Formation of Ammonia in the Reactions of a Tungsten Dinitrogen with Ruthenium Dihydrogen Complexes under Mild Reaction Conditions[1]

Yoshiaki Nishibayashi,† Shin Takemoto, Shotaro Iwai, and Masanobu Hidai*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received July 17, 2000

Treatment of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (**5**) with an equilibrium mixture of *trans*-[$RuCl(\eta^2\text{-}H_2)(dppp)_2$]X (**3**) with $pK_a = 4.4$ and [$RuCl(dppp)_2$]X (**4**) [X = PF_6, BF_4, or OTf; dppp = 1,3-bis(diphenylphosphino)propane] containing 10 equiv of the Ru atom based on tungsten in benzene−dichloroethane at 55 °C for 24 h under 1 atm of H_2 gave NH_3 in 45−55% total yields based on tungsten, together with the formation of *trans*-[$RuHCl(dppp)_2$] (**6**). Free NH_3 in 9−16% yields was observed in the reaction mixture, and further NH_3 in 36−45% yields was released after base distillation. Detailed studies on the reaction of **5** with numerous $Ru(\eta^2\text{-}H_2)$ complexes showed that the yield of NH_3 produced critically depended upon the pK_a value of the employed $Ru(\eta^2\text{-}H_2)$ complexes. When **5** was treated with 10 equiv of *trans*-[$RuCl(\eta^2\text{-}H_2)(dppe)_2$]X (**8**) with $pK_a = 6.0$ [X = PF_6, BF_4, or OTf; dppe = 1,2-bis(diphenylphosphino)ethane] under 1 atm of H_2, NH_3 was formed in higher yields (up to 79% total yield) compared with the reaction with an equilibrium mixture of **3** and **4**. If the pK_a value of a $Ru(\eta^2\text{-}H_2)$ complex was increased up to about 10, the yield of NH_3 was remarkably decreased. In these reactions, heterolytic cleavage of H_2 seems to occur at the Ru center via nucleophilic attack of the coordinated N_2 on the coordinated H_2 where a proton (H^+) is used for the protonation of the coordinated N_2 and a hydride (H^-) remains at the Ru atom. Treatment of **5**, *trans*-[$W(N_2)_2(PMePh_2)_4$] (**14**), or *trans*-[$M(N_2)_2(dppe)_2$] [M = Mo (**1**), W (**2**)] with $Ru(\eta^2\text{-}H_2)$ complexes at room temperature led to isolation of intermediate hydrazido(2−) complexes such as *trans*-[$W(OTf)(NNH_2)(PMe_2Ph)_4$]OTf (**19**), *trans*-[$W(OTf)(NNH_2)(PMePh_2)_4$]OTf (**20**), and *trans*-[$WX(NNH_2)(dppe)_2$]$^+$ [X = OTf (**15**), F (**16**)]. The molecular structure of **19** was determined by X-ray analysis. Further ruthenium-assisted protonation of hydrazido(2−) intermediates such as **19** with H_2 at 55 °C was considered to result in the formation of NH_3, concurrent with the generation of W(VI) species. All of the electrons required for the reduction of N_2 are provided by the zerovalent tungsten.

Introduction

Industrial ammonia (NH_3) production from dinitrogen (N_2) and dihydrogen (H_2) has successfully been carried out for more than 80 years by the use of Fe-based heterogeneous catalysts, but the reaction conditions are extremely drastic.[2,3] In contrast, biological nitrogen fixation is well-known to occur at ambient temperature and pressure.[3−6] The mechanism remains unclear although the X-ray structural model has recently been reported for the FeMo-cofactor, the site for conversion of N_2 to NH_3, of FeMo nitrogenase.[4] However, it is generally believed that N_2 is coordinated at the multimetallic site and converted to NH_3 by a sequential process of protonation followed by reduction.[5,6]

Extensive studies have long been continued to investigate the reactivities of coordinated N_2 in numerous N_2 complexes of transition metals.[7−10] Among them, molybdenum and tungsten N_2 complexes of the type [$M(N_2)_2(L)_4$] (M = Mo, W; L = tertiary phosphine)[7,10] have been most intensively studied since

* To whom correspondence should be addressed. Present address: Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan.

† Present address: Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan.

(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 69. Part 68: Nishibayashi, Y.; Wakiji, I.; Hirata, K.; DuBois, M. R.; Hidai, M. *Inorg. Chem.*, in press.

(2) (a) Ertl, G. In *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Plenum Press: New York, 1991 and references therein. (b) Appl, M. In *Ammonia*; Wiley-VCH: Weinheim, 1999 and references therein.

(3) Postgate, J. In *Nitrogen Fixation*; Cambridge University Press: Cambridge, 1998.

(4) (a) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677. (b) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 553. (c) Chan, M. K.; Kim, J.; Rees, D. C. *Science* **1993**, *260*, 792. (d) Rees, D. C.; Chan, M. K.; Kim, J. *Adv. Inorg. Chem.* **1993**, *40*, 89. (e) Kim, J.; Rees, D. C. *Biochemistry* **1994**, *33*, 389. (f) Eady, R. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2739. (g) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965. (h) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983. (i) Peters, J. W.; Stowell, M. H. B.; Soltis, S. M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C. *Biochemistry* **1997**, *36*, 1181.

(5) Recent theoretical studies, see: (a) Deng, H.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1062. (b) Stavrev, K. K.; Zerner, M. C. *Chem.—Eur. J.* **1996**, *2*, 83. (c) Dance, I. G. *Aust. J. Chem.* **1994**, *47*, 979. (d) Dance, I. G. In *Transition Metal Sulfur Chemistry*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; Chapter 7. (e) Dance, I. *Chem. Commun.* **1997**, 165. (f) Dance, I. *Chem. Commun.* **1998**, 523. (g) Zhong, S.-J.; Liu, C.-W. *Polyhedron* **1997**, *16*, 653. (h) Grönberg, K. L. C.; Gormal, C. A.; Durrant, M. C.; Smith, B. E.; Henderson, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 10613.

(6) (a) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460 and references therein. (b) Richards, R. L. *Coord. Chem. Rev.* **1996**, *154*, 83 and references therein. (c) Coucouvanis, D.; Demadis, K. D.; Malinak, S. M.; Mosier, P. E.; Tyson, M. A.; Laughlin, L. J. In *Transition Metal Sulfur Chemistry*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; Chapter 6 and references therein.

10.1021/ic000799f CCC: $19.00 © 2000 American Chemical Society
Published on Web 11/29/2000

the first preparation[11] of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane] (**1**) in this laboratory because of, at least in part, their possible relevance to the active site of nitrogenase and the unexpected rich chemistry of the coordinated N$_2$. The ligating N$_2$ can be transformed into NH$_3$ and/or hydrazine (NH$_2$NH$_2$) by treatment with inorganic acids such as H$_2$SO$_4$[12] and HCl.[13] A detailed mechanism for the protonation of the ligating N$_2$ leading to the formation of NH$_3$ and/or NH$_2$-NH$_2$ has been proposed on the basis of the reactivities of isolable intermediate complexes such as hydrazido(2−) complexes.[12,13] However, the N−H bond formation was not achieved by treatment of those N$_2$ complexes with H$_2$ because H$_2$ replaced the ligating N$_2$ to form hydride complexes [MH$_4$(L)$_4$].[14] Alternatively, acidic metal carbonyl hydrides such as [HCo(CO)$_4$] formally prepared from [Co$_2$(CO)$_8$] and H$_2$ could be employed for the N−H bond formation of the coordinated N$_2$ on tungsten.[15,16] Recently Morris and co-workers employed an acidic Ru(η^2-H$_2$) complex [CpRu(η^2-H$_2$)(dtfpe)]BF$_4$ {dtfpe=1,2-bis[bis(*p*-trifluoromethylphenyl)phosphino]ethane} with the pseudo-aqueous pK_a = 4.3 in order to protonate the ligating N$_2$ in *trans*-[W(N$_2$)$_2$(dppe)$_2$] (**2**).[17] Interestingly, the protonation occurred to form a hydrazido(2−) complex, although the Ru(η^2-H$_2$) complex was not available directly from H$_2$.[17] The pseudo-aqueous pK_a values are evaluated by acid−base reactions in organic solvents. We shall simply use the term pK_a values hereafter. Quite recently, Fryzuk and co-workers observed the N−H bond formation when a dinuclear zirconium complex with a side-on bridging N$_2$ ligand was treated with H$_2$.[18] However, the reaction stopped at the stage of N$_2$H, and no NH$_3$ was formed.[18]

Since the discovery of the first H$_2$ complex of a transition metal by Kubas and co-workers in 1984,[19] a great number of this unique class of complexes have been prepared and their structures and reactivities have been extensively studied.[20,21] Systematic investigation of ligand effects on the reactivity of coordinated H$_2$ led to findings of highly *acidic* M(η^2-H$_2$) complexes.[20,21] Especially, an acidic Ru(η^2-H$_2$) complex, *trans*-

(7) Recent advances in the chemistry of N$_2$ complexes can be followed in several excellent reviews, see: (a) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, Chapter 60. (b) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 13. (c) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, p 53. (d) Hidai, M.; Mizobe, Y. In *Molybdenum Enzymes, Cofactors and Model System*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993; Chapter 22. (e) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (f) Hidai, M.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 819. (g) Shilov, A. E. In *Metal Complexes in Biomimetic Chemical Reactions*; CRC Press: New York, 1997; Chapter 1. (h) Tuczek, F.; Lehnert, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2636. (i) Hidai, M.; Mizobe, Y. *Top. Organomet. Chem.* **1999**, *3*, 227. (j) Hidai, M. *Coord. Chem. Rev.* **1999**, *185*−*186*, 99.

(8) Rawls, R. L. *Chem. Eng. News* **1998**, June 22, 29.

(9) Recent reports of N$_2$ complexes, see: (a) Shan, H.; Yang, Y.; James, A. J.; Sharp, P. R. *Science* **1997**, *275*, 1460. (b) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. *Inorg. Chem.* **1998**, *37*, 112. (c) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 437. (d) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070. (e) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836. (f) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024. (g) Abbenhuis, R. A. T. M.; Rio, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749. (h) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, *37*, 5149. (i) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. (j) Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, *17*, 5591. (k) Campazzi, E.; Solari, E.; Floriani, C.; Scopelliti, R. *Chem. Commun.* **1998**, 2603. (l) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. *Inorg. Chem.* **1999**, *38*, 243. (m) Demadis, K. D.; El-Samanody, E.-S.; Coia, G. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 535. (n) Lehnert, N.; Tuczek, F. *Inorg. Chem.* **1999**, *38*, 1659. (o) Lehnert, N.; Tuczek, F. *Inorg. Chem.* **1999**, *38*, 1671. (p) Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053. (q) Tsai, Y.-C.; Johnson, M. J. A.; Mindiola, D. J.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10426. (r) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444. (s) Fomitchev, D. V.; Bagley, K. A.; Coppens, P. *J. Am. Chem. Soc.* **2000**, *122*, 532. (t) Tellers, D. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 954. (u) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **2000**, *122*, 3652. (v) Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T. A.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622.

(10) Our recent studies, see: (a) Nishibayashi, Y.; Iwai, S.; Hidai, M. *J. Am. Chem. Soc.* **1998**, *120*, 10559. (b) Harada, Y.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1999**, *574*, 24. (c) Harada, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chim. Acta* **1999**, *285*, 336. (d) Sasagawa, T.; Seino, H.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 425. (e) Ishino, H.; Tokunaga, S.; Seino, H.; Ishii, Y.; Hidai, M. *Inorg. Chem.* **1999**, *38*, 2489. (f) Arita, C.; Seino, H.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1999**, 611. (g) Seino, H.; Arita, C.; Nonokawa, D.; Nakamura, G.; Harada, Y.; Mizobe, Y.; Hidai, M. *Organometallics* **1999**, *18*, 4165. (h) Seino, H.; Mizobe, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 631. (i) Seino, H.; Nonokawa, D.; Nakamura, G.; Mizobe, Y.; Hidai, M. *Organometallics* **2000**, *19*, 2002.

(11) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *J. Chem. Soc., Chem. Commun.* **1969**, 1392.

(12) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature (London)* **1975**, *253*, 39. (b) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852. (c) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973.

(13) (a) Hidai, M.; Mizobe, Y.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1978**, 1187. (b) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405. (c) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461.

(14) (a) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110. (b) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079. (c) Pierantozzi, R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 1821. (d) Graff, J. L.; Sobieralski, T. J.; Wrighton, M. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 7526. (e) George, T. A.; Tisdale, R. C. *Inorg. Chem.* **1988**, *27*, 2909.

(15) Hidai, M.; Takahashi, T.; Yototake, I.; Uchida, M. *Chem. Lett.* **1980**, 645.

(16) (a) Nishihara, H.; Mori, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1980**, 667. (b) Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367.

(17) Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *30*, 593.

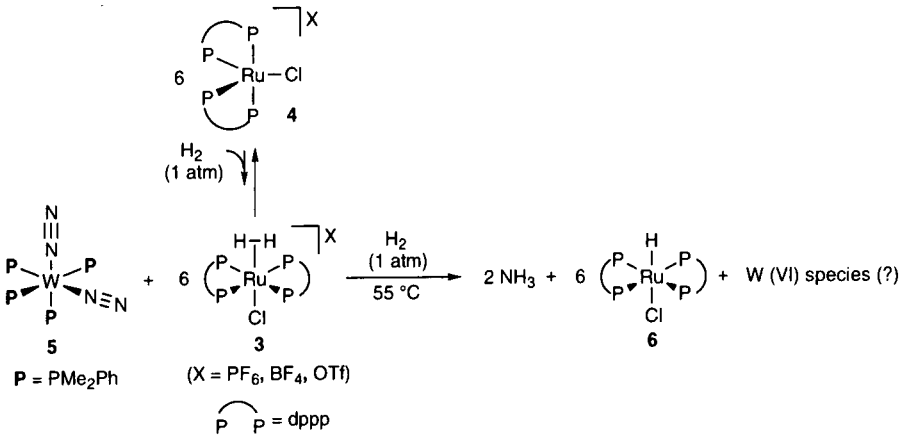
(18) (a) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445. (b) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 523. (c) Basch, H.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1999**, *121*, 5754.

(19) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120 and references therein.

(20) For recent reviews, see: (a) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913. (d) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (e) Morris, R. H. *Can. J. Chem.* **1996**, *74*, 1907. (f) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077. (g) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577.

(21) For recent examples, see: (a) Nishibayashi, Y.; Takei, I.; Hidai, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3047. (b) Bakhmutov, V. I.; Bianchini, C.; Maseras, F.; Lledos, A.; Peruzzini, M.; Vorontsov, E. V. *Chem.*−*Eur. J.* **1999**, *5*, 3318. (c) Basallote, M. G.; Duran, J.; Fernandez-Trujillo, M. J.; Manez, M. A. *Inorg. Chem.* **1999**, *38*, 5067. (d) Landau, S. E.; Morris, R. H.; Lough, A. J. *Inorg. Chem.* **1999**, *38*, 6060. (e) Hussein, K.; Marsden, C. J.; Barthelat, J.-C.; Rodriguez, V.; Conejero, S.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Chem. Commun.* **1999**, 1315. (f) Helleren, C. A.; Henderson, R. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1999**, 1213. (g) Basallote, M. G.; Duran, J.; Fernandez-Trujillo, M. J.; Gonzalez, G.; Manez, M. A.; Martinez, M. *J. Chem. Soc., Dalton Trans.* **1999**, 3379. (h) Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4475. (i) Borowshi, A. F.; Donnadieu, B.; Daran, J.-C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543. (j) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652.

Scheme 1



$[RuCl(\eta^2\text{-}H_2)(dppp)_2]PF_6$ [dppp = 1,3-bis(diphenylphosphino)-propane] (**3a**), has intrigued us because the Ru(η^2-H_2) complex is directly prepared from H_2 and $[RuCl(dppp)_2]PF_6$ (**4a**),[22] and the pK_a value of **3a** (pK_a = 4.4)[22] is almost the same as that of $[CpRu(\eta^2\text{-}H_2)(dtfpe)]BF_4$[17] employed by Morris for the protonation of coordinated N_2. This led to our recent findings of the formation of NH_3 from the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**5**) and complex **3a** under 1 atm of H_2. The presumed stoichiometry for the formation of NH_3 is shown in Scheme 1, indicating that the tungsten provides the six electrons for the reduction of N_2. Preliminary results have already been reported in a previous communication.[23] Here we will describe the detailed results of the reactions between tungsten N_2 and acidic ruthenium H_2 complexes, including the mechanism for the ruthenium-assisted protonation of coordinated N_2 on tungsten with H_2.

Results and Discussion

Formation of NH_3 from the Reactions of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (5) with 10 Equiv of Acidic Ru(η^2-H_2) Complexes. As reported by Mezzetti and co-workers,[22] an equilibrium mixture of **4a** and **3a** in a ratio of about 9:1 was obtained when a solution of **4a** in benzene−dichloroethane was stirred under 1 atm of H_2 at room temperature for 12 h. When **5** was added to the equilibrium solution containing 10 equiv of the Ru atom based on tungsten and the mixture was stirred under 1 atm of H_2 at 55 °C for 24 h, NH_3 was produced in 55% total yield based on tungsten, where free NH_3 in 10% yield was found in the reaction mixture, and further NH_3 in 45% yield was released after base distillation (Table 1; run 1). The ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture showed the complete consumption of **5** and the formation of *trans*-$[RuHCl(dppp)_2]$[22,24] (**6**) in 150% yield, concurrent with small amounts of PMe_2Ph and $[PMe_2PhH]^+$. Complex **6** has actually been isolated and characterized by spectroscopy. On the other hand, when complex **5** was directly treated with 10 equiv of **4a** under 1 atm of H_2 at 55 °C for 24 h, NH_3 was formed in 22% total yield (Table 1; run 2). This result indicates that the pretreatment of **4a** under 1 atm of H_2 and the subsequent addition of complex **5** to the solution is preferred to increase the yield of NH_3. The yield of NH_3 was lower when tetrahydrofuran (THF) was used as solvent (Table 1; run 3). The formation of NH_3 was not observed at 25 °C. Both the Ru complex **4a** and H_2 are essential to the formation of NH_3. This was unequivocally demonstrated by the experiments without complex **4a** or H_2 (Table 1; runs 4 and 5).

Table 1. Reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**5**) with an Equilibrium Mixture of *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]X$ (**3**) and $[RuCl(dppp)_2]X$ (**4**) Derived from 10 Equiv of **4**[a]

		yield of NH_3 (%)[b]		
run	Ru complex	free[c]	basic[d]	total
1	$[RuCl(dppp)_2]PF_6$ (**4a**)	10	45	55[e]
2[f]	$[RuCl(dppp)_2]PF_6$ (**4a**)	4	18	22
3[g]	$[RuCl(dppp)_2]PF_6$ (**4a**)	3	23	26
4[h]	$[RuCl(dppp)_2]PF_6$ (**4a**)	0	0	0
5[i]		0	0	0
6	$[RuCl(dppp)_2]BF_4$ (**4b**)	16	38	54[e]
7	$[RuCl(dppp)_2]OTf$ (**4c**)	9	36	45[e]

[a] All of the reactions were carried out in benzene−dichloroethane under 1 atm of H_2 at 55 °C for 24 h after 0.10 mmol of **5** was added to an equilibrium mixture of **3** and **4** derived from 10 equiv of **4** unless otherwise stated. [b] Yield of NH_3 was based on the W atom. [c] Free yield was before base distillation of the reaction mixture. [d] Basic yield was after base distillation to fully liberate NH_3. [e] Variation ±3% between experiments. [f] The reaction was carried out without pretreatment of **4a** under 1 atm of H_2 (see text). [g] THF was used as solvent in place of benzene−dichloroethane. [h] The reaction was carried out under 1 atm of N_2. [i] The reaction was carried out in the absence of the Ru complex.

Two analogous H_2 complexes *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]BF_4$ (**3b**) and *trans*-$[RuCl(\eta^2\text{-}H_2)(dppp)_2]OTf$ (**3c**) were also prepared in a similar way from $[RuCl(dppp)_2]BF_4$ (**4b**) and $[RuCl(dppp)_2]$-OTf (**4c**) under 1 atm of H_2, respectively. The efficiency for the formation of NH_3 did not significantly change when **4b** and **4c** were employed in place of **4a** (Table 1; runs 6 and 7). In all cases, a trace amount of NH_2NH_2 was observed. It is noteworthy that free NH_3 was observed in low but substantial yields in all cases using **4a**−**4c**. This provides clear-cut evidence that NH_3 is produced from the coordinated N_2 and H_2 under mild reaction conditions.

Reactions of complex **5** with a series of acidic Ru(η^2-H_2) complexes were then investigated to elucidate the relationship between N−H bond formation and the acidity constant pK_a of a η^2-H_2 ligand. Typical results are shown in Table 2. In sharp contrast to complex **4a**, Ru complexes $[RuCl(dppe)_2]X$ (X = PF_6, **7a**;[25a] BF_4, **7b**;[25b] OTf, **7c**; BAr_4, **7d**) [Ar = 3,5-$(CF_3)_2C_6H_3$] were quantitatively converted under 1 atm of H_2

(22) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Zotto, A. D.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711.
(23) Preliminary communication: Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540. A commentary of this work, see: Leigh, G. J. *Science* **1998**, *279*, 506.
(24) James, B. R.; Wang, D. K. W. *Inorg. Chim. Acta* **1976**, *19*, L17.
(25) (a) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278. (b) Polam, J. R.; Porter, L. C. *J. Coord. Chem.* **1993**, *29*, 109.

Table 2. Reaction of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (**5**) with Ru(η^2-H_2) Complexes[a]

run	Ru(η^2-H_2) complex	pK_a	yield of NH_3 (%)[b] free[c]	basic[d]	total
1	*trans*-[RuCl(η^2-H_2)(dppe)$_2$]PF_6 (**8a**)	6.0	3	52	55[e]
2	*trans*-[RuCl(η^2-H_2)(dppe)$_2$]BF_4 (**8b**)		0	71	71[f]
3	*trans*-[RuCl(η^2-H_2)(dppe)$_2$]BF_4 (**8b**)				79[g]
4	*trans*-[RuCl(η^2-H_2)(dppe)$_2$]OTf (**8c**)				74[g]
5	*trans*-[RuCl(η^2-H_2)(dppe)$_2$]BAr_4 [h] (**8d**)		0	3	3
6	[CpRu(η^2-H_2)(dppm)]OTf (**10**)	(7.5)[i]	3	31	34[j]
7	*trans*-[RuH(η^2-H_2)(dppe)$_2$]BF_4 (**11b**)	(10.2)[k]	0	0	0
8	*trans*-[RuH(η^2-H_2)(dppe)$_2$]OTf (**11c**)		0	6	6
9	*trans*-[RuH(η^2-H_2)(dppe)$_2$]BF_4 (**12b**)	15.0	0	0	0
10	*trans*-[RuH(η^2-H_2)(dppe)$_2$]OTf_4 (**12c**)		0	0	0

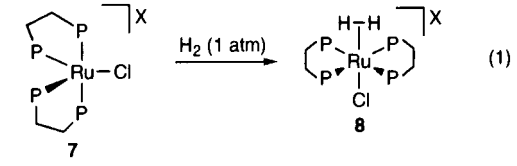
[a] All of the reactions were carried out in benzene−dichloroethane using 0.10 mmol of **5** and 1.00 mmol of Ru(η^2-H_2) complex under 1 atm of H_2 at 55 °C for 24 h unless otherwise stated. [b] Yield of NH_3 was based on the W atom. [c] Free yield was before base distillation of the reaction mixture. [d] Basic yield was after base distillation to fully liberate NH_3. [e] Variation ±10% between experiments. [f] Variation ±3% between experiments. [g] This yield of NH_3 was observed in the water extract of the reaction mixture (see text). [h] Ar = 3,5-$(CF_3)_2C_6H_3$. [i] The pK_a value of [CpRu(η^2-H_2)(dppm)]BF_4 was reported to be 7.5 (see ref 31). [j] Variation ±4% between experiments. [k] The pK_a value of *trans*-[RuH(η^2-H_2)(dppp)$_2$]PF_6 **(11a)** was reported to be 10.2 (see ref 32).

Table 3. ^1H and $^{31}P\{^1H\}$ NMR Data of *trans*-[RuCl(η^2-H_2)(dppe)$_2$]X (**8**)[a]

X	chemical shift of (η^2-H_2)[b]	chemical shift of $^{31}P\{^1H\}$ NMR[b]
PF_6	−11.8	51.8
BF_4	−11.9	51.5
OTf	−11.6	52.2
BAr_4	−12.5	49.4

[a] All of the samples were measured in $CDCl_3$ at 18 °C under 1 atm of H_2. [b] In ppm.

into the corresponding Ru(η^2-H_2) complexes *trans*-[RuCl(η^2-H_2)(dppe)$_2$]X (X = PF_6, **8a**;[25a] BF_4, **8b**;[25a] OTf, **8c**; BAr_4, **8d**) within several minutes at ambient temperature, respectively (eq 1).[25] The typical ^1H and $^{31}P\{^1H\}$ NMR data of **8** are shown in

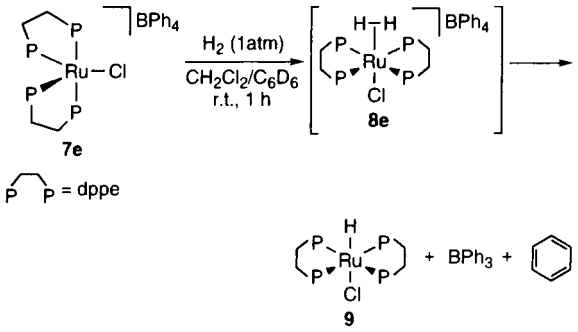


(X = PF_6 **7a**; BF_4 **7b**; OTf **7c**; BAr_4 **7d**)

P P = dppe

Table 3. The existence of the η^2-H_2 moiety in a new complex **8c** was confirmed by variable-temperature T_1 measurement and the observation of a large J_{HD} for the corresponding isotopomer.[20,21] A minimum T_1 value of 24 ms (400 MHz in CD_2Cl_2) at 250 K was obtained for the broad signal at −11.6 ppm assignable to the η^2-H_2. The deuterio derivative *trans*-[RuCl(η^2-HD)(dppe)$_2$]OTf (**8c**-d_1) was prepared by the reaction of *trans*-[RuHCl(dppe)$_2$][25,26] (**9**) with a stoichiometric amount of trifluoromethanesulfonic acid-d_1 (DOTf) in CD_2Cl_2 at room temperature. The complex (**8c**-d_1) has a J_{HD} coupling constant of 25.6 Hz in CD_2Cl_2 at 20 °C. These values of minimum T_1 and J_{HD} are in good agreement with those of a known complex **8a**.[25] These results show that the counteranion of complex **8** does not essentially affect the Ru(η^2-H_2) bonding except for BPh_4^- anion (vide infra). Although complex **8a** has lower acidity (pK_a = 6.0)[25] than complex **3a**, the ligating N_2 in **5** is expected to be protonated by the coordinated H_2 in **8a** because the ligating N_2 is protonated by a large excess of MeOH (pK_a = 15)[20b] to form NH_3 under some conditions.[12b,27] Actually, NH_3 was produced in 55% total yield at 55 °C (Table 2; run 1). Treatment of **5** with 10 equiv of **8b** under the same conditions produced NH_3 in 71% total yield (Table 2; run 2). When the reaction mixture of **5** and 10 equiv of **8b** under the same reaction conditions was extracted with an excess of water instead of base distillation, the amount of NH_4^+ in the water extract reached 79% yield based on tungsten (Table 2; run 3). The similar yield of NH_3 was obtained by using **8c** (Table 2; run 4). Furthermore, plausible hydrazido(2−) intermediate complexes, which might provide NH_3 by base treatment,[12c] were not detected by the NMR and IR spectra of the reaction mixture (vide infra). These results indicate that protonation of the coordinated N_2 did not stop at the stage of the hydrazido(2−) form, but proceeded further to form NH_4^+. Thus, the reaction mixture was treated with KOH aqueous solution to fully liberate NH_3 (base distillation). It is to be noted that no formation of NH_3 was observed when the above reactions were performed at ambient temperature.

Employment of [RuCl(dppe)$_2$]BPh_4 (**7e**) did not give NH_3 under the same conditions. This might be due to the degradation[28,29] of the initially formed H_2 complex *trans*-[RuCl(η^2-H_2)(dppe)$_2$]BPh_4 (**8e**) via nucleophilic attack of the BPh_4^- anion on the η^2-H_2 ligand. In fact, reaction of **7e** with 1 atm of H_2 at room temperature for 24 h gave **9** together with BPh_3 and benzene (eq 2). The formation of BPh_3 and benzene was



confirmed by GLC and GC−MS. On the other hand, Ru(η^2-H_2) complex **8d** with BAr_4^- anion[30] could be prepared in a similar way to complexes **8a**−**8c**; however, the yield of NH_3 from the reaction of **5** with **8d** was quite low (Table 2; run 5).

The Ru(η^2-H_2) complex [CpRu(η^2-H_2)(dppm)]OTf [31] [dppm = bis(diphenylphosphi**n**o)methane] (**10**) with relatively lower acidity[31] was less effective for the protonation of the coordinated N_2 in complex **5**, and the yield of NH_3 was moderate (Table 2;

(26) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 2605.

(27) (a) Hidai, M.; Yokotake, I.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1982**, 453. (b) Wakatabe, A.; Takahashi, T.; Jin, D.-M.; Yokotake, I.; Uchida, Y.; Hidai, M. *J. Organomet. Chem.* **1983**, *254*, 75.

(28) (a) Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7505. (c) Bianchini, C.; Moneti, S.; Peruzzini, M.; Vizza, F. *Inorg. Chem.* **1997**, *36*, 5818.

(29) Cooper, J. N.; Powell, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 1590.

(30) (a) The BPh_4^- anion is susceptible to protonolysis by H_2SO_4. The presence of the electron-withdrawing CF_3 substituent in the Ar group rendered the BAr_4^- anion virtually inert toward degradation by H_2SO_4. (b) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (c) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(31) (a) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (b) The pK_a value of [CpRu(η^2-H_2)(dppm)]BF_4 was estimated to be 7.5.[31a]

Table 4. Reactions of N_2 Complexes of Mo and W with *trans*-[RuCl(η^2-H_2)(dppe)$_2$]OTf (**8c**),[a] H_2SO_4,[b,c] or HOTf[a]

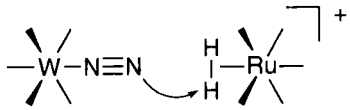
run	N_2 complex	proton source	yield of NH_3 (%)[d] free[e]	basic[f]	total
1	*cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**)	**8c**			74[g]
2	cis-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**)	H_2SO_4			198[c]
3	*cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**)	HOTf	0	122	122[h]
4	*cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**)	HOTf[i]	0	102	102[j]
5	*cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] (**13**)	**8c**	0	0	0
6	*cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] (**13**)	H_2SO_4			68[c]
7	*trans*- [W(N_2)$_2$($PMePh_2$)$_4$] (**14**)	**8c**	3	2	5[k]
8	*trans*-[W(N_2)$_2$($PMePh_2$)$_4$] (**14**)	H_2SO_4			190[c]
9	*trans*-[W(N_2)$_2$($PMePh_2$)$_4$] (**14**)	HOTf	0	109	109[l]
10	*trans*-[W(N_2)$_2$($PMePh_2$)$_4$] (**14**)	HOTf[i]	0	102	102[h]
11	*trans*-[W(N_2)$_2$(dppe)$_2$] (**2**)	**8c**	0	0	0

[a] The reactions with **8c** or HOTf were carried out in benzene−dichloroethane using 0.10 mmol of N_2 complex and 1.00 mmol of **8c** under 1 atm of H_2 or 1.00 mmol of HOTf under 1 atm of N_2 at 55 °C for 24 h. [b] The reactions with H_2SO_4 were carried out in methanol using ca. 15 equiv of H_2SO_4 at room temperature for 20 h. [c] See ref 12. [d] Yield of NH_3 was based on the W atom. [e] Free yield was before base distillation of the reaction mixture. [f] Basic yield was after base distillation to fully liberate NH_3. [g] This yield of NH_3 was observed in the water extract of the reaction mixture (see text). [h] Variation ±5% between experiments. [i] The reactions were carried out at room temperature for 24 h. [j] Variation ±8% between experiments. [k] Variation ±2% between experiments. [l] Variation ±3% between experiments.

run 6). Employment of Ru(η^2-H_2) complexes such as *trans*-[RuH(η^2-H_2)(dppp)$_2$]X[22,32] (X = BF_4, **11b**; OTf, **11c**) and *trans*-[RuH(η^2-H_2)(dppe)$_2$]X[33] (X = BF_4, **12b**;[33] OTf, **12c**) with much lower acidity[32,33] resulted in the formation of NH_3 in 0−6% total yields (Table 2; runs 7−10). Conventional hydrogenation catalysts such as [$RuCl_2(PPh_3)_3$], [$RuH_2(PPh_3)_4$], [$RhCl(PPh_3)_3$], and Pd/C (10%) as well as *trans*-[Mo(CO)(η^2-H_2)(dppe)$_2$][20a,34] afforded only trace amounts of NH_3.

In conclusion, when the acidity constant pK_a of a Ru(η^2-H_2) complex was increased up to about 10, the yield of NH_3 was remarkably decreased.

Reactions of Other N_2 Complexes of Mo and W with Acidic Ru(η^2-H_2) Complexes. Reactions of several N_2 complexes of Mo and W with an excess amount of Ru(η^2-H_2) complex **8c** were investigated. Typical results are shown in Table 4. No NH_3 was formed when *cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] (**13**) was used in place of **5**, although the protonation with H_2SO_4 gives NH_3 in 68% yield[12] (Table 4; runs 5 and 6). Previously, Chatt and co-workers reported that when **5** and *trans*-[W(N_2)$_2$($PMePh_2$)$_4$] (**14**) are treated with H_2SO_4 at ambient temperature, NH_3 is formed in 198% and 190% yields, respectively (Table 4; runs 2 and 8).[12] We have now found that treatment of **5** and **14** with 10 equiv of trifluoromethanesulfonic acid (HOTf) in benzene−dichloroethane under 1 atm of N_2 at 55 °C for 24 h gives NH_3 in 122% and 109% total yields, respectively (Table 4; runs 3 and 9). Even at room temperature, both of the reactions produced NH_3 in 102% yield (Table 4; runs 4 and 10). In sharp contrast to these findings, the protonation of **14** with **8c** at 55 °C afforded NH_3 in only 5% yield (Table 4; run 7), although the corresponding reaction of **5** with **8c** gave NH_3 in 74% yield (Table 4; run 1). If the protonation of the coordinated N_2 in either **5** or **14** with **8c** proceeded with a trace of protonic acid HOTf released from **8c**, NH_3 should have been formed even at ambient temperature and in almost the same yields in both cases. However, the reaction at ambient temperature did not give NH_3, and the yield of NH_3 by the reaction of **5** with **8c** at 55 °C was apparently higher than that of **14** with **8c** (vide supra). Therefore, we are inclined to the view that the N−H bond formation proceeds through the direct nucleophilic attack of the coordinated N_2 on W upon the coordinated H_2 on Ru, as shown in eq 3. This is



(3)

essentially the same as the intermolecular heterolytic cleavage of η^2-H_2 ligands by base.[20,21] Recently, various complexes containing intramolecular[35,36] or intermolecular[35,37] hydrogen bonds between a metal hydride and a hydrogen bond donor such as an O−H or an N−H group have been reported which represent plausible intermediates for the heterolytic cleavage of coordinated H_2.[35−37]

On the other hand, treatment of *trans*-[W(N_2)$_2$(dppe)$_2$] (**2**) with 10 equiv of **8c** in benzene−dichloroethane at 55 °C for 24 h under 1 atm of H_2 did not give any NH_3 (Table 4; run 11), however, the protonation of the coordinated N_2 proceeded to

(32) The pK_a value of *trans*-[RuH(η^2-H_2)(dppp)$_2$]PF_6 (**11a**) was estimated to be 10.2.[22]

(33) (a) Saburi, M.; Aoyagi, K.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1990**, 601. (b) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (c) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375. (d) The pK_a value of *trans*-[RuH(η^2-H_2)(dppe)$_2$]BF_4 (**12b**) was estimated to be 15.0.[33c]

(34) (a) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113. (b) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569.

(35) For recent reviews, see: (a) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. *Acc. Chem. Res.* **1996**, *29*, 348. (b) Shubina, E. S.; Belkova, N. V.; Epstein, L. M. *J. Organomet. Chem.* **1997**, *536*−*537*, 17. (c) Crabtree, R. H. *Science* **1998**, *282*, 2000. (d) Crabtree, R. H.; Eisenstein, O.; Sini, G.; Peris, E. J. *J. Organomet. Chem.* **1998**, *567*, 7. (e) Crabtree, R. H. *J. Organomet. Chem.* **1998**, *577*, 111.

(36) O−H: (a) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (b) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Yuo, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007. N−H: (d) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (e) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (f) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (g) Xu, W.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 1549. (h) Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001. (i) Lee, D.-H.; Patel, B. P.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **1999**, 297. S−H: (j) Schlaf, M.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 625. (k) Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1996**, *15*, 4423.

(37) O−H: (a) Peris, E.; Wessel, J.; Patel, B. P.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2175. (b) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105. (c) Belkova, N. V.; Shubina, E. S.; Ionidis, A. V.; Epstein, L. M.; Jacobsen, H.; Messmer, A.; Berke, H. *Inorg. Chem.* **1997**, *36*, 1522. (d) Ayllon, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000. (e) Guari, Y.; Ayllon, J. A.; Sabo-Etienne, S.; Chaudret, B.; Hessen, B. *Inorg. Chem.* **1998**, *37*, 640. (f) Gründemann, S.; Ulrich, S.; Limbach, H.-H.; Golubev, N. S.; Denisov, G. S.; Epstein, L. M.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1999**, *38*, 2550. N−H: (g) Wessel, J.; Lee, J. C. L., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (h) Patel, B.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *Chem. Commun.* **1996**, 991. (i) Abdur-Rashid, K.; Gusev, D. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 11826. (j) Gusev, D. G.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 13138. (k) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 834.

Table 5. Reactions of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**1**) or *trans*-[W(N$_2$)$_2$(dppe)$_2$] (**2**) with Ru(η^2-H$_2$) Complexes[a]

run	N$_2$ complex	Ru(η^2-H$_2$) complex	pK_a	yield (%) hydrazido(2−) complex[b]	yield (%) Ru−H complex[b,c]
1[d]	**2**	[RuCl(η^2-H$_2$)(dppp)$_2$]BF$_4$ (**3b**)[e]	(4.4)[f]	[WF(NNH$_2$)(dppe)$_2$]BF$_4$ (**16b**), 63%	146% (**6**)
2	**2**	[RuCl(η^2-H$_2$)(dppe)$_2$]BF$_4$ (**8b**)		[WF(NNH$_2$)(dppe)$_2$]BF$_4$ (**16b**), 99%	199% (**9**)
3	**2**	[RuCl(η^2-H$_2$)(dppe)$_2$]OTf (**8c**)		[W(OTf)(NNH$_2$)(dppe)$_2$]OTf (**15**), 75%	199% (**9**)
4	**1**	[RuCl(η^2-H$_2$)(dppe)$_2$]PF$_6$ (**8a**)	6.0	[MoF(NNH$_2$)(dppe)$_2$]PF$_6$ (**18**), 50%	117% (**9**)
5	**2**	[CpRu(η^2-H$_2$)(dppm)]OTf (**10**)	(7.5)[g]	[W(OTf)(NNH$_2$)(dppe)$_2$]OTf (**15**), 99%	160%[h]
6[i]	**2**	[RuH(η^2-H$_2$)(dppp)$_2$]OTf (**11c**)	(10.2)[j]	0%[k]	
7[i]	**2**	[RuH(η^2-H$_2$)(dppe)$_2$]OTf (**12c**)	(15.0)[l]	0%[m]	

[a] All of the reactions were carried out in benzene−dichloroethane using N$_2$ complex (**1** or **2**) and 2 equiv of Ru(η^2-H$_2$) complex under 1 atm of H$_2$ at room temperature for 24 h unless otherwise stated. [b] Yields of hydrazido(2−) and Ru−H complexes were estimated by ^{31}P{^{1}H} NMR (see text). [c] Yield of Ru−H complex was based on the W atom. [d] At 55 °C. [e] A mixture of **4b** and **3b** derived from treatment of 2 equiv of **4b** with 1 atm of H$_2$ was used for the protonation of coordinated N$_2$. [f] The pK_a value of *trans*-[RuCl(η^2-H$_2$)(dppp)$_2$]PF$_6$ (**3a**) was reported to be 4.4 (see ref 22). [g] The pK_a value of [CpRu(η^2-H$_2$)(dppm)]BF$_4$ was reported to be 7.5 (see ref 31). [h] [CpRuH(dppm)] and [CpRuCl(dppm)] were obtained in 100% and 60% NMR yields, respectively. In addition, unknown compounds were observed. It was confirmed that [CpRuH(dppm)] partly reacted with dichloroethane to give [CpRuCl(dppm)] under the same reaction conditions. Thus, the yield of Ru−H complex was estimated to be 160%. [i] THF was used as solvent. [j] The pK_a value of *trans*-[RuH(η^2-H$_2$)(dppp)$_2$]PF$_6$ (**11a**) was reported to be 10.2 (see ref 32). [k] [WH$_4$(dppe)$_2$] was obtained. In addition, unknown compounds were observed. [l] The pK_a value of *trans*-[RuH(η^2-H$_2$)(dppe)$_2$]BF$_4$ (**12b**) was reported to be 15.0 (see ref 33). [m] [WH$_4$(dppe)$_2$] was obtained in >95% NMR yield.

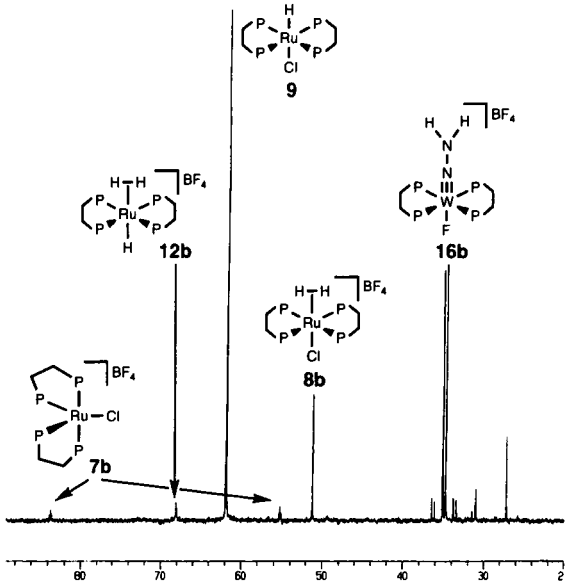
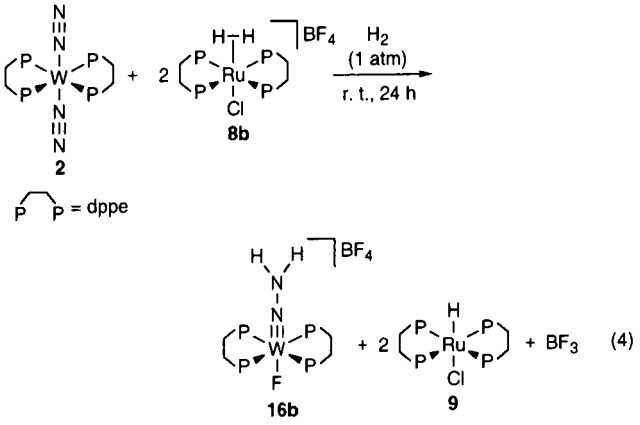


Figure 1. ^{31}P{^{1}H} NMR spectrum of the reaction mixture of *trans*-[W(N$_2$)$_2$(dppe)$_2$] (**2**) and 2 equiv of *trans*-[RuCl(η^2-H$_2$)(dppe)$_2$]BF$_4$ (**8b**) in benzene−dichloroethane at room temperature for 24 h under 1 atm of H$_2$.

afford the hydrazido(2−) complex *trans*-[W(OTf)(NNH$_2$)(dppe)$_2$]OTf (**15**) in high yield. The latter complex **15** was previously prepared by the protonation of **2** with HOTf.[38] The ruthenium-assisted protonation of coordinated N$_2$ affording the hydrazido(2−) complex occurred even at ambient temperature. Typical results of the reactions between *trans*-[M(N$_2$)$_2$(dppe)$_2$] [M = Mo (**1**), W (**2**)] and Ru(η^2-H$_2$) complexes at ambient temperature are shown in Table 5. The NMR yields of the metal products were determined by integration of the gated-{^{1}H}-decoupled ^{31}P resonances against PPh$_3$ added as an internal reference. Figure 1 shows the ^{31}P{^{1}H} NMR spectrum (in CDCl$_3$) of the crude reaction mixture of **2** and 2 equiv of **8b** in benzene−dichloroethane at room temperature for 24 h under 1 atm of H$_2$ (eq 4) (Table 5; run 2). This demonstrates that N$_2$ complex **2** was transformed into the hydrazido(2−) complex *trans*-[WF(NNH$_2$)(dppe)$_2$]BF$_4$[39] (**16b**), in 99% NMR yield, showing a doublet band with ^{183}W satellites at 35.0 ppm (J_{PF} = 39 Hz, J_{PW} = 290 Hz). With regard to Ru complexes, Ru−H



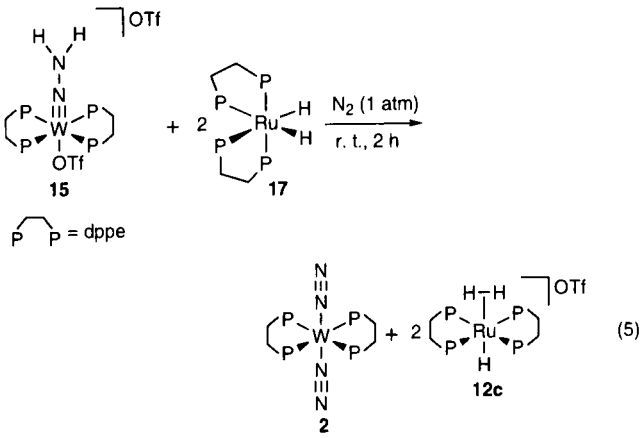
(4)

complex **9**, in 199% NMR yield, exhibiting a singlet at 61.9 ppm was a major product, although weak resonances assigned to Ru complexes **8b**, **7b**, and **12b** were also found in the reaction mixture. These results corroborate the view that the heterolytic cleavage of H$_2$ occurs at the Ru center where one H atom is used for the protonation of coordinated N$_2$ on the W atom and the other H atom remains at the Ru atom as a hydride. The direct transfer of a proton from the η^2-H$_2$ ligand in **8c** to the coordinated N$_2$ in **2** is also strongly supported by the experiment under 1 atm of D$_2$. ^{31}P{^{1}H} and ^{2}H NMR spectra of the reaction mixture of **2** and 2 equiv of *trans*-[RuCl(η^2-D$_2$)(dppe)$_2$]OTf (**8c**-d_2) in benzene−dichloroethane at room temperature for 0.5 h under 1 atm of D$_2$ showed that the deuterated hydrazido(2−) complex *trans*-[W(OTf)(NND$_2$)(dppe)$_2$]OTf (**15′**) was formed in ca. 70% NMR yield.

Employment of Ru(η^2-H$_2$) complexes **11** and **12** with a pK_a value of above 10 did not cause the protonation of coordinated N$_2$ in complex **2**; instead the tetrahydrido tungsten complex [WH$_4$(dppe)$_2$][14d] was obtained as a major product (Table 5; runs 6 and 7). It is to be noted that the tetrahydrido tungsten complex was produced in a much lower yield in the absence of **11** or **12** under the same conditions. Thus, treatment of **2** with 2 equiv of **12c** in THF at room temperature for 12 h under 1 atm of H$_2$ afforded [WH$_4$(dppe)$_2$] in 75% NMR yield. On the other hand, the formation of [WH$_4$(dppe)$_2$] in 30% NMR yield was observed in the absence of **12c** under the same reaction conditions. In both cases, unreacted **2** was recovered; however, no other W

(38) Field, L. D.; Jones, N. G.; Turner, P. *Organometallics* **1998**, *17*, 2394.
(39) (a) Chatt, J.; Heath G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074. (b) Chatt, J. C.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1520.

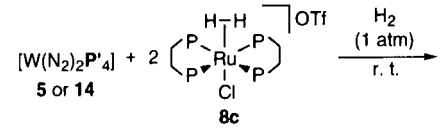
complex was formed. Interestingly, the hydrazido(2−) complex **15** was deprotonated by the dihydride complex *cis*-[RuH_2-$(dppe)_2$][40] (**17**) at room temperature for 2 h in THF under 1 atm of N_2 to give N_2 complex **2** and Ru(η^2-H_2) complex **12c** in 60% and 199% NMR yields, respectively (eq 5). This is not



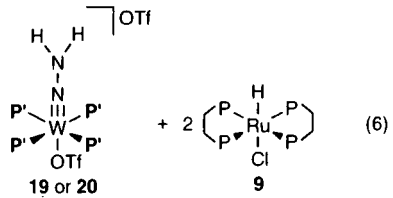
surprising because the NH proton in **15** is deprotonated by base like KO^{t}Bu or Et_3N.[38]

The protonation of the coordinated N_2 in **1** with **8a** also proceeded smoothly at ambient temperature. The hydrazido-(2−) complex *trans*-[MoF(NNH_2)$(dppe)_2$]PF_6[41] (**18**) was obtained in ca. 50% NMR yield, concurrent with the formation of **9** in 117% NMR yield (Table 5; run 4).

Isolation of Hydrazido(2−) Complexes *trans*-[W(OTf)-(NNH_2)(L)$_4$]OTf (L = PMe_2Ph, 19; $PMePh_2$, 20) and *trans*-[Mo(OTf)(NNH_2)$(PMe_2Ph)_4$]OTf (21). When the reaction of **5** and 2 equiv of **8c** was carried out at room temperature for 20 h in benzene−dichloroethane, the hydrazido(2−) complex *trans*-[W(OTf)(NNH_2)$(PMe_2Ph)_4$]OTf (**19**) was obtained in 63% NMR yield together with **9** in 199% NMR yield (eq 6).



(**5**, **P'** = PMe_2Ph; **14**, **P'** = $PMePh_2$)



(**19**, **P'** = PMe_2Ph; **20**, **P'** = $PMePh_2$)

Analogous hydrazido(2−) complexes *trans*-[WX(NNH_2)(PMe_2-$Ph)_4$]X [X = Cl, Br, and I] were previously prepared by the reaction of **5** with anhydrous HX (X = Cl, Br, and I) in dichloromethane.[39,42] Complex **19** was also isolated from the reaction of **5** and 2 equiv of HOTf in toluene in 76% yield. Complex **19** exhibits a single peak in the $^{31}P\{^1H\}$ NMR spectrum at −18.7 ppm with ^{183}W satellites (J_{PW} = 282 Hz), indicating the chemical equivalence of the four phosphorus atoms. The IR spectrum of **19** shows the ν_{NH} band at 3270 cm^{-1}.

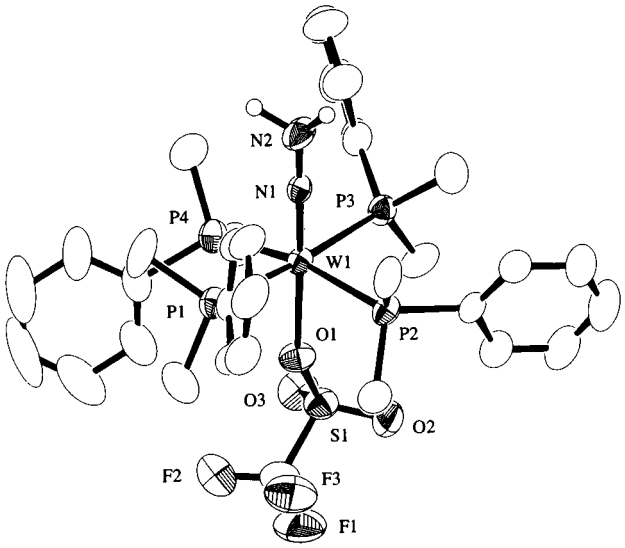


Figure 2. ORTEP drawing for *trans*-[W(OTf)(NNH_2)$(PMe_2Ph)_4$]OTf·$(THF)_{0.5}$ [(**19**)·$(THF)_{0.5}$]. Hydrogen atoms except for those attached to N(2), THF, and OTf anion are omitted for clarity.

Table 6. Selected Bond Lengths and Angles in *trans*-[W(OTf)(NNH_2)$(PMe_2Ph)_4$]OTf·$(THF)_{0.5}$ [**19**·$(THF)_{0.5}$]

Bond Lengths (Å)			
W(1)−P(1)	2.529(3)	W(1)−O(1)	2.218(5)
W(1)−P(2)	2.555(2)	W(1)−N(1)	1.722(6)
W(1)−P(3)	2.535(3)	S(1)−O(1)	1.479(5)
W(1)−P(4)	2.564(2)	N(1)−N(2)	1.320(9)
Bond Angles (deg)			
P(1)−W(1)−P(2)	90.31(7)	P(2)−W(1)−N(1)	94.6(2)
P(1)−W(1)−P(3)	175.28(7)	P(3)−W(1)−P(4)	88.58(7)
P(1)−W(1)−P(4)	89.37(7)	P(3)−W(1)−O(1)	96.9(1)
P(1)−W(1)−O(1)	87.1(1)	P(3)−W(1)−N(1)	86.9(2)
P(1)−W(1)−N(1)	89.2(2)	P(4)−W(1)−O(1)	83.2(1)
P(2)−W(1)−P(3)	92.62(7)	P(4)−W(1)−N(1)	98.3(2)
P(2)−W(1)−P(4)	167.16(7)	W(1)−N(1)−N(2)	178.6(6)
P(2)−W(1)−O(1)	84.0(1)	W(1)−O(1)−S(1)	151.0(4)

The molecular structure of **19** was unambiguously confirmed by X-ray analysis. An ORTEP drawing of **19**·$(THF)_{0.5}$ is shown in Figure 2. Selected bond lengths and angles are shown in Table 6. The complex adopts a slightly distorted octahedral geometry around the W center. The four phosphorus atoms occupy the equatorial coordination sites around the W center, and the W−P bond distances are almost equal. The hydrazido(2−) and OTf ligands occupy the remaining axial coordination sites. The W(1)−N(1)−N(2) linkage is essentially linear and typical of hydrazido(2−) complexes.[38,43] The W(1)−N(1) bond length of 1.722(6) Å indicates a metal−nitrogen triple bond.[38,43]

Treatment of hydrazido(2−) complex **19** with 10 equiv of **8c** in benzene−dichloroethane under 1 atm of H_2 at 55 °C for 24 h gave NH_3 in 50% total yield. This result indicates that the formation of NH_3 from **5** and **8c** proceeds through the protonation of hydrazido(2−) complex **19**.

The hydrazido(2−) complex *trans*-[W(OTf)(NNH_2)$(PMePh_2)_4$]-OTf (**20**) was prepared in 55% NMR yield by the reaction of **14** and 2 equiv of **8c** at room temperature for 1 h in benzene−dichloroethane (eq 6). Complex **20** was also isolated from the reaction of **14** and 2 equiv of HOTf in THF in 44% yield.

(40) Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 5569.
(41) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694.
(42) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766.
(43) For an example, see: Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

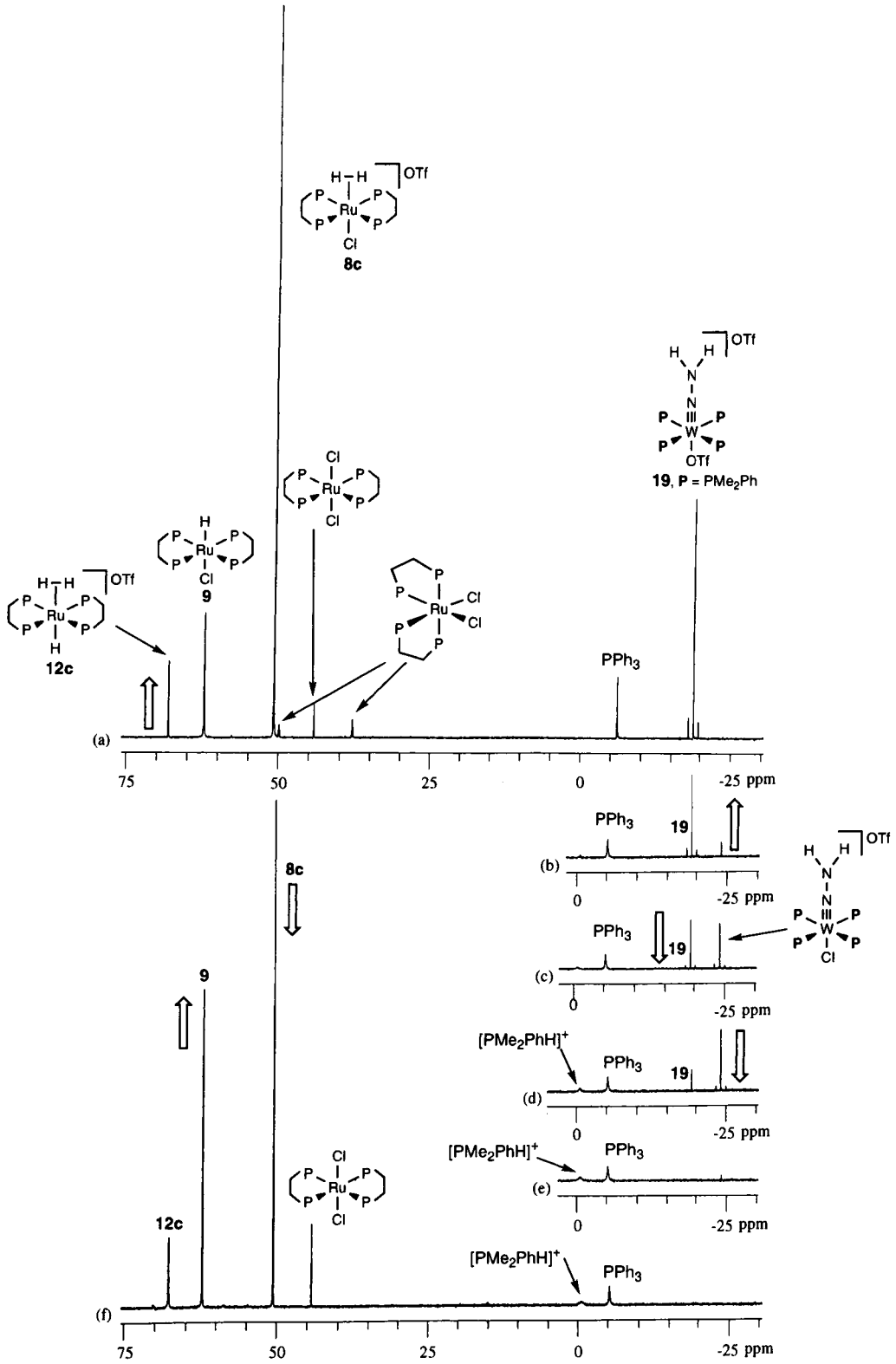
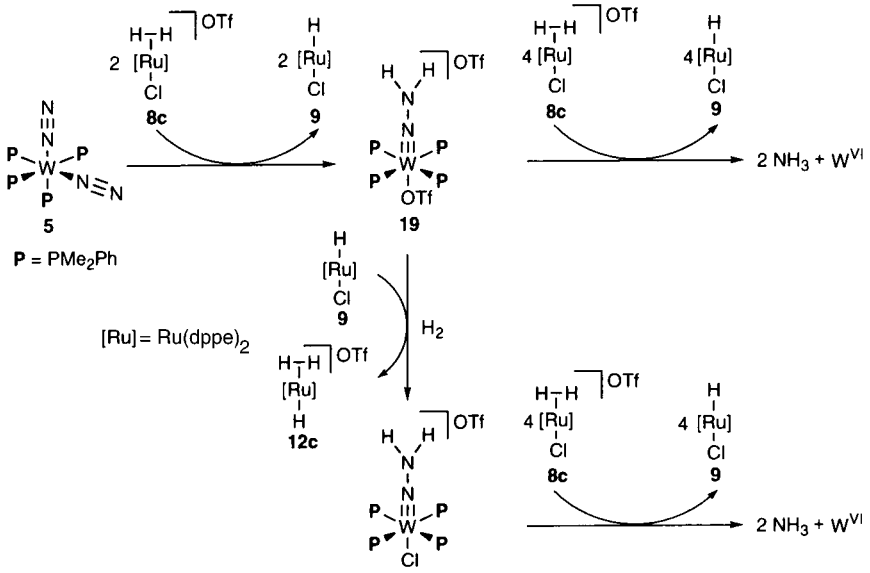


Figure 3. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (**5**) and 10 equiv of *trans*-[$RuCl(\eta^2\text{-}H_2)(dppe)_2$]OTf (**8c**) in benzene-d_6−dichloroethane under 1 atm of H_2: (a) the reaction mixture after 5 min at room temperature, (b) after 15 min as the reaction temperature was raised to 55 °C, (c) after 30 min as the reaction temperature was raised to 55 °C, (d) after 45 min as the reaction temperature was raised to 55 °C, (e) after 100 min as the reaction temperature was raised to 55 °C, and (f) after 150 min as the reaction temperature was raised to 55 °C.

Complex **20** exhibits a single peak in the $^{31}P\{^1H\}$ NMR spectrum at 19.5 ppm with ^{183}W satellites (J_{PW} = 170 Hz), indicating the chemical equivalence of the four phosphorus atoms. The IR spectrum exhibits the ν_{NH} band at 3220 cm^{-1}. These results show that the structure of **20** is similar to that of **19**. Previously it was reported that the hydrazido(2−) complex [$WHCl_3(NNH_2)(PMePh_2)_2$] was produced by the reaction of **14** with anhydrous HCl in dichloromethane.[44]

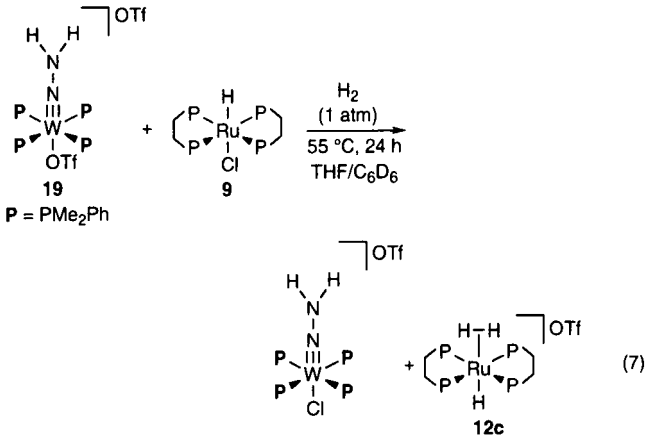
(44) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345.

Scheme 2



The hydrazido(2−) complex *trans*-[Mo(OTf)(NNH$_2$)(PMe$_2$Ph)$_4$]OTf (**21**) was prepared in 30% isolated yield by the reaction of Mo−N$_2$ complex **13** and 2 equiv of HOTf at room temperature for 5 min in toluene. Complex **21** exhibits a single peak in the ^{31}P{^{1}H} NMR spectrum at −1.80 ppm, indicating the chemical equivalence of the four phosphorus atoms. The IR spectrum exhibits the ν_{NH} band at 3249 cm^{-1}. It is to be noted that complex **21** was not obtained by treatment of **13** with 2 equiv of **8c** at room temperature under H$_2$, although the formation of hydride **9** was observed. This is compatible with the finding that no NH$_3$ was formed from the reaction of **13** with excess **8c** under H$_2$ (vide supra).

NMR Study on the Reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] (5) with 10 Equiv of *trans*-[RuCl(η^2-H$_2$)(dppe)$_2$]OTf (8c). To elucidate the mechanism for the formation of NH$_3$, the reaction of **5** and 10 equiv of **8c** in C$_6$D$_6$/ClCH$_2$CH$_2$Cl (1/3) at room temperature and 55 °C under 1 atm of H$_2$ was monitored by ^{31}P{^{1}H} NMR. The NMR spectra are shown in Figure 3, where PPh$_3$ was used as an internal reference because PPh$_3$ was confirmed not to react with **8c**. When **5** was added to the solution of **8c** at room temperature, **5** seemed to be almost completely consumed within 5 min and the hydrazido(2−) complex **19** with a resonance at −18.8 ppm was produced in 82% NMR yield, concurrent with the formation of hydride **9** (62.2 ppm) in 214% NMR yield based on tungsten. In addition, the formation of the hydrido−dihydrogen complex **12c** (68.0 ppm) in 31% NMR yield was observed, which was accompanied by the formation of a small amount of *cis*- and *trans*-[RuCl$_2$(dppe)$_2$], while a large amount of complex **8c** (50.2 ppm) remained in the mixture. In a separate run, the reaction of **8c** and hydride **9** was performed at room temperature for 1 h in C$_6$D$_6$/ClCH$_2$CH$_2$Cl (1/2) under H$_2$. The NMR analysis of the mixture showed the formation of **12c** and *cis*- and *trans*-[RuCl$_2$(dppe)$_2$] in 8% yields, respectively. Thus, this type of reaction explains the formation of **12c** at the early stage of the reaction. We were not able to observe any intermediates such as diazenido (N$_2$H) complexes because the transformation of **5** to **19** proceeded quite rapidly even at room temperature. As the reaction temperature was raised to 55 °C, **8c** was gradually consumed, accompanied by the increase of hydride **9**, and the hydrazido(2−) complex **19** was slowly transformed into another hydrazido(2−) complex *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]OTf which finally disappeared after 150 min. It is supposed that **19** reacts with **9** to afford *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]OTf and **12c**. Actually, the reaction of **19** with **9** at 55 °C for 24 h in THF/C$_6$D$_6$ (2/1) under 1 atm of H$_2$ afforded *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]OTf and **12c** in 71% and 44% NMR yields, respectively (eq 7). Subsequent protonation of hydrazido(2−) complexes **19**



(7)

and *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]OTf with H$_2$ complex **8c** at 55 °C results in the formation of NH$_3$, concurrent with the formation of [PMe$_2$PhH]$^+$. After 24 h at 55 °C, hydrides **9** and **12c** were formed in 260% and 330% NMR yields based on tungsten, respectively. It may be concluded that H$_2$ complex **8c** is consumed not only for the formation of NH$_3$ but also for the protonation of NH$_3$ produced and PMe$_2$Ph ligands released from the tungsten. All of the electrons required for the reduction of N$_2$ are supplied from the zerovalent tungsten in **5**. The presumed reaction pathway for the formation of NH$_3$ is summarized in Scheme 2.

It is noteworthy that the protonation of N$_2$ complexes **5** and **14** with 10 equiv of H$_2$ complex **8c** occurred rapidly even at room temperature to form the corresponding hydrazido(2−) intermediates, respectively; however, they remain unchanged at that temperature. When the reaction temperature was raised to 55 °C, subsequent protonation of the hydrazido(2−) intermediates with **8c** proceeded to eventually afford NH$_3$. The significant difference in the yield of NH$_3$ between N$_2$ complexes **5** and **14** in this protonation (vide supra) may arise from the different reactivity of the corresponding hydrazido(2−) inter-

mediates toward **8c**. We presume that hydrazido(2−) complex **19** with PMe_2Ph ligands reacts much more readily with H_2 complex **8c** to afford NH_3 than hydrazido(2−) complex **20** with $PMePh_2$ ligands, because PMe_2Ph is a stronger σ-donor than $PMePh_2$.

Conclusion

We have found a novel synthesis of NH_3 from the reactions of tungsten dinitrogen complex **5** with an excess of acidic ruthenium dihydrogen complexes (∼10 equiv) under mild conditions. In these reactions, heterolytic cleavage of H_2 proceeds at the Ru center through nucleophilic attack of the coordinated N_2 on the coordinated H_2 where a proton (H^+) is used for the protonation of the coordinated N_2 and a hydride (H^-) remains at the Ru atom. The protonation initially transforms the coordinated N_2 into the NNH_2 ligand. Hydrazido(2−) complexes have actually been isolated in some cases. We presume that further protonation of hydrazido(2−) intermediates at 55 °C results in the formation of NH_3 along with W(VI) species. The yield of NH_3 is up to 79% yield based on tungsten when H_2 complex **8b** is employed. However, in these reactions, only one proton formed by the heterolytic cleavage of H_2 is used for the N−H bond formation and all of the electrons required for the formation of NH_3 are supplied from the zerovalent tungsten. Thus, the remaining hydride is not used for either the N−H bond formation or reduction of the high-valent W species to regenerate the starting N_2 complex **5**. Our studies are now in progress toward development of bimetallic systems where both the hydrogen atoms of activated H_2 are effectively used for the catalytic nitrogen fixation.

Experimental Section

General Procedure. Preparation of complexes was performed under 1 atm of N_2 or Ar dried by passage through silica gel and P_2O_5. Reactions of N_2 complexes with Ru(η^2-H_2) complexes were carried out under 1 atm of H_2 dried by passage through silica gel and P_2O_5. D_2 (99.9%) was obtained from Takachiho Chemical Industrial Co. LTD. (Japan). Benzene, hexane, diethyl ether (Et_2O), and THF were freshly distilled over sodium benzophenone ketyl just before use. Dichloromethane and dichloroethane were distilled over P_2O_5. Unless otherwise noted, all manipulations were done by use of Schlenk techniques.

NMR spectra were recorded on a JEOL JNM-LA-400 or a JEOL JNM-EX-270 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer. Quantitative GLC analyses of organic compounds were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC−MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules in the crystals of new complexes were determined by both elemental analyses and ^{1}H NMR spectroscopy. Absorption spectra were recorded on a Shimadzu UV-2400PC.

Dinitrogen complexes[12,45,46] such as **1**, **2**, **5**, **13**, and **14**, hydrazido(2−) complexes such as **15**,[38] **16**,[39] **18**,[41] and *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]Cl,[42] and other complexes including [RuCl$_2$(PPh$_3$)$_3$],[47] [RuH$_2$(PPh$_3$)$_4$],[48] [RhCl(PPh$_3$)$_3$],[49] **4a**,[22] **7a**,**b**,[25] **11b**,[40] **12b**,[33] *trans*-[Mo(CO)(η^2-H$_2$)(dppe)$_2$],[34] **17**,[40] and *cis*-[RuCl$_2$(dppe)$_2$][33b] were prepared according to literature procedures.

Preparation of [RuCl(dppp)$_2$]X (4b and 4c·CH$_2$Cl$_2$). The following procedure for preparation of the complex [RuCl(dppp)$_2$]OTf·CH$_2$Cl$_2$ (**4c**·CH$_2$Cl$_2$) is representative.[22] A suspension of [RuCl$_2$(PPh$_3$)$_3$] (11.78 g, 12.3 mmol), dppp (10.0 g, 24.3 mmol), and NaOTf (6.35 g, 36.9 mmol) in EtOH (500 mL) was stirred at reflux temperature for 4 h under 1 atm of N_2. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (20 mL). Addition of *i*-PrOH to the concentrated CH_2Cl_2 solution gave **4c**·CH$_2$Cl$_2$ (5.93 g, 4.96 mmol) in 40% yield as dark red crystals. ^{1}H NMR ($CDCl_3$): δ 0.75 (br t, 2H), 1.62 (br s, 2H), 2.19 (br s, 3H), 2.61 (br s, 2H), 2.86 (br s, 3H), 6.82−7.81 (m, 40H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.32 (t, J = 33 Hz) and 43.5 (t, J = 33 Hz). Anal. Calcd for $C_{55}H_{52}ClF_3O_3P_4SRu\cdot CH_2Cl_2$: C, 56.27; H, 4.55. Found: C, 56.53; H, 4.48.

Similarly, **4b** was prepared by using NH_4BF_4. The physical, spectroscopic, and analytical data are as follows.

[RuCl(dppp)$_2$]BF$_4$ (4b). Yield: 83%. Dark red crystals. ^{1}H NMR ($CDCl_3$): δ 0.86 (br t, 2H), 1.68 (br s, 2H), 2.25 (br s, 3H), 2.63 (br s, 2H), 2.90 (br s, 3H), 6.95−7.82 (m, 40H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −4.09 (t, J = 33 Hz) and 43.1 (t, J = 33 Hz). Anal. Calcd for $C_{54}H_{52}BClF_4P_4Ru$: C, 61.88; H, 5.00. Found: C, 61.96; H, 5.04.

Preparation of [RuCl(dppe)$_2$]X (X = OTf, BAr$_4$) [7c·(CH$_2$Cl$_2$)$_{0.5}$ and 7d·CH$_2$Cl$_2$]. The following procedure for preparation of the complex [RuCl(dppe)$_2$]OTf·(CH$_2$Cl$_2$)$_{0.5}$ [**7c**·(CH$_2$Cl$_2$)$_{0.5}$] is representative.[25] A solution of NaOTf (2.13 g, 12.4 mmol) and *cis*-[RuCl$_2$(dppe)$_2$] (10.0 g, 10.3 mmol) in THF (100 mL) and EtOH (50 mL) was stirred at room temperature for 12 h under 1 atm of Ar. After evaporation of the solvents, the residue was extracted with CH_2Cl_2 (100 mL). The CH_2Cl_2 solution was washed with H_2O and dried over anhydrous $MgSO_4$. Addition of hexane to the concentrated CH_2Cl_2 solution gave **7c**·(CH$_2$Cl$_2$)$_{0.5}$ (8.96 g, 7.97 mmol) in 77% yield as dark red crystals. ^{1}H NMR ($CDCl_3$): δ 1.65 (br s, 4H), 2.56 (br s, 2H), 2.65 (br s, 2H), 6.78−7.76 (m, 40H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.6 (br t, J = 12 Hz) and 83.7 (br t, J = 12 Hz). Anal. Calcd for $C_{53}H_{48}ClF_3O_3P_4SRu\cdot(CH_2Cl_2)_{0.5}$: C, 57.12; H, 4.39. Found: C, 57.13; H, 4.57.

Similarly, **7d**·CH$_2$Cl$_2$ was prepared by using $NaBAr_4$. The physical, spectroscopic, and analytical data are as follows. Yield: 67%. Dark red crystals. ^{1}H NMR ($CDCl_3$): δ 1.66 (br s, 3H), 2.29 (m, 3H), 2.63 (br s, 2H), 6.60−7.80 (m, 52H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 56.0 (br t, J = 12 Hz) and 82.6 (br t, J = 12 Hz). Anal. Calcd for $C_{84}H_{60}BClF_{24}P_4Ru\cdot CH_2Cl_2$: C, 54.26; H, 3.32. Found: C, 54.07; H, 3.34.

Preparation of [RuCl(dppe)$_2$]BPh$_4$·(CH$_2$Cl$_2$)$_{1.5}$ [7e·(CH$_2$Cl$_2$)$_{1.5}$]. A mixture of *cis*-[RuCl$_2$(dppe)$_2$] (969 mg, 1.00 mmol) and $NaBPh_4$ (1.20 g, 3.50 mmol) in dry EtOH (30 mL) was stirred at reflux temperature for 1 h under 1 atm of Ar. The resulting red solid was collected, washed with EtOH, and dried under reduced pressure. The residue was extracted with CH_2Cl_2 (15 mL). Addition of methanol to the CH_2Cl_2 solution gave **7e**·(CH$_2$Cl$_2$)$_{1.5}$ (888 mg, 0.64 mmol) in 64% yield as red crystals. ^{1}H NMR ($CDCl_3$): δ 1.51 (br s, 2H), 2.15 (br s, 4H), 2.33 (br s, 2H), 6.60−7.80 (m, 60H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.8 (br t, J = 12 Hz) and 82.7 (br t, J = 12 Hz). Anal. Calcd for $C_{77.5}H_{71}BCl_4P_4Ru$: C, 67.45; H, 5.19. Found: C, 67.72; H, 5.13.

Conversion of [RuCl(dppe)$_2$]OTf (7c) into *trans*-[RuCl(η^2-H$_2$)(dppe)$_2$]OTf (8c). In a Schlenk tube was placed **7c**·(CH$_2$Cl$_2$)$_{0.5}$ (15.0 mg, 0.013 mmol) under 1 atm of N_2. Dry CD_2Cl_2 (0.75 mL) was then added under 1 atm of N_2. The reaction mixture was stirred at room temperature for 5 min under 1 atm of H_2. ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixture showed the complete conversion of **7c** into **8c**. ^{1}H NMR (CD_2Cl_2): δ −11.6 (br, 2H), 2.33 (br, 4H), 2.87 (br, 4H), 6.92−7.39 (m, 40H); a minimum T_1 value of 24 ms (400 HMz) at 250 K was obtained for the broad signal at −11.6 ppm, assignable to the η^2-H_2. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 52.2 (s).

Preparation of *trans*-[RuCl(η^2-HD)(dppe)$_2$]OTf (8c-d_1). The Ru(η^2-HD) complex (**8c**-d_1) was prepared in situ by the following procedure. To a solution of **9**[25,26] (19 mg, 0.02 mmol) in CD_2Cl_2 (0.75 mL) was added a mixture (15 mg) of HOTf and D_2O (1/1, w%) at room temperature under 1 atm of N_2. ^{1}H NMR spectra of the reaction mixture showed the formation of **8c**-d_1. ^{1}H NMR (CD_2Cl_2): δ −12.29 (tq, J_{PH} = 7.3 Hz, J_{HD} = 25.6 Hz).

Preparation of [CpRu(η^2-H$_2$)(dppm)]OTf (10). To a solution of

(45) Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703.
(46) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139.
(47) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.
(48) Young, R.; Wilkinson, G. *Inorg. Synth.* **1977**, *17*, 75.
(49) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

[CpRuH(dppm)][50] (257 mg, 0.466 mmol) in THF (10 mL) under 1 atm of N_2 was added HOTf (69.9 mg, 0.47 mmol), and the mixture was stirred for 10 min. After evaporation of the solvent, the residue was extracted with CH_2Cl_2. Addition of Et_2O to the CH_2Cl_2 solution afforded **10** (179 mg, 0.26 mmol) in 55% yield as colorless crystals. ^{1}H NMR ($CDCl_3$): δ −7.03 (br s, 2H, η^2-H_2), 5.13 (s, 5H, Cp), 4.28 (dt, 1H, J_{HH} = 16 Hz, J_{PH} = 11 Hz), 5.51 (dt, 1H, J_{HH} = 16 Hz, J_{PH} = 11 Hz), 7.4−7.7 (m, 20H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 4.0 (s). Anal. Calcd for $C_{31}H_{29}F_3O_3P_2SRu$: C, 53.07; H, 4.17. Found: C, 52.83; H, 4.13.

Preparation of *trans*-[RuH(η^2-H_2)(dppp)$_2$]OTf·CH_2Cl_2 (11c·CH_2Cl_2). To a solution of *cis*-[RuH_2(dppp)$_2$][40] (432 mg, 0.47 mmol) in THF (10 mL) under 1 atm of argon was added HOTf (69.9 mg, 0.47 mmol), and the mixture was stirred for 10 min. After evaporation of the solvent, the residue was extracted with CH_2Cl_2. Addition of Et_2O to the CH_2Cl_2 solution afforded **11c**·CH_2Cl_2 (417 mg, 0.36 mmol) in 77% yield as orange crystals. ^{1}H NMR (CD_2Cl_2): δ −8.08 (br s, 1H, RuH), −3.13 (br s, 2H, η^2-H_2), 1.31 (br s, 4H), 2.13 (br d, 8H), 6.9−7.6 (m, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.0 (br s). Anal. Calcd for $C_{56}H_{57}Cl_2F_3O_3P_4SRu$: C, 57.83; H, 4.94. Found: C, 57.62; H, 4.90.

Preparation of *trans*-[RuH(η^2-H_2)(dppe)$_2$]OTf·CH_2Cl_2 (12c·CH_2Cl_2). To a solution of *cis*-[RuH_2(dppe)$_2$][40] (3.00 g, 3.33 mmol) in THF (50 mL) under 1 atm of argon was added HOTf (500 mg, 3.33 mmol), and the mixture was stirred overnight. After evaporation of the solvent, the residue was extracted with CH_2Cl_2. Addition of hexane to the CH_2Cl_2 solution afforded **12c**·CH_2Cl_2 (3.45 g, 3.04 mmol) in 91% yield as colorless crystals. ^{1}H NMR (CD_2Cl_2): δ −10.17 (quint, 1H, J_{PH} = 18 Hz), −4.79 (br s, 2H, η^2-H_2), 2.15 (br d, 8H), 7.1−7.4 (m, 40H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 68.3 (s). Anal. Calcd for $C_{54}H_{53}Cl_2F_3O_3P_4SRu$: C, 57.15; H, 4.71. Found: C, 56.89; H, 4.78.

Formation of NH_3 in the Reactions of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] (5) with Ru(η^2-H_2) Complexes under 1 atm of H_2. A typical procedure for the reaction of **5** with 10 equiv of **8c** under 1 atm of H_2 is as follows. In a 500 mL flask was placed **7c**·$(CH_2Cl_2)_{0.5}$ (1.1 g, 1.00 mmol) under 1 atm of N_2. Dry dichloroethane (15 mL) and benzene (5 mL) were added, and then the mixture was magnetically stirred at 55 °C for 15 min. After the N_2 atmosphere was replaced by 1 atm of H_2 to convert **7c** into **8c**, **5** (80 mg, 0.10 mmol) was added portionwise. The reaction mixture was stirred at 55 °C for 24 h under 1 atm of H_2. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in dilute H_2SO_4 solution (1 N; 10 mL). Potassium hydroxide aqueous solution (40 wt %; 20 mL) was added to the residue, and the mixture was distilled into another dilute H_2SO_4 solution (1 N; 10 mL). NH_3 and NH_2NH_2 present in each of the H_2SO_4 solutions were quantitatively analyzed by using indophenol and *p*-(dimethylamino)-benzaldehyde reagents, respectively.[13c,51]

Alternatively, the reaction mixture was diluted with CH_2Cl_2 (50 mL), and the solution was extracted with H_2O (100 mL × 3). The combined aqueous extract was treated with activated charcoal and filtered through Celite. The amount of NH_4^+ ion in the aqueous solution was determined by the indophenol reagent.[13c,51]

Reaction of *trans*-[$W(N_2)_2$(dppe)$_2$] (2) with Ru(η^2-H_2) Complexes. A typical experimental procedure for the reaction of **2** with **8b** is as follows. In a 50 mL flask was placed **7b** (102 mg, 0.10 mmol) under 1 atm of N_2. Dry dichloroethane (3 mL) and benzene (3 mL) were added, and then the mixture was magnetically stirred at room temperature for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2 to transform **7b** into **8b**, **2** (52 mg, 0.05 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 24 h under 1 atm of H_2. The solvent was then removed under vacuum, and the residue was dissolved in $CDCl_3$ to measure the ^{31}P{^{1}H} NMR spectrum. PPh_3 (52 mg, 0.20 mmol) was added into the $CDCl_3$ solution as an internal reference because PPh_3 was confirmed not to react with **8b**. The NMR yields of the produced complexes were determined by integration of the gated-{^{1}H}-decoupled ^{31}P resonances against the PPh_3 standard. **16b**: ^{31}P{^{1}H} NMR ($CDCl_3$): δ 35.0 (d with ^{183}W satellites, J_{PF} = 39 Hz, J_{PW} = 290 Hz). **9**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 61.9 (s). **8b**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 51.3 (s).

Reaction of *trans*-[$W(N_2)_2$(dppe)$_2$] (2) with *trans*-[RuCl(η^2-D_2)(dppe)$_2$]OTf (8c-d_2) under 1 atm of D_2. In a 50 mL flask was placed **7c**·$(CH_2Cl_2)_{0.5}$ (112 mg, 0.10 mmol) under 1 atm of N_2. Dry dichloroethane (5 mL) was added, and then the mixture was magnetically stirred at room temperature for 5 min. After the N_2 atmosphere was replaced by 1 atm of D_2 to transform **7c** into **8c**-d_2, a solution of **2** (52 mg, 0.05 mmol) in benzene (5 mL) was added by syringe. The reaction mixture was stirred at room temperature for 0.5 h under 1 atm of D_2. The solvent was then removed under vacuum, and the residue was dissolved in $CDCl_3$ to measure the ^{31}P{^{1}H} NMR spectrum. PPh_3 (52 mg, 0.20 mmol) was added into the $CDCl_3$ solution as an internal reference. The NMR yields of the produced complexes were determined by integration of the gated-{^{1}H}-decoupled ^{31}P resonances against the standard PPh_3. Then the solvent was again evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 to measure the ^{2}H NMR spectrum. C_6D_6 was added into the CH_2Cl_2 solution as an internal reference. The amount of the deuterated species **15′** was determined by integration of the ^{2}H signal against the standard C_6D_6. **15′**: ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 37.5 (s with ^{183}W satellites, J_{PW} = 321 Hz); ^{2}H NMR (CH_2Cl_2) δ 4.60 (br s; WNND$_2$); ca. 70% NMR yield. **9′**: ^{31}P-{^{1}H} NMR ($CDCl_3$) δ 62.4 (s); ^{2}H NMR (CH_2Cl_2) δ −19.5 (br s; RuD); ca. 200% NMR yield.

Reaction of *trans*-[W(OTf)(NNH_2)(dppe)$_2$]OTf (15) with 2 equiv of *cis*-[RuH_2(dppe)$_2$] (17) under 1 atm of N_2. In a 20 mL flask were placed **15** (26 mg, 0.02 mmol) and **17** (36 mg, 0.04 mmol) under 1 atm of N_2. Dry THF (1 mL) was added, and then the mixture was magnetically stirred at room temperature for 2 h. After evaporation of the solvent under vacuum, the residue was dissolved in C_6D_6/$ClCH_2CH_2Cl$ (1/3) to measure the ^{31}P{^{1}H} NMR spectrum. PPh_3 (21 mg, 0.08 mmol) was added into the solution as an internal reference. The NMR yields of the produced complexes were determined by integration of the gated-{^{1}H}-decoupled ^{31}P resonances against the standard PPh_3. **2**: ^{31}P{^{1}H} NMR δ 45.5 (s with ^{183}W satellites, J_{PW} = 320 Hz); 60% NMR yield. **12c**: ^{31}P{^{1}H} NMR δ 68.5 (s); 199% NMR yield. **17**: ^{31}P-{^{1}H} NMR δ 64.9 (t, J = 15 Hz), 78.9 (t, J = 15 Hz); <5% NMR yield. In addition, unknown compounds were observed.

Preparation of *trans*-[W(OTf)(NNH_2)(PMe_2Ph)$_4$]OTf (19). To a solution of **5** (387 mg, 0.49 mmol) in toluene (7 mL) was added HOTf (147 mg, 0.98 mmol) under 1 atm of N_2. The reaction mixture was stirred at room temperature for 30 min. Then, Et_2O (10 mL) was slowly added to the reaction mixture to give **19** (393 mg, 0.37 mmol) in 76% isolated yield as pale brown needles. ^{1}H NMR ($CDCl_3$): δ 1.67 (br s, 24H, P*Me*$_2$Ph), 7.13 (s, 2H, NNH_2), 7.16−7.21 (m, 20H, PMe$_2$*Ph*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −18.7 (s with ^{183}W satellites, J_{PW} = 282 Hz). IR (KBr, cm^{-1}): 3270 (N−H). Anal. Calcd for $C_{34}H_{46}F_6N_2O_6P_4S_2W$: C, 38.36; H, 4.36; N, 2.63. Found: C, 38.00; H, 4.32; N, 2.62.

Complex **19** was also prepared from the reaction of **5** with 2 equiv of **8c** under 1 atm of H_2. In a 50 mL flask was placed **7c**·$(CH_2Cl_2)_{0.5}$ (112 mg, 0.10 mmol) under 1 atm of N_2. Dry dichloroethane (3 mL) and benzene (3 mL) were added, and then the mixture was magnetically stirred at room temperature for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2 to transform **7c** into **8c**, **5** (40 mg, 0.05 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 20 h under 1 atm of H_2. The solvent was then removed under vacuum, and the residue was dissolved in $CDCl_3$ to measure the ^{31}P{^{1}H} NMR spectrum. PPh_3 (52 mg, 0.20 mmol) was added into the $CDCl_3$ solution as an internal reference. The NMR yields of the produced complexes were determined by integration of the gated-{^{1}H}-decoupled ^{31}P resonances against the standard PPh_3. Complexes **19** and **9** were formed in 63% and 199% NMR yields, respectively.

Preparation of *trans*-[W(OTf)(NNH_2)($PMePh_2$)$_4$]OTf (20). To a solution of **14** (50 mg, 0.048 mmol) in THF (5 mL) was added HOTf (15 mg, 0.10 mmol) under 1 atm of N_2. The reaction mixture was stirred at room temperature for 30 min. Then, Et_2O (15 mL) was slowly added to the reaction mixture to give **20** (28 mg, 0.021 mmol) in 44% isolated yield as a brown solid. ^{1}H NMR ($CDCl_3$): δ 2.36 (br s, 12H, P*Me*Ph_2), 5.26 (br s, 2H, NNH_2), 7.23−7.70 (m, 40H, PMe*Ph*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.5 (s with ^{183}W satellites, J_{PW} = 170 Hz). IR (KBr, cm^{-1}):

(50) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747.
(51) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971.

3220 (N−H). Anal. Calcd for $C_{54}H_{54}F_6N_2O_6P_4S_2W$: C, 49.40; H, 4.15; N, 2.13. Found: C, 49.78; H, 4.39; N, 2.39.

Complex **20** was also prepared from the reaction of **14** with 2 equiv of **8c** under 1 atm of H_2. In a 50 mL flask was placed **7c**·$(CH_2Cl_2)_{0.5}$ (59 mg, 0.052 mmol) under 1 atm of N_2. Dry dichloroethane (3 mL) and benzene (3 mL) were added, and then the mixture was magnetically stirred at room temperature for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2 to transform **7c** into **8c**, **14** (30 mg, 0.029 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 1 h under 1 atm of H_2. The solvent was then evaporated under vacuum, and the residue was dissolved in $CDCl_3$ to measure the $^{31}P\{^1H\}$ NMR spectrum. PPh_3 (5 mg, 0.02 mmol) was added into the $CDCl_3$ solution as an internal reference. The NMR yields of the produced complexes were determined by integration of the gated-$\{^1H\}$-decoupled ^{31}P resonances against the standard PPh_3. Complexes **20** and **9** were formed in 55% and 199% NMR yields, respectively.

Preparation of *trans*-[Mo(OTf)(NNH$_2$)(PMe$_2$Ph)$_4$]OTf (21). To a solution of **13** (71 mg, 0.10 mmol) in toluene (4 mL) was added HOTf (30 mg, 0.20 mmol) under 1 atm of N_2. The reaction mixture was stirred at room temperature for 5 min. Then, Et_2O (8 mL) was slowly added to the reaction mixture to give **21** (29 mg, 0.030 mmol) in 30% isolated yield as orange crystals. ^1H NMR (CD_2Cl_2): δ 1.60 (br s, 24H, P*Me*$_2$Ph), 7.30−7.45 (m, 20H, PMe$_2$*Ph*), 8.37 (s, 2H, NNH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −1.80 (s). IR (KBr, cm^{-1}): 3249 (N−H). Anal. Calcd for $C_{34}H_{46}F_6MoN_2O_6P_4S_2$: C, 41.81; H, 4.75; N, 2.87. Found: C, 41.62; H, 4.90; N, 2.92.

$^{31}P\{^1H\}$ NMR Monitoring of the Reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] (5) with 10 Equiv of *trans*-[RuCl(η^2-H$_2$)(dppe)$_2$]OTf (8c) under 1 atm of H$_2$. A typical experimental procedure for the reaction described in Figure 3 is as follows. In a 20 mL flask were placed **7c**·$(CH_2Cl_2)_{0.5}$ (110 mg, 0.10 mmol) and PPh_3 (10 mg, 0.04 mmol) as an internal reference under 1 atm of N_2. Dry dichloroethane (1.5 mL) and C_6D_6 (0.5 mL) were added, and then the mixture was magnetically stirred at room temperature. After the N_2 atmosphere was replaced by 1 atm of H_2 to transform **7c** into **8c**, **5** (8 mg, 0.01 mmol) was added portionwise. A part of this homogeneous solution (0.5 mL) was transferred at room temperature into an NMR tube by syringe. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture after 5 min at room temperature is shown in Figure 3a. The NMR sample was then kept at 55 °C for 150 min under 1 atm of H_2. The time dependence of the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture is shown in Figure 3b−f. The NMR yields of the produced complexes were determined by integration of the gated-$\{^1H\}$-decoupled ^{31}P resonances against the standard PPh_3.

Reaction of *trans*-[RuCl(η^2-H$_2$)(dppe)$_2$]OTf (8c) with 1 Equiv of *trans*-[RuHCl(dppe)$_2$] (9) under 1 atm of H$_2$. In a 50 mL flask was placed **7c**·$(CH_2Cl_2)_{0.5}$ (28 mg, 0.025 mmol) under 1 atm of N_2. Dry dichloroethane (1 mL) and C_6D_6 (0.5 mL) were added, and then the mixture was magnetically stirred at room temperature for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2 to transform **7c** into **8c**, **9** (23 mg, 0.025 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 1 h under 1 atm of H_2. PPh_3 (26 mg, 0.10 mmol) was added into the solution as an internal reference. A part of this homogeneous solution (0.5 mL) was transferred at room temperature into an NMR tube by syringe. The NMR yields of the produced complexes were determined by integration of the gated-$\{^1H\}$-decoupled ^{31}P resonances against the standard PPh_3. **12c**: 8% NMR yield. *cis*- and *trans*-[$RuCl_2$(dppe)$_2$]: 8% NMR yield.

Reaction of *trans*-[W(OTf)(NNH$_2$)(PMe$_2$Ph)$_4$]OTf (19) with 1 Equiv of *trans*-[RuHCl(dppe)$_2$] (9) under 1 atm of H$_2$. In a 20 mL flask were placed **19** (21 mg, 0.02 mmol) and **9** (19 mg, 0.02 mmol) under 1 atm of H_2. Dry THF (1 mL) and C_6D_6 (0.5 mL) were added, and then the mixture was magnetically stirred at 55 °C for 24 h. PPh_3 (21 mg, 0.08 mmol) was added into the solution as an internal reference. The NMR yields of the produced complexes were determined by integration of the gated-$\{^1H\}$-decoupled ^{31}P resonances against the standard PPh_3. *trans*-[WCl(NNH$_2$)(PMe$_2$Ph)$_4$]OTf: $^{31}P\{^1H\}$ NMR δ −23.4 (s with ^{183}W satellites, J_{PW} = 277 Hz); 71% NMR yield. **12c**: $^{31}P\{^1H\}$ NMR δ 68.5 (s); 44% NMR yield. **9**: $^{31}P\{^1H\}$ NMR δ 62.5 (s); 25% NMR yield. In addition, unknown Ru compounds were observed.

Table 7. Crystallographic Data for *trans*-[W(OTf)(NNH$_2$)(PMe$_2$Ph)$_4$]OTf·(THF)$_{0.5}$ [**19**·(THF)$_{0.5}$]

formula	$C_{36}H_{50}N_2F_6O_{6.50}S_2P_4W$
fw	1100.66
cryst size (mm^3)	0.80 × 0.40 × 0.10
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	brown
a (Å)	11.818(5)
b (Å)	33.978(6)
c (Å)	12.163(4)
β (deg)	109.24(2)
V (Å^3)	4611(2)
Z	4
d_{calc} (g cm^{-1})	1.585
F (000)	2208.00
μ_{calc} (cm^{-1})	28.05
no. of unique data	8097
no. of data used ($I > 3\sigma(I)$)	5395
no. of params refined	504
R^a	0.039
$R_w{}^b$	0.033
goodness of fit indicator	1.68
max residuals (e Å^{-3})	0.96

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

X-ray Crystallographic Studies. Brown crystals of [**19**·(THF)$_{0.5}$] suitable for X-ray analysis were obtained by recrystallization from THF−hexane. The single crystal was sealed in a Pyrex glass capillary under Ar atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer at 20 °C. Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 reflections with 38.9° < 2θ < 40.0°. No significant decay was observed for three standard reflections monitored every 150 reflections during the data collection. Intensity data were corrected for Lorentz−polarization effects and for absorption (scans). Details of crystal and data collection parameters are summarized in Table 7. Structures solution and refinements were carried out by using the teXsan program package.[52] The positions of heavy atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY).[53] All non-hydrogen atoms except for those in the solvating THF molecule were refined anisotropically by full-matrix least-squares techniques (based on F). The C atoms in the solvating THF molecule were found at two disordered positions. These C atoms were refined as rigid groups with occupancies of 50%, respectively. The hydrogen atoms attached to the N(2) atom were found in the final difference Fourier map, while other hydrogen atoms were placed at the calculated positions; these hydrogen atoms were included in the final stage of refinement with fixed parameters. The atomic scattering factors were taken from ref 54, and anomalous dispersion effects were included; the values for $\Delta f'$ and $\Delta f''$ were taken from ref 55.

Acknowledgment. This work was supported by a Grant-in-Aid for Specially Promoted Research (09102004) from the Ministry of Education, Science, Sports, and Culture of Japan. We thank Dr. Dai Masui for assistance with ^2H NMR analysis.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **19**·(THF)$_{0.5}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000799F

(52) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.
(53) Patty: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallography Laboratory, University of Nijmegen: Nijimegen, The Netherlands, 1992.
(54) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(55) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.