Nitrogen Fixation

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

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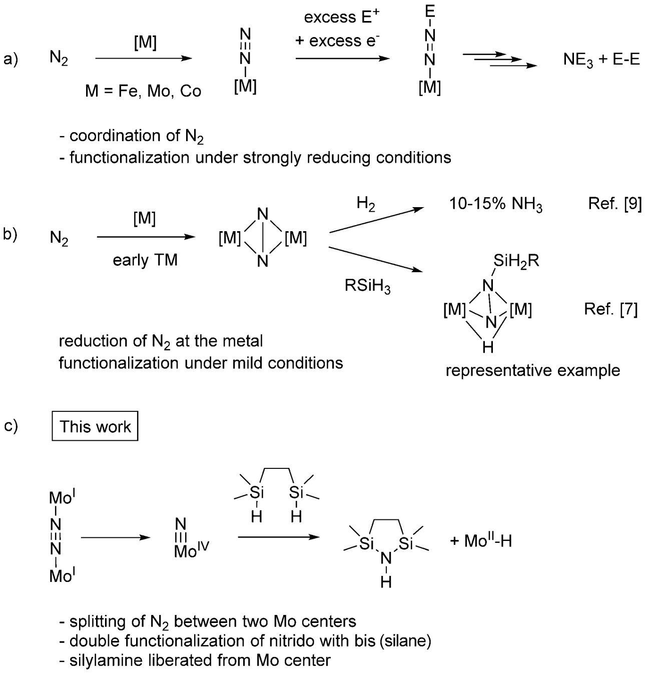
In memory of Pascal Le Floch

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.*

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 N_2 reduction, N_2, coordinated at metal a center(s), reacts with an electrophile (H^+, R^+, or $SiMe_3Cl$) 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 silylamine $N(SiMe_3)_3$[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 (H_2 or Si−Si compounds). In the second strategy, N_2, also coordinated and/or activated by a metal(s), reacts with the neutral compound E−H (E = H or SiH_2R; Scheme 1 b). 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, N_2 is split at the surface of the catalyst into a nitrido derivative. Functionalization of the nitrido into ammonia then requires activation of H_2 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 N_2 and H_2. For a homogeneous system, although early-transition-metal N_2 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 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 $\{[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu\text{-}N_2)\}$ complex is the only example that can be hydrogenated to yield substoichiometric amounts of NH_3 (10–15 %).[9] Herein we describe the first molybdenum(I)-based homogeneous system which is able to a) reduce and cleave N_2 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 1 c). Finally, the molybdenum(I) fragment reacts preferentially with N_2 in the presence of the bis(silane), and thus opens the way for the development of a catalytic process.



Scheme 1. Approaches to N_2 reduction and functionalization.

Our strategy for N_2 functionalization relied on the splitting of N_2 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 $[(P^{Ph}P_2^{Cy})Mo(N_2)_2(\mu\text{-}N_2)Mo(N_2)_2(P^{Ph}P_2^{Cy})]$ molybdenum(0) dimer complex did not result in N_2 splitting, although it could be used as catalyst for the reduction of N_2 into $N(SiMe_3)_3$ (Scheme 1 a).[13] The corresponding stoichiometric N_2 functionalization study allowed us to isolate the

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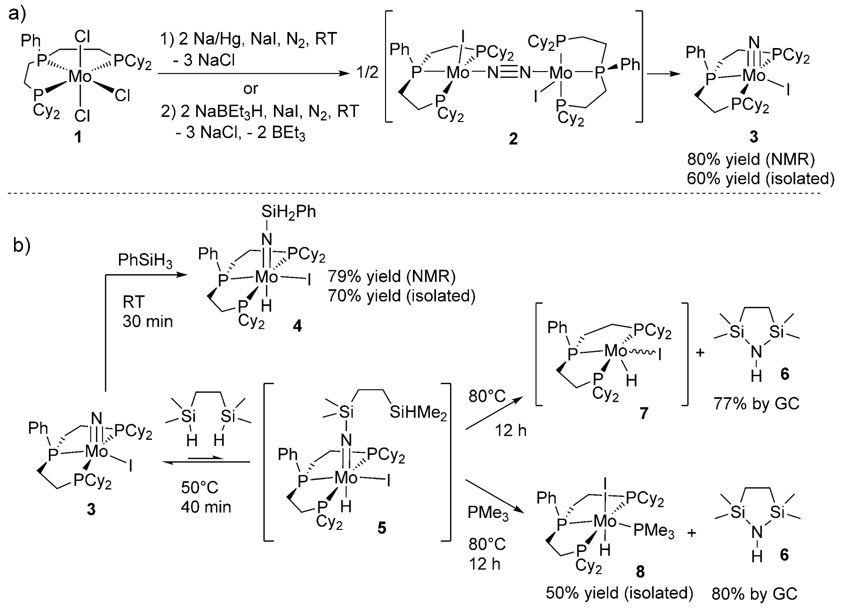
molybdenum(IV) nitrido complex. We postulated that the same complex could be obtained by the direct N_2 splitting (six-electron reduction) by two unsaturated molybdenum(I) fragments, which are generated in situ under N_2. Reduction of the $[(P^{Ph}P_2^{Cy})MoCl_3]$ complex **1** with two equivalents of Na/Hg in the presence of NaI was thus attempted under an N_2 atmosphere (1 atm) at room temperature (Scheme 2a). A single diamagnetic complex, the known $[(P^{Ph}P_2^{Cy})Mo(N)(I)]$ complex **3**,[13] was observed by ^{31}P NMR spectroscopy (two singlets at $\delta = 69$ and 121 ppm; see Figure S2 in the Supporting Information), and crystallized in 60 % yield.



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).

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 N_2 ligand, for example, the complex **2** (Scheme 2a). Alternatively, $NaHBEt_3$ (two equiv) can be used as a reducing agent, but it results in a lower yield of **3** (ca. 30 %). When labelled $^{15}N_2$ was used to prepare $[^{15}N]$**3**, the signal of the nitrido ligand was found at $\delta = 830$ ppm (^{15}N NMR spectroscopy).

Addition of an E−H bond to a terminal M≡N[14] and M=NR[15] has been reported in rare instances. Moreover, none of these complexes were prepared from N_2, except a single recent example of the addition to Fe=N−NR_2.[16] A metal fragment that can achieve N_2 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−SiR_3 was studied. No reaction between **3** and H_2 was observed but the same reaction with a stoichiometric amount of $PhSiH_3$ 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 $^{29}Si\{^1H, ^{31}P\}$ NMR spectrum ($\Delta\delta = 16$ ppm vs. $PhSiH_3$). Further evidence for 1,2-addition of the Si−H bond across the Mo≡N bond was given by a hydride resonance in the ^1H NMR spectrum at $\delta = -5.97$ ppm [dt, $^2J(P,H) = 60$ Hz, $^2J(P,H) = 51$ 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.

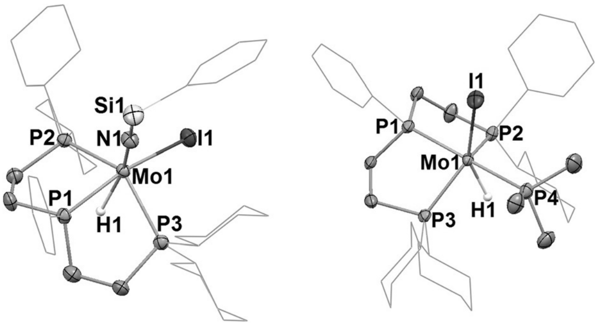


Figure 1. X-ray structures of $[(P^{Ph}P^{Cy}_2)Mo(H)(I)(NSiH_2Ph)]$ (**4**) and $[(P^{Ph}P^{Cy}_2)Mo(PMe_3)(H)(I)]$ (**8**).[20] Thermal ellipsoids shown at 50 % probability, except for the carbon atoms on silicon and the carbon atoms in the Cy and Ph groups. Hydrogen atoms, except for the hydrides,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

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) $HSiMe_2$-$(CH_2)_2SiMe_2H$ 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 R_3SiH versus $PhSiH_3$, and in turn results in a thermodynamically less favorable process. A twenty-fold excess of the bis(silane) was required to allow full displacement of the equilibrium toward **5** (see Figures S8–S10). Isolation 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, $^2J(P,H) = 56$ Hz, 1 H, Mo-*H*] in the ^1H NMR spectrum, along with two signals at $\delta = -2.5$ and -10.2 ppm in the $^{29}Si\{^1H,^{31}P\}$ spectrum for the NSi and SiH moieties, respectively. Together, these data confirmed the 1,2-addition of one Si−H bond of the bis(silane) to the Mo≡N bond. In a second stage, the crude mixture was heated at 80 °C to promote the second intramolecular Si–H insertion.

The ^{29}Si{^{1}H} 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 N_2-free, unsaturated complex, because of the lack of a Mo–N_2 IR stretch. We could however prove the reduction to molybdenum(II) when the reaction was carried out in the presence of PMe_3. 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 ^{15}N-labeled silylamine [^{15}N]**6** as the only amine as proved unambiguously by GC-MS and ^{29}Si NMR spectra (Figure 2). Not only did this experiment prove the origin of the N atom of the **6**, but it also proved the non-reversibility of the splitting of **2** into **3**. Heating **5** therefore resulted in the unprecedented overall apparent 1,1-addition of the second Si–H on the imido complex, followed by elimination of the amine from the coordination sphere.

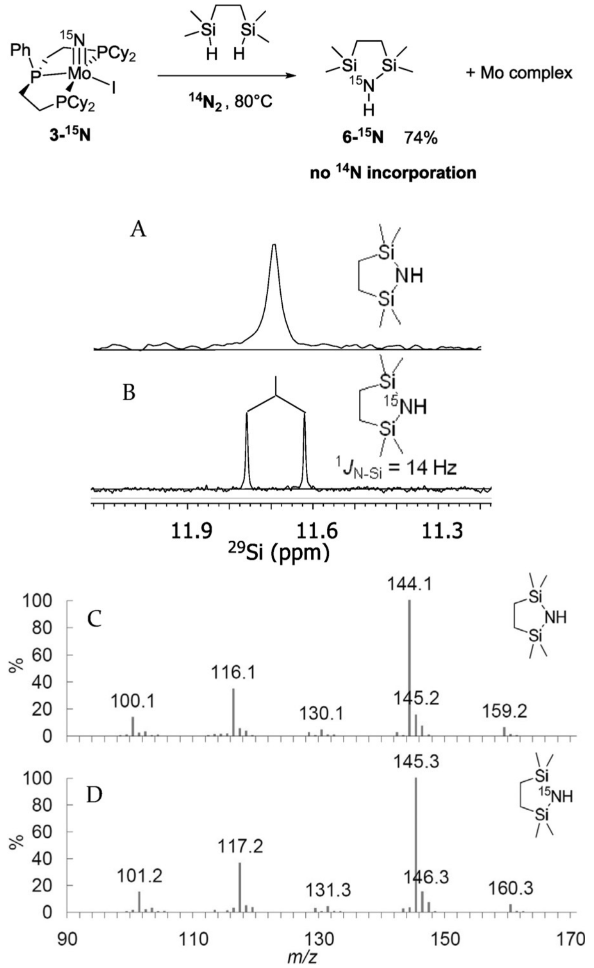
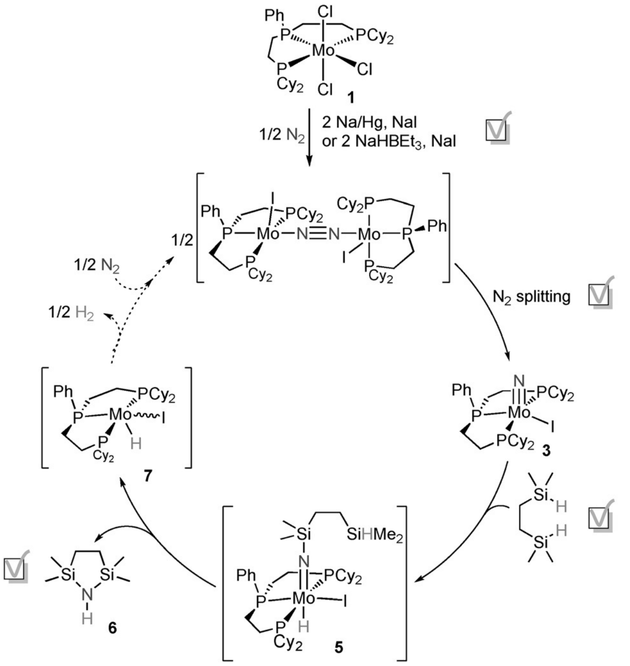


Figure 2. Reactivity of ^{15}N-labeled complex [^{15}N]**3** with bis(silane) under $^{14}N_2$. A,B) ^{29}Si{^{1}H} NMR spectra of compound **6** and [^{15}N]**6**. C,D) Mass spectra of **6** and [^{15}N]**6**.

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 N_2 reduction. We have thus performed the one-pot reaction between **1**, 2 equivalents of Na/Hg, and 20 equivalents of the bis(silane) under N_2 (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).[19] 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 N_2 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 three-electron 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.

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$_3$]·(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 freeze-pump-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 HMe$_2$SiCH$_2$CH$_2$SiMe$_2$H (0.80 mmol) were mixed in THF (4 mL) in a sealed tube and heated at 50 °C. After 40 min, PMe$_3$ (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 (≈2 × 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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