Mixed ligand dioxomolybdenum complex synthesis and evaluation of their potential for atomic layer deposition & catalytic applications

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Introduction
Molybdenum Oxide has interesting optical and electronic properties that make it useful for applications in microelectronics and nanoelectronics. As new technology gets smaller and smaller, the need for high precision nanofeatures in nanoelectronics becomes of increasing importance. Current thin layer deposition methods, namely chemical vapor deposition (CVD) cannot precisely control the thickness and uniformity of the thin film. Atomic layer deposition (ALD) is different deposition method as it is being explored for these applications because it is self-limiting, and the thickness of the film can be controlled by the number of cycles. (See figure 1) However, for ALD to work, suitable precursors need to be volatile (ALD occurs in gas phase), thermally stable (not decompose), reactive (to a co-reactant), and yield no corrosive by-products. This investigation analyzes the properties of dioxomolybdene mixed ligand systems, hoping to combine the properties of the different ligands, namely pyrazolato (high thermal stability, low reactivity) and amidinato (high reactivity, low thermal stability) groups.

Volatilization Data
Thermogravimetric analysis (fig. 4) was performed on the complexes. R=RtBu showed more weight loss than R=IPr at lower temperatures. What was most interesting was the slight change in concavity at ~220°C, suggesting a change in the form of weight loss. It indicates that maybe the compound was volatile before this point, where decomposition likely occurs.

Sublimation tests from 75°C-95°C indicated evidence of decomposition. However, equipment limitations prevented a strong vacuum from being formed, and more conclusive sublimation tests need to be done before a definitive evaluation of its volatility and potential for ALD can be determined.

Conclusions
This investigation elicited the synthesis of two novel oxy-molybdenum complexes along with the elucidation of their crystal structure using X-ray crystallography. This is a demonstration of two mixed ligand systems of pyrazolato and amidinato ligands, as well as the ability to adjust said complex by altering the R-group on the amidinato group to give slightly different properties. Thermogravimetric analysis suggest the possibility of volatility, but sublimation experiments showed evidence of decomposition. However, further sublimation experiments under a stronger vacuum need to be done before conclusive results on the volatility of the compound can be established.

The molybdenum complexes also showed evidence of catalysis of the oxidation triphenylphosphine, specifically when R=IrtBu. This was the first time an oxomolybdenum complex with an amidinato ligand has shown catalytic properties. Further evaluation of the catalytic power of the complexes and the ability to use it in different oxygen transfer reactions of interest is needed.

Overall the successful syntheses of these compounds open the door for a wide variety of different mixed ligand systems of not only molybdenum oxide, but other transition metals to potentially be synthesized and evaluated to similar applications.

Literature cited


Acknowledgments
Thank you so much to Ivo Vath and The Vouros Fund for funding me throughout this co-op. Thanks to Dr. Oussama ElKadi and the Department of Biology, Chemistry, and Environmental Sciences at the American University of Sharjah for hosting me and working with me on the project. And Thanks to Graham Jones and the Northeastern Department of Chemistry for helping me find this co-op in the first place!

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Table 1
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<tr>
<th>Bond/Angle</th>
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<td>IPr 4.50</td>
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Table 1. Bond Lengths & Angles Determined from X-Ray Crystalligraphy.

Figure 1. The four steps of ALD: (1) Volatile precursor deposits onto substrate. (2) Remaining precursor is blow away by inert gas. (3) Co-reactant reacts with layer of deposits onto substrate. (4) Remaining precursor is blow away by inert gas. These steps are repeated until desired thickness is achieved.

Figure 2. Oxygen transfer mechanism of previously synthesized compound containing a [MoO₂]³⁻ fragment

Synthetic methods
Synthesis of the compounds occurred under air sensitive condition in a glove box and Schlenk tube under an argon atmosphere. After much research, the reaction according to Fig. 3 was performed.

Figure 3. Crystal structure of Complex 2 (R=IrtBu) determined from X-Ray Crystalligraphy.

Figure 4. Thermogravimetric analysis data of the two oxomolybdenum complexes. R=RtBu shows more weight loss as lower temperatures. The slight change in concavity in the graph -220°C suggest that there is some change in the weight loss at that point. Maybe a shift from volatility to decomposition

Catalytic Data
The oxomolybdenum complexes, along with a previously synthesized amidinato complex (fig. 5a) were evaluated for their catalytic properties by being mixed with triphenylphosphine (TPP) and DMSO. With no catalyst, no reaction takes place, but with it, TPP oxidizes. This reaction was measured using 31P NMR (fig. 5b)

Figure 5a. Previously synthesized amidinato oxomolybdenum compound (1) with a IrtBu group was also evaluated for catalytic properties. 5b. 31P NMR of the reactions of triphenylphosphine (TPP) with DMSO using the synthesized oxomolybdenum complexes as catalysts. Compounds 1 & 2 both show good catalytic potential.

Figure 5b. 31P NMR of the reactions of triphenylphosphine (TPP) with DMSO using the synthesized oxomolybdenum complexes as catalysts. Compounds 1 & 2 both show good catalytic potential.

Figure 3. Synthesis of Mixed ligand dioxomolybdenum complexes containing a 3,5-tetraethylpyrazolato group and other N, N diisopropyl amidinato group (2) or a N, N-dicyclopropyl amidinato group (3)