Nitrogen−Nitrogen Double Bond Cleavage of Azobenzene by a Triruthenium Pentahydrido Complex, $(Cp'Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ ($Cp' = \eta^5\text{-}C_5Me_5$), and Catalytic Hydrogenation of Azobenzene and 1,2-Diphenylhydrazine

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The reaction of triruthenium pentahydrido, $(Cp'Ru)(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**1**), with azobenzene yielded $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu\text{-}H)_3$ (**7**) and $(Cp'Ru)_3(\mu_3\text{-}NPh)_2(\mu\text{-}H)$ (**8**) via independent routes. Mono(μ_3-NR) complexes, **3** (R = H), **9** (R = Et), **10** (R = CH_2Ph), and **7**, underwent hydrogenolysis to generate the corresponding amines, NRH_2, and **1**, while bis(μ_3-phenylimido) complex **8** offered resistance to the reaction with hydrogen. The rate of the hydrogenolysis likely depends on the bulkiness of the substituent at the triply bridging nitrogen atom. Polyhydrido cluster **1** catalyzed the hydrogenation of both azobenzene and 1,2-diphenylhydrazine to yield aniline.

Introduction

Transition metal-mediated reductive cleavage of the nitrogen−nitrogen single bond of hydrazine or hydrazido salts is crucial for nitrogen fixation, and the reaction of a transition metal hydrido complex with hydrazine derivatives would, therefore, provide deep insight into the conversion of dinitrogen to ammonia. Extensive studies dealing with activation of hydrazines have been reported,[1] and catalytic reduction of hydrazine has been attained by several groups in the presence of a proton source and a reducing agent.[2]

Recently, we have reported that the nitrogen−nitrogen bond of hydrazine and its derivatives is cleaved by triruthenium polyhydrido complexes, $(Cp'Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**1**) and $[(Cp'Ru)_3(\mu\text{-}H)_6]X$ (**2**) (X = BF_4, PF_6, and $(1/2)SO_4$), under mild conditions.[3,4] In the reaction of cationic complex **2** with hydrazine, mono(μ_3-NH) and bis(μ_3-NH) complexes, $(Cp'Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3$ (**3**) and $(Cp'Ru)_3(\mu_3\text{-}NH)_2(\mu\text{-}H)$ (**4**), respectively, were formed stepwise via a nitrogen−nitrogen bond cleavage, and they underwent hydrogenolysis to give ammonia and **1**. It is noteworthy that no protons and reducing agents are needed for the conversion of hydrazine into ammonia in this reaction system.

Neutral polyhydrido complex **1** effectively activates the nitrogen−nitrogen bond of substituted hydrazines, while the disproportionation to afford ammonia and dihydrogen predominates over the nitrogen−nitrogen bond cleavage in the reaction of **1** with hydrazine.[3,5] The reaction of **1** with an excess amount of monosubstituted hydrazine, such as $MeNHNH_2$ and $PhNHNH_2$, resulted in the exclusive formation of a nonsymmetrically capped bis(μ_3-imido) complex, $(Cp'Ru)_3(\mu_3\text{-}NR)(\mu_3\text{-}NH)(\mu\text{-}H)$ (**5**, R = Me; **6**, R = Ph) as a result of nitrogen−nitrogen bond cleavage. In contrast to the reaction with monosubstituted hydrazine, the reaction of **1** with 1,2-diphenylhydrazine predominantly yielded a mono-capped imido complex, $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu_3\text{-}H)_3$ (**7**), due to the steric hindrance between the Cp′ groups and the incoming bulky 1,2-diphenylhydrazine molecule (Scheme 1).

Thus, we have demonstrated that the ruthenium polyhydrido clusters effectively operate in the nitrogen−nitrogen bond cleavage of hydrazine derivatives. In relation to the activation of nitrogen, nitrogen−nitrogen bond cleavage of an azo compound is of great interest

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(1) For example: (a) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1971**, *31*, 275. (b) Evans, W. J.; Kociok-Köhn, G.; Leong, V. S.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 3592. (c) Schollhammer, P.; Guénin, E.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *Organometallics* **1998**, *17*, 1922. (d) Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1994**, *33*, 3619. (e) Bruce, M. I.; Humphrex, M. G.; Shawkataly, O. B.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *315*, C51. (f) Sellmann, D.; Hille. A.; Rösler, A.; Heinemann, F. W.; Moll, M.; Brehm, G.; Schneider, S.; Reiher, M.; Hess, B. A.; Bauer, W. *Chem. Eur. J.* **2004**, *10*, 819. (g) Albertin, G.; Antoniutti, S.; Bortoluzzi, M.; Castro-Fojo, J.; Garcia-Fontán S. *Inorg. Chem.* **2004**, *43*, 4511. (h) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385, and references therein.

(2) (a) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta *J. Am. Chem. Soc.* **1992**, *114*, 758. (b) Malinak, S. M.; Demadis, K. D.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 3126. (c) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725. (d) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760. (e) Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747.

(3) Nakajima, Y.; Suzuki, H. *Organometallics* **2003**, *22*, 959.

(4) Nakajima, Y.; Inagaki, A.; Suzuki, H. *Organometallics* **2004**, *23*, 4040.

(5) When the reaction of **1** with excess hydrazine was performed at elevated temperature, disproportionation and dehydrogenation of hydrazine proceeded catalytically to produce ammonia, dinitrogen, and hydrogen. The reaction rate was very fast, and 1300 equiv of ammonia and 970 equiv of dinitrogen were obtained from 4600 equiv of hydrazine after 14 h at 100 °C. Ammonia was quantified by indophenol metahod (Chaney, A. L.; Marbach, E. P. *Clin. Chem.* **1962**, *8*, 130), and dinitrogen was quantified by means of GC. Nakajima, Y.; Suzuki, H. To be published.

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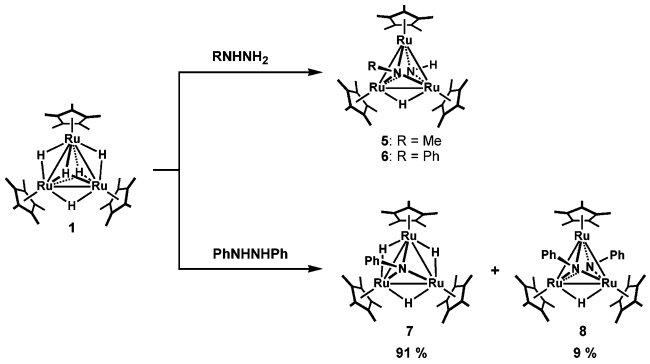
Scheme 1. Reaction of 1 with Substituted Hydrazines

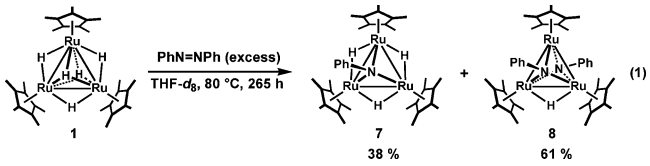


as well as that of hydrazine derivatives. Although catalytic hydrogenation of azo compounds was attained by heterogeneous catalysis such as Ni and Pt,[6] there is no example of hydrogenation of azo and hydrazine derivatives catalyzed by a soluble transition metal complex.

We report herein the cleavage of a nitrogen−nitrogen double bond of azobenzene in the reaction field of the ruthenium polyhydrido cluster and polyhydrido cluster-catalyzed hydrogenation of azobenzene and 1,2-diphenylhydrazine.

Results and Discussion

Nitrogen−Nitrogen Double Bond Cleavage of Azobenzene by Triruthenium Pentahydrido Complex 1. The reaction of triruthenium pentahydrido complex **1** with azobenzene proceeds very slowly at ambient temperature, but proceeds at a reasonable rate at elevated temperature. The reaction of **1** with excess amount of azobenzene in tetrahydrofuran-d_8 at 80 °C for 265 h resulted in the formation of $(Cp'Ru)_3(\mu_3\text{-NPh})(\mu\text{-H})_3$ (**7**) and $(Cp'Ru)_3(\mu_3\text{-NPh})_2(\mu\text{-H})$ (**8**) in 38% and 61% yield, respectively (eq 1).



Both **7** and **8** were formed as the result of nitrogen−nitrogen double bond cleavage and identified by comparison with the authentic samples prepared by the reaction of **1** with 1,2-diphenylhydrazine.[3] A single-crystal of **8** was obtained from tetrahydrofuran at −30 °C, and the structure was determined by means of X-ray diffraction studies. The resulting ORTEP diagram is shown in Figure 1, and relevant geometrical parameters are given in Table 1.

The structure shown in Figure 1 clearly demonstrates the structural identity of **8**, which has two triply bridging phenylimido ligands on both faces of the Ru_3 core. All distances and angles are comparable to those reported for known trinuclear ruthenium complexes that possess a μ_3-imido ligand.[3,7] The time-course curve of the reaction monitored by means of ^{1}H NMR spectroscopy is shown in Figure 2.

Figure 2 obviously shows that complexes **7** and **8** are independently formed, namely, via different pathways. Actually, it was confirmed that complex **8** was not formed via mono(μ_3-imido) complex **7** by a controlled

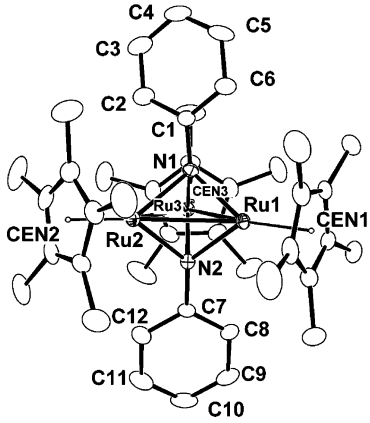


Figure 1. Molecular structure of **8**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) of 8[a]

distances (Å)		angles (deg)	
Ru1−Ru2	2.7358(4)	C1−N1−Ru1	136.5(2)
Ru2−Ru3	2.7221(5)	C1−N1−Ru2	124.8(2)
Ru3−Ru1	2.7637(5)	C1−N1−Ru3	122.4(2)
Ru1−N1	1.992(3)	C7−N2−Ru1	132.0(2)
Ru1−N2	2.004(3)	C7−N2−Ru2	131.8(2)
Ru2−N1	2.035(3)	C7−N2−Ru3	119.5(2)
Ru2−N2	2.021(3)	G1-Ru1−CEN1	177.6
N1−C1	1.402(5)	G1-Ru2−CEN2	171.9
N2−C7	1.427(5)	G1-Ru3−CEN3	175.6

[a] G1 and CEN1−3 are the center of the gravity of the Ru_3 triangle and the centroids of the Cp's, respectively.

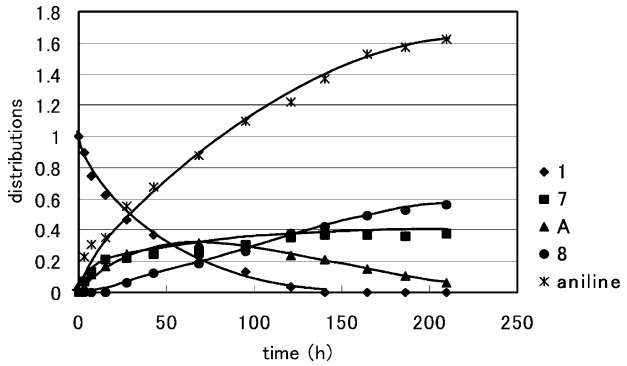
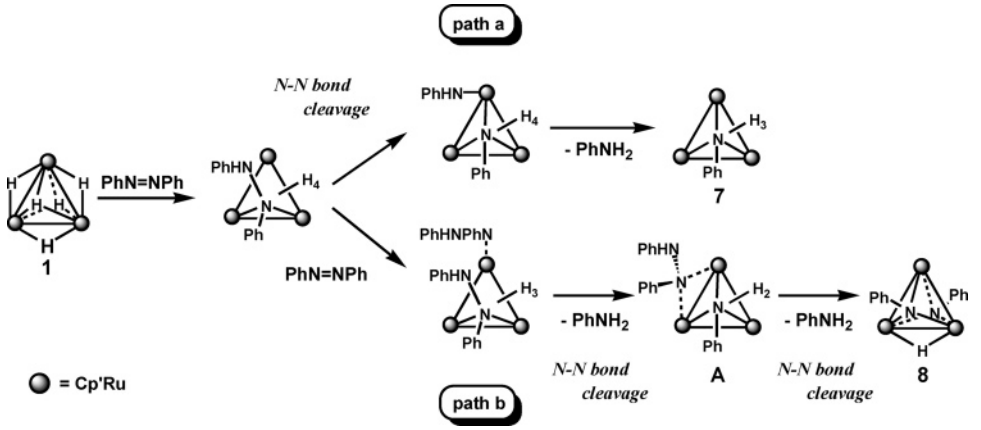


Figure 2. Time−distribution curve of the reaction of **1** with azobenzene

(6) (a) Nakamura, A.; Kamada, M.; Sugihashi, K.; Otsuka, S. *J. Mol. Catal.* **1980**, *8*, 353. (b) Gostikin, V. P.; Lefedova, O. V.; Marochko, A. V.; Nemtseva, M. P. *Kinet. Catal.* **1998**, *39*, 690. (c) Covert, L. W.; Adkins, H. *J. Am. Chem. Soc.* **1932**, *54*, 4116. (d) Andrews, L. H.; Lowy, A. *J. Am. Chem. Soc.* **1934**, *56*, 1411. (e) Whitmore, W. F.; Anthony, R. *J. Am. Chem. Soc.* **1937**, *59*, 1500. (f) Cieplik, M. K.; Louw, R. *Eur. J. Org. Chem.* **2004**, 3011.

(7) (a) Bhaduri, H.; Gopalkrishnan, K. S.; Sheldrich, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339. (b) Lausarot, P. M.; Operti, L.; Vaglio, G. A.; Valle, M.; Tiripicchio, A.; Camellini, M. T.; Graiboldi, P. *Inorg. Chim. Acta* **1986**, *103*, 122. (c) Lee, K. K.-H.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1996**, 1707. (d) Lee, K. K.-H.; Wong, W.-T. *J. Organomet. Chem.* **1999**, *577*, 323. (e) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2501. (f) Basu, A.; Bhaduri, S.; Khwaja, H.; Jones, P. G.; Meyer-Base, K.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2501. (g) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* **1988**, *105*, 356.

Scheme 2. Reaction Paths of 1 with Azobenzene



experiment. The reaction of **7** with a possible source of the μ_3-NPh ligand, such as aniline, azobenzene, or 1,2-diphenylhydrazine in tetrahydrofuran at 100 °C, resulted in the complete recovery of **7**.

Complex **1** was rapidly consumed in the early stage of the reaction, and 4% of **1** remained after 121 h. In the initial stage of the reaction, mono(μ_3-phenylimido) complex **7** and an intermediary species **A** were formed. The amount of **7** monotonically increased and reached about 37% after 121 h. After that, the amount of **7** remained fairly constant. The amount of the intermediate species reached the maximum value, ca. 32%, after 69 h and then decreased. The time-course curve for the formation of **8** was consistent with that of a typical consecutive reaction by way of **A**. Along with the decrease in the intermediate species **A**, the amount of **8** increased. After 210 h, the amount of **8** reached 56%. At the same time, aniline was formed along with the reaction. Molar ratios of aniline to the total for **7**, **A**, and **8** were 1.4 after 140 h and 1.6 after 265 h, respectively. It is noteworthy that the amount of aniline subsequently increased even after **1** was totally consumed.

The ^{1}H NMR spectrum of **A** revealed two C_5Me_5 signals with integral intensities of 15H and 30H at δ 1.49 and 1.96, respectively. On the other hand, a singlet signal for the hydrido ligands was observed at δ −19.49 with an integral intensity of 2H. These results strongly implied that the structure of **A** has a mirror plane, which bisects one of the Ru−Ru bonds.

We tentatively propose a μ_3-phenylimido-μ-phenylhydrazido species for the intermediate **A**. A possible reaction pathway for the formation of **7** and **8** is proposed on the basis of careful monitoring of the reaction (Scheme 2).

Mono(μ_3-phenylimido) complex **7** would be formed by the insertion of azobenzene into a ruthenium−hydrogen bond of **1** and subsequent cleavage of a nitrogen−nitrogen bond of the resulting μ-hydrazido ligand (path a). Notably, equimolar aniline and complex **7** would be formed in these steps. In contrast, bis(μ_3-imido) complex **8** would be formed via stepwise insertion of two azobenzene molecules into the ruthenium−hydrogen bond of **1** followed by reductive elimination of aniline (path b).

As mentioned above, mono-μ_3-phenylimido complex **7** reacts with neither aniline nor azobenzene. This shows that the bis(μ_3-imido) complex **8** was not formed by way of **7**. The three C_5Me_5 groups probably block access of aniline or azobenzene molecules to the reaction sites due to the steric repulsion. The second azobenzene molecule would be incorporated into the Ru_3 reaction space before the Ru_3(μ_3-NPh) framework was formed. Cleavage of the N−N bond of one of the hydrazide groups and subsequent liberation of aniline would generate intermediate **A**, which would undergo N−N bond cleavage of the μ-hydrazido ligand to yield **8** together with liberation of aniline. As a result, conversion from **1** to **8** should be accompanied by the formation of twice the molar amount of aniline. The amount of aniline formed in the reaction of **1** with azobenzene is estimated at 1.6 equiv on the basis of the yield of **7** (38%) and **8** (61%), and this value agrees with the observed value within experimental error.

This reaction mechanism is totally different from that for the reaction of **1** with 1,2-diphenylhydrazine, which produces **8** without liberation of aniline.[3]

Table 2. Hydrogenation of μ_3-Imido Complexes (Cp′Ru)$_3$(μ_3-NR)(μ-H)$_3$ (3, R = H; 9, R = Et; 10, R = Bz)

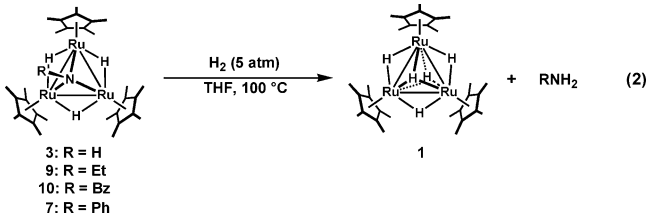
run	R	H_2 (atm)	temp (°C)	time	yield[b]
1	H (**3**)	5	100	5 min	100
2	Et (**9**)	5	100	250 min	88
3	Bz[a] (**10**)	5	100	65 h	100
4	Ph (**7**)	5	100	184 h	58

[a] Bz = $PhCH_2$. [b] The yield of complex **1** was determined by ^{1}H NMR spectroscopy.

Hydrogenation of μ_3-Imido Complexes. The above stoichiometric reaction between **1** and azobenzene resulted in the formation of mono(μ_3-phenylimido) complex **7** and bis(μ_3-phenylimido) complex **8** together with liberation of aniline as a result of cleavage of the nitrogen−nitrogen bond. Hydrogenolysis of **7** and **8**, which affords the starting compound **1** and aniline, is, therefore, crucial to realize the catalytic conversion of azobenzene into aniline.

We examined the reaction of a series of mono(μ_3-imido) complexes with hydrogen, and the results are listed in Table 2 along with the reaction conditions. Ethyl- and benzylimido complexes, **9** and **10**, were prepared by the reaction of **1** with acetonitrile and benzonitrile, respectively.[8] In all cases, the reaction of the imido complexes with hydrogen proceeds selectively to produce **1** and the corresponding amine (eq 2).

(8) Matsubara, K.; Suzuki, H. Unpublished result.



While a complex with a nonsubstituted μ_3-imido group, $(Cp'Ru)_3(\mu_3\text{-}NH)(\mu\text{-}H)_3$ (**3**), readily undergoes hydrogenolysis to yield **1** and ammonia, selectively, upon treatment with 5 atm of dihydrogen at 100 °C for 5 min,[4] the reaction of a substituted-imido complex with dihydrogen was seriously retarded. The conversion of ethylimido complex **9** and phenylimido complex **7** was only 88% and 58%, respectively, even after prolonged reaction time.

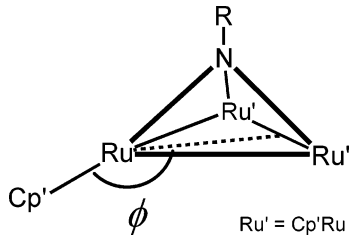
The X-ray diffraction studies of **3**, **9**, **10**,[9] and **7**[3] revealed that the Cp′ groups of these compounds tilted away from the μ_3-imido ligand with respect to the Ru_3 plane. We defined the term "tilt angle ϕ" as shown in Chart 1.

The average tilt angles for **3**, **9**, **10**, and **7** are 178.4°, 177.0°, 175.1°, and 175.3°, respectively. An empty space spread across the opposite face of the μ_3-imido ligand would be a reaction field. The smaller the tilt angle is, the narrower the reaction field becomes. The size of the reaction field is probably reflected in the reaction rate. If the hydrogen molecule accesses from the opposite face of the μ_3-imido group, the order of the reaction rates should, therefore, be H > Et > Bz ≥ Ph.

On the other hand, Tolman's electronic factor χ would be a quantitative criterion upon which to judge the electronic effect of the substituent. The χ values for H, ethyl, benzyl, and phenyl groups are 8.3, 1.8, 3.5, and 4.3 cm^{-1}, respectively.[10] Except for the case of **3**, the reaction is accelerated more as the substituent at the triply bridging nitrogen atom is a better electron donor. In contrast, the reaction of complex **3** is dominated chiefly by steric factors rather than electronic factors probably because complex **3** has a sterically undemanding μ_3-NH group.

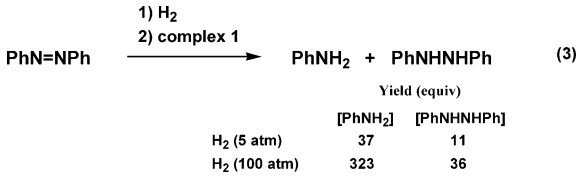
We also examined hydrogenation of coordinatively saturated bis(μ_3-phenylimido) complex **8**. When complex **8** was treated with 50 atm of hydrogen in tetrahydrofuran at 100 °C, more than 95% of **8** was recovered even after 7 days. The product was unidentified, and pentahydrido complex **1** was not obtained at all. This situation is significantly different from the hydrogenation of bis(μ_3-imido) complex **4**. Although complex **4** is coordinatively saturated as well as **8**, complex **4** undergoes hydrogenolysis to yield **1** and ammonia.[4] Particularly, addition of a proton source, such as ethanol, to the reaction system was effective for acceleration of hydrogenolysis of **4**. The reaction of **8** with hydrogen was not, however, affected by the addition of ethanol at all. This is probably due to the sterically demanding μ_3-phenylimido groups in **8**.

Chart 1. Tilt Angle, ϕ



Catalytic Hydrogenation of Azobenzene and 1,2-Diphenylhydrazine. Stoichiometric reaction of **1** with azobenzene generates mono(μ_3-phenylimido) complex **7** and bis(μ_3-phenylimido) complex **8**. The former undergoes hydrogenolysis to yield **1** and aniline upon treatment with hydrogen, while the latter does not react with hydrogen. According to this result, we examined the possibility of the catalytic hydrogenation of azobenzene of yielding aniline by using **1** as the catalyst.

The reaction was conducted at 100 °C for 5 days in ethanol using an autoclave. The reaction of azobenzene with 5 atm of hydrogen in ethanol in the presence of a catalytic amount (0.45 mol %) of **1** proceeded slowly to generate aniline and 1,2-diphenylhydrazine, selectively. It is noteworthy that the reaction proceeded catalytically although the conversion of azobenzene was low (13%). Turnover number for the complete reduction yielding twice the molar amount of aniline was 19, and that for the partial hydrogenation was 11. High turnover for the catalytic hydrogenation, which yielded aniline, was attained by increasing the pressure of hydrogen. When the reaction was conducted under 100 atm of hydrogen, conversion of azobenzene reached 68% and the molar ratio of aniline and 1,2-diphenylhydrazine to the catalyst was 323:36:1 (eq 3).



As mentioned previously, the reaction of **1** with azobenzene yields bis(μ_3-phenylimido) complex **8** together with **7**, and **8** does not react with hydrogen. Catalytically inactive complex **8**, therefore, accumulated in the reaction system with the progress of the catalytic reaction. Although the formation of **8** was considerably retarded under pressurized hydrogen, most of catalyst **1** had been converted into **8** after the reaction.

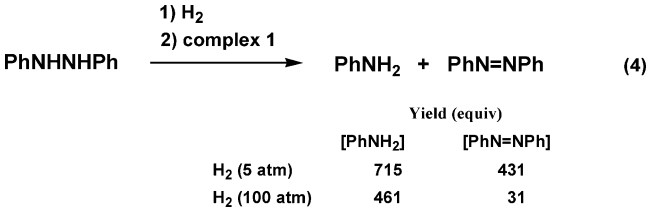
There are two possible routes for the formation of aniline in the catalytic hydrogenation of azobenzene. One is hydrogenolysis of the mono(μ_3-imido) complex **7**, which is directly formed in the reaction of catalyst **1** with azobenzene, and the other is catalytic hydrogenation of 1,2-diphenylhydrazine formed as the result of partial hydrogenation of azobenzene. The former process

(9) Matsubara, K.; Kawashima, T.; Kameo, H.; Suzuki, H. Unpublished result. Crystallographic Data for **3**. Formula: $C_{30}H_{49}NRu_3$, temp: 23 °C, crystal system: triclinic, space group: $P\bar{1}$(#2), cell parameters: a = 11.082(7) Å, b = 15.754(8) Å, c = 11.068 (5) Å, α = 108.98(4)°, β = 119.73(3)°, γ = 72.64(5)°, volume: 1564(1) Å^3, Z: 2, R = 0.041, wR_2 = 0.034. Crystallographic Data for **9**. Formula: $C_{32}H_{53}NRu_3$, temp: −50 °C, crystal system: triclinic, space group: $P\bar{1}$(#2), cell parameters: a = 11.137(15) Å, b = 11.064(13) Å, c = 15.72(2) Å, α = 96.42(4)°, β = 99.59(4)°, γ = 119.60(4)°, volume: 1617(4) Å^3, Z: 2, R = 0.0629, wR_2 = 0.1748. Crystallographic Data for **10**. Formula: $C_{37}H_{53}NRu_3$, temp: −120 °C, crystal system: monoclinic, space group: $P2_1/c$(#14), cell parameters: a = 11.272(6) Å, b = 19.196(12) Å, c = 49.179(13) Å, β = 94.30(5)°, volume: 10611(9) Å^3, Z: 12, R = 0.0401, wR_2 = 0.0825. Selected distances and angles as well as detailed crystallographic data for **3**, **9**, and **10** are listed in Supporting Information.

(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

has already been proved to be reasonable. The second process, catalytic hydrogenation of 1,2-diphenylhydrazine, is also plausible because complex **1** reacts with 1,2-diphenylhydrazine to form **7** in 91% yield.[3] This result implies the possibility of catalytic hydrogenation of 1,2-diphenylhydrazine.

When 1,2-diphenylhydrazine was treated with 5 atm of hydrogen at 100 °C in ethanol in the presence of a catalytic amount (S/C = 1100) of **1**, azobenzene and aniline were formed in the product/catalyst ratio of 431 and 715, respectively (eq 4).



Then, we examined the reactivity of 1,2-diphenylhydrazine toward **1** and **7**, which possibly existed in the above-mentioned reaction system. Complex **1** catalyzed disproportionation of 1,2-diphenylhydrazine, namely, a conversion of 2 mol of 1,2-diphenylhydrazine into 1 mol of azobenzene and 2 mol of aniline. In contrast, decomposition of 1,2-diphenylhydrazine giving equimolar azobenzene proceeded slowly in the presence of a catalytic amount of **7**. The ratio of 715:431 for the amount of the formed aniline to azobenzene in the above-mentioned reaction clearly shows the progress of both the disproportionation and the decomposition, and this result does not give evidence for the catalytic hydrogenation of 1,2-diphenylhydrazine. On the other hand, the ratio between aniline and azobenzene increased to 461:31 along with an increase in hydrogen pressure (100 atm) (eq 4). This result evidenced a catalytic hydrogenation of 1,2-diphenylhydrazine or azobenzene.

To the best of our knowledge, this is the first example of hydrogenation of azobenzene and 1,2-diphenylhydrazine catalyzed by transition metal complexes, although there have been, thus far, many precedents of reductive nitrogen−nitrogen bond cleavage of hydrazine with the aid of a proton source.

Summary and Conclusion

We previously pointed out the potential applicability of the transition metal polyhydrido clusters to the reduction of nitrogen.[3,4] In relation to the nitrogen activation, we examined nitrogen−nitrogen bond cleavage of azobenzene and 1,2-diphenylhydrazine.

Triruthenium pentahydrido, $(Cp'Ru)(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**1**), effectively cleaved a nitrogen−nitrogen double bond of azobenzene to yield $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu\text{-}H)_3$ (**7**) and $(Cp'Ru)_3(\mu_3\text{-}NPh)_2(\mu\text{-}H)$ (**8**). The resulting mono(μ_3-phenylimido) complex **7** underwent hydrogenolysis to generate aniline and **1**. Mono(μ_3-NR) complexes, **3** (R = H), **9** (R = Et), and **10** ($R = CH_2Ph$), also underwent hydrogenolysis to generate the corresponding amines and **1**, although bis(μ_3-phenylimido) complex **8** did not react with hydrogen.

Combination of the nitrogen−nitrogen bond cleavage and the hydrogenation of the mono(μ_3-imido) complex completed a formal catalytic cycle, and we demonstrated here catalytic hydrogenation of both azobenzene and 1,2-diphenylhydrazine to yield aniline using complex **1** as a catalyst.

This catalytic process is completely different from other examples of reduction of hydrazines so far reported, in which addition of a reducing agent and a proton source is essential. The results obtained here strongly imply the effectiveness of the polyhydrido clusters for the activation of hydrazines and nitrogen and provide important insight in connection with the proposed mechanism for the formation of ammonia from dinitorgen in a nitrogenase system.

Experimental Section

General Procedures. 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, 14599-85 for ethanol, and 40500-85 for toluene). Azobenzene and 1,2-diphenylhydrazine were obtained from Tokyo Kasei Kogyo Co., Ltd., and aniline was obtained from Sigma-Aldrich. For all substrates no further purification was performed. $(Cp'Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (**1**) was prepared as previously described.[11] Benzene-d_6 and tetrahydrofuran-d_8 were distilled, dried over sodium benzophenone ketyl, and stored under argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 Fourier transform spectrometer with tetramethylsilane as an internal standard. GC spectra were obtained by means of a Shimadzu GC 17A using a DB-5 column.

Reaction of $(Cp'Ru)_3(\mu_3\text{-}H)_2(\mu\text{-}H)_3$ (1) with Azobenzene. An NMR sample tube was charged with **1** (11.4 mg, 0.0158 mmol), PhN=NPh (22.0 mg, 0.121 mmol), cycloheptane (1 μL, 0.0083 mmol), and tetrahydrofuran-d_8 (0.4 mL). After the sample tube was sealed, the solution was warmed to 80 °C. The reaction was monitored by ^1H NMR spectroscopy. Molar distributions of **1** and resulting **7**, **8**, and **A** were calculated on the relative integral intensity of Cp′ ligands to cycloheptane. Also, aniline was quantified on the basis of relative integral intensity of the signal assigned for o-H (δ 6.53) to cycloheptane. After 141 h, complex **1** was fully consumed and **7**, **A**, and **8** were formed in yields of 37%, 21%, and 42%, respectively. At 265 h, although the yield of **7** remained almost unchanged (38%), **A** was decreased to 1% and the yield of **8** reached 61%.

A: ^1H NMR (400 MHz, rt, THF-d_8, δ/ppm) −19.49 (s, 2H, Ru-*H*), 1.49 (s, 15H, Cp′-*Me*), 1,96 (s, 30H, Cp′-*Me*). No signal assigned for N-*H* was observed. Signals of the phenyl group were obscured in the signals of excess azobenzene.

Reaction of $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu\text{-}H)_3$ (7) with Aniline. Tetrahydrofuran solution (5 mL) containing **7** (27.1 mg, 0.0337 mmol) and $PhNH_2$ (0.30 μL, 3.28 mmol) was stirred for 5 h at 100 °C. After removal of the solvent and excess $PhNH_2$ in vacuo at elevated temperature, complex **7** was fully recovered.

Reaction of $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu\text{-}H)_3$ (7) with Azobenzene. Tetrahydrofuran-d_8 solution (0.4 mL) of **7** (7.09 mg, 0.00882 mmol) and azobenzene (18.5 mg, 0.102 mmol) was charged in an NMR sample tube and was left for 25 h at 100 °C. ^1H NMR of the resulting residue exhibited no signals other than **7** and unreacted azobenzene.

Reaction of $(Cp'Ru)_3(\mu_3\text{-}NPh)(\mu\text{-}H)_3$ (7) with 1,2-Diphenylhydrazine. A 50 mL glass autoclave was charged with **7** (10.8 mg, 0.0135 mmol), 1,2-diphenylhydrazine (34.2 mg, 0.185 mmol), and tetrahydrofuran (5 mL). After the solution was stirred at 100 °C for 8 days, the solution was transferred

(11) Suzuki, H.; Kakigano, T.; Tada, K.; Igarashi, M.; Matsubara, K.; Inagaki, A.; Oshima, M.; Takao, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 67.

Table 3. Reaction Conditions of Hydrogenation of Azobenzene

run	H_2 (atm)	**1** (mmol)	added PhN=NPh	yield PhNHNHPh (mmol)	$PhNH_2$ (mmol)	conv (%) of PhN=NPh	total N balance (%)
1	5	0.00644	257.3 mg (1.41 mmol)	0.068	0.24	13	98
2	100	0.00619	325.0 mg (1.79 mmol)	0.22	2.0	68	80

Table 4. Reaction Conditions of Hydrogenation of 1,2-Diphenylhydrazine

run	H_2 (atm)	**1** (mmol)	added PhNHNHPh	yield PhN=NPh (mmol)	$PhNH_2$ (mmol)	conv of PhNHNHPh (%)	total N balance (%)
1	5	0.00137	277.2 mg (1.51 mmol)	0.59	0.98	72	98
2	100	0.00304	465.2 mg (2.53 mmol)	0.094	1.4	31	92

to a 50 mL Schlenk tube and the solvent was removed under reduced pressure. ^{1}H NMR spectra of the resulting residue revealed that complex **7** was fully recovered and all 1,2-diphenylhydrazine was converted to azobenzene.

Hydrogenolysis of (Cp′Ru)$_3$(μ_3-NEt)(μ-H)$_3$ (9). Tetrahydrofuran solution of **9** (32.7 mg, 0.0458 mmol) was equally divided into four 50 mL glass autoclaves, and H_2 gas was introduced into each autoclave at 5 atm after degassing. The reactions were performed at 100 °C, and the reactions were terminated after appropriate intervals (85, 115, 180, and 250 min) by removal of the solvent in vacuo. The ^{1}H NMR spectra of the residue revealed 88% of **9** was converted to **1** after 250 min.

Hydrogenolysis of (Cp′Ru)$_3$(μ_3-NCH$_2$Ph)(μ-H)$_3$ (10). A 50 mL glass autoclave was charged with **10** (50.6 mg, 0.0619 mmol) and 5 mL of tetrahydrofuran. After degassing of the autoclave, H_2 gas was introduced at 5 atm. After the mixture was stirred for 65 h at 100 °C, the solution was transferred to a 50 mL Schenk tube, and then, the solvent was removed under reduced pressure. Formation of **1** (100% by NMR) and benzylamine was detected by ^{1}H NMR spectra of the resulting residue.

Hydrogenolysis of (Cp′Ru)$_3$(μ_3-NPh)(μ-H)$_3$ (7). A 50 mL glass autoclave was charged with **7** (44.1 mg, 0.0550 mmol) and tetrahydrofuran (5 mL). After degassing of the autoclave, H_2 gas was introduced at 5 atm. After the reaction proceeded for 184 h at 100 °C, the reaction mixture was transferred to a 50 mL Schlenk tube and the solvent was removed under reduced pressure. ^{1}H NMR spectra of the resulting residue revealed the formation of **1** in 58% yield. At the same time, formation of a trace amount of aniline was detected.

Hydrogenolysis of (Cp′Ru)$_3$(μ_3-NPh)$_2$(μ-H) (8). Complex **8** (2.7 mg, 0.127 mmol) was solved in tetrahydrofuran/ethanol (5 mL/0.5 mL) solution and charged into a stainless steel autoclave. After H_2 gas was introduced at 50 atm, the mixture was heated to 100 °C and stirred for 7 days. The solution was transferred into the 50 mL Schlenk tube, and the solvent was removed in vacuo. ^{1}H NMR spectra of the resulting residue exhibited signals assigned for **8** and a new signal at δ 2.11 with the integral intensity of the Cp′ region of 95% and 5%, respectively.

Catalytic Hydrogenation of Azobenzene by (Cp′Ru)$_3$(μ_3-H)$_2$(μ-H)$_3$ (1). The reaction of **1** with excess azobenzene was performed in a glass/stainless steel autoclave under appropriate atmosphere of H_2 gas for 5 days at 100 °C. Ethanol (5 mL) was used as the solvent, and the compositions of **1** and substrate used for the reaction are listed in Table 3. After the solution was transferred to a 50 mL Schlenk tube and the solvent was removed under reduced pressure, a red oily compound was obtained. To the resulting mixture was added cyclooctane (50.0 μL, 0.368 mmol) as an internal standard. The ^{1}H NMR spectra were measured in C_6D_6, and the resulting aniline and the remaining azobenzene were quantified on the basis of integral intensity of each o-H signal (δ 6.43 for aniline and δ 7.92 for azobenzene) of the phenyl group to that of cyclooctane. 1,2-Diphenylhydrazine was calculated by dividing the integral intensity of o- and p-H of diphenylhydrazine from the total integral intensity of o- and p-H of diphenylhydrazine (δ 6.67 and 6.76, respectively) and p-H (δ 6.63) of anline.

Table 5. Crystallographic Data for 8

(a) Crystal Data

empirical formula	$C_{42}H_{56}N_2Ru_3$
fw	892.10
cryst description	block
cryst color	dark red
cryst size (mm)	0.10 × 0.10 × 0.10
crystallizing solution (temp)	THF (−30 °C)
cryst syst	triclinic
space group	$P\bar{1}$ (#2)
a (Å)	10.9707(11)
b (Å)	11.1817(10)
c (Å)	17.7671(13)
α (deg)	84.9770(17)
β (deg)	87.2000(17)
γ (deg)	64.1550(17)
V (Å^3)	1953.8(3)
Z	2
D_{calcd} (g/cm^{-3})	1.516
measurement temp (°C)	−50

(b) Intensity Measurements

diffractometer	R-AXIS RAPID
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
max 2θ (deg)	55
no. of reflns collected	19 044
no. of unique reflns	8780
no. of reflns used in refinement ($I > 2\sigma(I)$)	6962
abs correction type	numerical
abs transmn	0.9087 (min.), 0.9540 (max.)

(c) Refinement (SHELXL-97)

R_1 ($I > 2\sigma(I)$)	0.0373
wR_2 ($I > 2\sigma(I)$)	0.0792
R_1 (all data)	0.0518
wR_2 (all data)	0.0863
no. of data/restraints/params	8758/ 0/450
goodness of fit on F^2	1.042

It was independently certified that less than 0.1% of added aniline was detected in the solvent removed in vacuo by GC. As a result, the amount of aniline is considered to be almost completely detected by ^{1}H NMR.

Formation of (Cp′Ru)$_3$(μ_3-NPh)$_2$(μ-H)$_3$ (8). The reaction of **1** (20.0 mg, 0.028 mmol) with azobenzene (209.3 mg, 1.14 mmol) was carried out under 5 atm of H_2 for 13 days at 100 °C. In the ^{1}H NMR spectrum, quantitative formation of **8** was detected and both aniline and a trace of azobenzene were detected in the aromatic region (δ 6−8). After removal of volatile material at elevated temperature, the resulting residue was extracted with toluene and purified by the use of column chromatography on alumina. The solvent was removed in vacuo, the resulting red solid was dissolved in tetrahydrofuran, and the solution was cooled at −30 °C. Red crystals of **8** were obtained, which were suitable for X-ray analysis.

Catalytic Hydrogenation of 1,2-Diphenylhydrazine by (Cp′Ru)$_3$(μ_3-H)$_2$(μ-H)$_3$ (1). The reaction of **1** with excess 1,2-diphenylhydrazine was performed in a glass/stainless steel autoclave under atmosphere of H_2 gas for 5 days at 100 °C. Ethanol (5 mL) was used as a solvent, and the compositions of **1** and substrate used for the reaction are listed in Table 4.

After the solution was transferred to a 50 mL Schlenk tube and the solvent was removed under reduced pressure, a red oily compound was obtained. To the resulting mixture was added cyclooctane (3.0 μL, 0.2207 mmol) as an internal standard. The resulting aniline, 1,2-diphenylhydrazine, and the remaining azobenzene were quantified by ^{1}H NMR in the same manner as described in catalytic hydrogenation of azobenzene.

Monitoring the Reaction of (Cp′Ru)$_3$(μ_3-H)$_2$(μ-H)$_3$ (1) with 1,2-Diphenylhydrazine: Disproportionation of 1,2-Diphenylhydrazine. An NMR sample tube was charged with **1** (1.2 mg, 0.00168 mmol), 1,2-diphenylhydrazine (38.5 mg, 0.209 mmol), and tetrahydrofuran-d_8 (0.4 mL), with cyclooctane as an internal standard. The sample tube was sealed and heated to 80 °C. The changes in the molar distributions of 1,2-diphenylhydrazine, azobenzene, and aniline as well as **1**, **7**, and **8** were monitored by means of ^{1}H NMR spectroscopy. The reaction of **1** with 1,2-diphenylhydrazine resulted in the formation of **7** and **8** with yields of 90% and 10%, respectively, as mentioned in a previous paper.[3] At the same time, 1,2-diphenylhydrazine was converted to produce aniline and azobenzene in the ratio of 1:2. After 30 min, excess 1,2-diphenylhydrazine was almost consumed. Notably, the ratio of aniline to azobenzene remained 2:1. At this point, conversion of **1** was 44%. The molar ratio of **1** continued to decrease and completely disappeared to produce **7** and **8** after 27 h.

Decomposition of 1,2-Diphenylhydrazine by (Cp′Ru)$_3$(μ_3-NPh)(μ-H)$_3$ (7). It was confirmed by the reaction of **7** with 1,2-diphenylhydrazine shown above.

Single-Crystal X-ray Analysis of (Cp′Ru)$_3$(μ_3-NPh)$_2$(μ-H) (8). A crystal of **8** prepared as written above was mounted on glass fibers. The diffraction data of **8** were collected at −50 °C on an R-AXIS RAPID diffractometer. Reflections were collected in the range $6° < 2\theta < 55°$. The readout was performed with a pixel size of 100 μm × 100 μm. The structure was solved by direct methods using the SHELXS-97 program,[12] followed by successive cycles of full-matrix least-squares refinement on F^2. No H atom bound to the Ru atom was observed in the Fourier maps. Hydrogen atoms of the phenyl groups were included in the structure factor calculations in idealized positions. Least-squares refinement was carried out using SHELXL-97.[12] Details of crystal data and data collection refinement parameters are summarized in Table 5.

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Supporting Information Available: Tables of atomic coordinates and parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawings of **8** with full numbering schemes; crystallographic data are also available; selected bond lengths and angles as well as ORTEP drawings of **3**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049069W

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