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Supramolecular Structures from Polycarbene Ligands and Transition Metal Ions

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The synthesis of cylinder-type carbene complexes from polycarbene ligands and coinage metal ions via metal-controlled self-assembly has been explored. Imidazole reacts with 1,2,4,5-tetrabromobenzene or 1,3,5-tribromobenzene to give 1,2,4,5-tetrakis(1-imidazolyl)benzene (**1**) and 1,3,5-tris(1-imidazolyl)benzene (**3**), respectively. The tetrakisimidazolium salts of type H_4-**2a**,**b**$(Br)_4$ and the trisimidazolium salts of type H_3-**4a**,**b**$(Br)_3$ have been prepared by alkylation of the remaining free imines of the tetrakis- and trisimidazoles (H_4-**2a**$^{4+}$, H_3-**4a**$^{3+}$: R = *n*-butyl; H_4-**2b**$^{4+}$, H_3-**4b**$^{3+}$: R = ethyl). Polyimidazolium salts H_4-**2a**,**b**$(PF_6)_4$ and H_3-**4a**,**b**$(PF_6)_3$ have been synthesized by anion exchange from H_4-**2a**,**b**$(Br)_4$ and H_3-**4a**,**b**$(Br)_3$. Two equivalents of tetraimidazolium salt H_4-**2a**$(Br)_4$ or H_4-**2a**,**b**$(PF_6)_4$ reacts with four equivalents of Ag_2O to yield via self-assembly molecular cylinders of type $[Ag_4(\mathbf{2a})_2]Y_4$ (Y^- = $[AgBr_2]^-$ and/or Br^-) or $[Ag_4(\mathbf{2a,b})_2](PF_6)_4$, respectively. Similarly, reaction of two equivalents of trisimidazolium salts H_3-**4a**$(Br)_3$ or H_3-**4a**,**b**)$(PF_6)_3$ with three equivalents of Ag_2O yields the molecular cylinder $[Ag_3(\mathbf{4a})_2](Y)_3$ (Y^- = $[AgBr_2]^-$ and/or Br^-) or $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$, respectively. Transmetalation of $[Ag_4(\mathbf{2a,b})_2](PF_6)_4$ with four equivalents of $[AuCl(SMe_2)]$ leads to the formation of the tetranuclear gold(I) complex $[Au_4(\mathbf{2a,b})_2](PF_6)_4$ with retention of the metallosupramolecular assembly. Analogously, transmetalation of $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$ with three equivalents of $[AuCl(SMe_2)]$ or CuBr yields the trinuclear gold(I) complexes $[Au_3(\mathbf{4a,b})_2](PF_6)_3$ or the copper(I) complexes $[Cu_3(\mathbf{4a,b})_2](PF_6)_3$, respectively. Contrary to the metallosupramolecular assemblies of type $[M_4(\mathbf{2a})_2]^{4+}$ (M = Ag^+, Au^+), tetrakisimidazolium salt H_4-**2a**$(Br)_4$ reacts with K_2PtCl_4 in the presence of NaOAc to yield the square-planar dinuclear complex $[Pt_2(\mathbf{2a})Br_4]$.

1. Introduction

Metal-controlled self-assembly of supramolecular structures has attracted tremendous attention in the last two decades after the first report on dinuclear double-helical complexes by Lehn et al. from bipyridine and copper(I).[1] Subsequently, a large number of self-assembled metallohelicates[2] and other three-dimensional supramolecular structures[3] have been obtained by variation of the metal components and the ligands. Some of these supramolecular assemblies can act as molecular hosts by encapsulating small molecular guests, which might undergo selective chemical transformations within the host molcule.[4] A dramatic rate enhancement has been observed for selective transformations within metallosupramolecular hosts.[5]

Most of the three-dimensional metallosupramolecular structures are built from metal centers at the corners (often palladium or platinum species with *cis*-coordinated diamines or diphosphines as supporting ligands) that are linked by classical Werner-type polydentate ligands featuring nitrogen and/or oxygen donor atoms, such as pyrazine, 4,4′-bipyridine, or 2,4,6-tris(4-pyridyl)-1,3,5-triazine.[3,4] Polydentate ligands with carbon donors have rarely been used for the construction of metallosupramolecular assemblies, although some derivatives with bridging diisocyanide,[6] acyclic diaminocarbenes,[7] and remote N-heterocyclic carbene ligands[8] have been described. Metallosupramolecular structures containing

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the ubiquitous N-heterocyclic carbenes (NHCs)[9] as bridging ligands have been unknown until recently. In combination with the proper metal building blocks, such ligands would allow the construction of metallosupramolecular assemblies that feature only metal−carbon bonds, thereby generating organonometallic frameworks (OMFs) that might constitute an alternative to the intensely studied metal−organic frameworks (MOFs).[10]

From the polydentate NHC ligands known,[11] only few have found applications as bridging ligands in the construction of metallosupramolecular assemblies. The first example of a three-dimensional structure made up from three silver(I) cations and two tripodal tricarbene ligands was reported by Meyer.[12] The tricarbene ligand $(NHC-CH_2)_3C-CH_3$ used, however, could also be metalated under formation of "abnormal" NHCs,[13] leading to a different type of structure.[14] Later, the benzobis-NHCs first reported by Bielawski[15] have been used to synthesize dicarbene-bridged molecular rectangles.[16] A macrocyclic hexacarbene ligand has also been employed for the preparation of a hexasilver-dodecacarbene complex where six silver atoms are sandwiched in between two hexacarbene ligands.[17] Related silver complexes, also featuring exclusively $Ag-C_{NHC}$ bonds, have been obtained from macrocyclic tricarbene[18] and tetracarbene ligands.[19]

In our search for new polycarbene ligands that would allow the construction of three-dimensional metallosupramolecular structures, we have studied the coordination chemistry of disk-shaped NHC-functionalized benzenes. These ligands resemble the disk-like tridentate ligands described by Shionoya et al., which coordinate via the thiazolyl imine nitrogen atoms to give sandwich-shaped trinuclear complexes of type **[A]**$^{3+}$ (Figure 1).[20] In a preliminary publication we reported that related tetracarbene and tricarbene ligands react with silver(I) ions to yield tri- or tetranuclear complexes of types **[B]**$^{4+}$ and **[C]**$^{3+}$, respectively.[21] Herein we present a detailed account of the use of *in situ*-generated disk-like polyarbene ligands for the generation of cylindrical structures featuring three or four silver atoms sandwiched in between two tri- or tetracarbene ligands and the transmetalation of the NHC ligands from silver(I) to gold(I) or copper(I). In addition, the reaction of the tetracarbene ligand with d^8 metal ions like Pt^{II} leading to planar complexes of type *cis,cis*-$[(Br)_2Pt(NHC)_2\text{-}1,2\text{-}C_6H_2\text{-}4,5\text{-}(NHC)_2Pt(Br)_2]$ is described.

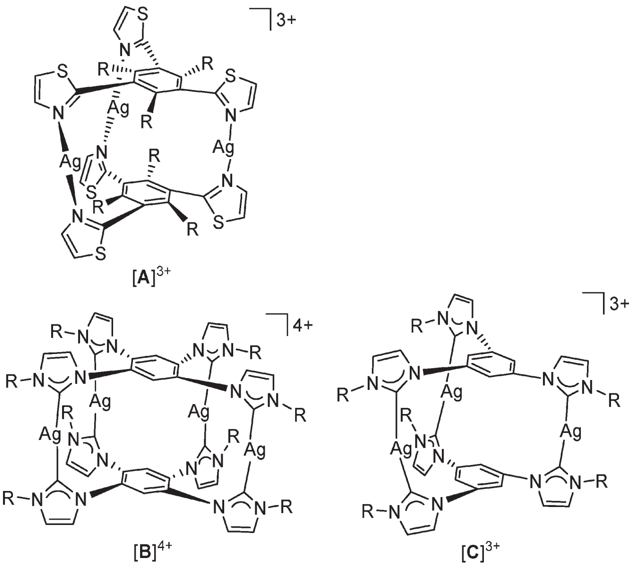

Figure 1. Molecular cyclinders obtained from trithiazolyl ligands **[A]**$^{3+}$ and molecular cylinders **[B]**$^{4+}$ and **[C]**$^{3+}$ made up from disk-like polycarbene ligands and silver(I).

2. Results and Discussions

2.1. Synthesis and Characterization of Polyimidazolium Salts. 1,2,4,5-Tetrakis(1-imidazolyl)benzene (**1**) was synthesized by the solid-state reaction of imidazole with 1,2,4,5-tetrabromobenzene using an Ullmann coupling protocol[22] in 40% yield. Subsequently, the remaining imine functions were alkylated in DMF as solvent using either *n*-butyl bromide or ethyl bromide to give the tetrakisimidazolium tetrabromide H_4-**2a**$(Br)_4$ and H_4-**2b**$(Br)_4$, respectively. Anion exchange with NH_4PF_6 in methanol gave H_4-**2a**$(PF_6)_4$ and H_4-**2b**$(PF_6)_4$ in yields of more than 80% (Scheme 1). All four tetrakisimidazolium salts are nonhygroscopic colorless solids. The hexafluorophosphate salts H_4-**2a**$(PF_6)_4$ and H_4-**2b**$(PF_6)_4$ are freely soluble in acetone, DMF, and acetonitrile but almost insoluble in solvents such as dichloromethane, tetrahydrofuran, and diethyl ether, while the bromide salts H_4-**2a**$(Br)_4$ and H_4-**2b**$(Br)_4$ are soluble in more polar solvents such as DMSO, methanol, and H_2O. This solubility difference determined the choice of the solvent for the subsequent metal complex formation reactions.

Compound 1,3,5-tris(1-imidazolyl)benzene (**3**) was prepared using a slightly modified protocol of the published procedure.[23] The trisimidazolium salts H_3-**4a**$(Br)_3$ and H_3-**4b**$(Br)_3$ were

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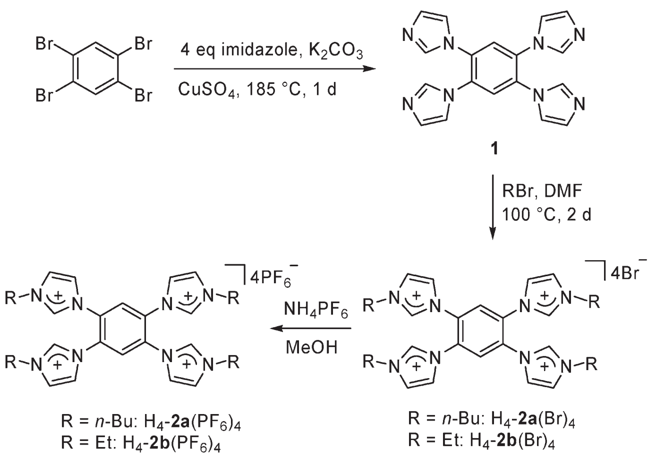
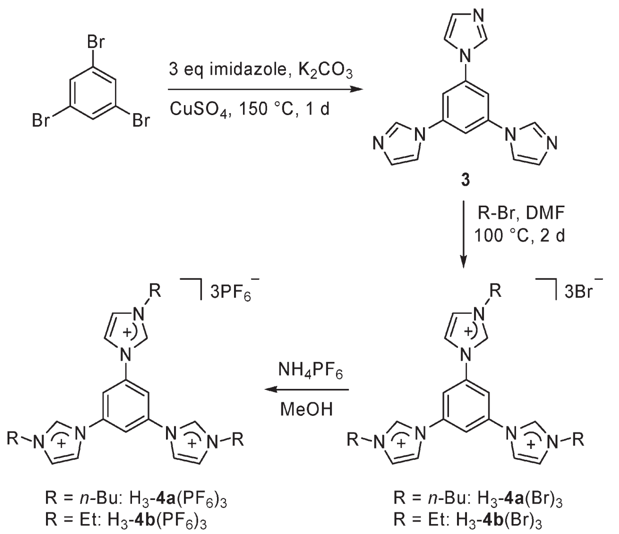
Scheme 1. Preparation of Tetrakisimidazolium Salts H_4-2a,b-$(Br)_4$ and H_4-2a,b$(PF_6)_4$



Scheme 2. Preparation of Trisimidazolium Salts H_3-4a,b$(Br)_3$ and H_3-4a,b$(PF_6)_3$



obtained by trisalkylation of **3** with the appropriate alkyl bromide. Anion exchange with NH_4PF_6 in methanol gave H_3-**4a**$(PF_6)_3$ and H_3-**4b**$(PF_6)_3$ (Scheme 2). The solubility properties of the trisimidazolium tribromide and trishexafluorophosphate salts resemble those of the tetrakisimidazolium salts of type H_4-**2a**,**b**$(X)_4$ with the bromide salts soluble in polar solvents such as DMSO, methanol, and H_2O, while the hexafluorophosphate salts are soluble in acetone, DMF, and acetonitrile.

Formation of the polyimidazolium salts can be detected by NMR spectroscopy. The C2−H resonances for the polyimidazolium salts are observed in the range typical for such derivatives[9a] (in [d_6]DMSO: H_4-**2a**$(PF_6)_4$ δ = 9.55 ppm, H_3-**4a**$(PF_6)_3$ δ = 9.89 ppm; in CD_3CN: H_4-**2b**$(PF_6)_4$ δ = 9.12 ppm; H_3-**4b**$(PF_6)_3$ δ = 9.15 ppm). The different counterions employed (Br^- vs PF_6^-) lead to a slight difference in the acidity of the C2−H protons due to different types of hydrogen bonding. The $^{13}C\{^1H\}$ NMR spectra showed the resonance for the C2 imidazolium carbon atoms of the hexafluorophosphate salts in the narrow range of $\delta \approx 136-138$ ppm, which are typical values for unsaturated imidazolium salts.[9a,19,24] Only one C2 and only one C2−H resonance was observed in the $^{13}C\{^1H\}$ and ^1H NMR spectra, respectively, of both the tetrakis- and the trisimidazolium salts, which indicates free rotation about the $C_{phenyl}-N_{imidazolium}$ bonds. This free rotation was also confirmed by the observation of only one resonance each for the C4 and C5 protons of the imdazolium rings. The resonances for the alkyl protons fall in the range previously reported for imidazolium salts.[19,24]

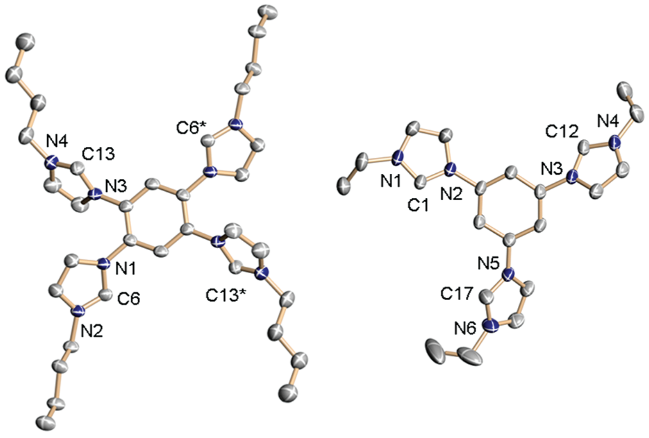


Figure 2. Molecular structures of the tetracation in H_4-**2a**-$(PF_6)_4 \cdot CH_3CN$ (left, one cation derived from one of the two independent halves of $[H_4\text{-}\mathbf{2a}]^{4+}$ in the asymmetric unit is shown) and the trication in H_3-**4b**$(PF_6)_3 \cdot CH_3CN$ (right). Anions, solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for H_4-**2a**$(PF_6)_4$ and [H_3-**4b**$(PF_6)_3$]: range $N-C_{NCHN}$ 1.299(5)−1.345(5) [1.318(4)−1.338(4)], $N-C_{NCHN}-N$ 107.9(4)−109.6(3) [108.0(3)−109.0(3)].

Single crystals of the polyimidazolium hexafluorophosphate salts have been obtained by slow diffusion of diethyl ether into saturated acetonitrile solutions of H_4-**2a**$(PF_6)_4$ and H_3-**4b**$(PF_6)_3$, respectively. The molecular structures of H_4-**2a**$(PF_6)_4 \cdot CH_3CN$ and H_3-**4b**$(PF_6)_3 \cdot CH_3CN$ have been determined by X-ray diffraction analysis. Figure 2 depicts the molecular structures of the polyimidazolium cations in H_4-**2a**$(PF_6)_4 \cdot CH_3CN$ and H_3-**4b**$(PF_6)_3 \cdot CH_3CN$. The imidazolium groups in both cations are not pointing in a common direction in the solid-state structures. They are also not oriented in a preferred direction with respect to the central phenyl ring. Important bond parameters in the polyimidazolium cations do not differ significantly from those observed for previously reported imidazolium salts.[9a,19,24] Both the tetrakisimidazolium cation and the trisimidazolium cation exhibit slightly shorter $N-C_{NCHN}$ bond lengths [range 1.299(5)−1.345(5) Å] and larger $N-C_{NCHN}-N$ angles [range 107.9(4)−109.6(3)°] than the free imidazolin-2-ylidenes,[9a,24a] in agreement with the previous observations and DFT calculations.[25]

2.2. Synthesis and Characterization of Tetranuclear Complexes. The tetranuclear silver(I) octacarbene complexes $[Ag_4(\mathbf{2a})_2](Y)_4$ ($Y^-=[AgBr_2]^-$ and/or Br^-) and $[Ag_4(\mathbf{2a,b})_2]$-$(PF_6)_4$ were synthesized in about 70% yield from 4 equiv of

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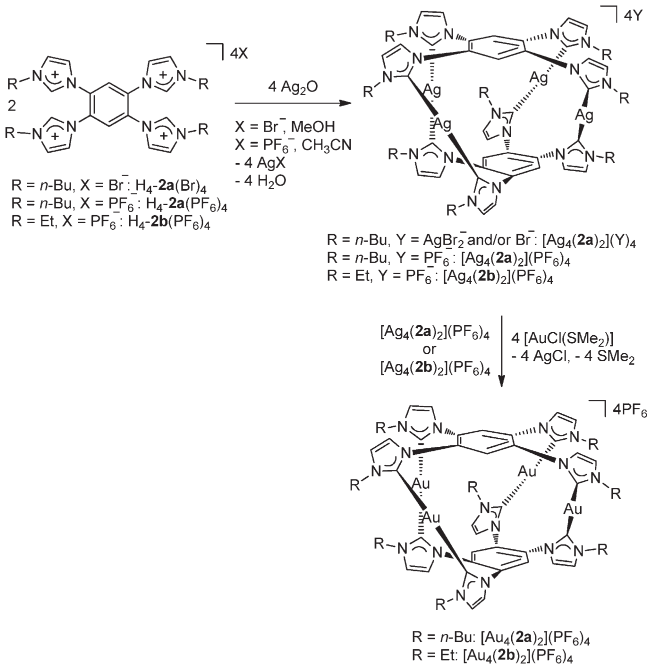
Scheme 3. Preparation of Tetranuclear Silver(I) Carbene Complexes and Transmetalation to Tetranuclear Gold(I) Carbene Complexes



Ag_2O and 2 equiv of H_4-**2a**$(Br)_4$ in methanol or H_4-**2a**,**b**$(PF_6)_4$ in acetonitrile, respectively, using the Ag_2O method developed by Lin et al.[26a] (Scheme 3). The silver(I) carbene complexes were isolated as white to pale brown solids after workup. Carbene complex $[Ag_4($**2a**$)_2](Y)_4$ dissolves well in methanol and DMSO, whereas complexes $[Ag_4($**2a**,**b**$)_2](PF_6)_4$ are well soluble in acetone, acetonitrile, and DMF. Complex $[Ag_4($**2a**$)_2](Y)_4$ is much less stable toward heat and light than the hexafluorophosphate salts $[Ag_4($**2a**,**b**$)_2](PF_6)_4$. Heating $[Ag_4($**2a**$)_2](Y)_4$ to temperatures above 55 °C leads to the formation of a silver mirror in the reaction vessel due to decomposition of the complex. Even though the imidazolium groups were not preorganized in the solid-state molecular structure of H_4-**2a**$(PF_6)_4$, the good solublity of all silver(I) complexes indicates that only the cylindrical tetranuclear structures depicted in Scheme 3 and no oligomers of higher nuclearity had formed. Upon carbene complex formation, all imidazolium groups or, after deprotonation, all imidazolin-2-ylidene donors must rotate in the same direction with respect to the central phenyl ring to form the cylindrical silver carbene complexes.

Formation of the carbene complexes $[Ag_4($**2a**$)_2](Y)_4$ and $[Ag_4($**2a**,**b**$)_2](PF_6)_4$ has been confirmed by both ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ^1H NMR spectra of the complexes, for example, the resonances for the imidazolium proton of the parent salts (in $[d_6]$DMSO: $\delta = 10.24$ ppm for H_4-**2a**$(Br)_4$ and $\delta = 9.55$ ppm for H_4-**2a**$(PF_6)_4$) were absent. The imidazolium C2 carbon resonance for H_4-**2a**$(PF_6)_4$ at $\delta = 137.68$ ppm was replaced with a new resonance for the C_{NHC} carbon atom at $\delta = 181.30$ ppm in the $^{13}C\{^1H\}$ NMR spectrum of $[Ag_4($**2a**$)_2](PF_6)_4$. The C_{NHC} resonance was found at $\delta = 182.50$ ppm in the $^{13}C\{^1H\}$ NMR spectrum of $[Ag_4($**2a**$)_2](Y)_4$, exhibiting the rarely observed coupling to both silver isotopes (dd, $^1J(C{-}Ag^{107}) = 184.3$ Hz, $^1J(C{-}Ag^{109}) = 212.9$ Hz).[17,27] The observed chemical shifts and $^1J(C{-}Ag^{107/109})$ coupling constants fall in the range previously described for $[Ag(NHC)_2]^+$ complexes.[17,27]

Observation of only one proton signal for the central phenyl ring and only two resonances for the imidazole C4 and C5 protons for both $[Ag_4($**2a**$)_2](Y)_4$ and $[Ag_4($**2a**,**b**$)_2](PF_6)_4$ indicates the formation of highly symmetric structures in solution. Upon complex formation, the $N{-}CH_2$ protons of the carbene substituents in complex $[Ag_4($**2a**$)_2](Y)_4$ become diastereotopic, giving rise to a multiplet for each proton at $\delta = 4.38$ and 4.21 ppm in the ^1H NMR spectrum. For complex $[Ag_4($**2a**$)_2](PF_6)_4$, the $N{-}CH_2$ proton resonances were observed as a multiplet at $\delta = 4.12{-}4.16$ ppm. The ^{109}Ag NMR spectrum of $[Ag_4($**2a**$)_2](PF_6)_4$ shows a resonance at $\delta = 676$ ppm.[17] Electrospray ionization (ESI) mass spectra (positive ions) of $[Ag_4($**2a**$)_2](Y)_4$ and $[Ag_4($**2a**,**b**$)_2](PF_6)_4$ show peaks for the complex cations $[Ag_4($**2a**,**b**$)_2(PF_6)_n]^{(4-n)+}$ (n = 1−4), supporting the formation of the tetranuclear complexes.

Salt $[Ag_4($**2a**$)_2](Y)_4$ could not be crystallized due to its light sensitivity and the presence of two different types of counterions (Br^- or $AgBr_2^-$). However, complex $[Ag_4($**2a**$)_2](PF_6)_4$ was crystallized by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at room temperature as $[Ag_4($**2a**$)_2](PF_6)_4\cdot 2CH_3CN$. The X-ray diffraction analysis confirmed the formation of cylindrical tetrasilver octacarbene complex (Figure 3, left). Complex $[Ag_4($**2a**$)_2](PF_6)_4$ cocrystallized with two molecules of acetonitrile. The acetonitrile molecules as well as the PF_6^- anions exhibit no remarkable interactions with the complex cation.

Complex cation $[Ag_4($**2a**$)_2]^{4+}$ is built from four silver(I) ions sandwiched in between two tetracarbene ligands related to each other by a pseudoinversion center. Each Ag^I is coordinated by two NHC donors from two different tetracarbene ligands **2a** in an almost linear fashion [range $C_{NHC}{-}Ag{-}C_{NHC}$ 175.2(2)−178.5(2)°]. The $Ag{-}C_{NHC}$ bond lengths [range $Ag{-}C_{NHC}$ 2.073(4)−2.089(4) Å] fall in the range previously observed for similar types of silver-dicarbene complexes.[17,27] For the complex formation, the planes of the NHC donors must rotate out of the plane of the central phenyl ring. The NHC ring planes are, however, not oriented perpendicularly with respect to the central phenyl ring. In order to avoid close contacts between the silver ions, the four imidazolin-2-ylidenes rings of both ligands rotate from an imaginary perpendicular orientation relative to the central phenyl ring in an anticlockwise direction. The torsion angles with respect to the central phenyl ring range from −54.256(6)° to −64.735(6)°. This results in a shorter than possible separation of 5.190 Å between the two phenyl ring centroids. In addition, the ring planes of two NHC donors coordinating to the same Ag^I ion are not oriented in a coplanar fashion (see the coordination environment around Ag2) to avoid interactions of the *N*-*n*-butyl substituents.

The four silver ions sandwiched between two tetracarbene ligands in $[Ag_4($**2a**$)_2](PF_6)_4$ form a slightly distorted rectangle (Figure 3, middle) featuring two short (Ag1−Ag2 3.4032(1) Å, Ag3−Ag4 3.5207(2) Å) and two long (Ag2−Ag3 5.8373(2) Å, Ag1−Ag4 5.9592(2) Å) Ag···Ag separations. The shortest Ag···Ag separation (3.4032(1) Å) is slightly shorter than the sum of van der Waals radii of two silver atoms.[28]

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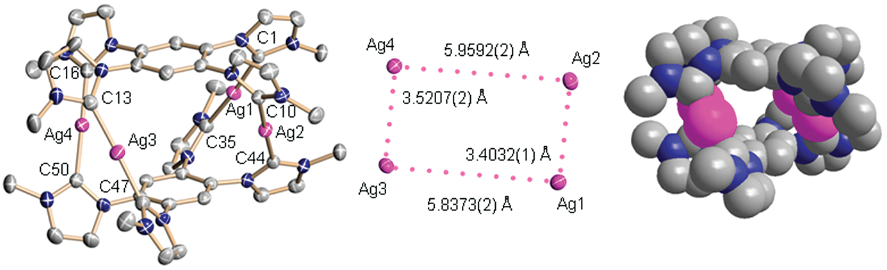


Figure 3. Molecular structure of the tetracation $[Ag_4(\mathbf{2a})_2]^{4+}$ in $[Ag_4(\mathbf{2a})_2](PF_6)_4\cdot 2CH_3CN$ (left, hydrogen atoms have been omitted for clarity, and only the first atom of each of the *N*-*n*-Bu substituents is depicted); view of the rectangular arrangement of the four silver ions (middle) and space-filling drawing of the tetracation showing the cavity inside the complex (right). Selected bond lengths (Å) and angles (deg): range $Ag-C_{NHC}$ 2.073(4)−2.089(4), range $C_{NHC}-Ag-C_{NHC}$ 175.2(2)−178.5(2), $N-C_{NHC}-N$ 103.4(4)−104.6(4).

The silver(I) NHC complexes $[Ag_4(\mathbf{2a})_2](PF_6)_4$ and $[Ag_4(\mathbf{2b})_2](PF_6)_4$ were expected[26] and found to be excellent carbene transfer agents. All four silver atoms in $[Ag_4(\mathbf{2a})_2](PF_6)_4$ and $[Ag_4(\mathbf{2b})_2](PF_6)_4$ can be substituted by Au^I to give the homonuclear complexes $[Au_4(\mathbf{2a})_2](PF_6)_4$ and $[Au_4(\mathbf{2b})_2](PF_6)_4$ in yields of about 65% yield without destruction of the three-dimensional metallosupramolecular assembly (Scheme 3). The gold(I) carbene complexes were isolated as white powders. Exclusively the homotetranuclear gold(I) complex $[Au_4(\mathbf{2a})_2](PF_6)_4$ was isolated when a mixture of $[Ag_4(\mathbf{2a})_2](PF_6)_4$ and 4 equiv of $[AuCl(SMe_2)]$ in acetonitrile was stirred at ambient temperature for 12 h. No heterobimetallic Ag/Au complex was observed when 1 equiv of $[Ag_4(\mathbf{2a})_2](PF_6)_4$ was treated with only 3 equiv of $[AuCl(SMe_2)]$.

Complexes $[Au_4(\mathbf{2a})_2](PF_6)_4$ and $[Au_4(\mathbf{2b})_2](PF_6)_4$ were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by mass spectrometry. The $^{13}C\{^1H\}$ NMR spectra showed the resonance for the carbene carbon atoms only slightly shifted downfield relative to the tetranuclear silver complexes to δ = 183.91 ppm (for $[Au_4(\mathbf{2a})_2](PF_6)_4$) and 183.99 ppm (for $[Au_4(\mathbf{2b})_2](PF_6)_4$), respectively. These C_{NHC} resonances were detected as singlets. The presence of only one C_{NHC} resonance in the $^{13}C\{^1H\}$ NMR spectra confirms the complete substitution of all the four Ag^I ions for Au^I ions. The NMR spectroscopic data for the tetranuclear gold complexes are quite similar to those of the corresponding silver(I) complexes and are in good agreement with data reported for similar gold(I) dicarbene complexes.[17,27] The ESI mass spectra of $[Au_4(\mathbf{2a})_2](PF_6)_4$ and $[Au_4(\mathbf{2b})_2](PF_6)_4$ showed the mass of tetracation $[Au_4(\mathbf{2a})_2]^{4+}$ and dication $[Au_4(\mathbf{2b})_2(PF_6)_2]^{2+}$, respectively, as intense peaks.

Complex $[Au_4(\mathbf{2a})_2](PF_6)_4$ was crystallized by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at room temperature. Multiple data sets were collected with different crystals. Identical molecular structures were found with all data sets collected. Refinement of these, however, proved difficult. The best refinement (R = 0.0791) was obtained with a model featuring Au, P, and N atoms with anisotropic and F and C atoms with isotropic thermal parameters. No hydrogen atoms were added to this structure model, which after refinement is only of sufficient quality to discuss the overall geometry of the $[Au_4(\mathbf{2a})_2]^{4+}$ cation.

The X-ray diffraction analysis with crystals of $[Au_4(\mathbf{2a})_2](PF_6)_4$ showed that the asymmetric unit contained two independent molecules of the complex exhibiting essentially identical bond parameters. The structure analysis (Figure 4) reveals that the complex cations $[Au_4(\mathbf{2a})_2]^{4+}$ and its precursor $[Ag_4(\mathbf{2a})_2]^{4+}$ are nearly isostructural. The major difference is the generally shorter $M-C_{NHC}$ bond distances in $[Au_4(\mathbf{2a})_2]^{4+}$ compared to $[Ag_4(\mathbf{2a})_2]^{4+}$. Similar behavior has been described previously for essentially isostructural Ag^I and Au^I complexes.[17] As a result, the separation of the centroids of the central phenyl rings shrinks from 5.190 Å for $[Ag_4(\mathbf{2a})_2]^{4+}$ to 5.073 Å for $[Au_4(\mathbf{2a})_2]^{4+}$. Similar to $[Ag_4(\mathbf{2a})_2]^{4+}$ the four gold ions in $[Au_4(\mathbf{2a})_2]^{4+}$ are arranged in a rectangular fashion with the Au···Au separations (short distances 3.4843(2) and 3.4405(2) Å, long distances 6.2568(5) and 6.1510(5) Å) in the range of Ag···Ag separation in $[Ag_4(\mathbf{2a})_2]^{4+}$.

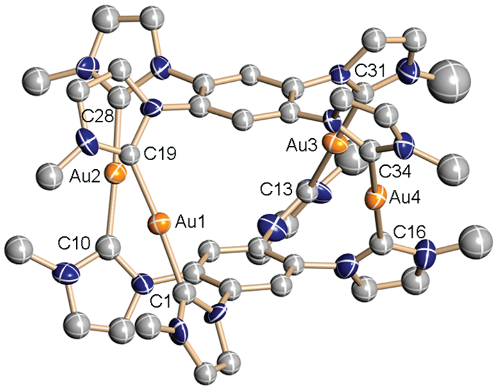
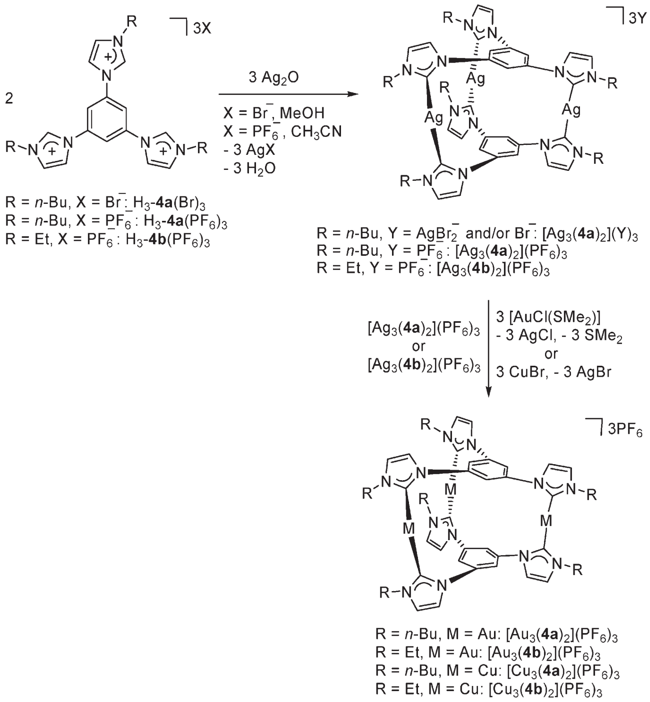


Figure 4. Molecular structure of one of the two independent tetracations $[Au_4(\mathbf{2a})_2]^{4+}$ in the asymmetric unit of $[Au_4(\mathbf{2a})_2](PF_6)_4$ (only the first atoms of the *N*-*n*-Bu substituents are shown, refinement of Au and N with anisotropic and C with isotropic thermal parameters). Selected bond lengths (Å) and angles (deg) for molecule 1 [molecule 2]: range $Au-C_{NHC}$ 1.984(18)−2.065(16) [1.987(16)−2.013(16)], range $C_{NHC}-Au-C_{NHC}$ 175.4(7)−179.9(8) [176.1(7)−178.1(8)], range $N-C_{NHC}-N$ 103.0(14)−106.4(14) [103.3(16)−107.2(17)].

2.3. Synthesis and Characterization of Trinuclear Coinage Metal(I) Carbene Complexes. The trinuclear hexacarbene silver(I) complexes $[Ag_3(\mathbf{4a})_2](Y)_3$ and $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$ have been prepared as described for the analogous tetranuclear silver(I) complexes from the trisimidazolium salts H_3-$\mathbf{4a}(X)_3$ ($X = Br^-$, PF_6^-) or H_3-$\mathbf{4b}(PF_6)_3$ (Scheme 4). Reaction of 3 equiv of Ag_2O with 2 equiv of H_3-$\mathbf{4a}(Br)_3$ (in methanol) or 2 equiv of H_3-$\mathbf{4a,b}(PF_6)_3$ (in acetonitrile) yielded exclusively the cylindrical trisilver hexacarbene complexes $[Ag_3(\mathbf{4a})_2](Y)_3$ ($Y^- = [AgBr_2]^-$ and/or Br^-, PF_6^-) and $[Ag_3(\mathbf{4b})_2](PF_6)_3$, respectively, as colorless solids. No significant amounts of insoluble polymeric compounds have been observed.

Again, the imidazolium groups (or after deprotonation, the imidazolin-2-ylidene donors) that were not preorganized for the formation of the cylindrical structure (Figure 2) rotate in the same direction with respect to the central phenyl ring

Scheme 4. Preparation of Trinuclear Cationic Silver(I) Carbene Complexes $[Ag_3(\mathbf{4a,b})_2]^{3+}$ and Transmetalation to the $[Au_3(\mathbf{4a,b})_2]^{3+}$ and $[Cu_3(\mathbf{4a,b})_2]^{3+}$ Complexes



upon complex formation. The NMR spectra of the silver(I) complexes indicate that highly symmetrical structures were obtained. Similarly to the synthesis of tetranuclear silver(I) complexes (Scheme 3), the counterions in the trisimidazolium salts H$_3$-**4a**,**b**(X)$_3$ (X = Br$^-$, PF$_6^-$) determine the solvent to be used for the synthesis of the trinuclear silver(I) carbene complexes. The solubility of the carbene complex salts [Ag$_3$(**4a**)$_2$](AgBr$_2^-$ and/or Br$^-$)$_3$ and [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ are similar to that of the corresponding tetranuclear silver salts. The silver carbene complex [Ag$_3$(**4a**)$_2$](AgBr$_2^-$ and/or Br$^-$)$_3$ is extremely light sensitive and turned yellowish-red when exposed to light, but the hexafluorophosphate salts [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ are more stable toward light.

Formation of the trinuclear hexacarbene complexes was monitored by both ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In the ^{1}H NMR spectra of the complexes, as expected, the resonances for the C2$-$H imidazolium protons of H$_3$-**4a**,**b**(PF$_6$)$_3$ (δ = 9.15$-$9.89 ppm) are absent. In the ^{13}C{^{1}H} NMR spectra, the C$_{NHC}$ resonances for all three complexes are observed around $\delta \approx 181.0$ ppm instead of the imidazolium C2 carbon resonances for H$_3$-**4a**(PF$_6$)$_3$ (δ = 135.66 ppm) or H$_3$-**4b**(PF$_6$)$_3$ (δ = 136.15 ppm). The C$_{NHC}$ resonance of [Ag$_3$(**4a**)$_2$](AgBr$_2^-$ and/or Br$^-$)$_3$ exhibits coupling to both of the silver isotopes (dd, ^1J(C$-$Ag^{107}) = 182.4 Hz, ^1J(C$-$Ag^{109}) = 209.7 Hz). Additional ^{1}H and ^{13}C{^{1}H} resonances for the trinuclear silver(I) complexes fall in the range previously reported for related silver dicarbene complexes.[27] The ESI mass spectra (positive ions) of both [Ag$_3$(**4a**)$_2$](AgBr$_2^-$ and/or Br$^-$)$_3$ and [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ show the mass of the cationic complex ions [Ag$_3$(**4a**,**b**)$_2$]$^{3+}$ as peaks of high intensity.

Again, the salt with AgBr$_2^-$ and/or Br$^-$ counterions could not be crystallized partly due to its decomposition upon exposure to light in addition to the presence of two different anions. Crystals of [Ag$_3$(**4b**)$_2$](PF$_6$)$_3\cdot$0.5(CH$_3$)$_2$CO$\cdot$0.25EtOH were obtained by diffusion of diethyl ether/ethanol into an aetonitrile/acetone solution of [Ag$_3$(**4b**)$_2$](PF$_6$)$_3$. The structure analysis confirmed the formation of the trinuclear cylindrical complex (Figure 5). The asymmetric unit contains two independent molecules of the cation [Ag$_3$(**4b**)$_2$]$^{3+}$, one of which is shown in Figure 5.

As observed for the tetranuclear complexes, the three imidazolin-2-ylidene rings are not oriented perpendicular to the central phenyl ring. For steric reasons, the imidazolin-2-ylidenes rings of both ligands are rotated from an imaginary perpendicular orientation relative to the central phenyl ring in a clockwise direction. The torsion angles with respect to the central phenyl ring range from 49.296(14)° to 54.352(14)°. These torsion angles are smaller than the corresponding torsion angles in [Ag$_4$(**2a**)$_2$](PF$_6$)$_4$, resulting in a smaller distance between the centroids of the phenyl rings (4.914 Å) than found in [Ag$_4$(**2a**)$_2$](PF$_6$)$_4$. The three silver atoms form a slightly distorted triangle sandwiched in between the two tricarbene ligands with nonbonding Ag$\cdots$Ag separations between 6.0091(3) and 6.1069(4) Å. These intermetallic distances are larger than those in the tetranuclear complexes due to the different substitution pattern of the central phenyl ring.

Bond lengths and angles in the cation [Ag$_3$(**4b**)$_2$]$^{3+}$ fall in the typical range observed previously for linear silver(I) dicarbene complexes.[17,27] The three hexafluorophosphate anions and the solvent molecules do not show any interaction with the complex cation.

Transmetalations of [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ with 3 equiv of CuBr in acetonitrile at ambient temperature yields exclusively the homotrinuclear copper(I) hexacarbene complexes [Cu$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ as white solids in about 70% yield with retention of the metallosupramolecular cylindrical structure (Scheme 4). Formation of heterobimetallic Ag/Cu complexes was ruled out on the basis of mass spectra and the observation of only one C$_{NHC}$ resonance for each complex in the ^{13}C{^{1}H} NMR spectra. When 1 equiv of the complexes [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ was treated with only 2 equiv of CuBr, the trisubstituted complexes [Cu$_3$(**2**)$_2$](PF$_6$)$_3$ were still isolated as the main product. It appears that the synthesis of heterometallic Ag/Cu complexes is not possible by a variation of the stoichiometry of the reagents in the transmetalation reaction.

The C$_{NHC}$ resonances were shifted to δ = 177.66 ppm for [Cu$_3$(**4a**)$_2$](PF$_6$)$_3$ and to δ = 177.46 ppm for [Cu$_3$(**4b**)$_2$](PF$_6$)$_3$, just slightly upfield from the C$_{NHC}$ resonances of the trisilver presursor complexes [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$. Apart from the C$_{NHC}$ resonances, equivalent ^{13}C{^{1}H} NMR spectral parameters of complexes [Ag$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ and [Cu$_3$(**4a**,**b**)$_2$](PF$_6$)$_3$ are essentially identical. The tricopper complexes were also identified by ESI-MS spectrometry with strong peaks observed for the cations [Cu$_3$(**4a**,**b**)$_2$(PF$_6$)$_2$]$^+$.

Crystals of [Cu$_3$(**4b**)$_2$](PF$_6$)$_3$ suitable for an X-ray diffraction analysis have been obtained by slow diffusion of diethyl ether into a saturated solution of the complex in acetonitrile at room temperature. The structure analysis confirmed the formation of the tricopper hexacarbene complex cation (Figure 6). The cation resides on a crystallographic 2-fold axis passing through atom Cu2 and bisecting the Cu1$\cdots$Cu1* vector. The asymmetric unit contains 1/2 formula unit.

Compound [Cu$_3$(**4b**)$_2$](PF$_6$)$_3$ is a rare example of a crystallographically characterized copper(I) polycarbene complex, and only one related tricopper complex featuring two tripodal tricarbene ligands has been described.[29] The Cu$-$C$_{NHC}$

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(29) Hu, X.; Costrao-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755–764.

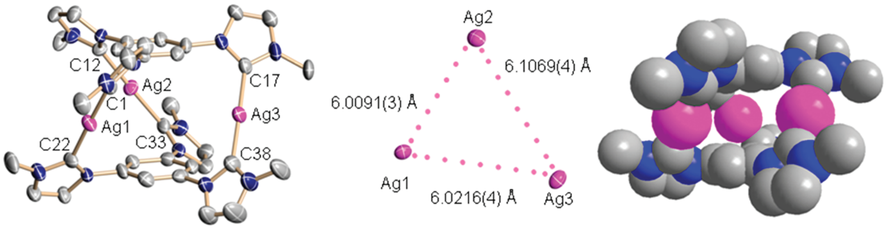


Figure 5. Molecular structure of one of the trications $[Ag_3(\mathbf{4b})_2]^{3+}$ in $[Ag_3(\mathbf{4b})_2](PF_6)_3 \cdot 0.5(CH_3)_2CO \cdot 0.25C_2H_5OH$ (left, hydrogen atoms and solvent molecules have been omitted for clarity, and only the first atom of each of the *N*-ethyl substituents is depicted); view of the triangular arrangement of the three silver ions (middle) and space-filling drawing of the trication (right). Selected bond lengths (Å) and angles (deg) for molecule 1 [molecuel 2]: range Ag$-$C$_{NHC}$ 2.073(7)$-$2.087(7) [2.064(8)$-$2.101(9)], range C$_{NHC}$$-Ag-C_{NHC}$ 176.1(3)$-$178.0(3) [176.5(3)$-$178.9(3)], N$-$C$_{NHC}$$-$N 103.0(6)$-$106.4(6) [102.4(7)$-$105.5(6)].

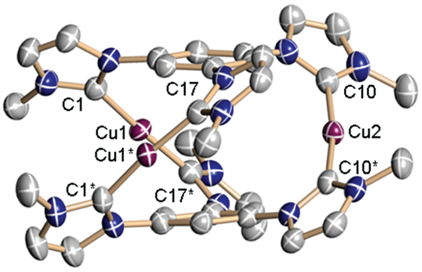


Figure 6. Molecular structure of the trication $[Cu_3(\mathbf{4b})_2]^{3+}$ in $[Cu_3(\mathbf{4b})_2](PF_6)_3$ (hydrogen atoms are omitted for clarity, and only the first atoms of the *N*-ethyl substituents are shown). The molecule resides on a crystallographic 2-fold axis passing through atom Cu2. Selected bond lengths (Å) and angles (deg): range Cu$-$C$_{NHC}$ 1.913(3)$-$1.925(3), range C$_{NHC}$$-Cu-C_{NHC}$ 170.30(12)$-$170.95(17), N$-$C$_{NHC}$$-$N 103.8(2)$-$104.4(3).

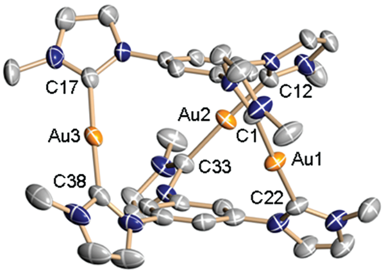


Figure 7. Molecular structure of the trication $[Au_3(\mathbf{4b})_2]^{3+}$ in $[Au_3(\mathbf{4b})_2](PF_6)_3 \cdot 1.5CH_3CN \cdot 0.5Et_2O \cdot 0.5(CH_3)_2CO$ (hydrogen atoms and solvent molecules are omitted for clarity, and only the first atoms of the *N*-ethyl substituents are shown). Selected bond lengths (Å) and angles (deg): range Au$-$C$_{NHC}$ 2.009(5)$-$2.018(6), range C$_{NHC}$$-Au-C_{NHC}$ 176.2(2)$-$177.7(2), N$-$C$_{NHC}$$-$N 104.5(5)$-$105.0(5).

distances [1.913(3)$-$1.925(3) Å] are shorter than the Ag$-$C$_{NHC}$ distances in $[Ag_3(\mathbf{4b})_2](PF_6)_3$ by about 0.15 Å and fall in the range previously reported for related copper dicarbene complexes.[29] In addition and contrary to the equivalent parameter in $[Ag_3(\mathbf{4b})_2](PF_6)_3$, the C$_{NHC}$$-Cu-C_{NHC}$ bond angles [170.30(12)$-$170.95(17)°] deviate significantly from linearity. The combination of the factors of nonlinear angles C$_{NHC}$$-Cu-C_{NHC}$ and short Cu$-$C$_{NHC}$ bond distances along with the small torsion angles for the rotation of the NHC donor planes relative to the plane of the central phenyl ring [38.34(2)$-$46.79(2)°] lead to a significant reduction of the distance between the two phenyl ring centroids to 4.239 Å, which is significantly shorter than the equivalent value (4.914 Å) found for the trisilver complex cation in $[Ag_3(\mathbf{4b})_2](PF_6)_3$. The intramolecular Cu$\cdots$Cu separations [5.9474(7)$-$5.9666(6) Å] are slightly shorter than the Ag$\cdots$Ag distances in $[Ag_3(\mathbf{4b})_2](PF_6)_3$.

The NHC ligands in complexes $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$ can also be transferred to gold(I), yielding complexes $[Au_3(\mathbf{4a,b})_2](PF_6)_3$. The reactions of 1 equiv of $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$ with 3 equiv of $[AuCl(SMe_2)]$ at ambient temperature resulted in the formation of the trinuclear gold(I) carbene complexes as air- and moisture-stable white solid with yields above 60%. The transmetalation reactions can be carried out in air using reagent-grade solvents. This observation indicates that the free carbenes are not intermediates in the transmetalation reaction. As observed in the transmetalation Ag→Cu, formation of heterobimetallic Ag^I/Au^I complexes was ruled out on the basis of ESI-MS spectrometry data showing only the formation of the homotrimetallic gold(I) complexes. In addition, only one C$_{NHC}$ resonance was observed in the $^{13}C\{^1H\}$ NMR spectra of $[Au_3(\mathbf{4a,b})_2](PF_6)_3$ at $\delta \approx 183.5$ ppm. Comparable NMR parameters of $[Au_3(\mathbf{4a,b})_2](PF_6)_3$ are essentially identical to those found for $[Ag_3(\mathbf{4a,b})_2](PF_6)_3$. The trigold complexes were identified by ESI-MS spectrometry, which showed the masses of trications $[Au_3(\mathbf{4a,b})_2]^{3+}$ as intense peaks.

An X-ray diffraction study with crystals of composition $[Au_3(\mathbf{4b})_2](PF_6)_3 \cdot 1.5CH_3CN \cdot 0.5Et_2O \cdot 0.5(CH_3)_2CO$ obtained by slow diffusion of diethyl ether into a saturated solution of $[Au_3(\mathbf{4b})_2](PF_6)_3$ in an acetone/actonitrile solution confirmed the composition and molecular structure of the $[Au_3(\mathbf{4b})_2]^{3+}$ cation (Figure 7).[21] The complex cation $[Au_3(\mathbf{4b})_2]^{3+}$ is essentially isostructural with cation $[Ag_3(\mathbf{4b})_2]^{3+}$. The major differences between the two cations is found in the slightly shorter Au$-$C$_{NHC}$ bond lengths [2.009(5)$-$2.018(6) Å], in agreement with previous reports.[17,27] This leads to a slight reduction of the distance between the centroids of the two phenyl rings in cation $[Au_3(\mathbf{4b})_2]^{3+}$ (4.762 Å) compared to cation $[Ag_3(\mathbf{4b})_2]^{3+}$ (4.914 Å). The Au$\cdots$Au separations [5.9893(6)$-$6.1572(9) Å] in $[Au_3(\mathbf{4b})_2]^{3+}$ are in the range of the Ag$\cdots$Ag separations in $[Ag_3(\mathbf{4b})_2]^{3+}$ but are slightly longer than the Cu$\cdots$Cu separation in cation $[Cu_3(\mathbf{4b})_2]^{3+}$.

Selected geometric parameters of the three trinuclear cations $[M_3(\mathbf{4b})_2]^{3+}$ (M = Ag, Au, Cu) are summarized in Table 1. Contrary to the tetranuclear octacarbene complexes with 1,2-substitution pattern of the central phenyl ring, no bonding intramolecular M$\cdots$M interactions were found in the trinuclear cations $[M_3(\mathbf{4b})_2]^{3+}$ (shortest M$\cdots$M separation 5.9474(7) Å in $[Cu_3(\mathbf{4b})_2]^{3+}$). The intramolecular separation between the phenyl ring centroids depends on the torsion angles between the planes of the phenyl ring and the NHC donors and, to a lesser extend, on the M$-$C$_{NHC}$ bond lengths and the C$_{NHC}$$-M-C_{NHC}$ bond angles.

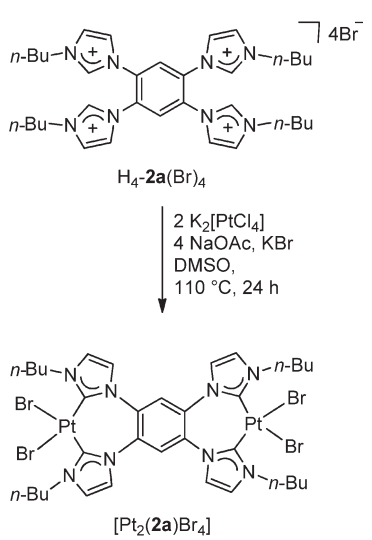
Table 1. Selected Geometric Parameters for Complexes $[M_3(\mathbf{4b})_2](PF_6)_3$ (M = Ag, Cu, Au)

parameter	M = Cu	M = Ag	M = Au
range angles $C_{NHC}-M-C_{NHC}$ (deg)	170.30(12)−170.95(17)	176.1(3)−178.9(3)	176.2(2)−177.7(2)
range lengths (Å) $M-C_{NHC}$	1.913(3)−1.925(3)	2.064(8)−2.101(9)	2.009(5)−2.018(6)
torsion angles (deg) phenyl/NHC	38.34(2)−46.79(2)	49.296(14)−54.352(14)	−43.96(2) to −53.95(2)
distance between centroids of phenyl ring (Å)	4.239	4.914	4.762
separation M···M (Å)	5.9474(7)−5.9666(6)	6.0091(3)−6.1069(4)	5.9893(6)−6.1572(9)

Shionoya et al. described related sandwich-shaped trinuclear silver(I) complexes with two disk-shaped ligands bearing three thiazolyl donor groups (Figure 1, $[\mathbf{A}]^{3+}$).[20] These helical complexes exhibit a dynamic flip motion between the *P* and *M* isomers in solution. The related complexes of type $[M_3(\mathbf{4b})_2](PF_6)_3$ ($M = Ag^I, Au^I, Cu^I$) are similarly built and also helical in nature, but no flip between the *M* and *P* isomers, which both occur in the solid state, was observed in solution. The reason for this difference is not found in the nature of the donor atoms (N vs C_{NHC}) but in the substitution pattern of the ligands. For the thiazolyl ligands, the transition state for the flip motion is assumed to contain N−Ag−N linkages parallel to the helix axis. This situation is easily achieved since the sulfur atoms of the thiazolyl donor groups are not substituted. Complexes of type $[M_3(\mathbf{4b})_2](PF_6)_3$ contain an alkyl-substituted nitrogen atom in α-position to the C_{NHC} donor atom, and these N-substituents appear to prevent a parallel orientation of the $C_{NHC}-M-C_{NHC}$ linkages, thereby preventing an interconversion of the *P* and *M* helical structures.

2.4. Synthesis and Characterization of a Dimetallic Platinum Carbene Complex. In previous studies we and others have noticed that the formation of metallosupramolecular structures from polycarbene ligands and selected metal centers depends on the coordination chemistry of the metal center employed. For example, macrocyclic ligands possessing NHC donors can form sandwich-like metallosupramolecular assemblies with linearly coordinated Ag^I in which the NHC donors rotate out of the plane of the macrocycle and the silver(I) centers are then sandwiched in between two macrocyclic ligands. Coordination of two carbene donors from the same ligand to the linearly coordinated silver(I) is impossible due to geometric constraints of the macrocycle.[17−19,30a,b] Alternatively, metal centers featuring a square-planar coordination geometry like Pd^{II}, Pt^{II}, Rh^I, and Ir^I will allow the coordination of two NHC donors from the same macrocycle to one metal center in *cis*-fashion.[30c−e] We were interested to find out if the coordination chemistry of the tetracarbene ligand obtained from H_4-**2a**$(Br)_4$ can also be influenced by the type of metal center offered. Specifically, we were interested in the coordination chemistry of the tetracarbene ligand **2a** with Pt^{II}. Reaction of H_4-**2a**$(Br)_4$ with 2 equiv of K_2PtCl_4 in the presence of sodium acetate and KBr (to avoid anion scambling) in DMSO gave in good yield of 73% the dinuclear complex $[Pt_2(\mathbf{2a})Br_4]$ (Scheme 5). Air-stable $[Pt_2(\mathbf{2a})Br_4]$ is soluble in polar organic solvents such as DMF, acetonitrile, and DMSO, but insoluble in THF, diethyl ether, and dioxane.

Scheme 5. Preparation of Dinuclear Platinum(II) Tetracarbene Complex $[Pt_2(\mathbf{2a})Br_4]$



Formation of the dinuclear complex $[Pt_2(\mathbf{2a})Br_4]$ was monitored by NMR spectroscopy. The ^1H NMR spectrum of the complex exhibits resonances shifted slightly upfield in comparison to the parent tetraimidazolium salt H_4-**2a**$(Br)_4$ with the imidazolium C2 proton signal missing. The $^{13}C\{^1H\}$ NMR spectrum showed the characteristic C_{NHC} signal at $\delta \approx 150.5$ ppm, well downfield shifted from the C2 resonance of the parent imidazolium salt ($\delta = 138.40$ ppm). Prolonged heating in DMSO was necessary to yield exclusively the complex $[Pt_2(\mathbf{2a})Br_4]$ with two bromide ligands. However, this complex still exhibited two separate sets of NMR signals (70:30), while microanalytical data and ESI-MS spectrometry showed exclusive formation of $[Pt_2(\mathbf{2a})Br_4]$. We attribute this behavior to the presence of two isomeric complexes (*syn* and *anti*).

An X-ray diffraction analysis with crystals of $[Pt_2(\mathbf{2a})Br_4]\cdot 2CH_3CN$ confirmed the composition of the complex (Figure 8). The asymmetric unit contains 1/2 formula unit related to each other half by a crystallographic inversion center located at the midpoint of the central phenyl ring. The platinum atoms are located above and below the plane of the central phenyl ring, and the analyzed crystal therefore was made up from the *anti*-isomer. The *syn*-isomer, featuring both metal atoms at the same side of the phenyl ring, apparently causes the second set of resonances in the NMR spectra, but this isomer was not detected crystallographically. In addition, no interconversion of the isomers was detected by NMR spectroscopy.

The platinum atoms in $[Pt_2(\mathbf{2a})Br_4]$ are surrounded in an almost perfect square-planar fashion by two C_{NHC} and two bromide donors. Two seven-membered chelate rings result from this coordination. The imidazolin-2-ylidene rings are not oriented in a coplanar fashion with respect to the central phenyl ring of the ligand. In fact, they are rotated out of the

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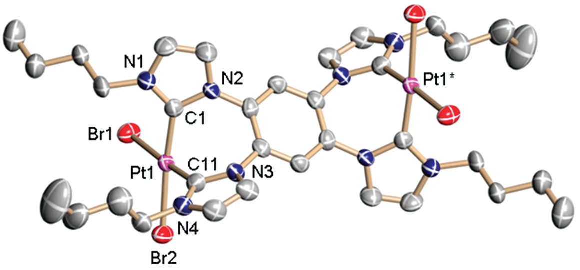

Figure 8. Molecular structure of the $[Pt_2(\mathbf{2a})Br_4]\cdot 2CH_3CN$ (hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths (Å) and angles (deg): Pt1−Br1 2.4887(5), Pt1−Br2 2.4777(5), Pt1−C1 1.956(4), Pt1−C11 1.960(4), N1−C1 1.342(5), N2−C1 1.370(5), N3−C11 1.360(5), N4−C11 1.343(5); Br1−Pt1−Br2 93.28(2), Br1−Pt1−C1 91.33(12), Br1−Pt1−C11 176.20(12), Br2−Pt1−C1 174.67(12), Br2−Pt1−C11 90.52(12), C1−Pt1−C11 84.9(2), N1−C1−N2 104.7(3), N3 − C11−N4 105.4(4).

plane of the central phenyl ring in opposite directions by 55.09° and −55.17°, respectively. These torsion angles are of the magnitude observed for the torsion angles for tricarbene ligand **4b** in the formation of cyclindrical trimetallic structures (see Table 1). However, in the cylinder-like trinuclear structures $[M_3(\mathbf{4b})_2]^{3+}$ (M = Ag^I, Au^I, Cu^I) all imidazolin-2-ylidene donors are rotated in the same direction, leading to a helical structure. To accommodate the platinum atoms with *cis*-coordination of the carbene donors, the planes of the NHC donors in $[Pt_2(\mathbf{2a})Br_4]$ are rotated in different directions relative to the plane of the central phenyl ring. This opposite rotation leads to the positioning of the platinum atoms outside the plane of the central phenyl ring. The differences in the coordination chemistry between linearly coordinated d^{10} metals (Ag^I, Au^I) and square-planar Pt^{II} with *cis*-geometry cause the formation of the two different coordination polyhedra. Metric parameters in $[Pt_2(\mathbf{2a})Br_4]$ resemble those reported for similar platinum complexes with two NHC ligands coordinated in *cis*-fashion.[31]

3. Conclusions

We have developed a straightforward high-yield synthesis of cylindrical polynuclear Ag^I carbene complexes from polyimidazolium salts via metal-controlled self-assembly. The tetra- and trinuclear silver polycarbene complexes undergo transmetalation with $[AuCl(SMe_2)]$ to give the homonuclear Au^I complexes with retention of the three-dimensional structure. In addition, the trisilver(I) NHC complexes undergo transmetalation with CuBr to yield the homonuclear tricopper(I) carbene complexes. The tetrakisimidazolium salt H_4-**2a**$(Br)_4$ reacts after deprotonation with Pt^{II} under formation of a dinuclear complex with two carbene donors coordinating in *cis*-fashion to the metal center. Current studies are directed toward expanding the size of the polycarbene ligands to generate three-dimensional complexes with larger cavities for the encapsulation of selected substrates by purely organometallic supramolecular structures.

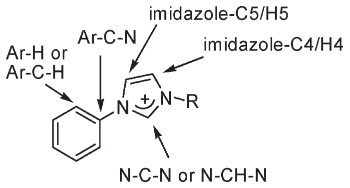

Figure 9. Assignment of NMR resonances.

4. Experimental Section

General Procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox. Glassware was oven-dried at 130 °C. Solvents were freshly distilled by standard procedures prior to use. ^1H, $^{13}C\{^1H\}$, and ^{109}Ag NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard (CD_3CN, ^1H 1.94 ppm and $^{13}C\{^1H\}$ 1.32, 118.26 ppm; CD_3OD, ^1H 3.31 ppm and $^{13}C\{^1H\}$ 49.00 ppm; [d_6]DMSO, ^1H 2.50 ppm and $^{13}C\{^1H\}$ 39.52 ppm; [d_7]DMF, ^1H 2.74, 2.91, 8.02 ppm and $^{13}C\{^1H\}$ 29.90, 35.24, 162.72 ppm). An external standard ($AgNO_3$ in D_2O) was used for recording the ^{109}Ag NMR spectra. All coupling constants are expressed in hertz and only for $^1H-^1H$ coupling unless mentioned otherwise. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen), Quattro LCZ (Waters-Micromass, Manchester, UK), or Varian MAT 212 spectrometers. 1,3,5-Tris(1-imidazolyl)benzene[23] and $[AuCl(SMe_2)]$[32] were prepared as described in the literature. 1,3,5-Tribromobenzene, 1,2,4,5-tetrabromobenzene, imidazole, *n*-butyl bromide, ethyl bromide, Ag_2O, CuBr, and $K_2[PtCl_4]$ were purchased from commercial sources and were used as received without further purification. For assignment of NMR resonances see Figure 9.

Synthesis of 1,2,4,5-Tetrakis(1-imidazolyl)benzene, 1. 1,2,4,5-Tetrabromobenzene (0.788 g, 2.0 mmol), imidazole (1.09 g, 16.0 mmol), K_2CO_3 (1.52 g, 11.0 mmol), and $CuSO_4$ (0.02 g, 0.08 mmol) were mixed in a 50 mL flask and heated under an argon atmosphere for 24 h to 185 °C. The reaction mixture was then cooled to ambient temperature and was washed three times with water. The remaining solid residue was extracted with methanol (70 mL). The methanol solution was decolorized with activated charcoal and filtered. The filtrate was brought to dryness to give a colorless solid. Yield: 0.273 g (0.8 mmol, 40%). ^1H NMR (400 MHz, CD_3OD): δ 8.08 (s, 2H, Ar-H), 7.79 (s, 4H, N−CH-N), 7.22 (s, 4H, imidazole-H5), 7.15 ppm (s, 4H, imidazole-H4). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 138.70 (N-C-N), 134.18 (Ar-C-N), 130.54 (imidazole-C4), 127.52 (Ar-C-H), 121.58 ppm (imidazole-C5). MS (EI, 20 eV): *m*/*z* (%) 341 (100) $[M - H]^+$. Anal. Calcd (%): C, 63.14; H, 4.12; N, 32.74. Found: C, 62.64; H, 3.54; N, 32.52.

Synthesis of 1,3,5-Tris(1-imidazolyl)benzene, 3 (ref 23**).** A 100 mL flask was charged with 1,3,5-tribromobenzene (1.26 g, 4.0 mmol), K_2CO_3 (2.21 g, 16.0 mmol), imidazole (1.63 g, 24.0 mmol), and $CuSO_4$ (0.025 g, 0.10 mmol). The mixture was heated for 24 h to 150 °C under an argon atmosphere. The mixture was then allowed to cool to ambient temperature. It was washed with water (3 × 20 mL). The solid residue was extracted with dichloromethane (3 × 50 mL), and the obtained dichloromethane solution was dried over $MgSO_4$. Removal of the solvent gave 1,3,5-tris(1-imidazolyl)benzene as a colorless solid. Yield: 0.83 g (3.0 mmol, 75%). ^1H NMR (400 MHz, [d_6]DMSO): δ 8.55 (s, 3H, N-CH-N), 8.03 (s, 3H, imidazole-H4/H5), 7.96 (s, 3H, Ar-H), 7.18 ppm (s, 3H, imidazole-H4/H5). $^{13}C\{^1H\}$ NMR (100 MHz, [d_6]DMSO): δ 139.54 (Ar-C-N), 136.57 (N-C-N), 130.56 (imizazole-C4/C5), 118.76 (Ar-C-H), 109.76 ppm

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(imidazole-C4/C5). MS (EI, 20 eV): *m*/*z* (%) 276 (100) $[M]^+$. Anal. Calcd (%): C, 65.20; H, 4.38; N, 30.42. Found: C, 65.27; H, 4.26; N, 30.35. The spectroscopic data match those reported in ref 23.

Synthesis of 1,2,4,5-Tetrakis(3-*n*-butyl-1-imidazolium)benzene Tetrabromide, H_4-2a(Br)$_4$. A sample of 1,2,4,5-tetrakis(1-imidazolyl)benzene (**1**; 0.7 g, 2.05 mmol) was dissolved in DMF (10 mL), and *n*-butyl bromide (2.263 g, 16.4 mmol) was added. The reaction mixture was heated for 40 h at 100 °C, during which time a white precipitate formed. The precipitate was isolated by filtration and washed with diethyl ether. The solid residue was dissolved in methanol and precipitated with diethyl ether to give H_4-**2a**(Br)$_4$ as a colorless solid after drying *in vacuo*. Yield: 1.25 g (1.41 mmol, 69%). ^{1}H NMR (400 MHz, [d_6]DMSO): δ 10.24 (s, 4H, N-CH-N), 8.97 (s, 2H, Ar-H), 8.14 (m, 8H, imidazole-H4 and imidazole-H5), 4.31 (t, ^3J = 7.18 Hz, 8H, NCH_2), 1.90 (m, 8H, NCH_2CH_2), 1.32 (m, 8H, $NCH_2CH_2CH_2$), 0.94 ppm (t, ^3J = 7.35 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_6]-DMSO): δ 138.40 (N-C-N), 130.40 (Ar-C-N), 128.40 (Ar-C-H), 123.60 (imidazole-C4), 122.70 (imidazole-C5), 49.40 (NCH_2), 30.80 (NCH_2CH_2), 18.70 ($CH_2CH_2CH_2$), 13.20 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 284.1987 (calcd for $[H_2\text{-}\mathbf{2a}]^{2+}$ 284.2001). Anal. Calcd (%) for H_4-**2a**(Br)$_4$·$2H_2O$: C, 44.08; H, 5.88; N, 12.10. Found: C, 44.25; H, 5.85; N, 11.75.

Synthesis of 1,2,4,5-Tetrakis(3-*n*-butyl-1-imidazolium)benzene Tetrakis(hexafluorophosphate), H_4-2a(PF$_6$)$_4$. A solution of NH_4PF_6 (0.896 g, 5.5 mmol) in methanol (3 mL) was added slowly to a solution of H_4-**2a**(Br)$_4$ (0.886 g, 1.0 mmol) in methanol (7 mL). The white hexafluorophosphate salt H_4-**2a**(PF$_6$)$_4$ precipitated immediately and was collected by filtration and washed with small portions of cold methanol and diethyl ether. Drying *in vacuo* gave H_4-**2a**(PF$_6$)$_4$ as a colorless solid. Yield: 1.024 g (0.89 mmol, 89%). ^{1}H NMR (400 MHz, [d_6]DMSO): δ 9.55 (s, 4H, N-CH-N), 8.64 (s, 2H, Ar-H), 8.13 (s, 4H, imidazole-H5), 7.91 (s, 4H, imidazole-H4), 4.30 (t, ^3J = 7.18 Hz, 8H, NCH_2), 1.84 (m, 8H, NCH_2CH_2), 1.31 (m, 8H, $CH_2CH_2CH_2$), 0.94 ppm (t, ^3J = 7.36 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_6]DMSO): δ 137.68 (N-C-N), 131.00 (Ar-C-N), 128.18 (Ar-C-H), 124.01 (imidazole-C4), 123.05 (imidazole-C5), 49.59 (NCH_2), 31.03 (NCH_2CH_2), 18.68 ($CH_2CH_2CH_2$), 13.20 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1005.3073 (calcd for $[H_4\text{-}\mathbf{2a}(PF_6)_3]^+$ 1005.3075), 430.1710 (calcd for $[H_4\text{-}\mathbf{2a}(PF_6)_2]^{2+}$ 430.1715), 238.4593 (calcd for $[H_4\text{-}\mathbf{2a}(PF_6)]^{3+}$ 238.4595). Satisfactory microanalytical data for H_4-**2a**(PF$_6$)$_4$ could not be obtained due to the large amount of fluorine present.

Synthesis of 1,2,4,5-Tetrakis(3-ethyl-1-imidazolium)benzene Tetrabromide, H_4-2b(Br)$_4$. A sample of 1,2,4,5-tetrakis(1-imidazolyl)benzene (**1**; 0.5 g, 1.462 mmol) was dissolved in DMF (8 mL), and ethyl bromide (1.275 g, 11.70 mmol) was added. The reaction mixture was heated for 40 h at 100 °C, during which time a white precipitate formed. The precipitate was isolated by filtration and washed with diethyl ether. Yield: 1.0 g (1.286 mmol, 88%). The crude bromide salt H_4-**2b**(Br)$_4$ obtained this way was not further purified but used directly for the preparation of H_4-**2b**(PF$_6$)$_4$.

Synthesis of 1,2,4,5-Tetrakis(3-ethyl-1-imidazolium)benzene Tetrakis-(hexafluorophosphate), H_4-2b(PF$_6$)$_4$. The hexafluorophosphate salt H_4-**2b**(PF$_6$)$_4$ was synthesized as described for the preparation of H_4-**2a**(PF$_6$)$_4$ starting from 1.0 g (1.286 mmol) of H_4-**2b**(Br)$_4$ and 1.152 g (7.07 mmol) of NH_4PF_6 as an off-white powder. Yield: 1.11 g (1.069 mmol, 83%). ^{1}H NMR (400 MHz, CD_3CN): δ 9.12 (s, 4H, N-CH-N), 8.29 (s, 2H, Ar-H), 7.65 (s, 4H, imidazole-H5), 7.48 (s, 4H, imidazole-H4), 4.32 (q, ^3J = 7.3 Hz, 8H, NCH_2), 1.56 ppm (t, ^3J = 7.3 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 137.88 (N-C-N), 133.14 (Ar-C-N), 130.03 (Ar-C-H), 125.34 (imidazole-C4), 124.17 (imidazole-C5), 47.31 (NCH_2), 15.08 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 893.1854 (calcd for $[H_4\text{-}\mathbf{2b}(PF_6)_3]^+$ 893.1826). Satisfactory microanalytical data for H_4-**2b**(PF$_6$)$_4$ could not be obtained due to the large amount of fluorine present.

Synthesis of 1,3,5-Tris(3-*n*-buyl-1-imidazolium)benzene Tribromide, H_3-4a(Br)$_3$. A sample of 1,3,5-tris(1-imidazolyl)benzene **3** (1.2 g, 4.35 mmol) and *n*-butyl bromide (6.0 g, 43.5 mmol) were dissolved in DMF (15 mL) and heated to 100 °C for 2 days. A white precipitate formed during this time, which was isolated by filtration, washed with diethyl ether (3 × 15 mL), and dried *in vacuo* to yield the bromide salt H_3-**4a**(Br)$_3$ as white solid. Yield: 2.10 g (3.05 mmol, 70%). ^{1}H NMR (400 MHz, [d_6]DMSO): δ 10.62 (t, ^4J = 1.4 Hz, 3H, N-CH-N), 8.81 (s, 3H, Ar-H), 8.78 (dd, ^3J = 2.2 Hz, ^4J = 1.4 Hz, 3H, imidazole-H5), 8.23 (dd, ^3J = 2.2 Hz, ^4J = 1.4 Hz, 3H, imidazole-H4), 4.35 (t, ^3J = 7.19 Hz, 6H, NCH_2), 1.97 (m, 6H, NCH_2CH_2), 1.36 (m, 6H, $CH_2CH_2CH_2$), 0.96 ppm (t, ^3J = 7.34 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_6]DMSO): δ 136.34 (Ar-C-N), 136.10 (N-C-N), 123.76 (imidazole-C4), 120.99 (imidazole-C5), 115.35 (Ar-C-H), 49.45 (NCH_2), 30.86 (NCH_2CH_2), 18.76 ($CH_2CH_2CH_2$), 13.22 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 223.1581 (calcd for $[H_2\text{-}\mathbf{4a}]^{2+}$ 223.1579). Anal. Calcd (%) for H_3-**4a**(Br)$_3$·H_2O: C, 45.97; H, 5.86; N, 11.92. Found: C, 45.38; H, 5.70; N, 12.02.

Synthesis of 1,3,5-Tris(3-*n*-buyl-1-imidazolium)benzene Tris-(hexafluorophosphate), H_3-4a(PF$_6$)$_3$. A solution of NH_4PF_6 (0.326 g, 2.0 mmol) in methanol (3 mL) was added slowly to a solution of H_3-**4a**(Br)$_3$ (0.342 g, 0.50 mmol) in methanol (5 mL). The white hexafluorophosphate salt H_3-**4a**(PF$_6$)$_3$ precipitated immediately and was collected by filtration and washed with small portions of cold methanol and diethyl ether. Drying *in vacuo* gave H_3-**4a**(PF$_6$)$_3$ as a colorless solid. Yield: 0.34 g (0.385 mmol, 77%). ^{1}H NMR (400 MHz, [d_6]DMSO): δ 9.89 (t, ^4J = 1.4 Hz, 3H, N-CH-N), 8.51 (s, 3H, Ar-H), 8.41 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 3H, imidazole-H5), 8.20 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 3H, imidazole-H4), 4.35 (t, ^3J = 7.25 Hz, 6H, NCH_2), 1.92 (m, 6H, NCH_2CH_2), 1.38 (m, 6H, $CH_2CH_2CH_2$), 0.97 ppm (t, ^3J = 7.37 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_6]DMSO): δ 136.40 (Ar-C-N), 135.66 (N-C-N), 124.01 (imidazole-C4), 121.12 (imidazole-C5), 116.19 (Ar-C-H), 49.56 (NCH_2), 30.99 (NCH_2CH_2), 18.75 ($CH_2CH_2CH_2$), 13.20 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 737.2500 (calcd for $[H_3\text{-}\mathbf{4a}(PF_6)_2]^+$ 737.2520), 296.1444 (calcd for $[H_3\text{-}\mathbf{4a}(PF_6)]^{2+}$ 296.1439), 223.1582 (calcd for $[H_2\text{-}\mathbf{4a}]^{2+}$ 223.1579). Satisfactory microanalytical data for H_3-**4a**(PF$_6$)$_3$ could not be obtained due to the large amount of fluorine present.

Synthesis of 1,3,5-Tris(3-ethyl-1-imidazolium)benzene Tribromide, H_3-4b(Br)$_3$. A sample of 1,3,5-tris(1-imidazolyl)benzene (**3**; 1.2 g, 4.35 mmol) and ethyl bromide (4.74 g, 43.5 mmol) were dissolved in DMF (15 mL) and heated to 100 °C for 2 days. A white precipitate formed during this time, which was isolated by filtration, washed with diethyl ether (3 × 15 mL), and dried *in vacuo* to yield the crude bromide salt H_3-**4b**(Br)$_3$. Yield: 1.97 g (3.26 mmol, 75%). The crude bromide salt H_3-**4b**(Br)$_3$ was not further purified but used directly for the preparation of H_3-**4b**(PF$_6$)$_3$.

Synthesis of 1,3,5-Tris(3-ethyl-1-imidazolium)benzene Tris-(hexafluorophosphate), H_3-4b(PF$_6$)$_3$. The crude bromide salt H_3-**4b**(Br)$_3$ was converted to H_3-**4b**(PF$_6$)$_3$ by adding a solution of NH_4PF_6 (2.119 g, 13 mmol) in methanol (4 mL) to a methanolic solution (30 mL) of H_3-**4b**(Br)$_3$ (1.97 g, 3.26 mmol). The precipitated white hexafluorophosphate salt was collected by filtration and washed with small portions of cold methanol and diethyl ether. Drying *in vacuo* gave H_3-**4b**(PF$_6$)$_3$ as a colorless solid. Yield: 2.08 g (2.61 mmol, 80%). ^{1}H NMR (400 MHz, CD_3CN): δ 9.15 (s, 3H, N-CH-N), 8.12 (s, 3H, Ar-H), 7.95 (s, 3H, imidazole-H5), 7.73 (s, 3H, imidazole-H4), 4.36 (q, ^3J = 7.33 Hz, 6H, NCH_2), 1.61 ppm (t, ^3J = 7.33 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 138.25 (Ar-C-N), 136.15 (N-C-N), 124.92 (imidazole-C4), 122.87 (imidazole-C5), 119.24 (Ar-C-H), 47.10 (NCH_2), 15.20 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 653.1566 (calcd for $[H_3\text{-}\mathbf{4b}(PF_6)_2]^+$ 653.1575), 254.0961 (calcd for $[H_3\text{-}\mathbf{4b}(PF_6)]^{2+}$ 254.0964). Satisfactory microanalytical data for H_3-**4b**(PF$_6$)$_3$ could not be obtained due to the large amount of fluorine present.

Synthesis of $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{Y})_4$ ($\mathrm{Y} = \mathrm{AgBr_2}^-$ and/or Br^-). A sample of $\mathrm{H_4}$-$\mathbf{2a}(\mathrm{Br})_4$ (0.089 g, 0.1 mmol) was dissolved in methanol (5 mL), and to this solution was added $\mathrm{Ag_2O}$ (0.049 g, 0.21 mmol). The resulting suspension was heated to 50 °C for 24 h under exclusion of light. After cooling to ambient temperature, the obtained suspension was filtered. The filtrate was concentrated to 2 mL, and diethyl ether (10 mL) was added, leading to the formation of a white microcrystalline solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.095 g (0.036 mmol, 72%) (assuming $\mathrm{AgBr_2}^-$ as counterion). ^{1}H NMR (400 MHz, [d_4]MeOH): δ 8.63 (s, 2H, Ar-H), 7.62 (s, 4H, imidazole-H4), 7.41 (s, br, 4H, imidazole-H5), 4.38 (m, 4H, $\mathrm{NC}\mathit{H}\mathrm{H}$), 4.21 (m, 4H, $\mathrm{NCH}\mathit{H}$), 1.93 (m, 8H, $\mathrm{NCH_2C}\mathit{H}_2$), 1.41 (m, 8H, $\mathrm{CH_2CH_2C}\mathit{H}_2$), 1.06 ppm (t, ^3J = 7.36 Hz, 12H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, [d_4]MeOH): δ 182.50 (dd, $^1J(\mathrm{C-Ag^{107}})$ = 184.3 Hz, $^1J(\mathrm{C-Ag^{109}})$ = 212.9 Hz, N-C-N), 137.70 (Ar-C-N), 130.12 (Ar-C-H), 124.70 (imidazole-C5), 124.30 (imidazole-C4), 53.40 ($\mathrm{NCH_2}$), 34.90 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 21.00 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2}$), 14.20 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 391.0995 (calcd for $[\mathrm{Ag_4}(\mathbf{2a})_2]^{4+}$ 391.0969). Consistent microanalytical data for $[\mathrm{Ag_4}(\mathbf{2a})_2]\mathrm{X_4}$ could not be obtained, as the relative amounts of the anions ($[\mathrm{AgBr_2}]^-$ or Br^-) varied.

Synthesis of $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$. A sample of $\mathrm{H_4}$-$\mathbf{2a}(\mathrm{PF_6})_4$ (0.115 g, 0.1 mmol) was dissolved in acetonitrile (7 mL), and to this solution was added $\mathrm{Ag_2O}$ (0.051 g, 0.22 mmol). The suspension was heated to 50 °C under exclusion of light until all of the $\mathrm{Ag_2O}$ was used up. After cooling to ambient temperature, the resulting suspension was filtered. The filtrate was concentrated to 3 mL, and addition of diethyl ether (15 mL) induced precipitation of a white solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.082 g (0.038 mmol, 76%). ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$): δ 7.95 (s, 2H, Ar-H), 7.38 (s, 4H, imidazole-H5), 6.82 (s, br, 4H, imidazole-H4), 4.12−4.16 (m, 8H, $\mathrm{NCH_2}$), 1.79 (m, br, 8H, $\mathrm{NCH_2C}\mathit{H}_2$), 1.28 (m, br, 8H, $\mathrm{CH_2CH_2C}\mathit{H}_2$), 0.94 ppm (t, ^3J = 7.33 Hz, 12H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_3CN}$): δ 181.30 (N-C-N), 136.96 (Ar-C-N), 129.71 (Ar-C-H), 124.31 (imidazole-C5), 118.50 (imidazole-C4), 53.11 ($\mathrm{NCH_2}$), 34.33 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 20.54 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2}$), 14.11 ppm ($\mathrm{CH_3}$). ^{109}Ag NMR (18.63 MHz, $\mathrm{CD_3CN}$): δ 676 ppm. MS (ESI, positive ions): m/z 927.1598 (calcd for $[\mathrm{Ag_4}(\mathbf{2a})_2(\mathrm{PF_6})_2]^{2+}$ 927.1586), 569.7846 (calcd for $[\mathrm{Ag_4}(\mathbf{2a})_2(\mathrm{PF_6})]^{3+}$ 569.7842), 391.1008 (calcd for $[\mathrm{Ag_4}(\mathbf{2a})_2]^{4+}$ 391.0969). Satisfactory microanalytical data for $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ could not be obtained due to the large amount of fluorine.

Synthesis of $[\mathrm{Ag_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$. Complex $[\mathrm{Ag_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ was synthesized as described for the synthesis of $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ from 0.208 g (0.2 mmol) of $\mathrm{H_4}$-$\mathbf{2b}(\mathrm{PF_6})_4$ and 0.096 g (0.414 mmol) of $\mathrm{Ag_2O}$. Yield: 0.134 g (0.07 mmol, 70%). ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$): δ 7.95 (s, 2H, Ar-H), 7.38 (s, 4H, imidazole-H5), 7.09 (s, br, 4H, imidazole-H4), 4.19 (m, 8H, $\mathrm{NCH_2}$), 1.44 ppm (t, ^3J = 7.12 Hz, 12H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_3CN}$): δ 181.4 (dd, $^1J(\mathrm{C-Ag^{107}})$ = 184.54 Hz, $^1J(\mathrm{C-Ag^{109}})$ = 212.07 Hz, N-C-N), 137.35 (Ar-C-N), 129.62 (Ar-C-H), 123.98 (imidazole-C5), 118.41 (imidazole-C4), 48.44 ($\mathrm{NCH_2}$), 17.56 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 815.0343 (calcd for $[\mathrm{Ag_4}(\mathbf{2b})_2(\mathrm{PF_6})_2]^{2+}$ 815.0337). Satisfactory microanalytical data for $[\mathrm{Ag_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ to $[\mathrm{Au_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$. A solution of $[\mathrm{Ag_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ (0.107 g, 0.05 mmol) in acetonitrile (8 mL) was treated with solid $[\mathrm{AuCl(SMe_2)}]$ (0.059 g, 0.2 mmol). During the addition a white and a purple solid precipitated from the reaction mixture. The reaction mixture was stirred at ambient temperature for 12 h and then slowly filtered to get a clear filtrate. The filtrate was added slowly into diethyl ether (20 mL). Upon this addition, a white solid precipitated, which was collected by filtration, washed with diethyl ether, and dried *in vacuo* without heating to give $[\mathrm{Au_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ as a colorless solid. Yield: 0.081 g (0.0324 mmol, 65%). ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$): δ 8.00 (s, 2H, Ar-H), 7.41 (s, br, 8H, imidazole-H4 and imidazole-H5), 4.21 (m, br, 8H, $\mathrm{NCH_2}$), 1.83 (m, br, 8H, $\mathrm{NCH_2C}\mathit{H}_2$), 1.31 (m, br, 8H, $\mathrm{CH_2CH_2C}\mathit{H}_2$), 0.96 ppm (t, ^3J = 7.23 Hz, 12H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_3CN}$): δ 183.91 (N-C-N), 136.30 (Ar-C-N), 130.3 (Ar-C-H), 124.60 (imidazole-C4 and imidazole-C5), 52.50 ($\mathrm{NCH_2}$), 34.20 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 20.50 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2}$), 14.10 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 688.5323 (calcd for $[\mathrm{Au_4}(\mathbf{2a})_2(\mathrm{PF_6})]^{3+}$ 688.5326), 639.8751 (calcd for $[\mathrm{Au_4}(\mathbf{2a})_2\text{-H}]^{3+}$ 639.8753), 480.1578 (calcd for $[\mathrm{Au_4}(\mathbf{2a})_2]^{4+}$ 480.1583). Satisfactory microanalytical data for $[\mathrm{Au_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ could not be obtained due to the large amount of fluorine present. The mass spectrometry data and presence of one N−C−N singnal (singlet) in the ^{13}C{^{1}H} NMR spectrum clearly show the successful transmetalation.

Transmetalation of $[\mathrm{Ag_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ to $[\mathrm{Au_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$. Complex $[\mathrm{Au_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ was synthesized as described for $[\mathrm{Au_4}(\mathbf{2a})_2](\mathrm{PF_6})_4$ from 0.129 g (0.067 mmol) of $[\mathrm{Ag_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ and 0.079 g (0.268 mmol) of $[\mathrm{AuCl(SMe_2)}]$. Yield: 0.10 g (0.044 mmol, 66%). ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$): δ 8.01 (s, 2H, Ar-H), 7.42 (s, br, 8H, imidazole-H4 and imidazole-H5), 4.24 (q, ^3J = 7.15 Hz, 8H, $\mathrm{NCH_2}$), 1.47 ppm (t, ^3J = 7.15 Hz, 12H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_3CN}$): δ 183.99 (N-C-N), 136.51 (Ar-C-N), 130.12 (Ar-C-H), 124.31 (imidazole-C4 and imidazole-C5), 47.88 ($\mathrm{NCH_2}$), 17.32 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 993.1595 (calcd for $[\mathrm{Au_4}(\mathbf{2b})_2(\mathrm{PF_6})_2]^{2+}$ 993.1561). Satisfactory microanalytical data for $[\mathrm{Au_4}(\mathbf{2b})_2](\mathrm{PF_6})_4$ could not be obtained due to the large amount of fluorine present.

Synthesis of $[\mathrm{Ag_3}(\mathbf{4a})_2](\mathrm{Y})_3$ ($\mathrm{Y} = \mathrm{AgBr_2}^-$ and/or Br^-). A sample of $\mathrm{H_3}$-$\mathbf{4a}(\mathrm{Br})_3$ (0.113 g, 0.164 mmol) was dissolved in methanol (6 mL), and to this solution was added $\mathrm{Ag_2O}$ (0.058 g, 0.25 mmol). The resulting suspension was heated to 50 °C under exclusion of light until all of the $\mathrm{Ag_2O}$ was consumed. After cooling to ambient temperature the obtained suspension was filtered. The filtrate was concentrated to 2 mL, and diethyl ether (10 mL) was added to yield a white microcrystalline solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.116 g (0.0574 mmol, 70%) (assuming $\mathrm{AgBr_2}^-$ as counterion). ^{1}H NMR (400 MHz, [d_4]MeOH): δ 8.01 (s, 3H, Ar-H), 7.76 (d, ^3J = 1.88 Hz, 3H, imidazole-H5), 7.67 (d, ^3J = 1.88 Hz, 3H, imidazole-H4), 4.38 (t, ^3J = 6.76 Hz, 6H, $\mathrm{NCH_2}$), 1.96 (m, 6H, $\mathrm{NCH_2C}\mathit{H}_2$), 1.39 (m, 6H, $\mathrm{CH_2CH_2C}\mathit{H}_2$), 1.05 ppm (t, ^3J = 7.37 Hz, 9H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, [d_4]MeOH): δ 181.1 (dd, $^1J(\mathrm{C-Ag^{107}})$ = 182.4 Hz, $^1J(\mathrm{C-Ag^{109}})$ = 209.7 Hz, N-C-N), 143.3 (Ar-C-N), 124.5 (imidazole-C4), 123.6 (imidazole-C5), 122.4 (Ar-C-H), 52.90 ($\mathrm{NCH_2}$), 34.60 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 20.80 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2}$), 14.24 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 629.1565 (calcd for $[\mathrm{Ag_3}(\mathbf{4a})_2\text{-}\mathrm{HCO_2}]^{2+}$ 629.1559), 404.4384 (calcd for $[\mathrm{Ag_3}(\mathbf{4a})_2]^{3+}$ 404.4378). Consistent microanalytical data for $[\mathrm{Ag_3}(\mathbf{4a})_2](\mathrm{Y})_3$ could not be obtained, as the relative amounts of anions ($[\mathrm{AgBr_2}]^-$ or Br^-) varied.

Synthesis of $[\mathrm{Ag_3}(\mathbf{4a})_2](\mathrm{PF_6})_3$. To a mixture of $\mathrm{H_3}$-$\mathbf{4a}(\mathrm{PF_6})_3$ (0.176 g, 0.2 mmol) and $\mathrm{Ag_2O}$ (0.074 g, 0.0.32 mmol) was added acetonitrile (6 mL). The suspension was heated to 60 °C for 24 h under exclusion of light. After cooling to ambient temperature, the suspension obtained was filtered. The filtrate was concentrated to 3 mL, and diethyl ether (15 mL) was added. Upon addition of diethyl ether, a white solid precipitated, which was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.115 g (0.07 mmol, 70%). ^{1}H NMR (400 MHz, $\mathrm{CD_3CN}$): δ 7.86 (s, 3H, Ar-H), 7.55 (d, ^3J = 1.9 Hz, 3H, imidazole-H5), 7.50 (d, ^3J = 1.9 Hz, 3H, imidazole-H4), 4.35 (t, ^3J = 6.80 Hz, 6H, $\mathrm{NCH_2}$), 1.96 (m, 6H, $\mathrm{NCH_2C}\mathit{H}_2$), 1.39 (m, 6H, $\mathrm{CH_2CH_2C}\mathit{H}_2$), 1.06 ppm (t, ^3J = 7.34 Hz, 9H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_3CN}$): δ 181.0 (N-C-N), 142.6 (Ar-C-N), 124.1 (imidazole-C4), 123.1 (imidazole-C5), 122.0 (Ar-C-H), 52.6 ($\mathrm{NCH_2}$), 34.1 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 20.3 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2}$), 14.2 ppm ($\mathrm{CH_3}$). MS (ESI, positive ions): m/z 679.1401 (calcd for $[\mathrm{Ag_3}(\mathbf{4a})_2(\mathrm{PF_6})]^{2+}$ 679.1391), 404.4394 (calcd for $[\mathrm{Ag_3}(\mathbf{4a})_2]^{3+}$ 404.4378). Satisfactory microanalytical data for $[\mathrm{Ag_3}(\mathbf{4a})_2](\mathrm{PF_6})_3$ could not be obtained due to the large amount of fluorine present.

Synthesis of $[\mathrm{Ag_3}(\mathbf{4b})_2](\mathrm{PF_6})_3$. Complex $[\mathrm{Ag_3}(\mathbf{4b})_2](\mathrm{PF_6})_3$ was synthesized as described for $[\mathrm{Ag_3}(\mathbf{4a})_2](\mathrm{PF_6})_3$ from 0.399 g

(0.5 mmol) of H_3-**4b**$(PF_6)_3$ and 0.179 g (0.77 mmol) of Ag_2O. Yield: 0.320 g (0.216 mmol, 86%). ^1H NMR (400 MHz, CD_3CN): δ 7.77 (s, 3H, Ar-H), 7.41 (d, ^3J = 1.92 Hz, 3H, imidazole-H5), 7.40 (d, ^3J = 1.92 Hz, 3H, imidazole-H4), 4.29 (q, ^3J = 7.3 Hz, 6H, NCH_2), 1.51 ppm (t, ^3J = 7.3 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 181.19 (N-C-N), 142.73 (Ar-C-N), 123.54 (imidazole-C4), 123.27 (imidazole-C5), 122.42 (Ar-C-H), 48.18 (NCH_2), 17.41 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1335.0643 (calcd for $[Ag_3(\mathbf{4b})_2(PF_6)_2]^+$ 1335.0551), 595.0459 (calcd for $[Ag_3(\mathbf{4b})_2](PF_6)]^{2+}$ 595.0452), 348.3745 (calcd for $[Ag_3(\mathbf{4b})_2]^{3+}$ 348.3752). Satisfactory microanalytical data for $[Ag_3(\mathbf{4b})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[Ag_3(\mathbf{4a})_2](PF_6)_3$ to $[Cu_3(\mathbf{4a})_2](PF_6)_3$. A solution of CuBr (0.018 g, 0.12 mmol) in 4 mL of acetonitrile was added dropwise to a solution of $[Ag_3(\mathbf{4a})_2](PF_6)_3$ (0.066 g, 0.04 mmol) in 2 mL of acetonitrile. The reaction mixture was left stirring for 12 h at ambient temperature. The resulting suspension was then brought to dryness. The solid residue was taken up in acetone and filtered slowly over Celite. The filtrate was concentrated to 2 mL, and 10 mL of diethyl ether was added, leading to the precipitation of a colorless solid. The precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Yield: 0.42 g (0.028 mmol, 70%). ^1H NMR (400 MHz, CD_3CN): δ 7.90 (s, br, 3H, Ar-H), 7.36 (s, br, 3H, imidazole-H5), 7.29 (d, ^3J = 1.9 Hz, 3H, imidazole-H4), 4.27 (t, ^3J = 6.72 Hz, 6H, NCH_2), 1.90 (m, 6H, NCH_2CH_2), 1.32 (m, 6H, $CH_2CH_2CH_2$), 0.99 ppm (t, ^3J = 7.34 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 177.66 (N-C-N), 141.94 (Ar-C-N), 123.89 (imidazole-C4), 121.54 (imidazole-C5), 118.59 (Ar-C-H), 52.36 (NCH_2), 34.27 (NCH_2CH_2), 20.45 ($CH_2CH_2CH_2$), 14.15 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1369.3133 (calcd for $[Cu_3(\mathbf{4a})_2(PF_6)_2]^+$ 1369.3151), 539.1881 (calcd for $[Cu_3(\mathbf{4a})_2-H]^{2+}$ 539.1892). Satisfactory microanalytical data for $[Cu_3(\mathbf{4a})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[Ag_3(\mathbf{4b})_2](PF_6)_3$ to $[Cu_3(\mathbf{4b})_2](PF_6)_3$. Complex $[Cu_3(\mathbf{4b})_2](PF_6)_3$ was prepared as described for $[Cu_3(\mathbf{4a})_2](PF_6)_3$ from $[Ag_3(\mathbf{4b})_2](PF_6)_3$ (0.080 g, 0.054 mmol) and CuBr (0.023 g, 0.162 mmol) in acetonitrile. Yield: 0.050 g (0.037 mmol, 68.5%). ^1H NMR (400 MHz, CD_3CN): δ 7.86 (s, 3H, Ar-H), 7.35 (s, 3H, imidazole-H5), 7.33 (s, 3H, imidazole-H4), 4.30 (q, ^3J = 6.96 Hz, 6H, NCH_2), 1.53 ppm (t, ^3J = 6.96 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 177.46 (N-C-N), 142.08 (Ar-C-N), 123.42 (imidazole-C4), 121.73 (imidazole-C5), 119.25 (Ar-C-H), 47.70 (NCH_2), 17.51 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1201.1262 (calcd for $[Cu_3(\mathbf{4b})_2(PF_6)_2]^+$ 1201.1285), 528.0807 (calcd for $[Cu_3(\mathbf{4b})_2(PF_6)]^{2+}$ 528.0813). Satisfactory microanalytical data for $[Cu_3(\mathbf{4b})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[Ag_3(\mathbf{4a})_2](PF_6)_3$ to $[Au_3(\mathbf{4a})_2](PF_6)_3$. A sample of $[Ag_3(\mathbf{4a})_2](PF_6)_3$ (0.077 g, 0.047 mmol) was dissolved in acetonitrile (6 mL), and to this solution was added solid $[AuCl(SMe_2)]$ (0.042 g, 0.141 mmol). A white solid started to precipitate immediately. The mixture was left stirring at ambient temperature for 12 h. The reaction mixture was then filtered until a clear filtrate was obtained. The filtrate was added slowly to diethyl ether (20 mL) to obtain a white microcrystalline solid, which was collected by filtration, washed with diethyl ether, and dried *in vacuo* without heating. Yield: 0.056 g (0.0291 mmol, 62%). ^1H NMR (400 MHz, CD_3CN): δ 7.85 (s, 3H, Ar-H), 7.42 (d, ^3J = 2.0 Hz, 3H, imidazole-H5), 7.41 (d, ^3J = 2.0 Hz, 3H, imidazole-H4), 4.32 (t, ^3J = 6.75 Hz, 6H, NCH_2), 1.93 (m, 6H, NCH_2CH_2), 1.34 (m, 6H, $CH_2CH_2CH_2$), 0.96 ppm (t, ^3J = 7.19 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 183.5 (N-C-N), 141.16 (Ar-C-N), 124.1 (imidazole-C4), 123.7 (Ar-C-H), 123.4 (imidazole-C5), 52.26 (NCH_2), 33.95 (NCH_2CH_2), 20.39 ($CH_2CH_2CH_2$), 14.13 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1769.4313 (calcd for $[Au_3(\mathbf{4a})_2](PF_6)_2]^+$ 1769.4278), 812.2331 (calcd for $[Au_3(\mathbf{4a})_2](PF_6)]^{2+}$ 812.2315), 493.1667 (calcd for $[Au_3(\mathbf{4a})_2]^{3+}$ 493.1666). Satisfactory microanalytical data for $[Au_3(\mathbf{4a})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present. The mass spectrometry data and the presence of one N-C-N singnal in the $^{13}C\{^1H\}$ NMR spectrum show the successful transmetalation.

Transmetalation of $[Ag_3(\mathbf{4b})_2](PF_6)_3$ to $[Au_3(\mathbf{4b})_2](PF_6)_3$. Complex $[Au_3(\mathbf{4b})_2](PF_6)_3$ was prepared as described for $[Au_3(\mathbf{4a})_2](PF_6)_3$ from $[Ag_3(\mathbf{4b})_2](PF_6)_3$ (0.104 g, 0.07 mmol) and $[AuCl(SMe_2)]$ (0.062 g, 0.21 mmol) in acetonitrile. Yield: 0.073 g (0.042 mmol, 60%). ^1H NMR (400 MHz, CD_3CN): δ 7.81 (s, 3H, Ar-H), 7.43 (d, ^3J = 1.98 Hz, 3H, imidazole-H5), 7.35 (d, ^3J = 1.98 Hz, 3H, imidazole-H4), 4.36 (m, 6H, NCH_2), 1.57 ppm (t, ^3J = 7.29 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 183.67 (N−C−N), 141.36 (Ar-C-N), 124.15 (imidazole-C4), 123.65 (Ar-C-H), 123.61 (imidazole-C5), 47.75 (NCH_2), 17.12 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1601.2362 (calcd for $[Au_3(\mathbf{4b})_2](PF_6)_2]^+$ 1601.2405), 728.1372 (calcd for $[Au_3(\mathbf{4b})_2](PF_6)]^{2+}$ 728.1381), 437.1033 (calcd for $[Au_3(\mathbf{4b})_2]^{3+}$ 437.1040). Satisfactory microanalytical data for $[Au_3(\mathbf{4b})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present. The mass spectrometry data and the presence of one N-C-N signal in the $^{13}C\{^1H\}$ NMR spectrum show the successful transmetalation.

Synthesis of $[Pt_2(\mathbf{2a})Br_4]$. A sample of $K_2[PtCl_4]$ (0.166 g, 0.4 mmol), tetraimidazolium salt H_4-**2a**$(Br)_4$ (0.177 g, 0.2 mmol), sodium bromide (0.082 g, 0.8 mmol), and sodium acetate (0.074 g, 0.90 mmol) were dissolved in DMSO (8 mL) and stirred for 24 h at 110 °C. After cooling of the reaction mixture to ambient temperature all solvents were removed *in vacuo*. The solid residue was taken up in 20 mL of acetonitrile and filtered over Celite. A clear solution was obtained, which was concentrated to about 50%, and diethyl ether was added until precipitation occurred. The precipitate was isolated by filtration, washed with a methanol/diethyl ether mixture (1:2, v/v), and dried *in vacuo*. Yield: 0.186 g (0.146 mmol, 73%). ^1H NMR (400 MHz, [d_7]DMF), for the major isomer: δ 8.45 (s, 2H, Ar-H), 8.07 (d, 4H, ^3J = 1.99 Hz, imidazole-H4), 7.86 (d, ^3J = 1.99 Hz, 4H, imidazole-H5), 4.76 (m, br, 4H, NC*H*H), 4.47 (m, br, 4H, NCH*H*), 2.01 (m, br, 8H, NCH_2CH_2), 1.45 (m, 8H, $CH_2CH_2CH_2$), 0.99 ppm (t, ^3J = 7.30 Hz, 12H, CH_3); for the minor isomer (30%): δ 8.42 (d, 4H, ^3J = 1.98 Hz, imidazole-H5), 8.33 (s, 2H, Ar-H), 7.85 (d, ^3J = 1.98 Hz, 4H, imidazole-H4), 4.74 (m, br, 4H, NC*H*H), 4.45 (m, br, 4H, NCH*H*), 2.01 (m, br, 8H, NCH_2CH_2), 1.45 (m, 8H, $CH_2CH_2CH_2$), 0.97 ppm (t, ^3J = 7.32 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_7]DMF), for the major isomer: δ 150.50 (N-C-N), 134.50 (Ar-C-N), 125.80 (Ar-C-H), 124.07 (imidazole-C4), 123.30 (imidazole-C5), 51.20 (NCH_2), 32.83 (NCH_2CH_2), 20.40 ($CH_2CH_2CH_2$), 13.90 ppm (CH_3); for the minor isomer: δ 150.9 (N-C-N), 134.4 (Ar-C-N), 125.6 (Ar-C-H), 124.13 (imidazole-C5), 123.30 (imidazole-C4), 51.10 (NCH_2), 32.77 (NCH_2CH_2), 20.30 ($CH_2CH_2CH_2$), 13.90 ppm (CH_3). MS (ESI, positive ions): *m*/*z* 1298.9750 (calcd for $[Pt_2(\mathbf{2a})Br_4 + Na]^+$ 1298.9722), 1229.0989 (calcd for $[Pt_2(\mathbf{2a})Br_3 + MeOH]^+$ 1229.0913), 1197.0678 (calcd for $[Pt_2(\mathbf{2a})Br_3]^+$ 1197.0650), 660.9806 (calcd for $[Pt_2(\mathbf{2a})Br_4 + 2Na]^{2+}$ 660.9807), 609.5286 (calcd for $[Pt_2(\mathbf{2a})Br_3 + Na]^{2+}$ 609.5273), 558.0745 (calcd for $[Pt_2(\mathbf{2a})Br_2]^{2+}$ 558.0735). Anal. Calcd (%) for $[Pt_2(\mathbf{2a})Br_4]$: C, 31.99; H, 3.63; N, 8.78. Found: C, 32.01; H, 3.85; N, 9.01.

X-ray Crystal Structure Determinations. X-ray diffraction data were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using either graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) or Mo Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97[33] package using direct methods and were refined with SHELXL-97[33] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms (for

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(33) *SHELXS-97*, *SHELXL-97*: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models on calculated positions.

H_4-2a$(PF_6)_4\cdot CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of H_4-**2a**$(PF_6)_4$. $C_{36}H_{61}N_9F_{24}P_4$, $M = 1199.82$, colorless crystal, $0.15 \times 0.08 \times 0.06$ mm^3, triclinc, space group $P\bar{1}$, $Z = 2$, $a = 13.0970(6)$ Å, $b = 13.8225(6)$ Å, $c = 14.2153(7)$ Å, $\alpha = 93.647(3)°$, $\beta = 103.371(4)°$, $\gamma = 93.993(3)°$, $V = 2489.2(2)$ Å^3, $\rho_{calc} = 1.601$ g$\cdot$cm^{-3}, Cu Kα radiation ($\lambda = 1.54178$ Å), $\mu = 2.596$ mm^{-1}, ω- and φ-scans, 14 356 measured intensities ($6.4° \leq 2\theta \leq 144.8°$), semiempirical absorption correction ($0.697 \leq T \leq 0.860$), 8375 independent ($R_{int} = 0.0575$) and 6584 observed intensities ($I \geq 2\sigma(I)$), refinement of 673 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0877$, $wR = 0.2404$, $R_{all} = 0.1030$, $wR_{all} = 0.2589$. The asymmetric unit contains two independent halves of the cation, four PF_6^- anions, and one acetonitrile molecule.

H_3-4b$(PF_6)_3\cdot CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of H_3-**4b**$(PF_6)_3$. $C_{23}H_{30}N_7F_{18}P_3$, $M = 839.45$, colorless crystal, $0.14 \times 0.14 \times 0.06$ mm^3, triclinc, space group $P\bar{1}$, $Z = 2$, $a = 11.1538(4)$ Å, $b = 13.5610(4)$ Å, $c = 13.7856(4)$ Å, $\alpha = 110.253(2)°$, $\beta = 95.935(3)°$, $\gamma = 114.094(2)°$, $V = 1711.35(9)$ Å^3, $\rho_{calc} = 1.629$ g$\cdot$cm^{-3}, Cu Kα radiation ($\lambda = 1.54178$ Å), $\mu = 2.793$ mm^{-1}, ω- and φ-scans, 9898 measured intensities ($7.1° \leq 2\theta \leq 143.0°$), semiempirical absorption correction ($0.696 \leq T \leq 0.850$), 5731 independent ($R_{int} = 0.0429$) and 4427 observed intensities ($I \geq 2\sigma(I)$), refinement of 467 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0595$, $wR = 0.1674$, $R_{all} = 0.0725$, $wR_{all} = 0.1768$. The asymmetric unit contains one formula unit.

$[Ag_4(2a)_2](PF_6)_4\cdot 2CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of $[Ag_4(\mathbf{2a})_2](PF_6)_4$. $C_{72}H_{98}N_{18}Ag_4F_{24}P_4$, $M = 2227.04$, colorless crystal, $0.18 \times 0.05 \times 0.03$ mm^3, monoclinc, space group $P2_1/n$, $Z = 4$, $a = 13.6501(6)$ Å, $b = 34.1296(14)$ Å, $c = 20.1054(8)$ Å, $\beta = 99.1950(10)°$, $V = 9246.2(7)$ Å^3, $\rho_{calc} = 1.600$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.002$ mm^{-1}, ω- and φ-scans, 94 622 measured intensities ($2.4° \leq 2\theta \leq 56.0°$), semiempirical absorption correction ($0.840 \leq T \leq 0.971$), 22 312 independent ($R_{int} = 0.0728$) and 14 468 observed intensities ($I \geq 2\sigma(I)$), refinement of 1108 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0508$, $wR = 0.1093$, $R_{all} = 0.0952$, $wR_{all} = 0.1287$. The asymmetric unit contains one formula unit. The terminal carbon atoms of some of the *N-n*-butyl substituents exhibit large anisotropic thermal parameters due to strong thermal motion. A potential disorder of these atoms could not be resolved.

$[Au_4(2a)_2](PF_6)_4$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of $[Au_4(\mathbf{2a})_2](PF_6)_4$. $C_{68}H_{92}N_{16}Au_4F_{24}P_4$, $M = 2501.32$, colorless crystal, $0.12 \times 0.07 \times 0.03$ mm^3, monoclinic, space group Pn, $Z = 4$, $a = 13.5089(10)$ Å, $b = 35.940(3)$ Å, $c = 19.3128(15)$ Å, $\beta = 92.0560(10)°$, $V = 9370.5(12)$ Å^3, $\rho_{calc} = 1.773$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 6.404$ mm^{-1}, ω- and φ-scans, 108 649 measured intensities ($1.1° \leq 2\theta \leq 60.0°$), semiempirical absorption correction ($0.514 \leq T \leq 0.831$), 52 753 independent ($R_{int} = 0.0655$) and 30 540 observed intensities ($I \geq 2\sigma(I)$), refinement of 1170 parameters against $|F^2|$ of all measured intensities. No hydrogen positions were added to the structure model. $R = 0.0791$, $wR = 0.2136$, $R_{all} = 0.1497$, $wR_{all} = 0.2539$. The asymmetric unit contains two formula units. In spite of the collection of multiple data sets, refinement did not proceed satisfactorily. Refinement was therefore carried out with anisotropic thermal parameters for atoms Au, P, and N, while the positional parameters for fluorine and carbon atoms were refined with isotropic thermal parameters. No hydrogen atoms were added to the structure model. The refinement allows the determination of the composition and geometry of the compound, while it is not sufficient for a detailed discussion of bond lengths and angles.

$[Ag_3(4b)_2](PF_6)_3\cdot 0.5(CH_3)_2CO\cdot 0.25EtOH$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether/ethanol into a saturated acetone/acetonitrile solution of $[Ag_3(\mathbf{4b})_2](PF_6)_3$. $C_{44}H_{52.5}N_{12}Ag_3F_{18}O_{0.75}P_3$, $M = 1520.00$, colorless crystal, $0.21 \times 0.13 \times 0.09$ mm^3, monoclinc, space group $C2$, $Z = 8$, $a = 34.493(2)$ Å, $b = 19.0350(13)$ Å, $c = 21.5033(15)$ Å, $\beta = 100.2160(10)°$, $V = 13895(2)$ Å^3, $\rho_{calc} = 1.453$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 0.992$ mm^{-1}, ω- and φ-scans, 81 217 measured intensities ($2.4° \leq 2\theta \leq 60.0°$), semiempirical absorption correction ($0.819 \leq T \leq 0.916$), 39 289 independent ($R_{int} = 0.0422$) and 28 304 observed intensities ($I \geq 2\sigma(I)$), refinement of 1410 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0673$, $wR = 0.1812$, $R_{all} = 0.1003$, $wR_{all} = 0.2089$. The asymmetric unit contains two molecules of $[Ag_3(\mathbf{4b})_2](PF_6)_3$, 1/2 molecule of ethanol, and one acetone molecule.

$[Cu_3(4b)_2](PF_6)_3$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of $[Cu_3(\mathbf{4b})_2](PF_6)_3$. $C_{42}H_{48}N_{12}Cu_3F_{18}P_3$, $M = 1346.45$, colorless crystal, $0.18 \times 0.12 \times 0.09$ mm^3, monoclinc, space group $C2/c$, $Z = 4$, $a = 19.720(3)$ Å, $b = 19.109(3)$ Å, $c = 15.484(2)$ Å, $\beta = 109.025(2)°$, $V = 5516.2(13)$ Å^3, $\rho_{calc} = 1.621$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.338$ mm^{-1}, ω- and φ-scans, 31 963 measured intensities ($3.1° \leq 2\theta \leq 60.0°$), semiempirical absorption correction ($0.795 \leq T \leq 0.889$), 8058 independent ($R_{int} = 0.0214$) and 6459 observed intensities ($I \geq 2\sigma(I)$), refinement of 361 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0520$, $wR = 0.1424$, $R_{all} = 0.0659$, $wR_{all} = 0.1562$. The cation resides on a crystallographic 2-fold axis passing through atom Cu2 and bisecting the Cu1$\cdots$Cu1* vector. The asymmetric unit contains 1/2 formula unit.

$[Au_3(4b)_2](PF_6)_3\cdot 1.5CH_3CN\cdot 0.5Et_2O\cdot 0.5(CH_3)_2CO$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetone/acetonitrile solution of $[Au_3(\mathbf{4b})_2](PF_6)_3$. $C_{48.5}H_{60.5}N_{13.5}Au_3F_{18}OP_3$, $M = 1874.41$, colorless crystal, $0.27 \times 0.13 \times 0.03$ mm^3, monoclinc, space group $P2_1/c$, $Z = 4$, $a = 15.020(2)$ Å, $b = 21.071(3)$ Å, $c = 22.150(3)$ Å, $\beta = 90.546(2)°$, $V = 7010(2)$ Å^3, $\rho_{calc} = 1.776$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 6.422$ mm^{-1}, ω- and φ-scans, 81 172 measured intensities ($2.7° \leq 2\theta \leq 60.0°$), semiempirical absorption correction ($0.276 \leq T \leq 0.831$), 20 444 independent ($R_{int} = 0.0386$) and 15 487 observed intensities ($I \geq 2\sigma(I)$), refinement of 781 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0392$, $wR = 0.1019$, $R_{all} = 0.0605$, $wR_{all} = 0.1135$. The asymmetric unit contains one formula unit. Positional parameters for the atoms of solvent molecules in the asymmetric unit ($3 \times 1/2$ CH_3CN, 1/2 $(CH_3)_2CO$, and 1/2 Et_2O, SOF = 1/2 for all solvent atoms) have been refined with isotropic thermal parameters, and no hydrogen positions have been calculated for the solvent molecules.

$[Pt_2(2a)Br_4]\cdot 2CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by cooling a saturated acetonitrile solution of $[Pt_2(2a)Br_4]$. $C_{38}H_{52}N_{10}Br_4Pt_2$, $M = 1358.72$, colorless crystal, $0.09 \times 0.05 \times 0.05$ mm^3, triclinc, space group $P\bar{1}$, $Z = 2$, $a = 12.5950(8)$ Å, $b = 14.1932(9)$ Å, $c = 14.3770(9)$ Å, $\alpha = 73.4480(10)°$, $\beta = 87.0100(10)°$, $\gamma = 66.5510(10)°$, $V = 2254.6(2)$ Å^3, $\rho_{calc} = 2.001$ g$\cdot$cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 9.781$ mm^{-1}, ω- and φ-scans, 25 570 measured intensities ($3.0° \leq 2\theta \leq 59.0°$), semiempirical absorption correction ($0.473 \leq T \leq 0.641$), 12 468 independent ($R_{int} = 0.0267$) and 10 164 observed intensities ($I \geq 2\sigma(I)$), refinement of 493 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0310$, $wR = 0.0752$, $R_{all} = 0.0432$, $wR_{all} = 0.0801$. The asymmetric unit contains two independent halves of the formula unit related to the other halves by a crystallographic inversion center at the midpoint of the central phenyl ring.

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Supporting Information Available: X-ray crystalographic files for H_4-**2a**$(PF_6)_4 \cdot CH_3CN$, H_3-**4b**$(PF_6)_3 \cdot CH_3CN$, $[Ag_4($**2a**$)_2](PF_6)_4 \cdot 2CH_3CN$, $[Au_4($**2a**$)_2](PF_6)_4$, $[Ag_3($**4b**$)_2](PF_6)_3 \cdot 0.5(CH_3)_2CO \cdot 0.25EtOH$, $[Cu_3($**4b**$)_2](PF_6)_3$, $[Au_3($**4b**$)_2](PF_6)_3 \cdot 1.5CH_3CN \cdot 0.5Et_2O \cdot 0.5(CH_3)_2CO$, and $[Pt_2($**2a**$)Br_4] \cdot 2CH_3CN$ (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.