Lewis acid activation of molybdenum nitrides for alkyne metathesis†

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The substantial kinetic barrier to molybdenum nitride–alkyne metathesis is facilitated by precomplexation of the borane Lewis acid $B(C_6F_5)_3$, providing convenient access to metathesis-active molybdenum alkylidynes. Spectroscopic and X-ray structural analysis suggest $Mo \equiv N$ bond weakening upon borane complexation.

Alkyne metathesis, once the underutilized cousin of olefin metathesis, has undergone a resurgence in the past ten years.¹ One major advance in this field has been the development of well-defined alkyne metathesis precatalysts based on molybdenum alkylidynes.² The preparation of Mo alkylidynes is not straightforward; highly air- and moisture-sensitive precursors and difficult multistep syntheses complicate facile preparation. The molybdenum nitrides, by contrast,³ are much easier to prepare from commercially-available precursors.⁴ In a seminal report, Gdula and Johnson reported that molybdenum nitrides could metathesize with aliphatic alkynes to generate the Mo-alkylidyne and an alkylnitrile irreversibly.⁵ The kinetic barrier for this reaction is high, as with many N-transfer reactions, and occurs slowly at elevated temperatures. Nevertheless, recently-reported precatalysts based on Mo-nitrides have demonstrated excellent activity for ring-closing metathesis of aliphatic alkynes.2b,4b

In this communication, we describe the activation of Mo-nitrides toward metathesis with alkynes *via* N-ligation of a Lewis acid. Activation of MoO_x precatalysts with oxophilic trialkylaluminiums for alkyne metathesis is well-known;⁶ however, the effects of Lewis acid addition to Mo-nitrides in alkyne metathesis have not been reported. The nitrogen atom in Mo-nitrides has sufficient nucleophilic character to display predictable reactivity with Brønsted acids,^{7a} Lewis acids,^{7b,c} and organic electrophiles.^{7d} We hypothesized that the typically high activation barrier to nitride–alkyne metathesis could be



Scheme 1 Promotion of molybdenum nitride–alkyne metathesis by precomplexation with borane.

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Scheme 2 Reactions of various Mo-nitrides with $B(C_6F_5)_3$.

overcome by precomplexation with a Lewis acid (Scheme 1), weakening the Mo \equiv N bond and making it more susceptible to metathesis. The borane B(C₆F₅)₃ was particularly attractive due to its strong Lewis acidity and relative inertness compared to other boranes.⁸

Our initial studies focused on pyridine complex 1, developed by Fürstner as a stable, convenient alkyne metathesis precatalyst and is now commercially available.^{4b} However, upon reaction of 1 with 1 equiv. $B(C_6F_5)_3$, we observed the formation of $B(C_6F_5)_3$.pyridine only (Scheme 2);⁹ 1-B was generated with 2 equiv. $B(C_6F_5)_3$. Catalytic amounts of 1-B reacted with 1-phenyl-1-butyne in toluene at 90 °C overnight to generate diphenylacetylene and 3-hexyne.

Encouraged by these results, we then turned our focus to Mo-nitride **2**, the precursor to **1**, which Fürstner reported to be active in alkyne metathesis upon *in situ* substitution with appropriate silanol ligands.^{4b} Reaction of **2** with $B(C_6F_5)_3$ in DCM solvent generated **2-B** in quantitative yield as a white solid. Crystals suitable for X-ray analysis were formed from slow diffusion of pentane into a DCM solution of **2-B** at $-30 \, ^\circ\text{C.‡}$ Analysis of the structure of **2-B** displayed some unusual attributes (Fig. 1a).^{10a} First, the Mo \equiv N bond length of 1.696(3) Å is elongated compared to terminal nitrido complexes of Mo.^{10b} Furthermore, the Mo–N–B bond angle is 159.3°, significantly distorted from the expected linearity. Neither **2** nor **2-B** were metathesis-active with 3-hexyne or 1-phenyl-1-butyne.

To directly compare the structural effects of Lewis acid addition to Mo-nitrides, the well-studied Mo-nitride 3^{11} was prepared and complexed with B(C₆F₅)₃ to generate **3-B** (Scheme 2). Crystals suitable for X-ray analysis were grown from slow diffusion of pentane into a DCM solution of **3** and B(C₆F₅)₃ (Fig. 1b).‡ The Mo \equiv N bond length in **3-B** (1.692(5) Å) is significantly longer (> 3σ) than in **3** (1.661(4) Å).^{11,12}

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[†] Electronic supplementary information (ESI) available: Synthesis procedures, compound characterization, crystal structures in CIF format for **2-B** and **3-B**. CCDC 788129 and 788130. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03113e



Fig. 1 Thermal ellipsoid plots (35% probability) of (a) 2-B and (b) 3-B. Hydrogens omitted for clarity.‡



Fig. 2 ATR-IR spectra of **3**, **3-B**, and $(C_6F_5)_3$. The reported (for **3**)¹¹ and proposed (for **3-B**) Mo \equiv N stretches are labelled.

Furthermore, a weakening of the Mo \equiv N bond is observed by IR (Fig. 2). This is in contrast to the Mo \equiv N bond length in MoN[(*t*-Bu)Ar]₃·BF₃, which does not deviate significantly from the free nitride.^{7b} As with **2**, neither **3** nor **3-B** were metathesis-active with 3-hexyne or 1-phenyl-1-butyne.

From these data, it became clear that a different strategy for nitride/alkyne metathesis was necessary, and the choice of ligand may be critical. We previously reported that the Mo-alkylidyne Mo(CEt)(Nt-BuAr)₃ in conjunction with an electron-poor phenol was extremely active toward alkyne metathesis.^{2a} With this in mind, we envisaged that Lewis acid complexation of Mo-nitrides, followed by ligand displacement with electron-poor phenols, may lead to enhanced rates of Mo-alkylidyne formation. Due to its ease of preparation, we decided on **2** as the Mo-nitride precursor of choice for use in catalytic reactions.

Reaction of 2 or 2-B in toluene with 3 equiv. 4-nitrophenol led to the precipitation of a red solid which was insoluble in non-coordinating solvents such as CCl_4 and toluene but very soluble in THF and MeCN. Attempts to metathesize this complex in any solvent were unsuccessful, possibly due to its insolubility in non-coordinating solvents and the known unreactivity of Mo-nitrides toward alkyne metathesis in coordinating solvents.⁵ The insoluble solid, as well as the adducts with coordinating solvents, resisted attempts at crystallization, both from solution and *via* sublimation. However, reaction of **2** and **2-B** with 3 equiv. 2-trifluoromethylphenol generated a complex soluble in non-coordinating solvents. Attempts to crystallize these complexes were unsuccessful.

The metathesis activity of **2** versus **2-B** with 2-trifluoromethylphenol was tested for the effect of borane addition. The results are summarized in Table 1. It is clear that the presence of borane accelerates metathesis with alkynes. Notably, metathesis of the diarylalkyne 4-methoxydiphenylacetylene (entries 5 and 6), which has not previously been reported to occur with Mo-nitrides, is rapid in the presence of $B(C_6F_5)_3$, establishing equilibrium at 90 °C *in 20 minutes*. By contrast, metathesis in the absence of borane led to less than 10% conversion after 12 h at 90 °C. Lewis acid activation of the nitride thus appears to be necessary to efficiently metathesize diarylalkynes.

Cross-metathesis of diphenylacetylene and 3-hexyne to generate 1-phenyl-1-butyne is also accelerated by the addition of borane (Table 1, entries 3 and 4). The reaction of 10 equiv. 3-hexyne with **2** or **2-B** and 2-trifluoromethylphenol at 90 $^{\circ}$ C

Table 1 Effect of borane addition on alkyne metathesis

$R_1 R_2$			2 (10 mol %) 2-(CF ₃)PhOH (30 mol %) B(C ₆ F ₅) ₃ (0-20 mol %) toluene, 90 °C		$R_1 R_3$	
Entry	R ₁	R ₂	R ₃	R ₄	Borane ^a	$\frac{-R_4}{\begin{array}{c} \text{Convn} \\ (\%) \ 1 \ h^b \end{array}}$
1 2 3 4 5 6	Ph Ph Ph Ph Ph Ph	Et Et Ph Ph 4-OMePh 4-OMePh	Ph Ph Et Et Ph Ph	Et Et Et 4-OMePh 4-OMePh	2-B 2 2-B 2 2-B 2	64 29 55 3 51 8
<i>a</i> 2-B w	/as ma	de <i>in situ</i> fr	om 10 r	nol% of 2 at	nd 20 mol%	$B(C_6F_5)_3.$

^b Percent conversion of starting material (R_1 - \equiv - R_2) by GC after 1 h.

led exclusively to alkyne polymerization and no alkylidyne was observed by ¹³C NMR.

In summary, the activation of Mo-nitrides with the Lewis acid $B(C_6F_5)_3$ significantly enhances the rate of metathesis of alkynes. The elongation of the Mo \equiv N bond upon complexation with borane has been directly established crystallographically and spectroscopically. Future work will elaborate on the mechanistic effects of Lewis acid addition on alkyne metathesis of Mo-nitrides.

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Notes and references

‡ Crystal data for **2-B**: C₃₀H₃₆BF₁₅MoN₂O₂Si₄, M = 960.70, monoclinic, space group $P2_1/n$, a = 14.367(5) Å, b = 17.170(6) Å, c = 16.896(6) Å, $\beta = 92.256(9)^\circ$, V = 4165(2) Å³, Z = 4, $D_c = 1.532$ g cm⁻³, μ (Mo-K) = 0.527 mm⁻¹, F(000) = 1936, T = 193 K. R_1 ($I > 2\sigma$) = 0.0541, wR₂ (all data) = 0.1559 for 7582 independent reflections with a goodness-of-fit of 1.032. Crystal data for **3-B**: C₃₀H₂₇BF₁₅MoNO₃, M = 841.27, orthorhombic, space group Fdd2, a = 21.3488(18) Å, b = 66.889(5) Å, c = 10.0299(10) Å, V = 14323(2) Å³, Z = 16, $D_c = 1.561$ g cm⁻³, μ (Mo-K) = 0.476 mm⁻¹, F(000) = 6720, T = 193 K. R_1 ($I > 2\sigma$) = 0.0472, wR₂ (all data) = 0.0866 for 6055 independent reflections with a goodness-of-fit of 0.962. Further information can be found in the ES1.†

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- 12 **3** undergoes a phase change in the solid state between $-90 \,^{\circ}C$ and $-160 \,^{\circ}C$. The Mo \equiv N bond length at $-90 \,^{\circ}C$ is 1.661(4) Å; at $-160 \,^{\circ}C$, the bond length is 1.673(5) Å. See ref. 11. Structural data for **3-B** was collected at $-80 \,^{\circ}C$.