Two novel reactions of ruthenated aniline. Structure and bonding in bis-chelated ruthenium complexes of quinone related ligands

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Two novel examples of oxidative *ortho* coupling of ruthenated aniline are described; the products are fully characterised by X-ray and other physicochemical data.

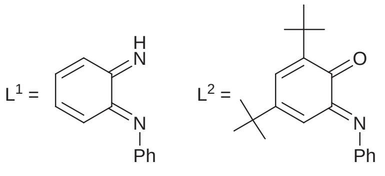
In a recent communication[1] we reported the formation of $\mathrm{RuCl_2(PhNH_2)_2(L^1)}$, **1** ($\mathrm{L^1}$ = *N*-phenyl-1,2-phenylenediimine), from the reaction of hydrated $\mathrm{RuCl_3}$ and $\mathrm{PhNH_2}$ [eqn. (1)].

$$\mathrm{RuCl_3{\cdot}3H_2O} \xrightarrow{\text{aniline}} \underset{\mathbf{1}}{\mathrm{RuCl_2(PhNH_2)_2(L^1)}} \qquad (1)$$

Although ruthenium(II) aniline complexes are known,[2] complex **1** represents the first example of a structurally characterised aniline complex of ruthenium. One of the principal interests in **1** was the possibility to study the chemical reactions of the coordinated aniline. In this report we present two such novel examples.

The reaction of $\mathrm{RuCl_2(PhNH_2)_2(L^1)}$ and 3,5-di-*tert*-butylcatechol occurs smoothly in methanol at room temperature to produce a blue compound of composition $\mathrm{RuCl_2(L^1)(L^2)}$, **2** [eqn. (2)], in 55% yield. This compound is highly soluble in common organic solvents and the solution shows an intense transition in the visible region at 627 nm. Verification of the composition and geometry of **2** was ascertained by the determination of its single crystal X-ray structure.‡ A view of the molecule is shown in Fig. 1 and selected bond distances are collected in Table 1. The results reveal the oxidative coupling of coordinated aniline and catechol to result in an *N*-phenyliminoquinone ligand, $\mathrm{L^2}$, with the formation of a C–N bond. This transformation was not known previously. The formulation of the diimine oxidation state of $\mathrm{L^1}$ (N,N) is evident[1] from the structural data of **2**. The imine C–N bond lengths, average 1.315(6) Å, are considerably shorter than the C7–N2 single bond, 1.444(6) Å, present in the same ligand. Considering the diimine oxidation state of the ligand $\mathrm{L^1}$, two charge distributions for the $\mathrm{RuL^2}$ moiety are possible in the above complex, either $\mathrm{Ru^{II}}$–$\mathrm{L^2}$ BQ (**2a**) or $\mathrm{Ru^{III}}$–$\mathrm{L^2}$ SQ (**2b**). Compound **2** is diamagnetic and shows two sharp *tert*-butyl proton resonances at δ 0.993 and 1.267. The C14–O bond length of the coordinated $\mathrm{L^2}$ is 1.280(5) Å and the C13–N3 bond length is 1.339(6) Å. This C–O bond length is longer than the C=O bond length [1.239(7) Å] observed[3] in free 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (Phenox BQ) but it falls below the range observed[4] (1.29 Å and above) for a coordinated semiquinone ligand. For comparison, the C–O bond length[3a] in $\mathrm{Ru(PPh_3)_2Cl_2}$(phenox SQ) (phenox SQ = 1-hydroxy-2,4,6,8-tetra-*tert*-butylphenoxyzinyl radical) is 1.300(4) Å and the average C–O bond length[5] in $\mathrm{Ru(bpy)_2(DBSQ)^+}$ (bpy = 2,2′-bipyridine, DBSQ = 3,5-di-*tert*-butyl-1,2-semiquinone) is 1.308 Å. The C–N bond length of coordinated $\mathrm{L^2}$ is within the range of values expected[6] for imine ligands. Moreover, the C15–C16 and C17–C18 bonds have almost localised double bond character which is also consistent[4b] with the iminobenzoquinone formulation (**2a**). Their average distance of 1.355(6) Å is significantly shorter than the other four bonds of the ring (Table 1). To the

$$\underset{\mathbf{1}}{\mathrm{RuCl_2(PhNH_2)_2(L^1)}} + \text{3,5-di-}\textit{tert}\text{-butylcatechol} \xrightarrow{\mathrm{CH_3OH}} \underset{\mathbf{2}}{\mathrm{RuCl_2(L^1)(L^2)}} \qquad (2)$$



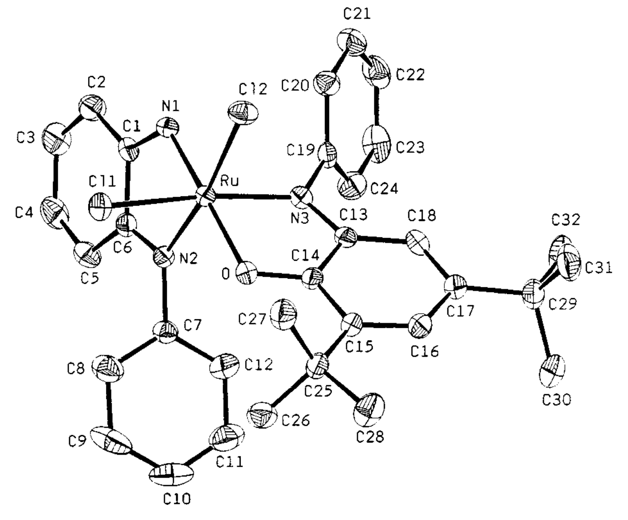
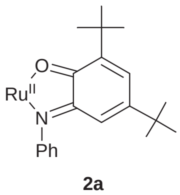


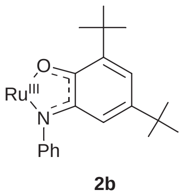
Fig. 1 Molecular structure of $\mathrm{RuCl_2(L^1)(L^2)}$ showing the atom numbering scheme

Table 1 Selected bond distances (Å) for $\mathrm{RuCl_2(L^1)(L^2){\cdot}CH_2Cl_2}$

Ru–O	2.022(3)	N3–C13	1.339(6)	C5–C6	1.434(6)
Ru–N1	1.950(4)	O–C14	1.280(5)	C6–C1	1.447(6)
Ru–N2	2.001(4)	N2–C7	1.444(6)	C13–C14	1.439(6)
Ru–N3	1.974(4)	N3–C19	1.446(6)	C14–C15	1.439(6)
Ru–Cl1	2.364(13)	C1–C2	1.421(7)	C15–C16	1.355(6)
Ru–Cl2	2.385(13)	C2–C3	1.341(7)	C16–C17	1.441(7)
N1–C1	1.317(6)	C3–C4	1.417(8)	C17–C18	1.355(7)
N2–C6	1.313(6)	C4–C5	1.338(8)	C18–C13	1.420(6)



2a



2b

best of our knowledge compound **2** represents the first example[7] of a mixed ligand compound containing both 1,2-diimine (N,N) and 1,2-iminoquinone (N,O) which gives an opportunity for the direct comparison of bonding between an (N,N) and an (N,O) donor. Furthermore, we wish to note here that structurally characterised Ru 1,2-diimines (N,N) are scarce[6] and there is only one example[3] of a ruthenium complex of 1,2-iminosemiquinone, the structure of which has been reported. Synthetic difficulties[7] have inhibited the study of iminoquinone complexes.

It was observed that prolonged exposure of a brown solution of **1** to air led to formation of a blue solution. A similar transformation occurs instantaneously and smoothly when a solution of **1** in CH_2Cl_2 is treated with H_2O_2. Chromatographic work up followed by crystallisation of the crude product yielded crystalline $RuCl_2(L^1)_2$, **3**, in 45% yield [eqn. (3)]. The three-dimensional X-ray structure of **3** authenticates the formation of the compound from reaction (3). The isomer geometry of the ruthenium complex is identical[8] to that of the analogous dibromo osmium complex, $OsBr_2(L^1)_2$. The bond distances of the coordinated diimine ligand in the above two ruthenium and osmium compounds are similar. (Details of the X-ray structure of **3** will be reported elsewhere.) The compound shows an intense transition at 590 nm in the visible region.

$$\underset{\mathbf{1}}{\mathrm{RuCl_2(PhNH_2)_2(L^1)}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{H_2O_2}} \underset{\mathbf{3}}{\mathrm{RuCl_2(L^1)_2}} \qquad (3)$$

The above coupling reactions [(2) and (3)] do not occur with uncoordinated aniline. These reactions therefore may be classified as reactions of the activated coordinated aniline. In reaction (2) one of the coordinated anilines coupled with externally added 3,5-di-*tert*-butyl catechol to form an *N*-phenyl substituted derivative of *o*-iminobenzoquinone.[7] It is possible that oxidation of catechol followed by condensation with the coordinated aniline have occurred during the above transformation. Reaction (3) formally involves many operations which are believed to occur simultaneously: isomerization of the starting compound to bring the two interacting aniline molecules into close proximity, oxidative coupling of two aniline molecules to *o*-semidine and further oxidation of *o*-semidine to diimine. For comparison, the reaction[8] of aniline with $[OsBr_6]^{2-}$ resulted in formation of a bis-chelated complex, $OsBr_2(L^1)_2$, directly. In contrast, a similar reaction[1] using hydrated $RuCl_3$ as the starting material yielded only a monochelated diimine complex, $RuCl_2(PhNH_2)_2(L^1)$, where two out of the four coordinated aniline molecules underwent oxidative dimerisation. Our present results have been able to demonstrate clearly that further oxidative coupling of the coordinated anilines in $RuCl_2(PhNH_2)_2(L^1)$ is possible by the use of a suitable oxidant. Our preliminary results in the area of oxidative coupling reactions of coordinated aromatic amines[2] in $[Ru(ArNH_2)_6]^{2+}$ and related substrates are highly encouraging and the scope of these reactions is very high.

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Notes and References

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‡ *Crystal data*: $[RuCl_2(L^1)(L^2)]\cdot CH_2Cl_2$ **2**: $C_{33}H_{37}N_3OCl_4Ru$, M = 734.55, monoclinic, space group $P2_1/n$, a = 12.1035(20), b = 14.7953(11), c = 19.718(3) Å, β = 104.715(11)°, U = 3415.2(8) Å^3, Z = 4, D_c = 1.429 g cm^{-3}, crystal dimensions 0.25 × 0.25 × 0.20 mm, T = 298 K, μ = 6.259 cm^{-1}. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). 6007 unique reflections were measured and 3728 with $I \geqslant 2\sigma(I)$ were used in the refinement. Refinement[9] of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R = 0.037. The final Fourier difference map showed residual extrema at 0.410, −0.430 e Å^{-3}. CCDC 182/919.

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