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# Closing the Loop on Transition-Metal-Mediated Nitrogen Fixation: Chemoselective Production of $HN(SiMe_3)_2$ from $N_2$, $Me_3SiCl$, and X—OH (X = R, $R_3Si$, or Silica Gel)

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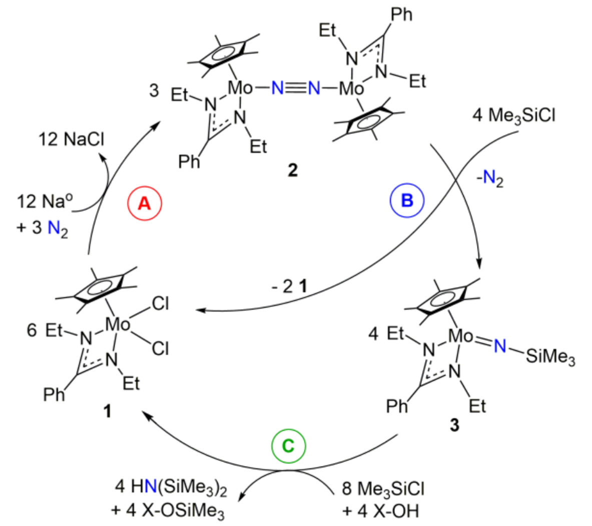
Supporting Information

**ABSTRACT:** Treatment of the Mo(IV) terminal imido complex, $(\eta^5\text{-}C_5Me_5)[N(Et)C(Ph)N(Et)]Mo(NSiMe_3)$ (**3**), with a 1:2 mixture of iPrOH and $Me_3SiCl$ resulted in the rapid formation of the Mo(IV) dichloride, $(\eta^5\text{-}C_5Me_5)[N(Et)C(Ph)N(Et)]MoCl_2$ (**1**), and the generation of 1 equiv each of $HN(SiMe_3)_2$ and $iPrOSiMe_3$. Similarly, a 1:2 mixture of $Me_3SiOH$ and $Me_3SiCl$ provided **1**, $HN(SiMe_3)_2$, and $O(SiMe_3)_2$. Finally, silica gel, when coupled with excess equivalents of $Me_3SiCl$, was also effectively used as the X—OH reagent for the generation of **1** and $HN(SiMe_3)_2$. A proposed mechanism for the **3** → **1** transformation involves formal addition of HCl across the Mo═N imido bond through initial hydrogen-bonding between X—OH and the N-atom of **3** to form the adduct **IIIb**, followed by chloride delivery from $Me_3SiCl$ to the metal center via a six-membered transition state (**IV**) that leads to the intermediate, $(\eta^5\text{-}C_5Me_5)[N(Et)C(Ph)N(Et)]Mo(Cl)(NHSiMe_3)$ (**V**), and $XOSiMe_3$ as a co-product. Metathetical exchange of the new Mo−N amido bond of **V** by a second equivalent of $Me_3SiCl$ then generates **1** and $HN(SiMe_3)$. These results serve to complete a highly efficient chemical cycle for nitrogen fixation that is mediated by a set of well-characterized transition-metal complexes.

The development of transition-metal-mediated catalytic processes that can convert abundant dinitrogen ($N_2$) into ammonia ($NH_3$), or other nitrogen-containing materials, through a sequence of steps involving N≡N bond cleavage, N-atom functionalization, and N-product-forming reactions remains a scientific "grand challenge" of significant importance to society.[1−3] A further desirable outcome for such synthetic nitrogen fixation schemes is that they proceed with high chemical efficiency and atom economy, and under relatively mild conditions, so as to minimize overall energy requirements and chemical waste.[2] In recent years, several significant advances have been made toward achieving these goals.[3] However, there still remains ample space for the development of alternative strategies for achieving nitrogen fixation that proceed through a mechanistically sound (catalytic) chemical cycle that is based on structurally well characterized transition-metal complexes. Herein, we now report the highly efficient nitrogen fixation cycle of Scheme 1 that *chemoselectively* converts $N_2$, chlorotrimethylsilane ($Me_3SiCl$), and a proton source, such as an alcohol (ROH), a triorganosilanol ($R_3SiOH$), or even partially dehydrated silica gel ($SiO_2$), into hexamethyldisilazane [$HN(SiMe_3)_2$].[4,5] As shown, the favorable features of this new cycle include (a) only three steps (steps **A**–**C**) and three intermediates (**1**–**3**) that collectively constitute a *formal* overall Mo(II)/Mo(IV) redox process, (b) a single metal-centered chemical reduction (step **A**), (c) a thermally promoted N≡N bond cleavage (step **B**), and (d) the use of innocuous chemical reagents for N-atom functionalization (steps **B** and **C**) that are chemically compatible with other intermediates in the cycle. Finally, in addition to all of the byproducts from the three steps of Scheme 1 being readily recyclable, the final product, $HN(SiMe_3)_2$, can be either converted to ammonium chloride ($H_4NCl$), with additional recycle of $Me_3SiCl$ upon acidolysis with hydrochloric acid (HCl), or employed directly as a useful chemical reagent.[4]

**Scheme 1**



We have previously reported the chemistry for steps **A** and **B** of Scheme 1 that proceed through mechanistically well-established intermediates and pathways.[6−8] To recap briefly, in **A**, chemical reduction of the cyclopentadienyl amidinate (CPAM) Mo(IV) dichloride complex, $Cp^*[N(Et)C(Ph)N(Et)]MoCl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**), with sodium amalgam

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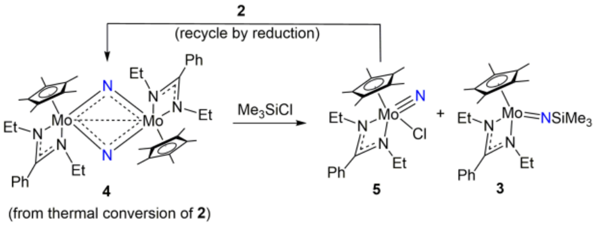
(NaHg) in tetrahydrofuran (THF), from −30 to 25 °C under an atmosphere of $N_2$, produces a high yield of the formal [Mo(II),Mo(II)] dinuclear "end-on-bridged" $\mu$-$N_2$ complex, {Cp*[N(Et)C(Ph)N(Et)]Mo}$_2$($\mu$-$\eta^1$:$\eta^1$-$N_2$) (**2**).[6,8] In **B**, addition of excess equivalents of $Me_3SiCl$ to a solution of **2** in toluene at 60 °C for 18 h directly provides 4 equiv of the CPAM Mo(IV) terminal imido derivative, Cp*[N(Et)C(Ph)-N(Et)]Mo(NSiMe$_3$) (**3**), *along with regeneration of 2 equiv of* ***1*** (see Scheme 1).[7,8] As clarified in Scheme 2, after quantitative thermal conversion of **2** into the formal [Mo(V),Mo(V)] dinuclear bis($\mu$-nitrido complex, {Cp*[N(Et)C(Ph)N(Et)]Mo-($\mu$-N)}$_2$ (**4**), the observed stoichiometry of step **B** arises from the critical role played by 1 equiv of **2** as a sacrificial reductant that is necessary for converting the intermediate Mo(VI) nitrido chloride co-product, Cp*[N(Et)C(Ph)N(Et)]Mo(N)-Cl (**5**), back into **4** for eventual complete conversion to **3** and **1**.[8]

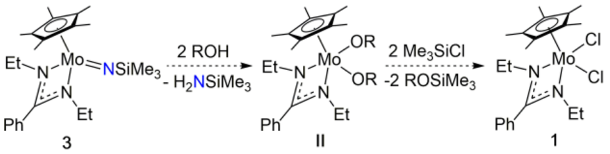
**Scheme 2**



In order to close the loop in Scheme 1 for a complete nitrogen fixation cycle, a step **C** was required that could convert **3** directly back into **1** while maintaining the Mo(IV) metal oxidation state that is common to both. A previously reported solution to this problem involved simultaneous nitrene group transfer (NGT) and oxygen atom transfer (OAT) between a structural analogue of **3** and carbon dioxide ($CO_2$) in the presence of excess equivalents of $Me_3SiCl$ at elevated temperature and pressure to effect the formal transformation: [CPAM]Mo═NSiMe$_3$ + $CO_2$ + 2 $Me_3SiCl$ → [CPAM]MoCl$_2$ + $Me_3SiNCO$ + O(SiMe$_3$)$_2$.[7] In addition to requiring exceedingly long reaction times, a significant disadvantage of this strategy is that the class of CPAM group 6 dinuclear ($\mu$-$\eta^1$:$\eta^1$-$N_2$) complexes to which **2** belongs also undergoes OAT with $CO_2$,[9] thereby negating the ability to achieve chemical compatibility within a complete nitrogen fixation cycle. In considering other alternatives that are based on existing precedents,[10−13] treatment of **3** with anhydrous HCl would seem to provide the most straightforward way in which to regenerate **1** while also producing 1 equiv of $H_4NCl$ and $Me_3SiCl$ through acidolysis of the initially formed trimethylsilylamine ($H_2NSiMe_3$).[11] Metathetical exchange of **3** with 1 equiv of $H_2O$ could also potentially serve to provide $H_2NSiMe_3$ and the Mo(IV) terminal oxo, Cp*[N(Et)C(Ph)N(Et)]Mo-(O) (**I**), which is a structural derivative for this class of complex that we have previously reported.[9,12] Subsequent treatment of **I** with 2 equiv of $Me_3SiCl$ should then provide a high yield of **1** along with coproduction of 1 equiv of hexamethyldisiloxane [O(SiMe$_3$)$_2$].[7] Unfortunately, in practice, **3** proved to be highly sensitive to even trace quantities of $H_2O$ in either nonpolar (benzene) or polar solvents (THF), leading to only a complex mixture of unidentifiable materials in each case. In addition, since neither HCl nor $H_2O$ is likely to be chemically compatible with other complexes involved in the nitrogen fixation cycle of Scheme 1, no further studies with these rather harsh hydrolytic reagents were pursued.

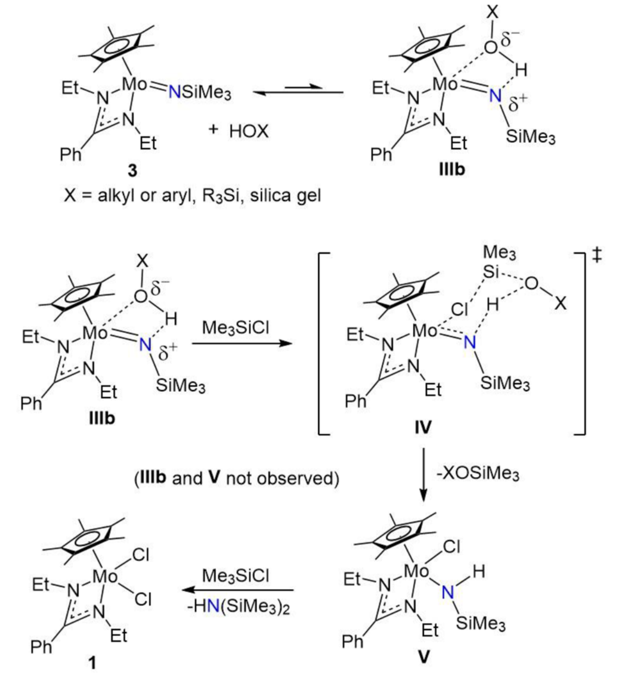
As an alternative means of converting **3** into **1** under more mild conditions, it was hypothesized that **3** might react with 2 equiv of an alcohol to form the Mo(IV) bisalkoxide intermediate, Cp*[N(Et)C(Ph)N(Et)]Mo(OR)$_2$ (**II**), along with $H_2NSiMe_3$.[13] Subsequent Mo−O bond metathesis with 2 equiv of $Me_3SiCl$ should then yield **1** and 2 equiv of a trimethylsilylether ($Me_3SiOR$) according to Scheme 3. In an effort to experimentally realize this goal, however, it was discovered that, unlike the case with $H_2O$, no *apparent* reaction (*vide infra*) occurred between **3** and excess equivalents of isopropanol (iPrOH) in benzene-$d_6$ solution after extended periods of time as monitored by $^1H$ NMR spectroscopy.[14] An attempt to drive formation of a Mo(IV) bisalkoxide product through chelation control using **3** in combination with pinacol (2,3-dimethyl-2,3-butanediol) also failed to elicit any apparent reaction.[13a,c] Finally, since triorganosilanols ($R_3SiOH$) are more acidic than alcohols,[15] excess equivalents of a commercial source of nearly pure $Me_3SiOH$ was added to a benzene-$d_6$ solution of **3**, but as before, no apparent reaction involving **3** occurred. On the other hand, addition of 2 equiv of phenol (PhOH) to a solution of **3** in benzene-$d_6$ rapidly produced a complex mixture of unidentifiable products, thus suggesting that an *acidity wall* for uncontrolled reactions of **3** with protic reagents does likely exist.

**Scheme 3**



Although no evidence for formation of the desired target **II** was obtained, variable temperature (VT) $^1H$ NMR spectra were successful in revealing the existence of a rapid dynamic process between **3** and iPrOH that presumably involves reversible formation of a 1:1 adduct (**III**).[14] Similar observations were made when iPrOH was substituted by *tert*-butanol (tBuOH) and $Me_3SiOH$, and qualitatively, the relative steric bulk of these protic reagents did not seem to have a major impact on the nature of this solution equilibrium. Accordingly, given (1) the lack of precedent for either the forward addition of RO—H across the M═N bond of a metal imido or for the formal reverse reaction, (2) the anticipated sensitivity of both of these processes to the steric and electronic features of the R group, and (3) the expected stability of a new Mo−O bond once formed, these collective observations strongly suggest that the identity of **III** is not the formal CPAM-Mo(IV) alkoxy amido complex, Cp*[N(Et)C(Ph)N(Et)]Mo(OR)(NHSiMe$_3$) (**IIIa**), but rather that of the resonance hybrid shown in Scheme 4 that exists along a continuum between **IIIa** at one end of the spectrum and a 1:1 adduct **IIIb** at the other end, in which the N-atom of the imido group of **3** serves as a hydrogen-bond acceptor. Using standard NMR methods,[16] the equilibrium constant, $K_{eq}$, for **3** and iPrOH (100 mM of each in toluene-$d_8$) forming **IIIb** (R = iPr), was determined to be 0.68 at 273 K, and this value establishes a concentration of **IIIb** of 6 mM under these solution conditions; in other words, 6% of **3** and iPrOH exist in the form of **IIIb** at equilibrium.

**Scheme 4**



Since **IIIb** has a finite concentration in solution, it was reasoned that this "activated" complex could potentially be chemically trapped upon addition of $Me_3SiCl$.[17] Gratifyingly, this hypothesis not only proved to be correct, but it provided an unexpected fortuitous result. Namely, upon addition of >2 equiv of $Me_3SiCl$ to a benzene-$d_6$ solution containing **3** and 1 equiv of iPrOH at ambient temperature, a near instantaneous and quantitative formation of **1** occurred along with 1 equiv each of $HN(SiMe_3)_2$ and $iPrOSiMe_3$, the identities of which were confirmed by gas chromatography/mass spectrometry (GC/MS) analysis.[14] Importantly, this chemistry not only now provides a highly efficient process by which to complete the chemical cycle of Scheme 1, but it establishes the first example of the chemoselective production of $HN(SiMe_3)_2$ through metal-mediated trimethylsilylation of $N_2$.[5] In terms of generality, both tBuOH and $Me_3SiOH$ are effective replacements for iPrOH, and the corresponding reactions with **3** and 2 equiv of $Me_3SiCl$ produce $tBuOSiMe_3$ and $O(SiMe_3)_2$, respectively, along with $HN(SiMe_3)_2$ and **1**. Quite surprisingly, even PhOH can now be used as the protic reagent in this reaction, and clean production of **1**, $HN(SiMe_3)_2$, and $PhOSiMe_3$ is observed.[14] For silanols, a variety of commercially available derivatives, $R_3SiOH$ (R = Me, Et, and Ph), could be used, and in these cases, the respective hexaorganodisiloxanes ($Me_3SiOSiR_3$) were the only products formed along with **1** and $HN(SiMe_3)_2$. Finally, it was determined that the protic reagent requirement could also be satisfied by simply adding a small quantity of partially dehydrated silica gel to a benzene-$d_6$ solution containing **3** and an excess of $Me_3SiCl$. Stirring the resulting heterogeneous mixture at room temperature for a short period of time once again cleanly produced **1** in good yield along with $HN(SiMe_3)_2$.[14,18]

In terms of mechanism, control experiments established that **3** is inert to excess equivalents of $Me_3SiCl$ in benzene-$d_6$ at elevated temperatures for extended periods of time. Further, under strictly anhydrous conditions, a 1:2 mixture of iPrOH and $Me_3SiCl$ in benzene-$d_6$ solution only very slowly produced $iPrOSiMe_3$ at ambient temperature as monitored by NMR spectroscopy, and a similar mixture of tBuOH and $Me_3SiCl$ in benzene-$d_6$ reacted even more slowly over the same period of time to form a trace amount of $tBuOSiMe_3$. However, to rule out the possibility that an adventitious amount of HCl from these silylation reactions might be catalyzing the conversion of **3** to **1**, an additional control experiment was performed in which a 1:2 mixture of iPrOH and $Me_3SiCl$ was added to a solution of **3** containing 0.1 equiv of 1,8-bis(dimethylamino)-naphthalene (also known as "proton sponge") in benzene-$d_6$ at room temperature.[14] Once again, however, rapid and quantitative formation of **1**, $HN(SiMe_3)_2$, and $iPrOSiMe_3$ occurred.[14] Finally, when a 1:1 mixture of tBuOH and $Me_3SiCl$ was added to a solution of **3**, the nature of the products remained the same, but now only 50% conversion of **3** was observed.

The above results are consistent with the mechanism presented in Scheme 4 in which a formal equivalent of "H—Cl" is added across the Mo═N imido bond through a six-membered ring transition state (**IV**) in which the X—OH (X = R, $R_3Si$, and $SiO_2$) protic reagent is activated through prior formation of **IIIb**. This proposal further accommodates the apparent lack of sensitivity of the process to the steric size of the XOH component since it avoids formation of a Mo−OX bonded intermediate. Further, although unique for metal imido chemistry, precedent does exist for a similar mechanism involving intramolecular hydrogen-bonding assisted trimethylsilylation of alcohols with $Me_3SiCl$.[19] Finally, as shown in Scheme 4, after formation of the CPAM Mo(IV) amido, chloride intermediate, Cp*[N(Et)C(Ph)N(Et)]Mo(Cl)-($NHSiMe_3$) (**V**), rapid metathetical exchange with a second equivalent of $Me_3SiCl$ serves to generate **1** while releasing $HN(SiMe_3)_2$.

Scheme 1 now represents perhaps the shortest chemical cycle yet reported for nitrogen fixation that is mediated by a set of well-characterized transition metal complexes.[3] The simplicity of each of the three steps, along with a verified chemical compatibility of complexes **1** and **2** to a mixture of $Me_3SiCl$ and iPrOH (or tBuOH) for extended periods of time,[14] bodes well for the eventual development of a catalytic cycle based on this chemistry. Indeed, we are currently exploring alternatives to NaHg for step **A** that can drive this cycle forward through the chemical or electrochemical reductive conversion of **1** to **2** that occurs in the presence of $R_3SiCl$ and XOH reagents and under more environmentally benign conditions. The results of these efforts will be reported in due course.

## ■ ASSOCIATED CONTENT

### S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08859.

Supporting spectra and characterization data (PDF)

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### Notes

The authors declare no competing financial interest.

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(17) The N-atom of the metal imido group is known to be basic, but its ability to serve in the capacity of a hydrogen-bond acceptor is a subject that has not received previous attention.[10]

(18) As an extension of this observation, hydrocarbon or ether solutions of **1** containing excess equivalents of $Me_3SiCl$ can be passed through a silica gel chromatography column without experiencing loss of the Mo(IV) dichloride. In contrast, in the absence of $Me_3SiCl$, **1** adheres (reacts) strongly with silica gel.

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