Articles

Unprecedented π-Bonded Rhodio- and Iridio-*o*-Benzoquinones as Organometallic Linkers for the Design of Chiral Octahedral Bimetallic Assemblies

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Received June 26, 2008

We report the first synthesis of π-bonded rhodio and iridio-*o*-benzoquinones [Cp*M(*o*-benzoquinone)] (M = Rh (**3a**); M = Ir (**3b**)) following a novel synthetic procedure. These compounds were fully characterized by spectroscopic methods; in particular the X-ray molecular structure of **3b** was determined. Compounds **3a**,**b** were used as chelating *organometallic linkers* for the design of a new family of chiral octahedral bimetallic complexes, **4**−**9**. The X-ray molecular structure of $[(bpy)_2Ru(\mathbf{3b})][OTf]_2$ (**5**) is presented and shows that the *organometallic linker* **3b** is chelating the ruthenium center. In particular, the carbocycle of the *organometallic linker* **3b** adopts a η^4-quinone form, where the Cp*Ir is also bonded to only four carbons. Further our strategy to design new assemblies with organometallic linkers is successfully achieved. These assemblies hold promise for new properties relative to those made from organic bidentate ligands.

Introduction

We recently described the synthesis of *p*-benzoquinone complexes of rhodium and iridium [Cp*M(*p*-benzoquinone)] (M = Rh (**1a**); M = Ir (**1b**)) as well as the related [Cp*Ir(*o*-dithiobenzoquinone)] and [Cp*Ir(*p*-dithiobenzoquinone)] complexes (Figure 1a).[1] The latter were successfully used as organometallic linkers, "OM-linkers", for the design of an impressive range of new supramolecular assemblies and coordination polymers when treated with cationic inorganic building blocks of different geometry.[2] Some of these complexes exhibited useful luminescent properties.[3] Unlike the *p*-benzoquinone metal complexes, the related *o*-benzoquinone compounds can be used as OM-chelates to generate new chiral assemblies, which may exhibit different properties when compared to those with *p*-benzoquinone metal complexes. The OM-linkers **1a**,**b** are obtained simply by treatment of $[Cp*M(solvent)_3]^{2+}$ (M = Rh, Ir), prepared *in situ*, and hydroquinone.[4] In stark contrast the reaction of the solvated species $[Cp*M(solvent)_3]^{2+}$ with catechol does not lead to a π-bonded compound. Instead a catecholato complex is formed where the Cp*M is chelated to the two oxygen atoms of the catechol as reported by Maitlis and co-workers (Figure 1b).[5] Although we have previously obtained the 3-methoxy-*o*-benzoquinone complex [Cp*Ir(η^4-(3-methoxy)-$C_6H_3O_2$] through a nucleophilic *ortho*-functionalization reaction,[1a] no direct method for the synthesis of Cp*M-π-bonded catechol compounds has been reported so far. On the other hand we note that clusters of ruthenium and palladium incorporating one or more catecholate ligands have been studied by Pierpont, Bohle, Churchill, and Keister.[6] However these examples cannot be considered as a rational synthetic method to prepare simple mononuclear π-bonded *o*-quinone complexes as described in the current work.

In this paper we report the first synthesis of π-bonded rhodio- and iridio-*o*-benzoquinones [Cp*M(*o*-benzoquinone)] (M = Rh

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10.1021/om800594g CCC: $40.75
Publication on Web 01/02/2009

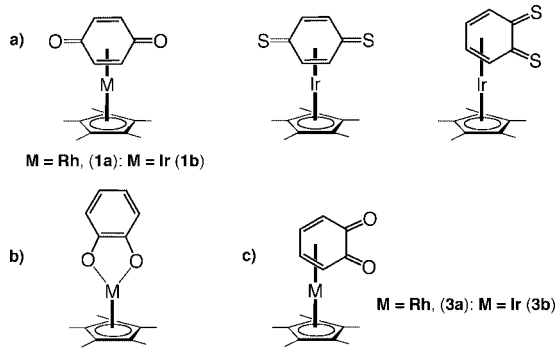

Figure 1. Schematic drawings of some π-bonded and O−O′-bonded benzoquinone and thiobenzoquinone complexes.

(**3a**); M = Ir (**3b**)) (Figure 1c) following a new synthetic procedure and their use as chelating OM-linkers for the design of a new family of chiral octahedral bimetallic complexes.

Results and Discussion

Treatment of $[Cp^*M(solvent)_3][OTf]_2$ prepared *in situ* with catechol in acetone, in the presence of excess $BF_3 \cdot 2H_2O$, followed by precipitation with Et_2O[7] provided the π-bonded catechol complexes $[Cp^*M(\eta^6\text{-}C_6H_6O_2)][BF_4]_2$ (M = Rh, **2a**; M = Ir, **2b**). Subsequent deprotonation with Cs_2CO_3 in acetone afforded the target π-bonded OM-linkers [Cp*M(*o*-benzoquinone)] (M = Rh (**3a**); M = Ir (**3b**)) in 85−92% yields (Scheme 1).

Unlike those reported by Maitlis, which are blue in color, our compounds are orange and yellow, respectively. Moreover the ^{1}H and ^{13}C NMR studies carried out on **3a** and **3b** confirmed that the *o*-benzoquinone moiety "η-$C_6H_4O_2$" is π-bonded[8] through the arene ring to the Cp*M fragment. Thus the ^{1}H NMR spectrum of **3b** recorded in MeOD at room temperature showed the presence of a singlet assigned to the methyl protons of Cp*Ir moiety at δ 2.03 ppm and two doublets of doublets centered at δ 5.22 and 5.75 ppm attributed to the protons of the η^4-bonded arene ring. In a similar fashion the ^{1}H NMR spectrum of complex **3a** showed a singlet at 1.85 ppm for the Cp*Rh unit and two doublets of doublets at δ 4.74 and 5.44 ppm, respectively. Furthermore, the ^{13}C NMR spectrum of **3a** showed two doublets for the CH groups of the carbocycle at δ 82.4 and 84.7 ppm. These doublets arise from the coupling with a rhodium nucleus with J_{C-Rh} = 8.7 and 7.3 Hz, respectively. Further the carbonyl groups appeared as a singlet at δ 168.2 ppm, proving clearly that the metal is η^4-bonded to *o*-benzoquinone. These compounds were fully characterized; see Experimental Section. In particular the structure of complex **3b** was confirmed by single-crystal X-ray diffraction study (*vide infra*).

X-ray Molecular Structure of 3b. Suitable crystals of **3b** for X-ray analysis were obtained from a CH_2Cl_2/hexane mixture using a slow evaporation technique. Complex **3b** crystallizes in the monoclinic space group $P2_1/m$. The structure confirms the formation of the desired compound as described by the spectroscopic data (Figure 2a).

The carbocyclic ring is π-bonded to the organometallic Cp*Ir moiety in the expected η^4-fashion. We note that the structure displays a crystallographic plane of symmetry that passes through O(1), C(1), C(4), and C(5) and Ir(1) and bisects the molecule into two equivalent disordered halves. Further the structure shows that the quinone moiety is slightly bent upward away from the metal center with angle θ = 4.7(8)° between the planes "C(3), C(4), C(3′), C(2a′)" and "C(3), C(2), C(1), C(2a′)".

At this stage a short comment on the resonance form of the π-bonded ring is required. Previously Pierpont and co-workers[9a] reported the X-ray structure of a disubstituted catecholate complex, $(t\text{-}Bu)_2\text{-}C_6H_2O_2Mn(CO)_3$. In this compound the $Mn(CO)_3$ fragment is σ-bonded to the oxygen atoms rather than π-bonded to the cyclic ring (Figure 3). Further the structure confirms that the carbocyclic ring is aromatic and is better described as a catecholate dianion. More recently Sweigart and co-workers[11a] reported the molecular structure of an isomeric complex to the precedent example where the $Mn(CO)_3$ moiety is π-bonded to the carbocylic ring; further, one of the carbonyl oxygens is coordinated to a sodium cation and the complex was isolated as a dimer (Figure 3). In this example the *o*-benzoquinone complex is not a free molecule as in our case but rather an "*organometallic ligand*" that coordinates to a sodium cation (*vide infra*).

In our example, the solid state structure of **3b** indicates that the major resonance form is that of a π-bonded η^4-quinone (**3b**) (Figure 4). Moreover in solution, the ^{1}H and ^{13}C NMR of this complex exhibited two multiplets shifted upfield, which is in accord with that of a diene, i.e., resonance form **3b**.[1a,b,4]

Further examination of the packing in the unit cell suggested that [Cp*Ir(*o*-quinone)] (**3b**) individual molecules interact through $\pi-\pi$ interactions (d = 3.38 Å, α = 18.23°) between the electron-rich Cp*Ir moiety and the η^4-quinone fragment, thus describing a 1D supramolecular chain (see Figure 2b). To our knowledge, this is the first X-ray molecular structure of an η^4-*o*-quinone π-bonded to the Cp*M family. In previous work we have isolated the first examples of *o*- and *p*-dithiobenzoquinone complexes $[Cp^*Ir(\eta^4\text{-}o\text{-}C_6H_4S_2)]$ and $[Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)]$.[1c,1d,2c] In order to understand the role of "Cp*Ir" in stabilization of the short-lived *p*-dithiobenzoquinone, we have taken an *ab initio* computational approach employing the hybrid density functional B3LYP method. Computational analyses using density functional theory confirm a net transfer of about 0.8 unit of electron density to the π^* ligand LUMO and 0.2 unit of electron density to each sulfur atom. This additional electron density is largely localized around the thiocarbonyl bonds, resulting in a reduction in C═S bond order as well as the anticipated decrease in C═C bond order. These calculations also prove that the sulfur atoms in the metalated thioquinone $[Cp^*Ir\text{-}p\text{-}(\eta^4\text{-}C_6H_4S_2)]$ (**2e**) are more nucleophilic and hence are good assembling organometallic ligands to construct novel supramolecular structures with transition metal electrophiles. Thus it is not surprising that the Cp*Ir moiety stabilizes the η^4-*o*-quinone form through back-donation, as illustrated by the solid state structure of **3b**.

Pierpont and co-workers[9] investigated the charge distribution in several catecholate complexes where the metal center is chelated to the oxygen atoms. In these compounds the quinone ligands bonded in both semiquinone and catecholate electronic

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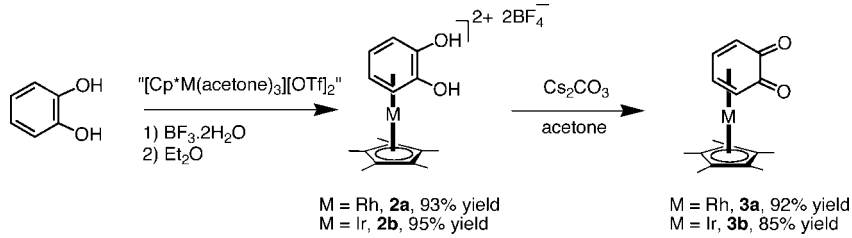
Scheme 1. Synthesis of the OM-Linkers 3a,b



forms. The latter is described as a "valence tautomerism" or "redox isomerization". The authors demonstrated that facile intramolecular electron transfer between the metal and the organic *o*-quinone unit occurs and is temperature dependent. The novelty in our work involves a Cp*M unit (M = Rh, Ir) instead of a first-row metal ion, and in our case the metal fragment is π-bonded to the *o*-quinone system.

Having elucidated the structures of these novel OM-linkers [Cp*M(*o*-benzoquinone)] (**3a**,**b**), we decided to explore their coordination chemistry toward cationic inorganic building blocks with adequate geometry, i.e., having two empty sites in a *cis*-position for chelation by the two O−O′ oxygen centers of the η^4-*o*-benzoquinone fragment of **3a**,**b**.

Indeed, treatment of the luminophore building blocks[10] such as "$(bpy)_2Ru(II)^{2+}$", "$(ppy)_2Rh(III)^{+}$", and "$(ppy)_2Ir(III)^{+}$ {bpy = 2,2′-bipyridine, ppy = 2-phenylpyridine} with our OM-linkers [Cp*M(*o*-benzoquinone)] (M = Rh (**3a**); M = Ir (**3b**)) provided after reaction workup the novel family of chiral octahedral homo- and heterobimetallic complexes with C_1-symmetry $[(bpy)_2Ru(\mathbf{3a})][OTf]_2$ (**4**, **RuRh**), $[(bpy)_2Ru(\mathbf{3b})][OTf]_2$ (**5**, **RuIr**), $[(ppy)_2Rh(\mathbf{3a})][OTf]$ (**6**, **RhRh**), $[(ppy)_2Rh(\mathbf{3b})][OTf]$ (**7**, **RhIr**), $[(ppy)_2Ir(\mathbf{3a})][OTf]$ (**8**, **IrRh**), and $[(ppy)_2Ir(\mathbf{3b})][OTf]$ (**9**, **IrIr**) (Figure 5). These compounds were obtained as racemates.

All these complexes (**4**−**9**) were fully characterized by spectroscopic techniques (^1H, ^{13}C NMR, IR) and elemental analysis (see Experimental Section). The NMR data suggest that in solution the bimetallic assembly is maintained. For each bimetallic compound, the ^1H and ^{13}C NMR spectra showed two series of resonances for the bicyclic "bpy" or "ppy" entities. We also note the ^{13}C NMR spectra of *o*-benzoquinone moieties permitted to distinguish the six different carbons, indicating clearly a loss of symmetry. For instance, the ^1H NMR spectrum of $[(ppy)_2Ir(\mathbf{3a})][OTf]_2$ (**8**, **IrRh**) presented 15 multiplets in a range of 6.05 to 8.75 ppm, corresponding to the two nonequivalent ppy ligands, three doublets of doublets at δ 5.51, 5.57, and 5.95 ppm, which are attributed to the coordinated *o*-benzoquinone, and a singlet at δ 1.86 ppm for the η-Cp*Rh. These latter signals are downfield relative to the free OM-linker **3a**.

The ^{13}C NMR spectrum of **8** permitted to distinguish 19 peaks for the two ppy patterns in the range 118.7−167.9 ppm. The *o*-benzoquinone moiety showed four doublets at δ 85.3 ppm (J_{C-Rh} = 6.8 Hz), 87.2 ppm (J_{C-Rh} = 6.8 Hz), 88.0 ppm (J_{C-Rh} = 7.6 Hz), and 89.1 ppm (J_{C-Rh} = 7.6 Hz) corresponding to the carbons in α- and β-positions relative to the ketonic groups and two singlets at δ 159.9 and 166.3 ppm attributed to the −C=O functions (Figure 6a). Finally a singlet at δ 9.3 ppm and one doublet at δ 103.0 ppm (J_{C-Rh} = 7.6 Hz) were attributed to the η-Cp*Rh moiety. Assignment of individual resonances was achieved using COSY (Figure 6b), HMQC, and HMBC

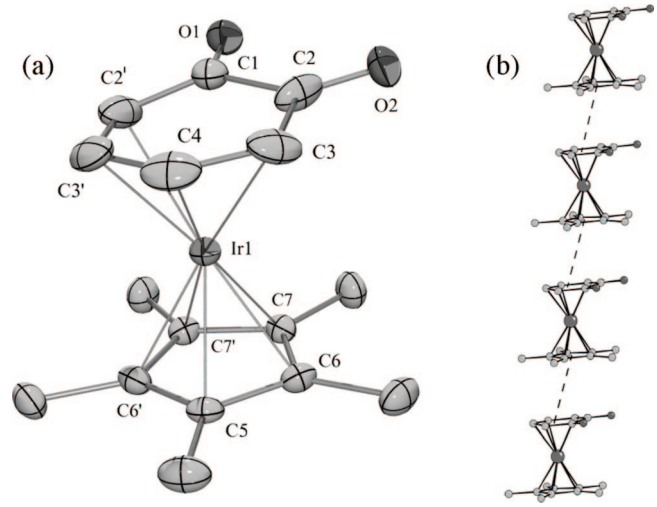


Figure 2. (a) X-ray molecular structure of **3b** with atom-numbering system. (b) 1D supramolecular chain formed through $\pi-\pi$ interactions between individual units of [Cp*Ir(*o*-quinone)] (**3b**). Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 2.574(5); Ir(1)−C(2) 2.51(2); Ir(1)−C(3)2.182(4); Ir(1)−C(4)2.144(6); Ir(1)−C(2′) 2.27(2); C(1)−O(1)1.250(7); C(2)−O(2) 1.27(1); C(2′)−C(1)−C(2) 116.7(7); C(1)−C(2)−C(3)112.3(9);C(2)−C(3)−C(4)125.1(6);C(3)−C(4)−C(3′) 118.9(5); C(4)−C(3′)−C(2′) 117.2(8); C(3′)−C(2′)−C1 128.0(1.5).

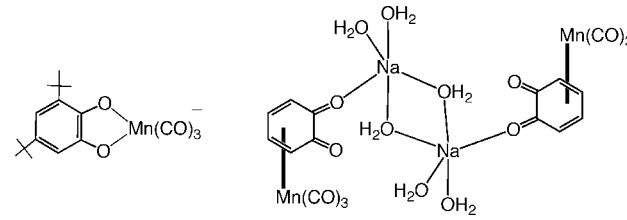


Figure 3. Some organometallic compounds displaying a catecholate ligand as a σ-bonded ligand or a benzoquinone as a π-bonded ligand.

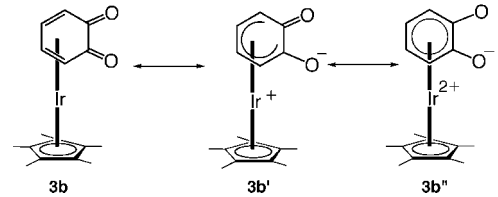


Figure 4. Possible resonance forms displayed by the π-bonded benzoquinone ligand in complex **3b**.

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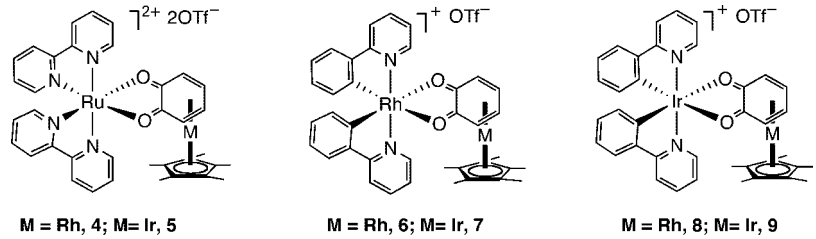

Figure 5. Schematic drawings of **4**−**9**.

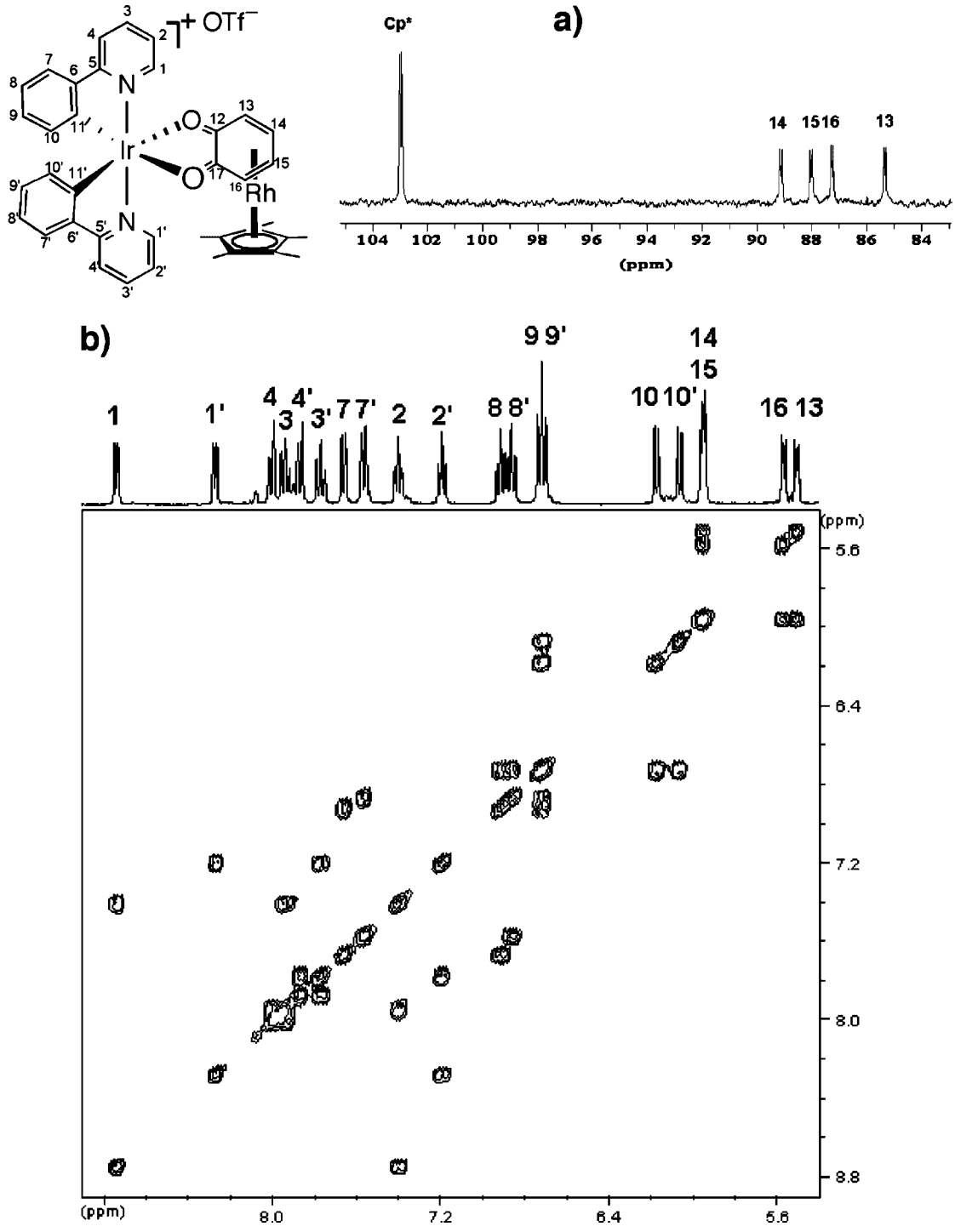

Figure 6. (a) Section of the $^{13}C\{^1H\}$ NMR spectrum of **8** showing doublets related to J_{C-Rh} coupling. (b) 2D COSY NMR spectrum of **8** showing full proton assignments.

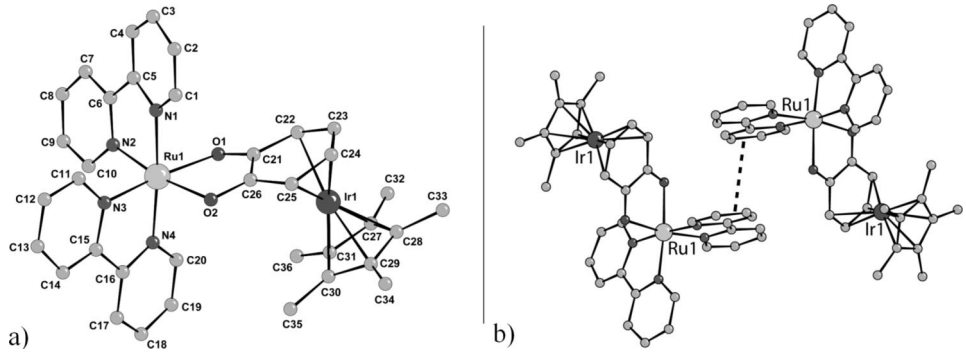

Figure 7. (a) X-ray structure of the cationic part of **5** (**RuIr**); (b) $\pi-\pi$ interactions between two bpy units describing a supramolecular dimer. Selected bond distances (Å) and angles (deg): Ru(1)−O(1) 2.143(4); Ru(1)−O(2) 2.125(4); Ru(1)−N(1) 2.057(4); Ru(1)−N(2) 2.040(4); Ru(1)−N(3) 2.026(5); Ru(1)−N(4) 2.066(5); Ir(1)−C(21) 2.548(6); Ir(1)−C(22) 2.241(6); Ir(1)−C(23) 2.191(6); Ir(1)−C(24) 2.187(6); Ir(1)−C(25) 2.259(6); Ir(1)−C(26) 2.597(6); O(1)−Ru(1)−O(2) 79.42(15); N(1)−Ru(1)−N(2) 79.08(18); N(3)−Ru(1)−N(4) 78.85(18).

2D experiments; the latter permitted in particular linking without ambiguity each phenyl group to its pyridine for the two ppy ligands.

A complete NMR study was carried out for all complexes **4**−**9**. In the case where [Cp*Rh(*o*-benzoquinone)] was used as a linker, it is noteworthy to mention that ^{13}C NMR spectra showed doublets for each *o*-benzoquinone "CH" carbon, except the carbonyl groups. These doublets arise from the coupling constants J_{C-Rh}. Interestingly the NMR studies highlight the nature of the η^4-bonded *o*-benzoquinone in the bimetallic complexes. All these NMR data confirm that our assemblies are also stable in solution. Further, the structure of one of these bimetallic assemblies (**5**, **RuIr**) was ascertained without ambiguity by single-crystal X-ray diffraction study (*vide infra*). For instance the ^1H NMR of $[(bpy)_2Ru(\mathbf{3b})][OTf]_2$ (**5**, **RuIr**) recorded in CD_2Cl_2 is very informative and showed a singlet for the η-Cp*Ir at δ 1.94 ppm. Further, as a result of loss of symmetry in **5**, four multiplets are now visible to the coordinated OM-linker **3b** and appear at δ 5.74, 5.76, 5.92, and 5.99 ppm, which are assigned to the four protons of the chelating η^4-bonded *o*-benzoquinone. These signals are downfield relative to the free OM-linker **3b**. Moreover, the lack of symmetry is also manifested by the appearance of 15 multiplets in the range 7.14−9.07 ppm and are attributed to the two nonequivalent bpy ligands.

The X-ray structure of **5** (Figure 7) confirms the O,O′ σ-chelating mode of the OM-linker **3b** to the Ru(II) core via both oxygen atoms. The Ru(II) center is also coordinated to four nitrogen atoms of two bpy ligands, which describes a distorted octahedral geometry around the metal center. The structure shows also that the *o*-benzoquinone is coordinated to the Cp*Ir(I) moiety via the four diene carbons in η^4-fashion similar to that of the free complex **3b**. The Ir---C21 and Ir---C26 distances are 2.548 and 2.597 Å, respectively, indicating absence of interaction. Further the C21---O1 and C26---O2 bond distances are 1.294 and 1.293 Å, suggesting a double-bond character. Moreover the two quinone functional groups are bent upward relative to the Cp*Ir moiety with a hinge angle θ = 12.74°. In summary, in the bimetallic assembly **5**, the carbocycle of the organometallic linker **3b** adopts a η^4-benzoquinone form. On the other hand, examination of the crystal packing revealed that the bimetallic assembly **5** undergoes $\pi-\pi$ interaction (d = 3.601 Å, α = 30.33°) with one of its neighbors via the bpy unit to form a supramolecular dimer.

All new octahedral assemblies (**4**−**9**) were stable in air and soluble in most organic solvents, and they can be stored under argon for a long period of time. It is worth mentioning that some neutral 2D networks were prepared from anionic [Na][(CO)$_3$Mn(*o*-benzoquinone)] and divalent transition metal ions; however the synthesis and structures of these compounds are completely different from those described here.[11] We believe that our OM-linkers may be used as assembling ligands to construct an impressive range of chiral supramolecular assemblies, which may present different properties than those made via classical organic linkers.[12−15]

In summary, we have reported the first synthesis of π-bonded rhodio- and iridio-*o*-benzoquinones [Cp*M(*o*-benzoquinone)] (M = Rh (**3a**); M = Ir (**3b**)) using a new efficient synthetic method. The X-ray molecular structure of complex **3b** was determined and shows that a η^4-quinone form is stabilized at least in the solid state. Complexes **3a**,**b** were used as OM-linkers to prepare a new family of octahedral bimetallic assemblies **4**−**9** via chelation of the appropriate inorganic building blocks such as "$(bpy)_2Ru(II)^{2+}$", "$(ppy)_2Rh(III)^{+}$", and "$(ppy)_2Ir(III)^{+}$" {bpy = 2,2′-bipyridine, ppy = 2-phenylpyridine}. The X-ray molecular structure of $[(bpy)_2Ru(\mathbf{3b})][OTf]_2$ (**5**, **RuIr**) was determined. The X-ray data of the binuclear assembly **5** show that the carbocycle of the organometallic linker **3b** adopts a η^4-quinone resonance form. Our future studies are devoted to the resolution of these chiral assemblies using optically pure anions.[16] Moreover the luminescent properties of **4**−**9** are currently under investigation.

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Experimental Section

General Procedures. All manipulations were carried out at room temperature under an argon atmosphere using standard Schlenk tube techniques. Solvents were dried and distilled under argon by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 300 or Avance 400 spectrometers. IR spectra were recorded on a Bruker Tensor 27 equipped with a Harrick ATR.

Synthesis of [Cp*Rh(η^6-catechol)][BF_4]$_2$ (2a). An acetone solution (10 mL) of AgOTf (415 mg; 1.60 mmol) was added to an orange suspension of [Cp*Rh(μ-Cl)Cl]$_2$ (249 mg; 0.40 mmol) in acetone (10 mL). The resulting white AgCl precipitate was filtered off through Celite after stirring for 15 min. The yellow filtrate was then directly added to catechol (340 mg; 3 mmol), the solution turned brown, and the solvent was removed under vacuum. Then $BF_3 \cdot 2H_2O$ (2 mL) was added to the sticky brown solid, and the mixture was stirred for 30 min. Then diethyl ether (50 mL) was added to precipitate the complex [Cp*Rh(η^6-catechol)][BF_4]$_2$ as a light yellow microcrystalline powder, which was filtered through cotton, washed twice with diethyl ether (30 mL each), and dried under vacuum (386 mg; 0.74 mmol). Yield: 93%. Anal. Calcd for $C_{16}H_{21}O_2B_2F_8Rh$: C, 36.82; H, 4.06. Found: C, 37.71; H, 3.85. ^{1}H NMR (300 MHz in CD_3OD): 2.01 (s, 15H, Cp*); 6.00 (dd, 2H, catechol); 6.22 (dd, 2H, catechol). IR (ATR): 3101; 1555; 1540; 1492; 1425; 1387; 1311; 1019; 876; 819; 764; 736; 637; 588; 540; 520; 463; 387; 339; 228 cm^{-1}.

Synthesis of [Cp*Ir(η^6-catechol)][BF_4]$_2$ (2b). This compound was prepared using the procedure described for complex **2a** using the following amounts: AgOTf (520 mg; 2.00 mmol), [Cp*Ir(μ-Cl)Cl]$_2$ (400 mg; 0.50 mmol), and catechol (340 mg; 3 mmol). Complex **2b** was obtained as a white microcrystalline powder (580 mg; 0.95 mmol). Yield: 95%. Anal. Calcd for $C_{16}H_{21}O_2B_2F_8Ir$: C, 31.44; H, 3.46. Found: C, 32.38; H, 3.41. ^{1}H NMR (300 MHz in CD_3OD): 2.14 (s, 15H, Cp*); 6.45 (dd, 2H, catechol); 6.82 (dd, 2H, catechol). IR (ATR): 3560; 3100; 1630; 1555; 1534; 1491; 1425; 1390; 1311; 1027; 889; 838; 819; 764; 735; 639; 578; 540; 520; 467; 388; 342; 309; 210 cm^{-1}.

Synthesis of [Cp*Rh(*o*-benzoquinone)] (3a). An acetone solution (10 mL) of **2a** (386 mg; 0.74 mmol) was added to a white suspension of Cs_2CO_3 (540 mg; 1.67 mmol) in acetone (10 mL). The reaction mixture was stirred for 1 h at room temperature and was then filtered through Celite. The yellow filtrate was allowed to evaporate under vacuum, and the residue was dissolved in methanol (50 mL) and filtered through basic alumina. Evaporation of methanol under vacuum provided complex **3a** as an orange microcrystalline solid, which was dried under vacuum (274 mg; 0.68 mmol). Yield: 92%. Anal. Calcd for $C_{16}H_{19}O_2Rh \cdot 3H_2O$: C, 47.74; H, 6.76. Found: C, 47.01; H, 5.48. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.85 (15H, s, Cp*); 4.74 (2H, dd, ^3J = 4.7 Hz, ^4J = 3.2 Hz, Hα); 5.44 (2H, dd, ^3J = 4.7 Hz, ^4J = 3.2 Hz, Hβ). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 8.6 (CH_3-Cp*); 82.4 (d, J_{C-Rh} = 8.7 Hz, Cα); 84.7 (d, J_{C-Rh} = 7.3 Hz, Cβ); 98.8 (d, J_{C-Rh} = 7.3 Hz, Cq-Cp*); 162.8 (s, C=O). IR (ATR): 3351; 2910; 1669; 1533; 1442; 1382; 1367; 1260; 1152; 1030; 869; 734; 679; 637; 585; 517; 456; 433; 353; 304; 218 cm^{-1}.

Synthesis of [Cp*Ir(*o*-benzoquinone)] (3b). This compound was prepared using the procedure described for complex **3a** using **2b** (580 mg; 0.95 mmol) instead of **2a** and Cs_2CO_3 (720 mg; 2.00 mmol). Complex **3b** was obtained as a yellow microcrystalline solid (380 mg; 0.81 mmol). Yield: 85%. Anal. Calcd for $C_{16}H_{19}O_2Ir \cdot 2H_2O$: C, 40.75; H, 4.92. Found: C, 40.86; H, 4.92. ^{1}H NMR (400 MHz in MeOD): 2.03 (15H, s, Cp*); 5.22 (2H, dd, ^3J = 4.7 Hz, ^4J = 2.7 Hz, Hα); 5.75 (2H, dd, ^3J = 4.7 Hz, ^4J = 2.7 Hz, Hβ). ^{13}C{^{1}H} NMR (100 MHz in MeOD): 9.1 (CH_3-Cp*); 77.9 (Cα); 80.6 (Cβ), 95.9 (Cq-Cp*); 161.1 (C=O). IR (ATR): 3362; 2919; 1670; 1555; 1473; 1425; 1385; 1353; 1046; 891; 732; 596; 521; 428; 250; 226 cm^{-1}.

Synthesis of [(bpy)$_2$Ru(3a)][OTf]$_2$ (4). An acetone solution (10 mL) of AgOTf (103 mg; 0.40 mmol) was added to a dark purple acetone solution (10 mL) of [(bpy)$_2$RuCl$_2$] (104 mg; 0.20 mmol). The reaction mixture was stirred for 30 min at room temperature and was then filtered through Celite. The dark red filtrate was added to **3a** (77 mg; 0.20 mmol), and the reaction mixture was stirred for 1 h at room temperature. Then the solvent was removed under vacuum and the residue was dissolved in dichloromethane (50 mL) and filtered through Celite. Evaporation of CH_2Cl_2 under vacuum provided complex **4** as a dark red microcrystalline solid, which was dried under vacuum (196 mg; 0.18 mmol). Yield: 90%. Anal. Calcd for $C_{38}H_{35}N_4O_8F_6RhRuS_2 \cdot 2H_2O$: C, 41.73; H, 3.59; N, 5.12. Found: C, 41.94; H, 3.69; N, 5.56. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.83 (15H, s, Cp*); 5.62 (1H, dd, ^3J = 6.2 Hz, ^4J = 1.2 Hz, H-13); 5.72 (1H, dd, ^3J = 6.2 Hz, ^4J = 1.2 Hz, H-16); 5.97 (1H, td, ^3J = 6.2 Hz, ^4J = 1.2 Hz, H-14); 6.01 (1H, td, ^3J = 6.2 Hz, ^4J = 1.2 Hz, H-15); 7.12−7.17 (2H, m, H-9′,9), 7.47 (1H, d, ^3J = 5.9 Hz, H-10′); 7.65 (1H, d, ^3J = 5.9 Hz, H-10); 7.66−7.71 (1H, m, H-2′); 7.74 (1H, td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-8′); 7.82 (1H, td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-8); 7.94−7.98 (1H, m, H-2); 8.06 (1H, td, ^3J = 8.2 Hz, ^4J = 1.2 Hz, H-3′); 8.25 (1H, d, ^3J = 7.8 Hz, H-7′); 8.29 (1H, td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-3); 8.38 (1H, d, ^3J = 8.2 Hz, H-4′); 8.41 (1H, d, ^3J = 7.8 Hz, H-7); 8.59 (1H, d, ^3J = 7.8 Hz, H-4); 8.67 (1H, d, ^3J = 5.9 Hz, H-1′); 9.12 (1H, d, ^3J = 5.9 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.4 (CH_3-Cp*); 84.8 (d, J_{C-Rh} = 6.7 Hz, C-13); 86.5 (d, J_{C-Rh} = 6.7 Hz, C-16); 88.1 (d, J_{C-Rh} = 7.8 Hz, C-15); 88.8 (d, J_{C-Rh} = 7.8 Hz, C-14); 103.4 (d, J_{C-Rh} = 6.7 Hz, Cq-Cp*); 122.9 (C-4′); 123.1 (C-7′); 123.3 (C-7); 123.5 (C-4); 125.4 (C-9′); 125.5 (C-9); 126.9 (C-2′); 127.0 (C-2); 134.7 (C-8′); 135.0 (C-8); 136.5 (C-3′); 136.7 (C-3); 150.1 (C-1′); 151.1 (C-1); 152.7 (C-10′); 153.4 (C-10); 157.5 (C-5′); 158.2 (C-5); 159.4 (C-6,6′); 161.0 (C-17); 167.3(C-12). IR (ATR): 3470; 3076; 2964; 2921; 1719; 1603; 1498; 1462; 1420; 1386; 1341; 1252; 1148; 1026; 878; 800; 760; 727; 659; 633; 591; 572; 538; 515; 422; 343; 254; 208 cm^{-1}.

Synthesis of [(bpy)$_2$Ru(3b)][OTf]$_2$ (5). This compound was prepared according to the procedure described for complex **4** and using compound **3b** (95 mg; 0.20 mmol) instead of **3a**. Complex **5** was isolated as a dark red microcrystalline solid (225 mg; 0.19 mmol). Yield: 95%. Anal. Calcd for $C_{38}H_{35}N_4O_8F_6IrRuS_2 \cdot 2H_2O$: C, 38.58; H, 3.32; N, 4.74. Found: C, 38.37; H, 3.45; N, 4.74. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.94 (15H, s, Cp*); 5.76 (1H, dd, ^3J = 6.3 Hz, ^4J = 1.2 Hz, H-13); 5.87 (1H, dd, ^3J = 6.3 Hz, ^4J = 1.2 Hz, H-16); 5.92 (1H, td, ^3J = 6.3 Hz, ^4J = 1.2 Hz, H-14); 5.99 (1H, td, ^3J = 6.3 Hz, ^4J = 1.2 Hz, H-15); 7.11−7.16 (2H, m, H-9′,9); 7.45 (1H, d, ^3J = 5.9 Hz, H-10′); 7.65 (1H, d, ^3J = 5.9 Hz, H-10); 7.70−7.76 (2H, m, H-2′, H-8′); 7.80 (1H, td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-8); 7.91−7.95 (1H, m, H-2); 8.08 (1H, td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-3′); 8.24−8.29 (2H, m, H-7′,3); 8.39 (2H, d, ^3J = 7.8 Hz, H-4′,7); 8.58 (1H, d, ^3J = 8.2 Hz, H-4); 8.72 (1H, d, ^3J = 5.9 Hz, H-1′); 9.07 (1H, d, ^3J = 5.4 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.2 (CH_3-Cp*); 76.1 (C-13); 78.3 (C-16); 80.2 (C-15); 80.5 (C-14); 97.0 (Cq-Cp*); 122.9 (C-7′); 123.0 (C-4′); 123.3 (C-7); 123.5 (C-4); 125.3 (C-9′); 125.4 (C-9); 126.9 (C-2); 127.0 (C-2′); 134.6 (C-8′); 135.0 (C-8); 136.5 (C-3′); 136.6 (C-3); 150.0 (C-1′); 150.9 (C-1); 152.7 (C-10′); 153.5 (C-10); 157.5 (C-5′); 158.1 (C-5); 159.4 (C-6,6′,17); 166.6 (C-12). IR (ATR): 3453; 3072; 2974; 1698; 1603; 1499; 1461; 1419; 1388; 1328; 1251; 1148; 1027; 879; 762; 728; 659; 634; 591; 572; 539; 423; 346; 256 cm^{-1}.

Synthesis of [(ppy)$_2$Rh(3a)][OTf] (6). This compound was prepared according to the procedure described for complex **4**

using AgOTf (52 mg; 0.2 mmol) and the precursor $[(ppy)_2Rh(\mu\text{-}Cl)]_2$ (89 mg; 0.1 mmol) instead of $[(bpy)_2RuCl_2]$. Complex **6** was isolated as an orange microcrystalline solid (169 mg; 0.18 mmol). Yield: 90%. Anal. Calcd for $C_{39}H_{35}N_2O_5F_3Rh_2S \cdot 2H_2O$: C, 49.69; H, 4.17; N, 2.97. Found: C, 49.64; H, 4.06; N, 2.77. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.86 (15H, s, Cp*); 5.41−5.43 (1H, m, H-13); 5.49−5.51 (1H, m, H-16); 5.86−5.89 (2H, m, H-14,15); 6.08 (1H, d, ^3J = 7.8 Hz, H-10′); 6.19 (1H, d, ^3J = 7.8 Hz, H-10); 6.79−6.84 (2H, m, H-9′,9); 6.97 (1H, t, ^3J = 7.8 Hz, H-8′); 7.01 (1H, t, ^3J = 7.8 Hz, H-8), 7.22 (1H, q, J = 5.0 Hz, H-2′); 7.44 (1H, t, ^3J = 5.9 Hz, H-2); 7.62 (1H, d, ^3J = 7.8 Hz, H-7′); 7.71 (1H, d, ^3J = 7.8 Hz, H-7); 7.88 (2H, d, ^3J = 4.0 Hz, H-3′,4′); 7.98−8.07 (2H, m, H-4,3); 8.25 (1H, d, ^3J = 5.0 Hz, H-1′); 8.74 (1H, d, ^3J = 5.9 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.4 (CH_3-Cp*); 83.8 (d, J_{C-Rh} = 7.3 Hz, C-13); 85.9 (d, J_{C-Rh} = 7.3 Hz, C-16); 87.4(d, J_{C-Rh} = 8.1 Hz, C-15); 88.5(d, J_{C-Rh} = 7.3 Hz, C-14); 102.3(d, J_{C-Rh} = 8.1 Hz, Cq-Cp*); 119.0(C-4′); 119.2 (C-4); 122.2 (C-2); 122.5 (C-2′,8,8′); 123.8 (C-7′); 124.0 (C-7); 128.9 (C-9′); 129.1 (C-9); 133.1 (C-10′); 133.6 (C-10); 137.7 (C-3′); 137.9 (C-3); 143.7 (C-6); 143.9 (C-6′); 147.8 (C-1′); 149.4 (C-1); 160.0 (C-17); 162.6 (C-11′); 162.8 (C-11); 164.3 (C-5′); 164.8 (C-5); 166.1 (C-12). IR (ATR): 2965; 1604; 1580; 1518; 1501; 1479; 1415; 1384; 1352; 1254; 1222; 1150; 1026; 863; 796; 755; 735; 636; 607; 579; 535; 514; 415; 318; 234; 219 cm^{-1}.

Synthesis of [(ppy)$_2$Rh(3b)][OTf] (7). This compound was prepared according to the procedure described for complex **4** using AgOTf (52 mg; 0.2 mmol), **3b** (95 mg; 0.20 mmol), and the precursor $[(ppy)_2Rh(\mu\text{-}Cl)]_2$ (89 mg; 0.1 mmol) instead of $[(bpy)_2RuCl_2]$. Complex **6** was isolated as a yellow microcrystalline solid (204 mg; 0.19 mmol). Yield: 98%. Anal. Calcd for $C_{39}H_{35}N_2O_5F_3IrRhS \cdot H_2O$: C, 46.20; H, 3.68; N, 2.76. Found: C, 46.71; H, 3.86; N, 2.58. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.96 (15H, s, Cp*); 5.54 (1H, dd, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-13); 5.63 (1H, dd, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-16); 5.83 (1H, td, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-14); 5.88 (1H, td, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-15); 6.06 (1H, d, ^3J = 7.8 Hz, H-10′); 6.18 (1H, d, ^3J = 7.8 Hz, H-10); 6.78−6.84 (2H, m, H-9′,9); 6.95−7.03 (2H, m, H-8′,8); 7.23−7.27 (1H, m, H-2′); 7.43 (1H, t, ^3J = 5.9 Hz, H-2); 7.63 (1H, d, ^3J = 7.8 Hz, H-7′); 7.70 (1H, d, ^3J = 7.8 Hz, H-7); 7.87−7.90 (2H, m, H-3′,4′); 7.99 (1H, d, ^3J = 7.8 Hz, H-4); 8.04 (1H, t, ^3J = 7.8 Hz, H-3); 8.29 (1H, d, ^3J = 5.9 Hz, H-1′); 8.66 (1H, d, ^3J = 5.5 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.2 (CH_3-Cp*); 74.8 (C-13); 77.3 (C-16); 79.3 (C-15); 80.0 (C-14); 95.9 (Cq-Cp*); 119.0 (C-4′); 119.2 (C-4); 122.2 (C-2); 122.5 (C-8,8′); 122.6 (C-2′); 123.8 (C-7′); 123.9 (C-7); 128.9 (C-9′); 129.1 (C-9); 133.0 (C-10′); 133.5 (C-10); 137.7 (C-3′); 137.8 (C-3); 143.7 (C-6); 143.9 (C-6′); 147.7 (C-1′); 149.2 (C-1); 160.0 (C-17); 162.2 (d, J_{C-Rh} = 37.0 Hz, C-11′); 162.6 (d, J_{C-Rh} = 37.0 Hz, C-11); 164.2.(C-5′); 164.7(C-5); 166.6(C-12). IR (ATR): 3520; 3066; 2960; 2911; 1698; 1605; 1525; 1502; 1479; 1418; 1386; 1350; 1335; 1257; 1222; 1149; 1062; 1027; 878; 797; 755; 735; 669; 636; 611; 580; 538; 515; 442; 418; 323; 256; 232; 216 cm^{-1}.

Synthesis of [(ppy)$_2$Ir(3a)][OTf] (8). This compound was prepared according to the procedure described for complex **4** using AgOTf (52 mg; 0.20 mmol), **3a** (77 mg; 0.20 mmol), and the precursor $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ (107 mg; 0.10 mmol) instead of $[(bpy)_2RuCl_2]$. Complex **8** was isolated as an orange microcrystalline solid (186 mg; 0.18 mmol). Yield: 90%. Anal. Calcd for $C_{39}H_{35}N_2O_5F_3IrRhS \cdot 2H_2O$: C, 45.39; H, 3.81; N, 2.71. Found: C, 45.57; H, 3.67; N, 2.62. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.86 (15H, s, Cp*); 5.51 (1H, dd, ^3J = 4.9 Hz, ^4J = 2.9 Hz, H-13); 5.57 (1H, dd, ^3J = 4.9 Hz, ^4J = 2.9 Hz, H-16); 5.95 (2H, dd, ^3J = 4.9 Hz, ^4J = 2.9 Hz, H-14,15); 6.06 (1H, dd, ^3J = 7.8 Hz, ^4J = 0.8 Hz, H-10′); 6.17 (1H, dd, ^3J = 7.8 Hz, ^4J = 0.8 Hz, H-10); 6.72 (2H, td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-9,9′); 6.86 (1H, td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-8′); 6.91 (1H, td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-8); 7.19 (1H, ddd, ^3J = 8.2 Hz, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-2′); 7.40 (1H, ddd, ^3J = 8.2 Hz, ^3J = 5.5 Hz, ^4J = 1.2 Hz, H-2); 7.56 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-7′); 7.66 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-7); 7.77 (1H, td, ^3J = 8.2 Hz, ^4J = 1.5 Hz, H-3′); 7.86 (1H, d, ^3J = 8.2 Hz, H-4′); 7.94 (1H, td, ^3J = 8.2 Hz, ^4J = 1.5 Hz, H-3); 8.00 (1H, d, ^3J = 8.2 Hz, H-4); 8.27 (1H, d, ^3J = 5.9 Hz, H-1′); 8.74 (1H, d, ^3J = 5.5 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.3(CH_3-Cp*); 85.3 (d, J_{C-Rh} = 6.8 Hz, C-13); 87.2 (d, J_{C-Rh} = 6.8 Hz, C-16); 88.0 (d, J_{C-Rh} = 7.6 Hz, C-15); 89.1 (d, J_{C-Rh} = 7.6 Hz, C-14); 103.0 (d, J_{C-Rh} = 7.6 Hz, Cq-Cp*); 118.6(C-4′); 118.9 (C-4); 121.2 (C-8′); 121.3 (C-8); 122.0 (C-2); 122.2 (C-2′); 123.9 (C-7′); 124.1 (C-7); 128.9 (C-9′); 129.1 (C-9); 131.8 (C-10′); 132.7 (C-10); 137.5 (C-3′); 137.6 (C-3); 141.1 (C-11,11′); 144.1 (C-6); 144.2 (C-6′); 147.2 (C-1′); 148.8 (C-1); 159.9 (C-17); 166.3 (C-12); 167.5 (C-5′); 168.1 (C-5). IR (ATR): 3470; 3064; 2966; 2927; 1719; 1607; 1582; 1501; 1460; 1418; 1385; 1341; 1256; 1223; 1152; 1062; 1028; 863; 796; 757; 730; 671; 636; 584; 537; 516; 459; 420; 380; 347; 231; 223 cm^{-1}.

Synthesis of [(ppy)$_2$Ir(3b)][OTf] (9). This compound was prepared according to the procedure described for complex **4** using AgOTf (52 mg; 0.20 mmol), **3b** (95 mg; 0.20 mmol), and the precursor $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ (107 mg; 0.10 mmol) instead of $[(bpy)_2RuCl_2]$. Complex **8** was isolated as an orange microcrystalline solid (189 mg; 0.17 mmol). Yield: 85%. Anal. Calcd for $C_{39}H_{35}N_2O_5F_3Ir_2S \cdot H_2O$: C, 42.46; H, 3.38; N, 2.54. Found: C, 42.47; H, 3.51; N, 2.35. ^{1}H NMR (400 MHz in CD_2Cl_2): 1.95 (15H, s, Cp*); 5.63 (1H, dd, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-13); 5.70 (1H, dd, ^3J = 5.9 Hz, ^4J = 1.2 Hz, H-16); 5.90−5.97 (2H, m, H-14,15); 6.01 (1H, d, ^3J = 7.4 Hz, H-10′); 6.13 (1H, d, ^3J = 7.4 Hz, H-10); 6.70 (2H, t, ^3J = 7.4 Hz, H-9,9′); 6.85 (1H, t, ^3J = 7.4 Hz, H-8′); 6.90 (1H, t, ^3J = 7.4 Hz, H-8); 7.23 (1H, ddd, ^3J = 7.8 Hz, ^3J = 5.9 Hz, ^4J = 1.5 Hz, H-2′); 7.38 (1H, ddd, ^3J = 7.8 Hz, ^3J = 5.9 Hz, ^4J = 1.5 Hz, H-2); 7.57 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-7′); 7.65 (1H, dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-7); 7.79 (1H, td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-3′); 7.88 (1H, d, ^3J = 7.8 Hz, H-4′); 7.93 (1H, td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-3); 7.99 (1H, d, ^3J = 7.8 Hz, H-4); 8.30 (1H, d, ^3J = 5.9 Hz, H-1′); 8.66 (1H, d, ^3J = 5.9 Hz, H-1). ^{13}C{^{1}H} NMR (100 MHz in CD_2Cl_2): 9.1 (CH_3-Cp*); 76.4 (C-13); 78.9 (C-16); 80.1 (C-15); 80.8 (C-14); 96.5 (Cq-Cp*); 118.7 (C-4′); 118.9 (C-4); 121.2 (C-8′); 121.3 (C-8); 122.1 (C-2); 122.3 (C-2′); 123.9 (C-7′); 124.1 (C-7); 129.0 (C-9′); 129.2 (C-9); 131.5 (C-10′); 132.4 (C-10); 137.5 (C-3′); 137.6 (C-3); 140.6 (C-11,11′); 144.2 (C-6); 144.4 (C-6′); 147.1 (C-1′); 148.6 (C-1); 159.2 (C-17); 166.3 (C-12); 167.4 (C-5′); 167.9 (C-5). IR (ATR): 3500; 3061; 2963; 2917; 1698; 1606; 1583; 1527; 1502; 1476; 1386; 1350; 1338; 1254; 1222; 1148; 1062; 1027; 878; 796; 756; 729; 670; 635; 611; 584; 572; 538; 513; 458; 419; 381; 332; 303; 240; 207 cm^{-1}.

Summary of the Crystallographic Details. Crystal data for 3b. Nonius KappaCCD diffractometer, ϕ and ω scans, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, T = 150 K, structure solution with SIR97, refinement against F^2 using SHELXL97 with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. Data collection for **3b**: yellow plate, 0.20 × 0.20 × 0.12 mm; monoclinic, $P2_1/m$, a = 7.121(5) Å, b = 13.743(1) Å, c = 8.296(1) Å, β = 105.022(1), V = 784.13(12) Å^3, Z = 2, ρ_{calc} = 1.997 g cm^{-3}, μ = 8.526 cm^{-1}, $F(000)$ = 456, θ_{max} = 30.01°, hkl ranges: −10 8; −19 17; −11 9, 5678 data collected, 2366 unique data (R_{int} = 0.0293), 2232 data with $I > 2\sigma(I)$,119 parameters refined, GOF(F^2) = 1.073, final R indices ($R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), R1 = 0.0260, wR2 = 0.0607, max/min residual electron density 1.841(0.161)/−2.7500(0.161) e A^{-3}. Disorder

is induced by a symmetry plane that contains O1, C1, C4, Ir1, and C5. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-702607. 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).

Crystal Data for [(bpy)$_2$Ru(3b)][OTf]$_2$ (5). Red plate-like crystals: $C_{38}H_{35}F_6IrN_4O_8RuS_2$, monoclinic, $P2_1/c$, $a = 8.6500(12)$ Å, $b = 39.336(4)$ Å, $c = 12.8186(17)$ Å, $\beta = 108.822(10)$, $V = 4128.4(9)$ Å^3, $Z = 4$, $T = 250(2)$ K, $\mu = 3.770$ mm^{-1}, 28 952 reflections measured, 8332 independent ($R_{int} = 0.0432$), 6044 observed [$I = 2\sigma(I)$], 545 parameters, final R indices R1 [$I = 2\sigma(I)$] = 0.0452 and wR2 (all data) = 0.1210, GOF on $F^2 = 1065$, max./min. residual electron density = 0.88/−1.71 e Å^{-3}. A single crystal of compound **5** was selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo Kα radiation. Unit-cell parameter determination, data collection strategy, and integration were carried out with the Nonius EVAL-14 suite of programs (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220). Multiscan absorption correction was applied (R. H. Blessing, *Acta Crystallogr.*, **1995**, *A51*, 33). The structure was solved by direct methods using the SHELXS-97 program (G. M. Sheldrick, University of Göttingen, 1997) and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, 1997).

Acknowledgment. This work was supported by Université Pierre et Marie Curie, Paris-6 and CNRS.

Supporting Information Available: Crystallographic data of **3b** and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800594G