Formation of a Chelating Bidentate Nitrosoalkane Complex of Ruthenium(II) through Reaction of H_2O with a High-valent Bis(imido)ruthenium Intermediate and X-Ray Crystal Structure of $[Ru(bpy)_2(ONCMe_2CMe_2NO)][ClO_4]_2{\cdot}Me_2CO$

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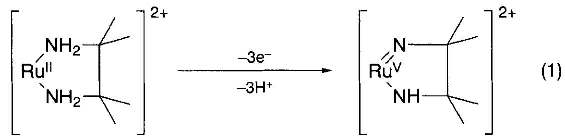
Oxidation of $[Ru^{II}(bpy)_2(NH_2CMe_2CMe_2NH_2)]^{2+}$ by Ce^{IV} in H_2O generates the highly reactive *cis*-bis(imido)ruthenium(VI) intermediate, which reacts with H_2O to give $[Ru^{II}(bpy)_2(ONCMe_2CMe_2NO)]^{2+}$, the structure of which has been determined by X-ray crystallography.

Because of their high $E°$ values, high-valent ruthenium complexes containing imido, nitrido and amido ligands are of prime importance to the study of nitrogen atom transfer reactions. While several neutral ruthenium imido complexes are known in the literature,[1] the chemistry of the cationic species remains unknown. In the electrochemical oxidation of bound ammonia to NO^+, Meyer and coworkers proposed an electrochemically generated $Ru^{IV}{=}NH$ intermediate, which reacts with water to give Ru–N(O)H and subsequently $Ru^{II}{-}NO$.[2] Here, we provide support to this mechanism through isolation of a ruthenium(II) complex having a chelating bidentate nitrosoalkane ligand.

The preparation and characterization of $[Ru(bpy)_2(NH_2CMe_2CMe_2NH_2)]^{2+}$ **1** has been previously described.[3] Previous studies showed that this complex cation displays a reversible proton-coupled $Ru^V{-}Ru^{II}$ couple in aqueous solution [eqn. (1)].



Electrochemical oxidation of **1** at $E°$ of this three-electron couple led to cleavage of the bidentate amine and to the formation of a bis(imine)ruthenium(II) complex. In this work, oxidation of **1** with $Ce(NO_3)_6{}^{2-}$ in 0.1 mol dm^{-3} CF_3CO_2H was found to give a brown solution, from which the brown crystalline solid $[Ru(bpy)_2(ONCMe_2CMe_2NO)][ClO_4]_2$ **2**[†] was isolated in ≈70% yield upon addition of perchloric acid (6 mol dm^{-3}). Complex **2** is diamagnetic and is stable in air and in solution for several days. Its ^1H NMR spectrum shows peaks at δ 1.06 and 1.71, which are due to CH_3. The IR spectrum shows an intense band at 1450 cm^{-1}, which is tentatively assigned to the ν(N=O) stretch. A similar ν(NO) stretch at 1446 cm^{-1} was previously reported in $[PtCl_2(PhNO)_2]$;[4] however, the ν(NO) stretches found in other ruthenium(II) nitrosoarene complexes are at 1270–1340 cm^{-1}.[5] The structure of **2** was established by an X-ray crystal analysis.[‡] Fig. 1 shows a perspective view of the complex cation of **2**. Unlike the previous case,[3] no cleavage of the chelating ligand is found and the complex contains a chelating bidentate nitrosoalkane ligand. Since the complex is diamagnetic, the ruthenium is assigned as Ru^{II}. The measured N=O distances of 1.222(4) and 1.234(4) Å are comparable to the related distances of 1.260(20) Å in $[Fe(tpp)(Pr^iNO)(Pr^iNH_2)]$ (H_2tpp = 5,10,15,20-tetraphenylporphyrin)[6] and 1.24–1.25 Å in tris(biolurato)ruthenium(II).[7] The Ru–N(O) distances are 1.923(4) and 1.937(4) Å. These values are shorter than that of a normal Ru–N single bond, but are not very much different from that of 1.963 Å in tris(violurato)ruthenium(II).[7] In MeCN containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate, complex **2** shows a reversible $Ru^{III}{-}Ru^{II}$ couple at $E_{\frac{1}{2}}$ = 0.76 V *vs.* $Ag/AgNO_3$ (0.1 mol dm^{-3} in MeCN). To our knowledge, this is the first metal complex containing a chelating bidentate nitrosoalkane ligand.

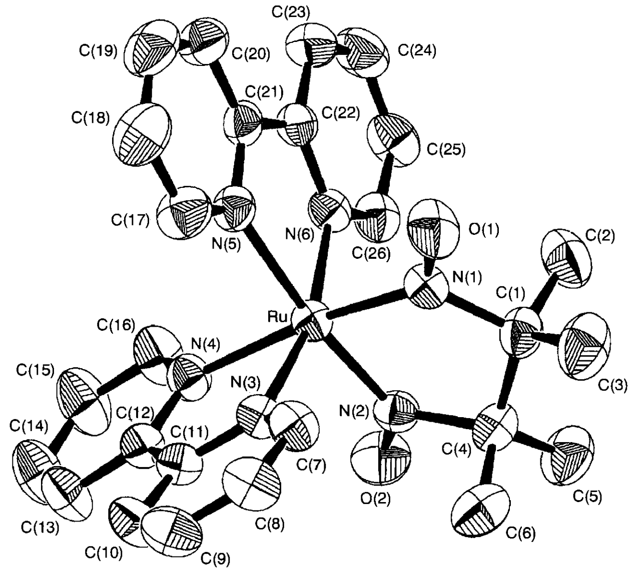
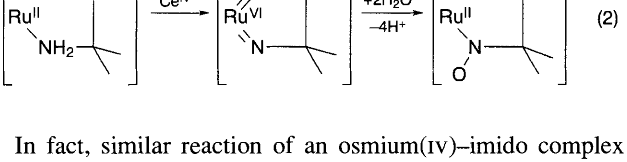


Fig. 1 Perspective view of the complex cation of **2**. Selected bond lengths (Å) and angles (°): Ru–N(1) 1.923(4), Ru–N(2) 1.937(4), Ru–N(3) 2.084(4), Ru–N(4) 2.130(4), Ru–N(5) 2.115(4), Ru–N(6) 2.082(4), O(1)–N(1) 1.222(4), O(2)–N(2) 1.234(4); Ru–N(1)–O(1) 126.9(3), Ru–N(1)–C(1) 117.8(3), O(1)–N(1)–C(1) 115.3(4), Ru–N(2)–O(2) 127.6(3), Ru–N(2)–C(4) 117.1(3), O(2)–N(2)–C(4) 115.3(4).

The isolation of **2** suggests that highly oxidizing ruthenium–imido complexes are very electrophilic and react with H_2O through a redox pathway. With reference to previous studies,[3] oxidation of **1** by Ce^{VI} in H_2O likely produces the very oxidizing bis(imido)ruthenium(VI) complex, the two imido moieties of which may have nitrene character. Nucleophilic attack of the electrophilic imido moieties by H_2O leads to an intramolecular redox reaction, resulting in the formation of complex **2** [eqn. (2)].



In fact, similar reaction of an osmium(IV)–imido complex with secondary amines has also been reported.[8]

We acknowledge support from the Hong Kong Research Grant Council and The University of Hong Kong.

Received, 17th November 1994; Com. 4/07026G

Footnotes

[†] *Selected data for* **2**: Analysis $C_{26}H_{28}Cl_2N_6O_{10}$. Calc: C, 41.27; H, 3.70; N, 11.11; Found: C, 40.88; H, 3.58; N, 10.88%. FAB MS: *m/z* 657 $(M - ClO_4)^+$, 558 $(M - 2ClO_4)^+$. IR: ν(NO)/cm^{-1} 1450. UV–VIS (MeCN) λ_{max}/

nm(ε_{max}/mol^{-1} dm^3 cm^{-1}), 246 (16770) (sh), 291.1 (9490) (sh), 318 (8420) (sh), 352 (6080) (sh).^{1} H NMR [$(CS_3)_2CO$]: δ 1.06 (s, Me, 12H), 1.71 (s, Me, *12H*), 7.86 (m, 4H), 8.15 (m, 2H), 8.43 (m, 4H), 8.61 (m, 2H), 8.82 (d, 2H), 8.92 (d, 2H).

‡ *Crystal data for* **2**·Me_2CO, $C_{29}H_{34}Cl_2N_6O_{11}Ru$, M = 814.60, monoclinic, space group $P2_1/c$, a = 13.863(4), b = 18.822(7), c = 13.342(3) Å, β = 102.59(2)°, V = 3397.6(3.3) Å^3, Z = 4, D_c = 1.592 g cm^{-3}, μ(Mo-Kα) = 6.86 cm^{-1}, $F(000)$ = 1664, crystal dimensions 0.10 × 0.10 × 0.15 mm. Intensity data were collected at 25 °C on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) using ω–2θ scans with ω-scan angle (1.31 + 0.344 tanθ)° at a scan speed of 16.0° min^{-1} and to $2\theta_{max}$ = 45°. A total of 4610 unique reflections were measured, 3503 of which with $I \geqslant 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure was solved by heavy-atom Patterson methods and refined by full-matrix least squares methods. All non-H atoms were refined anisotropically and H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 442 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.003F_o^2)^2]$ for reflections with $I \geqslant 3\sigma(I)$, was reached at R = 0.033 and R_w = 0.032 with a goodness of fit of 2.55. $(\Delta/\sigma)_{max}$ = 0.01. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.64 and 0.45 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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