# **Bis-Adducts of Substituted Phenylethynyl on a** Ru<sub>2</sub>(DMBA)<sub>4</sub> Core: Effect of Donor/Acceptor **Modifications**

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The reactions between arylethynes (either BuLi activated or Et<sub>3</sub>N assisted) and Ru<sub>2</sub>- $(RDMBA)_4X_2$ , where RDMBA is either N,N-dimethylbenzamidinate (R = H) or N,Ndimethyl-*m*-methoxybenzamidinate (R = m-MeO) and X is either Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>, resulted in the compounds  $Ru_2(RDMBA)_4(C \equiv CC_6H_4Y)_2$  (Y = H (1a,b), 4-NO<sub>2</sub> (2a,b), 4-CN (3a,b), 3-CN (4a,b),  $\hat{4}$ -NMe<sub>2</sub> (5a,b); R = H (a), m-MeO (b)). The single-crystal X-ray diffraction study of **1b** and **2a** revealed the linear alignment of the arylethynyl ligands along the Ru–Ru vector. All of the compounds display two Ru-based one-electron processes, an oxidation and a reduction, and their electrode potentials correlate linearly with the Hammett constants of substituent Y. Compounds 5a,b display an additional pair of one-electron processes attributed to the oxidation of 4-NMe<sub>2</sub> groups, on the basis of which an extensive electron delocalization along the metallayne backbone was inferred.

## Introduction

Dinuclear paddlewheel species continue to attract significant attention, due to the diversity in both metal centers and bridging ligands, as well as their interesting electrochemical, magnetic, and other properties.<sup>1,2</sup> Facile electron delocalizations between dinuclear units linked via a  $\pi$ -delocalized framework have been demonstrated by the laboratories of Cotton,<sup>3</sup> Bursten and Chisholm,<sup>4,5</sup> and Ren,<sup>6,7</sup> revealing the possibility of realizing molecular electronic wires based on these paddlewheel species.<sup>8,9</sup> To achieve this goal, the ability to precisely control the electronic properties of paddlewheel species is crucial. Previously, substituent effects in paddlewheel species were explored in our laboratory on a series of  $M_2(DArF)_4$  compounds with M = Mo, Ni, Ru, Rh and DArF = diarylformamidinate.<sup>10–16</sup> Initial studies of Mo<sub>2</sub> and Ni<sub>2</sub> series revealed that there is a linear correlation

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between electrode potentials of metal-based redox processes and the Hammett constants ( $\sigma$ ) of the phenyl substituent on DArF ligands, and both the optical and structural features were unaltered by the substituents.  $^{10-12}$ Similar results were found for the series of  $Rh_2(DArF)_4$ compounds and  $Ru_2(DArF)_4$  compounds bearing either chloro or phenylethynyl axial ligands in our laboratory, 13-16  $\operatorname{Re}_2(D\operatorname{Ar} F)_4\operatorname{Cl}_2$  and  $\operatorname{Cr}_2(D\operatorname{Ar} F)_4$  compounds in the laboratory of Eglin,<sup>17,18</sup> and Ru<sub>2</sub>(X-ap)<sub>4</sub>Cl compounds (X-ap = substituted 2-anilinopyridinates) in the laboratory of Bear and Kadish.<sup>19</sup> It was concluded that the phenyl substitution of the bridging ligands imparts an inductive effect on the dinuclear core.<sup>20</sup> The significance of substituent effects in the chemistry of transition-metal complexes of both alkynyl and other unsaturated carbon ligands such as allenylidene and cumulenylidene is also well documented.<sup>21,22</sup> For example, the presence of strong donor or acceptor groups has been a hallmark of mononuclear complexes with enhanced nonlinear optical properties.23

We reported recently the synthesis of  $Ru_2(DMBA)_4$ -Cl<sub>2</sub> and its reactions with lithiated alkynyls to yield Ru<sub>2</sub>- $(DMBA)_4(C_2R)_2$  (R = H, SiMe<sub>3</sub>, C<sub>2</sub>SiMe<sub>3</sub>, C<sub>2</sub>H, Ph).<sup>24</sup> The

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ease of alkynyl adduct formation at the Ru<sub>2</sub>(*DMBA*)<sub>4</sub> core prompts us to consider its utility as the platform for the exploration of substituent electronic effects. Reported herein are the synthesis and characterization of the bis-adducts of substituted phenylethynyl (YC<sub>6</sub>-H<sub>4</sub>C=C-) on both Ru<sub>2</sub>(*DMBA*)<sub>4</sub> and its derivative Ru<sub>2</sub>-(*m*MeO*DMBA*)<sub>4</sub> cores with their numerical designations defined in Chart 1.

#### **Results and Discussion**

Synthesis and Characterization of  $\sigma$ -Alkynyl Complexes. Synthesis of compound 1a via the reaction between Ru<sub>2</sub>(*DMBA*)<sub>4</sub>Cl<sub>2</sub> and LiC<sub>2</sub>Ph was reported previously.<sup>24</sup> However, the utility of lithiated alkynyl became less effective with phenylethynes bearing functional groups such as  $-NO_2$  and -CN. For example, Pt<sub>2</sub>- $(\mu$ -dppm)<sub>2</sub>(C=CC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>)<sub>4</sub> was prepared from Pt-(P,P'-dppm)Cl<sub>2</sub> and LiC=CC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> in only 21% yield.<sup>25</sup> We found that the newly reported complexes Ru<sub>2</sub>(*DMBA*)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and Ru<sub>2</sub>(*DMBA*)<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub> readily reacted with *unactivated* alkynes in the presence of Et<sub>3</sub>N at room temperature to yield the desired alkynyl derivatives:<sup>26</sup>

$$\frac{\text{Ru}_2(DMBA)_4(\text{NO}_3)_2 + 2\text{HC}_2\text{R}}{\xrightarrow{\text{Et}_3\text{N, THF, room temp}}} \\ \frac{-(\text{Et}_3\text{NH})\text{NO}_3}{\text{Ru}_2(DMBA)_4(\text{C}_2\text{R})_2}$$

Under these conditions, compounds 1-4 formed in quantitative yields (monitored by thin-layer-chromatography), and workups were fairly straightforward. However, compounds **5a**,**b** could not be obtained similarly. Instead, they were prepared using the appropriate lithiated alkynyl. Alkynylation of a mononuclear Ru complex by 1-alkyne under weakly basic conditions is a well-established reaction, and the mechanism may involve the formation of a Ru-( $\eta^2$ -HC $\equiv$ CR) intermediate and its subsequent conversion to a Ru-vinylidene moiety.<sup>27</sup> This mechanism may not be operative in the



**Figure 1.** ORTEP plot of **1b** with ellipsoids at the 30% probability level.



**Figure 2.** ORTEP plot of **2a** with ellipsoids at the 30% probability level.

current case, since the presence of four *N*-methyl groups will likely block the formation of a  $\eta^2$ -HC=CR adduct on the Ru<sub>2</sub> core. Instead, the reaction may proceed via simple anion metathesis.

The new compounds (**1b** and **2**–**5**) were characterized by combustion analysis, FAB mass spectrometry, <sup>1</sup>H NMR, visible–near-infrared (vis–near-IR), and IR spectroscopic techniques. The IR spectra generally display characteristic  $\nu$ (C=C) bands around 2070 cm<sup>-1</sup>, accompanied by a  $\nu$ (C=N) band between 2217 and 2226 cm<sup>-1</sup> in compounds **3** and **4**. The vis–near-IR spectra feature two intense absorption bands around ca. 515 and 883 nm, which are similar to the spectra reported for the series of Ru<sub>2</sub>(*DMBA*)<sub>4</sub>(C=CR)<sub>2</sub> compounds with R = SiMe<sub>3</sub>, C<sub>2</sub>SiMe<sub>3</sub>.<sup>24</sup> All the compounds reported herein are diamagnetic, with well-resolved <sup>1</sup>H NMR spectra, and the protons of the arylethynyl ligands can be unambiguously assigned in most cases.

Molecular structures of both compounds **1b** and **2a** determined via X-ray diffraction studies are shown in Figures 1 and 2, respectively, and the selected bond lengths and angles are collected in Table 1. Both molecules adopt the paddlewheel motif, and their general features are very similar to those reported earlier for  $\text{Ru}_2(DMBA)_4(\text{C}_2\text{R})_2$  with  $\text{R} = \text{SiMe}_3$ ,  $\text{C}_2\text{H}.^{24}$  The coordination spheres of the Ru centers can be described as pseudo-octahedral with four N centers from DMBA occupying the equatorial positions and the other Ru center and the alkynyl assuming two axial positions. The Ru–Ru bond length in **1b** (2.448(1) Å) is clearly

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

1b		2a	
Ru–Ru′	2.4478(9)	Ru–Ru′	2.459(1)
Ru-N(1)	2.058(5)	Ru-N(2)	1.980(5)
Ru-N(2)	2.036(5)	Ru-N(3)	2.028(5)
Ru-N(3)	2.023(5)	Ru-N(4)	2.137(5)
Ru-N(4)	2.052(5)	Ru-N(5)	2.015(5)
Ru-C(1)	1.996(7)	Ru-C(1)	1.982(7)
C(1)-C(2)	1.20(1)	C(1)-C(2)	1.190(9)
N(1)-Ru-Ru	84.6(1)	N(2)-Ru-Ru'	94.7(2)
N(2)-Ru-Ru	88.6(1)	N(3)-Ru-Ru'	86.8(1)
N(3)-Ru-Ru	88.8(1)	N(4)-Ru-Ru	78.5(1)
N(4)-Ru-Ru	84.9(1)	N(5)-Ru-Ru'	86.5(1)
C(1)-Ru-Ru'	175.1(2)	C(1)-Ru-Ru'	165.5(2)
C(2)-C(1)-Ru	177.5(6)	C(2)-C(1)-Ru	176.3(7)

Table 2. Electrode Potentials and Related DataDetermined using CV for Compounds 1–5

compd	$\sigma_{\rm Y}{}^a$	$E_{1/2}(A)/V, \Delta E/V, i_b/i_f^b$	$E_{1/2}$ (B)/V, $\Delta E$ /V, $i_b/i_f^{L}$
<b>1a</b> <sup>c</sup>	0	0.52, 0.058, 0.89	-1.10, 0.057, 0.79
1b	0	0.51, 0.058, 0.93	-1.10, 0.062, 0.80
2a	0.81	0.69, 0.069, 0.99	-0.87, 0.073, 0.92
2b	0.81	0.70, 0.067, 0.93	-0.86, 0.074, 0.68
3a	0.70	0.65, 0.065, 0.89	-0.92, 0.060, 0.93
3b	0.70	0.66, 0.065, 0.87	-0.94, 0.062, 0.98
<b>4a</b>	0.62	0.62, 0.063, 0.89	-0.98, 0.064, 0.93
<b>4b</b>	0.62	0.63, 0.066, 0.91	-0.98, 0.068, 0.99
5a	-0.83	0.31, 0.066, 0.95	$-1.17^{d}$
5b	-0.83	0.29,  0.069,  0.88	$-1.21^{d}$

<sup>*a*</sup> Taken from ref 32. <sup>*b*</sup>  $i_{\rm b}/i_{\rm f} = i_{\rm backward}/i_{\rm forward}$ . <sup>*c*</sup> Taken from ref 24. <sup>*d*</sup>  $E_{\rm pc}$ , irreversible process.

shorter than that in **2a** (2.459(1) Å), while the Ru–C distance in **1b** is slightly longer than that in **2a**. As discussed previously,<sup>9</sup> the lengthening of the Ru–Ru bond in bis-alkynyl adducts is generally attributed to the formation of a strong  $\sigma(\text{Ru}-\text{C})$  bond, which polarizes the  $d_z^2$  orbital toward the C center. The strong acceptor nature of 4-NO<sub>2</sub> groups in **2a** further enhances this effect. The ligand arrangement around the Ru<sub>2</sub> core in **2a** deviates significantly from the idealized  $D_4$  symmetry, an effect commonly observed for *trans*-Ru<sub>2</sub>(L)<sub>4</sub>-(C<sub>2</sub>Y)<sub>2</sub> complexes and attributed to second-order Jahn–Teller distortion.<sup>14</sup> Interestingly, the deviation is negligible in **1b**.

Electrochemical Studies. The results of cyclic voltammetric (CV) measurements of the ruthenium alkynyl compounds **1**–**5** are summarized in Table 2. Previous work with diruthenium metallaynes revealed rich redox characteristics,<sup>9</sup> and the compounds described here are no exception. Compounds 1-5 generally feature two one-electron Ru<sub>2</sub>-based couples: an oxidation (A), and a reduction (B), as shown by both the CVs of compounds **na** (n = 2-5) in Figure 3 and those of **nb** provided in the Supporting Information. Both the oxidation and reduction couples are (quasi)reversible in compounds **1**–**4**, as evidenced by both small  $\Delta E$  values and a nearunity *i*<sub>backward</sub>/*i*<sub>forward</sub> ratio. The reduction couples in compounds **5a**,**b** are irreversible, and the irreversibility is indicative of alkynyl dissociation upon reduction.<sup>24</sup> Compounds 2a, b also feature a second reduction around -1.29 V (C in the CV of **2a**), which is attributed to the reduction of the 4-NO<sub>2</sub> group on the basis of comparison with previous work.<sup>28-30</sup> Compounds 5a,b, on the other hand, feature two additional oxidations at ca. 0.70 and



**Figure 3.** Cyclic voltammograms of complexes *n* (n = 2-5) recorded in a 0.20 M THF solution of Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV/s.

0.90 V, respectively, which are clearly due to the sequential oxidations of two 4-NMe<sub>2</sub> groups.<sup>31</sup>

It is clear from Figure 3 that the electrode potentials for both the oxidation (A) and reduction couples (B) shift cathodically as the electron-withdrawing power of phenylethyne substituents decreases (NO<sub>2</sub> > CN > H > NMe<sub>2</sub>). This trend can be further quantified by fitting the plot of electrode potentials versus the Hammett constant of substituent Y ( $\sigma_{\rm Y}$ ) according to the following equation:<sup>32</sup>  $E_{1/2}(Y) = E_{1/2}(H) + \rho(2\sigma_Y)$ , where  $\rho$  is the reactivity constant. Both the plot and fit for compounds *n***a** (n = 1-5) are shown in Figure 4, and the reactivity constants are 110 and 86 mV for the oxidation ( $\rho(A)$ ) and reduction ( $\rho(B)$ ) processes, respectively. While the linear fit of oxidation potentials yields an excellent correlation coefficient (R = 99.5%), the linear fit of reduction potentials is of marginal quality (R = 95%), which is mainly due to the irreversibility of the reduction couple of compound 5a. Similar reactivity constants  $(\rho(A) = 121 \text{ mV} \text{ and } \rho(B) = 97 \text{ mV})$  were obtained for compounds *n***b** (n = 1-5), and the least-squares plots are provided in the Supporting Information (Figure S2). Comparison of both the  $\rho$  and electrode potentials in Table 2 between *na* and *nb* series reveals that the redox processes associated with the Ru<sub>2</sub> core are relatively insensitive to the presence of substituents on the phenyl ring of *DMBA* ligands. Such a substituent independence, although surprising, can be explained by the fact that the phenyl group of the DMBA ligand is always far from being coplanar with the amidine group, due to the

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**Figure 4.** Hammett plot of  $E_{1/2}$  vs  $2\sigma$ . The crosses (×) are the measured values of  $E_{1/2}$ (B), circles ( $\bigcirc$ ) are the measured values of  $E_{1/2}$ (A), and the solid lines are the least-squares fit.



**Figure 5.** Differential pulse voltammogram of compound **5a** in the anodic region recorded in a 0.20 M THF solution of  $Bu_4NPF_6$  at a scan rate of 4 mV/s.

presence of *N*-methyl groups, which effectively eliminates the propagation of electronic effect through conjugation.

The reactivity constants obtained for compounds 1-5are comparable to the largest obtained for the M<sub>2</sub>-(*D*Ar *F*)<sub>4</sub> series,<sup>20</sup> which is truly remarkable, considering that the substituted phenyl is only two bonds away from the M<sub>2</sub> center in the latter but three bonds away from the Ru<sub>2</sub> center in compounds 1-5. The enhanced response to the substituent in compounds 1-5 indicates that the  $\pi$ -conjugation along the Ph-C=C-Ru<sub>2</sub> backbone is extensive. Lapinte et al. reported the study of a comprehensive series of Cp\*Fe(dppe)(C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4-Y) compounds with Y = NO<sub>2</sub>, CN, CF<sub>3</sub>, F, Br, H, Me, 'Bu, OMe, NH<sub>2</sub>, NMe<sub>2</sub>.<sup>31,33,34</sup> While a large range in  $E^{\circ}$ (Fe<sup>3+</sup>/Fe<sup>2+</sup>) was observed, the electrode potentials do not correlate with  $\sigma_{\rm Y}$  at all, and the lack of correlation was attributed to the coexistence of several canonical structures.

The stepwise appearance of 4-NMe<sub>2</sub> oxidation waves (D and E) in **5a** indicates that the mixed-valence species generated by the second oxidation (D) is delocalized. Although the separation between **D** and **E** could not be determined from the CV, it is readily determined from the differential pulse voltammogram of **5a** (Figure 5) as 0.20 V. Considering the fact that two NMe<sub>2</sub> groups are separated by over 20.0 Å (estimated from the structural data of **2a**), such a coupling strength is remarkable. In comparison, a  $\Delta E$  value of 60 mV was reported for a bis(triarylamine) bridged by an organic linker over a distance of 19.3 Å.<sup>35</sup> The large  $\Delta E$  value determined for **5a** reveals the exceptional ability of the Ru<sub>2</sub> metallayne in mediating electron delocalization. Unfortunately, the instabilities of the oxidized species preclude probing the intervalence charge-transfer transition to provide more insight into the electron delocalization in the mixed-valence species.

### Conclusions

Alkynylation under weak base conditions adds a new dimension to the research of dinuclear alkynyl compounds and can be a powerful method to introduce other functionalized alkynes. Both the linear  $E_{1/2}-\sigma_Y$  correlation and large reactivity constants for the Ru<sub>2</sub>-based processes revealed the feasibility of achieving significant modulation of electronic structures of metallaynes through the substitution on axial phenylethynyls. We are currently investigating the synthesis of polar  $DC_6H_4C=C-Ru_2-C=CC_6H_4A$  type compounds (D and A are donor and acceptor substituents, respectively), which are similar to the molecular diode proposed by Ratner and Aviram.<sup>36</sup>

#### **Experimental Section**

General Conditions, Reagents, and Instruments. n-BuLi was purchased from Aldrich, PhC≡CH from Acros, and silica gel from Merck. Ru<sub>2</sub>(DMBA)<sub>4</sub>Cl<sub>2</sub>,<sup>24</sup> Ru<sub>2</sub>(m-MeODMBA)<sub>4</sub>- $Cl_{2}$ ,<sup>37</sup>  $Ru_{2}(DMBA)_{4}(NO_{3})_{2}$  and  $Ru_{2}(m-MeODMBA)_{4}(NO_{3})_{2}$ ,<sup>26</sup> and 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C≡CH and 3-/4-CN-C<sub>6</sub>H<sub>4</sub>C≡CH<sup>38</sup> were prepared as previously described. 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>I was prepared via the method of Fabbrini et al.<sup>39</sup> and converted to  $4-Me_2NC_6H_4C \equiv$ CH by the standard method. THF and hexanes were distilled over Na/benzophenone under a N2 atmosphere prior to use. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer using KBr disks. Absorption spectra were obtained with a Perkin-Elmer Lambda-900 UV-vis-near-IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 300 NMR spectrometer with chemical shifts  $(\delta)$  referenced to the residual CHCl<sub>3</sub>. Cyclic and differential pulse voltammograms were recorded in 0.2 M [NBu<sub>4</sub>]PF<sub>6</sub> solution (THF, N2-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 diruthenium species was always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.595 V (vs Ag/AgCl) under these experimental conditions. Elemental analysis was performed by Atlantic Microlab, Norcross, Georgia.

 $[\mathbf{Ru}_2(m-\mathbf{MeODMBA})_4(\mathbf{C}=\mathbf{CPh})_2]$  (1b).  $\mathbf{Ru}_2(m-\mathbf{MeODMBA})_4$ -(NO<sub>3</sub>)<sub>2</sub> (134 mg, 0.129 mmol) was suspended in 20 mL of THF, to which were added HC≡CPh (104 mg, 1.02 mmol) and NEt<sub>3</sub> (5 mL). After the mixture was stirred for 20 h under argon, the solvent was removed under reduced pressure. The residue

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was loaded onto a silica gel column deactivated by 10% Et<sub>3</sub>N in hexanes and eluted with ethyl acetate-hexanes-Et<sub>3</sub>N (30/ 70/5, v/v), giving pure **1b** as a deep red material. Yield: 103 mg (72% based on Ru). Data for **1b** are as follows.  $R_f$ 0.41 (ethyl acetate-hexanes-Et<sub>3</sub>N, 20/70/10, v/v; the same combination is also used for the determination of other  $R_f$ 's). Anal. Found (calcd) for C<sub>56</sub>H<sub>62</sub>N<sub>8</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 60.65 (60.42); H, 5.49 (5.61); N, 10.07 (9.98). MS-FAB (*m/e*, based on <sup>101</sup>Ru): 1114 [MH<sup>+</sup>]. UV-vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 874 (1500), 500 (9500). IR (cm<sup>-1</sup>):  $\nu$ (C $\equiv$ C), 2071 (w). Electrochemistry ( $E_{1/2}$ , V;  $\Delta E_p$ , V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.51, 0.058, 0.93; B, -1.10, 0.062, 0.80. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.80–6.40 (26H, Ph), 3.81 (12H, OMe), 3.25 (24H, NMe).

 $[Ru_2(DMBA)_4(C \equiv C - 4 - C_6H_4NO_2)_2]$  (2a).  $Ru_2(DMBA)_4(NO_3)_2$ (81.3 mg, 0.089 mmol) was suspended in 20 mL of THF, to which were added HC=C-4-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (52.5 mg, 0.357 mmol) and NEt<sub>3</sub> (5 mL). The solution changed from dark green to red immediately upon the addition of the alkyne. After the mixture was stirred overnight under argon, the solution was filtered through a plug of deactivated silica, which was rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under reduced pressure, and the resulting solid was triturated with hexanes to yield pure **2a** as a deep red material. Yield: 91 mg (94% based on Ru). Data for 2a are as follows.  $R_f 0.65$ . Anal. Found (calcd) for C52H52N10O4Ru2·C6H14·0.5CH2Cl2: C, 58.22 (57.98); H, 5.53 (5.57); N, 11.40 (11.56). MS-FAB (m/e, based on <sup>101</sup>Ru): 1084 [MH<sup>+</sup>]. UV-vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 859 (1820), 528 (24 100). IR (cm<sup>-1</sup>):  $\nu$ (C=C), 2060 (m). Electrochemistry ( $E_{1/2}$ , V;  $\Delta E_{\rm p}$ , V;  $i_{\rm backward}/i_{\rm forward}$ ): A, 0.69, 0.069, 0.99; B, -0.83, 0.073, 0.92, C, -1.29, 0.116, 0.79. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 8.03 ( $J_{\text{HH}} =$ 9 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.48-7.38 (12H, Ph), 7.12 (J<sub>HH</sub> = 9 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.01-6.94 (8H, Ph), 3.24 (24H, NMe).

**[Ru<sub>2</sub>(***m***-MeO***DMBA***)<sub>4</sub>(<b>C**≡**C**-4·**C**<sub>6</sub>**H**<sub>4</sub>**NO**<sub>2</sub>)<sub>2</sub>] (**2b**). The synthesis is similar to that of **2a**, with Ru<sub>2</sub>(*DMBA*)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> being replaced by Ru<sub>2</sub>(MeO-*m*-DMBA)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>. Yield: 74%. Data for **2b** are as follows. *R<sub>f</sub>*0.30. Anal. Found (calcd) for C<sub>56</sub>H<sub>60</sub>N<sub>10</sub>O<sub>8</sub>-Ru<sub>2</sub>: C, 55.65 (55.90); H, 5.22 (5.03); N, 11.13 (11.64). MS-FAB (*m*/*e*, based on <sup>101</sup>Ru): 1204 [MH<sup>+</sup>]. UV−vis (*λ*<sub>max</sub>, nm (*ε*, M<sup>-1</sup> cm<sup>-1</sup>)): 855 (2500), 523 (34 600). IR (cm<sup>-1</sup>): *ν*(≡CH), 2062 (m). Electrochemistry (*E*<sub>1/2</sub>, V; Δ*E*<sub>p</sub>, V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.70, 0.067, 0.93; B, −0.86, 0.074, 0.68, C, −1.29, 0.124, 0.64. <sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ*): 8.03 (*J*<sub>HH</sub> = 9 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.80−7.20 (4H, Ph), 7.12 (*J*<sub>HH</sub> = 9 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.00−6.40 (12H, Ph), 3.81 (12H, OMe), 3.26 (24H, NMe).

**[Ru<sub>2</sub>(***DMBA***)<sub>4</sub>(C≡C-4-C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] (3a).** The synthesis is similar to that of **2a**, with 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C≡CH being replaced by 4-CN-C<sub>6</sub>H<sub>4</sub>C≡CH. Yield: 83%. Data for **3a** are as follows. *R*<sub>7</sub>0.61. Anal. Found (calcd) for C<sub>54</sub>H<sub>52</sub>N<sub>10</sub>Ru<sub>2</sub>: C, 61.09 (61.18); H, 5.05 (5.36); N, 12.16 (12.41). MS-FAB (*m/e*, based on <sup>101</sup>Ru): 1044 [MH<sup>+</sup>]. UV−vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 869 (2900), 504 (18 800). IR (cm<sup>-1</sup>):  $\nu$ (C≡C), 2070 (m). Electrochemistry (*E*<sub>1/2</sub>, V;  $\Delta E_p$ , V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.65, 0.065, 0.89; B, −0.92, 0.060, 0.93. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.50−7.35 (16H, C<sub>6</sub>H<sub>4</sub> + Ph), 7.10 (*J*<sub>HH</sub> = 8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.00−6.95 (8H, Ph), 3.25 (24H, NMe).

**[Ru<sub>2</sub>(***m***-MeO***DMBA***)<sub>4</sub>(C≡C-4-C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] (3b)**. The synthesis is similar to that of **2b**, with PhC≡CH being replaced by 4-CN-C<sub>6</sub>H<sub>4</sub>C≡CH. Yield: 54%. Data for **3b** are as follows. *R*<sub>7</sub>0.25. Anal. Found (calcd) for C<sub>58</sub>H<sub>60</sub>N<sub>10</sub>O<sub>4</sub>Ru<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>(**3b**·CH<sub>2</sub>-Cl<sub>2</sub>): C, 56.98 (56.73); H, 5.01 (4.97); N, 11.12 (11.22). MS-FAB (*m*/*e*, based on <sup>101</sup>Ru): 1162 [(M − H)<sup>+</sup>]. UV−vis (*λ*<sub>max</sub>, nm (*ε*, M<sup>-1</sup> cm<sup>-1</sup>)): 860 (2600), 479 (17 700). IR (cm<sup>-1</sup>): *ν*(C≡ C), 2066 (w). Electrochemistry (*E*<sub>1/2</sub>, V; *ΔE*<sub>p</sub>, V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.66, 0.065, 0.87; B, −0.94, 0.062, 0.98. <sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ*): 7.41 (*J*<sub>HH</sub> = 8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.40−7.30 (4H, Ph), 7.05 (*J*<sub>HH</sub> = 8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.00−6.45 (12H, Ph), 3.81 (12H, OMe), 3.25 (24H, NMe).

**[Ru<sub>2</sub>(***DMBA***)<sub>4</sub>(C≡C-3-C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] (4a).** The synthesis is similar to that of **2a** with 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>C≡CH being replaced by 3-CN-C<sub>6</sub>H<sub>4</sub>C≡CH. Yield: 64%. Data for **4a** are as follows.  $R_{f}$ 0.63. Anal. Found (calcd) for C<sub>52</sub>H<sub>52</sub>N<sub>10</sub>Ru<sub>2</sub>: C, 61.53 (62.17);

H, 5.01 (5.02); N, 12.98 (13.43). MS-FAB (*m/e*, based on <sup>101</sup>Ru): 1046 [(MH)<sup>+</sup>]. UV-vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 860 (2600), 502 (13 700). IR (cm<sup>-1</sup>):  $\nu$ (C=C), 2073 (m);  $\nu$ (C=N), 2226 (w). Electrochemistry ( $E_{1/2}$ , V;  $\Delta E_p$ , V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.63, 0.063, 0.89; B, -0.98, 0.064, 0.93. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.80-6.90 (28H, C<sub>6</sub>H<sub>4</sub> + Ph), 3.25 (24H, NMe).

**[Ru<sub>2</sub>(***m***-MeODMBA)<sub>4</sub>(C≡C-3-C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] (4b).** The synthesis is similar to that of **1b**, with PhC≡CH being replaced by 3-CN-C<sub>6</sub>H<sub>4</sub>C≡CH. Yield: 64%. Data for **4b** are as follows. *R*<sub>*t*</sub>0.26. Anal. Found (calcd) for C<sub>58</sub>H<sub>60</sub>N<sub>10</sub>O<sub>4</sub>Ru<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>(**4b**·CH<sub>2</sub>-Cl<sub>2</sub>): C, 56.68 (56.73); H, 5.03 (4.97); N, 11.03 (11.22). MS-FAB (*m*/*e*, based on <sup>101</sup>Ru): 1165 [(MH)<sup>+</sup>]. UV−vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 857 (2600), 500 (14 100). IR (cm<sup>-1</sup>):  $\nu$ (C≡C), 2071 (m);  $\nu$ (C≡N), 2226 (w). Electrochemistry (*E*<sub>1/2</sub>, V;  $\Delta E_p$ , V; *i*<sub>backward</sub>/*i*<sub>forward</sub>): A, 0.63, 0.066, 0.91; B, −0.98, 0.068, 0.99. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.40−6.45 (4H, C<sub>6</sub>H<sub>4</sub> + Ph), 3.80 (12H, OMe), 3.26 (24H, NMe).

[Ru<sub>2</sub>(DMBA)<sub>4</sub>(C=C-4-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>] (5a). Ru<sub>2</sub>(DMBA)<sub>4</sub>Cl<sub>2</sub> (101 mg, 0.117 mmol) was dissolved in 20 mL of THF, to which was added LiC=C-4-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> (0.45 mmol) prepared in situ from  $HC \equiv C-4-C_6H_4NMe_2$  and *n*-BuLi. The solution changed from brown to dark red immediately upon the addition of the lithiated alkyne. After the mixture was stirred overnight under argon, the solvent was removed under reduced pressure. The residue was placed on a sintered funnel and washed with cold hexanes to give pure 5a as a purple material. Yield: 40 mg (32%). Data for **5a** are as follows.  $R_f$  0.66. Anal. Found (calcd) for C<sub>56</sub>H<sub>64</sub>N<sub>10</sub>Ru<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O (5a·2CH<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O): C, 54.55 (54.93); H, 5.25 (5.52); N, 10.87 (11.05). MS-FAB (m/e, based on <sup>101</sup>Ru): 1080 [MH<sup>+</sup>]. UV–vis ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 890 (2100), 511 (12 700). IR (cm<sup>-1</sup>): v(C≡C), 2078 (m). Electrochemistry ( $E_{1/2}$ , V;  $\Delta E_p$ , V;  $i_{backward}/i_{forward}$ ): A, 0.31, 0.066, 0.95; B, -1.17, 0.070, 0.41. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.45-7.33 (12H, Ph), 7.00–6.95 (12H,  $C_6H_4$  + Ph), 6.59 ( $J_{HH}$  = 9 Hz, 4H,  $C_6H_4$ ), 3.28 (24H, NMe), 2.88 (12H, NMe2).

[Ru<sub>2</sub>(*m*-MeODMBA)<sub>4</sub>(C=C-4-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>] (5b). Ru<sub>2</sub>(*m*-MeODMBA)<sub>4</sub>Cl<sub>2</sub> (208 mg, 0.212 mmol) was dissolved in 25 mL of THF, to which was added LiC=C-4-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> (0.854 mmol) prepared in situ from  $HC \equiv C-4-C_6H_4NMe_2$  and *n*-BuLi. The solution changed from brown to dark red immediately upon the addition of the lithiated alkyne. After the mixture was stirred for 1 h under argon, the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column deactivated by 10% Et<sub>3</sub>N in hexanes and eluted with ethyl acetate-hexanes-Et<sub>3</sub>N (30/70/5, v/v), giving pure 5b as a deep red material. Yield: 86 mg (34%). The reduced yield is due to slow decomposition of **5b** on silica. Data for **5b** are as follows. Rf 0.15. Anal. Found (calcd) for C<sub>66.5</sub>H<sub>87</sub>N<sub>10</sub>O<sub>4</sub>ClRu<sub>2</sub> (5b·C<sub>6</sub>H<sub>14</sub>·<sup>1</sup>/<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>): C, 61.07 (60.14); H, 6.74 (6.60); N, 10.07 (10.55). MS-FAB (m/e, based on <sup>101</sup>Ru): 1200 [MH<sup>+</sup>]. UV-vis  $(\lambda_{\text{max}}, \text{ nm } (\epsilon, \text{ M}^{-1} \text{ cm}^{-1}))$ : 851 (1800), 504 (9800). IR (cm<sup>-1</sup>):  $\nu$ (C=C), 2075 (w). Electrochemistry ( $E_{1/2}$ , V;  $\Delta E_p$ , V;  $i_{\text{backward}}$ *i*<sub>forward</sub>): A, 0.29, 0.069, 0.88; B, -1.21, 0.00, 0.41. <sup>1</sup>H NMR  $(\text{CDCl}_3, \delta)$ : 7.41  $(J_{\text{HH}} = 8 \text{ Hz}, 4\text{H}, C_6\text{H}_4)$ , 7.40–7.30 (4H, Ph), 7.05 ( $J_{\rm HH} = 8$  Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.00–6.40 (12H, Ph), 3.79 (12H, OMe), 3.28 (24H, NMe), 2.86 (12H, NMe2).

X-ray Data Collection, Processing, and Structure Analysis and Refinement. Single crystals of both compounds 1b and 2a were grown via slow evaporation of the fractions from column purification. The X-ray intensity data were measured at 300 K on a Bruker SMART1000 CCD-based X-ray diffractometer system using Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å). Crystals of dimension  $0.58 \times 0.46 \times 0.23$  mm<sup>3</sup> (1b) and  $0.39 \times 0.13 \times 0.06$  mm<sup>3</sup> (2a) were cemented onto a quartz fiber with epoxy glue for X-ray crystallographic analysis. Data were measured using  $\omega$  scans of  $0.3^{\circ}$  per frame such that a hemisphere (1271 frames) was collected. No decay was indicated for either data set by the re-collection of the first 50 frames at the end of each data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm,<sup>40</sup> which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS, supplied by George Sheldrick.

The structures of both **1b** and **2a** were solved and refined using the Bruker SHELXTL (version 5.1) software package in the space group  $C2/c.^{41-43}$  Positions of all non-hydrogen atoms of diruthenium moieties were revealed by direct methods. In each case, the asymmetric unit contains half of the diruthenium molecule, which is related to the other half via a crystallographic 2-fold axis orthogonal to and bisecting the Ru–Ru' vector. One of the phenyl rings of the *DMBA* ligand in **1b** was severely disordered and consequently refined as a rigid hexagon. With all non-hydrogen atoms being anisotropic and all hydrogen atoms in calculated position and riding mode, both structures were refined to convergence by least-squares methods 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 3.

**Acknowledgment.** We thank both the University of Miami and the National Science Foundation (Grant

 (41) SHELXTL 5.03 (Windows NT Version), Program Library for Structure Solution and Molecular Graphics; Bruker-AXS Inc., 1998.
 (42) Sheldrick, G. M. SHELXS-90, Program for the Solution of

(42) Sheldrick, G. M. SHELXS-90, Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1990.

(43) Sheldrick, G. M. SHELXL-93, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993.

Table 3. Crystal Data for Compounds 1b and 2a

	1b	$2a \cdot 2CH_2Cl_2$
formula	$C_{56}H_{62}N_8O_4Ru_2$	C <sub>54</sub> H <sub>56</sub> Cl <sub>4</sub> N <sub>10</sub> O <sub>4</sub> Ru <sub>2</sub>
fw	1113.3	1253.0
space group	C2/c	C2/c
a, Å	19.845(2)	21.366(3)
<i>b,</i> Å	15.222(2)	18.020(3)
<i>c</i> , Å	19.967(2)	16.741(3)
$\beta$ , deg	116.806(3)	115.581(2)
<i>V</i> , Å <sup>3</sup>	5383.6(9)	5814(2)
Ζ	4	4
$\rho_{\rm calcd}$ , g cm <sup>-3</sup>	1.374	1.432
$\mu$ , mm <sup>-1</sup>	0.613	0.755
T, °C	27	27
no. of rflns collected	13 691	21 507
no. of indep rflns	4740 (R(int) =	5107 (R(int) =
-	0.0763)	0.1162)
final R indices	R1 = 0.065,	R1 = 0.064,
$(I > 2\sigma(I))$	wR2 = 0.186	wR2 = 0.1372

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**Supporting Information Available:** Tables of X-ray crystallographic data and figures giving additional ORTEP views for the structure determination of compounds **1b** and **2a**; X-ray data are also available as electronic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030401Y

<sup>(40)</sup> SAINT V 6.035 Software for the CCD Detector System; Bruker-AXS Inc., 1999.