Oxidation of Coordinated Azomethine to Amide. Synthetic and Structural Studies on a Rhenium and a Ruthenium System

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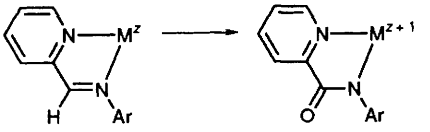
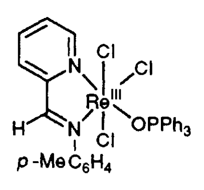
The title reaction is exemplified by the high yield conversions **1** → **2** and **3** → **4** by H_2O_2, and the X-ray structures of **2** and **4** are reported; the species $\mathbf{1}^+$ and $\mathbf{3}^+$ afford **2** and **4** respectively when treated with water.

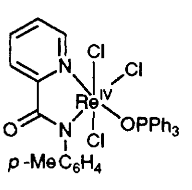
The transformation of organic functions activated by metal coordination is an important theme in chemical research. The reaction concerning us here, $-CH{=}NR + [O] \rightarrow -C({=}O)NHR$, could in principle open a convenient route for converting aldehydes (*via* Schiff bases) to amides. In practice, however, the reaction is not directly accessible. Herein we describe the transformation of a chelated *N*-aryl-pyridine-2-aldimine to the corresponding deprotonated *N*-aryl-2-picolinamide as in Scheme 1 (M = Re, Ru) which, to the best of our knowledge, constitutes the first realisation of such a reaction. Along with ligand oxidation the metal oxidation state (z) also increases to $z + 1$. For M = Re, Ar = *p*-tolyl and the metal is coordinated by one pyridylimine; for M = Ru, Ar = Ph, then the metal is doubly coordinated.



Scheme 1



1



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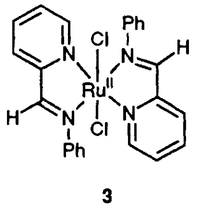

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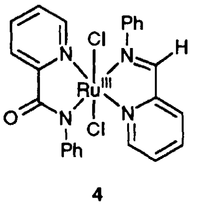

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An MeCN solution (30 cm^3) of the red Re^{III} complex **1** (25 mg) synthesised[1] from the corresponding Schiff base[2] and $ReOCl_3(PPh_3)_2$[3] was oxidised by aqueous H_2O_2 (30%) at room temperature and the brownish yellow residue left after removal of solvent was recrystallised from toluene affording the Re^{IV} amide complex **2** as the toluene adduct **2**·0.25 PhMe.†

The green Ru^{II} complex[4] **3** (100 mg) was similarly oxidised by 30% aqueous H_2O_2 in CH_2Cl_2 (30 cm^3). Here the red-brown residue obtained after solvent removal was recrystallised from PhMe–CH_2Cl_2 furnishing the Ru^{III} amide chelate **4** as the solvate **4**·PhMe in 75% yield.

The X-ray structures of **2** and **4** in their toluene adducts are shown in Figs. 1 and 2.‡ The lattice of **2**·0.25 PhMe consists of two metrically very similar but crystallographically distinct molecules of **2**. In the distorted octahedral $ReOCl_3N_2$ coordination sphere, the pyridine nitrogen lies *trans* to $OPPh_3$ oxygen and the Cl_3 fragment is meridional. The average distances within the planar amide function are C–O, 1.22(2) Å, and C–N, 1.35(2) Å. The average Re–O–P angle is 152.5(8)°.

In **4**·PhMe the coordination sphere (Fig. 2) involves RuN_4Cl_2; the two pyridine nitrogen atoms as well as the two chlorine atoms lie *trans* to each other. The chelating ligands display an interesting disorder. Even though **4** cannot be centrosymmetric, the metal atom in the lattice lies on a centre of inversion (0,0,0). Thus the molecules are packed in two equivalent but opposite orientations such that corresponding carbon and nitrogen atoms of the two bidentate ligands are nearly or completely superimposed and alternative peaks are not resolved in difference maps; the thermal parameters for some of the atoms appear to be somewhat large. In Fig. 2 only one (occupation factor of 0.5) of the two equivalent oxygen sites is shown. Owing to the disorder distinctive distances in the amide and azomethine fragments are not observable.

In MeCN (0.1 mol dm^{-3} in NH_4PF_6; Pt electrode) **1** displays a reversible one-electron cyclic voltammetric peak $\mathbf{1}^+/\mathbf{1}$ with

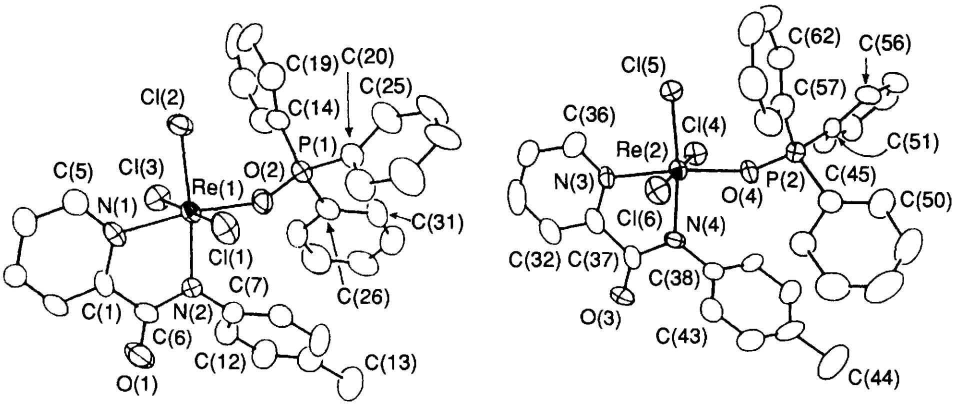

Fig. 1 ORTEP plot and atom labelling scheme for **2** in its toluene adduct **2**·0.25 PhMe. Selected bond distances (Å) and angles (°): Re(1)–Cl(1), 2.329(4); Re(1)–Cl(2), 2.358(5); Re(1)–Cl(3), 2.342(4); Re(1)–O(2), 2.034(10); Re(1)–N(1), 2.100(12); Re(1)–N(2), 2.066(14); Re(2)–Cl(4), 2.341(5); Re(2)–Cl(5), 2.352(4); Re(2)–Cl(6), 2.345(5); Re(2)–O(4), 2.019(10); Re(2)–N(3), 2.101(12); Re(2)–N(4), 2.074(11); C(6)–O(1), 1.23(3); C(37)–O(3), 1.22(2); N(1)–Re(1)–N(2), 78.4(5); N(3)–Re(2)–N(4), 77.9(5).

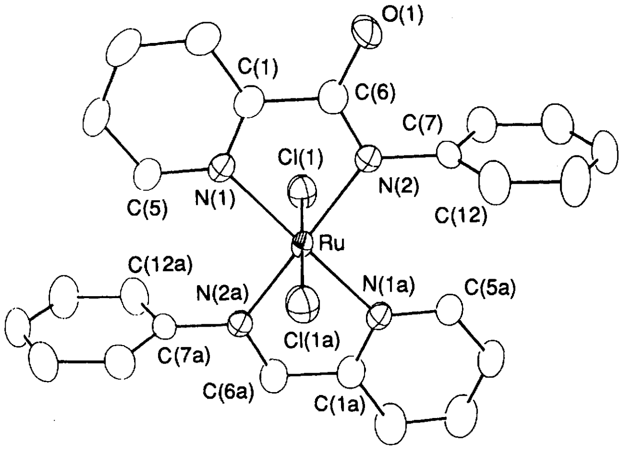

Fig. 2 ORTEP plot and atom labelling scheme for **4** in its toluene adduct **4**·PhMe. Selected bond distances (Å) and angles (°): Ru–Cl(1), 2.334(1); Ru–N(1), 2.089(3); Ru–N(2), 2.068(4); N(1)–Ru–N(2), 77.8(1).

$E_{\frac{1}{2}}$ 0.30 V *vs.* saturated calomel electrode (SCE) where $\mathbf{1}^+$ is the Re^{IV} analogue of **1**. For **2** the Re^{IV}/Re^{III} couple ($\mathbf{2}/\mathbf{2}^-$) has the much lower $E_{\frac{1}{2}}$ of −0.41 V signifying strong stabilisation of the higher oxidation state by the amide ligand as expected[5] (the Re^{V}/Re^{IV} couple $\mathbf{2}^+/\mathbf{2}$ is also observed, $E_{\frac{1}{2}}$ 1.21 V). Similarly the Ru^{III}/Ru^{II} couples $\mathbf{3}^+/\mathbf{3}$ and $\mathbf{4}/\mathbf{4}^-$ have $E_{\frac{1}{2}}$ values of 0.31 and −0.14 V respectively; the $E_{\frac{1}{2}}$ of $\mathbf{4}^+/\mathbf{4}$, *i.e.* Ru^{IV}/Ru^{III}, is 1.29 V. Stable yellow solutions of $\mathbf{1}^+$ can be quantitatively generated in dry MeCN *via* coulometry at 0.50 V. Upon addition of water (*e.g.*, 1 cm^3 of H_2O in 20 cm^3 of MeCN) $\mathbf{1}^+$ is spontaneously transformed into a mixture of **1** and **2**. The ruthenium system behaves similarly. Here $\mathbf{3}^+$, the Ru^{III} analogue of **3**, has been isolated in 75% yield as the perchlorate salt $[\mathbf{3}]^+ClO_4^-$ by careful oxidation of **3** (100 mg in 15 cm^3 of MeCN) by Cl_2(gas) followed by addition of $NaClO_4$. In warm aqueous MeCN solution $[\mathbf{3}]^+ClO_4^-$ is transformed spontaneously into a mixture of **3** and **4**.

In summary $\mathbf{1}^+$ (or $\mathbf{3}^+$) is converted into a mixture of **2**(**4**) and **1**(**3**) by water. Water possibly adds to the polarised azomethine function of $\mathbf{1}^+(\mathbf{3}^+)$ and the hydroxy-amine intermediate so formed is rapidly oxidised to **2**(**4**) by a part of $\mathbf{1}^+(\mathbf{3}^+)$ (when an external oxidant is not present) which is reduced to **1**(**3**). Some examples of the addition of hydroxylic solvents (H_2O, EtOH) to azomethine functions exist.[6] It is conceivable that in the reaction of Scheme 1, H_2O_2 first oxidises **1**(**3**) to $\mathbf{1}^+(\mathbf{3}^+)$ which adds water and the adduct is further oxidised by H_2O_2 affording **2**(**4**) in high yields.

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Footnotes

† Satisfactory elemental analyses were obtained in all cases. **1**: λ_{max}/nm (MeCN) 675 ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$ 2220), 475 (4100), 450 (2575) (sh) and 425 (2425) (sh); ν/cm^{-1} (KBr disc) $\nu_{C=N}$ 1591, ν_{OP} 1123; μ_{eff}/μ_B (298 K) 2.84 (t_2^4). **2**·0.25 PhMe : λ_{max}/nm (MeCN) 725 ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$ 85), 525 (540) (sh) and 400 (2260) (sh); ν/cm^{-1} (KBr disc) ν_{amide} 1642 and 1605, ν_{OP} 1121; μ_{eff}/μ_B (298 K) 3.64 (t_2^3). $[\mathbf{3}]^+ClO_4^-$: λ_{max}/nm (MeCN) 500 ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$ 2000) (sh), 470 (2665), 400 (3895) and 290 (7535); ν/cm^{-1} (KBr disc) $\nu_{C=N}$ 1602; μ_{eff}/μ_B (298 K) 1.82 (t_2^5); $\Lambda/\Omega^{-1}\,cm^2\,mol^{-1}$ (MeCN, 298 K) 134. **4**·PhMe : λ_{max}/nm (MeCN) 510 ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$ 2525), 350 (3750) (sh) and 280 (7350) (sh); ν/cm^{-1} (KBr disc) ν_{amide} 1595 and 1630, $\nu_{C=N}$ 1605; μ_{eff}/μ_B (298 K) 1.86 (t_2^5). (sh = shoulder).

‡ *Crystal data* for **2**·0.25 PhMe: $C_{32.75}H_{28}N_2O_2PCl_3Re$, M = 805.1, triclinic, space group $P\bar{1}$, Z = 4, a = 11.780(5), b = 12.092(3), c = 23.320(4) Å, α = 83.77(2), β = 78.93(3), γ = 79.75(3)°, V = 3199(2) Å^3, T = 295 K, D_c = 1.67 g cm^{-3}, μ(Mo-Kα) = 41.3 cm^{-1}, crystal dimension 0.22 × 0.16 × 0.18 mm^3. For **4**·PhMe: $C_{31}H_{18}N_4OCl_2Ru$, M = 634.5, triclinic, space group $P\bar{1}$, Z = 1, a = 9.454(4), b = 9.582(4), c = 9.902(4) Å, α = 69.40(3), β = 75.63(3), γ = 62.96(3)°, V = 743.6(5) Å^3, T = 295 K, D_c = 1.42 g cm^{-3}, μ(Mo-Kα) = 7.36 cm^{-1}, crystal dimension 0.18 × 0.20 × 0.48 mm^3. Data were collected by the ω-scan technique in the range $3 < 2\theta < 50°$ for both the crystals on a Siemens R3m/V four-circle diffractometer affording 10058 (**2**·0.25 PhMe) and 2653 (**4**·PhMe) unique reflections of which 5741 and 2345 [$I > 3\sigma(I)$] respectively were used for structure solution. All data were corrected for Lorentz and polarization effects and empirical absorption corrections were done on the basis of azimuthal scans.[7] Both structures were solved by the Patterson heavy-atom method and difference Fourier techniques, and subsequently refined by full=matrix least-squares procedures using the SHELXTL-Plus program package[8] on a MicroVAX II computer. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were added at their respective calculated positions with fixed U = 0.08 Å^2 in the final cycle of refinement. In both the crystals, the solvent molecule occupied a special position (centre of symmetry) but was disordered. The structures refined to R = 5.30% and R_w = 6.81% for **2**·0.25 PhMe and R = 3.17% and R_w = 3.40% for **4**·PhMe. The highest residual electron densities were, respectively, 1.28 and 0.39 e Å^{-3} near the metal atoms. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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