Reductive Cleavage of the N−N Bond of Hydrazine Induced by a Cationic Trinuclear Ruthenium Hexahydride Complex, $[(Cp'Ru)_3(\mu\text{-}H)_6]X$ ($Cp' = \eta^5\text{-}C_5Me_5$; $X = {}^1/_2\ SO_4, BF_4, PF_6, BPh_4$) and Dihydrogen

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The reaction of the monocationic triruthenium hexahydride $[(Cp'Ru)_3(\mu\text{-}H)_6]X$ (**1**; $X = {}^1/_2$ SO_4, BF_4, PF_6, BPh_4) with hydrazine leads to the formation of the mono(μ_3-imido) complex $(Cp'Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3$ (**3**) and the triruthenium pentahydride complex $(Cp'Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**2**). Complex **1** is in equilibrium with **2** in the presence of NH_4X or N_2H_5X, and complex **1** is regenerated upon treatment of **2** with such a protic salt. Complex **3** further reacts with hydrazine to yield the bis(μ_3-imido) complex $(Cp'Ru)_3(\mu_3\text{-}NH)_2(\mu\text{-}H)$ (**4**) as a result of cleavage of the nitrogen−nitrogen bond, which is formally catalyzed by a proton. Both **3** and **4** undergo hydrogenation to generate **2** together with ammonia. Thus, reductive cleavage of the nitrogen−nitrogen bond of hydrazine leading to ammonia is achieved by the use of the monocationic trinuclear hexahydride complex **1** and dihydrogen under conditions without any added proton source and a reducing agent.

Introduction

Despite a vast amount of research on nitrogenase and isolable transition-metal dinitrogen complexes, few details are known about how the nitrogen−nitrogen bond of dinitrogen is cleaved to give ammonia.[1,2] With regard to dinitrogen reduction by a metalloenzyme, much attention is now focused on transition-metal complexes of diazene and hydrazine. The N−N bond cleavage of hydrazines is a crucial step to attain the dinitrogen reduction from N_2 to NH_3.

The N−N bond cleavage has, thus far, been studied using many low-valent molybdenum and tungsten complexes.[3] On the other hand, Schrock revealed that the N−N single bond could be cleaved by using a tungsten complex having a Cp^*WMe_3 fragment, which is in a relatively high oxidation state.[4] Evans also reported the N−N bond cleavage of hydrazine derivatives on $Cp'_2Sm(THF)$.[5] Talarmin and co-workers investigated the transformation of hydrazine and its derivatives in detail by the use of a thiolato-bridged dimolybdenum complex, $Mo_2Cp_2(\mu\text{-}SMe)_3$ ($Cp = \eta^5\text{-}C_5H_5$), and provided good insight into the nitrogen activation by metalloenzymes.[6] In this system, the N−N double bond of PhN═NH is readily cleaved on the bimetallic molybdenum core by protonation coupled with electrochemical reduction.

The catalytic reduction of hydrazine has engaged the special attention of both inorganic and organometallic chemists.[7] Block et al. developed a catalytic reduction of hydrazine to produce ammonia (TON = ca. 1000) by using a sulfide-bridged dinuclear molybdenum complex, $[Mo_2Cl_4(2\text{-}SC_5H_3NH\text{-}3\text{-}SiPr^i{}_3)_2(\mu\text{-}S_2)(\mu\text{-}2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)]$, as a catalyst.[8] In this reaction, reduction of hydrazine was achieved via successive protonation and reduction using lutidine−HCl and Zn amalgam as a proton source and reducing agent, respectively. Most of the reduction systems of hydrazine reported thus far require both a reducing agent and a proton source together with a transition-metal complex as a catalyst. Otherwise, disproportionation proceeds, resulting in a decrease in selectivity of ammonia formation.

Recently, we have demonstrated the N−N bond cleavage of substituted hydrazines, such as methylhydrazine and phenylhydrazine, using a neutral polyhy-

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dride cluster.[9] For example, a bis(μ_3-imido) complex, (Cp′Ru)$_3$(μ_3-NMe)(μ_3-NH)(μ-H), is selectively formed in the reaction of (Cp′Ru)$_3$(μ-H)$_3$(μ_3-H)$_2$ (**2**) with MeNHNH$_2$ at elevated temperature. Detailed studies on the reaction mechanism indicated that the nitrogen−nitrogen bond cleavage was achieved by the cooperative action of the adjacent metal atoms. Namely, one of the three metals likely played the role of a binding site and another metal center took the part of an active site. Thus, polyhydride clusters such as [(Cp′Ru)$_3$(μ-H)$_6$](X) (**1**; X = monoanion such as BF$_4^-$) and (Cp′Ru)$_3$(μ-H)$_3$-(μ_3-H)$_2$ (**2**) were proved to be active for cleavage of chemically inert bonds, such as C−H and N−N bonds, and are possibly applicable to the nitrogen−nitrogen bond cleavage of unsubstituted hydrazine, NH$_2$NH$_2$.

As demonstrated so far, notable features of the transition-metal polyhydride clusters are the capabilities for multiple coordination of a substrate, multielectron transfer between the substrates, and hydrogen donation to the substrate. Accordingly, the trinuclear pentahydride complex of ruthenium [(Cp′Ru)$_3$(μ-H)$_6$](X) (**1**) is expected to be active for the nitrogen−nitrogen bond cleavage of hydrazine in the absence of both a proton source and a reducing agent. In this regard, there have been some research using a polyhydride cluster as an activator of the nitrogen−nitrogen bond of hydrazine and dinitrogen.[10]

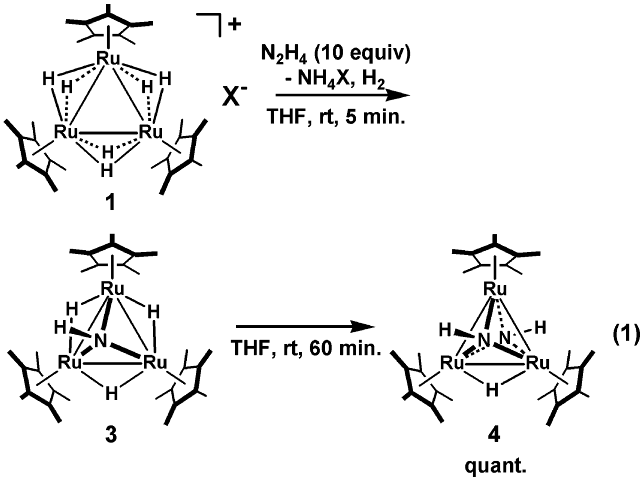
Here, we report effective reductive cleavage of the nitrogen−nitrogen bond of hydrazine leading to ammonia by the use of a monocationic trinuclear hexahydride complex, [(Cp′Ru)$_3$(μ-H)$_6$]X (**1**), in the absence of a proton source and a reducing agent.

Results and Discussion

Reaction of [(Cp′Ru)$_3$ (μ-H)$_6$]X (1) with Hydrazine. We previously demonstrated that the triruthenium pentahydride (Cp′Ru)$_3$(μ-H)$_3$(μ_3-H)$_2$ (**2**) reacted with substituted hydrazines such as PhNHNH$_2$ and MeNHNH$_2$ at elevated temperature to result in the formation of a bis(μ_3-imido) complex as a result of selective cleavage of the nitrogen−nitrogen bond. In contrast, a similar μ_3-imido complex was not formed in the reaction of complex **2** with the parent hydrazine N$_2$H$_4$. Disproportionation giving nitrogen and ammonia took precedence over the formation of a similar μ_3-imido complex upon heating, although no reaction proceeded at room temperature.

It is anticipated that a cationic hydride cluster is likely suitable for the incorporation of weakly basic hydrazine into its reaction field. The reaction of a monocationic hexahydride cluster, [(Cp′Ru)$_3$(μ-H)$_6$]X (**1**; X = $^1/_2$ SO$_4$, BF$_4$, PF$_6$), with hydrazine was, therefore, examined and proved that complex **1** was highly reactive toward the nitrogen−nitrogen bond cleavage of hydrazine.

The reaction of **1** with 10 equiv of N$_2$H$_4$ readily proceeded at room temperature in tetrahydrofuran (eq 1).



After 5 min, the solution turned dark green and ultimately turned dark orange after additional stirring for 60 min. Removal of the solvent under reduced pressure quantitatively afforded a bis(μ_3-imido) complex, (Cp′Ru)$_3$(μ_3-NH)$_2$(μ-H) (**4**). Color changes of the solution during the reaction imply the formation of an intermediate. An intermediate mono(μ_3-imido) complex, (Cp′Ru)$_3$(μ_3-NH)(μ-H)$_3$ (**3**), was isolated when the reaction of **1** with 3 equiv of hydrazine was terminated after about 10 min by removal of the solvent in vacuo. Dihydrogen formed in the reaction was detected by means of ^{1}H NMR spectroscopy when the reaction was conducted in the NMR sample tube, and formation of the ammonium salt was detected by the indophenol method.[11]

Complexes **3** and **4** formed in the reaction of **1** with hydrazine were identified by comparing their NMR spectral data with those of the authentic samples prepared independently. The mono(μ_3-imido) complex **3** is alternatively derived from **2** by a reaction with Me$_3$SiN$_3$ in the presence of methanol.[12] The bis(μ_3-imido) complex **4** is independently obtained by the treatment of **3** with methylhydrazine or phenylhydrazine in tetrahydrofuran at 100 °C.[9] Complex **3** displays the resonance signals for the Cp′ groups and the hydride ligands at δ 1.89 and −14.22, respectively, in an intensity ratio of 45H:3H. For complex **4**, its ^{1}H NMR spectrum exhibits two singlets for the Cp′ ligands at δ 1.86 and 1.92 in an intensity ratio of 1:2 and a singlet for the hydride ligand at δ −19.27.

The reaction of **1** with hydrazine was monitored by ^{1}H NMR spectroscopy. The reaction in the NMR sample tube is more retarded than that in the Schlenk tube because of the low efficiency of stirring. As a result, an intermediate was possibly detected. The molar ratio of each complex observed during the reaction was calculated on the basis of the integral intensity of the hydride signals, and the resulting time−distribution curves are shown in Figure 1. The time−distribution curves clearly show that the reaction proceeds consecutively by way of the intermediate **3**. The neutral triruthenium pentahydride **2** was formed immediately after the beginning of the reaction. The distribution of **2** reached its maximum value, ca. 75%, after several minutes and

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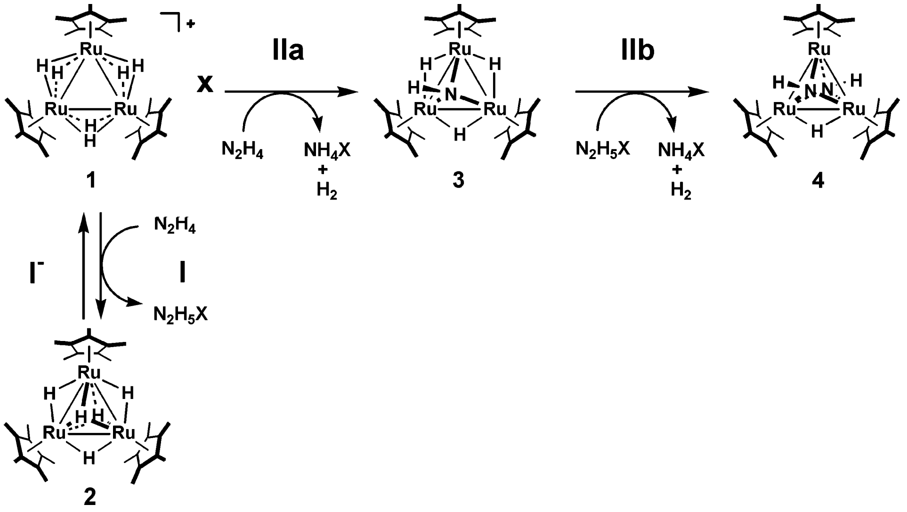
Scheme 1. Reaction Paths of 1 with Hydrazine



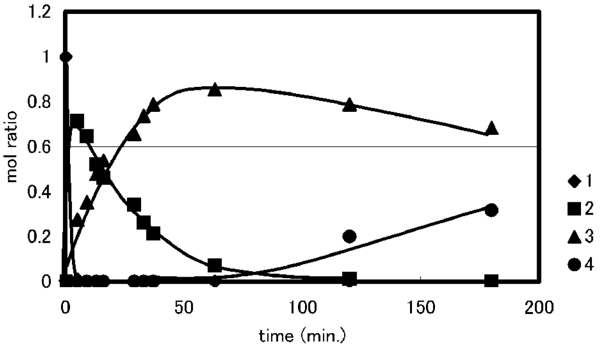


Figure 1. Time-distribution curve of the reaction of **1** with hydrazine.

then decreased gradually and almost disappeared after 120 min. The amount of the intermediate **3** increased with the progress of the reaction, and the yield reached its maximum value, ca. 85%, after 70 min and then decreased gradually. In contrast, the final product, the bis(μ_3-imido) complex **4**, appeared after about 50 min and the yield increased monotonically. After 180 min, the yield of **4** reached nearly 32%.

These results strongly imply that the cationic complex **1** equilibrates with **2** in the presence of hydrazine, and the mono(μ_3-imido) complex **3** was directly generated from **1** via the nucleophilic attack of hydrazine. The reaction between **2** and hydrazine is disregarded for the formation of **3** and **4**, as mentioned later.

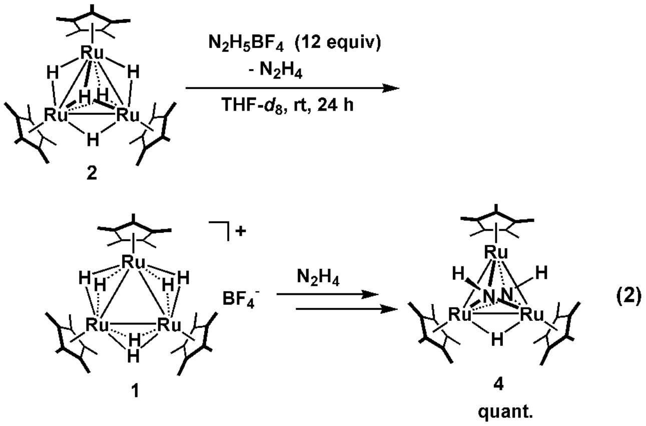
Possible reaction paths of the monocationic hexahydride complex **1** with hydrazine are illustrated in Scheme 1. The reaction consists of two independent paths, I and II. The "hydride" ligands in the cationic complexes likely have "protonic" character and would be abstracted by hydrazine. Deprotonation from **1** by hydrazine yields the neutral complex **2** and the hydrazonium salt N_2H_5X (path I). The reverse process, namely, protonation of **2** by N_2H_5X, regenerates **1** (path I$^-$). Path II involves two consecutive attacks of N-nucleophiles to the metal centers of the cationic complex **1**. Nucleophilic attack of hydrazine at **1** generates the mono(μ_3-imido) complex **3** and ammonium salt NH_4X as a result of nitrogen−nitrogen bond cleavage (path IIa). As proposed for the reaction of **2** with substituted hydrazine,[9] adjacent metal centers likely cooperate as a binding site and an activation site. Such cooperative action must be a characteristic feature of the "multimetallic system". Complex **3** sustained an attack by N_2H_5X to form the bis(μ_3-imido) complex **4** (path IIb). The source of the second μ_3-NH ligand in the final step, path IIb, was concluded to be N_2H_5X, on the basis of a control experiment mentioned later.

A series of control experiments using **1** and the isolated key intermediate **3** were carried out to verify each step of the proposed reaction mechanism shown in Scheme 1.

The reaction of **1** with hydrazine largely depends on the solvent used in the reaction. While the reaction of **1** with 10 equiv of hydrazine in tetrahydrofuran at room temperature resulted in the exclusive formation of the bis(μ_3-imido) complex **4** within 1 h as mentioned above, the reaction of **1** with 10 equiv of hydrazine conducted in toluene at room temperature led to formation of the neutral pentahydride complex **2** and bis(μ_3-imido) complex **4** in 44 and 56% yields, respectively. It is well established that the equilibrium between an ionic substrate and a neutral one is significantly affected by the polarlity of the solvent used. In a polar solvent, the equilibrium between **1** and **2** shifts toward the cationic complex **1** and shifts in the reverse direction in a nonpolar solvent, because complex **1** is more soluble in the polar solvent and, as a result, the irreversible path IIa is significantly accelerated. In contrast, complex **1** is sparingly soluble in a nonpolar solvent and, therefore, the conversion into **3** is seriously retarded in toluene. Consequently, the reaction leading to **4** was accelerated in tetrahydrofuran while a considerable amount of pentahydride complex **2** was formed and remained unreacted in toluene.

To establish each reaction step of the reaction mechanism shown in Scheme 1, the reaction of **2** or **3** with various N-acids and bases derived from hydrazine was carried out. At first, the protonation step of **2** giving **1** was examined. The neutral pentahydride complex **2** is basic enough to be protonated by ammonium or hydrazonium salt, which is possibly generated in the reaction of **1** with hydrazine. Whereas the hydrazonium salt N_2H_5X is formed in the initial stage of the reaction of **1** with hydrazine, the ammonium salt NH_4X is generated in step IIa as a result of nitrogen−nitrogen bond cleavage of hydrazine which is incorporated in the reaction site of **1**. Therefore, the reaction of **2** with $N_2H_5BF_4$ and that with NH_4BF_4 were examined.

The reaction of **2** with 12 equiv of $N_2H_5BF_4$ was carried out in tetrahydrofuran-d_8 at room temperature and monitored by means of ^{1}H NMR spectroscopy. With a monotonic decrease in ruthenium pentahydride **2**, cationic complex **1** and bis(μ_3-imido) complex **4** were formed in the early stages of the reaction. After 40 min, the percentage of complex **2** decreased to 50% and complex **1** and the final product, the bis(μ_3-imido) complex **4**, were produced in 43% and 7% yields, respectively. The molar distribution of **1** reached its maximum value, about 60%, after 100 min. Complex **2** was quantitatively converted into **4** after 24 h (eq 2).



(2)

Although ammonium salt is a weaker acid than hydrazonium salt, it can also protonate **2** to regenerate **1**. Treatment of **2** with 6 equiv of NH_4BF_4 in tetrahydrofuran-d_8 at room temperature selectively afforded the cationic complex **1**.

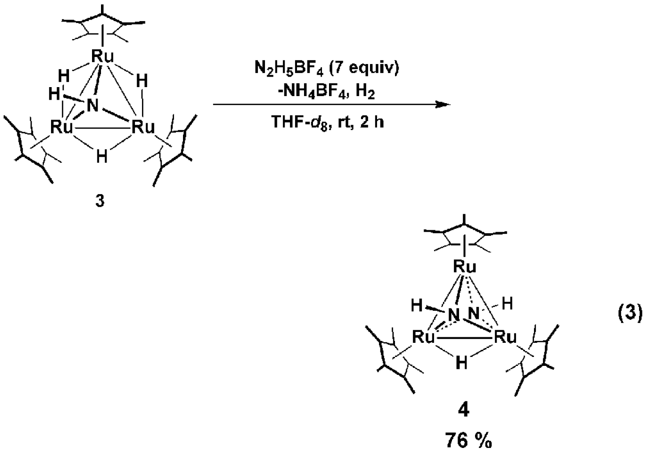
This implies that the hydrazonium salt contributes to the protonation of **2** in the early stages of the reaction, but the ammonium salt formed in step IIa also may act as a proton donor later.

The formation of the μ_3-imido complex **3** is followed by step IIb, in which the second μ_3-imido group is introduced into the Ru_3 core of **3** from the face opposite the first μ_3-NH group with respect to the Ru_3 plane to form the bis(μ_3-imido) complex **4**. In this reaction system, an ammonium salt, NH_4X, coexists with hydrazine because an excess amount of hydrazine is used in this reaction. The ammonium salt, therefore, reacts with excess hydrazine to yield a hydrazonium salt, N_2H_5X, although the equilibrium between the ammonium salt and the hydrazonium salt leans toward the ammonium salt. This was confirmed experimentally: i.e., the reaction of hydrazine with NH_4PF_6 in tetrahydrofuran-d_8 produced $N_2H_5PF_6$ accompanied by the evolution of gas. The hydrazonium salt, $N_2H_5PF_6$, was identified by comparing the ^{1}H NMR data with those of an authentic sample. As a result, three kinds of nitrogen-containing compounds, NH_4X, N_2H_4, and N_2H_5X, are nominated as candidates for the source of the second μ_3-imido ligand. The reaction of **3** with these nitrogen-containing compounds was examined to elucidate the reaction path.

The reaction of **1** with an excess amount of ammonium salt afforded very complicated mixtures. A complex mixture of unidentified products was also obtained, even when the reaction of **3** with less than 1 equiv of NH_4BF_4 was performed in tetrahydrofuran-d_8 at room temperature. However, the μ_3-imido complex **4** was not included in the mixture. This clearly shows that the ammonium salt does not participate in the formation of **4**.

In contrast, complex **4** was formed in the reaction of **3** with both hydrazine and hydrazonium salt. Monitoring the reaction of **3** with 12 equiv of hydrazine in tetrahydrofuran-d_8 at room temperature by means of ^{1}H NMR spectroscopy showed that the reaction was relatively slow and less selective. After 8 h, conversion of **3** reached 56% but the selectivity of the reaction for the formation of **4** remained at 26%. Complex **3** completely disappeared, and the bis(imido) complex **4** was formed in 40% yield after 35 h. The remaining 60% was attributed to unidentified complexes. As mentioned above, the reaction of **1** with excess hydrazine resulted in the quantitative formation of **4**. Therefore, this aspect of the reaction is different from that of the reaction of **3** with hydrazine.

The reaction of **3** with 7 equiv of $N_2H_5BF_4$ under similar conditions proceeded more rapidly and selectively than that of **3** with hydrazine. Seventy-six percent of **3** was consumed after 2 h, and no products other than **4** were formed (eq 3).



(3)

These results indicate that the second μ_3-imido ligand that is introduced into the Ru_3 core of **3** in path IIb in Scheme 1 stems from the hydrazonium salt. The reaction most likely proceeds via initial protonation of **3** by the hydrazonium salt and subsequent nucleophilic attack of hydrazine to generate **4** and ammonium salt. Thus, the N−N bond cleavage was formally catalyzed by a proton. The electron density at the ruthenium center in **3** is reduced due to protonation, and nucleophilic attack of the hydrazine molecule is accelerated to lead to the formation of **4** in a highly selective way. Thus, a cationic intermediate is presumably produced in the course of the reaction. Two possible structures of the intermediate can be proposed (Chart 1); one is a cationic μ_3-imido triruthenium tetrahydride, and the other is a cationic μ-amido triruthenium trihydride. The former is generated as a result of protonation at the ruthenium atom, and the latter is, in contrast, formed via protonation at the μ_3-imido group.

The results of these control experiments show that cationic complex **1** reacts stepwise with two hydrazine

Chart 1. Possible Structures of the Cationic Intermediate

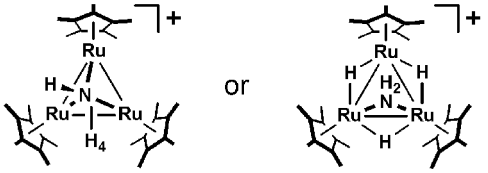
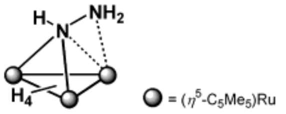


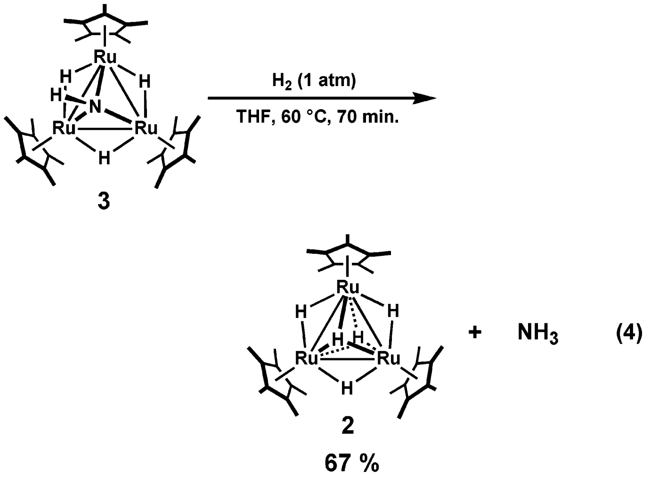
Chart 2. N−N Bond Cleavage of Hydrazine on the Ru$_3$ Core



molecules to generate **4** and two NH$_3$ molecules and a proton with liberation of two hydrogen molecules. Thus, the polyhydride complex **1** is remarkably active for the nitrogen−nitrogen bond cleavage of hydrazine. The nitrogen−nitrogen bond is effectively cleaved on the Ru$_3$ core of **1**, and no intermediary hydrazonium complexes were observed in any stage of the reaction. This is most likely due to the cooperation of the three ruthenium atoms. As mentioned in the previous paper,[9] the β-nitrogen atom of the hydrazonium (I) or hydrazonium (II) ligand in the intermediate is coordinated to the adjacent ruthenium atom and, as a result, these ruthenium atoms cooperatively work for the nitrogen−nitrogen bond cleavage (Chart 2).

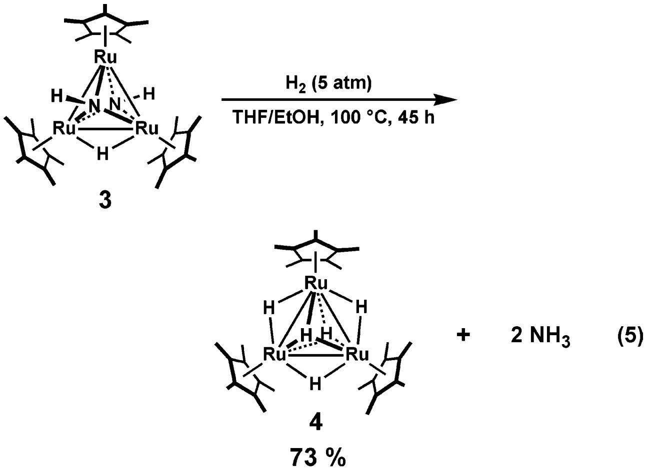
Although there have, thus far, been several reported examples of μ_3-imido complexes,[13] little is known about their reactivity. Hydrogenation of the μ_3-imido complex that generates ammonia seems to be crucial for success in the catalytic hydrogenation of hydrazine by the use of a polyhydride complex as a catalyst. We examined the reaction of μ_3-imido complexes **3** and **4** with hydrogen.

Reaction of the μ_3-imido complex **3** under atmospheric pressure of hydrogen in THF at 60 °C for 70 min resulted in the exclusive formation of the triruthenium pentahydride complex **2** in 67% yield (eq 4). Ammonia formed in the reaction was quantified by the indophenol method.[11]



The reaction was significantly accelerated at higher temperature or under the atmosphere of pressurized hydrogen. When the reaction was conducted at 60 °C under 5 atm of hydrogen, it took 70 min for the completion of the reaction. Under 5 atm of hydrogen at 100 °C, the reaction was complete within 5 min to give **2**, quantitatively.

The bis(μ_3-imido) complex **4** also undergoes hydrogenolysis to yield **2** and ammonia but the reaction is much slower than that of the mono(μ_3-imido) complex **3**. Complex **4** is coordinatively saturated, while **3** is an unsaturated 46e species. This is reflected in deceleration of the reaction of **4** with H$_2$ in comparison to that of **3**. When the reaction of **4** with 5 atm of hydrogen was conducted in a 5/1 (v/v) mixture of THF/EtOH at 100 °C, **2** was formed in the yield of 73% after 45 h (eq 5). Formation of ammonia was detected and quantified by means of the indophenol method.



Addition of ethanol is essential for acceleration of the reaction. The reaction slowed markedly in the absence of ethanol, and the yield of **2** was less than 50% even after 3 days.

In summary, complexes **3** and **4** were formed stepwise together with an ammonium salt in the reaction of **1** with hydrazine and both **3** and **4** were converted into **2** with formation of ammonia via hydrogenolysis. As the pentahydride complex **2** is convertible into the cationic hexahydride **1** by protonation, a stoichiometric cycle of hydrazine reduction is, thus, formally completed (Scheme 2).

Cycle A is a semicircular course of the reaction that consists of the nitrogen−nitrogen bond cleavage of hydrazine by **1** (path a), hydrogenolysis of the mono(μ_3-imido) complex **3** (path e), and protonation of **2** to regenerate **1** (path d). Cycle B consists of an entirely circular course and involves the nitrogen−nitrogen bond cleavage of the second hydrazine molecule to form the bis(μ_3-imido) complex **4** (path b) and hydrogenolysis of **4** (path c) in addition to paths a and d. The proton that stems from **1** plays a role of activator of the neutral μ_3-imido complex **3** and catalyzes the conversion from **3** into **4** in cycle B. Overall processes of both cycles A and B correspond to ammonia formation by the reaction of hydrazine with an equimolar amount of hydrogen, even though they are not catalytic but stoichiometric.

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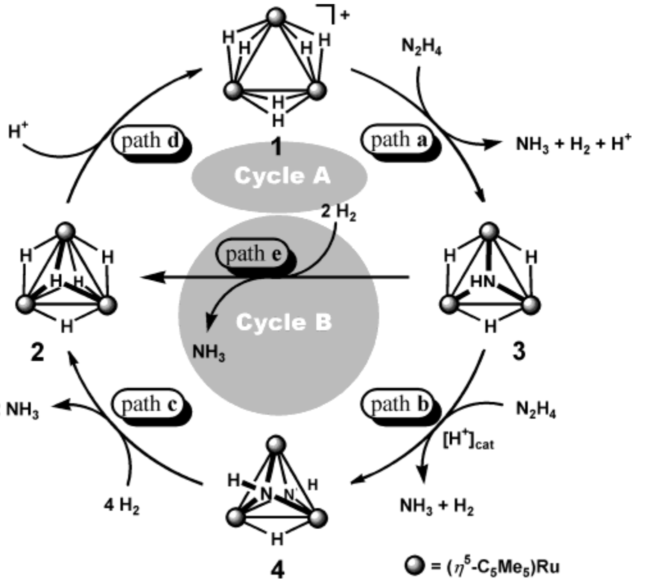
[13] (a) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255−7259. (b) Wuchere, E. J.; Tasi, M.; Hansert, B.; Powell, A. K.; Garland, M.-T.; Halet, J.-F.; Saillard, J.-Y.; Vahrenkamp, H. *Inorg. Chem.* **1989**, *28*, 3564−3572. (c) Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2301−2309. (d) Jordan, A. Y.; Meyer, T. Y. *J. Organomet. Chem.* **1999**, *591*, 104−113.

Scheme 2. Proposed Hydrazine Reduction Cycle



In summary, it was revealed that the cationic hexahydride complex **1** was highly active in the cleavage of the nitrogen−nitrogen bond of hydrazine. In the reaction with hydrazine, complex **1** plays the role of both an acid and an electrophile. Nucleophilic attack of hydrazine at the ruthenium center resulted in the formation of the μ_3-imido complex **3**, whereas the neutral triruthenium pentahydride complex **2** was formed as a result of proton abstraction by the hydrazine. It is noteworthy that only one proton is needed for the conversion of hydrazine into ammonia both in cycle A and in cycle B, and the hydrogen molecule directly participates in the ammonia formation via hydrogenolysis of the μ_3-imido complex. This is in clear contrast to the reactions reported thus far, which utilize a proton and a reducing agent for the reduction of hydrazine. Formally, hydrogen is separated into proton and electron by the action of the polyhydride cluster.

Work on the catalytic hydrogenation of hydrazine by the use of a polyhydride cluster is now under way.

Experimental Section

General Considerations. The compounds described below were handled under an argon atmosphere with rigorous exclusion of air and water using Schlenk techniques. Dehydrated solvents were purchased from Kanto Chemical Co. Ltd. (Cat. No. 41001-85 for tetrahydrofuran, 40500-85 for toluene, and 32053 for pentane). Hydrazine monohydrate was used in all experiments. Hydrazine hydrate and ammonium hexafluorophosphate, NH_4PF_6, were obtained from Tokyo Kasei Kogyo Co., Ltd., and no further purification was performed. The hydrazonium salt $N_2H_5BF_4$ and ammonium salt NH_4BF_4 were prepared by protonation of each reagent, N_2H_4 and NH_3. The remaining H_2O existing in $N_2H_5BF_4$ was dried in vacuo with additional azeotropic solution, C_6H_6. Benzene-d_6 and tetrahydrofuran-d_8 were distilled, dried over sodium benzophenone ketyl, and stored under an argon atmosphere. [(Cp′Ru)$_3$(μ-H)$_6$]X (**1**) was prepared as previously described.[14] ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 Fourier transform spectrometer with tetramethylsilane as an internal standard.

Reaction of 1-(SO$_4$)$_{1/2}$ with Hydrazine. A THF solution (5 mL) of **1**-(SO$_4$)$_{1/2}$ (59.3 mg, 0.0777 mmol) was charged in a 50 mL Schlenk tube, to which was added hydrazine (40 μL, 0.692 mmol). Soon the solution turned green, and after being stirred for 60 min, the solution turned dark orange. After removal of the solvent under reduced pressure, the residue was extracted with toluene and (Cp′Ru)$_3$(μ_3-NH)$_2$(μ-H) (**4**) was obtained as a red solid (51.7 mg, 0.0699 mmol, 90%).

Detection of Ammonium Salts. A mixture of **1**-BPh$_4$ (48.1 mg, 0.0599 mmol) and hydrazine (40 μL, 0.692 mmol) in tetrahydrofuran was charged in a 50 mL Schlenk tube and stirred for 5 h. After removal of solvent in vacuo, NH_4BPh_4 was extracted by 1 mL of H_2O. Though the amount of ammonium salt was small and out of the range of quantification, the indophenol color reaction clearly implied the production of ammonium salts.[11]

Isolation of the Intermediate (Cp′Ru)$_3$(μ_3-NH)(μ-H)$_3$ (3). A 50 mL Schlenk tube was charged with **1**-(SO$_4$)$_{1/2}$ (138.5 mg, 0.161 mmol) and tetrahydrofuran (5 mL). Then 3 equiv of hydrazine (30 μL, 0.519 mmol) was added to the reaction mixture. This mixture was stirred at room temperature for 10 min, and the solution turned dark green. Removal of the solvent under reduced pressure and extraction with toluene followed by another removal of the solvent afforded **3** as a green solid (89.8 mg, 0.121 mmol, 75%).

Monitoring the Reaction of 1 with Hydrazine. An NMR sample tube was charged with **1**-BF$_4$ (14.5 mg, 0.0181 mmol), cycloheptane (0.2 μL, 0.0165 mmol), and tetrahydrofuran-d_8 (0.4 mL). After an excess of hydrazine monohydrate (23.2 μL, 0.376 mmol) was added to the solution, the reaction was monitored by means of ^{1}H NMR spectroscopy. The change in the intensity ratio of the signals of hydrides to those of cycloheptane as an internal standard was plotted versus time (Figure 1).

Reaction of 1 with N_2H_4 in Toluene. To a stirred solution of **1**-(SO$_4$)$_{1/2}$ (29.1 mg, 0.0376 mmol) in toluene was added hydrazine monohydrate (23 μL, 0.376 mmol). After the solution was stirred for 20 h, the solvent was removed under reduced pressure. It is revealed that complexes **1** and **4** were formed in yields of 44% and 56%, respectively, each on the basis of the integral intensity of the Cp′ reagion.

Reaction of 2 with $N_2H_5BF_4$. An NMR sample tube was charged with **2** (3.3 mg, 0.00462 mmol), $N_2H_5BF_4$ (6.7 mg, 0.0559 mmol), tetrahydrofuran-d_8 (0.4 mL), and cyclooctane (1 μL, 0.00734 mmol). The reaction was monitored at room temperature by measurement of the integral intensity ratio of the Cp′ region to that of cyclooctane in the ^{1}H NMR spectrum. After 40 min, complex **2** decreased its percentage to 50% and complex **1** and the final product, the bis(μ_3-imido) complex **4**, were produced in 43% and 7% yields, respectively. The yield of **2** reached its maximum value, 60%, after 60 min and then decreased. After 24 h, complex **4** was formed quantitatively.

Reaction of 2 with NH_4BF_4. An NMR sample tube was charged with **2** (9.2 mg, 0.0129 mmol) and tetrahydrofuran-d_8 (0.4 mL). After NH_4BF_4 (8.2 mg, 0.0746 mmol) was added at room temperature, the solution turned dark purple gradually and the ^{1}H NMR spectrum revealed the exclusive formation of **1**-BF$_4$ (conversion 50%) after 1 h. The reaction was monitored at room temperature by measurement of the integral intensity ratio of the hydride region to that of grease in the ^{1}H NMR spectrum.

Reaction of NH_4PF_6 with Hydrazine: Formation of $N_2H_5PF_6$. A tetrahydrofuran-d_8 solution containing anhydrous hydrazine (10 μL, 0.313 mmol) was charged in an NMR sample tube. After NH_4PF_6 (32.7 mg, 0.196 mmol) was added to the reaction mixture at room temperature, evolution of the gas was observed. In the ^{1}H NMR spectrum, only the signal assignable for $N_2H_5PF_6$ was observed. $N_2H_5PF_6$: ^{1}H NMR (400 MHz, room temperature, THF-d_8) δ 4.68 (br s, $w_{1/2} = 5.65$ Hz).

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(14) Suzuki, H.; Kakigano, T.; Tada, K.; Igarashi, M.; Matsubara, K.; Inagaki, A.; Oshima, M.; Tanaka, M. Manuscript in preparation.

Reaction of 3 with NH_4BF_4. An NMR sample tube was charged with **3** (7.1 mg, 0.00977 mmol), NH_4BF_4 (0.9 mg, 0.0056 mmol), cyclooctane (2 μL, 0.0147 mmol) as an internal standard and tetrahydrofuran-d_8 (0.4 mL). After 3 h at room temperature, the ^{1}H NMR spectrum revealed that no bis-imido complex **4** but several unidentified products were formed though **3** decreased its population to 61%.

Reaction of 3 with Hydrazine. An NMR sample tube was charged with **3** (5.3 mg, 0.00729 mmol) and tetrahydrofuran-d_8 (0.4 mL). After hydrazine monohydrate (4.2 μL, 0.0863 mmol) was added, the reaction was monitored at room temperature by measurement of the integral intensity ratio of the hydride region to that of TMS in the ^{1}H NMR spectrum. After 8 h, conversion of **3** reached 56% but the selectivity of the reaction for the formation **4** was 26%. After 35 h, complex **3** completely disappeared and the bis(imido) complex **4** was formed in 40% yield. The remaining 60% was attributed to unidentified complexes.

Reaction of 3 with $N_2H_5BF_4$. An NMR sample tube was charged with **3** (9.4 mg, 0.0129 mmol) and tetrahydrofuran-d_8 (0.4 mL). Then, 7 equiv of $N_2H_5BF_4$ (10.4 mg, 0.0868 mmol) was added and the reaction was monitored by ^{1}H NMR spectroscopy. After 3 h, no signals other than complex **4** (76%), unreacted **3** (24%), and $N_2H_5BF_4$ were observed in the ^{1}H NMR spectrum.

Reaction of 3 with H_2. A 50 mL glass autoclave was charged with **3** (10.1 mg, 0.0141 mmol) and 3 mL of tetrahydrofuran. After degassing of the autoclave, H_2 gas was introduced at 1 atm. After the reaction proceeded for 70 min at 60 °C, the reaction mixture was transferred to a 50 mL Schlenk tube and the solvent was removed under reduced pressure. The ^{1}H NMR spectra of the residue revealed that complex **2** was formed with a yield of 67% and 33% of **3** remained. Formation of ammonia was separately confirmed in the following experiment.

Determination of Ammonia. A 50 mL glass autoclave was charged with **3** (21.0 mg, 0.0289 mmol) and 5 mL of tetrahydrofuran. After degassing of the autoclave, H_2 gas was introduced at 5 atm. After stirring for 30 min at 100 °C, complex **2** was formed quantitatively. Ammonia existing in the gas phase was trapped by plunging gas in dilute sulfuric acid, and 0.0049 mmol (17%) of ammonia was detected using the indophenol method. The amount of ammonia detected was small because ammonia existing only in the gas phase was quantified. Most of the ammonia presumably existed in the solution.

Reaction of 4 with H_2. A 50 mL glass autoclave was charged with **4** (17.9 mg, 0.0242 mmol) and a mixed solvent composed of 5 mL of tetrahydrofuran and 1 mL of ethanol. After the remaining air was expelled from the autoclave, H_2 gas was introduced at 5 atm. After the reaction proceeded for 45 h at 100 °C, the reaction mixture was transferred to a 50 mL Schlenk tube, and the solvent was removed under reduced pressure. The ^{1}H NMR spectra of the residue revealed that complex **2** was formed in a yield of 73%, and the rest was unreacted **4** (27%). Ammonia existing in the gas phase was trapped by plunging the gas into hydrochloric acid. In addition, the solvent was transferred in the acid solution using a trap-to-trap technique to capture the ammonia existing in the solution. Ammonia (0.030 mmol, 85%) was detected using the indophenol method.

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