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Formation of a Dinuclear Imido Complex from the Reaction of a Ruthenium(VI) Nitride with a Ruthenium(II) Hydride

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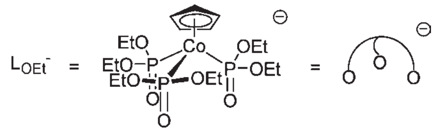
The treatment of $[Ru(L_{OEt})(N)Cl_2]$ (**1**; $L_{OEt}^- = [Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$) with Et_3SiH affords $[Ru(L_{OEt})Cl_2(NH_3)]$ (**2**), whereas that with $[Ru(L_{OEt})(H)(CO)(PPh_3)]$ (**3**) gives the dinuclear imido complex $[(L_{OEt})Cl_2Ru(\mu\text{-}NH)Ru(CO)(PPh_3)(L_{OEt})]$ (**4**). The imido group in **4** binds to the two ruthenium atoms unsymmetrically with Ru−N distances of 1.818(6) and 1.952(6) Å. The reaction between **1** and **3** at 25 °C in a toluene solution is first order in both complexes with a second-order rate constant determined to be $(7.2 \pm 0.4) \times 10^{-5}\ M^{-1}\ s^{-1}$.

Transition-metal complexes containing metal−nitrogen multiple bonds have attracted much attention because of their possible involvement in catalytic cycles of metal-mediated nitrogen fixation.[1,2] Of special interest is the formation of imido and amido species from the hydrogenation of metal nitrides, which may play a role in the metal-catalyzed reduction of N_2 to NH_3.[3−8] Peters and co-workers reported that the hydrogenation of a dinuclear iron(II) μ-nitrido complex gave a μ-imido μ-hydrido species.[4] Burger and co-workers synthesized an iridium(III) amido complex by the hydrogenation of an iridium(III) terminal nitrido complex.[5] Smith and co-workers reported the formation of NH_3 from the reaction of an iron(IV) terminal nitrido complex with hydrogen atom donors such as 1-hydroxy-2,2,6,6-tetramethylpiperidine, apparently via a hydrogen-atom-transfer (HAT) mechanism.[6] Inspired by these observations, we set out to explore the reactivity of more easily accessible ruthenium(VI) nitrido complexes toward hydrogen and hydride compounds. The formation of $RuNH_x$ (x = 1−3) species from Ru≡N is of particular interest given the significance of ruthenium-based catalysts in ammonia synthesis.[9]

Chart 1. Kläui Oxygen Tripodal Ligand L_{OEt}^-



Previously, we synthesized an electrophilic ruthenium(VI) nitrido complex with the Kläui oxygen tripodal ligand[10] $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (Chart 1, denoted as L_{OEt}^- hereafter), $[Ru(L_{OEt})(N)Cl_2]$ (**1**), which reacted with PPh_3, Me_3NO, and $S_2O_3^{2-}$ to give phosphiniminato, nitrosyl, and thionitrosyl complexes, respectively.[11] In this paper, we describe the reactivity of **1** toward hydride compounds. The formation of a dinuclear imido complex from **1** and a ruthenium(II) hydride complex will be reported.

No reaction was found between **1** and molecular hydrogen (1−3 atm) at room temperature. However, complex **1** could be reduced readily with main-group hydrides such as silanes and boranes (see the Supporting Information, SI). For example, the treatment of complex **1** with excess Et_3SiH (> 3 equiv) in toluene at room temperature afforded yellow crystals identified as $[Ru(L_{OEt})Cl_2(NH_3)]$ (**2**) in 85% yield

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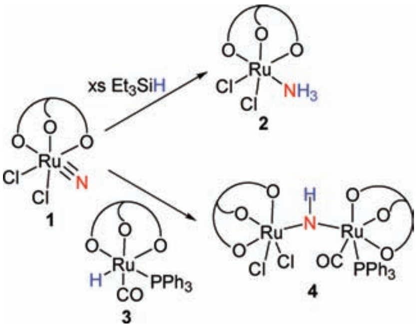
Scheme 1. Reduction of **1** with Et_3SiH and **3**



(Scheme 1 and the SI). The silicon-containing product(s) has not been fully characterized, although Et_3SiOH was detected in the reaction mixture by gas−liquid chromatography analysis. The measured magnetic moment for **2** of ca. 1.8 μ_B is consistent with the low-spin d^5 configuration for ruthenium(III). The IR spectrum displayed ν_{NH} bands at 3263 and 3333 cm^{-1}. The solid-state structure of **2** is shown in Figure 1. The Ru−O distances in **2** [2.059(5)−2.122(4) Å] are longer than those in **1** [2.030(5) and 2.031(5) Å, Ru−O (trans to Cl)].[11] The Ru−N distance of 2.061(6) Å is slightly shorter than those in reported ruthenium(III) ammine complexes (2.091−2.142 Å).[12] The formation of **2** apparently involves a multistep mechanism. No reaction was found between **1** and Brønsted acids such as acetic acid (pK_a = 4.75) and phenol (pK_a = 18.0 in dimethyl sulfoxide[13]), ruling out a proton transfer pathway. It is also unlikely that a simple HAT mechanism is involved because **2** was not formed[14] from reactions of **1** with conventional HAT reagents such as dihydroanthracene[15] (BDE = 78 kcal mol^{-1}; cf. 96 kcal mol^{-1} for Et_3SiH). We are inclined to believe that the first step for the formation of **2** from **1** involves the insertion of the Ru≡N group into the silane Si−H bond because a similar insertion reaction was found for **1** and ruthenium hydride (vide infra). Subsequent hydrolysis and reduction of the silylamido intermediate yielded **2**. An attempt to isolate/characterize the silylamido intermediate by reacting **1** with a stoichiometric amount of Et_3SiH was unsuccessful. **2** was also formed from **1** and *n*-Bu_3SnH. However, the reaction of **1** with *n*-Bu_3SnH is much faster (even at low temperature, e.g., −78 °C) than that with silane (see the SI). We have not been able to characterize the tin-containing product(s) and elucidate the mechanism for the reduction of **1** with tin hydride, which presumably is different from that for the silane reduction.

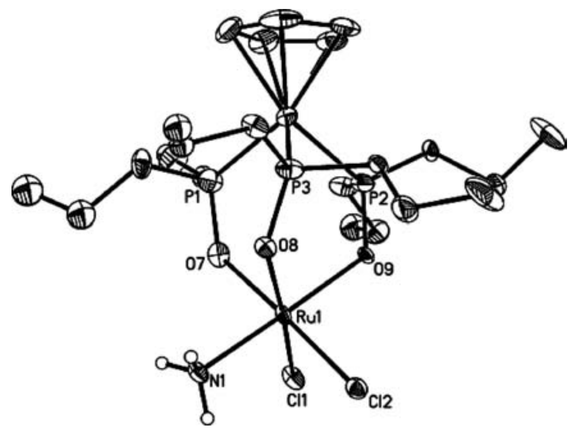


Figure 1. Molecular structure of **2**. Hydrogen atoms of the L_{OEt}^- ligand are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Ru1−N1 2.061(6), Ru1−Cl1 2.3209(18), Ru1−Cl2 2.3351(19), Ru1−O7 2.059(5), Ru1−O8 2.073(5), Ru−O9 2.122(4).

We next examined the reduction of **1** with transition-metal hydrides. The treatment of **1** with 1 equiv of $[Ru(L_{OEt})(H)(CO)(PPh_3)]$ (**3**)[16] afforded the air-stable dinuclear parent imido (NH) complex $[(L_{OEt})Cl_2Ru(\mu\text{-}NH)Ru(CO)(PPh_3)(L_{OEt})]$ (**4**; Scheme 1).[17] **1** was also found to react with other ruthenium(II) hydride complexes such as $[Ru(\eta^5\text{-}C_5H_5)(H)(CO)(PPh_3)]$, as evidenced by NMR spectroscopy. Unfortunately, we have not been able to crystallize the product(s) formed. The IR spectrum of **4** displayed the ν_{CO} band at 1949 cm^{-1}, which is higher than that for **3** (1908 cm^{-1}) but similar to that for the tosylamido complex $[Ru(L_{OEt})(NHTs)(CO)(PPh_3)]$ (1942 cm^{-1}).[16] The ^1H NMR spectrum of **4** displayed a signal at δ 40.6 ppm, which is tentatively assigned to the imido proton. The imido hydrogen atom has also been located in the Fourier map in a single-crystal X-ray diffraction study.[18] Attempts to prepare a μ-nitrido complex by deprotonation of **4** with bases were unusccessful. No reaction was found when **4** was treated with bases such as Et_3N in benzene-d_6. The reactions of **4** with stronger bases such as $LiN(SiMe_3)_2$ and *n*-BuLi resulted in decomposition of the complex. The structure of **4** consisting of a $\{Ru^{IV}(L_{OEt})Cl_2\}$ moiety and a $\{Ru^{II}(L_{OEt})(PPh_3)(CO)\}$ moiety linked by an NH group is shown in Figure 2. To our knowledge, this is the first ruthenium parent imido complex characterized by X-ray diffraction. The imido group binds to the two ruthenium atoms unsymmetrically with Ru−N distances of 1.818(6) and 1.952(6) Å, suggestive of the Ru^{IV}=N−Ru^{II} bonding description. The Ru^{IV}−N distance in complex **4** is longer than those in ruthenium terminal imido

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(17) Synthesis of **4:** To a solution of complex **1** (72 mg, 0.1 mmol) in toluene (4 mL) was added $[Ru(L_{OEt})(H)(CO)(PPh_3)]$ (93 mg, 0.1 mmol) in toluene (4 mL), and the mixture was stirred at room temperature for 4 h. After the solution was reduced to ca. 1 mL, cool hexane (30 mL) was added to a red solid precipitate of **4** (150 mg, 91%). Red crystals of **4** were obtained from tetrahydrofuran−hexane and were suitable for X-ray diffraction study. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.94 (6H, t, J = 5.6 Hz, CH_3), 1.12 (3H, t, J = 6.8 Hz, CH_3), 1.23−1.42 (24H, m, CH_3), 1.55 (3H, t, J = 6.8 Hz, CH_3), 3.02−3.11 (1H, m, CH_3), 3.25−3.35 (1H, m CH_3), 3.61−3.71 (1H, m, CH_3), 3.89−4.03 (2H, m, CH_3), 4.05−4.90 (19H, m, CH_3), 4.93 (5H, s, Cp), 5.10 (5H, s, Cp), 7.06−7.13 (9H, m, PPh_3), 7.78 (6H, m, PPh_3) 40.6 (1H, s, NH). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ 45.0 (d, $^3J_{PP}$ = 5.2 Hz, PPh_3), 107.5, 108.4, 108.9, 109.4, 109.8, 110.0, 110.7, 111.0, 112.2, 113.2, 113.6, 114.3, 116.8, 117.8, 118.8 (m, L_{OEt}). IR (KBr, cm^{-1}): 1949s (CO). Anal. Calcd for $C_{53}H_{86}C_{12}Co_2NO_{19}P_7Ru_2$: C, 38.61; H, 5.26; N, 0.85; Found: C, 38.75; H, 5.22; N, 0.77.

(18) Crystal data for **4**: $C_{53}H_{86}C_{12}Co_2NO_{19}P_7Ru_2$, M_r = 1648.92, 0.25 × 0.19 × 0.12 mm^3, T = 173(2) K, monoclinic, space group $P2_1/n$, a = 16.3311(11) Å, b = 23.7167(17) Å, c = 18.3823(12) Å, β = 100.870(7)°, V = 6992.1(8) $Å^3$, Z = 4, ρ_{calcd} = 1.566 Mg m^{-3}, μ(Mo Kα) = 9.852 mm^{-1}, θ_{max} = 33.7°; 45 215 reflections collected, and 12 530 unique (R_{int} = 0.1419). The final R1 = 0.0529 and wR2 = 0.0773 [$I > 2.0\,\sigma(I)$]; R1 = 0.1377 and wR2 = 0.0968 (all data); $\rho_{max/min}$ 0.604/−0.426 e $Å^{-3}$. CCDC 771482 (**2**) and 771481 (**4**) contain the supplementary crystallographic data for this paper.

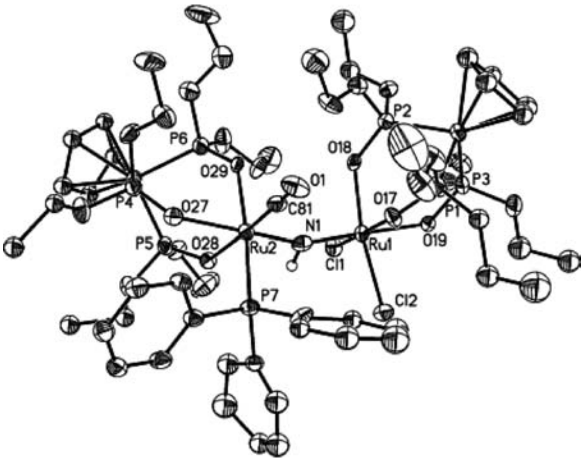
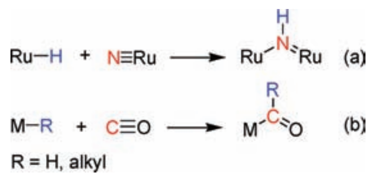


Figure 2. Molecular structure of **4**. Hydrogen atoms, except that with the imido group, are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angle (deg): Ru1−N1 1.818(6), Ru2−N1 1.952(6), Ru1−Cl1 2.3625(19), Ru1−Cl2 2.341(2), Ru2−P7 2.327(2), Ru2−C81 1.833(8), Ru1−O17 2.119(5), Ru1−O18 2.083(5), Ru1−O19 2.143(5), Ru2−O27 2.152(5), Ru2−O28 2.154(4), Ru2−O29 2.165(5); Ru1−N1−Ru2 153.6(3).

complexes such as $[Ru^{II}(\eta^6\text{-}p\text{-cymene})(NC_6H_2t\text{-}Bu_3\text{-}2,4,6)]$ [1.751(14) Å][19] and $[Ru^{VI}(TPP)(NC_6H_3(CF_3)_2\text{-}3,5)_2]$ [1.808(4) Å; TPP = the dianion of 5,10,15,20-tetraphenylporphyrin][20] but shorter than those in reported μ-imido complexes such as $[Ru^{II}(\eta^6\text{-}p\text{-cymene})(\mu\text{-}NC_6H_3i\text{-}Pr_2\text{-}2,6)]_2$ [1.977(7) and 1.959(8) Å].[19] The Ru^{II}−N distance in **4** is shorter than that in $[L_{OEt}(COD)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$ [2.174(5) Å].[16] The Ru^{IV}−N−Ru^{II} unit is bent, with an angle of 153.6(3)°.

Although reactions of electrophilic transition-metal nitrido complexes with nucleophiles have been studied extensively,[5,7d,21−23] to our knowledge, this is the first report of the insertion of a nitrido ligand into a metal−hydrogen bond. It may be noted that insertion of an osmium(VI) nitride into borane B−C and alkene C═C double bonds has been reported.[21] No reaction was found between **3** and $[Os(L_{OEt})(N)Cl_2]$ or $[Re(L_{OEt})(N)(PPh_3)Cl]$,[24] suggesting that the reactivity of ruthenium nitride is critically dependent on the electrophilic character of Ru^{VI}≡N and the ease of Ru^{VI}−Ru^{IV} reduction. Mayer et al. suggested that the Os≡N group of $[Os^{VI}Tp(N)Cl_2]$ [Tp^- = hyridotris(pyrazol-1-yl)borate(1−)] behaves like a π-acid ligand like CO as a result of the low-lying empty Os−N π^* orbitals.[25] In this work, we found that, similar to the migratory insertion of metal−alkyl/hydride with CO, the Ru≡N group inserts into the Ru−H bond to give an imido species (Scheme 2), although different mechanisms are involved in the two types of insertion. It should also be noted that the reaction of **3** with tosylazide yielded the tosylamido complex $[Ru(L_{OEt})(NHTs)(CO)(PPh_3)]$, presumably via insertion of the transient electrophilic tosylnitrene into the Ru−H bond.[16]

Scheme 2. Insertion of (a) Ru≡N into Ru−H and (b) C≡O into M−R/H



^{1}H NMR spectroscopy indicates that the reaction between **1** and **3** is a clean process that does not involve any detectable intermediates. The kinetics for the reaction under pseudo-first-order conditions ([**3**] ≫ [**1**]) has been studied by UV/vis spectroscopy (see the SI). The reaction was found to be first-order in both **1** and **3**, following a rate law of rate = k_2[**1**][**3**]. At 298 K, in a toluene solution, k_2 was determined to be $(7.2 \pm 0.4) \times 10^{-5}$ M^{-1} s^{-1}. The measured entropy of activation of $-(43.3 \pm 11.1)$ eu is suggestive of an associative pathway. The above kinetic data are consistent with a concerted mechanism for the nucleophilic attack of the nitride of **1** by ruthenium(II) hydride.

In summary, we have demonstrated that the electrophilic ruthenium(VI) nitrido complex **1** reacted with main-group and ruthenium(II) hydride compounds to give ammine and μ-imido complexes, respectively. The formation of an imido species from a metal nitride and a metal hydride may play a role in the ruthenium-catalyzed ammonia synthesis.

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Supporting Information Available: Full experimental details, kinetic studies of the reaction of **1** with **3**, and crystallographic data in CIF format and selected bond distances and angles for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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