JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

N–N Bond Cleavage of Hydrazines with a Multiproton-Responsive Pincer-Type Iron Complex

Kazuki Umehara, Shigeki Kuwata,* and Takao Ikariya*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Supporting Information

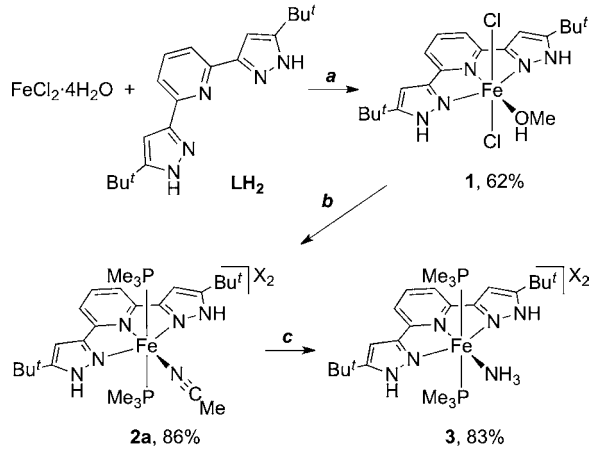
ABSTRACT: N–N bond cleavage of hydrazines on transition metals is of considerable importance in understanding the mechanism of biological nitrogen fixation under ambient conditions. We found that a metal–ligand-bifunctional complex of iron with a pincer-type ligand bearing two proton-responsive pyrazole arms catalyzes the disproportionation of hydrazine into ammonia and dinitrogen. The NH groups in the pyrazole ligands and hydrazines are crucial for the reaction, which most likely occurs through multiple and bidirectional proton-coupled electron transfer between the iron complex and hydrazine. The multiproton-responsive pincer-type ligand also stabilizes the intermediate diazene complex through a hydrogen-bonding network, as revealed by structural characterization of a κ^1N-phenylhydrazine complex.

Proton-coupled electron transfer (PCET) plays pivotal roles in a broad range of biological transformations and energy conversions with notable efficiency.[1] A representative example is enzymatic nitrogen fixation, which involves multiple and alternating flows of protons and electrons to the N_2 substrate without the formation of high-energy intermediates.[2] We envisioned that such multiple PCET may proceed smoothly at a redox-active metal center ligated by multiple proton-delivering functional groups. In such a bifunctional platform, transfer of the accumulated protons to the coordinated substrate would render the functional ligands more electron-donating to facilitate coupled metal-to-substrate electron transfer. This strategy has rarely been explored in functional modeling of nitrogenase enzymes,[3,4] although reductive transformations of dinitrogen[5,6] and related nitrogenous substrates[5,7−10] on transition-metal complexes have been extensively studied. Within this context, and in relation to our continuing study of metal–ligand cooperating bifunctional catalysts,[11−13] we recently reported stepwise and reversible deprotonation of a ruthenium complex bearing a multiproton-responsive pincer-type bis(pyrazole) ligand, 2,6-bis(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine ($\mathbf{LH_2}$ in Scheme 1), as well as N_2 coordination therein.[12] Here we describe multiple and bidirectional PCET in a related metal–ligand-bifunctional complex of iron with ligand $\mathbf{LH_2}$, leading to facile reduction and oxidation of hydrazine, which is a nitrogenase substrate.[14]

The reaction of iron(II) chloride with the pincer ligand $\mathbf{LH_2}$ in methanol afforded chlorido–methanol complex **1** (Scheme 1). The high-spin complex **1** (μ_{eff} = 5.0μ_B) was characterized by X-ray analysis (Figure S1).[15] Ligand exchange of **1** with PMe_3 and solvent acetonitrile, with addition of NaOTf to provide triflate counterions, led to the formation of the diamagnetic iron complex **2a**. The pyrazole NH signal at δ 12.40 in the ^{1}H NMR spectrum of **2a** was identified by exchange with added D_2O. The Brønsted acidic nature of the pyrazole protons is further suggested by the crystal structure of **2a** depicted in Figure 1, in which the pyrazole NH groups point to the triflate counteranions with hydrogen-bonding interactions (mean NH···O distance = 1.97 Å). While **2a** was inert toward dinitrogen, the nitrile ligand in **2a** was cleanly replaced by ammonia to give ammine complex **3**, whose ^{1}H NMR spectrum shows a resonance ascribed to the ammine ligand at δ 3.09.

The pincer-type complex **2a** having two ionizable NH groups around the labile nitrile ligand proved to effect the catalytic disproportionation of hydrazine into ammonia and dinitrogen. Treatment of **2a** with 5 equiv of hydrazine led to complete consumption of the hydrazine and the clean formation of ammonia and dinitrogen along with ammine complex **3**.[16] No dihydrogen evolution was observed. The product yields summarized in Table 1 clearly indicate that **2a** catalyzes the disproportionation of hydrazine according to the equation

Scheme 1. Synthesis of Protic Pincer-Type Iron Complexes 2a and 3[a]



[a]Reagents and conditions: (a) MeOH, rt. (b) NaOTf (excess), PMe_3 (2.3 equiv), MeCN, rt. (c) NH_3 (excess), CH_2Cl_2, rt. X = OTf (OSO_2CF_3).

Received: December 17, 2012
Published: April 23, 2013

   dx.doi.org/10.1021/ja3122944 | J. Am. Chem. Soc. 2013, 135, 6754–6757

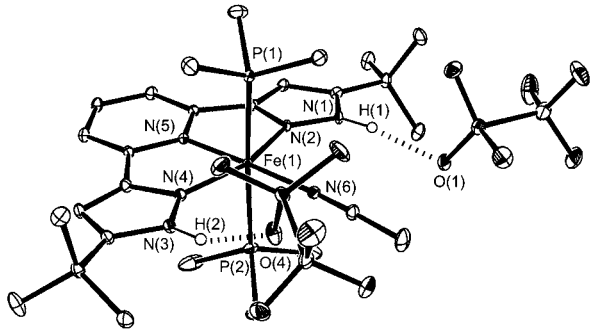
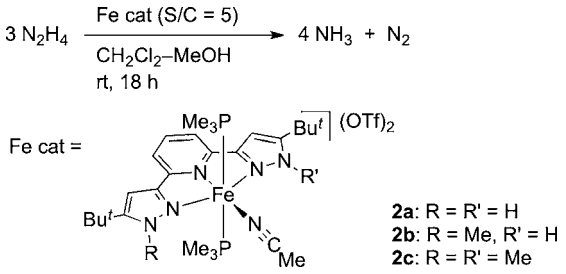


Figure 1. Structure of nitrile complex **2a**. H atoms except for the pyrazole NH hydrogens have been omitted for clarity. Ellipsoids are drawn at the 30% probability level.

Table 1. Catalytic Disproportionation of Hydrazine with Protic Pincer-Type Iron Complexes

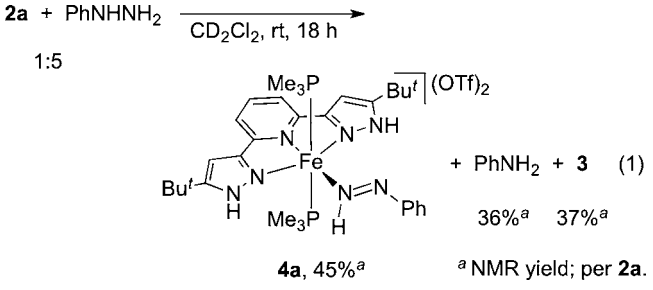


		yields[b]	
catalyst	conv. of N_2H_4 (%)[a]	NH_3[a]	N_2[c]
2a	>98[d]	5.5 (6.1)[d,e]	1.5[d]
2b	54	2.8	0.79
2c	37	0.34	0.52

[a]Determined by colorimetry. [b]In moles per mole of Fe complex. [c]Determined by GC. [d]Average value from three runs. [e]The value in parentheses includes the amount of ammine complex **3** estimated by ^{1}H NMR analysis. For details, see the Supporting Information.

shown therein with a reasonable material balance. Notably, the reactions with the N-methylated analogues **2b** and **2c**[15] were much slower and more complicated, suggesting that the importance of the NH groups in the catalysis.

Although disproportionation of hydrazine itself is catalyzed by a number of transition-metal complexes, including iron-based ones,[7−9] little is known about the detailed mechanism of N−N bond cleavage. To elucidate the mechanism of the catalytic disproportionation of hydrazine with **2a**, we next examined the reaction using substituted hydrazines. When **2a** was treated with phenylhydrazine, the N−N bond cleavage occurred in a substoichiometric manner to give the deep-violet phenyldiazene complex **4a**, aniline, and ammine complex **3** in a molar ratio of approximately 1:1:1 (eq 1):



In this reaction, complex **3** was derived from **2a** and free ammonia. When the reaction was carried out under a slightly reduced pressure to suppress the ammonia coordination, the isolated yield of **4a** increased to 63%. The overall reaction can thus be described as disproportionation of two molecules of phenylhydrazine to give phenyldiazene, aniline, and ammonia. X-ray analysis of **4a** revealed the κ^1N coordination of a *cis*-PhN=NH ligand, which is almost coplanar with the pincer ligand (Figure 2). The diazene ligand is involved in the hydrogen-

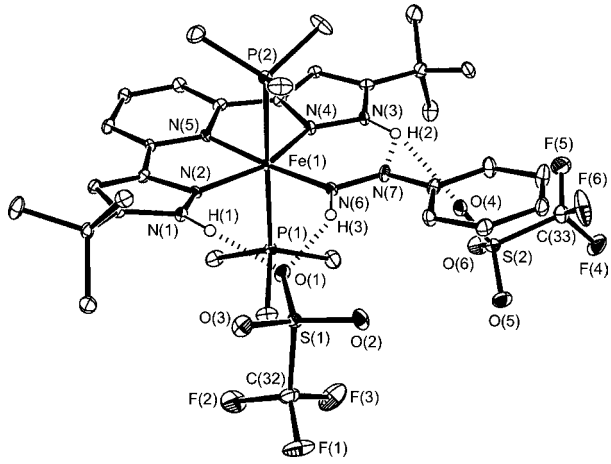
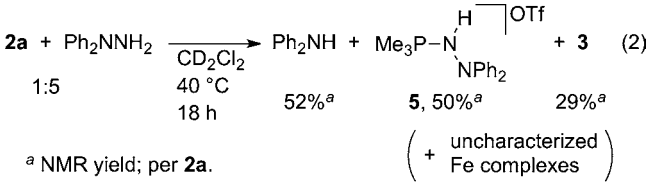


Figure 2. Structure of phenyldiazene complex **4a**. H atoms except for the NH hydrogens have been omitted for clarity. Ellipsoids are drawn at the 30% probability level.

bonding network with the protic pincer ligand and triflate anions [O(1)···H(3), 2.35(3) Å;[17] N(7)···H(2), 2.32 Å]. The Fe−$N_{proximal}$ and N=N distances of 1.875(3) and 1.270(3) Å, respectively, are comparable to those found in related diazene complexes.[4,7,8,18] The ^{1}H NMR spectrum of the diamagnetic complex **4a** exhibited a singlet at extremely low field (δ 17.46) that was assigned to the diazene proton on the basis of the observation that it split into a doublet upon ^{15}N labeling ($^1J_{NH}$ = 67.0 Hz). The ^{15}N{^{1}H} NMR resonances of **4a**-$^{15}\mathbf{N_2}$ appeared at δ 414.1 and 466.3. These spectroscopic parameters agree with the diazene formulation.[4,7,8,18−20] The two pyrazole NH protons at δ 12.27 were found to be equivalent even at −80 °C, indicating a rapid rotation about the iron−diazene bond in solution despite the presence of the hydrogen-bonding network. These NH signals disappeared upon treatment with D_2O, consistent with the expected Brønsted acidic nature of these protons.

On the other hand, the reaction of **2a** with 1,1-diphenylhydrazine afforded diphenylamine and an almost equimolar amount of hydrazinophosphonium triflate **5** along with ammine complex **3** and other paramagnetic iron complexes (eq 2):

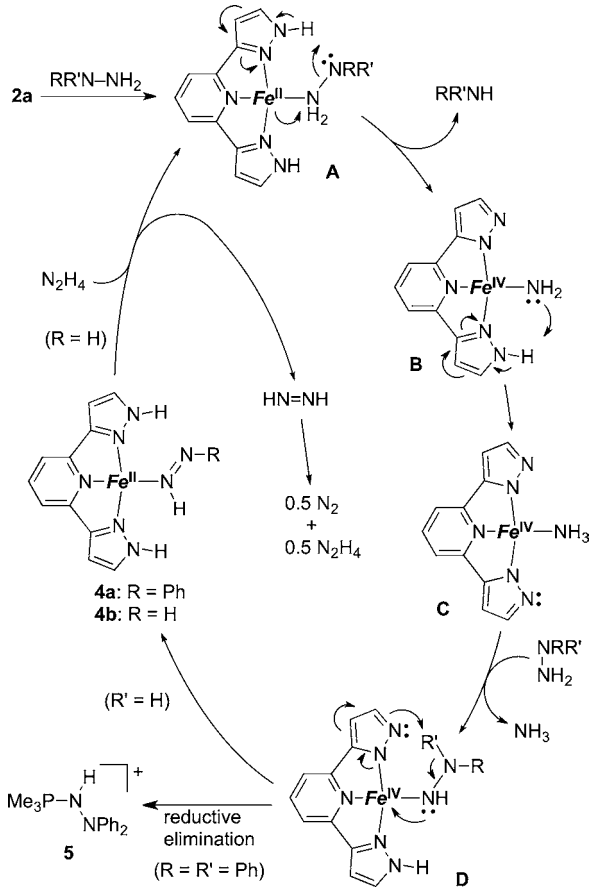


Triflate salt **5** was unambiguously characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, X-ray analysis (Figure S2), and an alternative synthesis of **5** from an iodophosphonium salt and 1,1-diphenylhydrazine.[15] Formation of the phosphorus(V) salt **5** strongly suggests that a high-valent iron−hydrazido species is involved in the early stage of the reaction of **2a** with hydrazines.

dx.doi.org/10.1021/ja3122944 | J. Am. Chem. Soc. 2013, 135, 6754−6757

The isolation of phenyldiazene complex **4a** and hydrazinophosphonium salt **5** along with the low catalytic activity of the N-methylated complexes **2b** and **2c** suggests a possible mechanism for the catalytic disproportionation of hydrazine (Scheme 2).

Scheme 2. Proposed Mechanism for N−N Bond Cleavage of Hydrazines[a]



[a] *Fe* = $Fe(PMe_3)_2^{2+}$. The total charges of the Fe complexes (2+) and the *tert*-butyl groups in the pincer ligands have been omitted.

First, a hydrazine binds to the iron through the less-hindered nitrogen atom to give hydrazine complex **A**. Hydrogen bonding between the pyrazole NH group and the uncoordinated nitrogen atom in the hydrazine ligand promotes reductive N−N bond cleavage, leading to the formation of iron(IV)−amido complex **B**.[21] In this step, hydrazine acts as an oxidant.[22] We note some similarity between this PCET process and the heterolytic O−O bond cleavage of hydrogen peroxide in heme peroxidase and catalases, in which distal peptide residues serve as acid−base catalytic groups.[23] In addition, we previously demonstrated that a protic N-heterocyclic carbene ligand promotes C−O bond cleavage of allyl alcohol through analogous PCET.[13] The NH_2 ligand in intermediate **B** then undergoes a proton transfer from the remaining pyrazole NH group and is converted to the more labile ammine ligand in **C**. Subsequent ligand substitution by a second molecule of hydrazine and a proton shift from the coordinated hydrazine to the pyrazolato arm give iron(IV)−hydrazido(1−) complex **D** and ammonia. This acid−base catalysis of the second pyrazole NH group rationalizes the lower reactivity of **2b** without this NH group. When a hydrogen atom on the distal nitrogen is available in **D** (R′ = H), subsequent PCET from the hydrazido(1−) ligand to the iron(IV)−pyrazolato moiety occurs, affording iron(II) diazene complex **4**, which is isolable for R = Ph (**4a**). Since such a PCET is not possible in the diphenylhydrazido(1−) analogue (R = R′ = Ph), reductive elimination of the hydrazido(1−) ligand and trimethylphosphine from the iron(IV) center would instead take place, generating phosphonium salt **5**. Finally, the labile HN═NH ligand in **4b** would be replaced[20] by hydrazine to regenerate hydrazine complex **A** and free diazene, the latter of which immediately undergoes bimolecular disproportionation to yield dinitrogen and hydrazine.[24]

In summary, we have demonstrated that the metal−ligand-bifunctional iron complex **2a** bearing a pincer-type bis(pyrazole) ligand cleaves the N−N bond of hydrazines. Mechanistic investigations using N-substituted pyrazoles and hydrazines led us to conclude that the reaction occurs through multiple proton and electron shuttling between hydrazine and the iron complex mediated by the two proton-responsive pyrazoles appropriately placed in the rigid pincer framework. It would be worth mentioning that the μ-sulfido ligands in the FeMo-cofactor of nitrogenase are proposed to mediate consecutive PCET to coordinated dinitrogen via the protonated hydrosulfido form.[25] Furthermore, the proton-responsive pincer ligand stabilizes the diazene intermediate through multiple hydrogen bonds. Efforts will be directed toward the application of multiproton-responsive ligands to more the challenging conversion of dinitrogen under mild conditions as well as other important multielectron reduction/oxidation processes such as carbon dioxide reduction and water oxidation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and X-ray crystallographic data for **1**, **2a**, **4a**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

skuwata@apc.titech.ac.jp; tikariya@apc.titech.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (S) (22225004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Prof. Hiroyuki Kawaguchi, Prof. Hiroharu Suzuki, and Mr. Kyo Namura (Tokyo Institute of Technology) are gratefully acknowledged for helping us to measure the magnetic susceptibility.

■ REFERENCES

(1) (a) Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Murphy, C. F.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; McCafferty, D. G.; Meyer, T. J. *Chem. Rev.* **2012**, *112*, 4016. (b) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961.

(2) (a) Howard, J. B.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17088. (b) Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. *Acc. Chem. Res.* **2009**, *42*, 609. (c) Dance, I. *Dalton Trans.* **2012**, *41*, 7647.

(3) (a) Sellmann, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460. (b) Kinney, R. A.; McNaughton, R. L.; Chin, J. M.; Schrock, R. R.; Hoffman, B. M. *Inorg. Chem.* **2011**, *50*, 418.

(4) Sellmann, D.; Hille, A.; Rösler, A.; Heinemann, F. W.; Moll, M.; Brehm, G.; Schneider, S.; Reiher, M.; Hess, B. A.; Bauer, W. *Chem.—Eur. J.* **2004**, *10*, 819.

(5) (a) Hazari, N. *Chem. Soc. Rev.* **2010**, *39*, 4044. (b) Crossland, J. L.; Tyler, D. R. *Coord. Chem. Rev.* **2010**, *254*, 1883. (c) Ballmann, J.; Munhá, R. F.; Fryzuk, M. D. *Chem. Commun.* **2010**, *46*, 1013. (d) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512.
(6) Recent examples: (a) Yuki, M.; Tanaka, H.; Sasaki, K.; Miyake, Y.; Yoshizawa, K.; Nishibayashi, Y. *Nat. Commun.* **2012**, *3*, 1254. (b) Semproni, S. P.; Margulieux, G. W.; Chirik, P. J. *Organometallics* **2012**, *31*, 6278. (c) Knobloch, D. J.; Semproni, S. P.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 3377. (d) Semproni, S. P.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 10406. (e) Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 18118. (f) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. *Science* **2011**, *334*, 780. (g) Curley, J. J.; Cozzolino, A. F.; Cummins, C. C. *Dalton Trans.* **2011**, *40*, 2429. (h) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120. (i) Ballmann, J.; Yeo, A.; Patrick, B. O.; Fryzuk, M. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 507.
(7) Saouma, C. T.; Moore, C. E.; Rheingold, A. L.; Peters, J. C. *Inorg. Chem.* **2011**, *50*, 11285.
(8) (a) Rozenel, S. S.; Arnold, J. *Inorg. Chem.* **2012**, *51*, 9730. (b) Chen, Y.; Liu, L.; Peng, Y.; Chen, P.; Liu, Y.; Qu, J. *J. Am. Chem. Soc.* **2011**, *133*, 1147.
(9) (a) Watanabe, D.; Gondo, S.; Seino, H.; Mizobe, Y. *Organometallics* **2007**, *26*, 4909. (b) Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. *Inorg. Chem.* **2005**, *44*, 3768. (c) Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747. (d) Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1994**, *33*, 3619. (e) Coucouvanis, D.; Mosier, P. E.; Demadis, K. D.; Patton, S.; Malinak, S. M.; Kim, C. G.; Tyson, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 12193. (f) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 758.
(10) (a) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2012**, *31*, 2953. (b) Chen, Y.; Zhou, Y.; Chen, P.; Tao, Y.; Li, Y.; Qu, J. *J. Am. Chem. Soc.* **2008**, *130*, 15250. (c) Zdilla, M. J.; Verma, A. K.; Lee, S. C. *Inorg. Chem.* **2008**, *47*, 11382. (d) Hoover, J. M.; Freudenthal, J.; Michael, F. E.; Mayer, J. M. *Organometallics* **2008**, *27*, 2238. (e) Sadique, A. R.; Gregory, E. A.; Brennessel, W. W.; Holland, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 8112. (f) Nakajima, Y.; Suzuki, H. *Organometallics* **2005**, *24*, 1860. (g) Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522. (h) Seino, H.; Masumori, T.; Hidai, M.; Mizobe, Y. *Organometallics* **2003**, *22*, 3424. (i) Le Grand, N.; Muir, K. W.; Pétillon, F. Y.; Pickett, C. J.; Schollhammer, P.; Talarmin, J. *Chem.—Eur. J.* **2002**, *8*, 3115. (j) Barkley, J. V.; Heaton, B. T.; Jacob, C.; Mageswaran, R.; Sampanthar, J. T. *J. Chem. Soc., Dalton Trans.* **1998**, 697.
(11) (a) Dub, P. A.; Ikariya, T. *ACS Catal.* **2012**, *2*, 1718. (b) Ikariya, T. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1. (c) Kuwata, S.; Ikariya, T. *Chem.—Eur. J.* **2011**, *17*, 3542. (d) Kashiwame, Y.; Kuwata, S.; Ikariya, T. *Organometallics* **2012**, *31*, 8444. (e) Dub, T. A.; Wang, H.; Watanabe, M.; Gridnev, I. D.; Ikariya, T. *Tetrahedron Lett.* **2012**, *53*, 3452. (f) Sato, Y.; Kayaki, Y.; Ikariya, T. *Chem. Commun.* **2012**, *48*, 3635. (g) Hasegawa, Y.; Gridnev, I. D.; Ikariya, T. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 316. (h) Kimura, T.; Ishiwata, K.; Kuwata, S.; Ikariya, T. *Organometallics* **2012**, *31*, 1204. (i) Watanabe, M.; Kashiwame, Y.; Kuwata, S.; Ikariya, T. *Eur. J. Inorg. Chem.* **2012**, 504. (j) Kimura, T.; Koiso, N.; Ishiwata, K.; Kuwata, S.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 8880.
(12) Yoshinari, A.; Tazawa, A.; Kuwata, S.; Ikariya, T. *Chem.—Asian J.* **2012**, *7*, 1417.
(13) Araki, K.; Kuwata, S.; Ikariya, T. *Organometallics* **2008**, *27*, 2176.
(14) Davis, L. C. *Arch. Biochem. Biophys.* **1980**, *204*, 270.
(15) See the Supporting Information.
(16) Ammine complex **3** would be a resting state of the catalyst since isolated **3** efficiently catalyzes the disproportionation of hydrazine as **2a**.[15]
(17) The diazene hydrogen atom H(3) was found in the difference Fourier map and isotropically refined.
(18) (a) Sutton, D. *Chem. Rev.* **1993**, *93*, 995. (b) Ittel, S. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4804. (c) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. (d) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627. (e) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829. (f) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271. (g) Sellmann, D.; Friedrich, H.; Knoch, F.; Moll, M. *Z. Naturforsch., B* **1993**, *48*, 76. (h) Cheng, T.-Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657. (i) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245. (j) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296. (k) Sellmann, D.; Blum, D. C. F.; Heinemann, F. W. *Inorg. Chim. Acta* **2002**, *337*, 1. (l) Saouma, C. T.; Müller, P.; Peters, J. C. *J. Am. Chem. Soc.* **2009**, *131*, 10358.
(19) (a) Albertin, G.; Antoniutti, S.; Bortoluzzi, M. *Inorg. Chem.* **2004**, *43*, 1328. (b) Crossland, J. L.; Balesdent, C. G.; Tyler, D. R. *Inorg. Chem.* **2012**, *51*, 439.
(20) (a) Smith, M. R., III; Cheng, T.-Y.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 8638. (b) Albertin, G.; Antoniutti, S.; Bacchi, A.; De Marchi, F.; Pelizzi, G. *Inorg. Chem.* **2005**, *44*, 8947. (c) Hanstein, W. G.; Lett, J. B.; McKenna, C. E.; Traylor, T. G. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 1314.
(21) Selected references on terminal Fe−NH_2 complexes: (a) Anderson, J. S.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 534. (b) Fox, D. J.; Bergman, R. G. *Organometallics* **2004**, *23*, 1656.
(22) (a) Hoover, J. M.; DiPasquale, A.; Mayer, J. M.; Michael, F. E. *Organometallics* **2007**, *26*, 3297. (b) Ohki, Y.; Takikawa, Y.; Hatanaka, T.; Tatsumi, K. *Organometallics* **2006**, *25*, 3111. (c) Verma, A. K.; Lee, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 10838. (d) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346. Also see refs 1b and 10g.
(23) (a) Erman, J. E.; Vitello, L. B. *Biochim. Biophys. Acta* **2002**, *1597*, 193. (b) Hiner, A. N. P.; Raven, E. L.; Thorneley, R. N. F.; García-Cánovas, F.; Rodríguez-López, J. N. *J. Inorg. Biochem.* **2002**, *91*, 27. (c) Fita, I.; Rossmann, M. G. *J. Mol. Biol.* **1985**, *185*, 21.
(24) Wiberg, N.; Bachhuber, H.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 829.
(25) (a) Doan, P. E.; Telser, J.; Barney, B. M.; Igarashi, R. Y.; Dean, D. R.; Seefeldt, L. C.; Hoffman, B. M. *J. Am. Chem. Soc.* **2011**, *133*, 17329. (b) Dance, I. *Dalton Trans.* **2010**, *39*, 2972.