Nitrogen Fixation

Direct Synthesis of Silylamine from N₂ and a Silane: Mediated by a Tridentate Phosphine Molybdenum Fragment

Qian Liao, Anthony Cavaillé, Nathalie Saffon-Merceron, and Nicolas Mézailles*

In memory of Pascal Le Floch

Abstract: A homogeneous system which is able to yield silylamine from N_2 and bis(silane) in one pot is reported. Mechanistically a {(triphosphine)molybdenum(I)} fragment, generated in situ, splits N_2 into the corresponding nitrido complex at room temperature. Then, functionalization of the molybdenum nitrido is achieved by double Si–H addition under mild reaction conditions. Moreover, the bis(silyl)amine product is decoordinated from the metal center.

 \mathbf{N}_2 fixation at ambient conditions has undergone tremendous advances in the past years, yet it still remains a challenge.^[1] In the first of the two common strategies for N₂ reduction, N₂, coordinated at metal a center(s), reacts with an electrophile (H^+ , R^+ , or SiMe₃Cl) and external electrons. In nature, this process is achieved by nitrogenase enzymes.^[2] Besides that, several carefully designed molecular catalysts have been reported for this transformation, thus affording $NH_3^{[3]}$ or the silvlamine $N(SiMe_3)_3^{[4]}$ (Scheme 1 a). It is to be noted that in these cases, the electrophile also consumes the electrons directly in an efficient competitive process which inevitably results in large amounts of unwanted side products (H₂ or Si-Si compounds). In the second strategy, N₂, also coordinated and/or activated by a metal(s), reacts with the neutral compound E-H (E = H or SiH₂R; Scheme 1b). The Haber-Bosch process, requiring high pressures and temperatures (350-550 °C, 150-350 atm), is a representative example of this strategy employing heterogeneous catalysts.^[5] In this case, N₂ is split at the surface of the catalyst into a nitrido derivative. Functionalization of the nitrido into ammonia then requires activation of H₂ at the catalyst surface followed by sequential hydrogen transfers to terminal nitrogen moieties.^[6] It allows the synthesis of about 100 million tons/year of ammonia from N2 and H2. For a homogeneous system, although early-transition-metal N2 complexes (group IV and V) display rich reactivity towards E-H bonds (E = H, Si, B),^[7] the strength of M-N bonds prevents the release of the

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Scheme 1. Approaches to N₂ reduction and functionalization.

nitrogen product.^[8] In most cases, a strong acid such as HCl has to be employed to cleave the M–N bond, thus preventing further development of catalytic systems. To date, the $\{[(\eta^5-C_5Me_4H)_2Zr]_2(\mu-N_2)\}\)$ complex is the only example that can be hydrogenated to yield substoichiometric amounts of NH₃ (10–15%).^[9] Herein we describe the first molybdenum-(I)-based homogeneous system which is able to a) reduce and cleave N₂ into the corresponding nitrido complex, as well as b) enables the double H–Si addition across the Mo≡N bond to afford bis(silyl)amine species (Scheme 1c). Finally, the molybdenum(I) fragment reacts preferentially with N₂ in the presence of the bis(silane), and thus opens the way for the development of a catalytic process.

Our strategy for N₂ functionalization relied on the splitting of N₂ in a first step, and this process has only been reported to occur at a few molybdenum,^[10] rhenium,^[11] and iron^[12] centers (thermally or photochemically). We recently reported that the $[(P^{Ph}P_2^{\ Cy})Mo(N_2)_2(\mu-N_2)Mo(N_2)_2(P^{Ph}P_2^{\ Cy})]$ molybdenum(0) dimer complex did not result in N₂ splitting, although it could be used as catalyst for the reduction of N₂ into N(SiMe₃)₃ (Scheme 1 a).^[13] The corresponding stoichiometric N₂ functionalization study allowed us to isolate the

molybdenum(IV) nitrido complex. We postulated that the same complex could be obtained by the direct N₂ splitting (six-electron reduction) by two unsaturated molybdenum(I) fragments, which are generated in situ under N₂. Reduction of the $[(P^{Ph}P_2^{\ CV})MoCl_3]$ complex **1** with two equivalents of Na/Hg in the presence of NaI was thus attempted under an N₂ atmosphere (1 atm) at room temperature (Scheme 2a). A



Scheme 2. N_2 splitting and hydrosilylation on molybdenum. a) Two alternative synthetic strategies for N_2 splitting. b) Reactivity of the nitrido complex **3** toward silane and bis(silane).

single diamagnetic complex, the known $[(P^{Ph}P_2^{Cy})Mo(N)(I)]$ complex **3**,^[13] was observed by ³¹P NMR spectroscopy (two singlets at $\delta = 69$ and 121 ppm; see Figure S2 in the Supporting Information), and crystallized in 60% yield.

It is to be noted that no $[Mo^0(N_2)]$ complex, resulting from over reduction, was observed in this reaction (either by NMR and IR). Mechanistically, the formation of **3** implies the intermediacy of a molybdenum(I) dimer featuring a bridging N₂ ligand, for example, the complex **2** (Scheme 2a). Alternatively, NaHBEt₃ (two equiv) can be used as a reducing agent, but it results in a lower yield of **3** (ca. 30%). When labelled ¹⁵N₂ was used to prepare [¹⁵N]**3**, the signal of the nitrido ligand was found at $\delta = 830$ ppm (¹⁵N NMR spectroscopy).

Addition of an E–H bond to a terminal $M\equiv N^{[14]}$ and $M\equiv NR^{[15]}$ has been reported in rare instances. Moreover, none of these complexes were prepared from N₂, except a single recent example of the addition to Fe=N–NR₂.^[16] A metal fragment that can achieve N₂ splitting, followed by nitride and imide functionalization by E–H bonds all the way to the free amine has never been reported.^[17] Thus the reactivity of Mo≡N with either H–H or H–SiR₃ was studied. No reaction between **3** and H₂ was observed but the same reaction with a stoichiometric amount of PhSiH₃ resulted in the formation of a single diamagnetic complex [**4**; 79% yield (NMR) vs. internal standard] within 30 minutes at room

temperature (Scheme 2b). It was isolated in 70% yield, and characterized by multinuclear NMR spectroscopy (see the Supporting Information). Formation of the N–Si bond was shown by a singlet at $\delta = -44.6$ ppm in the ²⁹Si{¹H, ³¹P} NMR spectrum ($\Delta \delta = 16$ ppm vs. PhSiH₃). Further evidence for 1,2-addition of the Si–H bond across the Mo≡N bond was given by a hydride resonance in the ¹HNMR spectrum at $\delta =$

-5.97 ppm [dt, ²*J*(P,H) = 60 Hz, ²*J*(P,H) = 51 Hz, 1 H, Mo-*H*]. Final proof was given by X-ray structure analysis (Figure 1, left). In **4**, the Mo–N bond distance of 1.787-(4) Å is much longer than in the starting **3** [1.656(2) Å] and is indicative of a decrease in bond order as expected upon functionalization.

Having achieved a first hydrosilylation of the molybdenum nitrido, we postulated that an intramolecular approach might favor a second Si-H addition, and the reaction between the bis(silane) HSiMe₂- $(CH_2)_2SiMe_2H$ and **3** was performed. Upon heating at 50°C, an equilibrium mixture of the starting nitrido complex and a new diamagnetic complex, 5, was formed. This result is readily explained by the lower reactivity of R₃SiH versus PhSiH₃, and in turn results in a thermodynamically less favorable process. A twentyfold excess of the bis(silane) was required to allow full displacement of the equilibrium toward 5 (see Figures S8-S10). Iso-



Figure 1. X-ray structures of $[(P^{Ph}P^{Cy}_2)Mo(H)(I)(NSiH_2Ph)]$ (4) and $[(P^{Ph}P^{Cy}_2)Mo(PMe_3)(H)(I)]$ (8).^[20] Thermal ellipsoids shown at 50% probability, except for the carbon atoms on silicon and the carbon atoms in the Cy and Ph groups. Hydrogen atoms, except for the hydrides, have been omitted for clarity.

lation of this complex in pure form was not possible because of the favorable reverse reaction to the nitrido. However, the spectra recorded from the crude mixture showed a signal at $\delta = -5.94$ ppm [q, ²*J*(P,H) = 56 Hz, 1H, Mo-*H*] in the ¹H NMR spectrum, along with two signals at $\delta = -2.5$ and -10.2 ppm in the ²⁹Si{¹H, ³¹P} spectrum for the NSi and SiH moieties, respectively. Together, these data confirmed the 1,2addition of one Si-H bond of the bis(silane) to the Mo=N

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bond. In a second stage, the crude mixture was heated at 80 °C to promote the second intramolecular Si–H insertion.

The ²⁹Si{¹H} NMR spectrum showed the formation of the bis(silyl)amine 6 ($\delta = 11.7$ ppm, compared to authentic sample) in 77% yield (based on 3) as determined by GC-MS analysis of the crude reaction mixture (Scheme 2b). The formation of 6 implies a reduction process at the molybdenum center to give molybdenum(II). Isolation of the complex 7 has not been achieved so far, but we propose it to be an N₂-free, unsaturated complex, because of the lack of a Mo-N2 IR stretch. We could however prove the reduction to molybdenum(II) when the reaction was carried out in the presence of PMe₃. The diamagnetic complex 8 was isolated in 50% yield from the crude reaction mixture (Figure 1, right). To definitely prove the functionalization of the nitrido N, the same reaction was carried out under ${}^{14}N_2$ with $[{}^{15}N]3$. This reaction yielded the ¹⁵N-labeled silylamine [¹⁵N]6 as the only amine as proved unambiguously by GC-MS and ²⁹Si NMR spectra (Figure 2). Not only did this experiment prove the origin of the N atom of the 6, but it also proved the nonreversibility of the splitting of 2 into 3. Heating 5 therefore resulted in the unprecedented overall apparent 1,1-addition



Figure 2. Reactivity of ¹⁵N-labeled complex [¹⁵N]3 with bis(silane) under ¹⁴N₂. A,B) ²⁹Si{¹H} NMR spectra of compound 6 and [¹⁵N]6. C,D) Mass spectra of 6 and [¹⁵N]6.

of the second Si-H on the imido complex, followed by elimination of the amine from the coordination sphere.

Finally, the development of a proper catalytic process requires that each intermediate reacts selectively with one of the reagents. So far, this has never been achieved. For example, the classical use of the strongly oxidizing Me⁺ to functionalize the nitrido intermediate^[18] to give nitrile/ isonitrile derivatives is incompatible with the reaction conditions required for N₂ reduction. We have thus performed the one-pot reaction between 1, 2 equivalents of Na/Hg, and 20 equivalents of the bis(silane) under N₂ (see Figure S18). Most satisfyingly, 6 was produced in 57%, which is higher than the yields of the two isolated steps, that is, 46% (60% for N_2 splitting and 77% for amine formation). $^{\left[19\right]}$ When the reaction was carried out under argon, two diamagnetic complexes featuring hydride ligands were observed. Although they have not been characterized so far, these complexes obviously result from oxidative addition in the Si-H bonds. Most importantly for our purposes, these two reactions prove that in situ generated molybdenum(I) species react much faster with N₂ to form the nitrido complex rather than with the silane, and this preference is a key for further developments.

In conclusion, we show for the first time that a homogeneous metal fragment, $\{(P^{Ph}P_2^{Cy})Mo^I\}$, is both able to split N_2 and allow subsequent functionalization of the generated nitrido complex by Si–H bonds all the way to the free amine under very mild reaction conditions (atm. pressure of N_2 , mild heating). In the first step, each metal fragment acts as a threeelectron reducing agent for N_2 , while the Si–H moieties provide the electrons needed for the two functionalizing steps. These findings pave the way for the development of a catalytic process as proposed in Scheme 3, and will require the



Scheme 3. Potential four-step homogeneous catalytic cycle for the functionalization of N_2 using bis(silane) built on the three stoichiometric steps presented herein.

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reduction of the molybdenum(II) into molybdenum(I) (dotted arrow in Scheme 3). Current work is dedicated to this goal.

Experimental Section

Synthesis of $[^{15}N]$ **3:** $[Mo(P^{Ph}P_2^{Cy})Cl_3] \cdot (THF)_2$ (**1**; 36.0 mg, 0.0400 mmol) and NaI (12.0 mg, 0.0800 mmol) were dissolved in 3 mL of THF in a schlenk tube. Then 182 mg of freshly prepared sodium amalgam (1.0 wt% Na) was put in another small test tube inside the schlenk tube. The solution was degassed by four freezepump-thaw cycles and then backfilled with ${}^{15}N_2$ (≈ 1 atm). After stirring for 15 min, the solution and the sodium amalgam were mixed by inverting the schlenk tube. The mixture was stirred for 4 hours, thus affording a light-brown solution. After the solvent was removed under vacuum, 5 mL of toluene were added to extract the residue. Insoluble residues were separated by centrifugation and the solution containing the product was dried under vacuum. Green crystals of $[Mo(P^{Ph}P_2^{Cy})({}^{15}N)(I)]$ ($[{}^{15}N]3$) were grown by vapor diffusion of *n*pentane into its THF solution. Then the mother liquor was filtered, and the crystals were collected, rinsed with minimum of n-pentane, and dried. Yield of isolated product: 16 mg, 50%.

Synthesis of 8: Complex 3, $[Mo(P^{ph}P_2^{Cy})(N)(I)]$ (31.9 mg, 0.0400 mmol) and HMe₂SiCH₂CH₂SiMe₂H (0.80 mmol) were mixed in THF (4 mL) in a sealed tube and heated at 50 °C. After 40 min, PMe₃ (0.040 mmol, 1.0 m in THF) was added and the solution was heated at 80 °C for another 12 h. Color of the solution changed from light-brown to blueish green. After the reaction, THF was removed under vacuum and about 1 mL of *n*-pentane was added to the residue. The mixture was stirred vigorously for 1 hour, thus affording some blue powder, which was further washed with minimum of pentane ($\approx 2 \times 1.5$ mL) and dried. Yield of isolated product: 17 mg, 50 %. Blue crystals were grown by heating the *n*-pentane solution of the compound in a sealed tube at 50 °C for 20 min then at 40 °C for 20 min.

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- [19] Alternative pathways resulting in the formation of the silylamine **6** were envisaged from the reactions between $(P^{Ph}P_2^{Cy})MoCl_3$, $(P^{Ph}P_2^{Cy})Mo^0(N_2)_x$ or $(P^{Ph}P_2^{Cy})Mo=N-N(SiMe_2-CH_2-CH_2-SiMe_2)$ with excess of bis(silane) (Ref. [13]). None of them led to formation of the desired product.
- [20] CCDC 1455338 (4) and 1455339 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Direct Synthesis of Silylamine from N_2 and a Silane: Mediated by a Tridentate Phosphine Molybdenum Fragment



Split up: Reaction of N_2 with an in situ generated molybdenum(I) fragment stabilized by a tridentate phosphine ligand, results in direct N_2 splitting and formation of the nitrido complex. Functionalization of the nitrido all the way to the formation of bis(silyl)amine can be achieved under mild reaction conditions with bis(silane).

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