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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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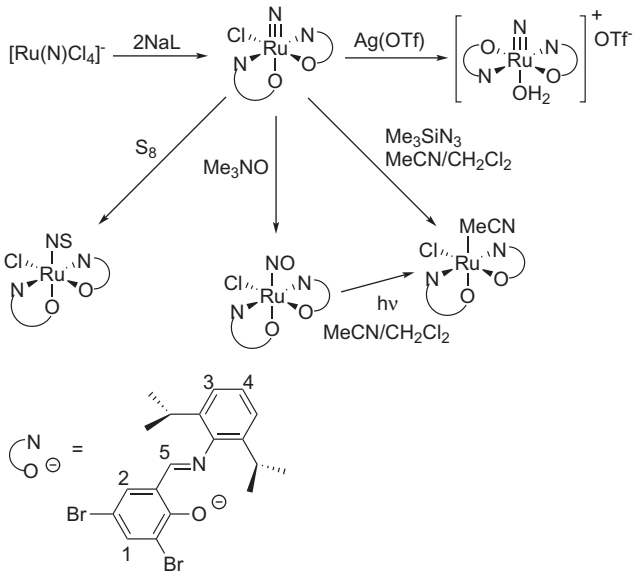

Scheme 1. Synthesis and reactivity of Ru^{VI} nitrido complexes.

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