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Conversion of Dinitrogen into Nitrile: Cross Metathesis of N₂-Derived Molybdenum Nitride with Alkynes

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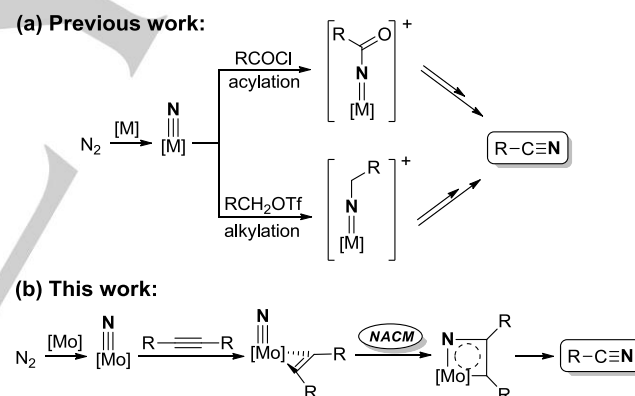
Supporting information for this article is given via a link at the end of the document.

Abstract: Direct synthesis of nitrile from N₂ under mild conditions is of great importance and has attracted much interest. Herein, we report a direct conversion of N₂ into nitrile via nitrile alkyne cross metathesis (NACM) process involving a N₂-derived Mo nitride. Treatment of the Mo nitride with alkyne in the presence of KOTf afforded an alkyne coordinated nitride, which was then transformed into Mo^(V) carbyne and corresponding nitrile upon 1e⁻ oxidation. Both aryl and alkyl substituted alkyne underwent this process smoothly. Experiments and DFT calculations have proved that the oxidation state of Mo center played a crucial role. This method does not rely on the nucleophilicity of the N₂-derived metal nitride, offering a novel strategy to the N₂ fixation chemistry.

Reduction of N₂ molecule under ambient condition has been a long-standing challenge in chemistry. During the past decades, many efforts were devoted to establish homogeneous metal complex systems that can catalyze N₂ reduction. Impressively, Mo, Fe, Co have been proved to be efficient catalytic system for NH₃ and N(TMS)₃ synthesis.^[1-3] Cr, Ti, Ru also showed some catalytic reactivity in these transformations very recently.^[4-6] Beyond that, direct transform N₂ molecule to value-added N-containing organic compound is even more challenging, and attracts much attention continuously.^[7] Nitriles, as fundamental organic compounds, have found many applications in organic chemistry and material science.^[8] Therefore, direct synthesis of nitrile derivatives from N₂ under mild condition is of great importance.

So far, few examples of transformation of N₂ into nitrile have been reported in the literature.^[9] In all cases, these transformations were initiated by the treatment of metal nitride with electrophiles. However, N₂-derived metal nitrides are typically poorly reactive, being poor nucleophiles.^[10] This property lead to harsh conditions for the functionalization of N₂-derived metal nitrides, relying on strong electrophiles such as acyl halide or alkyl triflate (Scheme 1). Moreover, subsequent transformation of the metal-imido complex into the desired nitrile required multistep processes. On the other hand, we have noticed that many molybdenum-nitrido complexes act as catalysts or intermediates in nitrile alkyne cross metathesis (NACM).^[11] If the N₂-derived metal nitrides were embedded in

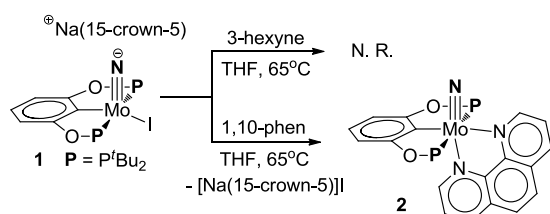
NACM, the synthesis of nitrile from N₂ could be envisioned. To the best of our knowledge, this process has never been reported. Herein, a direct transformation of N₂ into nitrile via an unprecedented metathesis involving N₂-derived Mo nitride is described, providing a novel strategy to the N₂ fixation chemistry.



Scheme 1. Strategies for nitrile synthesis through conversion of N₂-derived terminal metal nitrides.

Although it is widely reported that dinitrogen can be partially or completely cleaved when coordinated to polynuclear metal complexes^[12,13] or even boron compounds,^[14] examples of direct splitting N₂ into terminal metal nitride are remarkably scarce, and most of them rely on the use of Mo centers. In 1995, Cummins revealed the first homolytic cleavage of bridging N₂ on a Mo-trisamido complex.^[15] By using a heterodinuclear (Nb/Mo) system, a terminal Nb nitride was prepared from N₂ splitting.^[9d] Few years later, in 2012, Schrock reported the synthesis of (PCP)Mo-nitrido complex from N₂.^[16] A Re complex featuring a PNP ligand was also found to be able to homolytically cleave N₂ in 2014 by Schneider.^[17] Mézailles showed that the reduction of a Mo complexes with PPP pincer ligand under N₂ atmosphere in the presence of NaI led to the formation of a Mo^(IV) nitride.^[18] Shortly thereafter, Nishibayashi discovered a similar result on MoI₃ with PNP ligand.^[19] Recently, Schneider reported a direct

preparation of terminal Mo and W nitride by dinitrogen splitting coupled to ligand protonation.^[20] And very recently, Masuda has found a transformation of Mo(depe)₂ dinitrogen complex into terminal Mo nitride, induced by one-electron oxidation.^[21] Besides thermal N₂ cleavage, photochemical processes could also favor N₂ splitting to terminal nitride.^[22] Among the possible above mentioned candidates for our study, the anionic (PCP)Mo nitride (**1**) was selected and its reactivity towards alkyne was examined (Scheme 2). Indeed, we postulated that the complex being overall anionic, the iodide ligand would act as a good leaving group, allowing alkyne coordination under mild conditions. Disappointedly, when internal alkynes such as 3-hexyne were added, no reaction occurred even upon heating. Nevertheless, when 1,10-phenanthroline was added to (PCP)Mo^(IV)-nitrido iodide (**1**) Na(15-crown-5), a green compound was formed cleanly. This diamagnetic compound showed a singlet at 209.0 ppm in ³¹P{H} NMR, and could be crystallized from its concentrated diethyl ether solution. X-ray crystallography study revealed that this complex was a neutral Mo^(IV)-nitrido complex with a 1,10-phen ligand (Figure 1). Satisfyingly, the I⁻ anion no longer coordinated to the Mo center.



Scheme 2. Reactivity of complex **1** towards 3-hexyne and 1,10-phen.

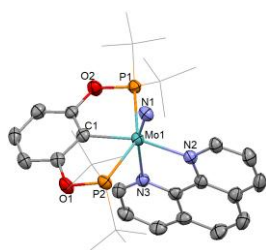
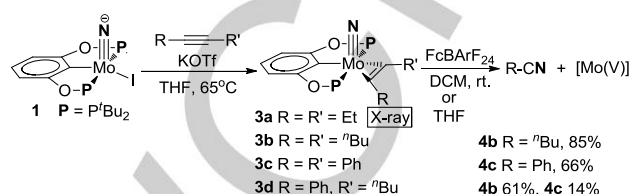


Figure 1. X-ray structure of complex **2**. Thermal ellipsoids shown at 50% probability, except for the carbon atoms of *tert*-butyl groups. Hydrogen atoms have been omitted for clarity. The CCDC number can be found in the Supporting Information.

Thus, a stronger driving force for I⁻ elimination than simple alkyne coordination had to be found. KOTf was therefore added to the mixture of (PCP)Mo(N)I⁻ (**1**) and 3-hexyne in THF (Scheme 3). To our delight, a very clean reaction happened, and a new diamagnetic complex (**3a**) with a singlet at 223.3 ppm in ³¹P{H} NMR was observed. In contrast, if only KOTf was added to (PCP)Mo(N)I⁻ (**1**), no such complex was observed by NMR. These results convinced us of the participation of the alkyne. When 5-decyne or diphenylacetylene was used in place of 3-hexyne, a similar result was obtained (complexes **3b** and **3c** resp.). While with 1-phenyl-1-hexyne, two doublets (217.4 and 221.8 ppm, ²J_{(P,P)} = 43.1 Hz) coupling with each other were observed in ³¹P{H} NMR, indicating that the P atoms became}

inequivalent in complex **3d**. After many attempts, complex **3a** was crystallized from a *n*-pentane solution. The X-ray structure analysis confirmed an alkyne coordinated Mo-nitrido complex (Figure 2, left), with the C≡C bond almost perpendicular to the Mo≡N bond (81.3°). The alkyne is located in the equatorial plane of the pseudo square pyramidal complex. These complexes do not lead to nitrile formation via metathesis even upon heating at 80°C for 36 h. This was rationalized by DFT calculations (*vide infra*).



Scheme 3. Cross metathesis of complex **1** with alkynes.

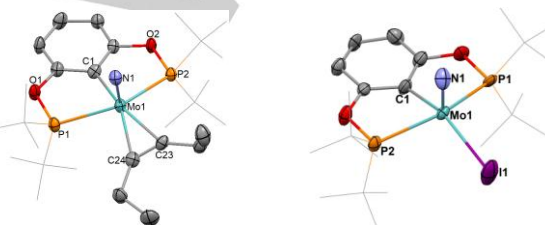


Figure 2. X-ray structure of complex **3a** (left) and **5** (right). Thermal ellipsoids shown at 50% probability, except for the carbon atoms of *tert*-butyl groups. Hydrogen atoms have been omitted for clarity. The CCDC number can be found in the Supporting Information.

It has been demonstrated that alkyne metathesis is catalyzed by high oxidation state carbyne complexes of Mo or W. The requirement for the process to occur is the intermediacy of a planar four membered ring.^[23] We thus anticipated that oxidation of the Mo^(IV) alkyne-nitrido complexes would favor the metathesis reaction, by allowing the coplanarity of the Mo≡N and C≡C bonds. Accordingly, when 1 eq. of [FcCp₂]⁺ was added to the 5-decyne coordinated Mo-nitrido complex (**3b**) at room temperature, *n*-pentanenitrile (**4b**) was detected and quantified by GC-MS analysis in 85% yield (compared to authentic sample). Similarly, diphenylacetylene also reacted smoothly in the same condition to give benzonitrile (**4c**) in 66% yield. When asymmetric internal alkyne such as 1-phenyl-1-hexyne was used, a mixture of *n*-pentanenitrile (61%) and benzonitrile (14%) was obtained (Scheme 3). At this point, the resulting paramagnetic Mo^(V) carbyne complexes could not be isolated in pure form, but mass spectra analyses proved their formation (see ESI). Furthermore, the reduction of the product mixture resulting from the Fc⁺ addition to complex **3b** gave two major compounds, one of which is **3b** again, and the other compound has two doublets in ³¹P{H} NMR (see ESI). These inequivalent phosphorus atoms strongly suggest a pseudo square pyramidal Mo^(IV)-carbyne with a nitrile coordinated in the equatorial plane, in which the C≡N bond is perpendicular to the Mo≡C bond (*vide infra*).

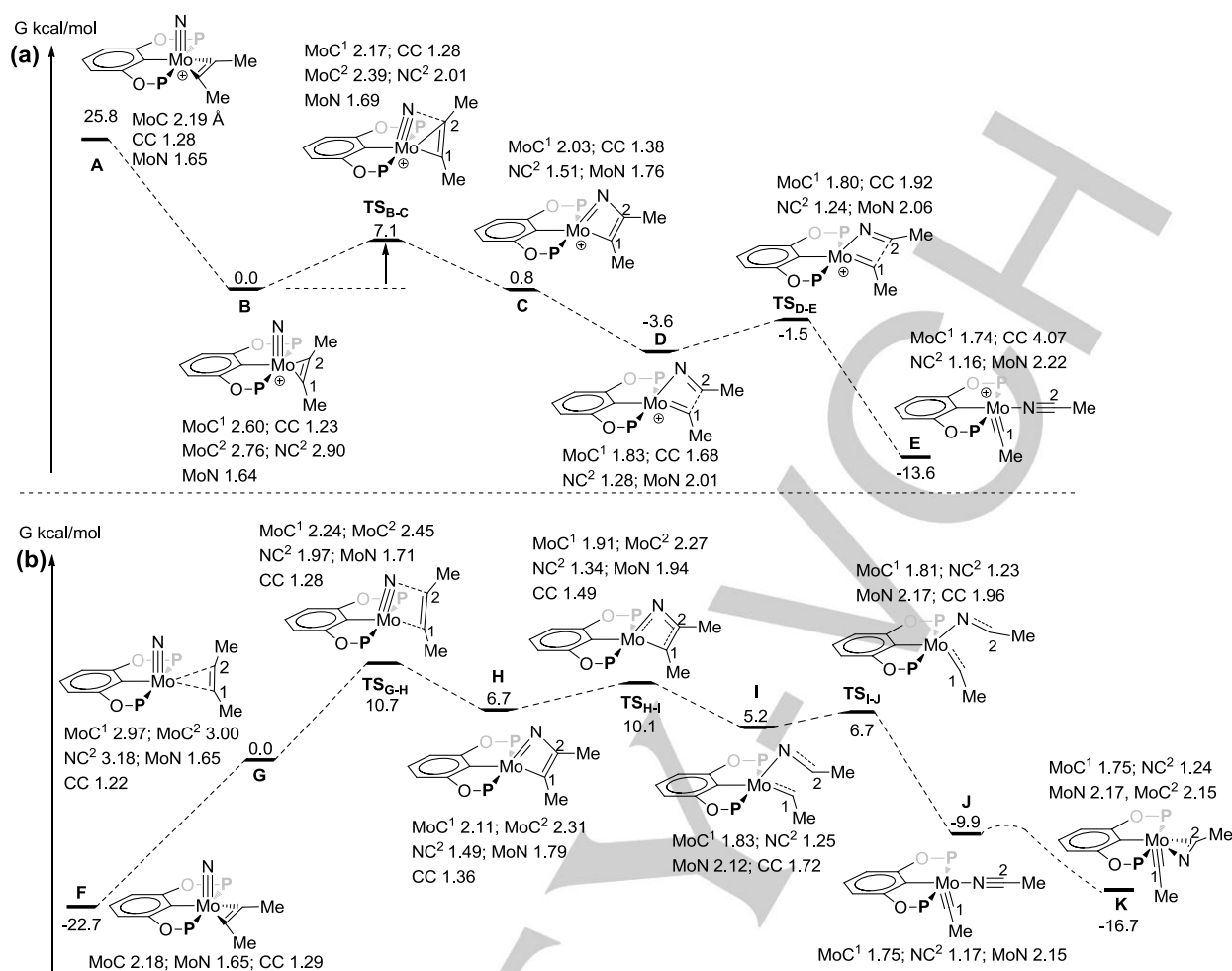
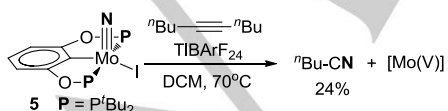


Figure 3. Energy profile of cross metathesis of Mo(V⁺) nitride (a) and Mo(IV) nitride (b) with alkyne.

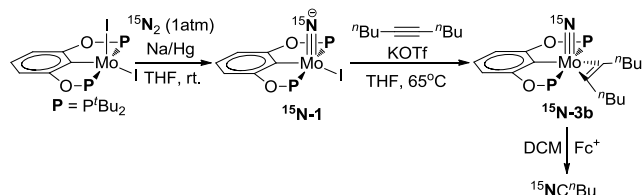
In order to further verify the participation of Mo(V) center, Mo(V)-nitrido complex, (PCP)Mo(N)I (**5**), was separately prepared by one-electron oxidation of (PCP)Mo(IV)(N)I⁻ (**1**). X-ray study of complex **5** (Figure 2, right) revealed a pseudo square pyramid geometry at Mo, similar to complex **1**. When TIBArF₂₄ and 5-decyne were added to complex **5**, *n*-pentanenitrile was quantified by GC-MS analysis in 24% yield (Scheme 4). Note that heating is needed to allow iodide abstraction by the Ti⁺ salt, which might be the reason for the poor yield of the nitrile. Nevertheless, this experiment confirmed the intermediacy of the N₂-derived Mo(V) nitride in the metathesis process.



Scheme 4. Cross metathesis of Mo(V) nitride (**5**) with 5-decyne.

For definitive proof of the origin of N-atom, ¹⁵N-labeling experiments were carried out. Mo(IV)-nitrido complex (¹⁵N-**1**) was prepared from ¹⁵N₂ and then treated with 5-decyne (Scheme 5). The corresponding ¹⁵N-labeled intermediate (¹⁵N-**3b**) exhibited a singlet at 832.1 ppm in ¹⁵N NMR and the final ¹⁵N-labeled nitrile

could also be observed by both ¹⁵N NMR (245.0 ppm) and GC-MS analysis (see ESI). These results unambiguously demonstrated that the N-atom in the nitrile indeed came from dinitrogen.



Scheme 5. Cross metathesis of ¹⁵N-labeled Mo(IV) nitride (¹⁵N-**1**) with 5-decyne.

DFT calculations were performed to provide insights into the mechanism of the metathesis as well as explain the differences in reactivity between the Mo(IV) and Mo(V⁺) nitrido complexes towards alkynes (see ESI for details). As a starting point, we took the X-ray structure of the neutral Mo(IV) alkyne complex, and performed the geometry optimization of the one electron oxidized Mo(V) cationic complex (Figure 3a). A local minimum was found, complex **A**, featuring the alkyne in the equatorial plane. Rotation of the alkyne led to strong stabilization and the

cationic complex **B** was found 25.8 kcal/mol lower than complex **A**. In this complex, the MoN and the alkyne moieties are nearly coplanar, adequately positioned for the [2+2] reaction. A transition state (**TS_{B-C}**) creating the N-C bond was accordingly found at 7.0 kcal/mol. In the TS the N-C distance is decreased to 2.01 Å (vs 2.90 Å in complex **B**) while the CC bond is slightly elongated at 1.28 Å (vs 1.23 Å in **B**). The transition state is then connected to a local minimum, complex **C** (at 0.8 kcal/mol), on the way to complex **D** (no TS localized between **C** and **D**) found at -3.6 kcal/mol (vs **B**). In complex **D**, although the aza metalacyclobutadiene structure is still apparent, the CC bond can be considered as broken (1.68 Å). In this complex the CN double bond is formed (1.28 Å), the MoN bond is now a single bond (2.01 Å vs 1.64 Å in complex **B**), while the MoC bond is short at 1.83 Å. A very low energy process then leads to the final complex featuring the carbyne moiety and the nitrile ligand. Indeed, the **TS_{D-E}** is found at -1.5 kcal/mol, a mere 2.1 kcal/mol higher than complex **D**, on the way to the final complex, **E**, found at -13.6 kcal/mol. In this complex, the nitrile ligand is found in the equatorial plane (*trans* to the strong aryl donor), while the carbyne ligand in an axial position, consistent with the *trans* effects of these ligands (weak and strong respectively). Overall, the C≡C and Mo≡N bonds breaking to form the Mo≡C and C≡N bonds is therefore exergonic by 13.6 kcal/mol, and the process is very facile with the highest TS at 7.1 kcal/mol.

The same process was computed from the Mo^(IV) alkyne complex. The PES is presented in the Figure 3b. The major results are as follows. As observed experimentally, complex **F** in which the alkyne is in the equatorial plane (*ca* perpendicular to the Mo≡N bond) is much more stable ($\Delta G = -22.7$ kcal/mol) than the one, complex **G**, in which the Mo≡N and alkyne are parallel. The final Mo^(IV)-carbyne-nitrile complex **K** is in this case higher in energy than the starting Mo^(IV)-nitrido-alkyne complex **F** ($\Delta G = +6.0$ kcal/mol) and the reaction is therefore endergonic, consistent with the lack of reactivity observed experimentally. Interestingly nonetheless, once the significant energy cost of rotating the alkyne is paid (22.7 kcal/mol), the [2+2] coupling process does not require much energy, with the highest TS to reach at only 10.7 kcal/mol. The DFT calculations thus rationalize that the one electron oxidation results in a strong destabilization of the alkyne-nitrido complex in which the alkyne is perpendicular to the Mo≡N fragment, thereby favoring the NACM process. They also rationalize experimental finding concerning reduction of Mo(V) nitrile-carbyne complex **E**. Indeed, complex **J** is initially generated, and evolves partly to complex **K**, featuring the nitrile η^2 coordinated and partly reverts back to nitride-alkyne complex **F**, since the highest TS is only 20.6 kcal/mol relative to complex **J**, thereby readily accessible at room temperature.

In conclusion, by the combination of N₂ splitting and NACM process, a direct synthesis of nitrile from dinitrogen under mild condition was achieved. This is a new strategy which does not rely on the nucleophilicity or basicity of the N₂-derived metal nitride. Both experiments and calculations have proved that the oxidation state of Mo center played a crucial role. The Mo^(V) nitride complex underwent metathesis efficiently whereas Mo^(IV) nitride only gave alkyne coordinated complex.

Acknowledgements

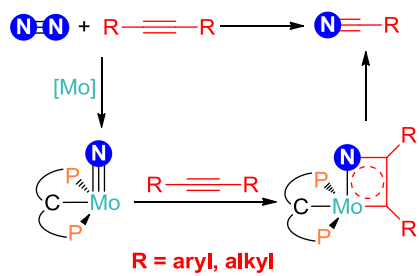
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Keywords: N₂ splitting, nitrile alkyne cross metathesis, molybdenum-nitrido complex, pincer ligand, nitrile synthesis

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Metathesis after split up: By the combination of N_2 splitting on Mo complex and sequent nitrile-alkyne-cross-metathesis process, a direct synthesis of nitrile from dinitrogen under mild condition was achieved. This provides a new strategy of functionalizing the N_2 -derived metal nitrido complex