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 RuCl₂(PhNH₂)₂(L₁), 1 (L₁ = N-phenyl-1,2-phenylenediimine), from the reaction of hydrated RuCl₃ and PhNH₂ [eqn. (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 RuCl₂(PhNH₂)₂(L₁) and 3,5-di-tert-butylcatechol occurs smoothly in methanol at room temperature to produce a blue compound of composition RuCl₂(L₁)(L₂), 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, L₂, with the formation of a C=N bond. This transformation was not known previously. The formulation of the diimine oxidation state of L₁ (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 L₁ (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 L₂, two charge distributions for the RuL₂ moiety are possible in the above complex, either Ru⁺⁺L₂ BQ (2a) or Ru⁺⁺L₂ 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 L₂ 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-butylphenoxyzin-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 3 in 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 L₂ 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 4 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

Fig. 1 Molecular structure of RuCl₂(L₁)(L₂) showing the atom numbering scheme

| Table 1 Selected bond distances (Å) for RuCl₂(L₁)(L₂)·CH₂Cl₂ |
|-----------------|-----------------|-----------------|-----------------|
| Ru–O            | 2.022(5)        | N3–C13          | 1.339(6)        |
| Ru–N1           | 1.950(4)        | O–C14           | 1.280(5)        |
| Ru–N2           | 2.001(4)        | N2–C7           | 1.444(6)        |
| Ru–N3           | 1.974(4)        | N3–C19          | 1.446(6)        |
| Ru–Cl1          | 2.364(13)       | C1–C2           | 1.421(7)        |
| Ru–Cl2          | 2.385(13)       | C2–C3           | 1.431(7)        |
| Ni–C1           | 1.317(6)        | C3–C4           | 1.417(8)        |
| N2–C6           | 1.313(6)        | C4–C5           | 1.338(8)        |
| C1–C2           | 1.420(6)        | C5–C6           | 1.434(6)        |

RuCl₂·SH₂O + aniline → RuCl₂(PhNH₂)₂(L₁) (1)

RuC₂(PhNH₂)₂(L₁) + 3,5-di-tert-butylcatechol → RuCl₂(L₁)(L₂) (2)

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best of our knowledge compound 2 represents the first example of a mixed ligand compound containing both 1,2-dimines (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-dimines (N,N) are scarce and there is only one example of a ruthenium complex of 1,2-iminoquinone, the structure of which has been reported. Synthetic difficulties 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 CH₂Cl₂ is treated with H₂O₂. Chromatographic work up followed by crystallisation of the crude product yielded crystalline RuCl₂(L¹)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 to that of the analogous dibromo osmium complex, OsBr₂(L¹)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.

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. 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 of aniline with [OsBr₃]²⁺ resulted in formation of a bis-chelated complex, OsBr₂(L¹)₂, directly. In contrast, a similar reaction using hydrated RuCl₃ as the starting material yielded only a monochelated diimine complex, RuCl₂(PhNH₂)₂(L¹), 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 RuCl₂(PhNH₂)₂(L¹) is possible by the use of a suitable oxidant. Our preliminary results in the area of oxidative coupling reactions of coordinated aromatic amines in [Ru(ArNH₂)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: [RuCl₂(L¹)₂]·CH₂Cl₂: C₃₇H₃₇N₃OCl₄Ru, M = 734.55, monoclinic, space group P2₁/n, a = 12.1035(20), b = 14.7953(11), c = 19.718(3) Å, β = 104.715(11)°, U = 3415.2(8) Å³, Z = 4, D₀ = 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 > 2σ(I) were used in the refinement. Refinement 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 182919.

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