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Article

One-Pot Synthesis of Symmetric and Asymmetric *p*-Quinone Ligands and Unprecedented Substituent Induced Reactivity in Their Dinuclear Ruthenium Complexes

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The compounds 2-[2-(trifluoromethyl)-anilino]-5-hydroxy-1,4-benzoquinone ($\mathbf{L^1}$), 2,5-di-[2-(trifluoromethyl)-anilino]-1,4-benzoquinone ($\mathbf{L^2}$), 2-[2-(methylthio)-anilino]-5-hydroxy-1,4-benzoquinone ($\mathbf{L^3}$), and 2,5-di-[2-(methylthio)-anilino]-1,4-benzoquinone ($\mathbf{L^4}$) were prepared in high yields by reacting 2,5-dihydroxy-1,4-benzoquinone with the corresponding amines in a one-pot synthesis in refluxing acetic acid. This straightforward and "green" synthesis delivers biologically relevant asymmetric *p*-quinones such as $\mathbf{L^1}$ and $\mathbf{L^3}$ in a rare, simple, one-step process. The proposed synthetic route is general and can be applied to generate a variety of such molecules with different substituents on the nitrogen atoms. Structural characterization of $\mathbf{L^2}$ and $\mathbf{L^4}$ shows electron delocalization across the "upper" and "lower" parts of the molecule, thus showing the importance of charge separated species in the proper description of such molecules. Reactions of these ligands with [Cl(η^6-Cym)Ru(μ-Cl)$_2$Ru(η^6-Cym)Cl] (Cym = *p*-Cymene = 1-isopropyl-4-methyl-benzene) in the presence of a base result in the formation of complexes [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^1}$)] (**1**), [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^2}$)] (**2**), [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^3}$)] (**3**), and [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^4}$)] (**4**). Structural characterization of **2** and **4** shows a rare *syn*-coordination of the chloride atoms. The SMe groups in **3** and **4** are not coordinated to the ruthenium center, and the bridging ligands thus function in a bis-bidentate form. Abstraction of the chloride atoms in these complexes with $AgClO_4$ in CH_3CN results in the expected formation of solvent substituted complexes [{(CH_3CN)(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^1}$)][ClO_4]$_2$ (**5**[ClO_4]$_2$) and [{(CH_3CN)(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^2}$)][ClO_4]$_2$ (**6**[ClO_4]$_2$) with the ligands where there are no additional donor atoms on the nitrogen substituents. The same chloride abstraction reaction in the cases of **3** and **4** leads to an unprecedented substituent induced release of the Cym ligand, resulting in complexes of the form [(CH_3CN)(η^6-Cym)Ru(μ-$\mathbf{L_{-2H}^3}$)Ru(CH_3CN)$_3$][ClO_4]$_2$ (**7**[ClO_4]$_2$) and [{(CH_3CN)$_3$Ru}$_2$(μ-$\mathbf{L_{-2H}^4}$)][ClO_4]$_2$ (**8**[ClO_4]$_2$), where the SMe groups are now coordinated to the metal center. In the case of complex **3**, which contains an asymmetric bridging ligand, Cym release is observed only at the side that contains an additional SMe donor, thus proving the necessity of such donor substituents for the observed reactivity. The increase in Lewis acidity at the ruthenium center on chloride abstraction is made responsible for SMe coordination and the rigidity of the ligand systems, and their concomitant failure to coordinate in a "*fac*" manner as is required for a piano stool configuration results in the eventual Cym release. The bridging ligand which then coordinates in a bis-meridional fashion in **8**[ClO_4]$_2$ results in a bis-pincer type of coordination. These observations were validated by a structural analysis of **8**[ClO_4]$_2$. The results show the potential hemilabile character of ligands such as $\mathbf{L^3}$ and $\mathbf{L^4}$. Electrochemical and spectroscopic investigations are reported on **8**[ClO_4]$_2$, and substitution reactions of the CH_3CN molecules are presented to show the use of **8**[ClO_4]$_2$ as a versatile precursor for other reactions.

Introduction

Quinones are ubiquitous in biological systems, being part of vital processes such as cellular respiration and photosynthesis.[1−3] Owing to their facile electron transfer properties, they are often found in combination with transition metal centers in biological systems.[3,4] They are also usually found in the paradoxical role of mutagenic agents as well as effective antitumor agents.[5] The biological activity of quinone molecules is often related to the presence of acidic

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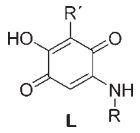
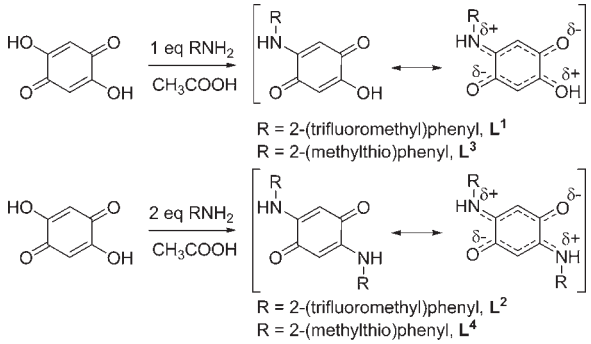


Figure 1. Quinone containing −OH substituent.

protons in these molecules.[6−8] Quinones of the form **L** (Figure 1) containing an OH substituent play an important role as inhibitors of tumors[9] and of hydroxyphenyl pyruvate dioxygenase.[10] Despite intensive research efforts in that direction, straightforward one-pot and green synthetic routes for access to such molecules are, to the best of our knowledge, nonexistent in the literature, with the existing procedures requiring multistep synthesis, extraction from natural products, or involved purification steps.[9−17]

Coordination compounds with quinone ligands have been studied for a variety of reasons, such as their interesting electron transfer properties,[18−22] magnetic behavior,[23,24] use in supramolecular chemistry,[25,26] as well as homogeneous catalysis.[27,28] Ligand noninnocence is a well-known phenomenon in metal complexes of quinones,[29−32] and recently valence ambiguities arising out of such a process have been extensively studied for diruthenium complexes containing

Scheme 1



potentially bridging quinone ligands.[20,33−35] Valence ambiguity as well as mixed valency are widely researched fields for di- and multiruthenium complexes with a variety of ligands.[36−43] Hemilability of ligands is an important phenomenon in catalysis.[44] Efforts at synthesizing potentially bridging quinone ligands with additional donor atoms capable of showing hemilability have been rare until now.[28] In view of our interest in developing easy, straightforward, and green routes for synthesizing various quinone ligands and exploring their use in coordination and organometallic chemistry, we ventured onto this present project.[45−49] We present here a one-pot synthesis of the ligands 2-[2-(trifluoromethyl)-anilino]-5-hydroxy-1,4-benzoquinone ($\mathbf{L^1}$), 2,5-di-[2-(trifluoromethyl)-anilino]-1,4-benzoquinone ($\mathbf{L^2}$), 2-[2-(methylthio)-anilino]-5-hydroxy-1,4-benzoquinone ($\mathbf{L^3}$), and 2,5-di-[2-(methylthio)-anilino]-1,4-benzoquinone ($\mathbf{L^4}$). $\mathbf{L^1}$ and $\mathbf{L^3}$ are rare examples of asymmetric *p*-quinones containing an additional OH group and are directly related to molecules of the form **L** (Scheme 1). $\mathbf{L^3}$ and $\mathbf{L^4}$ combine additional SMe donors at the nitrogen substituents, thus making these ligands potentially hemilabile, with $\mathbf{L^3}$ having this feature only on one side of the molecule. These ligands were used to form complexes [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^1}$)] (**1**), [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^2}$)] (**2**), [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^3}$)] (**3**), and [{Cl(η^6-Cym)Ru}$_2$(μ-$\mathbf{L_{-2H}^4}$)] (**4**) that contain the "[Ru(Cym)]" (Cym = *p*-Cymene = 1-isopropyl-4-methyl-benzene) fragment popularized

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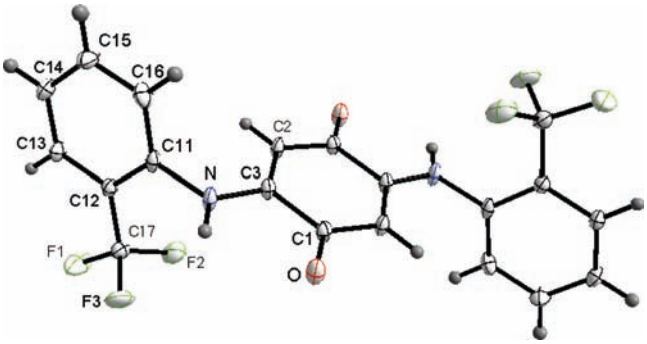

Figure 2. ORTEP plot of $\mathbf{L^2}$. Ellipsoids are drawn at 50% probability.

because of its anticancer properties and the catalytic activity of many of its metal complexes.[50,51] These complexes were further reacted with silver salts in acetonitrile to produce $[\{(CH_3CN)(\eta^6\text{-Cym})Ru\}_2(\mu\text{-}\mathbf{L}_{-2H}^{1})][ClO_4]_2$ (**5**$[ClO_4]_2$), $[\{(CH_3CN)(\eta^6\text{-Cym})Ru\}_2(\mu\text{-}\mathbf{L}_{-2H}^{2})][ClO_4]_2$ (**6**$[ClO_4]_2$), $[(CH_3CN)(\eta^6\text{-Cym})Ru(\mu\text{-}\mathbf{L}_{-2H}^{3})Ru(CH_3CN)_3][ClO_4]_2$ (**7**$[ClO_4]_2$), and $[\{(CH_3CN)_3Ru\}_2(\mu\text{-}\mathbf{L}_{-2H}^{4})][ClO_4]_2$ (**8**$[ClO_4]_2$). In the following, a detailed synthetic, spectroscopic, and crystallographic study on these ligands and complexes is presented. Reactivity studies are reported to determine the potential hemilabile character of ligands such as $\mathbf{L^3}$ and $\mathbf{L^4}$. Reasons for the unprecedented coordination induced release of Cym in complexes **3** and **4** to form **7**$[ClO_4]_2$ and **8**$[ClO_4]_2$ are stated and explained. Finally, electrochemical and spectroscopic investigations on **8**$[ClO_4]_2$ as well as the use of this compound as a versatile precursor are explored.

Results and Discussion

Synthesis of Ligands and Crystal Structures of $\mathbf{L^2}$ and $\mathbf{L^4}$. One of the reports on the synthesis of (aromatic)amino-substituted *p*-quinones deals with the reaction of the commercially available and relatively inexpensive 2,5-dihydroxy-1,4-benzoquinone with aromatic amines in *m*-cresol under reflux at temperatures of over 100 °C in the presence of catalytic amounts of trifluoroacetic acid.[52] This reaction, which is often used in the literature even up to now,[53] deals with *m*-cresol as a solvent, a substance that is highly toxic, and whose health hazards are well documented.[54] Additionally, polymer formation is often a problem while using the above-mentioned synthetic method.[52] In trying to unveil the possible mechanism of this reaction, we reasoned that the critical points in its functioning are relatively high temperatures and acid catalysis. Similar acid catalyzed reactions are found in several enzymatic processes which function in water.[55] Hence, we carried out the same reaction with nontoxic and environmentally benign acetic acid as a solvent. Gratifyingly, the reaction in acetic acid worked as good as or even better than that using *m*-cresol. No problems with polymer formation were observed, and we were able to isolate compounds $\mathbf{L^2}$ and $\mathbf{L^4}$ (Scheme 1) in high yields after just a one-step chromatographic purification. This route is general and can be extended to include all possible aliphatic and aromatic amines. The synthesis of $\mathbf{L^4}$ shows the possibility of building in additional donor atoms at the nitrogen substituents in such ligands, which can be crucial for hemilabile behavior and catalysis. To our surprise, repeating the same reactions with equimolar amounts of 2,5-dihydroxy-1,4-benzoquinone and the corresponding amine under the same conditions as stated above resulted in the formation of asymmetric *p*-quinone compounds $\mathbf{L^1}$ and $\mathbf{L^3}$ (Scheme 1). There are no reports in the literature of the synthesis of such compounds in *m*-cresol, as has been mentioned above for symmetrically amino-substituted *p*-quinones. Such compounds containing an additional OH group are very closely related to many biologically active *p*-quinones which function as bioinhibitors, and a simple and straightforward synthesis of such molecules has been rare and elusive up to now, to the best of our knowledge. $\mathbf{L^1}$ and $\mathbf{L^3}$ could be obtained in high yields with our method of using acetic acid as a solvent. $\mathbf{L^3}$ contains an additional SMe donor on only one side of the molecule. $\mathbf{L^1}$–$\mathbf{L^4}$ were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses. Whereas $\mathbf{L^2}$ and $\mathbf{L^4}$ show only one signal corresponding to the *p*-quinone ring C–H protons in their ^{1}H NMR spectra owing to symmetry equivalence, $\mathbf{L^1}$ and $\mathbf{L^3}$ show two different signals for the now inequivalent *p*-quinone ring C–H protons (see the Experimental Section), and this was the first indication for the formation of such asymmetrically substituted *p*-quinones. In the ^{13}C NMR spectra for $\mathbf{L^2}$ and $\mathbf{L^4}$, only one signal is seen for the "C=O" carbon; for $\mathbf{L^1}$ and $\mathbf{L^3}$ two different signals are observed owing to their inequivalence. In addition, the presence of the $-CF_3$ groups in $\mathbf{L^1}$ and $\mathbf{L^2}$ makes the assignment of signals in their ^{13}C NMR spectra convenient because of coupling to the ^{19}F nuclei (Experimental Section).

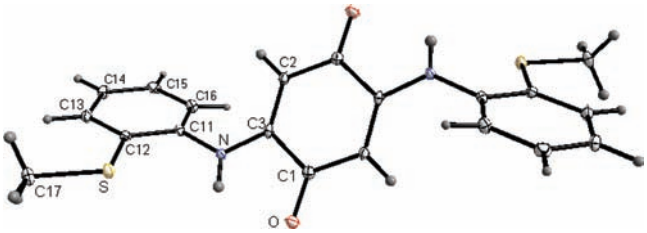

Figure 3. ORTEP plot of $\mathbf{L^4}$. Ellipsoids are drawn at 50% probability.

The ligand $\mathbf{L^2}$ could be crystallized from a dichloromethane/*n*-hexane (1/5, diffusion) solution and $\mathbf{L^4}$ from the slow evaporation of a $CHCl_3$/MeOH (4/1) solution at ambient temperatures (Figures 2 and 3). $\mathbf{L^2}$ and $\mathbf{L^4}$ crystallized in the *C*2/*c* and $P\bar{1}$ space groups, respectively (Table 1). Analysis of bond lengths within the six-membered *p*-quinone ring shows that the C1–O distances for $\mathbf{L^2}$ and $\mathbf{L^4}$ are 1.237(2) and 1.233(2) Å, respectively, and the C3–N distances are 1.337(2) and 1.344(2) Å, respectively. Accordingly, the C1–C2 distances are 1.418(2) and 1.432(2) Å, and the C2–C3 distances are 1.366(2) and 1.365(2) Å respectively for $\mathbf{L^2}$ and $\mathbf{L^4}$. These distances that are between those of typical single and double bonds point to electron delocalization and imply the formulation of these compounds as two C–C connected W-like merocyanine subunits (Scheme 1). The C1–C3 distances

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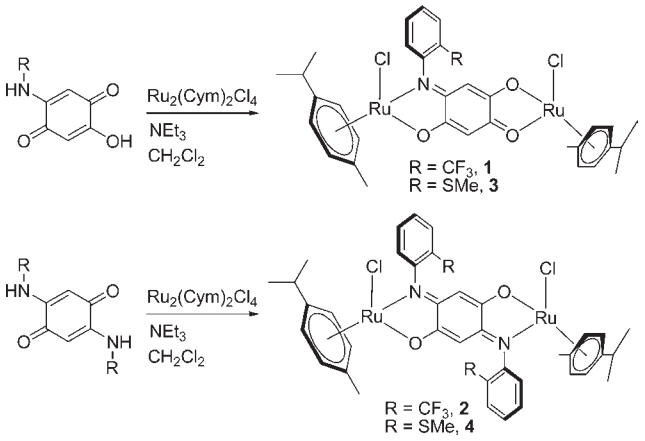
Table 1. Crystallographic Details

	$\mathbf{L^2}$	$\mathbf{L^4}$	**2**	**4**	**8**$[ClO_4]_2$
formula	$C_{20}H_{12}F_6N_2O_2$	$C_{20}H_{18}N_2O_2S_2$	$C_{40}H_{38}Cl_2F_6N_2O_2Ru_2$	$C_{43}H_{51}Cl_2N_3O_3Ru_2S_2$	$C_{35.5}H_{37.5}Cl_2N_8O_{10}Ru_2S_2$
M_r	426.32	382.48	965.76	995.03	1073.40
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
a (Å)	9.961(2)	3.8774(1)	17.592(4)	36.128(4)	8.0825(5)
b (Å)	11.829(2)	9.3734(3)	12.234(2)	11.652(1)	12.4651(7)
c (Å)	15.068(3)	11.8747(4)	19.212(4)	23.099(3)	12.4812(8)
α (deg)	90	93.894(2)	90	90	100.619(3)
β (deg)	93.10(3)	97.976(2)	107.35(3)	96.245(9)	101.953(3)
γ (deg)	90	95.969(2)	90	90	107.976(4)
V (Å^3)	1772.9(6)	423.60(2)	3946.8(1)	9666.0(2)	1127.7(1)
Z	4	1	4	8	1
D_{calc} (g cm^{-3})	1.597	1.499	1.625	1.367	1.580
T (K)	100(2)	100(2)	100(2)	173(2)	100(2)
μ Mo Kα (mm^{-1})	0.711	0.711	0.711	0.711	0.711
F(000)	864	200	1936	4064	541
measd/ ind. reflns	4072/2165	3665/2058	15417/8011	10790/9317	8432/4407
obsd. [$I > 2\sigma(I)$] reflns	1673	1865	4924	5553	3511
R (int)	0.026	0.022	0.075	0.106	0.045
R [$F^2 > 2\sigma(F^2)$]	0.042	0.034	0.078	0.109	0.062
wR (F^2)	0.119	0.084	0.175	0.255	0.150
S	1.308	1.107	1.286	1.319	1.133
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.327, −0.248	0.348, −0.299	2.677, −0.972	2.076, −2.237	1.049, −0.935

Scheme 2



of 1.519(2) and 1.524(2) Å respectively for $\mathbf{L^2}$ and $\mathbf{L^4}$ are typical C−C σ-bond distances, showing the presence of authentic single bonds that connect the merocyanine subunits. These data corroborate earlier observations and show the importance of charge separated species which must be invoked in order to explain the complete physicochemical properties of such color systems.[48,56] The trifluoromethyl(phenyl) substituents on the nitrogen atoms of $\mathbf{L^2}$ are almost perpendicular to the *p*-quinone plane.

Synthesis of 1−4 and Crystal Structures of 2 and 4. Reactions of $\mathbf{L^1}$−$\mathbf{L^4}$ with [Cl(η^6-Cym)Ru(μ-Cl)$_2$Ru(η^6-Cym)Cl] in the presence of a base resulted in the formation of **1**−**4**, respectively, in excellent yields (Scheme 2). The analytical purity of these complexes was determined by ^{1}H NMR spectroscopy, elemental analyses, and mass spectrometry. Of the possible *syn*- and *anti*- isomers that can form for such dinuclear compounds depending on the orientation of the chloro ligands with respect to the *p*-quinone plane, ^{1}H NMR spectroscopy showed the preferential formation of only one isomer under our reaction

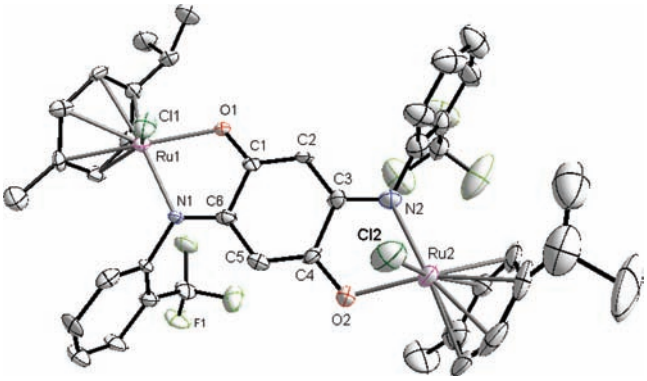


Figure 4. ORTEP plot of **2**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

conditions. Additionally, ^{1}H NMR spectroscopy as well as mass spectrometry showed the presence of two Cym groups in all of the complexes, including **3** and **4**, that have additional thioether donor groups on the substituent on nitrogen atoms (Experimental Section).

Compounds **2** and **4** could be crystallized from the slow evaporation of a dichloromethane solution and slow diffusion of ether into a CH_3CN/MeOH (1/1) solution, respectively, at ambient temperatures. ORTEP plots are presented in Figures 4 and 5, and selected bond lengths and bond angles are given in Tables 2 and 3.

Compound **2** crystallized in the $P2_1/c$ and **4** in the $C2/c$ space group. The quality of the crystallographic data for **4** is not very high, and despite several attempts of growing better crystals, we were not successful in improving their quality. However, the connectivity of the atoms can be stated with full confidence, confirming the presence of the chloride groups as well as the η^6-Cym ligands in **4**. From the crystal structure, we were also able to unambiguously identify the configuration of the complexes. To our surprise, the chloro ligands in **2** as well as **4** turned out to be in the *syn* orientation. This is in contrast to what has been reported in the literature for dinuclear complexes with similar ligands with the "Ir(Cp*)Cl" or "Rh(Cp*)Cl"

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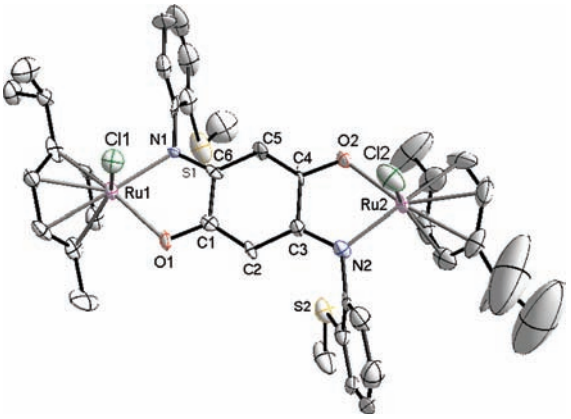

Figure 5. ORTEP plot of **4**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å)

	L^2	L^4	**2**	**4**	**8**$[ClO_4]_2$
C1−O1	1.237(2)	1.233(2)	1.281(8)	1.30(1)	1.287(7)
C4−O2			1.294(8)	1.31(1)	
C3−N[a]	1.337(2)	1.344(2)	1.311(9)	1.34(1)	1.336(7)
C6−N1			1.313(9)	1.32(1)	
C1−C2	1.418(2)	1.432(2)	1.34(1)	1.39(1)	1.384(8)
C1−C3/C1−C6[b]	1.519(2)	1.524(2)	1.511(9)	1.50(1)	1.503(8)
C2−C3	1.366(2)	1.365(2)	1.39(1)	1.43(1)	1.393(8)
C3−C4			1.498(9)	1.49(1)	
C4−C5			1.34(1)	1.36(1)	
C5−C6			1.41(1)	1.43(1)	

[a] C3−N refers to C3−N2 for **2** and **4** and C3−N1 for **8**$[ClO_4]_2$. [b] The bond C1−C6 in **2** and **4** is the same as the bond C1−C3 in the other molecules. A uniform numbering is not possible because certain molecules are centrosymmetric and others are not.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2** and **4**

bond lengths	**2**	**4**	bond angles	**2**	**4**
Ru1−O1	2.083(4)	2.078(7)	O1−Ru1−N1	76.2(2)	76.7(3)
Ru1−N1	2.083(5)	2.091(8)	O1−Ru1−Cl1	83.2(1)	85.9(2)
Ru1−Cl1	2.414(2)	2.437(3)	N1−Ru1−Cl1	85.0(2)	85.1(2)
Ru1−C[a]	1.669(8)	1.67(1)	O2−Ru2−N2	76.2(2)	77.4(3)
Ru2−O2	2.065(5)	2.064(7)	O2−Ru2−Cl2	83.6(2)	85.4(3)
Ru2−N2	2.092(6)	2.070(8)	N2−Ru2−Cl2	85.0(2)	83.8(2)
Ru2−Cl2	2.403(2)	2.430(3)			
Ru2−C[b]	1.669(8)	1.66(1)			
Ru1−S1		4.304(4)			
Ru2−S2		4.275(4)			
Ru1−Ru2	7.964(2)	8.051(1)			

[a] Ru1−C refers to the distance between the Ru center and the centroid of the p-Cym ring. [b] Ru2−C refers to the distance between the Ru center and the centroid of the p-Cym ring.

(Cp* = pentamethylcyclopentadienyl) fragments, where X-ray crystallography showed the presence of the chloro ligands in an *anti* configuration.[57] To the best of our knowledge, there are no reports of crystal structures of dinuclear complexes with substituted *p*-quinone ligands that have "Ru(Cym)Cl" fragments as in the present case. In cases where such complexes have been synthesized, the configuration has always been formulated as *anti* on the basis of comparison with related structures (for example, Ir(III)).[58,59] We found the reverse in our case from structural analyses. The chloride ions possibly adopt a *syn* orientation in order to avoid repulsive interactions with the $-CF_3$ or −SMe groups on the phenyl substituents of the bridge. The Ru−O, Ru−N, and Ru−Cl distances are typical for values reported in the literature for such complexes (Table 3). The η^6 coordination mode of the Cym ligand is seen in the similar Ru−C bond distances for all six carbon atoms of the arene ring. Thus, the ruthenium centers have a piano-stool-type configuration in these complexes. Analyses of the bond lengths within the *p*-quinone ring in **2** show a tendency toward localization of the double bonds in contrast to the free ligands (Table 2).[34,48] Thus, the C1−O1 and C3−N2 distances in **2** are 1.281(8) and 1.311(9) Å, respectively. The corresponding distances in $\mathbf{L^2}$ are 1.237(2) and 1.337(2) Å, respectively. Similarly, the C1−C2 and C2−C3 distances in **2** are 1.34(1) and 1.39(1) Å, respectively, and the corresponding distances in $\mathbf{L^2}$ are 1.418(2) and 1.366(2) Å, respectively. These results point to a localization of double bonds within the *p*-quinone ring and the concomitant binding of $\mathbf{L_{-2H}}^2$ through O^- and imine nitrogen atoms. These observations corroborate previous studies on dinuclear systems with similar ligands.[34,48] The C1−C6 and C3−C4 distances at about 1.5 Å remain authentic C−C σ bonds in both the free ligands and the metal complexes (Table 2). Although the bond lengths in **4** cannot be discussed with confidence because of the poor quality of the crystal data, the trends seem to match those described above for **2**, as one would intuitively expect. The Ru−S distance of more than 4 Å in case of **4** clearly shows that the SMe group does not coordinate to the metal centers in this case. The Ru−Ru intramolecular distances are 7.964(2) and 8.051(1) Å respectively for **2** and **4**.

Synthesis of 5−8 and Crystal Structure of 8. Reactions of **1** or **2** with two equivalents of $AgClO_4$ in acetonitrile resulted in chloride abstraction and the expected formation of **5**$[ClO_4]_2$ or **6**$[ClO_4]_2$, respectively, where the chloro ligands have been substituted by acetonitrile molecules (Experimental Section). Such reactions have been observed before, and compounds related to **5**$[ClO_4]_2$ or **6**$[ClO_4]_2$ are often intermediates in the formation of supramolecular systems.[58,59] While carrying out the same reaction under identical conditions with **4**, we observed that the ^{1}H NMR spectrum of the formed product (**8**$[ClO_4]_2$) showed no signals corresponding to the Cym group (Scheme 3). Since there are reports in the literature of Cym release from such molecules either through excitation by light or because of the presence of an oxidizing agent, we carried out the same reaction with **4** first in the dark and then by substituting $AgClO_4$ with $NaClO_4$ as a chloride abstracting agent. In both of these cases, there was again no sign of the Cym signals in ^{1}H NMR spectrum of the product. At this point, we thought of the possible importance of the SMe groups in the side arm of the ligand $\mathbf{L_{-2H}}^4$ in Cym release. In order to verify this hypothesis, we carried out the chloride abstraction reaction with **3** in acetonitrile. In keeping with our hypothesis, the product **7**$[ClO_4]_2$ formed in this case showed the presence of only one Cym group per molecule of **7**$[ClO_4]_2$, thus proving the importance of the SMe group since the bridging ligand $\mathbf{L_{-2H}}^3$ in this case has a SMe group on only one side of the molecule (Scheme 3).

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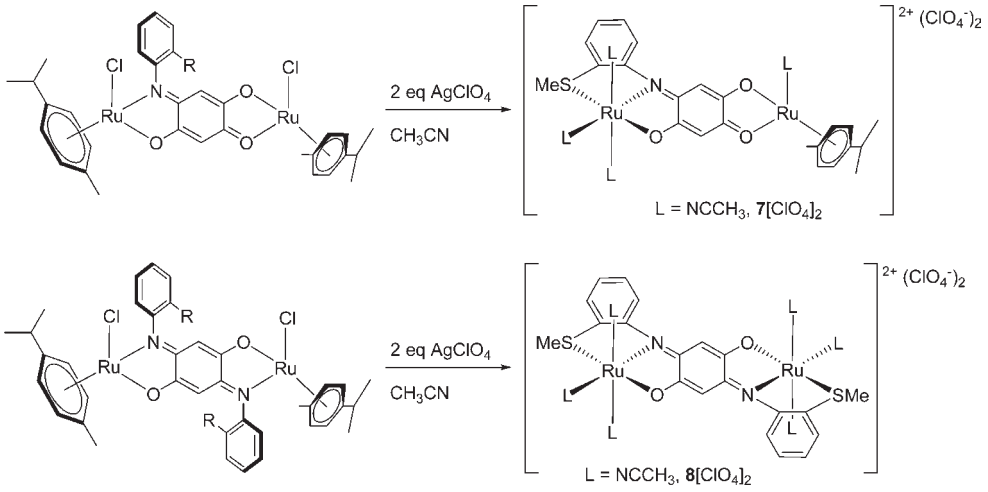
Scheme 3



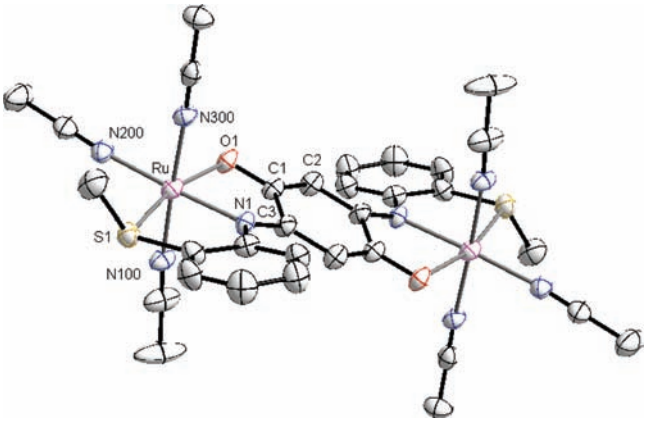


Figure 6. ORTEP plot of **8**$[ClO_4]_2$. Ellipsoids are drawn at 50% probability. Hydrogen atoms and perchlorate ions are omitted for clarity.

Final proof of the structure came from the successful growth of suitable single crystals of **8**$[ClO_4]_2$ as a toluene solvate (Figure 6). This compound crystallizes in the $P\bar{1}$ space group. Each ruthenium center is in a distorted octahedral environment, the distortion being imposed by the two chelating rings formed at each of the ruthenium centers by the bridging ligand. Accordingly, the O1−Ru−N1 and S1−Ru−N1 angles of 79.7(2)° and 86.0(1)° are smaller than the 90° angle expected for a perfect octahedron. The bridging ligand now binds in a bis-tridentate fashion with the SMe group also coordinated to the metal centers. The additional coordination sites are taken up by acetonitrile molecules. The Ru−O1, Ru−N1, and Ru−S1 distances to the donor atoms of the ligands $\mathbf{L_{-2H}}^4$ are in the typical range for such distances (Table 4). The Ru−N distances to the two acetonitrile molecules that are trans to each other are rather similar (Table 4). This is contrast to the Ru−N200 distance of 2.051(6) Å to the acetonitrile molecule that is trans to the imine N atom of the bridging ligand. The longer Ru−N distance in this case compared to the Ru−N distances to the two trans acetonitrile molecules is because of the better trans influence of the imine N atoms of the bridging ligand. The elongation of the C1−O1 distance and the shortening of the C1−C2 distance on complexation (Table 2) also points to a possible localization of double bonds within the *p*-quinone ring, as has been pointed out above for **2** and **4**.[34,48]

The bis-tridentate coordination mode of the bridging ligand $\mathbf{L_{-2H}}^4$ as confirmed by X-ray crystal structure raises some interesting points about binding modes and the resulting reactivity observed. Ruthenium complexes of η^6-arene ligands are text book examples of piano-stool complexes, and this has been observed in our case for **2** and **4**.[60] The η^6-arene ligand in a piano-stool complex "dictates" the *facial* coordination of the other three donor atoms at the metal center. In cases where ligand rigidity together with strong donation force a *meridional* coordination, a direct Cym release has been observed in the literature previously,[61] with bis(imino) pyridine ligands being an important example showing such an effect.[62] Substitution of one arene ring with another has also been studied in the context of hemilability.[63] In our case, the isolation of **4** proves that such a direct Cym release does not occur. The abstraction of chloride atoms from **4** certainly increases the Lewis acidity at the metal center. However, this increase of Lewis acidity alone is not sufficient for the binding of SMe and concomitant release of Cym, as has been proven by the observation of the $[M-2Cl^-]^{2+}$ peak for $\mathbf{4}^{2+}$ in mass spectrometry experiments in the gas phase (Experimental Section). This probably has to do with the need of finding suitable coordinating atoms for substituting the Cym ligand. On carrying out these chloride abstraction reactions in a coordinating solvent such as acetonitrile, we believe there are several phenomena that occur simultaneously. Chloride abstraction increases the Lewis acidity at the metal center, and this facilitates the binding of the SMe group, which stays otherwise uncoordinated in the chloro complex **4**. The rigidity of the ligand $\mathbf{L_{-2H}}^4$ because of partial double bond character of the bonds around the donor atoms prevents the *facial* binding mode of the O,N,S atoms and

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Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $\mathbf{8}[ClO_4]_2$

bond lengths		bond angles		bond angles	
Ru−O1	2.077(4)	O1−Ru−N1	79.7(2)	N1−Ru−N100	86.7(2)
Ru−N1	2.016(5)	O1−Ru−N100	88.3(2)	N1−Ru−N300	91.9(2)
Ru−S1	2.289(2)	O1−Ru−N200	95.9(2)	N100−Ru−N200	93.3(2)
Ru−N100	2.007(5)	O1−Ru−N300	89.6(2)	N200−Ru−N300	87.9(2)
Ru−N200	2.051(6)	S1−Ru−N1	86.0(1)	O1−Ru−S1	165.4(1)
Ru−N300	2.014(5)	S1−Ru−N100	87.9(2)	N1−Ru−N200	175.6(2)
Ru−Ru	7.8534(8)	S1−Ru−N200	98.4(2)	N100−Ru−N300	177.7(2)
		S1−Ru−N300	93.9(2)		

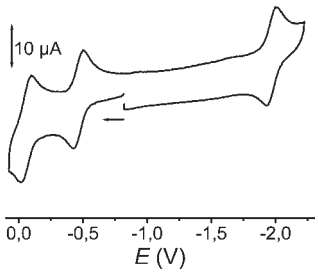

Figure 7. Cyclic voltammogram of $\mathbf{8}^{2+}$ in CH_2Cl_2/0.1 M Bu_4NPF_6 at 295 K. Scan rate: 100 mV/s. The ferrocene/ferrocenium couple was used as an internal standard.

the simple substitution of the Cl^- atom with the SMe group. The Lewis acidic metal center, however, now wants to bind the SMe group, which is possible only in a *meridional* fashion. This *meridional* coordination is incompatible with a piano-stool-type structure and the η^6-binding mode of the arene ligands. This leads to arene release, which is now aided by the coordination of the acetonitrile molecules which take up the other three *meridional* positions of the octahedron around the ruthenium centers. The bridging ligand $\mathbf{L_{-2H}}^4$ now has a bis-pincer-type coordination (Figure 6). Metal complexes of pincer ligands have found use in a variety of interesting and demanding chemical transformations in recent times.[64,65] The present reaction probably occurs in a concerted step that includes simultaneous chloride abstraction, acetonitrile coordination, and Cym release. We believe that the Cym ligand changes its denticity in this reaction before being finally displaced. However, attempts at identifying a defined intermediate via NMR spectroscopy were not successful. Thus, we have here an example of coordination "*on demand*" and concomitant reactivity associated with that. Such potentially hemilabile behavior can be extremely useful for various catalytic processes. Strong proof of our hypothesis of the need for chloride abstraction, donating solvent molecules, as well as an additional donor atom in a rigid bridging ligand also comes from the observation of the formation of $\mathbf{7}[ClO_4]_2$ from **3** (Scheme 3). The bridging ligand $\mathbf{L_{-2H}}^3$ has an additional SMe donor only on one side, and concomitantly Cym release is observed also from one side.

Electrochemistry, Spectroscopic Properties, and Substitution Reactions of 8. The presence of two Ru(II) centers and a redox-active quinone ligand as a bridge prompted us to investigate the electrochemical properties of $\mathbf{8}^{2+}$. $\mathbf{8}^{2+}$ shows two reversible oxidation processes at −0.46 and −0.06 V vs ferrocene/ferrocenium at 295 K in CH_2Cl_2/0.1 M Bu_4NPF_6 and a reversible reduction at −1.96 V (Figure 7). For comparison, the free ligand $\mathbf{L}^4$ shows an irreversible oxidation at 1.01 V and a reversible reduction process at −1.29 V under identical conditions. Further ill defined irreversible reduction processes were also observed for $\mathbf{L}^4$. The chloro precursors **1**−**4** as well as the complexes **5** and **6** showed only irreversible responses in their cyclic voltammogram.

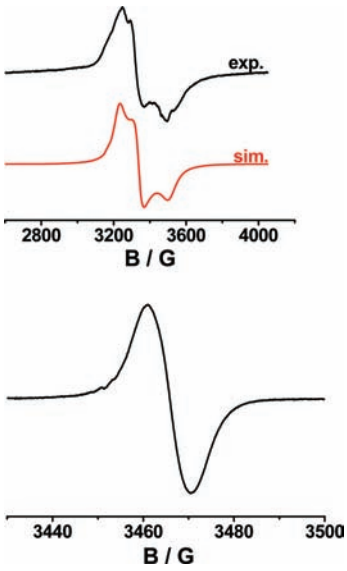

Figure 8. EPR spectrum of in situ generated $\mathbf{8}^{3+}$ in CH_2Cl_2/0.1 M Bu_4NPF_6 at 110 K with simulation (top) and $\mathbf{8}^+$ in CH_2Cl_2/0.1 M Bu_4NPF_6 at 295 K (bottom).

The UV−vis spectrum of $\mathbf{8}[ClO_4]_2$ shows a metal to ligand charge transfer (MLCT) band at 708 nm. A further band is observed at 371 nm, which can be assigned to a $\pi \rightarrow \pi^*$ transition based on the bridge. The in situ generated one-electron oxidized species $\mathbf{8}^{3+}$ is EPR silent at room temperature and shows a signal with rhombic symmetry at 110 K in CH_2Cl_2/0.1 M Bu_4NPF_6 which could be simulated with $g_1 = 2.143$, $g_2 = 2.074$, and $g_3 = 1.975$ (Figure 8). The g anisotropy ($\Delta g = g_1 - g_3$) of 0.168 and the g_{av} of 2.065 points to a metal-centered spin and the presence of a predominantly metal centered SOMO (singly occupied molecular orbital) on one-electron oxidation to $\mathbf{8}^{3+}$. In contrast to this, the one-electron reduced species $\mathbf{8}^+$ shows an isotropic EPR spectrum at 295 K with $g = 1.998$ (Figure 8), the closeness of which to the free electron g factor of 2.0023 points to a predominantly bridging ligand centered reduction. The hyperfine coupling expected from the ^{14}N ($I = 1$) nuclei was unfortunately not resolved, possibly due to unfavorable line width to hyperfine coupling constant ratios.

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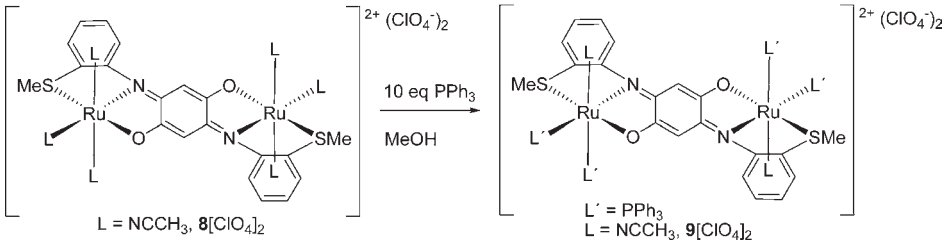
Scheme 4



Initial attempts at substituting the CH_3CN groups in **8**$[ClO_4]_2$ for other ligands met with success. The reaction of **8**$[ClO_4]_2$ with excess PPh_3 under refluxing conditions leads to the coordination of two PPh_3 molecules per ruthenium center, resulting in **9**$[ClO_4]_2$ (Scheme 4 and the Experimental Section). The product was characterized by ^1H and ^{31}P NMR spectroscopy as well as mass spectrometry. Attempts at substituting the third acetonitrile molecule from each ruthenium center did not meet with success even under forcing conditions. We believe this to be because of the steric bulk of the PPh_3 ligands. The presence of doublets in the ^{31}P NMR spectrum also confirmed the formation of a *cis* product. This would be expected on the basis of the structural analysis of **8**$[ClO_4]_2$, which showed a rather long Ru−N (acetronitrile) bond which is trans to the imine N atom of the bridging ligand.

Conclusion

We have reported here on a straightforward one-pot and green synthesis of symmetrically and rare asymmetrically substituted biologically relevant *p*-quinone ligands. Some of the ligands also contain an additional SMe donor group which could act as a potentially hemilabile donor. Structural characterization of the ligands shows a delocalization of the double bonds in these molecules and the importance of charge separated W-like merocyanine groups for their complete understanding. Complexes of the form [{Cl(η^6-Cym)Ru}$_2$(μ-**BL**$_{-2H}$)] (**BL**$_{-2H}$ = bridging quinine ligand) were synthesized with the doubly deprotonated forms of all the ligands. Structural characterization of some of these complexes has shown the η^6-coordination mode of the arene ligand and localization of the double bonds within the *p*-quinone bridge. Reactions of these complexes with $AgClO_4$ lead to the unprecedented substituent induced release of *p*-Cym from these complexes only in cases where an additional SMe group is present in the bridging ligand. Structural characterization of the thus formed complex [{$(CH_3CN)_3Ru$}$_2$-(μ-**L**$_{-2H}$^{4})][ClO_4]$_2$ shows that the bridging ligand binds in a bis-pincer-like meridional bis-tridentate fashion. The increase in the Lewis acidity at the metal center on chloride abstraction is made responsible for the coordination of the SMe group, and the inability of the rigid bridging ligand to take up a *facial* coordination as demanded by a piano-stool configuration is suggested to induce *p*-Cym release. Such stepwise reactivity of this complex shows the possible use of the SMe groups in hemilabile behavior. Electrochemical investigations on **8**$^{2+}$ show the presence of two one-electron oxidation processes at relatively low potentials as well as a reduction process. EPR spectroscopy confirms the first oxidation process as metal centered and the reduction process as ligand centered. The presence of the labile solvent molecules in **8**$[ClO_4]_2$ makes this a good starting material for subsequent reactions, and initial success in that direction has been observed with the substitution of CH_3CN molecules with PPh_3. In view of the observed *coordination on demand* behavior of the SMe groups and the ease of synthesizing such ligands with our new method, we will concentrate our future efforts in building up ligands with various additional donor atoms with different amounts of flexibility and probe their reactivities. In addition, compound **8**$^{2+}$ provides a unique opportunity of getting at systems with the potential of multielectron reservoirs because of its inherent redox-rich nature as well as the possibility of building in additional redox-active components in place of the labile acetonitrile ligands. Our current research is focused in that direction.

Experimental Section

General Considerations. 2,5-Dihydroxybenzoquinone, 2-(trifluoromethyl)aniline, 2-(methylthio)aniline, and PPh_3 were purchased from Sigma-Aldrich and $Ru_2(Cym)_2Cl_4$ from ABCR. For the metal complexes, all manipulations were carried out under an argon atmosphere. The solvents used for metal complex syntheses were dried and distilled under argon and degassed by common techniques prior to use.

Instrumentation. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer. Electronic absorption spectra were recorded on J&M TIDAS and Shimadzu UV 3101 PC spectrophotometers. EPR spectra in the X-band were recorded with a Bruker System EMX. EPR simulations were carried out by the Simfonia program of Bruker. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 solutions using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag wire as pseudoreference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as an internal reference. Elemental analyses were performed by the Perkin-Elmer Analyzer 240. Mass spectrometry experiments were carried out using a Bruker Daltronics Mictrotof-Q mass spectrometer

Syntheses. 2-[2-(Trifluoromethyl)-anilino]-5-hydroxy-1,4-benzoquinone (L^1). 2,5-Dihydroxybenzoquinone (300 mg, 2.15 mmol) was dissolved in acetic acid (40 mL), and 2-(trifluoromethyl)-aniline (345 mg, 2.15 mmol) was added dropwise. This was accompanied by a sudden color change from yellow to red. The solution was refluxed for 4 h and allowed to cool down to room temperature. After the addition of water (200 mL), a red solid precipitated and could be collected by filtration. The crude product was cleaned by column chromatography using silica and CH_2Cl_2/MeOH (10/1) as the eluent. After evaporation of the solvent, the product was obtained as a red solid (407 mg, 67%). Anal. Calcd for $C_{13}H_8F_3NO_3$: C, 54.19; H, 3.24; N, 4.95. Found: C, 54.42; H, 3.28; N, 4.64. ^1H NMR (250 MHz, $CDCl_3$): δ 5.84 (s, 1H, quinone-*H*), 6.03 (s, 1H, quinone-*H*), 7.39 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, aryl-*H*), 7.46 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, aryl-*H*), 7.62 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, aryl-*H*), 7.74 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, aryl-*H*), 7.92 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 95.9 (O=C−*C*−C−NHR), 103.1 (OH−C−*C*−C−C=O), 123.2 (q, $^1J_{C-F}$ = 273 Hz, CF_3), 125.1 (q, $^2J_{C-F}$ = 30 Hz, CF_3−*C*),

126.0 (aryl-*C*), 126.9 (aryl-*C*), 127.4 (q, $^3J_{C-F}$ = 5 Hz, CF_3-C-CH), 133.0 (aryl-*C*), 134.7 (q, $^3J_{C-F}$ = 2 Hz, $CF_3-C-C-NHR$), 147.0 (NHR−*C*−C═O), 157.9 (OH−*C*−C═O), 180.4 (O═*C*−C−NHR), 182.2 (O═*C*−C−OH). $^{19}F\{^1H\}$ NMR (235 MHz, $CDCl_3$): δ −61.5.

2,5-Di-[2-(trifluoromethyl)-anilino]-1,4-benzoquinone (L^2). The compound was prepared following the procedure for L^1 by using 2,5-dihydroxybenzoquinone (300 mg, 2.15 mmol) and two equivalents of 2-(trifluoromethyl)aniline (690 mg, 4.30 mmol). The crude product was cleaned by column chromatography using silica and CH_2Cl_2 as the eluent. After evaporation of the solvent, the product was obtained as a red solid (682 mg, 73%). X-ray-quality crystals could be grown by the slow diffusion of hexane into a dichloromethane solution. Anal. Calcd for $C_{20}H_{12}F_6N_2O_2$: C, 56.35; H, 2.84; N, 6.57. Found: C, 56.08; H, 2.83; N, 6.48. ^1H NMR (250 MHz, $CDCl_3$): δ 5.87 (s, 2H, quinone-*H*), 7.36 (t, $^3J_{H-H}$ = 8 Hz, 2H, aryl-*H*), 7.50 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, aryl-*H*), 7.62 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, aryl-*H*), 7.73 (d, $^3J_{H-H}$ = 8 Hz, 2H, aryl-*H*), 8.02 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 96.9 (O═C−*C*−C-NHR), 123.4 (q, $^1J_{C-F}$ = 273 Hz, *C*F_3), 124.9 (q, $^2J_{C-F}$ = 30 Hz, CF_3-C-CH)), 125.9 (aryl-*C*), 126.4 (aryl-*C*), 127.4 (q, $^3J_{C-F}$ = 5 Hz, $CF_3-C-CH-CH$)), 133.0 (aryl-*C*), 135.3 (q, $^3J_{C-F}$ = 2 Hz, $CF_3-C-C-NHR$), 146.8 (NHR−*C*−C═O), 180.3 (O═*C*−C−NHR). $^{19}F\{^1H\}$ NMR (235 MHz, $CDCl_3$): δ −61.5.

2-[2-(Methylthio)-anilino]-5-hydroxy-1,4-benzoquinone (L^3). The compound was prepared following the procedure for L^1 by using 2,5-dihydroxybenzoquinone (300 mg, 2.15 mmol) and one equivalent of 2-(methylthio)aniline (299 mg, 2.15 mmol). The crude product was cleaned by column chromatography using silica and CH_2Cl_2/MeOH (10/1) as the eluent. After evaporation of the solvent, the product was obtained as a red solid (332 mg, 51.5%). Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.28; H, 4.07; N, 5.33. ^1H NMR (250 MHz, $CDCl_3$): δ 2.06 (s, 3H, S*C*H_3), 5.27 (s, 1H, quinone-*H*), 5.97 (s, 1H, quinine-*H*), 7.24 (m, 2H, aryl-*H*), 7.37 (m, 2H, aryl-*H*), 8.33 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 16.6 (*C*H_3-SR), 95.2 (O═C−*C*−C−NHR), 103.3 (OH−C−*C*−C═O), 123.1 (aryl-*C*), 126.84 (aryl-*C*), 127.1 (aryl-*C*), 129.5 (aryl-*C*), 133.2 (aryl-C), 135.1 (NHR-*C*−C−S−CH_3), 146.2 (O═C−*C*−NHR), 158.5 (OH−*C*−C═O), 180.1 (O═*C*−C−NHR), 182.7 (O═*C*−C−OH).

2,5-Di-[2-(methylthio)-anilino]-1,4-benzoquinone (L^4). The compound was prepared following the procedure for L^1 by using 2, 5-dihydroxybenzoquinone (300 mg, 2.15 mmol) and two equivalents of 2-(methylthio)aniline (598 mg, 4.30 mmol). After the reaction, no further purification was necessary, and the red compound could be obtained after filtration (720 mg, 87%). Crystals for X-ray diffraction could be obtained from the slow evaporation of a $CHCl_3$/MeOH solution. Anal. Calcd for $C_{20}H_{18}N_2O_2S_2$: C, 62.50; H, 4.74; N, 7.32. Found: C, 62.44; H, 4.42; N, 7.30. ^1H NMR (250 MHz, CD_2Cl_2): δ 2.45 (s, 6H, S*C*H_3), 5.95 (s, 2H, quinone-*H*), 7.27 (m, 4H, aryl-*H*), 7.43 (m, 4H, aryl-*H*), 8.30 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 16.7 (*C*H_3−SR), 96.3 (O═C−*C*−C−NHR), 123.0 (aryl-*C*), 126.5 (aryl-*C*), 126.9 (aryl-*C*), 129.7 (aryl-*C*), 132.8 (aryl-*C*), 135.8 (NHR−*C*−C−S−CH_3), 146.3 (NHR−*C*−C═O), 180.4 (O═*C*−C−NHR).

[{**Cl(η^6-Cym)Ru**}$_2$(μ-L_{-2H}^1)] (**1**). $Ru_2(Cym)_2Cl_4$ (80 mg, 0.13 mmol) and the ligand L^1 (36.8 mg, 0.13 mmol) were dissolved in CH_2Cl_2 (30 mL) under an argon atmosphere. NEt_3 (1.0 mL) was added, and the solution was stirred overnight at room temperature. The solution was concentrated, and the product was precipitated by the addition of hexane. The compound was filtered, washed with hexane, and dried *in vacuo*. The compound was obtained as a reddish-purple solid (92 mg, 86%). Anal. Calcd for $C_{33}H_{34}Cl_2F_3NO_3Ru_2$: C, 48.18; H, 4.17; N, 1.70. Found: C, 47.86; H, 4.05; N, 1.66. MS (ESI) Calcd for $C_{33}H_{34}ClF_3NO_3Ru_2$ ([M − Cl^-]$^+$): *m*/*z* 788.03. Found: 788.03. ^1H NMR (250 MHz, $CDCl_3$): δ 1.09 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.16 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.26 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.27 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.89 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.46 (sept, $^3J_{H-H}$ = 7.9 Hz, 1H, $CH(CH_3)_2$), 2.86 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 4.92 (s, 1H, quinone-*H*), 4.96 (d, $^3J_{H-H}$ = 5.9 Hz, 1H, arene-*H*), 5.25 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, arene-*H*), 5.27 (d, $^3J_{H-H}$ = 5.6 Hz, 2H, arene-*H*), 5.40 (d, $^3J_{H-H}$ = 6.0 Hz, 2H, arene-*H*), 5.48 (d, $^3J_{H-H}$ = 4.6 Hz, 1H, arene-*H*), 5.50 (d, $^3J_{H-H}$ = 4.6 Hz, 1H, arene-*H*), 5.85 (s, 1H, quinone-*H*), 7.39 (t, $^3J_{H-H}$ = 7.9 Hz, 1H, aryl-*H*), 7.57 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, aryl-*H*), 7.67 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, aryl-*H*), 7.71 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, aryl-*H*).

[{**Cl(η^6-Cym)Ru**}$_2$(μ-L_{-2H}^2)] (**2**). The compound was prepared following the procedure for **1** by using $Ru_2(Cym)_2Cl_4$ (80 mg, 0.13 mmol) and ligand L^2 (55.4 mg, 0.13 mmol). The desired product was obtained as a purple solid (114 mg, 91%). Crystals for X-ray diffraction could be obtained from the slow evaporation of a CH_2Cl_2 solution. Anal. Calcd for $C_{40}H_{38}Cl_2F_6N_2O_2Ru_2$: C, 49.75; H, 3.97; N, 2.90. Found: C, 49.64; H, 3.86; N, 2.82. MS (ESI) Calcd for $C_{40}H_{38}ClF_6N_2O_2Ru_2$ ([M − Cl^-]$^+$) and $C_{40}H_{38}F_6N_2O_2Ru_2$ ([M − 2 Cl^-]$^{2+}$): *m*/*z* 931.06 and 447.44. Found: 931.06 and 447.56. ^1H NMR (250 MHz, CD_2Cl_2): δ 1.09 (d, $^3J_{H-H}$ = 7 Hz, 6H, $CH(CH_3)_2$), 1.16 (d, $^3J_{H-H}$ = 7 Hz, 6H, $CH(CH_3)_2$), 1.86 (s, 6H, CH_3), 2.31 (sept, $^3J_{H-H}$ = 7.0 Hz, 1H, $CH(CH_3)_2$), 2.40 (sept, $^3J_{H-H}$ = 7.0 Hz, 1H, $CH(CH_3)_2$), 4.89 (d, $^3J_{H-H}$ = 6.5 Hz, 2H, arene-*H*), 4.95 (s, 2H, quinone-*H*), 5.19 (d, $^3J_{H-H}$ = 6.0 Hz, 2H, arene-*H*), 5.31 (d, $^3J_{H-H}$ = 6.1 Hz, 4H, arene-*H*), 7.46 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, aryl-*H*), 7.63 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, aryl-*H*), 7.74 (m, 4H, aryl-*H*).

[{**Cl(η^6-Cym)Ru**}$_2$(μ-L_{-2H}^3)] (**3**). The compound was prepared following the procedure for **1** by using $Ru_2(Cym)_2Cl_4$ (80 mg, 0.13 mmol) and ligand L^3 (33.9 mg, 0.13 mmol). The compound was obtained as a reddish-purple solid (96 mg, 92%). Calcd for $C_{33}H_{37}Cl_2NO_3SRu_2$: C, 49.50; H, 4.66; N, 1.75. Found: C, 49.48; H, 4.60; N, 1.73. MS (ESI) Calcd for $C_{33}H_{37}ClNO_3SRu_2$ ([M − Cl^-]$^+$): *m*/*z* 766.02. Found: 766.00. ^1H NMR (250 MHz, $CDCl_3$): δ 1.08 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.16 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.24 (d, $^3J_{H-H}$ = 1.9 Hz, 3H, $CH(CH_3)_2$), 1.27 (d, $^3J_{H-H}$ = 2.0 Hz, 3H, $CH(CH_3)_2$), 2.20 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.53 (s, 3H, S*C*H_3), 2.85 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 3.70 (sept, $^3J_{H-H}$ = 2.6 Hz, 1H, $CH(CH_3)_2$), 5.03 (s, 1H, quinone-*H*), 5.06 (d, $^3J_{H-H}$ = 4.8 Hz, 1H, arene-*H*), 5.25 (d, $^3J_{H-H}$ = 5.8 Hz, 2H, arene-*H*), 5.34 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, arene-*H*), 5.47 (d, $^3J_{H-H}$ = 5.2 Hz, 3H, arene-*H*), 5.58 (d, $^3J_{H-H}$ = 5.4 Hz, 1H, arene-*H*), 5.83 (s, 1H, quinone-*H*), 7.12 (m, 1H, aryl-*H*), 7.21 (m, 2H, aryl-*H*), 7.36 (m, 1H, aryl-*H*).

[{**Cl(η^6-Cym)Ru**}$_2$(μ-L_{-2H}^4)] (**4**). The compound was prepared following the procedure for **1** by using $Ru_2(Cym)_2Cl_4$ (80 mg, 0.13 mmol) and ligand L^4 (49.8 mg, 0.13 mmol). The compound was obtained as a purple solid (120 mg, 93%). X-ray-quality crystals could be obtained by the slow diffusion of ether into a CH_3CN/MeOH solution. Anal. Calcd for $C_{40}H_{44}Cl_2N_2O_2Ru_2S_2 + 1/2CH_2Cl_2$: C, 50.44; H, 4.70; N, 2.90. Found: C, 50.33; H, 4.76; N, 3.14. HRMS (ESI) Calcd for $C_{40}H_{44}N_2O_2Ru_2S_2$ ([M − 2 Cl^-]$^{2+}$): *m*/*z* 426.0470. Found: 426.0461. ^1H NMR (400 MHz, CD_3CN): δ 1.07 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.15 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.82 (s, 6H, CH_3), 2.58 (s, 6H, S*C*H_3), 2.91 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 4.78 (s, 2H, quinone-*H*), 5.01 (d, $^3J_{H-H}$ = 5.8 Hz, 2H, arene-*H*), 5.39 (d, $^3J_{H-H}$ = 6.0 Hz, 2H, arene-*H*), 5.52 (d, $^3J_{H-H}$ = 5.9 Hz, 2H, arene-*H*), 5.55 (d, $^3J_{H-H}$ = 6.0 Hz, 2H, arene-*H*), 7.22 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, aryl-*H*), 7.30 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, aryl-*H*), 7.36 (t, $^3J_{H-H}$ = 7.1 Hz, 2H, aryl-*H*), 7.44 (d, $^3J_{H-H}$ = 8.1 Hz, 2H, aryl-*H*).

[{(**CH_3CN**)(**η^6-Cym**)**Ru**}$_2$(μ-L_{-2H}^1)][**ClO_4**]$_2$ (**5**[ClO_4]$_2$). Complex **1** (24.7 mg, 0.03 mmol) and $AgClO_4$ (12.0 mg, 0.06 mmol) were dissolved in CH_3CN (10 mL) under an argon atmosphere and refluxed for 3 h. After cooling down to room temperature, the solution was filtered and the filtrate collected. The solvent was

evaporated and the product dried *in vacuo*. The compound was obtained as a brown solid (20.0 mg, 78%). Anal. Calcd for $C_{37}H_{40}Cl_2F_3N_3O_{11}Ru_2$: C, 43.03; H, 3.90; N, 4.07. Found: C, 42.79; H, 3.65; N, 3.88. MS (ESI) Calcd for $C_{33}H_{34}F_3NO_3Ru_2$ ($[M - 2\ ClO_4^- - 2\ CH_3CN]^{2+}$): *m*/*z* 376.53. Found: 376.53. ^{1}H NMR (250 MHz, CD_3CN): δ 1.17 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.28 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.88 (s, 3H, CH_3), 2.09 (s, 3H, CH_3CN), 2.15 (s, 3H, CH_3CN), 2.21 (s, 3H, CH_3), 2.57 (sept, $^3J_{H-H}$ = 6.5 Hz, 1H, $CH(CH_3)_2$), 2.80 (sept, $^3J_{H-H}$ = 6.8 Hz, 1H, $CH(CH_3)_2$), 4.94 (s, 1H, quinone-*H*), 5.40 (d, $^3J_{H-H}$ = 6.5 Hz, 1H, arene-*H*), 5.59 (d, $^3J_{H-H}$ = 5.0 Hz, 1H, arene-*H*), 5.61 (d, $^3J_{H-H}$ = 6.0 Hz, 1H, arene-*H*), 5.69 (d, $^3J_{H-H}$ = 4.1 Hz, 2H, arene-*H*), 5.74 (d, $^3J_{H-H}$ = 4.1 Hz, 1H, arene-*H*), 5.85 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, arene-*H*), 5.87 (s, 1H, quinone-*H*), 7.18 (t, $^3J_{H-H}$ = 8.4 Hz, 1H, aryl-*H*), 7.66 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, aryl-*H*), 7.84 (d, $^3J_{H-H}$ = 5.8 Hz, 1H, aryl-*H*), 7.94 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, aryl-*H*).

[{$(CH_3CN)(\eta^6$-Cym)Ru$\}_2(\mu$-L_{-2H}^2)][ClO_4]$_2$ (6[ClO_4]$_2$). By using complex **2** (29.0 mg, 0.03 mmol) and $AgClO_4$ (12.0 mg, 0.06 mmol) and following the procedure for **5**[ClO_4]$_2$, the compound was obtained as a brown-red solid after washing with *n*-hexane (3 × 10 mL) and drying in vacuo (25 mg, 85%). Anal. Calcd for $C_{44}H_{44}Cl_2F_6N_4O_{10}Ru_2$: C, 44.94; H, 3.77; N, 4.76. Found: C, 44.96; H, 3.72; N, 4.80. HRMS (ESI) Calcd for $C_{40}H_{38}F_6N_2O_2Ru_2$ ($[M - 2\ ClO_4^- - 2\ CH_3CN]^{2+}$): *m*/*z* 448.0462. Found: 448.0470. ^{1}H NMR (250 MHz, CD_3CN): δ 1.13 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.78 (s, 6H, CH_3), 2.15 (s, 6H, CH_3CN); 2.30 (sept, $^3J_{H-H}$ = 5.1 Hz, 1H, $CH(CH_3)_2$), 2.55 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 5.01 (s, 2H, quinone-*H*), 5.08 (d, $^3J_{H-H}$ = 6.0 Hz, 1H, arene-*H*), 5.31 (d, $^3J_{H-H}$ = 6.5 Hz, 1H, arene-*H*), 5.56 (d, $^3J_{H-H}$ = 7.0 Hz, 4H, arene-*H*), 5.61 (d, $^3J_{H-H}$ = 5.6 Hz, 2H, arene-*H*), 7.44 (t, $^3J_{H-H}$ = 8.2 Hz, 1H, aryl-*H*), 7.65 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, aryl-*H*), 7.80 (t, $^3J_{H-H}$ = 6.7 Hz, 1H, aryl-*H*), 7.87 (d, $^3J_{H-H}$ = 6.6 Hz, 2H, aryl-*H*), 7.93 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, aryl-*H*).

[$(CH_3CN)(\eta^6$-Cym)Ru$(\mu$-L_{-2H}^3)Ru$(CH_3CN)_3$][ClO_4]$_2$ (7[ClO_4]$_2$). By using complex **3** (24.0 mg, 0.03 mmol) and $AgClO_4$ (12.0 mg, 0.06 mmol) and following the procedure for **5**[ClO_4]$_2$, the compound was obtained as a bluish green solid after washing with *n*-hexane (3 × 10 mL) and drying in vacuo (18.9 mg, 83%). Anal. Calcd for $C_{31}H_{35}Cl_2N_5O_{11}Ru_2S$: C, 38.84; H, 3.68; N, 7.30. Found: C, 38.47; H, 3.65; N, 7.05. HRMS (ESI) Calcd for $C_{25}H_{26}N_2O_3Ru_2S$ ($[M - 2\ ClO_4^- - 3\ CH_3CN]^{2+}$, $C_{23}H_{25}NO_4Ru_2S$ $[M - 2\ ClO_4^- - 4\ CH_3CN + H_2O]^{2+}$, and $C_{23}H_{23}NO_3Ru_2S$ $[M - 2\ ClO_4^- - 4\ CH_3CN]^{2+}$): *m*/*z* 318.9876, 307.4796, and 298.4743. Found: 318.9881, 307.4812, and 298.4736. ^{1}H NMR (250 MHz, CD_3CN): δ 1.34 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.14 (s, 9H, CH_3CN), 2.27 (s, 3H, CH_3CN), 2.57 (s, 3H, CH_3), 2.58 (s, 3H, SCH_3), 3.15 (sept, $^3J_{H-H}$ = 5.5 Hz, 1H, $CH(CH_3)_2$), 5.62 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, arene-*H*), 5.89 (d, $^3J_{H-H}$ = 6.4 Hz, 2H, arene-*H*), 5.95 (s, 1H, quinone-*H*), 6.66 (s, 1H, quinone-*H*), 7.48 (m, 2H, aryl-*H*), 7.72 (dd, $^3J_{H-H}$ = 10.2 Hz, $^4J_{H-H}$ = 1.6 Hz, 1H, aryl-*H*), 8.03 (dd, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 1.0 Hz, 1H, aryl-*H*).

[{$(CH_3CN)_3Ru\}_2(\mu$-L_{-2H}^4)][ClO_4]$_2$ (8[ClO_4]$_2$). By using complex **4** (27.7 mg, 0.03 mmol) and $AgClO_4$ (12.0 mg, 0.06 mmol) and following the procedure for **5**[ClO_4]$_2$, the desired compound was obtained as a green solid (yield: 26.0 mg, 85%). Crystals for X-ray diffraction could be obtained from a CH_3CN/toluene solution. Anal. Calcd for $C_{32}H_{34}Cl_2N_8O_{10}Ru_2S_2$: C, 37.39; H, 3.33; N, 10.90. Found: C, 37.00; H, 3.51; N, 10.32. HRMS (ESI) Calcd for $C_{24}H_{22}N_4O_2Ru_2S_2$ ($[M - 2\ ClO_4^- - 4\ CH_3CN]^{2+}$): *m*/*z* 332.9636. Found: 332.9645. ^{1}H NMR (250 MHz, CD_3CN): δ 2.22 (s, 18H, CH_3CN); 2.57 (s, 6H, SCH_3), 6.83 (s, 2 H, quinone-*H*), 7.30 (t, $^3J_{H-H}$ = 7.9 Hz, 2H, aryl-*H*), 7.47 (t, $^3J_{H-H}$ = 7.3 Hz, 2H, aryl-*H*), 7.73 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, aryl-*H*), 8.16 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, aryl-*H*).

[{$(CH_3CN)(PPh_3)_2Ru\}_2(\mu$-$L_{-2H}^4$)][$ClO_4$]$_2$ (9[ClO_4]$_2$). Complex **8**[ClO_4]$_2$ (103 mg, 0.10 mmol) and PPh_3 (262 mg, 1.00 mmol) were dissolved in MeOH (15 mL) under an argon atmosphere. The solution was refluxed overnight and the solvent evaporated. The crude product was purified by multiple column chromatography using alumina and CH_2Cl_2/CH_3CN (3/2) as the eluent (three different columns with the same packing material and the same eluent). The first deep-blue fraction was collected, and the solvent was evaporated under reduced pressure to afford the pure complex (34.0 mg 18%). Anal. Calcd for $C_{96}H_{82}Cl_2N_4O_{10}P_4Ru_2S_2$: C, 60.28; H, 4.32; N, 2.93. Found: C, 59.94; H, 4.16; N, 3.06. MS (ESI) Calcd for $C_{92}H_{76}N_2O_2P_4Ru_2S_2$ ($[M - 2\ ClO_4^- - 2\ CH_3CN]^{2+}$): *m*/*z* 816.12. Found: 816.13. ^{1}H NMR (250 MHz, CD_3CN): δ 2.34 (s, 6H, CH_3CN), 3.62 (s, 6H, SCH_3), 6.92 (s, 2H, quinone-*H*), 7.02−7.17 (m, 22H, aryl-*H*), 7.20−7.38 (m, 25H, aryl-*H*), 7.45−7.65 (m, 21H, aryl-*H*). ^{31}P NMR (250 MHz, CD_3CN): δ 35.45 (d, $^2J_{P-P}$ = 30.7 Hz, 2P), 37.65 (d, $^2J_{P-P}$ = 30.7 Hz, 2P).

X-Ray Crystallography. $\mathbf{L^2}$ was crystallized by the slow diffusion of a dichloromethane solution layered with *n*-hexane (1/5). Crystals for $\mathbf{L^4}$ were grown by slow evaporation of a $CHCl_3$/MeOH solution (1/4). Compound **2** was crystallized by the slow evaporation of a dichloromethane solution. X-ray-quality crystals of **4** could be obtained by the slow diffusion of ether into a CH_3CN/MeOH (1/1) solution. Crystals of **8**[ClO_4]$_2$ for X-ray diffraction could be obtained from a CH_3CN/toluene (1/1) solution. Data collection was made using either a four circle P4 diffractometer (Siemens, Madison (USA)) or a Kappa CCD diffractometer. The measurements were carried out at 173 K or 100 K by using Mo Kα radiation (graphite monochromator). Phase problems were solved using the program SHELXTL PC 5.03. Despite several attempts, we did not manage to improve the quality of crystals for **4**. The connectivity however is clearly observed in this case and can be discussed with confidence. CCDC 788042−788046 contain the CIF files for the structures reported in the work.

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Supporting Information Available: Crystallographic information files for **2**, **4**, **8**[ClO_4]$_2$, $\mathbf{L^2}$, and $\mathbf{L^4}$. This material is available free of charge via the Internet at http://pubs.acs.org.