Supporting Information for
Self-assembled half-sandwich polyhedral cages via flexible Schiff-base ligands: an unusual macrocycle-to-cage conversion
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Table S1. Crystallographic data and structure refinement parameters for complexes 1-5

1. Materials and instrumentations

All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. MeOH was purified by distilling with Mg rod and I$_2$. CH$_2$Cl$_2$ and CH$_3$CN solvents were purified by distilling with CaH$_2$. [Cp*MCl$_2$]$_2$ (M = Rh and Ir)$^{[1]}$, Schiff-base 4-pyridinecarbaldehyde isonicotinylhydrazone ligand (HL$_1$)$^{[2]}$ and 2,3-butanedione bis(isonicotinylhydrazone) ligand (H$_2$L$_2$)$^{[3]}$ were all prepared according to the literature methods. Elemental analyses were performed on an Elementar III Vario EI analyzer. $^1$H NMR (400/500 MHz) spectra were obtained on a Bruker AVANCE I 400 and VANCE-DMX 500 spectrometers. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm$^{-1}$ were measured on a Nicolet Avatar-360 spectrophotometer. ESI-MS spectra were recorded on a Micro TOF II
mass spectrometer using electrospray ionization.

2. Syntheses of complexes 1-5

Synthesis of 1. A mixture of \([\text{Cp}^*\text{RhCl}_2]_2\) (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, HL1 ligand (13.8 mg, 0.06 mmol) in acetonitrile were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of 1 for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of macrocycle 1 in methanol and acetonitrile. Yield: 20.5 mg (43%). Anal. Calcd (%) for C_{52}H_{56}N_{10}O_{14}S_{4}F_{12}Rh_2: C 38.86, H 3.51, N 8.72. Found: C 38.79, H 3.45, N 8.64. IR (KBr disk): 3112(w), 2968(w), 1685(s), 1609(m), 1551(w), 1491(w), 1418(m), 1375(m), 1351(w), 1282(vs), 1251(vs), 1225(m), 1160(vs), 1060(w), 1031(vs), 950(w), 895(w), 847(w), 760(w), 639(s), 575(m), 518(m)cm^{-1}. ESI-MS: m/z = 1375.07 (calcd for [Cp*_{2}Rh_{2}(HL1)_{2}(OTf)_{3}]^+ 1375.07).

Synthesis of 2. A mixture of \([\text{Cp}^*\text{RhCl}_2]_2\) (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, HL1 ligand (9.2 mg, 0.04 mmol) in acetonitrile were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of 2 for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of cage 2 in methanol and acetonitrile. Yield: 22.8 mg (63%). Anal. Calcd (%) for C_{120}H_{132}N_{18}O_{28}S_{8}F_{24}Rh_6: C 39.99, H 3.69, N 6.99. Found: C 39.90, H 3.60, N 6.91. IR (KBr disk): 2973(w), 2925(w), 1613(m), 1568(m), 1505(s), 1421(w), 1373(s), 1319(w), 1273(vs), 1277(vs), 1259(vs), 1225(m), 1159(vs), 1058(m), 1031(s), 901(w), 854(w), 824(w), 757(w), 709(w), 639(s), 602(w), 574(w), 518(w) cm^{-1}. ^1H NMR (400MHZ, CD_3OD): δ 8.70-8.12 (m, 36H, L1), δ 2.03 (s, 6H, CH_3CN), δ 1.81-1.70 (m, 90H, Cp*). ESI-MS: m/z = 1652.11 (calcd for [Cp^*_{6}Rh_{6}(L1)_{4}(CH_3CN)_2(OTf)_3]^2^+ 1652.11), 1024.41 (calcd for [Cp^*_{6}Rh_{6}(L1)_{4}(OTf)_3]^3^+ 1024.40).
Synthesis of 3. A mixture of [Cp*RhCl₂]₂ (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, H₂L₂ (9.8 mg, 0.03 mmol) in dichloromethane were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of 3 for an X-ray diffraction study were obtained by slow diffusion of hexane into a mixture solution of cage 3 in methanol and dichloromethane. Yield: 19.1 mg (58%). Anal. Calcd (%) for C₅₂H₇₆N₂₄O₃₂S₈F₂₄Rh₈: C 41.62, H 4.04, N 7.66. Found: C 41.55, H 3.96, N 7.59. IR (KBr disk): 2964(w), 2921(w), 1610(w), 1571(m), 1529(s), 1480(w), 1458(w), 1418(w), 1370(vs), 1262(m), 1158(s), 1058(w), 1031(vs), 903(w), 852(w), 755(m), 717(m), 702(w), 638 (vs), 573(w), 517(w)cm⁻¹. ¹H NMR (400MHz, CD₃OD): δ 8.66 (d, 16H, J = 6.4, Hα, L₂), δ 8.04 (d, 16H, J = 6.4, Hβ, L₂), δ 3.21 (s, 24H, Hγ, L₂), δ 1.69 (s, 120H, Cp*). ESI-MS: m/z = 2043.19 (calcd for [Cp*Rh₈(L₂)₄(OTf)₆]²⁺ 2043.18), 1312.47 (calcd for [Cp*Rh₈(L₂)₄(OTf)₅]³⁺ 1312.47).

Synthesis of 4. A mixture of [Cp*IrCl₂]₂ (24.0 mg, 0.03 mmol) and HL₁ ligand (4.6 mg, 0.02 mmol) in acetonitrile was stirred for 24h, then the mixture was obtained as solid by filtration, washed with diethyl ether and dried in vacuum. Crystals suitable of 4 for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of complex 4 in methanol and dichloromethane. Yield: 21.5 mg (78%). Anal. Calcd (%) for C₄₂H₅₄N₄OCl₃Ir₃: C 36.43, H 3.93, N 4.05. Found: C 36.37, H 3.87, N 3.98. IR (KBr disk): 2965(w), 2921(w), 1610(w), 1565(s), 1507(vs), 1457(m), 1418(w), 1383(s), 1319(w), 1241(w), 1162(w), 1081(w), 1056(m), 1031(s), 1012(m), 897(w), 859(w), 827(w), 756(w), 714(w), 694(w), 606(w), 583(w) cm⁻¹. ¹H NMR (400MHZ, DMSO): δ 8.82 (d, 2H, J = 6.4, H₉, L₁), δ 8.75 (d, 2H, J = 6.4, H₈, L₁), δ 8.36 (d, 2H, J = 6.4, H₇, L₁), δ 8.03 (s, 1H, Hγ, L₁), δ 7.98 (d, 2H, J = 6.4,H₆, L₁), δ 1.68 (s, 15H, Cp*), δ1.63 (s, 30H, Cp*). ESI-MS: m/z = 1349.19 (calcd for [Cp*₃Ir₃(L₁)Cl₄]⁺ 1349.19).

Synthesis of 5. A mixture of [(Cp*₂Rh₂(C₂O₄)Cl₂] (31.8mg, 0.05mmol) and AgOTf
(25.7mg, 0.10mmol) in methanol was stirred at room temperature for 5h. After filtration to remove AgCl, HL1 ligand (11.5mg, 0.05mmol) in acetonitrile was added to the filtrate, and the mixture was stirred for 24h. Then the solution was concentrated to give yellow solid, which was washed by diethyl ether and dried under vacuum. Crystals suitable of 5 for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of macrocycle 5 in methanol and acetonitrile.

Yield: 49.5 mg (91%). Anal. Calcd (%) for C_{72}H_{80}N_8O_{22}S_4F_{12}Rh_4: C 39.72, H 3.70, N 5.15. Found: C 39.69, H 3.61, N 5.10. IR (KBr disk): 2967(w), 2926(w), 1698(w), 1620(vs), 1560(w), 1489(w), 1458(w), 1281(w), 1258(vs), 1225(m), 1158(s), 1062(w), 1031(vs), 832(w), 796(w), 758(w), 639(s), 574(w), 518(w)cm\(^{-1}\). \(^1\)H NMR (400MHZ, DMSO): \(\delta\) 12.74 (s, 2H, -NH, HL1, trans), \(\delta\) 12.49 (s, 2H, -NH, HL1, cis), \(\delta\) 8.37 (s, 2H, H\(\gamma\), HL1, cis), \(\delta\) 8.29-8.30 (m, 6H, H\(\gamma\)+H\(\alpha\), HL1, trans; 4H, H\(\alpha\), HL1, cis), \(\delta\) 8.04-8.05 (m, 4H, H\(\alpha\)\', HL1, trans; 4H, H\(\alpha\)\', HL1, cis), \(\delta\) 7.60 (d, 4H, J = 6.4, H\(\beta\), HL1, trans), \(\delta\) 7.63 (d, 4H, J = 6.4, H\(\beta\), HL1, cis), \(\delta\) 7.60 (d, 4H, J = 6.4, H\(\beta\'), HL1, trans), \(\delta\) 1.55 (s, 60H, Cp*, cis), \(\delta\) 1.54 (s, 60H, Cp*, trans).

3. The \(^1\)H NMR and ESI-MS spectra of complexes 1-5

![Image](image.png)

Figure S1. The \(^1\)H NMR spectrum of cage 2 in methanol.
Figure S2. The ESI-MS spectrum ($2^{2+}$) and ($2^{3+}$) of cage 2.

Figure S3. The ESI-MS spectrum ($1^+$) of macrocycle 1.
Figure S4. Time course $^1$H NMR experiment of the crystalline macrocycle 1 displaying degradation and rearrangement to M$_6$(L1)$_4$ cage in DMSO-$d_6$ solvent. (a) Spectrum immediately after dissolution of macrocycle 1; (b)(c) Spectrum after dissolution of macrocycle 1, but measured 1 day and two weeks later, respectively; (d) Spectrum after redissolved cage 2 in DMSO-$d_6$ solvent.

Figure S5. The $^1$H NMR experiment of the crystalline macrocycle 1 displaying degradation and rearrangement to M$_6$(L1)$_4$ cage in DMSO-$d_6$ solvent. (a) Spectrum immediately after dissolution of macrocycle 1 (25°C); (b) Spectrum after dissolution of macrocycle 1 (80°C); (c) Spectrum after redissolved macrocycle 1 kept at 80°C for
1d; (d) Spectrum after redissolved cage 2 in DMSO-\textit{d}_6 solvent.

**Figure S6.** The ESI-MS spectrum after redissolved macrocycle 1 heated to 80°C in DMSO-\textit{d}_6 solvent, indicating that the formation of $M_6(L_1)_4$ cage.

**Figure S7.** The $^1$H NMR spectrum after mixing {Cp*Rh} fragments with HL1 ligands in a 1:1 ratio in MeOH solvent, then heated to 50°C, indicating that the formation of $M_6(L_1)_4$ cage.
Figure S8. The ESI-MS spectrum after mixing \{\text{Cp}^*\text{Rh}\} fragments with \text{HL1} ligands in a 1:1 ratio in MeOH solvent, then heated to 50°C, indicating that the formation of \text{M}_6(\text{L1})_4 cage.

Figure S9. The $^1$H NMR spectrum of cage 3.
Figure S10. The ESI-MS spectrum ($3^{2+}$) and ($3^{3+}$) of cage 3.

Figure S11. The $^1$H NMR and partial $^1$H COSY spectra of complex 4.
Figure S12. The ESI-MS spectrum (4⁺) of complex 4.

Figure S13. The $^1$H NMR and partial $^1$H COSY spectra of macrocycle 5.

4. DFT computational details

All the calculations were performed with the B97-D3 density functional method[^4] using the Gaussian 09 software package[^5]. The empirical long-range correction of Grimme et al was used for the B97-D3 functional[^6]. The basis sets used were: the 3-21G* basis set[^7] for C and H, the 6-31+G(d) basis set[^8] for N and O, and the SDD pseudo potential basis set[^9] for Rh. The solvent effect was
taken into consideration using the SMD solvation model of Truhlar et al.\textsuperscript{[10]} All geometries were fully optimized and harmonic vibrational frequencies were calculated to guarantee that the optimized structures are genuine minima.

**Figure S14.** Free-energy change at 298.15 K for the formation of $\text{M}_6(\text{L}_1)_4$ cage from $\text{M}_2(\text{HL}_1)_2$ macrocycle.

**Figure S15.** Free-energy change at 298.15 K for removing a CH$_3$CN or CH$_3$OH ligand from $\text{M}_2(\text{HL}_1)_2$ macrocycle in DMSO or CH$_3$OH solution, respectively.

5. Single-crystal structure determination of complexes 1-5

All the determinations of unit cell and intensity data were performed with
graphite-monochromated Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å) on the CCD-Bruker APEX DUO for complexes 1, 2, 4, 5 and especially Cu radiation ($\lambda = 1.54184$ Å) on the Bruker D8 ADVANCE for complex 3. All the data were collected at 173(2) or 150 K using the $\omega$ scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on $F2$ by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.\textsuperscript{[11]} Crystallographic data for complexes 1-5 are summarized in Table S1.

**Figure S16.** (a) X-ray crystal structure of complex 4; (b) Perspective image showing the triangle in 4. Hydrogen atom and solvent molecules are omitted for clarity.

**Figure S17.** X-ray crystal structure of macrocycle 5. Triflate anions and solvent molecules are omitted for clarity.
Table S1. Crystallographic data and structure refinement parameters for complexes 1-5

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REFERENCES


