A Cycle for Organic Nitrile Synthesis via Dinitrogen Cleavage

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Six-electron reductive cleavage of the N_2 molecule by soluble metal complexes has been observed for a handful of early transition-element systems to provide well-defined terminal or bridged nitridometal products.[1−9] We sought to couple dinitrogen cleavage chemistry with N-atom transfer reactivity,[4,10] keeping in mind the criterion that N-atom transfer should return the metal fragment in high yield and in a form that is suitable for subsequent, repeated dinitrogen cleavage. Dinitrogen cleavage by the three-coordinate molybdenum(III) complex $Mo(N[t\text{-}Bu]Ar)_3$ (**1**) provides 2 equiv of the terminal nitrido complex $N\equiv Mo(N[t\text{-}Bu]Ar)_3$ (**2**) in essentially quantitative yield.[1,2,11−13] Others have explored the use of nitrido **2** as an N-atom source in the synthesis of organonitrogen compounds upon treatment with TFAA ($(F_3CCO)_2O$), a regimen that did not satisfy the criterion articulated above.[14] We have developed a scheme for N-atom incorporation from **2** into organic nitriles, a scheme that until now has been entered into only via independent synthesis.[15,16] Herein we describe N-atom transfer from **2** into organic nitriles via a Lewis-acid induced reaction that returns molybdenum in the form of a chloromolybdenum(IV) complex[17] which in turn is reductively recycled[18] to dinitrogen-splitting complex **1**. Organic nitriles are useful nitrogen-containing building blocks for synthesis,[19,20] and the present methodology may find application in the ^{15}N-labeling of organic nitriles[21] and compounds derived therefrom.

The terminal nitride complex, **2**, is most conveniently prepared by stirring orange-red solutions of **1** with purified NaH[22,23] under an N_2 atmosphere. This method, a modification of published procedures,[11−13,24] requires little purification of the nitride product, as filtration of the reaction mixture followed by removal of solvent affords **2** as a golden-yellow powder. Nitrido complex **2** has proven to be a reluctant nucleophile. This is attributed, at least in part, to steric crowding of the nitrido functionality by three proximal *tert*-butyl residues. Accordingly, **2** is not acylated by acid chlorides in the absence of additives, even upon mild heating. On the other hand, nitrido **2** does take part in reactions with strong electrophiles. Recently described was the reaction of **2** with Me_3SiOTf leading rapidly to the silylimido salt $[Me_3SiNMo(N[t\text{-}Bu]Ar)_3][OTf]$ (**3**).[13] We recognized the latent potential of the Me_3Si^+ group as a Lewis acid capable of promoting a reaction between acid chlorides and **2**.[25−27] Indeed, in the presence of a catalytic amount of pyridine, mixtures of **3** and $PhC(O)Cl$ are converted to benzoylimido salt, $[PhC(O)NMo(N[t\text{-}Bu]Ar)_3][OTf]$ (**4**-Ph, 75%). This transformation creates a new N−C bond while introducing a carbonyl functional group into the molecule that is earmarked for synthetic elaboration.

Reduction of **4**-Ph by magnesium anthracene produces the purple $[Mg(THF)_2][PhC(O)NMo(N[t\text{-}Bu]Ar)_3]_2$ (**5**-Ph), which can be isolated from the reaction mixture as a crude material (82%). **5**-Ph participates in reactions with TFAA or $PhC(O)OTf$ to eliminate PhCN while forming molybdenum(IV) trifluoroacetate, F_3CCO_2-$Mo(N[t\text{-}Bu]Ar)_3$, or the structurally characterized benzoate, $PhCO_2$-$Mo(N[t\text{-}Bu]Ar)_3$.[28] However the molybdenum-containing products resulting from reactions of **5**-Ph could not be isolated as pure materials, therefore we sought to convert **5**-Ph into an easily

Scheme 1. A Synthetic Cycle that Incorporates N_2 into Organic Nitriles[a]
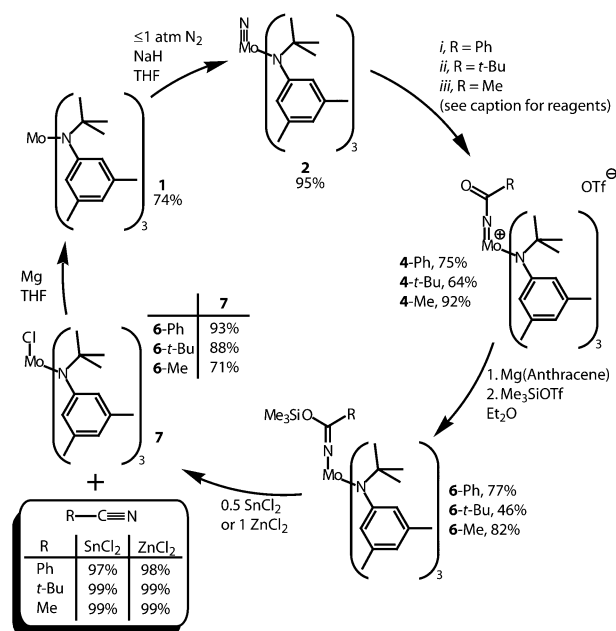
[a] (i) (a) Me_3SiOTf (b) 1.25 $PhC(O)Cl$, 0.2 py; (ii) 1.25 $t\text{-}BuC(O)Cl$, $[Me_3Si(py)][OTf]$; (iii) ($i\text{-}Pr)_3SiOTf$, $MeC(O)Cl$. Yields of RCN were determined by ^{1}H NMR versus an internal standard. The isolated yields of **7** shown were obtained from reactions using $SnCl_2$.

manipulated material. Accordingly, treatment of in situ generated **5**-Ph with Me_3SiOTf cleanly afforded a trimethylsiloxy-substituted ketimide, $Ph(Me_3SiO)CNMo(N[t\text{-}Bu]Ar)_3$ (**6**-Ph, 77%). Crystallographic data (Figure 1) obtained from single crystals of the dark green **6**-Ph show a short Mo−N single bond of 1.828(2) Å, an N═C bond of 1.280(2) Å, and a nearly linear Mo−N−C angle of 171.0(1)° for the ketimide moiety. The three anilide ligands, which are equivalent in solution, are found in an "up−down−sideways" conformation in the solid state.[15] Computational studies of **6**-Ph reveal that the HOMO is the back-bond between the d^2 metal center and the ketimide N═C π^* orbital. The LUMO is nonbonding and has the appearance of a d_{z^2} orbital.[29]

Complexes of the formula $Ph(X)CNMo(N[t\text{-}Bu]Ar)_3$ (X = O_2-CPh, SC_6F_5) are known to fragment giving $(X)Mo(N[t\text{-}Bu]Ar)_3$ and PhCN.[28] We therefore sought out reactions that would release PhCN from **6**-Ph. Both $ZnCl_2$ and $SnCl_2$ were found to react with **6**-Ph to evolve PhCN, with $ClMo(N[t\text{-}Bu]Ar)_3$ (**7**)[17,30] as the sole molybdenum-containing product. The reaction between $SnCl_2$ and **6**-Ph proceeds over 1 h producing **7** (93%) and PhCN (97%); the tin byproducts are removed by filtering the reaction mixture. The reaction between $ZnCl_2$ and **6**-Ph requires 3 h to yield PhCN (98%) and **7** (20%). The isolated yield of **7** is low because the soluble zinc byproducts must be separated by crystallization. The ^{15}N-labeled, $Ph(Me_3SiO)C^{15}NMo(N[t\text{-}Bu]Ar)_3$ (^{15}N NMR: $\delta = 404$ ppm) was prepared, and its reaction with $ZnCl_2$ was assayed by ^{15}N NMR. In the crude reaction mixture, only one resonance was
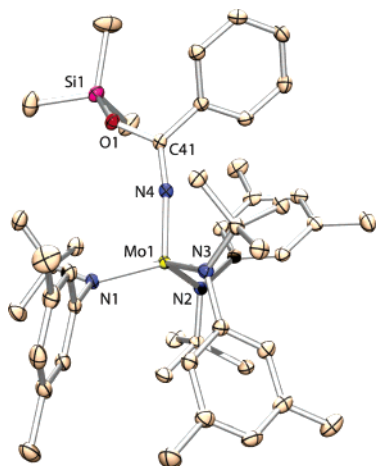
Figure 1. The molecular structure of **6**-Ph is shown with thermal ellipsoids at the 50% probability level.

observed over a spectral width of 0−1000 ppm corresponding to PhC^{15}N (260 ppm).[21] It is noteworthy that ZnCl$_2$ and SnCl$_2$ efficiently form PhCN and a single molybdenum-containing product from **6**-Ph when other Lewis acids do not behave similarly. Tolerance to the d^2 molybdenum center may be essential to avoid redox reactions; Zn(II) and Sn(II) salts are non-oxidizing Lewis acids.[31,32] Interestingly, ZnI$_2$ and Zn(OTf)$_2$ both failed to react with **6**-Ph, possibly implying that formation of a strong Mo−Cl bond is important to obtain favorable thermodynamics for nitrile loss. We favor a mechanism in which the Lewis acid binds to the trimethylsiloxy oxygen to form an intermediate that undergoes subsequent unimolecular fragmentation. This may occur via a six-membered transition state in which chloride bridges between Zn or Sn and Mo. Such a mechanism is analogous to the Lewis-acid induced decomposition of organic hydroximines to nitriles.[33] The reactions between **6**-Ph and ZnCl$_2$ or SnCl$_2$ differ in the required stoichiometry. In the presence of 0.58 equiv SnCl$_2$ **6**-Ph is completely consumed, whereas in the presence of 0.60 equiv ZnCl$_2$ only 60% of **6**-Ph is consumed. This observation implies that the Zn- and Sn-containing byproducts (possibly [ZnCl(OSiMe$_3$)(THF)]$_2$[34] and Sn(OSiMe$_3$)$_2$[35]) are expected to have different empirical formulas.

Reactions between **3** and aliphatic acid chlorides did not produce reasonable yields of corresponding acylimido species. However, treatment of a mixture of **2** and t-BuC(O)Cl with [Me$_3$Si(py)][OTf] affords [t-BuC(O)NMo(N[t-Bu]Ar)$_3$][OTf] (**4**-t-Bu, 64%).[36,37] Treatment of **4**-t-Bu with magnesium anthracene followed by Me$_3$SiOTf affords t-Bu(Me$_3$SiO)CNMo(N[t-Bu]Ar)$_3$ (**6**-t-Bu, 46%). Treatment of blue **6**-t-Bu with SnCl$_2$ cleanly produces both **7** (88%) and t-BuCN (99%). Similarly, ZnCl$_2$ and **6**-t-Bu react to yield **7** and t-BuCN (99%).

Use of the Lewis acid/Lewis base combination of Me$_3$SiOTf and pyridine turned out to be ineffective for synthesizing [MeC(O)-NMo(N[t-Bu]Ar)$_3$][OTf] (**4**-Me). To obtain **4**-Me we adopted a new acylation strategy, adding MeC(O)Cl to a mixture of (i-Pr)$_3$SiOTf and **2**.[25−27] This procedure is possible because (i-Pr)$_3$SiOTf itself does not react with **2** (as assessed by ^{1}H NMR), and the isolated yield of **4**-Me (92%) attests to the utility of this procedure. Treatment of **4**-Me with magnesium anthracene followed by the addition of Me$_3$SiOTf yields violet Me(Me$_3$SiO)CNMo(N[t-Bu]-Ar)$_3$ (**6**-Me, 83%). Treatment of **6**-Me with SnCl$_2$ cleanly produces both **7** (71%) and MeCN (99%). Similarly, treatment of **6**-Me with ZnCl$_2$ yields **7** and MeCN (99%).

The only molybdenum-containing product generated by the reactions of **4** with either SnCl$_2$ or ZnCl$_2$, **7**, is conveniently reduced by Mg^0 to **1** (74%). In this manner the precursor to **2** is regenerated, completing a synthetic cycle that progresses through three different nitrogen-containing triple bonds: 0.5 N≡N → N≡Mo → N≡CR.

A key feature of the cycle in Scheme 1 is the set of three acylation strategies that employ either Lewis acid/Lewis base combinations or a sterically hindered Lewis acid to promote the reaction of **2** with acid chlorides. The other essential feature is the use of SnCl$_2$ and ZnCl$_2$ as both Lewis acids and chloride donors.

Supporting Information Available: Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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