Supporting Information

**Stepwise Assembly of “Organometallic Boxes” with Half-Sandwich Ir, Rh and Ru Fragments**

Ying-Feng Han\(^1\), Yue-Jian Lin\(^1\), Lin-Hong Weng\(^1\), Heinz Berke\(^1\)\(^2\), and Guo-Xin Jin\(^*\)\(^1\)

\(^1\)Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai 200433 (P. R. China)

\(^2\)Institute of Inorganic Chemistry, University of Zurich, Winterthurer Strasse 190, 8057 Zurich (Switzerland)

E-mail: gxjin@fudan.edu.cn
Experimental Section

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System (4464) and collected just before use. \([\text{Cp}^*\text{IrCl}_2]_2\) (1a)[1], \([\text{Cp}^*\text{RhCl}_2]_2\) (1b)[1], [\((p\text{-cymene})\text{-RuCl}_2\] (1c)[2], [\((p\text{-cymene})_2\text{Ru}_2(\mu-\eta^4\text{-C}_2\text{O}_4)\] (4c)[3], [\((p\text{-cymene})_2\text{Ru}_2(\mu-\eta^4\text{-C}_2\text{O}_4)(\text{MeOH})_2\] (5c)[3], [(Cp*)_2Ir_2(\mu-\eta^4\text{-C}_2\text{O}_4)]Cl_2\] (4a)[4] and were prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, Elemental analyses were carried out by Elementar III Vario El Analyzer, the samples were dried in vacuum for 48 h before to analyses. \(^1\)H-NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in [D_6]-DMSO or CDCl_3 solution.

Synthesis of 2a \([\text{Cp}^*\text{Ir}_4(\mu-\text{H}_2\text{TPyP})\]Cl_8

To a solution of 1a (160 mg, 0.20 mmol) in CH_2Cl_2 (30 mL) was added H_2TPyP (62 mg, 0.10 mmol) at room temperature. After stirring for 18 h, the solvent was evaporated under reduced pressure and the dark red residue was washed by diethyl ether. The dark red solids (217 mg, 98%) were gained through recrystallization from CH_2Cl_2/hexane at -18°C. \(^1\)H-NMR (500 MHz, CDCl_3 , 25°C, TMS ): \(\delta = 9.47\) (m, 8H; Hpyridyl), 8.83 (d, 8H; Hpyrrole), 8.20 (m, 8H; Hpyridyl), 1.78 (s, 30H; Cp*), 1.56 (s, 30H; Cp*), -2.97 (s, 2H; NH) ppm; elemental analysis (%) calcd. for C_{80}H_{86}Cl_8Ir_4N_8: C 43.44, H 3.92, N 5.07; found: C 43.21, H 4.06, N 4.97.

Synthesis of 3a \([\text{Cp}^*\text{Ir}_8(\mu-\text{H}_2\text{TPyP})_2(\mu-\text{Cl})_8](\text{OTf})_8\)

AgOTf (102 mg, 0.40 mmol) was added to a solution of 2a (220 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL and diethyl ether was added. giving red solids of 3a (202 mg, 76%). \(^1\)H-NMR (500 MHz, [D_6]-DMSO, 25°C, TMS ): \(\delta = 9.08-9.36\) (m, 16H; Hpyridyl), 8.85 (m, 16H; Hpyrrole), 8.12 (d, 16H; Hpyridyl), 1.87 (s, 120H; Cp*), -2.92 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C_{168}H_{172}Cl_8F_4Ir_8N_16O_24S_8: C 37.84, H 3.25, N 4.20, S 4.81; found: C 37.59, H
Synthesis of 4b \([\text{Cp}^*\text{2}\text{Rh}_2(\mu-\eta^4-\text{C}_2\text{O}_4)\text{Cl}_2]\)

\((\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}\) (140 mg, 1 mmol) was added to a solution of 1b (618 mg, 1 mmol) in CH\(_3\)OH (20 mL). The suspension was kept stirring at 55°C for 5h. The solvent was then evaporated to dryness under vacuum, the residue was extracted with CH\(_2\)Cl\(_2\). Yield: 86%; \(^1\)H-NMR (500 MHz, [D\(_6\)]-DMSO, 25°C, TMS ): \(\delta = 1.65\) (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C\(_{22}\)H\(_{30}\)Cl\(_2\)O\(_4\)Rh\(_2\): C 41.60, H 4.76; found: C 41.92, H 4.84.

Synthesis of 5a \([\text{Cp}^*\text{2}\text{Ir}_2(\mu-\eta^4-\text{C}_2\text{O}_4)](\text{OTf})_2\)

AgOTf (51 mg, 0.20 mmol) was added to a solution of 4a (82 mg, 0.10 mmol) in CH\(_3\)OH (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH\(_2\)Cl\(_2\). The filtrate was concentrated to about 3 mL and diethyl ether was added, giving yellow solids of 5a (71 mg, 78%). \(^1\)H-NMR (500 MHz, [D\(_6\)]-DMSO, 25°C, TMS ): \(\delta = 1.63\) (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C\(_{24}\)H\(_{30}\)F\(_6\)Ir\(_2\)O\(_{10}\)S\(_2\): C 27.69, H 2.90, S, 6.16; found: C 27.34, H 3.04, S, 6.12.

Synthesis of 5b \([\text{Cp}^*\text{2}\text{Rh}_2(\mu-\eta^4-\text{C}_2\text{O}_4)](\text{OTf})_2\)

AgOTf (51 mg, 0.20 mmol) was added to a solution of 4b (64 mg, 0.10 mmol) in CH\(_3\)OH (20 mL) at room temperature and stirred for 3 h, The solvent was removed and the residue was extracted with CH\(_2\)Cl\(_2\). The filtrate was concentrated to about 3 mL and diethyl ether was added, giving yellow solids of 5b (71 mg, 83%). \(^1\)H-NMR (500 MHz, [D\(_6\)]-DMSO, 25°C, TMS ): \(\delta = 1.61\) (s, 30H; Cp*) ppm; elemental analysis (%) calcd. for C\(_{24}\)H\(_{30}\)F\(_6\)O\(_{10}\)Rh\(_2\)S\(_2\): C 33.42, H 3.51, S 7.44; found: C 33.64, H 3.68, S 7.85.

Synthesis of 6a \([\text{Cp}^*\text{8}\text{Ir}_8(\mu-\eta^4-\text{C}_2\text{O}_4)_{4}(\mu-\text{H}_2\text{TPyP})_{2}](\text{OTf})_8\)

The first method: (NH\(_4\))\(_2\)C\(_2\)O\(_4\)\cdot\text{H}_2\text{O}\) (28 mg, 0.2 mmol) was added to a solution of 3a (265 mg, 0.05 mmol) in CH\(_3\)OH (20 mL), The suspension was kept stirring at 55°C for 5h. The solvent was then
evaporated to dryness under vacuum, the residue was extracted with CH$_2$Cl$_2$. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 6a as purple solids. Yield: 143 mg, 65%.

The second method: AgOTf (0.2 mmol) was added to a suspension of 4a (0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H$_2$TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed and the residue was extracted with CH$_2$Cl$_2$. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 6a as purple solids. Yield: 110.5 mg, 82%; IR: $\nu$ = 1631 cm$^{-1}$(C=O); $^1$H-NMR (500 MHz, [D$_6$]-DMSO, 25°C, TMS): $\delta$ = 9.02-9.34 (m, 16H; H$_{\text{pyridyl}}$), 8.57-8.85 (m, 16H; H$_{\text{pyrrole}}$), 8.10 (d, 16H; H$_{\text{pyridyl}}$), 1.86 (m, 120H; Cp*), -2.93 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C$_{176}$H$_{172}$F$_{24}$Ir$_8$N$_{16}$O$_{40}$S$_8$: C 39.13, H 3.21, N 4.15, S 4.75; found: C 38.98, H 3.06, N 3.97, S 4.62.

Synthesis of 6b [Cp$_8$Rh$_8$(μ-η$^4$-C$_2$O$_4$)$_4$((μ-H$_2$TPyP)$_2$](OTf)$_8$

AgOTf (0.2 mmol) was added to a suspension of 4b (0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H$_2$TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed and the residue was extracted with CH$_2$Cl$_2$. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 6b as purple solids. Yield: 91.4 mg, 78%; IR: $\nu$ = 1634 cm$^{-1}$(C=O); $^1$H-NMR (500 MHz, [D$_6$]-DMSO, 25°C, TMS): $\delta$ = 9.06-9.08 (m, 16H; H$_{\text{pyridyl}}$), 8.88 (m, 16H; H$_{\text{pyrrole}}$), 8.17 (d, 16H; H$_{\text{pyridyl}}$), 1.57 (m, 120H; Cp*), -2.92 (s, 4H; NH) ppm; elemental analysis (%) calcd. for C$_{176}$H$_{172}$F$_{24}$Rh$_8$N$_{16}$O$_{40}$S$_8$: C 45.10, H 3.70, N 4.78, S 5.47; found: C 45.03, H 3.57, N 4.55, S 5.32.

Synthesis of 6c [(p-Cymene)$_8$Ru$_8$(μ-η$^4$-C$_2$O$_4$)$_4$((μ-H$_2$TPyP)$_2$](OTf)$_8$

AgOTf (0.2 mmol) was added to a suspension of 4c (0.1 mmol) in methanol (20 mL) at room
temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then H$_2$TPyP (0.05 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15h. The solvent was then removed and the residue was extracted with CH$_2$Cl$_2$. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give $6c$ as purple solids. Yield: 92.1 mg, 79%; IR: $\nu = 1630$ cm$^{-1}$ (C=O); $^1$H-NMR (500 MHz, [D$_6$]-DMSO, 25°C, TMS): $\delta = 8.96$-9.09 (m, 16H; H$_{\text{pyridyl}}$), 8.55 (m, 16H; H$_{\text{pyrrole}}$), 8.30 (d, 16H; H$_{\text{pyridyl}}$), 6.18-6.28 (m, 16H; Ar$_p$-cym), 5.99-6.15 (m, 16H; Ar$_p$-cym), 3.35 (m, 8H; CH(CH$_3$)$_2$), 3.35 (s, 24H; CH$_3$), 1.16-1.40 (m, 48H; CH(CH$_3$)$_2$), -3.07 (s, 4H; NH) ppm; elemental analysis (%): calcd. for C$_{176}$H$_{164}$F$_{24}$Ru$_8$N$_{16}$O$_{40}$S$_8$: C 45.32, H 3.54, N 4.80, S 5.50; found: C 45.13, H 3.37, N 4.65, S 5.21.

**X-ray Structure Determination.**

All single crystals were immersed in mother solution and sealed in thin-walled glass. Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the $\omega$ scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on $F^2$ by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL$^5$ program. In complex $6a$, three triflate anions could be well refined, but some carbon, oxygen and fluorine atoms in the other five anions were never found. Therefore, new data sets corresponding to omission of the missing anions were generated with the SQUEEZE algorithm$^6$ and the structures were refined to convergence. In the structure of $6a$, 93 restraints were used in the refinement: ISOR instructions were applied to restrain 15 atoms (atom N2, N4, N12, C4, C5, C10, C18, C20, C45, C89, C90, C125, C126, C159, C162, each ISOR command line corresponds to 6 restraints) and 3 bond distances were restrained by DFIX instructions. Similarly, in the structure of $6c$, 2 atoms were restrained by ISOR (C85, C112) and 3 bond distances by DFIX. All the
hydrogen atoms were included in calculated positions, one of the hydrogen atoms in the solvent water molecules could be found by differential Fourier method.

All of figures were drawn with Diamond.

Crystal data for 5b: C_{26}H_{34}Cl_{4}F_{6}Rh_{2}O_{10}S_{2}, \( M_r = 1032.27 \), Crystal dimensions 0.25 x 0.20 x 0.18 mm\(^3\), monoclinic, space group \( P2(1)/n \), \( Z = 2 \), \( \rho_{\text{calc}} = 1.823 \) g cm\(^{-3}\), \( \mu(\text{MoK}\alpha) = 1.352 \) mm\(^{-1}\), \( F(000) = 1028 \), \( a = 14.50(2) \), \( b = 9.437(14) \), \( c = 14.50(2) \) Å, \( \beta = 108.711(16)\)°, and \( V = 1880(5) \) Å\(^3\). \( R = 0.0738 \) [\( I > 2\sigma(I) \)], \( R_w = 0.1864 \) (for all data), GOF = 0.935.

**Figure S1** Molecular structure of 5b with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. The symmetry operators are: \( a = 1-x; b = 2-y; c = 1-z \).

**References**

**Figure S2** Crystal structure of the cationic part of 6a. Space-filling model of 6a viewed along the b axis showing the D (clockwise) configuration (left) and the L (counterclockwise) configuration (right). Carbon atoms are shown as gray, oxygen as red, nitrogen as blue and iridium as green.
**Figure S3** Crystal packing diagram of 6a showing the open channels. Hydrogen atoms, anions are omitted.
Figure S4 The existence of the counteranions and disordered H$_2$O molecules are located outside of box 6c. Carbon atoms are shown as black, oxygen as red, sulfur as yellow, fluorine as green and ruthenium as rosy.
Figure S5 Crystal packing diagram of 6c showing the open channels. Hydrogen atoms, anions and H₂O molecules are omitted.
**Figure S6** Crystal structure of the cationic part of 6c. Space-filling model of 6c viewed along the $b$ axis showing the **D** (clockwise) configuration (left) and the **L** (counterclockwise) configuration (right). Carbon atoms are shown as gray, oxygen as red, nitrogen as blue and iridium as green.
Figure S7 UV-vis absorption spectra in dichloromethane of 6a (red line), 6b (green line) and 6c (blue line) at room temperature.