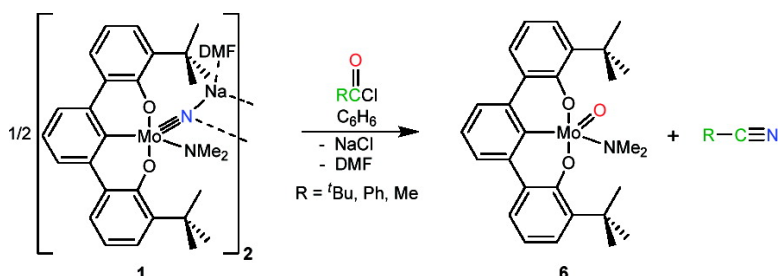Communication

Addition of Mild Electrophiles to a Mo#N Triple Bond and Nitrile Synthesis via Metal-Mediated N-Atom Transfer to Acid Chlorides

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Addition of Mild Electrophiles to a Mo≡N Triple Bond and Nitrile Synthesis via Metal-Mediated N-Atom Transfer to Acid Chlorides

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Transition metal-mediated N-atom transfer is an exceptionally difficult feat, owing in part to the strength of M−N triple bonds.[1] The nitride ligand, however, is not inert and can be synthetically incorporated into organic molecules.[2] The metal-mediated synthesis of nitriles, especially when the N-atom is derived from dinitrogen, is particularly challenging. Reduction of Cp_2TiCl_2 under N_2 followed by addition of ketones or acid chlorides provides amines and nitriles, respectively, but the identity of the Ti−N intermediate remains elusive.[3]

Cummins et al. established a well-defined system for benzonitrile extrusion via β-EPh (E = S, Se, and Te) elimination from [Ar(^{t}Bu)N]$_3$Mo–N≡CPh(EPh).[4] In addition, N-atom transfer to acid chlorides was accomplished via the four-coordinate tungsten nitride [Ar(^{i}Pr)N]$_3$W≡N (Ar = 3,5-$C_6H_3Me_2$).[5] Subsequently a complete cycle that, remarkably, incorporates dinitrogen into nitriles was reported for trisanilide niobium [Na][N≡Nb(N(Np)Ar)][6] and molybdenum [Ar(^{t}Bu)N]$_3$Mo≡N.[7]

Our approach to improve N-atom transfer reactions is to generate an isolable yet reactive nitrido fragment. Accordingly, we sought to marry the blueprint of stable group 6 nitrides with a constrained meridional tridentate ligand to create a nucleophilic M−N triple bond. To execute this plan we designed an OCO³⁻ pincer ligand (OCO³⁻ = [2,6-C_6H_3(6-$^tBuC_6H_3O)_2$]³⁻) to enable access to high oxidation state group 6 nitrides, to include alkoxide ligation, and to permit only meridional coordination by incorporating a rigid terphenyl backbone.[8] We now report the addition of mild electrophiles to the anionic terminal Mo-nitride {[^{t}BuOCO]Mo≡N(NMe₂)]Na(DMF)}₂ (1) and the synthesis of nitriles via metal-mediated N-atom transfer.
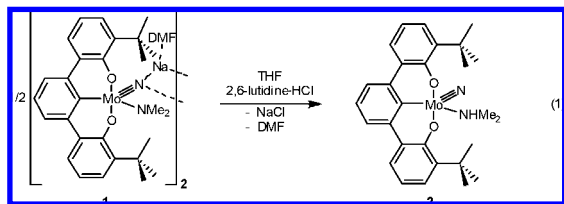
The terminal nitrido anion 1 was treated with 2,6-lutidinium·HCl to determine acid compatibility and protonation site. Upon addition of 2,6-lutidinium·HCl to 1, deep purple nitrido-amine [^{t}BuOCO]Mo≡N(NHMe₂) (2) forms within 15 min at 23 °C (eq 1). Analytically pure nitrido-amine 2 precipitates in 36% yield by dropping a concentrated THF solution of the reaction mixture into cold pentane. The ¹H NMR spectrum of 2 indicates the two diastereotopic amido-methyl resonances of 1 (4.10 and 2.60 ppm) collapsed to a doublet at 2.36 ppm (J = 6 Hz), which integrates as the six amine protons. The observation of a doublet confirms the addition ultimately occurs at the amido group of 1 to form dimethylamine. However, initial H⁺ addition to other positions, such as the alkoxide or terminal nitride, followed by rapid proton transfer to the amide cannot be ruled out.
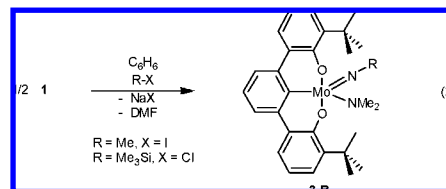
The imposed strain by the ligand and anionic charge elevates the reactivity of the terminal nitride, thereby permitting the addition of electrophiles. Indeed, treating 1 with the mild electrophiles Me₃SiCl and MeI forms the silylimido [^{t}BuOCO]Mo=NSiMe₃(NMe₂) (3-SiMe₃) and methylimido [^{t}BuOCO]Mo=NMe(NMe₂) (3-Me) complexes, respectively (eq 2). 3-Me is generated in an NMR tube reaction by treating 1 with excess MeI followed by heating at 60 °C for 10 h. Attempts to isolate 3-Me led only to intractable mixtures, thus precluding combustion analysis. However, 3-Me is stable in solution in the presence of excess MeI and is well characterized by ¹H and ¹³C{¹H} NMR spectroscopy. Two distinct singlets for the diastereotopic amido protons resonate at 4.23 and 3.59 ppm, and a third singlet is located at 2.86 ppm for the imido-methyl. In contrast to the formation of 3-Me, 3-SiMe₃ is generated rapidly at 23 °C upon addition of Me₃SiCl to 1. 3-SiMe₃ is isolable as an analytically pure orange solid in 71% yield. A ¹H NMR spectrum of 3-SiMe₃ again reveals distinct amido-methyls at 4.14 and 2.95 ppm and the silyl-methyl protons resonate at −0.21 ppm.

The reactivity of 1 toward electrophiles prompted its examination as an N-atom transfer reagent. A ¹H NMR spectrum obtained within minutes after combining C_6D_6 solutions of 1 and pivaloyl chloride indicates the pivaloylimido complex [^{t}BuOCO]Mo=NC(O)^{t}Bu(NMe₂)DMF (4-^{t}Bu) forms (Scheme 1). Similarly benzoylimido (4-Ph) and acylimido (4-Me) complexes are obtained in situ when PhC(O)Cl and MeC(O)Cl are employed. Figure 1 depicts the molecular structure of [^{t}BuOCO]Mo=N−C(O)^{t}Bu(NMe₂)DMF (4-^{t}Bu). The asymmetric unit consists of two chemically equivalent but crystallographically distinct molecules. The complex consists of a distorted octahedral coordination geometry containing the OCO trianionic pincer, the pivaloylimido group, a dimethylamide, and DMF.[9,10]

Gentle heating (60 °C) completes the N-atom transfer and nitrile expulsion. The reaction was monitored for each derivative of 4-R by ¹H NMR spectroscopy. Clear differences in the time required for complete nitrile formation are found with 4-Me (1.5 h) > 4-Ph (3 h) > 4-^{t}Bu (7.5 h), a reflection of the alkyl substituent size. Concomitant with nitrile formation is the growth of a new compound assigned as the oxo-amide [^{t}BuOCO]Mo=O(NMe₂) (7; Scheme 1). During nitrile expulsion the same ^{t}Bu (1.49 ppm) and amido-methyl resonances at 3.70 and 2.47 ppm, as well as pincer aromatic resonances appear for each 4-R. Oxo 6 is isolated as a brown solid in 66% yield.
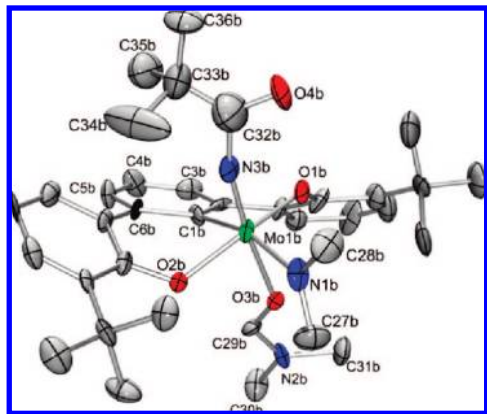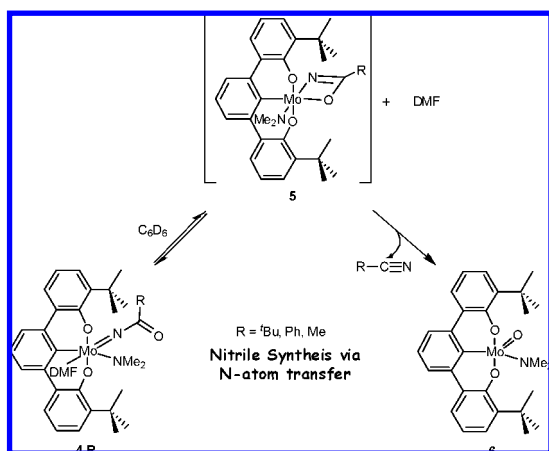
Figure 1. Selected interatomic distances (Å) and angles (°) for ['BuOCO]Mo=N−C(O)'Bu(NMe₂)DMF (**4-'Bu**): Mo1b−N3b, 1.727(9); N3b−C32b, 1.409(19); Mo1b−N1a, 1.985(8); Mo1b−O3b, 2.221(7); Mo1b−N3b-C32b, 164.7(10).

Scheme 1

Scheme 1 depicts the proposed mechanism for the N-atom transfer reaction. The key features include initial dissociation of a DMF molecule and simultaneous formation of an azametallocyclobutene intermediate **5**. Cummins proposed an identical reaction pathway but the azametallocyclobutene could not be detected prior to nitrile expulsion.[6b,10] In analogous phosphaalkyne synthesis, addition of 'BuC(O)Cl to [Na][P≡Nb(N[Np]Ar)₃] generated a phosphorus−metallacycle intermediate which was unambiguously assigned by single-crystal X-ray structural analysis.[11]

The mechanism is consistent with kinetic studies performed on complex **4-'Bu**. Comparing the NMe rotation $\Delta S^{\ddagger}$ values for **3-SiMe₃**, **6**, and **4-'Bu** provides the entropy of activation for DMF loss alone. Variable temperature NMR studies[12] indicate $\Delta S^{\ddagger}$ (cal/(mol·K), 273 K) for **3-SiMe₃** = −0.6(2) and **5** = −2.5(3) are small and negative, suggesting minimal entropy change during NMe equilibration and fitting a simple rotation around the Mo−NMe₂ bond. In contrast, a different mechanism must operate for **4-'Bu** since $\Delta S^{\ddagger}$ = 24.8(2) cal/(mol·K) and is large and positive. The value of +24 is entirely due to DMF dissociation since simple rotation in **3-SiMe₃** and **6** provides a value near zero.

Examining the rate of the overall reaction as a function of temperature provides evidence for cyclometalation. The rate of decay of **4-'Bu** was monitored by ¹H NMR spectroscopy using hexamethyldisiloxane as an internal standard over a 40 °C temperature range. The entropy of activation, obtained from an Eyring plot, is 1.5(3) cal/(mol·K). This is consistent with an increase in

entropy associated with DMF loss (24 cal/(mol·K)) followed by an approximately equal decrease in entropy connected to cyclometalation. Nitrile loss must be post rate-determining because additional entropy associated with nitrile release is expected to be large and positive.

Changing the concentration of DMF from 0.0 M, to 0.1 M, to 0.2 M results in a rate suppression. The inverse order in DMF indicates the first step involves reversible dissociation of DMF to form **5**.

We are now able to add evidence for the intermediacy of an azametallocyclobutene en route to nitrile expulsion during metal-mediated N-atom transfer to acid chloride. Intermediate **5** reemphasizes the prerequisite for at least one accessible coordination site to complete the N-atom transfer. The addition of mild electrophiles (MeI and Me₃SiCl) to the terminal nitride of **1** suggests the trianionic pincer ligand is an appropriate choice for generating reactive metal fragments and is the subject of ongoing studies.

Supporting Information Available: Full experimental procedures, ¹H, ¹³C{¹H} NMR spectra, kinetic data, and X-ray crystallographic details for **4-'Bu**. This material is available free of charge via the Internet at http://pubs.acs.org.

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