

Nitrogen fixation to cyanide at a molybdenum center†

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Facile methoxymethylation of N₂-derived nitride NMo(N[^tBu]Ar)₃ provided the imido cation [MeOCH₂NMo(N[^tBu]Ar)₃]⁺ as its triflate salt in 88% yield. Treatment of the latter with LiN(SiMe₃)₂ provided blue methoxyketimide complex MeO(H)CNMo(N[^tBu]Ar)₃ in 95% yield. Conversion of the latter to the terminal cyanide complex NCMo(N[^tBu]Ar)₃, which was the subject of a single-crystal X-ray diffraction study, was accomplished in 51% yield upon treatment with a combination of SnCl₂ and Me₂NSiMe₃.

An early commercialized nitrogen fixation process used barium carbide at temperatures of 700–800 °C, and produced barium cyanide exclusively; the process had been discovered in search of a source of cyanide for precious metal recovery.¹ Soon thereafter, Frank and Caro discovered the related calcium cyanamide process,² which supplanted that for barium cyanide due to the myriad chemical applications of cyanamide including use as a fertilizer. Cyanide as a primary product of nitrogen fixation also appeared in the work of Bucher according to eqn (1).



The Bucher process is noteworthy for its exceptional simplicity and lack of requirement for purified nitrogen, working even in air and in non-specialized apparatus at near 950 °C, by virtue of the presence of iron filings as catalyst.³ Ammonia is available from this method by hydrolysis of sodium cyanide.^{4,5}

In connection with our interest in the chemistry of N₂ cleavage by transition-metal complexes,⁶ and in the use of nitride complexes derived therefrom in the assembly of carbon-nitrogen triple bonds (organic nitriles),^{7,8} the present work illustrates a method for net carbon-atom addition to a terminal nitride resulting in the cyanide function. As illustrated in Scheme 1, the overall process can be divided into three conceptual steps: (i) dinitrogen cleavage to form the terminal nitride, (ii) transfer of methoxycarbene to the terminal nitride with carbon-nitrogen double bond formation, and (iii) removal of the elements of methanol, delivering bound cyanide. Accordingly, the process described herein is offered as a chemically distinct, low-temperature alternative to the earliest techniques for deriving cyanide from N₂.

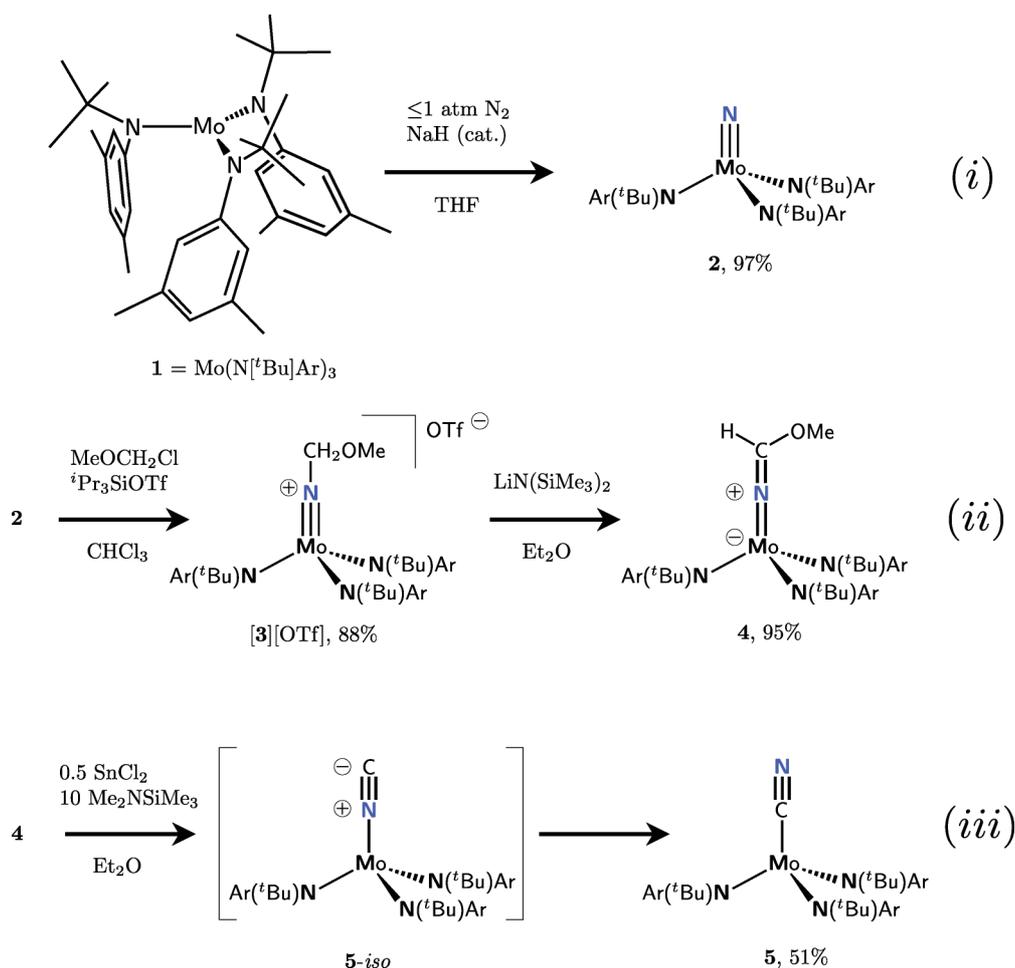
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The terminal nitride, **2**, undergoes a reaction with 1 equiv MeOCH₂I (MOMI) in CDCl₃ to rapidly form the cationic imido, [MeOCH₂NMo(N[^tBu]Ar)₃][I], **[3]I**. This reaction is more facile than the analogous reaction of **2** with MeI, which was best effected by stirring **2** in neat MeI for several hours.⁹ However, the oily **[3]I** proved difficult to isolate as a solid. Therefore, we sought to synthesize a salt of cation **3** with a counter-anion that would impart crystallinity. This was achieved by the treatment of **2** with a combination of MeOCH₂Cl and TIPSOTf (TIPS = tri-isopropylsilyl) to form a red solution containing [MeOCH₂NMo(N[^tBu]Ar)₃][OTf], **[3]OTf**, and TIPSCl. Such a synthetic procedure makes use of the steric bulk of the TIPS group to preclude a direct reaction with **3** that would unproductively yield a silyl imido cation.⁸ The TIPSCl byproduct is soluble in n-pentane and may be washed away from **[3]OTf**, which is isolated in 88% yield. This complex salt is a thermally robust, yellow powder that forms orange solutions in CHCl₃. The methoxymethyl group is easily displaced by a variety of nucleophiles and the complex decomposes in the coordinating solvents pyridine and THF. The ¹⁵N NMR resonance for **[3]OTf**, δ = 466 ppm, is nearly identical to that found for [MeNMo(N[^tBu]Ar)₃][I], δ = 462 ppm; the latter complex has been characterized both crystallographically and by solid-state ¹⁵N NMR spectroscopy.⁹

Crystals of **[3]OTf** suitable for X-ray diffraction were grown from CHCl₃ at –35 °C. The solid-state structure of **[3]OTf** exhibits a Mo–N bond length of 1.7119(14) Å that compares well with that of 1.708(9) Å found for [EtNMo(N[^tBu]Ar)₃][I] (Fig. 1).^{9,10} Interestingly, in **[3]OTf** the Mo–N–C bond angle is 172.24(12)° whereas in [EtNMo(N[^tBu]Ar)₃][I] this angle is 180°, coincident with a crystallographic C₃ axis. While imido systems are plentiful and important,¹¹ imido complexes bearing a –CH₂OR substituent appear not to have been described previously. Hence, the structure presented here for the **[3]**⁺ cation gives us the first glimpse of the MOM-imido moiety.

Addition of LiN(SiMe₃)₂ to yellow solutions of **[3]OTf** in Et₂O rapidly generates a dark blue solution. Evaporation of the solvent, followed by extraction into n-pentane to remove LiOTf affords MeO(H)CNMo(N[^tBu]Ar)₃, **4**, in 95% yield. The dark blue color of **4** is congruent with two absorption bands in the visible region: λ(ε) = 501 (1900), 615 (2500) nm (M⁻¹ cm⁻¹). The proton bound to the ketimide, HC=N, is shifted downfield from 6.1 ppm for **[3]OTf** to 7.4 ppm for **4**. Labeling **4** with ¹⁵N splits the NMR signal for this proton into a doublet for which ²J_{NH} = 2.5 Hz. A doublet with the same coupling was located in the ¹⁵N NMR spectrum at δ = 382 ppm. In contrast to **[3]OTf**, which maintains



Scheme 1 Sequence of (i) dinitrogen cleavage to form terminal nitride, (ii) two-step methoxycarbene addition with C=N bond formation, and (iii) removal of the elements of methanol revealing the cyanide function.

its integrity when stored at 20 °C for weeks, compound **4** is thermally sensitive and decomposes at ambient temperature within 12 h to form a myriad of products including the terminal cyanide NCMo(N^tBuAr)₃, **5**.¹² Because complex **4** gradually decomposes in the solid state at -35 °C, it was important to work with freshly prepared material.

We previously reported that complexes of the formula R¹O(R²)CNMo(N^tBuAr)₃ (R¹ = Me₃Si; R² = Me, Ph, ^tBu) extrude the organic nitriles, R²CN, and form known chloride ClMo(N^tBuAr)₃¹³ when treated with SnCl₂ or ZnCl₂.⁸ Therefore we attempted to liberate HCN by treatment of **4** with SnCl₂ under dynamic vacuum. This protocol did result in the formation of ClMo(N^tBuAr)₃; however, the reaction was not clean, as both the nitride complex **2** and free ligand HN^t(Bu)Ar were also formed. Moreover, attempts to collect HCN by vacuum transfer were unsuccessful.

The observed formation of chloride ClMo(N^tBuAr)₃ was consistent with the initial hypothesis that **4** may react with SnCl₂ in a fashion similar to previously reported ketimide complexes R¹O(R²)CNMo(N^tBuAr)₃. As a result, we postulated that when R² = H, an acidic proton is generated during the treatment of **4** with SnCl₂. Accordingly, we speculated that the addition of a suitable

proton base to the reaction mixture might intercept an acidic proton and afford a cleaner reaction. It was found that treatment of **4** with SnCl₂ in the presence of 10 equiv of Me₃SiNMe₂ afforded cyanide **5** as the major product. In an important control experiment, it was determined that **4** exhibits no reaction with Me₃SiNMe₂ on its own, in the absence of SnCl₂. The formation of **5** according to this protocol was confirmed by the appearance of characteristic ¹H NMR resonances and by MALDI-TOF mass spectrometry. In addition, cyanide **5** could be isolated in 51% yield by crystallization from the reaction mixture.

While an alternative synthesis of cyanide complex **5** has been reported previously,¹² we now present also a single-crystal X-ray structure analysis of this system; see Fig. 2.¹⁰ The key structural features observed are (i) linearity at cyanide carbon C4, (ii) a coordination geometry at Mo that is midway between tetrahedral and trigonal bipyramidal with C4-Mo-N(1-3) angles of approximately 100°, and a short cyano C-N distance, 1.122(2) Å. While there is nothing unusual about the structure of **5**, it is a fact that we have been unable to observe a ν_{CN} band in the infrared spectrum of this substance (Figure S8†). On the other hand, examples are known of molybdenum mono-cyanide complexes having a weak or absent ν_{CN} infrared feature.¹⁴⁻¹⁶

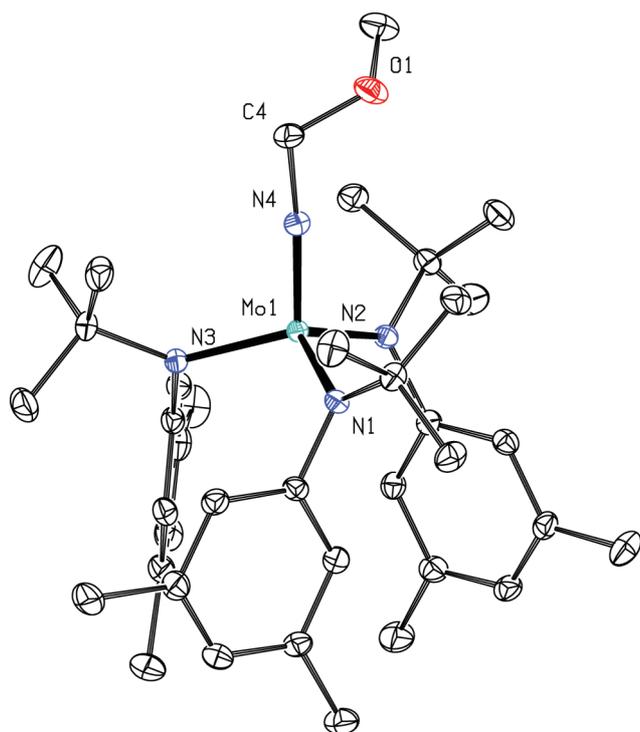


Fig. 1 Thermal ellipsoid plot (50% probability level) of imido cation [3]⁺ (CHCl₃ of crystallization, hydrogen atoms, and triflate counter-ion not shown).

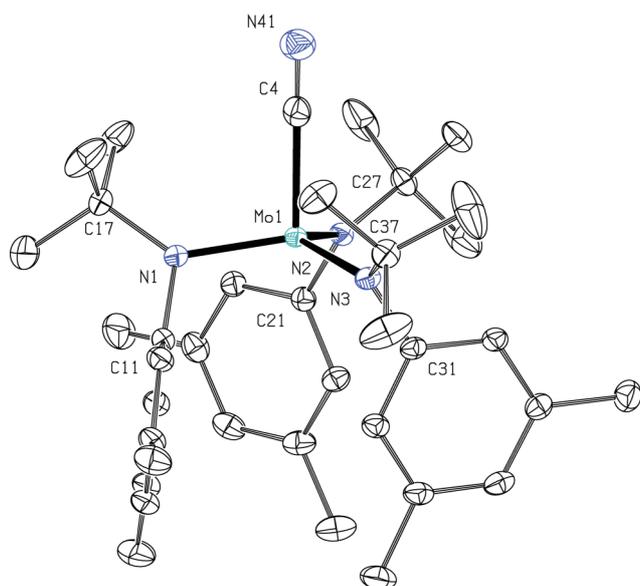


Fig. 2 Thermal ellipsoid plot (50% probability level) of cyanide complex $\text{NCMo}(\text{N}[\text{Bu}]\text{Ar})_3$, **5**. Selected interatomic distances (Å) and angles (°): C4 N41 1.122(2), C4 Mo1 2.0918(17), N1 Mo1 1.9574(12), N2 Mo1 1.9530(12), N3 Mo1 1.9637(12), N41 C4 Mo1 178.95(15), N2 Mo1 N1 116.51(5), N2 Mo1 N3 117.41(5), N1 Mo1 N3 118.12(5), N2 Mo1 C4 100.43(5), N1 Mo1 C4 98.51(6), N3 Mo1 C4 99.48(6).

The reaction that converts **4** to **5** (Scheme 1) proceeds over the course of approximately 30 min with a color change from a dark blue to red brown. When the heterogeneous reaction mixture is monitored by UV-vis spectroscopy, the intense band attributed to the metal-to-ligand charge transfer of **4**, = 615 nm,

decays away while an absorbance due to cyanide **5**, = 425 nm, gains in intensity (Fig. 3). The reaction by which **5** is formed from **4** poses a mechanistic question because the cyanide function may either dissociate from the metal or be retained on a single molybdenum center through the course of the reaction. For example, this reaction may proceed *via* the initial production of Me_3SiCN and $\text{ClMo}(\text{N}[\text{Bu}]\text{Ar})_3$ prior to the formation of **5**. Alternatively, a pathway in which the cyanide moiety does not leave the metal center may be operative. To test the first hypothesis, $\text{ClMo}(\text{N}[\text{Bu}]\text{Ar})_3$ was treated with Me_3SiCN . This protocol was found to afford compound **5** in 97% yield. However, this protocol for synthesizing **5** was found to require stirring for several hours at 20 °C to reach completion. The reaction is only about 33% complete after 1 h when carried out at concentrations similar to those employed for the conversion of **4** to **5**. As the latter reaction is complete within 30 min, it seems unlikely that a pathway that requires formation of Me_3SiCN predominates.

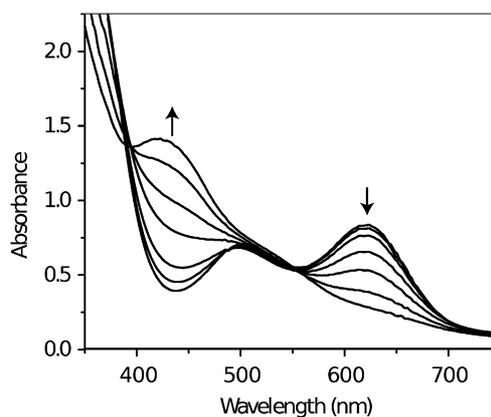


Fig. 3 UV-Vis spectral changes accompanying the **4**→**5** conversion with spectra shown at 5 min intervals.

Additional mechanistic information ensued from an isotope-labeling study. If trimethylsilyl cyanide were an intermediate, then adding this reagent to the reaction mixture containing ^{15}N -**4** would be expected to result in crossover of the nitrogen isotopomers. Accordingly, ^{15}N -**4**, prepared from $^{15}\text{N}_2$, was treated with SnCl_2 and 10 equiv $\text{Me}_3\text{SiNMe}_2$ in the presence of 1 equiv Me_3SiCN . Analysis of the crude reaction mixture by FT-IR showed a band at 2195 cm^{-1} corresponding to the added Me_3SiCN . No band consistent with $\text{Me}_3\text{SiC}^{15}\text{N}$ was observed in the spectrum, and all other bands were reproduced in the crude reaction mixture obtained without added Me_3SiCN . These observations are consistent with a mechanism in which the CN unit does not leave the metal. Although the metal isocyanide complex $\text{CNMo}(\text{N}[\text{Bu}]\text{Ar})_3$ (**5-iso**, Scheme 1) is not required to be an intermediate, linkage isomerism of the cyanide ligand has been studied.¹⁷ These studies indicated a rapid conversion of the $\text{M}-\text{N}\equiv\text{C}$ to $\text{M}-\text{C}\equiv\text{N}$ *via* an irreversible, first-order process.

Herein we have reported a surprising transformation of ketimide complex **4** into a corresponding terminal cyanide complex, **5**. As **4** is derived from simple alkylation and deprotonation of **2** (formal carbene transfer) the overall process converts a terminal N^3- ligand into a CN^- ligand that proceeds through three triply bonded atom pairs: $\text{N}\equiv\text{N} \rightarrow \text{Mo}\equiv\text{N} \rightarrow \text{C}\equiv\text{N}$. The net transformation may be viewed as the formal insertion of a carbon atom into the

Mo≡N triple bond. This work delivers a new synthetic method for terminal nitride functionalization *via* conversion to the rare methoxymethyl imido unit.

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