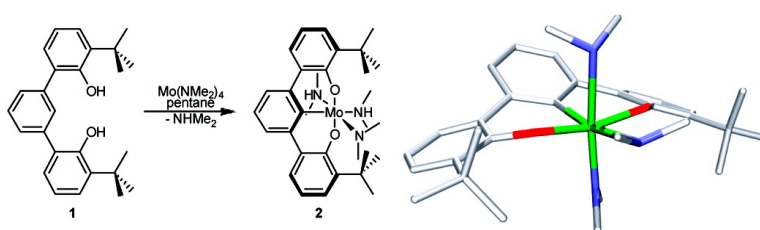


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Synthesis, Characterization, and Reactivity of a d^2 , Mo(IV) Complex Supported by a New OCO–Trianionic Pincer Ligand

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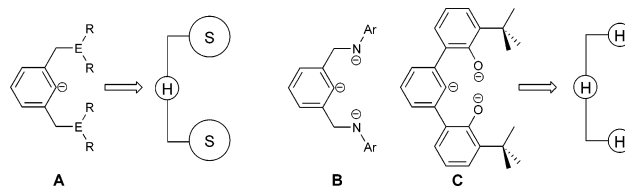
Early (groups 3–6) and late (groups 7–10) transition metal complexes have distinct structural and reactivity properties. Early metals favor high oxidation states, high coordination numbers, are typically electrophilic and are intolerant of many functional groups. The opposite is true for late metal complexes, in which low coordinate and low oxidation states prevail and a wide range of functional groups are tolerated.¹ By altering the properties of ancillary ligands, chemists are able to manipulate the inherent properties of a specific metal to promote and amplify reactions.

Pincer ligands are easily modified and offer an excellent opportunity to manipulate the electronic and geometric properties of metal complexes.² Classic pincer ligands (**A**, Scheme 1)³ are complementary to late transition metals due to their soft–hard–soft arrangement of donor atoms. However, only a few early metals have been supported by this original ligand design.⁴ Our approach is to match the harder early transition metals with a harder pincer ligand. Instead of a soft–hard–soft pincer motif, we have synthesized a series of new hard–hard–hard pincer ligands based on amido–arylide–amido linkages (**B**, Ar = 2,6-*i*-PrC₆H₃, and 3,5-MeC₆H₃, Scheme 1) and attached them to group IV metals,⁵ but significant challenges remain.

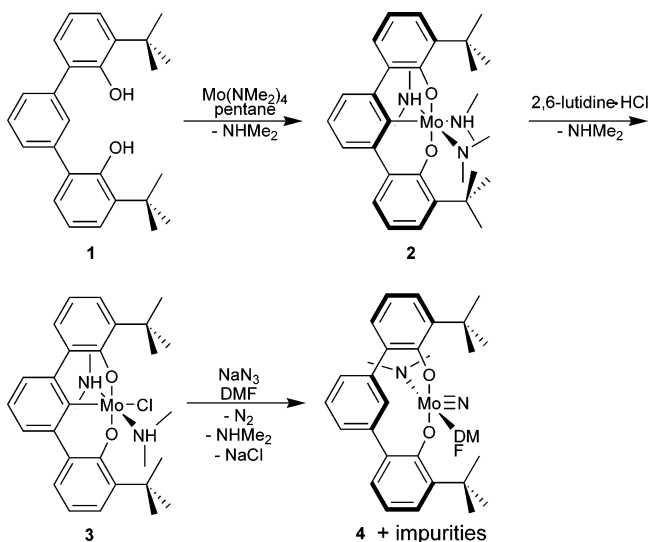
Lithium amides and arylides readily reduce metal substrates, thus complicating metalation. Alternatively, starting with neutral ligands requires the activation of distinctly different N–H and C–H bonds during metalation which can be difficult as separate problems, let alone in concert.⁶ To access group VI complexes supported by a trianionic pincer ligand, we began synthesizing ligands based on an OCO arrangement of donor atoms (**C**, Scheme 1).⁷ Herein we report a successful metalation via ArO–H and Ar–H bond activation to generate a d^2 , Mo(IV) complex supported by a new trianionic OCO terphenyl pincer ligand and its subsequent reactivity.

O–H and C–H bond activation to metalate **1** is achieved with remarkable ease under mild conditions. The Mo(IV), d^2 ($\mu_{\text{eff}} = 3.06 \mu_B$)⁸ amido–dimethylamine complex, [3,3''-di-*tert*-butyl-2,2''-di-(hydroxy- κ O)-1,1':3',1''-terphenyl-2'-yl- κ C²](*N*-methylmethanaminato)bis(*N*-methylmethanamine)molybdenum(IV), abbreviated as [BuOCO]Mo(NMe₂)(NHMe₂)₂ (**2**), is formed at –35 °C upon combining pentane solutions of **1** and Mo(NMe₂)₄ (Scheme 2). Compound **2** precipitates in 80% yield as an orange powder and can be further purified by recrystallization from concentrated solutions of 1,2-dimethoxyethane (DME) at –35 °C. The ¹H NMR spectrum of paramagnetic **2** revealed broad resonances that prohibited a detailed analysis, but some information could be gleaned. For example, ¹Bu protons appear at 2.83 ppm, the NHMe₂ protons are observed at 2.01 ppm, and three sets of aryl-H resonances are observed, with one appearing extremely downfield at 66.7 ppm while the others resonate at 9.74 ppm and upfield at –9.85 ppm. Ultimately, an X-ray structural analysis on a single crystal obtained from cooled concentrated DME solutions of **2** confirmed its identity.

Scheme 1. Classic Pincer (**A**, E = P, N: S–H–S) and New Trianionic Pincer Ligands (**B**, **C**: H–H–H)



Scheme 2



The solid-state structure of **2** is presented in Figure 1 and validates the assignment of a trianionic tridentate pincer ligand. The structure consists of an octahedral Mo(IV) center bound to the pincer ligand, two dimethylamines ($d(\text{Mo}1-\text{N}2) = 2.390(3) \text{ \AA}$, $d(\text{Mo}-\text{N}3) = 2.430(3) \text{ \AA}$) and one dimethylamido ($d(\text{Mo}-\text{N}1) = 1.928(3) \text{ \AA}$). The amido and amine ligands are easily distinguished since N1 is trigonal and N2 and N3 are pyramidal. In addition, the protons on N3 and N4 were located from the difference Fourier map, and the M–N bond lengths are significantly different. The Mo–NMe₂ ligand is twisted away from the N2–Mo–N3 plane by 35° to break the otherwise perfect solid-state C_s symmetry. A space-filling model indicates the twist is due to packing forces that place a DME solvent molecule atop the amido group.^{9a}

Considerable strain is imparted to the pincer backbone and is attributable to congestion caused by the dimethylamine ligand *trans* to C1. The N–Me groups are nearly parallel to the O1–C1–O2 plane which forces them into the 'Bu's of the pincer. As a result, the 'Bu groups are strained creating 33 and 32° torsion angles between the aryl backbone C2–C7 and C6–C17 connections, respectively, and the central ring is bent up by 30°.

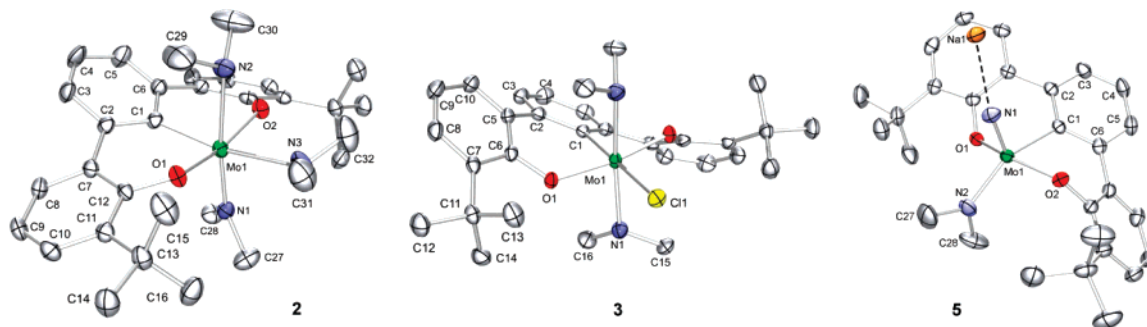
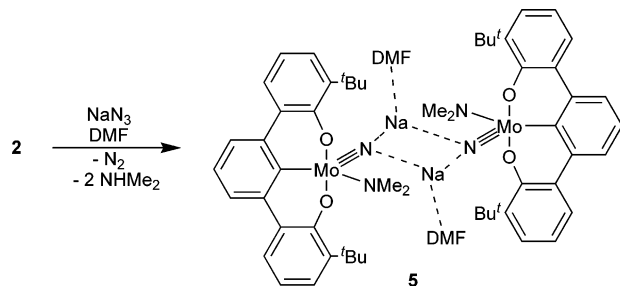


Figure 1. ORTEP molecular structures of compounds **2**, **3**, and **5** (half of dimer) with ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules for **2** (DME), **3** (benzene), and **5** (DMF) are removed for clarity.

Scheme 3



When benzene solutions of **2** are treated with 2,6-lutidine·HCl and left undisturbed, large purple-red crystals deposit within 2 h (Scheme 2). A ^1H NMR spectrum of the crystals revealed aryl-H resonances downfield at 28.81 ppm ($\nu_{1/2} = 12$ Hz) and upfield at -1.10 , -1.98 , and -5.34 ppm ($\nu_{1/2} = 7$ Hz). The $\text{N}-\text{Me}$ protons are broad and located at -2.18 ppm ($\nu_{1/2} = 153$ Hz).

With the aid of a single-crystal X-ray diffraction experiment, the crystals were identified as the d^2 ($\mu_{\text{eff}} = 2.56 \mu_{\text{B}}$) 8 Mo(IV) chloride complex $[\text{tBuOCO}]\text{MoCl}(\text{NHMe}_2)_2$ (**3**) presented in Figure 1. The octahedral Mo(IV) center is coordinated by the pincer ligand, *trans*-dimethylamines, and a chloride. C_2 symmetry now results from a 33° twist in the backbone along the $\text{Cl1}-\text{Mo}-\text{C1}$ axis, due to the smaller Cl^- ligand. The dimethylamine ligands orient off axis by 57° and are rotated 88° with respect to each other, which again can be attributed to sterics. 9a

The dimethylamines on **3** are bound tightly and do not release under vacuum nor substitute with THF, DME, or CO, even at elevated temperatures (80°C). Attempts to reduce **3** with Na/Hg or alkylate with MeMgCl were unsuccessful, providing only intractable mixtures and protonated **1**.

$[\text{tBuOCO}]\text{MoCl}(\text{NHMe}_2)_2$ (**3**) did not react with Me_3SiN_3 or NaN_3 in refluxing THF. Instead, the more polar DMF solvent had to be used. Red solutions of **3** in DMF turn yellow-orange when treated with NaN_3 at 25°C and release N_2 to provide a mixture of products that are inseparable. A single crystal of one species was procured from a mixture of solids and was identified as the yellow Mo(VI) nitride complex $[\text{tBuOCHO}]\text{Mo}=\text{N}(\text{NMe}_2)(\text{DMF})$ (**4**, Scheme 2). 9b

Since **4** is produced in low yield as part of a mixture of unidentifiable products, we sought other routes to nitrido species, and treating **2** with NaN_3 in DMF proved effective. Nitrido anion dimer $\{[\text{tBuOCO}]\text{Mo}=\text{N}(\text{NMe}_2)\text{Na}(\text{DMF})\}_2$ **5** is synthesized in excellent yield (86%) and purity according to Scheme 3; the molecular structure is presented in Figure 1. The nitride occupies

the apical position of a distorted square pyramid ($d(\text{Mo}=\text{N}) = 1.6601(15)$ Å), but unlike **4**, the OCO ligand is now attached as a trianionic pincer. To balance charge, a Na ion, solvated with DMF, is present $2.4453(17)$ Å from the nitride. Multinuclear NMR spectroscopic, elemental, and IR characterization of **5** are consistent with the X-ray findings.

Considering the facile C–H bond activation to form **2** and the observed attached/detached ring in **5** and **4**, we are currently exploring the reversible activation of the backbone C–H bond. The detached ring C–H bond represents a masked metal hydride that may be activated when needed. These preliminary results indicate that new OCO trianionic pincer ligands can support high oxidation state transition metal complexes.

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Supporting Information Available: Full experimental procedures, spectroscopic, and crystallographic (CIF) data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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