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Stepwise Formation of Tetra- and Hexanuclear Iridium and Rhodium Complexes Containing Oxalato Ligands

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The reactions of [Cp*$_2$Ir$_2$(μ-η^2-η^2-C$_2$O$_4$)Cl$_2$] **2a** and [Cp*$_2$Rh$_2$(μ-η^2-η^2-C$_2$O$_4$)Cl$_2$] **2b** with bidentate ligands such as 4,4′-bipyridine (bpy) and 2,5-bis(4-pyridyl)-1,3,5-oxadiazole (bpo) in the presence of AgOTf gave the corresponding tetranuclear complexes [Cp*$_4$M$_4$(μ-L)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_2$](OTf)$_4$ (**3a**: M = Ir, L = bpy; **3b**: M = Rh, L = bpy; **4a**: M = Ir, L = bpo; **4b**: M = Rh, L = bpo). The reactions of **2a** and **2b** with tridentate ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) in the presence of AgOTf gave the corresponding hexanuclear complexes [Cp*$_6$M$_6$(μ-tpt)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_3$](OTf)$_6$ (**5a**: M = Ir; **5b**: M = Rh).

Introduction

In the past decade, the design and synthesis of metal-containing supramolecules and coordination cages based on organometallic half-sandwich complexes is a rapid growing area of interest because there are many promising organometallic half-sandwich fragments available for the construction of novel supramolecular materials. In particular, platinum and palladium complexes, such as M(diamine)$_2^{2+}$, M(diphosphine)$_2^{2+}$ (M = Pd and Pt), and other similar entities as corner pieces have been used widespread by many groups.[1,2] Cotton and co-workers have reported a series of metal−metal bonded binuclear units of the type *cis*-M$_2$(μ-DArF)$_2$ (M = Mo, Rh, and Ru) and dicarboxylate dianions as linkers.[3]

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.[4] There are three available coordination sites of (arene)-Ru or (cyclopentadienyl)M (M = Rh, Ir) complexes that can be used to construct metallamacrocyclic complexes as well as coordination cages. Many tri-, tetra- and hexanuclear metallamacrocycles using the combination of half-sandwich complexes with trifunctional ligands were studied extensively by many groups.[5] Some "organometallic boxes" with cyanide-linked cubes that contain octahedral building blocks of rhodium and cobalt derivatives have been reported by Rauchfuss et al.[6] We and the Tatsumi group have reported a series of tetranuclear rhodium and iridium supramolecules bearing cyclopentadienyl ligands in combination with two different types of spacer ligands.[7] Several half-sandwich ruthenium tetra- and hexanuclear complexes containing bidentate oxygen ligands have been reported by Süss-Fink and Therrien et al.[8] In contrast, half-sandwich iridium and rhodium complexes containing bidentate oxygen ligands are still underdeveloped. Herein we report the stepwise formation of tetra- and hexanuclear iridium and rhodium complexes bearing pentamethylcyclopentadienyl and oxalato bridges, connected by two and three pyridyl-based subunits. Complexes [Cp*$_2$Rh$_2$(μ-η^2-η^2-C$_2$O$_4$)Cl$_2$] (**2b**), [Cp*$_4$Ir$_4$(μ-bpy)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_2$](OTf)$_4$ (**3a**), [Cp*$_4$Ir$_4$(μ-bpo)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_2$](OTf)$_4$ (**4a**) and [Cp*$_6$Ir$_6$ (tpt)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_3$](OTf)$_6$ (**5a**) (bpy = 4,4′-bipyridyl; bpo = 2,5-bis(4-pyridyl)-1,3,5-oxadiazole; tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine; Cp* = η^5-C$_5$Me$_5$; OTf = CF$_3$SO$_3$) were confirmed by X-ray analyses.

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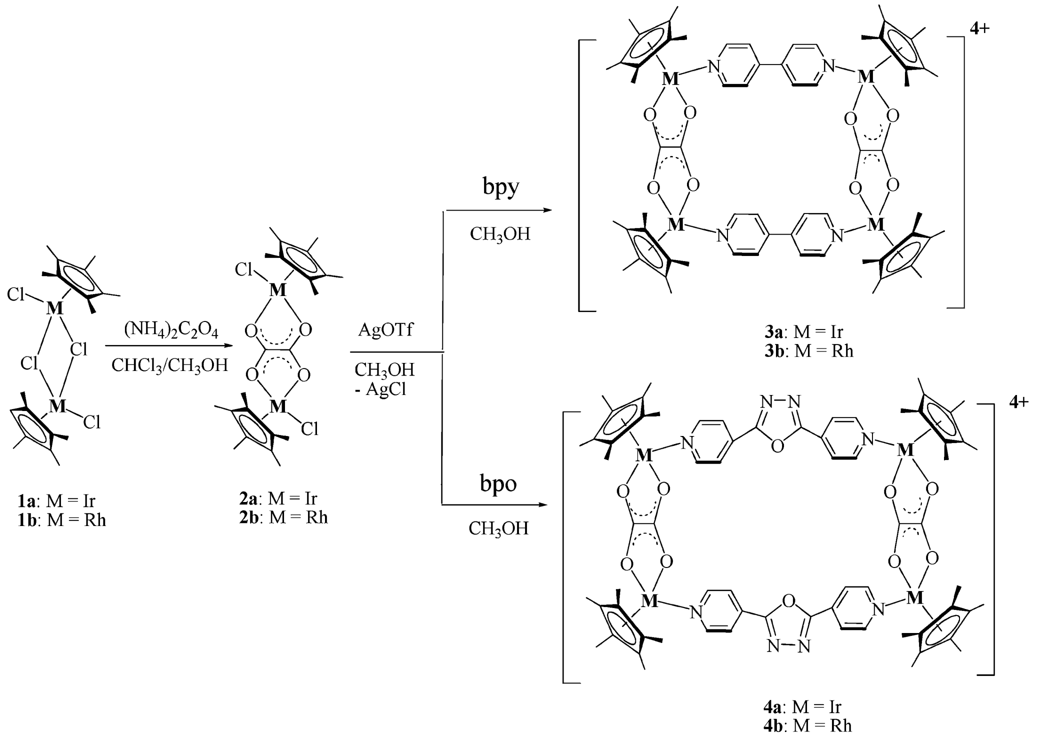
Scheme 1. Syntheses of Complexes 3a,b and 4a,b



Results and Discussion

The synthesis of the bridging oxalato complex $[Cp^*{}_2Ir_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)]Cl_2$ (**2a**) through $[Cp^*IrCl_2]_2$ reacted with $Ag_2C_2O_4$ in CH_2Cl_2 or THF solution have been reported by Grotjahn et. al.,[9] but if CH_3CN solvent was used, an oligomer or polymer was obtained. The *p*-cymene complex $[(p\text{-cymene})RuCl_2]_2$ reacts with $(NH_4)_2C_2O_4$ in $CHCl_3/CH_3OH$ solution to give the binuclear complex $[(p\text{-cymene})_2Ru_2((\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)Cl_2]$ as the only product that was reported by Süss-Fink et. al.[8a]When $[Cp^*IrCl_2]_2$ (**1a**) or $[Cp^*RhCl_2]_2$ (**1b**) reacted with $(NH_4)_2C_2O_4$ in $CHCl_3/CH_3OH$ solution at 55 °C to give the binuclear complexes $[Cp^*{}_2M_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)Cl_2]$ (**2a**: M = Ir; **2b**: M = Rh) in high yields, respectively. The IR spectra showed a strong band at about 1620 cm^{-1}, owing to the C═O stretching of the oxalate ligand,[8,10,11] and different from the two bands seen between 1650 and 1750 cm^{-1} for the most η^2-C_2O_4 complexes.[8,10−13] The ^1H NMR spectra showed a sharp singlet at $\delta = 1.62$ ppm for **2a** and a sharp singlet at $\delta = 1.64$ ppm for **2b** due to the Cp* protons, respectively. X-ray crystal analysis of **2b** confirmed the dimeric structure (Figure 1).

Tetranuclear complexes that bear the 4,4′-bipyridine ligand, $[Cp^*{}_4M_4(\mu\text{-bpy})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ (**3a**: M = Ir; **3b**: M = Rh), were prepared by direct reactions of **2a** or **2b** with 4,4′-bipyridine in the presence of Ag(OTf). The IR showed a strong band at 1630 cm^{-1} for **3a** and 1612 cm^{-1} for **3b** indicating the presence of the coordinated oxalate ligands. The ^1H NMR spectra for **3a** showed a singlet at $\delta = 1.63$ ppm due to Cp* protons and the multiple resonances at ca. $\delta = 8.4$ ppm due to bipyridine protons; that for **3b** had an analogue singlet at $\delta = 1.57$ ppm due to Cp* protons and the multiple resonances at ca. $\delta = 8.2$ ppm due to bipyridine protons. Detailed structure was confirmed by X-ray analyses of **3a** (Figure 3). It revealed that the complex cations has the rectangular structure bridged by two oxalato ligands and two 4,4′-bipyridine molecules.

The binuclear complexes **2a** and **2b** reacted readily with 2,5-bis(4-pyridyl)-1,3,5-oxadiazole (bpo) in the presence of AgOTf to give complexes formulated as $[Cp^*{}_4M_4(\mu\text{-bpo})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ (**4a**: M = Ir; **4b**: M = Rh). The IR showed a strong oxalate ligands band at 1630 and 1621 cm^{-1}, respectively.

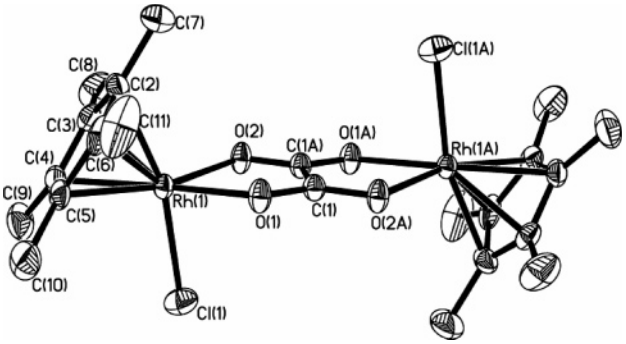


Figure 1. Molecular structure of **2b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−O(1), 2.138(3); Rh(1)−O(2), 2.141(3); Rh(1)−Cl(1), 2.3823(16); O(1)−C(1), 1.251(5); O(2)−C(1A), 1.248(5); C(1)−C(1A) 1.547(8); O(1)−Rh(1)−O(2), 77.66(11); O(1)−Rh(1)−Cl(1), 88.09(10); O(2)−Rh(1)−Cl(1), 88.10(10); C(1)−O(1)−Rh(1), 114.0(3); C(1A)−O(2)−Rh(1), 113.6(3); O(1)−C(1)−C(1A), 116.7(5).

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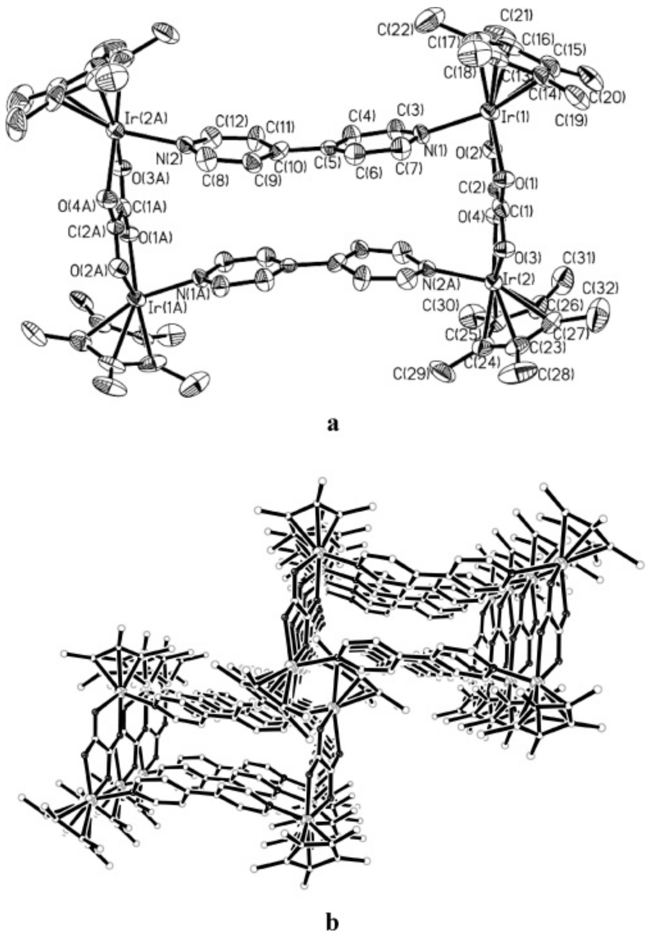


Figure 2. (a) Complex cation of the tetranuclear [Cp*$_4$Ir$_4$(μ-bpy)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_2$](OTf)$_4$ **3a** with thermal ellipsoids drawn at the 30% level. (b) The stacking of the molecules in crystals of **3a** viewed along the *b*-axis. All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−N(1), 2.124(7); Ir(1)−O(1), 2.142(6); Ir(1)−O(2), 2.158(6); Ir(2)−O(4), 2.151(6); Ir(2)−O(3), 2.159(6); N(1)−C(3), 1.312(11); N(1)−C(7), 1.320(10); N(2)−C(12), 1.283(10); N(2)−C(8), 1.360(11); O(1)−C(1), 1.297(10); O(2)−C(2), 1.240(10); O(3)−C(1), 1.242(10); O(4)−C(2), 1.273(10); C(1)−C(2), 1.491(12); C(5)−C(10), 1.501(12); N(1)−Ir(1)−O(1), 83.4(3); N(1)−Ir(1)−O(2), 83.7(3); O(1)−Ir(1)−O(2), 77.7(2); N(2A)−Ir(2)−O(4), 83.9(2); N(2A)−Ir(2)−O(3), 83.5(3); O(4)−Ir(2)−O(3), 76.7(2).

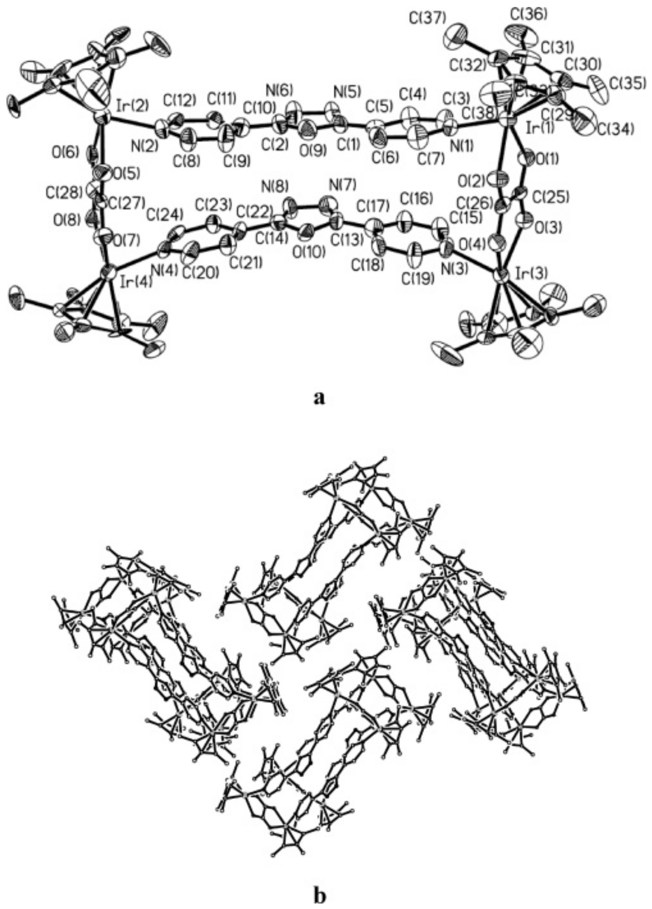


Figure 3. (a) Complex cation of the tetranuclear [Cp*$_4$Ir$_4$(μ-bpo)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_2$](OTf)$_4$ **4a** with thermal ellipsoids drawn at the 30% level. (b) The stacking of the molecules in crystals of **4a** viewed along the *a*-axis. All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−N(1), 2.1100(5); Ir(1)−O(1), 2.1442(5); Ir(1)−O(2), 2.1499(6); Ir(2)−O(6), 2.0133(6); Ir(2)−N(2), 2.1222(6); Ir(2)−O(5), 2.1449(5); Ir(3)−O(3), 2.1220(6); Ir(3)−N(3), 2.1344(6); Ir(3)−O(4), 2.1553(6); Ir(4)−N(4), 2.1016(7); Ir(4)−O(7), 2.1567(6); Ir(4)−O(8), 2.1623(6); N(1)−Ir(1)-O(1), 83.85(2); N(1)−Ir(1)−O(2), 84.88(2); O(1)−Ir(1)−O(2), 77.587(18); O(6)−Ir(2)−N(2), 85.113(19); O(6)−Ir(2)−O(5), 75.27(2); N(2)−Ir(2)−O(5), 83.84(3); O(3)−Ir(3)−N(3), 83.681(19); O(3)−Ir(3)−O(4), 77.456(13); N(3)−Ir(3)−O(4), 83.63(2); N(4)−Ir(4)−O(7), 82.518(16); N(4)−Ir(4)−O(8), 83.51(2); O(7)−Ir(4)−O(8), 76.29(2).

And the formation of **4a** is also confirmed by the appearance of the ^{1}H signals at $\delta = 1.63$ and ca. $\delta = 8.3$, 8.9 ppm, which can be ascribed to the Cp* protons and pyridyl protons. Similarly, the resonances of **4b** at $\delta = 1.64$ and ca. $\delta = 7.8$, 8.6 ppm in the ^{1}H NMR spectra demonstrate the coexistence of Cp* rings and pyridyl ligand. On the basis of the spectroscopy and the structures of 2,5-bis(4-pyridyl)-1,3,5-oxadiazole, complexes **4a** and **4b** were assumed to be a structure bridges by two oxalato ligands and two 2,5-bis(4-pyridyl)-1,3,5-oxadiazole molecules. X-ray crystal analysis of **4a** confirmed the structure (Figure 4).

Changing the ligand from 4, 4′-bipyridyl (bpy) or 2,5-bis(4-pyridyl)-1,3,5-oxadiazole (bpo) to 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt), hexanuclear metalloprisms formulated as [Cp*$_6$M$_6$(tpt)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_3$](OTf)$_6$ (**5a**: M = Ir; **5b**: M = Rh), which were bridged by oxalato ligands and connected by two 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) subunits, were isolated as yellow prismatic crystals (Scheme 2). The infrared spectrum of **5a** gives rise to only one very strong absorption at 1630 cm^{-1} for the C=O stretching of the oxalate ligand, whereas the corresponding stretching frequency in **5b** was found at 1620 cm^{-1}. The ^{1}H NMR spectra of **5a** and **5b** displayed similar signal patterns for the pyridyl protons with two multiples at $\delta = 8.66$ and 9.03 ppm for **5a** and at $\delta = 8.40$ and 9.00 ppm for **5b**. In addition, the structure of **5a** was determined by single-crystal X-ray analysis (Figure 4). Each Ir(III) atom is coordinated by one nitrogen atom from pyridyl, two oxygen atoms of oxalato ligands, and a Cp* moiety, resulting in a hexanuclear metalloprisms structure.

A perspective drawing of **2b** with the atomic numbering scheme and selected bond lengths and angles are given in Figure 1. The crystal structure of **2b** consists of binuclear units, connected by an oxalate ligand, and each rhodium atom is surrounded by two O atoms and one Cl atom. All of the rhodium centers are six-coordinate geometry, assuming that the Cp* ligand functions as a three-coordinate ligand. Angles between adjacent atoms around the rhodium atoms are nearly 90°. The Rh1-C11-O1 and Rh1-C11-O2 angles are 88.09(10)º and 88.10(10)º, respectively. Compared to binuclear tetrathiooxalate

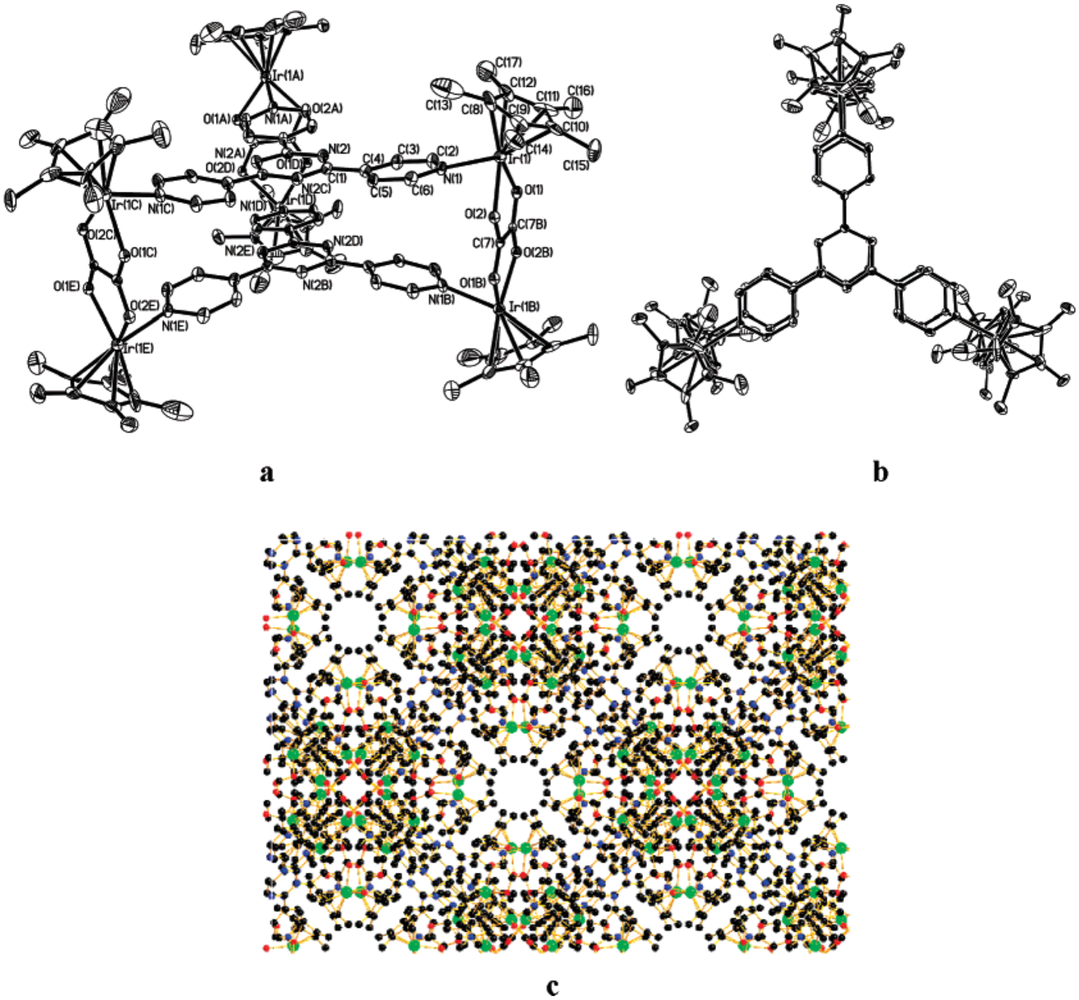
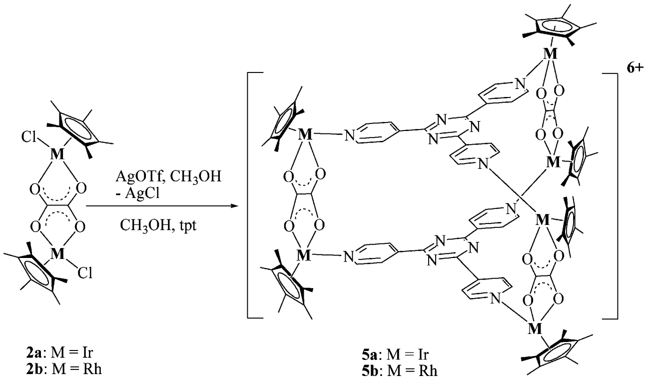


Figure 4. Complex cation of the hexanuclear $[Cp^*_6Ir_6(tpt)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_6$ **5a** with thermal ellipsoids drawn at the 30% level ((a) side and (b) top views). (c) Crystal packing of **5a**. All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Selected distances (Å) and angles (deg): Ir(1)−N(1), 2.132(7); Ir(1)−O(1), 2.135(6); Ir(1)−O(2), 2.137(6); N(1)−Ir(1)−O(1), 82.9(2); N(1)−Ir(1)−O(2), 82.6(2); O(1)−Ir(1)−O(2), 76.8(2).

Scheme 2. Syntheses of Complexes 5a and 5b



complex $[(C_5Me_4Et)_2Rh_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2S_4)]Cl_2$ (Rh−Cl bond length range: 2.4 Å),[14] **2b** has shorter Rh−Cl bond distances (2.38 Å), which are similar to other binuclear oxalato complexes $[(p\text{-cymene})_2Ru_2((\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)Cl_2]$ (Ru−Cl bond length range: 2.39 Å) and $[Cp^*_2Ir_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)]Cl_2$ (**2a**) (Ir−Cl bond length range: 2.38 Å).[9] The two Rh atoms are separated by 5.548 Å and the two Cl atoms are oriented in a trans manner. In addition, the two five-rings and rhodium atoms are coplanar.

Crystals of **3a** suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloromethane at low temperature. Perspective drawings of **3a** with the atomic numbering scheme and selected bond lengths and angles are given in Figure 2. The crystal structure of **3a** is composed of $[Cp^*_4Ir_4(\mu\text{-bpy})_2(\mu\text{-}\eta^4\text{-}C_2O_4)_2]^{4+}$ cations, OTf^- counteranions, and CH_2Cl_2 and H_2O solvent molecules in the solid. The cation part of **3a** has a crystallographically imposed inversion center in the middle of the Ir(1)···Ir(1A) or Ir(2)···Ir(2A) vector. Each Ir(III) atom is coordinated by one nitrogen atom from one N atom of bpy and two oxygen atoms of oxalato ligands, resulting in a tetranuclear rectangle structure, with the dimensions of 5.56 × 11.10 Å as defined by the iridium centers. The Ir(1)···Ir(1A) and Ir(2)···Ir(2A) diagonal lengths in the rectangular structure are 12.351 and 12.479 Å. The dihedral angle between the oxalato and bpy ligands is just 90.0°. The average Ir−O and Ir−N bond lengths are 2.153 and 2.124 Å. The structures also show that the two bpy ligands are close to each other with a distance of 3.83 Å, indicating the presence of $\pi-\pi$ interaction. As shown in Figure 2b, the molecular rectangles stack via the *b*-axis to form rectangle channels due to the $\pi-\pi$ interactions between the independent molecules. The overall free voids are 44.5% of the cell volume, which is omitted counteranions, solvent molecules, and hydrogen atoms. In addition, the H_2O molecules are seen within these channels, but the counteranions and CH_2Cl_2 molecules are located outside of the channels.

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A perspective drawing of **4a** with the atomic numbering scheme and selected bond lengths and angles are given in Figure 3. The crystal structure of **4a** is also composed of $[Cp^*{}_4Ir_4(\mu\text{-}bpo)_2(\mu\text{-}\eta^4\text{-}C_2O_4)_2]^{4+}$ cations and OTf^- counteranions in the solid. Each Ir center adopts three-legged piano-stool conformation, which is six-coordinate geometry, assuming that the Cp* ligand functions as a three-coordination ligand. Each Ir(III) atom is coordinated by one nitrogen atom from bpo and two oxygen atoms of bridging oxalato ligands resulting in a rectangle, with dimensions of 5.508 Å × 13.684 Å, as defined by iridium centers. The Ir(1)···Ir(4) and Ir(2)···Ir(3) diagonal lengths in the rectangular structure are 14.810 and 14.641 Å. The dihedral angle between the oxalato ligands and pyridyl rings of bpo ligands is just 90.0°. The Ir−O and Ir−N bond lengths are in the range of 2.0133(6)−2.1623(6) Å and 2.1016(7)−2.1344(6) Å, respectively. The structures also show that oxadiazole rings are parallel to each other with a distance of 3.49 Å, showing the presence of $\pi-\pi$ interaction. As shown in Figure 3, the molecular rectangles stack via *a*-axis to form rectangle channels. The overall free voids are 20.9% of the cell volume which is omitted counter anions, solvent molecules, and hydrogen atoms. In addition, the counterions are located outside of the channels.

A perspective drawing of **5a** with the atomic numbering scheme and selected bond lengths and angles are given in Figure 4. Complex **5a** consists of hexanuclear $[Cp^*{}_6Ir_6(tpt)_2(\mu\text{-}\eta^4\text{-}C_2O_4)_3]^{6+}$ cations, as well as OTf^- counteranions in the solid state. The empty spaces between cationic hexanuclear cations are filled with O_3SCF_3 anions. The cation part of **5a** contains six octahedral iridium centers, which are bridged by three oxalato ligands with an average Ir···Ir separation of 5.52 Å. It is surprising that unlike the ruthenium oxalato clips that are tilted and where the tpt ligands adopt an almost perfect eclipsed conformation, all of the iridium oxalato clips are nearly 90° and the two triazine rings of tpt ligands are parallel to each other.

However, the centroid···centroid distance (3.44 Å) shows the strong parallel π-stacking interactions between the two triazine moieties, which is similar to that found in related $[(C_6Me_6)_6Ru_6(tpt)_2(\mu\text{-}\eta^4\text{-}C_2O_4)_3](OTf)_6$ complex (3.42 Å). From the top views, the complex has a perfect trinuclear triangular structure, the volume of the box is approximately 250 $Å^3$ based on the Ir···Ir lengths of 13.057 Å. The average Ir−N and Ir−O bond lengths are 2.125 and 2.133 Å, similar to those of our previous reports.[7a] The remarkable feature of **5a** is the packing pattern along the *ab* plane. As shown in Figure 4, each molecular **5a** is surrounded by twelve neighboring molecules in the crystal lattice to form the beautiful carpetlike structure which consists of square units. The vertexes of the squares are made up of Cp* fragments and the iridium atoms and oxalate groups are inside the squares. Every square is connected with each other by two tpt ligands.

In summary, we have successfully developed the stepwise formation of tetra- and hexanuclear iridium and rhodium complexes containing bidentate oxygen ligands. 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 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 hexane was distilled over sodium/benzophenone ketyl just before use. All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. 2,5-Bis-(4-pyridyl)-1,3,5-oxadiazole (bpo),[15] 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt),[16] $[Cp^*IrCl_2]_2$(**1a**),[17] and $[Cp^*RhCl_2]_2$(**1b**)[17] were prepared according to the reported procedures, while other chemicals were obtained commercially and used without further purification. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer. Elemental analyses were carried out by Elementar III Vario EI Analyzer; the samples were dried in vacuum for 48 h before to analyses. ^1H NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in $[D_6]$-DMSO solution.

Synthesis of $[Cp^*{}_2Ir_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)Cl_2]$ 2a. $(NH_4)_2C_2O_4\cdot H_2O$ (140 mg, 1 mmol) was added to a suspension of $[Cp^*IrCl_2]_2$ (800 mg, 1 mmol) in $CHCl_3/CH_3OH$ (1:1, 20 mL); the suspension was kept stirring at 55 °C for 5 h. The solvent was then evaporated to dryness under vacuum, and the residue was extracted with CH_2Cl_2 to give yellow crystals of **2a** (740 mg, 91%). Anal. Calcd for $C_{22}H_{30}Cl_2O_4Ir_2$: C, 32.47; H, 3.72. Found: C, 32.30; H, 3.65. ^1H NMR (500 MHz, $[D_6]$-DMSO): $\delta = 1.62$ (s, 30H; Cp*) ppm. IR (KBr disk): $\nu = 1620$ cm^{-1}.

Synthesis of $[Cp^*{}_2Rh_2(\mu-\eta^2\text{-}\eta^2\text{-}C_2O_4)Cl_2]$ 2b. $(NH_4)_2C_2O_4\cdot H_2O$ (140 mg, 1 mmol) was added to a suspension of $[Cp^*RhCl_2]_2$ (618 mg, 1 mmol) in $CHCl_3/CH_3OH$ (1:1, 20 mL), The suspension was kept stirring at 55 °C for 5 h. The solvent was then evaporated to dryness under vacuum, and the residue was extracted with CH_2Cl_2 to give red crystals of **2b** (621 mg, 86%). Anal. Calcd for $C_{22}H_{30}Cl_2O_4Rh_2$: C, 41.60; H, 4.76. Found: C, 41.92; H, 4.84. ^1H NMR (500 MHz, $[D_6]$-DMSO): $\delta = 1.64$ (s, 30H; Cp*) ppm. IR (KBr disk): $\nu = 1612$ cm^{-1}.

Synthesis of $[Cp^*{}_4Ir_4(\mu\text{-}bpy)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ 3a. AgOTf (51 mg, 0.2 mmol) was added to a suspension of **2a** (81 mg, 0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds. 4,4′-Bipyridine (16 mg, 0.1 mmol) was added to the filtrate. The solution was kept at room temperature and stirred for 15 h. The solvent was then removed, and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL, and diethyl ether was added, giving **3a** as yellow solids (106 mg, 89%). Anal. Calcd for $C_{68}H_{76}F_{12}Ir_4N_4O_{20}S_4$: C, 34.11; H, 3.20; N, 2.34. Found: C, 33.83; H, 3.14; N, 2.28. ^1H NMR (500 MHz, $[D_6]$-DMSO): $\delta = 7.95-8.84$ (m, 16H; $H_{pyridyl}$), 1.63 (s, 60H; Cp*) ppm. IR (KBr disk): $\nu = 1632$ cm^{-1}.

Synthesis of $[Cp^*{}_4Rh_4(\mu\text{-}bpy)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ 3b. AgOTf (51 mg, 0.2 mmol) was added to a suspension of **2b** (64 mg, 0.1 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then 4,4′-bipyridine (16 mg, 0.1 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed, and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL, and diethyl ether was added, giving **3b** as yellow solids (80 mg, 79%). Anal. Calcd for $C_{68}H_{76}F_{12}Rh_4N_4O_{20}S_4$: C, 40.09; H, 3.76; N, 2.75. Found: C, 40.03; H, 3.25; N, 2.83. ^1H NMR (500 MHz, $[D_6]$-DMSO): $\delta = 7.76-8.84$ (m, 16H; $H_{pyridyl}$), 1.57 (s, 60H; Cp*) ppm. IR (KBr disk): $\nu = 1619$ cm^{-1}.

Synthesis of $[Cp^*{}_4Ir_4(\mu\text{-}bpo)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ 4a. It was prepared in the same procedure described above for **3a** using 2,5-bis(4-pyridyl)-1,3,5-oxadiazole instead of 4,4′-bipyridyl. The deposited yellow solid of **4a** was obtained (98 mg, 78%). Anal. Calcd for $C_{72}H_{76}F_{12}Ir_4N_8O_{22}S_4$: C, 34.17; H, 3.03; N, 4.43. Found: C, 34.32; H, 3.03; N, 4.29. ^1H NMR (500 MHz, $[D_6]$-DMSO): $\delta = 8.12-8.94$ (m, 16H; $H_{pyridyl}$), 1.63 (s, 60H; Cp*) ppm. IR (KBr disk): $\nu = 1630$ cm^{-1}.

Synthesis of $[Cp^*{}_4Rh_4(\mu\text{-}bpo)_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)_2](OTf)_4$ 4b. This compound was prepared in the same procedure described above

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Table 1. Crystallographic Data and Structure Refinement Parameters for 2b, 3a, 4a, and 5a

	2b	**3a**	**4a**	**5a**
formula	$C_{22}H_{30}Cl_2O_4Rh_2$	$C_{70}H_{84}Cl_4F_{12}Ir_4N_4O_{22}S_4$	$C_{72}H_{76}Cl_4F_{12}Ir_4N_8O_{22}S_4$	$C_{108}H_{114}F_{18}Ir_6N_{12}O_{30}S_6$
fw	635.18	2600.25	2530.45	3747.67
cryst syst	monoclinic	triclinic	monoclinic	cubic
space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$Fd\bar{3}c$
a (Å)	8.387(3)	12.685(10)	16.654(5)	50.627(10)
b (Å)	8.827(3)	14.250(11)	30.945(10)	50.627(10)
c (Å)	16.629(6)	15.672(12)	18.917(6)	50.627(10)
α (deg)		95.394(12)		
β (deg)	93.999(5)	111.274(10)	91.905(6)	
γ (deg)		116.316(9)		
V (Å^3)	1228.1(7)	2253(3)	9744(5)	129762(43)
Z	2	1	4	32
ρ_{calcd} (g/cm^3)	1.718	1.916	1.725	1.535
μ (Mo Ka)(mm^{-1})	1.586	6.191	5.620	5.061
no. of observe	5963	9948	40809	74734
no. of params	141	479	1059	255
GOF	1.044	0.826	0.871	1.010
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0422	0.0452	0.0710	0.0604
$wR_2{}^a$ ($I > 2\sigma(I)$)	0.1016	0.1100	0.1864	0.1516

[a] $R_1 = \sum||F_0| - |F_c||$(based on reflections with $F_0^2 > 2\sigma F^2$). $wR_2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (0.095P)^2]$; $P = [\max(F_0^2, 0) + 2F_c^2]/3$ (also with $F_0^2 > 2\sigma F^2$).

for **3b** using 2,5-bis(4-pyridyl)-1,3,5-oxadiazole instead of 4,4′-bipyridyl. The deposited yellow solid of **4b** was obtained (88 mg, 81%). Anal. Calcd for $C_{72}H_{76}F_{12}Rh_4N_8O_{22}S_4$: C, 39.79; H, 3.52; N, 5.16. Found: C, 39.95; H, 3.43; N, 5.09. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): $\delta = 7.55-8.99$ (m, 16H; H$_{pyridyl}$), 1.64 (s, 60H; Cp*) ppm. IR (KBr disk): $\nu = 1621$ cm^{-1}.

Synthesis of [Cp*$_6$Ir$_6$(tpt)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_3$](OTf)$_6$ 5a. AgOTf (77 mg, 0.3 mmol) was added to a suspension of **2a** (123 mg, 0.15 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then tpt (32 mg, 0.1 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL and diethyl ether was added, giving yellow solids of **5a** (159 mg, 85%). Anal. Calcd for $C_{108}H_{114}F_{18}Ir_6N_{12}O_{30}S_6$: C, 34.61; H, 3.07; N, 4.48. Found: C, 34.53; H, 3.06; N, 4.27. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): $\delta = 9.03$ (br, 12H; H$_{pyridyl}$), 8.66 (br, 12H; H$_{pyridyl}$), 1.65 (s, 90H; Cp*) ppm. IR (KBr disk): $\nu = 1630$ cm^{-1}.

Synthesis of [Cp*$_6$Rh$_6$ (tpt)$_2$(μ-η^2-η^2-C$_2$O$_4$)$_3$](OTf)$_6$ 5b. AgOTf (77 mg, 0.3 mmol) was added to a suspension of **2b** (96 mg, 0.15 mmol) in methanol (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble compounds, and then tpt (32 mg, 0.1 mmol) was added to the filtrate. The solution was kept at room temperature to stir for 15 h. The solvent was then removed and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to about 3 mL, and diethyl ether was added, giving yellow solids of **5b** (159 mg, 82%). Anal. Calcd for $C_{108}H_{114}F_{18}Rh_6N_{12}O_{30}S_6$: C, 40.39; H, 3.58; N, 5.23. Found: C, 40.18; H, 3.24; N, 4.98. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): $\delta = 9.00$ (br, 12H; H$_{pyridyl}$), 8.40 (br, 12H; H$_{pyridyl}$), 1.62 (s, 90H; Cp*) ppm. IR (KBr disk): $\nu = 1620$ cm^{-1}.

X-ray Structure Determination. All single crystals were immersed in mother solution and sealed in thin-walled glass. Data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo 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. All the calculations were carried out with the SHELXTL[18] program. Crystals for **2b** was obtained by the slow diffusion of hexane into a solution of the complexes in CH_2Cl_2. **3a**, **4a**, and **5a** are obtained by the slow diffusion of diethyl ether into a solution of the complexes in CH_2Cl_2.

All the calculations were carried out with the SHELXTL program. In complex **2b**, all of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. In complex **5a**, one of the triflate anions could be well-refined, and voids corresponding to solvent molecules and other disordered anions were observed. In complex **3a**, one dichloromethane molecule could be refined, but more voids were found. In complex **4a**, three of the four triflate anions could be well-refined, but voids corresponding to anions of another one and other disordered solvent molecules were observed. Therefore new data sets corresponding to omission of the missing solvent and anions were generated with the SQUEEZE algorithm,[19] and the structures were refined to convergence. For **5a**, the pentamethylcyclopentadienyl fragments have two idealized positions (50:50) because of its rotation in room temperature. Other non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. For **3a**, the non-hydrogen atoms of the cations, well-refined anions, and solvent molecules which were found were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions. For **4a**, the disorder of three pentamethylcyclopentadienyl fragments was observed, and all of them were included in two idealized positions (60:40 for C39−C48, 55:45 for C49−C58, 50:50 for C59−C68). Several carbon atoms (C28, C39′−C43′, C52, C55, C49′−C54′, C59, C60, C63, C60′−C62′) had to be refined isotropically because of non-positive definition, Other non-hydrogen atoms of the cations and anions were refined anisotropically, and hydrogen atoms were included in calculated positions.

Crystal data, data collection parameters, and the results of the analyses of compounds **2b**, **3a**, **4a**, and **5a** are listed in Table 1.

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Supporting Information Available: The crystallographic data for **2b**, **3a**, **4a,** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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