N–H Activation

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Cleavage of Nitrogen–Hydrogen Bonds of Ammonia Induced by Triruthenium Polyhydrido Clusters**

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N–H bond activation of amines has attracted increasing attention owing to its applicability to the synthesis of various amino compounds, and the development of a new and effective reaction system for the activation of ammonia must be one of the most important research targets in connection with the transformation of abundant and inexpensive ammonia into a useful amino compound.[1] However, successful examples of activation of the N–H bond of ammonia are still rare because of both the high N–H bond dissociation energy ($\approx 104 \pm 2$ kcal mol^{-1})[2] and the difficulty in forming an N–H σ complex.[3]

The groups of Milstein[1g,i,j] and Hartwig[1k,q] showed independently that some mononuclear iridium(I) complexes exhibited activity towards oxidative addition of ammonia. A highly unsaturated 14 e species with T-shaped geometry was proposed as a reactive intermediate for the N–H bond cleavage on the basis of kinetic studies.[1q] Some complexes containing a d^0 metal center, such as $[Cp^*_2MH_2]$ (M = Zr, Hf; Cp* = pentamethylcyclopentadiene),[1b,c,e] $[Cp^*_2ScR]$,[1f] and $[(neopentyl)_3Ta=C(H)(tBu)]$,[1h] also activated ammonia to generate amido and nitrido complexes. There have, thus far, been examples of bimetallic oxidative addition to ammonia. A trinuclear carbonyl cluster, $[Os_3(CO)_{11}(L)]$ (L = *c*-C_6H_8 or CH_3CN), effectively activates ammonia with the participation of the two osmium centers to produce the μ-amido complex $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NH_2)]$.[1a,d]

A multimetallic system may work more efficiently for bond activation than a monometallic complex owing to the cooperative action of the metal centers. Each metal center would be allotted a part as a binding site and an activation site, and the transition state of the bond-activation step may, therefore, be stabilized.

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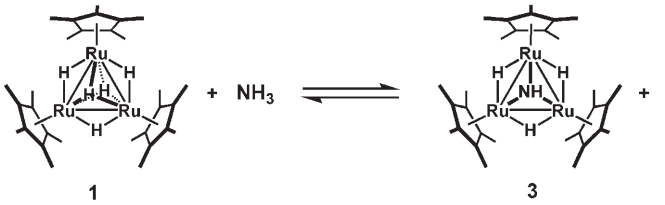
We have thus far demonstrated that a trinuclear pentahydrido complex of ruthenium, $[(Cp^*Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3]$ (**1**) [Eq. (1)], effectively activates a wide spectrum of chemical bonds, such as the C–H bond of alkanes and the N–H and N–N bonds of hydrazines.[4] Herein we report the first example of trinuclear oxidative addition of ammonia to form a μ_3-imido cluster in the reaction of **1** with ammonia. We also demonstrate acceleration of the oxidative addition of ammonia in the reaction with a μ_3-oxo complex, $[(Cp^*Ru)_3(\mu_3\text{-}O)(\mu\text{-}H)_3]$ (**2**) [Eq. (4)].[5]

Complex **1** reacts with ammonia to produce a known μ_3-imido complex, $[(Cp^*Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3]$ (**3**),[4h] and dihydrogen as a result of activation of the two N–H bonds [Eq. (1)].



1 + NH_3 ⇌ 3 + $2\,H_2$ (1)

The reaction is reversible, and treatment of **3** with dihydrogen quantitatively affords **1** and ammonia as reported recently.[4h] Therefore, the reaction reaches a stationary equilibrium when it is carried out in a closed reaction vessel. When the reaction of **1** (8.5×10^{-3} mmol) with ammonia (0.10 mmol) in $[D_8]$THF (0.4 mL) in a sealed tube was monitored by ^{1}H NMR spectroscopy at 80 °C, the reaction reached its equilibrium, **1**/**3** = 70:30, after standing for 3 days. As anticipated, the **1**/**3** ratio improved to 11:89 by reevacuation and recharging with ammonia.

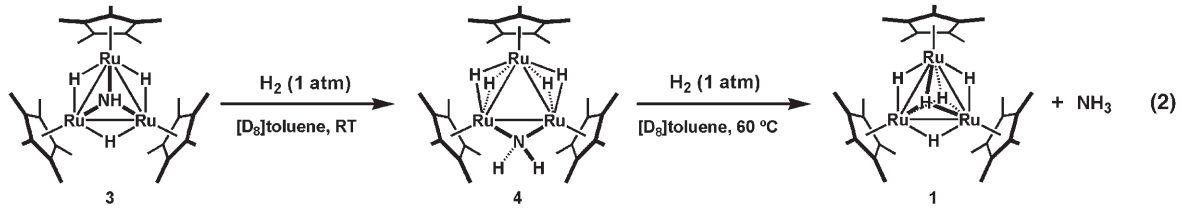
The reaction of **1** with ammonia likely proceeds via an intermediary μ-amido complex, $[(Cp^*Ru)_3(\mu\text{-}NH_2)(\mu\text{-}H)_4]$ (**4**), which would be formed in a sequence of steps, namely, ammonia coordination, N–H bond cleavage, and liberation of dihydrogen. Although no intermediate was detected upon monitoring the reaction by ^{1}H NMR spectroscopy, one plausible intermediate was prepared by partial hydrogenation of **3**.

When the reaction of **3** with dihydrogen (1 atm) in $[D_8]$toluene was monitored by ^{1}H NMR spectroscopy, signals assignable to the newly formed μ-amido complex were observed. The ^{1}H NMR spectrum recorded at −80 °C exhibits two broad signals of the amido hydrogen atoms protons at δ = 2.88 (1H) and 5.09 ppm (1H) and two singlets at $\delta = -17.71$ (2H) and −5.48 ppm (2H) for the metal-bound hydrogen atoms. This clearly indicates the formation of the μ-amido-μ-tetrahydrido complex **4** as a result of the partial hydrogenation of **3**. Two of the four hydrido ligands in **4** probably position on the same side of the μ-amido group with respect to the Ru_3 plane and the rest lies on the opposite side. Upon heating at 60 °C in $[D_8]$toluene, μ-amido complex **4** reacted further with dihydrogen to generate **1** quantitatively [Eq. (2)].

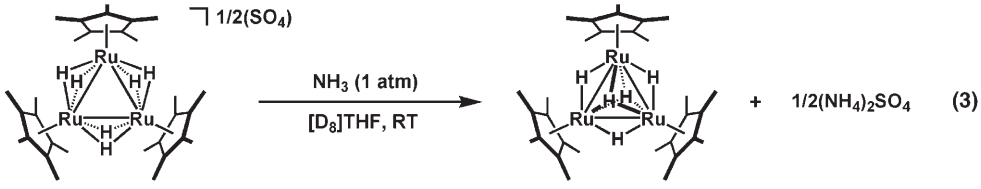
This result suggests that complex **4** is an intermediate species for the formation of μ_3-imido complex **3** from **1** and ammonia through N–H bond activation.

As shown in the reaction of hydrazine with triruthenium polyhydrido complexes **1** and $[(Cp^*Ru)_3(\mu\text{-}H)_6]^1/_2(SO_4)$ (**5**), a decrease in the electron density at the ruthenium center accelerates nucleophilic attack of the hydrazine molecule.[4g,h] On the basis of this observation, we examined the reaction of cationic **5** with ammonia. However, deprotonation to give **1** predominated over nucleophilic attack of ammonia at the metal center because of the protonic character of the hydrido ligand in **5** [Eq. (3)].

A neutral complex that has electron-deficient metal centers would, therefore, be suitable for the promotion of nucleophilic attack of ammonia. Hence we examined the reaction of ammonia with μ_3-oxo complex, $[(Cp^*Ru)_3(\mu_3\text{-}O)(\mu\text{-}H)_3]$ (**2**), in which the electron density of the metal



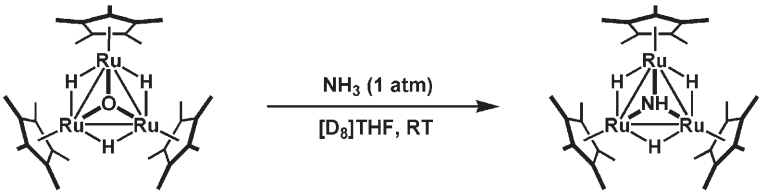
3 → 4 → 1 + NH_3 (2)



5 → 1 quant + $1/2(NH_4)_2SO_4$ (3)

centers should be lower owing to the polarization between the oxygen and the ruthenium atoms, and the hydrido ligands should be less protonic than those in **5**.

The reaction of **2** with ammonia (1 atm) proceeded smoothly even at room temperature to yield **3** quantitatively [Eq. (4)]. Notably, the formation of the water stemming from the μ_3-oxo ligand was confirmed by ^{1}H NMR spectroscopy ($\delta = 2.53$ ppm). The reactivity of **2** is remarkably higher than that of **1**, and the reaction is completed within 1 h at 80 °C.



+ H_2O (4)

We pursued a kinetic study by means of ^{1}H NMR spectroscopy to gain insight into the reaction paths. The entropy and the enthalpy of activation were estimated at -23.0 cal K^{-1} mol^{-1} and 16.7 kcal mol^{-1}, respectively. The relatively large and negative value of the entropy of activation implies that the reaction proceeds through an associative mechanism, and the initial step, namely incorporation of ammonia into the reaction site, is probably the rate-determining step. This is consistent with what we mentioned for the reaction of **1** with 1,1-dimethylhydrazine (-23.0 cal K^{-1} mol^{-1}) and phenylhydrazine (-22.7 cal K^{-1} mol^{-1}):[4g] these hydrazine molecules would be captured into the Ru_3 core from the less bulky $-NH_2$ terminus. The fact that no intermediate was observed when the reaction was monitored at room temperature by ^{1}H NMR spectroscopy also indicates that the initial step of the reaction, namely capture of the ammonia molecule, is the rate-determining step.

In contrast to the reaction with **2**, the reaction of ammonia with a bis(μ_3-oxo) complex, [(Cp*Ru)$_3$(μ_3-O)$_2$(μ-H)] (**6**),[5] resulted in the recovery of the starting complex **6**. This result implies that protonation of the bridging oxygen atom does not take place in the initial step of the reaction and that the presence of the vacant space on the opposite face of the μ_3-oxo ligand with respect to the Ru_3 plane is essential for the promotion of the reaction.

A key feature of this reaction system is that complex **2** is coordinatively unsaturated (46 e) and has a triply bridging oxo ligand. The ammonia molecule would be easily accessible to the reaction site owing to the coordinative unsaturation. The bridging oxo ligand induces polarization of charge between the ruthenium and the oxygen atoms and, as a result, accelerates the nucleophilic attack of ammonia at the ruthenium atom. Furthermore, formation of water would make the reaction exothermic and irreversible.[2] Thus, introduction of the μ_3-oxo ligand into the Ru_3 core makes the reaction not only kinetically but also thermodynamically favorable.

In summary, we have shown that triruthenium pentahydrido complex **1** exhibits considerable activity towards N–H bond cleavage of ammonia and that the introduction of a triply bridging oxo ligand into the Ru_3 core significantly enhances the activity. Although there have been, thus far, several successful examples of the activation of ammonia, this is to our knowledge the first example of "double activation" of ammonia. We are currently investigating a new catalytic process that takes full advantage of this feasible N–H bond cleavage of ammonia.

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[2] H_2NNH_2 ($D_{NH} = 76 \pm 2$ kcal mol^{-1}), NH_3 ($D_{NH} = 104 \pm 2$ kcal mol^{-1}), H_2O ($D_{OH} = 119.2 \pm 0.2$ kcal mol^{-1}): *Lange's Handbook of Chemistry*, *13th ed.* (Eds.: N. A. Lange, J. A. Dean), McGraw-Hill, New York, **1985**, pp. 3–131.

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