

Steric Switching from Photochemical to Thermal Reaction Pathways for Enhanced Efficiency in Metal-Mediated Nitrogen Fixation

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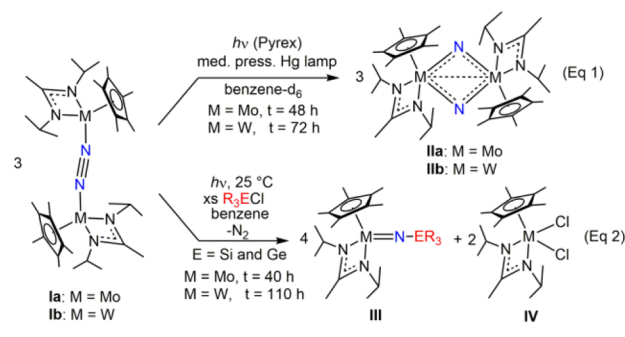
S Supporting Information

ABSTRACT: Programmed manipulation of the subtle interplay of nonbonded steric interactions within a supporting ligand environment has been used for the conversion of a photochemically driven chemical cycle for group 6 metal-mediated nitrogen fixation into a thermally promoted process with increased energy efficiency and atom economy for key transformations involving N≡N bond cleavage and N-atom functionalization of coordinated N₂.

The development of new industrial nitrogen fixation processes that can convert dinitrogen (N₂) into ammonia (NH₃), or other high-value N-containing products, with lower energy and environmental impact than the currently practiced century-old Haber–Bosch technology, remains a “holy grail” of scientific research.^{1–3} Central to the realization of this goal is the identification of new paradigms that can be used to cleave the strong N≡N bond of N₂ (BDE = 226 kcal/mol) in a manner that provides access to subsequent low-energy reaction pathways for N-atom functionalization and overall atom-economical substrate-to-product conversion within a catalytic cycle.⁴ Recently, we reported⁵ a *photochemically driven* chemical cycle for group 6 metal-mediated nitrogen fixation that converts N₂, carbon dioxide (CO₂), and trialkyl group 14 element chlorides, R₃ECl (E = Si and Ge), into the corresponding isocyanates, R₃EN=C=O, and dimetalloxanes, R₃E—O—ER₃, according to the overall stoichiometry N₂ + 2CO₂ + 6R₃ECl + 6Na → 2R₃ENCO + 2(R₃E)₂O + 6NaCl. Several key steps within this photochemical process, however, suffer from significant limitations that, in the absence of a solution, negatively impact the ultimate goal of translating it into a viable catalytic cycle. Herein, we report success in addressing many of these deficiencies through the programmed design development of an alternative *thermally driven* nitrogen fixation cycle that benefits from having significantly enhanced energy efficiency and atom economy for the primary transformations involving N≡N bond cleavage and N-atom functionalization of coordinated N₂. These results make an important contribution to the development of a set of “first principles” for the design, validation, and implementation of new dinuclear μ-N₂ complexes that can expand the scope of synthetic nitrogen fixation beyond NH₃.^{4,6}

The task of switching the underlying photochemically promoted reaction pathways for metal-mediated N≡N bond cleavage and N-atom functionalization within a nitrogen fixation cycle into more highly competitive, thermally promoted

Scheme 1



analogues represents an enormous challenge. Indeed, using the paradigm first established by Cummins et al.⁷ in 1995, only seven examples have ever been reported in which a structurally well-characterized dinuclear μ-N₂ complex has been unequivocally shown to engage in *chemically unassisted*⁸ N≡N bond cleavage through either thermal^{7,9,10} or photochemical^{5,11–14} reaction pathways to provide a discrete transition metal nitrido product.^{4,15} Quite surprisingly, for group 6 dinuclear μ-N₂ complexes undergoing thermally promoted N≡N bond cleavage, this number reduces further to the single original example set by the Cummins group with their now iconic {[ArN(C(CD₃)₂CH₃)₃Mo]₂(μ-η¹:η¹-N₂)} [Ar = 3,5-(Me₂)-C₆H_{3}] complex.⁷ Even here, the third-row tungsten congener has never been reported, despite a computational study that predicts a more favorable energy barrier for N≡N bond cleavage.¹⁶ A final consideration is that any significant change in the nature of the dinuclear μ-N₂ complex required to achieve thermal N≡N bond cleavage cannot have a deleterious impact on the ability to perform all subsequent chemical transformations that complete a chemical or catalytic nitrogen fixation cycle.}

Scheme 1 summarizes the limitations that existed with our previous photochemical nitrogen fixation process. To begin, the critical N≡N bond-cleaving step was originally achieved through photolysis of the *thermally stable* second- and third-row group 6 dinuclear “end-on-bridged” μ-η¹:η¹-N₂ complexes I¹⁷ into the corresponding dinuclear bis(μ-nitrido) complexes II according to eq 1 in Scheme 1. Although high-yielding, this process is unfortunately plagued by exceedingly slow rates of photolysis that greatly limit practicality for any scale-up considerations. As Scheme 1 further shows, in the presence of

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excess equivalents of R_3ECl , photolysis of **1** under otherwise identical conditions provides an excellent yield of the $M(IV)$ -terminal imido **III** along with the $M(IV)$ dichloride **IV** according to eq 2. However, similarly long photolysis times are now coupled with the requirement that one equivalent of **1** must serve as a sacrificial Cl-atom trap with release of N_2 . Thus, while **IV** can be recycled back to **1** through chemical reduction under an atmosphere of N_2 ,^{5,17} the reaction of eq 2 is hamstrung by both poor energy efficiency and atom economy. A final major issue is that the photochemical basis (mechanism) for eqs 1 and 2 is unknown.

Inspiration for a new design for securing a thermal equivalent of eq 1 came from structure–property relationships obtained for the growing family of structurally characterized, cyclopentadienyl amidinate (CPAM) early transition-metal dinuclear $\mu-N_2$ complexes with the general formula $\{(\eta^5-C_5R_5)[N(R^1)C(R^2)N(R^1)]M\}_2(\mu-N_2)$, which we have been developing over the past decade and which, inclusive of **1**, now encompasses derivatives where M = group 4 (Ti, Zr, Hf),^{17,18} group 5 (V, Nb, Ta),⁹ and group 6 (Mo, W) metals.^{5,17} More specifically, for M = Zr and Hf within CPAM group 4 dinuclear “side-on-bridged” $\mu-\eta^2:\eta^2-N_2$ complexes,¹⁸ the degree of $N\equiv N$ bond “activation” increases as the magnitude of steric interactions within the CPAM ligand environment decreases. Indeed, as typically evaluated on the basis of the crystallographically determined $N-N$ distance parameter, $d(NN)$, this degree of activation reaches a maximum for M = Hf, R = R^2 = Me, R^1 = Et, in which $d(NN)$ has the remarkable value of 1.635(3) Å. Moving on to second- and third-row CPAM group 5 dinuclear $\mu-N_2$ derivatives, the experimentally determined energy barrier height for thermally promoted $N\equiv N$ bond cleavage, which is proposed to proceed through an intramolecular $\mu-\eta^1:\eta^1-N_2 \rightarrow \mu-\eta^2:\eta^2-N_2$ rearrangement, was further observed to decrease as ligand nonbonded steric interactions decrease [for M = Ta, R = Me, R^1 = i Pr: $\Delta G_{\text{calc}}^\ddagger(338.15\text{ K}) = 26.6\text{ kcal/mol}$ (R^2 = Ph) $>$ 25.5 kcal/mol (R^2 = NMe_2) $>$ 24.3 kcal/mol (R^2 = Me)].^{9b} By extension of these correlations, we reasoned that the inability of **1** to engage in thermally promoted $N\equiv N$ bond cleavage might simply be due to too much steric crowding within the ligand sphere that prevents access to the required transition-state geometry. As a corollary, photolysis of **1** could then be serving to reduce the magnitude of steric interactions through a change in amidinate group ligation from κ^2 - to κ^1 -coordination.

To test our hypothesis, the series of new “sterically reduced” CPAM group 6 derivatives, $\{Cp^*[N(Et)C(Ph)N(Et)]M\}_2(\mu-\eta^1:\eta^1-N_2)$, where $Cp^* = \eta^5-C_5Me_5$, M = Mo (**1**) and W (**2**), were synthesized from the corresponding $M(IV)$ dichlorides, $Cp^*-[N(Et)C(Ph)N(Et)]MCl_2$ (**3** and **4**) (Scheme 2).¹⁹ The solid-state structures of **1** and **2** were obtained through single-crystal X-ray analyses, and, as exemplified by **1** shown in Figure 1a, both were found to adopt a $\mu-\eta^1:\eta^1-N_2$ geometry with $d(NN)$ values

Scheme 2

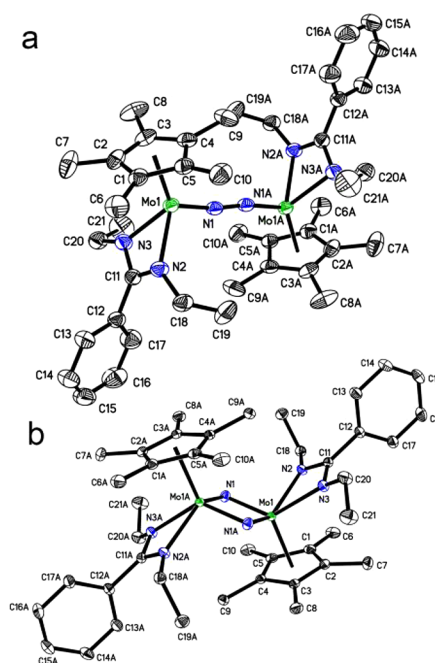
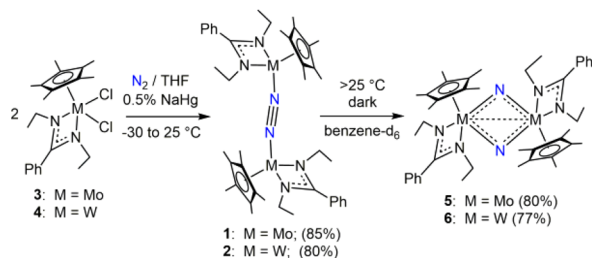


Figure 1. Molecular structures (30% thermal ellipsoids) of (a) **1** and (b) **5**. H-atoms have been removed for the sake of clarity.¹⁹

that are slightly longer than those previously reported for **1** [$d(NN) = 1.288(3)$ Å for **1** and 1.299(5) Å for **2**, vs 1.277(8) Å for **1b** and 1.267(2) Å for **1c** ($M = Mo$, $R = Me$, $R^1 = i$ Pr, $R^2 = NMe_2$)].^{17,19}

Gratifyingly, after an analytically pure sample of **1** was obtained, a series of 1H NMR (400 MHz, benzene- d_6 , 25 °C) spectra recorded over a period of several days at room temperature revealed the steady increase in intensity for 1H resonances of a single new species, **5**, at the expense of those of **1** (Figure 2a).¹⁹ Heating this NMR sample to 60 °C over a period of 70 h, in the dark, showed the eventual quantitative thermal conversion of **1** into **5**. Additional confirmation of the quantitative nature of this thermal conversion was provided by variable-temperature scanning UV/vis spectroscopy, in which a well-defined isosbestic point at $\lambda = 757\text{ nm}$ is observed for a series

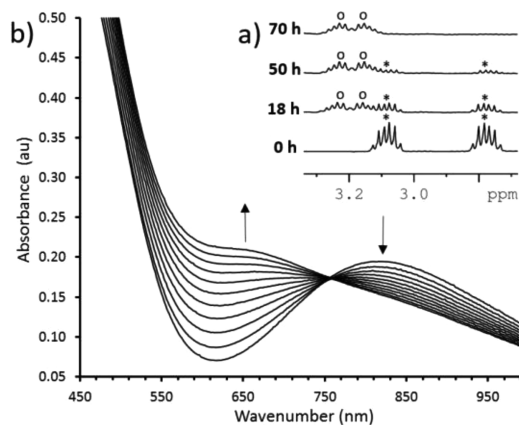


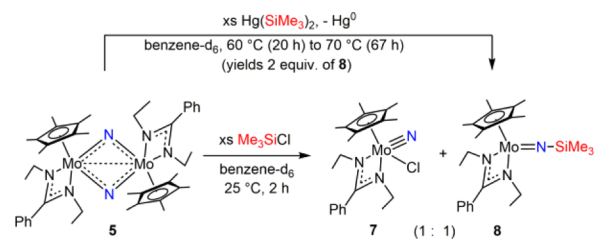
Figure 2. Thermal conversion of **1** \rightarrow **5**. (a) Partial 1H NMR (400 MHz, benzene- d_6) spectra recorded at 60 °C for different time intervals. The displayed 1H resonances are for the diastereotopic methylene (CH_2) protons of the N-ethyl substituents for (*) **1** and (O) **5**. (b) Partial display of a series of electronic spectra recorded by scanning UV/vis spectroscopy at 70 °C.¹⁹

of electronic spectra recorded at 70 °C (Figure 2b). Finally, and most importantly, performing thermolysis of **1** in toluene solution on a preparative scale provided an analytically pure crystalline sample of **5**, for which single-crystal X-ray analysis conclusively established the solid-state structure to be that of the dinuclear bis(μ -nitrido) complex, $\{\text{Cp}^*[\text{N}(\text{Et})\text{C}(\text{Ph})\text{N}(\text{Et})]\text{Mo}(\mu\text{-N})\}_2$ (Figure 1b).¹⁹ With respect to the structural parameters for **5**, the Mo_2N_2 core defines a planar four-membered ring with a pair of “long” and “short” Mo–N bonds for each formal M(V) metal center [$d(\text{Mo1}-\text{N1}) = 1.8917(12)$ Å and $d(\text{Mo1}-\text{N2}) = 1.9269(12)$ Å]. In contrast, the reported structure of **IIa** displays a nonplanar four-membered ring with Mo–N bonds paired into a “short” set for one metal center [$d(\text{Mo}_1\text{N}) = 1.8495(13)$ Å] and a “long” set for the other [$d(\text{Mo}_2\text{N}) = 1.9636(13)$ Å].⁵ The $d(\text{MoMo})$ distance is also slightly shorter in **5** vs **IIa** (2.6480(3) and 2.6764(3) Å, respectively). Finally, the physical difference between these two homologues, **5** and **IIa**, continues in the solution state, where the former exhibits diamagnetic character by NMR spectroscopy and the ¹H NMR resonances for the latter experience strong paramagnetic shifting. Additional studies to elucidate the ground-state electronic structure for the parent system of **5** and **II** are now in progress.

As Scheme 2 further reveals, the group 6 third-row congener **2** was also observed to cleanly convert at 60 °C in solution to the crystalline ditungsten bis(μ -nitrido) **6**, which was isolated and structurally characterized by single-crystal X-ray analysis (see Supporting Information). In this respect, only very slight differences exist between the geometric parameters of **6** vs **IIb**, and both complexes display diamagnetic character in solution.⁵ Qualitatively, the rate of **2** → **6** is much slower than that of **1** → **5**, and this difference appears to originate with the shorter M–N_{amidinate} bonds observed for **2** relative to **1**^{19,20} and the steric sensitivity of the N₂-splitting process. Additional support for this conclusion is provided by comparative ¹H NMR Eyring analyses conducted from 60 to 80 °C (five points) in benzene-*d*₆ that yielded, for **1** → **5**, $\Delta H^\ddagger = 23.2$ kcal/mol, $\Delta S^\ddagger = -10.6$ cal/(mol·K), and $\Delta G_{\text{calc}}^\ddagger(338.15 \text{ K}) = 26.8$ kcal/mol, and for **2** → **6**, $\Delta H^\ddagger = 20.4$ kcal/mol, $\Delta S^\ddagger = -20.6$ cal/(mol·K), and $\Delta G_{\text{calc}}^\ddagger(338.15 \text{ K}) = 27.4$ kcal/mol. These results are significant in that they serve to establish **1** and **2** as the first isostructural pair of second- and third-row group 6 dinuclear $\mu\text{-N}_2$ complexes that are known to undergo thermally promoted N≡N bond cleavage and **2** as the first ditungsten derivative to do so.

With the principal goal of developing a thermal N≡N bond cleavage process based on **1** and **2** to replace the photochemical step that employed **I** achieved (see Scheme 1), it next became of paramount importance to determine if the dinuclear bis(μ -nitrido) products, **5** and **6**, could still engage in the necessary subsequent chemical steps for nitrogen fixation to proceed, and what, if any, might be the additional advantages of having this new thermal N₂-splitting process being part of an ultimate catalytic cycle. For preliminary inquiries regarding these questions, only chemistry involving the **1** → **5** transformation has been considered. To begin, despite the diamagnetic character of **5**, vis-à-vis **IIa**, the former complex fortunately behaves in similar fashion to the latter upon addition of an excess quantity of Me₃SiCl by rapidly and quantitatively producing a 1:1 mixture of the Mo(VI) nitrido chloride, Cp* $[\text{N}(\text{Et})\text{C}(\text{Ph})\text{N}(\text{Et})\text{Mo}(\text{N})\text{Cl}$ (**7**), and the Mo(IV)-terminal imido, Cp* $[\text{N}(\text{Et})\text{C}(\text{Ph})\text{N}(\text{Et})\text{Mo}(\text{NSiMe}_3)$ (**8**) (Scheme 3). The structural identity and nature of **7** and **8** were confirmed through single-crystal X-ray analyses, and both compounds were further prepared through

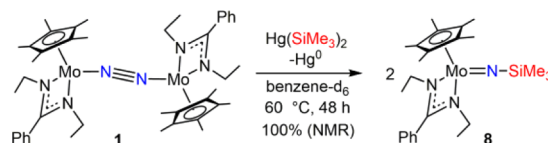
Scheme 3



alternative syntheses starting from **3**.¹⁹ As further shown in Scheme 3, reaction of **5** with a slight excess of bis(trimethylsilyl)mercury, $\text{Hg}(\text{SiMe}_3)_2$,²¹ at elevated temperature proceeded cleanly in benzene-*d*₆ to quantitatively produce 2 equiv of **8**, along with elemental mercury as the only co-product.¹⁹

With the ability to formally obtain **8** from **1** by going through isolated **5**, we were intrigued by the possibility of establishing a direct thermal **1** → **8** synthetic scheme in which **5** would now assume the role of a transient intermediate. Thus, as Scheme 4

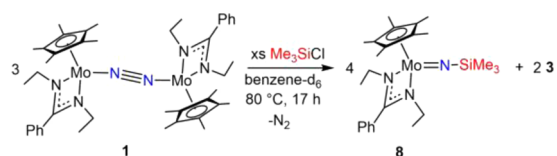
Scheme 4



reveals, simple thermolysis of **1** in benzene-*d*₆ solution at 60 °C in the presence of a slight excess of $\text{Hg}(\text{SiMe}_3)_2$ was now observed to provide a nearly quantitative yield of **8**, along with Hg^0 as the only co-product.¹⁹ Depending on the initial concentration of reactants, a small population of **5** does initially appear as an intermediate, but this diminishes as the conversion proceeds. It can also be noted that, qualitatively, the **1** → **8** conversion appears to occur faster and at lower temperature than the **5** → **8** transformation. Since it is possible that the two reaction schemes proceed through different mechanisms, more studies of the origin of this difference are warranted. Finally, it is significant that previous attempts to photochemically convert **I** using $\text{Hg}(\text{SiMe}_3)_2$ to the corresponding M(IV) imido complexes led only to a complex mixture of products due to uncontrolled photodecomposition of the latter reagent.

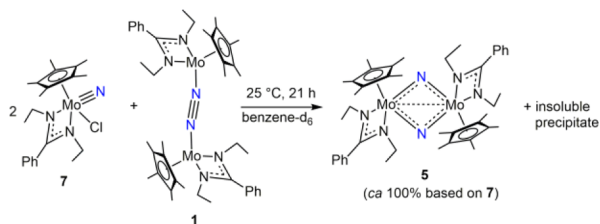
As a final consideration, it was of interest to determine if a thermal analogue for the photolytic “one-pot” N≡N bond cleavage/N-atom functionalization process of eq 2 in Scheme 1 using R₃ECl as a benign reagent could be developed.²² In practice, simply heating a solution of **1** in benzene-*d*₆ at 55 °C in the presence of excess equivalents of Me₃SiCl provided an excellent yield of **8**, as observed by ¹H NMR spectroscopy. When the reaction was conducted on a preparative scale in benzene-*d*₆ at 80 °C for 17 h, **8** and paramagnetic dichloride **3** were determined to be the only co-products, thereby suggesting the stoichiometry of Scheme 5, in which one equivalent of **1** must

Scheme 5



again be serving in a sacrificial capacity as a Cl-atom trap.¹⁹ Curiously, however, this thermal process proceeds with no NMR evidence for **5** as a transient intermediate, presumably due to this species reacting with Me₃SiCl as quickly as it is formed. On the other hand, if this were the case, one would also expect to see a steady buildup of mononuclear nitrido chloride **7** as a co-product (see Scheme 3). A solution to this conundrum was eventually found through determination that **1** formally functions as a chemical reductant that converts **7** back into **5** through Cl-atom abstraction, as verified by the results presented in Scheme 6.²³

Scheme 6



Surprisingly, however, when conducted in this fashion, the direct reaction of **1** and **7** did not provide ¹H NMR evidence for formation of paramagnetic **3**, and when it was performed on a larger preparative scale, production of **5** was accompanied by generation of an intractable, insoluble precipitate that presumably accounts for the missing chlorine. Importantly, the confirmed role of **1** as a formal reducing agent (via Cl-atom abstraction) complicates the task of elucidating the complete operative mechanisms of this and other nitrogen fixation schemes.

In summary, consideration of the ligand steric requirements for N₂ activation and N≡N bond cleavage by the family of early transition-metal CPAM dinuclear μ -N₂ complexes has led to the successful programmed development of new thermally promoted N≡N bond cleavage/N-functionalization processes for nitrogen fixation based on second- and third-row group 6 metal derivatives. The excellent versatility previously displayed by the CPAM ligand set further suggests that a number of new synthetic derivatives are likely accessible that can be used to fine-tune reaction energy barriers and the lifetimes of key intermediates that are necessary for the realization of competent and competitive nitrogen fixation catalytic processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b09789.

Experimental details and characterization data (PDF)

X-ray crystallographic data for **1**, **2**, **5**–**8** (CIF)

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Notes

The authors declare no competing financial interest.

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