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Self-Assembly of Molecular Cylinders from Polycarbene Ligands and Ag^I or Au^I

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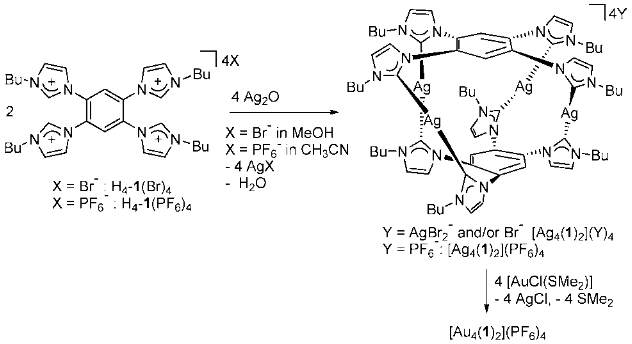
The formation of supramolecular structures via metal-directed self-assembly has become a field of intensive research initiated with the first report on dinuclear helicates obtained from Cu^I and 2,2′-bipyridine.[1] Subsequently, a large number of metallosupramolecular structures have been described.[2] Some of these can act as molecular hosts by encapsulating small molecular guests, which might undergo selective chemical transformations within the host molecule.[3] Most of the known “molecular containers” have been built from Werner-type metal centers (i.e., metal centers coordinated by nitrogen and/or oxygen donor atoms). Metallosupramolecular structures containing ligands with carbon donor atoms are rare,[2e] although some examples of such structures with bridging diisocyanides,[4] acyclic diaminocarbenes,[5a] or remote N-heterocyclic carbene (NHC) ligands[5b] are known. Metallosupramolecular structures derived from the ubiquitous NHC ligands[6] have been unknown until recently.

In our search for macrocyclic ligands with carbene donor groups,[7] we serendipitously prepared the first three-dimensional metallosupramolecular assembly featuring exclusively M−C(NHC) bonds[7b] from two hexa-NHC ligands and six silver(I) ions. This was followed by the planned preparation of a molecular rectangle[8] from two 4,4′-bipyridine and two rigid ditopic benzobis-NHC ligands.[9] In this contribution, we describe the use of in situ-generated poly-NHC ligands for the generation of cylindrical structures containing three or four silver atoms sandwiched between two tri- or tetra-NHC ligands.

The tetraimidazolium salts H_4-**1**$(X)_4$ ($X = Br^-$, PF_6^-; Scheme 1) were prepared by the reaction of imidazole with 1,2,4,5-tetrabromobenzene followed by alkylation of the remaining free imine with *n*-butyl bromide and, for H_4-**1**$(PF_6)_4$, anion exchange with NH_4PF_6 (see the Supporting Information). Salt H_4-**1**$(Br)_4$ is soluble only in methanol and dimethyl sulfoxide (DMSO), while H_4-**1**$(PF_6)_4$ is freely soluble in acetonitrile and acetone. These solubility differences determine the choice of solvent for the subsequent preparation of the silver complexes. The reactions of 4 equiv of Ag_2O with 2 equiv of H_4-**1**$(Br)_4$ (in methanol) and 2 equiv of H_4-**1**$(PF_6)_4$ (in acetonitrile) yielded the cyclindrical tetrasilver octacarbene complexes $[Ag_4(\mathbf{1})_2](Y)_4$ ($Y^- = [AgBr_2]^-$ and/or Br^-) and $[Ag_4(\mathbf{1})_2](PF_6)_4$, respectively, in ∼70% yield as white solids (Scheme 1). While salt $[Ag_4(\mathbf{1})_2](Y)_4$ is extremely sensitive toward light and soluble only in methanol and DMSO, the hexafluorophosphate salt $[Ag_4(\mathbf{1})_2](PF_6)_4$ is stable toward light and soluble in acetonitrile and acetone.

Formation of the carbene complexes $[Ag_4(\mathbf{1})_2](Y)_4$ and $[Ag_4(\mathbf{1})_2](PF_6)_4$ was confirmed by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra, for example, the resonance for the C2−H imidazolium proton in H_4-**1**$(PF_6)_4$ (9.55 ppm) disappeared upon complex formation. The imidazolium C2 resonance for H_4-**1**$(PF_6)_4$ (137.68 ppm) was absent in the ^{13}C NMR spectrum of $[Ag_4(\mathbf{1})_2](PF_6)_4$, and a new carbene resonance was observed at 181.30 ppm. This resonance was found at 182.50 ppm in the ^{13}C NMR spectrum of $[Ag_4(\mathbf{1})_2](Y)_4$, showing the rarely observed coupling to both silver isotopes [dd, $^1J(C{-}Ag^{107}) = 184.3$ Hz, $^1J(C{-}Ag^{109}) = 212.9$ Hz].[7b] The positive-ion electrospray ionization (ESI) mass spectra of both $[Ag_4(\mathbf{1})_2](Y)_4$ and $[Ag_4(\mathbf{1})_2](PF_6)_4$ showed the mass of the cationic complex ion $[Ag_4(\mathbf{1})_2]^{4+}$ as the peak of highest intensity.

Scheme 1. Preparation of Compounds $[Ag_4(\mathbf{1})_2](Y)_4$ ($Y = [AgBr_2]^-$, Br^-, PF_6^-) and Synthesis of $[Au_4(\mathbf{1})_2](PF_6)_4$



Crystallization of $[Ag_4(\mathbf{1})_2](Y)_4$ proved to be impossible because of its sensitivity to light and the different anions present. Crystals of $[Ag_4(\mathbf{1})_2](PF_6)_4 \cdot 2CH_3CN$ were grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of the salt at room temperature. The structure analysis (Figure 1) confirmed the formation of the cylindrical tetrasilver octacarbene complex cation, which exhibits some structural relationship to the assemblies of metal ions between disk-shaped template ligands reported by Shionoya.[10]

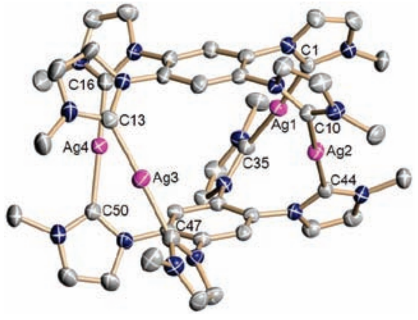


Figure 1. Molecular structure of the tetracation $[Ag_4(\mathbf{1})_2]^{4+}$ in $[Ag_4(\mathbf{1})_2](PF_6)_4 \cdot 2CH_3CN$ (hydrogen atoms have been omitted for clarity, and only the first atom of each *N*-*n*Bu substituent is depicted).

The metric parameters found in the $[Ag_4(\mathbf{1})_2]^{4+}$ cation [$Ag{-}C_{carbene}$, 2.073(4)−2.089(4) Å; $C_{carbene}{-}Ag{-}C_{carbene}$, 175.2(2)−178.5(2)°] fall in the ranges previously described for linear dicarbene silver complexes.[11] The four silver atoms form an essentially planar rectangle featuring two short [Ag1−Ag2, 3.4032(1)

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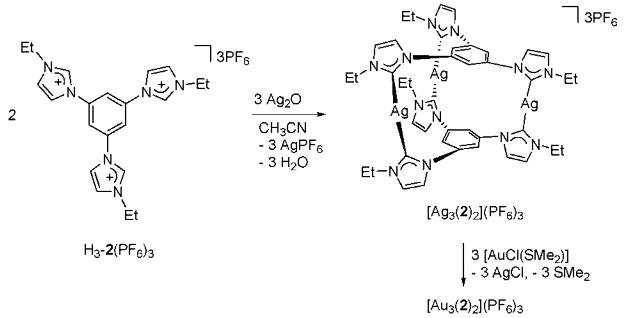
Å; Ag3−Ag4, 3.5207(2) Å] and two long [Ag2−Ag3, 5.8373(2) Å; Ag1−Ag4, 5.9592(2) Å] Ag···Ag separations.

Silver NHC complexes are excellent carbene transfer agents.[12] All four silver atoms in $[Ag_4(\mathbf{1})_2](PF_6)_4$ can be substituted by Au^I to give $[Au_4(\mathbf{1})_2](PF_6)_4$ in 65% yield without destruction of the supramolecular structure. Complete conversion was achieved by stirring a mixture of $[Ag_4(\mathbf{1})_2](PF_6)_4$ and 4 equiv of $[AuCl(SMe_2)]$ in acetonitrile for 12 h (Scheme 1). Complex $[Au_4(\mathbf{1})_2](PF_6)_4$ was characterized by NMR spectroscopy and mass spectrometry. The ^{13}C NMR spectrum showed the resonance for the carbene carbon atoms shifted only slightly to 183.91 ppm as a singlet. These spectroscopic data agree well with data reported for simple gold dicarbene complexes.[11b]

Supramolecular structures similar to $[M_4(\mathbf{1})_2]^{4+}$ ($M = Ag^I, Au^I$) can also be prepared from tricarbene ligands. The trisimidazolium salt H_3-$\mathbf{2}(PF_6)_3$ reacts with Ag_2O in acetonitrile to give the trisilver salt $[Ag_3(\mathbf{2})_2](PF_6)_3$ in an excellent yield of 86% (Scheme 2; also see the Supporting Information). The NMR spectroscopic data for $[Ag_3(\mathbf{2})_2](PF_6)_3$ [^{13}C NMR: $\delta(C_{carbene}) = 181.19$ ppm] resembled those of the tetrasilver salt $[Ag_4(\mathbf{1})_2](PF_6)_4$. The ESI mass spectrum showed the mass of cation $[Ag_3(\mathbf{2})_2]^{3+}$ as the most intense peak.

Scheme 2. Preparation of Compound $[Ag_3(\mathbf{2})_2](PF_6)_3$ and Transmetalation to $[Au_3(\mathbf{2})_2](PF_6)_3$



Transmetalation of $[Ag_3(\mathbf{2})_2](PF_6)_3$ with 3 equiv of $[AuCl(SMe_2)]$ gave exclusively the homotrinuclear gold(I) complex $[Au_3(\mathbf{2})_2](PF_6)_3$ in 60% yield with retention of the metallosupramolecular structure. Formation of heterobimetallic Ag/Au complexes was ruled out on the basis of the observation of only one carbene resonance in the ^{13}C NMR spectrum; this resonance, however, was shifted to $\delta(C_{carbene}) = 183.67$ ppm, just slightly downfield relative to the trisilver complex.

The trigold complex was also identified by ESI mass spectrometry, which showed the mass of cation $[Au_3(\mathbf{2})_2]^{3+}$ as the most intense peak.

An X-ray diffraction study with crystals of $[Au_3(\mathbf{2})_2](PF_6)_3 \cdot 0.5Et_2O \cdot 1.5CH_3CN \cdot 0.5(CH_3)_2CO$ confirmed the composition and molecular structure of the $[Au_3(\mathbf{2})_2]^{3+}$ cation (Figure 2). The Au−$C_{carbene}$ distances [2.009(5)−2.018(6) Å] are slightly shorter than the Ag−$C_{carbene}$ distances, in agreement with previous reports.[7b,11b] The Au···Au separations are longer than the Ag···Ag separations in $[Ag_4(\mathbf{1})_2]^{4+}$ and are almost equidistant [5.9893(6)−6.1572(9) Å].

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 complexes undergo transmetalation with $[AuCl(SMe_2)]$ to give the homonuclear Au^I complexes with retention of the three-dimensional structure. Current studies are focused on the incorporation of additional metal ions (Au^+) or small substrates (acetylenes) into the metallosupramolecular assemblies.

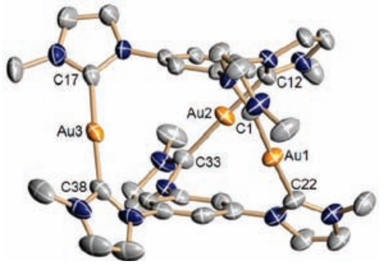


Figure 2. Molecular structure of the trication $[Au_3(\mathbf{2})_2]^{3+}$ in $[Au_3(\mathbf{2})_2](PF_6)_3 \cdot 0.5Et_2O \cdot 1.5CH_3CN \cdot 0.5(CH_3)_2CO$ (hydrogen atoms have been omitted for clarity, and only the first atom of each *N*-Et substituent is depicted).

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Supporting Information Available: Experimental details for the synthesis of all compounds and X-ray crystallographic data (CIF) for compounds $[Ag_4(\mathbf{1})_2](PF_6)_4 \cdot 2CH_3CN$ and $[Au_3(\mathbf{2})_2](PF_6)_3 \cdot 0.5Et_2O \cdot 1.5CH_3CN \cdot 0.5(CH_3)_2CO$. This material is available free of charge via the Internet at http://pubs.acs.org.

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