

Dimolybdenum– μ -cyanide complexes supported by *N*-*tert*-butylanilide ligation: in pursuit of cyanide reductive cleavage

Jonas C. Peters, Luis M. Baraldo, Thomas A. Baker, Adam R. Johnson,
Christopher C. Cummins *

Department of Chemistry, Massachusetts Institute of Technology, Room 2-227, Cambridge, MA 02139-4307, USA

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Abstract

The red cyanide complex $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ ($\text{R} = \text{C}(\text{CD}_3)_2\text{CH}_3$, $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) was prepared in 77% yield by reaction of iodide $\text{IMo}(\text{N}[\text{R}]\text{Ar})_3$ with tetra-*n*-butyl ammonium cyanide. By reaction of cyanide $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ with the three-coordinate molybdenum(III) complex $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ was prepared the dimolybdenum- μ -cyanide complex $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ as a violet solid in 80% yield. Reduction of μ -cyanide $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ by one electron would give a cyanide-bridged anion isoelectronic with the known $\mu\text{-N}_2$ complex $(\mu\text{-N}_2)\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$, an intermediate in dinitrogen cleavage to two equivalents of nitride $\text{NMo}(\text{N}[\text{R}]\text{Ar})_3$ by $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$. Instead of undergoing an analogous cleavage of cyanide upon one-electron reduction, μ -cyanide $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ was found to undergo expulsion of a ligand $\text{C}(\text{CD}_3)_2\text{CH}_3$ substituent upon exposure to reducing conditions, the product isolated in 50% yield being imido- μ -cyanide $(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}(\mu\text{-NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$. By reaction of $[\text{N}^t\text{Bu}_4][\text{CN}]$ with the 1-adamantyl-substituted molybdenum complex $\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$, the blue salt $[\text{N}^t\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ was obtained in 91% yield. Reaction of ferrocenium triflate or silver triflate with $[\text{N}^t\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ gave ferrocene or silver along with the neutral cyanide complex $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$, isolated in 74% yield. While reaction of $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ with $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ gave in 53% yield a burgundy-colored dimolybdenum- μ -cyanide complex $(\text{Ar}[\text{Ad}]\text{N})_3\text{Mo}(\mu\text{-CN})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$, the 1-adamantyl-substituted cyanide did not exhibit any reaction with the 1-adamantyl-substituted tricoordinate complex $\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$. The latter results indicate that cyanide is too small to serve as a bridge for two equivalents of the highly sterically encumbered $\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ fragment. A metathetical route to a heterodinuclear cyanide-bridged complex was explored involving addition of $[\text{N}^t\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ to the vanadium iodide complex $\text{IV}(\text{N}[\text{R}]\text{Ar}_F)_2$. By this reaction was obtained the orange-brown μ -cyanide complex $(\text{Ar}_F[\text{R}]\text{N})_2\text{V}(\mu\text{-NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ in 30% recrystallized yield. The latter was characterized by X-ray crystallography. The cyanide chemistry reported here is interpreted with the aid of bonding considerations and cyclic voltammetry studies on the new complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Cyano; *N*-*tert*-Butylanilide

1. Introduction

The reductive scission of molecular nitrogen by two equivalents of d^3 $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**, $\text{R} = \text{C}(\text{CD}_3)_2\text{CH}_3$, $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) established a paradigm for the six-electron reductive cleavage of a ten-valence-electron diatomic molecule [1–5]. In the case of dinitrogen as

the substrate, a substantial thermodynamic driving force can be traced to the formation of two extremely strong $\text{Mo}\equiv\text{N}$ triple bonds for each molecule of dinitrogen severed [6–8]. Following this line of reasoning, it was of interest to determine what chemistry would be manifested by **1** in conjunction with carbon monoxide, on the one hand [9], and cyanide ion on the other. Known carbon monoxide and cyanide reductive cleavage reactions are relevant [10–14], and a splitting of nitric oxide by a d^3 metal complex in conjunction with a d^2 metal complex has been documented [15].

* Corresponding author. Fax: +1-617-258-6989.
E-mail address: ccummins@mit.edu (C.C. Cummins)

Initial investigations into the carbonylation of **1** revealed a preference for formation of the mononuclear monocarbonyl (OC)Mo(N[R]Ar)₃ (**2**) [9]. No reaction was observed between **1** and carbonyl **2**, such that no CO splitting reaction is to be anticipated for this system. On the other hand, stepwise reduction and derivatization of carbonyl **2** was found to afford an unprecedented terminal carbide complex [M][CMo(N[R]Ar)₃], isolated as alkali metal salts (**3**, M = K(kryptofix) or K(benzo-15-c-5)₂) [9]. The anionic component of [M][CMo(N[R]Ar)₃] is a terminal carbide species isoelectronic with NMo(N[R]Ar)₃ (**4**) [3].

If cyanide ion were to undergo reductive scission in the presence of **1** (two equivalents), then a carbide product such as **3** is to be expected along with nitride **4**. Cyanide complex chemistry has been reviewed [16,17], and advances in the activation and functionalization of bound cyanide have been described [18–20]. The goal of the present work was to delineate the chemistry of **1** in the presence of cyanide ion. Also utilized in the course of this study is the more hindered, adamantyl-substituted analog of **1**, namely Mo(N[Ad]Ar)₃ (**5**, Ad = 1-adamantyl, Ar = 3,5-C₆H₃Me₂) [21,22], the supporting ligand [23] in this case having been introduced recently into zirconium [24], vanadium [25], niobium [26,27], and chromium [28,29] chemistries.

2. Results and discussion

2.1. Reaction of Mo(N[R]Ar)₃ (**1**) with [NⁿBu₄][CN]

An initial strategy for cyanide cleavage involved the addition of [NⁿBu₄][CN] to **1** in tetrahydrofuran solution. Addition of [NⁿBu₄][CN] (one equivalent) to a solution of **1** gave a rapid reaction in which a dramatic purple color appeared, the color persisting in the cold but fading to brown when the mixture was allowed to age at 25°C.

Spectroscopic monitoring by ²H-NMR reflected the aforementioned temperature-dependent color changes in that initial resonances in the 0–7 ppm range were observed to decay and be replaced by new signals. A compound exhibiting a resonance at ca. 6 ppm was tentatively assigned as the salt [NⁿBu₄][(NC)Mo(N[R]Ar)₃] (**6**). Repeated pentane extraction of the crude brown residue (obtained upon solvent removal) removed pentane-soluble impurities, leaving behind small amounts of the desired intense blue salt [NⁿBu₄][(NC)Mo(N[R]Ar)₃] (**6**). The IR spectrum (THF, KBr) of **6** featured an intense ν_{CN} stretch at 1941 cm⁻¹, while a ²H-NMR signal at 6 ppm was observed for the complex. Efforts to improve the synthesis of **6** by slow addition of **1** to a cold solution of [NⁿBu₄][CN] were successful in part, but unidentified decomposition pathways remained problematic.

Although slow addition of one equivalent of **1** to 0.5 equivalents of [NⁿBu₄][CN] was attempted as a direct route to the desired bridged species [NⁿBu₄][(μ-CN){Mo(N[R]Ar)₃}₂] (**7**), the reaction instead gave an uncharacterized mixture of products. Spectroscopic analysis of the crude mixture resulting from the latter 2:1 stoichiometry showed none of the anticipated NMo(N[R]Ar)₃ (**4**), an expected product of successful cyanide cleavage.

2.2. Synthesis of [NⁿBu₄][(NC)Mo(N[Ad]Ar)₃] (**8**)

It has been found that a dinitrogen-bridged species analogous to the well-characterized complex (μ-N₂){Mo(N[R]Ar)₃}₂ (**9**) [3] is sterically inaccessible for the more encumbered 1-adamantyl-substituted derivative Mo(N[Ad]Ar)₃ (**5**) [21,22]. Hence, dinitrogen is not split by **5**. Taking a hint from the dinitrogen results, it was elected to deliver cyanide ion to the more crowded Mo(N[Ad]Ar)₃ species, **5**. This approach was expected to minimize any side reactions involving a 2:1 Mo:cyanide stoichiometry.

Addition of a THF solution of [NⁿBu₄][CN] (1 equivalent) to a stirring solution of Mo(N[Ad]Ar)₃ (**5**) at 25°C resulted in a rapid color change from orange to intense blue. The blue color persisted, and an IR spectrum of the crude mixture featured a band at 1929 cm⁻¹, consistent with successful delivery of cyanide ion to **5**. The blue salt [NⁿBu₄][(NC)Mo(N[Ad]Ar)₃] (**8**) was isolated in 91% yield by removal of the THF solvent and subsequent thorough washing of the crude salt with pentane (see Fig. 1).

Probe experiments were performed in order to test the viability of **8** as a precursor to the unsymmetrical bridged dimolybdenum species [NⁿBu₄][(Ar[Ad]N)₃-Mo(μ-CN)Mo(N[R]Ar)₃] (**10**). Accordingly, **1** was added to **8** in THF under a dinitrogen atmosphere. The result was an unexpected nexus with the N₂ chemistry of **1**. Infrared spectra of the reaction mixture revealed the gradual appearance of a band at 1766 cm⁻¹, this band being a spectroscopic signature for the well-characterized N₂-complex anion derived from **1** [22], here being generated as the salt [NⁿBu₄][(N₂)Mo(N[R]Ar)₃] (**11**). It is known that, under N₂, complex **1** is in equilibrium with its neutral dinitrogen complex (N₂)Mo(N[R]Ar)₃ (**12**), which in turn is readily reduced to its monoanion [22]. Here the implication is that the cyanide salt complex **8** acts as the reducing agent, giving rise to [NⁿBu₄][(N₂)Mo(N[R]Ar)₃] (**11**) along with the new neutral molybdenum(IV) cyanide complex (NC)Mo(N[Ad]Ar)₃ (**13**). As described below, the independent synthesis of the neutral molybdenum(IV) cyanide **13** was accomplished via chemical oxidation of [NⁿBu₄][(NC)Mo(N[Ad]Ar)₃] (**8**) with both ferrocenium triflate [30] and silver triflate.

2.3. Synthesis and characterization of $(NC)Mo(N[R]Ar)_3$ (**14**)

In order to achieve a close comparison with the well-studied N_2 -cleavage reaction [1–5], the synthesis of the dinuclear cyanide-bridged species $(\mu-CN)\{Mo(N[R]Ar)_3\}_2$ (**15**, $R = C(CD_3)_2CH_3$) was required. A straightforward route to **15** was achieved via the neutral molybdenum(IV) cyanide complex $(NC)Mo(N[R]Ar)_3$ (**14**), which in turn was obtained by cyanide treatment of the green molybdenum(IV) iodide complex $IMo(N[R]Ar)_3$ (**16**). Iodide **16** itself is obtained in high yield upon treatment of **1** with 0.5 equivalents of I_2 . Fig. 2 summarizes the reaction chemistry involving $(NC)Mo(N[R]Ar)_3$ (**14**).

Addition of a chilled solution of $[N^rBu_4][CN]$ to a cold, brilliant green ether solution of **16** resulted (1 h) in smooth substitution of iodide by cyanide. Cyanide **14** exhibited a single 2H -NMR signal at 31 ppm, readily distinguished from the resonance for iodide **16** at 6 ppm. One equivalent of $[N^rBu_4][I]$ precipitated from the red reaction mixture upon addition of pentane, and the neutral molybdenum(IV) cyanide **14** was obtained as a red, semi-crystalline solid in 77% yield. Like iodide **16**, cyanide **14** was sparingly soluble in pentane and ether when pure. A ν_{CN} stretch was not observed for **14** by IR spectroscopy. Factors influencing the cyanide stretching frequency in mononuclear complexes and in

dinuclear cyanide-bridged assemblies have been discussed [31]. In addition, the relationship between ν_{CN} band intensity and π -bonding in the complexes has been explored for hexacyanometalates [32].

SQUID magnetometry data (5–300 K) were collected for **14**, yielding a μ_{eff} of $2.81 \mu_B$, consistent with assignment of the molybdenum(IV) complex as a ground state triplet. This is the expected result if the complex adopts C_3 symmetry, whereupon the d^2 configuration is represented by $(e)^2$ or $(d_{xz}, d_{yz})^2$. A molecular orbital analysis focusing on the embedded linear $NCMo$ framework of **14** gives the same result, with an indicated $(\pi_0)^4(\pi_1)^2(\pi_2)^0$ configuration (Section 2.10). A cyclic voltammetry study of cyanide **14** revealed reversible waves at -0.19 and -1.9 V (THF, $[N^rBu_4][PF_6]$, versus $[FeCp_2]^{+/0}$), assigned respectively as the reversible oxidation and reduction of **14**. The observed reduction potential of -1.9 V for neutral molybdenum(IV) cyanide **14** can be compared with that for the neutral molybdenum(III) N_2 complex **12** (-1.7 V) [22]. The apparent contradiction, that molybdenum(IV) is more difficult to reduce than molybdenum(III), can be reconciled in terms of the more π -acidic nature of dinitrogen vis-à-vis cyanide.

That cyanide **14** exhibits an electrochemically reversible reduction is taken to be an indication that $[N^rBu_4][(NC)Mo(N[R]Ar)_3]$ (**6**) is stable when prepared in the absence of **1**. If this is correct, then the low yield

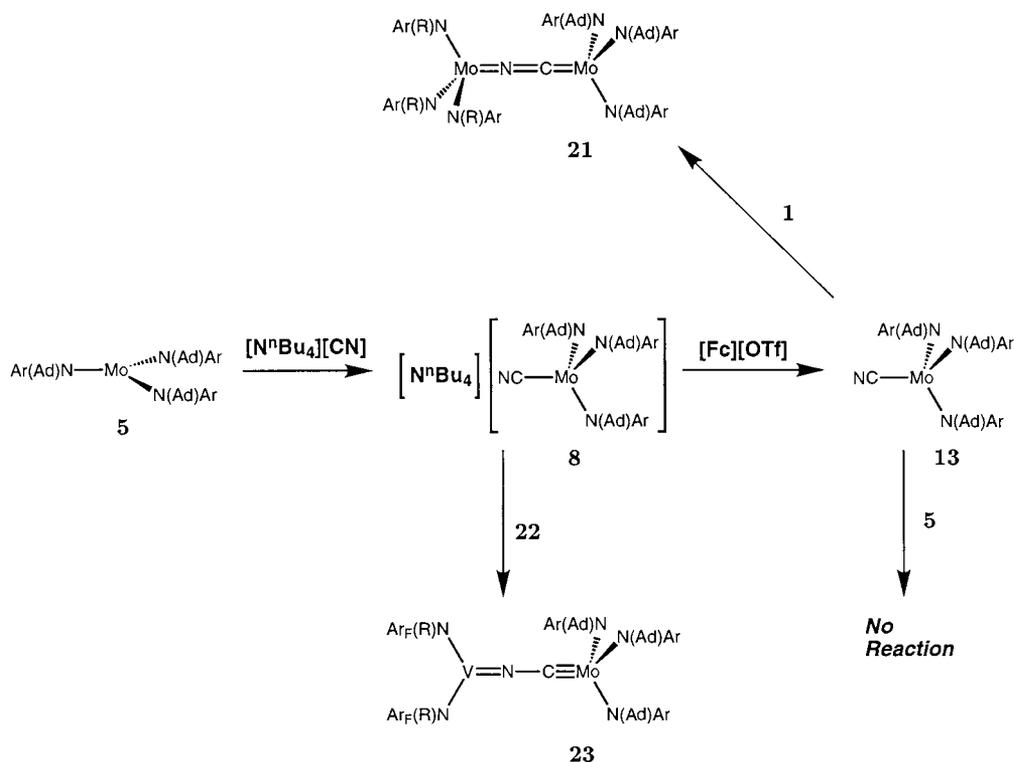


Fig. 1. Reaction scheme illustrating the synthesis of neutral cyanomolybdenum (IV) complex **13** and its incorporation into dinuclear- μ -cyanide complexes. Isolated yields of new compounds: **8**, 91%; **21**, 53%; **23**, 30%; **13**, 74%.

9 at -2.4 V [22]. Since cyanide-bridged **15** is formally a dimolybdenum(III/IV) complex, while dinitrogen-bridged **9** is formally a dimolybdenum(III/III) complex, it is reasonable that **15** should be more readily reduced. The monoanion derived from one-electron reduction of **15** is isoelectronic with neutral **9**.

2.5. Chemical reduction of $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (**15**): *t*-Bu-radical ejection instead of cyanide cleavage

Paramagnetic $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (**15**) underwent reaction upon treatment with a slight excess of sodium amalgam over 1 h, giving rise to a single diamagnetic product. Monitoring of the reaction mixture by ^2H -NMR spectroscopy over 1 h evinced a smooth decay of the two signals corresponding to μ -cyanide **15** and concomitant emergence of several new signals in the 0–10 ppm range, the data being indicative of one or more reduction products. After the reaction was deemed complete, a ^1H -NMR spectrum of a crude aliquot revealed that a single diamagnetic species had been formed in approximately 90% yield. This deep-orange species was pentane soluble and showed three distinct sets of resonances for aryl groups ($\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) in a 3:2:1 ratio. That the new complex exhibited no reaction with 12-crown-4, and that it was rather lypophilic suggested that a sodium cation was not likely to be present as part of the complex. In other words, the new orange product was a neutral species, not a salt.

The first-formed species in the reduction of μ -cyanide **15** is logically anticipated to be $[\text{Na}(\text{THF})_x][(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2]$ (**17**), but the data pertaining to the isolated material indicate that the anionic component of **17** has undergone both desymmetrization and a loss of counterion. Desymmetrization is explicable in terms of fragmentation at one of the six *N*-*t*-Bu bonds. Such a fragmentation leads to ejection of a *t*-Bu group, likely as the radical, and to formation of an imidometal functionality (e.g. $\text{Mo}=\text{NAr}$, where $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$). If the new imidometal-containing anion, namely $[\text{Na}(\text{THF})_x][(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}(\mu\text{-NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3]$ (**18**), is a highly-reducing species then formal loss of a sodium atom would convert it to the neutral imido- μ -cyanide complex $(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}(\mu\text{-NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**19**). Therefore, the orange complex formed in high yield upon exposure of μ -cyanide **15** to sodium amalgam is formulated as imido- μ -cyanide **19**. The overall transformation amounts to sodium-amalgam catalyzed ejection of a *tert*-butyl radical from **15**.

It has been documented previously that molybdenum(V) complexes possessing *tert*-butyl substituents in a position α to the metal can lose *tert*-butyl radical, giving rise to oxomolybdenum(VI) or imidomolybdenum(VI) functionalities [39,40]. Therefore it follows that the freshly-formed imido group of **19** resides on

the molybdenum center bonded to the cyanide nitrogen. In one resonance structure for imido- μ -cyanide **19**, both molybdenum centers are formally molybdenum(VI), the highly reduced cyanide behaving as an imido substituent to one Mo center, and as an alkylidyne substituent to the other Mo center.

It is likely that the reduction of μ -cyanide **15** by sodium amalgam is reversible, given the reduction potential of -2.2 V for the complex (see above). A cyclic voltammetry study of imido- μ -cyanide **19** showed the complex to be highly resistant to reduction, it being the case that an irreversible wave was observed at -3.2 V. The latter wave represented the only reduction manifested by the complex. Sodium amalgam (0.5%) is not competent to effect such a high-potential reduction so it therefore stands to reason that the putative anion of **18** would lose an electron, along with the sodium counterion, under the conditions of the synthesis of imido- μ -cyanide **19**.

Since it is postulated that *t*-Bu radical is ejected during the course of formation of **19**, an attempt was made to observe hexamethylethane, isobutylene, and isobutane. The latter are the conproportionation and disproportionation products, respectively, of the *t*-Bu radical [41–43]. Accordingly, the ^{13}C -NMR spectrum of the volatiles from the reaction was acquired, but only the solvent, tetrahydrofuran (THF), was observed. It is likely that *t*-Bu radical reacts with THF solvent readily, thus being diverted from undergoing disproportionation and conproportionation, and is converted to less volatile products. To get around this, the reduction of **15** was attempted in C_6D_6 , in the hope of identifying isobutane, isobutylene, and hexamethylethane. However, no reaction was observed in this solvent over a 48 h period. Therefore the statement that *t*-Bu radical ejection is a critical step in the mechanism of formation of **19** is not firmly established, though it remains a well-documented decomposition pathway for the $-\text{N}(\text{R})\text{Ar}$ ligand [39,40].

The electrochemistry of imido- μ -cyanide **19** was investigated further, with the result that a reversible wave was observed at -2.2 V, presumably corresponding to the oxidation of **19** to its monocation. The extremely low reduction potential of -3.2 V for **19** is approximately 1 V more negative than that exhibited by its precursor, neutral μ -cyanide **15**. These electrochemical data allow us to formulate a model illuminating the observed conversion of **15**–**19** under reducing conditions. Sodium amalgam (0.5%) readily reduces **15** to its monoanion, an electrochemically observable species. In the actual reaction mixture, this species is a salt such as **17**, and undergoes a homolytic C–N bond cleavage reaction to generate *t*-Bu radical and an extremely reducing anion, the anionic component of salt **18**. Salt **18** is oxidized by **15** or by mercury. The overall transformation, as indicated above, is a sodium amalgam catalyzed ejection of a *t*-Bu group from neutral μ -cyanide **15**.

2.6. Synthesis of $[Li(THF)_x][[NC)Mo(N[Ad]Ar)_3]$ (**20**)

A lithium for tetrabutyl ammonium cation replacement was effected by addition of excess lithium chloride to a blue THF solution of **8**. A color change from blue to intense violet occurred gradually, concomitant with a change in the IR absorbance of the mixture. Over a period of several hours the stretch at 1929 cm^{-1} , corresponding to precursor **8**, decayed and was replaced by two bands appearing at 1934 and 1915 cm^{-1} . The product is assigned as lithium molybdenum cyanide **20**.

The empirical observation of two ν_{CN} stretches for **20** is explicable in terms of two isomers of the complex, or in terms of its adopting an unsymmetrical dimeric structure. In either case, interactions between the lithium cation and the $3,5\text{-C}_6\text{H}_3\text{Me}_2$ substituents may be an essential component of the structure, as noted in other instances [9,44]. The increased hydrocarbon solubility of lithium salt **20** as compared with the tetrabutyl ammonium salt **8** is likewise an indication that the lithium cation is tightly associated with its counterion.

2.7. Chemical oxidation of the adamantyl-substituted anionic cyanide complex (**8**)

Oxidation of $[N^t\text{Bu}_4][[NC)Mo(N[Ad]Ar)_3]$ (**8**) with ferrocenium triflate [30] resulted in the formation of ferrocene along with the neutral cyanide complex **13**. Like its ^tBu-substituted analog **14**, neutral cyanide **13** is red in color and rather insoluble in pentane, the latter property facilitating its separation from ferrocene.

As was the case for ^tBu-substituted **14**, an IR spectrum of the neutral Ad-substituted cyanide **13** did not exhibit a ν_{CN} stretch.

2.8. Steric tuning of the cyanide-bridged dimolybdenum system

The results given above confirm that the cyanide ligand is capable of serving as a bridge to join together two molecules of $Mo(N[R]Ar)_3$ (**1**). Also, it has been shown [22] that the more sterically shielded three-coordinate molybdenum(III) complex $Mo(N[Ad]Ar)_3$ (**5**) does not form a dinuclear dinitrogen-bridged complex, and consequently does not split dinitrogen, in stark contrast to the results obtained for compound **1**. In keeping with the N_2 result with **5**, it was found here that the adamantyl-substituted cyanide **13** exhibits no reaction with $Mo(N[Ad]Ar)_3$ (**5**). With the cyanide chemistry uncovered in the present work, it became possible to see if the $Mo(N[R]Ar)_3$ (**1**) fragment could be linked to the $Mo(N[Ad]Ar)_3$ (**5**) fragment by a cyanide bridge. Given the known structural preferences for complexes of **5** and **1**, formation of the indicated ^tBu/1-Ad linked system requires the three ^tBu groups in

conjunction with the three 1-Ad substituents to form a shroud encapsulating the cyanide bridge.

Mixing of neutral adamantyl-cyanide **13** with a stoichiometric amount of **1** in tetrahydrofuran produced an intense violet color, very similar to the color of the all-^tBu neutral bridged-cyanide complex **15**. A ²H-NMR spectrum of the reaction mixture evinced a single broad resonance at 6.8 ppm ($\Delta\nu_{1/2} = 60\text{ Hz}$), reflecting attachment of the deuterated molybdenum complex **1** to the non-deuterated Ad-substituted species **13**, giving the mixed cyanide-bridged complex $(Ar[Ad]N)_3Mo(\mu-CN)Mo(N[R]Ar)_3$ (**21**, $R = C(CD_3)_2CH_3$). Compound **21**, which was found to be only sparingly soluble in alkane solvents, was obtained in 53% isolated yield.

2.9. A cyanide-bridged vanadium/molybdenum complex

One of the attractive features of monocyanometalates as in $[N^t\text{Bu}_4][[NC)Mo(N[Ad]Ar)_3]$ (**8**) is the potential for forming heterodinuclear cyanide-bridged complexes via metathetical reactions. This type of reactivity is illustrated by the reaction of **8** with the previously described [45] vanadium(III) iodide complex $IV(N[R]Ar_F)_2$ (**22**, $Ar_F = 2,5\text{-C}_6\text{H}_3\text{FMe}$, $R = C(CD_3)_2CH_3$). The indicated reaction generated the cyanide-bridged complex $(Ar_F[R]N)_2V(\mu-CN)Mo(N[Ad]Ar)_3$ (**23**), the reaction being carried out at low temperature for best results. Vanadium/molybdenum cyanide **23** was formed in ca. 60% yield, as estimated by a ²H-NMR spectrum of the crude reaction mixture. The isolated yield of complex **23** was 30%, subsequent to crystallization from ether. A magnetic susceptibility measurement by the method of Evans gave a μ_{eff} value of $1.70\ \mu_B$ for **23**, consistent with an $S = 1/2$ system.

An X-ray structural investigation of **23** revealed a $Mo-C-N-V$ linkage exhibiting a slight bend at the cyanide nitrogen. Another salient feature of the solid state structure of **23** is the unusually short $V-F(2)$ interaction ($2.147\ \text{\AA}$), $F(2)$ being an *ortho*-fluorine component of one of the two Ar_F substituents. Such chelation of fluoroaryl functional groups in the context of fluoroaryl amido chemistry has been described in some recent reports [46,47], and should be viewed as similar to an agostic interaction.

The $Mo-C-N-V$ tetratomic unit in **23** can be viewed in π -delocalized molecular orbital terms as being a $(\pi_0)^4(\pi_1)^4(\pi_2)^1(\pi_3)^0$ system (see Section 2.10). This configuration is consistent with the observed magnetic moment. Also consistent with the observed magnetic moment would be a Lewis description for the molecule in which molybdenum is assigned the +6 oxidation state and vanadium the +4 oxidation state. In such a description the molybdenum forms a formal triple bond to the cyanide carbon, while the vanadium forms an imido-like linkage to the cyanide nitrogen. That the

cyanide ligand is indeed highly reduced in complex **23** can be inferred from the relevant bond distances found in the structural investigation (Fig. 3).

2.10. Bonding considerations for multiply bonded systems derived from **1**

It has been mentioned previously [5] that $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**) is isolobal [48] with a ground state nitrogen atom. This isolobal analogy permits a first-order analysis of the bonding in linear multiply bonded systems that have $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**) as a terminus.

The analysis given here presumes a linear system of atoms, and stems from the equivalence of the x and y coordinates in a system (such as **1**) that is threefold symmetric about the z coordinate. Attention is focused on the π system of molecular orbitals, since this is where any unpaired electrons are expected to reside. For a triatomic system such as CO_2 , or for a system such as $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**14**) in which a triatomic NCMo system is embedded, it can be seen (Fig. 4) that there are three π energy levels. These are each doubly-degenerate due to the equivalence of the x and y coordinates, and they are referred to as π_0 , π_1 , and π_2 , the subscript being indicative of the number of interatomic nodes in each π -type molecular orbital.

For a tetraatomic linear system, for example two molecules of dinitrogen taken together, or dimolybdenum- μ -cyanide **15**, there are four π energy levels, each being doubly-degenerate and referred to as π_0 through π_3 (Fig. 5).

The configuration is arrived at by determining the number of π -type electrons in the system in question. In the case of $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ **14**, it is seen that the system is formally d^2 , and that the cyanide ligand contributes four π -symmetry electrons, for a total of six π -electrons. Thus the configuration for **14** is $(\pi_0)^4(\pi_1)^2(\pi_2)^0$, as indicated in Table 1. A triplet state therefore is indicated for **14**, consistent with its magnetic behavior.

A final point to be made is that the most stable systems are those with the $(\pi_0)^4(\pi_1)^4(\pi_2)^0$ configurations for triatomic systems, and those with the $(\pi_0)^4(\pi_1)^4(\pi_2)^0(\pi_3)^0$ configurations for tetraatomic systems. This can be understood with reference to CO_2 as a very stable diamagnetic closed-shell representative of this class.

Similar considerations of electronic structure apply to dinitrogen complexes in the molybdenum triamidoamine systems of Schrock and co-workers [49], and Bercaw has given a particularly lucid description of the bonding in dinitrogen-bridged dinuclear systems [50].

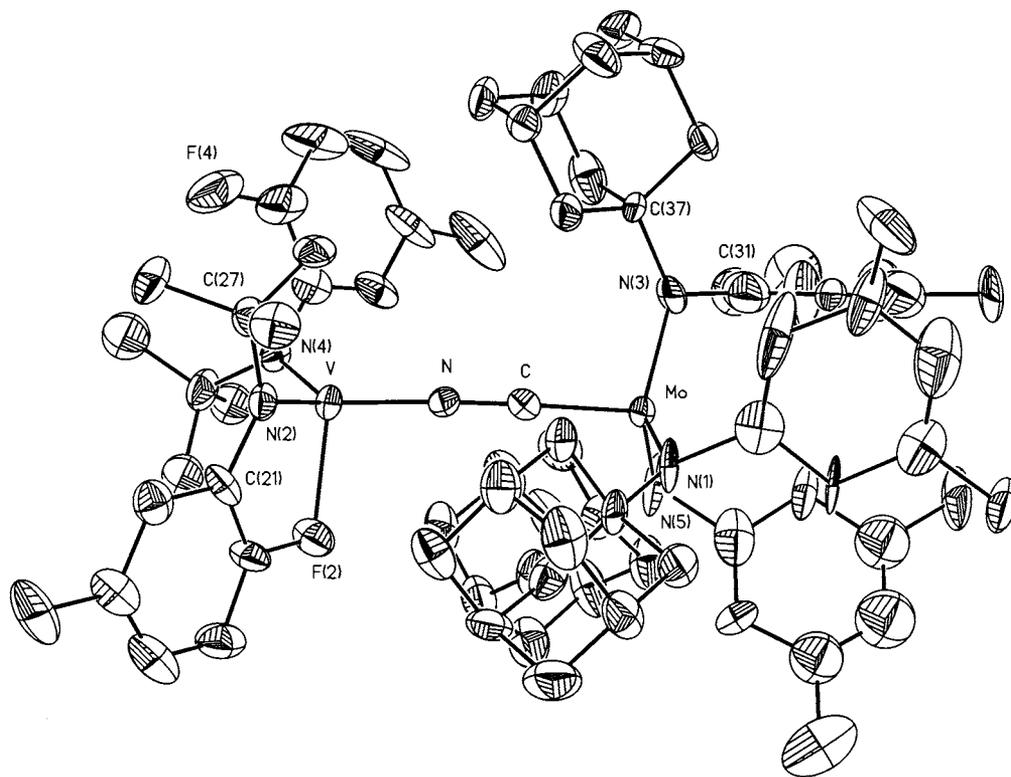


Fig. 3. Thermal ellipsoid representation of the structure of $(\text{Ar}_F[\text{R}]\text{N})_2\text{V}(\mu\text{-NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**23**) from a single-crystal X-ray diffraction study. Selected bond distances (Å) and angles ($^\circ$): Mo–C, 1.847(13); V–N, 1.799(11); C–N, 1.260(14); V–F(2), 2.148(7); Mo–N(1), 1.950(11); Mo–N(3), 1.933(12); Mo–N(5), 1.971(12); V–N(2), 1.962(10); V–N(4), 1.905(9); N–C–Mo, 176.1(9); C–N–V, 169.6(9); C–Mo–N(1), N(3), N(5), avg. = 100.8(4); N(2)–V–F(2), 121.9(4); N–V–N(4), 115.0(5).

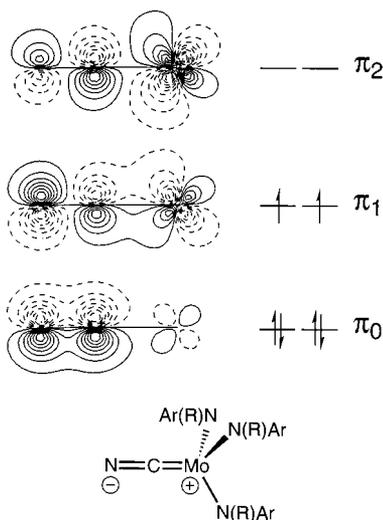


Fig. 4. Depiction of the π -symmetry molecular orbitals of the triatomic NCMo moiety embedded within the $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ molecule **14**. The designation π_0 refers to the π molecular orbital with zero interatomic nodes, and similarly the designation π_1 refers to the π molecular orbital with one interatomic node, and so on. The contour diagrams shown are intended to be schematic and are derived from an extended Hückel molecular orbital calculation [53] on $(\text{N}_2)\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**12**). Orbitals with the same general features are anticipated for any system having an electronegative diatomic molecule linearly coordinated to a transition metal fragment such as $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**).

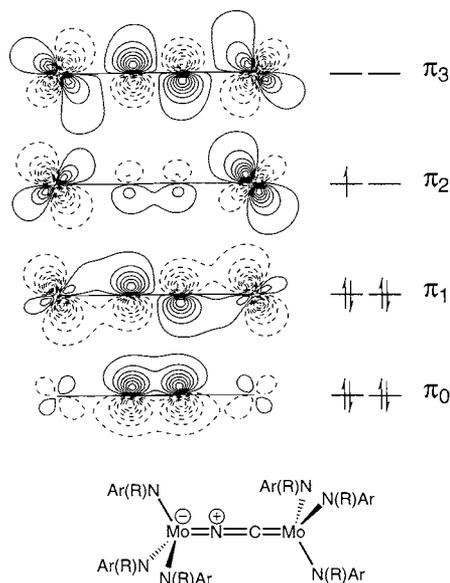


Fig. 5. Depiction of the π -symmetry molecular orbitals of the tetraatomic MoNCMo moiety embedded within the $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ molecule **15**. The designation π_0 refers to the π molecular orbital with zero interatomic nodes, and similarly the designation π_1 refers to the π molecular orbital with one interatomic node, and so on. The contour diagrams shown are intended to be schematic and are derived from an extended Hückel molecular orbital calculation [52] on $(\mu\text{-N}_2)\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (**9**). Orbitals with the same general features are anticipated for any system having an electronegative diatomic molecule linearly bridging two transition metal fragments such as $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**).

Table 1
 π -Bonding scheme for linear multiply bonded systems ^a

Compound	Configuration	Spin state
$[\text{Na}(\text{THF})_x][(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2]$ (17)	$(\pi_0)^4(\pi_1)^4(\pi_2)^2(\pi_3)^0$	Doublet
CO_2	$(\pi_0)^4(\pi_1)^4(\pi_2)^0$	Singlet
N_2O	$(\pi_0)^4(\pi_1)^4(\pi_2)^0$	Singlet
$(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (14)	$(\pi_0)^4(\pi_1)^2(\pi_2)^0$	Triplet
$(\text{N}_2)\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (12)	$(\pi_0)^4(\pi_1)^3(\pi_2)^0$	Doublet
$[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (8)	$(\pi_0)^4(\pi_1)^3(\pi_2)^0$	Doublet
$[\text{N}^n\text{Bu}_4][(\text{N}_2)\text{Mo}(\text{N}[\text{R}]\text{Ar})_3]$ (11)	$(\pi_0)^4(\pi_1)^4(\pi_2)^0$	Singlet
2N_2	$(\pi_0)^4(\pi_1)^4(\pi_2)^0(\pi_3)^0$	Singlet
$(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (15)	$(\pi_0)^4(\pi_1)^4(\pi_2)^1(\pi_3)^0$	Doublet
$[\text{Na}(\text{THF})_x][(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2]$ (17)	$(\pi_0)^4(\pi_1)^4(\pi_2)^2(\pi_3)^0$	Triplet
$(\mu\text{-N}_2)\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (9)	$(\pi_0)^4(\pi_1)^4(\pi_2)^2(\pi_3)^0$	Triplet
$2 \text{NMo}(\text{N}[\text{R}]\text{Ar})_3$ (4)	$(\pi_0)^4(\pi_1)^4(\pi_2)^0(\pi_3)^0$	Singlet

^a Configurations for triatomic systems are derived from Fig. 4, while those for tetraatomic systems derive from Fig. 5.

3. Conclusions

Inspired by the dinitrogen chemistry of the three-coordinate molybdenum(III) complex $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**) [1–3,5], this work has explored the cyanide chemistry of **1** [51] and its more sterically hindered adamantyl-substituted analog **5** [21,22]. Cyanomolybdenum and cyanodimolybdenum complexes have been prepared in the course of this study, the main goal of which was to probe the possibility that two equivalents of **1** might act cooperatively to effect the six-electron reductive cleavage of cyanide ion. Such a cleavage reaction, if successful, would generate one equivalent each of the known nitride [3] and carbide [9] complexes, $\text{NMo}(\text{N}[\text{R}]\text{Ar})_3$ (**4**) and $[\text{M}][\text{CMo}(\text{N}[\text{R}]\text{Ar})_3]$ (**3**), which have been synthesized independently. In the experiments that bear most strongly on this key issue it was found that a ligand degradation pathway, namely the ejection of a ligand 'Bu group, takes precedence over cyanide reductive cleavage. The observed C–N cleavage reaction, generating an imidometal unit, represents another example of a growing class of reactions in which a metal–ligand multiple bond is formed via formal radical expulsion [39,40].

It is difficult to compare directly the known dinitrogen cleavage reaction with the cyanide splitting reaction envisioned here, primarily because the anionic carbide complex isoelectronic with nitride **4** requires a counterion. The role of the said counterion in a hypothetical cyanide cleavage reaction is likely to be critical for stabilization of the developing negative charge on the carbide carbon with progress along the reaction coordinate.

Methods were developed for the synthesis of monocyano-metallate derivatives, potentially useful synthons for the construction of heterodinuclear cyanide-bridged

assemblies. The latter approach was illustrated via the assembly of a vanadium/molybdenum cyanide-bridged complex.

4. Experimental

4.1. General considerations

Unless stated otherwise, all operations were performed in a Vacuum Atmospheres dry box under an atmosphere of purified nitrogen, or using standard Schlenk techniques under an argon or dinitrogen atmosphere. Anhydrous ether and toluene were purchased from Mallinckrodt; *n*-pentane and *n*-hexane were purchased from EM Science. Ether was purified according to a published procedure [52]. Aliphatic hydrocarbon solvents were distilled under a nitrogen atmosphere from very dark blue to purple sodium benzophenone ketyl solubilized with a small quantity of tetraglyme. Distilled solvents were transferred under vacuum into Teflon-stopcocked glass vessels and stored, prior to use, in a vacuum atmospheres dry box. C₆D₆ was degassed and dried over activated 4 Å molecular sieves and transferred under vacuum into a storage vessel. Sieves (4 Å), Celite and alumina were activated in vacuo overnight at a temperature above 180°C. Mo(N[R]Ar)₃ (**1**) [3], ferrocenium triflate [30], LiN(Ad)Ar [23], and Mo(N[Ad]Ar)₃ (**5**) [21,22], were prepared according to published procedures. Other chemicals were purified and dried by standard procedures or were used as received. Infrared spectra were recorded on a Bio-Rad 135 Series FTIR spectrometer. UV–vis spectra were recorded on a Hewlett–Packard 8453 diode-array spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on Varian VXR-500, Varian XL-300, or Varian Unity-300 spectrometers. ¹H- and ¹³C-NMR chemical shifts are reported with reference to solvent resonances (residual C₆D₅H in C₆D₆, 7.15 ppm; C₆D₆, 128.0 ppm; CHCl₃ in CDCl₃, 7.24 ppm; CDCl₃, 77.0 ppm). ²H-NMR chemical shifts are reported with respect to external C₆D₆ (7.15 ppm). Solution magnetic susceptibilities were determined by ¹H-NMR at 300 MHz using the method of Evans. Routine coupling constants are not reported. Combustion analyses (C, H, and N) were performed by Microlytics, Southdeerfield MA. X-ray diffraction data were collected on a Siemens Platform goniometer with a charge coupled device (CCD) detector. Structures were typically solved by direct methods (SHELXTL V5.0, G.M Sheldrick and Siemens Industrial Automation, Inc., 1995) unless otherwise noted.

4.2. Electrochemical measurements

The electrochemical measurements were performed in THF solution containing the desired compounds and

0.5 M [NⁿBu₄][PF₆]. In a typical procedure 5 mg of the complex was dissolved in 0.75 ml of clean THF. To this solution was added 0.75 ml of 1.0 M THF solution of [NⁿBu₄][PF₆]. A platinum disk (1.6 mm diameter, Bio-analytical systems), a platinum wire, and a silver wire were employed as the working electrode, the auxiliary, and the reference, respectively. The electrochemical response was collected with the assistance of an Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software. An IR correction drop was always employed due to the high resistance of the solutions. A typical resistance value measured with the positive feedback technique for these solutions was 975 Ω. All of the potentials are reported against the [FeCp₂]^{+ / 0} couple measured in the same solution.

4.3. Synthesis of IMo(N[R]Ar)₃ (**16**)

To a solution of **1** (0.3494 g, 0.5435 mmol) in ether (10 ml) was added iodine (0.0706 g, 0.2782 mmol, 0.51 equivalents) as a solution in ether (5 ml). The resulting deep green solution was stirred for 30 min, whereupon the solvent was removed in vacuo. The green product was recrystallized from ether (0.3461 g, 0.4496 mmol, 83%). M.p. 122–124°C. ²H-NMR (46 MHz, ether): δ = 6.36 (Δ_{v_{1/2}} = 11 Hz). ¹H-NMR (300 MHz, C₆D₆): δ = 6.58 (C(CD₃)₂CH₃), 4.62 (aryl *ortho* C–H), 3.56 (aryl *para* C–H), 1.15 (aryl CH₃). μ_{eff} (300 MHz, C₆D₆, 25°C): 1.94 μ_B. Anal. Calc. for C₃₆H₃₆D₁₈MoN₃I: C, 56.17; H, 7.07; N, 5.46. Found: C, 56.15; H, 6.90; N, 5.34%.

4.4. Synthesis of (NC)Mo(N[R]Ar)₃ (**14**)

A solution of 494 mg [NⁿBu₄][CN] (1.841 mmol) in 3 ml of THF was chilled to –35°C and added via pipette to a chilled, brilliant green solution containing 1.181 g IMo(N[R]Ar)₃ (**16**, 1.534 mmol) in 20 ml of THF. The reaction mixture was allowed to warm to ambient temperature and was stirred for 2 h. At this time, 30 ml of pentane was added to precipitate the salts, and the slurry was then filtered through a sintered glass frit. The red filtrate was dried to a solid, and addition of 25 ml of OEt₂ partially dissolved the solid. The undissolved solid was collected by filtration as a first pure crop (502 mg), and storage of the ethereal filtrate afforded a second crop (284.6 mg) for an overall 77% yield of pure (NC)Mo(N[R]Ar)₃ (**14**). ²H-NMR (76 MHz, THF, 25°C): δ = 31.0 ppm (s, Δ_{v_{1/2}} = 13 Hz, C(CD₃)₂CH₃). SQuID (5–300K): μ_{eff} = 2.81 μ_B. μ_{eff} (300 MHz, 25°C, C₆D₆) = 2.46 μ_B. An FT-IR spectrum did not show a ν_{CN} stretch. Anal. Calc. for C₃₇H₃₆D₁₈N₄Mo: C, 66.44; H, 8.14; N, 8.37. Found: C, 66.19; H, 8.20; N, 7.99%.

4.5. Synthesis of $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (**15**)

Solid orange $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**, 378 mg, 0.588 mmol) was added to a stirring red solution of $(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**14**, 393.1 mg, 0.588 mmol) in 10 ml of a 4:1 ether/benzene mixture at 25°C. The mixture, which attained a brilliant violet color quickly upon mixing, was stirred for 1 h after which time the solvent was removed in vacuo. The resulting solid was collected on a sintered glass frit and washed thoroughly with pentane to remove a dark brown, pentane-soluble impurity. The violet solid which remained was sparingly soluble in both pentane and in ether. It was dried to a mass of 618 mg (80% yield) and was found to be spectroscopically and analytically pure. ^2H -NMR (46 MHz, THF, 25°C): $\delta = 6.6$ ppm (s, $\Delta\nu_{1/2} = 36$ Hz, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 3.3 ppm (s, $\Delta\nu_{1/2} = 21$ Hz, $\text{C}(\text{CD}_3)_2\text{-CH}_3$). SQUID (5–300K): $\mu_{\text{eff}} = 1.61 \mu_{\text{B}}$. UV–vis (THF): $\lambda = 350$ nm, 425 nm, 530 nm. FTIR (THF, KBr): 1575 cm^{-1} (overlapping with ligand aryl CC stretch). Anal. Calc. for $\text{C}_{73}\text{H}_{72}\text{D}_{36}\text{N}_7\text{Mo}_2$: C, 66.84; H, 8.30; N, 7.47. Found: C, 66.53; H, 8.32; N, 7.30%.

4.6. Synthesis of

$(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}(\mu\text{-NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**19**)

Solid $(\mu\text{-CN})\{\text{Mo}(\text{N}[\text{R}]\text{Ar})_3\}_2$ (**15**, 377 mg, 0.287 mmol) was added to a 0.40% w/w stirring sodium amalgam (9.5 mg Na in 2.38 g Hg, 0.413 mmol Na) in 5 ml of THF under N_2 . Within 30 min the solution had turned from the intense red–purple of **15** to a deep orange color. An FTIR spectrum after 45 min showed an intense stretch at 1584 cm^{-1} likely resulting from overlapping ν_{CN} and ν_{CC} vibrations. An aliquot of the reaction mixture was removed after 1 h, dried in vacuo, triturated with hexane, and extracted into C_6D_6 containing hexamethyldisiloxane as an internal standard. A ^1H -NMR spectrum of this aliquot showed that $(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}(\mu\text{-NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ had been generated in approximately 90% yield (based on the starting material **15**) by this time. Stirring was continued for an additional 2 h at 25°C, after which time the solvent was removed in vacuo and the crude mixture was triturated with hexane. The resulting product was extracted into pentane, filtered through Celite, and dried in vacuo. The product was difficult to recrystallize from hydrocarbon solvents due to its high lipophilicity, but was obtained in ca. 50% yield (215 mg) as a spectroscopically pure substance by precipitation from hexamethyldisiloxane. The orange powder thus obtained was then recrystallized to afford orange crystals in low yield. ^1H -NMR (300 MHz, C_6D_6 , 25°C): Assignments for respective ligands are listed separately for the two metal centers: $(\text{Ar}[\text{R}]\text{N})_2(\text{ArN})\text{Mo}$: 6.93 (aryl *ortho* C–H), 6.74 (aryl *para* C–H), 6.45 (imido aryl *para*

C–H), 6.41 (imido aryl *ortho* C–H), 2.23 (aryl CH_3), 2.16 (imido aryl CH_3), 1.60 ($\text{C}(\text{CD}_3)_2\text{CH}_3$). $(\text{Ar}[\text{R}]\text{N})_3\text{Mo}$: 6.70 (aryl *para* C–H), 6.08 (aryl *ortho* C–H), 2.13 (aryl CH_3), 1.62 ($\text{C}(\text{CD}_3)_2\text{CH}_3$). ^{13}C -NMR (125.66 MHz, C_6D_6 , 25°C): 153.4, 151.2, 137.8, 137.4, 131.3, 129.1, 127.8, 127.4, 159.8, 122.2, 116.3, 62.7, 61.5, 34.6, 32.7, 22.0, 21.9, 21.8. Anal. Calc. for $\text{C}_{70}\text{H}_{69}\text{D}_{30}\text{N}_7\text{Mo}_2$: C, 66.69; H, 7.95; N, 7.78. Found: C, 65.99; H, 8.09; N, 7.48%.

4.7. Synthesis of $[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**8**)

A solution of 419 mg $[\text{N}^n\text{Bu}_4][\text{CN}]$ (1.560 mmol) in 15 ml of THF was added to a stirring solution of 1.340 g $\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**5**, 1.560 mmol) in 20 ml of THF. The reaction mixture turned from the orange color of **5** to an intense blue upon mixing. Stirring was continued for 10 min after which time the solvent was removed in vacuo, leaving a blue residue. Pentane (10 ml) was added to the crude residue to form a slurry, filtration of which on a sintered glass frit provided a blue, pentane-insoluble solid. This solid was washed $\times 2$ with 5 ml of a 1:1 pentane–benzene mixture, and then it was washed with pentane until the washings were colorless. The blue powder, $[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**8**), was dried to a weight of 1.605 g (91% yield). FTIR: $\nu_{\text{CN}} = 1929$ cm^{-1} (THF, CaF_2). Anal. Calc. for $\text{C}_{71}\text{H}_{108}\text{N}_5\text{Mo}$: C, 75.63; H, 9.65; N, 6.21. Found: C, 75.46; H, 9.69; N, 6.15%.

4.8. Reaction of $[\text{N}^n\text{Bu}_4][\text{CN}]$ with $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**)

Solid white $[\text{N}^n\text{Bu}_4][\text{CN}]$ (181.5 mg, 0.679 mmol) was dissolved in 10 ml of THF in a scintillation vial. Crystalline $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**1**, 436.7 mg, 0.679 mmol) was added slowly to the solution in small portions. The color turned to an inky black–blue quickly, and an intense purple color was not observed. A crude ^2H -NMR spectrum showed a signal at 6.1 ppm and several peaks between 0 and 2 ppm. A repetitive pentane extraction process left behind 100 mg of an insoluble blue solid which was identified by spectroscopy as $[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3]$ (**6**). ^2H -NMR (76 MHz, THF, 25°C): $\delta = 6.1$ ppm (s, $\Delta\nu_{1/2} = 8$ Hz, $\text{C}(\text{CD}_3)_2\text{CH}_3$). FTIR: $\nu_{\text{CN}} = 1941$ cm^{-1} (THF, CaF_2). Elemental analysis was not obtained.

4.9. Synthesis of $[\text{Li}(\text{THF})_x][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**20**)

A slurry of 1.037 g of $\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**5**, 1.2071 mmol) was prepared in 15 ml of THF and cooled to -35°C . While stirring this mixture, 324.1 mg $[\text{N}^n\text{Bu}_4][\text{CN}]$ (1.207 mmol) was added to it as a solid, in one portion. After stirring for 45 min, 51.2 mg of

LiCl was added to the blue solution, effecting a color change to blue purple. After 16 h of stirring the mixture an FTIR spectrum was indicative of incomplete cation exchange. An additional 375 mg LiCl was added to the reaction mixture and stirring was continued for an additional 24 h. The solvent then was removed in vacuo, and the resulting residue was triturated with pentane. The powder thereby obtained was extracted into 25 ml pentane and filtered through celite. Storage of the pentane filtrate at -35°C afforded 618.1 mg of red-violet crystals. A $^1\text{H-NMR}$ spectrum showed broad signals at $\delta = 4.45, 3.75, 1.74, 1.50,$ and 1.40 ppm. An X-ray crystallographic study of one such crystal was consistent with the proposed formulation $[\text{Li}(\text{THF})_x][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**20**, where $x = 3$). Unfortunately, successful refinement of the structure was hampered by disorder problems involving the tetrahydrofuran moieties. Analytical data are presumed to be indicative of variable amounts of tetrahydrofuran solvent. Anal. Calc. for $\text{C}_{67}\text{H}_{96}\text{N}_4\text{LiMoO}_3$: C, 72.60; H, 8.73; N, 5.06. Found: C, 70.56; H, 7.61; N, 5.44. Chemical characterization of **20** was obtained via silver triflate oxidation (see Section 4.10), which was found smoothly to produce neutral $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**13**).

4.10. Synthesis of $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**13**)

Solid blue $[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**8**, 24.2 mg, 0.0215 mmol) and orange $[\text{FeCp}_2][\text{O}_3\text{SCF}_3]$ (7.2 mg, 0.0215 mmol) were weighed into a 20 ml scintillation vial equipped with a magnetic stir bar. Addition of ether (3.5 ml) with stirring effected a rapid color change to red. The ν_{CN} stretch for starting material **8** decayed away and no new ν_{CN} stretch was observed. Filtration of the mixture, followed by solvent removal in vacuo, gave a reddish residue the $^1\text{H-NMR}$ spectrum (C_6D_6) of which showed Cp_2Fe (4.00 ppm) and broad signals for $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**13**) as follows: $\delta = 13.5, 8.1, 4.1, 2.5, 1.3, -4.0, -7.8,$ and -13.6 ppm. The solid material was recovered by drying in vacuo. Subsequent pentane washing of this solid effected the removal of orange ferrocene and left behind a red powder, that once dried, was analytically pure $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**13**). Anal. Calc. for $\text{C}_{55}\text{H}_{72}\text{N}_4\text{Mo}$: C, 74.63; H, 8.20; N, 6.32. Found: C, 74.95; H, 8.38; N, 6.21%.

Compound **13** also was obtained in 74% yield subsequent to treatment of the lithium derivative **20** (0.319 mmol) with silver triflate (82 mg, one equivalent) in ether.

4.11. Synthesis of $(\text{Ar}[\text{Ad}]\text{N})_3\text{Mo}(\mu\text{-CN})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**21**)

Red $(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**13**, 190.9 mg, 0.2157 mmol) was stirred in 10 ml ether and the mixture was cooled to -35°C . Orange $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (1, 138.6 mg,

0.2157 mmol) was then added. The reaction mixture turned to an inky violet color rapidly and was stirred for an additional 15 min at 25°C . Some solid particulate material precipitated from solution and 2 ml of THF was added to achieve homogeneity. Filtration and storage of the solution at -35°C for 12 h produced 175 mg (53%) of solid burgundy $(\text{Ar}[\text{Ad}]\text{N})_3\text{Mo}(\mu\text{-CN})\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (**21**). $^2\text{H-NMR}$ (76 MHz, THF, 25°C): $\delta = 6.8$ ppm (s, $\Delta\nu_{1/2} = 60$ Hz, $\text{C}(\text{CD}_3)_2\text{CH}_3$). FTIR (THF, CaF_2): $\nu_{\text{CN}} = 1575$ cm^{-1} (overlapping with ligand aryl CC stretch). Anal. Calc. for $\text{C}_{91}\text{H}_{108}\text{D}_{18}\text{N}_7\text{Mo}_2$: C, 71.53; H, 8.31; N, 6.42. Found: C, 70.98; H, 8.29; N, 6.40%.

4.12. Synthesis of $(\text{Ar}_F[\text{R}]\text{N})_2\text{V}(\mu\text{-NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**23**)

A chilled (-35°C) green-brown solution of $\text{IV}(\text{N}[\text{R}]\text{Ar}_F)_2$ (**22**, 146.4 mg, 0.266 mmol) in ether (3 ml) was added dropwise over ca. 20 s to a chilled slurry of $[\text{N}^n\text{Bu}_4][(\text{NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3]$ (**8**, 300 mg, 0.266 mmol) in 5 ml of a 4:1 THF-ether mixture at -35°C . The reaction mixture began rapidly to turn orange-brown and stirring was continued for 1 h at 25°C , after which time pentane (5 ml) was added to induce salt precipitation. Filtration of the mixture through celite, drying in vacuo, and trituration with pentane provided 351 mg of a dark orange-brown powder. The crude powder thus obtained was ca. 60% pure judging by $^2\text{H-NMR}$ spectroscopy. Recrystallization from ether afforded $(\text{Ar}_F[\text{R}]\text{N})_2\text{V}(\mu\text{-NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**23**, 105 mg, 30%) as a dark orange solid. $^2\text{H-NMR}$ (76 MHz, OEt_2 , 25°C): $\delta = 17$ ppm (s, $\Delta\nu_{1/2} = 600$ Hz, $\text{C}(\text{CD}_3)_2\text{CH}_3$). μ_{eff} (300 MHz, 25°C , C_6D_6) = $1.70 \mu_{\text{B}}$. FTIR: ν_{CN} (tentative) = 1615 cm^{-1} (OEt_2 , KBr). Anal. Calc. for $\text{C}_{77}\text{H}_{90}\text{D}_{12}\text{F}_2\text{MoN}_6\text{V}$: C, 70.67; H, 7.86; N, 6.42. Found: C, 71.22; H, 7.53; N, 6.16%.

4.13. X-ray structure of $(\text{Ar}_F[\text{R}]\text{N})_2\text{V}(\mu\text{-NC})\text{Mo}(\text{N}[\text{Ad}]\text{Ar})_3$ (**23**)

Deep orange crystals of **23** were grown from an ether solution at -35°C . The crystals were transferred from a scintillation vial to a microscope slide and coated with Paratone N oil (an Exxon product). A dark orange plate was selected and mounted on a glass fiber using wax. A total of 11 301 reflections were collected ($-8 \leq h \leq 15$, $-18 < k \leq 17$, $-19 \leq l \leq 19$) in the θ range of 1.18 – 20.00° of which 6993 were unique ($R_{\text{int}} = 0.0626$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. A troublesome molecule of ether was present in the asymmetric unit and included during refinement (atom labels C1 C2, C3, C4, O1). This ether molecule did not refine very well but all atoms in the asymmetric unit were refined anisotropically. The ^tBu group connected to

N(4) was disordered and modeled as two positions at half occupancy. All non-hydrogen atoms were placed in calculated ($d_{C-H} = 0.96 \text{ \AA}$) positions. The largest peak and hole in the difference map were 1.043 and $-0.453 \text{ e \AA}^{-3}$, respectively. No absorption correction was applied. The least-squares refinement converged normally with residuals of R (based on F) = 0.1012, ωR (based on F^2) = 0.2323, and Goodness-of-fit = 1.109 based upon $I > 2\sigma(I)$. Crystal data for $C_{81}H_{103}F_2MoN_6V$: triclinic, space group = $P\bar{1}$, $z = 2$, $a = 13.5574(9) \text{ \AA}$, $b = 16.3838(11) \text{ \AA}$, $c = 17.5538(12) \text{ \AA}$, $\alpha = 92.6060(10)^\circ$, $\beta = 99.8760(10)^\circ$, $\gamma = 98.0680(10)^\circ$. $V = 3793.7(4) \text{ \AA}^3$, $\rho_{\text{calc.}} = 1.192 \text{ g cm}^{-3}$, $F(000) = 1444$.

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