Organometallics **2006,** *25,* 74−81

Synthesis and Structural Characterization of Macrocyclic Half-Sandwich Rhodium(III) and Iridium(III) Complexes Bearing Bipyridyl Derivatives and Terephthalate

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Received September 30, 2005

The reactions of half-sandwich rhodium and iridium complexes [Cp′MCl(μ-Cl)]$_2$ with bidentate ligands (L) such as pyrazine, 4,4′-bipyridine (bpy), and *trans*-4,4′-azopyridine gave the corresponding binuclear complexes [{Cp′MCl$_2$}$_2$(L)] (M = Ir, Cp′ = Cp* = η^5-C$_5$Me$_5$, L = pyrazine (**3a**), bpy (**3b**); M = Rh, Cp′ = Cp^t = η^5-1,3-^{t}Bu$_2$C$_5$H$_3$, L = bpy (**3c**), 4,4′-azopyridine (**3d**)), which can be converted into tetranuclear complexes [{Cp′$_2$M$_2$(μ-Cl)$_2$}$_2$(L)$_2$]$^{4+}$ (M = Ir, Cp′ = Cp*, L = bpy (**4a** and **4b**); M = Rh, Cp′ = Cp^t, L = bpy (**4c**, **4e**), L = 4,4′-azopyridine (**4d**)) on treatment with Ag(OTf) or AgBF$_4$ (OTf = CF$_3$SO$_3$). Treatment of Cl-bridged complexes **4c** and **4e** with terephthalate (L′) resulted in replacing the Cl bridges to produce macrocyclic complexes [(Cp′M)$_4${(L)(L′)}$_2$]$^{4+}$ (M = Rh, Cp′ = Cp^t, L = bpy, L′ = terephthalate (**5**)). The molecular structures of [{Cp*IrCl$_2$}$_2$(μ-pyrazine)] (**3a**), [{Cp*Ir}$_4$(μ-Cl)$_4$(μ-bpy)$_2$](BF$_4$)$_4$·6(CH$_2$Cl$_2$) (**4a**), [(Cp*Ir)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](OTf)$_4$·5(CH$_2$ClCH$_2$Cl) (**4b**), [(Cp^{t}Rh)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](OTf)$_4$ (**4c**), [(Cp^{t}Rh)$_4$(μ-Cl)$_4$(μ-*trans*-4,4′-azopyridine)$_2$](OTf)$_4$ (**4d**) and [(Cp^{t}Rh)$_4$(μ-terephthalate)$_2$(μ-bpy)$_2$] (BF$_4$)$_4$·2(C$_6$H$_{12}$) (**5**) have been determined by single-crystal X-ray analysis. The molecular structure of the cation in macrocyclic complex **5** contains two different types of ligand "edges", and the dimensions of the cavity are 10.8 × 11.2 Å.

Introduction

The design and synthesis of organometallic macrocyclic complexes is a rapid growing area of interest because there are many promising organometallic fragments available for the construction of novel supramolecular materials.[1,2] In particular, square-planar complexes of platinum and palladium are attractive as building blocks that occupy vertexes. By using mononuclear units, such as M(diamine)$_2$$^{2+}$, M(diphosphine)$_2$$^{2+}$ (M = Pd and Pt), and other similar entities as corner pieces, connected by appropriate linkers such as 4,4′-bipyridine, diverse polygonal molecules have been synthesized, which are often highly charged (Scheme 1a).[3] Cotton and co-workers have recently employed metal−metal bonded dinuclear units of the type *cis*-M$_2$(μ-DArF)$_2$ (M = Mo, Rh, and Ru) and dicarboxylate dianions as linkers (Scheme 1b).[4] This leads to neutral products, and depending on the nature of the linker, communication between the dimetal units through the linker has been detected by electrochemical means. So far, one of the advantages of this synthetic strategy for molecular squares is the spontaneous assembly of such structures from a mixture of ligands (edges) and metals (corners) in one step; the one-step synthesis of a rectangle is not possible.

Subsequent efforts were devoted to the synthesis of molecular rectangles to improve selectivity and sensitivity in molecular recognition and separation.[5] An alternative route for the formation of molecular rectangles involves the design of a binuclear complex with two parallel coordination sites. Hupp and Süss-Fink used this synthetic strategy successfully in a side-by-side assembly of a molecular rectangle (Scheme 1c,d).[6,7] Unfortunately, the cavity sizes for these rectangular species were too small to function as receptor sites, even for planar molecules such as benzene. Recent reports of the synthesis of molecular rectangles have appeared by Lu and Yamamoto (Scheme 1d,e).[8,9] These simple two-step routes to molecular rectangles demonstrate the important control offered by the directional-bonding approach over the shape of the resulting complex.

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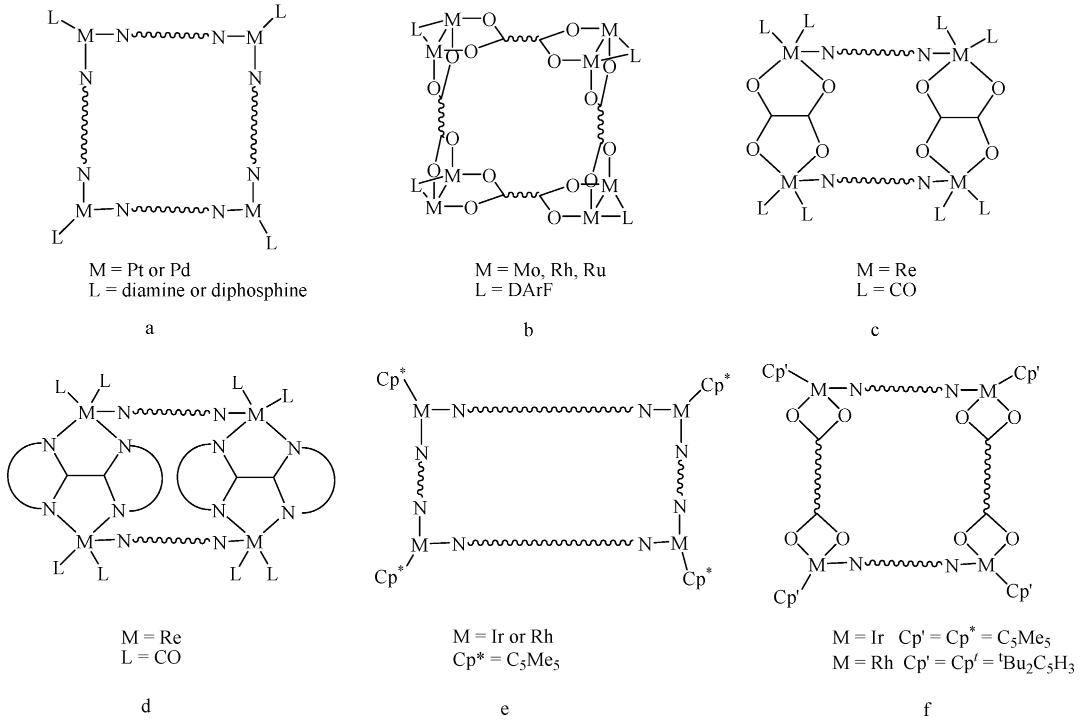
Scheme 1



M = Pt or Pd
L = diamine or diphosphine

a

M = Mo, Rh, Ru
L = DArF

b

M = Re
L = CO

c

M = Re
L = CO

d

M = Ir or Rh
$Cp^* = C_5Me_5$

e

M = Ir $Cp' = Cp^* = C_5Me_5$
M = Rh $Cp' = Cp^t = {}^tBu_2C_5H_3$

f

While these complexes are constructed from metal centers and pyridyl and/or diisocyanide neutral bridging ligands, it would be of interest to design and prepare tetranuclear molecular rectangles or squares containing carboxylate- and pyridyl-bridged ligands (Scheme 1f) with stepwise routes. We then designed and synthesized tetranuclear rhodium and iridium supramolecules bearing cyclopentadienyl derivatives and two different types of ligands. To the best of our knowledge, this is the first example of the control offered by cavity sizes for the rectangular species assisted by two different types of ligands. Complexes $[(Cp^*IrCl_2)_2(\mu\text{-pyrazine})]$ (**3a**), $[(Cp^*Ir)_4(\mu\text{-Cl})_4(\mu\text{-bpy})_2](BF_4)_4\cdot 6(CH_2Cl_2)$ (**4a**), $[(Cp^*Ir)_4(\mu\text{-Cl})_4(\mu\text{-bpy})_2](OTf)_4\cdot 5(CH_2ClCH_2Cl)$ (**4b**), $[(Cp^tRh)_4(\mu\text{-Cl})_4(\mu\text{-bpy})_2](OTf)_4$ (**4c**), $[(Cp^tRh)_4(\mu\text{-Cl})_4(\mu\text{-}trans\text{-}4,4'\text{-azopyridine})_2](OTf)_4$ (**4d**), and $[(Cp^tRh)_4(\mu\text{-terephthalate})_2(\mu\text{-bpy})_2](BF_4)_4\cdot 2(C_6H_{12})$ (**5**) (bpy = 4,4′-bipyridine; $Cp^* = \eta^5\text{-}C_5Me_5$, $Cp^t = \eta^5\text{-}1,3\text{-}{}^tBu_2C_5H_3$, OTf = CF_3SO_3) were confirmed by X-ray analyses.

Results and Discussion

Synthesis and Characterization. One of the most important considerations when designing the synthesis of organometallic macrocyclic assemblies is to have readily accessible or, at least, easily prepared building blocks. Most complexes are based on classical coordination compounds (e.g., $Pd(en)^{2+}$), but organometallic fragments such as $M(CO)_3$ (M = Re, Mo), Cp*Rh, and CpCo are increasingly used to build these structures.[10] Structurally related *tricationic* compounds with half-sandwich transition metal complexes at the corner have more special interest.[11,12] Using this kind of metal complexes as the building block offers a variety of advantages: (i) These six- or five-membered rings block three sites on the octahedron, benefiting building a bond between the metal and nitrogen or oxygen atom; (ii) introduction of other substituents on the cyclopentadienyl ring also can enhance solubility of the polymeric compound. Herein the stepwise synthesis of the tetranuclear rhodium(III) and iridium(III) supramolecules bearing cyclopentadienyl derivatives and binary ligands (Scheme 2) will be discussed.

Treatment of $[Cp^*IrCl(\mu\text{-Cl})]_2$ (**1**) with pyrazine in a 1:1 molar ratio at room temperature in dichloromethane generated orange crystals formulated as $[(Cp^*IrCl_2)_2(\mu\text{-pyrazine})]$ (**3a**). In the ^1H NMR spectrum in $CDCl_3$, two singlet resonances due to the Cp* and pyrazine protons appeared at about δ 1.56 and 7.26, respectively. These spectroscopic data indicate a dimeric structure in which the iridium centers are connected by a pyrazine ligand. X-ray crystal analysis confirmed the structure (Figure 1).

When $[Cp^*IrCl(\mu\text{-Cl})]_2$ (**1**) or $[Cp^tRhCl(\mu\text{-Cl})]_2$ (**2**) was treated with 4,4′-bipyridine (bpy), dinuclear complexes, $[(Cp^*IrCl_2)_2(\mu\text{-bpy})]$ (**3b**) and $[(Cp^tRhCl_2)_2(\mu\text{-bpy})]$ (**3c**), were formed in high yields. The ^1H NMR spectrum for **3b** showed a singlet at δ 1.63 due to Cp* protons and two resonances at approximately δ 7.83 (d) and 8.72 (d) due to bipyridyl protons; that for **3c** had three resonances at about δ 1.30 (s), 5.73 (d), and 6.03 (t) due to Cp^t protons and two singlets at δ 7.85 and 8.74 due to bipyridyl protons. Analogously, the reaction

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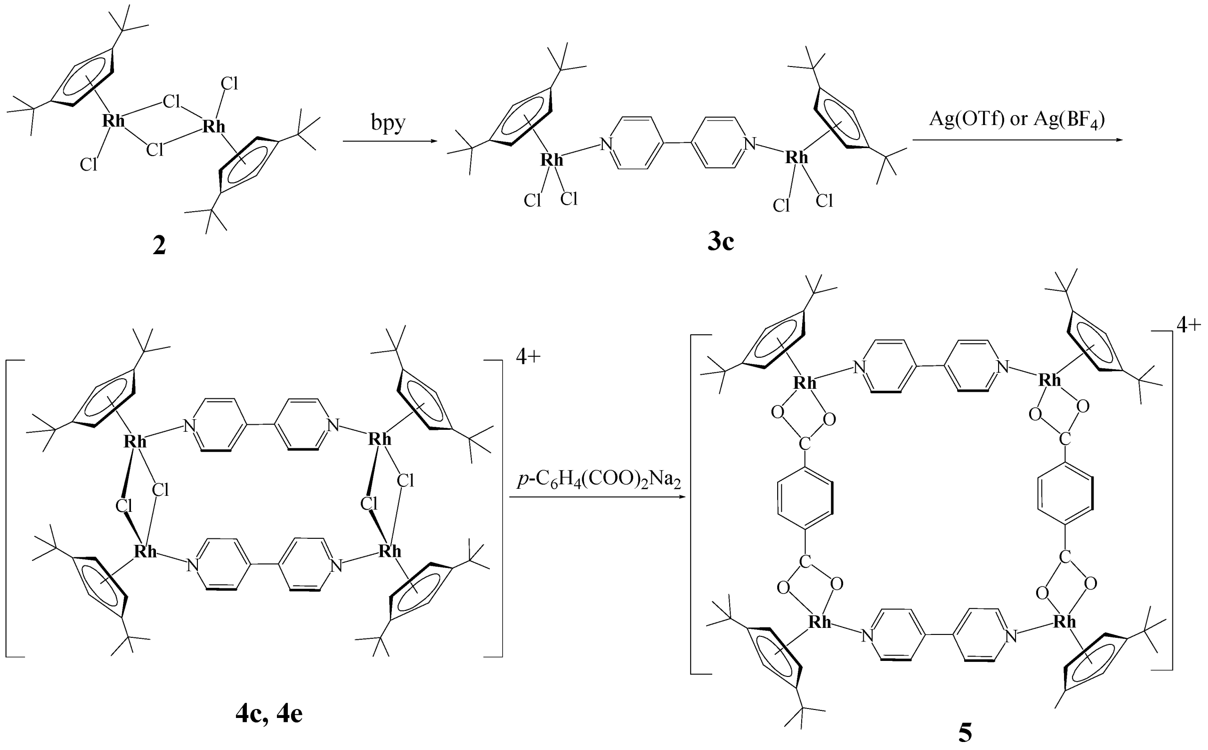
Scheme 2



of **2** with *trans*-4,4′-azopyridine gave dinuclear complex $[(Cp^tRhCl_2)_2(\mu\text{-}trans\text{-}4,4'\text{-azopyridine})]$ (**3d**). The ^{1}H NMR spectrum showed three sets of Cp^t ring ligands observed at δ 1.31, 5.35−5.50, and 6.02−6.11 and two resconances at δ 7.89 and 8.60 for azopyridyl protons.

When dinuclear complex **3b** was treated with $AgBF_4$ in a 1:2 molar ratio at room temperature, tetranuclear complex $[(Cp^*Ir)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2](BF_4)_4 \cdot 6(CH_2Cl_2)$ (**4a**) was formed. The ^{1}H NMR spectrum consists of three kinds of resonances at 1.63 (s), 7.88 (br), and 8.81 (br); the first is assigned to the Cp* protons, and the others are assigned to bipyridyl protons. The tetranuclear iridium complex $[(Cp^*Ir)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2](OTf)_4 \cdot 5(CH_2ClCH_2Cl)$ (**4b**) was obtained from **3b** and Ag(OTf) in a manner similar to the **4a** analogue.

Tetranuclear rhodium complexes that bear the 4,4′-bipyridyl or *trans*-4,4′-azopyridyl ligand, $[(Cp^tRh)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2](OTf)_4$ (**4c**), $[(Cp^tRh)_4(\mu\text{-}Cl)_4(\mu\text{-}trans\text{-}4,4'\text{-azopyridine})_2](OTf)_4$ (**4d**), and $[(Cp^tRh)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2](BF_4)_4$ (**4e**), were obtained by the reactions between the corresponding neutral dinuclear complexes (**3c**, **3d**) and silver salt. The ^{1}H NMR spectra for **4c** showed three resonances at δ 1.33 (s), 5.75 (d), and 6.23−6.42 (m) due to Cp^t protons and two resonances at δ 8.22 (m) and 9.07 (m) for bipyridyl protons; that for **4d** showed resonances for each of the Cp^t and *trans*-4,4′-azopyridine ligands, at δ 1.31, 5.93−6.10, and 6.33−6.47 for the former and at δ 8.12 and 9.10 for the latter, suggesting the presence of configurational isomers; and that for **4e** also showed two kinds of resonances for each of the Cp^t and bpy ligands, at δ 1.32, 5.66, and 6.18−6.33 for the former and at δ 8.21 and 9.01 for the latter. Detailed structures were confirmed by X-ray analyses of **4a**−**d**. They revealed that the complex cations have rectangular structures bridged by four Cl atoms, and two bpy or *trans*-4,4′-azopyridine ligands.

When μ-Cl-bridged complex **4e** was treated with 2 equiv of terephthalate sodium, the Cl bridges were replaced by terephthalate to produce orange crystals of $[(Cp^tRh)_4(\mu\text{-terephthalate})_2(\mu\text{-}bpy)_2](BF_4)_4 \cdot 2(C_6H_{12})$ (**5**) (Scheme 2). In the IR spectrum, the carboxyl band appeared at 1703 cm^{-1}. The ^{1}H NMR spectrum showed three kinds of resonances at δ 1.33 (s), 5.60 (d), and 6.32 (m) due to Cp^t; at δ 7.06−7.18 (m) due to terephthalate; and at δ 8.22 (m) and 9.07 (m) due to dipyridyl protons. Finally, the structure was determined by X-ray analysis. The complex has a tetranuclear rectanglar structure, and each rhodium atom is surrounded by a terephthalate, a bpy, and a Cp^t moiety.

Crystal Structures. Crystal Structure of 3a. The crystal structure of **3a** consists of binuclear units, in which there is one crystallographically independent Ir(III) atom and the pyrazine ligand adopts a bridge form (Figure 1). All of the iridium centers adopt a three-legged piano-stool conformation and have six-coordinate geometry, assuming that the Cp* ligand functions as a three-coordinate ligand. Angles between adjacent atoms around the iridium atoms are nearly 90°. All of the Cp* atoms fall in a fairly good plane. The Cp* ligands are symmetrically bound to the iridium atoms. The distance between Ir and the least-squares plane of the Cp* ring is 1.78 Å and compares well with those for other iridium complexes containing Cp*.[2b,13] A pyrazine unit bridges a pair of $[Cp^*IrCl_2]$ fragments to form a binuclear $[(Cp^*IrCl_2)_2(\mu\text{-pyrazine})]$ complex, and the distance of Ir(1)···Ir(1a) is 7.37 Å. The dihedral angle between

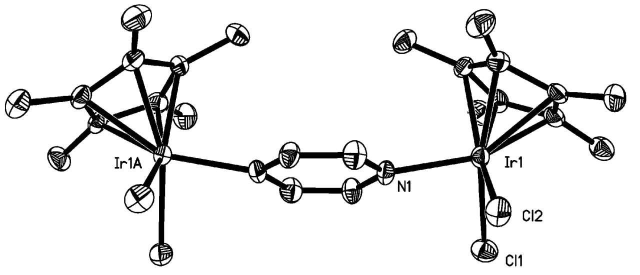


Figure 1. Molecular structure of **3a**. H atoms have been omitted by clarity. Selected distances (Å) and angles (deg): Ir1−N1, 2.095(8); Ir1−Cl1, 2.399(3); Ir1−Cl2, 2.383(3); Ir1···Ir1a, 7.37; N1−Ir1−Cl1, 88.7(2); N1−Ir1−Cl2, 85.1(2); Cl2−Ir1−Cl1, 89.4(1).

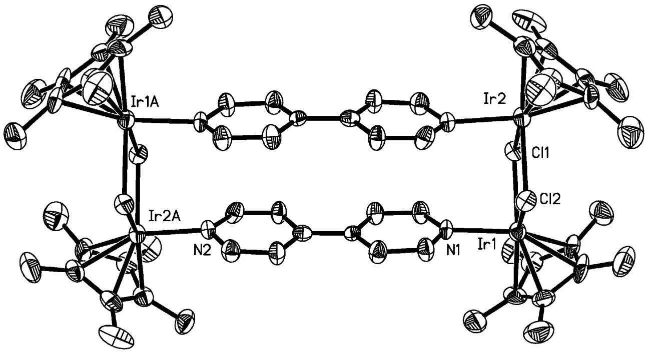


Figure 2. Molecular unit of the tetranuclear $[(Cp^*Ir)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2]^{4+}$ (**4a** and **4b**). All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): **4a**: Ir1−N1, 2.117(9); Ir1−Cl2, 2.457(4); Ir1−Cl1, 2.464(4); Ir2−N2a, 2.119(9); Ir2−Cl2, 2.439(4); Ir2−Cl1, 2.451(4); Ir1⋯Ir2, 3.733; Ir1⋯Ir2a, 11.268; Ir1⋯Ir1a, 11.940; Ir2⋯Ir2a, 11.799; N1−Ir1−Cl2, 87.6(3); N1−Ir1−Cl1, 87.9(3); Cl2−Ir1−Cl1, 80.61(11); N2a−Ir2−Cl2, 88.2(3); N2a−Ir2−Cl1, 87.3(3); Cl2−Ir2−Cl1, 81.23(11); Ir2−Cl1−Ir1, 98.83(12); Ir2−Cl2−Ir1, 99.33(12). **4b**: Ir1−N1, 2.113(6); Ir1−Cl1, 2.455(2); Ir1−Cl2, 2.463(3); Ir2−N2a, 2.121(6); Ir2−Cl1, 2.451(3); Ir2−Cl2, 2.465(2); Ir1⋯Ir2, 3.773; Ir1⋯Ir2a, 11.321; Ir1⋯Ir1a, 11.965; Ir2⋯Ir2a, 11.902; N1−Ir1−Cl1, 87.56(18); N1−Ir1−Cl2, 88.2(2); Cl1−Ir1−Cl2, 79.69(7); N2a−Ir2−Cl1, 88.5(2); N2a−Ir2−Cl2, 87.84(18); Cl1−Ir2−Cl2, 79.72(8); Ir2−Cl1−Ir1, 100.54(8); Ir1−Cl2−Ir2, 99.94(8).

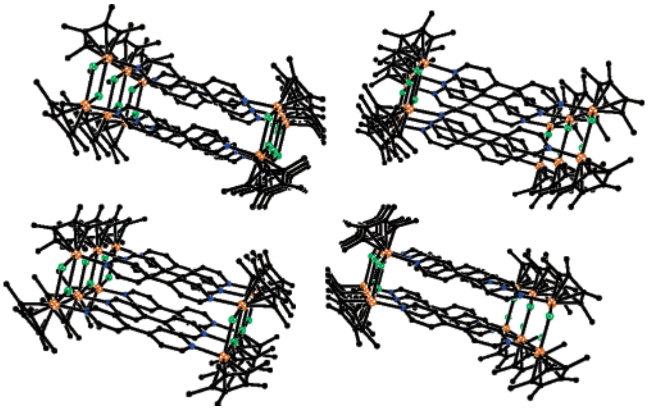


Figure 3. Stacking of the molecules in crystals of **4a** viewed along the *a*-axis. All anions and solvent molecules are omitted for clarity. Ir, Cl, N, and C atoms are represented by orange, green, blue, and black, respectively.

the Ir1−Cl1−Cl2 plane and pyrazine ligands is 83.9°. It is interesting to note that the two $[Cp^*IrCl_2]$ fragments take the *cis* conformation, being similar to that reported previously[2b,d] and different from the *trans* conformation.[2b,9b]

Complexes **4a** and **4b** consist of tetranuclear $[(Cp^*Ir)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2]^{4+}$ cations, as well as BF_4^- and OTf^- counteranions in the solid state, respectively. As illustrated in Figure 2, X-ray crystallographic analysis reveals that the complex cations have a rectangular macrocyclic structure bridged by four Cl atoms and two bpy molecules with dimensions of 3.733 × 11.268 Å for **4a** and 3.773 × 11.321 Å for **4b**, respectively. The corresponding rhodium structure was found in $[(Cp^*Rh)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2](OTf)_4$ with dimensions of 3.68 × 11.45 Å.[9b] The Ir(1)⋯Ir(1a) and Ir(2)⋯Ir(2a) diagonal lengths in the rectangular structure are 11.940 and 11.799 Å for **4a** and 11.965 and 11.902 Å for **4b**, and the bridged Cl(1)⋯Cl(2) separation is 3.183 Å

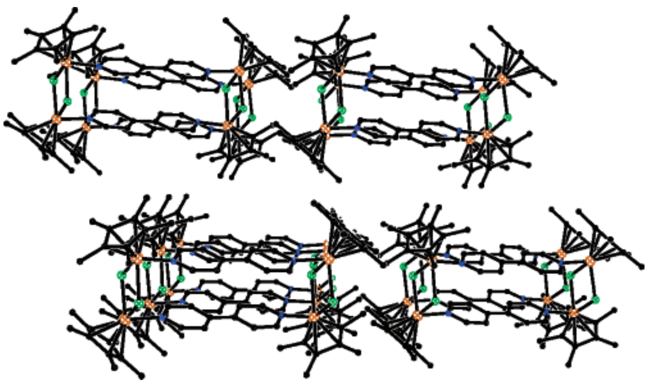


Figure 4. Stacking of the molecules in crystals of **4b** viewed along the *b*-axis. All anions and solvent molecules are omitted for clarity. Ir, Cl, N, and C atoms are represented by orange, green, blue, and black, respectively.

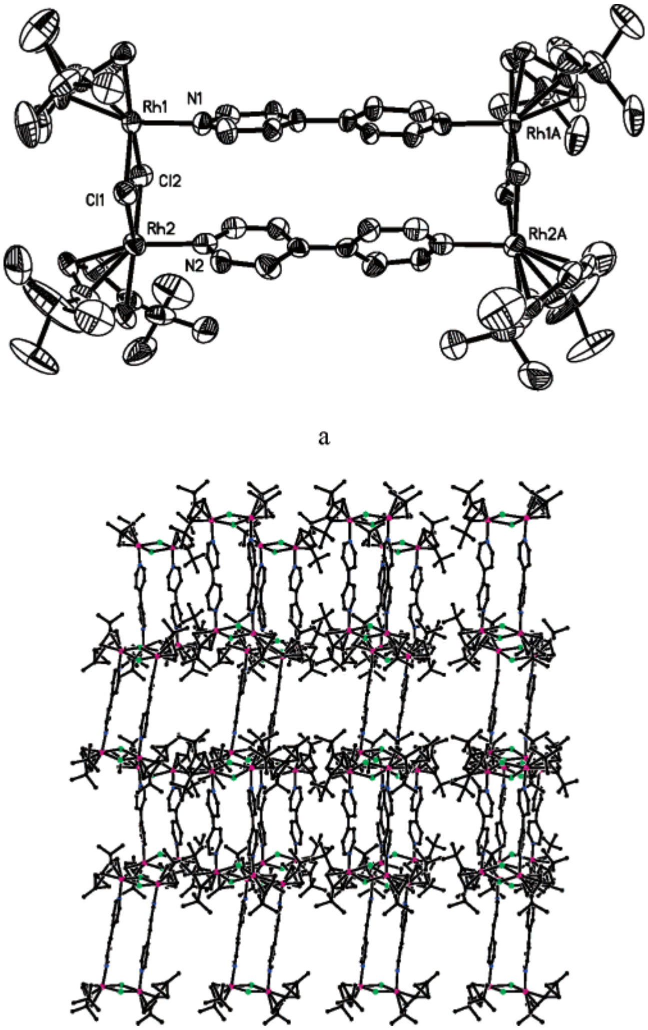


Figure 5. (a) Molecular unit of the tetranuclear $[(Cp^tRh)_4(\mu\text{-}Cl)_4(\mu\text{-}bpy)_2]^{4+}$ (**4c**). (b) Stacking of the molecules in crystals of **4c** viewed along the *c*-axis. All anions and solvent molecules are omitted for clarity. Rh, Cl, N, and C atoms are represented by pink, green, blue, and black, respectively. Selected distances (Å) and angles (deg): Rh1−N1, 2.122(11); Rh1−Cl2, 2.429(4); Rh1−Cl1, 2.436(4); Rh2−N2, 2.119(12); Rh2−Cl2, 2.428(5); Rh2−Cl1, 2.442(4); Rh1⋯Rh2, 3.693; Rh1⋯Rh1a, 11.971; Rh1⋯Rh2a, 11.314; Rh2⋯Rh2a, 11.831; N1−Rh1−Cl2, 87.8(3); N1−Rh1−Cl1, 87.7(3); Cl2−Rh1−Cl1, 81.32(14); N2−Rh2−Cl2, 88.1(4); N2−Rh2−Cl1, 87.5(3); Cl2−Rh2−Cl1, 81.24(13); Rh2−Cl2−Rh1, 99.00(15); Rh1−Cl1−Rh2, 98.40(14).

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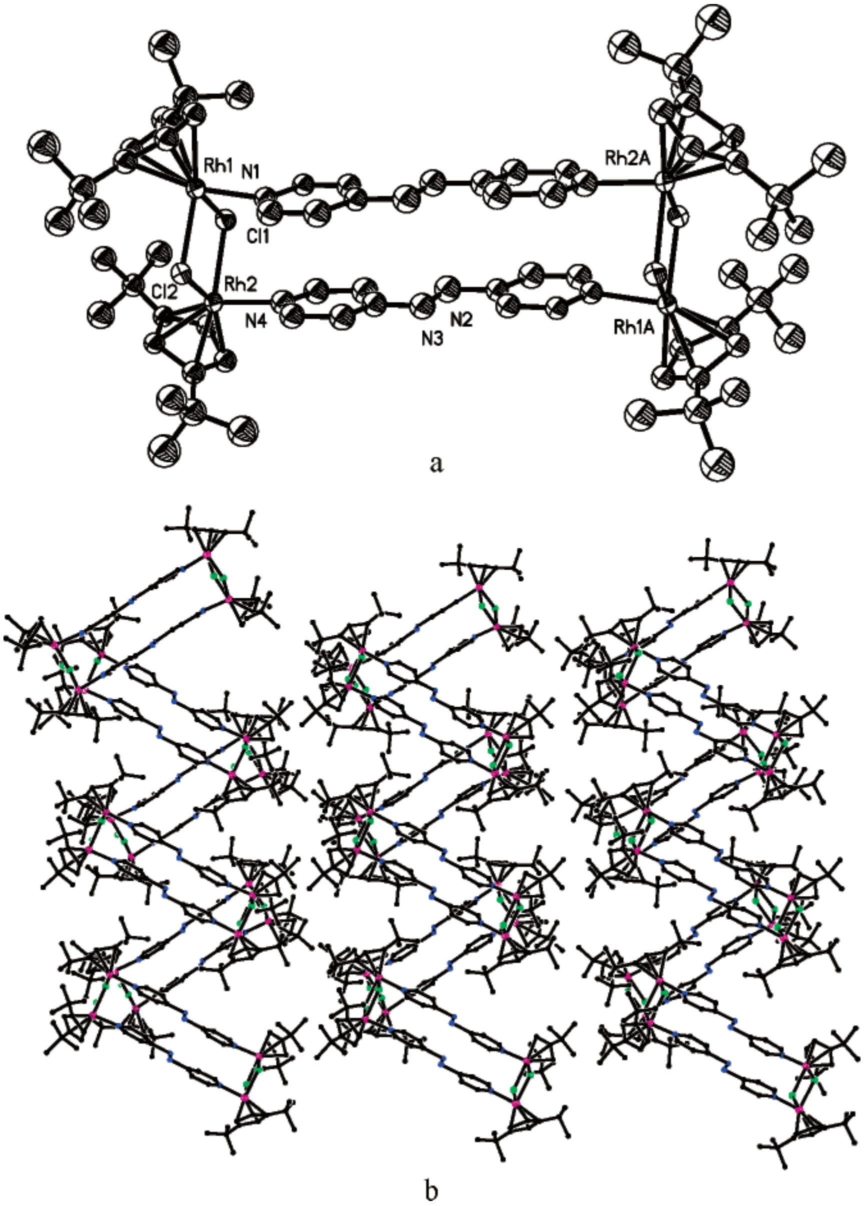

Figure 6. (a) Molecular unit of the tetranuclear $[(Cp^tRh)_4(\mu\text{-Cl})_4(\mu\text{-}trans\text{-}4,4'\text{-azopyridine})_2]^{4+}$ (**4d**). (b) Stacking of the molecules in crystals of **4d** viewed along the *c*-axis. All anions and solvent molecules are omitted for clarity. Rh, Cl, N, and C atoms are represented by pink, green, blue, and black, respectively. Selected distances (Å) and angles (deg): Rh1−N1, 2.128(12); Rh1−Cl2, 2.436(4); Rh1−Cl1, 2.455(4); Rh2−N4, 2.134(14); Rh2−Cl2, 2.438(4); Rh2−Cl1, 2.463(4); Rh1···Rh2, 3.708; Rh1···Rh1a, 13.497; Rh1···Rh2a, 13.172; Rh2···Rh2a, 13.869; N1−Rh1−Cl2, 87.2(4); N1−Rh1−Cl1, 89.4(4); Cl2−Rh1−Cl1, 81.61(14); N4−Rh2−Cl2, 90.5(4); N4−Rh2−Cl1, 85.6(4); Cl2−Rh2−Cl1, 81.43(14); Rh1−Cl1−Rh2, 97.87(16); Rh1−Cl2−Rh2, 99.05(16).

for **4a** and 3.151 Å for **4b**, respectively. The dihedral angles between the Ir1−Cl1−Ir2−Cl2 plane and bpy ligands are 91.6° for **4a** and 89.6° for **4b**. The structures also show that the bpy bridges are slightly twisted ($\phi = 4.7$ for **4a**, 2.8 for **4b**), a feature presumably absent in the bpy-bridged analogue, while the two bpy ligands are parallel to each other with a distance of 3.615 Å for **4a** and 3.534 Å for **4b**, showing the presence of $\pi-\pi$ interaction. As shown in Figures 3 and 4, the molecular rectangles **4a** and **4b** stack to form rectangle channels. The overall free voids are 51.2% for **4a** and 56.4% for **4b** of the cell volume, which is omitted counteranions, solvent molecules, and hydrogen atoms.[14] In addition, the anions and solvent molecules are not seen within these channels.

The crystal structures of complexes **4c** and **4d** are quite similar to that of **4a** and **4b**. As shown in Figures 5 and 6, X-ray crystallographic analysis reveals that the complex cations have a rectangular macrocycle bridged by four Cl atoms and two pyridyl ligands with dimensions of approximately 3.7 × 11.3 Å for **4c** and 3.7 × 13.2 Å for **4d**, and the bridged Cl(1)···Cl(2) and Cl(3)···Cl(4) separations are 3.170 and 3.200 Å for **4c** and 3.196 and 3.170 Å for **4d**, respectively. The two pyridyl rings of each bpy ligand are not coplanar, being inclined to one another by an angle of 30.8° and 52.5° for **4c**, while the structure of **4d** shows that the two pyridyl rings of *trans*-4,4′-azopyridine are slightly twisted ($\phi = 4.3°$ and 3.9°), and the two *trans*-4,4′-azopyridines are parallel to each other with a distance of 3.38 and 3.47 Å, showing the presence of $\pi-\pi$ interaction.

The intracyclic $\pi-\pi$ interactions of the two pyridyl ligands are mainly controlled by the coordination geometries of Cl anions. Generally, the stronger anion ligation to the metal atoms

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[14] Spek, Al. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003.

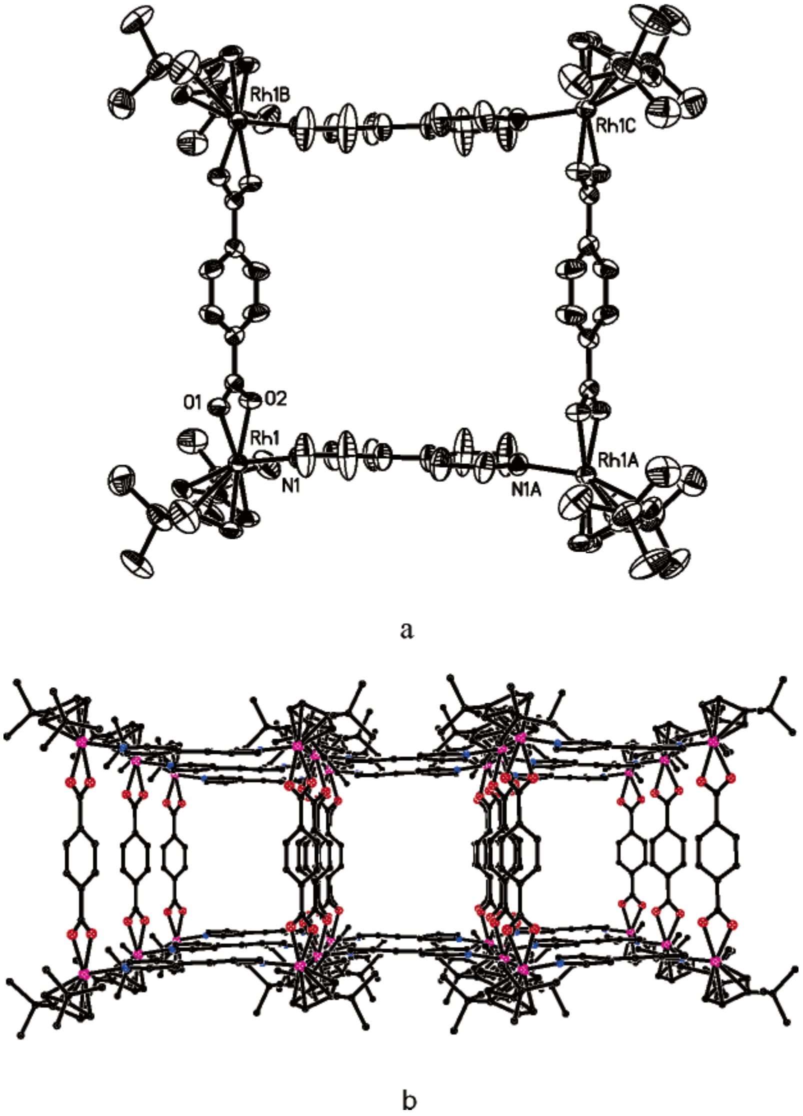

Figure 7. (a) Molecular unit of the tetranuclear $[(Cp'Rh)_4(\mu\text{-terephthalate})_2(\mu\text{-bpy})_2]^{4+}$ (**5**). (b) Stacking of the molecules in crystals of **5** viewed along the *a*-axis. All hydrogen atoms are omitted for clarity. Rh, O, N, and C atoms are represented by pink, red, blue, and black, respectively. Selected distances (Å) and angles (deg): Rh1−N1, 2.095(6); Rh1−O2, 2.148(5); Rh1−O1, 2.170(5); Rh1···Rh1a, 11.217; Rh1···Rh1b, 10.752; Rh1···Rh1c, 15.538; N1−Rh1−O2, 85.6(2); N1−Rh1−O1, 86.5(2); O2−Rh1−O1, 60.8(2).

can pull in the metal ions, giving rise to a shorter intramolecular $\pi-\pi$ distance.

A perspective drawing of **5** with the atomic numbering scheme and selected bond lengths and angles is given in Figure 7. The crystal structure of **5** is composed of $[(Cp^tRh)_4(\mu\text{-terephthalate})_2(\mu\text{-bpy})_2]^{4+}$ cations, BF_4^- counteranions, and cyclohexane solvent molecules in the solid. Each Rh center adopts a three-legged piano-stool conformation and has six-coordinate geometry, assuming that the Cp^t ligand functions as a three-coordinate ligand. Each Rh(III) ion is coordinated by one nitrogen atom from bpy and two oxygen atoms of terephthalate ligands, resulting in a rectangle, showing a cavity with dimensions of 10.752 × 11.217 Å, as defined by the rhodium centers. The Rh(1)···Rh(1a) diagonal length in the rectangular structure is 15.538 Å. The dihedral angle between the terephthalate and bpy ligands is just 90.0°. The structure also shows that the bpy bridges are slightly twisted ($\phi = 10.3°$). As shown in Figure 7b, the molecular rectangles stack via the *a*-axis to form rectangle channels. The overall free voids are 58.0% of the cell volume, which is omitted counteranions, solvent molecules, and hydrogen atoms.[14] In addition, two cyclohexanes are seen within these channels, but not within the molecular cavity. The counterions are located outside of the channels.

In summary, a new set of tetracationic rectangular molecules has been synthesized using iridium(III) or rhodium(III) that bear cyclopentadienyl derivative groups and two different types of ligands. This new type of tetranuclear complex is expected to play a role in the molecular architecture of supramolecules with ladder or cubic frameworks.

Experimental Section

General Comments. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2, and cyclohexane was distilled over sodium/benzophenone ketyl just before use. The starting material $[Cp^*IrCl(\mu\text{-Cl})]_2$ (**1**),[15] $[Cp^tRhCl(\mu\text{-Cl})]_2$ (**2**),[16] and *trans*-4,4′-azopyridine[17] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification. IR spectra are

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Table 1. Crystallographic Data for Compounds 3a, 4a, and 4b

	3a	**4a**	**4b**
empirical formula	$C_{24}H_{34}Cl_4Ir_2N_2$	$C_{66}H_{88}B_4Cl_{16}F_{16}Ir_4$	$C_{74}H_{96}Cl_{14}F_{12}Ir_4N_4O_{12}S_4$
fw	876.73	2620.64	2854.89
cryst syst	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	26.153(7)	9.414(8)	12.726(8)
b (Å)	7.357(2)	12.751(11)	13.736(9)
c (Å)	14.845(4)	20.270(17)	15.503(10)
α (deg)		98.667(12)	80.429(9)
β (deg)	112.385(5)	99.072(12)	71.022(8)
γ (deg)		100.045(12)	84.873(9)
V (Å^3)	2641(1)	2326(3)	2525(3)
Z	4	1	1
ρ_{calcd} (g/cm^3)	2.205	1.871	1.877
μ (Mo Kα) (mm^{-1})	10.488	6.234	5.782
no. of observ	2900	8048	8767
no. of params	145	506	570
goodness of fit	1.030	0.979	0.938
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0518	0.0524	0.0371
$wR_2{}^a$ ($I > 2\sigma(I)$)	0.1078	0.1492	0.094

[a] $R_1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o{}^2 > 2\sigma F^2$). $wR_2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.095P)^2]$; $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$ (also with $F_o{}^2 > 2\sigma F^2$).

measured on a Nicolet Avatar-360 spectrophotometer (as KBr pellet). ^{1}H{500 MHz} NMR spectra were obtained on a Bruker DMX-500 spectrophotometer in $CDCl_3$. Elemental analyses were performed on an Elementar III Vario EI analyzer.

Preparation of [(Cp*IrCl$_2$)$_2$(μ-pyrazine)] (3a). To a solution of **1** (80 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added pyrazine (8 mg, 0.1 mmol) at room temperature. After stirring for 18 h, the reaction mixture was filtered and the filtrate was reduced to about 5 mL under vacuum. Hexane was added slowly into the red solution, giving orange crystals of **3a** (73 mg, 83%). Anal. Calcd for $C_{24}H_{34}Cl_4Ir_2N_2$: C 32.88, H 3.91, N 3.19. Found (%): C 32.96, H 3.95, N 3.12. IR (KBr, cm^{-1}): 3522 (w), 3222 (w), 2920 (s), 1621 (w), 1451 (m), 1383 (m), 1262 (m), 1117 (s), 1080 (s), 1020 (s), 886 (m), 802 (m), 692 (w), 461 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (s, 30H, Cp*), 7.26 (s, 4H, pyrazine).

Preparation of [(Cp*IrCl$_2$)$_2$(μ-bpy)] (3b). It was prepared in the same procedure descibed above for **3a** using bpy instead of pyrazine. The deposited orange solid of **3b** was obtained (72 mg, 76%). Anal. Calcd for $C_{30}H_{38}Cl_4Ir_2N_2$: C 37.81, H 4.02, N 2.94. Found (%): C 37.80, H 4.02, N 2.95. IR (KBr, cm^{-1}): 3449 (w), 2962 (w), 2920 (w), 1603 (s), 1482 (m), 1406 (s), 1261 (m), 1085 (s), 1032 (s), 828 (m), 813 (m), 648 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.63 (s, 30H, Cp*), 7.83 (d, 4H, bipyridyl), 8.72 (d, 4H, bipyridyl).

Preparation of [(Cp^{t}RhCl$_2$)$_2$(μ-bpy)] (3c). To a solution of **2** (68 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added bpy (16 mg, 0.1 mmol) at room temperature. After stirring for 18 h, the reaction mixture was filtered and the filtrate was reduced to about 5 mL under vacuum. Hexane was added slowly into the red solution, giving orange crystals of **3c** (58 mg, 75%). Anal. Calcd for $C_{36}H_{50}Cl_4N_2Rh_2$: C 50.37, H 5.87, N 3.26. Found (%): C 50.36, H 5.85, N 3.23. IR (KBr, cm^{-1}): 3466 (m), 3175 (m), 2959 (s), 1602 (s), 1480 (s), 1405 (s), 1362 (m), 1254 (m), 1212 (m), 1061 (m), 808 (s), 625 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 36H, ^{t}Bu), 5.73 (d, 4H, Cp^t), 6.03 (t, 2H, Cp^t), 7.85 (d, J(H, H) = 6 Hz, 4H, bipyridyl), 8.74 (d, J(H, H) = 6 Hz, 4H, bipyridyl).

Preparation of [(Cp^{t}RhCl$_2$)$_2$(μ-*trans*-4,4′-azopyridine)] (3d). It was prepared in the same procedure described above for **3c** using μ-*trans*-4,4′-azopyridine instead of bpy. The deposited orange solid of **3d** was obtained (61 mg, 71%). Anal. Calcd for $C_{36}H_{50}Cl_4N_4Rh_2$: C 48,78, H 5.69, N 6.32. Found (%): C 48.73, H 5.62, N 6.30. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (s, 36H, ^{t}Bu), 5.35−5.50 (m, 4H, Cp^t), 6.02−6.11 (m, 2H, Cp^t), 7.89 (m, 4H, azopyridyl), 8.60 (m, 4H, azopyridyl).

Preparation of [(Cp*Ir)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](BF$_4$)$_4$·6(CH$_2$Cl$_2$) (4a). $AgBF_4$ (39 mg, 0.2 mmol) was added to a solution of **3b** (95 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h. The reaction mixture was filtered and the filtrate was concentrated to ca. 4 mL. Cyclohexane was added slowly into the red solution, giving red crystals of **4a** (82 mg, 63%). Anal. Calcd for $C_{60}H_{76}B_4Cl_4F_{16}Ir_4N_4 \cdot 6CH_2Cl_2$: C 30.25, H 3.38, N 2.14. Found (%): C 30.22, H 3.33, N 2.12. IR (KBr, cm^{-1}): 3494 (w), 3109 (w), 2978 (w), 1645 (w), 1466 (w), 1421 (m), 1259 (s), 1161 (s), 1030 (s), 817 (w), 754 (w), 638 (s), 517 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.63 (s, 60H, Cp*), 7.88 (br, 8H, dipyridyl), 8.81 (br, 8H, dipyridyl).

Preparation of [(Cp*Ir)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](OTf)$_4$·5(CH$_2$ClCH$_2$Cl) (4b). Ag(OTf) (51 mg, 0.2 mmol) was added to a solution of **3b** (95 mg, 0.1 mmol) in 1,2-dichloroethane (20 mL) at room temperature and stirred for 3 h. The mixture was filtered and the filtrate was concentrated to ca. 5 mL. Cyclohexane was added slowly into the red solution, giving red crystals of **4b** (97 mg, 67%). Anal. Calcd for $C_{64}H_{76}B_4Cl_4F_{12}Ir_4N_4O_{12}S_4 \cdot 5CH_2ClCH_2Cl$: C 30.67, H 3.34, N 1.93. Found (%): C 30.69, H 3.32, N 1.95. IR (KBr, cm^{-1}): 3504 (m), 3109 (w), 2913 (w), 1614 (s), 1456 (m), 1416 (m), 1381 (w), 1264 (s), 1221 (s), 1158 (s), 1031 (s), 819 (m), 753 (w), 639 (s), 573 (w), 517 (m).

Preparation of [(Cp^{t}Rh)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](OTf)$_4$ (4c). Ag(OTf) (51 mg, 0.2 mmol) was added to a solution of **3c** (86 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h. The mixture was filtered and the filtrate was concentrated to ca. 5 mL. Cyclohexane was added slowly into the red solution, giving red crystals of **4c** (78 mg, 72%). Anal. Calcd for $C_{76}H_{100}Cl_4F_{12}N_4O_{12}Rh_4S_4$: C 42.04, H 4.64, N 2.58. Found (%): C 42.08, H 4.65, N 2.55. IR (KBr, cm^{-1}): 3084 (m), 2965 (s), 1613 (w), 1487 (m), 1466 (m), 1371 (m), 1264 (s), 1223 (s), 1152 (s), 1031 (s), 870 (w), 805 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (s, 72H, ^{t}Bu), 5.75 (d, 8H, Cp^t), 6.23−6.42 (m, 4H, Cp^t), 8.22 (m, 8H, dipyridyl), 9.07 (m, 8H, dipyridyl).

Preparation of [(Cp^{t}Rh)$_4$(μ-Cl)$_4$(μ-*trans*-4,4′-azopyridine)$_2$](OTf)$_4$ (4d). Ag(OTf) (51 mg, 0.2 mmol) was added to a solution of **3d** (87 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) at room temperature and stirred for 3 h. The solution was filtered and the filtrate was concentrated to ca. 5 mL. Cyclohexane was added slowly into the red solution, giving red crystals of **4d** (72 mg, 65%). Anal. Calcd

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Table 2. Crystallographic Data for Compounds 4c, 4d, and 5

	4c	**4d**	**5**
empirical formula	$C_{76}H_{100}Cl_4F_{12}N_4O_{12}Rh_4S_4$	$C_{76}H_{100}C_{l4}F_{12}N_8O_{12}Rh_4S_4$	$C_{100}H_{132}B_4F_{16}N_4O_8Rh_4$
fw	2170.27	2227.32	2204.40
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2/c$	$P\bar{1}$	$P4_2/mbc$
a (Å)	23.406(4)	12.6755(18)	20.232(3)
b (Å)	12.868(2)	20.868(3)	20.232(3)
c (Å)	36.790(7)	22.048(3)	35.833(7)
α (deg)		81.406(3)	
β (deg)	91.095(3	80.098(2)	
γ (deg)		85.367(3)	
V (Å^3)	11 079(4)	5671.4(14)	14 668(4)
Z	4	2	4
ρ_{calcd} (g/cm^3)	1.301	1.304	0.998
μ (Mo Kα) (mm^{-1})	0.824	0.808	0.500
no. of observ	19 324	19 696	6543
no. of params	964	521	283
goodness of fit	0.818	0.793	0.916
$R_1{}^a$ ($I > 2\sigma(I)$)	0.1024	0.1004	0.0737
$wR_2{}^a$ ($I > 2\sigma(I)$)	0.3204	0.3144	0.2332

[a] $R_1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o{}^2 > 2\sigma F^2$). $wR_2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.095P)^2]$; $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$ (also with $F_o{}^2 > 2\sigma F^2$).

for $C_{76}H_{100}Cl_4F_{12}N_8O_{12}Rh_4S_4$: C 40.98, H 4.53, N 5.03. Found (%): C 40.99, H 4.53, N 5.04. IR (KBr, cm^{-1}): 3504 (m), 3081 (w), 2969 (w), 1640 (w), 1475 (w), 1418 (w), 1367 (w), 1259 (s), 1167 (m), 1032 (s), 845 (w), 640 (m), 581 (w), 522 (w). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.31 (s, 72H, ^{t}Bu), 5.93−6.10 (m, 8H, Cp^t), 6.33−6.47 (m, 4H, Cp^t), 8.12 (m, 8H, azopyridyl), 9.10 (m, 8H, azopyridyl).

Preparation of [(Cp^{t}Rh)$_4$(μ-Cl)$_4$(μ-bpy)$_2$](BF$_4$)$_4$ (4e). AgBF$_4$ (39 mg, 0.2 mmol) was added to a solution of **3c** (86 mg, 0.1 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature and stirred for 3 h. The solution was filtered to remove the undissolved compound. The filtrate was concentrated and cyclohexane was added slowly into the red solution, giving **4e** as a red solid (71 mg, 74%). Anal. Calcd for $C_{72}H_{100}B_4Cl_4F_{16}N_4Rh_4$: C 44.99, H 5.24, N 2.91. Found (%): C 45.02, H 5.22, N 2.93. IR (KBr, cm^{-1}): 3427 (w), 3081 (w), 2965 (w), 1612 (w), 1489 (w), 1466 (w), 1375 (w), 1261 (s), 1223 (m), 1159 (m), 1074 (m), 1030 (s), 903 (w), 814 (m), 638 (m), 573 (w), 518 (w), 468 (w). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.32 (s, 72H, ^{t}Bu), 5.66 (d, 8H, Cp^t), 6.18−6.33 (m, 4H, Cp^t), 8.21 (m, 8H, dipyridyl), 9.01 (m, 8H, dipyridyl).

Preparation of [(Cp^{t}Rh)$_4$(μ-terephthalate)$_2$(μ-bpy)$_2$](BF$_4$)$_4$·2(C$_6$H$_{12}$) (5). To a solution of **4e** (192 mg, 0.1 mmol) in CH$_2$Cl$_2$ (20 mL) was added terephthalate sodium (42 mg, 0.2 mmol) at room temperature. After stirring for 15 h, the mixture was filtered and the filtrate was reduced to about 5 mL under vacuum. Cyclohexane was added slowly into the red solution, giving orange crystals of **5** (157 mg, 69%). Anal. Calcd for $C_{100}H_{132}B_4F_{16}N_4O_8Rh_4$: C 52.75, H 5.84, N 2.46. Found (%): C 52.76, H 5.85, N 2.43. IR (KBr, cm^{-1}): 3428 (s), 2950 (w), 1703 (s), 1611 (m), 1414 (w), 1219 (m), 1196 (s), 1104 (s), 1045 (m), 1015 (m), 796 (m), 470 (w). ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.33 (s, 72H, ^{t}Bu), 5.6 (d, 8H, Cp^t), 6.32 (m, 4H, Cp^t), 7.06−7.18 (m, 8H, terephthalate), 8.22 (m, 8H, dipyridyl), 9.07 (m, 8H, dipyridyl).

X-ray Structure Determination. All single crystals were immersed in mother solution and sealed in thin-walled glass capillaries except **3a**. Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intersity data were performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. Non-hydrogen atoms of **3a**, **4a**, and **4b** were refined with anisotropic thermal parameters, and hydrogen atoms were used in calculated positions. For **4c**, non-hydrogen atoms were refined anisotropically with the exception of two disordered anions, which were refined isotropically. Hydrogen positions were included in idealized positions except those on the disordered *tert*-butyl. For **4d**, only the metal and chlorine atoms were refined anisotropically. Some carbon, oxygen, and fluorine from the anions were never found. Hydrogen atoms were included in idealized positions. Non-hydrogen atoms of **5** were refined anisotropically with the exception of anion and solvent molecules, which were refined isotropically. Hydrogen atoms were used in calculated positions. All the calculations were carried out with the SHELXTL[18] program. Crystal data, data collection parameters, and the results of the analyses of compounds **3a**, **4a**, **4b**, **4c**, **4d**, and **5** are listed in Table 1 and Table 2.

Acknowledgment. Financial support by the National Nature Science Foundation of China for Distinguished Young Scholars (20531020, 20421303), Shanghai Science and Technology Committee (05JC14003) and China Postdoctoral Science Foundation (2004036333) is gratefully acknowledged.

Supporting Information Available: The crystallographic data for **3a**, **4a**, **4b**, **4c**, **4d**, and **5** are available free of charge via the Internet at http://pubs.acs.org.

OM0508435

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