## Ruthenium Acetylide Complexes Supported by Trithiacyclononane and Aromatic Diimine: Structural, Spectroscopic, and Theoretical Studies

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Ruthenium(II)-acetylide complexes bearing 1,4,7-trithiacyclononane ([9]aneS3) and 1,10-phenanthroline (phen) have been prepared. The molecular structure of [([9]aneS3)(phen)Ru-C=CPh]<sup>+</sup> shows that the trans influence of the acetylide ligand is only slightly weaker than that of isocyanide and is stronger than that of chloride. The Ru(II/III) oxidation waves for the complexes are irreversible, with  $E_{pa} =$ 0.30-0.39 V vs Cp<sub>2</sub>Fe<sup>+/0</sup>. The lowest-energy dipole-allowed absorptions for the complexes ( $\lambda_{max} =$ 441-466 nm,  $\varepsilon_{max} = (4-5) \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) are assigned as  $d_{\pi}(Ru^{II}) \rightarrow \pi^*$ (phen) metal-to-ligand charge transfer (MLCT) transitions. The complexes are emissive in glassy MeOH/EtOH at 77 K upon photoexcitation and give emission at  $\lambda_{max} = 606-623$  nm. Density functional theory (DFT) calculations and charge decomposition analysis (CDA) have been used to probe the Ru–C bonding interaction in these complexes, and the results are compared with their isocyanide congeners. The rotational barrier for the phenyl ring in [([9]aneS3)(phen)Ru–C=CPh]<sup>+</sup> is calculated to be 0.53 kcal mol<sup>-1</sup>, suggesting that the Ru–C  $\pi$ -interaction in these complexes is weak and cannot lock the rotational motion of the acetylide ligand effectively.

Ruthenium(II) complexes containing aromatic diimine ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) represent an important class of luminophore based on transition metal complexes. They exhibit rich photophysical and photochemical properties, which originate from the triplet  $[d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(aromatic diimine)]$ metal-to-ligand charge transfer (<sup>3</sup>MLCT) excited state. The use of these complexes in photochemistry,<sup>1</sup> electron transfer reactions,<sup>2</sup> luminescent sensing,<sup>3</sup> light-emitting devices,<sup>4</sup> and

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photosensitizers<sup>5</sup> has attracted much attention, and the pursuit of  $[Ru(bpy)_3]^{2+}$ -related complexes exhibiting desirable photophysical properties continues unabated.<sup>6</sup>

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For ruthenium(II)-aromatic diimine complexes with general formula [Ru(diimine)<sub>x</sub>(L)<sub>y</sub>]<sup>n+</sup>, their photophysical properties can be fine-tuned by controlling the energy level of the  $\pi^*$ (diimine) orbital via modifying the degree of conjugation in the diimine ligands. An alternative approach would be tuning the energy of the d<sub> $\pi$ </sub>(Ru<sup>II</sup>) level via manipulating the Ru-L interaction. We previously probed the metal-carbon bonding interaction in [(Me<sub>3</sub>Tacn)(phen)Ru=C(OMe)R]<sup>2+</sup>, [(Me<sub>3</sub>Tacn)(phen)Ru=C=C=CR<sub>2</sub>]<sup>2+</sup>, [(Me<sub>3</sub>Tacn)(phen)Ru-(CNR)]<sup>2+</sup>, and [([9]aneS3)(phen)Ru(CNR)]<sup>2+</sup> (Me<sub>3</sub>Tacn = 1,4,7-triimethyl-1,4,7-triazacyclononane; [9]aneS3=1,4,7-triimethyl-1,4,7-triazacyclononane; [9]aneS3=1,4,7-triimethyl-1,4,7-triimethyl-1,4,7-triazacyclononane; [9]aneS3=

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**Figure 1.** Perspective view of the cation in  $1(PF_6)$  (thermal ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (deg): Ru(1)-C(1) 2.028(3), C(1)-C(2) 1.200(4), C(2)-C(3) 1.440(4), mean Ru(1)-N<sub>phen</sub> 2.089, mean Ru(1)-S<sub>[9]aneS3-cis</sub> 2.3018, Ru(1)-S<sub>[9]aneS3-trans</sub> 2.3553(7), Ru-(1)-C(1)-C(2) 175.0(2), C(1)-C(2)-C(3) 176.0(3).



thiacyclononane)<sup>7,8</sup> and demonstrated that manipulating the Ru–C bonding interaction can effectively modulate the photophysical properties of the [Ru(diimine)] luminophore. As an extension of this research, we now present the preparation and electrochemical, spectroscopic, and theoretical investigations for a series of luminescent ruthenium(II)–arylacetylide complexes bearing [9]aneS3 and phen.

## **Results and Discussion**

Acetylide complexes [([9]aneS3)(phen)Ru-C=CR]<sup>+</sup> (1-3) were prepared in ca. 80% yields by reacting HC≡CR with [([9]aneS3)(phen)RuCl]<sup>+</sup> in the presence of KOH in refluxing methanol (Scheme 1). Slow diffusion of Et<sub>2</sub>O into an acetone or acetonitrile solution yielded analytically pure bright yellow or orange crystalline solids, which are sufficiently stable to be handled in air under ambient conditions in solution and solid forms. For example, the UV-visible spectrum of 1 remains unchanged in CH<sub>3</sub>CN after 1 week. Complexes 1-3 feature four sets of <sup>1</sup>H NMR signals for the phen ligands and three sets of <sup>13</sup>C signals for the [9]aneS3 ligands, signifying that complexes 1-3 possess a pseudo plane of symmetry in solution on the NMR time scale at room temperature. This is consistent with the finding that the rotational barrier for the phenylacetylide ligand in 1 is low (calculated to be 0.53 kcal mol<sup>-1</sup>, see discussion below). The  $\nu(C \equiv C)$  stretching frequencies at

Table 1. Electrochemical Data for Complexes 1–3(PF<sub>6</sub>), [([9]aneS3)(phen)RuCl](PF<sub>6</sub>), and [([9]aneS3)(phen)Ru(t-BuNC)](PF<sub>6</sub>)<sub>2</sub><sup>a</sup>

complex	$E_{1/2}{}^{b}/V$ vs Cp <sub>2</sub> Fe <sup>+/0</sup>			
1 2 3 [([9]aneS3)(phen)RuCl] <sup>+</sup> [([9]aneS3)(phen)Ru( <i>t</i> -BuNC)] <sup>2+</sup>	-1.92 -1.92 -1.92 $-1.92^{c}$ $-1.76^{c}$	$\begin{array}{c} 0.39^{c} \\ 0.37^{c} \\ 0.30^{c} \\ 0.74 \\ 1.50 \end{array}$		

<sup>*a*</sup> Supporting electrolyte: 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>3</sub>CN. <sup>*b*</sup>  $E_{1/2} = (E_{pc} + E_{pa})/2$  at 298 K for reversible couples. <sup>*c*</sup> Irreversible; the recorded potential is the peak cathodic or anodic potential at scan rate of 100 mV s<sup>-1</sup>.

Table 2. UV-Visible Absorption and Emission Data for Complexes 1-3

complex	$\lambda_{\rm max}/{\rm nm}~(\varepsilon_{\rm max}/{\rm dm}^3~{\rm mol}^{-1}~{\rm cm}^{-1})^a$	$\lambda_{\rm em}/{\rm nm}^b$
1	267 (36 830), 297 (sh, 16 040), 441 (3970) 268 (41 170), 289 (ch, 25 510), 466 (4260)	606 617
3	268 (45 610), 289 (sh, 23 510), 460 (4200) 268 (45 610), 288 (sh, 28 790), 466 (4550)	623

<sup>*a*</sup>Solvent = CH<sub>3</sub>CN; 298 K. <sup>*b*</sup>Solvent = MeOH/EtOH (1:4 v/v); 77 K;  $\lambda_{ex} = 470$  nm.

2081-2085 cm<sup>-1</sup> for 1-3 are comparable to reported values for Ru(II)-acetylide complexes.<sup>9</sup>

The molecular structure of  $1(PF_6)$  was determined by X-ray crystallography (Figure 1). The Ru atom adopts a distorted octahedral geometry, with the [9]aneS3 facially coordinating to it. The Ru–C distance in 1 (2.028(3) Å) is similar to those in  $[Ru(C=CH)(cym)(phen)]^+$  (2.022(9) Å),<sup>10</sup>  $[Ru(Me_2bipy)(PPh_3)_2Cl(C \equiv CBu^t)]$  (2.053(5) Å),<sup>11</sup> and  $[Ru(tpy)(bpy)(C \equiv CAr)]^+$  (2.025(7)-2.025(9) Å),<sup>12</sup> and it is longer than that in the isocyanide congeners [([9]aneS3)- $(\text{phen})\text{Ru}(t-\text{BuNC})|^{2+}$  (1.984(3) Å)<sup>8</sup> by 0.044 Å. Interestingly, it is noted that within the  $[([9]aneS3)(phen)RuL]^{n+}$ series the structural trans influence of acetylide is only slightly weaker than that of isocyanide and is stronger than that of chloride: Ru-S<sub>[9]aneS3-trans</sub> distance in [([9]aneS3)- $(\text{phen})\text{Ru}(t\text{-BuNC})]^{2+}$  (2.3723(7) Å)<sup>8</sup>  $\approx$  1 (2.3553(7) Å) > [([9]aneS3)(phen)RuCl]<sup>+</sup> (2.272(2) Å).<sup>13</sup> This is consistent with the findings for trans-[PtL(Cl)(PR<sub>3</sub>)<sub>2</sub>] and AuL(PPh<sub>3</sub>), which indicate that the trans influence of acetylide ligands is significantly greater than that of chloride.9

Cyclic voltammetry was used to examine the electrochemistry of complexes 1–3, [([9]aneS3)(phen)RuCl]<sup>+</sup>, and [([9]aneS3)(phen)Ru(*t*-BuNC)]<sup>2+</sup> (Table 1; all values vs Cp<sub>2</sub>Fe<sup>+/0</sup>). Complexes 1–3 show a reversible couple at  $E_{1/2} = -1.92$  V and an irreversible wave at  $E_{pa} = 0.30$  to 0.39 V (scan rate = 100 mV s<sup>-1</sup>, 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>3</sub>CN as supporting electrolyte). The reduction couples for 1–3 are assigned as reduction of the phen ligands, whereas the oxidation waves are assigned as metal-centered Ru(II/III) oxidations. The span in the  $E_{pa}$  values for the Ru(II/III) oxidation from R = Ph (1) to C<sub>6</sub>H<sub>4</sub>OMe-4 (3) is 90 mV, suggesting that the highest-occupied molecular orbitals (HOMOs) of 1–3 may contain a contribution from the acetylide ligand. The more positive  $E_{1/2}$  values of the Ru(II/III) redox couple for

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Figure 2. Absorption (solid line; CH<sub>3</sub>CN; 298 K) and emission (dash line; MeOH/EtOH, 1:4, v/v; 77 K,  $\lambda_{ex} = 470$  nm) spectra of 1.

 $[([9]aneS3)(phen)RuCl]^+$  and  $[([9]aneS3)(phen)Ru(t-BuNC)]^{2+}$ compared with 1-3 can be rationalized by the fact that (1)  $Cl^{-}$  has a higher electronegativity than  $^{-}C \equiv CR$ , and (2) the electronic charge in the isocyanide complex (+2) is higher than those in acetylide complexes (+1).

The UV-visible spectral data for 1-3 are summarized in Table 2, and the absorption spectrum of 1 is depicted in Figure 2. All complexes exhibit intense high-energy absorption at  $\lambda_{\text{max}} \leq 350 \text{ nm}$  ( $\varepsilon_{\text{max}} \geq 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and moderately intense bands at  $\lambda_{\text{max}} = 441-466 \text{ nm}$  $(\varepsilon_{\text{max}} = (4-5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$  as their lowest-energy electronic transition. In the literature, ruthenium(II) complexes bearing aromatic diimine ligands such as  $[Ru(bpy)_3]^{2+}$  and  $[Ru(phen)_3]^{2+}$  feature two types of characteristic absorption bands: highly intense absorptions in the UV region, which are attributed to the diimine intraligand  $\pi \rightarrow \pi^*$  transitions, and moderately intense absorptions in the visible region, which are ascribed to  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(diimine)$  metal-to-ligand charge transfer (MLCT) transitions.<sup>1d</sup> In this work, the lowest-energy absorptions at  $\lambda_{\text{max}} = 441-466$  nm for 1-3 are assigned as  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(phen)$  metal-to-ligand charge transfer (MLCT) transitions. Assigning the lowest-energy absorptions for 1-3 to  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(C \equiv CR)$  MLCT transitions is unreasonable because the  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(C \equiv CR)$  MLCT transition for  $trans-[Ru(16-TMC)(C=CPh)_2]$  (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) occurs at 397 nm.14 In any case, the  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(C \equiv CR)$  MLCT transitions in 1-3 should appear at a higher energy than for derivates supported by 16-TMC because 16-TMC is a stronger  $\sigma$ -donor and weaker  $\pi$ -acceptor than the ([9]andS3)(phen) ligand set. It is noted that the  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(phen)$  MLCT transitions for 1-3 are not Gaussian in appearance, which is likely due to the presence of a strong (unresolved) vibronic sideband. A similar non-Gaussian  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(phen)$  MLCT transition profile has been observed in  $[(Me_3Tacn)(phen)Ru=C(OMe)R]^{2+}$ ,  $[(Me_3Tacn)(phen)Ru(CH_3CN)]^{2+}, [(Me_3Tacn)(phen)Ru(t [BuNC)]^{2+}$ , and  $[([9]aneS3)(phen)Ru(t-BuNC)]^{2+}$ .<sup>7,8</sup> The d<sub> $\pi$ </sub>- $(Ru^{II}) \rightarrow \pi^*$  (phen) MLCT transition for 1-3 is found to be redshifted compared with that of [([9]aneS3)(phen)Ru(t-Bu-NC)]<sup>2+</sup> ( $\lambda_{max} = 330 \text{ nm}$ ).<sup>8</sup> This suggests that the d<sub> $\pi$ </sub>(Ru<sup>II</sup>) level in the [([9]aneS3)(phen)Ru]<sup>2+</sup> core is destabilized to a greater extent by acetylide, revealing that acetylide is a greater  $\sigma$ -donor and weaker  $\pi$ -acceptor than isocyanide. It is also noted that the  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(phen)$  MLCT transition is sensitive to the change of substituent on the arylacetylide ligand: the  $\lambda_{max}$  of the MLCT transition is 441 nm for 1 (R = Ph) and 466 nm for 3 $(R = C_6H_4OMe-4)$ , consistent with the electrochemical finding

that the HOMOs of 1-3 may contain a contribution from the acetylide ligand. A similar argument was proposed in the photophysical studies of  $[(tpy)(bpy)Ru(C \equiv CR)]^+$  (tpy = 2,2':6',2"-terpyridine).<sup>12</sup> Importantly, our DFT calculations show that the acetylide ligand has a significant contribution in the HOMO of  $[([9]aneS3)(phen)Ru(C \equiv CR)]^+$  (see discussion below). Since complexes 1-3 are not highly emissive in solution form at room temperature, their emission properties were examined in glassy MeOH/EtOH (1:4, v/v; 77 K) solution. Excitation of 1-3 at  $\lambda = 470$  nm gives emission at  $\lambda_{max} =$ 606-623 nm (Figure 2, Table 2), which are red-shifted in energy compared with that of [([9]aneS3)(phen)Ru(*t*-Bu-NC)]<sup>2+</sup> ( $\lambda_{max} = 477 \text{ nm}$ ).<sup>8</sup> Since a similar red-shift is noted for the  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(phen)$  MLCT absorption energies, the emissions for [([9]aneS3)(phen)Ru(C≡CR)]<sup>+</sup> are ascribed as  $d_{\pi}(Ru^{II}) \rightarrow \pi^{*}(phen)^{3}MLCT$  in nature.

Density functional theory (DFT) calculations were performed on 1, 3, and  $[([9]aneS3)(phen)Ru(t-BuN=C)]^{2+}$  in order to provide more insight on the Ru-C bonding interaction in 1-3. The ground-state structures of these complexes were optimized at the DFT level (PBE1PBE).<sup>15</sup> The PBE1PBE functional was employed because it had been used to calculate ruthenium-acetylide,<sup>14</sup> -allenylidene,<sup>7</sup> -alkoxycarbene,<sup>7,16</sup> and isocyanide<sup>8</sup> systems, and satisfactory results had been obtained. Frequency calculations were also performed on the optimized structures. As no imaginary vibrational frequencies were encountered, the optimized stationary points were confirmed to be local minima. Detailed optimized structural data are summarized in the Supporting Information. Table 3 summarizes the compositions of the highest-occupied molecular orbitals (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs) for 1, 3, and [([9]aneS3)(phen)Ru(t-BuNC]<sup>2+</sup>. The calculated energies of the HOMOs are in the order  $3(-6.97 \text{ eV}) > 1(-7.39 \text{ eV}) \gg [([9]aneS3)(phen)Ru(t-$ BuNC)]<sup>2+</sup> (-12.19 eV), and those of the LUMOs are in the order 3 (-4.60 eV)  $\approx$  1 (-4.65 eV) > [([9]aneS3)(phen)Ru(t-BuNC)]<sup>2+</sup> (-7.61 eV). These parallel the experimental trends of the oxidation and reduction potentials for the corresponding complexes: (1) For oxidation waves,  $E_{pa} = 0.30$  V for **3**, 0.39 V for **1**, and  $E_{1/2} = 1.50$  V for [([9]aneS3)(phen)Ru(*t*-BuNC)]<sup>2+</sup>; (2) for reduction waves,  $E_{1/2} = -1.92$  V for 1 and 3, -1.76 V for [([9]aneS3)(phen)Ru(*t*-BuNC)]<sup>2+</sup>.

It is noted that the HOMOs and LUMOs of 1 and 3 are delocalized along the [Ru(C=CPh)] and [Ru(phen)] moieties, respectively. Moreover, the frontier orbitals of [([9]aneS3)(phen)RuL $|^{2+}$  are sensitive to the Ru-L bonding interactions: the HOMO-LUMO gaps for 1 and 3 are smaller than that for isocyanide-ligated complex [([9]aneS3)- $(\text{phen})\text{Ru}(t-\text{BuN}=C)]^{2+}$  by about 2 eV. Such sensitivity is important, as it provides a way to manipulate the photophysical properties of [([9]aneS3)(phen)RuL]<sup>2+</sup>, as demonstrated in the above photophysical studies. Charge decomposition analysis (CDA)<sup>17</sup> for the interaction between the closed-shell fragment [([9]aneS3)(phen)Ru]<sup>2+</sup> and <sup>−</sup>C≡CPh was performed (Table 4) and compared with the result for  $[([9]aneS3)(phen)Ru(t-BuN=C)]^{2+}$ . Since the residue terms  $(\Delta)$  are essentially zero, the Ru-acetylide complexes in this work can be discussed within the framework of the

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Table 3. HOMO and LUMO	Compositions of	Complexes 1	l, 3, and [([	9]aneS3)(phen	)Ru( <i>t</i> -BuN≡C)] <sup>2-</sup>
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	energy/eV	HOMO–LUMO gap/eV	% composition			
molecular orbital			Ru	C≡CR/t-BuN≡C	phen	[9]aneS3
HOMO	-7.387	2.737	25.38	65.15	3.59	5.88
HOMO	-6.969	2.372	15.93	77.07	2.72	4.28
LUMO HOMO LUMO	-4.597 -12.187 -7.612	4.576	9.69 47.94 9.03	1.54 5.32 1.18	83.99 31.72 85.02	4.78 15.02 4.77
	molecular orbital HOMO LUMO HOMO LUMO LUMO	molecular orbital         energy/eV           HOMO         -7.387           LUMO         -4.650           HOMO         -6.969           LUMO         -4.597           HOMO         -12.187           LUMO         -7.612	molecular orbital         HOMO-LUMO energy/eV         HOMO-LUMO gap/eV           HOMO         -7.387         2.737           LUMO         -4.650         2.372           HOMO         -6.969         2.372           LUMO         -4.597         4.576           HOMO         -12.187         4.576           LUMO         -7.612         4.576	molecular orbital         HOMO-LUMO energy/eV         Ru           HOMO         -7.387         2.737         25.38           LUMO         -4.650         9.54           HOMO         -6.969         2.372         15.93           LUMO         -4.597         9.69           HOMO         -12.187         4.576         47.94           LUMO         -7.612         9.03	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

Table 4. Charge Decomposition Analysis (CDA) for the [([9]aneS3)(phen)Ru]<sup>2+</sup>-L Interaction

L	$L \rightarrow M$ donation ( <i>d</i> )	$M \rightarrow L$ back-donation (b)	b/d	repulsion $(r)$	residue ( $\Delta$ )
<sup>-</sup> C=CPh (1)	1.774	0.102	0.057	-0.609	-0.038
<sup>−</sup> C≡CC <sub>6</sub> H <sub>4</sub> OMe-4 ( <b>3</b> )	1.793	0.096	0.054	-0.604	-0.038
t-BuN≡C	1.266	0.309	0.244	-0.637	-0.010



Figure 3. Optimized structure and HOMO and LUMO surfaces for complex 1 using the PBE1PBE functional (hydrogens are omitted for clarity, surface isovalue = 0.04 au).

Dewar–Chatt–Duncanson donor–acceptor model, as in the case for model complexes *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(C≡CAr)<sub>2</sub>] and *trans*-[Ru(PH<sub>3</sub>)<sub>4</sub>(C≡CAr)<sub>2</sub>].<sup>14</sup> The ratio of the values for [([9]aneS3)(phen)Ru]<sup>2+</sup> → C≡CPh back-donation (*b*) and C≡CPh → [([9]aneS3)(phen)Ru]<sup>2+</sup> donation (*d*), *b/d*, are 0.054–0.057, suggesting that the acetylide ligand is overall an electron donor (*b/d*≪1). The smaller *b/d* ratio for 1 and 3 compared with [([9]aneS3)(phen)Ru(*t*-BuN≡C)]<sup>2+</sup> (*b/d* = 0.244) is reasonable since acetylide is charged, whereas isocyanide is neutral. This is also consistent with the above spectroscopic investigation suggesting that acetylide is a greater *σ*-donor and weaker *π*-acceptor than isocyanide.

Defining the direction along the Ru-C as the z-axis and the Ru–N as the x- and y-directions in the fully optimized gas-phase structure for 1, it is noted that the plane of the phenyl ring is not coplanar with the xz- or yz-planes: the dihedral angle between the  $N_1{-}Ru{-}C_{\gamma}$  and  $Ru{-}C_{\gamma}{-}C'$ planes as defined in Figure 4 is  $-52.6^{\circ}$ . Moreover, the  $\pi$ system of the  $^{-}C = CPh$  ligand is found to be interacting with a  $d_{xz} + d_{yz}$  hybridized orbital of Ru(II) (Figure 3). A relaxed potential energy surface scan as a function of the dihedral angle for 1 was performed in order to gain further insight into the conformational landscape. In the relaxed potential energy surface scan calculations, the dihedral angle was rotated through 180° with 10° resolution and with geometry optimization at each step (rotation through 360° is not necessary since the  $^{-}C \equiv CPh$  has a  $C_{2v}$  symmetry). Figure 4 depicts the plot of energy as a function of the dihedral angle, and the rotational barrier for 1 is found to be  $0.53 \text{ kcal mol}^{-1}$ . It is noted that (1) points with the dihedral angles of ca. 0° and 90° in the plot are not local minima and (2) the energy of 1



**Figure 4.** Plot of energy and shortest  $H_{Ph} \cdots H_{[9]aneS3}$  distance as a function of dihedral angle between the  $Ru-C_{\gamma}-O$  and  $N(1)-Ru-C_{\gamma}$  planes for complex **1** (calculated in steps of 10°; energies are relative to the lowest-energy optimized structure).

increases with decreasing  $H_{Ph} \cdots H_{[9]aneS3}$  distance (the shortest). These reflect that the Ru–C  $\pi$ -interaction in 1 is not strong enough to lock the rotational motion of the acetylide, and the rotational barrier for 1 is dominated by intramolecular steric factors.

In conclusion, we have demonstrated that the  $d_{\pi}(Ru^{II}) \rightarrow \pi^*(\text{phen})$  MLCT absorption and emission energies for [([9]-aneS3)(phen)Ru(C=CR)]<sup>+</sup> are significantly red-shifted compared with their isocyanide analogue. This suggests that manipulation of Ru–C interactions is an effective way to modulate the photophysical properties of the [([9]aneS3)-(phen)RuL]<sup>n+</sup> luminophore (L=carbon-rich organic moiety). The Ru–C bonding interaction in complexes 1–3 has also been probed by structural and theoretical methods, which reveals that the Ru–C  $\pi$ -interaction is weak and cannot lock the rotational motion of the acetylide ligand effectively.

## **Experimental Section**

**General Procedures.** All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents were used as received, and solvents were purified by standard methods. [([9]aneS3)(phen)RuCl](PF<sub>6</sub>)

was prepared according to literature procedures.<sup>13</sup> <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Bruker 400 DRX FT-NMR spectrometers. Peak positions were calibrated with solvent residue peaks as internal standard. Electrospray mass spectrometry was performed on a PE-SCIEX API 3000 triple quadrupole mass spectrometer. Infrared spectra were recorded as KBr plates on a Perkin-Elmer FTIR-1600 spectrophotometer. UV-visible spectra were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer interfaced with an IBM-compatible PC. Elemental analyses were done on an Elementar Vario EL analyzer. Cyclic voltammetry was performed with a CH Instrument model 600C series electrochemical analyzer/workstation. The glassy-carbon electrode was polished with 0.05  $\mu$ m alumina on a microcloth and rinsed with acetonitrile before use. An Ag/AgNO<sub>3</sub> (0.1 M in CH<sub>3</sub>CN) electrode was used as reference electrode. All solutions were degassed with argon before experiments.  $E_{1/2}$  values are the average of the cathodic and anodic peak potentials for the oxidative and reductive waves. The  $E_{1/2}$  value of the ferroce-nium/ferrocene couple (Cp<sub>2</sub>Fe<sup>+/0</sup>) measured in the same solution was used as an internal reference.

[([9]aneS3)(phen)RuC=CR](PF<sub>6</sub>), 1-3(PF<sub>6</sub>). Excess HC=CR (0.60 mmol) was added to a methanolic solution (30 mL) containing [([9]aneS3)(phen)RuCl](PF<sub>6</sub>) (0.20 mmol) and KOH (2 mmol). After refluxing for 12 h, the reaction mixture was cooled and precipitated by addition of a saturated methanolic solution of NH<sub>4</sub>PF<sub>6</sub> (5 mL). The orange precipitates were washed with diethyl ether and dried under vacuum. The solid was then recrystallized by slow diffusion of Et<sub>2</sub>O into an acetonitrile or acetone solution to give bright orange crystals.

**Complex 1(PF<sub>6</sub>) (R = Ph):.** yield 0.12 g, 85%. Anal. Calcd for  $C_{26}H_{25}S_3N_2RuPF_6$ : C, 44.07; H, 3.56; N, 3.96. Found: C, 44.01; H, 3.61; N, 4.13. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  2.50–2.56, 2.60–2.79, 2.94–3.10 (m, 12H, [9]aneS<sub>3</sub>); 6.79 (d, J = 7.2 Hz, 2H, Ph); 6.89–7.02 (m, 3H, Ph); 7.87 (dd, 2H, J = 8.0, 5.0 Hz, phen); 8.15 (s, 2H, phen); 8.60 (dd, 2H, J = 8.0, 1.2 Hz, phen); 9.25 (dd, 2H, J = 5.0, 1.2 Hz, phen). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  32.6, 32.9, 36.0 ([9]aneS<sub>3</sub>); 106.7, 116.9 (C<sub>\alpha</sub> and C<sub>\beta</sub>); 125.2, 126.5, 128.8, 131.5, 131.7, 137.1, 139.4, 148.0, 153.6 (Ph and phen). IR (KBr, cm<sup>-1</sup>):  $\nu_{C=C}$  = 2085,  $\nu_{P-F}$  = 837. ESI-MS: m/z 562 [M<sup>+</sup>].

**Complex 2(PF<sub>6</sub>) (R = C<sub>6</sub>H<sub>4</sub>Me-4):.** yield 0.13 g, 90%. Anal. Calcd for C<sub>27</sub>H<sub>27</sub>S<sub>3</sub>N<sub>2</sub>RuPF<sub>6</sub>: C, 44.88; H, 3.77; N, 3.88. Found: C, 44.67; H, 3.92; N, 3.80. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  2.15 (s, 3H, Me); 2.50–2.55, 2.60–2.78, 2.93–3.09 (m, 12H, [9]aneS<sub>3</sub>); 6.68 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 6.81 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 7.86 (dd, 2H, *J* = 8.0, 5.2 Hz, phen); 8.14 (s, 2H, phen); 8.60 (dd, 2H, *J* = 8.0, 1.2 Hz, phen); 9.24 (dd, 2H, *J* = 5.2, 1.2 Hz, phen). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  21.1 (Me); 32.6, 32.9, 36.0 ([9]aneS<sub>3</sub>); 106.5, 114.9 (C<sub>α</sub> and C<sub>β</sub>); 126.5, 126.7, 128.5, 129.4, 131.5, 131.6, 134.8, 137.1, 148.0, 153.5 (C<sub>6</sub>H<sub>4</sub> and phen). IR (KBr, cm<sup>-1</sup>):  $\nu_{C=C} = 2083$ ,  $\nu_{P-F} = 837$ . ESI-MS: *m/z* 576 [M<sup>+</sup>].

**Complex 3(PF<sub>6</sub>) (R = C<sub>6</sub>H<sub>4</sub>OMe-4):.** yield 0.13 g, 88%. Anal. Calcd for C<sub>27</sub>H<sub>27</sub>S<sub>3</sub>N<sub>2</sub>ORuPF<sub>6</sub>: C, 43.90; H, 3.69; N, 3.79. Found: C, 43.81; H, 3.58; N, 3.82. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  2.48–2.55, 2.59–2.78, 2.93–3.10 (m, 12H, [9]aneS<sub>3</sub>); 3.62 (s, 3H, OMe); 6.55 (d, J = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 6.73 (d, J = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 7.84 (dd, 2H, J = 8.4, 5.2 Hz, phen); 8.10 (s, 2H, phen); 8.57 (dd, 2H, J = 8.4, 1.2 Hz, phen); 9.24 (dd, 2H, J = 5.2, 1.2 Hz, phen). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  32.6, 32.9, 36.0 ([9]aneS<sub>3</sub>); 55.7 (OMe); 105.9, 113.0 (C<sub> $\alpha$ </sub> and C<sub> $\beta$ </sub>); 114.3, 122.2, 126.5, 128.5, 131.4, 132.8, 137.0, 148.0, 153.5, 157.7 (C<sub>6</sub>H<sub>4</sub> and phen). IR (KBr, cm<sup>-1</sup>):  $\nu_{C=C}$  = 2081,  $\nu_{P-F}$  = 839. ESI-MS: m/z 592 [M<sup>+</sup>].

X-ray Crystallography. X-ray diffraction data for  $1(PF_6)$  were collected on an Oxford Diffraction Gemini S Ultra X-ray singlecrystal diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. The data were processed using CrysAlis.<sup>18</sup> The structure was solved and refined using full-matrix least-squares based on  $F^2$  with the programs SHELXS-97 and SHELXL-97<sup>19</sup> within WinGX.<sup>20</sup> The Ru and many non-H atoms were located according to the direct methods. The positions of the other nonhydrogen atoms were found after successful refinement by fullmatrix least-squares using the program SHELXL-97. A highly disordered solvent molecule was found to be present in the crystal. Since the disordered solvent could not be modeled reasonably, the SQUEEZE technique in PLATON was applied.<sup>21</sup> A void volume of 222 Å<sup>3</sup> was calculated to contain 30 electrons per unit cell. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. The positions of H atoms were calculated based on a riding mode with thermal parameters equal to 1.2 times that of the associated C atoms.

**Computational Methodology.** DFT calculations were performed on complexes 1, 3, and [([9]aneS3)(phen)Ru(*t*-BuN $\equiv$ C))<sup>2+</sup>. Their electronic ground states were optimized without symmetry constraints using the density functional PBE1PBE, <sup>15</sup> which is a hybrid of the Perdew, Burke, and Ernzerhof exchange and correlation functional and 25% HF exchange. The Stuttgart small core relativistic effective core potentials were employed for Ru atoms with their accompanying basis sets.<sup>22</sup> The 6-31G\* basis set was employed for C, H, N, and S atoms.<sup>23</sup> Tight SCF convergence (10<sup>-8</sup> au) was used for all calculations. The nature of the Ru–C bonds was examined using charge decomposition analysis (CDA).<sup>17</sup> All the DFT calculations were performed using the Gaussian 03 program package (revision D.01)<sup>24</sup> while CDA was performed with the QMForge program.<sup>25</sup>

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Supporting Information Available: Crystallographic information files (CIF) for  $1(PF_6)$ ; optimized geometries for 1, 3, and  $[([9]aneS3)(phen)Ru(t-BuN=C)]^{2+}$ . This material is available free of charge via the Internet at http://pubs.acs.org.

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