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Facile Formation of Molybdenum(VI) Monooxo Aryloxides $MoO(OAr)_{4-n}Cl_n$ from Molybdenum Dioxo Dichloride

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Molybdenum monooxo compounds $MoO(OAr)_{4-n}Cl_n$ ($n = 0$–2, Ar $= 2,6\text{-}Me_2C_6H_3$ or $2,6\text{-}i\text{-}Pr_2C_6H_3$) have been synthesized starting from the dioxo precursor MoO_2Cl_2. The complexes are characterized spectroscopically and by X-ray diffraction. The formation mechanism likely involves phenol precoordination followed by addition across the Mo=O bond.

Group VI metal aryloxides and oxo aryloxides have become prominent because of their utility as precursors for metathesis and metathesis polymerization catalysis. Compounds of the formula $M(OAr)_{6-n}Cl_n$ (M = W or Mo) and the monooxo compounds $WO(OAr)_{4-n}Cl_n$ have been shown to act as catalyst precursors in either the presence or absence of main group cocatalysts such as alkylaluminum complexes or organotin hydrides.[1,2] It is often suggested that the precursor undergoes substitution at chlorine sites to form the active metal carbene catalyst, and therefore, the fully aryloxylated derivatives tend to be less active than those with one or more chlorine substituents. Both W and Mo compounds are used, but Ivin et al. has noted that the Mo analogues are usually more active.[1] Considering the potential utility of these compounds, it is surprising that complexes $MoO(OAr)_{4-n}Cl_n$ have not yet appeared in the literature alongside their tungsten congeners. A report of some fully substituted derivatives, however, has recently appeared[3] and has triggered this publication of our unexpectedly easy route to both fully and partially substituted complexes.

Monooxo complexes $WO(OAr)_{4-n}Cl_n$ are reported to be readily accessible by reaction of the commercially available precursor $WOCl_4$ with either aryl alcohol or its anion,[4−8] but the corresponding Mo precursor $MoOCl_4$ is notoriously difficult to handle.[9] The molybdenum(VI) complex is photolabile and prone to disproportionation to chlorine and Mo(V) products, and it must be freshly prepared before use.[10] Although there is an old report of $MoOCl_4$ + ArOH yielding the corresponding oxo aryloxides,[11] this has never been confirmed and was not reproducible by us. Hayano et al. reported the successful formation of $MoO(OAr)_4$ for several mono- and multidentate aryloxy ligands by the low-temperature reaction of $MoOCl_4$ with the corresponding aryloxy anions, but the yields are low and the characterization minimal. They have, however, also demonstrated the utility of these materials as procatalysts for metathesis polymerization.[3]

Our interest in molybdenum oxo aryloxides has centered on dioxomolybdenum complexes that can model heterogeneous active sites in oxygen catalysis. We have reported the synthesis of the first four-coordinate aryloxide $MoO_2(OAr)_2$, **1**, from commercially available MoO_2Cl_2[12] and more recently the formation of the four-, five-, and six-coordinate analogues by manipulation of the steric environment of the aryloxy ligand.[13] The fifth and sixth coordination sites in the latter cases are filled by pyridine ligands. In the absence of pyridine or coordinating solvent, however, the reaction pathway is quite different, leading immediately to monooxo aryloxides

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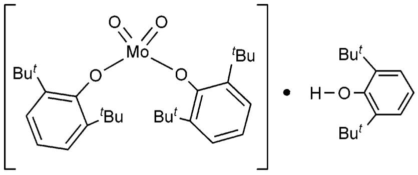
at room temperature. Here, we describe reactions leading to $MoO(OAr)_{4-n}Cl_n$ for $n = 2$, 1, and 0, as well as a proposed mechanism for the process. In a later full article, we will explore the generality of these reactions, as well as the suitability of these compounds as catalyst precursors.



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Synthesis and Characterization

The reaction of a suspension of MoO_2Cl_2 with LiO-2,6-$C_6H_3R_2$ (R = Me, ^{i}Pr) in ether (eq 1) at room temperature immediately forms a dark blue solution characteristic of d^0 group VI monooxo aryloxides.[8,14−16] The extent of product substitution is highly sensitive to ligand and stoichiometry.

$$MoO_2Cl_2 + x\mathrm{LiOAr} \rightarrow MoO(OAr)_{4-n}Cl_n \qquad (1)$$

$$x = 4,\ n = 0,\ \mathrm{Ar} = 2,6\text{-}^i\mathrm{Pr}_2C_6H_3,\ \mathbf{2}$$

$$x = 2,\ n = 1,\ \mathrm{Ar} = 2,6\text{-}\mathrm{Me}_2C_6H_3,\ \mathbf{3}$$

$$x = 1,\ n = 2,\ \mathrm{Ar} = 2,6\text{-}\mathrm{Me}_2C_6H_3,\ \mathbf{4}$$

If these compounds are combined in a 1:4 ratio, the fully substituted $MoO(O\text{-}2,6\text{-}^iPr_2C_6H_3)_4$ can be obtained in 35% yield after repeated recrystallization (yield is quantitative by ^{1}H NMR spectroscopy). By ^{1}H and ^{13}C NMR spectroscopies, the resonances of the aryl group are easily identified, and the Mo═O IR stretch of 954 cm^{-1} is characteristic of monooxomolybdenum(VI) complexes.[9] The dark blue color was initially surprising (UV/vis spectroscopy shows absorbances at 618, 315, and 278 nm), when compared to yellow or orange $MoO_2(OAr)_2$ or $MoO(OR)_4$ (R = alkyl) complexes, but it has been attributed to phenolate to molybdenum charge transfer in the Mo(VI) monooxo phenolate $[LMoO(OAr)_2](NO_3)$ [L^- = hydrotris(3,5-dimethyl-1-pyrazolylborate), OAr = p-O−C_6H_4−OC_2H_5].[16]

The trisubstituted complex was obtained for the dimethylphenoxy ligand. In this case, a similar reaction, but using a 1:2 Mo/LiOAr ratio, yielded crystalline $MoO(OAr)_3Cl$, **3**, in 41% yield (also quantitative by NMR spectroscopy). The spectroscopic data are quite similar to those of the tetrasubstituted complex.

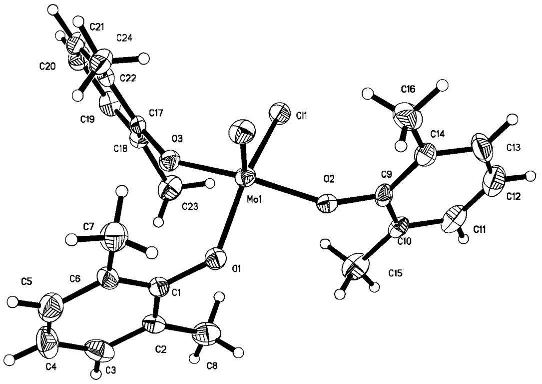

Figure 1. ORTEP diagram of the trisubstituted complex $MoO(OAr)_3Cl$, **3**.

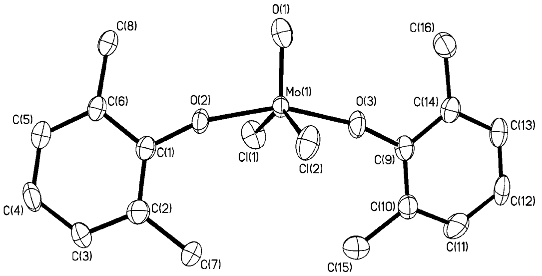

Figure 2. ORTEP diagram of the disubstituted complex $MoO(OAr)_2Cl_2$, **4**. Hydrogen atoms are not shown.

The crystal structure of **3** is shown in Figure 1. The structure is intermediate between square pyramidal with an apical molybdenum oxo group and trigonal bipyramidal with O(2) and O(3) in apical positions. The Mo(1)−O(1)−O(4)−Cl(1) fragment is planar within 0.022 Å, but the ArO−Mo−OAr and ArO−Mo−Cl angles [156.1(1)° and 144.4(1)°] are significantly distorted from ideal angles. The O═Mo−O(1,2,3) and O═Mo−Cl angles are 101.6(2)°, 101.2(2)°, 110.2(2)°, and 105.3(1)°, respectively. There is no coordinated water trans to the oxo group, in contrast to Floriani's[17] and our[18] calixarene-ligated molybdenum(VI) oxo complexes. The Mo═O bond length is 1.667(3) Å; the Mo−OAr bonds are 1.893(3), 1.862(3), and 1.891(4) Å; and the Mo−Cl bond is 2.345(2) Å. Few crystal structures of $Mo^{VI}O(OR)_4$ have been reported for comparison, but these distances are within normal ranges for other Mo(VI) oxo and aryloxide complexes.[9,19]

Finally, the disubstituted complex can be obtained by variation of the stoichiometry in eq 1 to produce $MoO(OAr)_2Cl_2$. In this case, however, a simpler and cleaner procedure is available, consisting of mixing the parent alcohol ArOH with MoO_2Cl_2 at room temperature, again in ether (equation 2). The NMR yield is again quantitative, and the dark blue product can be crystallized in 49% yield.

$$MoO_2Cl_2 + 2\mathrm{HOAr} \rightarrow MoO(OAr)_2Cl_2 \qquad (2)$$

$$\mathrm{Ar} = 2,6\text{-}\mathrm{Me}_2C_6H_3,\ \mathbf{4}$$

The X-ray structure of **4** is shown in Figure 2. The structure is similar to that of the trisubstituted complex **3**. The Mo(1)−Cl(1)−Cl(2)−O(1) fragment is planar within 0.016 Å, but the ArO−Mo−OAr and Cl−Mo−Cl angles

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[157.6(5) 144.65(19)°] are again distorted from ideal angles. The O═Mo−Cl angles [106.7(4)° and 108.6(4)°] are slightly larger than the O═Mo−OAr ones [101.0(5)° and 101.3(6)°]. The Mo═O bond, 1.628(13) Å, is slightly shortened from average,[19] possibly because of the small number of π-donating oxygen ligands in the basal "plane." The Mo−OAr [1.838(10), 1.856(11) Å] and Mo−Cl [2.319(5), 2.325(5) Å] bond distances are again within normal ranges.[9]

Reaction Mechanism

We suggest that the aryl alcohol adds across the Mo═O double bond to form an unstable intermediate, MoO(OAr)(OH)Cl_2, which immediately exchanges with further alcohol to form the product $MoO(OAr)_2Cl_2$, **4** (eq 2). This compound is stable in the presence of further phenol. The stoichiometric side product is 1 equiv of water, which was not detected by NMR spectroscopy. However, when the isolated material was exposed to 0.05 equiv of water, its stability was unchanged. No water was observed in the crystal lattice.

The addition of phenol across the Mo═O double bond can be viewed as a precoordination of phenol to the metal center, followed by protonation of the terminal oxo group on molybdenum. Although this reactivity is rarely seen in MoO_2^{2+} complexes, attack of protons and other cationic groups on metal oxo groups is well-precedented for several metals[20] and for other molybdenum-containing moieties.[21−27] Indeed, Kühn et al. recently proposed a similar precoordination followed by protonation of a MoO_2^{2+} group by *tert*-butylhydroperoxide.[28] We postulate a similar mechanism for the formation of monooxo molybdenum(VI) calixarene complexes formed from MoO_2Cl_2 and anionic calixarene precursors.[18]

The requirement for precoordination of phenol is supported by experimental observations. The attack of phenol on the oxo group in these molybdenum complexes can be contrasted with our previously reported molybdenum dioxo diaryloxide (**1**), which cocrystallizes with 1 equiv of phenol. No evidence of proton transfer is found in that system.[12] Presumably the difference is due to the steric environment of the metal center. In complex **1**, the steric bulk inhibits phenol coordination, and the free phenol is not sufficiently acidic to protonate the oxo group. Also consistent with a precoordination step, the formation of monooxo complexes $MoO(OAr)_4$ is not observed in the presence of pyridine (in which case the pyridine-ligated dioxo aryloxide is isolated[13]) or in coordinating solvents (e.g., acetonitrile, THF). When a weakly coordinating solvent is removed in vacuo, though, a dark blue solid is obtained that contains the monooxo aryloxide as its major component. These conditions, however, are less synthetically useful because of their lower yields.

The formation of $MoO(OAr)_4$ from the reaction of molybdenum dioxo dichloride and the lithium phenolate was less readily interpreted. Indeed, the compounds $MoO(OR)_4$ for R = alkyl have been reported to undergo ether loss to form the dioxo diaryloxides, implying that the dioxo form is more stable than the monooxo one.[29] We did find one report, also authored by Turova et al., of the disproportionation reaction of the dioxo complex $WO_2(OR)_2$ to form a mixture of uncharacterized insoluble oxoalkoxides and the monooxo compound $WO(OR)_4$.[30] Similar reactivity might be observed in our case; however, no excess LiOAr or other soluble side products are observed by ^{1}H NMR spectroscopy.

The more likely possibility, in our opinion, is a water-catalyzed reaction. Although we employ stringent techniques (see experimental details in the Supporting Information) to exclude water from our systems, the presence of *catalytic* quantities of water cannot be ruled out. Reactions 2−4 lead to the overall stoichiometry of eq 5.[31]

$$\begin{array}{llr}
2\mathrm{LiOAr} + \mathrm{H_2O} & \rightarrow 2\mathrm{HOAr} + \mathrm{Li_2O} & (3)\\
\mathrm{MoO_2Cl_2} + 2\mathrm{HOAr} & \rightarrow \mathrm{MoO(OAr)_2Cl_2} + \mathrm{H_2O} & (2)\\
\mathrm{MoO(OAr)_2Cl_2} + 2\mathrm{LiOAr} & \rightarrow \mathrm{MoO(OAr)_4} + 2\mathrm{LiCl} & (4)\\
\hline
\mathrm{MoO_2Cl_2} + 4\mathrm{LiOAr} & \rightarrow \mathrm{MoO(OAr)_4} + \mathrm{Li_2O} + 2\mathrm{LiCl} & (5)
\end{array}$$

Mixtures of complexes **2**−**4** are produced when LiOAr is added directly to $MoO(OAr)_2Cl_2$ in various ratios.

In conclusion, we have demonstrated the facile synthesis of molybdenum(VI) monooxo aryloxides from a convenient commercially available precursor, MoO_2Cl_2. These reactions likely proceed through an unusual addition of precoordinated phenol across a Mo(VI) terminal oxo group. Later publications will explore the generality of these reactions and the use of the oxo aryloxide products in catalysis.

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Supporting Information Available: X-ray crystallographic data in cif format for **3** and **4**, experimental details and characterization for syntheses of **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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