}, J^2 = 10.2 \text{ Hz}, 8\text{H}), 4.33 (t, J = 7.2 \text{ Hz}, 8\text{H}), 2.16$ (m, 8H), 2.02 (m, 8H). ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 75.5 MHz): δ 187.5, 141.9, 138.3, 130.6, 123.5, 122.0, 121.4, 115.7, 52.1, 31.3, 31.2. Calculated for C44H52Ag4I4N8: C, 32.38; H, 3.21; N, 6.87. Found: C, 32.47; H, 3.02; N, 7.13.

Bis(µ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-к-С)tetra- μ^3 -iodotetrasilver(1) (3d). 1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene diiodide (2d) (0.51 g, 0.88 mmol), Ag₂O (0.19 g, 0.84 mmol), KOH (0.087 g, 1.6 mmol), and CH₃CN (40 mL) were combined, protected from light and stirred for 18 h, vielding a white precipitate. The solid was collected and the KOH pellets were removed. The solid was washed with CH₃CN (10 mL), MeOH (5 mL) and Et₂O (2 \times 20 mL), and dried under reduced pressure affording an off-white solid (0.49 g, 73%). Crystals suitable for X-ray and elemental analysis were grown by slow vapor diffusion of CH₃OH into a saturated solution of complex 3d in DMSO. ¹H NMR (DMSO-d₆, 300 MHz): δ 9.05 (s, 2H), 8.49 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.36 (t, J = 8.3 Hz, 1H), 4.34 (s, 4H), 1.76 (m, 4H), 1.22 (m, 4H), 0.82 (t, J = 6.8 Hz, 6H). ¹³C{¹H} NMR (DMSO-d₆, 75.5 MHz): δ 186.5, 144.8, 140.0, 130.3, 121.8, 115.9, 48.2, 32.5, 18.9, 13.4. Anal. Calc. for C₃₆H₄₈Ag₄I₄N₁₂: C, 27.23; H, 3.05; N, 10.58. Found: C, 27.22; H, 3.05; N, 10.48.

Bis(µ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-к-С)tetra- μ^3 -bromotetrasilver(1) (3e). 1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene dibromide (2e) (0.890 g, 1.83 mmol), Ag₂O (0.466 g, 2.01 mmol), and CH₃CN (120 mL) were combined, protected from light and stirred overnight for 18 h, affording a white precipitate. The solid was collected and washed with acetone (3×50 mL). The filtrate was concentrated to dryness yielding a white powder (0.060 g, 7%). Crystals suitable for X-ray analysis were grown by slow vapor diffusion of MeOH into a saturated solution of complex 3e in DMSO. ¹H NMR (DMSO-d₆, 500 MHz): δ 9.15 (m, 2H), 7.91 (dd, J^1 = 7.9 Hz, $J^{2} = 1.7$ Hz, 2H), 7.74 (t, J = 7.7 Hz, 1H), 4.29 (t, J = 6.6 Hz, 4H), 1.81 (m, 4H), 1.26 (m, 4H), 0.80 (t, J = 7.1 Hz, 6H). ¹³C{¹H} NMR (DMSO-d₆, 75.5 MHz): δ 185.6, 144.5, 139.7, 130.8, 122.2, 115.6, 48.6, 32.7, 19.1, 13.5.

Alternate synthesis: 1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene dibromide (2e) (0.20 g, 0.67 mmol), Ag₂O (0.17 g, 0.74 mmol), molecular sieves (0.3 g, 4 Å beads), and CH₃CN (34 mL) were combined, protected from light and stirred overnight for 18 h, affording a white precipitate. The solution was filtered through celite, and the filter was washed with 3×20 mL of DMSO. The filtrate was concentrated to dryness yielding a free-flowing, off-white powder (0.37 g, 39%). Spectral data of the off-white solid was identical to data above.

Mixed synthesis

1,3-Bis(4'-butyl-1',2',4'-triazolium-1'-yl)benzene diiodide (2d) (0.25 g, 0.43 mmol), 1,3-bis(3'-butylimidazol-1'-yl)benzene diiodide (2a) (0.25 g, 0.44 mmol), Ag₂O (0.22 g, 0.97 mmol) and DMF (50 mL) were combined, protected from the light and stirred for 12 h. The solution was filtered through celite, concentrated to dryness, and DMF (10 mL) was added. The resulting solution was filtered through celite, concentrated under reduced pressure to ~2 mL. Et₂O (5 mL) was added to produce a white solid. The solid was washed with additional Et₂O (2 × 4 mL), yielding a free-flowing, white powder, which was dried overnight under reduced pressure yielding 0.35 g, 90%. See ESI[†] for spectral data.

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