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Hydrogenation of a Trinuclear μ_3-Imido Complex of Ruthenium: Homolytic or Heterolytic H–H Bond Cleavage?

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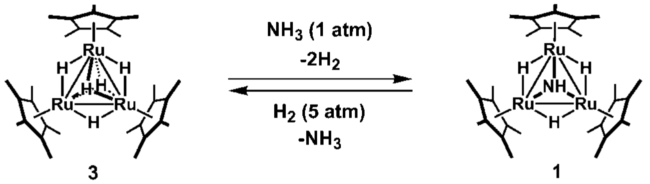
Keywords: Hydrido complexes / Ruthenium / Cleavage reactions / Imido complexes / Trinuclear complexes

To elucidate the mode of hydrogen–hydrogen bond cleavage at transition metal sites that cooperate with a heteroatom, the hydrogenation of trinuclear μ_3-imido complex $(Cp^*Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) with deuterium was carried out. The percentage of deuterium content in the amido ligand of $(Cp^*Ru)_3(\mu\text{-}NH_2)(\mu\text{-}H)_4$ (**2**), which was generated as an intermediate in the reaction of **1** with dihydrogen, proved that hydrogenation of **1** to **2** proceeded through homolytic cleavage of dihydrogen.

Introduction

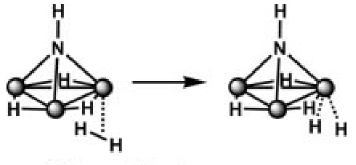
Activation of dihydrogen at transition metal sites is a critical issue in a wide field ranging from inorganic and organometallic chemistry to enzymology.[1] One focus of interest is the mode of hydrogen–hydrogen bond cleavage. Two possible pathways, namely homolysis and heterolysis, are proposed for the activation of dihydrogen. H–H bond cleavage by oxidative addition of dihydrogen to the metal center to form a dihydridometal species is a typical example of homolysis. In contrast, [FeFe]- and [FeNi]hydrogenase, of which the active site consists of iron and nickel ions bridged by two sulfur atoms and another heteroatom, is recognized to activate dihydrogen in a heterolytic manner to generate hydride and a proton.[2] In connection with the enzymatic reaction, the reaction of dihydrogen with a complex whose metal center cooperates with a heteroatom has engaged the attention of inorganic chemists.[3]

We have reported, thus far, that the reaction of triruthenium pentahydrido complex, $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**), with ammonia or hydrazine leads to the formation of the corresponding mono(μ_3-imido) complex, $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}NH)$ (**1**).[4,5] The resulting μ_3-imido complex **1** readily undergoes hydrogenation with 5 atm of dihydrogen to afford **3** and ammonia, quantitatively (Scheme 1).

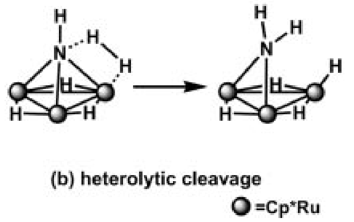


Scheme 1. Activation of N–H bonds of ammonia by trinuclear polyhydrido cluster **3** and hydrogenolysis of μ_3-imido complex **1**.

Complex **1** has a Lewis basic nitrogen atom directly bound to the ruthenium center and it would be of interest to determine whether the hydrogenation reaction proceeds by way of homolytic cleavage of dihydrogen at one of the ruthenium atoms or by heterolytic cleavage with participation of the adjacent nitrogen atom (Figure 1). In the homolysis step with the use of deuterium instead of hydrogen (Figure 1a), the deuterium molecule can access the ruthenium atom from the opposite face of the μ_3-NH ligand with respect to the Ru_3 plane as a result of the decreased steric hindrance; therefore, the deuterium molecule can undergo oxidative addition to form a dideuterido species. Alternatively, a deuterium molecule approaching the reaction site from the NH-bridged face might be expected to undergo heterolytic cleavage by interaction with both the nitrogen and ruthenium atoms (Figure 1b). We report herein a mech-



(a) homolytic cleavage



(b) heterolytic cleavage

Figure 1. Activation of dihydrogen on the metal imido cluster.

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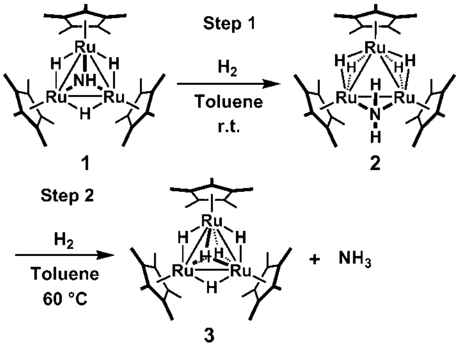
anistic study of the hydrogenation of μ_3-imido complex **1** where deuterium-labeling experiments showed conclusively that the reaction proceeds through oxidative addition of deuterium to the ruthenium atom.

Results and Discussion

Hydrogenation of μ_3-imido complex **1** proceeds via intermediary μ-amido complex **2**.[5] The reaction of **1** with 1 atm of hydrogen at room temperature was monitored by ^{1}H NMR spectroscopy, and the formation of μ-amido complex **2** was revealed; the yields of **2** and pentahydride **3** reached 91 and 6%, respectively, after 170 h. Intermediary μ-amido complex **2** underwent subsequent hydrogenation at 60 °C for 90 h to lead to the quantitative formation of **3** and ammonia (Scheme 2).



Scheme 2. Stepwise hydrogenolysis of μ_3-imido cluster **1** to generate **3** and NH_3 via μ-amido cluster **2**.

Compound **2** was isolated by crystallization from a cold (–30 °C) toluene solution of a mixture of **1**, **2**, and **3**. The structure of compound **2** was determined by an X-ray diffraction study with the use of a single crystal that was obtained from the NMR sample solution (Figure 2). The nitrogen atom of the amido ligand is located above the plane defined by the three ruthenium atoms. Notably, one of the hydrogen atoms attached to the nitrogen atom, H_A, is located inside the Ru_3N core and the other hydrogen atom, H_B, is located outside the Ru_3N core. The broad resonance signals which appeared at δ = 2.86 and 5.05 ppm in the ^{1}H NMR spectrum of **2** recorded at –60 °C were assigned to H_A and H_B, respectively, on the basis of shielding/deshielding effects of the aromatic ring current. The resonance signal of the proton located inside the Ru_3N core is shielded by the ring current, and as a result it is shifted upfield. Variable temperature ^{1}H NMR spectra exhibited broadening of signals for both H_A and H_B and a reduction in the difference of the chemical shifts between these two μ-amido protons along with the rise in temperature. This showed the site-exchange between H_A and H_B, possibly by a pivot motion (Scheme 3), and was confirmed by an SST experiment.[6] This type of dynamic process, namely, in-to-out site-exchange of protons, was reported for several trinuclear transition-metal clusters.[7]

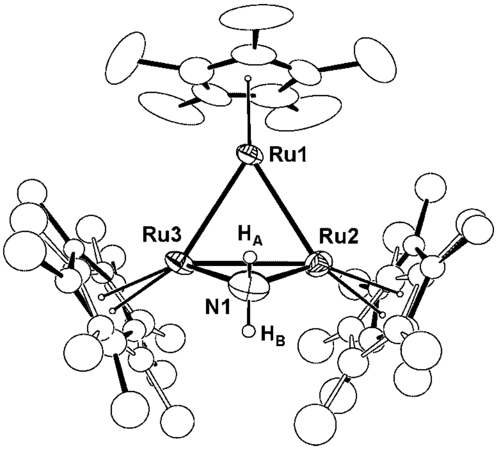
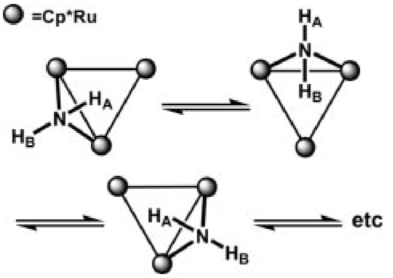


Figure 2. Molecular structure of μ-amido complex **2** with thermal ellipsoids at the 30% probability level.



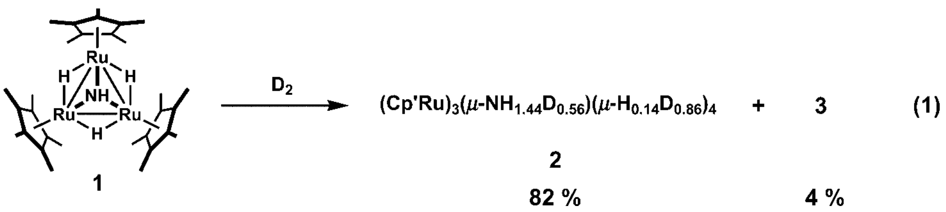
Scheme 3. Exchange of the sites between H_A and H_B.

Two sets of hydrido ligands of **2** exchange the coordination site with each other, and their resonance signals coalesce around room temperature. The enthalpy and entropy of activation for this exchange process were estimated at $\Delta H^{\ddagger} = 12.6 \pm 0.6\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\ddagger} = 3.6 \pm 0.1\ \mathrm{cal\,mol^{-1}\,K^{-1}}$, respectively, on the basis of line-shape analysis with the use of a *g*-NMR program package (vide infra). Interestingly, the hydrido ligands and the amido hydrogen of **2** do not undergo coordination site-exchange whereas the hydrido ligands mutually exchange the coordination sites. It should be noted that there is also no site-exchange process between the imido hydrogen and the hydrido ligands in **1**.

As mentioned above, amido complex **2** reacted with 1 atm of hydrogen to afford **3** with an equimolar amount of ammonia. In contrast, complex **2** underwent disproportionation to yield **1** and **3** in the absence of hydrogen, but the conversion of **2** is at most 4% after 120 h at room temperature.

On the basis of the above observations, the reaction of **1** with deuterium was examined to elucidate the mode of hydrogen activation in the hydrogenolysis of the ruthenium–nitrogen bond. The reaction was monitored by ^{1}H NMR spectroscopy, and the product and isotopomer ratios were estimated on the basis of the integral intensity of the resonance signals.[8]

The reaction of μ_3-imido complex **1** with 1 atm of deuterium in [D_8]toluene was monitored at ambient temperature by ^{1}H NMR spectroscopy by using cyclooctane (δ =



1.49 ppm, [D$_8$]toluene, 23 °C) as an internal standard. Conversion of **1** reached 86% after 125 h, and the molar ratio among **1**, μ-amido complex **2**, and pentahydrido complex **3** was 14:82:4 [Equation (1)].

In the hydrido region of the ^{1}H NMR spectrum, two singlet peaks assignable to the signal of the hydrido ligands of isotopomers (Cp*Ru)$_3$(μ-H)$_2$(μ-D)(μ$_3$-NH) (**1**-d_1) and (Cp*Ru)$_3$(μ-H)(μ-D)$_2$(μ$_3$-NH) (**1**-d_2) appeared at δ = –14.51 and –14.73 ppm, respectively. Notably, the hydrido signal of isotopomer **1**-d_0 (δ = –14.30 ppm) disappeared. Although the hydrido signal of isotopomer (Cp*Ru)$_3$(μ-D)$_3$(μ$_3$-NH) (**1**-d_3) was, of course, not observable, the amount of **1**-d_3 formed in the reaction was unambiguously estimated on the basis of the integral intensity ratio between the Cp* proton signal and the hydrido signals. As a result, the isotopomer ratio **1**-d_0/**1**-d_1/**1**-d_2/**1**-d_3 was estimated at 0:1:4:9, and the percentage of deuterium content in the hydrido ligand of unconverted **1** was 86%. Here, it should be stressed that the hydrogen of the imido ligand was not replaced by deuterium at all, and this clearly shows the absence of a direct exchange process between the hydrogen at the imido nitrogen and atmospheric deuterium.

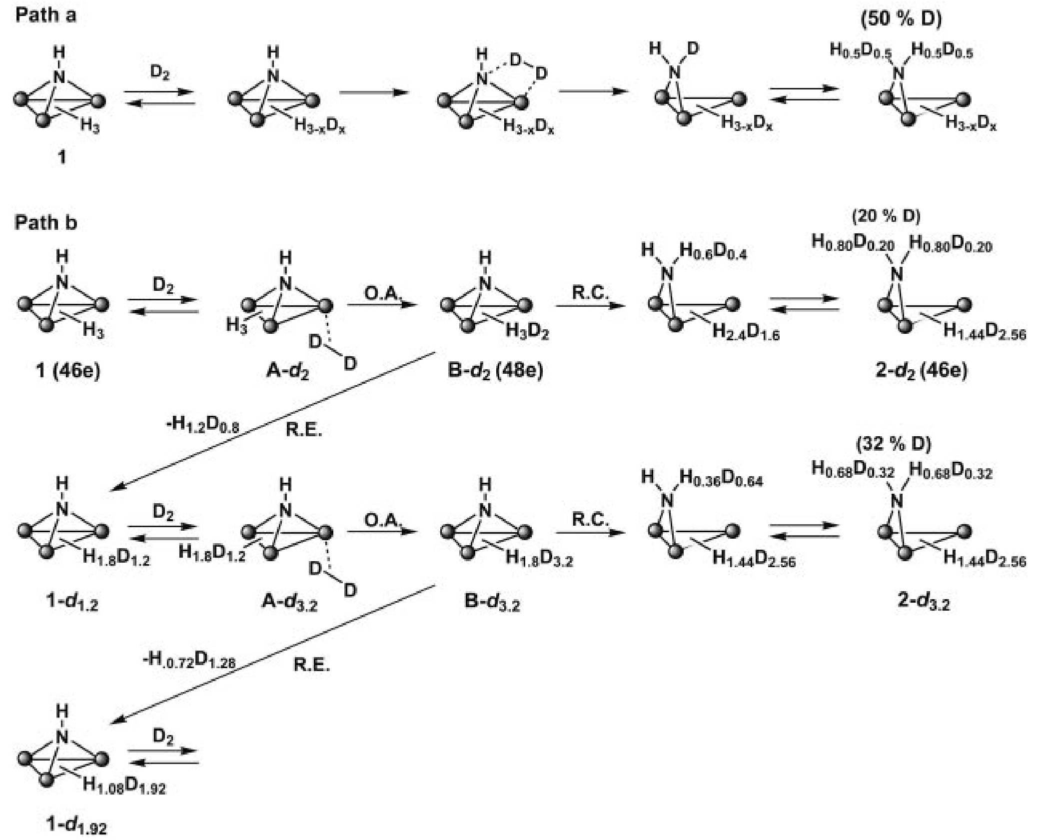
Conversely, the integral intensity of the signal for the amido proton of **2** formed in the reaction was 1.44 H, and the percentage of deuteration for the amido proton was estimated to be 28%, whereas that for the hydrido ligand was estimated at 86% (0.56 H). Interestingly, the percentage of deuteration was practically equal for both amido signals at δ = 2.86 and 5.05 ppm. This strongly supports the presence of a dynamic process, such as a pivot-motion mentioned above, which exchanges the site of the two amido protons, H$_A$ and H$_B$.

We then examined the reaction of **2**, which was isolated in the reaction of **1** with dihydrogen, with deuterium. The reaction of **2** with deuterium (1 atm) was monitored by ^{1}H NMR spectroscopy with the use of cyclooctane as an internal standard. The reaction proceeded slowly at ambient temperature, and the conversion yield from **2** to **3** is at most 4% after 280 h. The hydrido ligand of unconverted amido complex **2** was partially deuterated, and the percentage of deuteration of the hydrido ligand was estimated at 74%. In contrast to the hydrido ligand, the integral intensity of the amido proton signal remained almost unchanged despite a long reaction time, and the percentage of deuteration was estimated at less than 5%.

These results show that there is not any direct exchange process between the hydrogen atom of the amido ligand and atmospheric deuterium. According to these observations, we concluded that the deuterium was incorporated into the amido ligand of **2** through hydrogenolysis of the Ru–N bond of **1**, which involves the heterolytic activation of D$_2$ (path **a**) or through reductive coupling between the imido group and the deuterido ligand formed as a result of the homolytic activation, namely, oxidative addition of D$_2$ (path **b**). The two possible reaction paths are shown in Scheme 4.

If hydrogenation of **1** proceeded by path **a**, the percentage of deuteration of the amido ligand should be 50%. This value is far from the observed one, and path **a** should, therefore, be disregarded.

Path **b** involves the formation of μ$_3$-imido-pentahydrido species **B**. The formation of 48e species **B** is rationalized because the H/D exchange reaction between the hydrido ligand of **1** and D$_2$ likely proceeds through an associative pathway rather than a dissociative path by way of an intermediary μ$_3$-imido-monohydrido species (44e). In the first stage, deuterium would oxidatively add to μ$_3$-imido complex **1** via an intermediary σ-D$_2$ complex to generate isotopomer **B**-d_2 (48e), in which the coordination sites were exchanged between the deuterides and the hydrides. As a result, the deuterium atom would scramble around the coordination sites for the hydrido ligand. Rapid scrambling of the deuterido ligand is proved by the fact that the ^{1}H NMR spectroscopic signals for the three C$_5$Me$_5$ groups are observed to be equivalent at any percentage of deuterium content in **1**-d_n. Isotopomer **B**-d_2 would then undergo reductive coupling between the imido nitrogen and the hydrido ligand to yield μ-amido complex **2**-d_2. The percentage of deuterium content in the amido ligand should, therefore, be 20% (0.4 D/2 H). In contrast, the liberation of hydrogen (H$_{1.2}$D$_{0.8}$) from **B**-d_2 affords μ$_3$-imido complex **1**-$d_{1.2}$. Isotopomer **1**-$d_{1.2}$ would react again with deuterium to generate **2**-$d_{3.2}$, which should contain 0.64 D (32% deuterium content) at the amido nitrogen atom. The observed value of 28% for the percentage of deuterium content in the amido ligand in **2** is approximately consistent with that anticipated for the reaction paths involving homolytic activation, namely, oxidative addition of deuterium. This is strongly supported by the time-course of the yield of **2** and the percentage of deuterium content in the amido ligand (Figure 3). The percentage of deuterium content is about 20% in the early stage of the reaction, and grows gradually along with the progress of the reaction. The deuterium content finally reached 28% after 125 h. Path **b** rationally accounts for these results.



Scheme 4. Plausible mechanism for the reaction of **1** with D_2.

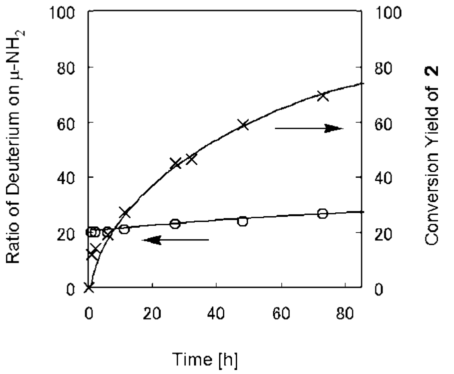


Figure 3. Time conversion regarding the reaction of **1** with D_2 (×: conversion yield of **2**, ○: the percentage of deuteration for the amido proton).

Conclusion

We have experimentally elucidated that hydrogenation of triruthenium μ_3-imido complex **1** to yield μ-amido complex **2** (Step 1, Scheme 2) proceeds through homolytic cleavage of dihydrogen. However, the reaction path for the hydrogenation of **2** to form **3** and ammonia (Step 2, Scheme 2) still remains unclear. Theoretical study is now in progress by using $[(C_5H_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{-}NH)$ as a model compound.

Experimental Section

General Procedure: The compounds described below were handled under an argon atmosphere with rigorous exclusion of air and water by using Schlenk techniques. Dihydrogen and deuterium were obtained from Fujii Co. Ltd., and no further purification was performed. $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}NH)$ (**1**), $(Cp^*Ru)_3(\mu\text{-}H)_4(\mu\text{-}NH)$ (**2**), and $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**3**) were prepared as described previously.[4,5] [D_8]toluene was dried with sodium benzophenone ketyl and distilled under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded with a Varian INOVA 400 Fourier transform spectrometer with tetramethylsilane as an internal standard.

Reaction of $(Cp^*Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3$ (1) with H_2. Formation of μ-Amido Complex 2: An NMR sample tube equipped with a Teflon stopcock was charged with **1** (6.1 mg, 0.0084 mmol), [D_8]toluene (0.4 mL), and cyclooctane (1 μL) as an internal standard. The sample tube was evacuated at –196 °C, and atmospheric pressure of dihydrogen (2.6 mL, 0.12 mmol) was introduced. The reaction was performed at room temperature and monitored by ^1H NMR spectroscopy. After 170 h, $(Cp^*Ru)_3(\mu\text{-}NH_2)(\mu\text{-}H)_4$ (**2**) and $(Cp^*Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**3**) were formed in 91 and 6% yield, respectively. The reaction was further carried out at 60 °C for 90 h to generate **3** quantitatively. Data for **2**: ^1H NMR (400 MHz, [D_8]toluene, –80 °C, TMS): δ = –17.71 (s, 2 H, Ru-*H*), –5.48 (s, 2 H, Ru-*H*), 1.81 (s, 30 H, Cp*-*Me*), 2.06 (s, 15 H, Cp*-*Me*), 2.88 (br. s, 1 H, $w_{1/2}$ = 10.5 Hz, N-*H*), 5.09 (br. s, 1 H, $w_{1/2}$ = 10.4 Hz, N-*H*) ppm. ^1H NMR (400 MHz, [D_8]toluene, 80 °C, TMS): δ = –11.83 (br. s, 4 H, $w_{1/2}$ = 45.2 Hz, Ru-*H*), 1.76 (s, 30 H, C_5Me_5), 1.96 (s, 15 H, C_5Me_5), 2.78 (br. s, 1 H, $w_{1/2}$ = 20.5 Hz, N-*H*), 4.85 (br. s, 1 H,

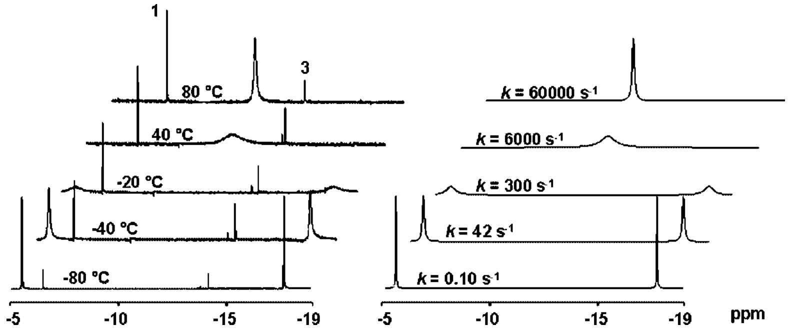


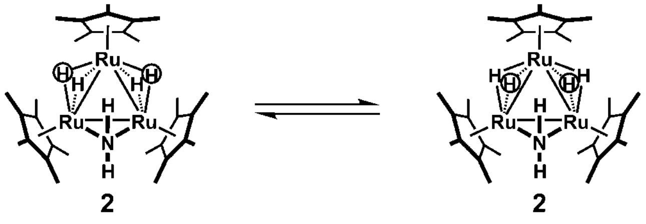
Figure 4. Experimental (left) and simulated (right) variable-temperature ^{1}H NMR spectra of **2**, which shows the region of the hydride protons.

$w_{1/2}$ = 20.3 Hz, N-*H*) ppm. ^{13}C NMR (100 MHz, [D$_8$]toluene, 23 °C, TMS): δ = 12.4 (q, J_{CH} = 125.6 Hz, Cp*-*Me*), 13.2 (q, J_{CH} = 125.4 Hz, Cp*-*Me*), 84.1 (s, Cp*-ring), 85.1 (s, Cp*-ring) ppm. $C_{30}H_{51}N_1Ru_3$ (728.9): calcd. C 49.57, H 6.79, N 1.92; found C 49.22, H 6.81, N 2.03.

X-ray Diffraction Studies: A single crystal of **2** for X-ray analysis was obtained directly from the preparations described above and mounted on glass fibers. The diffraction experiment was performed with a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at 173 K within 3.28° < θ < 27.48°. Cell refinement and data reduction were performed with the PROCESS-AUTO program.[9] Intensity data were corrected for Lorentz-polarization effects and for empirical absorption. The structure of **2** was solved by the Patterson method by using the SHELX-97 program package.[10] All non-hydrogen atoms were found by the difference Fourier synthesis and were refined anisotropically except for the disordered atoms described below. The refinement was carried out by least-squares methods based on F^2 with all measured reflections. For **2**, disorder at Cp* ligands bonded at Ru(2) and Ru(3) were refined in the ratio of 40:60. Crystal data for **2**: monoclinic, space group $P2_1/n$ (No. 14), a = 11.9713(10), b = 11.7390(10), c = 22.540(2) Å, β = 102.602(8)°, V = 3091.3(5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.566 Mg m^{-3}, $\mu(\mathrm{Mo}_{K\alpha})$ = 1.464 mm^{-1}, of the 24614 reflections that were collected, 7410 were unique (R_{int} = 0.0981), R_1 = 0.1089 [$I > 2\sigma(I)$], wR_2 = 0.3149 [$I > 2\sigma(I)$], GOF = 1.250, $\Delta\rho_{min/max}$ = +4.030/–1.855 e Å^{-3}. CCDC-630784 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of 2 by Variable-Temperature ^{1}H NMR Spectroscopy: An NMR sample tube equipped with a Teflon stopcock was charged with **2** (10.2 mg, 0.0014 mmol), [D$_8$]toluene (0.5 mL), and cyclooctane (1 μL) as an internal standard. Figure 4 shows the ^{1}H NMR spectra (hydride region) of **2** at variable temperatures. The signals on the left-hand side are the experimental set, and the right-hand side shows the signals simulated. The activation parameters were estimated by line-shape analysis using the g-NMR program. Temperature dependence of the rate constants gave activation parameters $\Delta H^\ddagger$ = 12.6 ± 0.6 kcal mol^{-1}, $\Delta S^\ddagger$ = 3.6 ± 0.1 cal mol^{-1} K^{-1}, and $\Delta G^\ddagger$ = 13.2 ± 0.6 kcal mol^{-1}. This exchange process is shown in Scheme 5.

Thermolysis of 2: An NMR sample tube equipped with a Teflon stopcock was charged with **2** (8.1 mg, 0.011 mmol), [D$_8$]toluene (0.4 mL), and cyclooctane (1 μL) as an internal standard. The reaction was performed at room temperature and monitored by ^{1}H NMR spectroscopy. After 120 h, the ^{1}H NMR spectrum showed that **2** underwent disproportionation to afford **1** and **3**, both in 2% yield.



Scheme 5. Coordination site exchange between the two sets of hydrido ligands of **2**.

Reaction of Complex 1 with Molecular Deuterium: An NMR sample tube equipped with a Teflon stopcock was charged with **1** (8.3 mg, 0.011 mmol), [D$_8$]toluene (0.4 mL), and cyclooctane (1 μL) as an internal standard. The sample tube was evacuated at –196 °C, and atmospheric pressure of molecular deuterium (2.6 mL, 0.12 mmol) was introduced. The reaction was performed at room temperature and monitored by ^{1}H NMR spectroscopy. After 125 h, the ^{1}H NMR spectrum showed the formation of **1**, **2**, and **3** in 14, 82, and 4% yield, respectively. The percentages of deuteration of unconverted **1** for the imido proton and the hydrido ligand were estimated at 0 and 86%, respectively. The percentages of deuteration of **2** for the amido proton and the hydrido ligand were estimated at 28 and 86%, respectively.

Reaction of Complex 2 with Molecular Deuterium: An NMR sample tube equipped with a Teflon stopcock was charged with **2** (7.5 mg, 0.010 mmol), [D$_8$]toluene (0.4 mL), and cyclooctane (1 μL) as an internal standard. The sample tube was evacuated at –196 °C, and atmospheric pressure of molecular deuterium (2.6 mL, 0.12 mmol) was introduced. The reaction was performed at room temperature and monitored by ^{1}H NMR spectroscopy. After 280 h, the ^{1}H NMR spectrum showed the formation of **2** and **3** in 96 and 4% yield, respectively. The percentage of deuteration of **2** for the hydrido ligand was estimated at 74%, and that for the amido proton was estimated at less than 5%.

Acknowledgments

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[6] The spin saturation transfer experiment was carried out at 80 °C with complex **2**. It was observed that irradiation of the amido peak at $\delta = 2.78$ ppm led to an approximately 80% decrease in intensity of another N–H signal at $\delta = 4.85$ ppm in the ^{1}H NMR spectrum. This observation can be interpreted to result from an in-to-out exchange process of the protons.

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[8] The longitudinal relaxation time T_1 of the amido proton signals at $\delta = 2.88$ and 5.09 ppm are 313 and 323 ms, respectively, at room temperature. The signals are sharpened at low temperature. We, therefore, recorded the ^{1}H NMR spectra at –80 °C with a relaxation delay (D1) of 10 s.

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