Metal Ion Cluster

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A Tray-Shaped, Pd^{II}-Clipped Au_3 Complex as a Scaffold for the Modular Assembly of [3 × *n*] Au Ion Clusters**

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Abstract: *A tray-shaped $Pd^{II}{}_3Au^{I}{}_3$ complex (**1**) is prepared from 3,5-bis(3-pyridyl)pyrazole by means of tricyclization with Au^I followed by Pd^{II} clipping. Tray **1** is an efficient scaffold for the modular assembly of [3 × n] Au^I clusters. Treatment of **1** with the $Au^I{}_3$ tricyclic guest **2** in H_2O/CH_3CN (7:3) or H_2O results in the selective formation of a [3 × 2] cluster (**1·2**) or a [3 × 3] cluster (**1·2·1**), respectively. Upon subsequent addition of Ag^I ions, these complexes are converted to an unprecedented Au_3–Au_3–Ag–Au_3–Au_3 metal ion cluster.*

The discrete assembly of metal ions into well-defined ionic clusters is an area of great interest in view of the potential new properties of the clusters, in particular, their catalytic activities.[1] Although the chemical and physical properties of the metal ion clusters are highly dependent on the number and array of the component metal ions,[2] the precise three-dimensional modulation of the metal ion array, especially in solution, is not easy and sophisticated and elaborate ligand designs are always required.[1a,3,4] We have recently found that the assembly of [3 × *n*] Au^I ion clusters[5] from a planar cyclic trinuclear Au^I complex[6,7] can be templated by a box-shaped cage complex, and that intermolecular Au^I–Au^I interactions contribute to the stabilization of the assembled entities. The stack number (*n*) of the Au^I ion clusters was precisely determined by the length of the lateral rigid pillars. Here we show that $Au^I{}_3$ tray-shaped molecules **1** act as shallow concave platforms that induce the assembly of [3 × *n*] Au^I ion clusters on their concave surface in a modular fashion (Figure 1). The stack number (*n*) of the ion clusters can be systematically tuned (*n* = 2–4) by changing the solvent conditions and the addition of Ag^I ions.

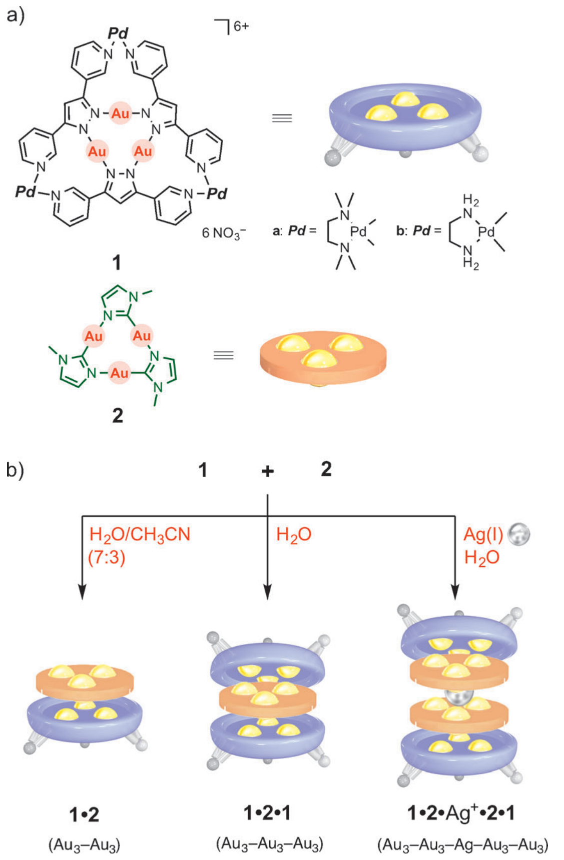

Figure 1. a) The tray-shaped $Au^I{}_3$ complexes **1** and guest $Au^I{}_3$ complex **2**. b) The formation of double, triple, and quadruple $Au^I{}_3$ stacks.

Tricyclic $Au^I{}_3$ ligand **3** was obtained in 75 % yield by the reaction of 3,5-di(3-pyridyl)pyrazole with $ClAuS(CH_3)_2$ in a 1:1 ratio under basic conditions. Only the pyrazolate moiety coordinated to Au^I to form the stable cyclic $Au^I{}_3$ core. When $Au^I{}_3$ ligand **3** was suspended in an H_2O/CH_3CN (7:3) solution of three equivalents of $(tmeda)Pd(ONO_2)_2$ (tmeda = tetramethylethylenediamine), tray-shaped molecule **1a** was quantitatively obtained (Figure 2a). ^1H NMR spectroscopy of the resulting clear solution revealed that the adjacent pyridyl groups of ligand **3** were clipped by $(tmeda)Pd^{II}$ units to give two diastereomers, tray *t*-**1a** and partial-tray *pt*-**1a**, in a 65:35 ratio (Figure 2b). The five intense signals in the aromatic region of the spectrum are attributed to the $H_{a\text{–}e}$ protons of *t*-**1a**, which has C_{3v} symmetry. In *pt*-**1a**, three signals in a 1:1:1 ratio are observed for each proton $H_{a\text{–}d}$, whereas two signals in a 2:1 ratio are observed for H_e; this is consistent with its C_s symmetry. A fluxional exchange between the two isomers was not observed on the NMR timescale, presumably because of the bulkiness of the tmeda ligand on the Pd center. In fact, when the less bulky $(en)Pd(ONO_2)_2$ (en = ethylenediamine) was employed in place of $(tmeda)Pd(ONO_2)_2$, the ^1H NMR spectrum of tray **1b** showed only five broad signals, which implies a fast exchange between *t*-**1b** and *pt*-**1b** (see the Supporting Information). Cold spray ionization MS (CSI-MS)

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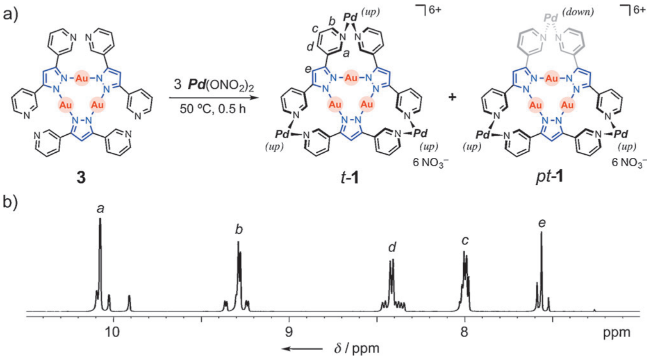

Figure 2. a) The self-assembly of tray complex **1** from Au$^I_3$ ligand **3** and three equivalents of Pd^{II} hinges. Two isomers exist: tray form *t*-**1** and partial-tray form *pt*-**1**. b) ^{1}H NMR spectrum of **1a** (*t*-**1a**:*pt*-**1a** = 65:35) [500 MHz, 300 K, D$_2$O/CD$_3$CN (7:3), aromatic region].

analysis of trays **1a** and **1b** clearly confirmed their molecular weights of 2294.5 and 2126.2 Da, respectively.

Single crystals of tray **1b** were obtained by cocrystallization with triphenylene (**4**), and X-ray analysis showed the 1:1 association complex, (*t*-**1b**)·**4** (Figure 3), in which the planar guest **4** was stacked in the shallow concave cavity of *t*-**1b**.

The stable formation of the stack structure (*t*-**1b**)·**4** indicated the good acceptor ability[8] of *t*-**1b** for electron-rich planar guests at the concave cavity. Inspired by this result, *t*-**1** was complexed with imidazolato-bridged, electron-rich Au$^I_3$ complex **2**[6a,8] to form double-deckered ionic Au$_3$–Au$_3$ cluster (*t*-**1**)·**2**. Complex **2** was suspended in an H$_2$O/CH$_3$CN (7:3) solution of **1a** (a 65:35 equilibrium mixture of *t*-**1a** and *pt*-**1a**; Figure 4a). After removal of the residual excess guest by filtration, ^{1}H NMR spectroscopy of the resulting solution revealed the formation of a 1:1 Au$_3$–Au$_3$ stacked complex (*t*-**1a**)·**2** in 93% yield as determined by NMR spectroscopy (Figure 4c). Signals of *pt*-**1a** were not observed because the equilibrium was entirely in favor of the association complex (*t*-**1a**)·**2**. Signals of guest **2** were shifted upfield (e.g., $\Delta\delta_{max} = -1.0$ ppm for H$_j$) as a result of shielding by the aromatic planes of *t*-**1a** (Figure 4b,c). A diffusion-ordered spectroscopy (DOSY) NMR experiment revealed the same diffusion coefficient ($D = 1.9 \times 10^{-10}$ m^{2}s^{-1}) for both *t*-**1a** and **2** in the complex, which indicates that Au$^I_3$ complex **2** was tightly bound to tray *t*-**1a**. Similarly, Au$^I_3$ tray **1b** gave the stable association complex (*t*-**1b**)·**2** in solution.

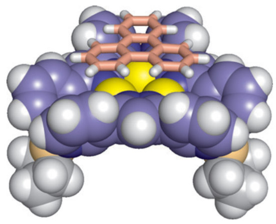

Figure 3. X-ray crystal structure of the association complex (*t*-**1b**)·**4**.

NMR studies showed that tray **1b** forms an Au$_3$–Au$_3$ self-stacked dimer, (*t*-**1b**)·(*t*-**1b**), in water, in which the trays are stacked in a face-to-face fashion with the hydrophobic Au$^I_3$ plane inside (see Figure 5b and the Supporting Information). When neutral Au$_3$ complex **2** was added to this solution (or when **1b** and **2** were directly mixed in D$_2$O), a discrete Au$_3$–Au$_3$–Au$_3$ triple stack (*t*-**1b**)·**2**·(*t*-**1b**) was formed (path a in Figure 5a). In this complex, neutral guest **2** was fully shielded by two cationic *t*-**1b** hosts, as confirmed by NMR spectroscopy (Figure 5c). In the ^{1}H NMR spectrum, the signals of guest **2** were considerably shifted upfield ($\Delta\delta_{max} = -2.1$ ppm for H$_j$). Two sets of *t*-**1b** signals were observed in a 1:1 ratio; this suggests a diastereomeric environment of the tray protons that results from the tight stack structure without inversion of guest **2**. The 2:1 tray/guest ratio and the equivalent tray signals strongly suggest that the whole association complex has a C_{3h} sandwich structure. The tray/guest ratio was saturated at 2:1 even if an excess of guest Au$^I_3$ complex **2** was employed. The fact that the association ratio is controlled by the solvent conditions means that the hydrophobic effect is the main driving force in this molecular recognition system. The addition of CH$_3$CN to the aqueous solution caused the disassembly of the Au$_3$–Au$_3$–Au$_3$ triple stack (*t*-**1b**)·**2**·(*t*-**1b**) to regenerate the Au$_3$–Au$_3$ double stack (*t*-**1b**)·**2**.

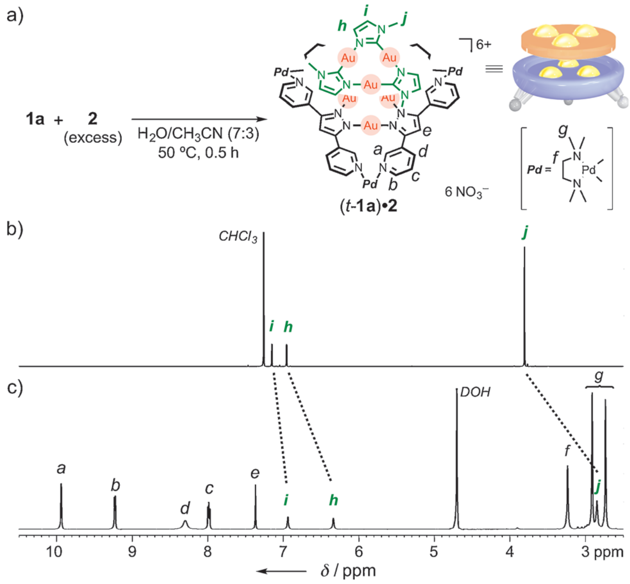

Figure 4. a) The formation of Au$^I_3$ double stack complex (*t*-**1a**)·**2**. b,c) ^{1}H NMR spectra (500 MHz, 300 K) of Au$^I_3$ guest complex **2** (in CDCl$_3$) (b) and 1:1 association complex (*t*-**1a**)·**2** [in D$_2$O/CD$_3$CN (7:3)] (c).

In order to build a higher stack of Au$^I_3$ complexes, we focused on metallophilic d^{10}–d^{10} interactions[9] in addition to the hydrophobic effects. Metallophilic interactions are observed for soft d^{10} metal ions such as Au^I and Ag^I and determine molecular geometries or arrays in the solution and crystalline states.[4,10] When the dimer of tray *t*-**1b** was mixed with an excess amount of guest **2** in the presence of AgNO$_3$ (1 equiv) in water, an Au$_3$–Au$_3$–Ag–Au$_3$–Au$_3$ association complex (*t*-**1b**)·**2**·Ag$^+$·**2**·(*t*-**1b**) was quantitatively obtained (path b in Figure 5a).[11] In the ^{1}H NMR spectrum, the integral ratio of guest **2** to tray *t*-**1b** was 1:1 (Figure 5d). Two sets of signals were observed for the C_{3h} symmetrical

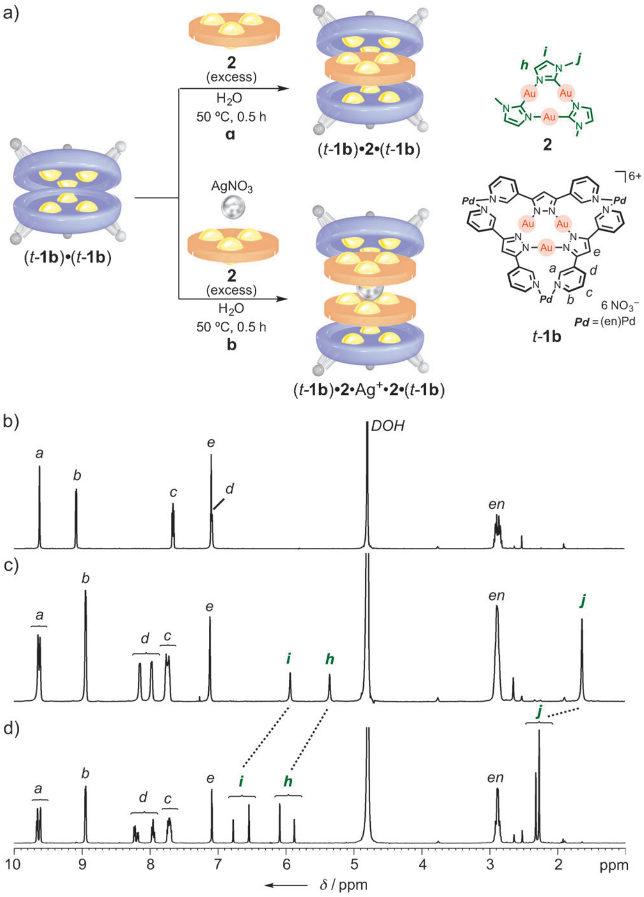

Figure 5. a) The formation of triple and quadruple Au^{I}_{3} stacks (t-**1b**)·**2**·(t-**1b**) and (t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**) from the Au^{I}_{3} tray dimer (t-**1b**)·(t-**1b**). b–d) ^{1}H NMR spectra (500 MHz, 300 K, D_2O) of each Au^{I}_{3} multiple stack: b) Au^{I}_{3} tray dimer (t-**1b**)·(t-**1b**), c) 2:1 association complex (t-**1b**)·**2**·(t-**1b**), and d) 2:2 complex (t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**).

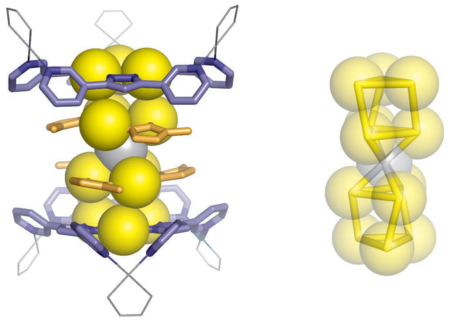

Figure 6. X-ray crystal structure of Au_3–Au_3–Ag–Au_3–Au_3 quadruple stack (t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**) (left) and highlighted Au^{I}–Ag^{I} ion arrays (right). The dimer of guest **2** (orange) and an Ag^{I} ion (gray) located at the center of the structure are sandwiched between two molecules of tray t-**1b** (blue). All counterions (NO_3^{-}) and solvents are omitted for clarity.

guest **2**, which indicates that two molecules of **2** are stacked tightly with either the same or opposite orientations. The dimer of **2** is sandwiched between two molecules of tray t-**1b** to form a 2:2 tray–guest association complex. The single Ag^{I} ion is selectively bound between the pair of electron-rich Au^{I}_{3} complexes **2**, not between guest **2** and the relatively electron-poor tray t-**1b**.[8] The location of the Ag^{I} ion was confirmed by the downfield-shifted signals of guests **2** in the ^{1}H NMR spectrum, compared to those in the Au_3–Au_3–Au_3 triple stack, (t-**1b**)·**2**·(t-**1b**) (Figure 5 c,d). The Ag^{I} ion is sandwiched by the electron-rich Au^{I}_{3} complexes **2** through Au^{I}–Ag^{I} interactions to form an Au_3–Ag–Au_3 triad.[5,12] The quadruple stack was stable even in H_2O/CH_3CN (7:3) mixed solvent, in which the 2:1 triple stack (t-**1b**)·**2**·(t-**1b**) was not maintained.

The structure of the quadruple Au^{I}_{3} stack (t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**) was unambiguously determined by X-ray crystallographic analysis (Figure 6). Pale yellow crystals were obtained by slow diffusion of THF vapor into an H_2O/CH_3CN (7:3) mixed solution of the complex. Au^{I}_{3} complex **2** was effectively fixed onto the shallow concave cavity of tray t-**1b**, yielding a columnar aromatic stack. The $Au_{12}Ag_1$ ion array in the stack has an hourglass structure, which consists of two vertical Au_6 prismatic units connected by a single Ag^{I} ion. The overall columnar metal array is significantly twisted around the vertical axis that passes through the central Ag^{I} site. The intermolecular Au⋅⋅⋅Au distances between trays t-**1b** and guests **2** [3.290(3)–3.372(3) Å] and the Au⋅⋅⋅Ag distances [2.745(3)–2.863(3) Å] are shorter than the sum of the van der Waals radii ($\approx$3.6 and 3.4 Å, respectively);[13] thus the complexes exhibit characteristic Au^{I}–Au^{I} and Au^{I}–Ag^{I} interactions. In particular, the Ag^{I} ion effectively acts as a glue connecting two Au^{I}_{3}–Au^{I}_{3} double stacks (t-**1b**)·**2** in a face-to-face fashion.

In summary, we have prepared an Au^{I}_{3} tray-shaped molecule as a scaffold, with which discrete stacks of Au_3 complexes were achieved in solution. The Pd^{II}-clipped pyridyl groups at the rim of the Au_3 complex provide a shallow concave cationic (6+) platform suitable for recognizing planar electron-rich molecules. The number of Au_3 stacks was systematically fine-tuned from two to four by changing the solvent conditions and the addition of Ag^{I} ions. We thus show that conventional confined cavities are not always necessary for the construction of discrete molecular stacks. Using the present shallow concave platform, we can manipulate dynamic molecular stacks at will in solution.

Experimental Section

Crystal data of (t-**1b**)·**4**: Orthorhombic space group *Pnma*, $T = 90(2)$ K, $a = 14.1734(15)$, $b = 19.427(2)$, $c = 32.499(3)$ Å, $V = 8948.6(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.594$ Mg m^{-3}, $F(000) = 4104$, reflection collected/unique 84007/8128 ($R_{int} = 0.0411$). The structure was solved by direct methods (*SHELXS-97*[14]) and refined by the full-matrix least-squares method on F^2 with 451 parameters (*SHELXL-2013*[14]). $R_1 = 0.0420$ ($I > 2\sigma(I)$), $wR_2 = 0.0887$. GOF = 1.170.

Crystal data of (t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**): Monoclinic space group *C*2/*m*, $T = 90(2)$ K, $a = 37.169(14)$, $b = 18.900(7)$, $c = 14.433(6)$ Å, $\beta = 111.246(4)$, $V = 9450(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.219$ Mg m^{-3}, $F(000) = 5876$, reflection collected/unique 41978/8340 ($R_{int} = 0.1321$). The structure was solved by direct methods (*SHELXS-97*[14]) and refined by the full-matrix least-squares method on F^2 with 479 parameters (*SHELXL-2013*[14]). $R_1 = 0.0941$ ($I > 2\sigma(I)$), $wR_2 = 0.1950$. GOF = 1.105.

CCDC 996175 ([(t-**1b**)·**2**·Ag^{+}·**2**·(t-**1b**)]) and CCDC 996176 ([(t-**1b**)·**4**]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

For full experimental details, characterizations, and crystallographic analysis, see the Supporting Information.

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