Inorg. Chem. **2006**, *45*, 10449–10456

Inorganic Chemistry
Article

Suzuki Coupling at the Periphery of Diruthenium Coordination and Organometallic Compounds

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Received April 29, 2006

A series of diruthenium compounds, $Ru_2(DArF)_3(L'')Cl$ (**2**), where the auxiliary ligand DArF is DmAniF or D(3,5-Cl_2Ph)F and L′′ is one of the diarylformamidinate ligands containing at least one biphenyl, were prepared from *Suzuki* reactions between $Ru_2(DArF)_3(L')Cl$ (**1**), where L′ is (4-I-Ph)NC(H)NPh (*N*-(4-iodophenyl)-*N*′-phenylformamidinate) or D(4-I-Ph)F (*N,N*′-di(4-iodophenyl)formamidinate), and $ArB(OH)_2$ (Ar = Ph and 4-$CH_3C(O)$Ph) in satisfactory yields. Alkynylation of the type **2** compounds with LiCCPh yielded the alkynyl derivatives $Ru_2(DArF)_3(L'')(CCPh)$ (**3**). Alternatively, type **3** compounds can be prepared from the *Suzuki* coupling reaction between $Ru_2(DArF)_3(L')(C_2Ph)$ and $ArB(OH)_2$. A structural comparison between the type **1** and **2** compounds revealed minimal changes in the coordination sphere of Ru_2 core. Cyclic voltammograms of *Suzuki* derivatives resemble those of the parent compounds, indicating the retention of the electrophore characteristic of diruthenium species upon peripheral modification.

Introduction

Transition metal alkynyl compounds and related metal−carbon-rich species continue to draw strong interest from both chemists and materials scientists[1] because of their potential applications as nonlinear optical materials[2] and molecular wires.[3] Our research in this area focuses on the utility of $RC{\equiv}C{-}Ru_2{-}C{\equiv}CR$-type compounds as both molecular wires and active species in molecular devices,[4] and results demonstrating both the charge-transfer efficiency and wire characteristics of diruthenium alkynyl species have been obtained.[5] It has been noted that diruthenium alkynyls are both excellent electrophores with multiple reversible and robust redox couples and intense visible and near-infrared chromophores.[4] These features make diruthenium alkynyls attractive as the building blocks for optoelectronic materials or as metalloprobes for biomolecules, provided that the electrophore/chromophore feature is retained in the materials synthesis and bioconjugation. To achieve the latter objective (i.e., to retain the electronic structure of Ru_2−alkynyl scaffold), the covalent chemistry should take place at the ligand periphery. Our approach is based on the introduction of ligands containing iodo-substituted aryls and subsequent covalent modification using well-established transition metal-catalyzed cross-coupling reactions. Successful preliminary results include the introduction of peripheral alkynyl groups through the *Sonogashira* coupling reaction[6,7] and the subsequent 1,3-dipole cycloaddition reaction with organic azides (the *click* reaction).[8] To expand the scope of our peripheral covalent chemistry, several other types of cross-coupling methods are being considered, including the *Heck* and *Suzuki* couplings.[9]

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Suzuki coupling is a powerful method for C−C bond formation in organic synthesis and has been practiced by numerous organic and medicinal chemists.[10] However, reports of direct Suzuki coupling on inorganic/organometallic fragments are rare. In one example, Bunz prepared a series of cymantrene-containing organometallic polymers via a Suzuki coupling reaction between 1,3-diiodocymantrene and 1,4-phenylenediboronic acid.[11] Suzuki coupling was also utilized to introduce a phenylene bridge between a pair of $[Ru(tpy)_2]^{2+}$ and ferrocene units by Sauvage and Launay.[12] Several starlike molecules with a diruthenium/dirhodium organometallic core were prepared by grafting oligo(phenylene) or oligo(thiophene) through Suzuki coupling by Cherioux.[13] In recent years, Suzuki coupling has become a preferred tool in either grafting porphyrins and porphyrin complexes[14] or assembling porphyrin supramolecules.[15] In this contribution, we wish to report successful peripheral functionalization of diruthenium paddlewheel species via Suzuki reaction and the characterization of these new derivatives.

Results and Discussion

Synthesis. As established in our recent studies, the key to peripheral modification is the synthesis of $Ru_2(L)_{4-n}(L')_n$-Cl-type compounds, where L is an auxiliary *N*,*N*′-bidentate bridging ligand and L′ is an *N*,*N*′-bidentate ligand bearing one or two iodo aryl substituents.[6−8] The $Ru_2(L)_{4-n}(L')_nCl$-type precursors are generally prepared from $Ru_2(L)_{4-n}(OAc)_nCl$ type compounds, which in turn were produced with methods developed and optimized in the laboratories of Cotton,[16,17] Jiménez-Aparicio,[18] and ours.[6] Two types of auxiliary *N*,*N*′-bidentate ligands are utilized in this study: *N*,*N*′-di(3-methoxyphenyl)formamidinate (DmAniF) and *N*,*N*′-di(3,5-dichlorophenyl)formamidinate (D(3,5-Cl_2Ph)F). The iodo-containing ligands are *N*-(4-iodophenyl)-*N*′-4-phenylformamidinate (**L1**) and *N*,*N*′-di(4-iodophenyl)formamidinate (**L2**). Compounds Ru_2(DmAniF)$_3$(**L1**)Cl (**1a**) and Ru_2(DmAniF)$_3$(**L2**)-Cl (**1b**) were prepared as previously described.[8] The new compound, Ru_2(D(3,5-Cl_2Ph)F)$_3$(**L2**)Cl (**1c**), was prepared from the reaction between Ru_2(D(3,5-Cl_2Ph)F)$_3$(OAc)Cl[19] and 2 equiv of *N*,*N*′-di(4-iodophenyl)formamidine in an excellent yield (89%) and fully characterized.

Table 1. Screening of Reaction Conditions[a] Based on Compound **1b**

entry	Pd source	base	solvents	result[b]
1	$Pd(OAc)_2$	K_2CO_3	THF/H_2O	decompositon
2	$Pd(OAc)_2$	K_2CO_3	THF	no reaction
3	$PdCl_2(PPh_3)_2$	Et_3N	THF	no reaction
4	$PdCl_2(PPh_3)_2$	^{t}BuOK	THF	50%

[a] $PhB(OH)_2$ (2 equiv/iodo substituent) was used in all cases, and the reactions were carried out at 80 °C. [b] For entries 1−3, the reactions were monitored by TLC; for entry 4, an isolated yield was listed.

The initial screening for optimal Suzuki coupling conditions was based on compound **1b**, and the conditions tested are summarized in Table 1. The only successful conditions found were $PdCl_2(PPh_3)_2$ as the catalyst, ^{t}BuOK as the base, and THF as the solvent (entry 4). The use of a strong base, such as ^{t}BuOK, in Suzuki coupling is uncommon, but it has been documented.[20] With the set of optimized conditions, the reactions between compounds **1a**/**1c** and $PhB(OH)_2$ produced the corresponding biaryl products **2a**/**2c** in moderate to good yields (40−50% after column purification). However, a substantial quantity of unreacted starting material was noted in the reaction between **1c** and 2 equiv of 4-MeC(O)Ph$B(OH)_2$, which may be the result of the decomposition of 4-$CH_3C(O)$-C_6H_4-$B(OH)_2$ through the attack on the active carbonyl group by ^{t}BuOK. The use of 4-MeC(O)Ph$B(OH)_2$ in a large excess (10 equiv) resulted only in compound **2d** in a yield of 20%. Intuitively, an alternative route to type **2** compounds would be to first carry out the Suzuki modification of free ligands (i.e., H**L1** and H**L2**), followed by a ligand metathesis reaction with Ru_2(D(3,5-Cl_2Ph)F)$_3$(OAc)Cl. However, the attempted Suzuki coupling between free ligand H**L1** and $PhB(OH)_2$ did not result in the desired biphenyl derivative.[21]

Similar to prior studies of $Ru_2(DArF)_4Cl$-type compounds,[22,23] compounds **2a**−**c** were alkynylated at one of the

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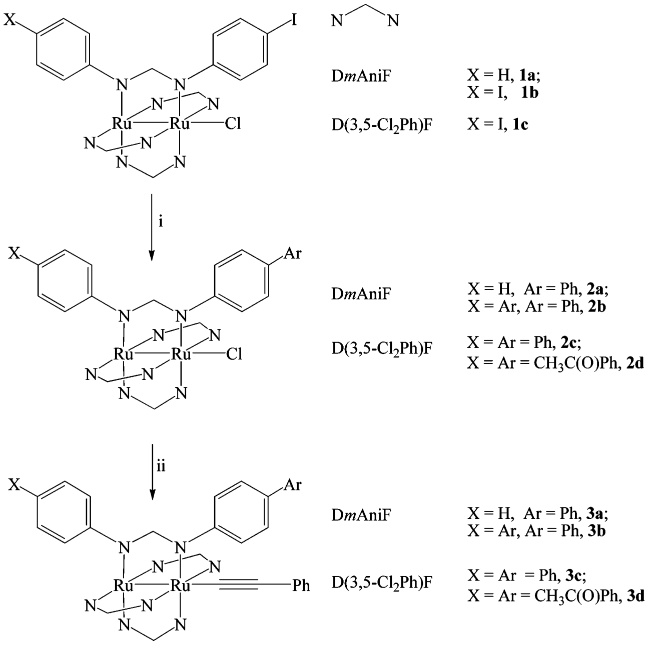
Scheme 1. Synthetic Routes for Suzuki Compounds **2a−d** and Their Alkynyl Derivatives **3a−d**[a]

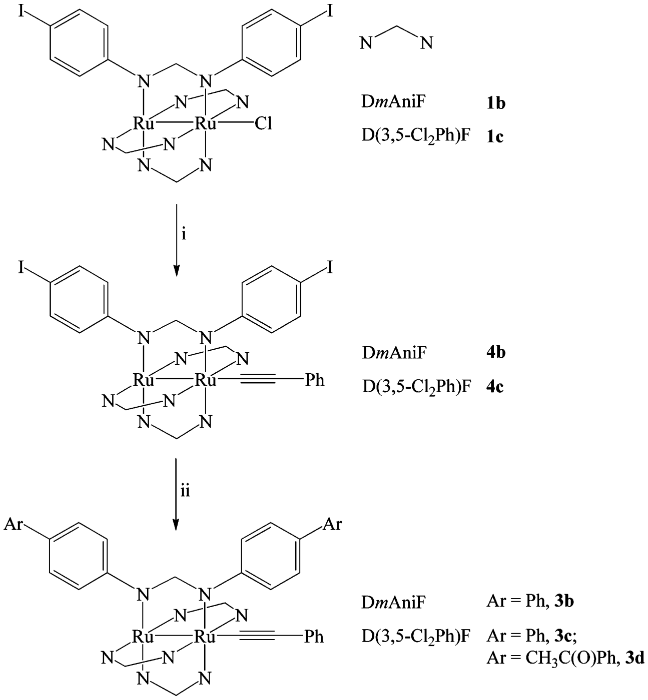


[a] Conditions: (i) $ArB(OH)_2$, ${}^tBuOK$, $PdCl_2(PPh_3)_2$ (10 mol%), PPh_3 (30 mol%); (ii) PhCCLi (5 equiv).

axial sites to yield monoadducts **3a−c** with excess lithium phenylacetylide (5 equiv, Scheme 1) in excellent yields. However, alkynylation of compound **2d** failed to yield compound **3d**, which is again a result of the sensitivity of the carbonyl group toward nucleophile. Attempts to produce bisphenylacetylide compounds have led to decomposition products so far.

Having succeeded in Suzuki coupling with the $Ru_2(L)_3(L')Cl$-type compounds, we also sought alternate routes to compounds **3**. As shown in Scheme 2, $Ru_2(L)_3(L')Cl$-type compounds (**1b**/**1c**) were readily converted to $Ru_2(L)_3(L')(C{\equiv}CPh)$-type compounds (**4b**/**4c**) following literature procedures.[22,23] The ensuing Suzuki coupling reactions between compounds **4b**/**4c** and either $PhB(OH)_2$ or $4\text{-}MeC(O)PhB(OH)_2$ under the conditions described in Scheme 1 yielded compounds **3c** and **3d**. To our knowledge, these reactions are the first examples of Suzuki coupling on a metal alkynyl species. The isolation of compound **3d**, albeit in a low yield, revealed the feasibility of preparing type **3** compounds containing a functional group sensitive to strong nucleophiles such as an acetylide. While Suzuki coupling on compounds **1a−c** required reflux in THF, reactions with alkynylated derivatives **4b−c** occurred at lower temperature (ca. 50 °C). These reaction temperatures are significantly lower than the typical temperature of Suzuki reactions on pure organic substrates (reflux in DMF/H_2O) when using commercial catalysts such as $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$, reflecting the activation of the iodo substituent by the DArF ligand coordination to the Ru_2 center.

Scheme 2. Alternate Route for Compounds **3**[a]



[a] Conditions: (i) PhCCLi (5 equiv); (ii) $ArB(OH)_2$, ${}^tBuOK$, $PdCl_2(PPh_3)_2$ (10 mol%), PPh_3 (30 mol%).

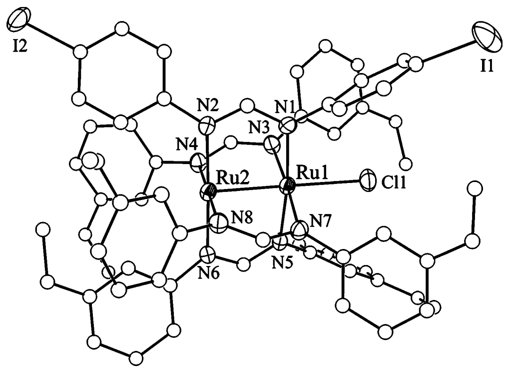


Figure 1. ORTEP plot of compound **1b**. Hydrogen atoms are omitted for clarity.

All compounds described in Schemes 1 and 2 are stable toward air and moisture and are paramagnetic species with magnetic moments ranging from 3.6 to 4.0 μ_B, a hallmark of the $Ru_2(II,III)$ species of a $S = 3/2$ ground state.[24] Compounds **1** and **2** are green crystalline solids, and compounds **3** and **4** are dark purple microcrystalline materials. All compounds reported were analyzed by combustion analysis with satisfactory results.

Molecular Structures. Single-crystal X-ray diffraction studies were performed for compounds **1b**, **1c**, and **2c**, and structural plots of these compounds can be found in Figures 1−3, respectively. Selected bond lengths and angles for all three compounds are listed in Table 2. Clearly, all three compounds adopt the paddlewheel motif with four bridging ligands occupying the equatorial positions and a chloro ligand at one of the axial positions of the Ru_2 core.[25] More importantly, the structural study of compound **2c** confirmed the formation of biphenyls from Suzuki coupling.

All three compounds crystallized in a monoclinic setting, and the asymmetric unit consists of one independent

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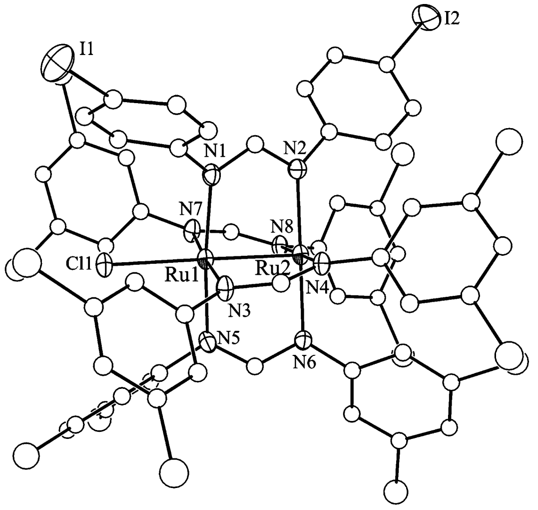

Figure 2. ORTEP plot of compound **1c**. Hydrogen atoms are omitted for clarity.

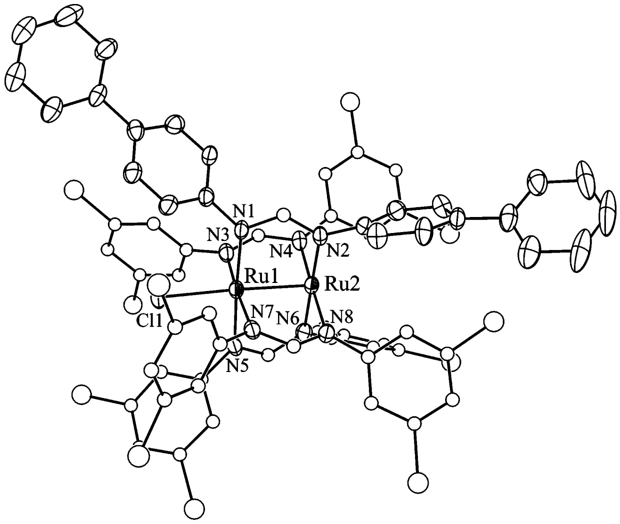

Figure 3. ORTEP plot of compound **2c**. Carbon atoms of biphenyl rings derived from the Suzuki coupling are shown as closed ellipsoids, and the hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Molecules **1b**, **1c**, and **2c**

	1b	**1c**	**2c**
Ru1−Ru2	2.3302(7)	2.3374(6)	2.3332(10)
Ru1−N1	2.095(5)	2.084(5)	2.091(6)
Ru1−N3	2.086(5)	2.084(4)	2.076(7)
Ru1−N5	2.086(5)	2.093(5)	2.090(7)
Ru1−N7	2.086(5)	2.092(4)	2.065(7)
Ru2−N2	2.044(5)	2.050(5)	2.018(7)
Ru2−N4	2.043(5)	2.078(4)	2.044(7)
Ru2−N6	2.045(5)	2.072(5)	2.051(7)
Ru2−N8	2.042(5)	2.055(4)	2.043(7)
Ru1−Cl1	2.4032(17)	2.3985(15)	2.375(2)
Ru2−Ru1−Cl1	178.51(6)	174.86(4)	177.65(7)

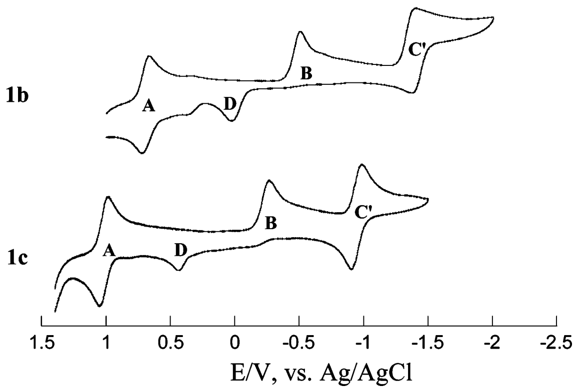

Figure 4. CVs of compounds **1b** and **1c** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

molecule in each case. The Ru−Ru bond length in **1b** (2.3302(7) Å) is significantly shorter than that in Ru_2(DmAniF)$_4$Cl (2.3855(8) Å).[26] The Ru−Ru bond length in **1c** (2.3374(6) Å) is also shorter than that in Ru_2(D(3,5-Cl_2-Ph)F)$_4$Cl (2.369(2) Å).[27] In fact, the Ru−Ru bond lengths in both **1b** and **1c** are very close to that of Ru_2(DPhF)$_4$Cl (2.339(1) Å),[28] where the bridging ligand DPhF has the least steric demand through its aryl−phenyl. Perhaps, the shortness of Ru−Ru bond in both **1b** and **1c** reflects that the presence of a D(4-I-Ph)F ligand that reduces the "strain" caused by other three DmAniF/D(3,5-Cl_2Ph)F ligands. In all three structurally characterized compounds, the Ru1 center is bonded to the axial Cl ligand and is formally 3+, while the Ru2 center is formally 2+. As shown by the parameters listed in Table 2, Ru1−N bonds (2.083−2.095 Å) are generally longer than Ru2−N bonds (2.018−2.079 Å), while one would expect an opposite trend on the basis of the covalent radii of the Ru^{2+} and Ru^{3+} centers. The contrast between the Ru1−N and Ru2−N bond lengths, however, is likely caused by Ru1 being six coordinated and therefore more crowded than the five-coordinated Ru2.

It is clear from the comparison of Figures 2 and 3 that the molecular structure of **2c** bears a significant similarity to its parent compound **1c**, indicating a minimal structural impact at the diruthenium core by Suzuki modification. This finding is consistent with those from the prior studies involving peripheral Sonagashira and click modifications.[6−8] The biphenyl moieties in **2c** have dihedral angles of about 40° (see the Supporting Information), which reveals the absence of a strong π−conjugation with the biphenyl group and thus a minimal electronic perturbation on the Ru_2 core upon Suzuki modification.

Voltammetric Studies. The electrochemical behaviors of all compounds were examined using cyclic voltammetry (CV). Within the potential window accessible in THF, all compounds display at least three Ru_2-based one-electron redox couples: one oxidation and two reductions. Selected CVs organized by the type of compounds are given in Figures 4−6, and the electrode potentials for all compounds are listed in Table 3.

The CVs of compounds **1a** and **1b** were reported in a previous paper,[8] and that of **1b** is included in Figure 4 for the sake of comparison. Similar to compound **1b**, compound **1c** features a reversible oxidation (A), one irreversible

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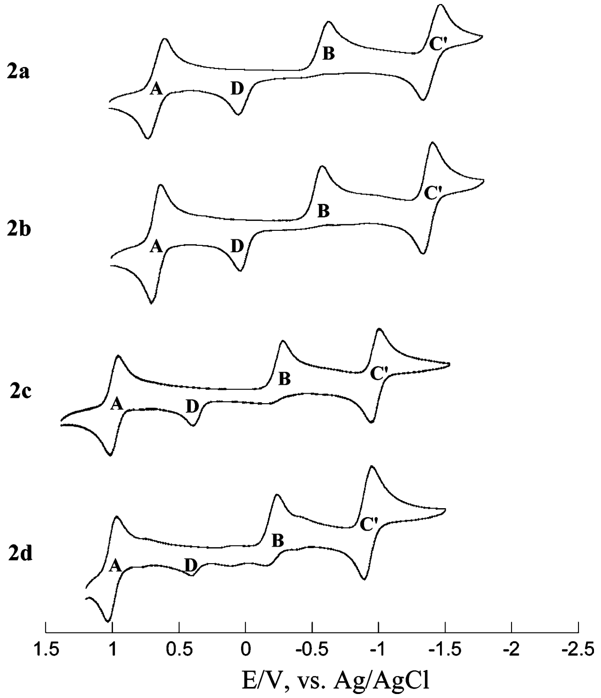


Figure 5. CVs of compounds **2a**−**d** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

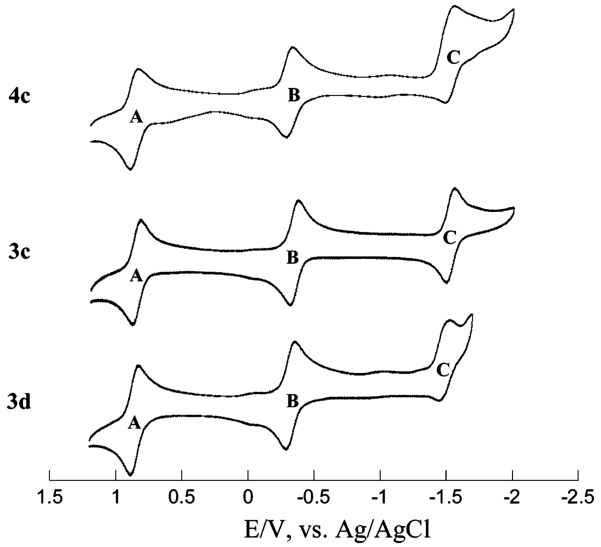


Figure 6. CVs of compounds **3c**, **3d**, and **4c** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.

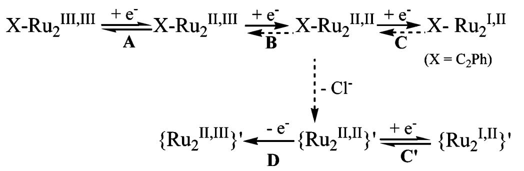
reduction couple (B), and one quasi-reversible reduction couple (C′). As first elaborated by Kadish[22] and illustrated in Scheme 3, the irreversibility of couple B is cased by a facile dissociation of the axial chloro ligand, and the resultant $Ru_2(DArF)_4$ moiety may be reoxidized at a more positive potential (D) or undergo a further reduction (C′). The electrode potentials of all couples of **1c** are shifted anodically by 0.3−0.4 V from those of **1b**, and the dramatic shift in potentials is attributed to the presence of strong electron-withdrawing substituents in $D(3,5\text{-}Cl_2Ph)F$.[29] The CVs of Suzuki products **2a**−**2d** are shown in Figure 5. The CVs of compounds **2a** and **2b** are nearly identical, indicating the insensitivity of the Ru_2 core toward single (**2a**) or double (**2b**) Suzuki modification. Surprisingly, very similar CVs were recorded for **2c** and **2d**, despite the latter compound having a strong electron-withdrawing group ($4\text{-}CH_3C(O)$) on each biphenyl ring. The absence of a potential shift corroborates the nonconjugated nature of the biphenyls, deduced from the preceding structural discussion.

Table 3. Redox Potentials Measured with Cyclic Voltammetry

	$E_{1/2}$(A) (V)	E(B)[a] (V)	E(C) or E(C′)[a] (V)	E_{pa}(***D***) (V)
1a[8]	0.66	−0.55	−1.41	0.01
1b[8]	0.68	−0.51	−1.38	0.04
1c	1.02	−0.27[b]	−0.95	0.44
2a	0.65	−0.65[b]	−1.42	0.03
2b	0.66	−0.59[b]	−1.38	0.03
2c	1.00	−0.26[b]	−0.94	0.42
2d	1.00	−0.24[b]	−0.92	0.41
4b	0.57	−0.68	−1.90[b]	NA
4c	0.87	−0.30	−1.52	NA
3b	0.52	−0.71	−1.95[b]	NA
3c	0.85	−0.34	−1.52	NA
3d	0.86	−0.32	−1.53[b]	NA

[a] $E_{1/2}$ or E_{pc} if irreversible couple as indicated. [b] Irreversible couple.

Scheme 3. Assignments of Ru_2-Based Redox Couples[a]



[a] X Stands for the axial ligand.

The mono-alkynyl derivatives, namely, compounds **3b**, **3c**, **3d**, **4b**, and **4c**, exhibit the voltammetric responses typical for $Ru_2(DArF)_4(C_2Ph)$-type compounds.[22,23] All CVs contain one oxidation and two reductions in the range of 1.5 to −2.5 V. Compared with the CVs of the chloro compounds (Figure 5), the CVs of the mono-alkynylated compounds show a greatly improved reversibility for couple B**,** on the basis of the measured ΔE_p and i_{pc}/i_{pa}, which is the testament to the robustness of the Ru−C(≡C) bond in monoanionic $[Ru_2(DArF)_4(C{\equiv}CPh)]^{1-}$. However, the Ru−C(≡C) bond is subject to cleavage at a more negative potential bias, which accounts for the quasireversible or irreversible nature of couple C in all mono-alkynyl species.

Conclusion

We have prepared a series of diruthenium compounds bearing peripheral biphenyls via Suzuki reactions. Significantly, the voltammetric characteristics of diruthenium compounds are unchanged upon Suzuki modification. The success in executing Suzuki coupling on alkynylated diruthenium complexes is an important step toward goals such as Ru_2-based bioconjugates and biosensors, which are being vigorously pursued in our laboratory.

Experimental Section

Phenylacetylene, triphenylphosphine, phenylboronic acid, 4-acetylphenylboronic acid, potassium *t*-butoxide, and copper(I) iodide were purchased from ACROS, and *n*BuLi was purchased from Aldrich. $PdCl_2(PPh_3)_2$ came from Strem Chemicals, and silica gel was

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(29) Ren, T. *Coord. Chem. Rev.* **1998**, *175*, 43.

obtained from Merck. *N,N′*-di(*m*-anisyl)formamidine (HDmAniF), *N,N′*-di(3,5-dichlorophenyl)formamidine (HD(3,5-Cl$_2$Ph)F), *N*-phenyl-*N′*-(4-iodophenyl)formamidine ((4-I−Ph)NC(H)N(H)Ph), *N,N′*-di-(4-iodophenyl)formamidine (HD(4-I−Ph)F), Ru$_2$(DmAniF)$_3$(OAc)-Cl, and Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(OAc)Cl were prepared according to modified literature procedures.[6,7,17,19,30] Ru$_2$(DmAniF)$_3$((4-I-Ph)-NCNPh)Cl (**1a**) and Ru$_2$(DmAniF)$_3$(D(4-I−Ph)F)Cl (**1b**) were prepared as described previously.[8] THF was either distilled over Na/benzophenone under an N$_2$ atmosphere prior to use or obtained from a solvent purification system (Innovative Technology Inc.). Magnetic susceptibility was measured at 294 K with a Johnson Matthey Mark-I magnetic susceptibility balance. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Vis−NIR spectra were obtained with a Varian Cary 50 UV−Vis−NIR spectrophotometer. Cyclic voltammograms were recorded in a 0.2 M (*n*-Bu)$_4$NPF$_6$ solution (THF, N$_2$-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. The concentration of the diruthenium species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.592 V (vs Ag/AgCl) under experimental conditions.

Synthesis of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)Cl (1c). A 200 mL flask was charged with Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(OAc)Cl (1.3 g, 1.0 mmol), H-D(4-I-Ph)F (0.896 g, 2 mmol), LiCl(excess), Et$_3$N (5 mL), and THF (150 mL). The color of the mixture changed gradually from dark red to dark brown upon refluxing overnight. The mixture was cooled to room temperature and filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was triturated with 100 mL of methanol and filtered to yield a green crystalline solid (1.5 g, 89% based on Ru). Anal. for $C_{52}H_{30}Cl_{13}I_2N_8Ru_2$ Found (Calcd): C, 37.12 (37.09); H, 2.04 (1.80); N, 6.48 (6.66). Vis−NIR λ_{max} (ϵ): 650 (sh), 492 nm (6190 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 1.018, 0.064, 0.92; C −0.269 (E_{pc}); D −0.947, 0.084, 1.00; E 0.440 (E_{pa}). Magnetism (μ_{eff}, 294 K): 4.03 μ_B.

Synthesis of Ru$_2$(D*m*AniF)$_3$((4-Ph-Ph)NCNPh)Cl (2a). A 100 mL Schlenck flask was charged with Ru$_2$(D*m*AniF)$_3$((4-I-Ph)-NCNPh)Cl (0.300 g, 0.23 mmol), PhB(OH)$_2$ (0.056 g, 0.46 mmol), ^{t}BuOK (0.103 g, 0.92 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.028 g, 0.04 mmol), PPh$_3$ (0.030 g, 0.12 mmol), and THF (60 mL). The color of the mixture changed immediately from dark green to dark red. The mixture was refluxed under N$_2$ overnight. Upon completion of the reaction, the mixture was cooled to room temperature and filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a mixture of ethyl acetate and hexanes (1/10−4/10, v/v). The first green band was collected and dried to yield a dark green powder (0.155 g, 53% based on Ru). Anal. for $C_{64}H_{60}ClN_8O_6Ru_2$ Found (Calcd): C, 60.66 (60.30); H, 4.98 (4.74); N, 8.34 (8.79). Vis−NIR λ_{max} (ϵ): 655 (2990), 474 nm (7280 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.649, 0.127, 0.94; C −0.648 (E_{pc}); D −1.422, 0.133, 0.95; E 0.032 (E_{pa}). Magnetism (μ_{eff}, 294 K): 3.60 μ_B.

Synthesis of Ru$_2$(D*m*AniF)$_3$(D(4-Ph-Ph)F)Cl (2b). A 100 mL Schlenck flask was charged with Ru$_2$(D*m*AniF)$_3$(D(4-I-Ph)F)Cl (0.433 g, 0.3 mmol), PhB(OH)$_2$ (0.110 g, 0.9 mmol), ^{t}BuOK (0.202 g, 1.8 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.063 g, 0.09 mmol), PPh$_3$ (0.071 g, 0.27 mmol), and THF (60 mL). The color of the mixture changed immediately from dark green to dark red. The mixture was refluxed under N$_2$ overnight. Upon completion of the reaction, the mixture was filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a mixture of THF and hexanes (1/5−2/5, v/v). The first green band was collected and dried to yield a dark green powder (0.200 g, 49% based on Ru). Anal. for $C_{70}H_{64}ClN_8O_6Ru_2\cdot 2H_2O$ Found (Calcd): C, 60.77 (60.62); H, 4.74 (4.94); N, 7.74 (8.08). Vis−NIR λ_{max} (ϵ): 654 (2940), 472 nm (6370 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.663, 0.071, 1.00; C −0.586 (E_{pc}); D −1.382, 0.133, 0.95; E 0.029 (E_{pa}). Magnetism (μ_{eff}, 294 K): 3.89 μ_B.

Synthesis of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-Ph-Ph)F)Cl (2c). A 100 mL Schlenck flask was charged with Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)Cl (0.393 g, 0.23 mmol), PhB(OH)$_2$ (0.112 g, 0.92 mmol), ^{t}BuOK (0.206 g, 1.84 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.063 g, 0.09 mmol), PPh$_3$ (0.071 g, 0.27 mmol), and THF (60 mL). The color of the mixture changed immediately from dark brown to dark red. The mixture was refluxed under N$_2$ for 4 h. Upon completion of the reaction, the mixture was filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a mixture of ethyl acetate and hexanes (2/100−3/100, v/v). The first brown band was collected, dried, and triturated with hexanes to yield a dark green powder (0.150 g, 41% based on Ru). Anal. for $C_{64}H_{40}Cl_{13}N_8Ru_2\cdot THF$ Found (Calcd): C, 49.60 (49.31); H, 2.92 (2.90); N, 6.77 (6.77). Vis−NIR λ_{max} (ϵ): 650 (sh), 490 nm (5750 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 1.004, 0.057, 0.95; C −0.257 (E_{pc}); D −0.940, 0.059, 1.00; E 0.415 (E_{pa}). Magnetism (μ_{eff}, 294 K): 3.99 μ_B.

Synthesis of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-CH$_3$C(O)Ph-Ph)F)Cl (2d). A 100 mL Schlenck flask was charged with Ru$_2$(D(3,5-Cl$_2$-Ph)F)$_3$(D(4-I-Ph)F)Cl (0.524 g, 0.31 mmol), 4-CH$_3$C(O)PhB(OH)$_2$ (0.492 g, 3.0 mmol), ^{t}BuOK (0.672 g, 6.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.042 g, 0.06 mmol), PPh$_3$ (0.047 g, 0.18 mmol), and THF (60 mL). The color of the mixture changed immediately from dark brown to dark red. The mixture was refluxed under N$_2$ for 4 h, and the formation of a significant amount of brownish precipitate was noticed during the course of reaction. Upon completion of the reaction, the mixture was filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a mixture of THF and hexanes (2/10−5/10, v/v). The first major brown band was collected and dried to yield a dark brown powder (0.100 g, 20% based on Ru). Anal. for $C_{68}H_{44}Cl_{13}N_8O_2Ru_2\cdot CH_2Cl_2\cdot C_4H_8O_2$ Found (Calcd): C, 47.21 (47.62); H, 2.85 (2.96); N, 5.56 (6.09). Vis−NIR λ_{max} (ϵ): 650(sh), 490 nm (4770 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 1.002, 0.068, 1.00; C −0.237 (E_{pc}); D −0.918, 0.058, 0.87; E 0.409 (E_{pa}). Magnetism (μ_{eff}, 294 K): 3.82 μ_B.

Synthesis of [Ru$_2$(D*m*AniF)$_3$(D(4-I-Ph)F)](CCPh) (4b). Five equivalents of LiC$_2$Ph was added to a 40 mL THF solution of Ru$_2$(D*m*AniF)$_3$(D(4-I-Ph)F)Cl (0.262 g, 0.18 mmol) at room temperature. The color of the reaction mixture changed from dark green to dark red upon the addition. The mixture was stirred under argon for 2 h. Upon completion of the reaction, the solvent was removed under vacuum prior to exposure to air. The residue was purified by column chromatography, eluted with a solvent mixture of CH$_2$Cl$_2$ and hexanes (1/10−3/10, v/v), and the first purple band was collected. Removal of the solvent yielded the pure product **4b** as a crystalline purple solid (0.180 g, 66% based on Ru). Anal. for $C_{66}H_{59}I_2N_8O_6Ru_2\cdot CH_2Cl_2$ Found (Calcd): C, 50.57 (50.26); H, 4.08 (3.84); N, 6.63 (7.00). Vis−NIR λ_{max} (ϵ): 540 nm (7760 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.573, 0.066, 0.82; C −0.682, 0.066, 1.00; D −1.897 (E_{pc}). Magnetism (μ_{eff}, 294 K): 3.62 μ_B.

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(30) Mandel, H. G.; Hill, A. J. *J. Org. Chem.* **1954**, *19*, 3978.

Synthesis of [Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)](CCPh) (**4c**). Five equivalents of LiC$_2$Ph was added to a 40 mL THF solution of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)Cl (0.197 mg, 0.12 mmol) at room temperature. The color of the reaction mixture changed from dark brown to dark red upon the addition. The mixture was stirred under argon for 2 h. Upon completion of the reaction, the solvent was removed under vacuum prior to exposure to air. The residue was purified by column chromatography, eluted with a solvent mixture of THF and hexanes (1/20−1/10, v/v), and the first purple band was collected. Removal of the solvent yielded the pure product **4c** as a crystalline purple solid (0.155 g, 74% based on Ru). Anal. for $C_{60}H_{35}Cl_{12}I_2N_8Ru_2 \cdot H_2O$ Found (Calcd): C, 40.34 (40.77); H, 2.46 (2.11); N, 6.50 (6.34). Vis−NIR λ_{max} (ϵ): 620 (sh), 530 nm (8400 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.866, 0.065, 1.00; C −0.301, 0.083, 0.52; D −1.519, 0.078, 0.45. Magnetism (μ_{eff}, 294 K): 3.95 μ_B.

Synthesis of [Ru$_2$(D*m*AniF)$_3$(D(4-Ph-Ph)F)](C$_2$Ph) (3b). Method A. Five equivalents of LiC$_2$Ph was added to a 40 mL THF solution of Ru$_2$(D*m*AniF)$_3$(D(4-Ph-Ph)F)Cl (0.067 mg, 0.05 mmol) at room temperature. The color of the reaction mixture changed from dark green to dark red upon the addition. The mixture was stirred under argon for 2 h. Upon completion of the reaction, the solvent was removed under vacuum prior to exposure to air. The residue was purified by column chromatography, eluted with a mixture of CH$_2$Cl$_2$ and hexanes (1/10−1/5, v/v), and the first purple band was collected. Removal of the solvents yielded **3b** as a crystalline purple solid (0.054 g, 76% based on Ru).

Method B. A 100 mL Schlenck flask was charged with [Ru$_2$(D*m*AniF)$_3$(D(4-I-Ph)F)](C$_2$Ph) (0.105 g, 0.069 mmol), PhB(OH)$_2$ (0.034 g, 0.276 mmol), ^{t}BuOK (0.062 g, 0.552 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.021 g, 0.03 mmol), PPh$_3$ (0.024 g, 0.09 mmol) ,and THF (40 mL). The color of the mixture changed immediately from dark purple to reddish purple. The mixture was heated at 50 °C under N$_2$ for 2 h. Upon completion of the reaction, the mixture was filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography eluted with a mixture of THF and hexanes (1/4−1/3, v/v). The first purple band was collected and dried to yield a dark purple solid (0.080 g, 49% based on Ru). The sample was identified to be the same compound as that prepared using method A by the comparison of TLC result.

Anal. for $C_{78}H_{69}N_8O_6Ru_2 \cdot 0.5CH_2Cl_2$ Found (Calcd): C, 64.24 (64.62); H, 4.98 (4.84); N, 7.42 (7.68). Vis−NIR, λ_{max} (ϵ): 540 nm (7760 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE$_p$ (V), $i_{backward}/i_{forward}$): B 0.523, 0.056, 1.00; C −0.714, 0.058, 0.52; D −1.949 (E_{pc}). Magnetism (μ_{eff}, 294 K): 3.88 μ_B.

Synthesis of [Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-Ph-Ph)F)](C$_2$Ph) (3c). Method A. Five equivalents of LiC$_2$Ph was added to a 40 mL THF solution of Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-Ph-Ph)F)Cl (0.079 g, 0.05 mmol) at room temperature. The color of the reaction mixture changed from dark brown to dark red upon the addition. The mixture was stirred under argon for 2 h. Upon completion of the reaction, the solvent was removed under vacuum prior to exposure to air. The residue was purified by column chromatography, eluted with a mixture of ethyl acetate and hexanes (0/10−1/10, v/v), and the first purple band was collected. Removal of solvents yielded **3c** as a purple crystalline solid (0.068 g, 83% based on Ru).

Method B. A 100 mL Schlenck flask was charged with [Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)](C$_2$Ph) (0.270 g, 0.154 mmol), PhB(OH)$_2$ (0.075 g, 0.616 mmol), ^{t}BuOK (0.138 g, 1.232 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.042 g, 0.06 mmol), PPh$_3$ (0.047 g, 0.18 mmol), and THF (40 mL). The color of the mixture changed immediately from dark purple to reddish purple. The mixture was heated to about 50 °C under N$_2$ for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature and filtered through a 2 cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a solvent mixture of THF and hexanes (1/20−1/10, v/v). The first purple band was collected and dried to yield a dark purple solid (0.140 g, 55% based on Ru). The sample was identified to be the same compound as that prepared using method A by the comparison of the TLC results.

Anal. for $C_{72}H_{45}Cl_{12}N_8Ru_2$ Found (Calcd): C, 52.55 (52.42); H, 2.91 (2.75); N, 6.65 (6.79). Vis−NIR λ_{max} (ϵ): 600 (sh), 534 nm (8150 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.852, 0.065, 1.00; C −0.341, 0.060, 0.99; D −1.522, 0.058, 0.91. Magnetism (μ_{eff}, 294 K): 3.79 μ_B.

Synthesis of [Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-CH$_3$C(O)Ph-Ph)F)](C$_2$Ph) (3d). Method B. A 100 mL Schlenck flask was charged with [Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-I-Ph)F)](C$_2$Ph) (0.300 g, 0.17 mmol), 4-CH$_3$C(O)PhB(OH)$_2$ (0.279 g, 1.7 mmol), ^{t}BuOK (0.381 g, 3.40 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.049 g, 0.07 mmol), PPh$_3$ (0.055 g, 0.21 mmol), and THF (40 mL). The color of the mixture changed immediately from dark purple to reddish purple. The mixture was heated at 50 °C under N$_2$ for 2 h, and significant precipitate formation was noticed. Upon completion of the reaction, the mixture was filtered through a 2-cm silicon gel pad. The filtrate was dried, and the residue was purified by column chromatography, eluted with a mixture of THF and hexanes (1/3−1/2, v/v). The first purple band was collected and dried to yield a dark purple solid (0.050 g, 17% based on Ru). Anal. for $C_{76}H_{49}Cl_{12}N_8O_2Ru_2 \cdot 2H_2O$ Found (Calcd): C, 51.53 (51.58); H, 2.93 (3.02); N, 6.50 (6.33). Vis−NIR λ_{max} (ϵ): 600 (sh), 530 nm (7550 M^{-1} cm^{-1}). Electrochemistry ($E_{1/2}$ (V), ΔE_p (V), $i_{backward}/i_{forward}$): B 0.855, 0.069, 1.00; C −0.323, 0.064, 0.87; D −1.528 (E_{pc}). Magnetism (μ_{eff}, 294 K): 3.80 μ_B.

X-ray Data Collection, Processing, and Structure Analysis and Refinement. Single crystals of compounds **1b**, **1c**, and **2c** were grown via either slow evaporation of an ethyl acetate and hexanes solution (**1b** and **1c**) or slow diffusion of hexanes into a toluene solution (**2c**). X-ray intensity data were measured at 300 K on a Bruker SMART1000 CCD-based X-ray diffractometer system using Mo Kα radiation (λ = 0.71073 Å). The crystals used for X-ray crystallographic analysis were either cemented onto a quartz fiber with epoxy glue (**1b** and **1c**) or wedged in a 0.30 mm capillary filled with mother liquor (**2c**). Data were measured using ω scans of 0.3° per frame such that a hemisphere (1271 frames) was collected. No decay was indicated for either data set by the recollection of the first 50 frames at the end of each data collection. The frames were integrated with the Bruker SAINT software package[31] using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS, supplied by George Sheldrick.

The structures were solved and refined using the Bruker SHELXTL (version 5.1) software package[32] in the space groups $P2_1/n$ (**1b** and **1c**) and $P2_1/c$ (**2c**). While each of the asymmetric unit cells of compounds **1b** and **1c** contains one independent molecule, the asymmetric unit cell of **2c** contains one independent molecule two toluene molecules and one H$_2$O molecule. The positions of all non-hydrogen atoms of the diruthenium moieties were revealed by direct method. Some structural disorders were also noted: one of 3-methoxyphenyl rings in **1b** is rotationally

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(31) *SAINT*, version 6.035; Bruker-AXS Inc.: Madison, WI, 1999.

(32) (a) *SHELXTL*, version 5.03; Bruker-AXS Inc.: Madison, WI, 1998. (b) Sheldrick, G. M. *SHELXS-90*, *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1990. (c) Sheldrick, G. M. *SHELXL-93*, *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

Table 4. Crystal Data for Compounds **1b**, **1c**, and **2c**

	1b	**1c**	**2c**·$2C_7H_8$·H_2O
formula	$C_{59}H_{56}ClI_2N_8O_7Ru_2$	$C_{52}H_{30}Cl_{14}I_2N_8Ru_2$	$C_{78}H_{56}Cl_{13}N_8ORu_2$
fw	1480.51	1719.08	1784.30
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	23.364(2)	11.294(1)	16.137(1)
b (Å)	11.436(1)	24.715(3)	28.440(3)
c (Å)	24.330(2)	21.414(2)	18.327(2)
β (deg)	116.180(2)	91.823(2)	99.270(2)
V (Å^3)	5833.8(9)	5975(1)	8301(1)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.686	1.911	1.428
μ (mm^{-1})	1.681	2.210	0.830
T (K)	300	300	300
R, wR2 ($I > 2\sigma(I)$)	0.054, 0.114	0.046, 0.110	0.069, 0.136
GOF on F^2	1.00	1.01	1.00

disordered, and the axial chloro ligand in **1c** was disordered in both axial positions. The disordered portions in both cases were refined with the occupancy constraints. With all non-hydrogen atoms being anisotropic and all hydrogen atoms in calculated positions and riding mode, the structure was refined to convergence by the least-squares method on F^2 (SHELXL-93, incorporated in SHELXTL.PC, version 5.03). Relevant information on the data collection and the figures of merit of final refinement are listed in Table 4.

Acknowledgment. We thank the National Science Foundation (CHE 0242623/0553564), the University of Miami (CCD diffractometer fund), and Purdue University for financial support.

Supporting Information Available: Vis−NIR absorption spectra of compounds **1**−**3**, fully labeled ORTEP drawings, and full table of bond lengths and angles for compound **2c** and X-ray crystallographic files in CIF format for compounds **1b**, **1c**, and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060734Y