

Cleavage and Formation of Molecular Dinitrogen in a Single System Assisted by Molybdenum Complexes Bearing Ferrocenyldiphosphine**

Takamasa Miyazaki, Hiromasa Tanaka, Yoshiaki Tanabe, Masahiro Yuki, Kazunari Nakajima, Kazunari Yoshizawa,* and Yoshiaki Nishibayashi*

Abstract: The N≡N bond of molecular dinitrogen bridging two molybdenum atoms in the pentamethylcyclopentadienyl molybdenum complexes that bear ferrocenyldiphosphine as an auxiliary ligand is homolytically cleaved under visible light irradiation at room temperature to afford two molar molybdenum nitride complexes. Conversely, the bridging molecular dinitrogen is reformed by the oxidation of the molybdenum nitride complex at room temperature. This result provides a successful example of the cleavage and formation of molecular dinitrogen induced by a pair of two different external stimuli using a single system assisted by molybdenum complexes bearing ferrocenyldiphosphine under ambient conditions.

Nitrogen fixation, the production of ammonia from molecular dinitrogen, is one of the most important chemical processes on earth because ammonia is widely used as an essential source of nitrogen fertilizers. Industrially, ammonia is produced from molecular dinitrogen and molecular dihydrogen using iron-based heterogeneous catalysts under harsh reaction conditions, such as quite high temperatures and pressures.^[1] In the Haber–Bosch process, the rate-determining step is the dissociative chemisorption of dinitrogen on the surface of the iron catalyst, which includes adsorption of dinitrogen, cleavage of the N≡N triple bond, and the bonding of two nitrogen atoms to the iron surface as nitride species.^[1] Although all these elementary steps are known to occur

reversibly, it is still quite difficult to understand the heterogeneous reaction in detail on the atomic and molecular levels.

Since the first discovery of a transition-metal–dinitrogen complex,^[2] various stoichiometric and catalytic transformations using transition-metal–dinitrogen complexes have been well investigated toward the development of the next generation nitrogen fixation system.^[3,4] During our study on the development of novel nitrogen fixation system under mild reaction conditions,^[4b,5] we have focused on use of ferrocenyldiphosphine as an auxiliary ligand chelating to molybdenum atom to capture and activate molecular dinitrogen.^[6] We have now found that molecular dinitrogen is cleaved and reformed on the pentamethylcyclopentadienyl molybdenum complexes in medium oxidation states bearing ferrocenyldiphosphine as an auxiliary ligand. In this reaction system, molecular dinitrogen bridging two molybdenum moieties is cleaved under visible light irradiation at room temperature to afford the corresponding molybdenum nitride complex. Conversely, the bridging molecular dinitrogen is reformed by oxidation of the molybdenum nitride complex at room temperature. This result provides a successful example of the cleavage and formation of molecular dinitrogen induced by a pair of two different external stimuli (both photochemically and oxidatively) using a single system under ambient conditions.

When the monocationic dinitrogen-bridged dimolybdenum complex chelated by 1,1'-bis(diethylphosphino)ferrocene (depf)^[6a] (**1**), which was prepared by the reaction of molybdenum(II)-dinitrogen hydride complex (**2**)^[6c] with the trityl cation, was reduced with KC₈ in dark or oxidized with FcBAR^F₄ (Fc = Fe(η⁵-C₅H₅)₂, Ar^F = 3,5-(CF₃)₂C₆H₃), the neutral dinitrogen-bridged dimolybdenum complex (**3**) or the dicationic dinitrogen-bridged dimolybdenum complex (**4**) was obtained in 34% or 96% yield, respectively (Scheme 1). A cyclic voltammetric study of **4** has revealed two consecutive one-electron reversible processes, leading us to examine the direct back-and-forth transformations between **3** and **4**. Thus, treatment of **4** with KC₈ afforded **3** in 94% yield (determined by the UV/Vis spectrum), while that of **3** with FcBAR^F₄ gave **4** in 53% yield (Scheme 1).

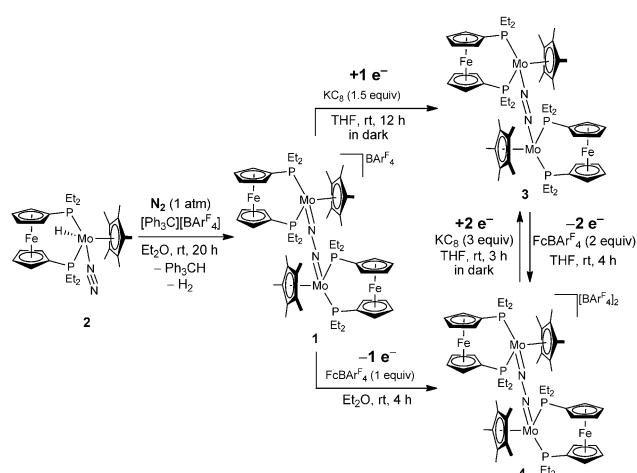
Detailed molecular structures of **1**, **3**, and **4** were determined by X-ray crystallographic analyses (Figure 1 a).^[7] In all these complexes, two {Cp*Mo(depff)} moieties are bridged by one dinitrogen ligand in an end-on fashion with an almost linear Mo–N–N–Mo backbone. However, other metric features around the Mo–N–N–Mo backbone depend on the oxidation states of molybdenum atoms in **1**, **3**, and **4**. In fact,

[*] Dr. T. Miyazaki, Dr. Y. Tanabe, Dr. M. Yuki, Dr. K. Nakajima, Prof. Dr. Y. Nishibayashi
Institute of Engineering Innovation, School of Engineering
The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: ynishiba@sogo.t.u-tokyo.ac.jp

Dr. H. Tanaka, Prof. Dr. K. Yoshizawa
Institute for Materials Chemistry and Engineering and
International Research Center for Molecular System
Kyushu University, Nishi-ku, Fukuoka 819-0395 (Japan)
E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp

[**] K.Y. thanks Grants-in-Aid for Scientific Research (No. 24109014) from the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) and the MEXT Projects of “Integrated Research on Chemical Synthesis” and “Elements Strategy Initiative to Form Core Research Center”. Y.N. thanks the Toyota Motor Corporation and the NEOS Hydrogen Trust Fund.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201405673>.



Scheme 1. Redox interconversions between dinitrogen-bridged dimolybdenum complexes chelated by depf.

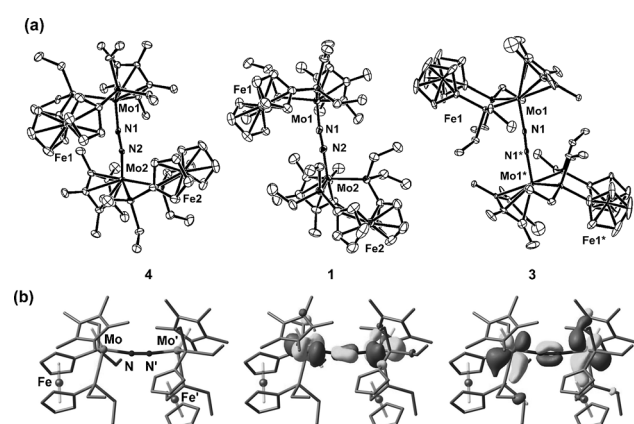


Figure 1. Molecular structures of dinitrogen-bridged dimolybdenum complexes. a) Crystallographic structures of the main parts of **4**, **1**, and **3**. b) Optimized structure of **3** in the triplet spin state and spatial distribution of the SOMOs (HOMO-1 (left) and HOMO (right)).

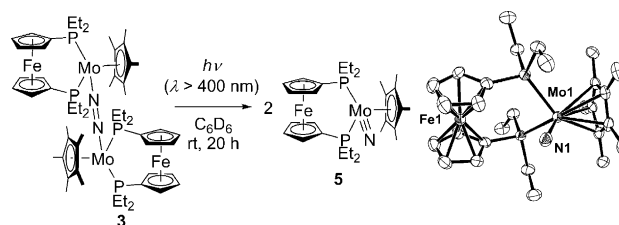
the N–N bond lengths of **4** (1.256(9) Å), **1** (1.226(4) Å) and **3** (1.182(5) Å) correspond to the bonding modes of the bridging dinitrogen ligand as $[\text{N}_2]^{4-}$, $[\text{N}_2]^{3-}$, and $[\text{N}_2]^{2-}$, respectively.^[8] Characteristics of the Mo–N–N–Mo backbone of **1**, **3**, and **4** have been investigated by using density-functional-theory (DFT) calculations at the BP86 level of theory. Table 1 summarizes the distances and Mayer bond orders^[9] of the N–

Table 1: Distances (*d*) and the Mayer bond orders (b.o.) of the N–N and Mo–N bonds of the dimolybdenum complexes **1'**, **3**, and **4'**.

Complex (total charge)	N–N			Mo–N		
	<i>d</i> _{exp}	<i>d</i> _{calc}	b.o.	<i>d</i> _{exp}	<i>d</i> _{calc}	b.o.
4' (+2)	1.256(9)	1.254	1.40	1.835(6)	1.853	1.22
				1.824(6)	1.852	1.22
1' (+1)	1.226(4)	1.228	1.60	1.888(3)	1.907	1.02
				1.874(3)	1.904	1.04
3 (0)	1.182(5)	1.208	1.80	1.955(4)	1.971	0.83
				1.955(4)	1.969	0.85

N and Mo–N bonds of **1'**, **3**, and **4'**, where **1'** and **4'** are the cationic part of **1** and **4**, respectively. Results of the BP86 functionals satisfactorily reproduce both the N–N and Mo–N distances in all the complexes. Two-electron reduction of **4** causes an increase in the N–N bond order (1.40 (**4'**)→1.60 (**1'**)→1.80(**3**)) with a decrease in the Mo–N bond order (1.22 (**4'**)→1.03 (**1'**)→0.84 (**3**)) in average, implying that the bridging dinitrogen ligand in the dimolybdenum complexes is reductively activated by at least two electrons, although the Mo–N–N–Mo backbone is close to linear in all the complexes. The structural differences in the Mo–N–N–Mo backbone can be understood from the singly-occupied molecular orbitals (SOMOs) of **3** (Figure 1b). Two SOMOs of **3**, which are occupied by two electrons added to the dicationic complex **4'**, have a bonding character between two nitrogen atoms, while they have an antibonding character between the molybdenum and nitrogen atoms.

When a benzene solution of **3** was irradiated by visible light ($\lambda > 400$ nm), cleavage of the bridging dinitrogen ligand occurred to give the corresponding molybdenum(IV) nitride complex (**5**) in 33% NMR yield (Scheme 2).^[8,10,11] In contrast,



Scheme 2. Photoinduced conversion of **3** into **5** and the X-ray crystallographic structure of **5**.

irradiation of visible light ($\lambda > 580$ nm) to **3** at room temperature or heating of **3** at 70 °C in dark did not give **5**, indicating that the cleavage of the dinitrogen ligand in **3** proceeds specifically under the photochemical conditions (400 nm < λ < 580 nm). Separately, we confirmed that irradiation of visible light to **1** and **4** did not give the corresponding molybdenum nitride complexes, where release of free depf was only observed by NMR spectra after reactions.

The molecular structure of **5** was characterized by ¹H and ³¹P{¹H} NMR spectra. The IR spectrum of **5** exhibits a moderate ν_{MoN} absorption at 1024 cm^{−1} that is assignable to the terminal nitride ligand. More detailed molecular structure of **5** was unequivocally characterized by an X-ray analysis (Scheme 2).^[7]

To obtain more information on the reaction pathway of the photo-induced cleavage of the coordinated dinitrogen, we investigated the time-course change of the absorption spectrum of **3** under irradiation ($\lambda > 400$ nm). As a typical absorbance at 292 nm derived from **3** decreased, shoulder peaks at 292 nm and 332 nm derived from **5** newly appeared (Figure 2a).

For the assignment of the absorption band responsible for the N≡N bond cleavage, electronic transition energies of **3** were obtained with a time-dependent DFT calculation using the BP86 functional. Use of the BP86 functional was

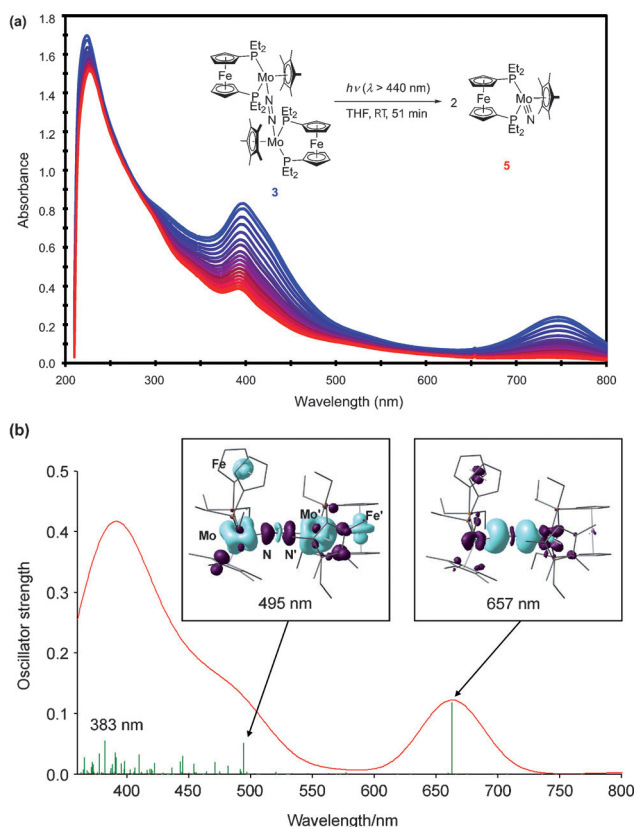
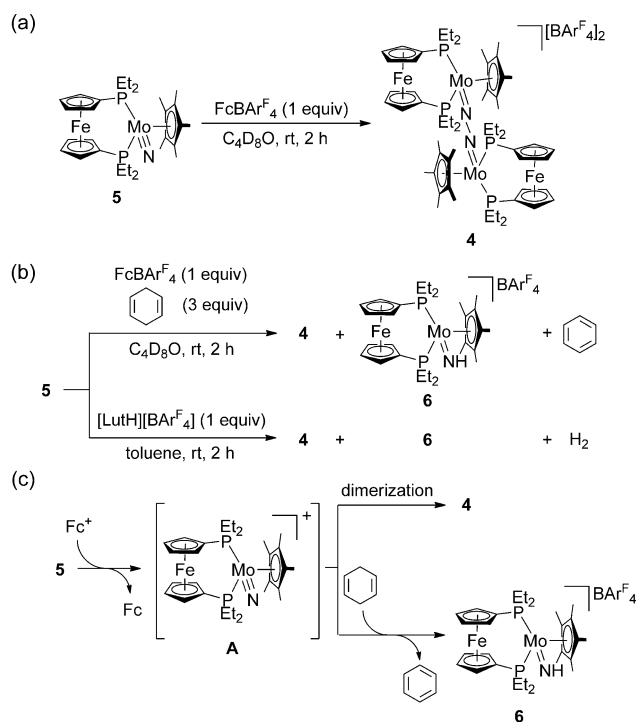


Figure 2. Time-dependent and simulated UV/Vis spectra of **3**. a) Time-dependent UV/Vis spectra of the conversion of **3** into **5** recorded every 3 min for 51 min under visible-light irradiation. b) UV/Vis spectrum of **3** simulated with the time-dependent BP86 method. Two inserts are electron density difference maps (EDDMs) showing isosurface plots of loss (light blue) and gain (purple) of electron density for the calculated electronic transitions.

validated by comparing UV/Vis spectra simulated with various functionals.^[12] As shown in Figure 2b, the calculated electronic transitions (200 transitions, $\lambda > \text{ca. } 400 \text{ nm}$) reasonably reproduced the shape of the measured UV/Vis spectrum of **3**. Three distinguished electronic transitions were found at 383, 495, and 657 nm in the simulated spectrum. Electron density differential maps (EDDMs) present isosurface plots of loss (light blue) and gain (purple) of electron density for the transitions at 495 and 657 nm. The loss of electron density between the two nitrogen atoms observed for the transition at 495 nm could be responsible for the cleavage of the bridging dinitrogen ligand induced by irradiation ($\lambda > 400 \text{ nm}$).

Oxidation of the nitride complex **5** with 1 equiv of $\text{FcBAR}^{\text{F}}_4$ led to its dimerization to generate the dinitrogen-bridged dimolybdenum complex **4** in 36% NMR yield (Scheme 3a). This result is in sharp contrast to the previously reported dimerization of electrophilic late-transition-metal-nitride complexes, where coupling of nitrides is not induced by oxidation.^[13] In fact, Schneider, de Bruin, and their co-workers have recently found that dimerization of iridium and rhodium nitride complexes bearing PNP-type pincer ligand is induced by reduction or photoirradiation, where the corre-



Scheme 3. Reactivity of **5**. a) Dimerization of **5** into **4**. b) Formation of **4** and **6** by the reaction with additives. c) A proposed reaction pathway for **4** and **6**.

sponding nitridyl complexes are proposed to work as key reactive intermediates.^[13j,k]

To investigate the reaction pathway for the oxidation-triggered dimerization of **5**, we next examined the effect of addition of a hydrogen source. When the oxidation of **5** with 1 equiv of $\text{FcBAR}^{\text{F}}_4$ was carried out in the presence of 1,4-cyclohexadiene as a hydrogen source, formation of **4** was observed in 16% NMR yield together with the cationic molybdenum(IV) imide complex (**6**) and benzene in 21% and 8% NMR yields, respectively (Scheme 3b). We also confirmed that no direct dimerization of **6** into **4** occurred under the similar reaction conditions, and thus **6** was revealed to be not a reaction intermediate for the dimerization of **5**. Rather surprisingly, treatment of **5** with $[\text{LutH}][\text{BAR}^{\text{F}}_4]$ ($\text{LutH} = 2,6\text{-lutidinium}$) as a protic acid also afforded a mixture of **6** and **4** in 39% and 37% NMR yields, respectively, together with molecular dihydrogen (H_2) in 9% GC yield (Scheme 3b), as we had expected that only protonation of **5** took place to afford **6** as the sole product. These results demonstrate that the one-electron oxidation of **5** rather preferentially takes place to afford an oxidized cationic nitride species (**A**), which further dimerizes into **4** via the homocoupling reaction or transfers a hydrogen atom from 1,4-cyclohexadiene to afford **6** and benzene (Scheme 3c). Furthermore, treatment of **5** with an excess amount of CoCp^*_2 as a reductant and an excess amount of $[\text{LutH}][\text{BAR}^{\text{F}}_4]$ as a proton source under an atmospheric pressure of argon in toluene at room temperature for 20 h in dark gave 0.37 equiv of ammonia based on **5**.^[12] This result provides a successful example of the formation of ammonia derived from the metal nitride

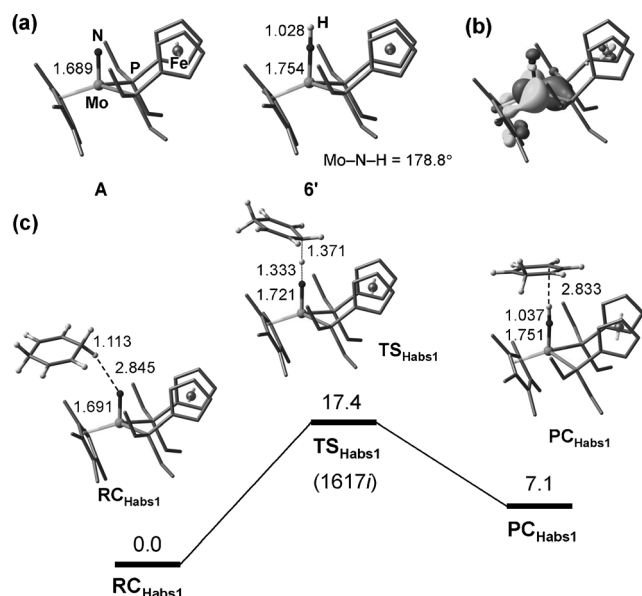


Figure 3. DFT study on the hydrogen transfer by **5**. a) Optimized structures of the intermediate **A** and the cationic part of imide complex **6** (**6'**). b) Spatial distribution of the SOMO of **6'**. c) Energy profile and optimized structures for hydrogen transfer from 1,4-cyclohexadiene by **A** to afford **6'**. RC and PC represent the reactant complex involving **A** and cyclohexadiene, and the product complex involving **6'** and the corresponding cyclohexadiene radical. Energies and interatomic distances are given in kcal mol^{−1} and Å, respectively.

complex formed via the light-induced cleavage of the nitrogen–nitrogen bond of molecular dinitrogen.^[14]

Herein we theoretically discuss the electronic structure and reactivity of the proposed intermediate **A**. Optimized structures of **A** and the cationic part of imide complex **6** (**6'**) are presented in Figure 3a. The Mo–N bond distance (Mayer bond order) of **A** is elongated from 1.689 Å (2.59) to 1.754 Å (1.91) after hydrogen transfer. Although the calculated Mo–N distance of **6'** is slightly longer than the experimental value (1.718(4) Å),^[7] the N–H stretching frequency of the imide moiety is reasonably reproduced (3444 cm^{−1}). The spin density of **6'** is localized at the molybdenum atom (0.91), while a negligibly small amount of the spin density is assigned to the nitrogen atom (−0.06). This spin localization reflects spatial distribution of the SOMO of **6'** (Figure 3b). These results are completely different from the iridium and rhodium nitride complexes reported by Schneider, de Bruin, and their co-workers.^[13j,k] Their metal nitride complexes possess a nitridyl M=N[•] radical character, where the spin density is almost equally distributed on both the metal and nitrogen atoms. Figure 3c shows an energy profile calculated for hydrogen transfer from 1,4-cyclohexadiene by intermediate **A** to afford **6'**. The calculated activation energy (17.4 kcal mol^{−1}) indicates that **A** is capable of picking a hydrogen atom up from cyclohexadiene at room temperature. Although this process is endothermic by 7.1 kcal mol^{−1}, the generated cyclohexadiene radical is readily converted into benzene by the following hydrogen transfer by **A**. Hydrogen transfer from the cyclohexadiene radical by **A** requires a lower activation energy of 10.7 kcal mol^{−1} in the triplet state, and the

resulting **6'** and benzene in the singlet state is 37.4 kcal mol^{−1} more stable than the reactant complex (Supporting Information, Figure S8).^[12] The DFT calculations demonstrate that the intermediate **A** is able to transfer hydrogen atoms from 1,4-cyclohexadiene at room temperature, despite no spin density at the nitride N atom, and therefore **A** is a possible candidate for the reactive species in the dimerization of **5**.

In summary, we have prepared a series of molybdenum–dinitrogen complexes bearing ferrocenyldiphosphine and have revealed their interconversions by redox and light-induced processes. We believe that our findings provide a new aspect in molybdenum–dinitrogen complexes in medium oxidation states.

Received: May 27, 2014

Revised: July 28, 2014

Published online: September 11, 2014

Keywords: dinitrogen complexes · Haber–Bosch process · iron · molybdenum · nitrogen fixation

- [1] R. Schlögl in *Handbook of Heterogeneous Catalysis*, Vol. 5, 2nd ed (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2501–2575.
- [2] A. D. Allen, C. V. Senoff, *Chem. Commun.* **1965**, 621.
- [3] a) J. Ballmann, R. F. Munhá, M. D. Fryzuk, *Chem. Commun.* **2010**, 46, 1013; b) Y. Shibata, H. Seino, Y. Mizobe, M. Hidai in *Encyclopedia of Catalysis* (Ed.: I. T. Horvath), Wiley-VCH, Weinheim, **2010**, DOI: 10.1002/0471227617.eoc016.pub2; c) J. L. Crossland, D. R. Tyler, *Coord. Chem. Rev.* **2010**, 254, 1883; d) N. Hazari, *Chem. Soc. Rev.* **2010**, 39, 4044; e) J. Sgrignani, D. Franco, A. Magistrato, *Molecules* **2011**, 16, 442; f) Y. Nishibayashi, *Dalton Trans.* **2012**, 41, 7447; g) S. Hinrichsen, H. Broda, C. Gradert, L. Sönksen, F. Tuczek, *Annu. Rep. Prog. Chem. Sect. A* **2012**, 108, 17; h) Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* **2013**, 257, 2551; i) K. C. MacLeod, P. L. Holland, *Nat. Chem.* **2013**, 5, 559; j) H.-P. Jia, E. A. Quadrelli, *Chem. Soc. Rev.* **2014**, 43, 547.
- [4] a) D. V. Yandulov, R. R. Schrock, *Science* **2003**, 301, 76; b) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, 3, 120; c) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, 501, 84.
- [5] a) H. Tanaka, K. Arashiba, S. Kuriyama, A. Sasada, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2014**, 5, 3737; b) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2014**, 136, 9719.
- [6] a) M. Yuki, Y. Miyake, Y. Nishibayashi, I. Wakiji, M. Hidai, *Organometallics* **2008**, 27, 3947; b) H. Tanaka, A. Sasada, T. Kouno, M. Yuki, Y. Miyake, H. Nakanishi, Y. Nishibayashi, K. Yoshizawa, *J. Am. Chem. Soc.* **2011**, 133, 3498; c) T. Miyazaki, Y. Tanabe, M. Yuki, Y. Miyake, K. Nakajima, Y. Nishibayashi, *Chem. Eur. J.* **2013**, 19, 11874.
- [7] CCDC 976705 (**1**), 976706 (**3**), 976707 (**4**-C₄H₁₀O-C₆H₁₄), 976708 (**5**), and 976709 (**6**-C₄H₈O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [8] a) C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George, I. J. Pickering, *J. Am. Chem. Soc.* **1996**, 118, 8623; b) J. J. Curley, T. R. Cook, S. Y. Reece, P. Müller, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, 130, 9394; c) P. P. Fontaine, B. L. Yonke, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2010**, 132, 12273.
- [9] I. Mayer, *Chem. Phys. Lett.* **1983**, 97, 270.

- [10] For photochemical cleavage of dinitrogen under ambient reaction conditions, see also: a) E. Solari, C. Da Silva, B. Iacono, J. Heschbrouck, C. Rizzoli, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed.* **2001**, *40*, 3907; *Angew. Chem.* **2001**, *113*, 4025; b) H. Kunkely, A. Vogler, *Angew. Chem. Int. Ed.* **2010**, *49*, 1591; *Angew. Chem.* **2010**, *122*, 1636; c) A. S. Huss, H. J. Curley, C. C. Cummins, D. A. Blank, *J. Phys. Chem. B* **2013**, *117*, 1429.
- [11] For thermal or reductive cleavage of dinitrogen at ambient reaction conditions, see also: a) C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861; b) J. S. Figueroa, N. A. Piro, C. R. Clough, C. C. Cummins, *J. Am. Chem. Soc.* **2006**, *128*, 940; c) F. Akagi, T. Matsuo, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2007**, *46*, 8778; *Angew. Chem.* **2007**, *119*, 8934; d) I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881 and references therein.
- [12] See the Supporting Information for details.
- [13] a) D. C. Ware, H. Taube, *Inorg. Chem.* **1991**, *30*, 4605; b) H.-W. Lam, C.-M. Che, K.-Y. Wong, *J. Chem. Soc. Dalton Trans.* **1992**, 1411; c) K. D. Demadis, T. J. Meyer, P. S. White, *Inorg. Chem.* **1997**, *36*, 5678; d) K. D. Demadis, E.-S. El-Samanody, G. M. Coia, T. J. Meyer, *J. Am. Chem. Soc.* **1999**, *121*, 535; e) C. Newton, K. D. Edwards, J. W. Ziller, N. M. Doherty, *Inorg. Chem.* **1999**, *38*, 4032; f) S. B. Seymore, S. N. Brown, *Inorg. Chem.* **2002**, *41*, 462; g) W.-L. Man, T.-M. Tang, T.-W. Wong, T.-C. Lau, S.-M. Peng, W.-T. Wong, *J. Am. Chem. Soc.* **2004**, *126*, 478; h) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 6252; i) W.-L. Man, G. Chen, S.-M. Yiu, L. Shek, W.-Y. Wong, W.-T. Wong, T.-C. Lau, *Dalton Trans.* **2010**, *39*, 11163; j) M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin, S. Schneider, *Nat. Chem.* **2012**, *4*, 552; k) M. G. Scheibel, Y. Wu, A. C. Stückl, L. Krause, E. Carl, D. Stalke, B. de Bruin, S. Schneider, *J. Am. Chem. Soc.* **2013**, *135*, 17719.
- [14] Formation of ammonia derived from the nitride complexes formed via reductive cleavage of dinitrogen has been reported: a) M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, *Science* **2011**, *334*, 780; b) T. J. Hebden, R. R. Schrock, M. K. Takase, P. Müller, *Chem. Commun.* **2012**, *48*, 1851.