

# Selective Formation of Heterometallic Ru–Ag Supramolecules via Stoichiometric Control of Multiple Different Tectons

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## Supporting Information

**ABSTRACT:** Stoichiometric control of Ru, Ag, and tetrazolyl ligands resulted in the formation of different heterometallic Ru–Ag supramolecular architectures. Although the reaction of Ru and 5-(2-hydroxyphenyl)-1H-tetrazolyl ( $LH_2$ ) in a molar ratio of 2:1 or 6:4 resulted in the formation of dimeric or hexameric Ru complexes, Ag metal ions caused the Ru complexes to form three-dimensional cylindrical  $Ru_6Ag_6L_6$  and double-cone-shaped  $Ru_6Ag_8L_6$  complexes by occupying vacant coordination sites.

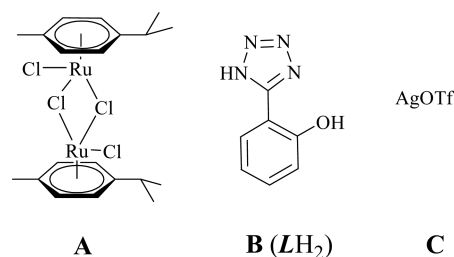
For a couple of decades, supramolecular chemistry has made significant contributions to the structural diversity and precise control of the sizes and shapes of molecules.<sup>1</sup> The use of various strong or weak interactions such as coordination and hydrogen bonding has enabled the synthesis of a variety of supramolecules that have been used in applications such as host–guest chemistry and catalysis.<sup>2</sup> In particular, their unique cavities provide suitable spaces for guest encapsulation and catalytic reactions.<sup>3</sup>

Recent research has focused on more complicated supramolecules.<sup>4</sup> Two major synthetic strategies have been developed for this purpose,<sup>5</sup> which include the use of (1) a number of reversible interactions between the same type of ligands for the formation of huge supramolecules such as cuboctahedra,<sup>6</sup> icosahedra, and dodecahedra;<sup>7</sup> (2) ligands with two different binding sites;<sup>8</sup> and (3) more than two kinds of ligands and two different weak interactions for the construction of heterometallic or multicomponent assemblies.<sup>9</sup> In this regard, we reported that stoichiometric control of electron-donor units such as pyridyl donors can lead to the formation of different discrete, single, two-dimensional (2D) supramolecular polygons.<sup>10</sup> While this concept was useful for the precise control of structures at the molecular level and for facile structure modification, it may also be applicable to the electron-acceptor metal units for the construction of various heterometallic supramolecular assemblies as a result of the diverse coordination modes of metal species.

To this end, the construction of different types of three-dimensional (3D) heterometallic supramolecular architectures has been achieved by stoichiometric control of different metal precursors and ligands as reported here. Among the metal species used for directional coordination-driven self-assembly, such as Ru, Pt, and Pd metal complexes, Ru species have a stronger

tendency to form chelate complexes with bidentate ligands than other metals. In particular, Ru-based half-sandwich units incorporating bridging O^O chelating ligands have received attention in supramolecular chemistry because of their rigid directionality toward pyridine electron donors from their restricted coordination sites.<sup>11</sup> However, the high rigidity often limits their structural variation, preventing versatile utilization. Thus, the use of Ru-based half-sandwich units containing a bidentate ligand system with additional binding sites for heterometallic supramolecular assemblies could be intriguing. We chose the tetrazolyl motif (Chart 1, B) because of its various coordination modes and strong tendency to form rigid coordination-bonded networks.<sup>12</sup>

**Chart 1. Structures of Ru (A), tetrazole (B), and Ag (C) tectons used in this work**

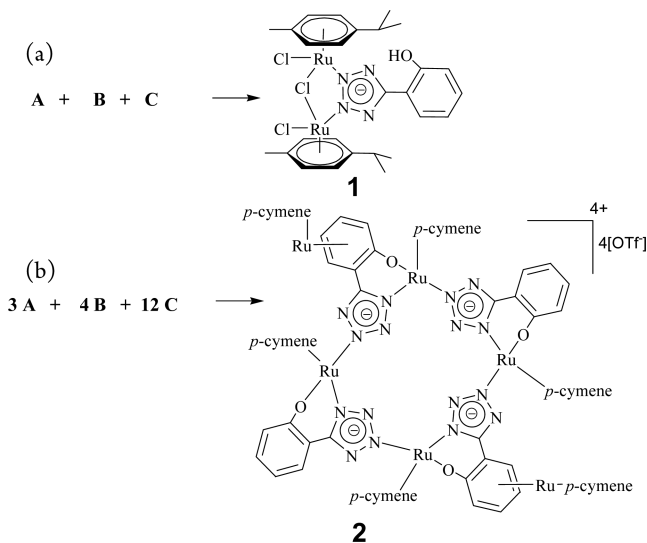


In addition, Ag ions may also be good candidates for the synthesis of heterometallic supramolecules because they can easily abstract Cl ions from metal chloride units and connect N-rich ligands to form network structures. Indeed, many high-dimensional coordination polymers and supramolecules of Ag and N-rich ligands have been reported.<sup>13,14</sup> We therefore chose Ru and Ag precursors as tectons for heterometallic supramolecular assemblies in combination with a tetrazolyl ligand (Chart 1).

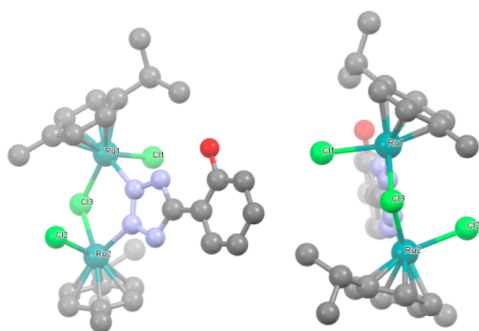
The reaction of  $[(p\text{-cymene})RuCl_2]_2$  with  $LH_2$  in the presence of an equimolar amount of silver triflate (AgOTf) produced diruthenium complex **1**, which is soluble in nitromethane and dimethyl sulfoxide (Scheme 1a). The molecular structure of **1** shows that one Cl ion and one  $LH^-$  ligand act as bridging units to form a dimeric Ru complex (Scheme 1 and Figure 1). It is worth

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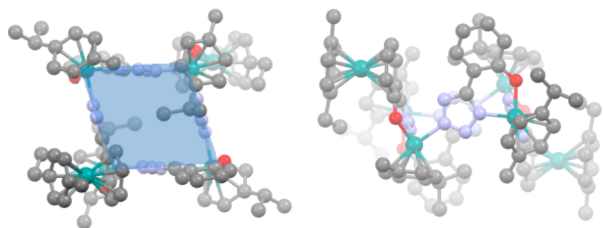
Scheme 1. Syntheses of (a) **1** and (b) **2**

noting that the tetrazole ligand is bound to the Ru centers in a  $\mu_2$ - $[N^2, N^3]$  fashion instead of the usual  $\eta^2$ -N<sup>1</sup>O binding mode.



**Figure 1.** Molecular structure of compound **1**. Color code: N, blue; O, red; C, gray; Ru, cyan; Cl, green.

The reaction of  $[(p\text{-cymene})\text{RuCl}_2]_2$ ,  $LH_2$ , and  $\text{AgOTf}$  in a 3:4:12 molar ratio produced the rectangular supramolecule **2**; its structure was determined using X-ray diffraction (Figure 2).



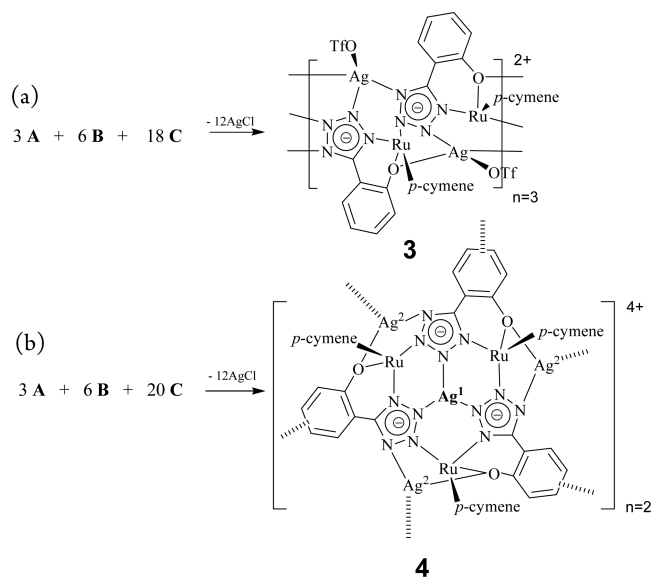
**Figure 2.** (a) Top view and (b) front view of the molecular structure of **2**. Color code: N, blue; O, red; C, gray; Ru, cyan.

There are two types of Ru metal ions with different coordination environments in the molecular structure of **2**. Four Ru metal ions of the first type are tetracoordinated with two  $L$  ligands and  $p$ -cymene. They are ligated to one  $L$  ligand via the  $\eta^2$ -N<sup>1</sup>O binding mode and bridged to the other  $L$  ligand by coordination of the N<sup>3</sup> atom to Ru (Scheme 1b). Two additional Ru metal ions are bonded to the phenyl rings of two  $L$  ligands via the  $\eta^6$  binding mode. Two  $\text{Ru}(\text{bz})_2^{2+}$  (bz = benzene) ruthenocene units are

formed by  $\eta^6$  binding with half of the four  $L$  ligands. The overall molar ratio of Ru to  $L$  ligands is 6:4.

In both complexes **1** and **2**, there are still free N binding sites, and therefore, we speculated that additional heterometallic supramolecular assemblies could be achieved with additional metal ions for extended coordination between the metal ions and the free N sites of the tetrazolyl units. Ag ions were chosen as the additional metal ions because they easily bind to tetrazole and were already used in the formation of complexes **1** and **2** to abstract Cl ions.

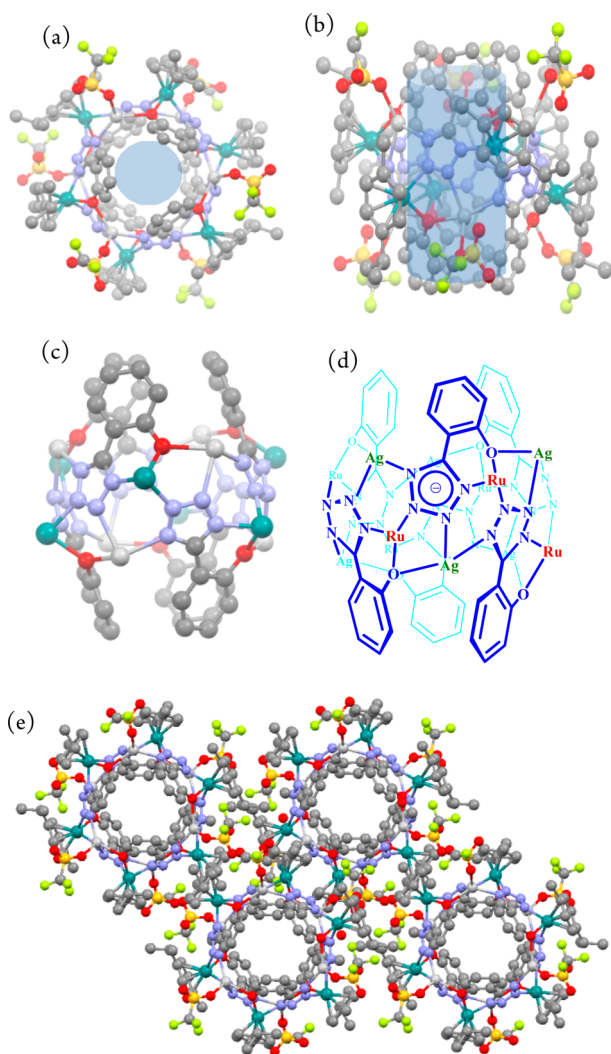
To investigate the effect of Ag ions,  $[(p\text{-cymene})\text{RuCl}_2]_2$ ,  $LH_2$ , and  $\text{AgOTf}$  were mixed in a 3:6:18 molar ratio in methanol (Scheme 2a). The reaction was monitored using  $^1\text{H}$  NMR

Scheme 2. Syntheses of (a) **3** and (b) **4**

spectroscopy, and crystals suitable for X-ray crystallography were obtained by simple recrystallization upon cooling. The solid-state structure was confirmed to be hexa-Ru metallosupramolecular complex **3** (Figure 3). Compound **3** has six Ru, six Ag, and six  $L^{2-}$  ligands. The Ru atoms are tetracoordinated with the N<sup>1</sup> and O atoms of one  $L$  ligand via an  $\eta^2$ -N<sup>1</sup>O-type binding mode, N<sup>3</sup> of another  $L$  ligand, and  $p$ -cymene. The Ag metal ions are also tetracoordinated with N<sup>2</sup>, N<sup>4</sup>, and O atoms from three different  $L$  ligands and one O atom of the triflate counteranion (Scheme 3a).

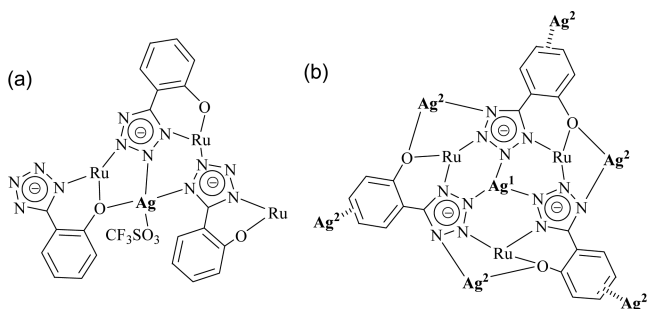
As expected, the Ag metal ions provide new coordination motifs to the tetrazole molecules, and all of the tetrazole N atoms have  $\eta^4$  coordination with four metal atoms (two Ru and two Ag; see Scheme 4c). Coordination of Ru, Ag, and  $L$  ligands results in the formation of a cylindrical structure (Figure 3c). There are two different tetrazolyl units, with phenyl groups placed toward the top and bottom of the main framework. The top and bottom of the cylinder are therefore each surrounded by three phenyl rings (Figure 3). The volume of the inside cylinder, which can be estimated using the six phenyl groups, is about  $320 \text{ \AA}^3$  (ca.  $11.5 \text{ \AA}$  in height and ca.  $6.0 \text{ \AA}$  in diameter) and may be used for the storage of small molecules or anions such as amino acids, triflate ions, and perchlorate ions. In the X-ray analysis, a methanol molecule is observed in the inside cavity of the cylinder and the triflate counterions are located outside, around the Ag metal ions.

An even more interesting metallosupramolecular architecture was achieved when the ratio of Ag units was increased. The reaction of  $[(p\text{-cymene})\text{RuCl}_2]_2$ ,  $LH_2$ , and  $\text{AgOTf}$  in a 3:6:20

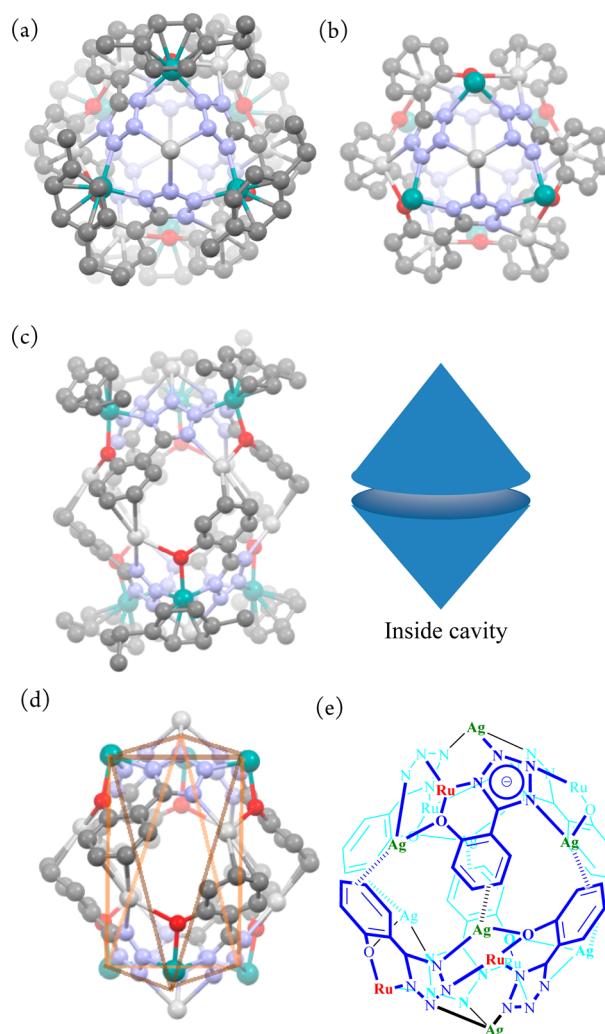


**Figure 3.** (a) Top view, (b) front view, (c) front view without p-cymene and triflate ions, (d) connectivity drawing, and (e) extended view along the *ac* plane of the molecular structure of **3**. Color code: N, blue; O, red; C, gray; Ru, cyan; Ag, light gray.

### Scheme 3. Coordination Modes of Ag in (a) **3** and (b) **4**



molar ratio in methanol resulted in a deep-yellow solution with a white precipitate, i.e., AgCl. After filtration, the reaction mixture was crystallized in a refrigerator to afford yellow crystals, which were shown by X-ray crystallography to be the double-cone-shaped  $\text{Ru}_6\text{Ag}_8\text{L}_6$  metallosupramolecule **4** (Figure 4). The coordination environments of the Ru metal ions are the same as those in complex **3**. However, there are two different types of Ag metal ions in the complex (Scheme 3b). Six Ag metal ions, labeled  $\text{Ag}^2$ , are coordinated to O and  $\text{N}^4$  of two different *L*

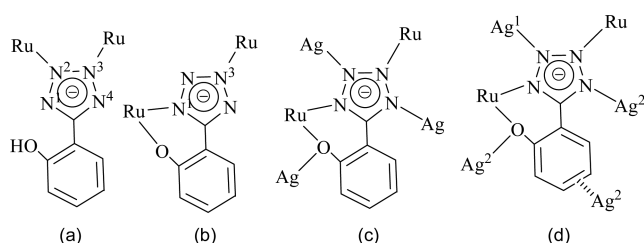


**Figure 4.** (a) Top view, (b) top view without *p*-cymene, (c) front view with cavity sketch, (d) front view without *p*-cymene and with trigonal antiprism sketch, and (e) connectivity drawing of the molecular structure of **4**. Hydrogen atoms and triflate ions have been omitted for clarity. Color code: N, blue; O, red; C, gray; Ru, cyan; Ag, light gray.

ligands and have  $\eta^2$  coordination with the phenyl group of the other *L* ligand. The overall coordination mode around  $\text{Ag}^2$  is  $\kappa^3$  coordination. Two other Ag metal ions, labeled  $\text{Ag}^1$ , are located on the top and bottom sides of the supramolecule (Scheme 3b). They are coordinated with N atoms from three different *L* ligands by  $\kappa^3$  coordination. Complex **4** has a relatively small double-cone-shaped inner cavity, in which each cone has a height of 6.3 Å and a radius of 2.8 Å. The volume of the double cone is about 100 Å<sup>3</sup>, which is suitable for encapsulation of small molecules such as methanol.

The different coordination behaviors of the tetrazole ligand are shown in Scheme 4. As a result of the addition of Ag ions, the tetrazole ligands in complexes **3** and **4** exhibit more diverse coordination behavior than those in the Ag-free complexes **1** and **2**. Electrospray ionization mass spectrometry data of complexes **1–4** also confirmed the existence of these complexes in solution.

The stoichiometric ratios and the coordination modes of the tetrazole ligands and metal ions are compared in Table 1. It is noteworthy that systems omitting Ag produced only one-dimensional (1D) or 2D complexes with limited coordination. However, the Ag systems showed more complicated binding

Scheme 4. Coordination Modes of the *L* Ligand in (a) **1**, (b) **2**, (c) **3**, and (d) **4**Table 1. Comparison of Coordination Modes and Shapes in Complexes **1**–**4**

| complex  | Ru:L:Ag | Ru–L  | Ag–L  | shape          |
|----------|---------|---|---|----------------|
| <b>1</b> | 2:1:0   | $\mu_2$   |   | 1D dimer       |
| <b>2</b> | 6:4:0   | $\eta^2\text{-N}_2\text{O}; \eta\text{-N}^3;$<br>$\eta^6$ |   | 2D rectangle   |
| <b>3</b> | 6:6:6   | $\eta^2\text{-N}_2\text{O}; \eta\text{-N}^3$              | $\kappa^3\text{-[N}_2\text{N}_2\text{O]}$   | 3D cylinder    |
| <b>4</b> | 6:6:8   | $\eta^2\text{-N}_2\text{O}; \eta\text{-N}^3$              | $\kappa^3\text{-[N}_2\text{N}_2\text{O}]; \eta^2;$<br>$\kappa^3\text{-[N}_2\text{N}_2\text{N]}$ | 3D double cone |

modes and formed 3D heterometallic supramolecular cages. Moreover, the stoichiometric ratio of Ag strongly influenced the shape of the complex, resulting in the selective formation of cylindrical compound **3** or double-cone-shaped compound **4**.

In conclusion, Ag metal ions played an important role in the formation of the metallosupramolecules reported herein. Whereas Ru and tetrazolyl ligands (*L*) formed only dimeric  $\text{Ru}_2\text{L}$  or hexameric 2D rectangular  $\text{Ru}_6\text{L}_4$  molecules, heterometallic cylindrical  $\text{Ru}_6\text{Ag}_6\text{L}_6$  and double-cone-shaped  $\text{Ru}_6\text{Ag}_8\text{L}_6$  metallosupramolecules were constructed selectively by stoichiometric control of AgOTf. Heterometallic supramolecular cages are rare, and shape control of the cages via stoichiometric control of the multiple metal precursors in supramolecular assembly has not previously been reported. We believe that these complexes may be used in specific host–guest chemistry or electrochemical material science. Studies of their photophysical and electrochemical properties and host–guest chemistry are in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details,  $^1\text{H}$  NMR and mass spectra of **1**–**4**, and crystallographic data for **1**–**4** (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b01253.

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### Notes

The authors declare no competing financial interest.

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