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Insertion of an electron-rich alkyne into a molybdenum amido bond

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A pseudo-octahedral molybdenum dimethylamido complex that readily inserts 3-hexyne forming a new C–N bond has been characterized.

Hydroamination of carbon–carbon double and triple bonds is a reaction of great potential utility for which several classes of catalysts have been designed.[1] For some late transition metal,[2] group 3,[3] and lanthanide[4] systems, the key C–N bond forming step may involve *cis* 1,2-insertion of the unsaturated organic into a metal–nitrogen bond.[5]

Clean, stoichiometric examples of alkyne insertion into metal–nitrogen bonds are rare, being largely restricted to insertions of highly electron deficient alkynes, *e.g.* dimethyl acetylenedicarboxylate, into late transition metal amide bonds.[6] Although 2-aminovinyl complexes are likely intermediates in many alkyne hydroaminations,[1–4] structurally characterized examples resulting from insertion of electron-rich alkynes into amide bonds are uncommon.

In the course of investigating synthetic strategies for the synthesis of molybdenum bis(amido) complexes incorporating the di-*N*,*N*-(pyrrolyl-α-methyl)-*N*-methylamine (dpma)[7] ligand, we found that treatment of $Mo(NMe_2)_4$[8] with H_2dpma (Fig. 1) generated $Mo(NMe_2)_2(NHMe_2)$(dpma)† (**1**).[9] The paramagnetic molybdenum(IV) complex is somewhat thermally sensitive. Nevertheless, a structure of reasonable quality was obtained by single-crystal X-ray diffraction.‡

Several structural features of **1** (Fig. 1) are noteworthy. The angles about the pseudo-octahedral metal center are very nearly ideal except those defined by the chelate-restricted pyrrolyl nitrogens (N1 and N2). For example, the N1–Mo–N3 and N2–Mo–N3 angles refined as 76.3(2) and 78.5(2)°, respectively. The average Mo–N(amido) distance of 2.004(7) Å is somewhat longer than found for $Mo(NMe_2)_4$ of 1.926(6) Å, which may be attributed to the higher coordination number of **1**. Of special note, the angle between the N4–C41–C42 and N5–C51–C52 planes is only 10.0(5)°, indicating that the two dimethylamido substituents are approximately coplanar.

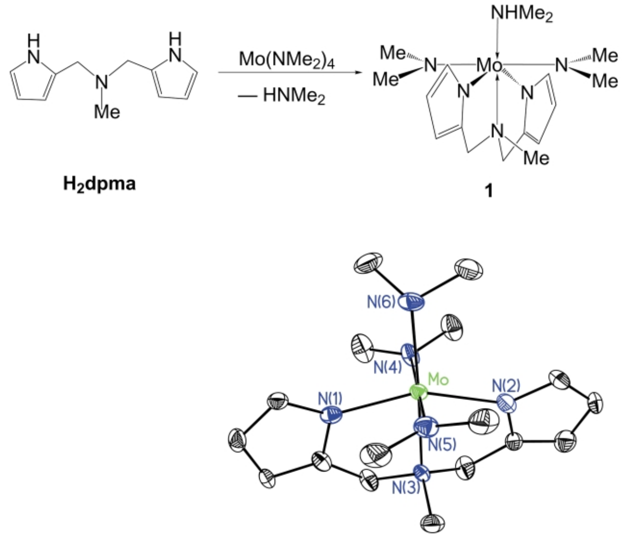

Fig. 1 Synthesis and structure of $Mo(NMe_2)_2(NHMe_2)$(dpma) (**1**) found by X-ray diffraction.

Unlike $Mo(NMe_2)_4$,[8] **1** displays a triplet ground state. A simple molecular orbital analysis is informative (Fig. 2). Taking N3–Mo–N6 as the *z*-axis for the pseudo-octrahedral complex, the three d-orbitals with π-symmetry are d_{xz}, d_{yz}, and d_{xy}. In the solid state geometry, the d_{xz} and d_{xy} orbitals can potentially engage in ligand-to-metal π-bonding with the amido and pyrrolyl nitrogen lone pairs, while d_{yz} is nonbonding. We have recently proposed that pyrrolyl moieties are weak π-donors, which is substantiated by the triplet ground state for **1**.[10] Hence, the only orbital for which π-interactions are significant is d_{xz}. In-phase and out-of-phase ligand π-basis sets can be generated from the amido lone pairs. The out-of-phase ligand π-donor orbital can interact with d_{xz}, but the in-phase combination can only interact with the metal-based p_z orbital. Since p_z is quite high in energy due to interaction with axial donors, the in-phase combination is effectively nonbonding. Considering the relatively high-energy filled orbital with amido character, the amido nitrogens of **1** may be expected to exhibit substantial nucleophilicity.

As shown in Fig. 3, $Mo(NMe_2)_2(NHMe_2)$(dpma) (**1**) reacts rapidly with 3-hexyne to give $Mo(NMe_2)[\eta^2\text{-}C(Et)=C(Et)NMe_2\text{-}C,N]$(dpma) (**2**).† Owing to the thermal instability of **1**, the 2-aminovinyl complex **2** is most readily prepared by generation of **1** *in situ* followed by the addition of excess alkyne. By this method, **2** was obtained as a thermally-stable, brown solid with a triplet ground state in 69% yield after purification.

In contrast to the reactivity noted for **1**, $Mo(NMe_2)_4$ reacts with excess 3-hexyne to give rapid formation of poly(3-hexyne). Complex **2** does not react further with 3-hexyne at room temperature.

Reaction of **1** with alkyne likely proceeds by initial displacement of dimethylamine to form an unobserved η^2-

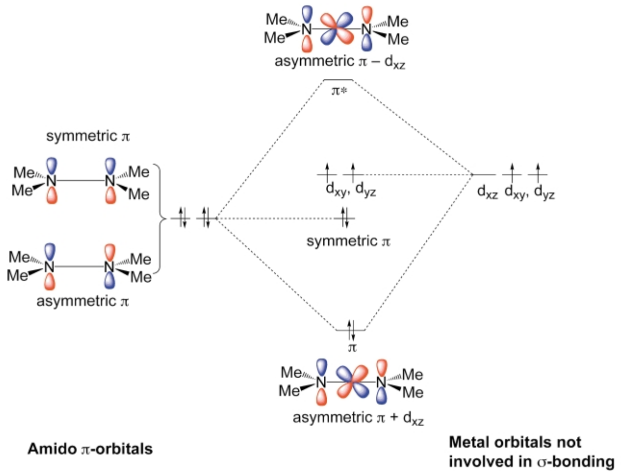

Fig. 2 Part of the molecular orbital diagram for $Mo(NMe_2)_2(NHMe_2)$(dpma) (**1**) illustrating the amido π-interactions.

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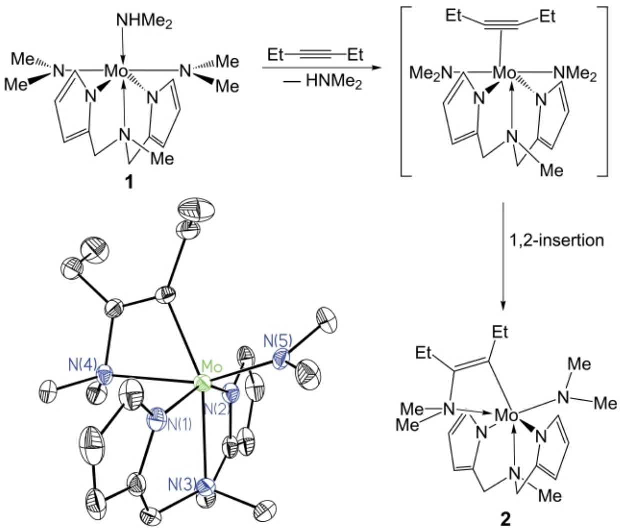

Fig. 3 Synthesis of Mo(NMe$_2$)[η^2-C(Et)=C(Et)NMe$_2$-*C*,*N*](dpma) (**2**). The structure of **2** found by X-ray diffraction is shown as an ORTEP diagram.

alkyne intermediate. Coordination of the alkyne may enable intramolecular nucleophilic attack by the basic dimethylamido substituent forming a new C–N bond. Alternatively, the C–N bond forming step may be described as an interaction between the filled Mo(NMe$_2$)$_2$ asymmetric π-interaction (Fig. 2) and the C–C π* LUMO of the coordinated alkyne; in this way, the metal center may be viewed as directly mediating the C–N bond forming reaction by enabling amido lone pair to alkyne π* donation.

X-Ray diffraction‡ on a single crystal of **2** (Fig. 3) provided an Mo–C3 distance of 2.098(4) Å. The Mo–N4 distance of 2.380(4) Å is *ca.* 0.15 Å longer than the other Mo–N(donor) distances of **1** and **2**; the weakening of this donor interaction is reasonably attributed to strain in the metalloazacyclobutene ring.

The facile reactivity of Mo(NMe$_2$)$_2$(NHMe$_2$)(dpma) (**1**) with alkynes appears to be driven by the electronic structure of this somewhat unusual bis(amido) complex. In addition to further stoichiometric reaction chemistry, catalytic schemes for the hydroamination of alkynes by secondary amines incorporating derivatives of **1** are currently under investigation.

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Notes and references

† Mo(NMe$_2$)$_2$(NHMe$_2$)(dpma) (**1**): under an inert atmosphere of purified nitrogen, a near frozen solution of Mo(NMe$_2$)$_4$ (0.844 g, 3.10 mmol) in 5 mL of diethyl ether was treated with H$_2$dpma (0.586 g, 3.10 mmol) in 5 mL of diethyl ether. The reaction was allowed to warm until the purple of the starting material faded to brown, then 10 mL of pentane was layered on the reaction. The layered solution was stored at −35 °C, which gave the product as a brown solid in 41% yield (0.476 g). Thus far, air sensitivity and thermal instability of **1** have prevented adequate elemental analysis. Magnetic susceptibility (Evans' method) μ_{eff} = 2.34 μ_{B}.

Mo(NMe$_2$)[η^2-C(Et)=C(Et)NMe$_2$-*C*,*N*](dpma) (**2**): under an inert atmosphere of purified nitrogen, a near frozen solution of Mo(NMe$_2$)$_4$ (0.186 g, 0.683 mmol) in 3 mL of diethyl ether was added a cold solution of H$_2$dpma (0.129 g, 0.683 mmol) in 4 mL of diethyl ether. The reaction was allowed to warm and stir for 15 min. A diethyl ether (3 mL) solution of 3-hexyne (0.137 g, 1.67 mmol) was added rapidly. After stirring for 10 min, volatiles were removed *in vacuo*. The product was extracted into diethyl ether and filtered. The compound crystallized as brown parallelopipeds at −35 °C in 68% yield (0.208 g). Magnetic susceptibility (Evans' method) μ_{eff} = 2.73 μ_{B}. Anal. calc. for C$_{21}$H$_{35}$MoN$_5$: C, 55.62; H, 7.78; N, 15.44. Found: C, 55.34; H, 7.54; N, 15.75%.

‡ *Crystal data* for **1**: C$_{17}$H$_{32}$MoN$_6$, M = 416.43, orthorhombic, a = 15.12(2), b = 15.30(3), c = 17.118(13) Å, U = 3958(10) Å^3, space group $Pbca$, Z = 8, μ(Mo-Kα) = 0.674 mm^{-1}, θ range 2.24–23.32°, 2853 independent reflections (R_{int} = 0.2544). The final $wR(F^2)$ = 0.1202 and $R(F)$ = 0.0599 for reflections $I > 2\sigma$.

For **2**: C$_{21}$H$_{35}$MoN$_5$, M = 453.48, monoclinic, a = 7.9289(12), b = 31.762(4), c = 8.9905(17) Å, β = 101.546(13)°, U = 2218.4(6) Å^3, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 0.606 mm^{-1}, θ range 2.40–23.27°, 3180 independent reflections (R_{int} = 0.0291). Final $wR(F^2)$ = 0.0989 and $R(F)$ = 0.0413 for reflections $I > 2\sigma$.

CCDC reference numbers 179378 and 179379.

See http://www.rsc.org/suppdata/cc/b2/b201389d/ for crystallographic data in CIF or other electronic format.

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