Ruthenium(III)-promoted oxidative dimerization of aniline to *N*-phenyl-1,2-phenylenediimine. Definitive proof for the template reaction

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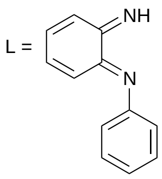
Two novel examples of ruthenium-promoted oxidative *ortho*-dimerization of aniline are described which demonstrate that the dimerization reaction proceeds *via* coordination of anilines to the metal ion.

In a recent communication[1] we described unusual examples of osmium-promoted oxidative dimerization of primary aromatic amines [eqn. (1)] to *N*-aryl-1,2-arylenediimine (L). It was

$$[Os^{IV}Br_6]^{2-} \xrightarrow{PhNH_2} \underset{\mathbf{1}}{[Os^{II}L_2Br_2]} \qquad (1)$$



proposed that prior *cis*-coordination of amines to the metal ion is the key step for the dimerization reaction.

Here, we further demonstrate two more novel examples of ruthenium-promoted oxidative dimerization reactions of aniline which established that coordination of amines takes place during the course of reaction.

The first reaction [eqn. (2)] is the reaction of $[Ru(acac)]_3]$[2]

$$[Ru(acac)_3] \xrightarrow{PhNH_2} \underset{\mathbf{2}}{[Ru(acac)_2L]} \qquad (2)$$

with neat aniline at 130 °C. Chromatographic work-up of the reaction mixture afforded $[Ru(acac)_2L]$, which was recrystallised from an aqueous acetonitrile solution and obtained as bown needles in 30% yield. Addition of NEt_3, which acts as a proton sink, to the reaction mixture increases the yield considerably to 65%. The compound $[Ru(acac)_2L]$ is soluble in common organic solvents and is diamagnetic. The N–H stretch occurs[3] as a sharp feature of moderate intensity in the range 3300–3200 cm^{-1}. The presence of a strong C=N stretch near 1600 cm^{-1} characterizes the presence of diimine chromophore in the compound. The ^1H NMR spectrum of the complex consists of three methyl resonances at δ 1.76(3 H), 1.83(6 H) and 2.35 (3 H); resolved aromatic proton resonances between δ 6.5 and 7.4 and the N–H resonance is observed[4] as a relatively broad singlet at δ 10.8. Suitable crystals for an X-ray structure determination† were obtained upon slow evaporation of a saturated solution of the compound in hexane, and a view of the molecule is shown in Fig. 1. 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. The imine, C–N bond lengths, average 1.341(8) Å, are considerably shorter than a C–N single bond, 1.433(9) Å. The analytical, spectral and X-ray data collectively conform to the formulation of **2** as $[Ru(acac)_2L.]$

To gain a better insight into the course of above metal-promoted oxidation reaction, we used $RuCl_3{\cdot}3H_2O$ as a starting material to carry out a similar reaction. $RuCl_3{\cdot}3H_2O$ was selected since first, as in $[Ru(acac)_3]$, ruthenium is trivalent and secondly, the chloride salt is much more labile towards substitution than is $Ru(acac)_3$. Therefore, a higher degree of amine coordination was anticipated.

This reaction proceeded very smoothly and recrystallisation of the crude product from dichloromethane–hexane [eqn. (3)]

$$RuCl_3{\bullet}3H_2O \xrightarrow{PhNH_2} \underset{\mathbf{3}}{[RuCl_2(PhNH_2)_2L]} \qquad (3)$$

resulted a highly crystalline compound **3** (yield, 60%), which contains one diimine (L), two *trans*-anilines and two *cis*-chlorides in the co-ordination sphere.

Unlike **2**, compound **3** is sparingly soluble in common organic solvents. The IR spectrum shows[3] multiple sharp ν_{NH} between 3300 and 3100 cm^{-1}, sharp $\nu_{C=C}$ and $\nu_{C=N}$ at 1600 and 1580 cm^{-1} and two ν_{Ru-Cl} stretches[5] at 360 and 340 cm^{-1}. The

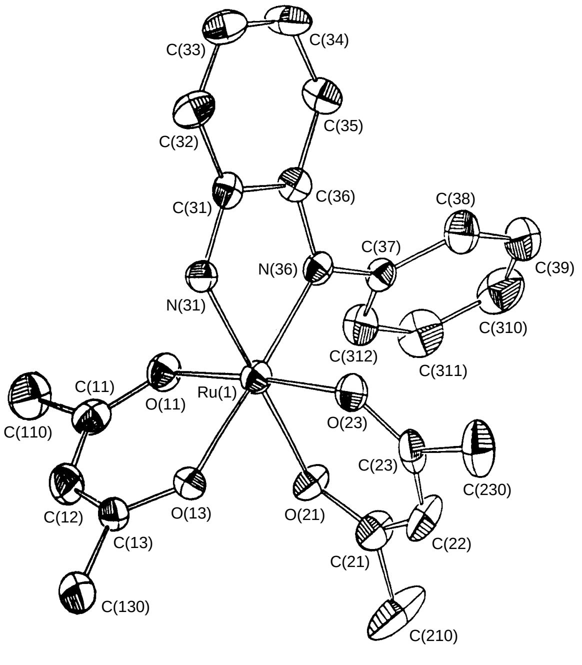


Fig. 1 Molecular structure of $[Ru(acac)_2L]$ **2** showing the atom numbering scheme. The asymmetric unit consists of two crystallographically distinct molecules. The figure shows a view of molecule 1. Selected bond distances (Å): Ru(1)–N(31) 1.958(5), Ru(1)–N(36) 1.996(5), Ru(1)–O(11) 2.019(5), Ru(1)–O(13) 2.068(4), Ru(1)–O(21) 2.050(4), Ru(1)–O(23) 2.031(5), N(31)–C(31) 1.333(8), N(36)–C(36) 1.352(8), N(36)–C(37) 1.429(8).

^{1}H NMR spectrum shows two doublet NH resonances[6] at δ 5.09 and 4.84 assigned to NH_2. Verification of the composition as well as the geometry of the compound was ascertained by single-crystal X-ray diffraction,† and a view of the molecule is shown in Fig. 2. There are three types of Ru–N distances in the molecule. The two Ru–N(aniline) single bonds are identical and are longer than the Ru–N(imine) bonds indicating a relatively weak bond between Ru and aniline. The two diimine, C=N bonds are much shorter than the C–N bonds. To the best of our knowledge compound **3** represents the first authentic example of aniline coordinated to ruthenium. Indications are strong that it can act as a good starting compound for substitution reactions and for performing reactions at the coordinated aniline.

It is worthwhile to compare the results of the three reactions (1)–(3). For osmium [eqn. (1)] a bis(diimine) complex was obtained whereas only a monodiimine complex resulted from reaction (2). It is noteworthy that the difference of the oxidation states of the metal ions in the starting compound and the end product is two in reaction (1) but is one in reaction (2). Interestingly, in reaction (3) only two of the four coordinated anilines have undergone oxidative dimerization and notably, the metal centre has undergone only a one-step reduction. From the above results it appears reasonable that the difference in the oxidation levels of the reactant and the product is equal to the number of diimine ligands formed in the reaction.

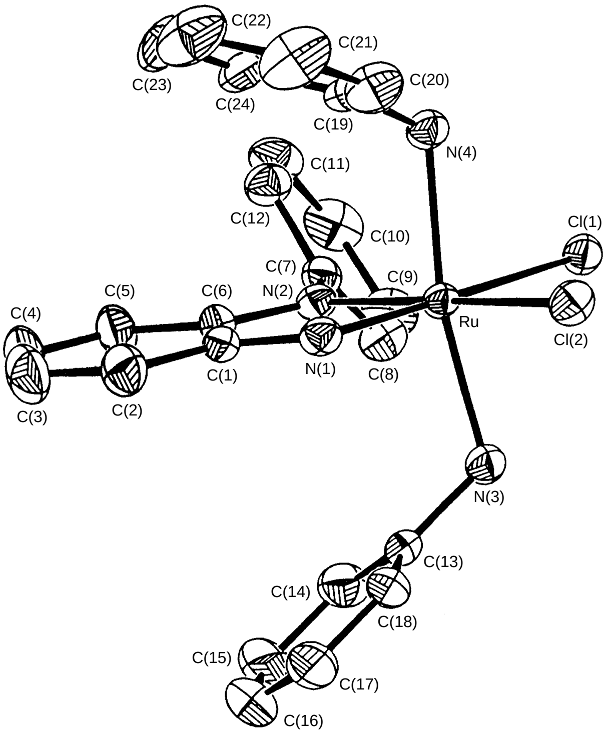


Fig. 2 Molecular structure of $[RuCl_2(PhNH_2)_2L]$ **3** showing the atom numbering scheme. Selected bond distances (Å): Ru–N(1) 1.940(4), Ru–N(2) 1.997(4), Ru–N(3) 2.135(4), Ru–N(4) 2.135(4), Ru–Cl(1) 2.422(1), Ru–Cl(2) 2.429(1), N(1)–C(1) 1.319(7), N(2)–C(6) 1.343(7), N(2)–C(7) 1.445(6), N(3)–C(13) 1.451(7), N(4)–C(19) 1.449(7).

In conclusion, it may be stated that the above results are a clear manifestation of template dimerization of primary aromatic amines to yield novel coordination complexes of arylene diimines which otherwise are not achievable.[7]

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Footnotes

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† *Crystal data*: $[Ru(acac)_2L]\cdot 0.25H_2O$ **2**: $C_{22}H_{25}N_2O_{4.25}Ru$, $M = 486.51$, monoclinic, space group $C2/c$, $a = 33.578(9)$, $b = 9.922(2)$, $c = 26.354(5)$ Å, $\beta = 93.114(10)°$, $U = 8768(3)$ Å^3, $Z = 16$, $D_c = 1.474$ g cm^{-3}, crystal dimensions 0.20 × 0.25 × 0.30 mm. Intensity data were collected on Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan mode with $2\theta_{max} = 32.4°$. 12 707 unique reflections were measured and 12 705 with $I \geqslant 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods[8] by a full-matrix least-squares procedure based on F^2 which smoothly converged to $R = 0.0805$. The final Fourier difference map showed residual extrema at 0.62, −0.80 e Å^{-3}.

$[RuCl_2(PhNH_2)_2L]\cdot CH_2Cl_2$ **3**: $C_{25}H_{26}N_4Cl_4Ru$, $M = 625.38$, monoclinic, space group $P2_1/n$, $a = 9.390(5)$, $b = 19.225(2)$, $c = 15.631(3)$ Å, $\beta = 101.91(3)°$, $U = 2761(16)$ Å^3, $Z = 4$, $D_c = 1.504$ g cm^{-3}, crystal dimensions 0.25 × 0.45 × 0.60 mm. Intensity data were collected on Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan mode with $2\theta_{max} = 50.0°$. 4848 unique reflections were measured and 3093 with $I \geqslant 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R = 0.040$. The final Fourier difference map showed residual extrema at 0.680, −0.510 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/486.

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