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Cp*Rh-Based Heterometallic Metallarectangles: Size-Dependent Borromean Link Structures and Catalytic Acyl Transfer

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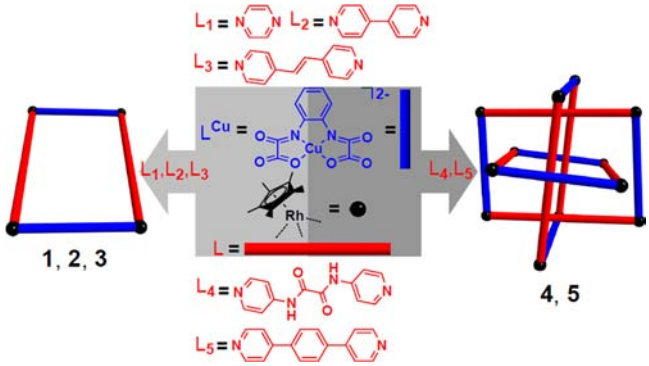
Supporting Information

ABSTRACT: A series of Cp*Rh-based functional metallarectangles have been synthesized from metallaligands. Enlargement of one linker leads to the isolation of two novel Borromean link architectures. All these complexes are intact in solution, as evident from ESI-MS spectroscopic analysis. Arising from the combination of open Cu centers and favorable cavity space, $\{(Cp^*Rh)_4(bpe)_2[Cu(opba)\cdot 2MeOH]_2\}4(OTf)\cdot 6MeOH$ shows extraordinary catalytic abilities with high efficiency and wide substrate selectivity in the acyl-transfer reaction.

In the past two decades, metallasupramolecular compounds have attracted a great deal of attention not only because of their intriguing structures[1] but also for their potential electronic,[2] magnetic,[3] host−guest,[4] drug delivery,[5] and catalytic properties.[6,7] These have led to significant interest in the construction of various molecular architectures[1] with desirable shapes, sizes, and ultimately function. In particular, the molecular flask-like catalytic prototypes[6] are developing rapidly due to their special suprastructures and the associated catalytic characteristic. Furthermore, the cavity size of frameworks could be easily regulated by modulating the linker length, which may give the opportunity to study the size-dependent interlocked architectures[8] and their related catalytic efficiency.[7]

In discrete system, the molecular species consist of interlinked ring-like molecules which are of great interest due to their fascinating structures, the topological importance, and potential applications in smart materials and nanoscale devices.[9] More specifically, the molecular Borromean link represents one of the most intriguing entangled bodies based on its structural integrity and aesthetic beauty.[10] For chemists, the topological complexity of discrete Borromean systems poses a formidable synthetic challenge. The only reported syntheses have originated in DNA[11] and metal ion templates.[12] It is important to note that the clever use of metal−ligand interactions could facilitate the assembly of Borromeates;[12d] further demetalation results in metal-template-free Borromeands with real Borromean link structures.[13] Encouraged by the enhanced stability of interpenetrating structures compensating weak coordination bonds, we focused on understanding size-dependent interlinked metallarectangles with two varying linkers offering more flexible length regulation. Herein we report a surprising observation that enlarging just one arm of the rectangle led to the isolation of two nontrivial 3-interlocked frameworks with Borromean link structures (Scheme 1). To the best of our knowledge, in the absence of a metal ion template, these one-pot self-assembled molecular Borromean rings are previously unknown.

Scheme 1. Size-Dependent Formation of Borromean Link Structures



The most popular methods for the preparation of coordination cycles are ligand substitution with building blocks of limited space. Since the first report on the organometallic Cp*Rh ($Cp^* = \eta^5$-C_5Me_5) fragment used as a building block for the construction of metallasupramolecular frameworks in 1998,[14] Cp*Rh-based supramolecular chemistry has grown rapidly.[15] In the assembly of these structures from metallaligands,[16] the frameworks are readily functionalized with Lewis acid sites. Here, the molecular precursor $L^{Cu} = [Cu(opba)]^{2-}$ [opba = *o*-phenylenebis(oxamato)] was used as a metallaligand complex which provides not only the bis-chelating coordination sites (oxalate-like) but also catalytic copper centers. Each Cp*Rh-based metal corner comprises three available coordination sites, besides the bis-chelating ligand L^{Cu}, and a monodentate bifunctional pyridine derivative (for example, 4,4′-bipyridine) is also needed. The two types of arms (spacers) are joined at the metal corners to give the rectangular architectures.

We used a different synthetic methodology from the reported method for Cp*Rh-based metallasupramolecular complexes[15f] from the same starting material, viz. $[Cp^*RhCl_2]_2$ (Scheme 2). A stoichiometric (1:1) mixture of $[Cp^*RhCl_2]_2$ and the

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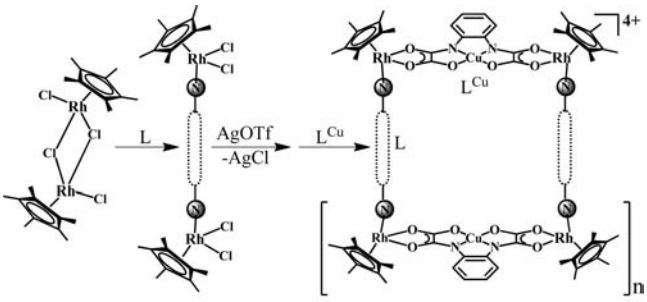
Scheme 2. Synthesis of Complexes 1−5



$L_1 + L^{Cu}$, n = 1 (**1**); $L_2 + L^{Cu}$, n = 1 (**2**); $L_3 + L^{Cu}$, n = 1 (**3**); $L_4 + L^{Cu}$, n = 3 (**4**); $L_5 + L^{Cu}$, n = 3 (**5**).

corresponding monodentate bifunctional pyridine derivative L_1−L_5 [L_1 = pyrazine (pz); L_2 = 4,4′-bipyridyl (bpy); L_3 = 1,2-bis(4-pyridyl)ethylene (bpe); L_4 = *N*,*N*′-4-dipyridyloxalamide (dpo); L_5 = 1,4-bis(4-pyridyl)benzene (bpb)] in MeOH at room temperature gave the binuclear complexes with four coordination sites as linear connecting units in almost quantitative yields. Chloride abstraction by AgOTf (Tf = O_2SCF_3) followed by addition of Na_2L^{Cu} gave rise to green solutions containing molecular rectangles. Complexes **6** and **7** were obtained through guest exchange of **1** with NO_3^- and **2** with H_2O (Figures S5 and S6), respectively.

All the basic units of complexes **1**−**5** are metallarectangles based on the common [4Rh+2Cu] nuclear core with different component units. The three coordination sites of the half-sandwich Rh fragment are occupied by pyridyl donor L and chelating group L^{Cu}. A representative structure, **3** (Figure S2), shows three crystallographically independent metal centers, viz. Rh(1), Rh(2), and Cu. The Cu(II) has approximately square pyramidal surroundings, with two nitrogen and two oxygen atoms from the opba group in the equatorial plane and two MeOH oxygen atoms in the axial positions. In these complexes, the lengths of pyridyl arms change significantly from 7.00 to 15.62 Å (Figure 1). Complexes **1**−**3** are monomeric rings; upon enlargement of pyridyl arms through the use of the longer linker *N*,*N*′-4-dipyridyloxalamide, trimeric complex **4** was obtained. It was surprising that no two rectangles are interlocked (i.e., catenated), yet each is threading through

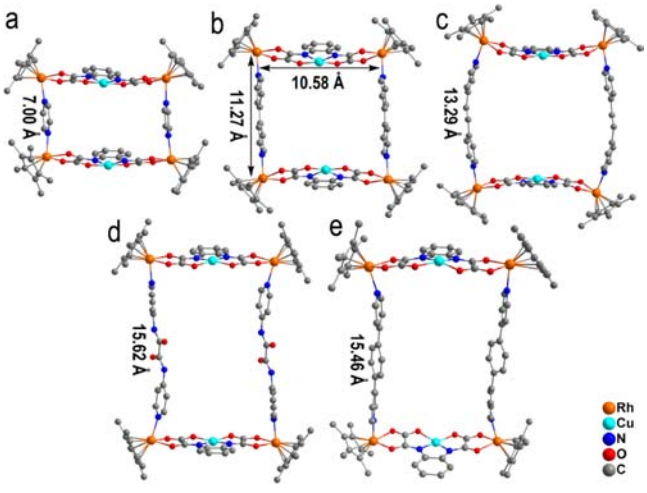


Figure 1. Single-crystal X-ray structures of complexes **6** (a), **2** (b), **3** (c), **4** (d), and **5** (e). All hydrogen atoms have been omitted for clarity.

one of the other rings and threaded by the other one (1→2, 2→3, 3→1). Although no rectangle is interlocked with any other individual rectangle, all three constitute an inseparable ensemble; scission of any one of the rings severs the union of the three (Figure 2). Another noteworthy feature of this

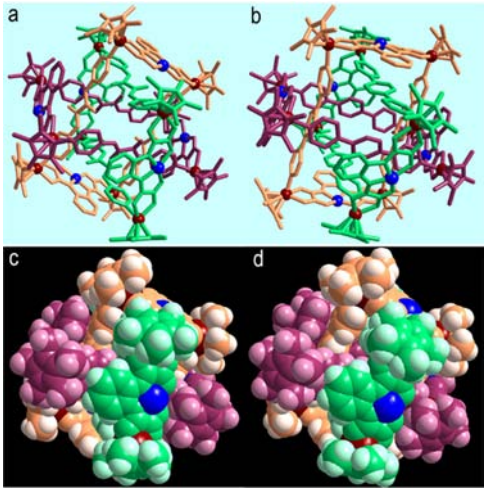


Figure 2. Borromean link structures. View of the X-ray structures of **4** (a,c) and **5** (b,d) as ball-and-stick and space-filling presentations. Counteranions are omitted for clarity.

structure is the presence of amide hydrogen bonds between N atoms of the outer rectangle and N−H moieties of the inner rectangle, which is reminiscent of some reported amide H-bond-directed catenanes.[17] To determine whether the main driving force for the formation of this molecular Borromean ring is the longer pyridyl arms or the templated amide hydrogen bonds, we tested 1,4-bis(4-pyridyl)benzene, with nearly equivalent N···N distance of the two 4-pyridyl groups but without an obvious hydrogen-bonding unit, as a ligand. This resulted in the formation of complex **5** also with Borromean link structure like **4** (Figure 2), which clearly pointed to the pyridyl arm length as the key factor that promoted interpenetration.

In support of the solid-state structures as evidenced from the X-ray diffraction analysis, the electrospray ionization mass spectrometry (ESI-MS) data of complexes **2**−**5** also point to the same species as their trifluoromethanesulfonate salts in solution. Peaks on the parent complexes **2** and **3** minus some counteranions, e.g., $[\mathbf{2} \times 2 - 2\mathrm{OTf}]^{2+}$ (m/z = 2335.46, Figure S8) and $[\mathbf{3} \times 2 - 3\mathrm{OTf}]^{3+}$ (m/z = 1541.68, Figure S9), were observed, strongly suggesting that the rectangular structures are intact in solution. The experimental peaks were all isotopically resolved and in good agreement with their theoretical distributions. Do the intact rectangular structures of **2** and **3** in solution imply that the structures of Borromean link complexes **4** and **5** are also preserved? The ESI-MS spectrum indicated **4** and **5** in solution would not split into monomeric rectangles but would preserve their 3-interlocked trimeric structures: $[\mathbf{4} - 3\mathrm{OTf}]^{3+}$ (m/z = 2507.65) and $[\mathbf{5} - 3\mathrm{OTf}]^{3+}$ (m/z = 2487.70) (Figure 3).

To demonstrate the size effect on catalytic activities of these metallacycle catalysts, we conducted the acyl-transfer reaction between *N*-acetylimidazole (NAI) and *x*-pyridylcarbinol (*x*-PC; *x* = 2, 3, 4).[18] The NAI and *x*-PC substrates could achieve suitable orientation and alignment for highly efficient acyl transfer through binding within the cavity of the metallacycle by

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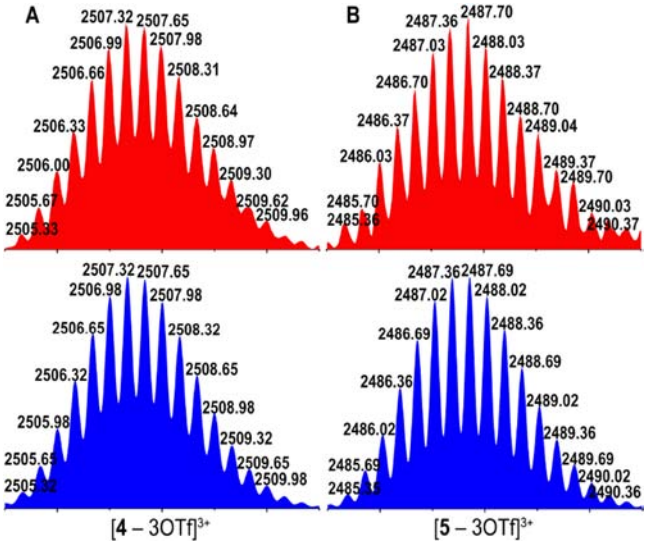

Figure 3. Calculated (bottom, blue) and experimental (top, red) ESI-MS spectra (3^+) of (A) **4** and (B) **5**.

open Cu centers. Furthermore, only the combination of substrates with the right distance can span the cavity and react at an accelerated rate. Their significantly different cavity sizes provided a basis for evaluation of the efficiency of different metallacycle catalysts in acyl-transfer reaction. For 3-PC, both **2** and **3** significantly accelerate the reaction rate. Complex **3** is almost 3 times more active than **2** (Figure 4), which may be

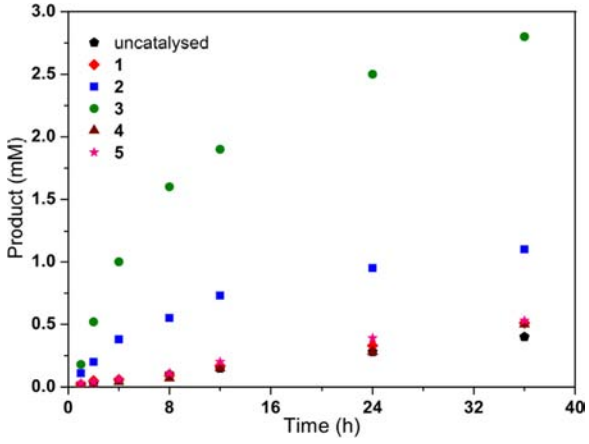

Figure 4. Progress curves for the acyl-transfer reaction between *N*-acetylimidazole and 3-pyridylcarbinol.

ascribed to **3** having highly favorable cavity size for accommodating the two reactants. 4-PC has longer distance between the N atom and carbinol group than 3-PC, and hence needs a more favorable and enlarged cavity size; complex **3** catalyzed the acyl-transfer reaction with medium rate (Figure S14 and S15). For 2-PC, all the rates drop significantly relative to 3- and 4-PC (Figure S12). This can be understood as the Cu-bound carbinol group of 2-PC and the imidazole *N*-acetyl group bound to the other side are positioned in opposite directions, resulting in an unfavorable transition state for acyl-transfer reaction. It is also noticeable that, regardless of 2-, 3-, or 4-PC, complexes **1**, **4**, and **5** catalyzed the reaction with low rate, only a little stronger than without catalyst. This is not surprising since **4** and **5** cannot split into monomeric rectangles, thus leaving no space for substrate entry into these Borromean link structures. But for **1**, its cavity is inherently narrow. These findings lead to the postulate that this acyl-transfer reaction proceeded through the constrained proximity of two reactive species and a tightly bound intermediate (Figure 5). The nitrogen atoms of NAI and 3-

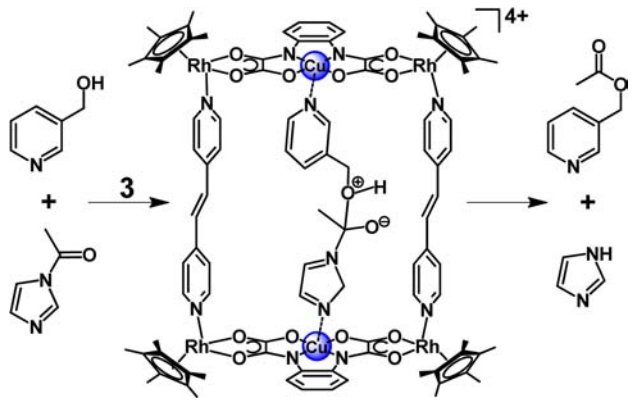

Figure 5. Tetrahedral intermediate doubly bound inside the cavity of complex **3**.

PC could be easily coordinated to the inner Cu centers of metallarectangle **3**, forming the cooperatively bound intermediate with low activation energy, thus facilitating the subsequent catalytic cycle based on the weak binding ability.

In conclusion, we have prepared a series of cavity-specific Cp*Rh-based heterometallic metallarectangles from a metal-laligand. Using an enlarged linker led to interpenetrating structures as a compensation of the weak coordination bonds. The two coordination-driven self-assembled metallasupramolecules with real Borromean link structures are unprecedented. The synthetic simplicity and readily tunable and easily modifiable modular design are distinct advantages of this function-oriented assembly. With appropriate cavity size, catalyst **3** shows remarkable catalytic abilities with high efficiency and wide substrate selectivity in the acyl-transfer reaction between *N*-acetylimidazole and *x*-pyridylcarbinol. These exciting results suggest the potential biomimicking effect of metallasupramolecular catalysis, but its development vis-à-vis understanding of interpenetration phenomenon and purpose-driven design of such suprastructures is still in its infancy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic data, IR and ESI-MS spectra, and progress curves for the acyl-transfer reaction for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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