Cooperative Effects

DOI: 10.1002/ange.201408725

Synthesis and Ligand Modification Chemistry of a Molybdenum Dinitrogen Complex: Redox and Chemical Activity of a Bis(imino)pyridine Ligand**

*Grant W. Margulieux, Zoë R. Turner, and Paul J. Chirik**

Abstract: *The bis(imino)pyridine 2,6-(2,6-iPr$_2$-C$_6$H$_3$N=CPh)$_2$-C$_5$H$_3$N (^{iPr}BPDI) molybdenum dinitrogen complex, [{(^{iPr}BPDI)Mo(N$_2$)}$_2$(μ_2,η^1,η^1-N$_2$)] has been prepared and contains both weakly (terminal) and modestly (bridging) activated N$_2$ ligands. Addition of ammonia resulted in sequential N−H bond activations, thus forming bridging parent imido (μ-NH) ligands with concomitant reduction of one of the imines of the supporting chelate. Using primary and secondary amines, model intermediates have been isolated that highlight the role of metal–ligand cooperativity in NH$_3$ oxidation.*

The synthesis of ammonia from its elements, nitrogen and hydrogen, is a long-standing challenge in coordination chemistry and homogeneous catalysis.[1] While the Haber–Bosch ammonia synthesis has transformed fertilizer production and hence global food supplies,[2–4] the fossil fuel inputs and associated CO$_2$ pollution inspires the search for methods compatible with renewable H$_2$.[5] Catalytic methods that rely on proton-coupled electron transfer (PCET),[6] similar to those operative in nitrogenase enzymes,[7] are particularly attractive. Yandulov and Schrock's seminal report of a tris(amido)amine molybdenum(III) complex which catalytically reduced N$_2$ to NH$_3$ using protons and electrons was transformative for demonstrating the utility of well-defined molecular entities for nitrogen fixation at ambient conditions in solution.[8,9] Nishibayashi and co-workers reported the second example of a molecular catalyst for N$_2$ fixation using a bis(phosphine)pyridine-pincer-ligated molybdenum(0) complex.[10,11] While the performance of the catalyst is highly sensitive to ligand substitution,[11,12] these findings have inspired the study of other pincer-ligated molybdenum complexes in the context of N$_2$ functionalization chemistry and to understand the mechanism of action of the catalytic system.[13,14]

The reverse of the ammonia synthesis reaction, the oxidation of NH$_3$ to N$_2$ and H$_2$, is also of interest for potential applications in hydrogen storage and fuel-cell chemistry.[5,15] Compared to ammonia synthesis, much less is known about NH$_3$ oxidation and few molecular catalysts are known to promote the reaction.[16] The first step in such a cycle likely involves N-H oxidative addition of ammonia, a relatively challenging transformation as the preference for M–NH$_3$ dative interactions must be overcome.[17] Metal–ligand cooperativity,[18] where both the transition metal and supporting ligand are directly involved in bond-breaking and bond-making events has emerged as an effective strategy for the synthesis of metal amides (M−NH$_2$) from NH$_3$.[19]

Aryl-substituted bis(imino)pyridine pincers are attractive because of their ease of preparation, synthetic modularity, and ability to support a variety of catalytically active transition-metal complexes.[20] The redox activity of these complexes, the ability to undergo reversible electron-transfer reactions with the transition metal,[21] distinguishes these chelates from PNP-type pincers and may enable unique reactivity relevant to N$_2$ fixation. Notable examples include the hydrogenation of iron imide complexes to yield free anilines[22] and the cleavage of the N−N bonds of azo compounds[23] and hydrazines[24] with bis(imino)pyridine vanadium derivatives where the reducing equivalents derive from both the metal and the supporting ligands. These observations, coupled with catalytic ammonia synthesis reported with [(PNP)Mo] compounds, inspired the study of reduced bis(imino)pyridine molybdenum derivatives. Herein we describe the synthesis of a molybdenum dinitrogen complex supported by a redox-active bis(imino)pyridine and an unusual example of ammonia oxidation to a parent imido ligand involving metal–ligand cooperativity. Insight into reaction intermediates was obtained from chemistry with primary and secondary amines and diphenyl hydrazine.

To prevent possible deprotonation reactions at the imine methyl positions,[25,26] the phenyl-substituted variant of the ligand, 2,6-(2,6-*i*Pr$_2$-C$_6$H$_3$N=CPh)$_2$C$_5$H$_3$N (^{iPr}BPDI) was selected. The molybdenum precursor, [(^{iPr}BPDI)MoCl$_3$], was isolated as a blue-green powder in 94 % yield by refluxing a toluene solution of the free ligand with [MoCl$_3$(thf)$_3$] for 12 hours. The target dinitrogen complex, [{(^{iPr}BPDI)Mo(N$_2$)}$_2$(μ_2,η^1,η^1-N$_2$)] (**1**) was synthesized by stirring [(^{iPr}BPDI)MoCl$_3$] with excess 0.5 % Na(Hg) under 1 atm N$_2$ (Scheme 1). Diamagnetic brown crystals were isolated in 41 % yield and, in contrast to the [{(^{tBu}PNP)Mo(N$_2$)$_2$}$_2$(μ_2-N$_2$)] derivative,[10] **1** contains only three equivalents of N$_2$ per two molybdenum centers. This formulation was established by Toepler pump experiments, combustion analysis, infrared and NMR spectroscopies, and X-ray diffraction.

The solid-state structure of **1** was determined by X-ray diffraction (Figure 1)[31] and established a dimeric molecule

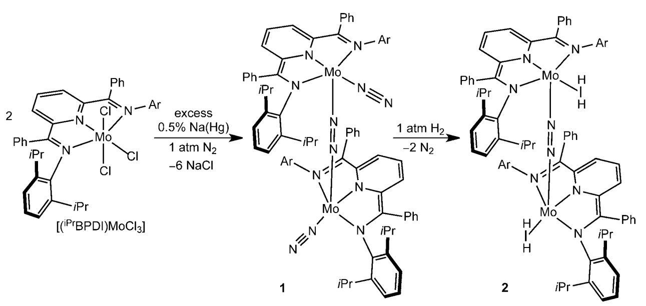
---

[*] G. W. Margulieux,[+] Z. R. Turner,[+] Prof. P. J. Chirik
Department of Chemistry, Princeton University
Frick Laboratory 292, Princeton, 08544 (USA)
E-mail: pchirik@princeton.edu

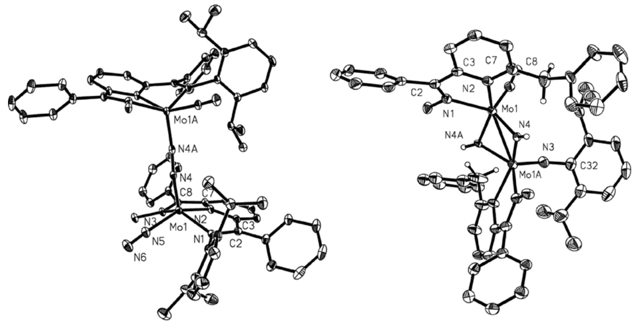
[+] These authors contributed equally to this work.

[**] We thank the Air Force Office for Scientific Research (FA9550-11-10252) for financial support. Z.R.T. thanks the US-UK Fulbright Commission for a fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408725.



Scheme 1. Synthesis and hydrogenation chemistry of **1**.



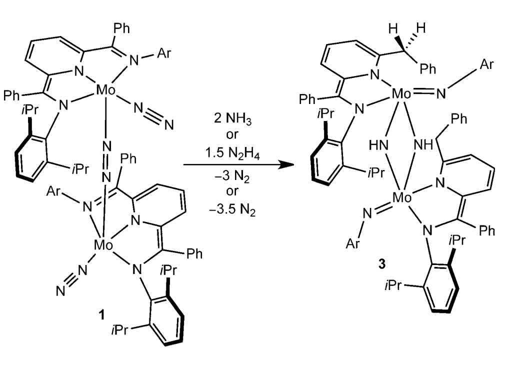
1 3

Figure 1. Solid-state structure of **1** and **3**.[31] Thermal ellipsoids shown at 30% probability. Chelate hydrogen atoms and selected 2,6-diisopropylphenyl groups are omitted for clarity.

where the two [(^{iPr}BPDI)Mo] subunits are best described as highly distorted square pyramidal and connected by an apical, bridging N_2 ligand. In agreement with the solution IR data ($\tilde{\nu}_{NN} = 2037\ \mathrm{cm}^{-1}$), weakly activated, end-on dinitrogen ligands [$d_{NN} = 1.109(5)$ Å] complete the coordination sphere of each molybdenum with each metal lifted out of the idealized plane of the bis(imino)pyridine chelate. Notably, the bridging dinitrogen ligand is more strongly activated than the terminal ones with an N−N distance of 1.246(4) Å, thus signaling formation of $[N_2]^{2-}$. While this degree of activation is distinct from [{(^{tBu}PNP)Mo(N_2)$_2$}$_2$(μ_2-N_2)] where only $[N_2]^0$ ligands are present, two-electron reduction of the bridging N_2 has been observed in bis(imino)pyridine chromium and vanadium compounds.[23,25a,26] The in-plane bond distances of the bis(imino)pyridine chelate, a diagnostic measure of participation of the ligand in the electronic structure,[21] are consistent with two-electron reduction, [^{iPr}BPDI]$^{2-}$. Based on the metrical data, each molybdenum in **1** is best described as Mo^{III}. Curiously, increased dinitrogen activation is observed upon replacement of the relatively electron-rich (^{tBu}PNP) pincer with the relatively electron-poor and redox non-innocent bis(imino)pyridine ligand, and may ultimately be a result of the fewer number of dinitrogen ligands per molybdenum center. We note that in the figures highlighting the synthetic sequences, the spectroscopic oxidation states of the molybdenum complexes are not depicted. These will be highlighted in a summary scheme (Scheme 5).

The [D$_6$]benzene ^{1}H NMR spectrum of **1** exhibits the number of resonances consistent with a C_2-symmetric dimeric compound, thus indicating that the solid-state structure is preserved in solution. The ^{15}N-isotopologue, [($^{15}N_2$)$_3$]**1** was prepared by reduction of [(^{iPr}BPDI)MoCl$_3$] under $^{15}N_2$ gas and exhibits a singlet centered at $\delta = 400.00$ ppm for the bridging dinitrogen linkage and two doublets at $\delta = 369.55$ and 527.75 ppm for the end-on ligand. Selective substitution of terminal N_2 ligands was achieved by addition of $^{15}N_2$ gas to **1**. Addition of 4 atm of H_2 to a [D$_6$]benzene solution of **1** also resulted in substitution of the terminal N_2 ligands to yield **2**. While not readily observed by ^{1}H NMR spectroscopy because of overlap with an aryl C−H resonance, repeating the experiment with D_2 gas identified the {Mo(η^2-H_2)} resonance as a broad singlet centered at $\delta = 6.89$ ppm. Monitoring this experiment by ^{2}H NMR spectroscopy over the course of hours at 23 °C revealed incorporation of the isotopic label into the methyl groups of the 2,6-isopropyl groups, thus demonstrating that both reversible H−H and C−H oxidative addition are operative under these reaction conditions. Exposure of **2** to vacuum resulted in decomposition to an intractable mixture of products while addition of 1 atm of N_2 cleanly regenerated **1**. While the bridging N_2 ligand appears resistant to substitution, no N−H bond-forming chemistry was observed.[27]

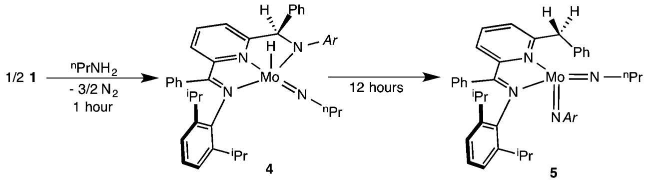
Ammonia synthesis from **1** was attempted by addition of proton and electron sources. Using conditions described by Nishibayashi and co-workers for catalytic NH_3 formation with [{(^{tBu}PNP)Mo(N_2)$_2$}$_2$(μ_2-N_2)],[10] **1** was treated with [LutH]OTf and [Cp$_2$Co]. Ammonia formation was not observed under the aforementioned catalytic conditions or from addition of excess hydrochloric acid. To gain further insight into this lack of reactivity, a series of stoichiometric experiments were performed. Addition of four equivalents of NH_3 gas to a thawing diethyl ether solution of **1** yielded a diamagnetic, red-brown molybdenum product identified as [{(^{iPr}BPIBn)Mo(=NAr^{Dipp})}$_2$(μ_2,η^1,η^1-NH)$_2$] (**3**; ^{iPr}BPIBn = 2,6-(2,6-iPr$_2$-C$_6$H$_3$N=CPh)(CH$_2$Ph)-C$_5$H$_3$N; Scheme 2). The bond distances in the κ^2-imino(pyridine) ligand are consistent with a one-electron-reduced bidentate ligand,[28] thus supporting Mo^V oxidation states. Performing the NH_3 addition and collecting the liberated gas with a Toepler pump confirmed loss of three equivalents of dinitrogen. This product was also obtained from addition of 1.5 equivalents of hydrazine with loss of N_2 and is likely a result of initial disproportionation of hydrazine to form ammonia, which engages in similar chemistry with **1**. Metal-catalyzed disproportionation of N_2H_4 to NH_3 is well established.[29]



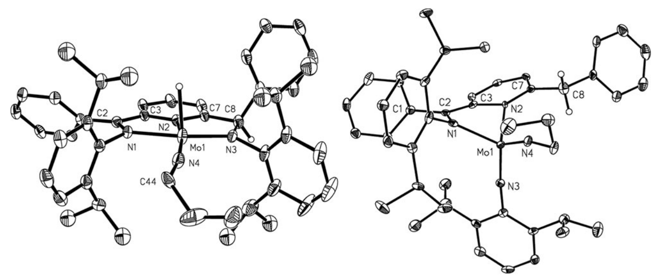
Scheme 2. Addition of NH_3 or N_2H_4 to **1** highlighting the chemical participation of the bis(imino)pyridine ligand.

The solid-state structure of **3** was determined by X-ray diffraction (Figure 1) and established gross structural reorganization upon ammonia addition. Each molybdenum subunit is best described as a C_2 symmetric, distorted trigonal bipyramid with the bridging NH and pyridinyl substituent occupying the axial positions. One of the imine portions of the bis(imino)pyridine chelate was reduced to a benzyl substituent and the former aryl nitrogen fragment was transformed into a terminal molybdenum imido. The fate of the ammonia is accounted for by the presence of two bridging imido ligands. The Mo1-Mo1A distance of 2.6397(5) Å is consistent with a metal–metal single bond and accounts for the observed diamagnetism. Performing the addition with ND_3 placed the isotopic labels on bridging NH ligands and benzylic C–H bonds, thus confirming ammonia as the source of hydrogen in the reduction of the imine unit.

To gain additional insight and potentially observe intermediates for the ligand modification process resulting from ammonia addition to **1**, reactivity with both primary and secondary amines was explored. Addition of two equivalents of nPrNH$_2$ to a diethyl ether solution of **1** followed by recrystallization from diethyl ether furnished red crystals, identified as **4**, in low yield (Scheme 3). Routine characterization of **4** was hampered by the lack of ^{1}H NMR and X-band EPR signals. The X-ray structure (Figure 2)[31] confirms the identity of the compound as a pseudo-square-pyramidal molybdenum imido hydride where the bis(imino)pyridine has been modified by addition of one hydrogen. The metrical parameters of the modified κ^3-amido imino(pyridine) chelate are consistent with one electron reduction, thus supporting assignment as a Mo^V compound. Stirring a diethyl ether solution of **4** at ambient temperature for 12 hours resulted in conversion into a new NMR and EPR-silent, paramagnetic product, **5** (Scheme 3). Determining the progress of the reaction was difficult because of the physical similarities of the reactant and product and the lack of spectroscopic handles. However, the product was characterized by X-ray diffraction and definitively establishes the identity of the compound as the bis(imido) molybdenum pyridine imine complex where one of the chelate arms has been reduced to a benzyl group, thus supporting the intermediacy of molybdenum hydrides in the imine reduction process. The observed distortions to the imino(pyridine) ligand again support a monoreduced chelate and Mo^V oxidation state. The overall geometry of the compound is best described as pseudotetrahedral with bond angles between nitrogen vertices ranging from 110.4(3)° to 119.9(3)°, thus excluding the value 80.4(2)° because of the constraints of the imino(pyridine) chelate. Consistent with this geometry, the solid-state magnetic moment (23 °C) of 2.8(2) μB was measured, thus establishing an $S = 1$ ground state. One of the DFT-computed SOMOs (see Figure S12 in the Supporting Information) is principally of molybdenum character while the other is essentially ligand based. In this symmetry, the orbital of the metal and ligand have poor overlap and hence antiferromagnetic coupling is minimized.



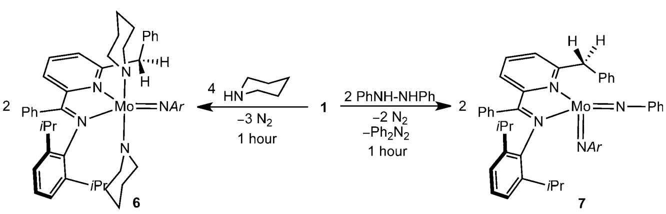
Scheme 3. N-H addition and ligand modification of **1** with nPrNH$_2$.



4 **5**

Figure 2. Solid-state structures of **4** and **5**.[31] Thermal ellipsoids shown at 30 % probability. Hydrogen atoms, except molybdenum hydrides and those on the benzylic positions of the chelate omitted for clarity.

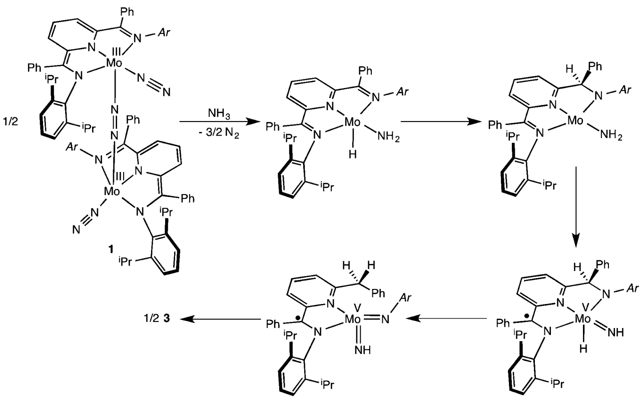
Piperidine was selected as a representative secondary amine and it too resulted in ligand modification. Addition of four equivalents of piperidine to a thawing toluene solution of **1** yielded, following recrystallization from diethyl ether, a new diamagnetic, red compound, **6** (Scheme 4). The [D$_6$]benzene ^{1}H NMR spectrum exhibited the number of resonances consistent with formation of κ^2-imino(pyridine) ligand arising from transfer of two hydrogen atoms from the amine to the imine position of the former bis(imino)pyridine. Single-crystal X-ray diffraction data confirmed formation of a five-coordinate molybdenum complex with a κ^2-imino(pyridine), a terminal imido derived from the bis(imino)pyridine, and two piperidide ligands defining the coordination sphere (see Figure S6). When less than four equivalents of amine were added, only partial conversion of **1** was observed, thus negating the possibility of detecting intermediates. The bond distances in the κ^2-imino(pyridine) are consistent with one-electron reduction,[25] thus supporting a ligand radical and a Mo^V center. Antiferromagnetic coupling between the two spins accounts for the overall diamagnetism of the compound. We do note however that additional spectroscopic measurements are needed to fully corroborate this electronic structure description.



Scheme 4. Reactivity of secondary amines and substituted hydrazines with **1**, thus resulting in ligand modification on molybdenum imido formation.

Because **1** proved to be an effective reagent for observing fundamental transformations relevant to ammonia and amine oxidation, the reactivity with hydrazines was also of interest. Treatment of a benzene solution of **1** with two equivalents of 1,2-diphenyl hydrazine resulted in disappearance of all starting materials and the formation of one equivalent of 1,2-diphenylazine which was identified by comparison of the ^{1}H NMR spectrum and GC-MS to an authentic sample. The molybdenum product was identified as the bis(imido) κ^2-imino(pyridine) molybdenum compound based on X-ray diffraction[31] and arises from transfer of two hydrazine hydrogen atoms to one of the imine positions of the former bis(imino)pyridine (see Figure S7). The molecular geometry of **7** is best described as distorted tetrahedral with bond angles and distances about the metal center nearly identical to **5**. Accordingly, **7** adopts an $S=1$ ground state with a measured solution magnetic moment of 2.7(2) μB at 23 °C.

In summary, the molybdenum dinitrogen complex supported by the redox active bis(imino)pyridine pincer promotes a rare example of NH_3 oxidation to a bridging metal imide.[31] Isolation and characterization of model intermediates provides insight into the role of the redox- and chemical activity of the bis(imino)pyridine ligand (Scheme 5). Metal hydride intermediates are formed during the oxidative process and are able to reduce the imine position to that of a benzyl group. This reactivity along with concomitant metal-imide formation likely drives the conversion of ammonia into a parent imido ligand. Such insights, particularly those involving metal–ligand cooperativity, may ultimately prove valuable in the synthetic schemes for the interconversion of ammonia with its elements.



Scheme 5. Proposed synthetic sequence for conversion of **1** into **3**. Spectroscopic oxidation states are depicted on examples where model intermediates have been isolated and characterized.

Received: September 1, 2014

Keywords: cooperative effects · ligand effects · molybdenum · nitrogen · oxidation

---

[1] M. Appl, *Ammonia*, Wiley-VCH, Weinheim, **2006**, and references therein.
[2] V. Smil, *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*, MIT Press, Cambridge, MA, **2001**.
[3] R. Schlögl, *Angew. Chem. Int. Ed.* **2003**, *42*, 2004; *Angew. Chem.* **2003**, *115*, 2050.
[4] P. Häussinger, R. Lohmüller, A. M. Watson, *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18*, Wiley-VCH, Weinheim, **2012**, p. 249.
[5] a) R. F. Service, *Science* **2014**, *345*, 610; b) S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau, S. Liu, *Science* **2014**, *345*, 637.
[6] M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, *107*, 5004.
[7] a) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983; b) R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013; c) D. Rehder, *Coord. Chem. Rev.* **1999**, *182*, 297; d) Y. Zhao, S. M. Bian, H. N. Zhao, J. F. Huang, *J. Integr. Plant Biol.* **2006**, *48*, 745.
[8] D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 5629.
[9] R. R. Schrock, *Acc. Chem. Res.* **2005**, *38*, 955.
[10] K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, *3*, 120.
[11] S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2014**, *136*, 9717.
[12] a) K. Arashiba, K. Sasaki, S. Kuriyama, Y. Miyake, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, *31*, 2035; b) E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, R. Shimazaki, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, *31*, 8437.
[13] T. J. Hebden, R. R. Schrock, M. T. Takase, P. Müller, *Chem. Commun.* **2012**, *48*, 1851.
[14] Y. Tiun, A. W. Pierpont, E. R. Batista, *Inorg. Chem.* **2014**, *53*, 4177.
[15] a) C. H. Christensen, T. Johannessen, R. Z. Sorensen, J. K. Norskov, *Catal. Today* **2006**, *111*, 140; b) A. Klerke, C. H. Christensen, J. K. Norskov, T. Vegge, *J. Mater. Chem.* **2008**, *18*, 2304.
[16] a) N. Hanada, S. Hino, T. Ichikawa, H. Suzuki, K. Takai, Y. Kojima, *Chem. Commun.* **2010**, *46*, 7775; b) G. M. Coia, K. D. Demadis, T. J. Meyer, *Inorg. Chem.* **2000**, *39*, 2212; c) D. D. Thusius, H. Taube, *J. Phys. Chem.* **1967**, *71*, 3845; d) O. Ishitani, E. Ando, T. J. Meyer, *Inorg. Chem.* **2003**, *42*, 1707; e) R. S. Wise, E. J. Markel, *J. Catal.* **1994**, *145*, 335.
[17] a) T. Kimura, N. Koiso, K. Ishiwata, S. Kuwata, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 8880; b) J. Zhao, A. S. Goldman, J. F. Hartwig, *Science* **2005**, *307*, 1080; c) T. Braun, *Angew. Chem. Int. Ed.* **2005**, *44*, 5012; *Angew. Chem.* **2005**, *117*, 5138; d) M. M. Banaszak-Holl, P. T. Wolczanski, G. D. van Duyne, *J. Am. Chem. Soc.* **1990**, *112*, 7989.
[18] a) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270; b) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588.
[19] a) Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa, K. F. Ozawa, *J. Am. Chem. Soc.* **2013**, *135*, 11791; b) D. V. Gutsulyak, W. E. Piers, J. Borau-Garcia, M. Parvez, *J. Am. Chem. Soc.* **2013**, *135*, 11776; c) E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang, D. Milstein, *J. Am. Chem. Soc.* **2010**, *132*, 8542.
[20] V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745.
[21] a) B. de Bruin, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936; b) P. H. M. Budzelaar, D. de Bruin, A. W. Gal, K. Weighardt, J. H. van Lenthe, *Inorg. Chem.* **2001**, *40*, 4649; c) Q. Knijnenburg, S. Gambarotta, P. H. M. Budzelaar, *Dalton Trans.* **2006**, 5442; d) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Weighardt, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13901.
[22] S. C. Bart, E. Lobkovsky, E. Bill, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 5302.

[23] C. Milsmann, Z. R. Turner, S. P. Semproni, P. J. Chirik, *Angew. Chem. Int. Ed.* **2012**, *51*, 5386; *Angew. Chem.* **2012**, *124*, 5482.

[24] C. Milsmann, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, 136, 12099.

[25] a) D. Reardon, F. Conan, S. Gambarotta, G. Yap, Q. Wag, *J. Am. Chem. Soc.* **1999**, *121*, 9318; b) S. Milione, G. Cavallo, C. Tedesco, A. Grassi, *Dalton Trans.* **2002**, 1839; c) I. Vidyaratne, J. Scott, S. Gamboratta, P. H. M. Budzelaar, *Inorg. Chem.* **2007**, *46*, 7040; d) J. Scott, I. Vidyarante, I. Korobkov, S. Gambarotta, P. H. M. Budzelaar, *Inorg. Chem.* **2008**, *47*, 896; e) M. W. Bouwkamp, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2006**, *45*, 2; f) C. C. Hojilla Atienza, C. Milsmann, S. P. Semproni, Z. R. Turner, P. J. Chirik, *Inorg. Chem.* **2013**, *52*, 5403.

[26] I. Vidyaratne, S. Gamboratta, I. Korobkov, P. H. M. Budzelaar, *Inorg. Chem.* **2005**, *44*, 1187.

[27] J. A. Pool, E. Lobkovsky, P. J. Chirik, *Nature* **2004**, *427*, 527.

[28] C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe, K. Wieghart, *J. Am. Chem. Soc.* **2008**, *130*, 3181.

[29] a) E. Block, G. Ofori-Okai, *J. Am. Chem. Soc.* **1992**, *114*, 758; b) P. B. Hitchcock, D. L. Hughes, M. J. Maguire, K. Marjani, R. L. Richards, *Dalton Trans.* **1997**, 4747; c) P. Schollhammer, F. Y. Petillon, S. Poder-Guillou, J. Y. Saillard, J. Talarmin, K. W. Muir, *Chem. Commun.* **1996**, 2633.

[30] During the preparation of this manuscript, the preparation of molybdenum carbonyl complexes with a pentadentate bis(imino)pyridine ligand was reported, see:R. Pal, T. L. Groy, A. C. Bowman, R. J. Trovitch, *Inorg. Chem.* **2014**, *53*, 9357.

[31] CCDC 1010713 [(^{iPr}BPDI)MoCl$_3$], 1010714 [{(^{iPr}BPDI)Mo(N$_2$)}$_2$(μ_2,η^1,η^1-N$_2$)] (**1**), 1010715 [{(^{iPr}BPIBn)Mo(=NAr^{Dipp})}$_2$(μ_2,η^1,η^1-NH)$_2$] (**3**), 1010717 [(^{iPr}BPIA)MoH(=NC$_3$H$_7$)] (**4**), 1010712 [(^{iPr}BPIBn)MoH(=NAr^{Dipp})(=NC$_3$H$_7$)] (**5**), 1010716 [(^{iPr}BPIBn)Mo(=NAr^{Dipp})(−NC$_5$H$_{10}$)$_2$] (**6**), and 1010711 [(^{iPr}BPIBn)Mo(=Nar^{Dipp})(=NPh)] (**7**) 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.