A Novel Dinuclear Ruthenium Complex Bridged through a Substituted Phenazine Ligand Formed by Ruthenium-Promoted Oxidative Assembly of 1,3-Diaminobenzene

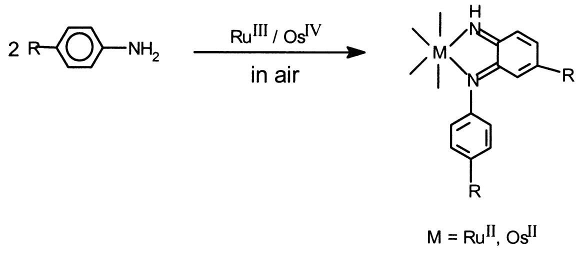
Partha Majumdar,[a] Larry R. Falvello,[b] Milagros Tomás,[b] and Sreebrata Goswami*[a]

Abstract: The reaction of $[Ru(acac)_3]$ (acac = acetylacetonate) with molten 1,3-diaminobenzene affords the crystalline monometallic compound $[Ru(L^1)(acac)_2]$ (**1**: L^1 = *N*-(3′-aminophenyl)1,2-(3-amino)benzoquinone diimine) along with an unstable dimetallic compound $[Ru_2(\mu\text{-}L^2)(acac)_4]$ (**2**: L^2 = *N*-4,6-bis(3′-aminophenyl)imino-3,5-diimino-hex-1-ene). Compound **2** transforms to a stable dimetallic compound $[Ru_2(\mu\text{-}L^3)(acac)_4]$ (**3**: L^3 = 2-amino-6(3′-aminophenyl)imino-9-imino-phenazine) in boiling 2-methoxyethanol. The above compounds are formed by ruthenium-mediated oxidative di- or trimerization of the diamine with the formation of several new C–N bonds. The products have been thoroughly characterized. FAB mass spectra, along with other physicochemical data, were used for their formulations. The compounds **1**, **2**, and **3** display intense peaks due to their parent molecular ions at *m*/*z* 512, 916, and 914, respectively. Final characterization of complex **3** was made by single-crystal X-ray structure determination. The structure of **3** confirmed the formation of three new C–N bonds and the bridging ligand L^3 from 1,3-diaminobenzene. The conversion, **2** → **3** is an oxidative ring-closure reaction, which is associated with dehydrogenation reactions. The monometallic compound **1**, showed a reversible metal-based anodic response at 0.35 V. On the other hand, both the compounds **2** and **3** showed a pair of well-resolved metal-based anodic oxidations, for which the separation between the two successive anodic responses were high (> 0.4 V). In addition, all of them showed multiple cathodic responses that were in the range −1.0 to −2.0 V.

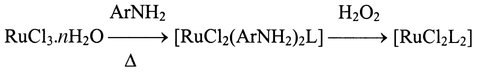
Keywords: C–H activation · C–N coupling · diimines · ruthenium · structure elucidation

Introduction

Metal-promoted organic reactions belong to important class of chemical transformations[1, 2] as these provide facile synthetic routes for the synthesis of many novel molecules, which are otherwise difficult, or in some cases even impossible, to synthesise following conventional synthetic procedures. In recent years we have noted[3, 4] a number of metal-promoted C–N bond-forming processes including the oxidative dimerization of primary aromatic monoamines leading to the synthesis of metal complexes of 1,2-diimines, which are otherwise inaccessible. For example, *N*-aryl-1,2-diiminoarenes were directly obtained[3] from the reaction of primary aromatic monoamines with suitable metal substrates (Scheme 1). It has also been shown[3d] that *cis* coordination of primary aromatic monoamines to a redox-active metal center and oxidative dehydrogenation are the two key steps for the amine → 1,2-diimine transformation (Scheme 2).



Scheme 1. Metal-promoted oxidative *ortho*-dimerization of an aromatic amine.



$$RuCl_3.nH_2O \xrightarrow[\Delta]{ArNH_2} [RuCl_2(ArNH_2)_2L] \xrightarrow{H_2O_2} [RuCl_2L_2]$$

L = *N*-aryl-1,2-diimino arene

Scheme 2. Oxidative dimerization of a ruthenium complex that contains two coordinated aromatic amines.

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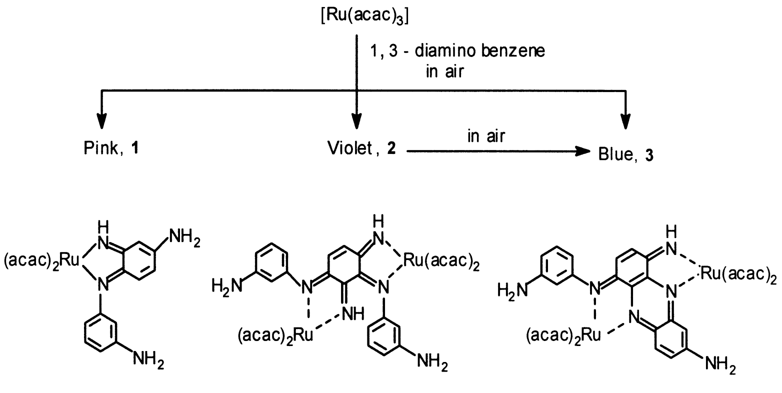
The success in this area persuaded us to explore the corresponding reactions of aromatic diamines, for which more C–N bond-forming processes were anticipated. In this respect, we have chosen 1,3-diaminobenzene as the reactant. It was hoped that this reaction might lead to complexes of higher nuclearity. It is noteworthy that two other isomers of the above diamine (1,2- and 1,4-diaminobenzene) are known to act as a bidentate chelate and monodentate bridging ligand, respectively.[5, 6] However, the coordination of 1,3-diaminobenzene is practically unknown.[7]

Herein we introduce an example of [Ru(acac)$_3$]-mediated oxidative di-, and trimerization reaction of 1,3-diaminobenzene leading to two major products (**1** and **2**, Scheme 3). The pink compound **1** is monometallic, and the violet compound **2** is dimetallic. The product **2** is unstable, particularly in solution, and is converted almost quantitatively to the blue dimetallic compound **3** on boiling in an alcoholic solvent, for example, 2-methoxyethanol. All the above compounds are formed through several C–N bond-forming processes. These metal-promoted transformations were unprecedented in the literature.



1 **2** **3**

Scheme 3. The synthetic reaction scheme.

Results and Discussion

The reaction: The synthetic reaction (Scheme 3) involved heating a mixture of [Ru(acac)$_3$] in molten 1,3-diaminobenzene (neat) for 30 min. The initial red solution gradually changed color to pink, and finally it became blue-violet. The crude product obtained from the reaction was soluble in common organic solvents. TLC showed the presence of a pink band followed by a violet band, and chromatographic purification yielded the pink **1**, and then violet compound **2**, as the two major products. A minor blue fraction **3** was eluted using a more polar eluent. Compound **2** was unstable in solution at room temperature and, with time, was slowly converted to a mixture of products that contained **3** as the major fraction. The **2** → **3** transformation was much faster in boiling 2-methoxyethanol. Working up the mixture, followed by column chromatography over basic alumina, yielded the blue crystalline compound **3**. The overall yields of the products were good. There were a few minor fractions which could not be purified, and their identities remain uncertain.

We wish to note that the above reactions only occur in the presence of molecular oxygen, and do not proceed in an inert atmosphere. Notably, this chemical transformation became much faster, and there was a significant increase in the yields of **1** and **2**, on addition of few drops of triethylamine at the initial stage of the reaction. The chemical transformations are associated with the loss of protons and triethylamine therefore acts as a proton sink.

Formulation and spectroscopic characterization: All the complexes gave satisfactory analyses (see Experimental Section). The compounds were soluble in common organic solvents and are diamagnetic. These showed $\nu_{C=N}$ stretch[8] near 1600 cm^{-1}, which characterizes the presence of a diimine chromophore in these compounds. The lowering of this stretching frequency, relative to that for the free imine, may be attributed to the presence of strong d(Ru) – π*(L) back-bonding[9] in the ground state of ruthenium(II) complexes. Here π*(L) is the LUMO of the diimine chromophore. The N–H stretching frequencies[10] appeared in the range 3230 – 3000 cm^{-1}. In addition, all the complexes showed all the characteristic stretches[11] of coordinated acetylacetonate.

^{1}H NMR data of the compounds were obtained in CDCl$_3$. They showed complex spectral patterns in the aromatic region ($\delta = 6.30$ to 7.25) due to extensive overlap of resonances. However, other resonances were diagnostic and have been used for the characterization of the compounds. The methyl proton resonances of **1**–**3** appeared in the range $\delta = 1.70$–2.30 (Table 1). For compound **1** four methyl resonances were

Table 1. ^{1}H NMR and UV-visible spectral data.

Compound	$\delta^{[a]}$				
	Me	CH	N–H	NH$_2$	λ_{max} [nm] (ε [M^{-1}cm^{-1}])[b]
1	1.74, 1.79, 1.81, 2.28	5.04, 5.22	9.01	3.80	550(13870), 345[c], 273(21400)
2	1.75, 1.79, 1.88, 1.90, 1.91, 1.94, 2.16, 2.29	5.00, 5.15, 5.27, 5.43	10.80, 11.53	3.66	562(24600), 350[c], 270(30000), 242[c]
3	1.75, 1.82, 1.89, 1.96, 2.00, 2.02, 2.09, 2.29	5.01, 5.15, 5.20, 5.35	12.56	3.73, 4.16	600(26450), 445[c], 265(44200)

[a] In CDCl$_3$; SiMe$_4$ used as internal standard; aromatic proton resonance occur in the region $\delta = 6.30$ to 7.25. [b] In CH$_2$Cl$_2$. [c] Shoulder.

observed, while eight such resonances were seen for both **2** and **3**. The ^{1}H NMR data thus confirmed the presence of two or four acac ligands, in **1**, or **2** and **3**, respectively. The methylene proton signals of the coordinated acac ligands appeared as sharp singlets in the range $\delta = 5.00 - 5.45$. The complex **1** showed two broad resonances at $\delta = 3.80$ and 9.01 assignable to N–H(amine) and N–H(imine) resonances, respectively.[12] Complex **2**, on the other hand, displayed two imine resonances at $\delta = 11.53$ and 10.80, which were associated with a broad resonance at $\delta = 3.66$ due to N–H(amine). In contrast, complex **3** had only one resonance at $\delta = 12.56$ assignable to N–H(imine), and the N–H(amine) resonance appeared at $\delta = 3.73$ and 4.16.

FAB mass spectra of the present complexes are available as Supporting Information (Figure S1). Compounds **1** and **3** displayed peaks due to their parent molecular ions at *m/z* 512 and 914, respectively. The spectrum of compound **1** confirmed that it was the monometallic [Ru(L^1)(acac)$_2$] (L^1 = *N*-(3′-aminophenyl)1,2-(3-amino)benzoquinone diimine). Apart from the molecular ion, two ions at *m/z* 413 and 313 due to the stepwise elimination of two coordinated acetylacetonates were observed. Interestingly and expectedly, four such peaks, at intervals of approximately 100 mass units, were observed in the case of dimetallic compound **3**, which contains four coordinated acac ligands. The FAB mass spectral pattern of the intermediate **2** was quite similar to that observed for **3**. An intense peak due to molecular ion at *m/z* 916 was observed, which was accompanied by four less intense peaks at *m/z* 816, 715, 615, and 516, which were due to stepwise dissociation of four coordinated acac ligands. It is noteworthy that the simulated isotopic patterns for the above formulations of compounds corresponded very well to the observed spectral pattern. Simulated spectra for the proposed molecular ions are available as Supporting Information (Figure S2).

Characterization of the dimetallic compounds **2** and **3** were made from their physicochemical data. However, the X-ray crystal analysis of **3** confirmed its structure (vide infra). It was possible to propose both the composition and structure of the intermediate **2**, from the identity of **3**, and from the comparison of physicochemical data of **2** and **3**. From the foregoing discussion it should be clear that while complex **1** is a congener of the reported diimine complexes [Ru(acac)$_2$-(diim)] (diim = *N*-phenyl-(1,2-benzoquinone)diimine),[3a] obtained from the reaction of [Ru(acac)$_3$] and ArNH$_2$, the dimetallic complexes obtained here are formed by previously unknown organic transformations.

Crystal structure of $3 \cdot 1.5\,C_6H_5CH_3$: After repeated trials, we obtained single crystals of **3**, as $3 \cdot 1.5\,C_6H_5CH_3$, from a toluene-hexane mixture, suitable for its X-ray structure determination. A view of molecule **3** is shown in Figure 1. The structure determination of **3**, which was derived from poor quality diffraction data, suffices to establish the connectivity of the molecule. It would not be appropriate to use these results in fine comparisons with similar entities. The coordination sphere around each ruthenium involves RuN$_2$O$_4$ and is coordinated in a distorted octahedral geometry by the four oxygen atoms of two acetylacetonate ligands and by the two nitrogen atoms of the bridging substituted phenazine ligand. We observe consistency among the shapes of the four acac groups. The bridging ligand is formed by the oxidative *ortho*-fusion of three 1,3-diaminobenzene residues. To achieve this, three new C–N bonds, C(21)–N(4), C(23)–N(3), and C(17)–N(2), were formed. This unusual transformation resulted in the formation of a bridging ligand, which would otherwise be unachievable. It is relevant to add that the common bridging ligands of N-donor atoms are usually derived from the pyridine bases.[13] There are also examples of bridging ligands that are made of imidazole basic units.[14] The structural data reveals that the bridging ligand, thus formed, is a conjugated planar system. The five-membered chelate rings in this compound have the expected bite angles (N(2)–Ru(1)–N(3), 79.5(6)°; N(4)–Ru(2)–N(6), 78.9(6)°), and the bite angles of the six-membered acac-containing chelate rings also have the expected values of near 90°.

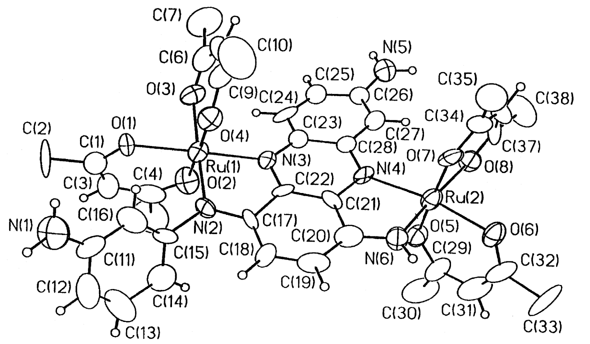


Figure 1. View of the dimetallic complex **3**.

The intermediate **2** underwent chemical transformation in solution and X-ray quality crystals could therefore not be obtained. However, the formulation of intermediate **2** could be made by comparing its physicochemical data with those of **3**, whose formulation had been authenticated (vide supra) through structure determination. The violet intermediate **2**, on heating in high-boiling alcoholic solvents in the presence of air, produced **3** quantitatively. The molecular weight of the compound **2** was 916, which is two mass units higher than that of the final blue product **3**. The ^{1}H NMR spectrum of **2** showed two N–H signals, while that of **3** showed only one signal (vide supra). The nature of electronic spectra and voltammograms (vide infra) of compounds **2** and **3** indicated the presence of two ruthenium centers. Based on the above physicochemical data we proposed the structure of **2** shown in Scheme 3. It has two imine N–H functions, one of which is close to an *ortho*-carbon of a pendent arylamino group. It is believed that on boiling in the presence of molecular oxygen, a new C–N bond is formed (ring closure) with the elimination of molecular hydrogen, which is responsible for the formation of the blue dinuclear compound **3**. This also explains the difference of two mass units between **2** and **3**, which is observed in FAB mass spectra.

The compounds **1**–**3** are formed by a series of C–N bond-forming processes due to activation[3, 4, 15] of C–H bonds, which presumably occurs through the coordination of diamine residues to the metal center(s). These are associated with dehydrogenation reactions. Ruthenium-catalyzed oxidative dehydrogenation processes with molecular oxygen as the oxidant are documented in the literature.[3f, 16] The formation of monometallic pink complex **1** is the result of oxidative dimerization processes of 1,3-diaminobenzene, which is similar to our earlier observations[3] in which *N*-aryl-(1,2-diimino) complexes were obtained from the reaction of [Ru(acac)$_3$] and ArNH$_2$ (Scheme 1). The present diamine may be viewed as a 3-amino-substituted primary aromatic amine. The formations of the two dinuclear compounds from the above reaction are much more complex. The actual mechanism and the steps involved are uncertain to us, and we therefore refrain from making any speculation on this.

Electronic spectra (UV-visible) and redox: The electronic spectral data for the complexes are given in Table 1 and spectra are presented in Figure 2. The electronic spectra of the complexes are dominated in the visible range by an intense transition in the range 600–540 nm, which is characteristic for similar 1,2-diimine complexes.[3] For example, [Ru(acac)$_2$(diim)], obtained from the reaction of [Ru(acac)$_3$] and aniline, showed an intense transition at 519 nm (ε 19050 M^{-1}cm^{-1}). This transition has been assigned to charge transfer between two heavily mixed orbitals.[3c] The mononuclear complex **1** similarly showed a strong absorption at 550 nm (ε 13870 M^{-1}cm^{-1}). The corresponding transitions for the dinuclear complexes **2** and **3** are almost twice as intense as expected.[17] Notably, the transition energy for the violet dimer **2** is similar to that observed for the pink monomer **1**. However, the corresponding transition for the blue dimer **3** shifts towards the blue appreciably ($\lambda = 600$ nm). This rather large shift may be due to differences of chromophoric groups in **3**, which are more or less similar in **1** and **2**. The rest of the transitions in the three complexes appeared in the UV region. The origin of these bands at high energies are either intraligand n → π* or π → π* transitions centered primarily on the imine group, or involve metal and higher energy ligand orbitals.

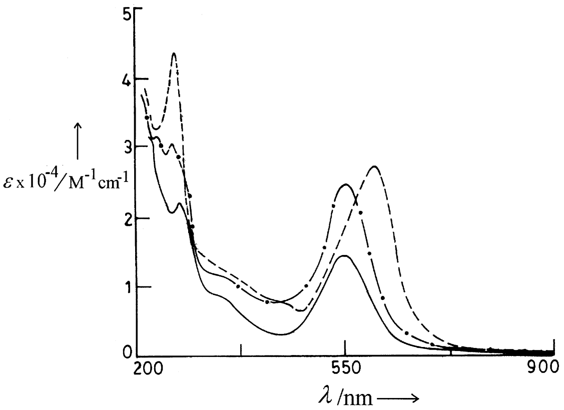


Figure 2. Electronic spectra of the complexes: **1** (——), **2** (•–•–), and **3** (- - - -).

We used cyclic voltammetry and differential pulse voltammetry to study the redox behavior of the complexes. The redox behavior of the complexes were studied in acetonitrile (0.1 M NEt$_4$ClO$_4$) in the potential range 2.0 to –1.5 V by using platinum and glassy carbon working electrodes. The reported potentials (Table 2, Figure 3) are referenced to the saturated calomel electrode (SCE). The value for the ferrocene–ferrocenium couple under our experimental conditions was 0.42 V.

Table 2. Electrochemical data.[a]

Compound	Metal oxidation $E_{1/2}$ [V] (ΔE_p [mV])[b]	Ligand reduction $-E_{1/2}$ [V] (ΔE_p [mV])[b]
1	0.35(70)	1.14(80), 1.82[d]
2	0.22(80), 0.80[c]	1.17(70), 1.77[d]
3	0.08(80), 0.54(80)	1.16(80), 1.50 (120), 1.82(80)

[a] Conditions: solvent, acetonitrile; supporting electrolyte, NEt$_4$ClO$_4$ (0.1 M); working electrode, platinum for oxidation and glassy carbon for reduction processes; reference electrode, SCE; solute concentration, ca. 10^{-3} M; scan rate, 50 mV s^{-1}. [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = (E_{pa} - E_{pc})$. [c] Irreversible E_{pa}. [d] Irreversible E_{pc}.

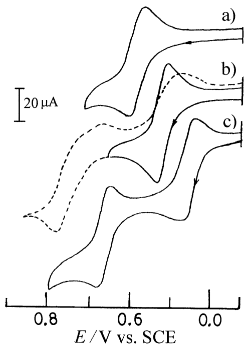


Figure 3. Cyclic voltammogram for the compounds: a) **1**, b) **2**, and c) **3** recorded in CH$_3$CN at a scan rate of 50 mV s^{-1}.

The mononuclear compound **1** showed three one-electron redox processes in the potential range 1.5 to –2.0 V. One was oxidative in nature, occurring at +0.35 V, whilst the other two were reductive responses and appeared at –1.14 and –1.82 V. The oxidative response is electrochemically reversible and assigned to a Ru^{II} $\rightleftharpoons$ Ru^{III} process. The waves at negative potentials formally correspond to ligand reductions. It is known that the coordinated diimine ligands are susceptible to two-step reductions.[3f] Similar responses were observed for [Ru(acac)$_2$(diim)] complexes. The potentials for these diimine complexes depend linearly on the Hammett parameter[18] of the substituent on the coordinated diimine ligands. Thus the observed anodic potential for compound **1** falls on the E°_{298} versus 2σ (σ = substitution constant) linear plot (Supporting Information Figure S3 and Table 3). This further confirms the formulation of the pink complex as a monometallic compound (Scheme 3). The dimetallic compound **3** showed a pair of oxidative waves at 0.08 and 0.54 V, both of which are

Table 3. Observed potentials for the Ru^{II}/Ru^{III} couple for a series of [Ru(acac)$_2$(L)] complexes.

R[a]	σ[b]	$E^{\circ}_{1/2}$ [V]	Reference
H	0.00	0.47	[3c]
p-CH$_3$	– 0.17	0.33	[3c]
p-OCH$_3$	– 0.27	0.27	[3c]
p-Cl	+0.23	0.52	[3c]
m-NH$_2$	– 0.16	0.35	this work

[a] R is the substituent on the aromatic diimine ligand L. [b] Ref. [18].

reversible. The cathodic scans showed three reversible waves at -1.16, -1.50, and -1.82 V. The two anodic responses were assigned to stepwise redox processes at the two metal centers. Compound **2** also displayed a pair of anodic (0.22 and 0.80 V) and a pair of cathodic (-1.17 and -1.77 V) waves; the first anodic and cathodic responses were electrochemically reversible. The anodic responses were assigned to metal oxidations. The two oxidative responses in **2** appeared at more anodic potentials than those for **3**. This may be attributed to the presence of more diimine chromophores in this compound. It is known that diimine chromophores stabilize the bivalent state of ruthenium, owing to stronger $d\pi-p\pi$ interactions.

Notably, the separation between the two successive anodic responses in **2** and **3** are quite high (>0.4 V). The coordination environments around the two ruthenium centers in **3** are not strictly identical, hence this separation (ΔE), in principle, cannot be taken as a direct measure of electronic interactions between the metal centers across the bridging ligand. However, we note that the violet dimer **2** is more symmetrical in this respect, and the large ΔE in this case indeed indicates strong communication between the two ruthenium centers.[19] This is expected since the two ruthenium centers in these bimetallic complexes are bound through planar, conjugated bridging ligands, suitable for effective $d\pi-p\pi$ interactions. Moreover, the peripheral acetylacetonate ligands also have significant contributions on this high metal–metal interaction across the bridging ligand. The peripheral acac ligand is a potential σ donor without any acceptor ability. As a result, the $d\pi$ orbitals of ruthenium centers are raised[20] in energy and, hence, the gap from the bridging π^* orbitals decreases. The multiple cathodic responses are assigned to ligand reductions occurring at the bridging ligand.

Conclusion

Three new ruthenium compounds **1**–**3** were obtained from the reaction of [Ru(acac)$_3$] and 1,3-diaminobenzene. The end products were isolated and fully characterized. The reagent 1,3-diaminobenzene underwent a novel metal-promoted transformation to afford ligands with varying denticities. To authenticate this transformation, X-ray structure analysis of one of the diruthenium compounds was performed. Physicochemical data, including ^{1}H NMR, FAB mass, IR, and electronic spectra of the compounds, fully support our assignments of the products. Electrochemical studies revealed high metal–metal interactions in the dinuclear complexes.

Experimental Section

Materials: The tris(acetylacetonato)ruthenium(III) was synthesized by the reaction of aqueous $RuCl_3 \cdot nH_2O$ with a large excess of acetylacetone.[21] Solvents and chemicals used for syntheses were of analytical grade. The supporting electrolyte (tetraethylammonium perchlorate) and solvents for electrochemical work were obtained as before.[3a]

Physical measurements: A Shimadzu UV2100 UV/Vis spectrophotometer was used to record electronic spectra in solution. Infrared spectra were recorded with a Perkin–Elmer 783 spectrophotometer. ^{1}H NMR spectra were measured in $CDCl_3$ with a Bruker–Avance DPX300 spectrometer and $SiMe_4$ was used as the internal standard. A Perkin–Elmer 240C elemental analyzer was used to record microanalytical data. Electrochemical measurements were done under a dry nitrogen atmosphere on a PAR 370-4 electrochemistry system as described earlier.[3a] All potentials in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium–ferrocene couple under our experimental condition was 0.42 V.

The reaction of Ru(acac)$_3$ with 1,3-diaminobenzene: A mixture of [Ru(acac)$_3$] (0.2 g, 0.5 mmol) and 1,3-diaminobenzene (0.4 g, 3.7 mmol) was heated on an oil bath at 150 °C for 30 min in presence of few drops of NEt_3. The initial red color gradually changed to blue-violet. The crude product, thus obtained, was dissolved in chloroform and purified on a silica-gel column (diameter, 2 cm; height, 70 cm). First, a dirty band was eluted with pure chloroform. A pink band was then eluted with acetonitrile/chloroform (1:9). An intense violet band was then eluted with acetonitrile/chloroform (7:3). A minor blue band was finally eluted from the column using acetonitrile/chloroform (4:1) as the eluant. A dark band remained uneluted at the top of the column.

The pink solution, on evaporation of the eluant under reduced pressure and recrystallization (dichloromethane/hexane 1:1), yielded compound **1** (0.1 g, 40%). IR (KBr): $\tilde{\nu} = 3210$ (N–H), 1590 (C=N), 1380 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{22}H_{26}N_4O_4Ru$: C 51.65, H 5.13, N 10.95; found: C 52.12, H 4.90, N 10.16; MS: *m/z*: 512 $[M]^+$.

Evaporation of the solution that contianed the violet band gave compound **2** (0.14 g, 30%). This compound is unstable, particularly in solution. IR (KBr): $\tilde{\nu} = 3220$ (N–H), 1600 (C=N), 1380 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{38}H_{44}N_6O_8Ru_2$: C 49.88, H 4.86, N 9.19; found: C 48.94, H 4.82, N 8.28; MS: *m/z*: 916 $[M]^+$.

Evaporation of the third, blue eluant produced compound **3** in only 7–10% yield. However, compound **2** was converted, almost quantitatively, to **3** in boiling 2-methoxyethanol (see below).

The conversion of 2 → 3: Compound **2** (0.10 g, 0.11 mmol) was dissolved in 2-methoxyethanol (25 mL), and the solution was heated at reflux on an oil bath (at 130 °C) for 4 h. The violet solution became intense blue during this period and was then evaporated to dryness. The crude product was extracted with chloroform and subjected to chromatography on a basic alumina column (diameter 1 cm; height 30 cm). An intense ink-blue band was eluted with an acetonitrile/chloroform (1:20) solvent mixture. A dark band remained at the top of the column. The blue eluant was evaporated under reduced pressure and dried under vacuum. The compound was then recrystallized (toluene/hexane) to give **3** (0.09 g, 90%): IR (KBr): $\tilde{\nu} = 3200$ (N–H), 1610 (C=N), 1390 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{38}H_{42}N_6O_8Ru_2$: C 49.99, H 4.65, N 9.21; found: C 49.26, H 4.11, N 9.47; MS: *m/z*: 914 $[M]^+$.

X-ray structure determination of $3 \cdot 1.5\,C_6H_5CH_3$: Crystallographic data along with refinement details for the compound are collected in Table 4. Single crystals for X-ray studies were obtained at RT by slow diffusion of a solution of compound **3** in toluene into hexene. It crystallized as a solvate: **3**·1.5 toluene. The crystals were found to undergo rapid decomposition when removed from the mother liquor. Several techniques were tried for mounting a specimen for the X-ray analysis. It was found that crystals mounted on glass fibers, surrounded with epoxy cement did not maintain sufficient quality for the analysis; neither did crystals mounted in a perfluorinated oil (Reidel de Haën RS3000) and then placed in a cold nitrogen stream. In the end, a crystal mounted in a capillary tube, along with some of its mother liquor, was used for the analysis, which was conducted at RT. A small amount of epoxy cement was placed in contact with the crystal and the wall of the capillary tube to prevent movement of the crystal within the tube.

After the initial reflection search and indexing,[22] intensity data were gathered in two shells $-4.0 \leq 2\theta \leq 38.0°$ and $37.9 \leq 2\theta \leq 50.0°$. Scan parameters were determined from two-dimensional ($\omega-\theta$) scans of eight reflections. During data collection, the orientation of the crystal was checked after every 800 measurements, and three monitor reflections were measured after every half-hour of X-ray exposure. These showed an average 23% decay through the 110.8 h of total beam time, and the measured intensities were corrected accordingly during data reduction.[23] Absorption corrections were based on Ψ-scans of 24 reflections with bisecting-mode Eulerian angle χ in the range of -47.3 to $+56.1°$.

Table 4. Crystal data and refinement results for $[Ru_2(\mu\text{-}L^3)(acac)_4] \cdot 1.5\,C_6H_5CH_3$.

formula	$C_{48.5}H_{54}N_6O_8Ru_2$
M_r	1051.12
crystal system	Triclinic
space group	$P\bar{1}$
a [Å]	10.5956(19)
b [Å]	14.234(3)
c [Å]	20.373(3)
α [°]	109.320(10)
β [°]	96.845(13)
γ [°]	90.402(13)
V [Å^3]	2875.4(9)
ρ_{calcd} [mg m^{-3}]	1.214
Z	2
crystal size [mm]	0.24 × 0.20 × 0.07
measured reflections	10160
unique reflections	10096
T [K]	298(2)
transmission factors (max/min)	0.957/0.780
θ range [°]	2.09–25.04
μ [cm^{-1}]	5.74
$R1$, $wR2$	0.1311, 0.2599
GOF	1.017

The structure was solved by direct methods[24] and refined by full-matrix least-squares.[25] The crystallographic asymmetric unit was found to consist of one molecule of the dinuclear Ru complex and three sites were occupied by toluene moieties. For these solvent molecules the methyl group was located for only one of the sites, and for the other two it was presumed to be randomly disordered. Each of the toluene sites was modeled as having occupancy of 0.5, after various values had been tested and refined. All non-hydrogen atoms in the asymmetric unit were refined with anisotropic displacement parameters. For the Ru complex, hydrogen atoms whose positions were easily predictable were placed at calculated positions and refined as riding atoms with isotropic displacement parameters set equal to 1.2 times the isotropic equivalent U values of their respective parent atoms. Attempts to locate the methyl hydrogen atoms of the acac ligands, by using local slant Fourier maps, gave inconclusive results, and so the methyl hydrogens were not included in the structural model. Neither were the hydrogen atoms at the toluene sites. The atoms located at each of the toluene sites were refined with a set of anisotropic displacement parameters common to the site; a restraint to isotropic behavior was used for one of the toluene moieties. Isotropic restraints were also used for two atoms of the Ru complex, namely for C(23) and C(25). In all, 523 variable parameters were refined to all 10096 unique reflection data (used as F_o^2) and to 55 observational restraints, giving an observation-to-parameter ratio of 19.4:1. The final residuals are listed in Table 4. A difference Fourier map at the end of the refinement showed several peaks above 1.0 e Å^{-3}, all in the vicinity of one of the toluene sites. We were not able to attribute geometrical significance to these peaks in such a way as to include them in the structural model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 161775 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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