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Stepwise Functionalization of N_2 at Mo: Nitrido to Imido to Amido. Factors Favoring Amine Elimination from the Amido Complex.

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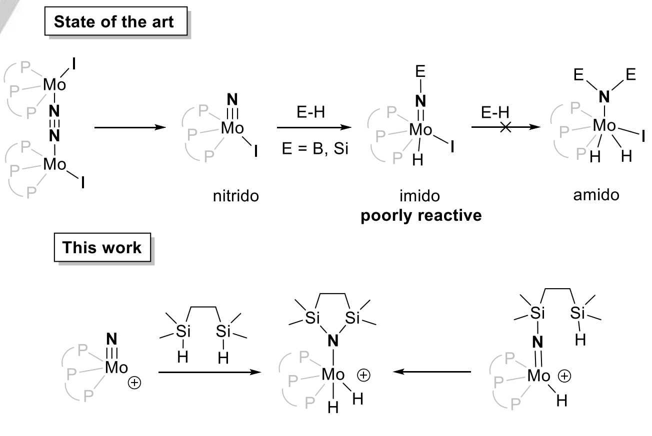
Dedication: In the memory of Prof. P. Le Floch.

Abstract: Functionalization of nitrido complex $[(P^{Ph}P_2^{Cy})Mo(N)(I)]$ by a bis-silane in concentrated medium generates the hydrido-imido complex $[(P^{Ph}P_2^{Cy})Mo(H)(=NSiMe_2CH_2CH_2SiMe_2H)(I)]$. Abstraction of the iodide by thallium salt TlX (X = PF_6, OTf) results in a second N–Si bond formation and forms the bis-hydride amide complex $[(P^{Ph}P_2^{Cy})Mo(H)_2(NSiMe_2CH_2CH_2SiMe_2)]^+$. An alternative synthesis relies on the abstraction of the iodide from the nitride complex $[(P^{Ph}P_2^{Cy})Mo(N)(I)]$ to generate the corresponding cationic complex $[(P^{Ph}P_2^{Cy})Mo(N)]^+$ followed by addition of the bis-silane. Addition of PMe_3 to the $[(P^{Ph}P_2^{Cy})Mo(H)_2(NSiMe_2CH_2CH_2SiMe_2)]^+$ complex liberates the silylamine and forms the $Mo^{(II)}$ cationic complex $[(P^{Ph}P_2^{Cy})Mo(H)(PMe_3)]^+$. DFT calculations rationalizing the observed reactivity are presented.

N_2 functionalization under mild conditions represents one of the biggest challenges for chemists as well as a major societal concern.[1–6] N_2 to NH_3 transformation involves a multistep process that forms six N–H bonds and breaks the $N{\equiv}N$ bond. Several pathways can be envisioned to create and break these bonds. Nature uses protons and electrons in a stepwise formation of N–H bond and reduction of the N–N bond order.[7–11] In the Haber Bosch process, metal atoms of a heterogeneous catalyst provide the six electrons to split N_2 in a first step, while the NH bonds are created in subsequent steps.[12–15] The latter process is appealing since it uses a neutral molecule, H_2, to provide simultaneously the functionalizing moiety and the electrons (stored in the H–H bond).[16] By design, it avoids the use of charged species (H^+ and e^-) that can react together rather than form the desired N–H bonds. Several molecular complexes have been shown to split N_2 under mild conditions,[17–22] opening functionalization pathways of N_2 *via* the transition metal (TM) nitrido complex. Elegant transformations to nitrile derivatives were reported by Cummins (with Mo) and Schneider (with Re) upon the use of strong electrophiles to circumvent the low nucleophilic character of the nitride N in the high valent $Mo^{(VI)}$ and $Re^{(V)}$.[23–27]

We have recently shown that Si–Cl, Si–H bonds as well as B–H bonds react with the $(PP_2)Mo^{IV}$-nitrido complex to generate the corresponding imido complexes in a very facile process (Scheme 1 top).[28–30] However, at this point, and it is a general feature of imido complexes of Mo, the nucleophilic character of the N is drastically reduced, which hampers further functionalization under mild conditions. We successfully circumvented this problem by using bis-silane in excess and heating. Indeed, double Si–H bond functionalization of the $Mo{\equiv}N$ moiety was achieved,[29] as well as amine decoordination from the Mo center. Alternatively, creation of a vacant coordination site at the Mo center of the boryl-imido complex allowed a second B–H bond addition to occur at room temperature. The ensuing (bis-boryl)amido $Mo^{(IV)}$ complex proved very reactive toward excess of B–H substrate, which prevented its isolation in pure form. In fact, amido complexes synthesized by two subsequent functionalizations of a nitrido derivative are very rare. It was the goal of the present study to devise a facile entry to such complexes. To meet success, two strategies were employed, either from the nitrido or the imido cationic derivatives (Scheme 1 bottom). We also report studies directed toward N–H bond formation from the amido derivative. Finally, DFT calculations rationalizing our experimental findings are presented in this article.



- Increased reactivity at N despite charge at Mo?
- Synthesis of amido complex by double Si-H functionalization

Scheme 1. Stepwise functionalization of $Mo^{(IV)}$-nitrido complex and approaches to the cationic amido intermediate

The starting point of this study is the known nitrido complex **1** $[(P^{Ph}P_2^{Cy})Mo(N)(I)]$, obtained *via* the N_2 splitting between two Mo centers (Scheme 2). We have reported previously that complex **1** reacts with an excess (20 equiv.) of

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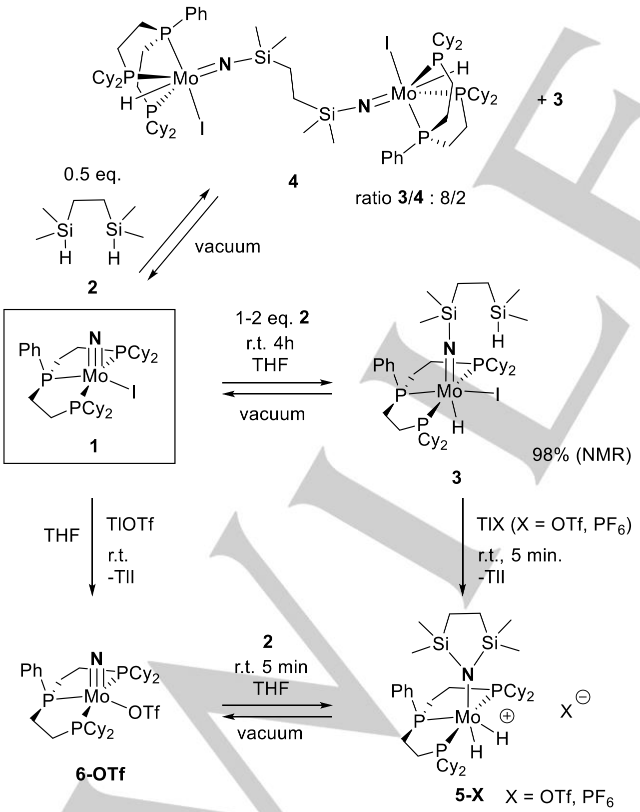
the bis-silane **2** to form the imido derivative **3** under mild conditions.[29] We reinvestigated the addition reaction of Si─H across the MoN bond under stoichiometric conditions. In fact, complex **3** can be synthesized with only one equiv. of bis-silane, yet more concentrated medium is required. Performing the reaction in deuterated solvent allowed its full NMR characterization. In particular, the two inequivalent P centers appear as two singlets at 91.3 and 108.8 ppm (2:1 ratio) in the $^{31}P\{^{1}H\}$ spectrum, while the two different Si centers appear as singlets at ─2.5 and ─10.5 ppm for the N─Si and Si─H moieties respectively. It is interesting to note that the complex is not stable under vacuum, because of the facile reversible process. In that case, the low boiling point of the bis-silane favors the reformation of the nitrido complex **1**. When only half equiv. of bis-silane **2** was reacted with **1**, few crystals slowly deposited from the solution over the course of 2 days, and a mixture of complex **3** and a novel complex, **4**, in *ca* 8:2 ratio, together with remaining nitrido was observed in the supernatant (Figure S4). Complex **4** is characterized in the ^{31}P spectrum by two singlets at 91.0 and 109.5 ppm (2:1 ratio), close to the chemical shifts of complex **3** which suggested the formation of another imido complex. Complex **4** was only observed in mixture with complex **3**.. Note here that when an excess of bis-silane **2** is added to the mixture of 3 and 4, a slow evolution to bissilylamine (Figure S5) and paramagnetic Mo(II) complex occurs. This is consistent with our previous observation of reactivity of complex 3 with bis-silane.



Scheme 2. Stepwise functionalization of nitrido complex **1** by Si─H bonds.

X-ray diffraction study proved the addition of the two Si─H bonds to two nitrido complexes **1** to form complex **4** (Figure 1). Bond distances and angles are presented below the structure. The Mo─N bond distance of 1.787(3) Å is elongated compared to the Mo─N bond in complex **1** (1.656(2) Å), as expected. All bond distances are similar to those measured in the related Mo-imido complex obtained by addition of $PhSiH_3$ on complex **1**.[29]

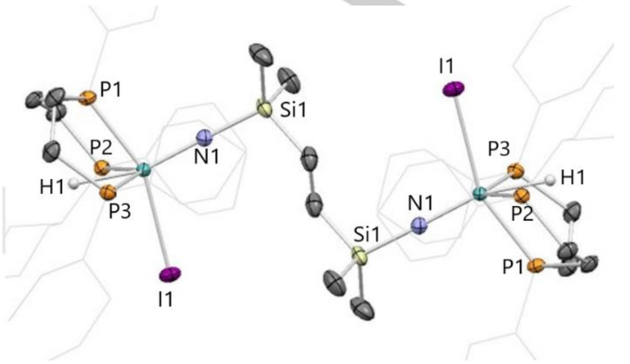


Figure 1. X-ray structure of complex **4**: 50% thermal ellipsoids are shown. Solvent molecule and hydrogen atoms, except for the hydride, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1-N1 1.787(3), Mo1-P1 2.388(1), Mo1-P2 2.466(1), Mo1-P3 2.441(1), Mo1-I1 2.835(1), Mo1-H1 1.85(4), N1-Si1 1.755(3); N1-Mo1-P1 99.9(1), N1-Mo1-P3 113.0(1), P1-Mo1-P3 81.0(1), N1-Mo1-P2 115.9(1), P1-Mo1-P2 80.1(1), P3-Mo1-P2 129.8(1), N1-Mo1-I1 103.9(1), P1-Mo1-I1 156.2(1), P3-Mo1-I1 90.0(1), P2-Mo1-I1 89.2(1), N1-Mo1-H1 162.7(11), P1-Mo1-H1 62.9(11), P3-Mo1-H1 64.1(11), P2-Mo1-H1 65.9(11), I1-Mo1-H1 93.3(11), Si1-N1-Mo1 175.5(2)

Pure complex **3** does not evolve at room temperature *via* a second Si─H bond addition onto the Mo=N moiety to form the amido-dihydride complex **5-I**. However, when this complex was reacted with one equiv. of TlX (X = OTf or PF_6), an instantaneous reaction occurred to afford **5-X**, as evidenced by a color change from brown to dark purple and by the two signals at 116.0 (d, $J_{P\text{-}P}$ = 5.2 Hz, 2P) and 133.3 (t, $J_{P\text{-}P}$ = 5.2 Hz, 1P) ppm in the ^{31}P NMR spectrum. Complex **5-X** was isolated in very good yield (80%) and fully characterized by multinuclear NMR spectroscopy. In particular, a single signal for the two hydrides was observed at –16.7 ppm in ^{1}H NMR as a broadened pseudo-quartet (J_{HP} = 48.2 Hz), for apparent equivalent H centers. In an attempt to slow down the process of fast position exchange of the two hydrides, the spectrum was also recorded at ─80°C. At that temperature, the signal sharpened yet remained a pseudo-quartet proving a low energy process for hydride interconversion. A $T_{1,min}$ of 135 ms was measured for the hydride signal, which is consistent with complex **5-X** to feature two hydride ligands rather than a dihydrogen ligand.[31,32] The complex is also characterized by two singlets in the $^{29}Si\{^{1}H\}$ spectrum at 13.6 and 14.7 ppm, corresponding to the two Si centers with different chemical environment. Importantly, the signal for Si─H bond in complex **3** found at ─10.2 ppm is now absent, also proving the second N─Si bond formation.

Complex **5-X** is stable at room temperature for extended periods, and even at 80°C for several hours but degrades upon prolonged heating. This observation points to difficult reductive elimination of the bis-silylamine **8** along with the corresponding

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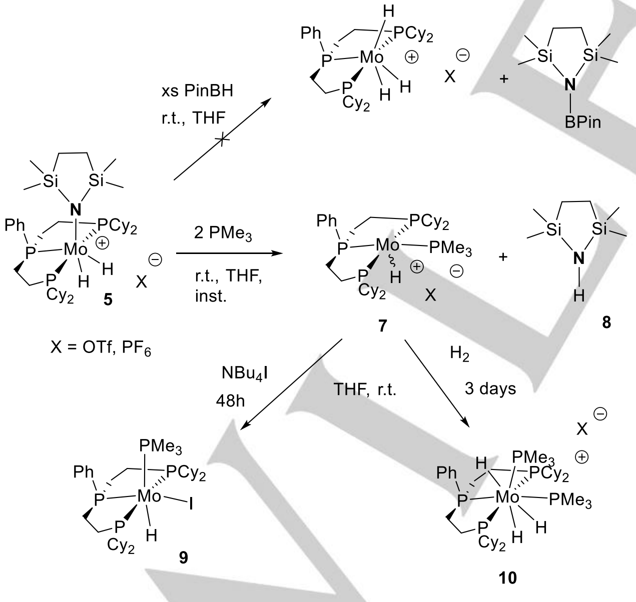
(PPP)Mo$^{(II)}$(H)$^{+}$ complex, which was rationalized by DFT calculations (*vide infra*).

In light of the facile second Si─H bond formation upon halide abstraction, the reactivity of the cationic nitrido complex toward the bis-silane **2** was envisaged. Abstraction of I^{-} from complex **1** with TlOTf proved also very facile and efficient. Indeed, a sharp color change from dark orange to dark green could be observed instantaneously. Isolation of complex **6-OTf** in 85% yield was achieved after filtration of the insoluble TlI salts and drying. Quite surprisingly, the chemical shifts in the ^{31}P{^{1}H} NMR spectrum are almost identical to those of complex **1**. The ^{19}F spectrum nonetheless proved the OTf moiety to be present in the complex. Reaction of **6-OTf** with one equivalent of the bis-silane **2** proved almost instantaneous, leading quantitatively by ^{31}P NMR to complex **5-OTf**. It is interesting to note that a solution of complex **5-OTf** put under vacuum evolves back to complex **6-OTf**, by evaporation of the low boiling point bis-silane **2**. This reactivity proves the reversible character of the double 1,2 Si─H bond addition across the Mo≡N bond.

Conditions to favor N─H bond formation *via* reductive elimination and thus liberation of the amine were then sought.

We have shown previously that an *in situ* generated (bis-boryl)amido-dihydride cationic complex does react at room temperature with PinBH to form a mixture of (BPin)$_3$N and (BPin)$_2$NH together with the (PP$_2$)Mo(H)$_3^{+}$ complex.[30] We thus hoped that complex **5-PF$_6$** would react with PinBH to form the corresponding boryl-(bis-silyl)amine, which was disapointingly not observed. However polymerization of THF was observed after several hours of reaction which we have previously observed when (PPP)Mo(H)$_3^{+}$ is formed.



Scheme 3. Reactivity of complex **5-X**

A distinct strategy was then envisioned relying on the addition of PMe$_3$, a small strongly donating 2e^{-} ligand in order to stabilize the coordinatively unsaturated (PPP)Mo^{II}-fragment resulting from the reductive elimination of the cyclic (bis-silyl)amine **8** from **5-X**. Pleasingly, upon addition of two equiv. of PMe$_3$ to a solution of complex **5-X** an instantaneous reaction was observed, indicated by a color change from purple to dark green. The ^{31}P{^{1}H} NMR spectrum of the crude mixture revealed the formation of a new complex, in addition to free PMe$_3$ and a very minor, unknown species (Fig S10, ESI). Integration of the signals as well as coupling pattern for complex **7-X** (AM$_2$X spin system) proved the coordination of a single PMe$_3$ to the cationic Mo center. Indeed, the ^{31}P{^{1}H} NMR spectrum showed a very characteristic set of multiplets at 111.0 ppm (d, $^{2}J_{P\text{-}P}$ = 61.0 Hz, P^{Ph}), 89.6 (d, $^{2}J_{P\text{-}P}$ = 18.8 Hz, P^{Cy2}), and ─7.3 (dt, $^{3}J_{P\text{-}P}$ = 18.4 Hz, 61.2 Hz, PMe$_3$). The ^{1}H NMR spectrum presents a highly coupled signal centered at ─7.1 ppm for a single hydride (Fig. 3 and ESI). Selective decoupling sequences with the three different P centers allowed isolation of the individual $^{2}J_{P\text{-}H}$ coupling constants (ddt, $J_{(H\text{-}PMe3)}$= 25.2 Hz, $J_{(H\text{-}PCy)}$= 56.1 Hz, $J_{(H\text{-}PPh)}$ = 40.3 Hz). The ^{29}Si{^{1}H} spectrum, recorded on the crude mixture revealed the formation of the known (bis-silyl)amine **8** which was quantified in *ca* 66% yield after extraction and hydrolysis to NH$_4^{+}$. Unfortunately, complex **7-X** has resisted crystallization to date, and several derivatization experiments were carried out to finally ascertain its formulation.

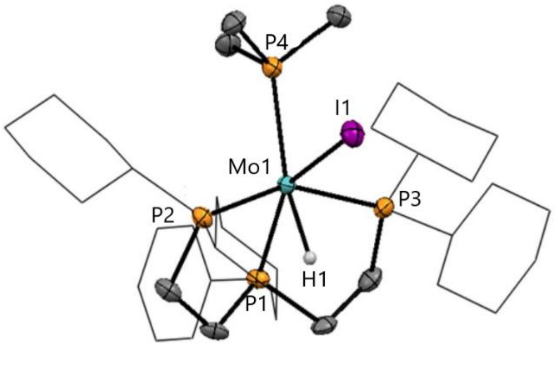


Figure 2. X-ray structure of complex **9**: 50% thermal ellipsoids are shown. Hydrogen atoms, except for the hydride, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1-P1 2.344(1), Mo1-P2 2.482(1), Mo1-P3 2.487(1), Mo1-P4 2.501(1), Mo1-I1 2.932(1), Mo1-H1 1.77(4); P1-Mo1-P2 81.5(1), P1-Mo1-P3 81.7(1), P2-Mo1-P3 150.9(1), P1-Mo1-P4 137.7(1), P2-Mo1-P4 104.1(1), P3-Mo1-P4 104.5(1), P1-Mo1-I1 144.3(1), P2-Mo1-I1 90.3(1), P3-Mo1-I1 89.7(1), P4-Mo1-I1 77.9(1), P1-Mo1-H1 63.0(13), P2-Mo1-H1 75.0(13), P3-Mo1-H1 76.2(13), P4-Mo1-H1 159.3(13), I1-Mo1-H1 81.3(13).

First, complex **7-X** was reacted with I^{-} sources (NaI, NBu$_4$I) in order to form the corresponding Mo$^{(II)}$ neutral complex. The reaction was surprisingly slow (*ca* 48h) and provided several complexes, likely isomers. Crystals were grown from the crude mixture, and X-ray diffraction analysis was carried out on complex **9**, which structure is presented in Figure 2. It is an isomer of a (PPP)Mo(H)(I)(PMe$_3$) complex reported by our group from the reaction between complex **1**, bis-silane **2** (excess) and PMe$_3$.[29]

In a second experiment, complex **7-X** was mixed with H$_2$ in the presence of PMe$_3$. ^{1}H and ^{31}P{^{1}H} NMR reaction monitoring indicated rather slow kinetics and *ca* 50% of the expected complex $[(PPP)Mo(H)_3(PMe_3)_2]^+$ **10** is formed after 12h. Nearly full conversion was achieved after 4 days at room temperature. Representative ^1H NMR spectra at different stages are presented in Figure 3.

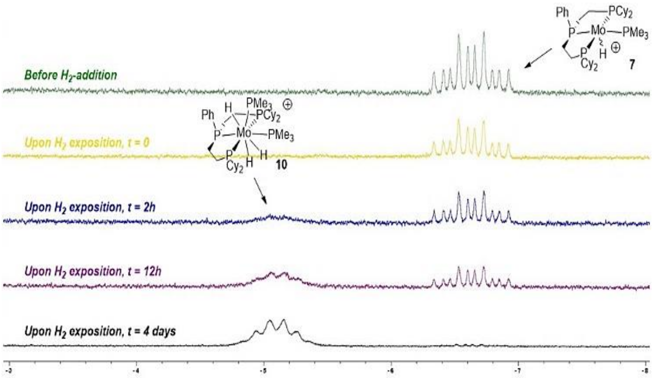
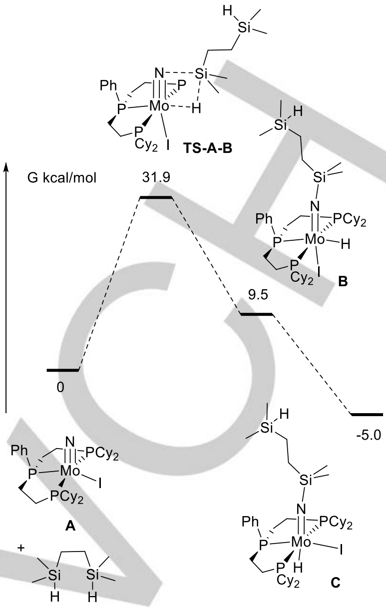


Figure 3. Hydride region of ^1H spectra of the reaction between complex **7-X**, PMe_3 and H_2 showing the formation of complex **10-X**.

To gain insight into the mechanisms of the various transformations observed experimentally, DFT(PBE0-D3) calculations were carried out on the actual experimental systems (see ESI for computational details; geometries of all the optimized structures are available in a single file in xyz format).

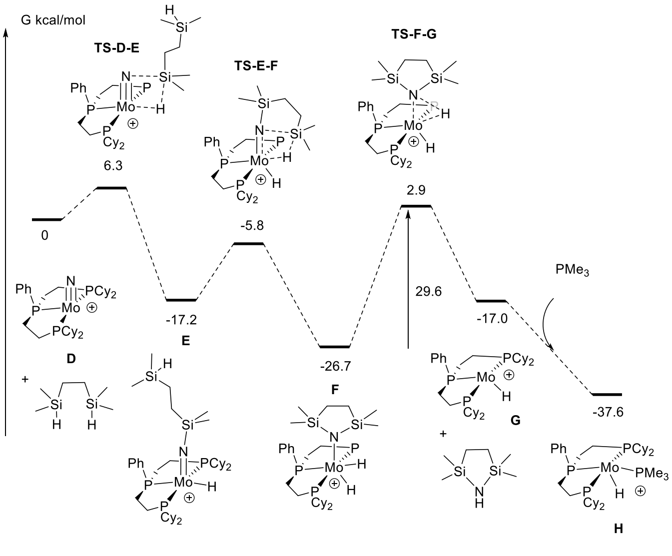
The reactivity of the $Mo^{(IV)}$ nitrido complex **A** with the bis-silane $HMe_2Si\text{-}(CH_2)_2\text{-}SiMe_2H$ was studied computationally (Scheme 4). The first Si─H bond activation is effective through **TS-A-E** with an activation barrier of $\Delta G^{\#} = 31.9$ kcal mol^{-1} with respect to **A**. In **TS-A-B**, the Mo─N bond lengthens (1.685 Å) and the N$\cdots$Si distance (2.200 Å) is relatively long. Concomitantly the hydrogen atom significantly interacts with the metal (Mo$\cdots$H = 1.775 Å), while the Si─H bond has lengthened to 1.754 Å (1.502 Å in the free bis-silane). The Mo-imido hydride product **B** is computed to be less stable than **A** by $\Delta G = 9.5$ kcal mol^{-1} (N─Si = 1.764 Å, Mo─N = 1.740 Å, and Mo─H = 1.704 Å in **B**). The isomer **C**, where the respective positions of H and I have been swapped is computed to be significantly more stable than **B** by $\Delta G = -14.5$ kcal mol^{-1}. The relative energy of **A** and **C** (Scheme 4) is in perfect agreement with the experimental observations of the formation of **3** (Scheme 2). However, the computed activation barrier for the formation of **B** is too high for a transformation complete in 4 hours at room temperature under stoichiometric conditions. At present, we suspect the involvement of a second Si-H moiety to assist the Si-H addition across the Mo-nitride bond via a more accessible transition state, but have not yet found the corresponding pathway by calculations.



Scheme 4. Computed mechanism for the Si─H bond activation on the neutral $Mo^{(IV)}$ nitrido starting complex **1**. Gibbs free energies (kcal mol^{-1}) are given relative to "**A** + bis-silane". Most H atoms have been omitted for clarity.

Experimentally, abstraction of the iodide results in an increased reactivity of the $Mo^{(IV)}$ nitride complex (Scheme 2). Even though the formation of the cationic nitrido complex **D** is computed to be endoergic ($\Delta G = 19.6$ kcal mol^{-1} with respect to **A**), further precipitation of TlI will shift the equilibrium toward formation of **D**. This cationic complex activates much more easily the Si─H bond of the bis-silane with a computed activation barrier of $\Delta G^{\#} = 6.3$ kcal mol^{-1} for **TS-D-E** (Scheme 5). Inspection of selected geometrical parameters indicates that the TS is a late transition state compared to **TS-A-B** (Mo─N = 1.685 Å, Mo─H = 1.775 Å, N─Si = 2.200 Å, Si─H = 1.754 Å in **TS-A-B**; Mo─N = 1.661 Å, Mo─H = 1.745 Å, N─Si = 2.178 Å, Si─H = 1.947 Å in **TS-D-E**). The reaction is strongly exoergic with $\Delta G = -17.2$ kcal mol^{-1}, whereas it was endoergic in the neutral case with iodide still coordinated to Mo. From this mono-activation intermediate, the second Si─H bond activation process is effective through **TS-E-F** with an activation barrier of only $\Delta G^{\#} = 11.4$ kcal mol^{-1}. The formation of the cationic amido-dihydride **F** is computed to be exoergic with $\Delta G = -9.5$ kcal mol^{-1} from **E**.

The calculations are in perfect agreement with the experimental observations (Scheme 2). Abstraction of the iodide in **1** to form **6⁺** opens up a pathway for very fast activation of the two Si─H bonds in the bis-silane to form the dihydride **5⁺**. Iodide abstraction in **3** also leads to easy Si─H bond activation to form the dihydride **5⁺**. In addition the transition state **TS-F-G** associated with the N─H bond formation step delivering the (bis-silyl)amine product **8** was located on the potential energy surface (Scheme 4). The activation barrier of $\Delta G^{\#} = 29.6$ kcal mol^{-1} to form complex **G** is not only high but more importantly this transformation is computed to be endergonic by $\Delta G = 9.7$ kcal mol^{-1}. It is therefore in agreement with experimental results, which show that complex **5-X** is the only observed complex.

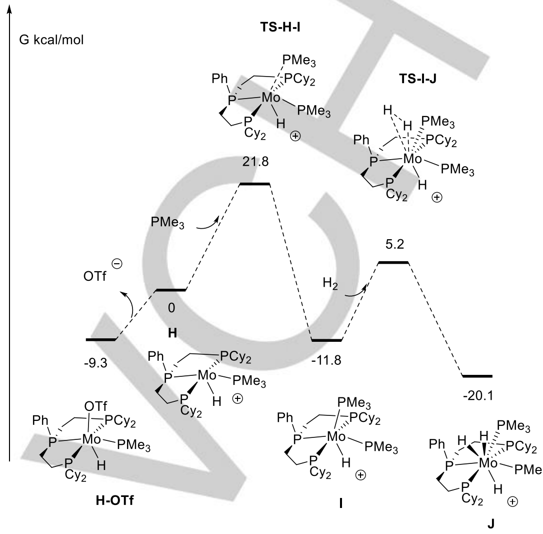


Scheme 5. Computed mechanism for the Si-H bond activations on the cationic $Mo^{(IV)}$ nitride complex. Gibbs free energies (kcal mol^{-1}) are given relative to “**D** + bissilane”. Most H atoms have been omitted for clarity.

The reactivity of complex **5-X** with an additional PMe_3 was subsequently probed. Two cases were computed. First, coordination of PMe_3 on complex **F** resulted in an increased barrier for amine elimination (> 30 kcal mol^{-1}), and is therefore not the path followed. Secondly, coordination of PMe_3 to **G** to form **H** is stabilizing with $\Delta G = -20.6$ kcal mol^{-1}, thus an overall 10.9 kcal mol^{-1} stabilization from complex **F**, which does explain amine formation upon addition of phosphine (Scheme 3), although the calculated overall barrier of 29.6 kcal mol^{-1} is high for a reaction occurring at room temperature.

Finally, the reactivity of complex **7-X** toward H_2 in the presence of PMe_3 was evaluated. Addition of PMe_3 on complex **H** is favorable by 11.8 kcal mol^{-1} to form complex **I**, and the transition state **TS-H-I** was located at $\Delta G^{\#} = 21.8$ kcal mol^{-1}. This is too low an activation barrier to be consistent with experimental observation (complex **7-X** is stable in the presence of additional phosphine). We therefore considered the influence of triflate on the stability of complexes **H** and **I**. Coordination of triflate trans to the H atom is evidenced in **H-OTf**, while complex I being saturated, **I-OTf** is optimized as an ion pair. The energy difference is now only 2.5 kcal/mol in favor of **I-OTf**, which indicates a 9.3 kcal/mol stabilization of unsaturated complex **H** by triflate coordination. Importantly, this translates into an additional energy cost to reach **TS-H-I** as OTf has to decoordinate prior to PMe_3 coordination. .

The transition state for H_2 addition to **I**, **TS-I-J**, was located on the potential energy surface at $\Delta G^{\#} = 17.0$ kcal mol^{-1} above **I**. The product of the H_2 oxidative addition, **J**, is computed to be more stable than **I** by $\Delta G = -9.3$ kcal mol^{-1}, and thus 20.1 kcal mol^{-1} lower than **H**. The computed results are qualitatively in agreement with the experimental observations for the transformation **7** → **10** (Scheme 3), and the calculated values indicate a strongly exoergic transformation with coordination of the second phosphine following OTf^- decoordination more energy demanding than H_2 oxidative addition.



Scheme 6. Computed mechanism for H_2 addition to complex **H** in the presence of PMe_3. Gibbs free energies (kcal mol^{-1}) are given relative to “**H** + PMe_3 + H_2”. Most H atoms have been omitted for clarity.

In conclusion, we have explored a new route of stepwise functionalization of a nitride complex to silylamine under mild conditions. We have shown that the liberation of a free coordination site on the imido complex **3** through halide abstraction facilates the second 1,2 addition of Si–H on the Mo–N bond, affording the stable cationic (bis-hydride)-amide complex **5-X**. Alternatively, complex **5-X** can be obtained directly from the reaction of the cationic nitride complex **6-X** and bis-silane **2**. This amido-bis-hydride complex is rather stable and reluctant to reductive elimination. However, the liberation of the silylamine was achieved at room temperature by addition of PMe_3. DFT calculations rationalizing our experimental findings are presented.

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CCDC-1966908 (4) and CCDC-1966909 (9) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Keywords: N_2 reduction • Molybdenum • bis-silane • nitride functionalization • hydride ligands

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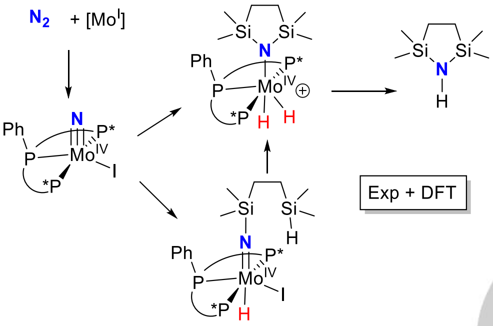
Article

A Mo-Nitride complex is functionalized by a bis-silane to form the Mo-imide-hydride complex then the corresponding Mo-amide-bishydride complex en route to the silylamine derivative. DFT calculations supporting the experimental findings are presented.



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Stepwise Functionalization of N_2 at Mo: Nitrido to Imido to Amido. Factors Favoring Amine Elimination from the Amido Complex.