Factors Influencing the Metathesis of Group VI Transition Metal Complexes Containing Nitrido and Alkylidyne Ligands.

A Thesis Submitted in Partial Fulfillment of the Requirements for
The Masters of Science Degree at The Ohio State University

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A series of molecules \((\text{RO})_3\text{M}≡\text{N}\) (\(\text{R} = \text{iPr}, \text{tBu}, \text{CMe}_2\text{CF}_3\) and \(\text{M} = \text{Cr}, \text{Mo}\) and \(\text{W}\)) have been synthesized and their electronic structure investigated with gas phase photoelectron spectroscopy and density functional calculations. For the most part the frontier molecular orbitals are of similar content. The frontier molecular orbitals are comprised of a nitrogen lone pair, metal-nitrogen \(\pi\) bonding and oxygen lone pairs. The ordering of these orbitals does change upon changing the metal and ligand character.

A qualitative molecular orbital diagram has been constructed that fits the predicted and observed results. The Molden™ plots of the frontier molecular orbitals for the inorganic nitrides and organic nitriles (\(\text{CH}_3\text{C}≡\text{N}\) and \(\text{CF}_3\text{C}≡\text{N}\)) are shown in the body of this work and the appendix for comparison purposes. Other properties of the nitrides have been calculated and are given, i.e. the bond dissociation energies and the bond polarities.

Metathesis reactions of the metal nitrides and some related metal alkylidyynes \(\left(\text{tBuO}\right)_3\text{M}≡\text{CR}\) (\(\text{R} = \text{Me}, \text{iPr}, \text{Ph}\) and \(\text{M} = \text{Mo}\) and \(\text{W}\)) have been investigated. The chromium nitride compound \(\left(\text{tBuO}\right)_3\text{Cr}≡\text{N}\) proves to be the best nitride transfer reagent both experimentally and computationally. In reaction studies where the tungsten nitride compound \(\left(\text{tBuO}\right)_3\text{W}≡\text{N}\) is a starting material there is no observed metathesis. One exception to this was in a labeling...
experiment where (tBuO)$_3$W$\equiv^{15}$N was allowed to react with (tBuO)$_3$Mo=\text{N} and the labeled molybdenum product (tBuO)$_3$Mo$\equiv^{15}$N was observed.
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VITA

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</tr>
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<td>(\pi)</td>
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<td>lowest unoccupied molecular orbital</td>
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<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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SHOMO = second highest occupied molecular orbital
THOMO = third highest occupied molecular orbital
THF = tetrahydrofuran
Introduction

Metal-ligand multiple bonds and metal-metal multiple bonds are reactive functional groups.\textsuperscript{1} Metathesis reactions that incorporate a metal-ligand multiple bond encompass a large area of inorganic chemistry. Some important reactions of this type include: olefin metathesis, alkyne metathesis, imido metathesis and nitrido transfer.\textsuperscript{1} Olefin metathesis is a long standing industrial process.\textsuperscript{1} This type of metathesis incorporates the use of a metal-carbon double bond, $\sigma^2\pi^2$ with a carbon-carbon double bond also $\sigma^2\pi^2$. For the most part the reactions of olefin substitution are believed to follow a four center mechanism as shown in Equation \textbf{1}.

\begin{equation}
\begin{array}{c}
R + R' \\
\downarrow M \downarrow \\
\end{array}
\rightarrow
\begin{array}{c}
\left[ \begin{array}{c}
R \quad R' \\
\downarrow M \downarrow \\
\end{array} \right] \\
\end{array}
\rightarrow
\begin{array}{c}
R = R' \\
M = R' \\
\end{array}
\end{equation}

Alkyne metathesis reactions begin with the use of a metal-carbon triple bond, and a carbon-carbon triple bond, both having a $\sigma^2\pi^4$ configuration. Similar to the metallacyclobutane of Equation \textbf{1}, a metallacyclobutadiene has been suggested for alkyne metathesis reactions. Equation \textbf{2} shows the analogous reaction pathway.
There is now a large body of evidence to support these mechanisms.\textsuperscript{2} A good example of alkyne metathesis was given by Schrock and coworkers who have shown the tungsten alkylidyne molecule \((\text{Bu}^\text{t})_3\text{WO}≡\text{C}^\text{t}\text{Bu}\) catalyzes the metathesis of acetylene.\textsuperscript{3}

Metal-nitrogen multiple bonds comprise another related area of metathesis chemistry. Typically we use the term imido for the \(M=\text{NR}\) moiety and nitrido for the \(M=\text{N}\) moiety. A common example of a metathesis reaction involving the imido ligand is that in Equation 3 which is used to catalyze the exchange in carbodiimides.\textsuperscript{1}

\[
\begin{align*}
R-N≡C≡N-R & + \quad \text{WCl}_{\text{4}}=\text{NR} & \rightarrow & \quad \text{2 R-N≡C≡N-R} \\
\end{align*}
\]

The metal nitrogen triple bond (nitride) is a common side product in the formation of metal alkylidyne products. Equation 4 is one such example.

\[
\begin{align*}
\text{W}_2(\text{OBu}^\text{t})_6 + \text{MeC≡N} & \xrightarrow{0^\circ \text{C}} \text{hexane} \quad \text{(Bu}^\text{t})_3\text{WO}≡\text{N} + (\text{Bu}^\text{t})_3\text{WO}≡\text{CMe} \\
\end{align*}
\]

In 1973, Griffith and Pawson reported the use of the nitride ion \((\text{N})^3\) as a terminal ligand to group VI transition metals.\textsuperscript{4} Several reviews have been written
describing the structure and bonding of transition metal nitrido compounds.\textsuperscript{1,5} The nitride ion is one of the most strongly $\pi$ donating ligands known, allowing it to be used to support high metal oxidation states. There is a vast amount of chemistry known for transition metal nitrido compounds.\textsuperscript{1,5} Many of the metal-ligand multiple bonds studied in this thesis including alkylidyynes and nitrides are formed from a metathesis reaction between a metal-metal multiple bond and an acetylene or nitrile as seen in Equation 4.

Transition metal-metal multiple bonds have been investigated since the early 1960's.\textsuperscript{6} The nature of the metal-metal multiple bonding varies depending on the transition metal used and on the ligands bound to the metal.\textsuperscript{7} For the group VI transition elements molybdenum and tungsten the multiple bonds formed for homonuclear compounds are a widely studied class of multiple bond.\textsuperscript{6,7} The first molybdenum-molybdenum triple bond was discovered in 1971 by Wilkinson and coworkers in the molecule $\text{Mo}_2\text{R}_6$, where $\text{R} = \text{CH}_2\text{SiMe}_3$.\textsuperscript{8} At a similar time the Chisholm group had begun to explore the chemistry of the $\text{M}_2\text{R}_6$ molecules, where $\text{M} = \text{Mo, W, R} = \text{NMe}_2$ and $\text{O}^{\prime}\text{Bu}$ etc.\textsuperscript{9} $\text{M}_2(\text{OR})_6$ ($\text{M} = \text{Mo, W}$ and $\text{R} = ^{\prime}\text{Bu}$) have been called “ethane-like” dimer molecules due to similarities to ethane in point group, rotational behavior about the C-C and M-M bond and the substituent number on carbon and the metal.\textsuperscript{7,10} Likewise, the compound discovered in 1982 by Schrock and coworkers, $(^\prime\text{BuO})_3\text{W}=\text{N}$ can be classified as an inorganic nitrile due to its similarity to organic nitriles.\textsuperscript{11} Again there is a similarity in point group, although now there are other similarities which include: a common bond
order between metal or carbon and the nitrogen atom and interesting reactivity towards the “ethane-like” metal dimers.

The discovery of \( (\text{^1BuO})_3\text{W} ≜ \text{N} \) in 1982 was soon followed by the discovery of the analogous molybdenum nitride.\(^{12}\) Subsequently, several groups prepared a variety of molybdenum and tungsten nitride compounds by varying the alkoxide ligands.\(^{12,13}\) More recently, the analogous chromium compound has been synthesized.\(^{14}\) The solid state structure of the alkoxide compounds varies significantly based solely on the ligand. Figure 1 shows some of the solid-state structures found by varying the alkoxide ligand. The chromium analog is monomeric.\(^{14}\)

![Diagram of tungsten nitrides](image)

Figure 1. Some known solid state structures of tungsten nitrides.
The $d^3$-$d^3$ dimers Mo$_2$(OR)$_6$ ($R=$Pr$^i$, Bu$^t$, and CH$_2$Bu$^t$) have been synthesized and characterized. For comparison, the $d^3$-$d^3$ dimer for W$_2$(OBU$^t$)$_6$ has also been synthesized but has a marked difference in reactivity from its molybdenum counterpart.$^{11,15,16}$ This must be attributed to energetic differences given the common metal-metal triple bond with one σ and two π bonds and similar alkoxide ligands. Schrock and co-workers found the compound Mo$_2$(OBU$^t$)$_6$ exhibited no reactivity toward organic nitriles, although the tungsten analogue cleaves them as illustrated in Equation 4.$^1$

Ancillary ligands such as alkoxides play an important role in tuning the frontier molecular orbitals of the metal-metal bond and therefore the reactivity of the M$_2$(OR)$_6$ complexes. Alkoxide ligands are strong π electron donors, which help to stabilize medium to high oxidation states for these transition elements. For the previous tungsten species, these effects can be demonstrated through changing the alkoxide ligands from R=Bu$^t$ to R=CM$_2$CF$_3$. The chemistry of the metal center changes from that in Equation 4 to that shown in Equation 5.$^{16}$

$$W_2(OCMe_2CF_3)_6 + 2\text{MeC} \rightleftharpoons W_2(OCMe_2CF_3)_6(\text{NMe})_2$$ (5)

Upon addition of the nitrile there is a reversible binding to the metal centers, instead of binding and C≡N cleavage. The fluorinated alkoxide groups are much more electronegative, making the metal centers more Lewis acidic and therefore more likely to bind a Lewis base such as an acetonitrile nitrogen or an ether oxygen. By increasing the fluorine content of the alkoxide ligands the trend
towards a greater Lewis acidity can be seen at the metal. Fluorine is the most electronegative element in the periodic table. Introducing a strongly electron withdrawing element into the system leads to less $\pi$ donation to the metal center and therefore greater Lewis acidity. The $pK_a$'s of the alcohols roughly track with their donicity, as can be seen by comparison of HOBu ($\sim 18$) and (CF$_3$)$_3$COH ($\sim 5$) $pK_a$'s. A similar trend can be seen in the $^1$H NMR spectrum. The increased fluorine content leads to less electronic shielding of the methyl protons which causes a downfield shift for these protons in the $^1$H NMR spectrum. There are however, more direct ways to probe the electronic structure of these metal systems.

Transition metal nitrides have bonding similar to that described above for $d^2$-$d^2$ dimers. For a mononuclear M≡N unit there is one $\sigma$ and two $\pi$ bonds forming a cylindrical $\sigma^2\pi^4$ multiple bond. The approximate $C_3$ symmetry is maintained in these cylindrical molecules, which maintains the degeneracy of the $\pi$-orbitals.
The Current Study.

The starting point of this work involves a closer look at the electronic structure of the group VI metal nitrido molecules ((^{\textit{t}}\textit{BuO})_{3}\textit{M}=\textit{N}) (where \textit{R} = ^{\textit{t}}\textit{Bu}, ^{\textit{t}}\textit{Pr}, \textit{CMe}_{2}\textit{CF}_{3} and \textit{M} = \textit{Cr}, \textit{Mo} and \textit{W}) based on changing the attendant alkoxide ligand and then on changing the metal center. One very powerful tool used to study the electronic structure of valence electrons in molecules is ultraviolet photoelectron spectroscopy (UPS). The ionization energy (\textit{E}_{\text{i}}) of electrons is directly investigated using an ultra-violet photon source. Equation 6 is used to calculate the \textit{E}_{\text{i}} given the photon energy (\textit{hv}) and by measuring the kinetic energy of the ejected electron (\textit{E}_{k}(\textit{e}^{-})).^{17}

\[
\textit{E}_{\text{i}} = \textit{hv} - \textit{E}_{k}(\textit{e}^{-})
\]  

(6)

Chisholm and co-workers have studied the bonding in a series of \textit{W}_{2}(\textit{NMe})_{2}(\textit{OR})_{4} (\textit{R}=\textit{CMe}_{2}\textit{CF}_{3}, \textit{CMe}(\textit{CF}_{3})_{2} and \textit{C}(\textit{CF}_{3})_{3}) compounds using ultraviolet photoelectron spectroscopy.\textsuperscript{18}

In addition to using this powerful experimental method, density functional calculations have been employed to elucidate the electronic structure of an analogous series of molecules. This allows for an investigation of the frontier
molecular orbitals, the ionization potentials (using both Hartree-Fock and density functional methods), the bond polarities and the bond dissociation energies. These results can be compared to the physically observable chemical properties. The calculations were performed using the Gaussian 98™ package of software at the B3LYP level of theory and using effective core potentials (ECP).¹⁹

To complete the understanding of the behavior of the \((\text{BuO})_3\text{M=E}\) compounds (where \(\text{E} =\) nitride or alkylidyne) species, several reactivity studies were employed to investigate their susceptibility to ligand exchange. Some studies were complimented by using isotopically labeled carbon (\(^{13}\text{C}\)) and nitrogen (\(^{15}\text{N}\)).
Results and Discussion

To more fully understand the chemistry in group VI alkoxide compounds the group of compounds with the formula \((\text{RO})_3\text{Mo}≡\text{N}\) (\(\text{R}=^\text{t-}\text{Bu}, \text{CMe}_2\text{CF}_3, {}^\text{1Pr}\)), and \((^\text{tBuO})_3\text{M}≡\text{N}\) (\(\text{M}=\text{Cr}\) and \(\text{W}\)) have been synthesized and UPS spectra have been obtained. Comparison of \(E_1\) values to other \(\text{C}_3\) symmetric and isolobal molecules like the \(\text{M}_2(\text{OR})_6\) series, \(\text{MeC}≡\text{N}\), and \(\text{CF}_3\text{C}≡\text{N}\) can give a better understanding of the properties of these molecules.

A good example of differences in reactivity include the alcoholysis of the nitrides. From Reactions 7-9 one can see that seemingly very similar molecules possess very different reactivity.\(^{31}\)

\[
(^\text{tBuO})_3\text{Cr(N)} + \text{xs } \text{HO}^\text{tPr} \quad \xrightarrow{\large \times} \quad (^\text{tPrO})_3\text{Cr(N)} + \text{xs } \text{HO}^\text{tBu} \quad (7)
\]

\[
(^\text{tBuO})_3\text{Mo(N)} + \text{xs } \text{HO}^\text{tPr} \quad \longrightarrow \quad (^\text{tPrO})_3\text{Mo(N)} + \text{xs } \text{HO}^\text{tBu} \quad (8)
\]

\[
(^\text{tBuO})_3\text{W(N)} + \text{xs } \text{HO}^\text{tPr} \quad \longrightarrow \quad \text{W}(\text{O}^\text{tPr})_6 + \text{HO}^\text{tBu} + \text{NH}_3 \quad (9)
\]
There is also a difference in the solid state structures of the molecules. The (tBuO)_3Cr=N is a monomer in the solid state while the molybdenum and tungsten nitride t-butoxide compounds are infinite linear polymers.\textsuperscript{12,14} There are two major factors contributing to these differences in reactivity. First, the effects of the ancillary ligands and secondly, the valence configuration of the metal centers (the frontier molecular orbitals).\textsuperscript{7} If possible, the two factors should be studied and understood separately and then understood in combination.

The structure and reactivity of group VI nitrido compounds can vary greatly as a function of the attendant alkoxide ligands and the metal center. This was illustrated to some extent in Figure 1 and Reactions 7-9. Initially it was decided to look at the electronic structure of a series of group VI metal nitrides by varying the ligand and then by varying the metal in an attempt to understand some of these differences.
Photoelectron Spectroscopy.

A common method in inorganic chemistry used to explore the frontier molecular orbitals is photoelectron spectroscopy. The orbital ionizations energies and to some extent the atomic orbital contributions to the molecular orbitals ionized can be retrieved.

The series of compounds \((RO)_3\text{Mo}≡\text{N}\) (\(R = ^1\text{Pr}, ^1\text{Bu}\) and \(\text{CM}_{2}\text{CF}_3\)) were synthesized and sent to the University of Arizona for the photoelectron experiments. The first spectrum is shown in Figure 2. Figure 2 shows the change in ionization pattern and energy upon changing the alkoxide ligand from \(^1\text{Bu}\) to \(^1\text{Pr}\) to \(\text{CM}_{2}\text{CF}_3\). The threshold ionization for the compounds where the ligand is \(^1\text{Bu}\) is \(\sim 8.77\) eV, for \(^1\text{Pr}\) ligand it is \(\sim 9.10\) eV and for \(\text{CM}_{2}\text{CF}_3\) ligand it is \(\sim 9.73\) eV. This general trend is intuitively pleasing given the increasing electronegativity of the alkyl group in going from \(^1\text{Bu}\) to \(\text{CM}_{2}\text{CF}_3\). One might expect to observe that the oxygen lone pair ionizations in the corresponding free alcohols would have the same trend and, indeed, the free alcohols do follow this trend; \((\text{CH}_3)_3\text{COH}, (\text{CH}_3)_2\text{HCOH},\) and \((\text{CH}_3)_2\text{CF}_3\text{COH}\) have ionizations of \(10.22\) eV, \(10.36\) eV and \(11.11\) eV, respectively. The spectra also show three distinct regions of ionizations. Region A is comprised of ionizations for the oxygen p orbital (lone pair) that is perpendicular to the C-O-M plane, the nitrogen lone pair...
electrons and the metal nitrogen \( \pi \) bonding electrons. Region B consists of ionizations for the oxygen p orbital (lone pair) that is in the C-O-M plane. Region C can be assigned to the O-C(\( \sigma \)), the C-C(\( \sigma \)), the C-H(\( \sigma \)) and the M-O(\( \sigma \)) ionizations.

The frontier molecular orbitals are the orbitals which are involved in chemical bonding and reactivity. Thus we are mainly interested in the most easily ionized electrons that correlate with ionizations from these frontier molecular orbitals. Upon looking more closely at region A of the spectrum the observation of three distinct ionizations can be determined. Figure 3 is the close-up of region A from Figure 2. These ionizations are assigned to electrons from metal-nitrogen \( \sigma \) and \( \pi \) bonds and oxygen lone pairs and will be discussed in more detail.

When thinking of electrons in a molecule and the ionizations that arise from the excitation of these electrons it is useful to employ molecular orbital diagrams (MOD). This is a useful method in helping to determine the assignments for the ionizations and sometimes the reactivity of the molecule itself. An isolobal approach can be used in generating molecular orbital diagrams. For example, a MOD can be generated by viewing the molybdenum nitride unit \((L_3M\equiv N)\) as the combination of a \(L_3M\) fragment with a N atom. The metal fragment enters the diagram with a \(4d^3\) valence electron configuration and the N atom enters the diagram with a \(2s^22p^3\) valence electron configuration. The \(L_3M\equiv N\) molecule can be viewed as the inorganic analog of acetonitrile, the \(\text{CH}_3\text{C} \equiv \text{N} \)
Figure 2. Full He I UPS of the molecules \((RO)_3\text{Mo=N,}

where \(R = \text{^1Bu (top), ^2Pr (middle) and CMe}_2\text{CF}_3 (bottom).}
fragment of CH$_3$C≡N is isolobal with the L$_3$M fragment. Another isolobal unit is the CF$_3$C fragment from trifluoroacetanitride. The comparison of the UPS for these compounds gives a feeling for the range of possibilities for the M≡N functionality. The UPS spectra of acetonitrile and trifluoroacetanitride are shown in Figure 4.\textsuperscript{20,21}

Another way of looking at the L$_3$Mo≡N unit is to consider that the metal has no 4d electrons (Mo\textsuperscript{VI}) and the nitrogen is a nitride ion (N\textsuperscript{3-}) giving it 8 valence electrons and a 2s\textsuperscript{2}2p\textsuperscript{6} valence configuration. The generation of the MOD for this approach is seen in Figure 5.\textsuperscript{22-24} The diagram shows that in the frontier molecular orbitals for the general case of L$_3$M≡N, the highest occupied molecular orbital (HOMO) arises from the interaction between the symmetry related orbitals metal d$_z^2$ and nitrogen 2p$_z$ with some mixing of the nitrogen 2s orbital. The HOMO is primarily nitrogen 2p$_z$ in character and is considered the nitrogen lone pair. The second highest molecular orbital (SHOMO) is a doubly degenerate set of \pi molecular orbitals that arise from the overlap between the metal d$_{xz}$ and nitrogen 2p$_x$ as well as, the metal d$_{yz}$ and nitrogen 2p$_y$. Because the molecule has approximate C$_3$ symmetry, and group theory tells us that the orbitals belong to the same transformation group, the resulting \pi orbitals are degenerate. The lower lying molecular orbital is the metal nitrogen \sigma bond. Comparing this MOD to the PES one can see that the left hand side fragment would be stabilized with the addition of less electron donating L ligands. The first ionization in all three molecules is predicted to be from a primarily nitrogen based lone pair.
Figure 3. Close-up of region A from figure 2.
The second ionization is from the metal-nitrogen $\pi$ bond and the third ionization is from the oxygen based lone pair.

In comparison to the acetonitrile and trifluoroacetonitrile where the nitrogen lone pairs are not the highest occupied molecular orbital (HOMO) but the second highest occupied molecular orbital (SHOMO), we can see that the nitrogen lone pair becomes even more difficult to ionize as the electronegativity of the ligand set increases. The $C\equiv N$ $\pi$ bonds are now the HOMO and they take 12.12 and 14.3 eV to ionize followed closely by the nitrogen lone pairs at 13.11 and 14.4 eV, respectively.\textsuperscript{20,21} Upon changing the metal center one might expect to see a similar trend. Figure 6 shows the PES of the altered metal compounds and the free alcohol for comparison purposes. The difference to the altered ligand spectra is that the threshold ionizations are all very similar, 8.77, 8.89 and 8.75 eV for chromium, molybdenum and tungsten, respectively. The expected ionization trend is Cr>Mo>W. The difference from the expected trend arises because of the relative sizes and Lewis acidity of the metal atoms. Chromium is smaller and more Lewis acidic in comparison to the similar molybdenum and tungsten atoms. This leads to a more closely bound set of alkoxide ligands which causes a filled-filled interaction and destabilizes the oxygen lone pair electrons. In the case of chromium the MOD shown as Figure 5 is altered by the raising of the third highest molecular orbital to be the HOMO.
Figure 4. The ultraviolet Photoelectron Spectra for acetonitrile and trifluoroacetonitrile.\textsuperscript{20,21} (reproduced without permission)
Figure 5. Schematic Molecular Orbital Diagram for a L₃M≡N molecule.
Density Functional Calculations.

Another way to help verify the assignments of the orbitals and to predict trends of the ionizations is to use density functional calculations. To complete the synthesis and characterization of the metal nitride chemistry a series of Gaussian 98 calculations were performed. The DFT calculations use the B3LYP level of theory with a LANLMB, LANLDZ and CEP-121G* basis set and effective core potentials (ECP) and are used to determine relative orbital energies, ionization energy trends, bond polarities and bond dissociation energies. For verification purposes Hartree-Fock calculations were also performed to support the ionization potentials. The calculation set consists of using a minimum basis set followed by a double zeta basis set and then finally by a triple zeta basis set. The bond dissociation energies used molecular fragment energies in comparison to the complete molecule. For calculational simplicity (RO)₃M≡N molecules were calculated as R = CH₃, H and CF₃ for molybdenum and only H for chromium and tungsten. Table 1 summarizes the metric parameters used for a starting point in the calculations as well as the calculated geometries. The oxygen hydrogen distances were set at 0.95 Å. Molden plots of the HOMO’s are pictured in Figures 7-11. The orbitals are shown as cross sectional views in different planes depending on the molecule.
The plane shown is indicated in the upper right corner of the respective figure. For the chromium compound the HOMO is purely oxygen lone pair in character and shows no metal or nitrogen mixing. The rest of the chromium orbitals follow the same trend as for the molybdenum and tungsten analogs. For molybdenum and tungsten the HOMO is a nitrogen based lone pair. This is as predicted given the PES data and shown MOD. There is some metal \(d_z^2\) (\(\sigma\)) and oxygen lone pair mixing in these calculated orbitals. The SHOMO is primarily metal to nitrogen \(\pi\) bonding with oxygen lone pair character.

For the alkoxide substituted molybdenum nitrides the HOMO remains the nitrogen based lone pair with some metal \(d_z^2\) (\(\sigma\)) and oxygen lone pair character. It is of some interest in comparing the orbitals that are primarily nitrogen lone pair. When looking at the Molden™ plots of these calculated orbitals the contours given by the red circles around nitrogen show the amount of associated electron density. In changing from methyl to hydroxy to trifluoromethyl it is easy to see the less diffuse nature of the contours about nitrogen. This implies a greater Lewis basicity for the nitrogen for the methyl analog as compared to the hydroxyl analog and likewise for hydroxyl analog as compared to the tri-fluoro methyl analog. Table 2 summarizes the frontier molecular orbital contributions. The Molden™ plots for the lowest unoccupied molecular orbitals (LUMO), the second highest occupied molecular orbitals (SHOMO) and the third highest occupied molecular orbitals (THOMO) are included in the appendix.
Figure 6. UPS of the compounds $(\text{BuO})_3M\equiv N$ ($M = \text{Cr, Mo and W}$) with the free alcohol $\text{BuOH}$ for reference.
Observed:

\[
\begin{align*}
\text{Cr-N} & \quad 1.538(5) \text{ Å} & \quad \text{Mo-N} & \quad 1.673(5) \text{ Å} & \quad \text{W-N} & \quad 1.740(15) \text{ Å} \\
\text{Cr-O} & \quad \sim 1.74 \text{ Å} & \quad \text{Mo-O} & \quad \sim 1.89 \text{ Å} & \quad \text{W-O} & \quad \sim 1.87 \text{ Å} \\
\text{N-Cr-O} & \quad \sim 108.1^\circ & \quad \text{N-Mo-O} & \quad \sim 103.5^\circ & \quad \text{N-W-O} & \quad \sim 101.6^\circ \\
\text{Cr-O-C} & \quad \sim 137.5^\circ & \quad \text{Mo-O-C} & \quad \sim 134.3^\circ & \quad \text{W-O-C} & \quad \sim 136.6^\circ
\end{align*}
\]

Calculated:

\[
\begin{align*}
\text{Cr-N} & \quad \sim 1.533 \text{ Å} & \quad \text{Mo-N} & \quad \sim 1.682 \text{ Å} & \quad \text{W-N} & \quad \sim 1.702 \text{ Å} \\
\text{Cr-O} & \quad \sim 1.75 \text{ Å} & \quad \text{Mo-O} & \quad \sim 1.90 \text{ Å} & \quad \text{W-O} & \quad \sim 1.89 \text{ Å} \\
\text{N-Cr-O} & \quad \sim 107.4^\circ & \quad \text{N-Mo-O} & \quad \sim 105.9^\circ & \quad \text{N-W-O} & \quad \sim 106.1^\circ \\
\text{Cr-O-H} & \quad \sim 127.8^\circ & \quad \text{Mo-O-H} & \quad \sim 131.5^\circ & \quad \text{W-O-H} & \quad \sim 134.5^\circ
\end{align*}
\]

Table 1. Metric parameters used from crystal structure data (references 14, 12 and 11) and the calculated output from DFT calculations.
For comparison the organic nitriles were also calculated using density functional methods. The HOMO in both cases is the carbon-nitrogen π bond. The Molden™ frontier molecular orbital plots have also been included in the appendix. It is easy to see the effect of adding three more electronegative groups to the molecule in going from acetonitrile to trifluoroacetonitrile in that there is a ~2 eV increase in the energy to ionize the nitrogen lone pair for the fluorinated analog. The orbital plot also appears to be less diffuse about the π bond for the trifluoro analog. The results fit well with the observed PES from Figure 4. Table 3 is a complete summary of the calculated IP’s and the observed IP’s. As stated before the IP’s were calculated using both DFT and Hartree-Fock methods. The DFT method incorporates the use of calculations on the neutral molecule and the +1 species and comparing the total energy difference. The Hartree-Fock method uses the calculated HOMO energy as the IP.
Figure 7. Molden™ plot for the (HO)$_3$Cr=N HOMO.
Figure 8. Molden™ plot for the (HO)₃Mo≡N HOMO.
Figure 9. Molden™ plot for the (HO)$_3$W≡N HOMO.
Figure 10. Molden™ plot for the (CH$_3$O)$_3$Mo≡N HOMO.
Figure 11. Molden™ plot for the (CF$_3$O)$_3$Mo≡N HOMO.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular Orbitals</th>
<th>Contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(N)(OH)$_3$</td>
<td>LUMO</td>
<td>Cr3d((\pi))-O2p((\pi^*))</td>
</tr>
<tr>
<td></td>
<td>HOMO</td>
<td>O2p((\pi))(l.p.)</td>
</tr>
<tr>
<td></td>
<td>SHOMO</td>
<td>N2p(l.p.) + Cr-N((\sigma^*))</td>
</tr>
<tr>
<td></td>
<td>THOMO</td>
<td>Cr3d-N2p((\pi)) + O(l.p.)</td>
</tr>
<tr>
<td></td>
<td>FHOMO</td>
<td>O2p((\pi))</td>
</tr>
<tr>
<td>Mo(N)(OH)$_3$</td>
<td>LUMO</td>
<td>Mo4d((\pi))-O2p((\pi^*))</td>
</tr>
<tr>
<td></td>
<td>HOMO</td>
<td>N2p(l.p.) + Mo-N((\sigma^*))</td>
</tr>
<tr>
<td></td>
<td>SHOMO</td>
<td>Mo4d((\pi))-N2p((\pi))</td>
</tr>
<tr>
<td></td>
<td>THOMO</td>
<td>O2p((\pi))(l.p.)</td>
</tr>
<tr>
<td></td>
<td>FHOMO</td>
<td>O2p((\pi))</td>
</tr>
<tr>
<td>W(N)(OH)$_3$</td>
<td>LUMO</td>
<td>W5d((\pi))-O2p((\pi^*))</td>
</tr>
<tr>
<td></td>
<td>HOMO</td>
<td>N2p(l.p.) + W-N((\sigma^*))</td>
</tr>
<tr>
<td></td>
<td>SHOMO</td>
<td>W5d((\pi))-N2p((\pi))</td>
</tr>
<tr>
<td></td>
<td>THOMO</td>
<td>O2p((\pi))(l.p.)</td>
</tr>
<tr>
<td></td>
<td>FHOMO</td>
<td>O2p((\pi))</td>
</tr>
<tr>
<td>Mo(N)(OCH)$_3$</td>
<td>LUMO</td>
<td>Mo4d((\pi))-O2p((\pi^*))</td>
</tr>
<tr>
<td></td>
<td>HOMO</td>
<td>N2p(l.p.) + Mo-N((\sigma^*))</td>
</tr>
<tr>
<td></td>
<td>SHOMO</td>
<td>O2p((\pi))(l.p.)</td>
</tr>
<tr>
<td></td>
<td>THOMO</td>
<td>Mo4d((\pi))-N2p((\pi))</td>
</tr>
<tr>
<td></td>
<td>FHOMO</td>
<td>O2p((\pi))</td>
</tr>
<tr>
<td>Mo(N)(OCF)$_3$</td>
<td>LUMO</td>
<td>Mo4d((\pi))-O2p((\pi^*))</td>
</tr>
<tr>
<td></td>
<td>HOMO</td>
<td>N2p(l.p.) + Mo-N((\sigma^*))</td>
</tr>
<tr>
<td></td>
<td>SHOMO</td>
<td>Mo4d((\pi))-N2p((\pi))</td>
</tr>
<tr>
<td></td>
<td>THOMO</td>
<td>O2p((\pi))(l.p.)</td>
</tr>
<tr>
<td></td>
<td>FHOMO</td>
<td>O2p((\pi))</td>
</tr>
</tbody>
</table>

Table 2. Calculated orbital contributions for the frontier molecular orbitals.
Experimentally observed physical characteristics of the nitrido compounds are also predicted by the calculations. The (\(^{1}\text{BuO}\))\(_3\text{Cr}≡\text{N}\) molecule is very soluble in hydrocarbon solvents. The molybdenum molecule is reasonably soluble and the tungsten analog is only sparingly soluble in hydrocarbons. Table 4 shows the calculated Mulliken charge densities of the molecules. The smallest difference in charge between metal and nitrogen is for the chromium compound (\(~\sim\sim .9\) and the largest is for the tungsten analog (\(~\sim\sim 1.6\) ). This shows that the calculated trend of increasing bond polarity for the \(\text{M}≡\text{N}\) bond agrees with the experimentally observed trend of \(\text{Cr}≡\text{N}<\text{Mo}≡\text{N}<\text{W}≡\text{N}\) which manifests itself in the \(\text{M}≡\text{N}→\text{M}\) association. This trend may also be seen in the temperatures of sublimation for the (\(^{1}\text{BuO}\))\(_3\text{M}≡\text{N}\) (\(\text{M} = \text{Cr, Mo and W}\) ) molecules. At a pressure of 1.0 x 10\(^{-1}\) torr and \(~\sim\sim 40 \text{ °C}\) the chromium nitride sublimes. At a pressure of 5.0 x 10\(^{-3}\) torr the molybdenum nitride sublimes at \(~\sim\sim 85 \text{ °C}\) and the tungsten analog sublimes at \(~\sim\sim 110 \text{ °C}\). This trend shows a difference in physical property that is in agreement with the calculated results.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calculated I.P. (eV) (DFT/HF)</th>
<th>Observed I.P. (eV)</th>
</tr>
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<tbody>
<tr>
<td>(HO)$_3$Cr≡N</td>
<td>10.9/9.86</td>
<td>9.2</td>
</tr>
<tr>
<td>(t-BuO)$_2$Cr≡N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HO)$_3$Mo≡N</td>
<td>10.5/9.79</td>
<td>9.5</td>
</tr>
<tr>
<td>(t-Pro)$_2$Mo≡N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HO)$_3$W≡N</td>
<td>10.2/9.48</td>
<td>9.2</td>
</tr>
<tr>
<td>(t-BuO)$_3$W≡N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$O)$_2$Mo≡N</td>
<td>9.6/9.09</td>
<td>9.3</td>
</tr>
<tr>
<td>(t-BuO)$_3$Mo≡N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CF$_3$O)$_3$Mo≡N</td>
<td>11.6/10.9</td>
<td>10.3</td>
</tr>
<tr>
<td>(Me$_2$CF$_3$CO)$_3$Mo≡N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$C≡N</td>
<td>11.9/12.74</td>
<td>12.1</td>
</tr>
<tr>
<td>CF$_3$C≡N</td>
<td>13.9/14.54</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Table 3. Calculated (density functional method and Hartree-Fock) and observed I.P.'s for the nitriles.
Reactivity studies.

The known reactivity of $W_2(O^tBu)_6$ towards acetonitrile prompted interest in its reactivity towards the inorganic nitriles. Several reactions were undertaken to investigate this chemistry.

\[
\begin{align*}
(\,^tBuO)_3W &\equiv N + Mo_2(O^tBu)_6 \xrightarrow{\text{hexane}} MoW(O^tBu)_6 + (\,^tBuO)_3Mo \equiv N & (10) \\
(\,^tBuO)_3Mo &\equiv N + W_2(O^tBu)_6 \xrightarrow{-70^\circ C}\ (\,^tBuO)_3W &\equiv N + W_2(O^tBu)_6 \\
&\text{Mo}_2(O^tBu)_6 & (11) \\
&\text{MoW(O^tBu)}_6 & \\
(\,^tBuO)_3Cr &\equiv N + Mo_2(O^tBu)_6 \xrightarrow{\text{hexane}} (\,^tBuO)_3Mo &\equiv N + Cr(O^tBu)_4 + \text{unrecoverable products} & (12) \\
(\,^tBuO)_3Cr &\equiv N + W_2(O^tBu)_6 \xrightarrow{-70^\circ C}\ (\,^tBuO)_3W &\equiv N + Cr(O^tBu)_4 + \text{unrecoverable products} & (13)
\end{align*}
\]
<table>
<thead>
<tr>
<th>Molecule:</th>
<th>M</th>
<th>N</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HO)$_3$Cr≡N</td>
<td>0.783</td>
<td>-0.118</td>
<td>-0.622</td>
</tr>
<tr>
<td>(HO)$_3$Mo≡N</td>
<td>1.166</td>
<td>-0.269</td>
<td>-0.701</td>
</tr>
<tr>
<td>(HO)$_3$W≡N</td>
<td>1.263</td>
<td>-0.335</td>
<td>-0.720</td>
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<tr>
<td>(CH$_3$O)$_3$Mo≡N</td>
<td>1.142</td>
<td>-0.304</td>
<td>-0.541</td>
</tr>
<tr>
<td>(CF$_3$O)$_3$Mo≡N</td>
<td>1.405</td>
<td>-0.118</td>
<td>-0.508</td>
</tr>
</tbody>
</table>

Table 4. Mulliken charge density analysis for the calculated atoms in the given molecules.
The reactions were carried out at room temperature in hydrocarbon solvents. The inorganic nitriles do show some reactivity towards group VI metal dimers. This is not surprising given the reactivity of the analogous molybdenum oxide (\(\text{BuO})_4\text{Mo}==\text{O}\) toward the ditungsten hexa-alkoxide.\(^30\) The reaction of the molybdenum oxo species can be compared to Reaction 11. The oxygen atom was transferred to tungsten and a mixed metal species was formed, similarly the nitrogen atom is transferred to tungsten and a mixed metal species was formed for Reaction 11. This is perhaps the most interesting of the four inorganic nitrile reactions. This reaction likely goes through two steps. The first is the formation of one equivalent of the tungsten nitride and one equivalent of a mixed metal dimer \(\text{WMo(O')Bu}_6\). This dimer then reacts with another equivalent of the molybdenum nitride thus forming the dimolybdenum dimer and another equivalent of the tungsten nitride. The reactions suggested would explain the formation of all products and the relative amounts observed in the \(^1\text{H}\) NMR spectra. The dimer is the first known group VI \(d^3-d^3\) mixed metal molecule. Attempts to purify this compound proved unsuccessful. This chemistry was briefly studied by a previous Chisholm group member with similar results.\(^31\)

Based on calculated results for the bond dissociation energies (bde's), one driving force for Reaction 11 is the formation of the tungsten nitride unit (see Table 5). Calculations were performed on the metal alkoxide fragment and the nitrogen fragment. The combined fragment energies were compared to the complete molecule total energy. The driving force suggested for Reaction 11 is
not present for the previously studied Reaction 10. Therefore, it makes sense that there is no reaction observed.

The reaction of the chromium nitride with the metal dimers was so rapid at room temperature that it needed to be cooled with a dry ice bath. Even at this reduced temperature the reaction was too vigorous to isolate all products. One key product that was isolated from Reactions 12 and 13 was the blue volatile compound Cr(OtBu)₄. The presence of this molecule implies a different path of reactivity and one that incorporates redox chemistry that is not necessarily present in the other inorganic nitride transfer reaction.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>bde (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HO)₃Cr≡N</td>
<td>~75.6</td>
</tr>
<tr>
<td>(HO)₃Mo≡N</td>
<td>~133.5</td>
</tr>
<tr>
<td>(HO)₃W≡N</td>
<td>~151.0</td>
</tr>
</tbody>
</table>

Table 5. Calculated bond dissociation energies (bde’s) for the metal nitride units in (HO)₃M≡N (M = Cr, Mo and W).

The calculated relatively weak chromium nitride bond dissociation energy may give the insight necessary to understand the rapid conversion to the (tBuO)₃M≡N (M = Mo and W) and Cr(OtBu)₄. Given the lower Cr≡N bde, the
chromium nitride should be a better nitrogen transfer reagent compared to the molybdenum and tungsten species.

The analogous Reaction 4 involving Mo₂(O'Bu)₆ is known to not proceed to give the molybdenum nitride and alkylidyne complexes. The reaction also does not occur for benzonitrile and the dimolybdenum hexa-alkoxide. Consequently we examined the reverse reaction to see if benzonitrile and the molybdenum dimer would form from the back reaction between the molybdenum nitride and the molybdenum benzylidyne, Reaction 14.

\[
\text{Mo(CPh)(O'Bu)₃ + Mo(N)(O'Bu)₃ } \rightarrow \text{ No observable reaction } \quad (14)
\]

The mixture did not show any observable reactivity with NMR scale reactions. Even after several days of heating there were no observable changes in the \(^1\text{H}\) NMR spectra. The metathesis of the nitride and alkylidyne does not occur, however this does not mean that there is not some form of exchange that is not observable. This consideration led us to investigate a series of reactions to detect nitride or alkylidyne transfer in molybdenum and tungsten species. The chemistry was monitored primarily by \(^1\text{H}\) NMR spectroscopy although some isotopically labeled \(^{13}\text{C}\) and \(^{15}\text{N}\) NMR were studied.

Reactions 15-24 show the reactions studied. Reactions 15 and 16 have the thermodynamically favored product \((\text{BuO})_3\text{W=N}\) as a reactant and thus may have no thermodynamic driving force.
\[
\begin{align*}
W(N)(O^1Bu)_3 + Mo(CPh)(O^1Bu)_3 & \quad \rightarrow \quad \text{No observable reaction} \quad (15) \\
W(N)(O^1Bu)_3 + Mo(N)(O^1Bu)_3 & \quad \rightarrow \quad \text{No observable reaction} \quad (16) \\
W(CMe)(O^1Bu)_3 + Mo(N)(O^1Bu)_3 & \quad \rightarrow \quad W(N)(O^1Bu)_3 + Mo(CMe)(O^1Bu)_3 \quad (17) \\
W(CMe)(O^1Bu)_3 + Mo(CPh)(O^1Bu)_3 & \quad \rightarrow \quad W(CPh)(O^1Bu)_3 + Mo(CMe)(O^1Bu)_3 \quad (18) \\
W_2(O^1Bu)_6 + Mo(CPh)(O^1Bu)_3 & \quad \rightarrow \quad \text{No observable reaction} \quad (19) \\
W(C^{13}Pr)(O^1Bu)_3 + Mo(CPh)(O^1Bu)_3 & \quad \rightarrow \quad W(CPh)(O^1Bu)_3 + Mo(C^{13}Pr)(O^1Bu)_3 \quad (20) \\
W(C^{13}Pr)(O^1Bu)_3 + Mo(N)(O^1Bu)_3 & \quad \rightarrow \quad W(N)(O^1Bu)_3 + Mo(C^{13}Pr)(O^1Bu)_3 \quad (21) \\
W(^{15}N)(O^1Bu)_3 + MeCN + PhCN & \quad \rightarrow \quad W(N)(O^1Bu)_3 + Me^{15}N + Ph^{15}N \quad (22) \\
W(CPh)(O^1Bu)_3 + Mo(CPh)(O^1Bu)_3 & \quad \rightarrow \quad \text{No observable reaction} \quad (23) \\
W(CPh)(O^1Bu)_3 + Mo(N)(O^1Bu)_3 & \quad \rightarrow \quad W(N)(O^1Bu)_3 + Mo(CPh)(O^1Bu)_3 \quad (24)
\end{align*}
\]
There was no dinitrogen formed or any of the observable mixed metal dimer seen in the $^1$H NMR spectrum for Reaction 16. After observing no change in reactants for Reaction 16 a second experiment was performed with $^{15}$N labeled tungsten nitride. The reaction was performed on the NMR scale and showed the formation of a new peak at 828.8 ppm in $d_8$-THF. The new peak is considered to be the formation of the $^{15}$N labeled molybdenum nitride, which is the first known example of this molecule. To support the evidence, mass spectral analysis of the mixture was performed which showed the isotope pattern for some $^{15}$N in the molybdenum nitride mass range. There is further support that nitrogen atom transfer occurs from Reactions 17, 21, 22 and 24. Reaction 17 seems to continue in a second reaction of two equivalents of the molybdenum ethylidyne to form the dimolybdenum hexa-alkoxide. There is no observable peak for 2-butyne in the $^1$H or $^{13}$C NMR however the spectrum does show the growth of a new alkylidyne peak. This peak is likely due to the new product molybdenum alkylidyne. Reaction 19 seems to follow the same trend. For both reactions the $^1$H NMR spectrum was used to show ligand transfer. $^{13}$C NMR was used to verify the findings and then to show the new alkylidyne peaks. Given the equilibrium of Reaction 18 it is not surprising that Reaction 20 also shows some ligand transfer. Because there are different levels of reactivity towards the nitriles for the group VI dimers it was thought that there may be some slight differences in reactivity given different steric and electronic factors for the alkylidyne ligand. In the specific case of Reaction 20 there was no observable difference in reactivity. Reaction 21 is similar to Reaction 17 but does not show the tendency to continue
on and have the secondary reaction forming the dimolybdenum hexa-alkoxide. Reaction 22 was performed to show that the most stable nitrido bond in this study, both by calculation and empirical methods (('BuO)₃W≡N), would undergo ligand exchange with organic nitriles. The reactivity or lack thereof, for Reaction 16 is similar to that of Reaction 23. There appears to be no change in the contents of the reaction flask for Reaction 23. Finally, Reaction 24 shows an equilibrium similar to that in Reactions 17 and 21. This is expected given the formation of the tungsten nitride unit. It is important to note that all of the equilibrium reactions favor the left hand side of the equations shown with the exception of one. The equilibrium in Reaction 20 favors the right hand side of the equation. The ¹⁵N labeled reactions do not favor the left or right hand side. There is a 1:1 mixture formed of labeled:unlabeled as might be expected given a lack of preference for nitrogen with a single mass unit difference.
Conclusions

Metal-ligand multiple bonds and metal-metal multiple bonds have been studied for many years. There are many examples of these functional groups being involved in metathesis reactions. The factors that govern metathesis reactions are many including, the transition metal used and the ligands bound to that metal. A complimentary mixture of experimental and theoretical approaches were used to explore these molecules. A series of compounds of the type (\(\text{RO}_3\text{M}=\text{N}\)) (where \(\text{R} = ^1\text{Bu}, ^1\text{Pr}, \text{CMe}_2\text{CF}_3\) and \(\text{M} = \text{Cr}, \text{Mo}\) and \(\text{W}\)) have been synthesized. UPS was used to probe the electronic structure of these compounds. When keeping the metal as molybdenum the IP is seen to increase by adding a more electronegative alkoxide ligand. When varying the metal center the IP values are approximately the same but the orbitals in which the electrons ionize from change in order.

Theoretical approaches to elucidating the electronic structure include Gaussian 98™ calculations and a schematic MOD. Simplified versions of the molecules i.e (\(\text{RO}_3\text{M}=\text{N}\) (\(\text{R} = \text{Me}, \text{H}, \text{CF}_3\) \(\text{M} = \text{Cr}, \text{Mo}\) and \(\text{W}\)) were used with the Gaussian 98™ package of software to obtain electronic structure, ionization potentials, bond dissociation energies and qualitative molecular orbital contributions. The results reasonably fit those predicted from the UPS. For \((^1\text{BuO})_3\text{Mo}=\text{N}\) and the other molybdenum analogs the ordering is nitrogen lone
pair for the HOMO, metal nitrogen \(\pi\) bond for the SHOMO and oxygen lone pair for the THOMO. This is also true for the tungsten analog. For the chromium analog the oxygen lone pair orbital has been pushed up in energy to be the HOMO with the rest of the orbitals remaining the same. These results have been compared to the organic nitriles MeC\(\equiv\)N and CF\(_3\)C\(\equiv\)N.

Because a trend in bond dissociation energies for the nitrides were also calculated a quantitative ordering of bond strength was known and showed that the (RO)\(_3\)Cr\(\equiv\)N molecule would be a good nitrogen atom transfer reagent. This led to some interesting reactivity studies. It has been shown that Mo\(_2\)(O\(^1\)Bu)\(_6\) does not react with PhC\(\equiv\)N or MeC\(\equiv\)N as the tungsten analog W\(_2\)(O\(^1\)Bu)\(_6\) does. The reaction between \((\text{^1BuO})_3\)Mo\(\equiv\)N and \((\text{^1BuO})_3\)Mo\(\equiv\)CPh does not proceed to give Mo\(_2\)(O\(^1\)Bu)\(_6\) and PhC\(\equiv\)N. The final part of the study investigates the reaction of several nitrides and or alkylidyne species to see if metathesis occurs. For some of the reactions there is an equilibrium that forms. \(^{15}\)N labeling experiments show nitrogen atom transfer for some of the reactions between the tungsten nitride \((\text{^1BuO})_3\)W\(\equiv\)N and the molybdenum nitride \((\text{^1BuO})_3\)Mo\(\equiv\)N or organic nitriles (MeC\(\equiv\)N and PhC\(\equiv\)N).
Continuing Work

Calculational work that helps to understand the energetics of nitrogen atom transfer is underway. The molybdenum nitride (\(\text{PrO}_2\)\(\text{Mo}=\text{N}\)) has been shown to react with the dimolybdenum hexa-isopropoxide (\(\text{Mo}_2(\text{OPr})_6\)) in a 2:1 ratio to form an unusual ladder shaped molecule.\(^{31}\) It is believed that this molecule and the neopentoxide analog are paramagnetic. A detailed study of the properties of these molecules is underway. The neopentoxide analog needs to be successfully synthesized and crystallized to compare to the isopropoxide analog.
**Experimental**

General Methods.

All manipulations were carried out using an Argon (Ar) or dinitrogen (N₂) atmosphere and standard air and moisture sensitive techniques in Vacuum Atmospheres and Mbraun Gloveboxes or a Schlenk line. Solvents were distilled from CaH₂ or Na/Benzophenone ketyl, purged of oxygen with either Ar or N₂ and stored over 4 Å sieves. All reagents were purchased from Aldrich unless otherwise stated and used without further purification. Fluoroalcohols (Lancaster Synthesis) were distilled under Ar and stored over 4 Å sieves. Molybdenum pentachloride and tungsten hexachloride (Strem Chemicals) were used as purchased. Lithium, sodium or potassium alkoxide salts were purchased (LiOBuᵗ, Aldrich) or prepared using a previously reported method.³² Molybdenum tetrachloride-bisacetonitrile (MoCl₄(CH₃CN)₂) was prepared via a reported method.³³,³⁴ Chromium nitrido tris-t-butoxide (⁵BuO)₃Cr=N, tungsten nitrido tris-t-butoxide (⁵BuO)₃W=N and M₂(O'Bu)₆ (where M = Mo and W) were prepared via reported syntheses.¹⁴,¹¹,³⁵-³⁶ The molybdenum nitrido alkoxides and fluoroalkoxides were prepared via a modification of a reported synthesis.¹² All alkylidyne species were prepared and purified according to a previously reported literature procedure.³⁷

Spectroscopic methods.
Proton (\(^1\text{H}\)) and fluorine (\(^19\text{F}\)) NMR spectra at Indiana University were obtained on a Varian Gemini 2000 spectrometer operating at a 300 MHz proton and 282 MHz fluorine NMR Larmor frequencies. Proton (\(^1\text{H}\)), carbon (\(^{13}\text{C}\)) spectra at The Ohio State University were obtained on a Bruker Avance 250 and 400 spectrometer operating at 250 and 400 MHz proton and 100 MHz carbon NMR Larmor frequency. Nitrogen (\(^{15}\text{N}\)) spectra were obtained on a Bruker Avance 500 MHz spectrometer at 50 MHz nitrogen NMR Larmor frequency. Infrared (IR) spectra were taken as KBr pellets on a Nicolet 510P FT-IR spectrophotometer using OMNI E. S. P. software at Indiana University. At The Ohio State University infrared spectra were taken on a Perkin-Elmer Spectrum GX FT-IR spectrophotometer using the Perkin-Elmer Spectrum v3.01 package of software. Mass spectra were taken on a Kratos MS 80 high resolution mass spectrometer using negative ion CI with methane (CH\(_4\)) as reagent gas at Indiana University and at The Ohio State University they were taken on a Kratos MS 25 RFA double focusing magnetic sector mass spectrometer. A positive ion EI source with a trap current of 100 \(\mu\text{A}\) at a temp of 225 \(^0\text{C}\) at 52 eV. A 3 kV analyzer was used with a resolution of 2000 using the 5% peak height definition. The scanning rate was 5 sec/decade with a mass range of 1100 to 275. A third party (MSS) data system was used. Photoelectron spectra were recorded at the University of Arizona using an instrument that features a 36 cm radius hemispherical analyzer (McPherson) with an 8 cm gap between sphere and specially designed photon sources and power supplies. The argon \(^2\text{P}_{3/2}\) ionization at 15.759 eV was used as an internal calibration lock for the energy scale.
Resolution (measured as full-width-at-half-maximum of the argon $^2P_{3/2}$ ionization) was 0.018-0.020 eV during data collection.

Samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue.

Calculational Methods.

Calculations were performed on the (RO)$_3$M≡N molecules (where M = Cr, Mo, W and R = H, CH$_3$ and CF$_3$) using the Gaussian98$^{TM}$ suite of programs utilizing the B3LYP method and standard basis sets.$^{19,25-28}$ The CEP-121G* basis set was used for the metals and ligands.$^{25-28}$ The bond length and angles were taken from the crystal structures of ($^t$BuO)$_3$M≡N (M = Cr, Mo, W) and optimized in C$_3$v symmetry.$^{12-14}$ The oxygen-hydrogen distances were set to 0.95 Å. Orbital analyses were completed with Molden$^{TM}$.29

**Reaction of ($^t$BuO)$_3$Mo≡N with W$_2$(O$^t$Bu)$_6$, 11.** The reaction was a modification of a previously reported reaction.$^{31}$ W$_2$(O$^t$Bu)$_6$ (0.25 g) and hexanes (10 mL) were added to a Schlenk flask and allowed to stir. Separately ($^t$BuO)$_3$Mo≡N (0.20 g) and hexanes (10 mL) were added to a second Schlenk flask and allowed to stir. The ($^t$BuO)$_3$Mo≡N solution was added to the W$_2$(O$^t$Bu)$_6$ solution via cannula. The mixture was left to stir at room temperature overnight. A white precipitate had formed and the solution was filtered via cannula away from the precipitate into a clean Schlenk flask. The filtrate was concentrated in
vacuo. The white precipitate was identified as \((^{13}\text{BuO})_3\text{W}=\text{N}\) by comparison of the \(^1\text{H}\) NMR spectra with that of known \((^{13}\text{BuO})_3\text{W}=\text{N}\).

**Reaction of \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) with \(\text{Mo}_2(\text{O}^{13}\text{Bu})_6\), 12.** \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) (0.057 g, 0.2 mmol) was added with hexanes (10 mL) to a Schlenk flask and allowed to stir. Separately, \(\text{Mo}_2(\text{O}^{13}\text{Bu})_6\) (0.126 g, 0.2 mmol) was added with hexanes (10 mL) to a Schlenk flask and allowed to stir. Both flasks were placed in a dry ice/acetone bath and were allowed to stir for 1 h until the solutions had cooled to \(-78\,^\circ\text{C}\). The \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) solution was slowly (15 min) added via cannula to the \(\text{Mo}_2(\text{O}^{13}\text{Bu})_6\) solution. The mixture was kept at \(-78\,^\circ\text{C}\) and was allowed to stir for 2 h. The solvent was removed in vacuo. As the flask slowly warmed a blueish-green liquid formed around the stopper of the flask. The blueish-green volatile compound was identified as \(\text{Cr}(\text{O}^{13}\text{Bu})_4\) by comparison of the infrared spectrum with that of known \(\text{Cr}(\text{O}^{13}\text{Bu})_4\). \(^1\text{H}\) NMR of reaction 12 (\(\text{C}_6\text{D}_6\) solvent, \(\text{C}_6\text{D}_5\text{H}\) reference, ppm): \(\delta\) 1.59 (b.s.), \(\delta\) 1.57 (s), \(\delta\) 1.55 (s), \(\delta\) 1.48 (s, \((^{13}\text{BuO})_3\text{Mo}=\text{N}\)). The mass spectrum of the dried reaction product has the correct peak range for \((^{13}\text{BuO})_3\text{Mo}=\text{N}\).

**Reaction of \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) with \(\text{W}_2(\text{O}^{13}\text{Bu})_6\), 13.** \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) (0.063 g, 0.22 mmol) was added with hexanes (10 mL) to a Schlenk flask and allowed to stir. Separately, \(\text{W}_2(\text{O}^{13}\text{Bu})_6\) (0.177 g, 0.22 mmol) was added with hexanes (10 mL) to a Schlenk flask and allowed to stir. Both flasks were placed in a dry ice/acetone bath and were allowed to stir for 1 h until the solutions had cooled to \(-78\,^\circ\text{C}\). The \((^{13}\text{BuO})_3\text{Cr}=\text{N}\) solution was slowly (15 min) added via cannula to the
W₂(O'Bu)₆ solution. The mixture was kept at −78 °C and was allowed to stir for 2 h. The solvent was removed in vacuo. As the flask slowly warmed a blueish-green liquid formed around the stopper of the flask. The blueish-green volatile compound was identified as Cr(O'Bu)₄ by comparison of the infrared spectrum with that of known Cr(O'Bu)₄. ¹H NMR of reaction 13 (C₇D₈ solvent, C₇D₃H reference, ppm): δ 3.42 (s), δ 2.1 (s), δ 1.59 (s, (BuO)₃W≡N), δ 1.48 (s), δ 1.45 (s). The mass spectrum of the dried reaction product has the correct peak range for (BuO)₃W≡N.

**Reaction of (BuO)₃W=¹⁵N with (BuO)₃Mo≡N, 16.** (BuO)₃W=¹⁵N (0.0209 g, 0.05 mmol) and (BuO)₃Mo≡N (0.0165 g, 0.05 mmol) were added to a NMR tube and allowed to react in d₈-THF at room temperature for 1 week. The ¹H NMR spectrum of reaction 16 shows no change from starting materials. The ¹⁵N NMR spectrum of reaction 16 (d₈-THF solvent, d₇-THF reference, ppm): δ 828.8 (s, (BuO)₃Mo=¹⁵N), δ 731.8 (s, (BuO)₃W=¹⁵N). Mass spectral analysis of the reaction products verifies the presence of (BuO)₃Mo=¹⁵N.

**Reaction of (BuO)₃W≡CMe with (BuO)₃Mo≡N, 17.** (BuO)₃W≡CMe (0.0215 g, 0.05 mmol) was made in an NMR tube according to a previously reported method.³⁷ (BuO)₃Mo≡N (0.0165 g, 0.05 mmol) was added to the tube and allowed to react at room temperature for 1 week. ¹H NMR of reaction 17 (C₆D₆ solvent, C₆D₃H reference, ppm): δ 3.57 (s, 3, Jₜₜ = 7.2 Hz, (BuO)₃W≡CMe), δ 2.58 (s, 3, (BuO)₃Mo≡CMe), δ 1.48 (s, 27, (BuO)₃Mo≡N), δ 1.46 (s), δ 1.443 (s, 27, (BuO)₃W≡CMe), δ 1.439 (s), δ 1.422 (s). ¹³C{¹H} NMR
of reaction 17 (C₆D₆ solvent, C₆D₅H reference, ppm): δ 333.1 (s), δ 279.6 (s, 1, (BuO)₂Mo≡CMe), δ 254.1 (s, 1, Jₖₕ = 306.5 Hz (BuO)₂W≡CMe.

Reaction of (BuO)₃W≡CMe with (BuO)₃Mo≡CPh, 18.

(BuO)₃W≡CMe (0.0054 g, 0.0125 mmol) was made in an NMR tube according to a previously reported method.³⁷ (BuO)₃Mo≡CPh (0.0051 g, 0.0125 mmol) was added to the tube and allowed to react at room temperature for 1 week. ¹H NMR of reaction 18 (C₆D₆ solvent, C₆D₅H reference, ppm): δ 7.49 (d, 2, (BuO)₃Mo≡CPh), δ 7.33 (d, 2, (BuO)₃W≡CPh), δ 7.23 (t, 2, (BuO)₃Mo≡CPh), δ 7.09 (t, 2, (BuO)₃Mo≡CPh), δ 6.87 (t, 1, (BuO)₃Mo≡CPh), δ 6.82 (t, 1, (BuO)₃Mo≡CMe), δ 3.57 (s, 3, Jₖₕ = 7.2 Hz, (BuO)₃W≡CMe), δ 2.58 (s, 3, (BuO)₃Mo≡CMe), δ 1.49 (s, 27, (BuO)₃Mo≡CPh), δ 1.48 (s, δ 1.44 (s, 27, (BuO)₃W≡CMe), δ 1.42 (s, 27, (BuO)₃W≡CPh). ¹³C{¹H} NMR of reaction 18 (C₆D₆ solvent, C₆D₅H reference, ppm): δ 333.1 (s), δ 307.8 (s), δ 279.8 (s, 1, (BuO)₃Mo≡CPh), δ 254.1 (s, 1, Jₖₕ = 306.5 Hz (BuO)₂W≡CMe.

Reaction of (BuO)₃W≡CPr with (BuO)₃Mo≡CPh, 20. (BuO)₃W≡CPr (0.0229 g, 0.05 mmol) and (BuO)₃Mo≡CPh (0.0202 g, 0.05 mmol) were added to a NMR tube and allowed to react at room temperature for 1 day. ¹H NMR of reaction 20 (C₆D₆ solvent, C₆D₅H reference, ppm): δ 7.50 (d, 2, (BuO)₃Mo≡CPh), δ 7.33 (d, 2, (BuO)₃W≡CPh), δ 7.22 (t, 2, (BuO)₃W≡CPh), δ 7.09 (t, 2, (BuO)₃Mo≡CPh), δ 6.87 (t, 1, (BuO)₃Mo≡CPh), δ 6.82 (t, 1, (BuO)₃Mo≡CPh), δ 4.05 (sept, 1, Jₖₕ = 6.85 Hz, (BuO)₃W≡CPr), δ 3.11 (sept, 1, (BuO)₃Mo≡CPr), δ 1.48 (s, 27, (BuO)₃Mo≡CPh), δ 1.47 (s, 27,
(\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr, \( \delta \) 1.46 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 1.45 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}W=CPh), \( \delta \) 1.242 (d, 6, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 1.16 (d, 6, (\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr). \textsuperscript{13}C{\{H\} NMR of reaction 20 (C\textsubscript{6}D\textsubscript{6} solvent, C\textsubscript{6}D\textsubscript{5}H reference, ppm): \( \delta \) 292.7 (s, 1, (\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr), \( \delta \) 268.3 (s, 1, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 257.8 (s, 1, (\textsuperscript{1}BuO)\textsubscript{3}W=CPh).

**Reaction of (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr with (\textsuperscript{1}BuO)\textsubscript{3}Mo=N, 21.** (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr (0.0229 g, 0.05 mmol) and (\textsuperscript{1}BuO)\textsubscript{3}Mo=N (0.0165 g, 0.05 mmol) were added to a NMR tube and allowed to react at room temperature for 1 week. \textsuperscript{1}H NMR of reaction 21 (C\textsubscript{6}D\textsubscript{6} solvent, C\textsubscript{6}D\textsubscript{5}H reference, ppm): \( \delta \) 4.05 (sept, 1, J\textsubscript{HW} = 6.85 Hz, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 3.11 (sept, 1, (\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr), \( \delta \) 1.48 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}Mo=N), \( \delta \) 1.47 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr), \( \delta \) 1.46 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 1.45 (s, 27, (\textsuperscript{1}BuO)\textsubscript{3}W=N), \( \delta \) 1.242 (d, 6, (\textsuperscript{1}BuO)\textsubscript{3}W=\textsuperscript{C}Pr), \( \delta \) 1.16 (d, 6, (\textsuperscript{1}BuO)\textsubscript{3}Mo=\textsuperscript{C}Pr).

**Reaction of (\textsuperscript{1}BuO)\textsubscript{3}W\textsuperscript{15}N with MeC=N and PhC=N, 22.** (\textsuperscript{1}BuO)\textsubscript{3}W\textsuperscript{15}N (0.0209 g, 0.05 mmol), MeC=N (2.6 \textmu L, 0.05 mmol) and PhC=N (5.1 \textmu L, 0.05 mmol) were added to a NMR tube and allowed to react at room temperature for 1 day. The \textsuperscript{1}H NMR spectrum of reaction 22 shows no change from starting materials. \textsuperscript{15}N NMR of reaction 22 (C\textsubscript{6}D\textsubscript{6} solvent, C\textsubscript{6}D\textsubscript{5}H reference, ppm): \( \delta \) 258.1 (s, 1, PhC=\textsuperscript{15}N), \( \delta \) 246.9 (s, 1, MeC=\textsuperscript{15}N).

**Reaction of (\textsuperscript{1}BuO)\textsubscript{3}W=CPh with (\textsuperscript{1}BuO)\textsubscript{3}Mo=N, 24.** (\textsuperscript{1}BuO)\textsubscript{3}W=CPh (0.0246 g, 0.05 mmol) and (\textsuperscript{1}BuO)\textsubscript{3}Mo=N (0.0165 g, 0.05 mmol) were added to a NMR tube and allowed to react at room temperature for 1 week. \textsuperscript{1}H NMR of reaction 24 (C\textsubscript{6}D\textsubscript{6} solvent, C\textsubscript{6}D\textsubscript{5}H reference, ppm): \( \delta \) 7.49 (d, 2, (\textsuperscript{1}BuO)\textsubscript{3}Mo=CPh), \( \delta \) 7.33 (d, 2, (\textsuperscript{1}BuO)\textsubscript{3}W=CPh), \( \delta \) 7.23 (t, 2, (\textsuperscript{1}BuO)\textsubscript{3}W=CPh), \( \delta \)
7.09 (t, 2, (′BuO)₃Mo≡CPh), δ 6.87 (t, 1, (′BuO)₃Mo≡CPh), δ 6.82 (t, 1, (′BuO)₃W≡CPh), δ 1.48 (s, 27, (′BuO)₃Mo≡N), δ 1.47 (s, 27, (′BuO)₃Mo≡CPh), δ 1.46 (s, 27, (′BuO)₃Mo≡CPh).
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