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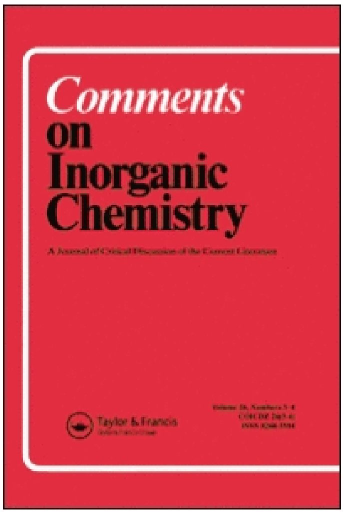

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Transition Metal Promoted Oxidative C–N Fusion Reactions of Aromatic Amines and Their Coordination Chemistry

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Some unusual examples of metal promoted oxidative dimerization and polymerization, via C–N bond formation, of aromatic mono- as well as di-amines are described. Successful isolation and thorough characterization of the products follow these reactions. Electrochemical and spectral studies of the complexes are reported and compared with related systems. While the heavier transition metal ions like ruthenium(III) and osmium(IV) mediate ortho-dimerization of primary amines, $ArNH_2$, Fe(III), on the other hand, promotes polymerization. Similar fusion reaction of 1,3-diaminobenzene with the mediator complex, $[Ru(acac)_3]$ (acac = acetyl acetonate), led to the formation of diruthenium complexes.

Keywords: metal-mediation, organic transformation, metal-diimines, X-ray structures, redox

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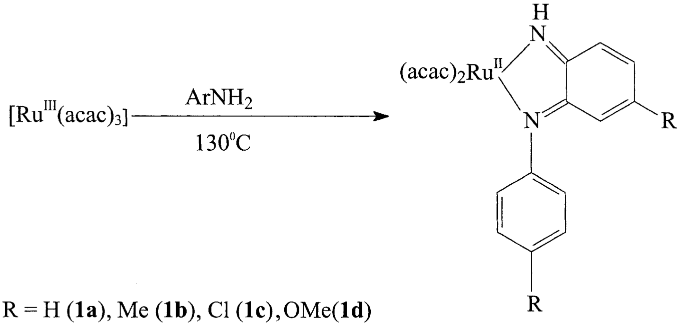
1. INTRODUCTION

Metal promoted organic reactions[1–3] belong to an important class of chemical transformations as these provide facile synthesis of many novel molecules, which are otherwise difficult, or in some cases even impossible, to synthesize following conventional procedures. In this respect, the use of transition metal ions as templates is found to be effective since these not only can gather and offer suitable orientations to various functionalized ligands by imposing a strict coordination geometry, but also can take part in redox reactions. In recent years, we have been interested in transition metal mediated aromatic amine fusion reactions that occur with formation[4] of new C-N bond(s). This report details the progress and identifies key features of the chemical reactions, which have been studied in our laboratory. We have also been concerned with coordination chemistry of the transformed organic compounds (ligands), which are interesting with many novel features. It may be worth noting that the reaction products described herein are otherwise not possible to synthesize. The results of the related work from other groups are mentioned in the context of our own work.

2. RUTHENIUM(III) PROMOTED OXIDATION OF PRIMARY AROMATIC AMINES

Our chemistry on amine fusion reactions built on an accidental reaction in which we noted[5] that the red complex, trisacetylacetonatoruthenium(III), reacted with aniline (neat) at 130°C to result a pink ruthenium complex $[\mathrm{Ru(acac)_2L^{1a}}]$ (**1a**) (acac = acetylacetonate and $\mathrm{L^1}$=N-aryl-1,2-benzoquinonediimine) (Eq. 1). It was later observed [6]



R = H (**1a**), Me (**1b**), Cl (**1c**), OMe(**1d**)

1

(1)

that substituted anilines also reacted similarly. The results of this reaction were totally unexpected and identification of the product was made by X-ray structure determination of a representative complex, **1a** (Figure 1). To look for the generality of this organic transformation, two other trivalent

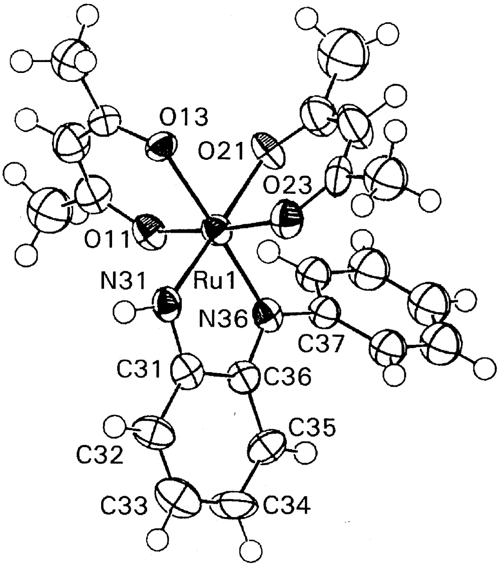
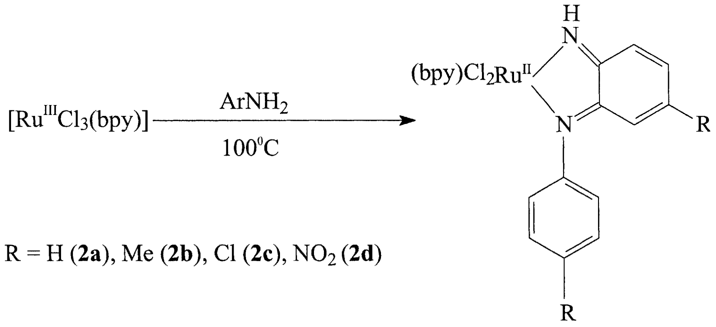


FIGURE 1 ORTEP plot and atom numbering scheme for [Ru(acac)$_2$(L^{1a})], **1a**. Hydrogen atoms are not shown for clarity. Reproduced with permission of RSC (Reference: 5).

ruthenium starting compounds, *viz.* [RuCl$_3$(bpy)] and RuCl$_3$.nH$_2$O, were chosen to carry out similar reactions with primary aromatic amines. The following reactions (Eq. 2 and 3) took place[5,7] and the products from each of the reactions were authenticated by X-ray structure solutions of the representative complexes *viz.* **2c** and **3a**, respectively (Figures 2 and 3).



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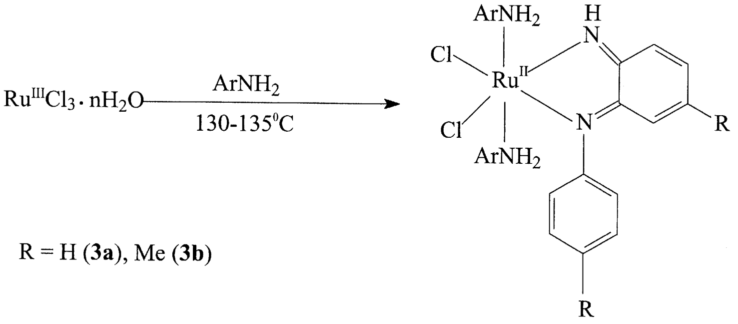
(2)



3 (3)

The three reactions, described above, exemplify ruthenium mediated oxidative dimerization of primary aromatic amines to N-aryldiimines. The organic transformation, under consideration, is a combination of two primary steps (Scheme 1): (i) oxidative *ortho* dimerization of $ArNH_2$ with a new C-N

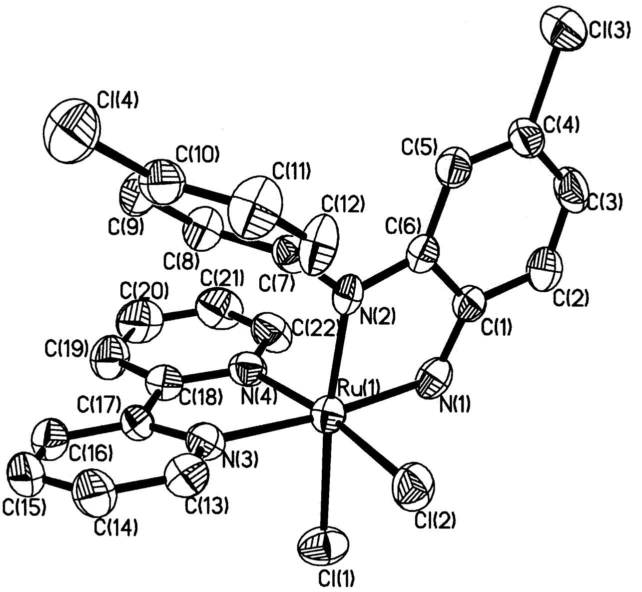


FIGURE 2 ORTEP plot and atom numbering scheme for $[RuCl_2(bpy)(L^{1c})]$, **2c**. Hydrogen atoms are not shown for clarity. Reproduced with permission of RSC (Reference: 7).

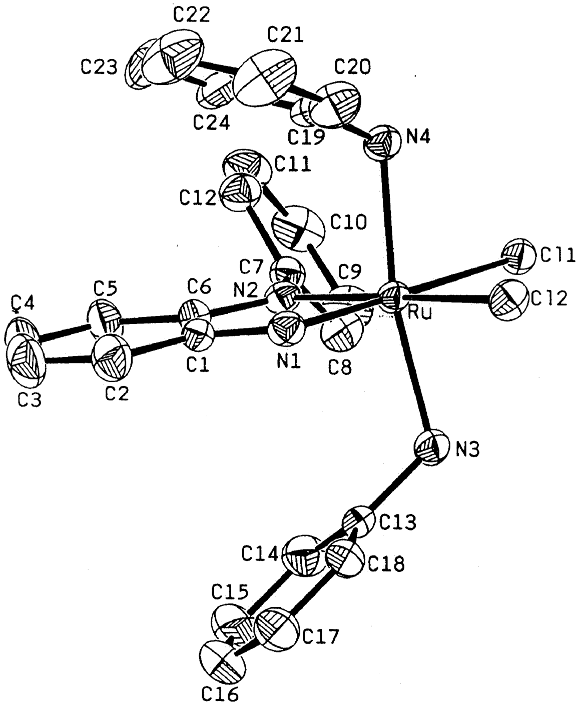
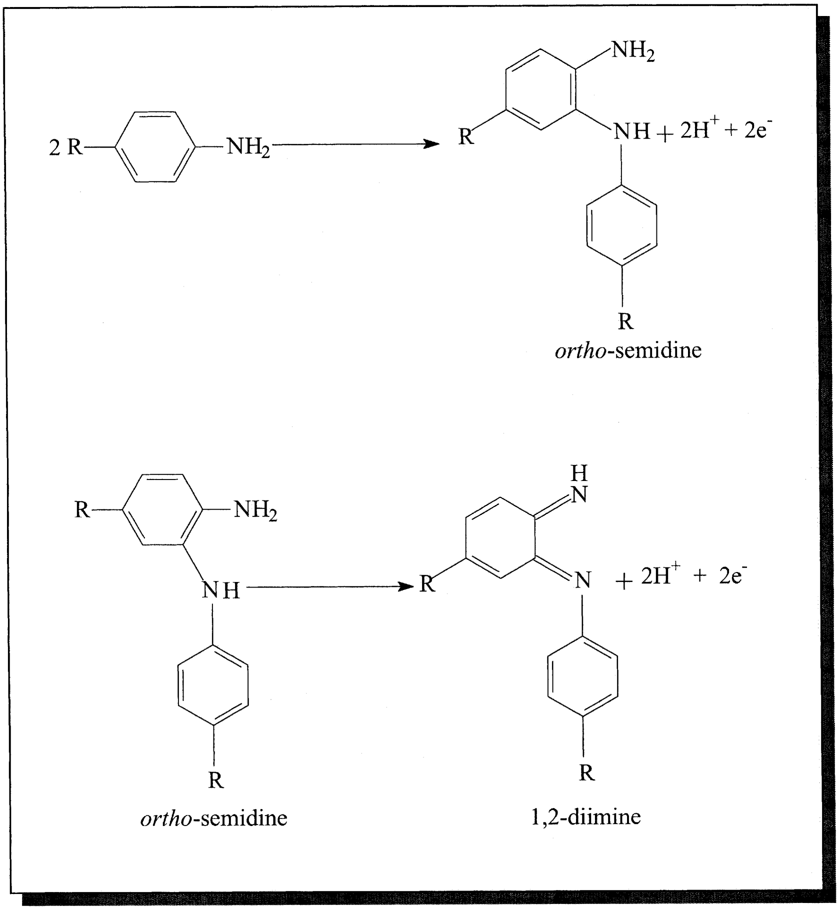


FIGURE 3 ORTEP plot and atom numbering scheme for [RuCl$_2$(PhNH$_2$)$_2$(L^{1a})], **3a**. Hydrogen atoms are not shown for clarity. Reproduced with permission of RSC (Reference: 5).

bond formation; and (ii) dehydrogenation of the resultant dimer (*ortho*-semidine) to corresponding 1,2-diimines.

A literature survey on chemical and electrochemical oxidations of primary aromatic amines revealed that oxidative dimerization of aromatic amines leading to *ortho*-semidine was not known. However, *para*-coupling reactions[8] producing *p*-semidine or benzidine and N,N coupling reactions resulting azo-arenes were commonly known. It may also be worth noting here that *o*-semidine is generally synthesized from hydrazoarene, Ar–NH–NH–Ar, which may be viewed as a dimer of the monoamine, ArNH$_2$. It is believed that initial dimerization of aromatic monoamines is essential to bring the amine nitrogen and *ortho*-carbon of the second aryl ring in close proximity for an *ortho*-C–N fusion reaction. Thus, for the same reason *cis*-coordination of aromatic amine residues in a metal promoted fusion reaction may be thought to be an essential prerequisite. This is shown to

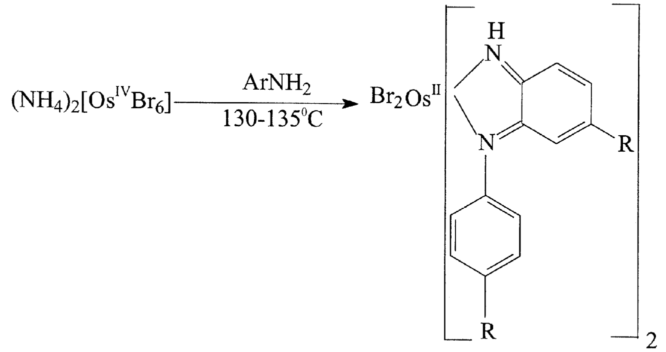


SCHEME 1 C–N fusion of an aromatic monoamine.

be so in a later section. It is important to note that the above reactions (1)-(3) occurred only in neat and in the presence of air. Furthermore, the reactions became faster and there was notable increase of yields on addition of NEt_3 at the initial stage of the reactions. It is therefore concluded that the amine oxidation reactions presumably occur *via* aerial oxidation. Ruthenium promoted dehydrogenation of amine→imine in the presence of air has been documented[9] in literature. Triethylamine, in these reactions, acts as proton sink to facilitate the release of protons.

3. OSMIUM(IV) PROMOTED REACTION

Our success in the ruthenium(III) promoted amine oxidation reactions prompted us to investigate similar reactions with osmium mediators. In this respect, we chose the common osmium salt, $(NH_4)_2[OsBr_6]$, as a mediator. The dark brown salt reacted slowly with neat aniline to produce a dibromo bisdiimine complex[10,11] of osmium(II), $[OsBr_2L_2{}^{1a}]$, **4a** (Eq. 4). The corresponding hexachloro salt, $(NH_4)_2[OsCl_6]$, reacted similarly to yield the dichloro analogue of **4**. These diimine complexes, **4**, represent the first examples of the osmium-1,2-diimine family (Figure 4). X-ray structure of a representative osmium complex, **4a**, was solved to authenticate the product from the above reaction.



(4)

4

R = H (**4a**), Me (**4b**), Cl (**4c**), OCH_3 (**4d**)

4. COORDINATION CHEMISTRY OF RUTHENIUM AND OSMIUM-DIIMINES

Metal complexes of the redox non-innocent diimine ligand sereies (1,2-benzoquinone diimine, bqdi; diiminosemiquinone, dsq and diamide, opda forms, Scheme 2) have been the subject of considerable interest[12–14] because of (i) their exceptionally rich redox and spectroscopic behavior and (ii) intramolecular electron transfer and the oxidation state formalism for highly delocalized systems. Both of these phenomena are related to a strong degree of orbital mixing between metal dπ and ligand pπ frontier orbitals, which can render conventional oxidation-state assignments difficult.

Previous studies on ruthenium quinone diimines have largely been confined to symmetrical diimines derived from 1,2-benzoquinonediimine and 9,10-phenanthrenequinonediimines. X-ray structures of metal complexes of benzoquinonediimines and their redox partners are still rare.[14b,15]

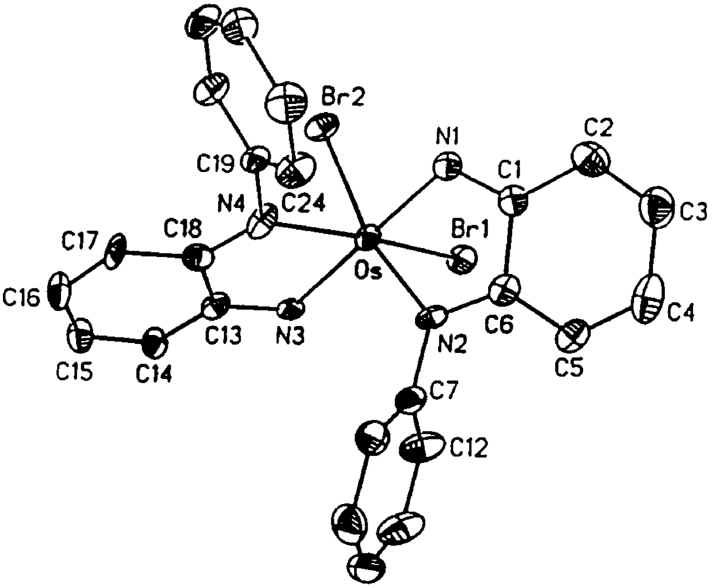
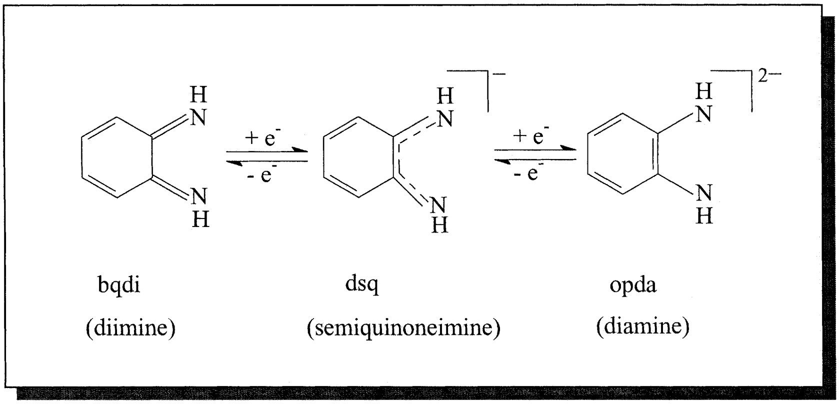


FIGURE 4 ORTEP plot and atom numbering scheme for $[OsBr_2(acac)_2(L^{1a})]$, **4a**. Hydrogen atoms are not shown for clarity. Reproduced with permission of ACS (Reference: 11).



SCHEME 2 1, 2-diaminobenzene and its redox partners.

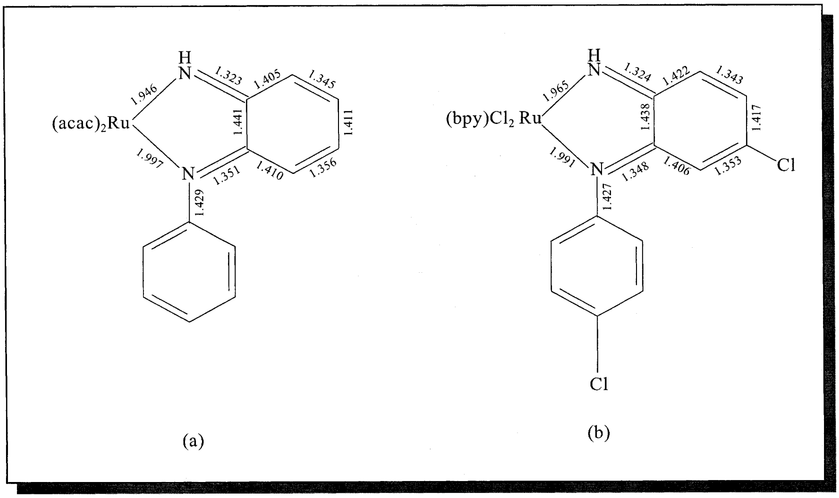
An example of ethylenediimine was reported by Meyer et al.,[16] which formed by the oxidative dehydrogenation of coordinated ethylenediamine. Beside these, there have been several reports[14b,14c,14e,17] on the orbital mixing in Ru–bqdi and Ru–dsq complexes. The dependency of the electron distribution on the extent of mixing between metal-ligand orbitals has been thoroughly investigated using different physicochemical techniques, *viz.* Electro chemistry, ESR and spectral studies. The ambiguity in assignment of the oxidation states to the metal or to the ligand ($\mathrm{Ru^{II}}$bqdi versus $\mathrm{Ru^{III}}$sqdi) was rationalized in terms of the specific orbitals involved in the various electronic transitions and the strong mixing between metal and ligand orbitals. In this context, the effect of substituents on $[\mathrm{Ru^{II}(bpy)_2(diim)}]$ complexes was also studied.[17b] There have been some studies to determine the relationship between charge-transfer emission energies and redox potentials for a large set of ruthenium diimine complexes.[17c] In comparison, osmium complexes of bqdi and their redox partners are rare.[18] About a decade ago, Danopoulos et al. reported[19] the synthesis of *trans*-$[\mathrm{Os^{VIII}O_2(opda)_2}]$ and we recently have reported[20] a trischelate $[\mathrm{Os^{II}(bqdi)_3}](\mathrm{ClO_4})_2$ by osmium mediated dehydrogenation of 1,2- benzoquinonediamine. The reference diimine ligand, $\mathrm{L^1}$, is not directly achievable from arylamines and consequently its coordination chemistry was not available in the literature.

A. Ruthenium Diimines

(i) Structures

One major interest in the complexes of quinone related ligands is the ambiguity in charge distributions. In this respect, structure analysis has been found to be one of the powerful tools for the assignment of charge distributions in these complexes. The status of the ligand in the two ruthenium complexes, *viz.* **1a** and **2c**, is revealed clearly on comparing the mean light-atom bond parameters in the chelate rings (Scheme 3).

In both the complexes, there are two types of C–N bonds: the lengths of immines bonded quinonoid ring are appreciably shorter than the C–N length of the N–aryl group. The former lengths fall in the expected range[13,15,21] of coordinated imine C=N length. The diimine oxidation state of the ligand in the above complexes has been further assessed by the examination of the C–C lengths within the quinonoid ring. Notably, the two reference lengths in the quinonoid ring are appreciably shorter than the other four lengths of the same ring. For example, average of C(2)–C(3) and C(4)–C(5) lengths (1.348(5) Å) in the structure in **2c** is shorter than the average of the rest four C–C lengths (av. 1.421(5) Å) of the same ring. The presence of two localized double bonds characterizes [22] a quinonoid ring and confirms the diimine oxidation state of the ligand in these compounds. The C–N(imine) lengths in these complexes are less elongated than a true C=N length. This is attributed to strong Ru(dπ)– diim(pπ) interactions, and as a result, the Ru–N



SCHEME 3 Bond lengths in two Ru^{II}-diimine complexes.

(imine) lengths (av. 1.978(3) Å) are shorter compared to the Ru–N(py) lengths (av. 2.064(3) Å) in the same compound **2c**.

(ii) Redox

The diimine complexes provide a unique opportunity for probing redox reactions pertaining to both metal oxidations as well as ligand reductions. For example, the cyclic voltammogram of a typical $[Ru(acac)_2L^{1a}]$ complex is displayed in Figure 5, which shows four one-electron redox processes in the potential range 2.0 to -2.5 V. In principle, a coordinated diimine ligand can undergo two reductions to give diiminosemiquinone monoanion and then the diamide dianion in exactly the same way as for the related dioxolene series. Thus, two responses at negative potentials are assigned as two successive reductions of the coordinated ligand L^1. Of the two positive potential redox responses, the first one is reversible, which is due to a $Ru^{III} \rightleftharpoons Ru^{II}$ process. The $Ru^{III} \rightarrow Ru^{IV}$ process, on the other hand, is irreversible and occur at high potential(>1.5 V). Interestingly, the potentials of all the above redox couples depend linearly on the Hammet parameters $\sum \sigma_p$ of the substituent on L^1. The value of electode potentials shift anodic as the electron withdrawing ability of substituent increases (Figure 6). The most significant observation of this diagram is the dependence of $Ru^{II} \rightleftharpoons Ru^{III}$ on the nature of the substituents essentially parallels that of the first reduction potential of the diimine ligands. The observation, in turn, confirms[23] considerable mixing of metal-ligand orbitals in these complexes.

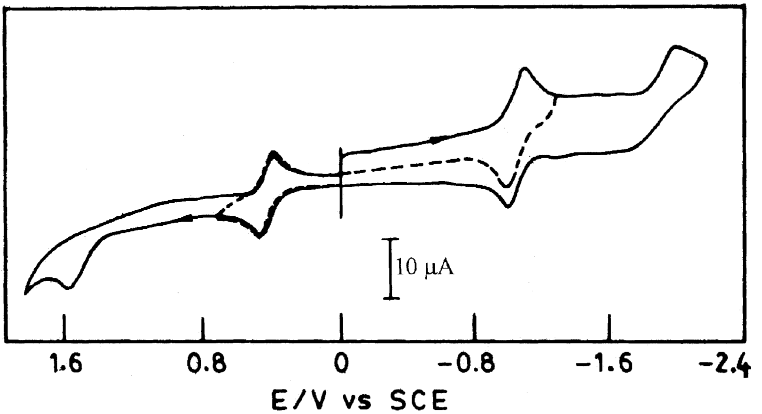


FIGURE 5 CV of [Ru(acac)$_2$(L^{1a})], **1a** in CH$_3$CN at 50 mVs^{-1}. Reproduced with permission of RSC (Reference: 6).

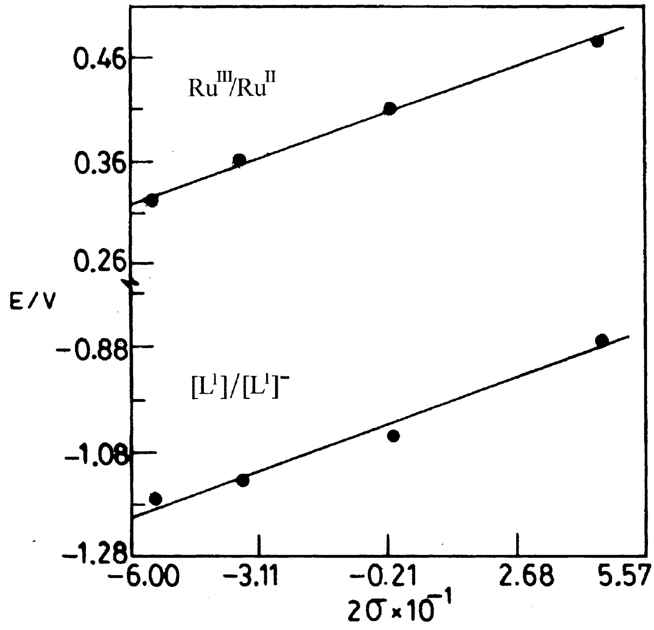
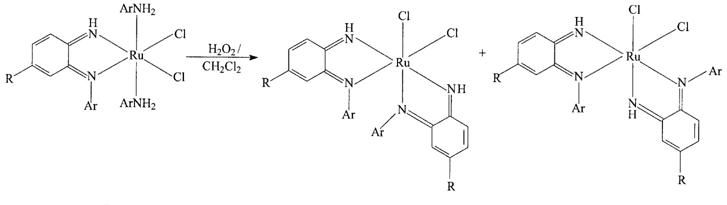


FIGURE 6 Hammett correlation diagram for the Ru^{III}/Ru^{II} and [L^1]/[L^1]$^-$ couples in **1**.

(iii) Reactions of Ruthenated Amines in [RuCl$_2$(ArNH$_2$)$_2$(diim)], 3

In order to have further insight into the above noted metal mediated reactions of aromatic amines, we explore chemical transformations at coordinated aromatic amines in the ruthenium complex, **3**.

It was observed[24,25] that prolonged exposure of a brown solution of **3** to air led to the formation of a blue solution, which otherwise did not form in anaerobic conditions. A similar transformation was found to occur instantaneously and smoothly when a solution of **3** in CH_2Cl_2 was treated with H_2O_2. Preliminary work up followed by chromatographic purification yielded two geometrical isomers of [RuCl$_2$(L^1)$_2$], *viz.* **5** and **6** in moderate yields. The relative orientations (*trans*/*cis*) of the coordinated imine nitrogen atoms [N(H), N(H)] and [N(Ar), N(Ar)] in the isomeric [RuCl$_2$(L^1)$_2$] are designated as *trans*, *cis* (*tc*) and *cis*, *cis* (*cc*), respectively (Eq. 5).

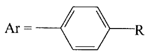


3, Brown

5, Blue

6, Blue

(5)



	R = H	R = Me
[RuCl$_2$(ArNH$_2$)$_2$(L^1)$_2$], **3**	**3a**	**3b**
tc- [RuCl$_2$(L^1)$_2$], **5**	**5a**	**5b**
cc- [RuCl$_2$(L^1)$_2$], **6**	**6a**	**6b**

Of the above two isomers, the *tc*-[RuCl$_2$(L^{1a})$_2$], **5a** formed good X-ray quality crystals while the geometry of the corresponding *cc*-isomer, **6** was revealed by the spectral data. The ORTEP of **5a** is shown in Figure 7. The isomer geometry and the pattern of bond lengths of ruthenium complex is identical to that of the analogous dibromo osmium complex, **4**. Selected bond lengths of the diimine complexes are collected in Table 1. The present chemical reaction (Eq. 5) is a combination of many operations, which occur simultaneously: (i) *trans* to *cis* isomerization of the starting complex, **3** for bringing the two aromatic amines in close proximity; (ii) oxidative dimerization with a new C–N bond formation (N-phenyl1,2–diaminobenzene); followed by (iii) oxidative dehydrogenation of diamine to diimine.

At this stage it is relevant to compare the results of four reactions, (Eq. (1), (2), (3) and (4)) that are described above. In the case of osmium, a bis-diimine complex was obtained from the reaction of [Os^{IV}Br$_6$]$^{2-}$ and ArNH$_2$, while in the remaining three cases where trivalent ruthenium promoters were used, only monodiimine complexes resulted. In this respect, the most notable result is the formation of a monodiimine complex in the reaction (3). In this reaction, only two of the four coordinated amines underwent oxidative

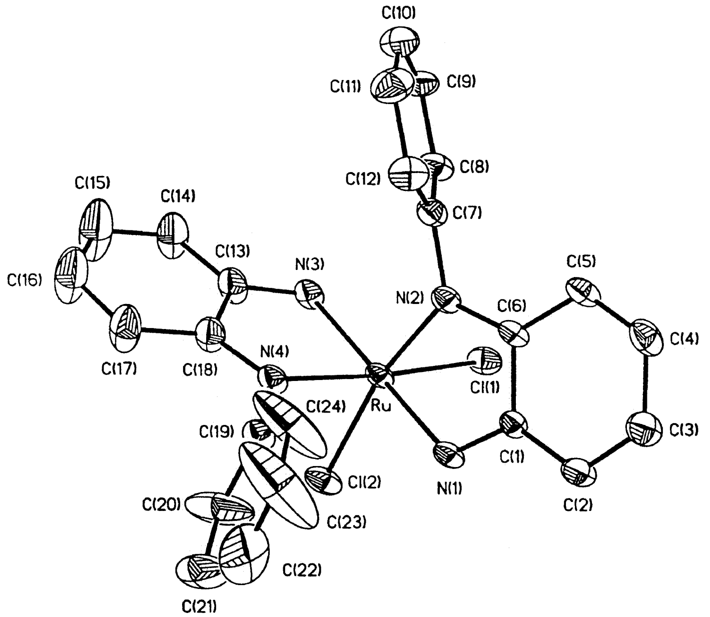


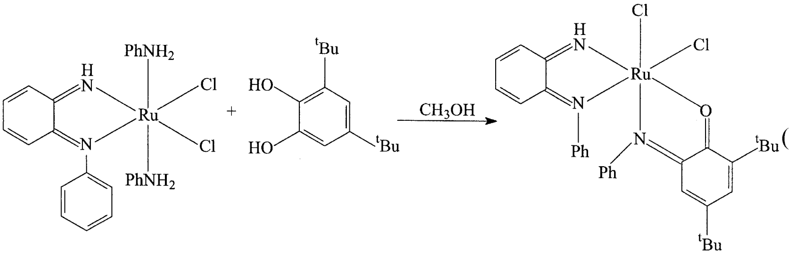
FIGURE 7 ORTEP plot and atom numbering scheme for $[\mathrm{RuCl_2(L^{1a})_2}]$, **5a**. Hydrogen atoms are not shown for clarity. Reproduced with permission of Elsevier Science (Reference: 25).

dimerisation and the rest two remained coordinated as amines. Further dimerization of these amines did occur but only in the presence of an external oxidant like H_2O_2. It is noteworthy that the difference of oxidation states of the metal ions in the starting compound and the end product is two in reaction (4) $(\mathrm{Os^{IV}} \overset{+2e}{\rightleftharpoons} \mathrm{Os^{II}})$, but is one in other reactions (1), (2) and (3) $(\mathrm{Ru^{III}} \overset{+e}{\rightleftharpoons} \mathrm{Ru^{II}})$. Therefore, it seems reasonable that the number of diimines formed from these reference reactions is equal to the difference in oxidation levels of the reactants and products. However, we have been in search of other similar examples to establish our proposition.

Interestingly, the complex, **3a** reacted instantaneously[24] with catechol or its substituted derivative to result, a mixed ligand ruthenium complex, **7**, containing both 1,2-diimine (N,N) and 1,2-iminoquinone (N,O) donors (Eq. 6). This unusual reaction was authenticated by the single crystal X-ray structure of a representative complex (Figure 8). The bond parameters (Table 1) indeed revealed that the ligands are coordinated as diimine and iminobenzoquinone forms. This type of mixed complex is rare and allows the direct comparison of bonding between[17a] two types of redox non-innocent benzoquinone ligands.

TABLE 1 Selected bond distances of compounds 1a·0.25 H_2O, 2c, 3a·CH_2Cl_2, 4a, 5a·THF and 7 in Å

1a·0.25 H_2O		**2c**		**3a**·CH_2Cl_2		**4a**		**5a**·THF		7	
Ru1–N31	1.946(5)	Ru1–N1	1.965(3)	Ru–N1	1.940(4)	Os–N1	1.998(11)	Ru–N1	1.996(5)	Ru–N1	1.950(4)
Ru1–N36	1.997(5)	Ru1–N2	1.991(3)	Ru–N2	1.997(4)	Os–N2	2.000(11)	Ru–N2	2.005(5)	Ru–N2	2.001(4)
Ru1–O11	2.018(5)	Ru1–N3	2.082(3)	Ru–N3	2.135(4)	Os–N3	1.994(10)	Ru–N3	1.982(6)	Ru–O	2.022(3)
Ru1–O13	2.067(4)	Ru1–N4	2.047(3)	Ru–N4	2.135(4)	Os–N4	2.017(11)	Ru–N4	1.999(6)	Ru–N3	1.974(4)
Ru1–O21	2.050(4)	Ru1–Cl1	2.3971(12)	Ru–Cl1	2.4221(14)	Os–Br1	2.519(2)	Ru–Cl1	2.402(2)	Ru–Cl1	2.3644(13)
Ru1–O23	2.030(5)	Ru1–Cl2	2.3914(10)	Ru–Cl2	2.4288(15)	Os–Br2	2.523(3)	Ru–Cl2	2.388(2)	Ru–Cl2	2.3852(13)
C31–N31	1.323(8)	C1–N1	1.324(4)	C1–N1	1.319(7)	C1–N1	1.317(19)	C1–N1	1.314(8)	C1–N1	1.317(6)
C36–N36	1.351(8)	C6–N2	1.348(4)	C6–N2	1.343(7)	C6–N2	1.338(19)	C6–N2	1.333(8)	C6–N2	1.313(6)
C37–N36	1.429(8)	C7–N2	1.427(4)	C7–N2	1.445(6)	C7–N2	1.417(15)	C7–N2	1.436(9)	C7–N2	1.444(6)
C31–C32	1.405(9)	C1–C2	1.422(5)	C13–N3	1.451(7)	C13–N3	1.325(19)	C13–N3	1.302(10)	C14–O	1.280(5)
C32–C33	1.345(9)	C2–C3	1.343(5)	C19–N4	1.449(7)	C18–N4	1.312(20)	C18–N4	1.314(9)	C13–N3	1.339(6)
C33–C34	1.411(10)	C3–C4	1.417(5)	C1–C2	1.418(8)	C19–N4	1.458(11)	C19–N4	1.432(8)	C19–N3	1.446(6)
C34–C35	1.356(9)	C4–C5	1.353(4)	C2–C3	1.347(9)			C1–C2	1.429(9)	C1–C2	1.421(7)
C35–C36	1.410(9)	C5–C6	1.406(5)	C3–C4	1.423(10)			C2–C3	1.360(10)	C2–C3	1.341(7)
C36–C31	1.441(9)	C6–C1	1.438(5)	C4–C5	1.360(9)			C3–C4	1.422(11)	C3–C4	1.417(8)
				C5–C6	1.409(8)			C4–C5	1.337(11)	C4–C5	1.338(8)
				C6–C1	1.440(8)			C5–C6	1.413(9)	C5–C6	1.434(6)
								C6–C1	1.453(9)	C6–C1	1.447(6)
								C13–C14	1.429(12)	C14–C15	1.439(6)
								C14–C15	1.332(14)	C15–C16	1.355(6)
								C15–C16	1.420(2)	C16–C17	1.441(7)
								C16–C17	1.362(14)	C17–C18	1.355(7)
								C17–C18	1.445(11)	C18–C13	1.420(6)
								C18–C13	1.447(10)	C13–C14	1.439(6)



(6)

6a **7**

B. Osmium Diimines

Although homoleptic and mixed ligand osmium-dioxolene complexes have been known for a while, osmium complexes[10,11] of 1,2-diimines and its redox partners are rare. As far as we are aware, the present osmium complexes of N-arylbenzoquinonediimine represent the first examples[20] of osmium complexes of above family. The X-ray structure of $[OsBr_2(L^{1a})_2]$

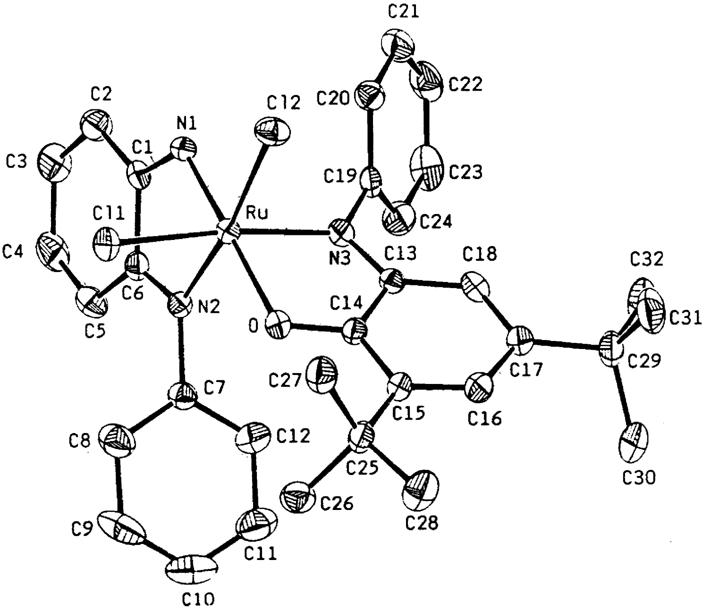
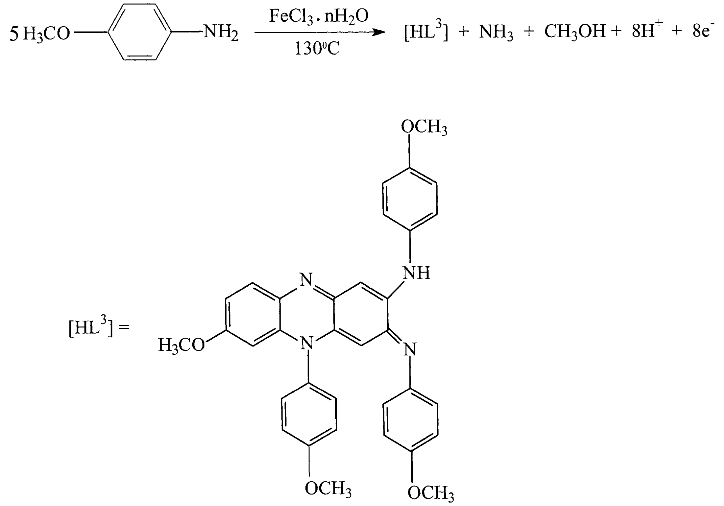


FIGURE 8 ORTEP plot and atom numbering scheme for $[RuCl_2(L^2)(L^{1a})]$, **7**. Hydrogen atoms are not shown for clarity. Reproduced with permission of RSC (Reference: 24).

authenticated the formation of Os^{II}-diimine complexes from an unusual metal mediated chemical transformation (Eq. 4). The bond length trend within the chelate as well as aromatic ring in this compound (Table 1) is consistent with a diimine character of the ligand bound to bivalent oxidation state of osmium. The complexes showed a reversible oxidative redox process due to Os^{III}/Os^{II} couple in the potential range 0.50 to 0.95 V, which varied linearly on the Hamett $\sum \sigma_p$ parameter of the substitution on L^1. Assignment of the reference redox couple was confirmed by the examination of EPR of the electrogenerated complex, $[\mathbf{4a}]^+$, in acetonitrile-toluene glass at 77 K. It showed a rhombic EPR as expected for a low spin d^5-system. Heteroleptic tris chelates of type $[Os(L^1)_2(N^\wedge N)]^{2+}$ were synthesized from $[OsBr_2(L^1)_2]$ by the use of silver-assisted[26] *trans*-metallation synthetic strategy. The tris chelates showed multiple redox responses.

5. POLYMERIZATION OF PRIMARY AROMATIC AMINES

The reaction of hydrated ferric chloride and p-anisidine afforded[27] yet another unusual transformation resulting in brown 6-*p*-anisyl-2-(*p*-anisylamino)-9-methoxy phenazine-3(4H)- *p*-anisylimine, $[HL^3]$, **8**, in moderate yield (Eq. 7).



(7)

8

6-*p*-anisyl-2-(*p*-anisylamino)-9-methoxy phenazine-3(4H)- *p*-anisylimine

The brown solution of $[HL^3]$, upon acidification, became violet. There was a sharp isobestic point at 508 nm, which indicated an acid-base equilibrium between HL^3 and $[H_2L^3]^+$ with pk, 6.62 ± 0.2 at 300 K. The chloride salt of the protonated phenazine [H_2L^3]Cl formed X-ray quality crystals suitable for its structure determination. X-ray structure analysis was used to authenticate the formation of [H_2L^3]Cl. A view of the molecule is shown in Figure 9, which indeed confirms the formation of a substituted phenazine from the reaction (7). ^{1}H NMR spectra of [HL^3] and its conjugate acid salt [H_2L^3]Cl are shown in Figure 10 for comparison.

A close examination of the bond angles and distances of the salt, [H_2L^3]Cl (Table 2) reveals that the long chain, N15–C2–C1–C14–N13–C12–C11–C10–C9–C8–C7–N6–C5–C4–C3–N22, contains hybrid bonds. The ranges of bond lengths in this chain are C–C = 1.372 to 1.410 Å and C–N = 1.337 to 1.399 Å. Moreover, a least-square plane calculated through the 14 atoms of the dibenzopyrazine fragment indicates that the skeleton is approximately planar; the largest deviation from the mean plane is 0.09 Å. The planarity of the phenazine fragment, together with the bond length trends, indicates extensive delocalization. This may be due to considerable contributions of the different resonance forms of the molecule. The lowest visible range absorptions in [HL^3] and [H_2L^3]Cl are assigned to intra ligand $\pi - \pi^*$ transitions (Figure 11). Notably, the lowest energy transition in [HL^3] occurs at 490 nm, which shifts red upon acidification due to increased planarity in the ligand frame.

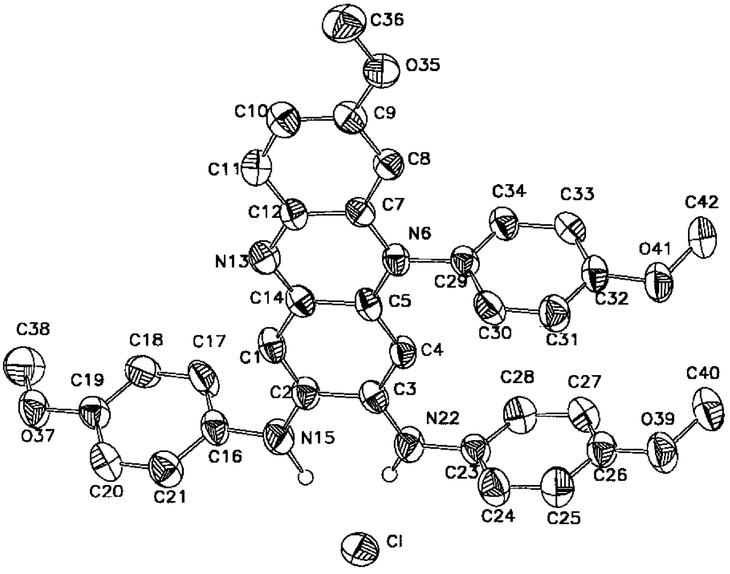


FIGURE 9 ORTEP plot and atom numbering scheme for [H_2L^3]Cl, **8**.HCl. Hydrogen atoms are not shown for clarity. Reproduced with permission of Wiley-VCH (Reference: 27).

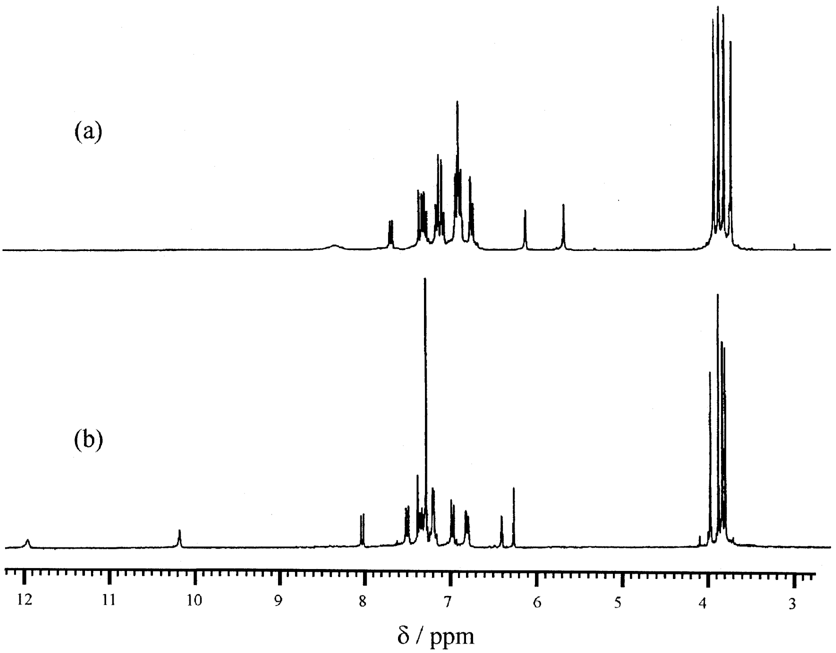


FIGURE 10 ^{1}H NMR spectra of (a) [HL^3] and (b) [H_2L^3]Cl in $CDCl_3$. Reproduced with permission of Wiley-VCH (Reference: 27).

The formation of [HL^3] directly from *p*-ansidine is an $8e^- + 8H^+$ transfer process and is accompanied by the elimination of one molecule each of CH_3OH and NH_3. Oxidative dimerization of *ortho*-substituted aromatic amines, for example 1,2-diiamino benzene or 2-aminophenol, are documented[28] in the literature. These dehydrogenation processes proceed *via* radical intermediates that have been detected by EPR spectroscopy. We have proposed that the first and key step of *p*-anisidne→[HL^3] transformation is the dimerization of the monoamine to produce N-aryl-1,2-diaminoarene. The N-aryl diamine, thus formed, then undergoes further dimerization and amination in the presence of excess amine to result [HL^3]. The major steps involved in this reaction are shown in Scheme 4. Thus the first step of this transformation is identical to that of ruthenium and osmium promoted amine→1,2-diimine oxidation reaction. However, in the presence of heavier transition metal ions dehydrogenation of the diamine occurs instantaneously, which is trapped by the reduced metal ions (Scheme 5).

The reaction (7), however, was not observed in the cases of other substituted or unsubstituted primary aromatic amines like $PhNH_2$, *p*-chloroaniline, *p*-toluidine, etc. The non-reactivity of these primary aromatic amines may be

TABLE 2 Selected Bond Distances of Compounds **8**·HCl and **11**·$1.5C_6H_5CH_3$ in Å

8·HCl		**11**·$1.5C_6H_5CH_3$	
C23–N22	1.432(7)	Ru1–N2	1.989(13)
C3–N22	1.356(7)	Ru1–N3	2.008(13)
C5–N6	1.368(6)	Ru1–O1	2.057(11)
C7–N6	1.399(6)	Ru1–O2	2.013(13)
C29–N6	1.451(6)	Ru1–O3	2.075(12)
C14–N13	1.337(6)	Ru1–O4	2.022(13)
C12–N13	1.359(6)	Ru2–N4	2.084(13)
C2–N15	1.363(7)	Ru2–N6	1.902(13)
C16–N15	1.448(7)	Ru2–O5	2.020(12)
C1–C2	1.381(7)	Ru2–O6	2.053(11)
C2–C3	1.463(7)	Ru2–O7	2.031(12)
C3–C4	1.390(7)	Ru2–O8	2.079(11)
C4–C5	1.383(7)	C23–N3	1.377(18)
C5–C14	1.444(7)	C22–N3	1.323(19)
C14–C1	1.410(7)	C28–N4	1.395(19)
		C21–N4	1.347(18)
		C20–N6	1.340(2)
		C17–N2	1.334(19)
		C15–N2	1.440(2)

explained by the fact that a similar mechanistic pathway (Scheme 4) demand elimination of H_2, HCl, CH_4, respectively, which is rather a difficult process. Hence, this reaction did not proceed up to Step 3 and thus phenazines were not obtainable. On the other hand, ruthenium and osmium promoted oxidative dehydrogenation reactions indeed proceeded smoothly for all the above amines to result in metal complexes of diimines.

The coordination abilities of the phenazines are now being explored; ruthenium complexes[28] of it show rich redox and spectral properties.

6. POLYMERIZATION OF 1,3–DIAMINO BENZENE

We then set out to explore[29] the reactions of a diaminoarene. We chose 1,3-diaminobenzene as the substrate. Due to the presence of two diamine functions in 1,3-diaminobenzene, it was anticipated that fusion of this in the presence of a suitable mediator metal complex might lead to the synthesis of complexes of high nuclearity. It may be noted here that the two other isomers of this diamine (1,2-and 1,4-diaminobenzene) are known[14,30] to act as a bidentate chelate and a monodentate bridging ligand, respectively. In comparison, the 1,3-isomer is not a good ligand and its coordination chemistry is very poorly developed.[31]

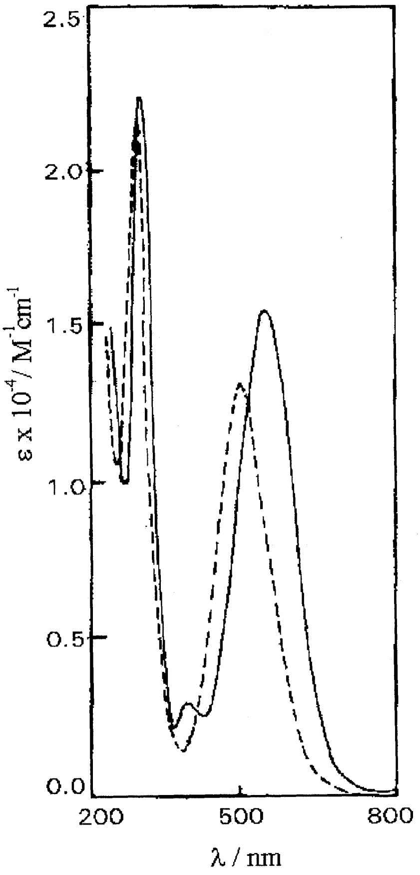
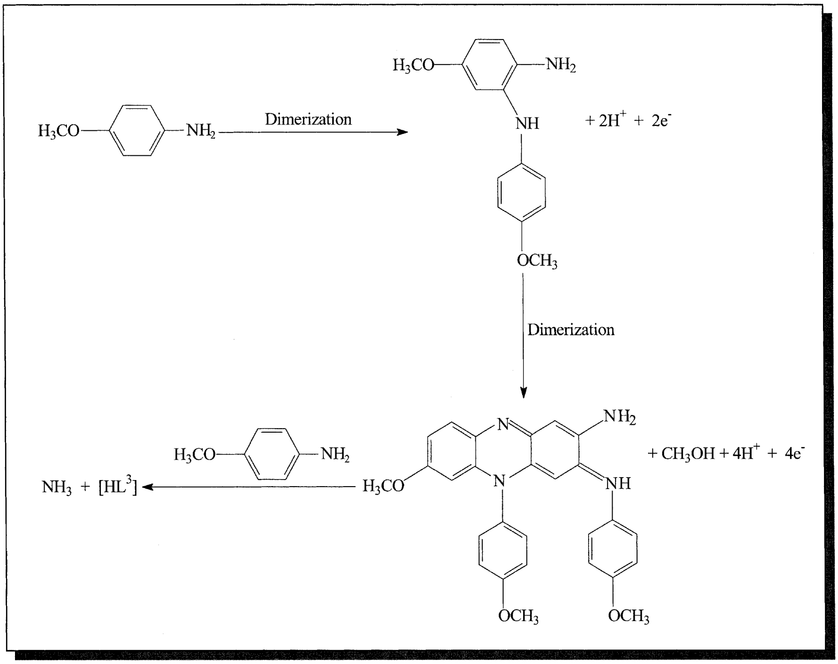


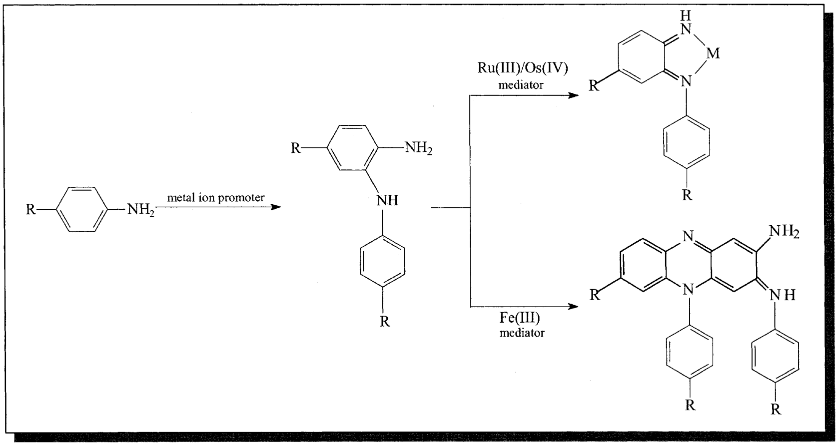
FIGURE 11 Electronic spectra of [HL^3] (- - - - -) and [H_2L^3]Cl (—) in CH_3CN. Reproduced with permission of Wiley-VCH (Reference: 27).

The reaction of molten 1,3-diaminobenzene with the mediator complex, [$Ru(acac)_3$], at 150°C produced a blue-violet mass in about 0.5 h. Three major products were obtained on usual work-up and purification on chromatographic silica gel column (Scheme 6). Of the three complexes, one was monometallic and pink in color (**9**) and the rest two were dimetallic, violet (**10**) and blue (**11**). The identities of the products were established based on their FAB mass as well as other physicochemical data.

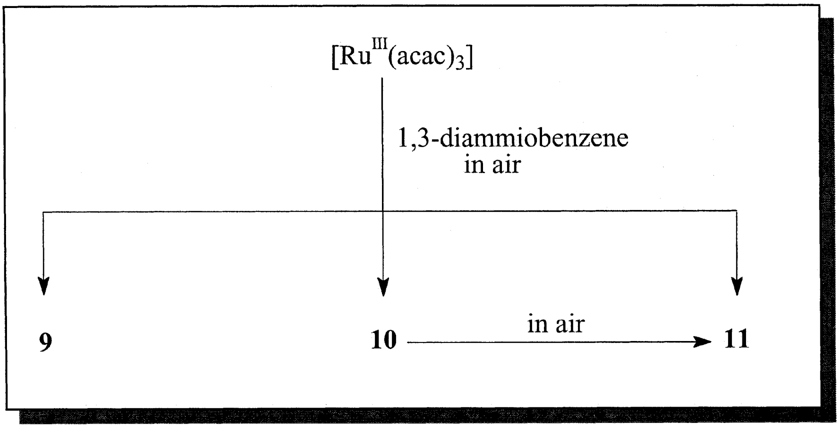
Selected ^{1}H NMR spectral data of the above three-ruthenium complexes are collected in Table 3. For example the monometallic complex, **9**, showed four methyl resonances while eight such resonances were observed for both the dimetallic compounds, *viz* **10** and **11**. This result thus confirmed the



SCHEME 4 Steps for the formation of $[HL^3]$ from *p*-anisidine.



SCHEME 5 Fusion of $ArNH_2$ in presence of different metal mediators.



SCHEME 6 Ruthenium(III) promoted fusion of 1,3-diaminobenzene.

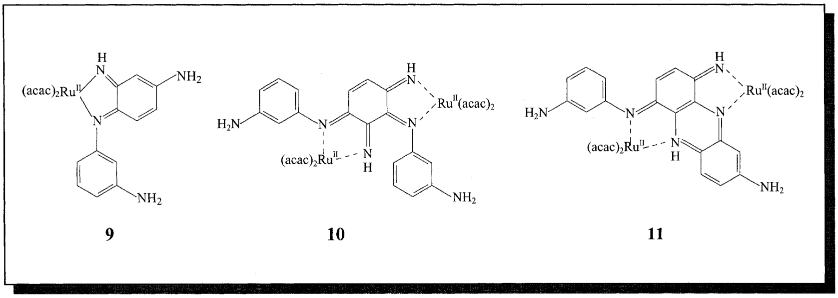
presence of two (**9**) and four acac ligands (**10, 11**) in these complexes. The complex **9**, showed two broad resonances at 3.80 and 9.01 ppm assignable to N–H (amine) and N–H (imine), respectively. The dimetallic complex **10**, on the other hand, displayed two N–H (imine) and one broad N–H (amine) resonances at 11.53, 10.83 and 3.66 ppm. In comparison the blue dimetallic complex, **11**, showed only one N–H (imine) resonance at 12.56 ppm and two N–H(amine) resonance at 3.73 and 4.16 ppm. FAB mass spectra of the compounds **9**, **10** and **11** showed intense peaks due to their

TABLE 3 ^{1}H NMR Spectral Data in δ (ppm) and FAB Mass Data for Compounds **9**, **10** and **11**

	^{1}H NMR^a				
Compound	Me(acac)	CH(acac)	N–H	NH$_2$	FAB Mass
9	1.74, 1.79, 1.81, 2.28	5.04, 5.22	9.01	3.80	512, 413,^{b} 313^b
10	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	916, 816,^{b} 715,^{b}615,^{b} 516^b
11	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	914, 814,^{b} 715,^{b} 613^b

[a] In CDCl$_3$; SiMe$_4$ as internal standard; aromatic proton resonance occur in the region 6.30 to 7.25δ

[b] Daughter peaks originated due to the fragmentation of the parent compound



SCHEME 7 Line drawings of the compounds **9, 10** and **11**.

parent molecular ions at m/z 512, 916 and 914, respectively. Their isotopic patterns as well as analyses of the daughter peaks indeed corroborate with the formulation of the above complexes (Scheme 7).

Of the three above complexes, the blue dimatellic complex, **11**, formed single X-ray quality crystals. A view of the molecule is shown in Figure 12. In this compound two [Ru(acac)$_2$] moieties are bridged across a bridging ligand (L^4), which was formed by the oxidative *ortho*-fusion of three 1,3-diaminobenzene residues. To achieve this, three new C–N bonds, *viz.*

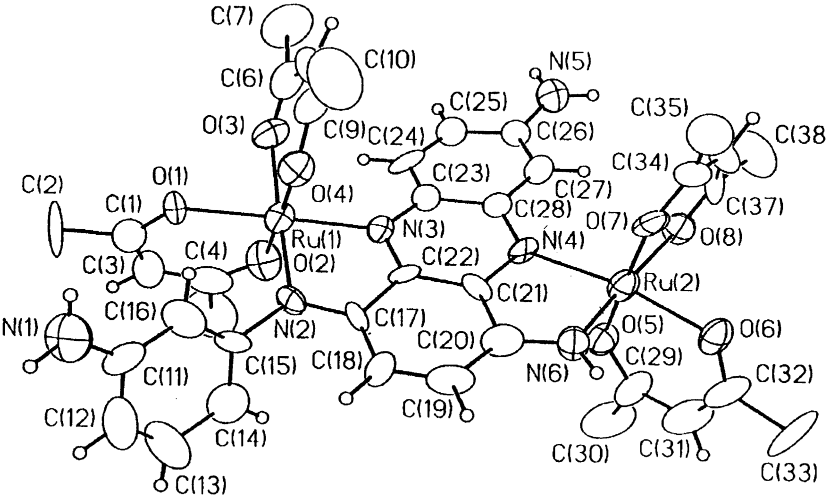


FIGURE 12 ORTEP plot and atom numbering scheme for [Ru$_2$(acac)$_4$(μ -L^4), **11** Hydrogen atoms are not shown for clarity. Reproduced with permission of Wiley-VCH (Reference: 29).

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 otherwise was not achievable. The coordination sphere around each ruthenium involves RuN_4O_2 and is coordinated in distorted octahedral geometry by the four oxygen of two acetylacetonate ligands and by the two nitrogens of the bridging phenazine ligand. The structural data revealed that the bridging ligand of **11** is a conjugated planar system. The other diruthenium complex, **10**, underwent chemical transformation in solution and its X-ray structure could not be obtained. However, it was noted that it produced **11** quantitatively upon heating in high boiling alcoholic solvents in the presence of air. It is believed that a new C–N bond was formed in this reaction (ring closure) with the elimination of molecular hydrogen. Thus the transformation **10**→**11** is an oxidative ring closure process. Notably, the compounds **10** and **11** are formed *via* a series of C–N bond formation processes due to activation of C–H bonds, which presumably occur through the coordination of diamine residues to the metal center(s). The formation of monometallic pink complex, **9**, is the result of oxidative dimerization processes of 1,3-diaminobenzene.

All the three above complexes showed multiple redox responses. The mono nuclear compound **9** displayed a reversible anodic wave at 0.35 V, which is assigned to a Ru^{III}/Ru^{II} couple. Interestingly, the potential of **9** falls on the $E°_{298}$ versus 2σ linear plot (Figure 6) for the $[Ru(acac)_2L^1]$ complexes. The dimetalic complex, **11**, showed a pair of anodic waves at 0.08 and 0.54 V due to two successive oxidations of the ruthenium centers. The violet complex **10** also showed two such responses at 0.22 and 0.80 V. Segmented cyclic voltammograms of these complexes are shown in Figure 13. The responses at cathodic potentials are due to the ligand reductions.

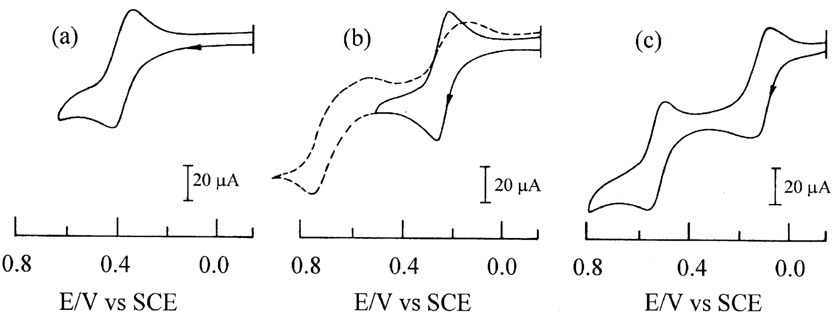


FIGURE 13 Segmented CVs for the compounds: (a) **9** (b) **10** and (c) **11** in CH_3CN at scan rate 50 mVs^{-1}. Reproduced with permission of Wiley-VCH (Reference: 29).

7. CONCLUSIONS

Herein we have presented some novel examples of oxidative fusion reactions of aromatic amines with metal mediation. The reactions occur due to enhancement of reactivity of amines as a consequence of metal coordination. It has been manifested that relative geometry of the interacting amine residues in the metal complex intermediates is important for the fusion reactions. The mediator metal complex holds the reactants in proximity by imposing a strict geometry and thereby promotes the fusion reactions. In addition, the mediators also take part in the redox reactions that are associated with the transformations. Two synthetic strategies have been successfully used to control the degree of fusion reactions. For example, ruthenium and osmium mediator complexes favored only dimerization of mono aromatic amines while their congener ferric ion promoted polymerization reaction to result N-substituted phenazines wherein fusion of five amine residues occur. Moreover, trimerization of a non chelating diamine, *viz.* 1,3-diaminobenzene, clearly demonstrated that the presence of an additional amine function favors higher degree of C–N fusion reaction.

The coordination chemistry of the products is also noteworthy. The present examples of ruthenium and osmium complexes of the diim ligand have opened up new avenues of research in the area of metal 1,2-imines. Previous studies[14,17,18] on metal quinone related diimines were largely confined to complexes of related diimines derived from 1,2-diaminobenzene and its derivatives. It may be noted here that unsymmetrical diimine of above type are not otherwise achievable. An unprecedented type of heteroleptic complexes containing both quinoneimine and diimine ligands was achieved by the fusion reaction of catechol on a coordinated amine function. All these complexes show rich redox as well as spectral properties. The solution electronic spectra of these are dominated by strong absorption in the visible region. The orbitals involved in these transitions are primarily a mixture of metal as well as ligand orbitals. Furthermore dimetallic ruthenium complex, obtained from the reaction of [Ru(acac)$_3$] and 1,3-diaminobenzene, reveals strong metal-metal interactions.

Our work on metal promoted fusion of aromatic amines continued. We are now in search of more examples of poly-metallic complexes that are suitable for study of electronic as well as magnetic interactions. It would also be interesting to see whether these fusion reactions can be applied for di- and polymerization between hetero-amines.

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