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Ruthenium(VI) nitrido complexes with a sterically bulky bidentate Schiff base ligand

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ABSTRACT

Ruthenium(VI) complexes with a sterically bulky bidentate Schiff base ligand, 2-[(2,6-diisopropylphenyl)imino]methyl-4,6-dibromophenolate (L^-), have been synthesized and their reactivity studied. Treatment of $[Bu^n_4N][Ru(N)Cl_4]$ in tetrahydrofuran with 2 equivalents of NaL afforded *cis*-$[Ru(N)Cl(L)_2]$ (**1**) that reacted with Ag(OTf) (OTf^- = triflate) in acetone to give *trans*-$[Ru(N)(H_2O)L_2][OTf]$ (**2**). Reactions of complex **1** with Me_3NO and elemental sulfur afforded *cis*-$[Ru(NO)(Cl)L_2]$ (**3**) and *cis*-$[Ru(NS)(Cl)L_2]$ (**4**), respectively. Reaction of complex **1** with Me_3SiN_3 in MeCN afforded $[Ru(MeCN)(Cl)L_2]$, which could alternatively be prepared by photolysis of complex **3** in CH_2Cl_2–MeCN with UV light. The crystal structures of complexes **1** and **2** have been determined.

1. Introduction

Late transition-metal terminal nitrido complexes have attracted attention due to their potential applications in metal-mediated nitrogen atom transfer [1–11]. Of special interest are nitrido complexes of ruthenium that are found to exhibit interesting electrophilic reactivity [7–9,12–16]. Lau and co-workers demonstrated that Ru^{VI} nitrido complexes with tetradentate Schiff base (salen) ligands are considerably more reactive than the Os^{VI} congeners. The reactivity of Ru^{VI}(salen) nitrido complexes toward phosphine, isocyanides, thiols and alkenes has been investigated [12]. In polar solvents, *trans*-$[Ru(N)(MeOH)(salen)]^+$ undergoes facile intermolecular N···N coupling to give dinitrogen and Ru^{III}(salen) complexes [12a]. A synthetic route to *trans*-$[Ru^{III}L_2(salen)]^+$ complexes based on ligand-accelerated nitrido coupling of *trans*-$[Ru(N)(MeOH)(salen)]^+$ has been reported [12b].

In an effort to explore the potential of electrophilic nitrido complexes for nitrogen atom transfer, we sought to synthesize Ru^{VI} nitrido complexes stabilized by sterically bulky coligands, which can inhibit the intermolecular coupling of the nitrido group. The sterically bulky bidentate Schiff base ligand 2-[(2,6-diisopropylphenyl)imino]methyl-4,6-dibromophenol (HL, Scheme 1) can form stable complexes with transition metals [17]. However, to our knowledge, Ru–L complexes have not been isolated. We herein describe the synthesis and structures of Ru^{VI} nitrido complexes, which are stable with respect to N···N coupling, and their reactions with Me_3NO and elemental sulfur.

2. Experimental

2.1. General remarks

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were dried by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400.1, 376.5 and 162.0 MHz for ^1H, ^{19}F and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and $CF_3C_6H_5$ (^{19}F). IR spectra were recorded on a Perkin-Elmer 16 PC Fourier transform infrared spectrophotometer. Electrospray ionization mass spectrometry was recorded on an Applied Bio-system QSTAR mass spectrometer. Magnetic moments of paramagnetic complexes were determined by Evans method [18] in $CDCl_3$ solutions at room temperature. Elemental analyses were performed by Medac Ltd., Surrey, UK. The compound $[Bu^n_4N][Ru(N)Cl_4]$ [19] was prepared according to a literature method. The hydrogen atom labelling scheme for the ligand L^- is shown in Scheme 1.

2.2. Preparation of the ligand HL

A mixture of 2,6-diisopropylaniline (18 mg, 0.1 mmol) and 3,5-di-bromo-2-hydroxylbenzaldehyde (28 mg, 0.1 mmol) in methanol (5 mL) was refluxed for 1.5 h. The solvent was removed *in vacuo* and the residue washed with ethanol (3 × 5 mL). Recrystallization from methanol–diethyl ether afforded a yellow solid. Yield: 31 mg (67%). ^1H NMR ($CDCl_3$): δ = 1.17 (d, J = 7 Hz, 12H, $(CH_3)_2CH$), 2.92 (sept, J = 7 Hz, 2H, $(CH_3)_2CH$), 7.21 (d, J = 2 Hz, 2H, H^3), 7.24 (t, J = 2 Hz, 1H, H^4), 7.44 (d, J = 2 Hz, 1H, H^2), 7.80 (d, J = 2 Hz, 1H, H^1), 8.20 (s, 1H, H^5, —HC = N) ppm. The sodium salt NaL was

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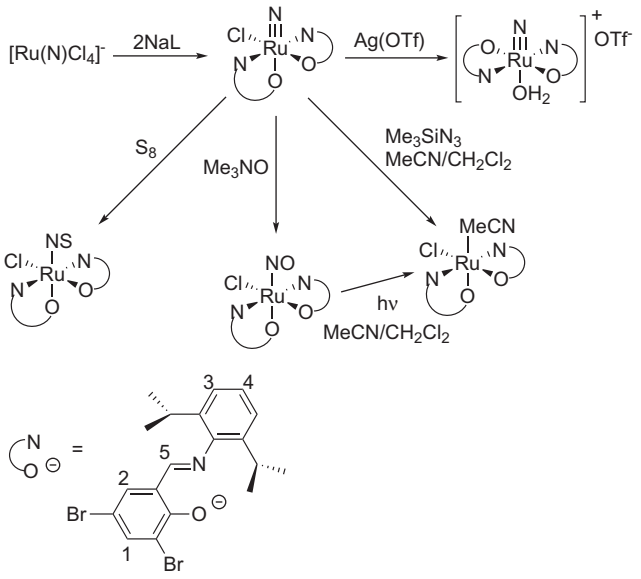

Scheme 1. Synthesis and reactivity of Ru^{VI} nitrido complexes.

prepared by reaction of HL (44 mg, 0.1 mmol) with 60% NaH (4 mg, 0.17 mmol) in tetrahydrofuran (THF) (10 mL) at room temperature for 1.5 h and recrystallized from THF–hexane.

2.3. Synthesis of complexes

2.3.1. Preparation of cis-[Ru(N)Cl(L)$_2$] (**1**)

To a solution of [Bu^n_4N][Ru(N)Cl_4] (50 mg, 0.1 mmol) in THF (10 mL) was added 2 equivalents of NaL (92 mg, 0.2 mmol) in THF (10 mL) dropwise. The mixture was stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the residual solid was extracted by Et_2O-hexane (v/v, 1:1, 3 × 10 mL). The extract was concentrated to 3 mL and cooled at −18 °C to give block red crystals which were suitable for the X-ray diffraction study. Yield: 52 mg (50%). ^{1}H NMR (C_6D_6): δ = 0.74 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.87 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.88 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.08 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.27 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.40 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.41 (d, J = 7 Hz 3H, (CH_3)$_2$CH), 1.54 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 3.12 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 3.80 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 3.99 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 4.78 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 6.83 (d, J = 2 Hz, 1H, H^3), 6.94 (d, J = 2 Hz, 2H, H^3), 6.97 (d, J = 2 Hz, 1H, H^3), 7.05 (t, J = 2 Hz, 1H, H^4), 7.12 (t, J = 2 Hz, 1H, H^4), 7.20 (d, J = 2 Hz, 1H, H^2), 7.22 (d, J = 2 Hz, 1H, H^2), 7.37 (d, J = 2 Hz, 1H, H^1), 7.40 (d, J = 2 Hz, 1H, H^1), 7.51 (s, 1H, H^5, —*H*C = N), 7.85 (s, 1H, H^5, —*H*C = N) ppm. IR (KBr, cm^{-1}): 1025 [ν(Ru≡N)], 1611 [ν(C=N)]. *Anal.* Calc. for $C_{38}H_{40}Br_4ClN_3O_2Ru{\cdot}1.5Et_2O$: C, 46.44; H, 4.87; N, 3.69. Found: C, 46.74; H, 4.97; N, 3.72%.

2.3.2. Preparation of trans-[Ru(N)(H_2O)L$_2$][OTf] (**2**)

To a solution of complex **1** (103 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was added 1 equivalent of AgOTf (26 mg, 0.1 mmol), and the mixture was stirred at room temperature for 6 h and filtered. The solvent was removed *in vacuo* and the residual solid was extracted with Et_2O–CH_2Cl_2 (v/v, 1:1, 3 × 10 mL). Concentration (to ca. 8 mL) and cooling at −18 °C afforded reddish-brown blocks which were suitable for the X-ray diffraction study. Yield: 87 mg (83%). ^{1}H NMR ($CDCl_3$): δ = 1.23 (d, J = 7 Hz, 6H, (CH_3)$_2$CH), 1.43 (d, J = 7 Hz, 6H, (CH_3)$_2$CH), 1.66 (d, J = 7 Hz, 6H, (CH_3)$_2$CH), 1.83 (d, J = 7 Hz, 6H, (CH_3)$_2$CH), 2.35 (br, 2H, H_2O), 3.29 (sept, J = 7 Hz, 2H, (CH_3)$_2$C*H*), 3.56 (sept, J = 7 Hz, 2H, (CH_3)$_2$C*H*), 7.08 (d, J = 2 Hz, 2H, H^3), 7.14 (d, J = 2 Hz, 2H, H^3), 7.28 (t, J = 2 Hz, 1H, H^4), 7.56 (t, J = 2 Hz, 1H, H^4), 7.67 (d, J = 2 Hz, 2H, H^2) 7.90 (d, J = 2 Hz, 2H, H^1), 7.91 (s, 2H, H^5, —*H*C = N) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ = −77.47 (s) ppm. MS (ESI): 991.99 (M^+−H_2O). IR (KBr, cm^{-1}): 1029 [ν(Ru≡N)], 1600 [ν(C = N)]. *Anal.* Calc. for $C_{39}H_{42}Br_4ClF_3N_3O_6RuS{\cdot}1/2\ CH_2Cl_2$: C, 39.50; H, 3.61; N, 3.50. Found: C, 39.85; H, 3.86; N, 3.54%.

2.3.3. Preparation of cis-[Ru(NO)(Cl)L$_2$] (**3**)

To a solution of complex **1** (103 mg, 0.1 mmol) in THF (10 mL) was added 1 equivalent Me_3NO (8 mg, 0.1 mmol), and the mixture was stirred at room temperature for 12 h, during which the color of solution changed from red to yellow. The solvent was removed in *vacuo* and the residual solid was extracted with Et_2O–hexane (v/v, 1:1, 3 × 10 ml). Concentration and cooling at −18 °C to give yellow crystals which were suitable for the X-ray diffraction study. Yield: 94 mg (90%). ^{1}H NMR (C_6D_6): δ = 0.79 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.95 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.97 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.10 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.13 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.21 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.23 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.29 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 2.99 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 3.48 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 3.65 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 4.43 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 7.06 (d, J = 2 Hz, 1H, H^3), 7.09 (d, J = 2 Hz, 1H, H^3), 7.10 (d, J = 2 Hz, 1H, H^3), 7.14 (d, J = 2 Hz, 1H, H^3), 7.23 (t, J = 2 Hz, 1H, H^4), 7.28 (t, J = 2 Hz, 1H, H^4), 7.31 (d, J = 2 Hz, 1H, H^2), 7.33 (d, J = 2 Hz, 1H, H^2), 7.40 (d, J = 2 Hz, 1H, H^1), 7.42 (d, J = 2 Hz, 1H, H^1), 7.64 (s, 1H, H^5, —*H*C = N), 7.95 (s, 1H, H^5, —*H*C=N) ppm. IR (KBr, cm^{-1}): 1859 [ν(N≡O)], 1618 [ν(C = N)]. *Anal.* Calc. for $C_{38}H_{40}Br_4ClN_3O_3Ru{\cdot}1/2\ C_6H_{14}$: C, 45.35; H, 4.36; N, 3.87. Found C, 44.87; H, 4.15; N, 3.53%. Despite two attempts, we have not been able to obtain satisfactory carbon analysis for complex **3**. However, the identity of complex **3** has been established by spectroscopic methods and X-ray diffraction.

2.3.4. Preparation of cis-[Ru(NS)(Cl)L$_2$] (**4**)

A mixture of complex **1** (103 mg, 0.1 mmol) and elemental sulfur (3.2 mg, 0.1 mmol) in THF (10 mL) was heated at reflux for 12 h, during which the color of solution changed from red to orange. The solvent was removed *in vacuo* and the residue was extracted by Et_2O–hexane (v/v, 1:1, 3 × 10 ml). Concentration and cooling at −18 °C afforded an orange crystalline solid. Yield: 92 mg (87%). ^{1}H NMR (C_6D_6): δ = 0.79 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.83 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.87 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 0.90 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.08 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.10 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.40 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.42 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 1.65 (d, J = 7 Hz, 3H, (CH_3)$_2$CH), 2.88 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 3.86 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 4.07 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 4.21 (sept, J = 7 Hz, 1H, (CH_3)$_2$C*H*), 7.05 (d, J = 2 Hz, 1H, H^3), 7.09 (d, J = 2 Hz, 2H, H^3), 7.11 (d, J = 2 Hz, 2H, H^3), 7.12 (d, J = 2 Hz, 1H, H^3), 7.20 (t, J = 2 Hz, 1H, H^4), 7.27 (t, J = 2 Hz, 1H, H^4), 7.32 (d, J = 2 Hz, 1H, H^2), 7.35 (d, J = 2 Hz, 1H, H^2), 7.40 (d, J = 2 Hz, 1H, H^1), 7.42 (d, J = 2 Hz, 1H, H^1), 7.63 (s, 1H, H^5, −*H*C = N), 7.92 (s, 1H, H^5, —*H*C=N) ppm. MS (ESI): 1058.76 (M^+), 1023.69 (M^+−Cl). IR (KBr, cm^{-1}): 1613 [ν(C=N)], 1284 [ν(N≡S)]. *Anal.* Calc. for $C_{38}H_{40}Br_4ClN_3O_2RuS{\cdot}1/2C_6H_{14}$: C, 44.68 H, 4.30; N, 3.81; S, 2.91: Found C, 45.57; H, 4.18; N, 3.71; S, 3.29%. Despite two attempts, we have not been able to obtain satisfactory carbon analysis for complex **4**. However, complex **4** has been well characterized by spectroscopic methods.

2.3.5. Preparation of cis-[Ru(MeCN)(Cl)L$_2$] (**5**)

Method A: a solution of complex **1** (104 mg, 0.1 mmol) in CH_2Cl_2–MeCN (100 mL, v/v, 9:1) was irradiated with UV light (Hg

lamp, 9 W) for 2 h, during which the color of solution changed from red to green. The solvent was removed *in vacuo* and the residue was extracted by Et_2O (10 mL). Concentration and cooling of the extract at −18 °C gave a green crystalline solid. Yield: 72 mg (68%). μ_{eff} (Evans method) = 1.7 μ_B. MS (ESI): 1052.91 (M^+-1), 1018.42 (M^+-Cl). *Anal.* Calc. for $C_{40}H_{43}Br_4ClN_3O_2Ru$: C, 45.58; H, 4.11; N, 3.99. Found: C, 45.74; H, 4.23; N, 3.78%.

Method B: to a solution of complex **1** (104 mg, 0.1 mmol) in CH_2Cl_2–MeCN (10 mL, v/v, 9:1) was added 1 equivalent of Me_3SiN_3 (1.3 μL, 0.1 mmol). The mixture was stirred for 12 h. The solvent was removed *in vacuo* and the residue was extracted by Et_2O (5 mL). Concentration and cooling of the extract at −18 °C gave a green crystalline solid characterized as complex **5**. Yield: 59 mg (56%).

2.4. X-ray crystallography

Complexes **2** and **3** have been characterized by X-ray diffraction. However, due to the positional disorder problem of the ligands (vide infra), the bond distances and angles of complex **3** have not been analyzed. Intensity data were collected on a Bruker 1000 or APEX 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT [20]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [21]. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters and with suitable restraints. However, disordered atoms were refined isotropically. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

3. Results and discussion

3.1. Ruthenium nitrido complexes

The synthesis and reactivity of Ru^{VI} nitrido complexes with the bidentate Schiff base ligand L^- are summarized in Scheme 1. Treatment of $[Bu^n_4N][Ru(N)Cl_4]$ (**1**) with 2 equivalents of NaL in tetrahydrofuran (THF) afforded *cis*-$[Ru(N)(Cl)L_2]$ (**1**). A preliminary X-ray diffraction study confirmed the cis arrangement between the nitride and chloride ligands in complex **1**. Unfortunately, the structure has not been refined satisfactorily because the nitrido ligand is disordered. Nevertheless, the identity of complex **1** has been fully confirmed. It may be noted a similar disorder problem has been observed in a related Cr^V nitrido chloride complex [22]. Complex **1** is soluble in common organic solvents including hexane, and air stable in both the solid state and solution. The imine protons of L^- in **1** appeared as two singlets at δ = 7.51 and 7.85 ppm in the ^1H NMR spectrum, consistent with the solid-state structure. This is in contrast with analogous Ru(N)(X)(salen)-type complexes containing quadridentate Schiff base ligands, which usually exhibit *trans* geometry. The IR spectrum of complex **1** displayed a peak at 1025 cm^{-1}, which is absent in the related nitrosyl complex (see later section). This peak is tentatively assigned as the Ru—N stretch. Similar Ru—N stretching frequencies have been found in related salen complexes.

The treatment of complex **1** with Ag(OTf) (OTf = triflate) afforded the cationic aqua complex *trans*-$[Ru(N)(H_2O)L_2][OTf]$ (**2**). Unlike **1**, complex **2** exhibits a *trans* geometry with the nitrido and aqua ligand opposite to each other. The reason (steric and/or electronic) for the difference in geometry between complexes **1** and **2** is not clear. Complex **2** is soluble in common organic solvents except Et_2O and hexane. The ^1H NMR spectrum of **2** showed a singlet at δ = 7.91 ppm for the imine proton, consistent with the *trans* geometry of the molecule. The IR spectrum displayed the ν(Ru≡N) band at 1029 cm^{-1}. Unlike *trans*-$[Ru(N)(MeOH)(salen)]^+$, complex **2** is stable in polar solvents such as acetonitrile and dimethylsulfoxide. No nitrido coupling was found even when **2** was reacted with pyridine in C_6D_6 at 50 °C. This result indicates that the intermolecular N···N coupling of the Ru nitride can be inhibited by the bulky, electron-deficient Schiff base coligand.

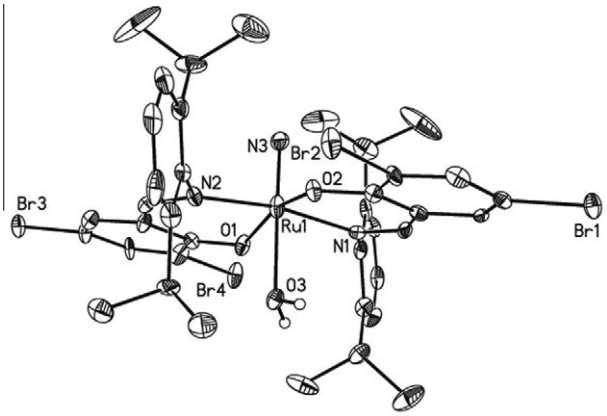

Fig. 1. Structure of the complex cation in *trans*-$[Ru(N)(H_2O)(L)_2][OTf]$ (2). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Ru(1)—O(1) 1.983(5), Ru(1)—O(2) 1.960(5), Ru(1)—O(3) 2.225(5), Ru(1)—N(1) 2.129(6), Ru(1)—N(2) 2.070(6), Ru(1)—N(3) 1.651(6).

Complex **2** has been characterized by X-ray diffraction.[1] Fig. 1 shows the molecular structure of complex **2**. Unlike complex **1**, the nitrido and aqua ligands complex **2** are *trans* to each other. The two imino groups of L^- are *trans* to each other in order to minimize the repulsion between the sterically demanding 2,6-diisopropylphenyl groups. The Ru-nitrido distance of 1.651(6) Å in **2** is longer than that in $[Ru(N)(MeOH)(salchda)]^+$ (salchda = *N,N′*-bis(salicylidene)-*o*-cyclohexyldamine dianion, 1.592(4) Å) [12a], possibly due to steric effects. The Ru—O(H_2O) distance of 2.225(5) Å in **2** is consistent with the formulation of an aqua ligand. The Ru—O [1.972(5) Å] and Ru—N [2.100(6) Å] distances for the Schiff base ligands are normal.

3.2. Reactivity of complex *1*

Unlike the salen analogue, no reactions were found between **1** and nucleophiles such as triphenylphosphine, tricyclohexylphosphine and morpholine. However, complex **1** reacted readily with PMe_3 to give an unidentified paramagnetic species. Reaction of complex **1** with Me_3NO led to formation of the nitrosyl complex *cis*-$[Ru(NO)(Cl)L_2]$ (**3**). The IR spectrum of complex **3** is similar to that of **1** except that an intense N-O band was found at 1859 cm^{-1}. The N—O stretching frequency of complex **3** is lower than those of related salen-type complexes, e.g. 1830 cm^{-1} for *trans*-[Ru(L1)(NO)C] (L1 = (*R,R*)-(−)-cyclohexanebis(3,5-di-*tert*-butylsalicylidene aminate)) [23], indicating that the Ru center in complex **3** is less electron-rich than those in the salen analogues. Such an electronic difference together with the steric factors may lead to the lower reactivity of complex **3** (e.g. N—N coupling and reactions with nucleophiles) compared with the salen analogues. The ^1H NMR spectrum displayed two imine proton signals at

[1] Crystal data for complex **2**·0.75CH_2Cl_2: $C_{39.75}H_{43.5}Br_4Cl_{1.5}F_3N_3O_6RuS$, Mr = 1222.22, T = 100(2) K, monoclinic, space group $P21/n$, a = 11.3057(6), b = 13.2964(7), c = 31.8107(16) Å, β = 97.747(1)°, V = 4738.3(4) $Å^3$, Z = 4, ρ_{calc} = 1.481 Mg m^{-3}, μ(Mo Kα) = 3.794; 23349 reflections collected, and 8140 unique (R_{int} = 0.0416). The final R_1 = 0.0458 and wR_2 = 0.1077 [$I > 2.0\ \sigma(I)$]; R_1 = 0.0571 and wR_2 = 0.1127 (all data).

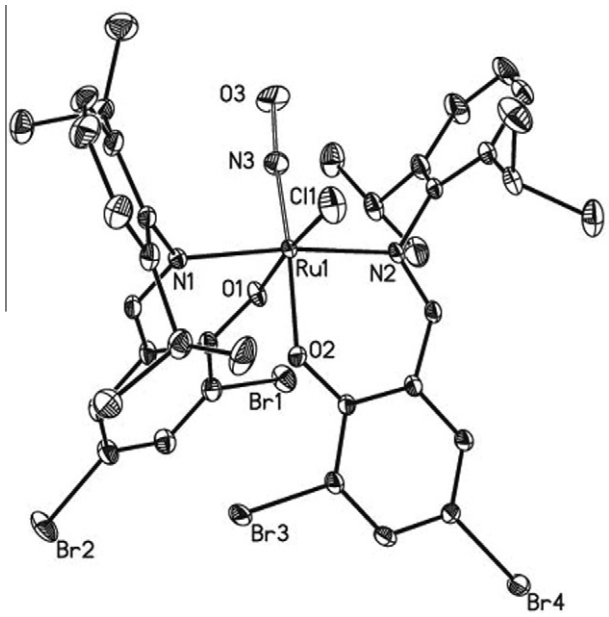

Fig. 2. Structure of $[Ru(NO)Cl(L)_2]$ (**3**). The chloride and nitrosyl ligands are 50:50 disordered. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level.

δ = 7.64 and 7.95 ppm, consistent with the *cis* geometry. The identity of complex **3** has been established by an X-ray diffraction study (Fig. 2)[2]. Unfortunately, the metal–ligand distances in **3** have not been analyzed due to the positional disorder found for the chloride and nitrosyl ligands.

Refluxing complex **1** with elemental sulfur led to formation of the thionitrosyl complex $[Ru(NS)(Cl)L_2]$ (**4**). It may be noted that a related Ru thionitrosyl complex, $[Ru(L_{OEt})(NS)Cl_2]$ (L_{OEt}^- = $[Co(\eta^5\text{-}C_5H_5)(P(O)Et)_3]^-$) has been prepared by reaction of $[Ru(L_{OEt})(N)Cl_2]$ with $S_2O_3^{2-}$ [14b]. Similar to complex **3**, the ^1H NMR spectrum of complex **4** showed two signals at δ = 7.63 and 7.92 ppm for the imine protons, indicative of the *cis* geometry of the molecule. The IR spectrum of complex **4** displayed the N—S stretch at 1284 cm^{-1}, which is similar to that for $[Ru(L_{OEt})(NS)Cl_2]$ (1307 cm^{-1}) [14b]. An attempt to prepare a selenonitrosyl complex by refluxing complex **1** with elemental selenium failed.

Treatment of complex **1** with Me_3SiN_3 in acetonitrile led to formation of the acetonitrile complex $[Ru(MeCN)(Cl)L_2]$ (**5**). Alternatively, complex **5** could be prepared by photolysis of the nitrosyl complex with UV light in CH_2Cl_2–MeCN. The measured magnetic moment of complex **5** of ca. 1.7 μ_B is consistent with formulation of a low-spin d^5 configuration of Ru^{III}. The ESI mass spectrum showed peaks at *m*/*z* 1052.91 and 1018.42 corresponding to M^+-1 and M^+-Cl, respectively. It is likely that the formation of complex **5** involves nucleophilic attack of the nitrido group by azide and subsequent decomposition of the azido(imido) intermediate. It may be noted that an Os^{IV} azido(imido) complex has been prepared by reaction of an Os^{VI} nitride with azide previously [24]. Additional work is needed in order to elucidate the mechanism of the formation of complex **5**.

[2] Crystal data for complex **3**: $C_{41}H_{40}Br_4Cl_1N_4O_2Ru$, Mr = 1076.93, *T* = 173(2) K, triclinic, space group $P\bar{1}$, *a* = 9.0029(2) Å, *b* = 15.4893(4) Å, *c* = 15.8688(4) Å, α = 87.688(2)°, β = 80.721(2)°, γ = 78.804(2)°, *V* = 2142.27(9) Å^3, *Z* = 2, ρ_{calc} = 1.670 - Mg m^{-3}, μ(Mo Kα) = 8.211 mm^{-1}, 11587 reflections collected, and 7412 unique (R_{int} = 0.0400). The final R_1 = 0.0433 and wR_2 = 0.1156 [$I > 2.0\ \sigma(I)$]; R_1 = 0.0448 and wR_2 = 0.1169 (all data).

4. Conclusions

In summary, we have synthesized a Ru^{VI} nitrido complex containing a sterically bulky bidentate Schiff base ligand, *cis*-$[Ru(N)(Cl)L_2]$ (**1**). Chloride abstraction of complex **1** afforded a cationic aqua complex, *trans*-$[Ru(N)(H_2O)L_2]^+$ (**2**), which has a *trans* geometry. In contrast with the salen analogues, complex **2** is stable with respect to intermolecular nitrido coupling in solutions. No reactions were found between complex **1** and nucleophiles including triphenylphosphine and morpholine. This result demonstrates that the steric and electronic factors of the coligand have an influence on the stability/reactivity of Ru^{VI} nitrido complexes. Complex **1** reacts with Me_3NO, S_8 and Me_3SiN_3–MeCN to give the nitrosyl, thionitrosyl and acetonitrile complexes, respectively. The investigation of reactivity of Ru^{VI} nitrido complexes with bulky, electron-deficient Schiff base ligands is underway.

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Appendix A. Supplementary material

CCDC 838645 and 838646 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.07.025.

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