

Stepwise Formation of Quasi-Octahedral Macrocyclic Complexes of Rhodium(III) and Iridium(III) Bearing a Pentamethylcyclopentadienyl Group

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Abstract: Reactions of $[\{MCl_2(Cp^*)\}_2]$ (**1**: M = Ir, **2**: M = Rh) with bidentate ligands (L) such as 1,4-diisocyno-2,5-dimethylbenzene (**a**), 1,4-diisocyno-2,3,5,6-tetramethylbenzene (**b**), pyrazine (**c**) or 4,4'-dipyridyl (**d**) gave the corresponding dinuclear complexes $[\{MCl_2(Cp^*)\}_2(L)]$ (M = Ir: **3a**, **3b**, **5c**, **5d**; M = Rh: **4b**, **6c**, **6d**), which were converted into tetranuclear complexes $[\{M_2(\mu-Cl)_2(Cp^*)_2\}_2(L)_2](OTf)_4$ (M = Ir: **7c**, **7d**, **9a**, **9b**; M = Rh: **8c**, **8d**, **10b**) on treatment with Ag(OTf). X-ray analyses of **8c** and **8d** revealed that each of four pentamethylcyclopentadienyl met-

al moieties was connected by two μ -Cl-bridged atoms and a bidentate ligand to construct a rectangular cavity with the dimensions of 3.7×7.0 Å for **8c** and 3.7×11.5 Å for **8d**. Both the Rh_2Cl_2 and pyrazine (or 4,4'-dipyridyl) ring planes are perpendicular to the Rh_4 plane. Treatment of Cl-bridged complexes (**7c**, **7d**, **8c**, **8d**, **9b**, and **10b**) with a different ligand (L') resulted in cleavage

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of the Cl bridges to produce two-dimensional complexes $[\{MCl(Cp^*)\}_4(L)(L')_2](OTf)_4$ (**11ac**, **11bc**, **11bd**, **12bc**, and **12bd**) with two different ligand "edges". Complex **10b** reacted readily with 1,4-diisocyno-2,3,5,6-tetramethylbenzene (**b**) to give a tetranuclear rhodium(III) complex **12bb**. The structure of tetranuclear complexes was confirmed by X-ray analysis of **11bc**. Each $\{MCp^*\}$ moiety is surrounded by a Cl atom, isocyanide, and pyrazine (or 4,4'-dipyridyl) and the dimensions of its cavity are 7.0×11.6 Å.

Introduction

Metal-containing supramolecules and coordination polymers have attracted interests in recent years because there are many promising metal fragments available for the construction of novel supramolecular materials.^[1] In particular, square-planar complexes of platinum and palladium are attractive as building blocks which occupy vertices. For example, diphosphines and diamine derivatives as ligands in metallic building blocks have been used widespread by many groups.^[2] The sixfold bridging capability of the octahedral unit leads to compounds with diverse dimensionality, in comparison with those that are square planar.^[3–7] We were interested in supramolecular complexes based on quasi-octahedral geometries that bear arene, cyclopentadienyl, or pentamethylcy-

clopentadienyl groups, and their derivatives, since a new type of supramolecular series would be developed by introduction of these organic moieties. Since these six- or five-membered rings block three sites on the octahedron, they reduce the dimensionality of the polymeric derivatives and render them particularly amendable to processing. Octahedral building blocks can be assembled to form cubic or ladder-shaped structures. Introduction of three-coordinate ring ligands also can enhance solubility of polymeric compounds. We report here stepwise assembly of the tetranuclear rhodium and iridium supramolecules bearing pentamethylcyclopentadienyl and binary ligands. Complexes reported here are novel because they contain two-dimensional architectures with two different ligand "edges", that is, molecular rectangles. The only self-assembled supramolecules with pentamethylcyclopentadienyl or cyclopentadienyl groups, to our knowledge, have been reported by Rauchfuss et al.:^[8, 9] $[Co_4Rh_4(CN)_{12}-(Cp)_4(Cp^*)_4]^{4+}$, $[Rh_7(Cp^*)_7(CN)_{12}]^{2+}$, and $[Ir_4Rh_3(CN)_{12}-(Cp^*)_7]^{2+}$ ($Cp^* = C_5Me_5$). They are cyanide-linked molecular squares and cubes that contain octahedral building blocks of rhodium and cobalt derivatives. Recently Darensbourg et al. reported the preparation of diamond-shaped heterometallic complexes of cyclopentadienyl iron(II) and copper(I) bridged by cyanide groups.^[10]

A preliminary account of our work has been published.^[11]

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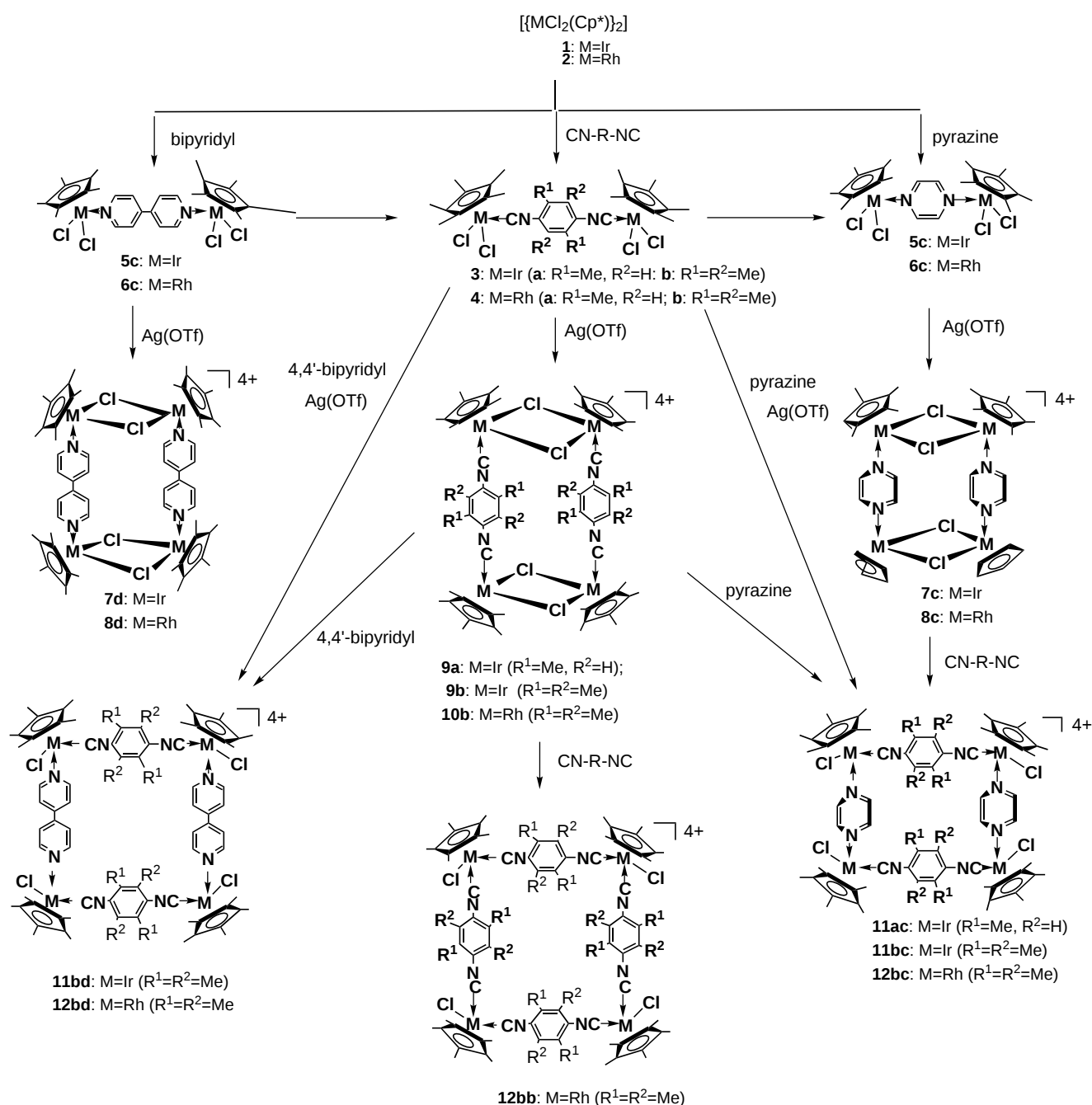
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Results and Discussion

Di- and tetranuclear complexes: When bis[dichloro(pentamethylcyclopentadienyl)iridium(III)] (**1**) was treated with 1,4-diisocyano-2,5-dimethylbenzene (**a**) or 1,4-diisocyano-2,3,5,6-tetramethylbenzene (**b**) in a 1:1 molar ratio at room temperature, yellow crystals formulated as $[\{\text{IrCl}_2(\text{Cp}^*)\}_2(\text{CN-R-NC})]$ (**3a**: $\text{R} = 2,5\text{-Me}_2\text{C}_6\text{H}_2$; **3b**: $\text{R} = 2,3,5,6\text{-Me}_4\text{C}_6$) by FAB mass spectroscopy, were formed in high yields (Scheme 1). The IR spectra showed a strong band at approximately 2140 cm^{-1} due to a terminal isocyanide group. In the ^1H NMR spectra two singlet resonances due to the Cp^* and Me protons appeared at about $\delta = 1.86$ and 2.40 , respectively. These spectroscopic data indicate a dimeric structure in which the Ir

centers are connected by a μ -diisocyanide ligand. X-ray crystal analysis of **3a** confirmed the structure (Figure 1 below). The rhodium analogue **4b**, $[\{\text{RhCl}_2(\text{Cp}^*)\}_2(\mu\text{-}1,4\text{-(NC)}_2\text{-}2,3,5,6\text{-Me}_4\text{C}_6)]$, was prepared as orange crystals in high yield by the reaction of $[\{\text{RhCl}_2(\text{Cp}^*)\}_2]$ (**2**) with **b** (Scheme 1).

Treatment of **1** or **2** with pyrazine (**c**) also generated the dinuclear complexes, **5c** ($\text{M} = \text{Ir}$) and **6c** ($\text{M} = \text{Rh}$) $[\{\text{MCl}_2(\text{Cp}^*)\}_2(\mu\text{-C}_4\text{H}_4\text{N}_2)]$. In the ^1H NMR spectra in $[\text{D}_6]\text{DMSO}$, two singlets appeared at about $\delta = 1.62$ and 8.65 , due to Cp^* and pyrazine protons, respectively. Analogously, the reactions with 4,4'-dipyridyl (**d**) gave dinuclear complexes, $[\{\text{MCl}_2(\text{Cp}^*)\}_2(\mu\text{-}4,4'\text{-dipyridyl})]$ **5d** ($\text{M} = \text{Ir}$) and **6d** ($\text{M} = \text{Rh}$). The ^1H NMR spectra in $[\text{D}_6]\text{DMSO}$ showed



Scheme 1.

three resonances at approximately $\delta = 1.60$ (s), 7.80 (d) and 8.70 (d); the first is assigned to the Cp* protons, and the others are assigned to dipyrindyl protons.

When dinuclear complex **6c** was treated with AgOTf (Tf = CF₃SO₂) in a 1:2 molar ratio in a mixture of CH₂Cl₂ and MeCN at room temperature, tetranuclear complex **8c**, formulated as [RhCl(Cp*)₄(μ -pyrazine)₂](OTf)₄ from the FAB mass spectroscopy (m/z 1254 ([$M+1$]⁺) and elemental analysis, was formed (Scheme 1). The ¹H NMR spectrum consists of two characteristic singlets at $\delta = 1.61$ and 8.65 in a 60:8 intensity ratio, suggesting a symmetric tetranuclear structure. A tetranuclear iridium complex **7c** was obtained from **5c** and AgOTf in a manner similar to the rhodium analogue. The ¹H NMR spectrum showed two kinds of resonances for each of the Cp* and pyrazine ligands; at $\delta = 1.58$ and 1.74 for the former and at $\delta = 8.84$ and 8.97 for the latter, suggesting the presence of configurational isomers.

Tetranuclear complexes that bear the 4,4'-dipyridyl ligand, [M(μ -Cl)(Cp*)₄(μ -bipyridyl)₂](OTf)₄ (**7d**: M = Ir; **8d**: M = Rh), were obtained by the reactions between the corresponding neutral dinuclear complexes and Ag(OTf). The ¹H NMR spectra for **7d** showed a singlet at $\delta = 1.60$ due to Cp* protons and a complex resonance at about $\delta = 8.5$ due to dipyrindyl protons; that for **8d** had two kinds of singlets at $\delta = 1.59$ and 1.61 due to Cp* protons and a complex resonance at about $\delta = 8.5$ due to dipyrindyl protons. The spectra of complex **8d** indicated the presence of configurational isomers, as did that in the case of **7c**. Detailed structures were confirmed by X-ray analyses of **8c** and **8d** (Figures 2 and 3 later). They revealed that the complex cations have the rectangular structures bridged by four Cl atoms, and two pyrazine or 4,4'-dipyridyl molecules.

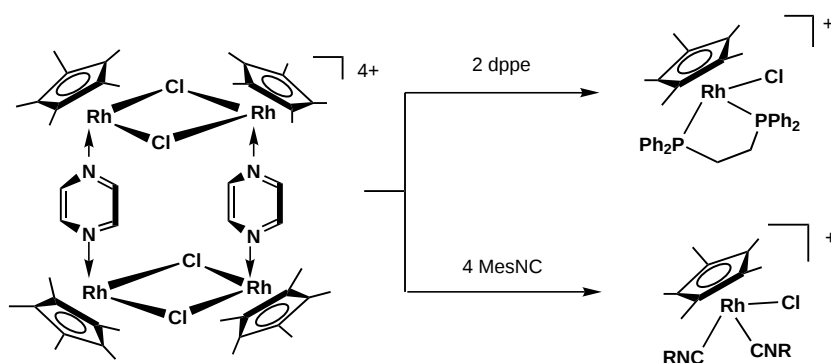
The dinuclear isocyanide complexes **3b** and **4b** reacted readily with Ag(OTf) to give complexes formulated as [M(μ -Cl)(Cp*)₄(μ -1,4-(NC)₂-2,3,5,6-Me₄C₆)₂](OTf)₄, **9b** (M = Ir) and **10b** (M = Rh) (Scheme 1). The IR spectra of **9b** and **10b** showed a terminal isocyanide bands at 2186 and 2182 cm⁻¹, respectively. The ¹H NMR spectra showed two sharp singlets at $\delta = 1.94$ and 2.42 for **9b** and at $\delta = 1.85$ and 2.37 for **10b**, due to Cp* and methyl protons of the isocyanide ligand, respectively. Based on the spectroscopy and structures of pyrazine and 4,4'-dipyridyl complexes **9b** and **10b** were assumed to be a structure bridged by four Cl atoms and two isocyanide ligands.

When μ -chloro-bridged complex **7c** was treated with two equivalents of **b**, the Cl bridges were replaced by **b** to produce yellow crystals **11bc** formulated as [IrCl(Cp*)₄(μ -pyrazine)₂][μ -1,4-(NC)₂-2,3,5,6-Me₄C₆]₂-(OTf)₄. This complex can be also obtained by the reaction between **9b** and pyrazine or the direct reaction of **3b** with pyrazine in the presence of Ag(OTf) (Scheme 1). The tetranuclear complex with a 4+ charge was revealed by the ESI technique. The isotopically resolved signal centered at m/z 495 and 455

correspond to the [M]⁴⁺ and [$M-2$ pyrazine]⁴⁺ charge state species, respectively, where M is a cationic species. The masses of the 4+ ion were determined to be 1981.6 and 1821.2, which are in nearly agreement with the theoretical masses of 1980.23 and 1820.05, respectively. In the IR spectrum, the CN band appeared at 2176 cm⁻¹. The ¹H NMR spectrum showed three singlets at $\delta = 1.94$, 2.42, and 8.65 in a 30:12:4 intensity ratio, due to Cp*, isocyanide, and pyrazine protons, respectively. Finally, the structure was determined by X-ray analysis (Figure 4 later). The complex has a tetranuclear rectangular structure, and each iridium atom is surrounded by an isocyanide, a pyrazine, a Cl atom, and a Cp* moiety. Tetranuclear complex **11ac**, [IrCl(Cp*)₄(μ -pyrazine)₂][μ -1,4-(NC)₂-2,5-Me₂C₆H₂]₂-(OTf)₄, which bears the 1,4-diisocyanato-2,5-dimethylbenzene (**a**) and pyrazine (**c**) ligands, was prepared by a direct reaction of **3a** with pyrazine in the presence of Ag(OTf) (Scheme 1). The rhodium analogue **12bc** was obtained in 49% yield from a direct reaction of **4b** with pyrazine in the presence of Ag(OTf). Tetranuclear iridium and rhodium complexes **11bd** and **12bd** bearing isocyanide and 4,4'-dipyridyl ligands were prepared by the direct treatment of **3b** or **4b** with 4,4'-dipyridyl (**d**). Complex **10b** reacted readily with **b** to give the rectangular complex **12bb** in which the four sides were surrounded by isocyanide ligands. The IR spectrum showed a terminal isocyanide at 2186 cm⁻¹. The ¹H NMR spectrum showed two singlets at $\delta = 1.85$ and 1.87 due to Cp* protons and a broad resonance at $\delta = 2.39$ due to methyl protons, which suggests the presence of isomers.

Reactions of **8c** with Lewis bases and of **3c** with K[Ag(CN)₂]:

Reaction of **8c** with four equivalents of mesityl isocyanide at room temperature replaced pyrazine ligands and Cl atoms to give [RhCl(Cp*)(MesNC)₂](OTf) together with recovery of the starting compound **8c**. A similar reaction with bis(diphenylphosphino)ethane (dppe) gave [RhCl(Cp*)(dppe)](OTf). These reactions arose from strong coordination ability of dppe and isocyanide (Scheme 2). In an attempt to prepare a complex bearing a silver atom, the reaction of **3a** with K[Ag(CN)₂] was carried out and led to the replacement of two Cl anions with CN anions to give yellow crystals formulated as [IrCl(CN)(Cp*)₂][μ -1,4-(NC)₂-2,3,5,6-Me₄C₆]₂ from the FAB mass spectroscopy and elemental analysis. The IR spectrum showed two NC stretching frequencies at 2170 and 2128 cm⁻¹. The ¹H NMR spectrum showed two characteristic



Scheme 2.

resonances at $\delta = 1.98$ and 2.41 , assignable to Cp^* and methyl protons, respectively. The spectroscopic data suggest a symmetric structure in which each iridium center was surrounded by Cp^* , Cl, CN, and isocyanide ligands.

Molecular structures: Detailed discussion of distances and angles is avoided here because of the low accuracy of the X-ray data, especially the methyl groups on the Cp^* rings, for the complexes **3a**, **8c**, **8d**, and **11bc**, but the tables of selected bond lengths and angles are given.

Crystal structure of 3a: A perspective drawing of **3a** with the atomic numbering scheme is given in Figure 1 and selected bond lengths and angles are listed in Table 1. The crystal unit has a crystallographically imposed inversion center in the middle of the $\text{Ir} \cdots \text{Ir}$ vector. The molecule has a dimeric structure connected by a μ -diisocyanide ligand, and the iridium atoms are surrounded by two Cl atoms and isocyanide. Angles between adjacent atoms around the iridium atoms are nearly 90° . The two Ir atoms are separated by $11.6 \text{ \AA}$. The Ir1-C11-N1 and C11-N1-C12 angles are 176 and 172° , respectively, and compare well with those for other isocyanide complexes.

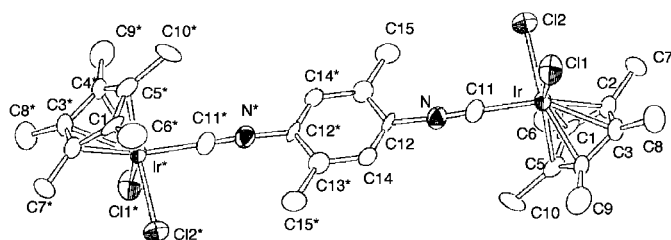


Figure 1. Molecular structure of $[[\text{IrCl}_2(\text{Cp}^*)]_2(\mu\text{-1,4-(NC)}_2\text{-2,5-Me}_2\text{C}_6\text{H}_2)]$ (**3a**).

Crystal structures of 8c and 8d: Perspective drawings of **8c**·2MeOH and **8d** with the atomic numbering schemes are given in Figures 2 and 3, respectively, and selected bond lengths and angles are listed in Tables 2 and 3. The crystal units of **8c** and **8d** also consist of the molecule with a crystallographically imposed inversion center in the middle of the $\text{Rh1} \cdots \text{Rh1}^*$ or $\text{Rh2} \cdots \text{Rh2}^*$, respectively, vector similar to the structure of **3a**. Methanol is contained as a solvent molecule in the crystal unit of **8c** (but outside of the square framework). The complex cations have a rectangular cavity bridged by four Cl atoms and two pyrazine or 4,4'-dipyridyl molecules with the dimensions of $3.68 \times 7.02 \text{ \AA}$ for **8c**, and of $3.68 \times 11.45 \text{ \AA}$ for **8d**, respectively. The molecular rectangle of $[[\text{ReBr}(\text{CO})_3]_4(\mu\text{-pyrazine})_2(\mu\text{-4,4'-dipyridyl})_2]$ is known to

Table 1. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **3a**.

Ir1-Cl1	2.393(4)	Ir1-Cl2	2.411(4)
Ir1-C11	1.96(1)	C11-N1	1.13(2)
Cl1-Ir1-Cl2	88.9(2)	Cl1-Ir1-C11	92.1(4)
Cl2-Ir1-C11	87.7(5)	Ir1-C11-N1	176(1)
C11-N1-C12	172(1)		
intramolecular interacts			
$\text{Ir1} \cdots \text{Ir1}^*$	11.6		

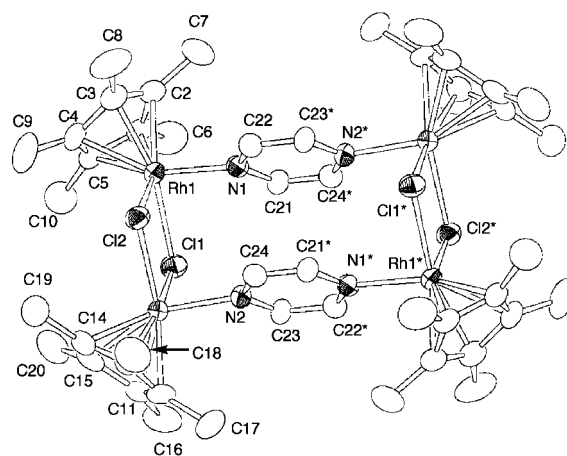


Figure 2. Complex cation of $[[\text{Rh}(\mu\text{-Cl})(\text{Cp}^*)]_4(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4 \cdot 2\text{MeOH}$ (**8c**·2MeOH).

consist of a cavity with the dimensions of $11.44 \times 7.21 \text{ \AA}$.^[12] These values are closely similar to that of the corresponding dimension for **8c** or **8d**. The Rh1-Rh1^* and Rh2-Rh2^* diagonal lengths in the rectangular structure are approximately 7.9 and $12.0 \text{ \AA}$ for **8c** and **8d**, respectively. The bridged $\text{Cl1} \cdots \text{Cl2}$ separation is $3.28 \text{ \AA}$. The dihedral angles between the Rh1-Rh2-Cl1-Cl2 plane and pyrazine (4,4'-dipyridyl) ligands are 90.9 and 92.2° for **8c** and 90.5° and 91.4° for **8d**, respectively. The dihedral angles between two pyridine rings of the dipyrindyl ligand for **8d** is 5.8° , compared with that of 1.4° between two pyrazine ligands for **8c**. The stacking

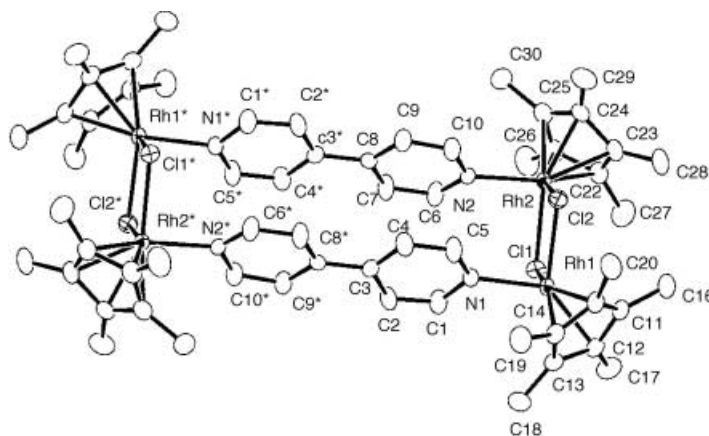


Figure 3. Complex cation of $[[\text{Rh}(\mu\text{-Cl})(\text{Cp}^*)]_4(\mu\text{-4,4'-$

Table 2. Selected bond lengths [Å] and angles [°] for compound **8c**.

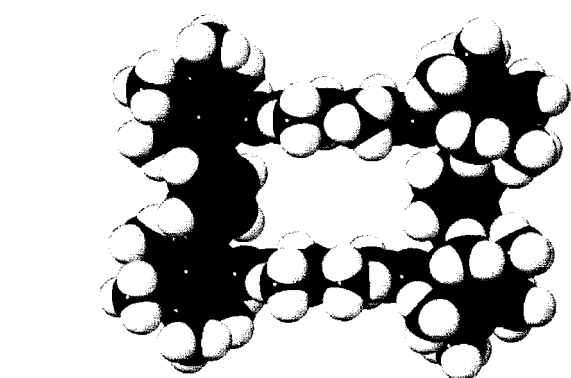
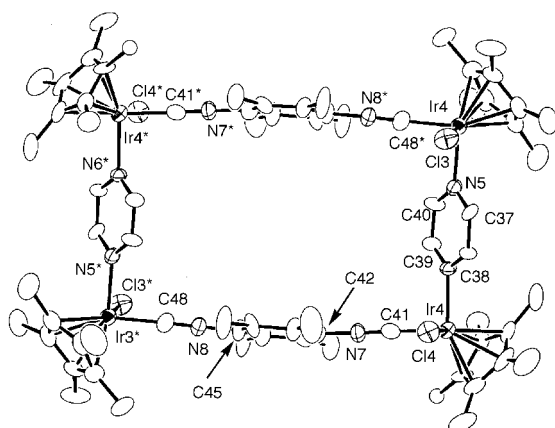
Rh1–Cl1	2.466(3)	Rh1–Cl2	2.467(2)
Rh1–N1	2.133(7)	Rh2–Cl2	2.474(3)
Rh2–Cl2	2.459(2)	Rh2–N2	2.153(8)
Cl1–Rh1–Cl2	83.50(8)	Cl1–Rh1–N1	88.0(2)
Cl2–Rh1–N1	87.8(2)	Cl1–Rh2–Cl2	83.47(8)
Cl1–Rh2–N2	88.5(2)	Cl2–Rh2–N2	88.5(2)
intramolecular interacts			
Rh1...Rh2	3.68	Rh1...Rh2*	7.98
Rh1...Rh1*	7.02	Cl1...Cl2	3.28

Table 3. Selected bond lengths [Å] and angles [°] for compound **8d**.

Rh1–Cl1	2.4632(9)	Rh1–Cl2	2.447(1)
Rh1–N1	2.134(3)	Rh2–Cl1	2.4760(9)
Rh2–Cl2	2.454(1)	Rh2–N2	2.134(3)
Cl1–Rh1–Cl2	83.64(3)	Cl1–Rh1–N1	88.31(8)
Cl2–Rh1–N1	89.55(8)	Cl1–Rh2–Cl2	83.21(3)
Cl1–Rh2–N2	89.49(8)	Cl2–Rh2–N2	89.10(9)

patterns of macrocycles **8c** and **8d** in the solid state showed that the cationic squares are stacked along the *c* axis, resulting in long channel-like cavities. The Rh–X bond lengths and X–Rh–X' angles around the Rh atom for **8c** and **8d** are not different from each other.

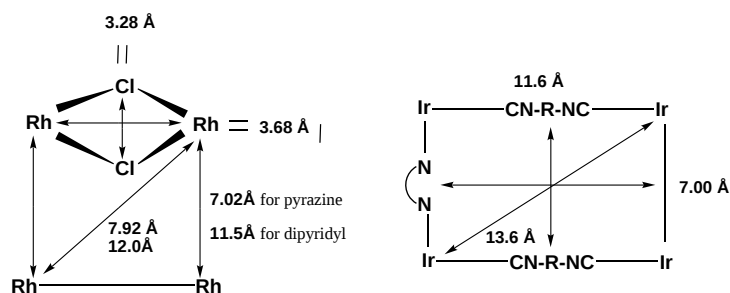
Crystal structure of 11bc: A perspective drawing of **11bc** with the atomic numbering scheme is given in Figure 4, and selected bond lengths and angles are listed in Table 4. An

Figure 4. Complex cation of $[[\text{IrCl}(\text{Cp}^*)]_4(\mu\text{-}1,4\text{-(NC)}_2\text{-}2,3,5,6\text{-Me}_4\text{C}_6)_2\text{-(}\mu\text{-pyrazine)}_2](\text{CF}_3\text{SO}_3)_4$ (**11bc**).Table 4. Selected bond lengths [Å] and angles [°] for **11bc**.

Ir1–Cl1	2.379(5)	Ir1–N1	2.12(1)
Ir1–Cl2	1.92(2)	Cl2–N4	1.18(2)
Ir2–Cl2	2.368(5)	Ir2–N2	2.11(1)
Ir2–C5	1.96(2)	C5–N3	1.14
Ir3–Cl3	2.408(5)	Ir3–N5	2.11(1)
Ir3–C48	1.98	C48–N8	1.14(2)
Ir4–Cl4	2.395(4)	Ir4–N6	2.12(1)
Ir4–C41	1.98(2)	C41–N7	1.13(2)
Cl1–Ir1–N1	87.5(4)	Cl1–Ir1–Cl2	86.7(6)
N1–Ir1–Cl2	87.2(6)	Cl2–Ir2–N2	86.5(4)
Cl2–Ir2–C5	87.7(5)	N2–Ir2–C5	90.8(6)
Cl3–Ir3–N5	86.0(4)	Cl3–Ir3–C48	88.8(5)
N5–Ir3–C48	90.5(6)	Cl4–Ir4–N6	86.0(4)
Cl4–Ir4–C41	87.8(5)	N6–Ir4–C41	93.2(6)
intramolecular interactions			
Ir...Ir	6.986(1), 7.0145(9); 11.6459(9), 11.668(1)		

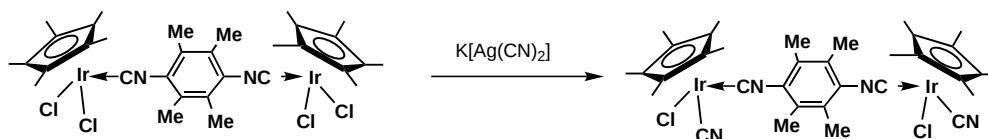
asymmetric unit of the crystal of **11bc** consists of two halves of the molecules, and each has a crystallographically imposed inversion center in the middle of the Ir...Ir* vector. The complex has a tetranuclear rectangular structure with Ir...Ir* lengths of 6.986(1) Å (7.0145(9) Å) and 11.6459(9) Å (11.668(1) Å). Methanol is contained as a solvent molecule in the crystal unit similar to **8c** (but outside of the square framework). The dihedral angles between Ir₄ plane and pyrazine are 49.44° (48.82°) and those between the Ir₄ plane and the phenyl rings of diisocyanides are 83.55° (83.58°) and 75.75° (75.95°). The Ir1–Ir1* and Ir2–Ir2* diagonal lengths in the rectangular structure are approximately 13.5 Å, similar to those found for **8c**.

Dimensions of cavity: The dimensions of the rectangular cavity of complexes obtained here are summarized in Figure 5. On the basis of X-ray analyses, the complex **12bb**

Figure 5. The dimensions of cavity for tetranuclear complexes **8c**, **8d**, and **11bc**.

surrounded by four diisocyanide ligand edges is estimated to be a square structure with the dimensions of 11.7 × 11.7 Å. Complexes **11bd** and **12bd**, which both contain two diisocyanide and two 4,4'-dipyridyl edges, are also calculated to be a rectangular structure with the dimensions of 11.7 × 11.5 Å.

In conclusion, the chemistry described above indicates the stepwise formation and structures of the tetranuclear complexes of iridium(III) and rhodium(III) that bear pentamethylcyclopentadienyl groups and two different ligands. These new types of tetranuclear complex are expected to play a role as



Scheme 3.

the molecular architecture of supramolecules with ladder or cubic frameworks.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Isocyanides were prepared by modifying the literature method.^[13] $[\text{RhCl}_2(\text{Cp}^*)]_2$ (**1**) was prepared according to the literature method.^[14] $[\text{IrCl}_2(\text{Cp}^*)]_2$ was prepared by refluxing pentamethylcyclopentadiene and $\text{H}_2\text{IrCl}_6 \cdot n\text{H}_2\text{O}$ in MeOH. Dichloromethane was distilled over CaH_2 and diethyl ether was distilled over LiAlH_4 . The IR spectra were measured on an FT/IR-5300 spectrometer. The ^1H NMR spectra were measured at 250 MHz and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured at 101 MHz with 85% H_3PO_4 as an external reference. Electrospray ionization (ESI) mass spectroscopy was performed on a Parkin–Elmer Sciex Instruments equipped by LC2Tune 1.2 software.

Preparation of 1,4-diisocyano-2,5-dimethylbenzene (a): Diisopropylamine (15 mL, 0.106 mol) was added to a solution of 2,5-dimethyl-1,4-phenylenediformamide (2.9 g, 0.015 mol) in CH_2Cl_2 (100 mL). The mixture was stirred for 20 min and POCl_3 (5.0 mL, 0.054 mol) was added dropwise at room temperature. The mixture was heated at 35°C for 4 h. Aqueous Na_2CO_3 (10%; 50 mL) was added at ice-cooling temperature and stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL) three times. The CH_2Cl_2 solution was dried over Na_2SO_4 . The solvent was removed, and the residue was purified by chromatography on alumina (containing 10% H_2O), with benzene as an eluant. The work-up of the eluate gave the title compound (1.58 g 68.7%). Analogously, 1,4-diisocyano-2,3,5,6-tetramethylbenzene (70%) was prepared from 2,3,5,6-tetramethyl-1,4-phenylenediformamide (6.6 g).

Preparation of dinuclear complexes

$[\{\text{IrCl}_2(\text{Cp}^*)\}_2\{\mu\text{-1,4-(NC)}_2\text{-2,5-Me}_2\text{C}_6\text{H}_3\}]$ (**3a**): Ligand **a** (49.5 mg, 0.32 mmol) was added to a solution of **1** (225.0 mg, 0.28 mmol) in CH_2Cl_2 (15 mL) at room temperature. After stirring for 3 h, the solvent was concentrated and diethyl ether was added, giving yellow crystals of **3a** (198.4 mg, 75%). IR(nujol): $\tilde{\nu} = 2137\text{ cm}^{-1}$; ^1H NMR (250 MHz, CDCl_3): $\delta = 1.86$ (s, 30H; Cp^*), 2.42 (s, 6H; Me), 7.29 (s, 2H; Ph); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Ir}_2$: C 37.81, H 4.02, N 2.94; found: C 37.26, H 4.04, N 2.97.

$[\{\text{IrCl}_2(\text{Cp}^*)\}_2\{\mu\text{-1,4-(NC)}_2\text{-2,3,5,6-Me}_4\text{C}_6\}]$ (**3b**): This complex (orange, 86%) was obtained from **1** (707 mg, 0.89 mmol) and ligand **b** (212.4 mg, 1.15 mmol) by a procedure similar to that described for **3a**. FAB MS: m/z (%): 981 (5) $[M+1]^+$; IR(nujol): $\tilde{\nu} = 2150\text{ cm}^{-1}$; ^1H NMR (250 MHz, CDCl_3): $\delta = 1.86$ (s, 30H; Cp^*), 2.39 (s, 12H; Me); elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{42}\text{N}_2\text{Cl}_4\text{Ir}_2$: C 39.18, H 4.32, N 2.86; found: C 38.67, H 4.26, N 2.95.

$[\{\text{RhCl}_2(\text{Cp}^*)\}_2\{\mu\text{-1,4-(NC)}_2\text{-2,3,5,6-Me}_4\text{C}_6\}]$ (**4b**): Diisocyanide **b** (59.7 mg, 0.32 mmol) was added to a solution of **2** (154.1 mg, 0.25 mmol) in CH_2Cl_2 (15 mL) at room temperature and stirred for 3 h. The solvent was concentrated to about 3 mL and diethyl ether was added, giving **4b** as an orange solid (146.5 mg, 73%). FAB MS: m/z (%): 802 (5) $[M]^+$. IR(nujol): $\tilde{\nu} = 2176\text{ cm}^{-1}$; ^1H NMR (250 MHz, CDCl_3): $\delta = 1.83$ (s, 30H; Cp^*), 2.40 (s, 12H; Me); elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{42}\text{N}_2\text{Cl}_4\text{Rh}_2$: C 47.90, H 5.28, N 3.49; found: C 48.26, H 5.46, N 4.24.

$[\{\text{RhCl}_2(\text{Cp}^*)\}_2\{\mu\text{-1,4-(NC)}_2\text{-2,5-Me}_2\text{C}_6\text{H}_3\}]$ (**4a**): This complex (orange, 73%) was obtained from **2** (142 mg, 0.23 mmol) and **a** (36.0 mg, 0.23 mmol) by a procedure similar to that described for **4b**. IR(nujol): $\tilde{\nu} = 2160\text{ cm}^{-1}$; ^1H NMR (250 Hz, CDCl_3): $\delta = 1.83$ (s, 30H; Cp^*), 2.44 (s, 6H; Me), 7.35 (s, 2H, Ar); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Rh}_2$: C 46.54, H 4.95, N 3.62; found: C 46.63, H 5.17, N 4.10.

$[\{\text{IrCl}_2(\text{Cp}^*)\}_2(\mu\text{-pyrazine})]$ (**5c**): Pyrazine **c** (8.8 mg, 0.11 mmol) was added to a solution of **1** (80 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) at room temperature and stirred for 3 h. The resulting yellow precipitate (73.4 mg, 83%) was separated and washed with diethyl ether. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.62$ (s, 30H; Cp^*), 8.65 (s, 4H; pyrazine); elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Cl}_4\text{Ir}_2$: C 32.88, H 3.91, N 3.20; found: C 32.51, H 3.81, N, 3.27.

$[\{\text{RhCl}_2(\text{Cp}^*)\}_2(\mu\text{-pyrazine})] \cdot \text{H}_2\text{O}$ (**6c**): This complex (orange, 281.0 mg, 82%) was obtained from **2** (302.6 mg, 0.49 mmol) and pyrazine **c** (43.1 mg, 0.54 mmol) by a procedure similar to that described for **5c**. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.61$ (s, 30H; Cp^*), 8.66 (s, 4H; pyrazine); elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Cl}_4\text{Rh}_2 \cdot \text{H}_2\text{O}$: C 40.25, H 5.07, N 3.91; found: C 40.29, H 4.84, N 4.04.

$[\{\text{IrCl}_2(\text{Cp}^*)\}_2(\mu\text{-dipyridyl})]$ (**5d**): This complex (yellow, 139.3 mg, 82%) was obtained from **1** (142.1 mg, 0.18 mmol) and dipyridyl **d** (30.6 mg, 0.20 mmol) by a procedure similar to that described for **5c**. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.62$ (s, 30H; Cp^*), 5.73 (s, CH_2Cl_2), 7.83 (d, $^3J(\text{H,H}) = 6\text{ Hz}$, 4H; dipyridyl), 8.72 (d, $^3J(\text{H,H}) = 6\text{ Hz}$, 4H; dipyridyl); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Ir}_2 \cdot \text{CH}_2\text{Cl}_2$: C 35.88, H 3.88, N 2.70; found: C 35.93, H 3.91, N 2.70.

$[\{\text{RhCl}_2(\text{Cp}^*)\}_2(\mu\text{-dipyridyl})]$ (**6d**): This complex (orange, 83.8 mg, 84%) was obtained from **2** (80.0 mg, 0.13 mmol) and dipyridyl **d** (22.2 mg, 0.14 mmol) by a procedure similar to that described for **5c**. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.61$ (s, 30H; Cp^*), 5.73 (s, CH_2Cl_2), 7.83 (br, 4H; dipyridyl), 8.72 (br, 4H; dipyridyl); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Rh}_2 \cdot 0.6\text{CH}_2\text{Cl}_2$: C 44.54, H 4.79, N 3.39; found: C 44.42, H 5.21, N 3.36.

Preparation of tetranuclear complexes

$[\{\text{Ir}(\mu\text{-Cl})(\text{Cp}^*)\}_4(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4$ (**7c**): $\text{Ag}(\text{CF}_3\text{SO}_3)$ (31.1 mg, 0.12 mmol) in acetonitrile (10 mL) was added to a solution of **5c** (50.9 mg, 0.06 mmol) in CH_2Cl_2 (10 mL) at room temperature and stirred for 15 h. The solvent was removed, and the residue was extracted with CH_2Cl_2 , followed by filtration through a glass filter (G5) to remove undissolved compounds. The filtrate was concentrated, and diethyl ether was added, giving yellow crystals of **7c** (43.8 mg, 64%). ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.58$ (s, 30H; Cp^*), 1.74 (s, 30H, Cp^*), 2.05 (s, 12H; pyrazine), 8.84 (s, 4H; pyrazine), 8.97 (s, 4H, pyrazine); elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{80}\text{N}_8\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Ir}_4$: C 30.43, H 3.23, N 4.73; found: C 30.24, H 3.48, N 4.59.

$[\{\text{Rh}(\mu\text{-Cl})(\text{Cp}^*)\}_4(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4$ (**8c**): This complex (reddish orange, 67%) was obtained from **6c** (36.0 mg, 0.05 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (29.1 mg, 0.11 mmol) by a procedure similar to that described for **7c**. FAB MS m/z (%): 1254 (4) $[M+1]^+$; ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.61$ (s, 60H; Cp^*), 8.65 (s, 8H; pyrazine); elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{68}\text{N}_4\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Rh}_4$: C 33.75, H 3.70, N 3.03; found: C 33.55, H 3.67, N 3.19.

$[\{\text{Ir}(\mu\text{-Cl})(\text{Cp}^*)\}_4(\mu\text{-4,4'-dipyridyl})_2](\text{CF}_3\text{SO}_3)_4$ (**7d**): This complex (yellow, 70.3 mg, 96%) was obtained from **5d** (56.1 mg, 0.06 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (33.3 mg, 0.13 mmol) by a similar procedure to that described for **7c**. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.60$ (s, 60H; Cp^*), 8.25–8.96 (m, 16H; dipyridyl); elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{76}\text{N}_4\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Ir}_4$: C 32.57, H 3.25, N 2.34; found: C 33.01, H 3.43, N 2.56.

$[\{\text{Rh}(\mu\text{-Cl})(\text{Cp}^*)\}_4(\mu\text{-4,4'-dipyridyl})_2](\text{CF}_3\text{SO}_3)_4$ (**8d**): This complex (reddish orange, 34.7 mg, 73%) was obtained from **6d** (56.1 mg, 0.06 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (33.3 mg, 0.13 mmol) by a procedure similar to that described for **7c**. ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.59$, 1.61 (s, 60H; Cp^*), 7.91–8.89 (m, 16H; 4,4'-dipyridyl); elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{76}\text{N}_4\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Rh}_4$: C 38.38, H 3.82, N 2.80; found: C 37.85, H 3.83, N 2.82.

$[\{\text{Ir}(\mu\text{-Cl})(\text{Cp}^*)\}_4(\mu\text{-1,4-(NC)}_2\text{-2,3,5,6-Me}_2\text{C}_6\text{H}_3)](\text{CF}_3\text{SO}_3)_4$ (**9b**): This complex (yellow crystals, 64.5 mg, 75%) was obtained from **3b** (70.0 mg,

0.07 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (40.4 mg, 0.16 mmol) by a similar procedure to that described for **7c**. IR(nujol): $\tilde{\nu}$ = 2186 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.94 (s, 60H; Cp*), 2.42 (s, 24H; Me); elemental analysis calcd (%) for $\text{C}_{68}\text{H}_{84}\text{N}_4\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Ir}_2 \cdot 4\text{MeCN}$: C 35.37, H 3.75, N 4.34; found: C 35.16, H 3.76, N 4.27.

[{RhCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2](\text{CF}_3\text{SO}_3)_4 (**10b**): This complex (orange, 26.5 mg, 75 %) was obtained from **4b** (31.0 mg, 0.04 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (20.8 mg, 0.08 mmol) by a similar procedure to that described for **7c**. IR(nujol): $\tilde{\nu}$ = 2182 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.85 (s, 60H; Cp*), 2.37 (s, 24H; Me).

[{IrCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4 (**11bc**): $\text{Ag}(\text{CF}_3\text{SO}_3)$ (40.3 mg, 0.16 mmol) in acetonitrile (12 mL) was added to a solution of **3b** (70 mg, 0.07 mmol) in CH_2Cl_2 (10 mL) at room temperature and stirred for 15 h. A solution of pyrazine (6.3 mg, 0.08 mmol) in CH_2Cl_2 was added to the mixture and stirred for 15 h. The solvent was removed and the residue was extracted with CH_2Cl_2 , followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give **11bc** as a yellow solid (39.1 mg, 59 %). IR(nujol): $\tilde{\nu}$ = 2176 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.94 (s, 60H; Cp*), 2.42 (s, 2H; Me), 8.66 (s, 8H; pyrazine); elemental analysis calcd (%) for $\text{C}_{76}\text{H}_{92}\text{N}_8\text{F}_{12}\text{O}_{12}\text{S}_4\text{Cl}_4\text{Ir}_4$: C 34.78, H 3.53, N 4.27; found: C 34.87, H 3.71, N 4.61; ESI MS: m/z (%): 495 (5) $[M]^{4+}$, 475 (6) $[M - \text{pyrazine}]^{4+}$, 455 (94) $[M - 2\text{pyrazine}]^{4+}$.

[{IrCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,5-\text{Me}_2\text{C}_6\text{H}_2)_2(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4 (**11ac**): This complex (yellow, 39.1 mg, 59 %) was obtained from **3a** (50.0 mg, 0.05 mmol) and $\text{Ag}(\text{CF}_3\text{SO}_3)$ (29.7 mg, 0.12 mmol) by a procedure similar to that described for **11bc**. IR(nujol): $\tilde{\nu}$ = 2170 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.94 (s, 60H; Cp*), 2.42 (s, 24H; Me), 5.73 (s, CH_2Cl_2), 7.96 (s, 4H; Ar), 8.65 (s, 8H; pyrazine); elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{88}\text{N}_8\text{F}_{12}\text{O}_{12}\text{S}_4\text{Cl}_4\text{Ir}_4 \cdot \text{CH}_2\text{Cl}_2$: C 33.65, H 3.33, N 4.30; found: C 33.39, H 3.63, N 4.62.

[{RhCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2(\mu\text{-pyrazine})_2](\text{CF}_3\text{SO}_3)_4 (**12bc**): This complex (orange, 41.1 mg, 49 %) was obtained from **4b** (60.0 mg, 0.07 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (42.3 mg, 0.15 mmol), and pyrazine (6.7 mg, 0.08 mmol) by a similar procedure to that described for **11bc**. IR(nujol): $\tilde{\nu}$ = 2186 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.88 (s, 60H; Cp*), 2.43 (s, 24H; Me), 5.73 (s, CH_2Cl_2), 8.65 (s, 8H; pyrazine); elemental analysis calcd (%) for $\text{C}_{76}\text{H}_{92}\text{N}_8\text{Cl}_{10}\text{F}_{12}\text{O}_{12}\text{S}_4\text{Rh}_4 \cdot 3\text{CH}_2\text{Cl}_2$: C 38.35, H 3.99, N 4.53; found: C 38.35, H 4.39, N 4.20.

[{RhCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2(\mu-4,4'\text{-dipyridyl})_2](\text{CF}_3\text{SO}_3)_4 (**11bd**): This complex (yellow, 38.7 mg, 70 %) was obtained from **3b** (40.0 mg, 0.041 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (23.1 mg, 0.082 mmol), and bipyridyl (7.0 mg, 0.045 mmol) by a procedure similar to that described for **11bc**. IR(nujol): $\tilde{\nu}$ = 2168 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.77, 1.80 (s, 60H; Cp*), 2.21 (s, 12H; Me), 2.31 (s, 12H; Me), 5.73 (s, CH_2Cl_2), 8.65 (s, 16H; dip); elemental analysis calcd (%) for $\text{C}_{88}\text{H}_{100}\text{N}_8\text{Cl}_4\text{F}_{12}\text{O}_{12} \cdot \text{S}_4\text{Ir}_4 \cdot 3\text{CH}_2\text{Cl}_2$: C 36.63, H 3.58, N 3.76; found: C 36.48, H 3.78, N 4.19.

[{RhCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2(\mu-4,4'\text{-dipyridyl})_2](\text{CF}_3\text{SO}_3)_4 (**12bd**): This complex (orange, 22.3 mg, 33 %) was obtained from **4b** (45.0 mg, 0.056 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (31.7 mg, 0.123 mmol), and 4,4'-dipyridyl (9.6 mg, 0.062 mmol) by a procedure similar to that described for **11bc**. IR(nujol): $\tilde{\nu}$ = 2182 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.85, 1.89 (s, 60H; Cp*), 2.40 (br, 12H; Me), 7.84–8.80 (m, 16H; dipy).

[{RhCl(Cp*)}_4(\mu-1,4-(\text{NC})_2-2,3,5,6-\text{Me}_4\text{C}_6)_2](\text{CF}_3\text{SO}_3)_4 (**12bb**): This complex (orange, 35.2 mg, 58 %) was obtained from **4b** (40.3 mg, 0.050 mmol), $\text{Ag}(\text{CF}_3\text{SO}_3)$ (28.4 mg, 0.10 mmol), and **b** (13.9 mg, 0.075 mmol) by a procedure similar to that described for **11bc**. IR(nujol): $\tilde{\nu}$ = 2186 cm^{-1} ($\text{N}\equiv\text{C}$); ^1H NMR (250 MHz, $[\text{D}_6]\text{DMSO}$): δ = 1.85, 1.87 (s, 60H; Cp*), 2.39 (br, 48H; Me); elemental analysis calcd (%) for $\text{C}_{92}\text{H}_{108}\text{N}_8\text{Cl}_4\text{F}_{12}\text{O}_{12}\text{S}_4\text{Rh}_4 \cdot 2\text{CH}_2\text{Cl}_2$: C 43.47, H 4.35, N 4.31; found: C 43.74, H 4.58, N 4.71.

Reaction of 8c with 1,2-bis(diphenylphosphino)ethane (dppe): Dppe (23.1 mg, 0.06 mmol) was added to a solution of **8c** (50 mg, 0.03 mmol) in MeOH (5 mL) and CH_2Cl_2 (5 mL) at room temperature and stirred for 15 h. The solution was concentrated to about 3 mL and diethyl ether was added to give orange crystals of $[\text{RhCl}(\text{Cp}^*)(\text{dppe})](\text{OTf})$ (29.7 mg, 42 %). Concentration of the mother liquor and addition of diethyl ether gave orange solid of **8c**. FAB MS: m/z : 672 $[M]^+$. These complexes were identified by comparison with spectroscopic data of the authentic complexes.

Reaction of 8c with mesityl isocyanide (MesNC): A mixture of **8c** (53.9 mg, 0.03 mmol) and mesityl isocyanide (19.8 mg, 0.14 mmol) in acetonitrile (10 mL) was stirred for 15 h at room temperature. The solution was concentrated to about 3 mL and diethyl ether was added to give yellow crystals of $[\text{RhCl}(\text{Cp}^*)(\text{MesNC})_2](\text{OTf})$ (28.5 mg, 47 %), identified by the authentic complex obtained from the reaction of **2** with MesNC in the presence of $\text{Ag}(\text{OTf})$. The presence of the starting material after workup of the mother liquor was proven spectroscopically.

Table 5. Crystal data for **3a**, **8c**·2MeOH, **8d**, and **11bc**.

	3a	8c ·2MeOH	8d	11bc ·4MeOH
formula	$\text{C}_{30}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Ir}$	$\text{C}_{54}\text{H}_{76}\text{N}_4\text{O}_{14}\text{S}_4\text{F}_{12}\text{Cl}_4\text{Rh}_4$	$\text{C}_{68}\text{H}_{88}\text{N}_4\text{O}_{16}\text{F}_{12}\text{Cl}_4\text{S}_4\text{Rh}_4$	$\text{C}_{78}\text{H}_{98}\text{N}_8\text{O}_{14}\text{F}_{12}\text{Cl}_4\text{S}_4\text{Ir}_4$
M_r	952.90	1914.87	2127.12	2638.6
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
a [Å]	7.54(1)	13.245(7)	12.2258(9)	13.1339(9)
b [Å]	16.571(7)	20.417(6)	12.5307(9)	16.203(1)
c [Å]	12.800(7)	14.419(4)	15.076(1)	26.309(2)
α [°]	90.0	90.0	114.3439(5)	73.953(2)
β [°]	95.69(7)	108.31(2)	91.9892(7)	87.9327(7)
γ [°]	90.0	90.0	95.143(1)	81.7369(6)
V [Å ³]	1590(2)	3701(1)	2089.2(2)	5324.7(6)
Z	2	2	1	2
ρ_{calcd} [g cm ⁻³]	1.989	1.718	1.691	1.646
μ [cm ⁻¹]	87.38	12.20	10.92	52.51
$F(000)$	908	1920	1072	2564
scan rate [° min ⁻¹]	4	4	0	0
reflections (< 2 θ [°])	2915 (< 50)	6705 (< 50)	9479 (< 55)	24272 (< 55)
reflections observed [$I > 2\sigma(I)$]	2798	6485 ^[a]	8293	14760
parameters	172	433	513	1072
R/R_w	0.111/0.116 ^[b]	0.100/0.170 ^[b]	0.045/0.061 ^[c]	0.086/0.089 ^[c]
$G1$	0.041 ^[d,e]	0.050 ^[d,f]	0.045 ^[c,g]	0.086 ^[c]
GOF ^[h]	1.28	1.62	3.87	2.20

[a] $[I > 10\sigma(I)]$ [b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). [c] $R = R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$). [d] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [e] For 2790 reflections. [f] For $[I > 2\sigma(I)]$. [g] For 8293 reflections. [h] $\text{GOF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(n - p)]^{1/2}$, where n = number of data, p = number of parameters.

X-ray crystallography—data collection: Complexes, **3a**, **8c**·2MeOH, **8d**, and **11bc**·4MeOH were recrystallized from CH₂Cl₂/diethyl ether/MeOH or CH₂Cl₂/diethyl ether/MeCN. Cell constants of **3a** and **8c**·2MeOH were determined from 20 reflections on Rigaku four-circle automated diffractometer AFC5S. Data collection was carried out on a Rigaku AFC5S refractometer at room temperature by using the 2θ - ω scan method. Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. An absorption correction was applied with ψ scan methods. Crystals of **8d** and **11bc** were mounted at the top of quartz fibers using perfluoro(polyoxypropylene ethylether), which were set on a MSC/ADSC Quantum CCD/Rigaku AFC7 diffractometer (**8d**) and on a MSC/ADSC Quantum CCD/Rigaku AFC8(ultraX 18) diffractometer (**11c**). The measurements were made by using MoK α radiation at -90°C to -80°C under a cold nitrogen stream. Four preliminary data frames were measured at 0.5° increments of ω , in order to assess the crystal quality and preliminary unit cell parameters were calculated. The cell parameters were refined using the all reflections measured in the range $2.8^\circ < 2\theta < 55.0^\circ$. The intensity images were measured at 0.5° intervals of ω for a duration of 20 s for **8d** and 108 s for **11bc**. The frame data were integrated using a d*TREK program package, and the data sets were corrected for absorption using a REQAB program. The crystal parameters along with data collections are summarized in Table 5. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from Cromer and Waber with the usual tabulation.^[15] Anomalous dispersion effects were included in F_o ;^[16] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.^[17] All calculations were performed using the teXsan crystallographic software package.^[18]

Determination of the structures: All structures were solved by Patterson methods. The positions of all non-hydrogen atoms except the solvent molecules were refined with anisotropic thermal parameters by using full-matrix least-squares methods. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151901 (**3a**), CCDC-151902 (**8c**), CCDC-151903 (**11bc**), and CCDC-171089 (**8d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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