Self-assembled half-sandwich polyhedral cages via flexible Schiff-base ligands: an unusual macrocycle-to-cage conversion†‡

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An edge-directed strategy was adopted to construct highly ordered polyhedral structures using flexible functions. Half-sandwich M₆(L₁)₄ octahedral and M₈(L₂)₄ cubic cages have been assembled by flexible Schiff-base ligands upon coordination to Cp*Rh(III) organometallic acceptors. In particular, the rearrangement from a Rh(III)-based half-sandwich M₂(HL₁)₂ macrocycle to M₆(L₁)₄ cage was found to occur in a solution.

The metal-mediated self-assembly of organic bridging ligands into discrete 3D polyhedral cages has emerged in supramolecular chemistry owing to their aesthetic appeals, as well as potential applications in host–guest chemistry and catalysis. Such MₓLₘ cages constructed from relatively simple components have displayed elaborate polyhedral shapes of striking complexity such as tetrahedral, octahedral, and cubic assemblies. The reported works in this area mostly focus on the self-assembly of rigid building blocks and metal corners with square-planar or octahedral geometries into the final discrete cages. However, the technique still remains relatively limited for half-sandwich organometallic polyhedral cages, particularly M₄L₄ or M₈L₄ species, due to the difficulties associated with highly efficient synthetic strategies and finding appropriate building blocks. To achieve predictable architectures, one of the central tenets in the design is that the available metal coordination sites are controlled by using polytopic ligands with inherent flexibility.

Multidentate Schiff-base ligands have the potential to form different types of complexes due to their rich coordination centres, such as tetrahedral, octahedral, and cubic assemblies. The metal-mediated self-assembly of organic bridging ligands into discrete 3D polyhedral cages has emerged in supramolecular chemistry owing to their aesthetic appeals, as well as potential applications in host–guest chemistry and catalysis. Such MₓLₘ cages constructed from relatively simple components have displayed elaborate polyhedral shapes of striking complexity such as tetrahedral, octahedral, and cubic assemblies. The reported works in this area mostly focus on the self-assembly of rigid building blocks and metal corners with square-planar or octahedral geometries into the final discrete cages. However, the technique still remains relatively limited for half-sandwich organometallic polyhedral cages, particularly M₄L₄ or M₈L₄ species, due to the difficulties associated with highly efficient synthetic strategies and finding appropriate building blocks. To achieve predictable architectures, one of the central tenets in the design is that the available metal coordination sites are controlled by using polytopic ligands with inherent flexibility.

Multidentate Schiff-base ligands have the potential to form different types of complexes due to their rich coordination sites and can be successively deprotonated, showing the tautomeric effect of keto and enol forms. When suitable metal centres exist, Schiff-base functional groups can chelate a metal centre with one carbonyl O atom and two imine N atoms, creating an excellent building unit for the assembly. Furthermore, the flexibility of such ligands, afforded by the varied angles of Schiff-base functional groups around the pyridine-based arms between their coordination vectors to complement the other partners, is simultaneously essential and exhilarating.

Based on an edge-directed strategy, the formation of cages could make use of half-sandwich organometallic fragments [Cp*M] (M = Rh, Ir; Cp* = η⁵-pentamethylcyclcopentadienyl) to occupy the corners of the polyhedron, and thus need to adopt flexible linear components connected at corners. In the present study, we exhibit how simple 4-pyridinecarbaldehyde isonicotinoyl hydrazine (HL₁) acts as a flexible linker in the self-assembly with Cp*Rh(III) acceptor to form half-sandwich M₆(HL₁)₂ macrocycle and M₆(L₁)₄ octahedral cage. Solution studies reveal that there could be a complicated dynamic behavior between the simplest M₂(HL₁)₂ and the largest M₆(L₁)₄ species in a solution. Moreover, a unique half-sandwich organometallic cubic cage of M₈(L₂)₄ composition has been synthesized utilizing 2,3-butanedione bis(isonicotinyl hydrazine) (HL₂) with an Cp*Rh(III) acceptor in the assembly. The coordination behavior of these flexible ligands with different metal subunits allows further structural diversification in this system.

M₆(HL₁)₂ macrocycle 1 was synthesized by activation of [Cp*RhCl₂] in methanol with 4 equivalents of silver salt AgOTf ([TF = O₂SCF₃]), followed by reaction with HL₁ ligands in a 1 : 1 (M : L) ratio in acetonitrile (yields: 43%). Similarly, M₆(L₁)₄ cage 2 was formed by treatment of [Cp*Rh] fragments with HL₁ ligands based on a 6 : 4 (M : L) ratio in methanol and acetonitrile (yields: 63%).

Single crystals of macrocycle 1 suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into the mixed methanol and acetonitrile solvents of 1. It is crystallized in the orthorhombic Pecn space group. As shown in Fig. 1, two bridging HL₁ ligands wrap around two [Cp*Rh] fragments to form a binuclear M₆(HL₁)₂ macrocycle with two bound acetonitrile...
molecules. The coordination sphere of each \{Cp*Rh\} centre is completed with two \textit{N}pyridine atoms (Rh–\textit{N}pyridine = 2.14 and 2.12 Å) and an acetonitrile molecule (Rh–NMeCN = 2.11 Å). The intramolecular distance between two metal centres is 10.62 Å. Notably, the \textit{HL1} ligands adopt a “U” shape, in which two pyridyl rings are not coplanar and form a dihedral angle of 57.3° in macrocycle 1.

Cage 2 was also structurally characterized in a procedure similar to that of 1. The compound crystallized in the monoclinic \textit{P}2\textsubscript{1}/\textit{n} space group. The assembly is composed of six \{Cp*Rh\} fragments and four \textit{L1} ligands, forming an octahedral cage, in which each bridging ligand connects three metal ions, and each metal centre is located at the meeting point of three edges. As shown in Fig. 2, the \textit{HL1} ligand is successively deprotonated and acts as a tetradentate ligand, not only adopting a linear form but also chelating an additional metal centre. In addition, to meet the requirements of the 18-electron rule, four \{Cp*Rh\} fragments have a typical three-legged piano-stool geometry with one anionic [N*O]-type chelating site and one \textit{N}pyridine atom. Another two \{Cp*Rh\} centres are coordinated by two \textit{N}pyridine atoms from two \textit{HL1} ligands, thus each requires one small solvent molecule to close off the cage and provide coordinative saturation. The distances of Rh1–NMeCN and Rh6–NMeCN are 2.13 and 2.03 Å, respectively. The edges of the octahedral cage range from 8.96 to 11.65 Å; however, the Rh1…Rh6 separation reaches up to 16.57 Å. Four \textit{L1} ligands in cage 2 are bent into an “L” shape with angles in the range 76.4°–79.5°. From the viewpoint of topology, cage 2 has four open “windows”.

Cage 2 has good solubility in the most common organic solvents and was further characterized by \textit{1}H NMR and ESI-MS spectroscopy confirming that cage 2 still retains its structure in a solution. The \textit{1}H NMR spectra of cage 2 displayed complicated multiple peaks in the range from \(\delta\) 8.70 ppm and \(\delta\) 8.12 ppm attributable to the protons of \textit{L1} ligands, and multiple peaks from \(\delta\) 1.81 to \(\delta\) 1.70 ppm corresponding to Cp* protons, respectively (see Fig. S1†). Presumably, such broad peaks are a result of the dynamic effects in a solution. The ESI-MS measurement showed fragment ions \([\text{Cp*}^\text{\textit{L1}}]_\text{2}(\text{CH}_3\text{CN})_\text{2}(\text{OTf})_\text{6}]^{2+}\) and \([\text{Cp*}^\text{\textit{L1}}]_\text{4}(\text{OTf})_\text{5}]^{3+}\) at \(m/z = 1652.11\) and 1024.41, respectively (see Fig. S2†). As evidenced by \textit{19}F NMR spectra analysis, there is one signal at chemical shifts of \(\sim 79.59\) ppm, indicating that all trilate guest anions have no close association with the host framework 2.

Unlike 2, macrocycle 1 is stable in the solid state, but less soluble in common organic solvents (except DMSO). Although the ESI-MS spectrum of 1 showed the expected fragment peak for the charged state \([\text{Cp*}^\text{\textit{HL1}}]_\text{2}(\text{OTf})_\text{3}]^{2+}\), the \textit{1}H NMR spectrum in DMSO exhibited a complicated series of peaks that could not be readily assigned. Nevertheless, it still reveals diagnostic signals at \(\delta\) 1.36 ppm corresponding to Cp* protons and at \(\delta\) 9.24 ppm corresponding to the H\textsubscript{e} atom consistent with the presence of the Rh\textsubscript{2}(HL1\textsubscript{2}) macrocycle. Therefore, macrocycle 1 can exist in DMSO, at least on a time scale of the measurement. However, we further observed that a sample of 1, left in a solution, showed gradual changes significantly in its \textit{1}H NMR spectrum over time at room temperature (see Fig. S4†). The peaks associated with the Rh\textsubscript{2}(HL1\textsubscript{2}) macrocycle slowly diminished in intensity and were replaced by a new set of peaks, which are the same as those of the crystalline cage 2 re-dissolved in DMSO–\textit{d}_\text{6} (complicated multiple peaks in the range of \(\delta\) 8.72 ppm and \(\delta\) 7.91 ppm attributable to the protons of \textit{L1} ligands, and a broad peak at \(\delta\) 1.68 ppm corresponding to Cp* protons, respectively). Some intangible peaks are supposed to be related to the release of free ligands and hydrogen ions. When the same sample of 1 was kept at 80 °C, it converted more rapidly to the Rh\textsubscript{2}(HL1\textsubscript{4}) cage, which was also evidenced by \textit{1}H NMR (see Fig. S5†) and the ESI-MS spectrum (see Fig. S6†). It showed two peaks at \(m/z = 1611.08\) and 1024.40 corresponding to the intact \([\text{Cp*}^\text{\textit{HL1}}_\text{2}(\text{OTf})_\text{3}]^{2+}\) and \([\text{Cp*}^\text{\textit{HL1}}_\text{4}(\text{OTf})_\text{5}]^{3+}\) structures, respectively. These observations are sufficient to allow us to identify the conversion from the Rh\textsubscript{2}(HL1\textsubscript{2}) macrocycle to the Rh\textsubscript{2}(HL1\textsubscript{4}) cage in DMSO (see Scheme 1).
A metal/ligand assembly experiment was conducted in reverse, i.e., by combining \{Cp*Rh\} fragments with H\textsubscript{L1} ligands in a 1:1 ratio in MeOH and following their evolution in the \textsuperscript{1}H NMR and ESI-MS spectra. Due to limited solubility, after mixing the components, it quickly formed numerous insoluble substances, which dissolved with continued heating at 50 °C. The \textsuperscript{1}H NMR spectrum clearly showed the formation of a \(\text{Rh}_6(\text{L1})_4\) cage (see Fig. S7\textsuperscript{‡}). The ESI-MS spectrum also exhibited one peak at \(m/z = 1024.41\), corresponding to the octahedral species \([\text{Cp*}_6\text{Rh}_6(\text{L1})_4(\text{OTf})_5]^{3+}\) (see Fig. S8\textsuperscript{‡}). Therefore, the \(\text{Rh}_2(\text{H}_{\text{L1}})_2\) macrocycle is the initial (meta-stable) product, which then slowly rearranges to an \(\text{Rh}_6(\text{L1})_4\) cage in a solution. By the Gibbs free energy calculation, the corresponding \(\Delta G\) value going from the \(\text{Rh}_2(\text{H}_{\text{L1}})_2\) macrocycle to the \(\text{Rh}_6(\text{L1})_4\) cage is \(-11.6\) kcal mol\(^{-1}\), indicating that the \(\text{Rh}_6(\text{L1})_4\) cage with higher octahedral symmetry is the thermodynamically favored product (see Fig. S14\textsuperscript{‡}). This conversion is supposed to be also associated with the solvent system. The \(\Delta G\) values for removing a CH\textsubscript{3}CN or CH\textsubscript{3}OH ligand from the \(\text{Rh}_2(\text{H}_{\text{L1}})_2\) macrocycle are 2.8 and 1.0 kcal mol\(^{-1}\), respectively. Therefore, it is easier for transformation to occur in MeOH than that in DMSO (see Fig. S15\textsuperscript{‡}).

In order to further explore the validity of the edge-directed synthetic strategy, as depicted in Scheme 2, a \(\text{M}_8\text{L}_4\) cubic cage 3 was prepared through two-step reactions. After treatment of \([\text{Cp*RhCl}_2]\_2\) with 4 equivalents of AgOTf in methanol, an equimolar amount of ligand H\textsubscript{L2} in dichloromethane solution was added, providing a 58% yield of 3. It has good solubility in the most common organic solvents. The \textsuperscript{1}H NMR spectrum of cage 3 displayed one complete set of proton resonances, as evidenced by two doublet signals at \(\delta = 8.66\) and \(\delta = 8.04\) ppm assignable to pyridyl rings, and one singlet at \(\delta = 3.21\) ppm for the methyl protons of the \textsubscript{L2} ligands, along with one singlet at \(\delta = 1.69\) ppm for the methyl protons of the Cp* rings (see Fig. S9\textsuperscript{‡}). Electrospray ionization mass spectrometry (ESI-MS) provided further evidence for the formation of the \(\text{M}_8(\text{L}_2)_4\) cage, with signals corresponding to \([\text{Cp*}_8\text{Rh}_8(\text{L}_2)_4(\text{OTf})_6]^{2+}\) and \([\text{Cp*}_8\text{Rh}_8(\text{L}_2)_4(\text{OTf})_5]^{3+}\) at \(m/z = 2043.19\) and 1312.47, respectively (see Fig. S10\textsuperscript{‡}). Thus, the \(\text{M}_8(\text{L}_2)_4\) cage 3 is stable both in the solid state and solution.

Single crystals of cage 3, grown by diffusion of hexane into methanol and dichloromethane, crystallized in the monoclinic space group \(C2/c\). X-ray diffraction analysis revealed that the \(\text{H}_4\text{L}_2\) ligand, with two active carboxyls, can lose the protons on the amido N atoms to form the corresponding dianion and can further coordinate through anionic \([\text{N}^+=\text{O}]\)-chelating five-membered rings, in addition to the Npyridyl atoms, when binding to Rh(III) ions. The \textsubscript{L2} bridging ligands adopt a “Z” shape, bent at the two chelating positions, with the pyridyl groups at the termini. This flexibility allows them to accommodate a number of metal centres. The presence of eight metal corners and twelve edges in a cube requires a 2:1 \(\text{M}/\text{L}\) ratio. As shown in Fig. 3, eight Rh(III) ions are arrayed at the corners of a pseudo-cube with four \textsubscript{L2} ligands spanning the twelve edges. Each \{Cp*Rh\} centre, being at the juncture of three
edges, therefore interacts with one bidentate chelating unit and one pyridine donor in a saturated three-legged piano-stool geometry. The separations between Rh⋯Rh centres along the edges in cage 3 lie in the range between 7.48 and 9.00 Å. The Rh1⋯Rh4 (9.00 Å) and Rh1⋯Rh4 (–x; y; 0.5 – z) (8.99 Å) distances are effectively identical, providing a 2D square. The squares sit nearly directly above one another, further extended by the Rh2⋯Rh3 separations providing a 3D cubic structure.

We attempted to introduce different metal subunits into this system to further study the self-assembly behavior and possible conformations of these flexible ligands. Half-sandwich trinuclear complex 4 was obtained simply by reaction of [Cp*IrCl2]2 and H3L1 ligands in a 3 : 2 ratio. A graphical representation of the crystal phase is depicted in Fig. S16,† where complex 4 is a neutral trinuclear complex. Accordingly, the bridging ligand L1 is bent with an angle of 81.6° at the Ir2 metal chelating site. The Ir1⋯Ir2, Ir2⋯Ir3 and Ir1⋯Ir3 distances are 9.05, 9.26 and 11.96 Å, respectively. The series of peaks characterized by 1H NMR in DMSO for complex 4 were observed at δ 8.82, 8.75, 8.36, 8.03 and 7.98 ppm corresponding to protons of asymmetrical L1 ligands. Moreover, the other two singlet peaks at δ 1.68 and 1.63 ppm arise from the methyl protons of one central and two terminal Cp* rings, respectively. There is a clear evidence of fragmentation in ESI-MS spectra with a peak for [Cp*3Ir3(L1)Cl4]+ at m/z = 1349.19 (see Fig. S11 and S12).†

Obviously there is a wide range of conformations that these flexible ligands could adopt in metal–ligand assemblies. We envisage that the use of rigid binuclear building units as building blocks could be an effective method for imposing linearity on these flexible ligands during self-assembly. When binuclear [Cp*Rh(CO4)2Cl2] was treated with AgOTf, followed by an equimolar amount of the HL1 ligand, macrocycle 5 was obtained in high yield (91%). X-ray analyses of 5 revealed that it is a rectangular macrocycle with dimensions of 5.5 × 15.4 Å. The HL1 ligands were found to adopt linear shapes, as depicted in Fig. S17.‡ The 1H NMR spectrum of the assembly indicated both trans and cis conformations in a solution (see Fig. S13‡).

Conclusions

In this study, we demonstrated a family of discrete half-sandwich polyhedral cages based on half-sandwich [Cp*Rh] metal centres and flexible Schiff-base ligands. By variation of the building blocks, we were able to substantially and selectively change the size and the topology of the cages. Notably, the Cp*Rh(m-based half-sandwich octahedral M9(L1), cage 2 and the cubic M9(L2), cage 3 are rare examples of assemblies based on flexible ligands as edges and half-sandwich organometallic fragments as corners. Interestingly, the Rh(m-based organometallic macrocycle M9(HL1), is metastable in a solution and was found to rearrange to a M9(L1), cage. From DFT calculations, the ΔG values agree well with the experimental observations. Our system highlights the modular function of flexible Schiff-base ligands and provides an insightful synthetic approach to the assembly of discrete half-sandwich coordination cages.

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Notes and references


