A Cyclometalated Resting State for a Reactive Molybdenum Amide: Favorable Consequences of β-Hydrogen Elimination Including Reductive Cleavage, Coupling, and Complexation

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Whereas dimethylamide ligation of molybdenum(III) supports Mo≡Mo triple bond formation,[1] and *N-tert*-butylanilide ligation engenders reactive yet isolable monomeric three-coordinate derivatives,[2,3] it is now shown that ligation of Mo(III) by *N*-isopropylanilide gives rise to the cyclometalated[4] (β-H eliminated) species $Mo(H)(\eta^2\text{-}Me_2C=NAr)(N[^iPr]Ar)_2$ (**1**, Ar = 3,5-$C_6H_3Me_2$, Figure 1), which can be thought of alternatively as an imine complex or as a metallaziridine derivative. β-H elimination for complexes of organoamide ligands is a rarely documented phenomenon.[5–9]

Compound **1**, which is freely soluble in hydrocarbon and ethereal solvents, was obtained as a brown solid in 70% yield from the reaction of $Li(N[^iPr]Ar)(OEt_2)$ with $MoCl_3(THF)_3$. Characterization of **1** includes Evans method magnetic susceptibility ($\mu_{eff} = 2.1\ \mu_B$) and ^2H NMR spectra for the d_{18} isotopomer $Mo(H)(\eta^2\text{-}(D_3C)_2C=NAr)(N[^iPr\text{-}d_6]Ar)_2$ (**1**-d_{18}). Three ^2H NMR signals in a 1:1:1 ratio are observed, consistent with a pseudo-C_s structure, as sketched in Figure 1. The three ^2H NMR signals for **1**-d_{18} were observed to coalesce under observation at ~70 °C (benzene, 500 MHz), consistent with the β-H elimination process being reversible. Infrared spectroscopy substantiates the presence of the terminal hydride ligand ($\nu_{MoH} = 1876\ cm^{-1}$).

X-ray crystallography was used to interrogate the structure of **1**-d_{18}. The structural parameters thereby determined are consistent with the ^2H NMR data. The effect of β-H elimination from the methine position is to give a short Mo−C(27) distance of 2.166-(7) Å. A conformational feature of interest is that the aryl ring component of the cyclometalated amide is favorably oriented for π-interaction with the contiguous nitrogen atom, the opposite of what is observed normally for unperturbed ligands of the $-N[^tBu]Ar$ variety.[10]

Single-crystal neutron diffraction also was used to characterize **1**, due to interest in the exact position of the presumed hydride ligand (Figure 2). Suffice it to say that the neutron structure of **1** is directly in accord with the X-ray structure, giving a Mo−H distance of 1.69(5) Å. No bonding interaction between the hydride ligand and C(27) is indicated by the relevant internuclear C···H distance of 2.36(6) Å. Density functional theory calculations were found to corroborate the structure of **1** as determined by the X-ray and neutron diffraction studies.

Initially it was presumed that the cyclometalated nature of **1** would inhibit the type of reaction chemistry observed for related three-coordinate derivatives.[2,3] This proved not to be the case. For example, the reaction of **1**-d_{18} with dinitrogen was found to give, in high yield, the nitrido-bridged dimolybdenum complex $(\mu\text{-N})[Mo(N[^iPr\text{-}d_6]Ar)_3]_2$ (**2**). Here, as in the other reactions of **1** to be described, the hydrido ligand is observed to have migrated *back* to carbon, rendering all three $-N[^iPr]Ar$ ligands per Mo center equivalent.

The X-ray structure of **2** shows that it possesses a linear Mo≡N≡Mo core, as found previously for the dimethylamide analogue.[11] Additionally, an inversion center at the bridging nitrogen atom is indicated by the crystallography. According to magnetic susceptibility studies, **2** is a ground-state doublet.

The ultimate step in the formation of **2** is thought to be the combination of the terminal nitrido complex $N\equiv Mo(N[^iPr\text{-}d_6]Ar)_3$ (**3**) with **1**-d_{18}. Formation of **3** presumably occurrs via dinuclear N_2 reductive cleavage,[10,12] a process evidently slow relative to consumption of **1**-d_{18}. Terminal nitride **3** was prepared independently by reaction of **1**-d_{18} with $N\equiv Cr(O^tBu)_3$,[13] and in control experiments was found to combine rapidly with **1**-d_{18} to produce purple **2**. These results are in stark contrast with those obtained for $Mo(N[R]Ar)_3$ (R = ^tBu), inasmuch as a μ-nitrido linkage was obviated sterically in that system.

Divergent pathways were observed for the reaction of **1** with benzonitrile (PhCN). Under conditions of rapid mixing of solutions of **1** and PhCN in a 1:1 ratio, nitrile coupling chemistry[14–18] was the result, leading to $(\mu\text{-N}[Ph]C-C[Ph]N)$-$[Mo(N[^iPr]Ar)_3]_2$ (**4**). Compound **4** is thought to arise from dimerization of putative intermediate adduct $(PhCN)Mo(N[^iPr]\text{-}Ar)_3$ (**5**). An analogue **16** of diamagnetic **4**, prepared from acetonitrile and $Mo(N[R]Ar)_3$ (R = ^tBu), was characterized by X-ray diffraction and found to have a C−C bond distance of 1.43-(2) Å. All indications are that **4** is a 1e (per Mo) coupling product.

In addition to the coupling of PhCN, **1** was found to effect the *cleavage* of this substrate. This reaction was optimized with a 3:1 ratio of **1**:PhCN; the products are benzylidyne $PhC\equiv Mo(N[^iPr]Ar)_3$ (**7**) (the ^{13}C NMR spectrum shows a resonance for the α-C at 294.9 ppm) and **2**. Slow addition of PhCN to a solution of **1** produced the best yields of **7**. Splitting of the nitrile functionality to alkylidyne and nitride components is known for ditungsten compounds.[19] A possible mechanism for the new PhCN cleavage reaction involves attack on putative intermediate adduct **5** by **1**, giving a dinuclear intermediate which can fragment to **3** and **7**. Finally, capture of **3** by the third equivalent of **1** produces **2**. The low solubility of **2** enables its facile separation from benzylidyne **7**.

Treatment of **1** with benzophenone (1 equiv) produced not the pinacol−coupling product, as might have been imagined,[20,21] but rather an adduct **8** with the carbonyl moiety complexed in an η^2

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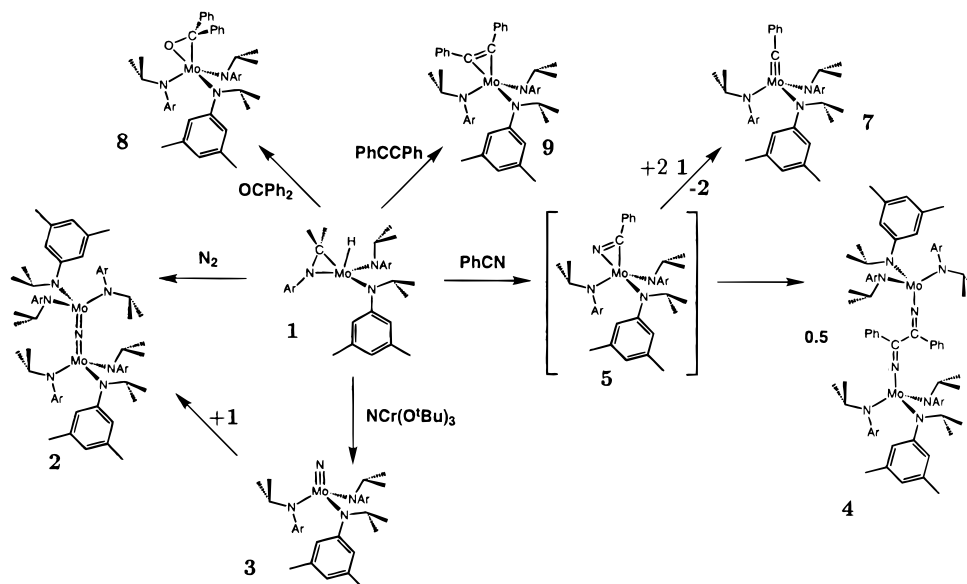
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Figure 1. Reaction pinwheel highlighting the chemistry of imine−hydride **1** (Ar = 3,5-C$_6$H$_3$Me$_2$).
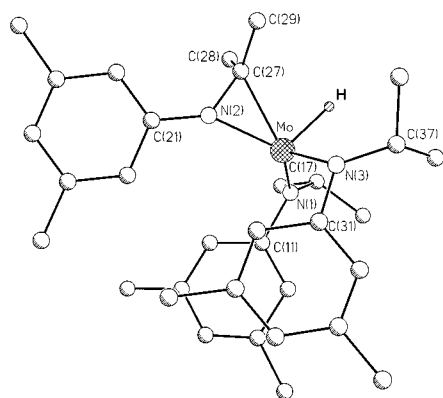

Figure 2. Ball-and-stick drawing of Mo(H)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$ (**1**) from a single-crystal neutron diffraction study. Selected distances (Å) and angles (deg): Mo−H, 1.69(5); Mo−N(1), 1.93(2); Mo−N(2), 1.95-(2); Mo−N(3), 2.02(2); Mo−C(27), 2.18(2); N(1)−C(17), 1.56(2); N(2)−C(27), 1.44(2), N(3)−C(37), 1.47(2); N(1)−Mo−N(2), 117(1); N(1)−Mo−N(3), 117(1); N(2)−Mo−N(3), 122(1); N(1)−Mo−C(27), 116(1); N(2)−Mo−C(27), 40.3(7); N(3)−Mo−C(27), 122(1).

fashion to Mo (Figure 3). Note that the *tert*-butyl-substituted analogue of **1**, namely Mo(N[R]Ar)$_3$ (R = ^{t}Bu), does not exhibit *any* reaction with benzophenone. The observed η^2-complexation of benzophenone by **1** raises the question of whether nitriles, as in putative **5**, also would prefer to engage in η^2-binding.[22]

As for alkynes, it was hoped that **1** would be competent for their cleavage to corresponding alkylidyne species.[19] However, treatment of **1** with tolane produced only the green adduct (η^2-PhCCPh)Mo(N[^{i}Pr]Ar)$_3$ (**9**), even under conditions of excess **1**.

In conclusion, an attempt to prepare the putative ^{i}Pr-substituted three-coordinate[2,3] molybdenum(III) complex Mo(N[^{i}Pr]Ar)$_3$ (**10**) led instead to the isolation and characterization of a new type of reactive hydride−imine complex, **1**. In all reactions studied thus far, **1** behaves as a source of **10**, serving to transfer the tricoordinate Mo fragment. Hydride **1** is electrochemically versatile, in that it serves as a 3e reductant in its dinitrogen and PhC≡N splitting reactions and as a 1e reductant in its coupling of PhCN. The PhCN-coupling reaction, producing **4**, was found to be unaffected by the presence of 1 equiv of ethyl acetate, an observation hinting at the functional-group-selective nature of **1**.

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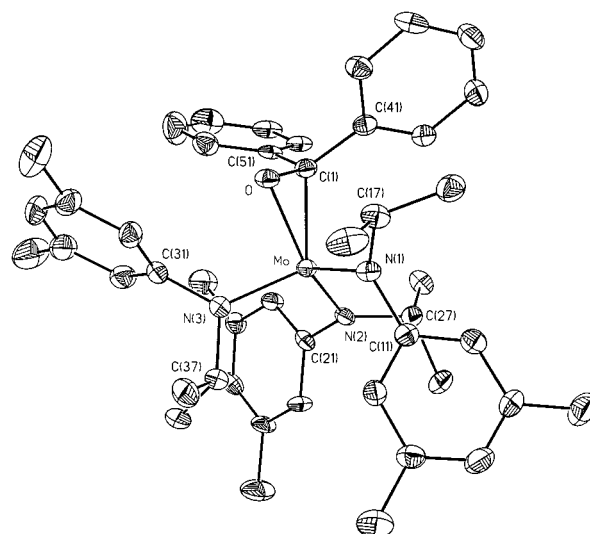

Figure 3. 35% thermal ellipsoid plot of (η^2-O=CPh$_2$)Mo(N[^{i}Pr]Ar)$_3$ (**8**). Selected distances (Å) and angles (deg): Mo−N(1), 1.954(4); Mo−N(2), 1.980(4); Mo−N(3), 1.950(5); Mo−C(1), 2.149(5); Mo−O, 2.049(3); O−C(1), 1.377(6); N(3)−Mo−N(1), 114.8(2); N(3)−Mo−N(2), 106.3-(2); N(1)−Mo−N(2), 108.1(2); N(3)−Mo−O, 88.3(2); N(1)−Mo−O, 93.4(2); N(2)−Mo−O, 144.9(2); N(3)−Mo−C(1), 115.6(2); N(1)−Mo−C(1), 103.7(2); N(2)−Mo−C(1), 108.1(2); O−Mo−C(1), 38.2(2); C(1)−Mo−O, 74.8(3); Mo−C(1)−O, 67.0(2).

Supporting Information Available: Synthetic, spectroscopic and analytical data for complexes **1**, **1**-d_{18}, **2**−**4**, **6**−**9**; tables of crystal data, atomic coordinates, structure solution and refinement, bond lengths and angles, and anistropic thermal parameters for compounds **1** (neutron study), **1**-d_{18} (X-ray study), **2**, **3**, **6**, and **8**; and information pertaining to the density functional theory study of hypothetical Mo(H)(η^2-H$_2$C=NH)-(NH$_2$)$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.