# **ORGANOMETALLICS**

### Comparative Study on *ortho*-C–H vs *ortho*-C–X (X = C, Cl, S) Bond Activation in *ortho*-C<sub>aromatic</sub>–N Bond Fusion in Substituted Anilines Using Ruthenium(II) Mediators: Isolation and Characterization of Unusual Ru<sub>2</sub> Complexes

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**Supporting Information** 

**ABSTRACT:** The chemical reactions of a selection of *ortho*mono- and disubstituted anilines with two ruthenium polyene mediator complexes,  $CpRu^{II}Cl(PPh_3)_2$  ( $Cp^- = cyclopenta$ dienyl anion) and  $(Bnz)_2Ru^{II}_2Cl_4$  (Bnz = benzene), have been undertaken with a primary aim to make a comparison between *ortho*-C-H and *ortho*-C-X (X = Cl, C, S) bond activation processes in *ortho*-C-N bond fusion reactions. The reaction of *ortho*-monosubstituted anilines, viz., 2-chloroaniline (HL<sup>1a</sup>), 2methylaniline (HL<sup>1c</sup>), and 2-methylthioaniline (HL<sup>1b</sup>), with  $CpRu^{II}Cl(PPh_3)_2$  yielded mononuclear complexes [ $CpRu^{II}L^{2a-c}Cl$ ] (1, 3, and 5), containing *in situ* generated ligands *N*-(aryl)-*ortho*-quinonediimine,  $L^{2a-c}$ , along with



#### INTRODUCTION

During the past decade we have been engaged in transition metal promoted regioselective *ortho*- $C_{arom}$ -N bond fusion reactions in anilines.<sup>1</sup> Our research in this area began with the studies on dimerization of anilines using ruthenium(III) and osmium(III) chelates as mediators.<sup>1a</sup> Subsequently, using the more potent oxidant OsO<sub>4</sub> as the mediator we were successful in regioselective *ortho*-kniting of up to six anilido substrates.<sup>2</sup> To gain insight into the above aniline fusion reactions, we have established the role of the central metal ion in  $C_{arom}$ -N bond fusion reactions using two polyene ruthenium(II) mediator complexes, CpRu<sup>II</sup>Cl(PPh<sub>3</sub>)<sub>2</sub> (Cp<sup>-</sup> = cyclopentadienyl anion) and (Bnz)<sub>2</sub>Ru<sup>II</sup><sub>2</sub>Cl<sub>4</sub> (Bnz = benzene).<sup>3</sup> In this work we have investigated the effect of *ortho*-substitution in aromatic amines

in the context of the above chemical transformations. For this purpose a selection of *ortho*-mono- and disubstituted aromatic amines (Chart 1) have been chosen as the substrates. The primary objective of this work is to make a comparison of different  $C_{arom}-X$  bond activation processes that are operative in the above *ortho*- $C_{arom}-N$  bond forming reactions. Accordingly the amines, as shown in Chart 1, were reacted separately with the two mediator complexes,  $CpRu^{II}Cl(PPh_3)_2$  and  $(Bnz)_2Ru^{II}_2Cl_4$ . While the redox-active  $Ru^{II}-Cp$  complex mediates the C–N bond fusion reactions successfully, the

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redox-innocent  $Ru^{II}$ -Bnz complex failed to bring about the above reactions.<sup>3</sup>

In the reactions between the above ortho-monosubstituted aromatic amines and the Ru<sup>II</sup>-Cp mediator complex, it was anticipated that C-H bond activation would compete with the C-X (X = C, Cl, S) bond activation processes. In this respect the coordination ability of 2-methylthioaniline<sup>4</sup> also plays an important role in the formation of the isolated compounds. The reactions of two ortho-disubstituted anilines, viz., 2,6-dichloroaniline and 2,6-dimethylaniline, were also studied. While we could successfully follow the reaction of 2.6-dichloroaniline via isolation of products, the substrate 2,6-dimethylaniline, on the other hand, failed to produce any isolable compound. The product from the reaction of 2,6-dichloroaniline is a cationic binuclear Ru(III) complex of a newly formed N-(2,6dichlorophenyl)-6-chloro-ortho-quinonediimine ligand. The new ligand was formed in situ as a result of aromatic C-Cl bond activation and ortho-C-N bond fusion reactions. Interestingly the coordination modes of 2,6-dichloroanilide and the new reference ligand in the above complex are unusual in that they include aromatic C-Cl group coordination to a Ru(III) center and a rare type of  $\eta^2$ -binding of an imine (= NH) nitrogen atom, respectively. It is relevant to note here that due to the expected relatively low electron donor capability of the aromatic-chlorine atom, its coordination to a Ru(III) center is a rare phenomenon. There are only a few reports on the complexes of p-block elements having such structural motifs.<sup>5</sup> The aromatic-chlorine atom coordination mode was first argued to exist in solution in the cases of nickel and cobalt complexes of a bidentate ligand, triazene-3-(2-halophenyl)-1oxide.<sup>6</sup> However, subsequent X-ray structure analysis of the cobalt complex indicated the presence of only secondary interactions having a long M-Cl bond.<sup>66</sup>

#### RESULTS AND DISCUSSION

**A. Chemical Reactions.** As it was noted before,<sup>1</sup> the polyene mediator complexes  $CpRu^{II}Cl(PPh_3)_2$  and  $(Bnz)_2Ru^{II}_2Cl_4$  allow the incoming substrates (aromatic amines in these reactions) to occupy only the *cis*-positions, which in fact is a prerequisite for the *ortho*- $C_{arom}$ -N bond formation in aromatic amines. While the complex  $(Bnz)_2Ru^{II}_2Cl_4$  is redox inert, the  $CpRu^{II}Cl(PPh_3)_2$  is oxidizable at 0.5 V vs SCE, and consequently their reactivity patterns are totally different.<sup>5</sup> In the following sections each of the above reactions has been dealt with separately by isolation and complete characterization of the products. The above reactions have yielded some unusual complexes that are not otherwise accessible.

1.a. Reaction of  $CpRu^{II}CI(PPh_3)_2$  and ortho-Monosubstituted Anilines: 2-Chloroaniline (HL<sup>1a</sup>), 2-Methylthioaniline (HL<sup>1b</sup>), and 2-Methylaniline (HL<sup>1c</sup>). The chemical reaction of  $CpRu^{II}Cl(PPh_3)_2$  in neat 2-chloroaniline (HL<sup>1a</sup>) for two hours at 80 °C afforded a brownish-red mass (Scheme 1). Rapid





crystallization of the crude reaction mixture from a dichloromethane-hexane solvent mixture furnished a major product, 1 (intense red), along with a minor product, 2 (yellowishbrown). While compound 1 is highly soluble in common nonpolar solvents, compound 2 is sparingly soluble in the above solvents. Thus fractional crystallization of the mixture using dichloromethane-hexane was useful for their separation. Compound 1 is a mononuclear ruthenium(II) compound that contains an N-(2-chlorophenyl)-6-chloro-ortho-quinonediimine ligand, L<sup>2a</sup>, formed in situ via ortho-C-H bond activation and dimerization of HL<sup>1a</sup>. Compound 2 is a symmetrical binuclear Ru<sup>III</sup><sub>2</sub> complex containing a Ru–Ru bond and bridged by two 2-chloroanilide, (L<sup>1a</sup>)<sup>-</sup>, ligands. Similar products (complexes 3 and 4) were isolated from the reaction of 2-methylaniline,  $HL^{1c}$ , and the above mediator complex (Scheme 1). Characterization of the isolated compounds is discussed in the following sections (vide infra).

A similar reaction with 2-methylthioaniline, HL<sup>1b</sup>, with the reference mediator complex under identical reaction conditions afforded the mononuclear red compound **5** as a minor product, which is an analogue of complexes **1** and **3**, and a new type of binuclear green complex, **[6]**Cl<sub>2</sub>, as the major product. The chemical reaction is depicted in Scheme 2. Though the compound **[6]**Cl<sub>2</sub> has a similar composition to that of compounds **2** and **4** (Scheme 1), its coordination mode and geometry are distinctly different. This is primarily because of the presence of an additional thioether binding site, which has led to a  $\mu$ - $\eta^2$ : $\eta^1$  mode of coordination of the anilido nitrogen and thiomethyl sulfur atom. This coordination mode of a closely related system, viz., 2-aminothiophenol, has been known<sup>7</sup> in a few selected examples. However such coordination of a 2-monothioether function is new.

Microanalytical, positive-ion ESI-MS spectra, together with the <sup>1</sup>H NMR spectral data of the compounds  $1-[6]Cl_2$  convincingly support their formulations as shown in Schemes 1 and 2. For example, the ESI-MS spectra of these compounds

#### Scheme 2



showed high-intensity peaks at m/z 417, 292, 377, 639, 441, and 304 amu, respectively, corresponding to the molecular ion peak of  $[M - CI]^+$  for 1, 3, and 5,  $[M/2 - CI]^+$  for 2,  $[M + Na]^+$  for 4, and  $[M/2]^+$  for [6]Cl<sub>2</sub> where M represents the molecular mass of the respective compounds. The binuclear complexes 2 and [6]Cl<sub>2</sub> also showed a low-intensity peak at m/z583 and 608 amu, respectively, which correspond to the molecular ion peak of  $[M - (H^+ + 2CI^-)]^+$  and  $[M]^+$ , respectively. The experimental spectral features of the above compounds correspond very well to their simulated isotopic patterns. Experimental and simulated ESI-MS spectra of all the compounds  $1-[6]Cl_2$  are submitted as Supporting Information (Figures S1-6).

The molecular compounds 1-5 showed reasonably resolved <sup>1</sup>H NMR spectra in chloroform-*d* solvent. The spectrum of the cationic compound [6]Cl<sub>2</sub>, however, was recorded in methanol $d_4$  solvent. Characteristic resonances due to the imine proton (=NH) of the coordinated ligands, viz.,  $L^{2a-c}$ , appeared at  $\delta$ 12-13 ppm for complexes 1, 3, and 5. The cyclopentadienyl ring proton resonances in these complexes appeared as a single peak near 5 ppm. In addition, aromatic proton resonances of the phenyl ring in  $L^{2a-c}$  ligands appeared in the range  $\delta$  6.5 to 7.8 ppm. For compounds 3 and 5 methyl  $(-CH_3)$  and thiomethyl (-SCH<sub>3</sub>) proton resonances appeared between  $\delta$ 2.1 and 2.5 ppm. The resonance due to the anilido (-NH-)proton in the binuclear complex  $[6]Cl_2$  appeared at 5.0 ppm, whereas in the case of the complexes 2 and 4 it shifted to the low-field region at 9.0 and 14.9 ppm, respectively. These disappeared on D<sub>2</sub>O shake as expected. This shift of the anilido proton resonance may be attributed to the presence of adjacent electronegative chlorine atoms in the latter complexes. <sup>1</sup>H NMR spectra of compounds  $1-[6]Cl_2$  are submitted as Supporting Information (Figures S7-12).

1.b. X-ray Crystal Structure. Three-dimensional X-ray structures of the compounds 1, 2, 5, and  $[6]Cl_2$  further confirm their formulations as well as geometries. The methyl-substituted compounds 3 and 4 are analogous to the complexes 1 and 2, respectively, and hence no attempt to solve their X-ray structures was made. Suitable single crystals for X-ray diffraction studies of complexes 1, 2, and 5 were obtained by slow evaporation of a dichloromethane—hexane solution of the corresponding compounds; single crystals of the compound  $[6]Cl_2$  were, however, grown by slow evaporation of its solution in methanol. ORTEP drawings and atom-numbering schemes of these complexes are shown in Figures 1–4. Selected

bond parameters of 2, 5, and  $[6]Cl_2$  are collected in Table 1, and for 1 these are submitted in Table S1.



**Figure 1.** ORTEP drawing and atom-numbering scheme of **1** with 30% probability thermal ellipsoids. All hydrogen atoms except at N11 are omitted for clarity.



**Figure 2.** ORTEP drawing and atom-numbering scheme of **5** with 30% probability thermal ellipsoids. All hydrogen atoms except at N1 are omitted for clarity.

X-ray crystal structure analysis of mononuclear compounds (1 and 5) reveal that the central ruthenium atom is coordinated to three different ligands, viz., a monoanionic chloro, a  $\eta^{5}$ -bonded cyclopentadienyl anion, and a bidentate *N*-(aryl)-*ortho*-



**Figure 3.** ORTEP drawing and atom-numbering scheme of **2** with 30% probability thermal ellipsoids. All the hydrogen atoms except at N1 and N2 are omitted for clarity.



Figure 4. ORTEP drawing and atom-numbering scheme of  $[6]Cl_2$  with 30% probability thermal ellipsoids. All hydrogen atoms except at N1 and N2 are omitted for clarity.

quinonediimine ligand (L<sup>2a</sup> for 1, Figure 1, and L<sup>2b</sup> for 5, Figure 2). The most notable feature in their structure is the elongation of C-N bonds of the imine chromophore compared to the normal imine C-N bond length:<sup>8</sup> 1.292-1.315 Å. In comparison the two C-N bond lengths in representative compound 5 are C(1)-N(1)H = 1.327(3) and C(6)-N(2)Ph= 1.343(3) Å. This bond length is an indicator of the oxidation state of the coordinated imine group, and the above C-N lengths lie intermediate between an anionic ortho-semiquinonediimine and a neutral ortho-quinonediimine formulation.<sup>8</sup> Moreover, these two bond lengths are shorter than the N(2)-C(8)Ph single bond (1.432(3) Å) present in the same molecule. Furthermore, the two meta-C-C lengths, viz.,  $d_{C(2/4)-(3/5)}$  at 1.367(4) and 1.363(4) Å, indicate a quinonediimine oxidation state. The oxidation state of the N,N-donor ligand in this case may best be argued in favor of an oxidized

ortho-quinonediimine state. The elongation of  $C_{arom}-N_{imine}$  lengths may be attributed to strong d(Ru) $-\pi^*$ (ligand) backbonding in the ground state of the complexes. A similar situation was noted<sup>8b</sup> in the bivalent ruthenium complexes of very closely similar diimine ligands. This issue on oxidation state assessment has been considered again by the analyses of EPR spectra of the electrogenerated complexes and examination of the results of DFT calculations (*vide infra*).

Single-crystal X-ray structure determination of the molecular complex 2 has revealed that it is a metal-metal-bonded Ru<sub>2</sub> system with a Ru-Ru distance of 2.683(8) Å, which is very similar to a typical<sup>9</sup> Ru–Ru single bond length (Figure 3, Table 1). Here the two ruthenium centers are bridged by the anilidonitrogen (-NH-) atoms of two deprotonated 2-chloroanilide ligands, and as a result, a four-membered Ru<sub>2</sub>N<sub>2</sub> metallocyclic ring is formed. The average Ru-N<sub>anilido</sub> distance is 2.062(6) Å, which indicates a monoanionic amido state of the coordinated 2-chloroanilide ligand.<sup>10</sup> In addition each ruthenium center is coordinated to a monoanionic  $\eta^5$ -cyclopentadienyl ring and a terminal monoanionic chloride, and thus the oxidation state of each Ru center is +3. Each of the two Ru(III) centers has 17 valence electrons with an unpaired spin, and thus the EAN of these two Ru(III) centers is achieved via the formation of a Ru-Ru single bond. A nearly similar situation exists in the dicationic complex  $[6]^{2+}$ . However, the difference here arose due to the presence of an ortho-SCH<sub>3</sub> group in the two bridging amido ligands. Two terminal chloride ligands present in 2 are substituted by SCH<sub>3</sub> coordination, leading to the formation of two five-membered chelates (Figure 4). Since the thiomethyl function binds as a neutral donor, the resultant compound as a whole is dicationic. The  $\mu$ - $\eta^2$ : $\eta^1$  coordination of the 2methylthioanilide ligand supported by the coordination of the thiomethyl sulfur atom makes it more rigid<sup>11</sup> in comparison to complex 2. Furthermore, in complex  $[6]^{2+}$  the two cyclopentadienyl rings are oriented on the same side of the Ru<sub>2</sub>N<sub>2</sub>

parameter	2	5	[ <b>6</b> ]Cl <sub>2</sub>	[7]Cl	$[9]Cl_2^a$
Ru1-Ru2	2.683(8)	×	2.646(7)	2.596(9)	3.299(5)
Ru1-N1	2.067(4)	1.996(2)	2.042(4)	1.961(5)	2.125(4)
Ru1-N2	2.063(5)	2.006(2)	2.096(4)	2.087(5)	2.146(4)
Ru2-N1	2.068(4)	×	2.101(4)	×	2.146(4)
Ru2-N2	2.050(4)	×	2.047(4)	×	2.125(4)
Ru1-S1	×	×	2.363(13)	×	2.382(13)
Ru2-S2	×	×	2.358(13)	×	2.382(13)
Ru1-Cl4	×	×	×	2.441(19)	×
Ru1-Cl6	×	×	×	2.358(2)	×
N1-C1	1.430(9)	1.327(3)	1.428(6)	1.296(8)	1.423(6)
N2-C6	×	1.343(3)	×	1.321(8)	×
N2-C8	×	×	1.432(7)	×	×
N2-C7	1.419(8)	×	×	×	×
C1-C6		1.442(3)	1.405(7)	1.465(9)	1.409(7)
C2-C3		1.367(4)	1.392(7)	1.328(11)	1.389(8)
C4-C5		1.363(4)	1.389(10)	1.346(13)	1.386(9)
N1-Ru1-N2	81.99(19)	76.93(9)	93.93(15)	77.0(2)	78.82(16)
N1-Ru2-N2	82.25(18)	×	93.64(15)	×	78.82(16)
Ru2-Ru1-N1	49.57(12)	×	51.31(10)	48.43(15)	×
Ru2-Ru1-N2	49.10(11)	×	49.48(10)	×	×
Ru1-Ru2-N1	49.52(13)	×	49.31(10)	48.55(16)	×
Ru1-Ru2-N2	49.49(11)	×	51.14(12)	×	×

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) of Complexes 2, 5, [6]Cl<sub>2</sub>, [7]Cl, and [9]Cl<sub>2</sub>

<sup>*a*</sup>For [9]Cl<sub>2</sub> N2  $\equiv$  N1\_a, Ru2  $\equiv$  Ru1\_a, and S2  $\equiv$  S1\_a because its two halves are related by an inversion center.

heterocyclic ring, and this ring is puckered. This geometry is favored because of the better overlap between the lone-pair orbitals on the anilido-nitrogen and acceptor orbitals on the ruthenium(III) atoms.<sup>10a-d</sup>

Isolation of the products from the reactions, discussed above, has led to new insights into the ortho-Carom-N bond forming reactions in ortho-monosubstituted aromatic amines. Clearly the Carom-N bond fusion reactions in these examples proceeded via involvement of an ortho-C-H bond activation process, revealing that the aromatic-C-H bond activation process is more facile over the aromatic-C-X (X = Cl, S, C) bond activation process. With this background we now turn our focus to the reactions of ortho-disubstituted anilines with the aforesaid mediator complex with the hope of isolating some intermediate(s) complex of higher oxidation state with terminal amido or imido ligands, which have been argued<sup>3</sup> to be the intermediate in the reference dimerization of aromatic amines. Accordingly, we chose 2,6-dichloroaniline, HL<sup>3a</sup>, and 2,6dimethylaniline, HL<sup>3b</sup>, as the substrates. While the reaction with HL<sup>3b</sup> did not produce any isolable product, the reaction with HL<sup>3a</sup> was smooth and is described below.

2.a. Reaction of  $CpRu^{II}Cl(PPh_3)_2$  and 2,6-Dichloroaniline ( $HL^{3a}$ ). The reaction of  $CpRu^{II}Cl(PPh_3)_2$  with 2,6-dichloroaniline ( $HL^{3a}$ ) under similar reaction conditions proceeded slowly to form an unsymmetrical binuclear dark red complex, [7]Cl, of a new ligand, *N*-(2,6-dichlorophenyl)-6-chloro-*ortho*-quinone-diimine,  $L^{2d}$ , as shown in Scheme 3. This new ligand is formed



as a result of ortho-dimerization of 2,6-dichloroaniline via a less facile ortho-Carom-Cl bond activation (vide supra) and an ortho-C<sub>arom</sub>-N bond fusion reaction (Scheme 3a). However, in 2,6dichloroaniline there indeed exists a possibility of a para-C-H bond activation reaction.<sup>12</sup> Thus formation of the orthoquinonediimine ligand via an ortho-C-Cl bond activation reaction here clearly points to the occurrence of coordination of aromatic amine residues to the metal center prior to the reference ortho-C-N bond formation reaction. The monocationic complex [7]<sup>+</sup> is a Ru<sup>III</sup><sub>2</sub> compound containing a single Ru-Ru bond and supported by three bridging ligands: one ortho-quinonediimine ligand coordinated by an imine nitrogen  $(C_{\text{phenvl}} = \text{NH})$  atom in a  $\eta^2$ -fashion, one deprotonated 2,6dichloroanilide ligand coordinated by an anilido nitrogen atom in a  $\eta^2$ -fashion, and an *in situ* generated acetate ligand coordinated via O,O-coordination. We wish to note here that the coordination modes of the reference ortho-quinonediimine ligand and 2,6-dichloroanilide ligand are unique and discussed

in detail in a Section, 2.b. The carboxylate anion, in the isolated complex, originated from contaminated ethanol in the reference mediator complex, which got oxidized to carboxylic acid during the course of the reaction. To establish the issue further, a similar reaction was performed in the presence of sodium acetate, and the isolated yield of the complex increased substantially (cf. Experimental Section).

Electrospray ionization mass spectral data (ESI-MS) of compound [7]Cl has provided strong support in favor of the formulation of the complex as shown in Scheme 3a. It showed an intense peak at m/z 806 amu, which corresponds to the molecular ion peak of  $[M - Cl]^+$ , where M represents the molecular mass of the compound. The observed spectrum exactly corroborates with its simulated spectrum and is submitted as Supporting Information (Figure S13). Compound [7]Cl is diamagnetic and showed a resolved <sup>1</sup>H NMR spectrum in methanol- $d_4$  solvent. The characteristic resonances due to cyclopentadienyl and methyl protons of the acetate moiety appeared at  $\delta$  5.8 and 1.5 ppm, respectively. Signals of aromatic proton resonances of the reference quinonediimine and 2,6-dichloroanilide ligands appeared in the range  $\delta$  6.8–7.6 ppm (Supporting Figure S14).

2.b. X-ray Crystal Structure. The formulation and geometry of compound [7]Cl are further authenticated by its X-ray crystal structure determination. The ORTEP drawing and atom-numbering scheme of the compound is displayed in Figure 5, and selected bond lengths and angles are collected in



**Figure 5.** ORTEP drawing and atom-numbering scheme of [7]Cl with 30% probability thermal ellipsoids. All hydrogen atoms except at N3 are omitted for clarity.

Table 1. X-ray crystal structure analysis has revealed that complex [7]Cl is a binuclear cationic compound consisting of two ruthenium centers that are connected by a single bond  $(d_{\text{Ru1-Ru2}}: 2.596(9) \text{ Å})$ . Here the two ruthenium centers, Ru1 and Ru2, are bridged by three ligands, viz., a new *N*-(2,6-dichlorophenyl)-6-chloro-*ortho*-quinonediimine ligand, a 2,6-dichloroanilide ligand, and an acetate ligand, as noted in the previous section and in Scheme 3a.

The new ortho-quinonediimine ligand here acts as a bridge connecting the two Ru1 and Ru2 centers through the imine (=N(1)H) nitrogen atom in a  $\eta^2$ -fashion, and the second imine nitrogen atom (=N(2)Ph) coordinates the Ru1 center in a normal  $\eta^1$ -fashion. While the bidentate N,N-donor chelation mode (A) of the ortho-quinonediimine ligand is common in the literature, <sup>1-3,8</sup> the  $\eta^2$ -coordination mode along

with simultaneous bidentate N,N-donor chelation (B) of the reference ligand is unknown in the literature (Scheme 4).

## Scheme 4. Coordination Mode of *ortho*-Quinonediimine Ligand



Selected bond parameters of compound [7]Cl are as follows: C(1)=N(1)H, 1.296(8) Å; C(6)=N(2)Ph, 1.321(8) Å; and C(2/4)=C(3/5)(meta), 1.328(11) and 1.346(13) Å, which indicate<sup>8</sup> a neutral *ortho*-quinonediimine oxidation state of the reference *ortho*-quinonediimine ligand.

In this complex, the 2,6-dichloroanilide ligand also acts as a bridge between Ru1 and Ru2 centers via the anilido (-N(3)H-) nitrogen atom in a  $\eta^2$ -fashion, which is similar to that observed in the previous two binuclear complexes, 2 and [6]Cl<sub>2</sub> (Schemes 1 and 2). The two Ru(1/2)-anilido nitrogen (-N(3)H-) distances are 2.024(5) and 2.096(6) Å, indicating a monoanionic amido state<sup>9</sup> of the coordinated 2,6-dichloroanilide ligand. The most significant observation in this structure is the presence of a distinct Ru(1)-Cl(4) (aromatic Cl) bond. A chloro group (attached to an aryl or alkyl group) is normally considered to be a very poor donor, and only a few compounds of p-block elements are known to form such bonds.<sup>5</sup> However, in the cases of transition metal complexes such a coordination mode of an aromatic-Cl atom is virtually unknown. As far as we are aware there exists only one report<sup>6</sup> in which the existence of such an unusual bond between Co/Ni and Cl(aromatic) atoms has been argued in the respective transition metal complexes of the ligand, triazene-2-(2halophenyl)-1-oxide. The bonding was primarily characterized by the analyses of their spectral data in solution. The Ru(1)-Cl(4) distance in compound [7]Cl is 2.441(19) Å, which is substantially shorter than the sum of their van der Waals radii. 3.75 Å. For comparison, the reported Co-Cl bond length (av 2.98 Å) in the above-noted cobalt-triazene complex is too long to be regarded as a real coordination bond and may be considered only as a weak Co-Cl interaction.<sup>6b</sup> Hence we wish to claim that the compound [7]Cl is the first example of an authentic transition metal complex  $(M = Ru^{III} in this case)$  with genuine crystallographic evidence of a M-Cl(aromatic) coordination. The above bonding phenomenon is further supported by the calculated atomic charge density of the chlorine atoms by the natural population analysis method, which shows more positive atomic charge density on the coordinated Cl(4) atom (0.241) in comparison to the similar uncoordinated Cl(5) atom (0.072). Moreover the C(18)-Cl(4) length (1.760(7) Å) is appreciably longer than the otherwise identical bond C(14)-Cl(5) (1.703(8) Å). Coordination of the anionic acetate ligand in this complex is usual and binds Ru1 and Ru2 centers via two oxygen atoms in a typical  $\eta^1$ -fashion.

Besides the coordination of three bridging ligands, the Ru1 center is terminally coordinated to a monoanionic chloride ligand, and the Ru2 center is coordinated to a monoanionic  $\eta^{5}$ -

cyclopentadienyl anion. As a whole, the structural analysis thus has revealed the trivalent oxidation state of both Ru1 and Ru2 centers in the complex [7]Cl.

3.a. Reaction of  $(Bnz)_2Ru''_2Cl_4$  and ortho-Mono- and Disubstituted Anilines. To explore the role of metal ion in ortho-C–N bond fusion in amines, the aforesaid aromatic amines were reacted separately with another polyene mediator complex,  $(Bnz)_2Ru''_2Cl_4$ . In a recent communication we have shown that the precursor Ru''–Bnz complex strongly resists oxidation of the metal center, and hence no dimerization of aromatic amines is possible. Similar expected complexes<sup>3</sup> were isolated from the reaction of 2-chloroaniline, 2-methylaniline, 2,6-dichloroaniline, and 2,6-dimethylaniline with the above mediator complex. The results are summarized in Scheme Sa,

Scheme 5



and an ORTEP diagram, as revealed by X-ray structure determination of a representative compound, **8**, is submitted as Supporting Information (Figure S15). These results are not discussed any further. However, the reaction of  $(Bnz)_2Ru^{II}_2Cl_4$  with 2-methylthioaniline under identical reaction conditions produced an interesting anilido-bridged binuclear  $Ru^{II}_2$  compound, [9]Cl<sub>2</sub>, in 42% yield (Scheme 5b). Here, the two deprotonated 2-methylthioanilide ligands coordinate in a  $\mu$ - $\eta^2:\eta^1$ -fashion, bridging the two Ru centers as shown in Scheme 5b. The compound was cleaned by removing the unreacted amines via washing with diethyl ether and subsequent crystallization from its solution in methanol.

The complex [9]Cl<sub>2</sub> gave satisfactory elemental analyses (cf. Experimental Section). The ESI-MS spectrum of the compound showed an intense peak at m/z 317 amu, corresponding to the molecular ion peak of  $[M/2]^+$  where M represents the molecular mass of the compound. The experimental spectral feature of the complex corroborates its simulated isotopic pattern, and these are submitted as Supporting Information (Figure S16). The complex is

diamagnetic and showed a well-resolved <sup>1</sup>H NMR spectrum in methanol- $d_4$  solvent. The resonance due to a characteristic aromatic  $\eta^6$ -benzene proton appeared at  $\delta$  6.0 ppm, and for the anilido (-NH-) proton it appeared at 7.8 ppm. The signals due to aromatic proton resonances of the coordinated ligand (L<sup>1b</sup>)<sup>-</sup> appeared in the range  $\delta$  6.5–8.0 ppm. The <sup>1</sup>H NMR spectrum of the compound [9]Cl<sub>2</sub> is submitted as Supporting Information (Figure S17).

3.b. X-ray Crystal Structure. The identity of complex  $[9]Cl_2$  was finally confirmed by solution of its single-crystal X-ray structure. Suitable single crystals were developed by slow evaporation of its methanolic solution. The ORTEP diagram and atom-numbering scheme of complex  $[9]Cl_2$  is shown in Figure 6, and selected bond lengths and angles are summarized



Figure 6. ORTEP drawing and atom-numbering scheme of  $[9]Cl_2$  with 30% probability thermal ellipsoids. All hydrogen atoms except at N1 and N1 a are omitted for clarity.

in Table 1. The asymmetric unit of the complex consists of the cationic complex  $[9]^{2+}$ , two Cl<sup>-</sup> as counteranions, and two water molecules as solvate. It is a homobinuclear  $Ru_{2}^{II}$  complex in which the two halves are related by an inversion center. Two units of 2-methylthioanilide bridge the two ruthenium centers by a  $\mu$ - $\eta^2$ : $\eta^1$  coordination mode through anilido nitrogen and thiomethyl sulfur atoms with the formation of a stable Ru<sub>2</sub>N<sub>2</sub> metallocyclic ring. The situation here is somewhat similar to that in the previously described compound  $[6]Cl_2$ . In addition, each ruthenium atom is coordinated by a  $\eta^6$ -Bnz ligand. In complex [9]Cl<sub>2</sub> two phenyl rings of the bridging ligands are disposed trans, which is opposite (cis) to that in the complex [6]Cl<sub>2</sub>. The Ru<sub>2</sub>N<sub>2</sub> metallocyclic ring is completely planar, whereas in the complex  $[6]Cl_2$  it is puckered. The two Ru(II) centers in [9]Cl<sub>2</sub> are widely separated ( $d_{Ru1-Ru2}$ : 3.299(5) Å), signifying the absence of any metal-metal bond.

**B.** Cyclic Voltammetry and EPR. Redox properties of all the complexes were examined by cyclic voltammetry in acetonitrile solution containing 0.1 M TEAP as the supporting electrolyte in the potential range +1.5 to -1.5 V using platinum as the working electrode. The potentials are referenced to the saturated Ag/AgCl electrode, and the results are summarized in Table 2. The  $E_{1/2}$  of the ferrocenium–ferrocene couple under our experimental conditions was 0.39 V.

Cyclic voltammetry of complex 1 exhibits two irreversible responses at potentials -0.93 and -1.27 V and one reversible oxidative response at potential 0.82 V (Figure 7). For irreversible waves the one-electron redox response has been

Table 2. Cyclic Voltammetric Data<sup>a</sup>

compound	$E_{1/2}^{b} V (\Delta E_{p}, mV)$	$E_{1/2}^{b} V (\Delta E_{p}, mV)$
1	0.82 (100)	$-0.93$ , <sup>c</sup> $1.27^{c}$
2	1.02 (100)	$-0.70^{c}$
3	0.54 (100)	$-1.04^{c}$
4	$1.20^{c}$	-0.69 (100)
5	0.67 <sup>c</sup>	$-0.70,^{c}$ $-1.11^{c}$
[ <b>6</b> ]Cl <sub>2</sub>	$0.76^{c}$	-0.42 (40), -0.71 (30)

"In acetonitrile solution, supporting electrolyte TEAP, reference electrode Ag/AgCl.  ${}^{b}E_{1/2} = 0.5(E_{\rm pa} + E_{\rm pc})$  where  $E_{\rm pa}$  and  $E_{\rm pc}$  are anodic and cathodic peak potentials, respectively,  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$  scan rate 50 mV s<sup>-1</sup>. "Quasireversible/irreversible."



Figure 7. Cyclic voltammogram of complex 1 in  $CH_3CN-0.1$  M  $NEt_4ClO_4$  and (inset) EPR spectrum of electrochemically generated  $[1]^+$  in  $CH_2Cl_2-0.1$  M  $Bu_4NClO_4$  at 77 K.

confirmed by comparison of the current height with the redox response of the ferrocene/ferrocenium couple under identical experimental conditions, and the reversible wave showed one electron stoichiometry in constant potential electrolysis experiments. To gain further insight into the electron transfer phenomena associated with the reversible redox process in complex 1, the EPR spectrum of the electrogenerated oneelectron-oxidized species was studied at 77 K. The oneelectron-oxidized compound, [1]<sup>+</sup>, showed a ruthenium(III)centered rhombic spectrum with  $\langle g \rangle_{av} = 2.0675$  (g1 = g2 = 2.1160 and  $g_3 = 1.9670$ ), confirming that the oxidation process primarily occurs at the Ru<sup>II</sup> center (Figure 7). Irreversibility of the first cathodic wave is presumably due to the reduction of the quinonediimine ligand and was supported by the DFT studies (cf. below) of the reduced complex, [1]<sup>-</sup>. A similar type of electrochemical response with small potential shift was exhibited by the other two mononuclear complexes, viz., 3 and 5, and the data are collected in Table 2 for comparison. The binuclear complex 2, on the other hand, displayed one irreversible cathodic response at -0.70 V and one reversible anodic response at 1.02 V (Figure 8). The one-electronoxidized species  $[2]^+$ , generated by exhaustive electrolysis of compound 2 at 1.25 V, showed an axial EPR spectrum with  $\langle g \rangle_{av} = 2.0313$  (g1 = 2.5292, g2 = 2.4417, and g3 = 1.8786, Figure 8), confirming the presence of a Ru(III) center. Thus the oxidative response may be assigned to the oxidation of one of the two Ru(III) centers, producing a mixed-valent Ru(III)-Ru(IV) or Ru(3.5)-Ru(3.5) compound. This ambiguity was further clarified by DFT calculations (cf. below). Another binuclear compound, 4, exhibited similar redox properties with



Figure 8. Cyclic voltammogram of complex 2 in  $CH_3CN-0.1$  M NEt<sub>4</sub>ClO<sub>4</sub> and (inset) EPR spectrum of electrochemically generated [2]<sup>+</sup> in  $CH_2Cl_2-0.1$  M Bu<sub>4</sub>NClO<sub>4</sub> at 77 K.

insignificant shift of redox potentials. The redox behavior of the binuclear complex [6]Cl<sub>2</sub> showed two reductive responses at -0.42 and -0.70 V (Figure S18). However, our efforts to trap the reduced species [6]<sup>+</sup> and [6] were unsuccessful. These electrogenerated species revert to the parent compound quickly. The complex [9]Cl<sub>2</sub>, on the other hand, is redox inert within the above potential window.

C. Electronic Structures of the Complexes 1 and 2. The above-noted N,N-donor ligands can exist in multiple oxidation states, and hence the electronic structures of the two representative complexes 1 and 2 were analyzed by density functional theory (DFT). Complex 1 was optimized in three conditions: singlet closed shell, singlet broken symmetry (BS) open shell, and triplet open shell (Table S1). The attempts to locate the open-shell singlet  $[Ru^{III}(Cp)(Q^{\bullet-})Cl]$  configuration for the native state of compound 1 using the BS-DFT approach converged back to the closed-shell configuration,  $[Ru^{II}(Cp)-$ (Q)Cl], where Q stands for the guinonediimine formulation of the ligand N-(2-chlorophenyl)-6-chloro-ortho-quinonediimine, L<sup>2a</sup>. The energies of singlet, triplet, and BS-singlet states of compound 1 are  $-8.28903 \times 10^5$ ,  $-8.28888 \times 10^5$ , and 8.28902 $\times$  10<sup>5</sup> kcal/mol, respectively. Compound 2 was also optimized in both closed-shell singlet (18.76252  $\times$  10<sup>5</sup> kcal/mol) and in open-shell triplet (18.76237  $\times$  10<sup>5</sup> kcal/mol) configurations (Table S1). The triplet state was found to reside much higher in energy (15.16 kcal/mol) relative to the singlet state. In addition compound 2 showed a resolved <sup>1</sup>H NMR spectrum in the normal range for diamagnetic compounds, indicating a further closed-shell singlet configuration. There is a good agreement between the calculated bond lengths and angles with the crystallographically established metrical parameters of the complexes 1 and 2 (Tables S2 and S3). The energies and compositions of the DFT calculated frontier orbitals of the complexes 1 and 2 are summarized in the Supporting Information (Tables S4 and S5). Analyses of the frontier molecular orbitals of complex 1 reveal that the highest occupied MO (HOMO) is a combination of metal (major) and coordinated N-(2-chlorophenyl)-6-chloro-ortho-quinonediimine ligand (minor) orbitals (1: Ru: 53%; Cl: 17%; L<sup>2a</sup>: 16%; Cp: 14%). Closely lying occupied HOMO-1 is formed by nearly equal contributions of metal (38%) and N-(2chlorophenyl)-6-chloro-ortho-quinonediimine ligand orbitals (41%). The lowest unoccupied MO (LUMO) is primarily

delocalized over the ligand (62%) orbitals; the metal orbitals contribute 28% to this orbital. The next lowest unoccupied orbital (LUMO+1) consists of metal (43%) and ligand orbitals (*N*-(2-chlorophenyl)-6-chloro-*ortho*-quinonediimine: 22% and cyclopentadienyl: 26%). However for the binuclear complex **2** both HOMO and LUMO orbitals are primarily localized over the metal orbitals with very little contributions of Cl<sup>-</sup> and 2-chloroanilide ligand, (L<sup>1a</sup>)<sup>-</sup> (HOMO: Ru: 45%; Cl: 26%; (L<sup>1a</sup>)<sup>-</sup>: 11%; Cp: 08%; and LUMO: Ru: 54%; Cp: 11%; (L<sup>1a</sup>)<sup>-</sup>: 27%; Cl: 08%).

The most probable electronic structure in the native state of compound 1 is  $[Ru^{II}(Cp)(Q)CI]$ , and accordingly, the oneelectron-reduced and oxidized species are  $[Ru^{II}(Cp)(Q^{\bullet-})CI]^{-}$ ,  $[1]^{-}$ , and  $[Ru^{III}(Cp)(Q)CI]^{+}$ ,  $[1]^{+}$ , respectively. In line with these descriptions, the Mulliken spin density population in the reduced complex  $[1]^{-}$  is more populated (0.5845) over the ligand center (Figure 9a), whereas in the oxidized complex  $[1]^{+}$ 



Figure 9. Spin density plots of (a)  $[1]^+$  and (b)  $[1]^-$ .

(Figure 9b) it is more populated over the metal center (0.7379). We believe that a similar electronic structure description is valid for the analogous complexes 3 and 5. In the case of binuclear complex 2, however, the two ruthenium centers are present in a trivalent oxidation state and are connected by two bridging deprotonated ligands,  $(L^{1a})^{-}$ . Accordingly, the electronic structure of complex 2 in its native state is  $[CpClRu^{III}{\mu-\eta^2-(L^{1a})^-}_2Ru^{III}ClCp]$ . Thus the possible descriptions for the one-electron-oxidized and reduced species are as follows: unsymmetrical mixed-valent formulation with different valences  $(CpClRu^{III} \{\mu - \eta^2 - (L^{1a})^-\}_2 Ru^{IV}ClCp], [2]^+,$ and  $[CpClRu^{III}{\mu-\eta^2-(L^{1a})^-}_2Ru^{II}ClCp]^-$ ,  $[2]^-$ , respectively, or symmetrical alternative mixed-valent formulation with average net metal valences [CpClRu<sup>3.5</sup>{ $\mu$ - $\eta$ <sup>2</sup>- $(L^{1a})^{-}_{2}Ru^{3.5}ClCp], [2]^{+}, and [CpClRu^{2.5}\{\mu, \eta^{2}-(L^{1a})^{-}\}_{2}Ru^{2.5}Cl$ Cp]<sup>-</sup>, [2]<sup>-</sup>, respectively. Since the unpaired spin densities in species  $[2]^+$  and  $[2]^-$  are populated nearly equally on the two metal centers ([2]<sup>+</sup>: Ru1: 0.383739, Ru2: 0.380776 and [2]: Ru1: 0.3420; Ru2: 0.3426, and the rest are populated on the coordinated ligands) (Figure 10), the best descriptions for both [2]<sup>+</sup> and [2]<sup>-</sup> are completely delocalized symmetrical mixedvalent formulations.

**D. Electronic Spectra.** Electronic spectra of all the complexes reported herein were recorded in acetonitrile solvent, and data are collected in Table 3. To assign the transitions of the complexes, time-dependent DFT (TD-DFT) calculations were performed on the two representative complexes 1 and 2, and the data are collected in Tables S6 and S7. Their electronic spectra are displayed in Figure 11.

The mononuclear complex **1** exhibited an intense broad transition at 488 nm. TD-DFT calculations revealed that this low-energy transition compared well with the calculated values

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Figure 10. Spin density plots of (a)  $[2]^+$  and (b)  $[2]^-$ .

Table 3. UV–Vis–NIR Absorption Spectral Data of Complexes 1–[7]Cl in Acetonitrile

complex	$\lambda_{ m max}/ m nm~(arepsilon/ m M^{-1}~ m cm^{-1})$
1	489(18311), 278(30492)
2	448(31487), 365(43667), 260(109548)
3	495(15901), 268(37288)
4	475(96688), 288(24064)
5	495(3941), 256(sh)(7199)
[ <b>6</b> ]Cl <sub>2</sub>	872(34802), 461(7051), 269(sh)(20329)
[7]Cl	477(2424), 398(1664), 357(1867)



Figure 11. UV-vis-NIR absorption spectra of the compounds 1 (red), 2 (orange), and  $[6]Cl_2$  (green) in  $10^{-5}$  M acetonitrile solution. Inset: [7]Cl in  $10^{-4}$  M acetonitrile solution.

for HOMO-1  $\rightarrow$  LUMO+1 and HOMO-2  $\rightarrow$  LUMO transitions. Although these four participating orbitals are delocalized over both metal and ligand orbitals, the metal orbitals have major contributions in the donor orbital (HOMO-2: 72%) and the ligand orbitals have major contributions in the acceptor orbital (LUMO: 62%). Thus the above transition may best be described as a metal to ligand charge transfer (MLCT) transition (Table S6). This transition was computationally predicted to appear at 466 nm. The analogous complexes 3 and 5 also showed similar MLCT transition near 500 nm (cf. Table 3). However, the neutral binuclear complex 2 exhibited a broad transition in the visible region at 447 nm. This transition is computationally predicted to appear at 468 nm and is attributed to HOMO-1  $\rightarrow$  LUMO +1 and HOMO-2  $\rightarrow$  LUMO+1 transitions. Since, both donor (HOMO–1 and HOMO–2) and acceptor (LUMO+1) orbitals here are delocalized primarily over the metal orbitals, one can assign this low-energy transition as a d(Ru)–d(Ru) transition (Table S7). Similarly the analogous complex 4 displayed this transition at 475 nm (cf. Table 3). In comparison the dicationic complex [6]Cl<sub>2</sub> showed an intense transition at 860 nm (Figure 11). DFT analyses on this (Tables S8 and S9) revealed that the HOMO is nearly equally populated over metal (48%) and ligand orbitals (40%) and the LUMO is composed of metal (55%) and ligand orbitals (35%). Further TD-DFT analysis (Table S10) has indicated that the above near-IR range transition compares well with the calculated value of the HOMO → LUMO transition. This type of low-energy transition in anilido-bridged Ru<sup>III</sup><sub>2</sub> complexes has been rarely observed.<sup>5a</sup>

#### CONCLUSION

In summary, using ortho-mono- and disubstituted anilines we have discussed competitive C-H vs C-X bond (X = Cl, C, S) activation reactions in ruthenium-mediated ortho-Carom-N bond fusion reactions. It has been found that the C-H bond activation process is undoubtedly preferable over the above C-X bond activation processes. However, the C-Cl bond activation reaction did occur in the case of ortho-disubstituted 2,6-dichloroaniline in more forceful conditions. The reactions of monosubstituted anilines have afforded the anilido-bridged binuclear ruthenium(III) complexes  $(2, 4, and \lceil 6 \rceil Cl_2)$  in addition to the mononuclear ruthenium(II) complexes (1, 3, and 5) containing N-aryl-ortho-quinonediimine ligands  $(L^{2a-c})$ . The reaction of  $CpRu^{II}Cl(PPh_3)_2$  with 2,6-dichloroaniline has resulted in an unusual binuclear ruthenium(III) complex, [7]Cl, in which the new N-(2,6-dichlorophenyl)-6-chloro-orthoquinonediimine ligand (L<sup>2d</sup>) is formed via ortho-C-Cl bond activation and ortho-C-N bond fusion reactions. As far as we are aware, this compound is the first example of an authentic transition metal complex ( $M = Ru^{III}$  in this case) with genuine crystallographic evidence of a M-Cl(aromatic) coordination. In the courses of these reactions several metal-metal-bonded  $Ru_{2}^{II}$  complexes (2, [6]Cl<sub>2</sub>, and [7]Cl) have been isolated and characterized. These complexes are rich in both spectral and redox properties and have been thoroughly studied by cyclic voltammetry, UV-vis spectra, and EPR, and the conclusions are supported by DFT studies. Finally, the chemical reactions reported herein not only have generated new scopes in the area of metal-mediated ortho-Carom-N bond fusion reaction but also have produced new classes of novel organometallic compounds that otherwise are not achievable following the available synthetic protocols.

#### EXPERIMENTAL SECTION

**Materials.** The ruthenium salt RuCl<sub>3</sub> was obtained from Arora-Matthey, Kolkata, and aromatic amines, viz., 2-chloroaniline, 2methylthioaniline, and 2,6-dichloroaniline, were obtained from Sigma-Aldrich. The mediator complexes  $CpRu^{II}Cl(PPh_3)_2^{-13}$  and  $(Bnz)_2Ru^{II}_2Cl_4^{-14}$  and the supporting electrolytes tetraethylammoniumperchlorate (TEAP) and tetrabuthylammoniumperchlorate (TBAP) for the electrochemical measurements were prepared and crystallized following the published procedures.<sup>15</sup> Solvents and other chemicals used for syntheses were of analytical grade and used as received.

**Instrumentation.** UV–vis–NIR absorption spectra were recorded either on a Perkin-Elmer Lambda 950 UV/vis spectrophotometer or on a J&M TIDAS instrument. The IR spectra were recorded with a Perkin-Elmer 783 spectrophotometer. Cyclic voltammetry was carried out in 0.1 M TEAP solutions using a three-electrode configuration

#### Table 4. Crystallographic Data of Complexes 1, 2, 5, [6]Cl<sub>2</sub>, [7]Cl, and [9]Cl<sub>2</sub>

parameter	1	2	5	[ <b>6</b> ]Cl <sub>2</sub>	[7]Cl	[9]Cl <sub>2</sub>
empirical formula	$C_{17}H_{13}Cl_3N_2Ru$	$\mathrm{C}_{22}\mathrm{H}_{20}\mathrm{Cl}_4\mathrm{N}_2\mathrm{Ru}_2$	C19H19ClN2RuS2	$C_{48}H_{52}N_4Ru_4S_4Cl_3O_7\\$	$C_{25}H_{18}Cl_7N_3O_4Ru_2\\$	$C_{26}H_{28}N_2Ru_2S_2Cl_4O_4\\$
fw	452.71	656.34	476.02	1435.85	874.71	840.58
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$Pca2_1$	$P2_1/n$	$P\overline{1}$	C2/c	$P\overline{1}$	$P\overline{1}$
a (Å)	20.932(4)	18.964(3)	9.422(11)	36.395(6)	10.178(17)	9.089(8)
b (Å)	7.503(17)	15.138(2)	10.710(12)	8.770(13)	12.442(2)	9.413(8)
c (Å)	20.915(4)	19.467(3)	11.157(14)	18.326(3)	13.129(2)	10.684(9)
$\alpha$ (deg)	90	90	64.183(2)	90	83.865(4)	64.083(10)
$\beta$ (deg)	90	100.946(4)	85.266(2)	108.519(3)	77.925(4)	76.070(2)
γ (deg)	90	90	72.337(2)	90	69.202(4)	74.921(2)
$V(\text{\AA}^3)$	3284.8(12)	5486.9(14)	964.1(2)	5546.5(15)	1518.9(4)	785.37(12)
Ζ	8	8	2	4	2	1
$D_{\rm calcd}~({\rm g/cm^3})$	1.831	1.589	1.640	1.719	1.913	1.777
cryst dimens (mm <sup>3</sup> )	0.06 × 0.08 × 0.11	$0.07 \times 0.17 \times 0.20$	$0.05 \times 0.09 \times 0.12$	$0.06\times0.10\times0.19$	0.11 × 0.13 × 0.16	$0.10\times0.10\times0.10$
$\begin{array}{l} \theta \text{ range for data collection} \\ (\text{deg}) \end{array}$	2.0-26.0	1.4-20.2	2.0-26.3	1.2-25.0	1.6-27.4	2.1-25.0
GOF on $F^2$	1.08	0.99	0.78	1.10	1.07	1.12
reflns collected	35 623	31 902	10 002	25 431	20 488	9111
unique reflns	3327	5232	3874	4887	6743	2765
final R indices $[I > 2\sigma(I)]$	R1 = 0.0419	R1 = 0.0306	R1 = 0.0262	R1 = 0.0353	R1 = 0.0540	R1 = 0.0376
	wR2 = 0.1198	wR2 = 0.0684	wR2 = 0.0760	wR2 = 0.1055	wR2 = 0.1692	wR2 = 0.1157
temperature (K)	120	293	293	293	293	293

(platinum working electrode, platinum counter electrode, Ag/AgCl reference electrode) and a PC-controlled PAR model 273A electrochemistry system. The  $E_{1/2}$  for the ferrocenium–ferrocene couple under our experimental conditions was 0.39 V. EPR spectra in the Xband were recorded with a JEOL JES-FA200 spectrometer. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). <sup>1</sup>H NMR spectra were taken on a Bruker Avance DPX 300 spectrometer, and SiMe<sub>4</sub> was used as the internal standard. C–H protons are assigned according to their labeling scheme in the respective figures as shown in the Supporting Information. Due to the presence of overlapping protons, assignments have not been made for the compound [7]Cl. ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263).

A. Chemical Reactions of  $CpRu^{II}Cl(PPh_3)_2$  with ortho-Monosubstituted Anilines. 1. 2-Chloroaniline ( $HL^{1a}$ ). A 200 mg (0.28 mmol) amount of  $CpRu^{II}Cl(PPh_3)_2$  in 3 mL of 2-chloroaniline was heated at 80 °C in air for six hours. During this period the color of the solution changed from orange to reddish-brown. The reaction mixture was then washed with a dichloromethane-hexane solvent mixture (1:10) several times to remove unreacted ligand. Rapid crystallization of the crude reaction mixture from 30 mL of a dichloromethane-hexane (1:10) solvent mixture furnished a major product, 1 (intense red), along with a minor product, 2 (yellowish-brown). Compound 2 was precipitated from this solvent mixture, and compound 1 was collected by the evaporation of solvent. These two compounds were recrystallized by slow evaporation of their solutions in a dichloromethane-hexane solvent mixture. Yield and characterization data of the compounds are as follows:

**1.** Yield: 62 mg (49%). ESI-MS, m/z: 417  $[M - Cl]^+$  (M =  $C_{17}H_{13}Cl_3N_2Ru$ ). Anal. Calcd for  $C_{17}H_{13}Cl_3N_2Ru$ : C, 45.13; H, 2.88; N, 6.19. Found: C, 45.07; H, 2.91; N, 6.15. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 12.79(s, 1H, N-H), 7.95(d, 1H, *J* = 7.5 Hz, H4), 7.42(d, 1H, *J* = 9.0 Hz, H7), 7.36(t, 1H, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 9.0 Hz, H5), 7.30(t, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 7.5 Hz, H6), 7.14(d, 1H, *J* = 6.5 Hz, H1), 6.89(t, 1H, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 7.0 Hz, H2), 6.84(d, 1H. *J* = 9.0 Hz, H3), 4.96(s, 5H, Cp).

**2.** Yield: 32 mg (17%). ESI-MS, m/z: 292  $[M/2 - Cl]^+$  (M =  $C_{22}H_{20}Cl_4N_2Ru_2$ ). Anal. Calcd for  $C_{22}H_{20}Cl_4N_2Ru_2$ : C, 40.24; H, 3.05; N, 4.27. Found: C, 40.28; H, 3.10; N, 4.22. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 9.0(s, 1H, N–H), 7.23(d, 1H, *J* = 9.0 Hz, H3), 7.01(m, 2H, H2, H4), 6.43(d, 1H, *J* = 9.0 Hz, H1), 5.26(s, SH, Cp).

2. 2-Methylaniline ( $HL^{1}$ ). The reaction of CpRu<sup>II</sup>Cl(PPh<sub>3</sub>)<sub>2</sub> with 2methylaniline under identical reaction conditions to those described in the previous section produced the mononuclear red compound 3 and the binuclear yellow compound 4. Their yield and characterization data are as follows:

**3.** Yield: 61 mg (53%). ESI-MS, m/z: 377 [M - Cl]<sup>+</sup> (M =  $C_{19}H_{20}ClN_2Ru$ ). Anal. Calcd for  $C_{19}H_{20}ClN_2Ru$ : C, 55.27; H, 4.85; N, 6.78. Found: C, 55.22; H, 4.90; N, 6.75. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 12.23(s, 1H, N-H), 7.75(d, 1H, *J* = 7.5 Hz, H4), 7.25 (d, IH, *J* = 7.5, H5), 7.15(t, 1H, *J* = 7.5 Hz, H7), 7.11(d, 1H, *J* = 7.5 Hz, H6), 6.71(d, 2H, *J* = 5.5 Hz, H2, H3), 6.61(t, 1H, *J*<sub>1</sub> = 5.5 Hz, J<sub>2</sub> = 5.0 Hz, H1), 4.73(s, SH, Cp), 2.54(s, 3H), 2.22(s, 3H, CH<sub>3</sub>).

**4.** Yield: 24 mg (14%). ESI-MS, m/z:  $639 [M + Na]^+$  (M =  $C_{24}H_{26}Cl_2N_2Ru_2$ ). Anal. Calcd for  $C_{24}H_{26}Cl_2N_2Ru_2$ : C, 46.75; H, 4.22; N, 4.24. Found: C, 46.72; H, 4.26; N, 4.22. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 14.99(s, 1H, N-H), 6.72(d, 1H, *J* = 7.5 Hz, H2), 6.71(t, 1H, *J*<sub>1</sub> = 7.5, *J*<sub>2</sub> = 8.0 Hz, H4), 6.42(d, 1H, *J* = 6.5 Hz, H3), 6.14(d, 2H, *J* = 9.0 Hz, H1), 4.98(s, 5H, Cp), 2.96(s, 3H, CH<sub>3</sub>).

3. 2-Methylthioaniline  $(HL^{1b})$ . A similar reaction with 2methylthioaniline produced the red complex 5 and the binuclear green complex [6]Cl<sub>2</sub>. Yield and characterization data of these compounds are as follows:

**5.** Yield: 37 mg (28%). ESI-MS, m/z: 441 [M - Cl]<sup>+</sup> (M = C<sub>19</sub>H<sub>19</sub>ClN<sub>2</sub>RuS<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>ClN<sub>2</sub>RuS<sub>2</sub>: C, 47.90; H, 3.99; N, 5.88. Found: C, 47.94; H, 3.95; N, 5.91. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 12.93(s, 1H, N-H), 7.71(d, 1H, *J* = 8.0 Hz, H7), 7.26(t, 1H, *J* = 7.5 Hz, H5), 7.15(t, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 7.5 Hz, H6), 7.10(d, 1H, *J* = 7.5 Hz, H4), 6.97(d, 1H, *J*<sub>1</sub> = 7.0 Hz, H1), 6.82(t, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 7.0 Hz, H2), 6.69(d, 1H, *J* = 8.5, H3), 4.86(s, 5H, Cp), 2.46(s, 3H, CH<sub>3</sub>), 2.24(s, 3H, CH<sub>3</sub>).

[6]Cl<sub>2</sub>. Yield: 48 mg (25%). ESI-MS, m/z: 304 [M/2]<sup>+</sup> (M = C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub>). Anal. Calcd for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 47.37; H, 4.28; N, 4.60. Found: C, 47.34; H, 4.25; N, 4.63. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): 4.94(s, 1H, N–H), 7.64(d, 1H, *J* = 13.5 Hz, H1), 7.41(t, 1H, *J*<sub>1</sub> = 11.8 Hz, *J*<sub>2</sub> = 13.5 Hz, H3), 7.27(t, 1H, *J*<sub>1</sub> = 13.4 Hz, *J*<sub>2</sub> = 11.8 Hz, H2), 7.14(d, 1H, *J* = 11.8 Hz, H4), 5.92(s, 5H, Cp), 2.54(s, 3H, CH<sub>3</sub>).

B. Reaction of  $CpRu^{II}Cl(PPh_3)_2$  and 2,6-Dichloroaniline (HL<sup>3a</sup>). A mixture of 200 mg (0.28 mmol) of  $CpRu^{II}Cl(PPh_3)_2$  and 3 mL of 2,6-dichloroaniline (HL<sup>3</sup>) was stirred for 24 hours at 80 °C in air. During this period, the color of the mixture became reddish-brown. The

reaction mixture was then cooled and washed with a dichloromethane–hexane solvent mixture (1:10) several times to remove excess 2,6-dichloroaniline. The crude mass thus obtained was dissolved in a minimum volume of dichloromethane and purified by rapid crystallization using hexane as the precipitant. The compound [7]Cl was recrystallized by slow evaporation of a methanolic solution of the compound. Its yield and characterization data are as follows:

[7]Cl. Yield: 68 mg (29%). ESI-MS, m/z: 806 [M]<sup>+</sup> (M =  $C_{25}H_{18}Cl_6N_3O_2Ru_2$ ). Anal. Calcd for  $C_{25}H_{18}Cl_6N_3O_2Ru_2$ : C, 49.42; H, 2.96; N, 6.92. Found: C, 49.37; H, 3.99; N, 6.88. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): 7.66(m, 3H), 7.52(m, 1H), 7.35(m, 4H), 6.88(m, 1H), 5.73(s, 5H, Cp), 4.85(s, 1H, N-H), 1.53(s, 3H, CH<sub>3</sub>).

The reaction in the presence of sodium acetate under identical reaction conditions produced the complex  $[7]Cl_2$  with a higher yield of 45%.

C. Reactions of  $(Bnz)_2Ru^{I_2}Cl_4$  with 2-Methylthioaniline (HL<sup>1b</sup>). A 200 mg (0.45 mmol) portion of  $(Bnz)_2Ru^{I_2}Cl_4$  was added to 3 mL of 2-methylthioaniline, and the mixture was stirred for 80 °C in air for six hours. During this reaction period the color of the solution became yellowish-brown. The reaction mixture was then cooled and washed with diethyl ether several times to remove excess ligand. The crude mass thus obtained was dissolved in a minimum volume of dichloromethane and purified by rapid crystallization using diethyl ether as the precipitant. Purification of the crude mass furnished a yellow-colored compound, [9]Cl<sub>2</sub>. It was recrystallized by slow evaporation of the methanolic solution of the compound. Its yield and characterization data are as follows:

[9]Cl<sub>2</sub>. Yield: 132 mg (42%). ESI-MS, m/z: 317 [M/2]<sup>+</sup> (M =  $C_{26}H_{28}N_2Ru_2S_2$ ). Anal. Calcd for  $C_{26}H_{28}N_2Ru_2S_2$ : C, 49.21; H, 4.41; N, 4.41. Found: C, 49.18; H, 4.45; N, 4.44. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): 7.87(s, N–H), 7.37(d, 1H, J = 13.5 Hz, H1), 7.11(m, 2H, H2, H4), 6.97(m, 1H, H3), 6.08(s, 6H, Bnz), 3.31(s, 3H, CH<sub>3</sub>).

**Computational Details.** Full geometry optimizations were carried out using the density functional theory method at the B3LYP level.<sup>16</sup> All elements except ruthenium were assigned the 6-31G(d) basis set. The SDD basis set with effective core potential was employed for the ruthenium atom.<sup>17</sup> The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive Eigen values. All calculations were performed with the Gaussian03 program package.<sup>18</sup> Natural bond orbital analyses were performed using the NBO 3.1 module of Gaussian03.<sup>19</sup> Vertical electronic excitations based on B3LYPoptimized geometries were computed using the TD-DFT formalism<sup>20</sup> in acetonitrile using the conductor-like polarizable continuum model.<sup>21</sup> GaussSum<sup>22</sup> was used to calculate the fractional contributions of various groups to each molecular orbital.

Crystallography. Crystallographic data for the compounds 1, 2, 5, [6]Cl<sub>2</sub>, [7]Cl, and [9]Cl<sub>2</sub> are collected in Table 4. Suitable X-ray quality crystals of the compounds 1, 2, 5, and [7]Cl were obtained by slow evaporation of a dichloromethane-hexane solution of the corresponding compounds. Suitable crystals for the cationic compounds  $[6]Cl_2$  and  $[9]Cl_2$ , on the other hand, were obtained by slow evaporation of their methanolic solutions. All data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), and were corrected for Lorentz-polarization effects. 1: A total of 35 623 reflections were collected, out of which 3327 were unique ( $R_{int}$  = 0.064), satisfying the  $I > 2\sigma(I)$  criterion, and were used in subsequent analysis. 2: A total of 31 902 reflections were collected, out of which 5232 were unique ( $R_{int} = 0.068$ ). 5: A total of 10 002 reflections were collected, out of which 3874 were unique ( $R_{int} = 0.030$ ). [6]Cl<sub>2</sub>: A total of 25 431 reflections was collected, out of which 4887 were unique ( $R_{int} = 0.034$ ). [7]Cl: A total of 20488 reflections were collected, out of which 6743 were unique ( $R_{int} = 0.043$ ). [9]Cl<sub>2</sub>: A total of 9111 reflections were collected, out of which 2765 were unique  $(R_{int} = 0.019)$ . The structures were solved by employing the SHELXS-97 program package<sup>23a</sup> and refined by full-matrix least-squares based on  $F^2$  (SHELXL-97).<sup>23b</sup> Hydrogen atoms were added in calculated positions.

#### ASSOCIATED CONTENT

#### Supporting Information

X-ray crystallographic files in CIF format for the complexes 1, 2, 5,  $[6]Cl_2$ , [7]Cl, and  $[9]Cl_2$ ; figures of ESI-MS and <sup>1</sup>H NMR of 1-[7]Cl and  $[9]Cl_2$ ; DFT and TD-DFT results of complexes 1, 2, and  $[6]Cl_2$  are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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