

Stepwise Formation of Molecular Rectangles of Half-Sandwich Rhodium and Ruthenium Complexes Containing Bridging Chloranilate Ligands

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Binuclear complexes $[\text{Cp}^*\text{Rh}_2(\mu\text{-CA})\text{Cl}_2]$ (**2a**) and $[(p\text{-cymene})_2\text{Ru}_2(\mu\text{-CA})\text{Cl}_2]$ (**2b**) (CA = chloranilate) were obtained by the reactions of $[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]$ (**1a**) or $[(p\text{-cymene})\text{RuCl}(\mu\text{-Cl})_2]$ (**1b**) with H_2CA in the presence of base, respectively. Treatment of **2a** or **2b** with bidentate ligands (L) such as pyrazine, 4,4'-dipyridine (bpy), 2,5-bis(4-pyridyl)-1,3,5-oxadiazole (bpo), and *E*-1,2-bis(4-pyridyl)ethene (bpe) in the presence of AgOTf (OTf = CF_3SO_3) in CH_3OH gave the corresponding tetranuclear complexes, with the general formulas $[\text{Cp}^*\text{Rh}_4(\mu\text{-CA})_2(\mu\text{-L})_2](\text{OTf})_4$ (**3a–d**) and $[(p\text{-cymene})_4\text{Ru}_4(\mu\text{-CA})_2(\mu\text{-L})_2](\text{OTf})_4$ (**4a–d**), respectively. The molecular structures of $[\text{Cp}^*\text{Rh}_4(\mu\text{-CA})_2(\mu\text{-bpy})_2](\text{OTf})_4$ (**3b**), $[(p\text{-cymene})_4\text{Ru}_4(\mu\text{-CA})_2(\mu\text{-bpy})_2](\text{OTf})_4$ (**4b**), and $[(p\text{-cymene})_4\text{Ru}_4(\mu\text{-CA})_2(\mu\text{-bpe})_2](\text{OTf})_4$ (**4d**) have been determined by single-crystal X-ray analysis and revealed that the metal centers were connected by pyridyl ligands and bis-bidentate chloranilate (CA) ligands to construct a rectangular cavity with different dimensions and strong π interactions between independent molecules to form rectangle channels in the solid state.

Introduction

In the past decade, the metal-directed self-assembly of supramolecular architectures, such as two-dimensional triangles, squares, rectangles, and polygons and three-dimensional cages and polyhedra, has attracted interest.^{1,2} Most of the available systems, which are derived from platinum or palladium species, such as diphosphines and diamine derivatives as ligands in metallic building blocks, have been used extensively by many groups.³ A series of metal–metal bonded binuclear units of the type *cis*- $\text{M}_2(\mu\text{-DArF})_2$ (M = Mo, Rh, and Ru) and dicarboxylate dianions as linkers have been reported by Cotton and co-workers.⁴ A family of Re-based molecular rectangles using 2,2'-bipyrimidine, dianionic benzimidazolate, sulfides, selenides, or alkoxide bridging ligands have also been synthesized recently.⁵

In recent years, supramolecular chemistry with organometallic half-sandwich complexes based on Ir, Rh, and Ru fragments has received considerable attention because they can be used to build metallamacrocyclic receptors as well as coordination cages. Many tri-, tetra-, and hexanuclear metallamacrocycles using a combination of half-sandwich complexes with trifunctional ligands were studied extensively by some groups.⁶ “Organometallic boxes” with cyanide-linked cubes that contain octahedral building blocks of rhodium and cobalt derivatives have been described by the group of Rauchfuss.⁷

On the other hand, 1,4-dihydroxybenzoquinone and its homologues ($\text{H}_2\text{C}_6\text{X}_2\text{O}_4$) are the most useful multifunctional ligands, which can provide a variety of binding sites for metal cations. As a result, many coordination compounds containing chloranilate (CA) as bis-bidentate ligands have been widely prepared and studied.^{8,9} Recently, the self-assembly of rhenium-based rectangular boxes containing chloranilate ligands has been reported; the rectangular box shows size and shape selectivity

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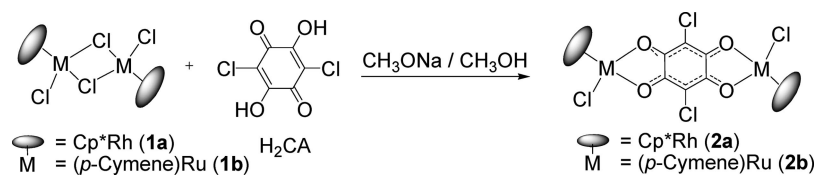
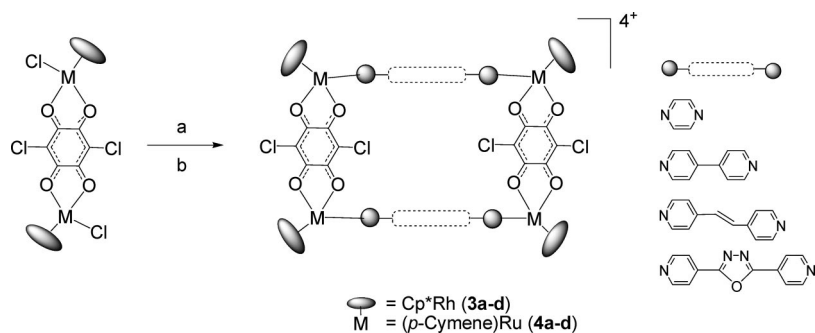
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Scheme 1. Synthesis of Binuclear Complexes **2a,b**Scheme 2. Synthesis of Tetranuclear Complexes **3a–d** and **4a–d**: (a) AgOTf, CH₃OH, Room Temperature; (b) Dipyridyl Ligands, CH₃OH, Room Temperature

toward aromatic guest molecules.^{10a} At the same time, one ruthenium-based hexanuclear metalloprism, which incorporates *p*-cymene ruthenium building blocks, bridged by 2,5-dihydroxy-1,4-benzoquinonato (dmbq) ligands and connected by two 2,4,6-tri(4-pyridyl)-1,3,5-triazine subunits, was reported.^{10b,c} However, metal compounds with the chloranilate ligands to build two-dimensional organometallic rectangles have not been studied extensively, although these supramolecular structures may display interesting functional properties and applications in various fields, including host–guest chemistry, redox activity, magnetic behavior, photo- and electrochemical sensing, and catalysis.^{10d}

We were interested in supramolecular complexes based on quasi-octahedral geometries that bear arene or cyclopentadienyl groups, and their derivatives, since a new type of supramolecular series has been developed by introduction of these organic moieties.¹¹ The stepwise formation of tetra- and hexanuclear half-sandwich complexes bearing organic π -ligands and oxalato bridges connected by two and three pyridyl-based subunits has been reported.^{12,13} Recently, the stepwise formation of “organometallic boxes” with half-sandwich Ir, Rh, and Ru fragments also has been realized.¹⁴ The general design strategy for the formation of molecular architectures involves the design of a binuclear complex with two parallel coordination sites, and the complexes contain two-dimensional architectures with two different ligands “edges”.

Herein we report the stepwise formation of bi- and tetranuclear rhodium and ruthenium complexes bridged by chloranilate ligands and connected by pyridyl-based subunits. A new series of bi- and tetranuclear rhodium and ruthenium complexes were synthesized and characterized. Tetranuclear complexes [Cp*₄Rh₄(μ -CA)₂(μ -bpy)₂](OTf)₄ (**3b**), [(*p*-cymene)₄Ru₄(μ -CA)₂(μ -bpy)₂](OTf)₄ (**4b**), and [(*p*-cymene)₄Ru₄(μ -CA)₂(μ -bpe)₂](OTf)₄ (**4d**) were confirmed by X-ray analyses.

Results and Discussion

Synthesis and Characterization of Binuclear Complexes **2a and **2b**.** As shown in Scheme 1, when [Cp*₂RhCl(μ -Cl)]₂ (**1a**) or [(*p*-cymene)₂RuCl(μ -Cl)]₂ (**1b**) was treated with H₂CA in the presence of CH₃ONa in a 1:1:2 ratio in CH₃OH at room temperature, the binuclear complexes [Cp*₂Rh₂(μ -CA)Cl₂] (**2a**) and [(*p*-cymene)₂Ru₂(μ -CA)Cl₂] (**2b**), respectively, were formed

in high yields. The IR spectra showed a strong band at approximately 1530 cm⁻¹ for **2a** and 1491 cm⁻¹ for **2b**, owing to the C=O stretching of the bridging chloranilate ligands. The ¹H NMR spectra of **2a** in [D₆]DMSO exhibited a sharp singlet at about $\delta = 1.63$ ppm due to the Cp* protons, and the ¹H NMR spectrum of **2b** showed four characteristic resonances for the *p*-cymene protons. Compounds **2a** and **2b** are air- and moisture-stable, but they are insoluble in common polar organic solvents, such as CHCl₃, CH₂Cl₂, CH₃OH, and CH₃CN.

Synthesis and Characterization of Tetranuclear Complexes **3a–d and **4a–d**.** Tetranuclear complexes bearing dipyridyl ligands, which are formulated as [Cp*₄Rh₄(μ -CA)₂(μ -L)₂](OTf)₄ (**3a**, L = pyrazine; **3b**, L = bpy; **3c**, L = bpo; **3d**, L = bpe) were prepared by direct reactions of **2a** with the corresponding dipyridyl ligands in the presence of AgOTf (Scheme 2). When pyrazine was added to the filtrate that was obtained from binuclear complex **2a** and AgOTf in a 1:2 molar ratio in CH₃OH at room temperature, tetranuclear complex **3a** was formed. The ¹H NMR spectrum consists of two characteristic singlets at $\delta = 1.67$ and 8.76 ppm in a 60:8 intensity ratio due to Cp* and pyrazine ligands, suggesting a symmetric tetranuclear structure. A tetranuclear complex bearing the 4,4'-dipyridyl ligands, [Cp*₄Rh₄(μ -CA)₂(μ -bpy)₂](OTf)₄ (**3b**), was obtained from the reaction between **2a** and 4,4'-dipyridine. The IR showed a strong band at 1511 cm⁻¹ indicating the presence of the coordinated bis-bidentate chloranilate ligands. The ¹H NMR spectra showed three resonances at approximately at $\delta = 1.65$ (s), 7.90 (d), and 8.37 (d) ppm; the first is assigned to Cp* protons and the others are assigned to dipyridyl protons. Similarly, tetranuclear complexes [Cp*₄Rh₄(μ -bpo)₂(CA)₂](OTf)₄ (**3c**) and [Cp*₄Rh₄(μ -

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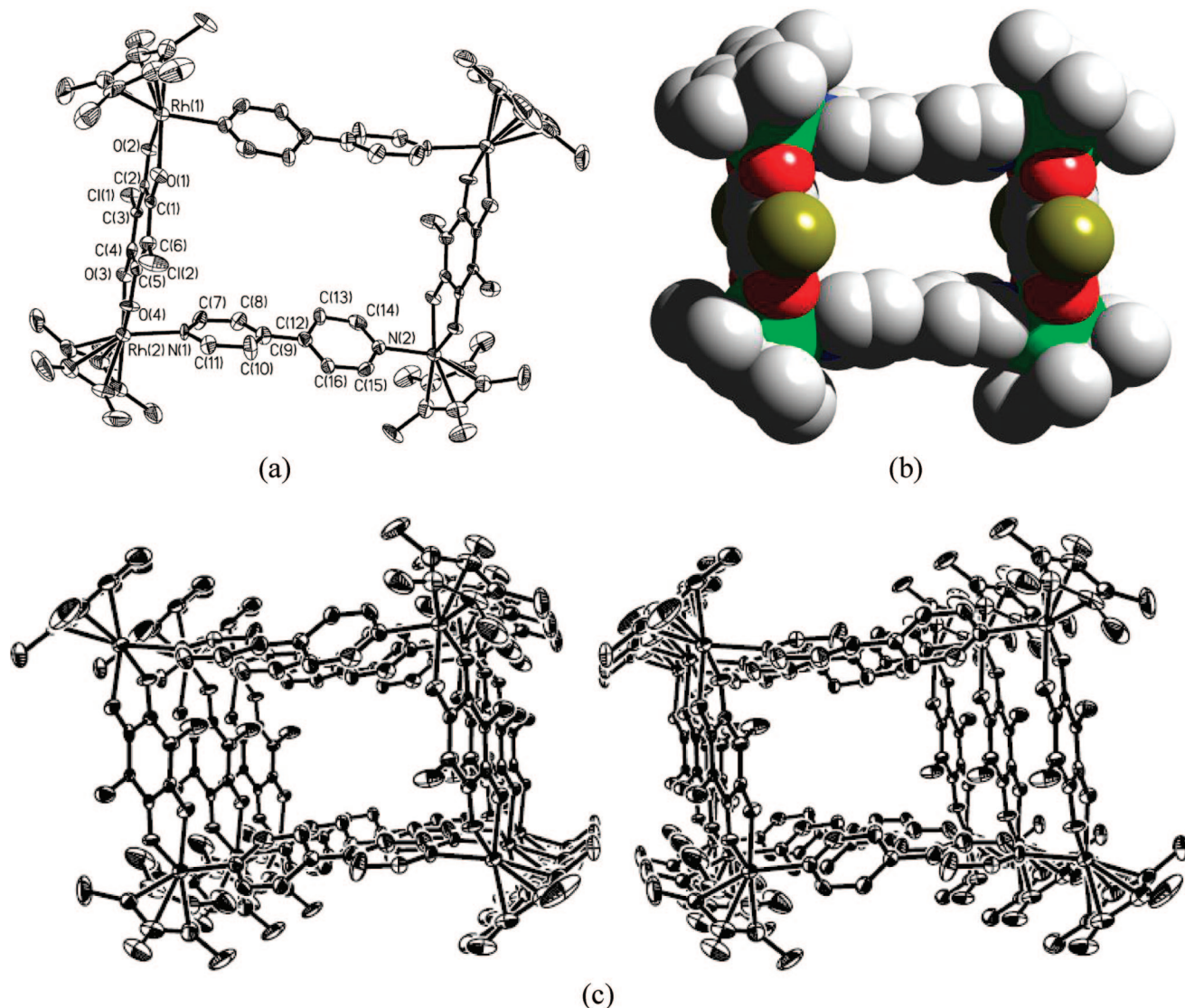


Figure 1. (a) Complex cation of **3b** with thermal ellipsoids drawn at the 30% level. (b) Space-filling model of cationic molecular rectangle **3b** based on its X-ray coordinates (Rh green; O red; N blue; C gray; Cl dark yellow). (c) Stacking of the molecules in crystals of **3b** viewed along the *c*-axis. All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

bpe)₂(CA)₂](OTf)₄ (**3d**) can be prepared readily from binuclear complex **2a** and 2,5-bis(4-pyridyl)-1,3,5-oxadiazole or 1,2-bis(4-pyridyl)ethylene under similar experimental conditions in 62% and 69% yield, respectively. In the ¹H NMR spectra, the Cp* methyl protons appear at 1.62 ppm for **3c** and **3d** as a singlet, respectively, while the resonances for the pyridyl are around $\delta = 8.15$ (d), 8.49 (d) for **3c** and 7.61 (d), 8.21 (d) ppm for **3d**. Both of them indicate the high molecular symmetry in these complexes, and the bands at around 1505 cm⁻¹ for **3c** and **3d**, in the IR spectra, can be assigned to the C=O stretching.

Ruthenium-based molecular rectangles of general formula [(*p*-cymene)₄Ru₄(μ -CA)₂(μ -L)₂](OTf)₄ (**4a**, L = pyrazine; **4b**, L = bpy; **4c**, L = bpo; **4d**, L = bpe) were synthesized following a similar procedure using [(*p*-cymene)₂Ru₂(μ -CA)Cl₂] (**2b**) instead of [Cp*₂Rh₂(μ -CA)Cl₂] (**2a**). In the ¹H NMR spectra, **4a–d** display similar signal patterns for the protons of the *p*-cymene ligands. The infrared spectra of **4a–d** are dominated by absorption of the coordinated chloranilate ligands (ca. 1504 cm⁻¹), which are slightly shifted as compared to that of the complex **2b** (1491 cm⁻¹).

Molecular Structures. Crystal structure of **3b**: A single-crystal X-ray diffraction analysis showed that compound **3b**

adopts a tetranuclear rectangular architecture. Crystals of **3b** suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane at low temperature. Perspective drawings of **3b** with the atomic numbering scheme are given in Figure 1, and selected bond lengths and angles are given in Table 1. Each Rh center adopts a three-legged piano-stool conformation, which are six-coordinate geometry, assuming that Cp* ligands function as three-coordinate ligands. Each Rh center is coordinated with one Cp* ring, one nitrogen atom from 4,4'-bipyridine, and two oxygen atoms of chloranilate ligands. The pyridyl plane in bridging bpy is twisted by 25°, which is close to the commonly observed twist angle for bpy in metallacycles. The dianion of chloranilic acid chelates to the two rhodium atoms through the four oxygen atoms, acting as a tetradentate ligands. The average Rh–N and Rh–O bond distances are 2.124 and 2.126 Å, respectively. The chloranilate C1–C2 and average C–O bond distances are 1.532 and 1.263 Å, respectively. The average bite distance of two oxygen atoms in the chloranilate five-membered chelate ring is 2.610 Å. As shown in Figure 1c, the molecular rectangles stack via the *c*-axis to form rectangle channels due to the π – π interactions between the independent

Table 1. Selected Bond Distances and Angles for **3b**

Bond Distances (Å)			
Rh(1)–O(1)	2.110(7)	Rh(1)–O(2)	2.137(7)
Rh(2)–O(3)	2.136(7)	Rh(2)–O(4)	2.090(7)
Rh(2)–N(1)	2.136(7)	Rh(1)–N(2A)	2.135(8)
Cl(1)–C(3)	1.689(10)	Cl(2)–C(6)	1.705(11)
O(1)–C(1)	1.255(10)	O(2)–C(2)	1.264(10)
O(3)–C(4)	1.246(10)	O(4)–C(5)	1.285(11)
C(1)–C(6)	1.382(13)	C(1)–C(2)	1.532(13)
C(2)–C(3)	1.397(12)	C(3)–C(4)	1.400(13)
C(4)–C(5)	1.507(13)	C(5)–C(6)	1.382(14)
Cl(1)–C(3)	1.689(10)	Cl(2)–C(6)	1.705(11)
Bond Angles (deg)			
O(1)–Rh(1)–O(2)	75.8(2)	O(4)–Rh(2)–O(3)	76.3(2)
O(4)–Rh(2)–N(1)	83.8(3)	O(4)–Rh(2)–O(3)	76.3(2)
N(1)–Rh(2)–O(3)	86.6(3)	C(1)–O(1)–Rh(1)	117.3(6)
C(2)–O(2)–Rh(1)	116.1(6)	C(4)–O(3)–Rh(2)	114.6(6)
C(5)–O(4)–Rh(2)	116.7(7)	C(11)–N(1)–Rh(2)	126.8(9)
C(7)–N(1)–Rh(2)	117.3(7)	C(14)–N(2)–Rh(1A)	120.7(7)
C(15)–N(2)–Rh(1A)	120.0(7)	O(1)–C(1)–C(6)	124.8(9)
O(1)–C(1)–C(2)	115.4(8)	C(6)–C(1)–C(2)	119.8(8)
O(2)–C(2)–C(3)	124.8(9)	O(2)–C(2)–C(1)	115.3(8)
C(3)–C(2)–C(1)	119.9(8)	C(2)–C(3)–C(4)	119.6(9)
O(3)–C(4)–C(3)	122.8(9)	O(3)–C(4)–C(5)	117.8(9)
C(3)–C(4)–C(5)	119.4(8)	O(4)–C(5)–C(6)	124.7(9)
O(4)–C(5)–C(4)	113.9(9)	C(6)–C(5)–C(4)	121.4(8)
C(1)–C(6)–C(5)	119.6(9)		

molecules. The counteranion molecules are located outside of the channels. The dimensions of the rectangular box were 11.2 × 8.0 × 6.3 Å.

Crystal structures of **4b** and **4d**: Perspective drawings of **4b** and **4d** with the atomic numbering schemes are given in Figures 2 and 3, and selected bond lengths and angles are listed in Tables 2 and 3, respectively. The complex cations have a rectangular cavity bridged by two CA²⁻ ligands and two 4,4'-dipyridyl or 1,2-bis(4-pyridyl)ethylene molecules with the dimensions 11.2 × 7.9 × 6.3 Å for **4b** and 13.5 × 7.9 × 6.3 Å for **4d**. The rectangle box of [(CO)₃Re(μ -CA)Re(CO)₃]₂(μ -bpy)₂ with the dimensions 11.4 × 8.1 × 6.3 Å was reported recently. These values are closely similar to that of the corresponding dimensions for **3b** or **4b**.^{10a} The Ru1...Ru1A and Ru2...Ru2A diagonal lengths in the rectangular structure are approximately 13.65, 13.86 Å for **4b** and 14.56, 16.68 Å for **4d**, respectively. The dihedral angles between the two pyridine rings of the dipyridyl ligands for **4b** are 22.4°, compared with that of 25° for **3b**.

The average Ru–N and Ru–O bond distances are 2.108, 2.084 Å for **4b** and 2.092, 2.087 Å for **4d**, respectively. The chloranilate C1–C2 bond distances are 1.506 Å for **4b** and **4d**, and the average C–O bond distances are 1.265 Å for **4b** and 1.254 Å for **4d**, respectively. As shown in Figure 2c, the molecular rectangles of complex **4b** stack via the *b*-axis to form rectangle channels due to the π – π interactions between the independent molecules. In addition, the H₂O molecules are seen within these channels, but the counteranions and toluene molecules are located outside of the channels. Unlike the molecular rectangles of complexes **3b** and **4b**, which can stack to form rectangle channels in the solid state, no regular channels can be formed in the solid state of complex **4d**.

Conclusion

In conclusion, a new series of tetranuclear half-sandwich rhodium and ruthenium complexes containing chloranilate

ligands have been synthesized and characterized. The structures indicate that the tetranuclear metal complexes bear half-sandwich fragments and two different ligands to construct rectangular cavities with different dimensions and strong π interactions between independent molecules to form rectangle channels in the solid state. Similar procedures have the potential to lead to many new and interesting forms of molecular architecture, and the use of molecular materials are now in progress.

Experimental Section

General Data. All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. CH₂Cl₂ was dried over CaH₂; CH₃OH was distilled over Mg/I₂; and THF, diethyl ether, hexane, and toluene were dried over Na and then distilled under nitrogen immediately prior to use. [Cp**RhCl*(μ -Cl)]₂,¹⁵ [(*p*-cymene)RuCl(μ -Cl)]₂,¹⁶ and 2,5-bis(4-pyridyl)-1,3,5-oxadiazole¹⁷ were prepared according to the literature. 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, H₂CA) and other reagents were obtained from commercial sources and used without further purification.

The ¹H NMR spectra were measured on a VAVCE-DMX 400 spectrometer. Elemental analysis was performed on Elementar vario EL III analyzer, and all of the samples were dried under vacuum at 80 °C over 24 h before analysis. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer.

Preparation of Binuclear Complexes. [Cp*₂Rh₂(μ -CA)Cl₂] (2a**).** 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (H₂CA) (208 mg, 1 mmol) was added to a solution of CH₃ONa (108 mg, 2 mmol) in CH₃OH (80 mL). The mixture was stirred for 1 h, and [Cp**RhCl*(μ -Cl)]₂ (618 mg, 1 mmol) was added at room temperature. After stirring for 6 h, the solvent was removed, and the residue was washed with H₂O, giving yellow crystals of **2a** (656 mg, 87%). IR (KBr): ν_{CO} 1530 cm⁻¹. ¹H NMR (400 Hz, DMSO): δ 1.63 (s, 30H; Cp*). Anal. Calcd (%) for C₂₆H₃₀Cl₄O₄Rh₂: C 41.41, H 4.01. Found: C 41.24, H 3.95.

[(*p*-cymene)Ru₂(μ -CA)Cl₂] (2b**).** 2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (H₂CA) (208 mg, 1 mmol) was added to a solution of CH₃ONa (108 mg, 2 mmol) in CH₃OH (80 mL). The mixture was stirred for 1 h, and [(*p*-cymene)RuCl(μ -Cl)]₂ (612 mg, 1 mmol) was added at room temperature. After stirring for 6 h, the solvent was removed, and the residue was washed with H₂O, giving dark red crystals of **2b** (636 mg, 85%). IR (KBr): ν_{CO} 1491 cm⁻¹. ¹H NMR (400 Hz, DMSO): δ 1.26, 1.34 (s, 12H; CH(CH₃)₂), 2.20 (s, 6H; CH₃), 2.83 (m, 2H; CH(CH₃)₂), 5.58 (d, 4H; *J* = 6.2 Hz, C₆H₄), 6.06 (d, 4H; *J* = 6.2 Hz, C₆H₄). Anal. Calcd (%) for C₂₆H₂₈Cl₄O₄Ru₂: C 41.72, H 3.77. Found: C 41.65, H 3.62.

Preparation of Tetranuclear Complexes. [Cp*₄Rh₄(μ -CA)₂(μ -pyrazine)₂](CF₃SO₃)₄ (3a**).** Ag(CF₃SO₃) (51 mg, 0.2 mmol) was added to a solution of **2a** (75 mg, 0.1 mmol) in CH₃OH (20 mL) at room temperature and stirred for 6 h, followed by filtration to remove insoluble materials. Pyrazine (8 mg, 0.1 mmol) was added to the filtrate and stirred for 10 h. The mixture was filtered and the filtrate was concentrated to about 3 mL. Diethyl ether was added slowly to the solution, giving green crystals of **3a** (72 mg, 68%). IR (KBr): ν_{CO} 1504 cm⁻¹. ¹H NMR (400 Hz, CD₃OD): δ 1.67 (s, 60H; Cp*), 8.76 (s, 8H; pyrazine). Anal. Calcd (%) for C₆₄H₆₈Cl₄F₁₂Rh₄N₄O₂₀S₄: C 36.21, H 3.23, N 2.64. Found: C 36.18, H 3.19, N 2.68.

[Cp*₄Rh₄(μ -CA)₂(μ -4,4'-dipyridyl)₂](CF₃SO₃)₄ (3b**).** Ag(CF₃SO₃) (51 mg, 0.2 mmol) was added to a solution of **2a** (75 mg, 0.1 mmol) in CH₃OH (20 mL) at room temperature and stirred for 6 h,

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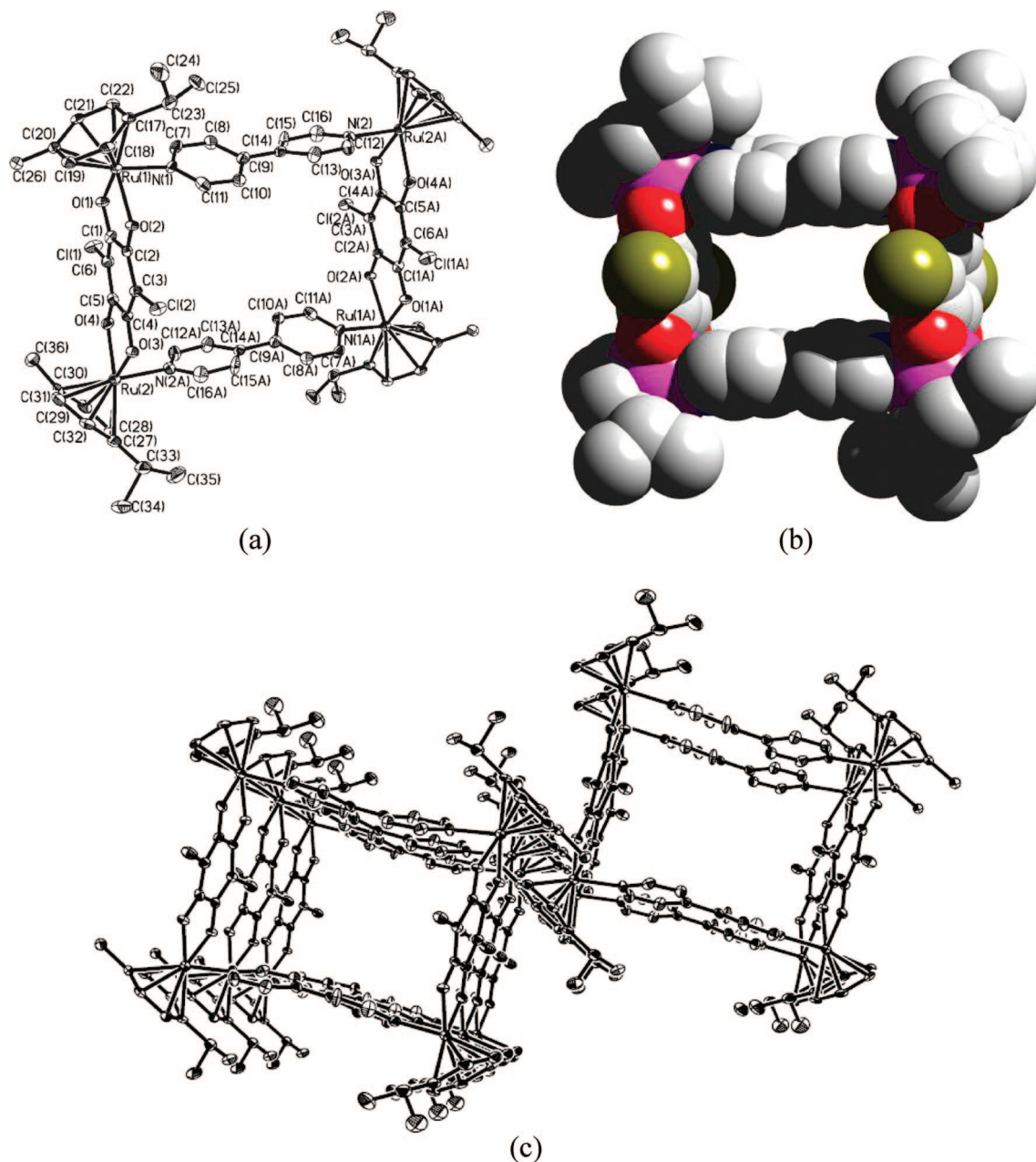


Figure 2. (a) Complex cation of **4b** with thermal ellipsoids drawn at the 30% level. (b) Space-filling model of cationic molecular rectangle **4b** based on its X-ray coordinates (Ru rose; O red; N blue; C gray; Cl dark yellow). (c) Stacking of the molecules in crystals of **4b** viewed along the *b*-axis. All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

followed by filtration to remove insoluble materials. 4,4'-Dipyridyl (16 mg, 0.1 mmol) was added to the filtrate and stirred for 10 h. The solvent was removed, and the residue was extracted with CH_2Cl_2 ; this extract was concentrated to about 3 mL. Diethyl ether was added slowly to the solution, giving green crystals of **3b** (82 mg, 72%). IR (KBr): ν_{CO} 1511 cm^{-1} . $^1\text{H NMR}$ (400 Hz, CD_3CN): δ 1.65 (s, 60H; Cp*), 7.90 (d, 8H; $J = 6.0$ Hz, dipyrindyl), 8.37 (d, 8H; $J = 6.0$ Hz, dipyrindyl). Anal. Calcd (%) for $\text{C}_{76}\text{H}_{76}\text{Cl}_4\text{F}_{12}\text{Rh}_4\text{N}_4\text{O}_{20}\text{S}_4$: C 40.12, H 3.37, N 2.46. Found: C 40.05, H 3.14, N 2.30.

$[\text{Cp}^*_4\text{Rh}_4(\mu\text{-CA})_2\{\mu\text{-2,5-bis(4-pyridyl)-1,3,4-oxadiazole}\}_2(\text{CF}_3\text{SO}_3)_4$ (**3c**). This complex (green, 74 mg, 62%) was obtained from **2a** (75 mg, 0.1 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (51 mg, 0.2 mmol), and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (22 mg, 0.1 mmol) by a similar procedure to that described for **3b**. IR (KBr): ν_{CO} 1504 cm^{-1} . $^1\text{H NMR}$ (400 Hz, CD_3CN): δ 1.62 (s, 60H; Cp*), 8.15 (d, 8H; $J =$

5.6 Hz, pyridyl), 8.49 (d, 8H; $J = 5.6$ Hz, pyridyl). Anal. Calcd (%) for $\text{C}_{80}\text{H}_{76}\text{Cl}_4\text{F}_{12}\text{Rh}_4\text{N}_8\text{O}_{22}\text{S}_4$: C 39.85, H 3.18, N 4.65. Found: C 39.83, H 3.11, N 4.72.

$[\text{Cp}^*_4\text{Rh}_4(\mu\text{-CA})_2\{\mu\text{-E-1,2-bis(4-pyridyl)ethene}\}_2(\text{CF}_3\text{SO}_3)_4$ (**3d**). This complex (green, 82 mg, 69%) was obtained from **2a** (75 mg, 0.1 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (51 mg, 0.2 mmol), and *E*-1,2-bis(4-pyridyl)ethene (18 mg, 0.1 mmol) by a similar procedure to that described for **3b**. IR (KBr): ν_{CO} 1505 cm^{-1} . $^1\text{H NMR}$ (400 Hz, CD_3CN): δ 1.62 (s, 60H; Cp*), 7.39 (s, 4H; $\text{CH}=\text{CH}$), 7.61 (d, 8H; $J = 6.0$ Hz, pyridyl), 8.21 (d, 8H; $J = 6.0$ Hz, pyridyl). Anal. Calcd (%) for $\text{C}_{80}\text{H}_{80}\text{Cl}_4\text{F}_{12}\text{Rh}_4\text{N}_4\text{O}_{20}\text{S}_4$: C 41.29, H 3.06, N 2.65. Found: C 41.14, H 2.98, N 2.52.

$[(p\text{-cymene})_4\text{Ru}_4(\mu\text{-CA})_2(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4$ (**4a**). $\text{Ag}(\text{CF}_3\text{SO}_3)$ (51 mg, 0.2 mmol) was added to a solution of **2b** (75 mg, 0.1 mmol) in CH_3OH (20 mL) at room temperature and stirred for 6 h, followed by filtration to remove insoluble materials. Pyrazine (8

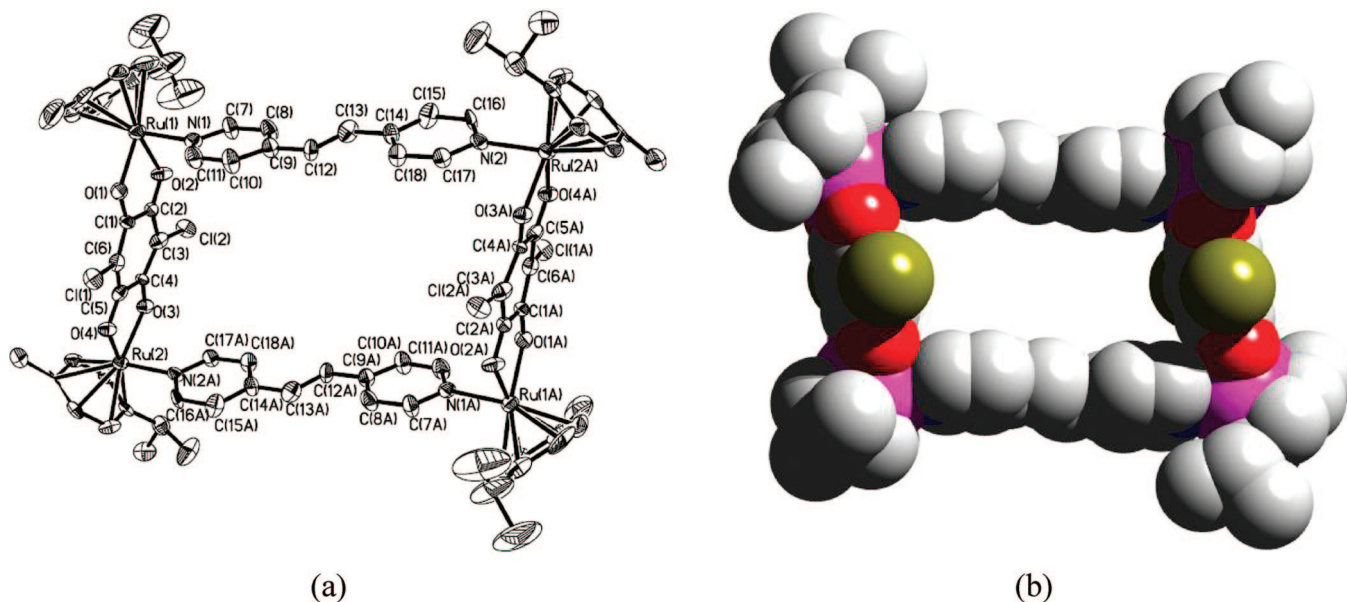


Figure 3. (a) Complex cation of **4d** with thermal ellipsoids drawn at the 30% level. (b) Space-filling model of cationic molecular rectangle **4d** based on its X-ray coordinates (Ru rose; O red; N blue; C gray; Cl dark yellow). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

Table 2. Selected Bond Distances and Angles for **4b**

Bond Distances (Å)			
Ru(1)–O(2)	2.071(5)	Ru(1)–O(1)	2.096(5)
Ru(1)–N(1)	2.112(6)	Ru(2)–O(3)	2.082(5)
Ru(2)–O(4)	2.084(5)	Ru(2)–N(2A)	2.104(6)
O(1)–C(1)	1.266(8)	O(2)–C(2)	1.257(8)
O(3)–C(4)	1.254(8)	O(4)–C(5)	1.283(8)
Cl(1)–C(6)	1.716(8)	Cl(2)–C(3)	1.732(8)
C(1)–C(6)	1.394(10)	C(1)–C(2)	1.506(10)
C(2)–C(3)	1.409(9)	C(3)–C(4)	1.387(9)
C(4)–C(5)	1.492(11)	C(5)–C(6)	1.372(10)
Bond Angles (deg)			
O(2)–Ru(1)–O(1)	76.98(19)	O(2)–Ru(1)–N(1)	86.0(2)
O(1)–Ru(1)–N(1)	82.4(2)	O(3)–Ru(2)–O(4)	77.3(2)
O(3)–Ru(2)–N(2A)	85.1(2)	O(4)–Ru(2)–N(2A)	82.5(2)
C(1)–O(1)–Ru(1)	115.6(5)	C(2)–O(2)–Ru(1)	116.3(5)
C(4)–O(3)–Ru(2)	114.9(5)	C(5)–O(4)–Ru(2)	115.4(5)
O(1)–C(1)–C(6)	125.0(7)	O(1)–C(1)–C(2)	115.0(7)
C(6)–C(1)–C(2)	119.9(7)	O(2)–C(2)–C(3)	124.8(7)
O(2)–C(2)–C(1)	116.0(6)	C(3)–C(2)–C(1)	119.1(7)
C(4)–C(3)–C(2)	120.2(7)	O(3)–C(4)–C(3)	123.7(7)
O(3)–C(4)–C(5)	117.4(6)	C(3)–C(4)–C(5)	118.8(7)
O(4)–C(5)–C(6)	123.4(7)	O(4)–C(5)–C(4)	114.5(7)
C(6)–C(5)–C(4)	122.1(7)	C(5)–C(6)–C(1)	118.8(7)

mg, 0.1 mmol) was added to the filtrate and stirred for 10 h. The mixture was filtered, and the filtrate was concentrated to about 3 mL. Diethyl ether was added slowly to the red solution, giving dark red crystals of **4a** (75 mg, 71%). IR (KBr): ν_{CO} 1504 cm^{-1} . ^1H NMR (400 Hz, CD_3CN): δ 1.39 (s, 24H; $\text{CH}(\text{CH}_3)_2$), 2.32 (s, 12H; CH_3), 2.91 (m, 4H; $\text{CH}(\text{CH}_3)_2$), 5.83 (d, 8H; $J = 6.4$ Hz, C_6H_4), 6.06 (d, 8H; $J = 6.4$ Hz, C_6H_4), 8.77 (s, 8H; pyrazine). Anal. Calcd (%) for $\text{C}_{64}\text{H}_{64}\text{Cl}_4\text{F}_{12}\text{Ru}_4\text{N}_4\text{O}_{20}\text{S}_4$: C 36.40, H 3.06, N 2.65. Found: C 36.34, H 3.02, N 2.72.

[(p-cymene) $_4$ Ru $_4$ (μ -CA) $_2$ (μ -4,4'-dipyridyl) $_2$](CF $_3$ SO $_3$) $_4$ (4b**).** Ag(CF $_3$ SO $_3$) (51 mg, 0.2 mmol) was added to a solution of **2b** (75 mg, 0.1 mmol) in CH_3OH (20 mL) at room temperature and stirred for 6 h, followed by filtration to remove insoluble materials. 4,4'-Dipyridyl (16 mg, 0.1 mmol) was added to the filtrate and stirred for 10 h. The solvent was removed, and the residue was extracted with CH_2Cl_2 ; this extract was concentrated to about 3 mL. Diethyl ether was added slowly to the red solution, giving dark red crystals of **4b** (84 mg, 74%). IR (KBr): ν_{CO} 1503 cm^{-1} . ^1H NMR (400 Hz,

Table 3. Selected Bond Distances and Angles for **4d**

Bond Distances (Å)			
Ru(1)–O(2)	2.075(6)	Ru(1)–O(1)	2.096(6)
Ru(1)–N(1)	2.098(6)	Ru(2)–O(3)	2.084(6)
Ru(2)–O(4)	2.093(5)	Ru(2)–N(2A)	2.086(7)
Cl(1)–C(6)	1.732(8)	Cl(2)–C(3)	1.719(9)
O(1)–C(1)	1.268(9)	O(2)–C(2)	1.230(9)
O(3)–C(4)	1.270(8)	O(4)–C(5)	1.251(9)
C(1)–C(6)	1.357(11)	C(1)–C(2)	1.506(11)
C(2)–C(3)	1.400(11)	C(3)–C(4)	1.386(11)
C(4)–C(5)	1.513(11)	C(5)–C(6)	1.405(11)
C(12)–C(13)	1.302(12)		
Bond Angles (deg)			
O(2)–Ru(1)–O(1)	77.0(2)	O(2)–Ru(1)–N(1)	87.1(2)
O(1)–Ru(1)–N(1)	84.4(2)	O(3)–Ru(2)–N(2A)	85.5(2)
O(3)–Ru(2)–O(4)	76.8(2)	N(2A)–Ru(2)–O(4)	82.6(2)
C(1)–O(1)–Ru(1)	114.6(5)	C(2)–O(2)–Ru(1)	115.6(5)
C(4)–O(3)–Ru(2)	116.2(5)	C(5)–O(4)–Ru(2)	116.1(5)
O(1)–C(1)–C(6)	124.3(8)	O(1)–C(1)–C(2)	115.0(7)
C(6)–C(1)–C(2)	120.7(7)	O(2)–C(2)–C(3)	125.2(8)
O(2)–C(2)–C(1)	116.7(7)	C(3)–C(2)–C(1)	118.1(8)
C(4)–C(3)–C(2)	120.6(8)	O(3)–C(4)–C(3)	124.7(7)
O(3)–C(4)–C(5)	114.9(7)	C(3)–C(4)–C(5)	120.3(7)
O(4)–C(5)–C(6)	126.6(8)	O(4)–C(5)–C(4)	115.9(7)
C(6)–C(5)–C(4)	117.5(8)	C(1)–C(6)–C(5)	121.3(8)
C(13)–C(12)–C(9)	126.2(9)	C(12)–C(13)–C(14)	127.0(9)

CD_3CN): δ 1.37 (s, 24H; $\text{CH}(\text{CH}_3)_2$), 2.20 (s, 12H; CH_3), 2.89 (m, 4H; $\text{CH}(\text{CH}_3)_2$), 5.79 (d, 8H; $J = 6.4$ Hz, C_6H_4), 5.98 (d, 8H; $J = 6.4$ Hz, C_6H_4), 7.86 (d, 8H; $J = 6.9$ Hz, dipyrindyl), 8.36 (d, 8H; $J = 6.9$ Hz, dipyrindyl). Anal. Calcd (%) for $\text{C}_{76}\text{H}_{72}\text{Cl}_4\text{F}_{12}\text{Ru}_4\text{N}_4\text{O}_{20}\text{S}_4$: C 40.32, H 3.21, N 2.47. Found: C 40.28, H 3.17, N 2.36.

[(p-cymene) $_4$ Ru $_4$ (μ -CA) $_2$ (μ -2,5-bis(4-pyridyl)-1,3,4-oxadiazole) $_2$](CF $_3$ SO $_3$) $_4$ (4c**).** This complex (dark red, 74 mg, 62%) was obtained from **2b** (75 mg, 0.1 mmol), Ag(CF $_3$ SO $_3$) (51 mg, 0.2 mmol), and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (22 mg, 0.1 mmol) by a similar procedure to that described for **4b**. IR (KBr): ν_{CO} 1504 cm^{-1} . ^1H NMR (400 Hz, CD_3CN): δ 1.39 (s, 24H; $\text{CH}(\text{CH}_3)_2$), 2.21 (s, 12H; CH_3), 2.92 (m, 4H; $\text{CH}(\text{CH}_3)_2$), 5.81 (d, 8H; $J = 5.8$ Hz, C_6H_4), 6.00 (d, 8H; $J = 5.8$ Hz, C_6H_4), 8.10 (d, 8H; $J = 6.8$ Hz, dipyrindyl), 8.47 (d, 8H; $J = 6.8$ Hz, dipyrindyl). Anal. Calcd (%) for $\text{C}_{80}\text{H}_{72}\text{Cl}_4\text{F}_{12}\text{Ru}_4\text{N}_8\text{O}_{22}\text{S}_4$: C 40.04, H 3.02, N 4.67. Found: C 39.84, H 3.01, N 4.73.

Table 4. Crystallographic Data for Compounds **3b**, **4b**, and **4d**

	3b	4b	4d
empirical formula	C ₇₆ H ₇₆ Cl ₄ F ₁₂ N ₄ O ₂₀ Rh ₄ S ₄	C ₇₆ H ₇₂ Cl ₄ F ₁₂ N ₄ O ₂₄ Ru ₄ S ₄ · 2PhMe · 2H ₂ O	C ₈₀ H ₇₆ Cl ₄ F ₁₂ N ₄ O ₂₀ Ru ₄ S ₄
temperature (K)	173(2)	293(2)	293(2)
fw	2275.09	2520.03	2315.77
cryst size (mm ³)	0.15 × 0.12 × 0.10	0.12 × 0.10 × 0.08	0.15 × 0.12 × 0.10
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	16.385(9)	21.293(6)	19.72(2)
<i>b</i> (Å)	18.966(10)	10.919(3)	14.441(15)
<i>c</i> (Å)	16.274(9)	23.103(7)	20.72(2)
β (deg)	92.407(7)	91.099(5)	115.138(16)
<i>V</i> (Å ³)	5053(5)	5371(3)	5342(10)
<i>Z</i>	2	2	2
ρ_{calcd} (g/cm ³)	1.495	1.558	1.440
μ (Mo K α) (mm ⁻¹)	0.913	0.818	0.813
limiting indices	-19 ≤ <i>h</i> ≤ 17, -22 ≤ <i>k</i> ≤ 22, -18 ≤ <i>l</i> ≤ 19	-25 ≤ <i>h</i> ≤ 24, -12 ≤ <i>k</i> ≤ 12, -25 ≤ <i>l</i> ≤ 27	-23 ≤ <i>h</i> ≤ 23, -17 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 24
no. collected reflns	19 938	21 805	21 701
no. unique reflns	8784	9446	9377
no. params	451	636	582
goodness of fit	1.024	0.872	0.865
R1 ^a , wR2 ^a [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0964 wR2 = 0.2460	R1 = 0.0619, wR2 = 0.1477	R1 = 0.0626, wR2 = 0.1453
R1, wR2 (all data)	R1 = 0.1617 wR2 = 0.2867	R1 = 0.1110, wR2 = 0.1610	R1 = 0.1339, wR2 = 0.1828
max./min. residual density (e Å ⁻³)	1.576 and -2.172	0.902 and -0.539	1.910 and -1.535

^a R1 = $\sum ||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

[(*p*-cymene)₄Ru₄(μ -CA)₂{ μ -*E*-1,2-bis(4-pyridyl)ethene}₂(CF₃SO₃)₄ (**4d**). This complex (dark red, 68 mg, 59%) was obtained from **2b** (75 mg, 0.1 mmol), Ag(CF₃SO₃) (51 mg, 0.2 mmol), and *E*-1,2-bis(4-pyridyl)ethene (18 mg, 0.1 mmol) by a similar procedure to that described for **4b**. IR (KBr): ν_{CO} 1504 cm⁻¹. ¹H NMR (400 Hz, CD₃CN): δ 1.36, 1.39 (s, 24H; CH(CH₃)₂), 2.18, (s, 12H; CH₃), 2.88, (m, 4H; CH(CH₃)₂), 5.75 (d, 8H; *J* = 6.4 Hz, C₆H₄), 5.94 d, 8H; *J* = 6.4 Hz, C₆H₄), 7.43 (d, 4H; CH=CH), 7.57–7.59 (m, 8H; dipyrityl), 8.18–8.20 (m, 8H; dipyrityl). Anal. Calcd (%) for C₈₀H₇₆Cl₄F₁₂N₄O₂₀S₄: C 41.49, H 3.31, N 2.42. Found: C 41.39, H 3.27, N 2.43.

X-ray Crystallography. Suitable crystals for X-ray analysis of **3b** and **4d** were obtained by slow diffusion of diethyl ether into CH₂Cl₂ solutions of the corresponding compound. A suitable crystal for X-ray analysis of **4b** was obtained by slow diffusion of toluene into CH₂Cl₂ solutions. 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 α radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature for **3b** and **4d** and at -100 °C under a cold nitrogen stream for **4b** using the ω -scan technique. The structures were solved by Patterson methods and refined by full-matrix least-squares calculations, using the program system SHELXTL-97,¹⁸ and

SADABS¹⁹ absorption corrections were applied to the data. The positions of all non-hydrogen atoms except the solvent molecules were refined with anisotropic thermal parameters by using full-matrix least-squares methods. Details of the data collection and refinement are summarized in Table 4.

In complexes **3b**, **4b**, and **4d**, there are disordered guest molecules in the voids of the crystal structure. One of the two triflate anions in **3b** is also disordered. Hence, new data sets corresponding to omission of the disordered anions and solvents were generated with the SQUEEZE algorithm, and the structures were refined to convergence. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules in the asymmetric unit of **4b** were not found, and other hydrogen atoms of all the complexes were placed in geometrically calculated positions with fixed isotropic thermal parameters.

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

OM800490S

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