Stepwise formation of “organometallic boxes” with half-sandwich Ir, Rh and Ru fragments†

Ying-Feng Han,[a] Yue-Jian Lin,[a] Lin-Hong Weng,[a] Heinz Berke[ab] and Guo-Xin Jin*[a]

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***Octa*nuclear complexes with half-sandwich Ir, Rh and Ru fragments and *tetra*(4-pyridyl)porphyrin (L1) and oxalate (L2) spacer ligands $[(Cp^*M)_4L1]_2[L2]_4$ (M = Ir (6a) M = Rh (6b)), $[((cymene)Ru)_4(L1)]_2[L2]_4$ were prepared and characterized.**

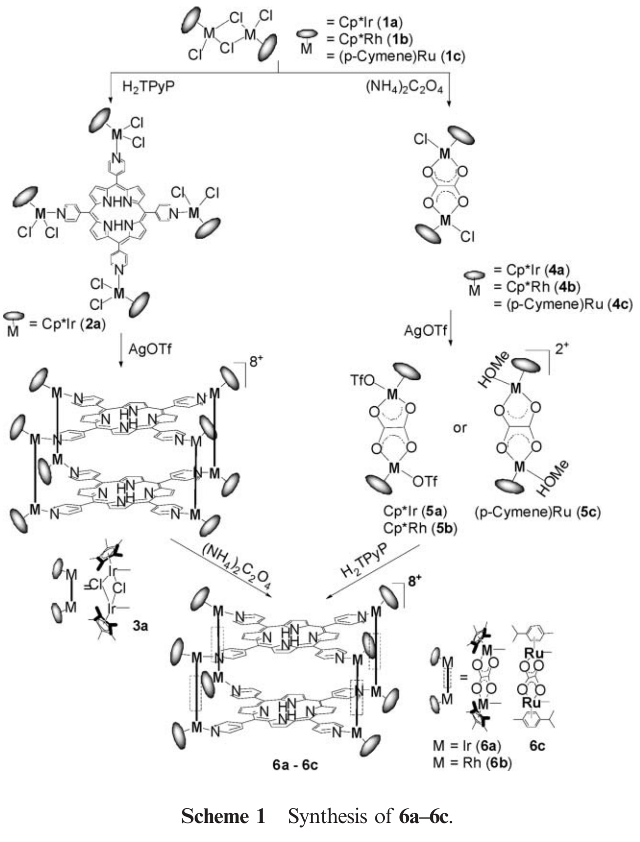
The directional properties of coordinative bonds can be used to construct supramolecular structures with transition metal centers by rational design. Closed structures provide cage properties and may have molecular filling of their cavities or not. In either case their unique physical and chemical properties were exploited as various types of sensors, different kinds of sorters, and as catalysts and templates in shape-selective synthesis.[1]

Except for the metalorganic species “MOF”,[2] which contain multinuclear connecting corners, the construction of metalorganic or organometallic cubane-type supramolecular structures with corners of single transition metal centers is as yet rarely approached. Among these the organometallic species with tightly binding ancillary ligand sets often possess corners with lower connectivities. As an exception may be viewed the example reported by the Rauchfuss group[3] which contain rhodium and cobalt octahedra and cyanide linkers and are infinitely connected. Corners with low connectivities are more suited for the build-up of molecular structures, such as metallamacrocyclic complexes and coordination cages. It was for instance shown that half-sandwich Ir, Rh and Ru fragments can serve as three-fold connectors in such compounds.[4] μ-Oxalato ligands were also demonstrated to be suitable spacers in half-sandwich Ru pseudo-prisms.[4b] We and the Tatsumi group have reported a series of tetranuclear rhodium and iridium supramolecules bearing ancillary cyclopentadienyl ligands in combination with two different types of spacer ligands.[5] Considering the fact that for the build-up of boxes a square subunit could not only be obtained from four rigid 2-connecting edges, but also from a 4-connecting rigid cross of square diagonals, we wondered, if the tetradentate slightly bent *meso*-tetra(4-pyridyl)porphyrin (H_2TPyP) with crossing *trans* donor axes could be used for this task. Furthermore, if we could connect up two of these squares by aid of μ-oxalato binuclear bridging units as short edges, we could obtain shapes of distorted cubanes compressed along a prominent tetragonal axis may be also refered to as “organometallic boxes”.

Following this idea, we indeed could develop a facile route to respective mixed ligand organometallic structures allowing first the assembly of one *meso*-tetra(4-pyridyl)porphyrin (H_2TPyP) square with caps of four half-sandwich chloro Ir units followed by clipping of two of these squares first with eight μ-chlorides and then with four oxalates by substitution of the chlorides (Scheme 1). Stirring a solution of $[Cp^*IrCl_2]_2$ (**1a**) and H_2TPyP in 2 : 1 molar ratio in CH_2Cl_2 at room temperature, the square-type *tetra*nuclear complex **2a** was obtained in almost quantitative yield.

Subsequent addition of AgOTf (Tf = O_2SCF_3) to **2a** caused chloride abstraction and μ-dichloro linkage of two squares, which constitute the shorter edges of the cationic “organometallic box” **3a** obtained as a red crystalline triflate (O_3SCF_3) salt.‡

3a was used as a synthetic intermediate exchanging the μ-Cl by μ-oxalato bridges by treatment of **3a** with 4 equivalents of ammonium oxalate. The porphyrin/oxalato mixed bridge species **6a** was obtained as a purple solid by a route, which could be denoted as “porphyrin before oxalate”.§ As depicted in Scheme 1, complex **6a** could also be prepared by an alternative “oxalate



Scheme 1 Synthesis of **6a–6c**.

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[a] *Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai, 200433, P. R. China. E-mail: gxjin@fudan.edu.cn; Fax: (+86)-21-65643776*
[b] *Institute of Inorganic Chemistry, University of Zurich, Winterthurer Strasse 190, 8057, Zurich, Switzerland*

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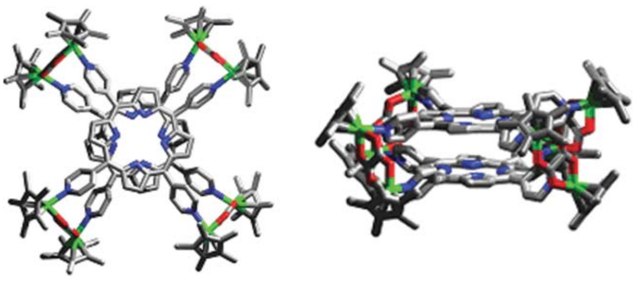

Fig. 1 X-Ray crystal structures of the cationic part of **6a**. Top view (left) and side view (right). Hydrogen atoms are omitted for clarity. Carbon atoms are shown in gray, oxygen in red, nitrogen in blue, iridium in green.

before porphyrin" synthetic pathway, which starts from the *bi*nuclear oxalato complex **4a**. The required coordinatively unsaturated intermediate **5a** was prepared by the reaction of **4a** with two equivalents of AgOTf. After separation from AgCl and subsequent reaction with H_2TPyP in methanol, the purple solid **6a** was isolated by filtration and washing with diethyl ether.‡

As shown in Fig. 1, the cation **6a** possesses a somewhat distorted "organometallic box" structure. It does indeed contain eight pseudo-octahedral iridium centers, four bridging oxalato ligands and two such H_2TPyP units. However, despite the porphyrin planes being approximately parallel, they are twisted along their normal in the direction of a square antiprism and as a consequence the iridium oxalato clips follow this motion. This distortion brings the H_2TPyP ring planes in closer contact optimizing their π-stacking interaction. N–H···N hydrogen bonding between the porphyrin rings can be excluded as a cause for the closing up of the porphyrin rings. The shortest inter-ring N···N distance is 4.4 Å, too far for any such contact. Complex **6a** crystallizes in the monoclinic space group $P2_1/n$, thus, the molecular structure is expected to possess two helical "propeller" type isomers,[6] the (clockwise) configuration **D** and the (counter-clockwise) configuration **L** as a result of the porphyrin plane twist. Both of the two configurations were indeed found in the single crystal of **6a**. As a second major distortion the "organometalic box" of **6a** has "squares" which are rectangles with two Ir···Ir distances of 13.684 Å (13.808 Å) and 14.140 Å (14.093 Å), best seen when viewed down the *b* crystallographic axis. The "square" edges are approximately 2.5 times longer than the oxalate edges.

As a distortion with apparently minor overall structural consequences the pyridine substituents are twisted by 56.9° from the in-plane conformation with the porphyrin. A crystal packing diagram of **6a** then also revealed open channels (Fig. 2). The volume of the box is approximately 800 $Å^3$ based on the distance between the two porphyrin planes of about 4.05 Å.

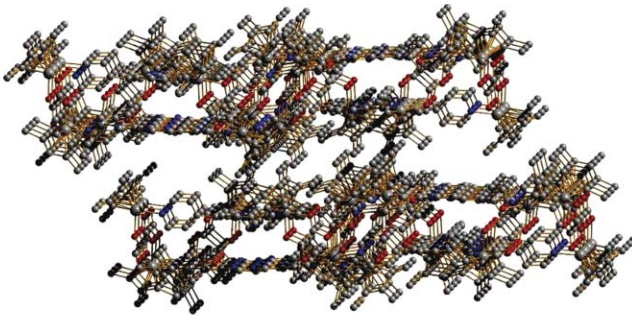

Fig. 2 Crystal packing diagram of **6a** showing the open channels. Hydrogen atoms, anions are omitted.

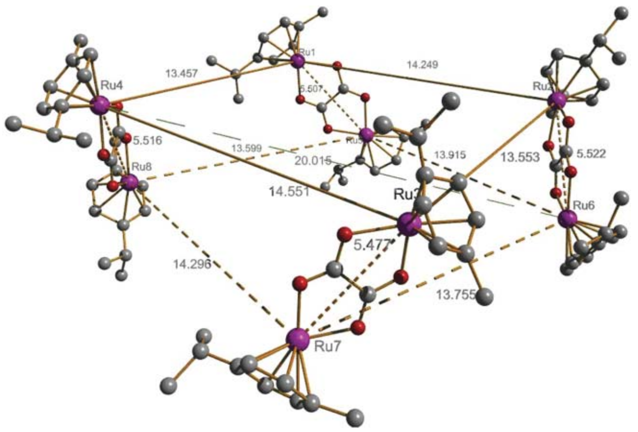

Fig. 3 The Ru···Ru distances of the complex **6c**. Hydrogen atoms and H_2TPyP are omitted for clarity. Carbon atoms are shown as gray, oxygen as red and ruthenium as rose.

When the reactions was carried out with the starting complexes $[Cp^*RhCl_2]_2$ or $[(p\text{-cymene})RuCl_2]_2$ in a fashion applying the "oxalate before porphyrin" route of **6a**, the complexes **6b** and **6c** were obtained in high yields. As intermediates of the build-up of the "organometallic box", the triflate salts **5b** and **5c** were obtained and structurally characterized.‡ **5b** turned out to be structurally totally related to **5a**,§ but **5c** additionally coordinates methanol.[7] The X-ray crystal structure determination of **6c** revealed the presence of disordered solvate molecules, but otherwise the "organometallic box" structure of **6c** resembles even in its distortions that of **6a** and contains eight pseudo-octahedral ruthenium centers, with four bridging oxalato ligands and two H_2TPyP units in the "squares" (Fig. 3).§ The "squares" of **6c** show also a distortion related to **6a**, being rectangles with two Ru···Ru distances of 13.457 Å (13.553 Å) and 14.551 Å (14.249 Å). The crystal packing diagram of **6c** also revealed open channels. The volume of the box **6c** is again approximately 800 $Å^3$ based on the distance between the two porphyrin planes, which is about 4.1 Å. The crystal of **6c** is also racemic with two enantiomeric "boxes" identified.

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Notes and references

‡ All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were purified by standard methods prior to use. $[Cp^*IrCl_2]_2$ (**1a**),[8] $[Cp^*RhCl_2]_2$ (**1b**),[8] $[(p\text{-cymene})\text{-}RuCl_2]_2$ (**1c**),[9] $[(p\text{-cymene})_2Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)]Cl_2]$ (**4c**),[7] $[(p\text{-cymene})_2Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2](OTf)_2$ (**5c**),[7] $[Cp^*{}_2Ir_2(\mu\text{-}\eta^4\text{-}C_2O_4)]Cl_2]$ (**4a**)[10] were prepared according to the reported procedures. Satisfactory analytical data were obtained for the new complexes. *Synthesis of* **6a**: *First method*: $(NH_4)_2C_2O_4{\cdot}H_2O$ (28 mg, 0.2 mmol) was added to a solution of **3a** (265 mg, 0.05 mmol) in CH_3OH (20 mL), The suspension

was kept stirring at 55 °C for 5 h. The solvent was then evaporated to dryness under vacuum, the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **6a** as purple solids. Yield: 143 mg, 65%. *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_2TPyP (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_2Cl_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): δ 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 (%): calc. for $C_{176}H_{172}F_{24}Ir_8N_{16}O_{40}S_8$: 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**: 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_2TPyP (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_2Cl_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): δ 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 (%): calc. for $C_{176}H_{172}F_{24}Rh_8N_{16}O_{40}S_8$: 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**: 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_2TPyP (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_2Cl_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): δ 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$_{p\text{-cym}}$), 5.99–6.15 (m, 16H; Ar$_{p\text{-cym}}$), 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 (%): calc. for $C_{176}H_{164}F_{24}Ru_8N_{16}O_{40}S_8$: 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.

§ *Crystal data*: for **5b**·$2CH_2Cl_2$: $C_{26}H_{34}Cl_4F_6O_{10}Rh_2S_2$, $M = 1032.27$, monoclinic, space group $P2_1/n$, $a = 14.50(2)$, $b = 9.437(14)$, $c = 14.50(2)$ Å, $\beta = 108.711(16)^\circ$, $V = 1880(5)$ Å^3, $Z = 2$, $D_c = 1.823$ g cm^{-3}, $F(000) = 1028$, μ(Mo-Kα) = 1.352 mm^{-1}, GOF = 0.978, $R_1 = 0.0721$ ($I > 2\sigma(I)$). For **6a**: $C_{176}H_{172}F_{24}Ir_8N_{16}O_{40}S_8$, $M = 5401.55$, monoclinic, space group $P2_1/n$, $a = 30.733(12)$, $b = 21.788(9)$, $c = 31.101(13)$ Å, $\beta = 90.037(7)^\circ$, $V = 20826(15)$ Å^3, $Z = 4$, $D_c = 1.723$ g cm^{-3}, $F(000) = 10480$, μ(Mo-Kα) = 5.263 mm^{-1}, GOF = 0.920, $R = 0.1012$ [$I > 2\sigma(I)$]. For **6c**: $C_{176}H_{164}F_{24}Ru_8N_{16}O_{40}S_8 \cdot 3H_2O$, $M = 4718.32$, triclinic, space group $P\bar{1}$, $a = 20.378(9)$, $b = 21.748(10)$, $c = 25.173(11)$ Å, $\alpha = 114.470(7)$, $\beta = 96.638(7)$, $\gamma = 103.749(7)^\circ$, $V = 9570(8)$ Å^3, $Z = 2$, $D_c = 1.644$ g cm^{-3}, $F(000) = 4776$, μ(Mo-Kα) = 0.804 mm^{-1}, GOF = 1.107, $R = 0.1041$ [$I > 2\sigma(I)$].

All data were measured at 293 K on a Bruker SMART APEX CCD diffractometer [λ(Mo-Kα) = 0.71073 Å], graphite monochromator. Refinement and solution.[11–13]

CCDC 644102 (**5b**), 644103 (**6a**) and 644104 (**6c**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711809k

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