# Reactions of Organic Nitriles with a Three-Coordinate Molybdenum(III) Complex and with a Related Molybdaziridine-Hydride

Yi-Chou Tsai, Frances H. Stephens, Karsten Meyer, Arjun Mendiratta,
Mircea D. Gheorghiu, and Christopher C. Cummins*

*Department of Chemistry, Room 2-227, Massachusetts Institute of Technology,*
*77 Massachusetts Avenue, Cambridge, Massachusetts 02139*

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Reactions of nitriles RCN with the sterically encumbered $Mo(N[t\text{-}Bu]Ar)_3$ (**1**, Ar = 3,5-$C_6H_3Me_2$) or the somewhat less hindered $Mo(H)(\eta^2\text{-}Me_2CNAr)(N[i\text{-}Pr]Ar)_2$ (**2**) have been investigated. Where R = Me or Ph, reaction with **1** results in reductive nitrile coupling and the formation of a diiminato product $[\mu\text{-}NC(R)C(R)N][\mathbf{1}]_2$. In contrast, reaction of **1** with $Me_2NCN$ surprisingly results in a stable, albeit highly congested, $\eta^2$ adduct of the nitrile. When the less sterically hindered **2** is used, reaction with PhCN gives the diiminato product analogous to the one mentioned for the *tert*-butyl system, $[\mu\text{-}NC(Ph)C(Ph)N][Mo(N[i\text{-}Pr]Ar)_3]_2$, where molybdaziridine-hydride **2** has provided access to the three-coordinate $Mo(N[i\text{-}Pr]Ar)_3$ (**3**) moiety. Use of a more bulky nitrile such as MesCN (Mes = 2,4,6-$C_6H_2Me_3$) results in formation of a bis-$\eta^1$ compound, $(\eta^1\text{-}MesCN)_2[\mathbf{3}]$. Use of 9-anthracenylcarbonitrile results in head-to-tail C−C coupling of two monomers via the anthracenyl moiety. Detailed variable-temperature EPR and $^2H$ NMR data are included for both molybdenum-containing starting materials and selected reaction intermediates and products.

## Introduction

For several years, we have investigated molybdenum trisamide fragments $Mo(N[t\text{-}Bu]Ar)_3$ (**1**, Ar = 3,5-$C_6H_3Me_2$) and $Mo(N[i\text{-}Pr]Ar)_3$ (**3**) because of their remarkable capacity for informative small-molecule activation; while the former *tert*-butyl-substituted complex is isolable as a three-coordinate monomer with a quartet ground state,[1−8] the latter isopropyl-substituted derivative reacts as though it were three-coordinate but is obtained as its doublet ground-state molybdaziridine-hydride tautomer $Mo(H)(\eta^2\text{-}Me_2CNAr)(N[i\text{-}Pr]Ar)_2$ (**2**).[9−11]

An operating hypothesis has been that the *tert*-butyl-substituted variant is sufficiently crowded that its Mo center can expand to a maximum coordination number of four,[7] either through the binding of terminal functionality or through the addition of a single atom, as in the system's terminal nitride,[1−3,12,13] phosphide,[4,14,15] and carbide[8,16,17] complexes. On the other hand, due to its more open nature, the *iso*-propyl-substituted system can not only expand its coordination number to five, it may coordinate substrates in an $\eta^2$ fashion.[9−11] An example of this is the ready complexation of benzophenone giving $(\eta^2\text{-}OCPh_2)[\mathbf{3}]$ for the isopropyl system while, in contrast, the *tert*-butyl system exhibits *no reaction* with benzophenone when an equimolar solution of the two is prepared. Generally speaking, reaction chemistry is simplified for the *tert*-butyl system in relation to the more open isopropyl derivative.

While originally begun as a comparative study of the reactivity of these two systems with organic nitriles, this work became substantially enriched due to the many unexpected phenomena encountered. Discussed are examples of nitriles capable of coordinating $\eta^2$ to the crowded *tert*-butyl-substituted system, nitriles that couple head-to-head or head-to-tail upon treatment with either Mo system, and nitriles that bind $\eta^1$ to the isopropyl-substituted system.

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* Address correspondence to this author. Fax: (617) 258-5700. E-mail: ccummins@mit.edu.

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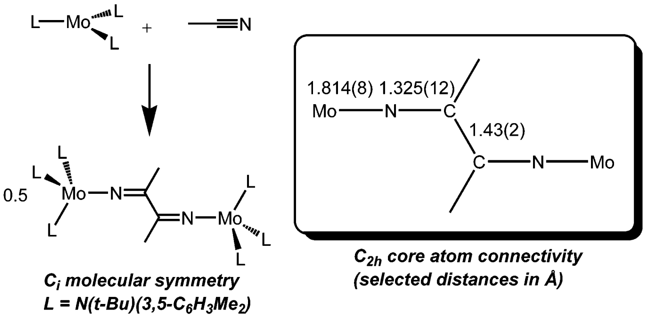

*$C_i$ molecular symmetry*
*L = N(t-Bu)(3,5-$C_6H_3Me_2$)*

*$C_{2h}$ core atom connectivity (selected distances in Å)*

**Figure 1.** Acetonitrile coupling to form ($\mu$-NC($CH_3$)C($CH_3$)N)[**1**]$_2$.

It has been possible to study many reactions of the molybdenum trisamides by $^2$H NMR and EPR spectroscopies. In certain cases, analogues of the intermediates in the nitrile coupling reactions could be rendered isolable by judicious substitution; such isolable analogues served as models and as aids to the interpretation of the spectra of reacting systems. Since the molybdaziridine-hydride system has a doublet ground state and a very characteristic EPR spectrum, a careful EPR study of it and several deuterated variants was carried out before attempting to interpret EPR spectra obtained upon interaction with organic nitriles. Thus, this work has provided not only a wealth of information concerning available modes of organonitrile manipulation by reducing, low-coordinate metal fragments, but also some fundamental characterization data pertaining to such fragments.

## Results and Discussion

**Dimerization of Nitriles by Mo(N[*t*-Bu]Ar)$_3$.** A new, facile, inexpensive synthesis of *N*-*tert*-butyl-3,5-dimethylaniline has been developed. Reaction of 2,4,6-trimethylpyrillium tetrafluoroborate with *tert*-butylamine in acetonitrile yields HN[*t*-Bu]Ar on scales greater than 100 g. Subsequent synthesis of **1** via addition of $MoCl_3(THF)_3$ to LiN[*t*-Bu]Ar·$OEt_2$ proceeds as reported previously.[1] Mixing **1** with 1 equiv of acetonitrile in ethereal solution leads to 1:1 binding and dimerization as depicted in Figure 1. The green dimer so obtained was isolated in 77% yield after it precipitated from the reaction mixture; the dimer may be considered the product of reductive coupling where each nitrile has been reduced by one electron in a fashion reminiscent of pinacol coupling. The X-ray crystal structure of this diiminato product, [$\mu$-NC(Me)C(Me)N][**1**]$_2$, has been reported previously in brief.[18] Important structural parameters are included in Figure 1. A crystallographic center of inversion resides at the midpoint of the newly furnished C−C bond, such that the bridging NC(Me)−C(Me)N ligand is, neglecting hydrogen atoms, perfectly planar.

The nitrile-derived nitrogen atoms in this dimer may be thought to bind to Mo essentially as would those in typical monodentate ketimide (N=CR$^1$R$^2$) ligands,[19,20] with the perturbation that two such functionalities are now juxtaposed and conjugated. Back-bonding from the d$^2$ molybdenum centers to the nitrile-derived NC $\pi$* orbitals is permitted in the plane *perpendicular* to that defined by the $C_{2h}$-symmetric Mo−N−C−C−N−Mo molecular core, as part of a topologically linear 8-electron $\pi$ system spanning the six core atoms. With reference to the $C_{2h}$ molecular core, $\pi$ donation from the two N lone pairs to otherwise empty Mo d orbitals is permitted by symmetry *within* the $\sigma_h$ plane.

Due to acetonitrile's frequent use as a solvent in coordination chemistry, there are several previous reports of its participation in both 2e and 4e reductive coupling leading to respectively bridging diiminato and enediimido moieties. McCarley and co-workers showed in 1975 that, under reducing conditions involving added zinc, tantalum and niobium halides effect the reductive coupling of acetonitrile, with {[$\mu$-NC(Me)C(Me)N][$NbCl_4$(NCMe)]$_2$}$^{2-}$ having been characterized crystallographically.[21] An enediimido formulation for the inversion-symmetrical diamagnetic dimer is suggested by the pertinent bond distances C=C, 1.35(1) Å, and C−N, 1.378(8) Å. Such a formulation was embraced by Cotton and Hall, who carried out a crystal structure determination on the related ditantalum complex, [$\mu$-NC(Me)=C(Me)N][$TaCl_3(THF)_2$]$_2$.[22] The latter evinced a central C=C distance of 1.347(16) Å and an N−C distance of 1.405(10) Å. As shown by de Bier and Teuben,[23] a pair of titanium(III) centers can be used in combination to effect 2e reductive coupling of organic nitriles; in this way they isolated diiminato derivatives of formula [$\mu$-NC(R)C(R)N][$Cp_2TiR$]$_2$, structures for which have not been reported. Gambarotta and co-workers isolated the diamagnetic enediimido complex [$\mu$-*trans*-NC(Me)=C(Me)N][$TiCl_2$(TMEDA)]$_2$ upon dissolution of their titanium(II) precursor in neat acetonitrile,[24] postulating carbene-like character for the unobserved $\eta^1$-coordinated nitrile complex intermediate. Their enediimido derivative exhibited a central C=C bond distance of 1.337(10) Å and an N−C distance of 1.384(5) Å. In contrast, Templeton and co-workers found that treatment of {HB($Me_2pz)_3$}W(CO)$_3$Br with NaS-*i*-Pr in refluxing acetonitrile led to formation of a 2,3-butanediiminato derivative, [$\mu$-NC(Me)C(Me)N][W(CO)$_2${HB($Me_2pz)_3$}]$_2$.[25] The latter complex is characterized by a central C−C bond distance of 1.40(4) Å and a C=N bond distance of 1.28(3) Å; interestingly, the bridging diiminato functionality was found in this case to deviate strongly from planarity (dihedral angle 54.4 °).

To summarize, it is clear from the foregoing discussion of structural parameters that enediimido bridging ligands are readily distinguished from their diiminato counterparts in that the central C−C bond is shorter than the flanking C−N bonds in the enediimido case, but longer in the diiminato formulation.

As discussed above, reductive dimerization of organic nitriles (in a fashion reminiscent of pinacol coupling)

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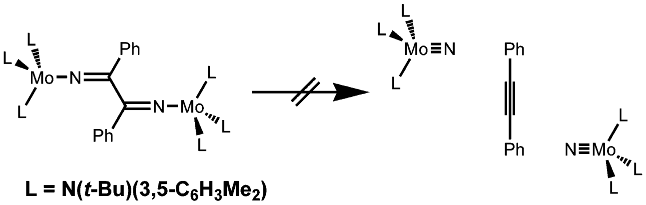

**Figure 2.** Thermolysis of the diiminato does not result in the formation of an alkyne and 2 equiv of molybdenum nitride.

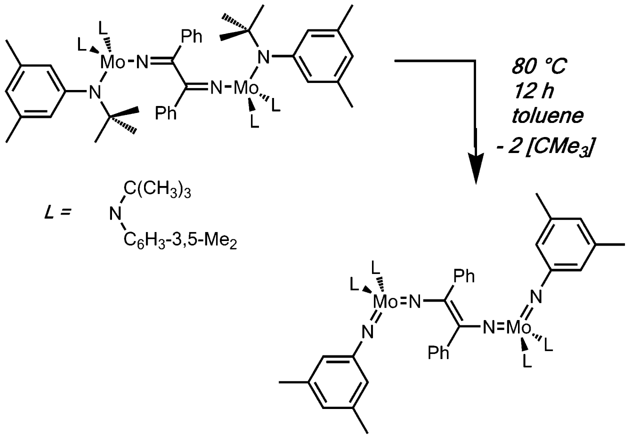

**Figure 3.** Thermal ejection of two *tert*-butyl radicals from **1** thereby generating the enediimido ($\mu$-N-CPh=CPh-N)-[Mo(NAr)(N[*t*-Bu]Ar)$_2$]$_2$.

has been effected previously by well-defined coordination complexes and organometallic systems, but *not* by any that result in a d$^2$/d$^2$ coupling product. This is significant because, as portrayed in Figure 2, double C−N homolysis from the dimer could in principle occur to provide 2 equiv of the known d$^0$ terminal nitrido complex NMo(N[*t*-Bu]Ar)$_3$ ($D_{\text{MoN}}$ = 155 kcal/mol)[7,12,13] along with diphenylacetylene. Such a transformation would be a 3-electron aza-analogue of the 2-electron McMurry reaction.[26] However, the type of fragmentation of ($\mu$-NC(Ph)C(Ph)N)[**1**]$_2$ suggested in Figure 2 was observed neither at room temperature nor upon extended heating (2 h in toluene-$d_8$ at 100 °C). Instead, upon thermolysis a double *tert*-butyl radical ejection was observed, as illustrated in Figure 3. This unusual reaction provides a pathway for conversion of molybdenum from its +4 to its +6 oxidation state, the redox being coupled with Mo−N multiple bond formation. In fact, the bridging diiminato ligand formally accepts 2 electrons and becomes an enediimido function, while 1e reduction each of two N−C bonds accounts for expulsion of two *tert*-butyl radicals; *tert*-butyl radical disproportionation and combination products isobutylene, isobutene, and hexamethylethane were observed by $^1$H NMR spectroscopy. Although the N(*t*-Bu)(3,5-C$_6$H$_3$Me$_2$) ancillary ligand is generally quite robust and resistant to intramolecular decomposition reactions, *tert*-butyl radical ejection from it—coupled with oxidation of the metal center—has been seen previously.[27]

**$^2$H NMR Investigation of Nitrile Coupling Reactions of Mo(N[*t*-Bu]Ar)$_3$.** In no case to date has a detailed mechanistic study been carried out to address the nature of intermediates involved in nitrile reductive coupling reactions. Reactions of transition metal-coordinated nitriles were reviewed in 1996,[28] while a more recent (2002) review of additions to metal-activated organonitriles provides little new information on nitrile reductive coupling.[29] In the present work, $^2$H NMR and EPR studies of reaction mixtures have provided substantial mechanistic insight.

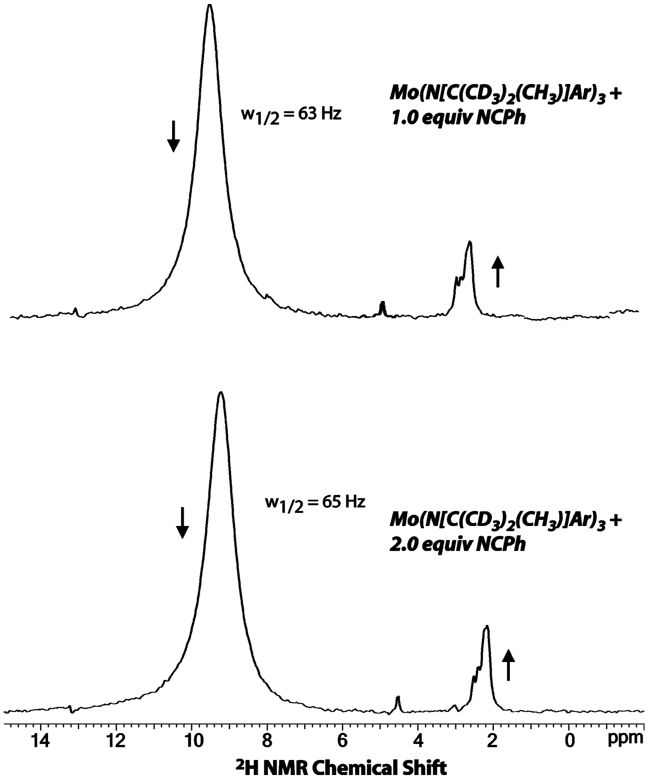

**Figure 4.** $^2$H NMR spectra of a mixture of **1**-$d_{18}$ and 1 (top) and 2 (bottom) equiv of PhCN recorded in Et$_2$O.

Monitoring in situ the progress of paramagnetic reaction mixtures by $^2$H NMR spectroscopy is facilitated by the use of the $d_{18}$ variant Mo(N[C(CD$_3$)$_2$CH$_3$]Ar)$_3$ (**1**-$d_{18}$); this complex exhibits a diagnostic $^2$H NMR signal at 64 ppm.[3] Interrogation of a 1:1 or 1:2 mixture of **1**-$d_{18}$ and PhCN in ether by $^2$H NMR spectroscopy revealed complete conversion upon mixing to a single new species exhibiting a peak at 9.5 ppm ($w_{1/2}$ = 65 Hz, Figure 4). Because the extra added equivalent of benzonitrile had no effect on the observed $^2$H NMR spectrum, the new complex can be assigned as the mononuclear 1:1 adduct (PhCN)[**1**-$d_{18}$]. A small peak close to 2.0 ppm corresponds to the diamagnetic dimeric coupling product [$\mu$-NC(Ph)C(Ph)N][**1**-$d_{18}$]$_2$, which is formed quantitatively and irreversibly upon concentration of the mixture. Solutions containing the intermediate 1:1 adduct develop an intense blue-purple color, whereas upon workup and isolation, solutions of the dimeric coupling product are a very dark green color. Providing a stark contrast with the prompt dimerization of MeCN described above, it is most intriguing that the 1:1 adduct with benzonitrile displays a long lifetime in dilute solution at 25 °C.

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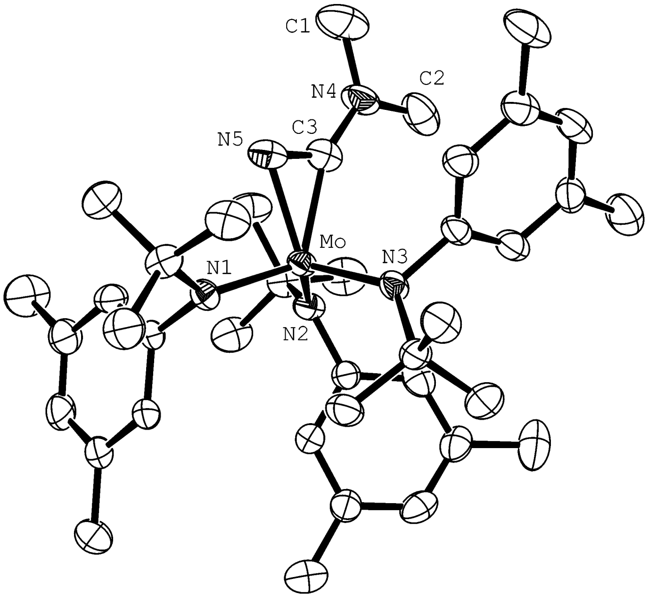
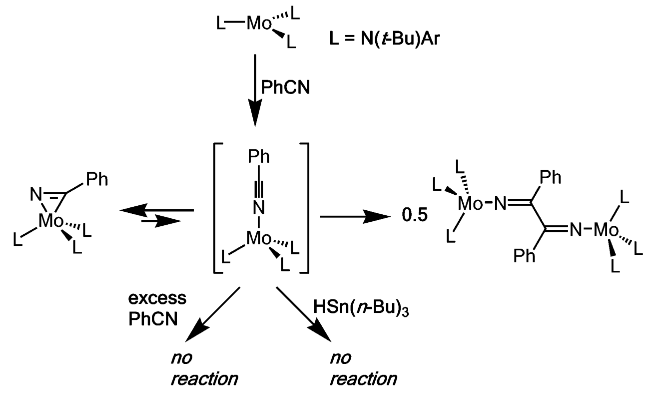


**Figure 5.** Thermal ellipsoid plot (35% probability) of ($\eta^2$-$Me_2NCN$)[**1**]. Selected bond distances (Å): Mo−N5, 2.030(5); Mo−C3, 2.037(6); N5−C3, 1.267(8); C3−N4, 1.346(8). Selected bond angles (deg): Mo−N5−C3, 72.1(4); Mo−C3−N5, 71.5(3); N5−Mo−C3, 36.3(2); N5−C3−N4, 130.9(6).

**Reaction of Mo(N[*t*-Bu]Ar)$_3$ with Dimethylcyanamide.** Interestingly, the reaction of $Me_2NCN$ (dimethylcyanamide) with **1**-$d_{18}$ permitted not only the spectroscopic *observation* of a 1:1 adduct ($^2$H NMR, $\delta$ = 7.1 ppm), but also its *isolation* in 63% yield. The 1:1 adduct was obtained as a green crystalline solid upon mixing of the reagents in *n*-hexane followed by concentration and cooling to −35 °C. An X-ray diffraction study (Figure 5) revealed an extremely surprising $\eta^2$ binding mode for the cyano functionality of the dimethylcyanamide ligand in the complex, ($\eta^2$-$Me_2NCN$)[**1**]. This is the first evidence that **1** *can* expand its binding pocket sufficiently to accommodate an $\eta^2$ interaction with unsaturated functionality. Normally, three N[*t*-Bu]Ar ligands pack in a pseudo-$C_3$ three-bladed propeller fashion in complexes of **1**;[3] here we are confronted with an unusual, splayed, low-symmetry ancillary ligand arrangement that presumably is forced by the strain of having to accommodate the $Me_2NCN$ ligand in an $\eta^2$ binding mode.

Complexation of organonitriles in an $\eta^2$ fashion is fairly well-documented. The first structurally characterized member of this class, described in 1986 by Wilkinson and co-workers, was $Cp_2Mo(\eta^2\text{-}NCCH_3)$.[30] This compound was found to have an N−C distance of 1.200(10) Å. As has been shown by Harman and co-workers,[31] the strong $\pi$-donating metal fragment $[W(bipy)(PMe_3)_2Cl]^+$ binds acetonitrile in an $\eta^2$ fashion and also gives rise to lengthening of the N−C bond, the observed bond distance being 1.267(7) Å, which is longer by ca. 0.12 Å than in free acetonitrile. Harman and co-workers subsequently prepared the neutral tungsten(II) $\eta^2$ acetonitrile complex, $W(PMe_3)_3Cl_2(\eta^2\text{-}NCCH_3)$, which was found by X-ray crystallography to have a C−N bond distance of 1.27(1) Å.[32] Our complex ($\eta^2$-$Me_2NCN$)[**1**] (Figure 5) exhibits a similar N−C bond distance for the coordinated nitrile functionality, namely 1.267(8) Å, which is consistent with the strong $\pi$-donor nature of the molybdenum trisamide fragment.

**Scheme 1**



Perhaps most relevant to the discussion of ($\eta^2$-$Me_2NCN$)[**1**] is Chisholm's study of dimethylcyanamide complexation by $Mo_2(ONp)_6$, where Np is neopentyl.[33] A crystal structure determination showed that the dimethylcyanamide ligand binds in a $\mu$-$\eta^1$,$\eta^2$ fashion in the complex $Mo_2(\mu\text{-}\eta^1,\eta^2\text{-}Me_2NCN)(\mu\text{-}ONp)(ONp)_5$, which also exhibits a dramatically lengthened *N*−*C*NMe$_2$ bond distance of 1.333(4) Å (longer by ca. 0.2 Å than that of the nitrile functionality in free dimethylcyanamide). As found for our complex, the dimethylcyanamide ligand is planar (ignoring hydrogen atoms) such that the $NMe_2$ lone pair is conjugated with the $\pi$ system of the azamolybdacyclopropene moiety.

Based on the similar $^2$H NMR chemical shift and line width properties for both the $Me_2NCN$ and PhCN adducts of **1**-$d_{18}$, it is probable that the long-lived 1:1 PhCN adduct has an $\eta^2$-bonded structure as demonstrated in Figure 5 for the $Me_2NCN$ adduct. If this is so, then the persistent nature of the benzonitrile adduct in solution can be explained as outlined in Scheme 1. As also depicted in Scheme 1, a fruitless attempt was made to intercept the putative $\eta^1$-PhCN adduct: dimerization to the corresponding diiminato derivative was not interrupted by addition of *n*-$Bu_3SnH$ to the system. The idea behind the *n*-$Bu_3SnH$ experiment was that the putative $\eta^1$-PhCN adduct central to Scheme 1 would have radical character at the nitrile carbon atom. It might therefore be able to abstract an H atom from *n*-$Bu_3SnH$ to give the ketimide derivative (PhCH=N)[**1**]. Ketyl complex intermediates have been intercepted and converted to alkoxides in such a fashion.[34−36] Evidently the $\eta^1$-PhCN adduct is not a potent H atom abstractor.

**Electron Paramagnetic Resonance Investigation of Mo(H)($\eta^2$-$Me_2CNAr$)(N[*i*-Pr]Ar)$_2$ and Its Isotopomers.** Prior to investigation of its reactions with nitriles, molybdaziridine-hydride **2** was subjected to a detailed EPR study. To aid the interpretation of the EPR

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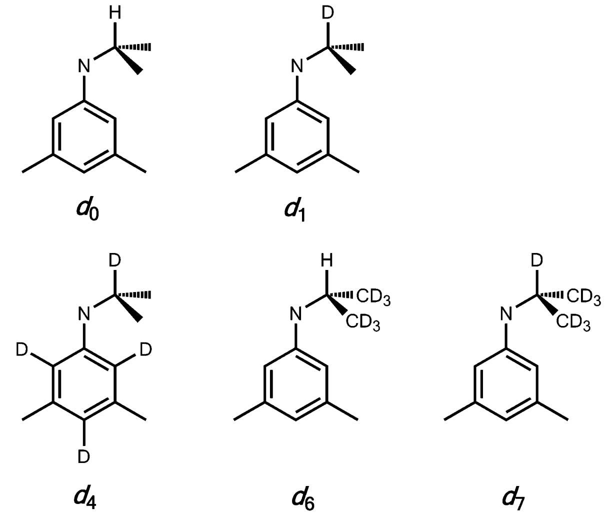

**Figure 6.** Isotopomers of the isopropyl ligand.

data, we prepared five isotopomers of the N(*i*-Pr)(3,5-$C_6H_3Me_2$) ligand as shown in Figure 6. In addition to the molybdaziridine-hydride/deuteride complexes derived from ligands $d_0$ and $d_1$, we have prepared additionally those derived from ligands $d_4$, $d_6$, and $d_7$; EPR spectra of the latter three derivatives contained no new or additional information. Incorporation of deuterium into the isopropyl methine position was accomplished by $LiAlD_4$ reduction of the appropriate acetone imine precursor, $Me_2C{=}NAr$, while exchange of deuterium into the aryl ring 2,4,6 positions as in the $d_4$ ligand variant employed conditions described in the literature.[37]

The most obvious feature in the EPR spectrum of **2** (Figure 7)[38] is the doublet splitting ($A_{iso}[^1H] = 16.4$ G) attributable to the presence of the terminal hydride ligand. Successful simulation of the observed spectrum was achieved by specifying four hyperfine couplings: $A_{iso}[^{95/97}Mo\ (25.5\%)] = 32.6$ G, $A_{iso}[^1H\ (99.99\%)] = 16.4$ G, $A_{iso}[^{14}N\ (99.63\%)] = 2.7$ (2 amido nitrogens) and 1.35 G (molybdaziridine nitrogen). To confirm our assignment of the doublet feature, the $d_3$-isotopomer Mo(D)($\eta^2$-$(CH_3)_2CNAr$)(N[CD$(CH_3)_2$]Ar$)_2$ (**2**-$d_3$) was prepared and likewise studied by EPR spectroscopy (Figure 8).[38] Successful simulation of the EPR spectrum of **2**-$d_3$ was achieved by using the same $A_{iso}$ $^{95/97}$Mo and $^{14}$N hyperfine coupling constants given above for the natural abundance isotopomer, substituting the value $A_{iso}[^2H\ (99.63\%)] = 2.4$ G for the hydride coupling. Clearly, upon replacement of the terminal hydride with deuteride, the doublet splitting collapses because the gyromagnetic ratio of $^2$H is approximately one-seventh that of $^1$H. The assignment is thus confirmed.

**Reaction of Molybdaziridine-Hydride with Benzonitrile.** Upon treatment with 1 equiv of benzonitrile, the molybdaziridine-hydride complex **2** provides access to the three-coordinate trisamide Mo(N[*i*-Pr]Ar$)_3$ (**3**). A benzonitrile adduct of **3**, presumed to be $\eta^2$ bonded, is formed that undergoes subsequent dimerization to a $\mu$-diiminato dimolybdenum complex. Noteworthy is the fact that the very distinctive EPR signals (Figure 7)[38] characteristic of **2** are lost completely upon nitrile binding. EPR characterization data for the intermediate $\eta^2$-PhCN adduct have been obtained and are compared in Figure 9[38] with those for the structurally characterized $\eta^2$-$Me_2NCN$ adduct of **1**, as well as with those for the previously described[9] and structurally characterized $\eta^2$-$OCPh_2$ adduct of **3**. The EPR data depicted in Figure 9[38] reveal that $S = {}^1/_2$ systems consisting of a molybdenum trisamide fragment bonded to a $\eta^2$ ketone or nitrile functionality have characteristic rhombic spectra. Confirmation that this should be so has been obtained with the aid of DFT calculations carried out on the full ($\eta^2$-$Me_2NCN$)[**1**] molecule, using structural data from the X-ray diffraction study. Observed and calculated (the latter in parentheses) *g* values for this system are as follows: $g_{11}$, 1.972 (1.987); $g_{22}$, 1.954 (1.972); $g_{33}$, 1.896 (1.916).

As in the case of PhCN coupling by the *tert*-butyl derivative, concentration of solutions 1:1 in PhCN and compound **2** gives rise irreversibly to an inversion-symmetrical coupling product. Due to its oily nature in this case the dimer was characterized most easily by conversion to its maroon monocation (triiodide salt). [(PhCN)(**3**)$]_2[I_3]$ was isolated in 86% yield following treatment of **2** with benzonitrile (1.1 equiv) in ether, solvent removal and replacement, and treatment of the resulting green solution with 1.5 equiv of molecular iodine. While the neutral coupled product [(PhCN)(**3**)$]_2$ is seen by cyclic voltammetry (Figure 10)[38] to be difficult to reduce, the complex displays *two* reversible oxidation waves −0.6 and −1.1 V versus the ferrocene/ferrocenium couple. Disproportionation of the monocation to equivalent amounts of dication and neutral is not an issue due to the disparity in $E_{1/2}$ values for the two oxidation products. Accordingly, the salt [(PhCN)(**3**)$]_2[I_3]$ was amenable to manipulation and could be crystallized from a methylene chloride/*n*-hexane mixture at −35 °C in a form suitable for study by X-ray diffraction.

Reported previously[9] was the X-ray structure of the neutral acetonitrile-coupled product ($\mu$-NC(Me)C(Me)N)[**1**$]_2$. Important structural parameters are the interatomic distances 1.814(8), 1.325(12), and 1.43(2) Å that correspond respectively to the MoN, NC, and CC′ distances in the molecule's central Mo−N−C(Me)−C(Me) core; a crystallographic center of inversion was situated at the midpoint of the newly furnished C−C bond (Figure 1). Note that 1.82 Å can be taken as the expectation value for a MoN double bond since this is the distance found for $C_i$-symmetric ($\mu$-N)[**3**$]_2$,[9] the molecular orbital picture for which entails a molybdenum−nitrogen bond order of *exactly* two. Thus, the valence bond picture that best describes the structurally characterized acetonitrile-coupled system is Mo=N=C(Me)−C(Me)=N=Mo.

The structure of [(PhCN)(**3**)$]_2^+$ (Figure 11) also incorporates a crystallographic center of inversion at the midpoint between the two coupled nitrile carbon atoms. The C−C interatomic distance at the point of coupling is 1.368(12) Å, and is sandwiched between two C−N bonds associated with an 1.393(8) Å interatomic distance. These values, along with a Mo−N interatomic distance of 1.740(5) Å, suggest that a substantial electronic reorganization has occurred upon 1e oxidation of the neutral coupled dimer. Most intriguing is the

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[37] Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783.

[38] Tsai, Y.-C. Ph.D. Thesis, Massachusetts Institute of Technology, 2002.

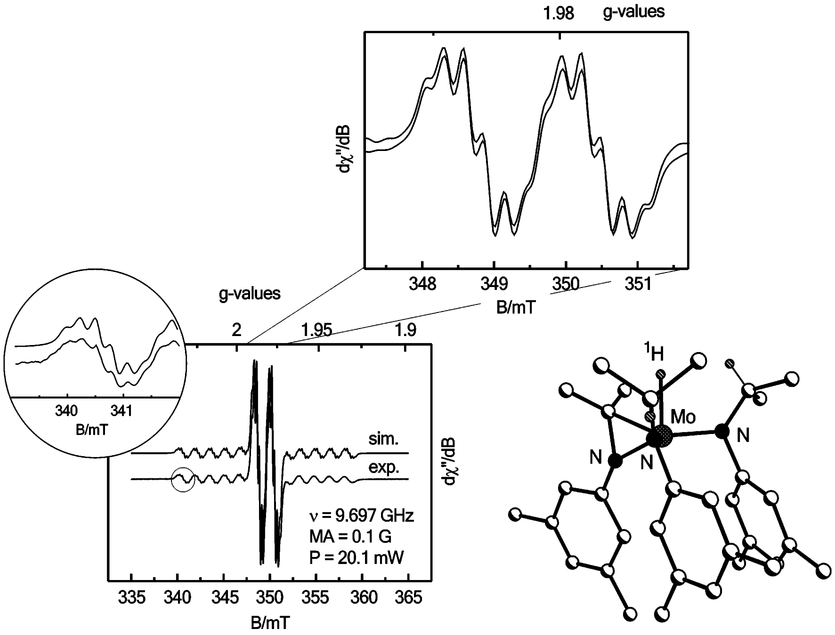

**Figure 7.** X-band EPR spectrum of **2** with inset of enlarged low-field signal and enlargement of main signal recorded in $Et_2O/n\text{-}C_5H_{12}$ (1:1) at 300 K. Experimental conditions: microwave frequency, $\nu = 9.697$ GHz; power, 20.1 mW; modulation amplitude, 0.1 G. Simulated parameters: $g_{iso} = 1.9825$; $A_{iso}[^{95/97}Mo\ (25.5\%)] = 32.6$ G (90.41 MHz); $A_{iso}[^{1}H\ (99.99\%)] = 16.4$ G (45.48 MHz); $A_{iso}[^{14}N\ (99.63\%)] = 2.75$ (2 amido ligands, 7.63 MHz) and 1.35 G (imino ligand, 3.74 MHz); line width, 1.94 G.

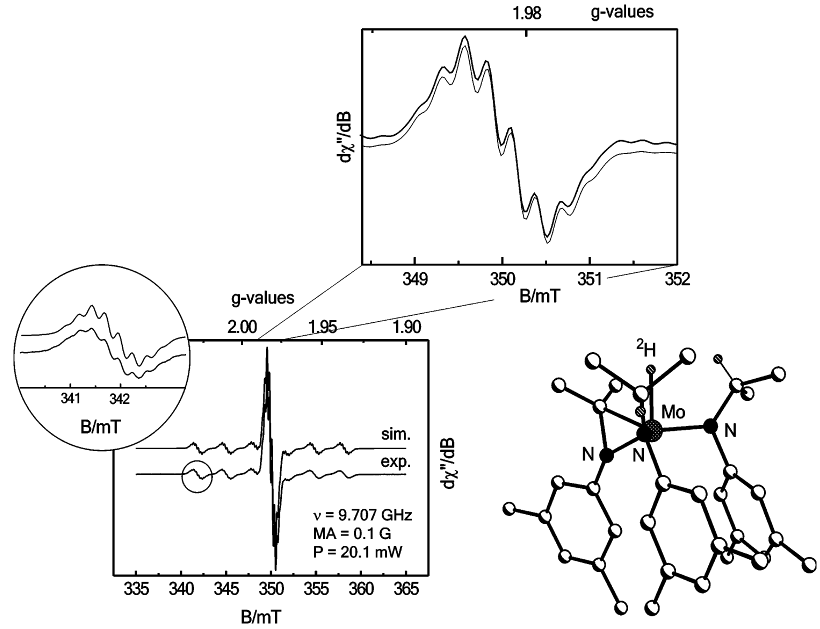

**Figure 8.** X-band EPR spectrum of **2**-$d_3$ with inset of enlarged low-field and enlargement of main signal recorded in $Et_2O/n\text{-}C_5H_{12}$ (1:1) at 300 K. Experimental conditions: microwave frequency, $\nu = 9.707$ GHz; power, 20.1 mW; modulation amplitude, 0.1 G. Simulated parameters: $g_{iso} = 1.9825$; $A_{iso}[^{95/97}Mo\ (25.5\%)] = 32.6$ G (90.41 MHz); $A_{iso}[^{2}H\ (99.63\%)] = 2.4$ G (6.66 MHz); $A_{iso}[^{14}N\ (99.63\%)] = 2.75$ (2 amido ligands, 7.63 MHz) and 1.35 G (imino ligand, 3.74 MHz); line width, 1.94 G.

contraction of the central C−C bond length upon oxidation; in effect, removal of an electron from the system converts the bridging ligand from the diiminato to the enediimido form. DFT studies carried out on the neutral model system ($\mu$-NC(H)C(H)N)[**1**]$_2$ in $C_i$ point symmetry reveal, as expected, that the HOMO belongs to the $A_g$ irreducible representation and is strongly C−C $\pi$ antibonding in character. An illustration is provided in Figure 12. This explains the ready 1- and 2-electron oxidations shown in Figure 10,[38] as well as the observed contraction in C−C bond distance upon oxidation.

**Variable-Temperature $^2$H NMR Study of Molybdaziridine-Hydride.** Further characterization data for molybdaziridine-hydride include variable-temperature $^2$H NMR spectra of the $d_{18}$-isotopomer Mo(H)($\eta^2$-$(D_3C)_2CNAr$)(N[CH(CD$_3$)$_2$]Ar)$_2$ (**2**-$d_{18}$) over the range 20−80 °C (see the Supporting Information). At ambient temperature are observed two relatively sharp peaks at 6 and 8 ppm, along with a rather broad peak at −18 ppm, consistent with the complex's time-averaged $C_s$ point group symmetry. Assignment of the signals can be made based on chemical shift and line width consid-

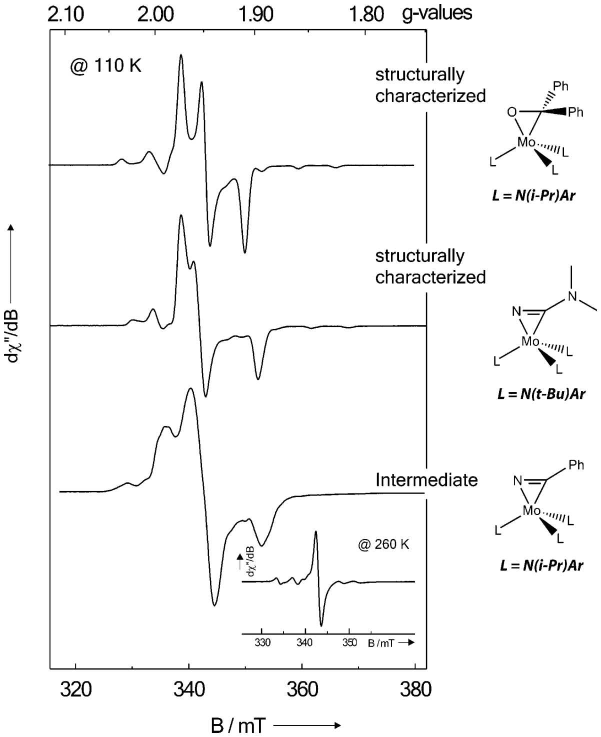

**Figure 9.** X-band EPR spectra of $(\eta^2\text{-OCPh}_2)$[**3**] (top): microwave frequency, $\nu = 9.351$ GHz; power, 1 mW; modulation amplitude, 5 G. $(\eta^2\text{-Me}_2\text{NCN})$[**1**] (middle): microwave frequency, $\nu = 9.707$ GHz; power, 1 mW; modulation amplitude, 5G. $(\eta^2\text{-NCPh})$[**3**] (bottom): microwave frequency, $\nu = 9.351$ GHz; power, 1 mW; modulation amplitude, 5 G. All spectra were recorded in frozen toluene solution at $T = 110$ K. The inset shows the isotropic spectrum of $(\eta^2\text{-NCPh})$[**3**] in liquid solution at $T = 260$ K. Experimental conditions: microwave frequency, $\nu = 9.351$ GHz; power, 1 mW; modulation aplitude, 5 G.

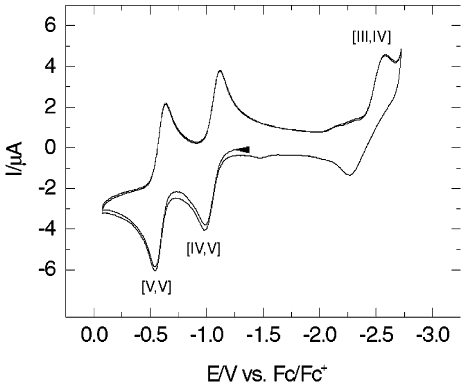

**Figure 10.** Cyclic voltammogram of [(PhCN)(**3**)]$_2$ recorded in THF solution containing 0.50 M TBAP. Scan rate is 0.10 V s$^{-1}$.

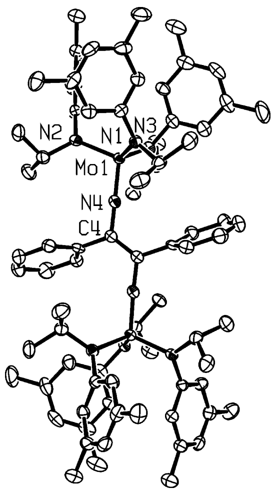

**Figure 11.** Thermal ellipsoid plot (35% probability) of [(PhCN)(**3**)]$_2$[I$_3$] (hydrogen atoms and counterion removed for clarity). Selected distances (Å): Mo1−N1, 1.921(5); Mo1−N2, 1.918(5); Mo1−N3, 1.929(5); Mo1−N4, 1.740(5); N4−C4, 1.393(8); C4−C4′, 1.368(12); I1−I2, 2.938(1); I2−I3, 2.896(1). Selected angles (deg): N1−Mo1−N2, 110.7(2); N2−Mo1−N3, 110.2(2); N3−Mo1−N1, 111.3(2); N4−Mo1−N1, 107.5(2); N4−Mo1−N2, 107.4(2); N3−Mo1−N4, 109.6(2); C4−N4−Mo1, 175.6(5); N4−C4−C4′, 120.6(7); I3−I2−I1, 177.22(3).

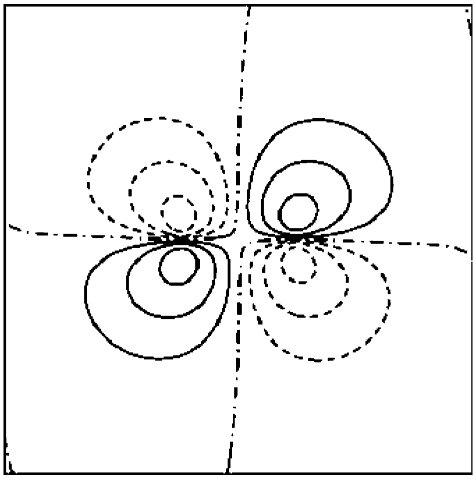

**Figure 12.** Contour plot (*xz* plane) of the $A_g$ HOMO, passing through the two carbon atoms, in the model structure $(\mu\text{-NC(H)-C(H)N})[\text{Mo(NH}_2)_3]_2$. The molecule is oriented such that the planar diiminato bridging ligand lies in the *yz* plane with the carbon atoms defining the *z* axis. Nodal surfaces are indicated by dash−dot−dash contours.

erations: the two sharp peaks are for the diastereotopic CH(CD$_3$)$_2$ groups while the broad signal signifies the $\eta^2$-bound (D$_3$C)$_2$C=NAr ligand. Upon raising the temperature to 80 °C, coalescence of the two sharp signals into a single peak is observed, and the −18 ppm signal is seen to broaden further into the baseline and to move downfield by approximately 5 ppm. Presumably, at temperatures of ca. 150−200 °C, coalescence of all three resonances would be observed. While the molybdaziridine-hydride exhibits thermal stability as judged by reversibility of the coalescence observed at 80 °C upon cooling back to room temperature, we have not yet pushed the highly reactive/sensitive system to still more extreme temperatures. The most plausible mechanism accounting for the observed coalescence is reversible $\beta$-H elimination as depicted in Figure 13: i.e., equilibration of **2** with its three-coordinate isomer **3**. Since the latter has in no case been observed, no data are available to determine if putative **3** would (like its *tert*-butyl-substituted counterpart) have a 3-fold symmetrical structure and a quartet ground state, or else perhaps one or more Mo−H−C agostic interactions and a doublet ground state.

$^2$H NMR spectroscopy is a convenient way to monitor the reaction between the deuterated molybdaziridine-hydride complex **2**-$d_{18}$ and 1 or 2 equiv of benzonitrile. Upon mixing with nitrile, the three peaks in a 1:1:1 ratio

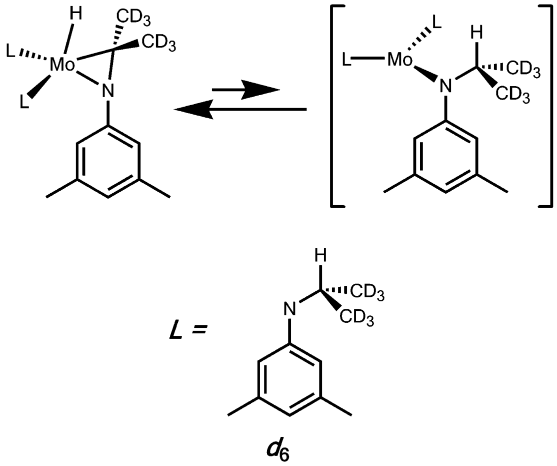

**Figure 13.** Reversible $\beta$-H elimination.

that correspond to the starting material are lost. Dominating the spectrum when 1 equiv of PhCN is used is a peak at 8.2 ppm ($w_{1/2} = 38$ Hz) that may be assigned to the $\eta^2$ adduct, ($\eta^2$-PhCN)[**3**-$d_{18}$]. Present in both cases, but far more abundant when 2 equiv of benzonitrile are employed, is a complex with a sharp ($w_{1/2} = 10$ Hz) signal at 4.4 ppm. This complex is formulated as the bis-$\eta^1$ adduct, ($\eta^1$-PhCN)$_2$[**3**-$d_{18}$].

The above assignments are supported by comparison with the $^2$H NMR spectra involving the previously described *t*-Bu system. In particular, the isolated and structurally characterized adduct ($\eta^2$-Me$_2$NCN)[**1**] exhibited a $^2$H NMR signal similar in chemical shift and line width to that for the sole adduct observed en route to benzonitrile coupling. Fitting this profile both in terms of line width and chemical shift is the dominant species observed upon mixing 1 equiv of PhCN with the isopropyl-substituted molybdenum trisamide.

**Reaction of Cyanomesitylene with Molybdaziridine-Hydride.** In further defense of the foregoing assignments, reference can be made to the fact that it has been possible to isolate and characterize a stable example of an ($\eta^1$-nitrile)$_2$[**3**] complex by employing a nitrile so substituted as to disfavor *both* $\eta^2$-binding *and* coupling via dimerization. Thus, addition of 2,4,6-trimethylbenzonitrile (cyanomesitylene, MesCN), either 2 equiv or in excess, to **2**-$d_{18}$ in hexane produced a blue, *EPR-silent* species exhibiting a single $^2$H NMR signal at 3.2 ppm ($w_{1/2} = 22$ Hz) and an effective magnetic moment of 1.6 $\mu_B$.[39] The new complex, ($\eta^1$-MesCN)$_2$[**3**-$d_{18}$] was collected by filtration in 52% yield as a dark blue powder following concentration of the spectroscopically pure solution.

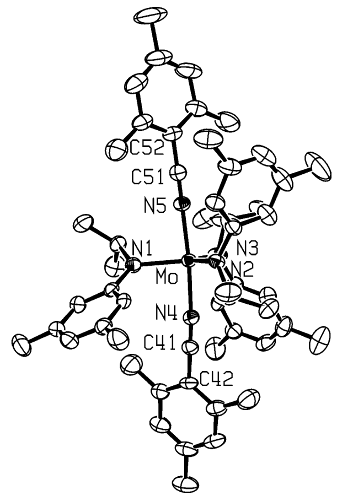

**Figure 14.** Thermal ellipsoid plot (35% probability) of ($\eta^1$-MesCN)$_2$[**3**]. Selected distances (Å): Mo–N1, 2.050(4); Mo–N2, 1.992(4); Mo–N3, 1.979(4); Mo–N4, 2.097(4); Mo–N5, 2.081(4); N4–C41, 1.158(6); N5–C51, 1.153(6). Selected angles (deg): N1–Mo–N2, 124.9(2); N2–Mo–N3, 117.5(2); N3–Mo–N1, 117.6(2); N1–Mo–N4, 86.9(2); N2–Mo–N4, 93.5(2); N3–Mo–N4, 89.4(2); N1–Mo–N5, 88.3(2); N2–Mo–N5, 89.6(2); N3–Mo–N5, 92.4(2).

Crystals of the bis-cyanomesitylene complex suitable for X-ray diffraction were grown at 25 °C from hexane solution in the presence of excess MesCN; a thermal ellipsoid plot is provided in Figure 14, and it illustrates several important points. First, the structure of ($\eta^1$-MesCN)$_2$[**3**] illustrates dramatically the manner in which isopropyl-substitution makes five-coordination available to the molybdenum center. The two cyanomesitylene ligands are disposed in a mutually trans arrangement at the axial positions (defining the *z* axis) of a trigonal bipyramid. This geometry is expected to place the three d electrons in the pair of near-degenerate *xz* and *yz* orbitals, giving a doublet ground state and allowing for back-bonding into the nitrile CN $\pi$* orbitals. That such back-bonding is in effect is indicated by the Mo–N(nitrile) distances of 2.097(4) and 2.081(4) Å, just slightly (ca. 0.1 Å) longer than the Mo–N(anilide) distances in the same complex. On the other hand, the nitrile CN interatomic distances (1.158(6) and 1.153(6) Å) and infrared stretching frequency (2218 cm$^{-1}$, Nujol mull) are not indicative of substantial reduction of the nitrile CN bond order, consistent with the fact that in dilute solution, the complex is observed to lose cyanomesitylene and revert to the molybdaziridine-hydride starting material. In other words, and by virtue of careful $^2$H NMR spectroscopic monitoring, it was possible to conclude that cyanomesitylene coordination to molybdenum is reversible.

To recap the observations thus far, we find that while a *single* intermediate (or possible kinetic cul-de-sac) is observed en route to benzonitrile coupling by the *tert*-butyl-substituted molybdenum trisamide, *two* species are observed en route to coupling in the case of the isopropyl-substituted variant. By virtue of similarities in both $^2$H NMR and X-band EPR profiles to the structurally characterized dimethylcyanamide complex, the species observed in the case of N[*t*-Bu]Ar ligation is assigned to be ($\eta^2$-PhCN)[**1**]. On the other hand, when N[*i*-Pr]Ar ligation is in effect, both an EPR-active mono-$\eta^2$ adduct and an EPR-silent bis-$\eta^1$ adduct are seen, and these are presumably in a state of equilibrium due to reversible formation of the trigonal-bipyramidal bis-$\eta^1$ adduct. Thus, while it is still our working hypothesis that **1** is reluctant to attain coordination number 5 complexes,[40] we must now recognize that $\eta^2$-binding, at least of organic nitriles, is a favorable phenomenon. *Not observed* are what are possibly the most interesting reactive intermediates involved in the molybdenum/nitrile system, namely the mono-$\eta^1$ adducts, direct dimerization of which would lead with little reorganiza-

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(39) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(40) Tsai, Y.-C.; Cummins, C. C. *Inorg. Chim. Acta* **2003**, *345*, 63.

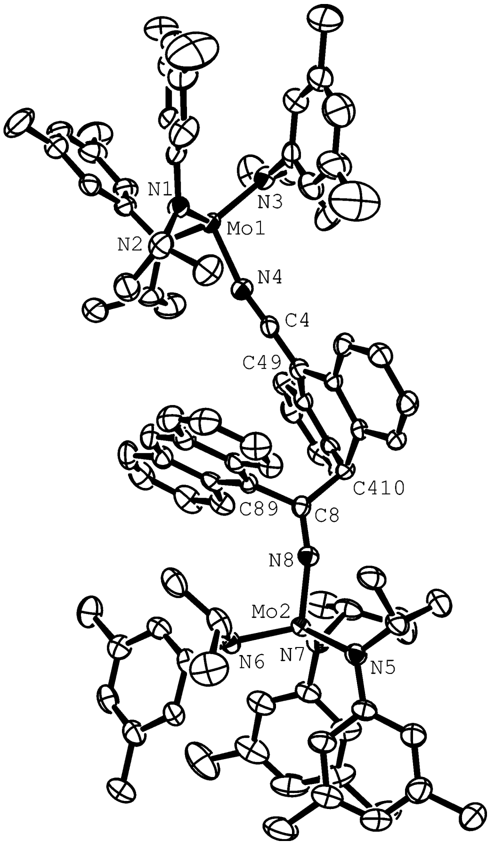

**Figure 15.** Thermal ellipsoid plot (35% probability) of [(AnthCN)(**3**)]$_2$. Selected distances (Å): Mo1−N1, 1.961(5); Mo1−N2, 1.948(5); Mo1−N3, 1.941(5); Mo1−N4, 1.917(5); Mo2−N5, 2.008(5); Mo2−N6, 1.947(5); Mo2−N7, 1.931(5); Mo2−N8, 1.833(5); N4−C4, 1.213(7); C4−C49, 1.347(7); C8−N8, 1.291(7). Selected angles (deg): N1−Mo1−N2, 111.6(2); N2−Mo1−N3, 115.3(2); N3−Mo1−N1, 118.7(2); N4−Mo1−N1, 104.3(2); N2−Mo1−N4, 97.1(2); N3−Mo1−N4, 106.5(2); C4−N4−Mo1, 168.4(5); N4−C4−C49, 178.0(6).

tion to the observed thermodynamic sink in the system: inversion-symmetrical nitrile-coupled products.

**Reaction of 9-Anthracenylcarbonitrile with Molybdaziridine-Hydride.** In contrast to the cases with PhCN and MesCN, when **2** is treated with 1 equiv of 9-anthracenylcarbonitrile, a head-to-tail dimer is formed, the X-ray crystal structure of which is depicted in Figure 15. Presumably, the increased steric demands of 9-anthracenylcarbonitrile disfavor a head-to-head coupled product. Structural features of note include the nearly linear N(4)−C(4)−C(49) keteneimine moiety ($\nu_{NCC}$ = 1944 cm$^{-1}$) as well as the pyramidalization at C(410), a manifestation of the electronic reorganization of the anthracene unit upon reductive coupling.

## Conclusions

In conclusion, we have illustrated the ability of both *tert*-butyl and isopropyl-substituted variants of the molybdenum trisamide fragment to engage in the reductive coupling of simple organic nitriles to form bridging diiminato complexes. NMR and EPR spectroscopic monitoring of this process with benzonitrile indicate that the initial product is a 1:1 $\eta^2$ bound nitrile complex; while this is the sole observable intermediate in the case of **1**, the reduced steric bulk of **2** allows for the formation additionally of a bis-$\eta^1$ complex, the equilibrium formation of which can be driven by the addition of excess nitrile. Judicious choice of nitrile and ligand set has allowed for the isolation and X-ray structural characterization of a representative 1:1 $\eta^2$ adduct, in the form of ($\eta^2$-Me$_2$NCN)[**1**], and also a representative 2:1 $\eta^1$ adduct, in the form of ($\eta^1$-MesCN)$_2$[**3**]. Finally, treatment of **2** with 9-anthracenyl carbonitrile results in the formation of a head-to-tail dimer.

In addition to comprising essential data on the chemical consequences of the differing steric demands manifested by the *tert*-butyl- and isopropyl-substituted molybdenum tris-amide fragments, these results provide valuable insights into the mechanism of reductive nitrile coupling by low-valent early metals. Future work will utilize kinetic measurements to further develop the mechanistic framework of nitrile reductive coupling now that several of the key players have been identified.

## Experimental Section

**General Considerations.** Unless otherwise stated, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified dinitrogen or by using Schlenk techniques under an argon atmosphere. Complexes Mo(H)($\eta^2$-Me$_2$CNAr)(N[*i*-Pr]Ar)$_2$, Mo(H)($\eta^2$-(CD$_3$)$_2$CNAr)(N[CH-(CD$_3$)$_2$]Ar)$_2$, and Mo(N[*t*-Bu]Ar)$_3$ were prepared according to the literature.[3,9] 9-Anthracenylcarbonitrile, benzonitrile, and 2,4,6-trimethylbenzonitrile were used as purchased from Lancaster Synthesis and dimethylcyanamide was obtained from Aldrich. Diethyl ether, benzene, *n*-pentane, *n*-hexane, and toluene were dried and deoxygenated by the method of Grubbs.[41] THF was distilled from purple Na/benzophenone ketyl and collected under nitrogen. C$_6$D$_6$ was degassed and dried over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were dried in vacuo overnight at a temperature above 200 °C. X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with an Oxford Instruments Helium flow cryostat (Model ESP 310) in the temperature range 20−300 K. Spectra were recorded in liquid and frozen toluene solution as well as mixtures of pentane/Et$_2$O. Room-temperature spectra were simulated by using Bruker's perturbation-theory based software packages SimFonia and WinEPR.[42] Frozen solution EPR data were analyzed and simulated by using a program provided by Frank Neese, MPI Mülheim, Germany.[43] Cyclic voltammetry measurements were carried out with an Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software in conjunction with a three-electrode cell, using 0.5 M [N$^n$Bu$_4$][PF$_6$] solutions in tetrahydrofuran. $^1$H, $^2$H, and $^{13}$C NMR spectra were recorded on a Varian VXR-500 or a Varian XL-301 spectrometer. $^1$H, $^2$H, and $^{13}$C chemical shifts are reported with respect to internal solvent (7.15 ppm and 128.38 (t) ppm (C$_6$D$_6$)). Elemental analyses (C, H, N) were conducted by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Rühr, Germany.

**Synthesis of HN[*t*-Bu]Ar.[45] (1) Synthesis of 2,4,6-Trimethylpyrillium Tetrafluoroborate.** Acetic anhydride (1 kg, 9.79 mol, 10 equiv) was placed in a 2-L, two-necked round-bottom flask. At room temperature, 4-hydroxy-4-methyl-2-pentanone (122 mL, 0.98 mol, 1 equiv) was added over 5 min, using a pressure equalizing dropping funnel, and the solution was stirred for 5 min. HBF$_4$ (127 mL, 48% solution in water, 0.97 mol, 1 equiv) was added dropwise, using a pressure equalizing dropping funnel, over a period of 1 h. The temper-

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[41] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[42] www.bruker-biospin.de/EPR/software/index.html
[43] Neese, F. *QCPE Bull.* **1995**, *15*, 5.

ature of the reaction mixture was ~90 °C during the addition. The color of the solution gradually changed from colorless to light orange to dark brown. The reaction mixture was heated at ~80 °C with stirring for another hour, then was allowed to cool to room temperature. The light-colored precipitate was filtered by suction and washed with a total of 1 L of diethyl ether to give 135 g (0.64 mol, 66%) of pale yellow, crystalline 2,4,6-trimethylpyrillium tetrafluoroborate. Melting point (uncalibrated): 219.6−220.3 °C dec. $^1$H NMR (CD$_3$CN, 300 MHz, 20 °C): $\delta$ 7.72 (s, 2H, *m*-methyl), 2.80 (s, 6H, *o*-methyl), 2.65 (s, 3H, *p*-methyl) ppm.

**(2) Synthesis of *N-tert*-Butyl-3,5-dimethylaniline.** Acetonitrile (100 mL) and *tert*-butylamine (200 mL, 1.90 mol, 4.40 equiv) were placed in a 4-L, two-necked round-bottom flask. The flask was purged with nitrogen and kept under nitrogen during the course of the following operations. 2,4,6-Trimethylpyrillium tetrafluoroborate (40 g, 0.19 mol, 0.44 equiv) was dissolved in acetonitrile (600 mL) and added dropwise over 2.5 h, using a pressure equalizing dropping funnel. Upon addition, the reaction mixture turned red. To the same reaction mixture was added a second fraction of pyrillium salt (50 g, 0.24 mol, 0.55 equiv) in acetonitrile (700 mL) over 5 h. Preserving the ratio of *tert*-butylamine to pyrillium salt at 4.4, the procedure was repeated in a second flask. Acetonitrile (35 mL) and *tert*-butylamine (70 mL, 0.66 mol, 1.54 equiv) were placed in a 2-L, two-necked round-bottom flask, as above. 2,4,6-Trimethylpyrillium tetrafluoroborate (30 g, 0.15 mol, 0.35 equiv) was dissolved in acetonitrile (600 mL) and added dropwise over 2.5 h. The volatiles were removed by rotary evaporation and the residues were combined. Water (400 mL) was added and the mixture was extracted three times with petroleum ether (300, 300, 200 mL). The organic fractions were dried over anhydrous MgSO$_4$ and filtered. The volatiles were removed by rotary evaporation to give a dark brown oil. GC-MS of the crude product showed ~90% content of the desired amine. Vacuum distillation (44 °C at 15 mTorr) allowed isolation of the desired *N-tert*-butyl-3,5-dimethylaniline (63.0 g, 0.36 mol, 62%) as a pale yellow oil. $^1$H NMR (C$_6$D$_6$, 300 MHz, 20 °C): $\delta$ 6.46 (s, 1H, para), 6.37 (s, 2H, ortho), 2.93 (s, 1H, N-*H*), 2.21 (s, 6H, *m*-methyl), 1.19 (s, 9H, *tert*-butyl methyl) ppm. By selective irradiation of the aryl methyl signal, H$_{\mathrm{para}}$ becomes a triplet ($J$ = 1.65 Hz) and H$_{\mathrm{ortho}}$ becomes a doublet ($J$ = 1.65 Hz). $^{13}$C NMR (C$_6$D$_6$, 300 MHz, 20 °C): $\delta$ 147.84 (ipso), 138.59 (meta), 121.03 (para), 116.35 (ortho), 51.63 (*t*-Bu quaternary), 30.77 (*t*-Bu methyl), 22.29 (Aryl methyl) ppm.

**Synthesis of ($\mu$-NC(CH$_3$)C(CH$_3$)N)[1]$_2$.** To a solution of **1** (331 mg, 530 $\mu$mol) in 5 mL of Et$_2$O contained in a 20-mL glass vial was added acetonitrile (26.1 mg, 636 $\mu$mol). The solution became green quickly, and green solid precipitated out in 5 min. After an hour, the green precipitate was collected by filtration, washed with cold Et$_2$O, and dried under vacuum (272 mg, 204 $\mu$mol, 77%). $^1$H NMR (C$_6$D$_6$, 22 °C): 6.7 (9 H, overlapping aryl ortho and para), 2.3 (21 H, overlapping aryl C*H*$_3$ and $\mu$-NC(C*H*$_3$)-C(C*H*$_3$)N), 1.5 (27 H, br, NC(C*H*$_3$)$_3$). Anal. Calcd for C$_{76}$H$_{114}$Mo$_2$N$_8$: C, 68.54; H, 8.63; N, 8.41. Found: C, 68.04; H, 8.55; N, 8.36.

**Synthesis of ($\eta^2$-Me$_2$NCN)[1].** In 8 mL of *n*-hexane was dissolved 1.278 g of compound **1**. To this stirring solution was added 0.168 g of dimethylcyanamide in 2 mL of *n*-hexane. Immediately the reaction mixture turned green. After 10 min, the reaction mixture volume was reduced in vacuo to 3 mL and the solution was stored at −35 °C. Crystalline product (1.097 g, 77%) was collected by filtration and rinsed with cold *n*-pentane. $^1$H NMR (C$_6$D$_6$, 20 °C): $\delta$ ca. 6.5 (br s), 0.762 ppm. $^2$H NMR of $d_{18}$ isotopomer (diethyl ether, 20 °C): $\delta$ 7.06 ($\Delta\nu_{1/2}$ = 76.6 Hz) ppm. $\mu_{\mathrm{eff}} = 1.83\,\mu_{\mathrm{B}}$ (Evans' method, C$_6$D$_6$, 19.9 °C).[39] Anal. Calcd for C$_{39}$H$_{60}$N$_5$Mo: C, 67.41; H, 8.70; N, 10.08. Found: C, 67.46; H, 8.62; N, 10.06.

**Synthesis of [(PhCN)(1)]$_2$.** To a diethyl ether solution of **1** (2.5422 g, 4.067 mmol) was added a diethyl ether solution of benzonitrile (0.4228 g, 4.105 mmol, 1.01 equiv). Upon mixing at 20 °C, a purple color was observed. This purple color persisted until concentration of the solvent to dryness 72 h later at which time a blue-green color was observed. Extraction and subsequent crystallization from cold THF yielded 1.833 g of dark green microcrystalline solid (70.3% yield). $^1$H NMR (C$_6$D$_6$, 20 °C, 500 MHz): $\delta$ 8.05 (br s, 2H, phenyl para), 7.50 (t, 4H, phenyl ortho, $J$ = 8 Hz), 6.94 (q, 4H, phenyl meta, $J$ = 7 Hz), 6.67 (s, 6H, aryl para), 6.41 (br s, 12H, aryl ortho), 2.18 (s, 36H, aryl methyl), 1.32 (s, 54H, *tert*-butyl methyl) ppm. $^{13}$C NMR (C$_6$D$_6$, 20 °C, 125 MHz): $\delta$ 153.32 (bridge), 137.09, 129.15 (aryl ortho), 128.42 (phenyl ortho), 127.92 (phenyl para), 127.34 (aryl para), 125.49 (phenyl meta), 116.30, 64.56 (*tert*-butyl quaternary), 32.47 (*tert*-butyl methyl), 22.02 (aryl methyl) ppm. Anal. Calcd for C$_{86}$H$_{118}$N$_8$Mo$_2$: C, 70.95; H, 8.17; N, 7.69. Found: C, 70.10; H, 8.39; N, 7.24.

**Thermolysis of [(PhCN)(1)]$_2$ with Concomitant Formation of the Enediimido [(PhCN)Mo(NAr)(N[*t*-Bu]-Ar)$_2$]$_2$.** A toluene solution of [(PhCN)(**1**)]$_2$ (ca. 50 mg in 7 mL toluene) was sealed in a Schlenk tube and thermolyzed in a 105 °C oil bath for 1.5 h. During this time the solution changed color from green to red-purple, and bubbling was observed. There was evidence in the $^1$H NMR spectrum of isobutene, isobutylene, and hexamethylethane consistent with *tert*-butyl radical ejection.[27,46−48] $^1$H NMR (C$_6$D$_6$, 20 °C, 500 MHz): $\delta$ 7.55 (d, 4H, phenyl ortho, $J$ = 7.5 Hz), 7.16 (t, 4H, phenyl meta), 7.07 (t, 2H, phenyl para), 6.74 (s, 8H, amido aryl ortho), 6.71 (s, 4H, amide aryl para), 6.45 (s, 2H, imido aryl para), 5.75 (s, 4H, imido aryl ortho), 2.22 (s, 24H, amido aryl methyl), 2.10 (s, 12H, imido aryl methyl), 1.24 (s, 36H, *tert*-butyl) ppm. $^{13}$C NMR (C$_6$D$_6$, 20 °C, 125 MHz): $\delta$ 157.85, 154.35, 148.69, 142.31, 137.57, 130.97 (phenyl ortho), 128.94, 128.88 (amido aryl ortho), 128.68 (phenyl meta), 126.92 (amido aryl para), 126.55, 125.94 (imido aryl para), 121.48 (imido aryl ortho), 60.72 (*tert*-butyl quaternary), 32.49 (*tert*-butyl methyl), 21.91 (amido aryl methyl), 21.68 (imido aryl methyl) ppm. Anal. Calcd for C$_{78}$H$_{100}$N$_8$Mo$_2$: C, 69.83; H, 7.51; N, 8.35. Found: C, 69.29; H, 7.08; N, 7.91.

**Synthesis of DN[CDMe$_2$]Ar and DN[CDMe$_2$](3,5-C$_6$D$_3$Me$_2$) (Ar = 3,5-C$_6$H$_3$Me$_2$).** Since the preparations of these two anilines were carried out in essentially the same way, the preparation of DN(CDMe$_2$)Ar is given in detail as an example. To a frozen solution of 9.377 g (0.223 mol) of lithium aluminum deuteride suspended in 250 mL of tetrahydrofuran was added dropwise a solution of 30 g (0.186 mol) of the imine Me$_2$CNAr in 50 mL of tetrahydrofuran. Upon complete addition, the reaction mixture was stirred at room temperature and became light gray-green overnight. The reaction vessel was cooled in an ice water bath and D$_2$O was slowly added, followed by several portions of a dilute solution of sodium potassium tartrate in D$_2$O, followed by two more portions of D$_2$O. All organic materials were extracted with 300 mL of petroleum ether. The organic layer was separated from the aqueous layer and dried over anhydrous MgSO$_4$. A pale yellow oil was obtained upon removing all volatiles in vacuo. DN[CDMe$_2$]Ar was obtained by vacuum distillation (23.552 g, 0.143 mol, 77%). $^1$H NMR of DN[CDMe$_2$]Ar (C$_6$D$_6$, 300 MHz, 20 °C): $\delta$ 6.40 (s, 1H, para), 6.15 (s, 2H, ortho), 2.21 (s, 6H, *m*-methyl), 0.92 (6H, −CD(C*H*$_3$)$_2$) ppm. $^1$H NMR of DN[CDMe$_2$](3,5-C$_6$D$_3$Me$_2$) (C$_6$D$_6$, 300 MHz, 19.8 °C): $\delta$ 2.21 (s, 6H, *m*-methyl), 0.93 (6H, −CD(C*H*$_3$)$_2$) ppm.

**Synthesis of Li(N[CDMe$_2$]Ar)·Et$_2$O and Li(N[CDMe$_2$]-(3,5-C$_6$D$_3$Me$_2$))·Et$_2$O (Ar = 3,5-C$_6$H$_3$Me$_2$).** Since the prepara-

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**Table 1. Crystallographic Data for ($\eta^2$-Me$_2$NCN)[1], ($\eta^1$-MesNC)$_2$[3], [(PhCN)(3)]$_2$[I$_3$], and [(AnthCN)(3)]$_2$**

| | ($\eta^2$-Me$_2$NCN)[**1**] | ($\eta^1$-MesNC)$_2$[**3**] | [(PhCN)(**3**)]$_2$[I$_3$] | [(AnthCN)(**3**)]$_2$ |
|---|---|---|---|---|
| formula | $C_{39}H_{60}MoN_5$ | $C_{53}H_{70}MoN_5$ | $C_{83}H_{110}Cl_6I_6Mo_2N_8$ | $C_{192}H_{228}Mo_4N_{16}$ |
| fw | 694.86 | 873.08 | 2385.77 | 3143.66 |
| space group | $P2_1/n$ | $P2_1/c$ | $C2/c$ | $P\bar{1}$ |
| $a$, Å | 12.9183(13) | 23.7364(2) | 20.0607(5) | 18.6762(2) |
| $b$, Å | 19.099(2) | 11.0300(2) | 19.6646(5) | 21.63490(10) |
| $c$, Å | 15.748(2) | 19.2358(4) | 24.8443(7) | 21.8544(3) |
| $\alpha$, deg | 90 | 90 | 90 | 85.1420(10) |
| $\beta$, deg | 95.313(2) | 93.6860(10) | 95.3800(10) | 85.3770(10) |
| $\gamma$, deg | 90 | 90 | 90 | 76.6580(10) |
| $V$, Å$^3$ | 3868.7(7) | 5025.75(14) | 9757.5(4) | 8544.2(2) |
| $Z$ | 4 | 4 | 4 | 2 |
| cryst description | green block | blue rod | red block | red plate |
| $D_{\text{calcd}}$, g·cm$^{-3}$ | 1.193 | 1.154 | 1.624 | 1.222 |
| $\mu$, mm$^{-1}$ | 0.371 | 0.299 | 0.236 | 0.343 |
| $F$(000) | 1484 | 1860 | 4672 | 3320 |
| GOF on $F^2$ | 1.129 | 1.322 | 1.103 | 1.328 |
| $R_1$ ($F_o$) for $I > 2\sigma I$ | 0.0750 | 0.0663 | 0.0516 | 0.0736 |
| $wR_2$ ($F_o^2$) for $I > 2\sigma I$ | 0.1481 | 0.1294 | 0.1265 | 0.1661 |

tions of these two lithium anilides were carried out in essentially the same way, the preparation of LiN[CDMe$_2$]Ar·Et$_2$O is given in detail. To a frozen solution of 23.0 g (0.139 mol) of DN[CDMe$_2$]Ar in 100 mL of *n*-pentane were added cold *n*-BuLi (105 mL, 1.6 M in hexanes, 0.168 mol). The resulting yellow solution was stirred for 60 min at room temperature and white precipitate formed. Upon reducing the volume of the slurry to one-third in vacuo, 18 mL of diethyl ether was added. After the resulting mixture was stirred for 1 h, the mixture was placed in the cold well of the glovebox for 30 min. A fine white powder (29.886 g, 0.233 mol, 87.7%) was collected by filtration, rinsed with cold *n*-pentane, and dried in vacuo. For Li(N[CDMe$_2$]Ar)·Et$_2$O, $^1$H NMR (C$_6$D$_6$, 300 MHz, 20 °C): $\delta$ 6.49 (s, 2H), 6.13 (s, 1H), 2.97 (q, 4H), 2.33 (s, 6H), 1.43 (s, 6H), 0.77 (t, 6H) ppm. $^{13}$C NMR (C$_6$D$_6$, 75 MHz, 20 °C): $\delta$ 160.38 (aryl ipso), 139.31 (aryl meta), 113.16 (aryl para), 111.00 (aryl ortho), 65.16 (O*C*H$_2$CH$_3$), 47.34 (*C*D(CH$_3$)$_2$), 29.93 (CD(*C*H$_3$)$_2$), 22.10 (Ar-*C*H$_3$), 14.31 (OCH$_2$*C*H$_3$) ppm. For LiN[CDMe$_2$](3,5-C$_6$D$_3$Me$_2$)·Et$_2$O, $^1$H NMR (C$_6$D$_6$, 300 MHz, 19.9 °C): $\delta$ 2.97 (q, 4H), 2.33 (s, 6H), 1.43 (s, 6H), 0.77 (t, 6H) ppm. $^2$H NMR (C$_6$H$_6$, 19.6 °C): $\delta$ 6.49 (s, 2D), 6.13 (s, 1D), 3.37 (s, 1D) ppm.

**Syntheses of Molybdaziridine Deuteride Complexes 2-*d*$_3$ and 2-*d*$_4$.** Since the preparations of these two complexes were carried out in essentially the same way, that for **2**-*d*$_3$ is given in detail. To 22.0 g of Li(N[CDMe$_2$]Ar)·Et$_2$O (0.090 mol) in 350 mL of diethyl ether was added orange solid MoCl$_3$(THF)$_3$ (18.84 g, 0.045 mol). The flask containing the resulting suspension was evacuated for 3 min and then stirred at room temperature for 5.5 h. The resulting orange-brown suspension was filtered through a plug of Celite to remove LiCl and excess MoCl$_3$(THF)$_3$. A black solid was obtained upon removing all volatiles of the filtrate. The resulting solid was redissolved in 200 mL of diethyl ether and the resulting solution was concentrated to 180 mL in vacuo in a 300-mL Schlenk flask. Big blocks of black crystals formed upon storing the solution under vacuum at −35 °C overnight. The desired product was isolated by filtration (2 crops totaling 10.67 g, 0.018 mol, 60.0%). $^2$H NMR of **2**-*d*$_3$ (C$_6$H$_6$, 19.6 °C): $\delta$ 5.84 ($\Delta\nu_{1/2} = 41.8$ Hz, 2D, amido isopropyl), −12.3 ($\Delta\nu_{1/2} = 412.6$ Hz, 1D, deuteride) ppm. $\mu_{\text{eff}} = 2.04\ \mu_B$ (Evans' method, C$_6$D$_6$, 20 °C).[39] For **2**-*d*$_4$, $^2$H NMR (C$_6$H$_6$, 19.6 °C): $\delta$ 9.48 ($\Delta\nu_{1/2} = 43.2$ Hz), 3.45 ($\Delta\nu_{1/2} = 95.7$ Hz), −2.91 ($\Delta\nu_{1/2} = 401.5$ Hz) ppm. $\mu_{\text{eff}} = 2.11\ \mu_B$ (Evans' method, C$_6$D$_6$, 19.9 °C).[39]

**Synthesis of ($\eta^1$-MesCN)$_2$[3-*d*$_{18}$].** To 0.756 mmol of **2-*d*$_{18}$** in 10 mL of *n*-hexane was added 0.220 g (1.51 mmol) MesCN in 5 mL of *n*-hexane. The resulting mixture became dark blue quickly. The solution was concentrated to approximately 3 mL in vacuo. A crop of spectroscopically pure solid was collected by filtration as a dark blue powder (0.394 mmol, 52.1%). $^2$H NMR (diethyl ether, 20 °C): $\delta$ 3.21 ($\Delta\nu_{1/2} = 22.1$ Hz) ppm. $\mu_{\text{eff}} = 1.58\ \mu_B$ (SQuID). Anal. Calcd for C$_{53}$H$_{70}$N$_5$Mo: C, 72.91; H, 7.93; N, 7.86. Found: C, 73.05; H, 7.96; N, 8.04.

**Synthesis of [(PhCN)(3-*d*$_{18}$)]$_2$[I$_3$].** To 0.313 g (0.537 mmol) of **2**-*d*$_{18}$ in 10 mL of diethyl ether was added 0.061 g (0.591 mmol) of PhCN. The resulting solution quickly turned to dark blue-green. An oily material was obtained upon removal of all volatiles in vacuo. The oily residue was redissolved in 5 mL of diethyl ether to yield a green solution. To this solution was added 0.103 g (0.812 mmol) of I$_2$ in 5 mL of diethyl ether. Maroon solid precipitated rapidly, was isolated by filtration, and was rinsed with *n*-hexane until the filtrate became colorless (0.406 g, 86.2%). $^2$H NMR (THF, 20 °C): $\delta$ 0.81 ($\Delta\nu_{1/2} = 16.0$ Hz) ppm. $\mu_{\text{eff}} = 1.31\ \mu_B$ (Evans' method, C$_5$D$_5$N, 19.9 °C).[39] Anal. Calcd for C$_{80}$H$_{106}$N$_8$I$_3$Mo$_2$: C, 54.83; H, 6.10; N, 4.80. Found: C, 54.91; H, 6.16; N, 4.73.

**Synthesis of [(AnthCN)(3)]$_2$.** To 0.680 mmol of **2** in 6 mL of diethyl ether was added 0.646 mmol of 9-anthracenecarbonitrile suspended in 10 mL of diethyl ether. The resulting mixture became purple quickly, and a purple precipitate formed in approximately 1 min. After the solution was stirred for 1 h, the purple solid was collected by filtration, rinsed with diethyl ether, and dried in vacuo (0.462 g, 0.294 mmol, 91%). $^1$H NMR (C$_6$D$_6$, 19.9 °C): $\delta$ 8.21 (s, 1H), 8.16 (t, 2H), 7.76 (t, 2H), 7.22 (m, 4H), 7.06 (m, 4H), 7.00 (d, 2H), 6.56 (s, 6H), 6.37 (s, 6H), 6.32 (s, 6H), 4.62 (q, 3H), 4.21 (q, 3H), 2.10 (s, 18H), 2.08 (s, 18H), 1.14 (d, 18H), 1.06 (d, 18H) ppm. IR (Et$_2$O): $\nu_{\text{NCC}}$ 1944 cm$^{-1}$. Anal. Calcd for C$_{96}$H$_{114}$N$_8$Mo$_2$: C, 73.35; H, 7.31; N, 7.13. Found: C, 73.24; H, 7.46; N, 7.02.

**X-ray Crystal Data: General Procedure.** Crystals grown from concentrated solutions at −35 °C were coated with Paratone N oil (an Exxon product) on a microscope slide. Samples were selected and mounted with wax on a glass fiber. Data collection was carried out at a temperature of 183(2) K on a three-circle goniometer Siemens Platform with a CCD detector with Mo K$\alpha$ ($\lambda = 0.71073$ Å, $\mu = 2.362$ mm$^{-1}$). The data were processed and refined by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in caluculated ($d_{\text{CH}} = 0.96$ Å) positions. Some details regarding refined data and cell parameters are available in Table 1. Selected bond distances and angles are supplied in the captions of Figures 5, 11, 13, and 15.

**DFT Calculations.** Calculations were performed with version 2002.02 of the Amsterdam DFT program package, ADF.[49−51] Atomic coordinates from the X-ray diffraction study of ($\eta^2$-Me$_2$NCN)[**1**] were employed, adjusting the C−H bond distances all to a value of 1.096 Å. The calculation was carried out with all the electrons considered explicitly, i.e., no frozen core approximation was utilized. The atomic basis sets employed were the ZORA/TZ2P bases supplied with the program, and accordingly, scalar relativistic effects were included with the ZORA treatment. The calculation was carried out in spin-restricted mode as required for **g**-tensor calculation, using the ESR block key within the ADF program.[52,53] The local density approximation functional used was that of Vosko, Wilk, and Nusair, while the functionals for the generalized gradient approximations took the form of Becke (exchange) and Perdew (correlation).[54−56]

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**Supporting Information Available:** $^2$H NMR spectra of **2**-$d_{18}$ in toluene at various temperatures and the simulation of these spectra; tables with bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structures of ($\eta^2$-Me$_2$NCN)[**1**], [(PhCN)(**3**)]$_2$[I$_3$], ($\eta^1$-MesCN)$_2$[**3**], and [(AnthCN)(**3**)]$_2$; details of the DFT calculations; X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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