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Highly Electrophilic (Salen)ruthenium(VI) Nitrido Complexes

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Recently, a number of osmium(VI) nitrido species containing nitrogen ligands, such as *cis*- and *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ (tpy = 2,2′:6′,2″-terpyridine), $[Os^{VI}(N)(tpm)(Cl)_2]^+$ (tpm = tris(1-pyrazolyl)methane), $[Os^{VI}(N)(Tp)(Cl)_2]$ (Tp = hydrotris(1-pyrazolyl)-borate anion), and $[Os^{VI}(N)(bpy)(Cl)_3]$ (bpy = 2,2′-bipyridine), have been shown to exhibit novel electrophilic properties.[1−3] They undergo a variety of redox reactions that are initiated by nucleophilic attack at the nitrido ligand to produce osmium species containing N−C, N−N, N−P, or N−E (E = O, S, Se) bonds. It is anticipated that the corresponding ruthenium(VI) nitrido complexes would be much more electrophilic, because high-valent ruthenium oxo complexes are in general much stronger oxidants than that of osmium.[4] Surprisingly, the electrophilic chemistry of Ru≡N is largely unexplored, most of the existing ruthenium nitrides contain strongly electron-donating anionic ligands, and they either show nucleophilic or weak electrophilic properties.[5] Ruthenium nitrides containing porphyrin ligands undergo amination reactions with hydrocarbons and silyl enol ethers in the presence of trifluoroacetic anhydride; however, the active electrophilic intermediate is an imido species rather than a nitrido species.[6] We report here the synthesis and reactivities of a series of highly electrophilic, cationic ruthenium(VI) nitrido species containing the cyclohexyl-bridged salen ligand and its derivatives, $[Ru^{VI}(N)(L)]^+$ (L = *N*,*N*′-bis(salicylidene)-*o*-cyclohexyldiamine dianion). These are also the first examples of high-valent salen complexes of ruthenium. Although salen ligands have played important roles in oxidation chemistry in recent years and they are known to stabilize complexes in high oxidation states,[7] high-valent ruthenium salen chemistry has not been explored.

Treatment of $[NBu^n{}_4][Ru^{VI}(N)Cl_4]$ with H_2L in methanol followed by the addition of X^- produced the diamagnetic $[Ru^{VI}(N)(L)(CH_3OH)]X$ (X = ClO_4, **1a** or PF_6, **1b)** as orange microcrystalline solids.[8] The neutral $[Ru^{VI}(N)(L)Cl]$ (**1c**) can be prepared by adding $[NBu^n{}_4]Cl$ to **1a** or **1b** in acetone. Other 5,5′-disubstituted (Cl, Br, MeO) salen complexes can also be prepared by the same procedures. The ν(Ru≡N) stretching frequencies for **1a**, **1b**, and **1c** occur at the same frequency at 1059 cm^{-1}, and as expected this peak is shifted to 1030 cm^{-1} upon ^{15}N labeling.

The X-ray structure of **1a** is shown in Figure 1. The Ru−N(nitrido) distance is 1.592 Å, which is longer than that of the starting material $[Ru^{VI}(N)Cl_4]^-$ (1.570 Å),[9] but is shorter than those in other ruthenium nitrido complexes (1.594−1.656 Å).[5,6]

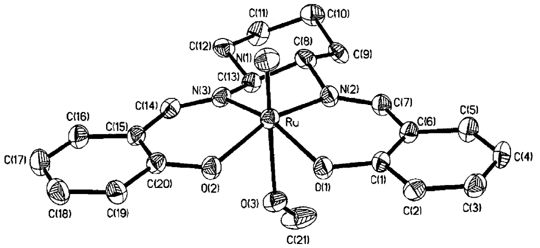

Figure 1. ORTEP diagram of the cation of **1a** (H atoms are omitted). Selected bond lengths (Å): Ru−N(1) 1.592(4), Ru−N(2) 2.018(4), Ru−N(3) 2.030(3), Ru−O(1) 1.977(3), Ru−O(2) 1.972(3), Ru−O(3) 2.431(3).

1 is stable to air in the solid state. However, in solvents such as DMF or DMSO, a facile N···N coupling reaction occurs at room temperature. A 0.01 M solution of **1a** in DMF turns from orange to green within minutes in an NMR tube, and gas bubbles can be seen. Analysis by GC-MS indicates that the gas released is N_2. When the 50% ^{15}N-labeled complex $[Ru(^{15}N)(L)(CH_3OH)]ClO_4$ is used, the gas evolved is found to be a mixture of $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$, and the ratio of $^{14}N^{15}N$ to $^{15}N_2$ is approximately 2:1. The electrospray ionization mass spectrum of the resulting green solution shows peaks at *m*/*z* = 422 and 568, which are assigned to $[Ru^{III}(L)]^+$ and $[Ru^{III}(L)(DMF)_2]^+$, respectively; these assignments are supported by the excellent agreement between the experimental and theoretical isotopic distribution patterns. These observations are consistent with a N···N coupling process represented by eqs 1 and 2.

$$2[Ru^{VI}(N)(L)]^+ \rightarrow [(L)Ru^{III}N{\equiv}NRu^{III}(L)]^{2+} \quad (1)$$

$$[(L)Ru^{III}N{\equiv}NRu^{III}(L)]^{2+} + 4DMF \rightarrow 2[Ru^{III}(L)(DMF)_2]^+ + N_2 \quad (2)$$

This is the first report of N···N coupling between ruthenium nitrides. Previously, coupling of metal nitrides to form dinitrogen has only been observed with Os−Os[10] and Os−Mo.[11] Coupling of Os^{VI}−Os^{VI} is very slow and usually requires heating to over 100 °C. Coupling of Os^{VI}−Mo^{VI} is faster, but still requires heating to 50 °C. On the other hand, coupling of Os^{VI}−Os^{V} or Os^{V}−Os^{V} occurs readily at room temperature. In contrast, facile coupling of **1** occurs with Ru^{VI}−Ru^{VI}. Cyclic voltammetry of **1a** in CH_3CN shows an irreversible peak at −0.67 V (vs Fc^+/Fc), which is assigned to the reduction of Ru^{VI} to Ru^{V}; this rather low redox potential suggests that reduction of Ru^{VI} to Ru^{V} by the solvent prior to coupling is very unlikely.

In nonpolar solvents such as CH_2Cl_2 or $CHCl_3$, **1** is stable with respect to N···N coupling for over 1 day at room temperature. Dilute solutions of **1** ($<1 \times 10^{-4}$ M) in CH_3CN and CH_3OH are also reasonably stable at room temperature ($t_{1/2} > 1$ h). Thus, it is possible to study the reactivities of the ruthenium nitrides in these solvents. These ruthenium nitrides are found to react rapidly with a variety of nucleophiles, including amines, phosphines, alkenes, thiols, azide, and cyanide. Their reactions with secondary amines are described below to illustrate that these complexes are highly electrophilic.

1a reacts rapidly with secondary amines such as pyrrolidine (HNC_4H_8), to produce a Ru^{IV}−hydrazido(1−) species, $[Ru^{IV}(N(H)NC_4H_8)(L)(HNC_4H_8)]^+$, isolated as the $PF_6{}^-$ salt (**2**).[12] **2** is found to be diamagnetic (solid sample, Gouy method), consistent with its Ru^{IV} formulation. The ^1H NMR spectrum in CD_3CN exhibits a

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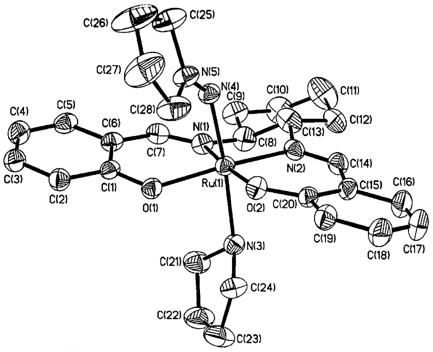

Figure 2. ORTEP diagram of the cation of **2**. (H atoms are omitted.) Selected bond lengths (Å) and bond angles (deg): Ru(1)−N(1) 2.002(5), Ru(1)−N(2) 2.009(5), Ru(1)−O(1) 2.024(4), Ru(1)−O(2) 2.038(4), Ru(1)−N(3) 2.157(5), Ru(1)−N(4) 1.940(5), N(4)−N(5) 1.279(6), N(5)−N(4)−Ru(1) 129.4(4).

N−H resonance at 13.3 ppm that disappears upon addition of D_2O; this is assigned to the hydrazido N−H. For Mo(VI)−hydrazido(1−) complexes, the N−H resonances also occur at around 13 ppm.[13] The IR spectrum (KBr) of **2** shows a strong and a weak band at 3217 and 3276 cm^{-1}, respectively, which are assigned to ν(N−H) stretching.

The structure of **2** has been determined by X-ray crystallography (Figure 2). Although there is no evidence for N(3)−H and N(4)−H in the X-ray determination, the rather long Ru−N(hydrazido) distance of 1.940 Å and the very acute Ru−N−N angle (129.4°) are consistent with a Ru^{IV}−hydrazido(1−) rather than a Ru^{V}−hydrazido(2−) species.[14] In the case of osmium, the Os−N(hydrazido) distances in $[Os^{V}(tpm)(Cl)_2(NN(CH_2CH_3)_2)]BF_4$ and $[Os^{IV}(tpm)(Cl)_2(N(H)N(CH_2)_4O)]PF_6$ are 1.855 and 1.904 Å, respectively.[15] The N−N distance (1.279 Å) lies within the range found in other transition metal hydrazido complexes (1.17−1.42 Å) and is indicative of a double bond.[15,16]

The kinetics of the reaction between **1a** and morpholine have been studied by UV−vis stopped-flow spectrophotometric methods. The reaction is first order in Ru^{VI} and second order in morpholine with $k(CH_3CN, 25.0\ °C) = 2.08\ (\pm 0.07) \times 10^6\ M^{-2}\ s^{-1}$. This rate constant is over 4 orders of magnitude larger than that of the corresponding reaction of the electrophilic osmium nitride *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ with morpholine, which has a similar rate law with $k = 58.1\ (\pm 1.2)\ M^{-2}\ s^{-1}$.[15]

In conclusion, we have prepared a series of highly electrophilic (salen)ruthenium(VI) nitrido complexes which are probably the most electrophilic transition metal nitrido complexes reported so far. The facile N···N coupling in polar solvents and the reaction with amines have not previously been observed with other ruthenium nitrides. N···N coupling for Ru occurs readily in the +VI oxidation state, while that of Os occurs readily only in the +V oxidation state; this difference could have implications on the mechanism of the reverse N≡N splitting process. The reaction of R_2NH with $Ru^{VI}{\equiv}N$ results in the formation of $Ru^{IV}-N(H)NR_2$, while with $Os^{VI}{\equiv}N$ the product is $Os^{V}-NNR_2$; because the products are different, it is likely that the mechanisms are also different.

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Supporting Information Available: NMR, kinetics, and crystallographic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Preparation of **1a**: H_2L (64 mg, 0.2 mmol) was added to a solution of $[N^nBu_4][Ru(N)Cl_4]$ (100 mg, 0.2 mmol) in methanol (10 mL), and the mixture was stirred for 15 min. $LiClO_4$ (106 mg, 1 mmol) was added, and the resulting orange microcrystalline solid was filtered and washed with cold methanol and then diethyl ether. Yield: 44%. Anal. Calcd for $C_{21}H_{24}N_3O_7ClRu$: C, 44.49; H, 4.27; N, 7.41. Found: C, 44.60; H, 4.47; N, 7.32. ^1H NMR (300 MHz, CD_3CN): δ 8.89 (s, 1H), 8.68 (s, 1H), 7.70−7.86 (m, 4H), 7.26−7.35 (q, 2H), 7.03−7.12 (m, 2H), 4.07−4.14 (t, 1H), 3.90−3.97 (t, 1H), 3.00−3.04 (d, 1H), 2.81−2.85 (d, 1H), 2.07−2.10 (t, 2H), and 1.47−1.60 (t, 2H). UV/vis (CH_3CN): λ_{max} [nm] (ϵ [$mol^{-1}\ dm^3\ cm^{-1}$]) 233 (4.46×10^4), 257 (2.33×10^4), 314 (1.29×10^4), 436 (2.73×10^3). **Warning:** Although we have not encountered any explosions so far, perchlorate salts of ruthenium nitrido complexes should be handled with extreme caution and in quantities not greater than 100 mg.

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(12) Preparation of **2**: Pyrrolidine (100 μL; 1.20 mmol) was added under argon to a suspension of **1b** (100 mg; 0.16 mmol) in diethyl ether (15 mL), and the mixture was stirred at room temperature for 3 h. The resulting dark red solid was recrystallized from CH_2Cl_2. Yield: 90%. Anal. Calcd for $C_{28}H_{38}N_5O_2PF_6Ru\cdot 0.5CH_2Cl_2$: C, 44.74; H, 5.14; N, 9.15. Found: C, 44.65; H, 5.00; N, 9.32.

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