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# Dinuclear Ruthenium Nitrido Complexes Supported by an Oxygen Tripodal Ligand

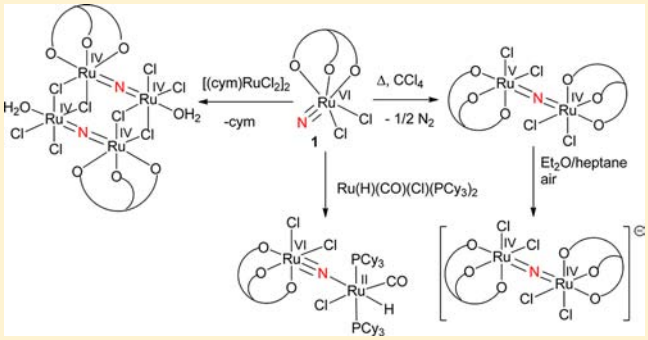
Xiao-Yi Yi,[†,‡] Ho-Yuen Ng,[‡] Wai-Man Cheung,[‡] Herman H. Y. Sung,[‡] Ian D. Williams,[‡] and Wa-Hung Leung*,[‡]

[†]School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, People's Republic of China

[‡]Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

Supporting Information

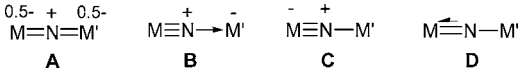
**ABSTRACT:** Dinuclear ruthenium nitrido complexes supported by the Kläui's tripodal ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ ($L_{OEt}^-$) have been synthesized starting from the ruthenium(VI) nitrido precursor $[L_{OEt}Ru^{VI}(N)Cl_2]$ (**1**). Heating a solution of **1** in $CCl_4$ at reflux, followed by recrystallization from hexane under nitrogen, afforded the mixed-valence ruthenium(V)−ruthenium(IV) $\mu$-nitrido complex $[L_{OEt}Cl_2Ru^{V}(\mu\text{-}N)Ru^{IV}Cl_2L_{OEt}]$ (**2**). The cyclic voltammogram of **2** exhibited reversible couples at 0.19 and 1.13 V versus $Cp_2Fe^{+/0}$, which are assigned as the $Ru^{V}-Ru^{IV}/Ru^{IV}-Ru^{IV}$ and $Ru^{V}-Ru^{V}/Ru^{V}-Ru^{IV}$ couples, respectively. Recrystallization of **2** from $Et_2O$/heptane in air yielded the diamagnetic $Ru^{IV}-Ru^{IV}$ complex $[H_{13}O_6][\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]$ ($[H_{13}O_6][\mathbf{2}]$), which underwent cation exchange with $n$-$Bu_4NOH$ to give $[n\text{-}Bu_4N][\mathbf{2}]$. X-ray diffraction revealed that the complex anions in $[H_{13}O_6][\mathbf{2}]$ and $[n\text{-}Bu_4N][\mathbf{2}]$ contain linear, symmetric Ru−N−Ru bridges. Treatment of **1** with $[(\eta^6\text{-}p\text{-cymene})Ru^{II}Cl_2]_2$ in benzene afforded the tetranuclear ruthenium(IV) complex $[L_{OEt}Cl_2Ru^{IV}(\mu\text{-}N)Ru^{IV}(H_2O)Cl_2]_2$ (**3**) containing symmetric $Ru^{IV}-N-Ru^{IV}$ bridges. The reaction of **1** with $[Ru^{II}(H)(Cl)(CO)(PCy_3)_2]$ (Cy = cyclohexyl) gave the ruthenium(VI)−ruthenium(II) nitrido complex $[L_{OEt}Cl_2Ru^{VI}(\mu\text{-}N)Ru^{II}(H)Cl(CO)(PCy_3)_2]$ (**4**). The observed short $Ru^{II}-N$ bond distance [1.915(5) Å] and high C−O stretching frequency (1985 $cm^{-1}$) in **4** are suggestive of $\pi$ interaction between $Ru^{II}$ and the nitride.




## INTRODUCTION

The nitrido group is a versatile bridging ligand that can bind to two metal ions symmetrically or asymmetrically (Scheme 1).[1]

**Scheme 1. Symmetric and Asymmetric Bridges in Dinuclear Nitrido Complexes[1]**




The symmetric $\mu$-nitrido complex can be viewed as consisting of two formal M=N double bonds (**A**), whereas in the asymmetric nitrido bridge, the interaction between M≡N and M′ is of either the donor−acceptor (**B**) or covalent (**C**) type. Type **C** nitride is reminiscent of organoimido complexes and therefore has also been described as a "metallonitrene" (**D**).[2]

Ruthenium nitrido complexes have attracted much attention recently because of their electrophilic behavior and potential applications in nitrogen-atom transfer.[3−7] Although polynuclear ruthenium complexes containing capping (e.g., $[(Cp^*Ru)_3(\mu_3\text{-}N)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CHC_6H_4)(\mu\text{-}H)]$, where $Cp^* = \eta^5\text{-}C_5Me_5$) and interstitial (e.g., $[Ru_{10}(\mu\text{-}N)(CO)_{24}]^-$) nitrido ligands are well-known,[8,9] relatively few dinuclear ruthenium $\mu$-nitrido complexes have been synthesized.[10−12] The most common diruthenium nitrido complexes are those containing symmetric bridges (type **A**) with antiferromagnetically coupled $Ru^{IV}$ $d^4$ centers, as exemplified by $[Ru^{IV}_2(\mu\text{-}N)Cl_{10}]^{3-}$.[10a]

Our interest in $\mu$-nitrido complexes is stimulated by a recent report that dinuclear iron(IV) $\mu$-nitrido phthalocyanine complexes can catalyze the oxidation of hydrocarbons, presumably via iron oxo intermediates, whereas the $\mu$-carbido analogues are inactive.[13] This result demonstrates the ability of the bridged nitrido group to stabilize high-valent metal−oxo species. Inspired by this work, we synthesize dinuclear ruthenium $\mu$-nitrido complexes and explore their redox chemistry and catalytic activity.

Kläui's tripodal ligand, $[CpCo\{P(O)(OEt)_2\}_3]^-$ (denoted as $L_{OEt}^-$ hereafter; Chart 1), has been recognized as an oxygen analogue of cyclopentadienyl.[14] Recently, we have isolated a ruthenium(VI) nitrido complex containing facially coordinating $L_{OEt}^-$, $[L_{OEt}Ru^{VI}(N)Cl_2]$ (**1**),[15] which was found to exhibit electrophilic behavior and interesting reactivity, e.g. insertion into the Ru−H bond.[16] Unlike the salen analogues $[Ru^{VI}(N)$-

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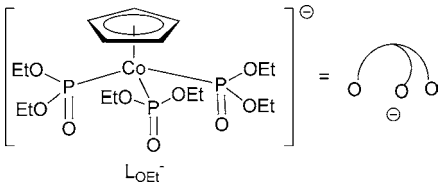
**Chart 1. Kläui's Tripodal Ligand $L_{OEt}^-$**




(salen)(MeOH)]$^+$,[17] **1** is stable with respect to intermolecular N−N coupling in polar solvents such as acetonitrile at room temperature. In this work, we found that heating **1** in solution resulted in the formation of a mixed-valence nitrido-bridged complex, $[L_{OEt}Cl_2Ru^V(\mu\text{-}N)Ru^{IV}Cl_2L_{OEt}]$ (**2**). This finding led us to explore the synthesis of new ruthenium $\mu$-nitrido complexes from **1** and lower-valent organoruthenium starting materials. Herein, we describe the reactions of **1** with $[(\eta^6\text{-}p\text{-cymene})Ru^{II}Cl_2]_2$ and $[Ru^{II}(H)Cl(CO)(PCy_3)_2]$ (Cy = cyclohexyl) and the crystal structures of the resulting $\mu$-nitrido complexes.

## ■ EXPERIMENTAL SECTION

**General Considerations.** 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 and 162.0 MHz for $^1$H and $^{31}$P, respectively. Chemical shifts ($\delta$, ppm) were reported with reference to $SiMe_4$ ($^1$H) and $H_3PO_4$ ($^{31}$P). IR spectra were recorded on a Perkin-Elmer 16 PC Fourier transform infrared spectrophotometer. UV/vis spectra were recorded on a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrometer. Electrospray ionization (ESI) mass spectra were recorded on an Applied Biosystem QSTAR mass spectrometer. Cyclic voltammetry was performed using a CH Instrument model 600D potentiostat. The working and reference electrodes were glassy carbon and Ag/$AgNO_3$ (0.1 M in MeCN), respectively. Potentials were reported with reference to the ferrocenium/ferrocene ($Cp_2Fe^{+/0}$) couple. The magnetic susceptibility was measured by a Sherwood Mark II magnetic susceptibility balance. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

The complexes **1**[15] and $[Ru^{II}(H)Cl(CO)(PCy_3)_2]$[18] were prepared according to literature methods. $[(\eta^6\text{-}p\text{-cymene})Ru^{II}Cl_2]_2$ was purchased from Aldrich Ltd. and used as received.

**Preparation of $[L_{OEt}Cl_2Ru^V(\mu\text{-}N)Ru^{IV}Cl_2L_{OEt}]$ (2).** A solution of **1** (72 mg, 0.1 mmol) in $CCl_4$ (10 mL) was heated at reflux for 2.5 h. The color of the solution changed from purple to dark red. The solvent was removed in vacuo, and the residual solid was extracted by hot hexane (3 × 10 mL). Concentration and cooling of the extract at −18 °C gave dark-red blocks. Yield: 56 mg (78%). $\mu_{eff}$ (solid sample, 295 K): 1.72 $\mu_B$. UV/vis [$CH_2Cl_2$; $\lambda_{max}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$)]: 534 (1279). MS (ESI): $m/z$ 1357.78 (M − 2Cl + 1). Anal. Calcd for $C_{34}H_{70}Co_2Cl_4NO_{18}P_6Ru_2\cdot0.6C_6H_{14}$: C, 30.51; H, 5.34; N, 0.95. Found: C, 30.94; H, 5.06; N, 0.92.

**Preparation of $[H(H_2O)_6][\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]$ ($[H_{13}O_6][2]$).** **2** was synthesized as described above, and the reaction mixture was extracted with undistilled heptane/$Et_2O$ (3 × 20 mL; 3:1, v/v). Slow evaporation in air for 4 days afforded yellow-brown blocks. Yield: 46 mg (64%). $^1$H NMR ($CDCl_3$): $\delta$ 1.20−1.29 (m, 36H, $CH_3$), 4.04−4.12, 4.20−4.27, 4.42−4.43 (m, 24H, $OCH_2$), 4.04 (br, 12H, $H_2O$), 5.01 (s, 10H, Cp). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 113.3 (m), 119.0 (m). Despite two attempts, we have not been able to obtain satisfactory analytical data (Table 1). Nevertheless, the compound has been well characterized spectroscopically and by X-ray diffraction.

**Preparation of $[n\text{-}Bu_4N][\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]$ ($[n\text{-}Bu_4N][2]$).** To a solution of $[H(H_2O)_6][2]$ (148 mg, 0.1 mmol) in tetrahydrofuran (THF; 10 mL) was added $n$-$Bu_4NOH$ (66 $\mu$L, 40 wt % in water, 0.1 mmol), and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue was washed with $Et_2O$. Recrystallization from THF/hexane afforded brown needles, which were suitable for the X-ray diffraction study. Yield: 159 mg (95%). $^1$H NMR ($CDCl_3$): $\delta$ 0.94−0.98 (t, $J$ = 5.4 Hz, 12H, $CH_3$), 1.17−1.24 (m, 36H, $CH_3$), 1.43−1.46 (m, 8H, $CH_2$), 1.60−1.70 (m, 8H, $CH_2$), 3.35−3.39 (m, 8H, $CH_2$), 4.01−4.05 (m, 4H, $OCH_2$), 4.11−4.15 (m, 4H, $OCH_2$), 4.22−4.29 (m, 12H, $OCH_2$), 4.47−4.51 (m, 4H, $OCH_2$), 4.96 (s, 10H, Cp). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 113.0

**Table 1. Crystallographic Data and Experimental Details for $[H_{13}O_6][2]$, $[n\text{-}Bu_4N][2]$, 3, and 4**

| | $[H_{13}O_6][2]$ | $[n\text{-}Bu_4N][2]\cdot{}^1/_4THF\cdot H_2O$ | $3\cdot4C_6H_6\cdot H_2O$ | $4\cdot4THF\cdot{}^1/_4C_6H_{14}$ |
|---|---|---|---|---|
| formula | $C_{34}H_{83}Cl_4Co_2NO_{24}P_6Ru_2$ | $C_{51}H_{110}Cl_4Co_2N_2O_{19.25}P_6Ru_2$ | $C_{58}H_{100}Cl_8Co_2N_2O_{21}P_6Ru_4$ | $C_{59.5}H_{117.5}Cl_3CoNO_{11}P_5Ru_2$ |
| fw | 1536.63 | 1707.03 | 2152.96 | 1544.81 |
| cryst syst | triclinic | monoclinic | triclinic | orthorhombic |
| space group | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ | $Pca2_1$ |
| $a$, Å | 10.3949(8) | 42.3383(12) | 12.9953(15) | 26.5336(2) |
| $b$, Å | 10.6252(6) | 13.6577(3) | 16.180(2) | 12.50800(10) |
| $c$, Å | 15.4506(10) | 28.3023(6) | 21.548(3) | 44.8977(3) |
| $\alpha$, deg | 109.191(6) | 90 | 81.223(2) | 90 |
| $\beta$, deg | 101.791(6) | 112.410(3) | 81.015(2) | 90 |
| $\gamma$, deg | 94.294(6) | 90 | 73.090(2) | 90 |
| $V$, Å$^3$ | 1558.91(18) | 15129.7(6) | 4254.1(9) | 14900.75(19) |
| $Z$ | 1 | 8 | 2 | 8 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.637 | 1.499 | 1.681 | 1.377 |
| $T$, K | 173(2) | 173(2) | 203(2) | 173(2) |
| wavelength, Å | 1.54178 | 1.54178 | 0.71073 | 1.54178 |
| $\mu$, mm$^{-1}$ | 11.586 | 9.565 | 1.500 | 7.380 |
| $F$(000) | 785 | 7072 | 2172 | 6480 |
| no. of reflns | 9031 | 40275 | 27616 | 34925 |
| no. of indep. reflns | 5716 | 13550 | 16329 | 20189 |
| $R_{int}$ | 0.0534 | 0.0604 | 0.0750 | 0.0391 |
| GOF$^a$ | 1.026 | 1.012 | 1.016 | 1.013 |
| R1,$^b$ wR2$^c$ [$I > 2\sigma(I)$] | 0.0384, 0.0715 | 0.0486, 0.1044 | 0.0618, 0.0789 | 0.0327, 0.0603 |
| R1, wR2 (all data) | 0.0612, 0.0754 | 0.0756, 0.1099 | 0.1575, 0.0955 | 0.0500, 0.0644 |

$^a$GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. $^b$R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. $^c$wR2 = $[(\sum w|F_o| - |F_c|)^2/\sum w^2|F_o|^2]^{1/2}$.

(m), 116.9 (m). Anal. Calcd for $C_{50}H_{106}Cl_4Co_2N_2O_{18}P_6Ru_2$·THF: C, 37.21; H, 6.59; N, 1.61. Found: C, 36.86; H, 6.92; N, 1.82.

**Preparation of $[L_{OEt}Cl_2Ru^{VI}(\mu\text{-}N)Ru^{II}(H_2O)Cl_2]_2$ (3).** A mixture of **1** (72 mg, 0.1 mmol) and 0.5 equiv of $[(\eta^6\text{-}p\text{-cymene})Ru^{II}Cl_2]_2$ (31 mg, 0.05 mmol) in benzene (8 mL) was heated at 60 °C for 12 h, during which the color of the solution changed from brown to dark orange. The solvent was removed in vacuo, and the residue was washed with cold hexane. Recrystallization from benzene/hexane in air afforded orange crystals, which were suitable for the X-ray diffraction study. Yield: 128 mg (70%). $^1$H NMR ($CDCl_3$): $\delta$ 1.19−1.33 (m, 36H, $CH_3$), 4.02−4.09 (m, 8H $OCH_2$), 4.14−4.28 (m, 16H, $OCH_2$), 4.98 (br, 4H, $H_2O$), 5.05 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 121.8 (s). Anal. Calcd for $C_{34}H_{74}Cl_8Co_2N_2O_{20}P_6Ru_4$: C, 22.41; H, 4.09; N, 1.54. Found: C, 22.08; H, 4.17; N, 1.41.

**$[(L_{OEt})Cl_2Ru^{VI}(\mu\text{-}N)Ru^{II}(H)Cl(CO)(PCy_3)_2]$ (4).** A mixture of **1** (72 mg, 0.1 mmol) and 1 equiv of $[Ru^{II}(H)Cl(CO)(PCy_3)_2]$ (73 mg, 0.1 mmol) in THF (10 mL) was stirred at room temperature for 12 h. The solvent was removed in vacuo, and the residue was washed with cold hexane. Recrystallization from THF/hexanes afforded orange crystals, which were suitable for X-ray diffraction. Yield: 116 mg (80%). $^1$H NMR ($CDCl_3$): $\delta$ 0.87−0.91 (m, 8H, $CH_3$), 1.12−1.31 (m, 12H, $CH_3$), 1.32−1.41, 1.57−1.60, 1.77−1.80, 1.83−1.86, 1.90−1.92, 1.98−2.02, 2.32−2.35, 1.53−1.55, 2.74−2.90 (m, 66H, Cy), 4.25−4.43 (m, 16H, $OCH_2$), 4.51−4.56 (m, 8H, $OCH_2$), 4.84 (s, 5H, Cp), −12.7 (t, $J$ = 26 Hz, 1H, Ru−H). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 50.6 (s, $PCy_3$), 108.9 (m, $L_{OEt}^-$), 117.3 (m, $L_{OEt}^-$). IR (KBr, $cm^{-1}$): 1985 [$\nu$(C−O)], 1938 [$\nu$(Ru−H)]. Anal. Calcd for $C_{54}H_{102}Cl_3CoNO_{10}P_5Ru_2$·$C_6H_{14}$: C, 46.98; H, 7.62; N, 0.91. Found: C, 47.31; H, 7.41; N, 0.89.

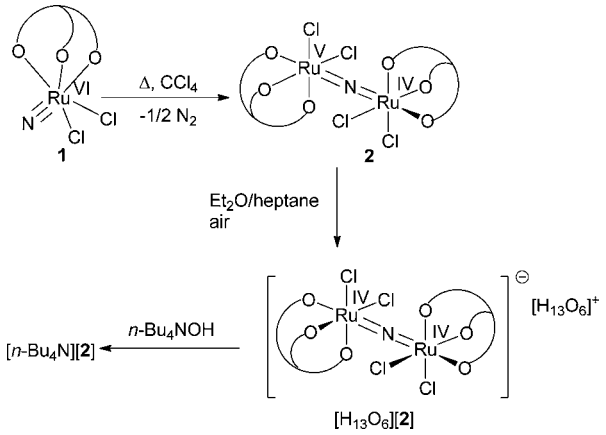
**X-ray Crystallography.** *Crystal Structure Determinations.* Diffraction data of **3** were recorded on a Bruker CCD diffractometer with monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The collected frames were processed with the software *SAINT*.[19] Diffraction intensity data of $[H_{13}O_6][\mathbf{2}]$, $[n\text{-}Bu_4N][\mathbf{2}]$, and **4** were collected on an Oxford Diffraction GeminiTMS Ultra with a CCD area detector with monochromatized Cu K$\alpha$ radiation ($\lambda$ = 1.54178 Å). Data collection and reduction were carried out using *CrysAlisPro 171.32.5*. Absorption correction was performed using *SADABS* built into the *CrysAlisPro* program suite. Structures were solved by direct methods and refined by full-matrix least squares on $F^2$ using the *SHELXTL* software package.[20] Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

In $[H_{13}O_6][\mathbf{2}]$, two ethyl groups of the tripodal ligands are disorder and have been refined with an occupancy of 0.5 each. In $[n\text{-}Bu_4N][\mathbf{2}]$, the $n$-butyl group of $[n\text{-}Bu_4N]^+$ is disordered and has been refined with the appropriate partial occupancies. The Cp rings of the tripod ligands are rotationally disordered and refined with an occupancy of 0.5 each. Two ethoxy groups in the tripod ligand were also found to be disordered. In the tripodal ligands of complex **4**, the Cp rings are rotationally disordered with occupancies of 0.6 and 0.4, whereas the ethyl groups are 55:45, 30:30, and 40:60 disordered.

## ■ RESULTS AND DISCUSSION

**Ruthenium(V)−Ruthenium(IV) Nitrido Complex.** In contrast with $[Ru^{VI}(salen)(N)(MeOH)]^+$,[17] **1** is stable with respect to intermolecular N−N coupling in polar solvents such as methanol, acetonitrile, and *N*,*N*-dimethylformamide at room temperature. However, heating **1** in benzene-$d_6$ at 50 °C led to the formation of a paramagnetic species, as evidenced by NMR spectroscopy. Evaporation of the solvent and recrystallization from hot hexane under nitrogen afforded dark-red crystals identified as the mixed-valence complex **2** (Scheme 2). **2** could be isolated in ca. 78% yield (with respect to Ru) by refluxing **1** in $CCl_4$ for 2.5 h. **2** is tentatively formulated as a mixed valence $Ru^V$−$Ru^{IV}$ complex, although the alternative $Ru^{VI}$−$Ru^{III}$ formulation cannot be ruled out. The $Ru^V$−$Ru^{IV}$ formulation is preferred because, like the $Ru^{IV}$−$Ru^{IV}$ analogue

**Scheme 2. Synthesis of $\mu$-Nitrido Complexes 2 and $[\mathbf{2}]^-$**




$[\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]^-$ (vide infra), the two ruthenium centers in **2** have identical ligand environments (namely, two chlorides, one nitride, and three oxygens), and it seems unlikely that they have very different oxidation states. In addition, **2** was formed readily by the chemical oxidation of $[\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]^-$ with oxidants such as $Ce^{IV}$, presumably via a simple one-electron oxidation of one of the two $Ru^{IV}$ centers in $[\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]^-$ to give a $Ru^V$−$Ru^{IV}$ species. Additional spectroscopic and theoretical studies are needed to confirm the ruthenium oxidation states in **2**. The magnetic moment of **2** was determined to be 1.72 $\mu_B$, which is consistent with the $S$ = $^1/_2$ spin state. The UV/vis spectrum of **2** in $CH_2Cl_2$ showed an absorption band centered at 534 nm, which is absent in the $Ru^{IV}$−$Ru^{IV}$ complexes. Although the exact type of electronic transition (d−d or charge transfer) responsible for this band is not clear, this absorption is possibly associated with the $Ru^V$ center because it not observed in related $Ru^{IV}$ complexes such as $[L_{OEt}RuCl_3]$ and $[\{L_{OEt}Ru^{IV}Cl_2\}_2(\mu\text{-}N)]^-$. We were not able to assign the $\nu$(Ru−N−Ru) band in the IR spectrum because of overlap with intense absorption of the $L_{OEt}^-$ ligand in the 1000−1250 $cm^{-1}$ region.

**2** has been characterized by X-ray crystallography.[21] The structure of **2** featuring a linear-symmetric Ru−N−Ru bridge (type **A**, Scheme 1) is shown in Figure 1. Unfortunately, because of the poor quality of the crystal, the structure has not been refined satisfactorily. Nevertheless, the identity of **2** and its

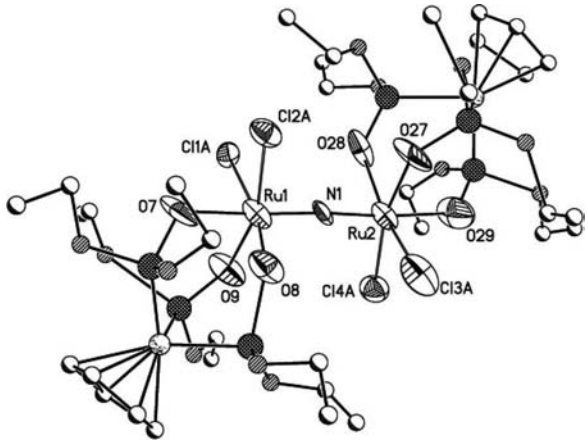



**Figure 1.** Molecular structure of **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level.

core structure has been unambiguously established. It may be noted that while a majority of reported diruthenium nitrido complexes are of the $Ru^{IV}$–$Ru^{IV}$ type,[10] **2** is a rare example of a mixed-valence ruthenium $\mu$-nitrido complex.[10c,g,12]

The N–N coupling of ruthenium and osmium nitrido complexes to give dinitrogen is well documented.[17,22,23] For example, $[Ru^{VI}(N)(salen)(MeOH)]^+$ undergoes intermolecular N–N coupling in the presence of a ligand L (L = monodentate nitrogen-donor ligand) to afford the $Ru^{III}$ complexes $[Ru(salen)L_2]^+$ and dinitrogen.[17] Therefore, it seems reasonable to assume that the formation of **2** involves the coupling of **1** with a $Ru^{III}$ species, "$L_{OEt}Ru^{IV}Cl_2$", derived from the N–N coupling of **1**. The thermally induced transformation of metal nitrides to $\mu$-nitrido complexes is well precedented. For example, thermolysis of $[Os^{VI}(N)Cl_3L_2]$ (L = substituted pyridine) afforded the trinuclear nitrido complexes $[Os^{IV}_3(N)_2L_8]$ accompanied by the formation of dinitrogen and $[Os^{IV}Cl_4L_2]$.[23]

**Ruthenium(IV)–Ruthenium(IV) Nitrido Complexes.** The cyclic voltammogram of **2** in acetonitrile (Figure 2a)

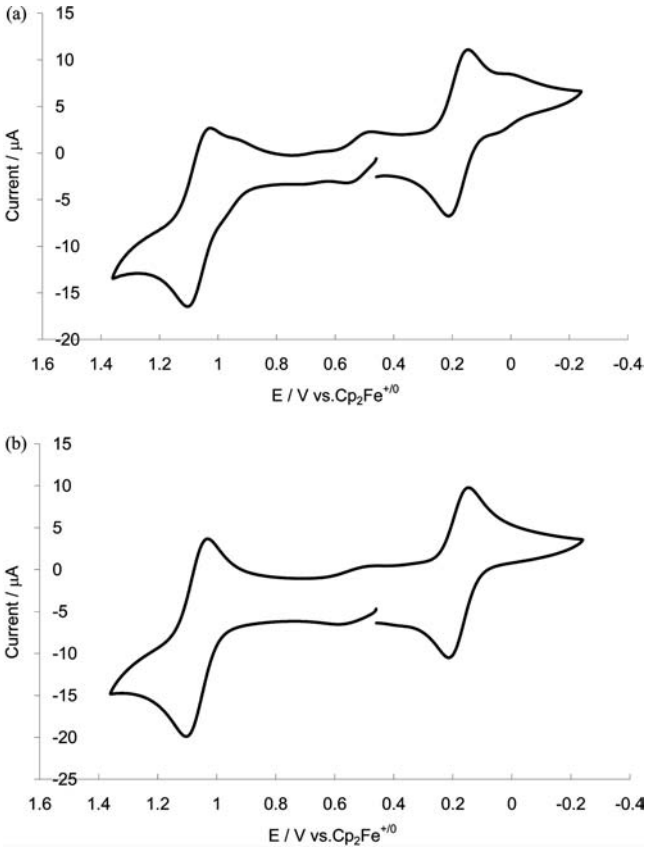



**Figure 2.** Cyclic voltammograms of **2** (a) and $[n\text{-}Bu_4N][\mathbf{2}]$ (b) in acetonitrile with 0.1 M $[n\text{-}Bu_4N]PF_6$ (working electrode, glassy carbon; scan rate = 100 mV $s^{-1}$).

displayed two reversible couples ($\Delta E_p \sim 60$ mV, $i_a/i_c \sim 1$) at 0.19 and 1.13 V versus $Cp_2Fe^{+/0}$, which are assigned as the metal-centered $Ru^V$–$Ru^{IV}$/$Ru^{IV}$–$Ru^{IV}$ and $Ru^V$–$Ru^V$/$Ru^V$–$Ru^{IV}$ couples, respectively. The observation of the $Ru^V$–$Ru^{IV}$/$Ru^{IV}$–$Ru^{IV}$ couple at 0.19 V suggests that **2** is an oxidizing agent and can be reduced to a $Ru^{IV}$–$Ru^{IV}$ complex easily. Indeed, recrystallization of **2** from undistilled $Et_2O$/heptane in air for 4 days led to isolation of the anionic $Ru^{IV}$–$Ru^{IV}$ complex $[\mathbf{2}]^-$. The completion of the reduction of **2** to $[\mathbf{2}]^-$ was indicated by the disappearance of the 534-nm band of **2** in the UV/vis spectrum. The cation was found to be the hydrated proton, $H_{13}O_6^+$, according to an X-ray diffraction study (vide infra). Although the mechanism for the formation of $[H_{13}O_6][\mathbf{2}]$ has not been elucidated, it is clear that water (and perhaps impurities of the solvent) plays a role in the reduction of the $Ru^V$–$Ru^{IV}$ complex. The reduction of **2** was very slow (as evidenced by UV/vis spectroscopy) if recrystallization was carried out in strictly anhydrous, distilled $Et_2O$ under nitrogen. In addition, the reduction of **2** was found to be accelerated by a Brønsted acid such as hydrochloric acid. Thus, in the presence of a few drops of 1 M HCl(aq), the reduction of **2** in $Et_2O$ in air completed overnight. Cation metathesis of $[H_{13}O_6][\mathbf{2}]$ with $n$-$Bu_4NOH$ yielded the tetra-$n$-butylammonium salt $[n\text{-}Bu_4N][\mathbf{2}]$. As expected, both $[H_{13}O_6][\mathbf{2}]$ and $[n\text{-}Bu_4N][\mathbf{2}]$ are diamagnetic as a result of antiferromagnetic coupling of the $Ru^{IV}$ $d^4$ centers. In each of these complexes, the Cp protons of the $L_{OEt}^-$ ligands appeared as a singlet (at $\delta$ 4.96 and 5.10, respectively) in the $^1H$ NMR spectrum. The cyclic voltammogram of $[n\text{-}Bu_4N][\mathbf{2}]$ in acetonitrile (Figure 2b) is virtually the same as that of $[\mathbf{2}]^-$ with a lower rest potential.

The structures of $[H_{13}O_6][\mathbf{2}]$ and the complex anion in $[n\text{-}Bu_4N][\mathbf{2}]$ are shown in Figures 3 and 4, respectively. The structure of the $H_{13}O_6^+$ cation (Figure 3a), which can be described as a tetrahydrate of the hydronium ion $H_5O_2^+$ (Chart

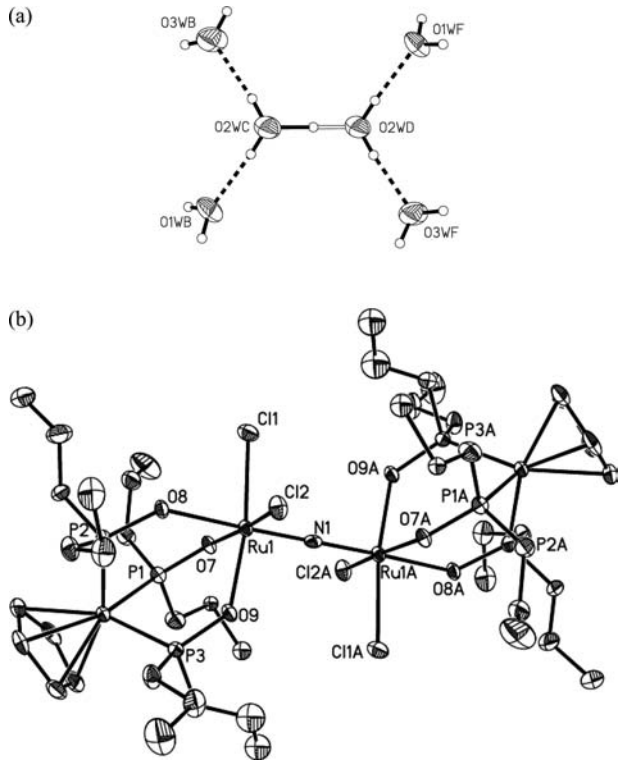



**Figure 3.** Structures of the cation (a) and complex anion (b) of $[H_{13}O_6][\mathbf{2}]$. Hydrogen atoms of the $L_{OEt}^-$ ligands are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): hydrogen bond, O2WC–O2WD 2.459(3), O2WC–O3WB 2.630(2), O1WB–O2WC 2.609(5); O2WC–H4WA–O1WB 166.0(4), O2WC–H3W–O3WB 164.5(6); Ru1–O7 2.076(3), Ru1–O8 2.095(3), Ru1–O9 2.069(3), Ru1–N1 1.7325(4), Ru1–Cl1 2.3538(12), Ru1–Cl2 2.3640(11). Symmetry code: A = $-x + 2, -y + 2, -z + 1$.

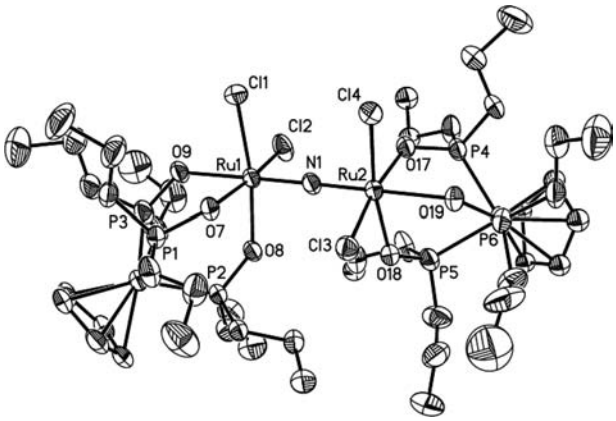
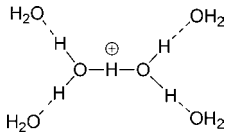



**Figure 4.** Molecular structure of the complex anion in [*n*-$Bu_4N$][**2**]. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru1−O7 2.076(3), Ru1−O8 2.110(3), Ru1−O9 2.139(3), Ru2−O17 2.096(3), Ru2−O18 2.079(3), Ru2−O19 2.123(3), Ru1−N1 1.737(4), Ru2−N1 1.718(4), Ru1−Cl1 2.3412(16), Ru1−Cl2 2.3357(15), Ru2−Cl3 2.3483(13), Ru2−Cl4 2.3465(14); Ru1−N1−Ru2 178.1(3).

2), is similar to that found in $[(C_9H_{18})_3(NH)_2Cl]Cl$.[24] The O···O distance in the conjugated O−H−O group, where the

**Chart 2. Structure of the $H_{13}O_6^+$ Cation**

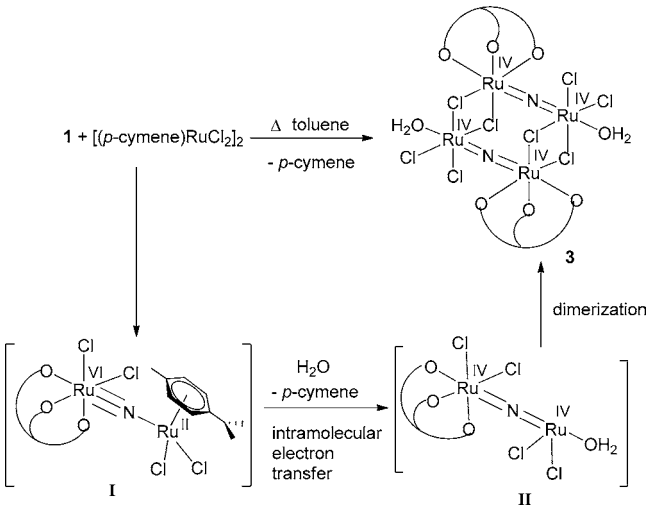



excess proton resides, is 2.459(3) Å, which compares well with that in the literature.[24]

The structures of the two complex anions (Figures 3b and 4) are very similar except that the two $L_{OEt}^-$ ligands in the former are in an anti arrangement, whereas those in the latter are syn. In the former, a center of inversion is located at the nitride ligand. The Ru−N distances for the two complexes [1.7325(4) Å for the former and 1.734(4) and 1.718(4) Å for the latter] compare well with those in $[Ru^{IV}_2(\mu\text{-}N)Cl_{10}]^{3-}$ [1.718(3) Å],[25] indicative of the symmetric binding mode of the $\mu$-nitrido ligand. The two Ru−N−Ru units [180° and 178.1(3)°, respectively] are essentially linear. The average Ru−O (2.080 and 2.014 Å, respectively) and Ru−Cl (2.359 and 2.343 Å, respectively) distances are similar to those in $[L_{OEt}Ru^{IV}Cl_2(NPPh_3)]$.[15]

**Reaction of 1 with $[(\eta^6\text{-}p\text{-Cymene})Ru^{II}Cl_2]_2$.** Previously, Strähle and co-workers reported the syntheses of heterobimetallic osmium(VI) and rhenium(V) nitrido complexes from metal nitrides and low-valent organometallic complexes.[26] This led us to prepare diruthenium nitrido complexes by reacting **1** with lower-valent organoruthenium starting materials. The treatment of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with **1** afforded a dark material that did not crystallize. No reaction was found between $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and **1** in benzene-$d_6$ at room temperature, as evidenced by NMR spectroscopy. However, when the reaction mixture was heated at 60 °C, the resonance signals of **1** dropped and a new diamagnetic species was produced. Recrystallization from benzene-$d_6$/hexane afforded red crystals identified by X-ray crystallography as the tetranuclear ruthenium(IV) nitrido complex **3** (Scheme 3). The $^1$H NMR spectrum of **3** displayed well-resolved resonances

**Scheme 3. Synthesis of Tetranuclear 3 and the Proposed Mechanism for Its Formation**




due to the magnetically equivalent $L_{OEt}^-$ ligands, indicative of the diamagnetic nature of the compound. Contrary to [**2**]$^-$, **3** is redox-inactive in the potential range −2.0 to +1.5 V versus $Cp_2Fe^{+/0}$.

The molecular structure of **3** is shown in Figure 5. The structure consists of two symmetry-related $[L_{OEt}Cl_2Ru^{IV}(\mu\text{-}N)Ru^{IV}Cl_2(H_2O)]$ fragments linked together via four chloro bridges. An inversion center is located at the center of the molecule. Like [**2**]$^-$, the nitrido bridge in **3** is linear and symmetric with Ru−N distances of 1.725(6) and 1.731(6) Å and a Ru−N−Ru′ angle of 174.5(4)°. The average Ru−O($L_{OEt}$) and Ru−$\mu$-Cl distances of the $\{L_{OEt}Ru^{IV}\}$ fragment are 2.060 and 2.372 Å, respectively. The Ru−$OH_2$, Ru−Cl, and Ru−$\mu$-Cl distances of the $\{Ru^{IV}Cl_2(H_2O)\}^{2+}$ fragment are 2.204(4), av 2.408, and av 2.337 Å, respectively.

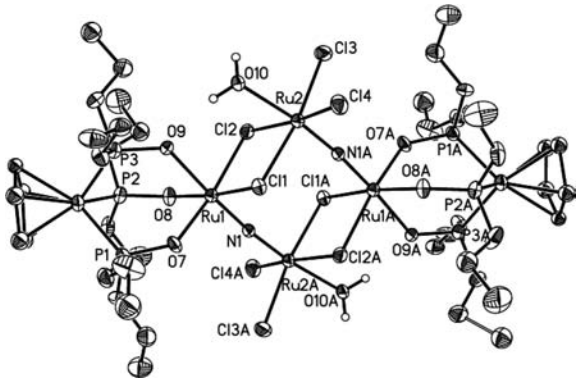



**Figure 5.** Molecular structure of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru1−O7 2.021(4), Ru1−O8 2.036(5), Ru1−O9 2.123(5), Ru1−N1 1.725(6), Ru1−Cl1 2.365(2), Ru1−Cl2 2.3784(18), Ru2−O10 2.204(4), Ru2−N1A 1.731(6), Ru2−Cl1 2.4025(18), Ru2−Cl2 2.413(2), Ru2−Cl3 2.343(2), Ru2−Cl4 2.331(2); Ru1−N1−Ru2A 174.5(4), Ru1−Cl1−Ru2 94.54(7), Ru1−Cl2−Ru2 93.93(7), N1A−Ru2−O10 173.3(2). Symmetry code: A = −*x*, −*y* + 1, −*z*.

A plausible mechanism for the formation of **3** is shown in Scheme 3. The reaction of $[(\eta^6\text{-}p\text{-cymene})Ru^{II}Cl_2]_2$ with **1** results in cleavage of the chloride bridges and the formation of a dinuclear nitrido intermediate, $\{(\eta^6\text{-}p\text{-cymene})Cl_2Ru^{II}(\mu\text{-}N)Ru^{VI}Cl_2L_{OEt}\}$ (**I**). It may be noted that a related rhenium(V)−ruthenium(II) nitrido complex, $[(PMe_2Ph)_3Cl_2Re^{V}(\mu\text{-}N)Ru^{II}Cl_2(\eta^6\text{-}C_6H_6)]$,[26c] has been isolated previously. Dissociation of the *p*-cymene ligand in **I**, followed by intramolecular electron transfer, affords the $Ru^{IV}$−$Ru^{IV}$ species $\{(H_2O)Cl_2Ru^{IV}{=}N{=}Ru^{IV}Cl_2L_{OEt}\}$ (**II**), which dimerizes to tetranuclear **3**.

**Reaction of 1 with $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$.** The reaction of **1** with hydride complexes is of special interest because in a previous work we found that **1** underwent migratory insertion with $[L_{OEt}Ru(H)(CO)(PPh_3)]$ to give a $\mu$-imido complex, $[L_{OEt}Cl_2Ru(\mu\text{-}NH)Ru(CO)(PPh_3)L_{OEt}]$.[15] The treatment of **1** with $[Ru(H)Cl(CO)(PPh_3)_3]$ led to rapid formation of the phosphoraminato complex $[L_{OEt}Ru^{IV}Cl_2(NPPh_3)]$,[15] indicating that attack of the nitride by dissociated $PPh_3$ is faster than nitride insertion into the Ru−H bond. Next, we studied the reaction of **1** with the 16-electron hydride complex $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$. Instead of nitride insertion, the reaction of **1** with $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ afforded the ruthenium(IV)−ruthenium(II) $\mu$-nitrido complex **4** (Scheme 4). On the other hand, no reaction was found between $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ and the less electrophilic $Os^{VI}$ analogue $[L_{OEt}Os^{VI}(N)Cl_2]$.[27] In the $^1H$ NMR spectrum, the hydride in **4** appeared as a triplet at $\delta$ −12.7 ($J_{PH}$ = 26 Hz), which is more downfield than that in $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ ($\delta$ −24.7).[28] The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at $\delta$ 50.6 due to the magnetically equivalent $PCy_3$ ligands along with the $L_{OEt}^-$ resonances at $\delta$ 108.9 and 117.3. The IR C−O stretching frequency of **4** was determined to be 1984 $cm^{-1}$, which is higher than those of the starting material $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ (1906 $cm^{-1}$) and six-coordinated $[Ru^{II}(H)(CO)Cl(PCy_3)_2(py)]$ (1882 $cm^{-1}$).

**Scheme 4. Synthesis of 4**

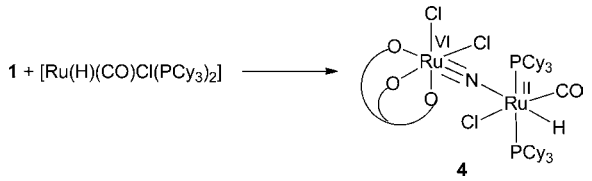



Figure 6 shows the molecular structure of **4**. The geometry around the two ruthenium centers is pseudooctahedral. The nitrido bridge in **4** is linear [Ru−N−Ru angle = 172.0(3)°] and asymmetric [$Ru^{VI}$−N 1.682(5) Å; $Ru^{II}$−N 1.915(5) Å] (type **C**), consistent with the $Ru^{VI}{\equiv}N{-}Ru^{II}$ formulation. The $Ru^{VI}$−N distance in **4** is intermediate between those for the terminal nitride [1.573(6) Å in **1**[15]] and symmetric $\mu$-nitride [1.718(4)−1.734(4) Å in $\mathbf{2}^-$ and **3**] analogues. The ligand environment of the $Ru^{II}$ fragment is the same as that of $[Ru^{II}(CO)(H)Cl(PCy_3)_2]$ except that a nitride is located opposite to the hydride. The $Ru^{II}$−N bond is shorter than typical $Ru^{II}$−N single bonds, indicative of multiple-bond character. The Ru−CO and $Ru^{II}$−Cl distances [1.841(6) and av 2.430 Å, respectively] in **4** compare well with those in $[Ru(H)(CO)Cl(PCy_3)_2]$, whereas the Ru−P distance [av 2.430 Å] is longer than that in the latter [2.3865(5) Å][29] possibly because of steric effects.

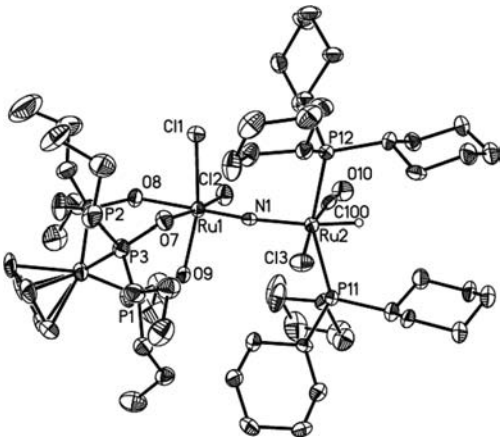



**Figure 6.** Molecular structure of **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ru1−O7 2.046(4), Ru1−O8 2.188(4), Ru1−O9 2.091(4), Ru1−N1 1.682(5), Ru1−Cl1 2.3258(16), Ru1−Cl2 2.3447(16), Ru2−N1 1.915(5), Ru2−C100 1.841(6), Ru2−P11 2.4271(15), Ru2−P12 2.4328(16), Ru2−Cl3 2.4382(15); Ru1−N1−Ru2 172.0(3).

Two factors may play a role in disfavoring the nitride insertion into the ruthenium-hydrogen bond in $[Ru^{II}(CO)(H)Cl(PCy_3)_2]$: (a) trans arrangement between the hydride and incoming nitride; (b) absence of a ligand opposite to the hydride (a P=O group in the case of $[L_{OEt}Ru^{II}(H)(CO)(PPh_3)]$), which can weaken the Ru−H bond. To test whether a ligand opposite to hydride is essential for the nitride insertion, the reaction between six-coordinated $[Ru^{II}(H)(CO)Cl(PCy_3)_2(py)]$ and **1** was studied. The treatment of $[Ru^{II}(H)(CO)Cl(PCy_3)_2(py)]$ with 1 equiv of **1** in benzene-$d_6$ resulted in dissociation of the pyridine ligand and formation of **4** almost quantitatively, suggesting that the electron-rich $Ru^{II}$ center prefers the ruthenium(VI) nitride to pyridine. Mayer and coworkers proposed that the electrophilic M≡N group (e.g., M = Os) behaves like a $\pi$-acid ligand like CO because of the presence of low-lying empty M−N $\pi^*$ orbitals. Thus, the Pt−N bond [1.868(8) Å] in $[(Me_2S)Cl_2Pt^{II}(\mu\text{-}N)Os^{VI}Cl_2Tp]$ [$Tp^-$ = hydridotris(pyrazol-1-yl)borate] is shorter than a normal Pt−N single bond as a result of the $\pi$ interaction between Pt and Os≡N[30] (cf. back-bonding in MCO complexes). This is in contrast with early-transition-metal nitrides, e.g., $[V(N)(OSiMe_3)_3]^-$, which bind to late transition metals primarily via $\sigma$ interaction.[2,31] In this work, we also found that the $Ru^{II}$−N bond in **4** is shorter than a Ru−N single bond, indicative of multiple-bond character. The $\pi$-acid-like character of the ruthenium(VI) nitride can explain why **1** binds to $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ more tightly than does pyridine. Also, no reaction was found between $[Ru^{II}(H)(CO)Cl(PCy_3)_2]$ and the "weaker" $\pi$ acceptor $[L_{OEt}Os^{VI}(N)Cl_2]$. **4** can therefore be described by two resonance forms, $Ru^{VI}{\equiv}N{-}Ru^{II}$ (type **C**, Scheme 1) and $Ru^{IV}{=}N{=}Ru^{IV}$ (type **A**, Scheme 1), with the former being the predominant one. The observation of a high C−O stretching frequency for **4** is consistent with the contribution of the latter resonance form. Complete delocalization of the $\pi$ bond to give a $Ru^{IV}$−$Ru^{IV}$ complex did not occur for **4** presumably because the $Ru^{II}$ center in **4** is stabilized by the carbonyl ligand. By contrast, dissociation of the labile *p*-cymene ligand from **3** facilitates $Ru^{II}/Ru^{IV}$ oxidation and the formation of a $Ru^{IV}{=}N{=}Ru^{IV}$ complex.

## CONCLUSIONS

In summary, the terminal ruthenium(VI) nitrido complex **1** proved to be a useful precursor to dinuclear ruthenium nitrido complexes. Heating **1** in a $CCl_4$ solution resulted in the formation of mixed-valence $\mu$-nitrido complex **2**, presumably a $Ru^{V}$−$Ru^{IV}$ species, which can be reduced to the more stable $Ru^{IV}$−$Ru^{IV}$ form, $[\mathbf{2}]^-$. Diruthenium nitrido complexes can be obtained readily from **1** and lower-valent organoruthenium complexes. The treatment of **1** with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ afforded the tetranuclear ruthenium(IV) nitrido complex **3**, whereas that with $[Ru(H)Cl(CO)(PCy_3)_2]$ gave the dinuclear ruthenium(VI)−ruthenium(II) nitrido complex **4**. Consistent with Mayer's suggestion, the ruthenium(VI) nitride can act as a $\pi$-acidic metalloligand. In **4**, the $Ru^{II}$ to $Ru^{VI}{\equiv}N$ "back-donation" results in a short $Ru^{II}$−N bond and a high C−O stretching frequency. For the reaction of **1** with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$, after dissociation of the cymene ligand, the $Ru^{II}$ to $Ru^{VI}{\equiv}N$ "backdonation" is so strong that $Ru^{II}/Ru^{IV}$ oxidation occurred and a $Ru^{IV}{=}N{=}Ru^{IV}$ complex is formed.

## ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION


### Corresponding Author

*E-mail: chleung@ust.hk.


### Notes

The authors declare no competing financial interest.

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