

Ruthenium- and osmium-promoted oxidation of aromatic amines. Some observations in the area of metal-diimines

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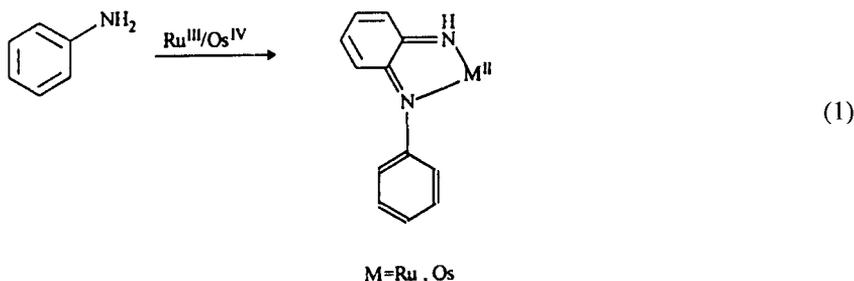
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Abstract. Three reactions of aniline with $\text{Ru}(\text{acac})_3$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $(\text{NH}_4)_2[\text{OsBr}_6]$ are reported. The isolated complexes are $\text{Ru}(\text{acac})_2\text{L}$, $\text{RuCl}_2(\text{aniline})_2\text{L}$ and OsBr_2L_2 ($\text{L} = \text{N-phenyl-1,2-phenylene diimine}$) respectively. In all the cases oxidation of aniline has occurred to result in diimine chelates. The products of the above reactions have been fully characterized and their X-ray structures are reported. The bond length trends within the chelate as well as the aromatic rings are consistent with the diimine character of the coordinated ligand. A qualitative pathway for the formation of L is suggested. A correlation between the metal oxidation levels in the starting compounds and the products with the number of ligand formation is noted.

Keywords. Aromatic amine oxidation; template dimerization; diimines; ruthenium; osmium.

1. Introduction

The selective transformation of organic functions via metal binding is an attractive area of chemical research. This report reviews¹⁻³ some novel results of oxidative dimerization reactions of primary aromatic amines, Ar-NH_2 , leading to coordinated N-aryl-1,2-arylene diimines. The general reaction is as shown in (1).



The resultant diimine complexes belong to the family of complexes of 1,2-arylene diimines which are of interest⁴ in contemporary research. These ligands may be reduced to semiquinone imines and further to diimine forms. Thus, there remains different

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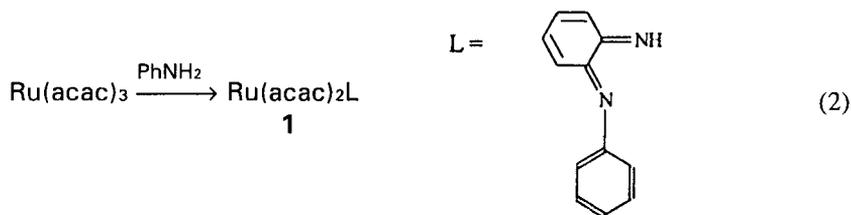
possibilities of charge distributions in the complexes of these ligands. We note here that previous studies in this area have been largely confined to the complexes of symmetrical 1,2-phenylenediimine⁵ and 9,10-phenanthrene quinone diimine⁶. The metal complex of the unsymmetrical diimine of the above type was, however, not known.

2. Results

Three examples, describing the title reaction, are elaborated below.

2.1 Reaction of $Ru(acac)_3$ and aniline

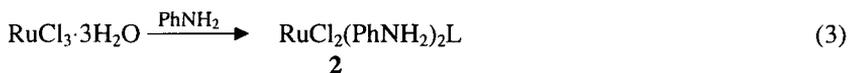
The first example, which has been described in (2), involves $Ru(acac)_3$ promoted oxidation of aniline to coordinated *N*-phenyl-1,2-phenylene diimine (L). Dark red crystals of $Ru(acac)_3$ reacts with aniline in neat at 130°C to afford a violet mixture. Chromatographic workup of the above resulted in a highly crystalline Ru^{II} -diim



compound, $Ru(acac)_2L$ (**1**) in 65% yield. This compound $Ru(acac)_2L$ is soluble in common organic solvents and is diamagnetic. The N–H stretch occurs as a sharp feature of moderate intensity in the range 3300–3200 cm^{-1} . The presence of strong C=N stretch near 1600 cm^{-1} characterizes the presence of diim chromophore in the compound. The 1H NMR spectral feature of the complex consists of a set of methyl resonances at 1.76 (3H), 1.83 (6H) and 2.35 (3H) δ . Resolved aromatic proton resonances appear in between 6.5 and 7.4 δ . The N–H resonance is observed⁷ as a relatively broad singlet at 10.8 δ . Fortunately, this compound formed a suitable crystal for X-ray structure determination from a saturated solution of the compound in hexane. A view of the molecule is shown in figure 1. In this compound ruthenium is coordinated by the four oxygens of two acetylacetonato ligands and by the two nitrogens of a diimine ligand in a distorted octahedral geometry about ruthenium. The imine, C–N bond lengths, average 1.341 Å, are considerably shorter than the C–N single bond, 1.433 Å. There are two localised double bonds in the quinoid ring (table 1).

2.2 Reaction of $RuCl_3 \cdot 3H_2O$ and aniline

This reaction also proceeded smoothly in neat aniline and the temperature was maintained at 140°C. Recrystallization of the crude product from dichloromethane-hexane mixture resulted in a highly crystalline compound (yield, 60%), **2** (3) which contains one diimine (L), two *trans* anilines and two *cis* chlorides in the coordination sphere.



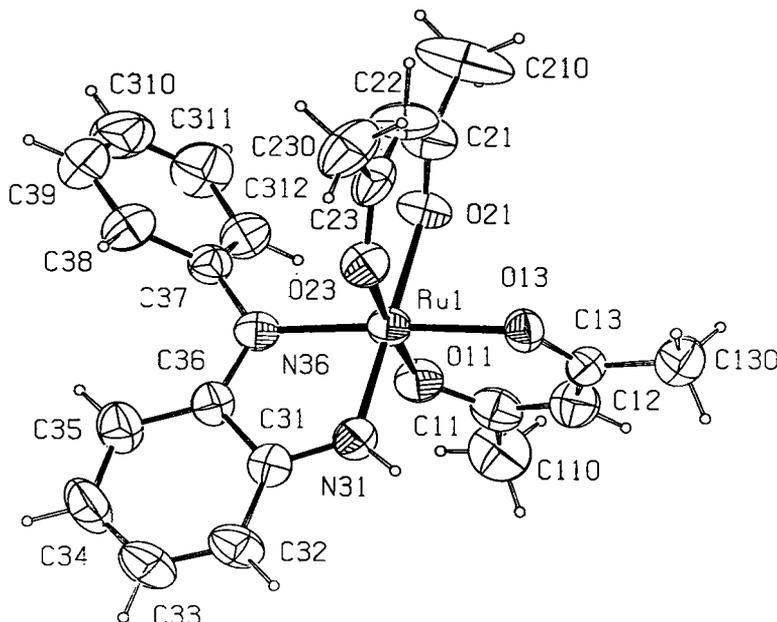


Figure 1. ORTEP plot and atom labelling scheme for $\text{Ru}(\text{acac})_2\text{L}$, **1**.

Table 1. Selected bond distances in the compounds **1**, **2** and **3**.

$\text{Ru}(\text{acac})_2\text{L}^a$, 1			
$\text{Ru}(1)-\text{N}(31)$	1.958(5)	$\text{N}(36)-\text{C}(36)$	1.352(8)
$\text{Ru}(1)-\text{N}(36)$	1.996(5)	$\text{C}(31)-\text{C}(32)$	1.410(9)
$\text{Ru}(1)-\text{O}(11)$	2.019(5)	$\text{C}(35)-\text{C}(36)$	1.413(9)
$\text{Ru}(1)-\text{O}(13)$	2.068(4)	$\text{C}(32)-\text{C}(33)$	1.348(9)
$\text{Ru}(1)-\text{O}(21)$	2.050(4)	$\text{C}(34)-\text{C}(35)$	1.357(9)
$\text{Ru}(1)-\text{O}(23)$	2.031(5)	$\text{C}(33)-\text{C}(34)$	1.407(10)
$\text{N}(31)-\text{C}(31)$	1.333(8)	$\text{C}(31)-\text{C}(36)$	1.447(9)
$\text{N}(36)-\text{C}(37)$	1.429(8)		
$\text{RuCl}_2(\text{PhNH}_2)_2\text{L}^b$, 2			
$\text{Ru}-\text{N}(1)$	1.940(4)	$\text{N}(1)-\text{C}(1)$	1.319(7)
$\text{Ru}-\text{N}(2)$	1.997(4)	$\text{N}(2)-\text{C}(6)$	1.343(7)
$\text{Ru}-\text{N}(3)$	2.135(4)	$\text{N}(2)-\text{C}(7)$	1.445(6)
$\text{Ru}-\text{N}(4)$	2.135(4)	$\text{N}(3)-\text{C}(13)$	1.451(7)
$\text{Ru}-\text{Cl}(1)$	2.422(1)	$\text{N}(4)-\text{C}(19)$	1.449(7)
$\text{Ru}-\text{Cl}(2)$	2.429(1)		
$\text{OsBr}_2\text{L}_2^c$, 3			
$\text{Os}-\text{N}(1)$	1.998(11)	$\text{N}(1)-\text{C}(1)$	1.317(19)
$\text{Os}-\text{N}(2)$	2.000(11)	$\text{N}(2)-\text{C}(6)$	1.338(19)
$\text{Os}-\text{N}(3)$	1.994(10)	$\text{N}(2)-\text{C}(7)$	1.417(15)
$\text{Os}-\text{N}(4)$	2.017(11)	$\text{N}(3)-\text{C}(13)$	1.325(19)
$\text{Os}-\text{Br}(1)$	2.519(2)	$\text{N}(4)-\text{C}(18)$	1.312(20)
$\text{Os}-\text{Br}(2)$	2.523(3)	$\text{N}(4)-\text{C}(19)$	1.458(11)

^aAtom labelling scheme is as in figure 1. The molecule contains 0.25H₂O as solvent of crystallization. ^bAtom labelling scheme is as in figure 2 below. The molecule contains CH₂Cl₂ as solvent of crystallization. ^cAtom labelling scheme is as in figure 3 below

Unlike **1**, the compound **2** is sparingly soluble in common organic solvents. The IR spectrum of it consists of multiple sharp $\nu_{\text{N-H}}$ between 3300 and 3100 cm^{-1} , sharp $\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$ at 1600 and 1580 cm^{-1} respectively; two $\nu_{\text{Ru-Cl}}$ stretches occur⁸ at 360 and 340 cm^{-1} . The proton NMR spectral investigation reveals the presence of two doublet N-H resonances occurring at 5.09 and 4.84 δ assigned⁹ to δ_{NH_2} . Final verification of the composition as well as the geometry of the compound were ascertained from the single crystal X-ray data. A view of the molecule is shown in figure 2. It indeed authenticated the composition of the compound, **2** as $\text{RuCl}_2(\text{PhNH}_2)_2\text{L}$. There are two types of Ru-N distances in the molecule (table 1). Two Ru-N (aniline) single bonds are identical and are longer than Ru-N (imine) bonds indicating a relatively weak bond between Ru and aniline. Two diimine, C=N bonds are much shorter than the C-N bonds.

2.3 Reaction of $(\text{NH}_4)_2[\text{OsBr}_6]$ and aniline

The third reaction of this series (4) is the reaction of $(\text{NH}_4)_2[\text{OsBr}_6]$ and aniline at 120–130°C. The compound OsBr_2L_2 , **3**, was obtained by chromatographic workup. Recrystallization from a 1:1 dichloromethane-hexane mixture gives X-ray quality crystals in 50% yield.



The molecular complex is freely soluble in common organic solvents. The moderate N-H and strong C=N stretches in its IR spectrum occur at 3250–3150 and 1600 cm^{-1}

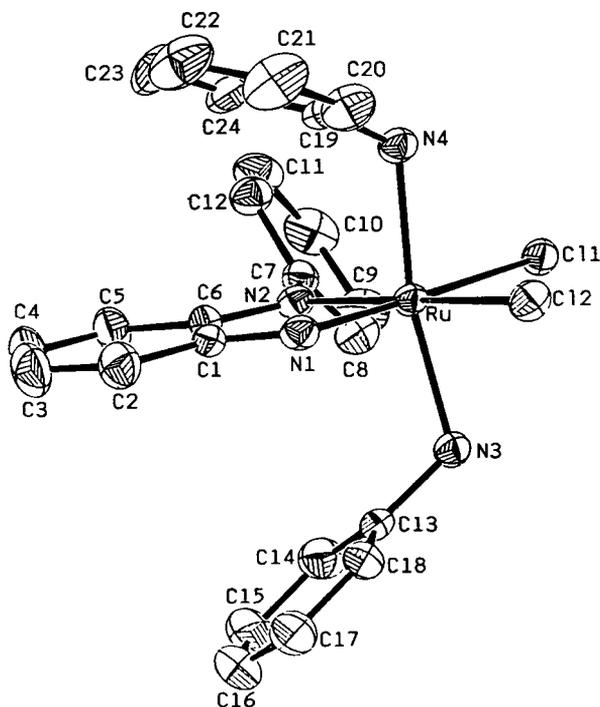


Figure 2. ORTEP plot and atom labelling scheme for $\text{RuCl}_2(\text{PhNH}_2)_2\text{L}$, **2**.

respectively. This complex is diamagnetic and shows highly resolved aromatic proton resonances at 5.2 to 7.8 δ . The N-H resonance was identified⁷ as a relatively broad singlet near 13.5 δ (width at half height 0.06 ppm). Interestingly, each kind of proton gave rise to one signal. Thus the two ligands in **3** are magnetically equivalent and therefore, a two-fold axis of symmetry is required. Due to the unsymmetric nature of L, there exist¹⁰ five geometric possibilities of OsBr₂L₂. The final characterization of the osmium-diimine complex was made by a structure determination of OsBr₂L₂. A molecular view of **3** is represented in figure 3. The coordination sphere involves OsBr₂N₄. The X-ray structure reveals a *cis* geometry with respect to two coordinated bromides. The bond length trends within the chelate as well as the aromatic rings are consistent with a diimine character of L bound to osmium in its bivalent oxidation state. The two-fold axis bisects the angles N(1)-Os-N(4) and N(2)-Os-N(3).

3. Discussion

The three reactions described above, exemplify the novel ruthenium and osmium promoted oxidative dimerization of aniline to N-aryl diimine ligand(s). The mechanism of the above transformation of the organic substrate (5) is a combination of two major processes.



These are the oxidative *o*-dimerization of PhNH₂ to *o*-semidine and further oxidation of *o*-semidine to the diimine ligand, L. Anodic oxidation¹¹ of aromatic amines followed by para coupling leading to *p*-benzidine or *p*-semidine are common. There are also examples

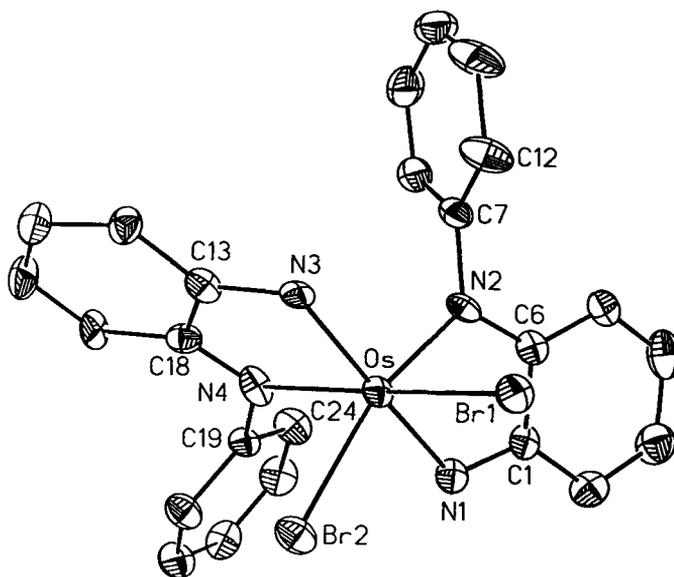


Figure 3. ORTEP plot and atom labelling scheme for OsBr₂L₂, **3**.

of oxidation of PhNH_2 to diazo compound¹², Ph-N=N-Ph . The oxidative ortho coupling of aniline leading directly to *o*-semidine¹³, however, is not known. It may be noted here that *cis* coordination of two aniline residues (or its deprotonated form) to the metal ion would bring them in close proximity to promote ortho dimerization. Moreover, the reactions, under consideration, do not occur in the absence of O_2 . Ruthenium promoted oxidation of amines to imines by O_2 is documented in the literature^{14,15}. It is, therefore, believed that the oxidation reactions presumably occur via aerial oxidation. Interestingly and expectedly, 2,6-dimethyl aniline does not react under a similar condition. We wish to note here that the coordination chemistry of N-substituted diimines was not known. The formation of the mixed ligand complex $\text{RuCl}_2(\text{aniline})_2\text{L}$ (**2**) from the reaction of RuCl_3 and aniline is interesting. In this compound only two, out of four coordinated aniline molecules, have undergone oxidative coupling to form L. The two anilines which are coordinated in relative *trans* positions remain unaffected. However, this compound can be further oxidised to a blue compound whose physical data indicate a *bis* diimine chelation¹⁶. Furthermore, this **2** and the osmium compound **3** are highly reactive and are suitable for studying chemical reaction. Our work in this area is continuing.

We now wish to note an interesting trend with regard to the compositions of the products obtained from the reactions (2)–(4). In the case of reaction (2) the difference of oxidation states of the metal ion ($\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{II}}$) is one while that in the reaction (4) ($\text{Os}^{\text{IV}} \rightarrow \text{Os}^{\text{II}}$) is two. Interestingly, in the reaction (3) the metal ion has undergone only one step reduction and as a result only one diimine ligand formation could occur. For further oxidative dimerization in **2**, an external oxidant like H_2O_2 or air is needed. From the above results it appears reasonable that the difference in the metal oxidation levels of the reactant and the product is the number of diimine ligand(s) formed in the above reactions.

4. Conclusions

In conclusion it may be stated that the results, discussed here, are a clear manifestation of template dimerization of aniline to yield some novel coordination complexes of N-phenyl-1,2-phenylene diimines which were otherwise not achievable. Strong π -interaction has been noted in these complexes which is reflected in the short M-N(diimine) distances (table 1). The compounds **2** and **3** are reactive and undergo different and interesting chemical reactions. For example, silver (I) assisted^{17,18} substitution of the two *cis* bromides in **3** by 2,2'-bipyridine results in a mixed *tris* chelate, $[\text{Os}(\text{L})_2(\text{bpy})]^{2+}$, which showed successive 5-electron transfer, presumably at the ligand centre.

Our research in this area is continuing and the results indeed show that the prospect of this type of reaction is bright. The preliminary results of the reaction of $\text{Ru}(\text{acac})_3$ and meta phenylene diamine reveal the possibility of formation¹⁹ of a bimetallic ruthenium complex with diimine bridging chelates. The reaction results of FeCl_3 , CrCl_3 with Ar-NH_2 are also highly promising²⁰ and are believed to form N-substituted phenazines.

Acknowledgements

Financial support received from the Department of Science and Technology, New Delhi and the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. We also thank Professors S-M Peng and A Castiñeiras and Dr P Ghosh for crystallographic studies.

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