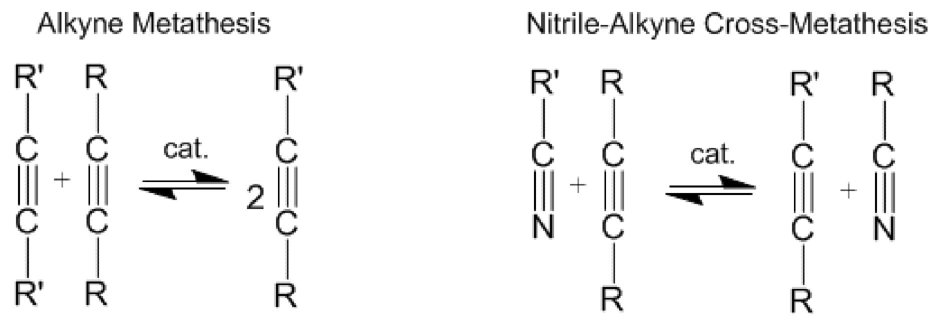
Chapter One:

Overview of Triple-Bond Metathesis

1.1 Introduction

Olefin and alkyne metathesis have revolutionized the synthesis of carbon-carbon bonds in natural products, polymers, pharmaceuticals, and many other materials.[1-5] Unlike olefin metathesis, alkyne metathesis is still in its infancy in terms of catalyst development and breadth of synthetic application. Although several alkyne metathesis systems have been developed, drawbacks for each system exist. These shortcomings include but are not limited to: (i) catalyst instability, (ii) lack of extensive functional group tolerance, (iii) sensitivity to air and water, (iv) low catalyst activity, (v) high temperature requirements, and (vi) difficult, multistep syntheses of catalysts.[2] These limitations have caused alkyne metathesis to be underutilized.

Despite these weaknesses, recent applications in the fields of natural product and polymer synthesis demonstrate the utility of alkyne metathesis.[1,4] Stereoselective reduction of the installed alkyne moiety can be effected through Lindlar or trans-hydrosilylation methodologies.[4,6-8] Moreover, these dual alkyne metathesis-reduction manifolds avoid the difficulties of stereoselective carbon-carbon double bond formation present in olefin metathesis.[6] From these examples, the necessity of developing a metathesis system that can be readily applied in the synthesis of a wide range of target molecules is apparent.



Scheme 1.1. General reactions for alkyne metathesis and proposed nitrile-alkyne cross-metathesis.

Currently, *all* alkyne metathesis systems are limited by the requirement of a pre-existing carbon-carbon triple bond in each substrate as shown in Scheme 1.1. Extension of alkyne metathesis to include not only carbon-carbon triple bonds but also carbon-nitrogen triple bonds would increase the utility of the system (Scheme 1.1). Carbon-nitrogen triple bonds can frequently be more readily installed in molecules in comparison to carbon-carbon triple bonds.[9,10] For instance, both nucleophilic substitution of a halide with cyanide and dehydration of an amide allow one to readily access the nitrile functionality.[11] Additionally, many nitrile-substituted compounds are commercially available, increasing the attractiveness of nitrile precursors. With these advantages in mind, my research objective is to develop and investigate metal complexes that will catalyze the formation of alkynes via cross-metathesis of an alkyne with a nitrile.

1.2 Early Heterogeneous and Homogeneous Catalyst Systems

The first alkyne metathesis systems were developed in the late 1960s using silica-supported tungsten oxide catalysts.[12,13] These heterogeneous systems operate at atmospheric pressure and temperatures between 100^{o}C and 550^{o}C. They are tolerant of internal alkynes, but not terminal alkynes, which undergo cyclotrimerization reactions.

System optimization to overcome low activity is complicated by the elusive nature of the active catalyst.

The inability to apply the heterogeneous systems on a preparative scale led to the development of homogenous catalysts systems consisting of $Mo(CO)_6$ and phenols.[14] Mortreux's systems are operationally simple, relying on commercially available chemicals and displaying only slight sensitivity to air and water. Similar to the heterogeneous systems, these systems require elevated temperatures (140-150^{o}C) and display low activity. Although recent improvements to the system, such as addition of more acidic phenols, have assisted in increasing activity and functional-group tolerance, systematic optimization is difficult due to the unknown identity of the active catalyst. [15,16]

An analogous homogeneous tungsten system was developed several years later.[17] Unlike the corresponding molybdenum system, some phenol incompatibility is observed along with sensitivity to water and air. Further drawbacks including, elevated reaction temperatures, high catalyst loadings and functional group incompatibility limit the system's utility.

1.3 Development of Well-Defined Alkyne Metathesis Catalysts

1.3.1 Tungsten-Based Alkylidyne Catalysts

The first well-defined catalysts in the field of alkyne metathesis were synthesized by Schrock's group in 1981.[18] The first of these species, $Me_3CC{\equiv}W(OCMe_3)_3$, displays increased reaction rates (< 4 hours to equilibrium) and product yields at 25°C in hydrocarbon solvents relative to earlier systems. Schrock-type tungsten alkylidyne catalysts (Figure 1.1) can be readily synthesized from $Me_3CC{\equiv}W(CH_2CMe_3)_3$ (**1.1**). As outlined in Scheme 1.2, treatment of **1.1** with 3 equivalents of hydrochloric acid in the presence of DME followed by ligand substitution with a variety of alkoxide ligands affords the desired alkylidyne complexes (Figure 1.1).[19,20] Alternatively, facile tungsten-tungsten triple bond scission of $W_2(OR)_6$ complexes upon reaction with various internal alkynes affords desired alkylidyne species in high yields (Scheme 1.2).[21,22]

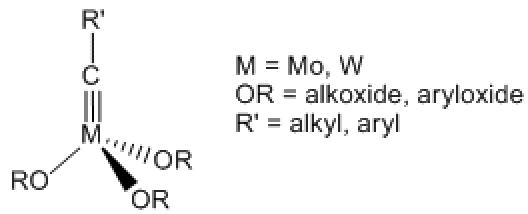
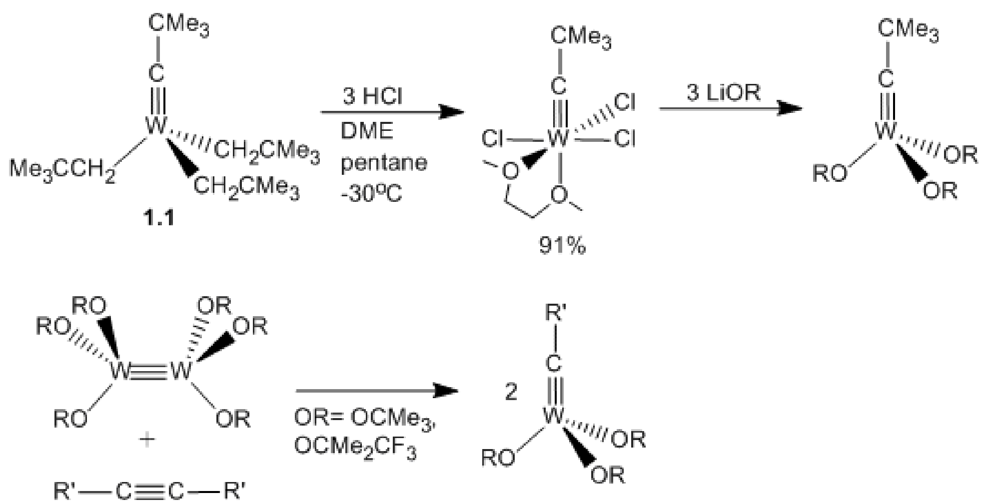


Figure 1.1. Structure of Schrock-type alkylidyne complexes.

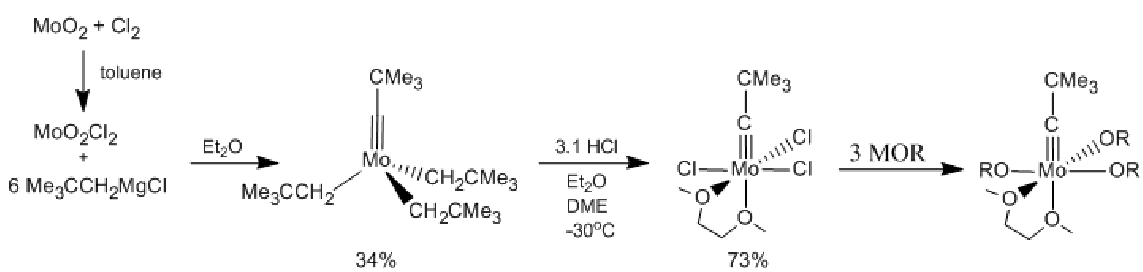
Schrock found that careful selection of the alkoxide is the key to designing efficient, active alkyne metathesis catalysts.[23] Increasing the degree of fluorination of the alkoxide ligand leads to a general trend of increased reaction rates.[19] Meanwhile, decreasing the steric profile of the alkoxide ligand favors alkyne polymerization over alkyne metathesis.[24] Although well-developed, these catalysts are highly sensitive to air and water and are incompatible with some functional groups, including pyridines, thioethers, thiocarbamates, thiophenes, alcohols, crown ethers and amines.[2,4] Additionally, alkyne metathesis is usually only successful with internal alkynes, as terminal alkynes preferentially undergo alkyne polymerization.[25]



Scheme 1.2. Syntheses of Schrock-type tungsten alkylidyne complexes.

1.3.2 Molybdenum-Based Alkylidyne Catalysts

Shortly after synthesizing the first metathesis-active tungsten alkylidyne catalyst, Schrock and co-workers followed up with the molybdenum analogues (Figure 1.1).[26] Although $Me_3CC{\equiv}Mo(OCMe_3)_3$ is catalytically inactive, increased fluorination of the alkoxide leads to increasingly active species as observed with the corresponding W-based complexes. Since molybdenum is less electrophilic than tungsten increased functional group compatibility with Lewis basic substrates is observed.



Scheme 1.3. General synthesis of Schrock-type molybdenum alkylidyne complexes.

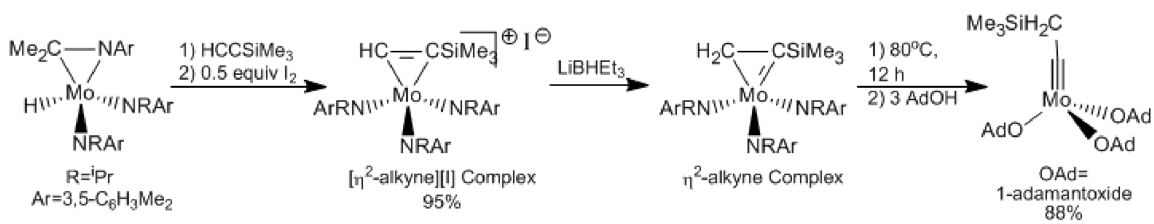
Unlike tungsten, $Mo_2(OR)_6$ complexes are reported not to undergo Mo-Mo triple bond scission with internal alkynes to form molybdenum alkylidyne species[27] (However, see Chapter 4). Although terminal alkynes do permit cleavage of the triple bond, the yields of alkylidyne complexes are relatively low due to isolation difficulty and decomposition of the presumed molybdenum methylidyne complex.[28] As a result, molybdenum alkylidyne complexes are generally accessed through a tedious, low-yielding synthesis involving the treatment of MoO_2 with chlorine gas followed by addition of six equivalents of neopentyl Grignard to produce $Me_3CC{\equiv}Mo(CH_2CMe_3)_3$. The neopentylidyne complex can then be subjected to 3 equivalents of HX (X=Cl, Br) followed by salt metathesis with the desired alkoxide to afford the desired alkylidyne catalysts (Scheme 1.3).[29] Accounting for the multitude of steps and the air-sensitive nature of the complexes, unless made commercially available (currently unviable) only chemists highly skilled in air-sensitive techniques can readily access the catalysts. This fact decreases the attractiveness of the molybdenum alkylidyne complexes.

1.4 Recent Catalyst Synthesis Developments

In order to overcome the difficult syntheses of the Schrock-type catalysts, several alkyne metathesis pre-catalyst systems and new methods of catalyst synthesis have been developed. Most of this work has focused on homogeneous systems due to the general ability to readily optimize the active species. However, Moore has expanded his work to include heterogeneous systems in order to avoid bimolecular catalyst decomposition.[30] Although several systems and new alkylidyne species have been designed, no pre-catalyst system or alkylidyne complex works well for all conversions and all are air sensitive. Variations in functional group tolerance, commercial availability, synthetic ease, temperature requirements, and successful applications exist with each material.[2]

1.4.1 Cummins

Nearly two decades after Schrock's initial work with molybdenum alkylidyne complexes Cummins designed an alternative route to these complexes (Scheme 1.4).[31] A metalaaziridine-hydride complex is treated with trimethylsilylacetylene and then oxidized with iodine to produce a cationic η^2-alkyne complex. The η^2-vinyl derivative is then accessed via reaction with $[Li][BHEt_3]$. Isomerization through 1,2-trimethylsilyl migration is induced by heating. At this point alcoholysis delivers the desired alkylidyne complex. Although this route is an improvement over previous efforts, the metalaaziridine-hydride complex serves as a source of $Mo(N^iPrAr)_3$, which is known to readily cleave dinitrogen.[32] Thus manipulation of this material in a nitrogen-filled glove box is not facile.



Scheme 1.4. Cummins's method of synthesizing Schrock-type alkylidyne complexes.

1.4.2 Fürstner

Taking advantage of Cummins's $Mo(N^tBuAr)_3$ complexes, Fürstner discovered that activation of these materials with CH_2Cl_2 and various other geminal dihalide sources leads to an alkyne-metathesis-active mixture of species.[33,34] A variety of materials were isolated from these mixtures and their catalytic competence was examined. Three of the species shown in Figure 1.2 are catalytically active. Surprisingly, the methylidyne complex displays only sluggish reactivity relative to the other species. Since complexes other than alkylidyne complexes are competent catalysts, this emphasizes that routes of alkyne metathesis beyond those involving the traditional alkylidyne complex may exist. Due to the vast number of reactive materials present in these systems, the actual active species and its reaction pathway is still unknown. Additional limitations of this system include intolerance toward thiophenes and secondary amides.

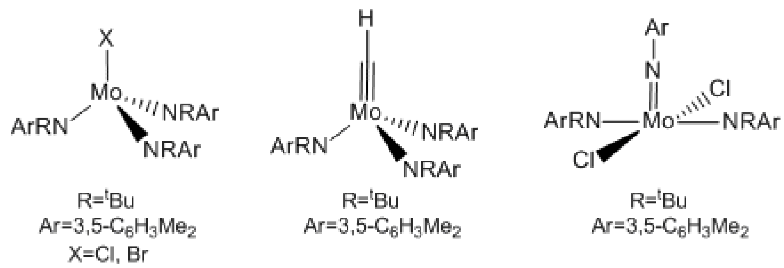
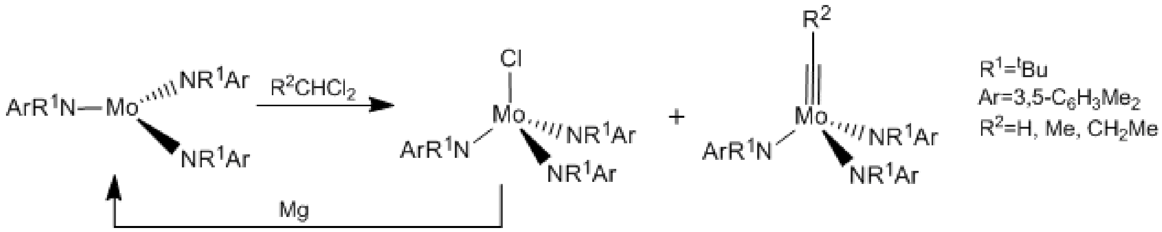


Figure 1.2. Alkyne-metathesis-active species from activation of Mo(N^{t}BuAr)$_3$ with halogens.

1.4.3 Moore

Inspired by Fürstner's *in-situ* alkyne metathesis system, Moore sought to guide the system towards selective alkylidyne complex formation.[35] Activation of Mo(N^{t}BuAr)$_3$ with a geminal dihalide in the presence of magnesium results in the reduction of the molybdenum (IV) monochloride to the original three-coordinate molybdenum complex while leaving the alkylidyne complex unaffected (Scheme 1.5). This "reductive recycle" method results in a high-yielding synthesis of the molybdenum alkylidyne species. Alcoholysis of the alkylidyne complex affords *in-situ* metathesis-active alkylidyne complexes, as the alkylidyne complexes could not be isolated. This leads to some questioning of the actual active species, since the aniline is still present in the reaction mixture. Although an attractive system in terms of broad functional group tolerance, it is extraordinarily sensitive and difficult to manipulate as even magnesium grain size appears to influence the reductive recycle step.



Scheme 1.5. Moore's reductive recycle methodology for the formation of alkylidyne complexes.

Continuing work with EtC≡Mo(N^{t}BuAr)$_3$, Moore elected to coordinate this complex to amorphous silica to avoid bimolecular decomposition.[30] Addition of the alkylidyne complex to a suspension of silica results in successful impregnation of the silica (Figure 1.3). The system does not appear to oligimerize alkyne substrates and displays some potential for recyclability. Although somewhat recyclable, there is a significant reduction in yield during the third cycle, thus indicating that further optimizations of the system are needed to be useful on an industrial scale. An exhaustive survey of the functional group tolerance still needs to be completed.

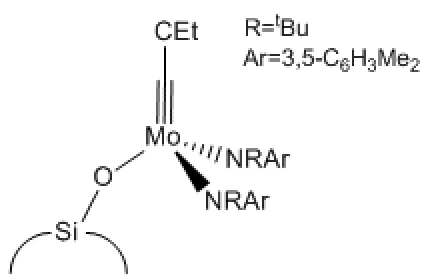


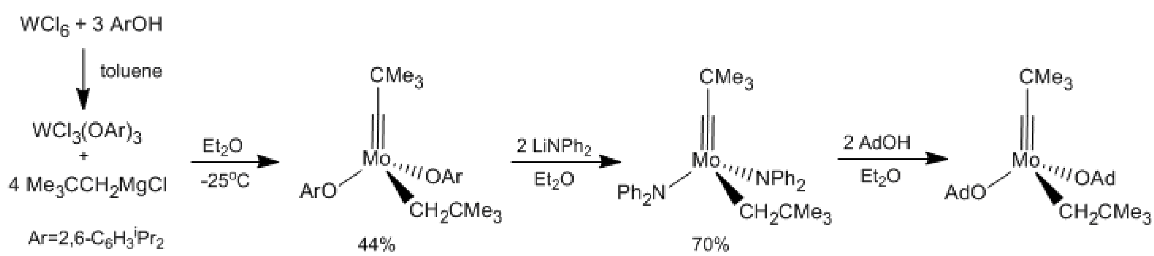
Figure 1.3. Moore's heterogeneous alkyne metathesis catalyst.

Attracted by the absence of alkyne polymerization in the heterogeneous system, Moore sought to extend the silica substituted format to a homogeneous system.[36]

Substitution of $EtC{\equiv}Mo(N^tBuAr)_3$ was achieved on incompletely condensed polyhedral oligomeric silsesquioxane (POSS). Several different substituted POSS's were examined; alkyne metathesis activity varied. Bulkier POSS's precluded alkyne polymerization, while multidentate POSS's did not. Although functional group tolerance has not been surveyed, this system can be applied in the synthesis of large macrocyles.[36]

1.4.4 Schrock

Recent developments within Schrock's group have focused on creating relatively "direct" routes to alkylidyne complexes from simple tungsten-containing precursors.[37] As outlined in Scheme 1.6, treatment of WCl_6 with ArOH (Ar = 2,6-diisopropylphenoxide) affords $W(OAr)_3Cl_3$. Addition of 4 equivalents of $MeCCH_2MgCl$ to $W(OAr)_3Cl_3$ yields readily isolable $Me_3CC{\equiv}W(OAr)_2CH_2CMe_3$. Further manipulation of this neopentylidyne complex via addition of $LiNPh_2{\bullet}Et_2O$ followed by alcoholysis results in the formation of $Me_3CC{\equiv}W(OR)_2CH_2CMe_3$.



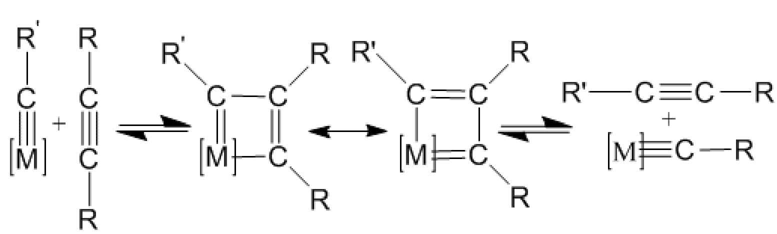
Scheme 1.6. Schrock's synthesis of alkyl-aryloxide alkylidyne complexes.

Schrock noted that Ar group identity is important for alkyne metathesis activity, as adamantoxide- and 2,6-diisopropylphenoxide-ligated alkylidyne complexes have different catalyst resting states. The former consists of a propylidyne complex in the presence of 3-hexyne, whereas the latter exists as primarily a metalacycle. The adamantoxide-substituted complex achieves an equilibrium mixture of alkynes in the presence of 50 equivalents of 3-heptyne within 3 h at 23 °C. In comparison, the analogous 2,6-diisopropylphenoxide derivative reaches equilibrium at a much slower rate, requiring over 24 h at 22 °C and produces a large amount of poly(alkyne). This suggests that the sluggish break-up of the stable tunsgtacyclobutadiene intermediate hinders metathesis and possibly favors alkyne polymerization. Currently entry into this system has only worked when Ar = 2,6-diisopropylphenoxide in $W(OAr)_3Cl_3$. Extension to 2,6-dimethylphenoxide does not produce an isolable neopentylidyne compound. The functional group compatibility of these alkylidyne complexes has not yet been investigated.

1.5 Mechanism

1.5.1 Alkyne Metathesis

In 1975, Katz proposed the accepted mechanism of alkyne metathesis involving the [2+2] cycloaddition of a metal alkylidyne complex and an alkyne to form a metalacyclobutadiene intermediate followed by cycloreversion to produce a new alkyne and metal alkylidyne complex (Scheme 1.7).[38]



Scheme 1.7. Accepted mechanism of alkyne metathesis.

Two different intermediates, a metalatetrahedrane and a metalacyclobutadiene (Figure 1.4), have been proposed for alkyne metathesis. Theoretical calculations on a model system consisting of HC≡$MoCl_3$ and 2-butyne reveal that the pathway leading to the metalacyclobutadiene intermediate has a lower barrier to formation and is fully symmetry allowed, unlike the metalatetrahedrane intermediate.[39] Experimental data support these conclusions as several isolated metalatetrahedrane complexes do not display alkyne metathesis activity.[40] In contrast, some isolated tungstacyclobutadiene species are active in alkyne metathesis.[24]

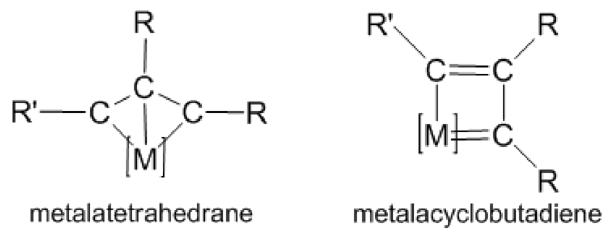
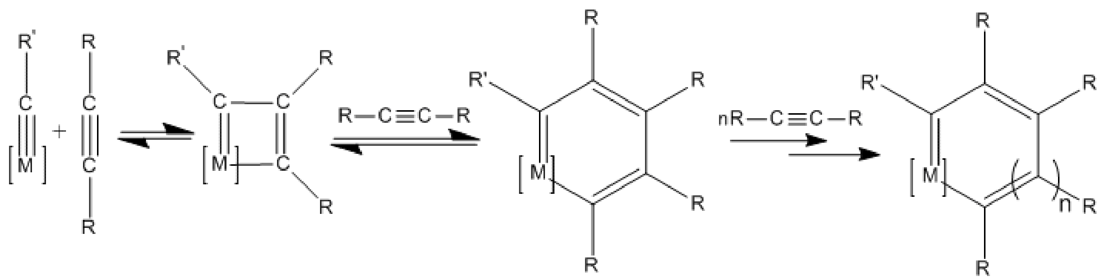


Figure 1.4. Plausible intermediates of alkyne metathesis.

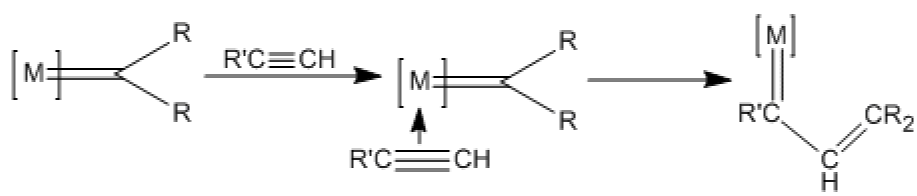
1.5.2 Alkyne Polymerization

A common competing reaction with alkyne metathesis is alkyne polymerization. Unlike alkyne metathesis, the mechanism of alkyne polymerization is currently under debate. One postulated method of alkyne polymerization involves a ring expansion mechanism (Scheme 1.8).[35]



Scheme 1.8. Proposed ring expansion mechanism of alkyne polymerization.

This entails the formation of a metalacyclobutadiene that undergoes alkyne insertion instead of cycloreversion. Support for this mechanism is found in the "molybdenabenzene"-like complexes that have been isolated from the reaction between $Me_3CC{\equiv}W(OR)_3$ and terminal alkynes.[41] A second mechanism requires the presence of trace alkylidenes in the reaction mixture, which also polymerize alkynes (Scheme 1.9).[25,41,42] A third mechanism involves a bimolecular decomposition. This type of mechanism is supported through Moore's work with heterogeneous alkyne metathesis catalysts, which would prevent a bimolecular interaction. In the heterogeneous alkyne metathesis system, alkyne polymerization is not observed, which is contrary to some of the homogeneous system.[30]



Scheme 1.9. Alkylidene-based alkyne polymerization.

1.6 Electronic Influences

Alkyne metathesis can be described as an electrophilic attack of the metal alkylidyne center on an alkyne. Both metal and alkoxide selection are found to influence the catalyst resting state and rate of alkyne metathesis. For instance, the increased propensity of molybdenacyclobutadiene complexes to release acetylene relative to tungstacylcobutadienes is likely due to the reduced d-orbital spatial extent of molybdenum with respect to tungsten.[23,29] This accounts for the inability to isolate an alkyne-metathesis-active molybdenum cyclobutadiene complex; the alkylidyne complexes are more stable than their cyclobutadiene counterparts. As detailed in Section 1.3.1, the use of increasingly fluorinated alkoxides results in an overall increase in alkyne metathesis rate as the metal center becomes increasingly Lewis acidic.

A recent study by Lin sought to explain the influence of metal center and alkoxide identity on alkyne metathesis activity from a theoretical perspective.[43] Four model catalyst systems and their interaction with 2-butyne were investigated, including $MeC{\equiv}W(OMe)_3$, $MeC{\equiv}W(NMe_2)_3$, $MeC{\equiv}Mo(OMe)_3$ and $MeC{\equiv}W(OCH_2F)_3$. These models were selected to mimic known alkylidyne complexes $Me_3CC{\equiv}W(OCMe_3)_3$, $Me_3CC{\equiv}W(NMe_2)_3$, $Me_3CC{\equiv}Mo(OCMe_3)_3$ and $Me_3CC{\equiv}W(OCCF_3Me_2)_3$.[23,44] The free energy barriers for each catalyst to metalacycle formation are summarized in Figure 1.5. The source of these energy differences was probed via energy-decomposition studies. This study looked at energy changes associated with binding of the alkyne and deformations of the alkylidyne and alkyne required for metalacyclobutadiene formation.

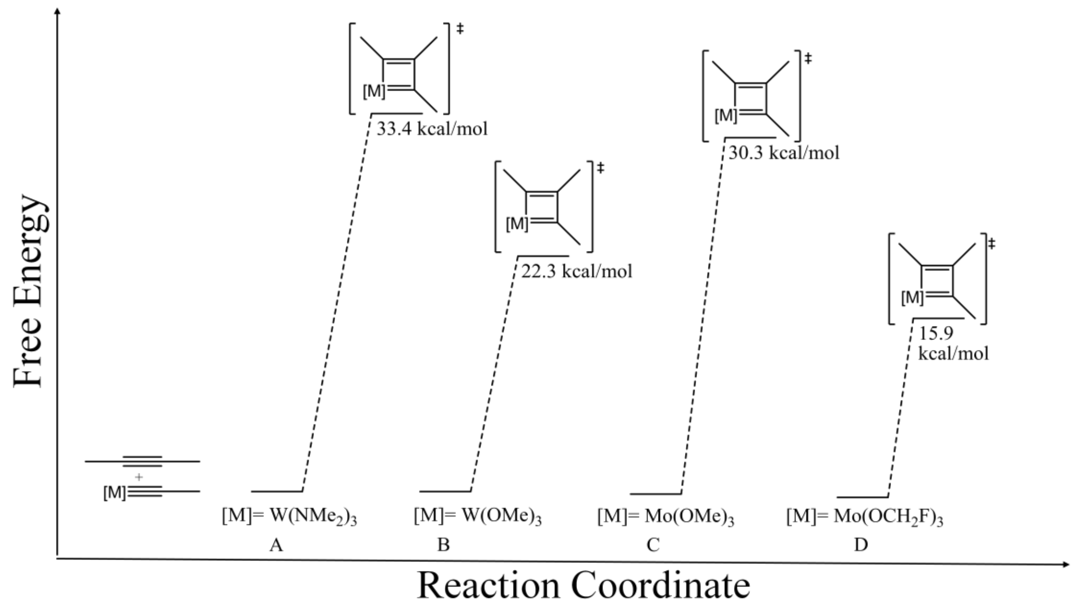


Figure 1.5. Relative free energy plots of metal alkylidyne and transition states.

As reported by Lin (Figure 1.5),[43] the energetic barrier for metalacycle formation is greater for molybdenum than for tungsten when the same ancillary ligand set is present (B,C). Energy decomposition studies indicate that this is likely due to the increased distortion of the starting materials required for metalacyle formation with the molybdenum-based systems in comparison to the corresponding tungsten systems. This can be accounted for through the smaller d-orbital spatial extent of molybdenum with respect to tungsten. This would require the alkyne to approach the alkylidyne moiety much more closely with molybdenum than tungsten, necessitating larger starting material deformations. As a result, the main bonding interaction between the metal alkylidyne complex and the alkyne is between the LUMO of the alkylidyne fragment and the HOMO of the alkyne fragment (Figure 1.6).[39,43] These theoretical calculations agree with experimental data as $Me_3CC{\equiv}W(OCMe_3)_3$ is alkyne metathesis active at room temperature whereas $Me_3CC{\equiv}Mo(OCMe_3)_3$ is not.[23]

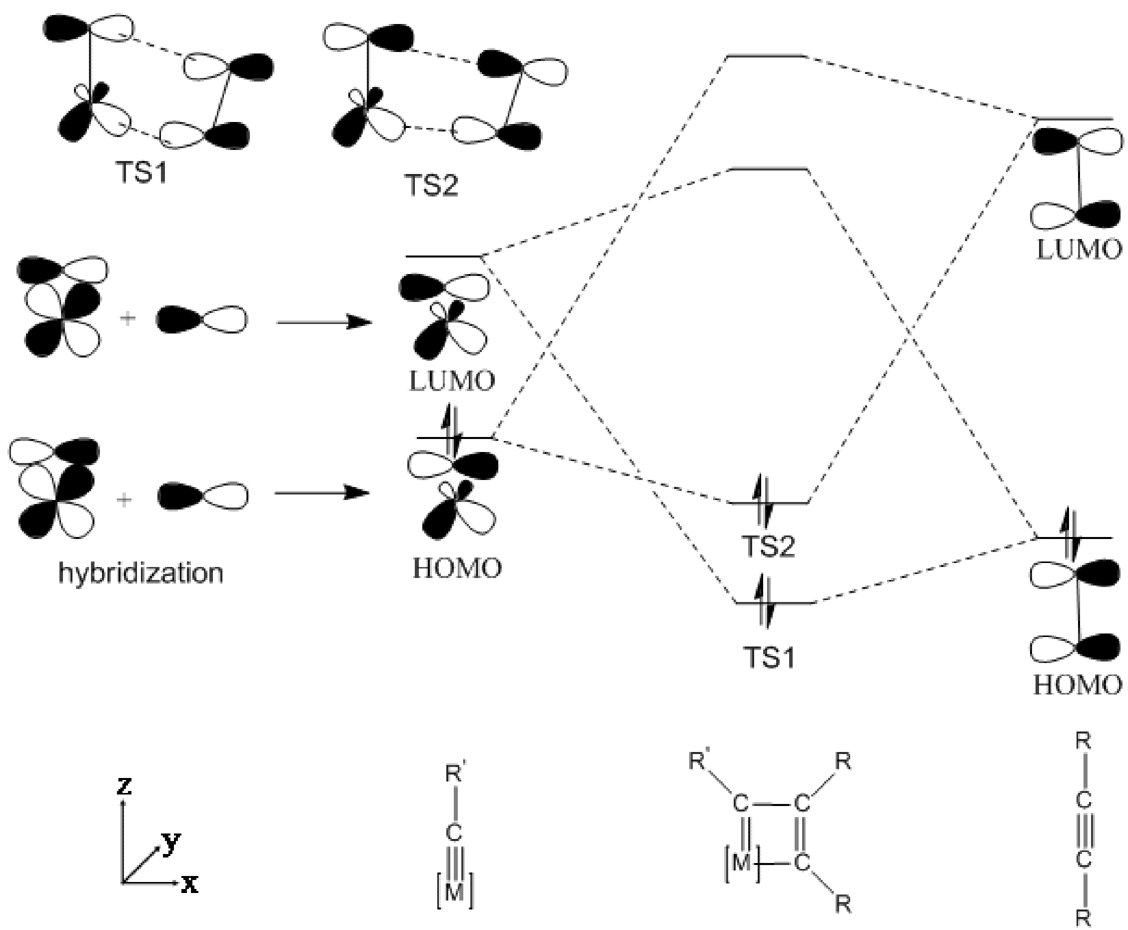


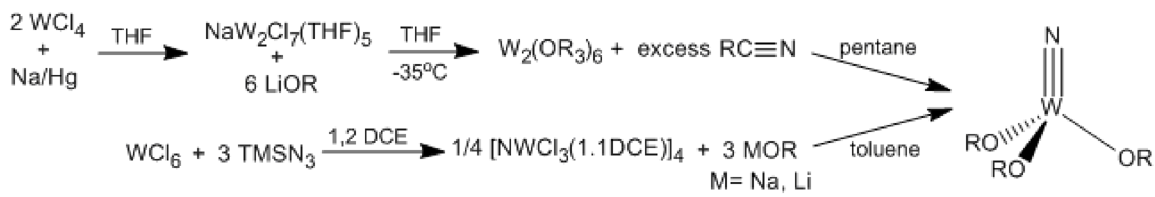
Figure 1.6. Electronic interactions in metalacyclobutadiene formation.

Comparing ancillary ligand sets for a given metal alkylidyne species, moving to more electron donating ancillary ligands increases the barrier to metalacycle formation (Figure 1.5). The energy barrier decomposition analysis largely attributes this to the binding energy of the alkyne, as the difference in the energies associated with deformation of the alkyne and alkylidyne complex is minimal. Experimental data further support these studies; $Me_3CC{\equiv}W(NMe_2)_3$ is almost inactive while $Me_3CC{\equiv}W(OCMe_3)_3$ is a very active alkyne metathesis catalyst.[23,44]

1.7 Tungsten and Molybdenum Nitride Species

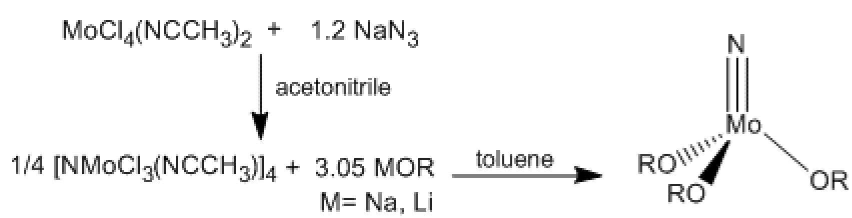
1.7.1 Synthesis

Two major methods can be used to access tungsten nitride complexes. Triple-bond scission of $W_2(OCMe_3)_6$ with nitriles affords RC≡W$(OCMe_3)_3$ and N≡W$(OCMe_3)_3$.[27] Addition of excess nitrile leads to solely tungsten nitride complex formation as the RC≡W$(OCMe_3)_3$ readily converts to the nitride complex.[27] Alternatively, treatment of WCl_6 with trimethylsilylazide yields [N≡$WCl_3]_4$•1.1DCE.[45] Then salt metathesis of [N≡$WCl_3]_4$•1.1DCE with alkoxide salts yields N≡W$(OR)_3$ complexes (Scheme 1.10).[27]



Scheme 1.10. General syntheses of tungsten nitride complexes.

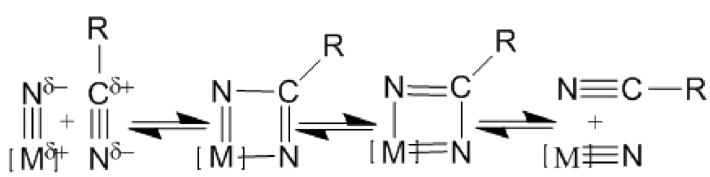
Simple methods for synthesizing molybdenum nitride complexes were developed by Chisholm.[46] Treatment of $MoCl_4(THF)_2$ or $MoCl_4(NCMe)_2$ with azide sources including NaN_3 and trimethsilylazide leads to the formation of [N≡$MoCl_3]_4$. Addition of alkoxide salts to [N≡$MoCl_3]_4$ affords the desired N≡Mo$(OR)_3$ complexes (Scheme 1.11). The actual structures of the metal nitride complexes vary depending on alkoxide identity and the presence of solvent adducts.[47]



Scheme 1.11. General synthesis of molybdenum (VI) nitride complexes.

1.7.2 Reactivity

Some molybdenum and tungsten nitride species are active for triple bond metathesis, undergoing degenerate N-atom exchange with nitriles (Scheme 1.12).[48,49] The ability of the metal nitride complex to exchange nitride moieties is dependent on the Lewis acidity of the metal center, which can be tuned by ligand selection as described in Section 1.5.[46] For instance, at room temperature $N{\equiv}Mo(OCMe_3)_3$ is inactive towards degenerate metathesis while $N{\equiv}Mo(OC(CF_3)_2Me)_3$ is active. The degenerate exchange is favored over dinitrogen production due to the polarization of the metal-nitride moiety. The metal center carries a positive partial charge and the nitrogen carries a partial negative charge.[46] As the nitrile approaches, the negatively charged nitrogen of the nitrile aligns with the positively charged metal center, resulting in degenerate N-atom exchange. (Scheme 1.12)

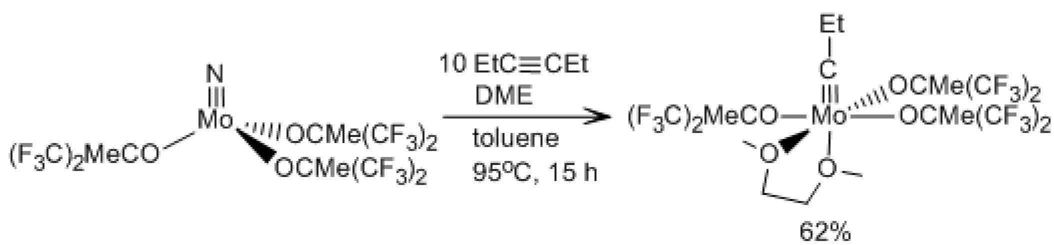


Scheme 1.12. Mechanism of degenerate N-atom exchange.

Another example of triple bond metathesis with a molybdenum nitride complex can be found in Chisholm's interchange reaction of $N{\equiv}Mo(OCMe_3)_3$ and $(Me_3CO)_3W{\equiv}W(OCMe_3)_3$.[50] This reaction proceeds rapidly at room temperature to produce $N{\equiv}W(OCMe_3)_3$ and $(Me_3CO)_3W{\equiv}Mo(OCMe_3)_3$. In this case, favorable reduction-oxidation reaction of the metal centers drive the reaction: $Mo^{6+} + W^{3+} \rightarrow Mo^{3+} + W^{6+}$.

1.8 Converting Nitride and Alkylidyne Species

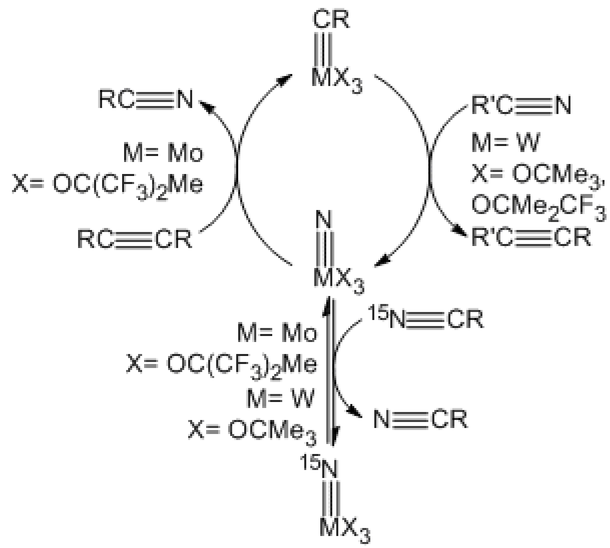
In 2006, our research group reported the first conversions of molybdenum nitride complexes to molybdenum propylidyne species via metathesis with 3-hexyne.[51] This *irreversible* conversion works well with N≡Mo(OC(CF$_3$)$_2$Me)$_3$ and N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) at 95 °C. Addition of DME to the reaction mixtures permits isolation of EtC≡Mo(OC(CF$_3$)$_2$Me)$_3$(DME) on multi-gram scales (Scheme 1.13). Interestingly, only the reverse conversion has been shown with tungsten alkylidyne complexes.[47,52,53] This is a simple method for accessing alkylidyne complexes from readily synthesized molybdenum nitride species.



Scheme 1.13. Formation of a molybdenum alkylidyne complex from a nitride complex.

Much of my work focuses on broadening the utility of known interconversions of alkylidyne and nitride complexes (Scheme 1.14) and developing new interconversions, including: (1) Extending current and development of new methodologies for formation of alkylidyne complexes; (2) altering reaction conditions to encourage formation of alkylidyne complexes from nitride complexes with more electron donating alkoxides; (3) developing a triple-bond metathesis system that *reversibly* converts nitride and alkylidyne moieties. Accordingly, Chapter 2 details the development of nitrile-alkyne cross-metathesis (NACM). Chapter 3 includes mechanistic investigations and applications of NACM. Chapter 4 discusses the interconversion of Mo$_2$(OR)$_6$ and RC≡Mo(OR)$_3$

complexes. Chapter 5 introduces alkyne metathesis assisted by Lewis acids with N≡Mo(OR)$_3$ and $Mo_2(OR)_6$ complexes.



Scheme 1.14. Known interconversions of alkylidyne and nitride complexes.

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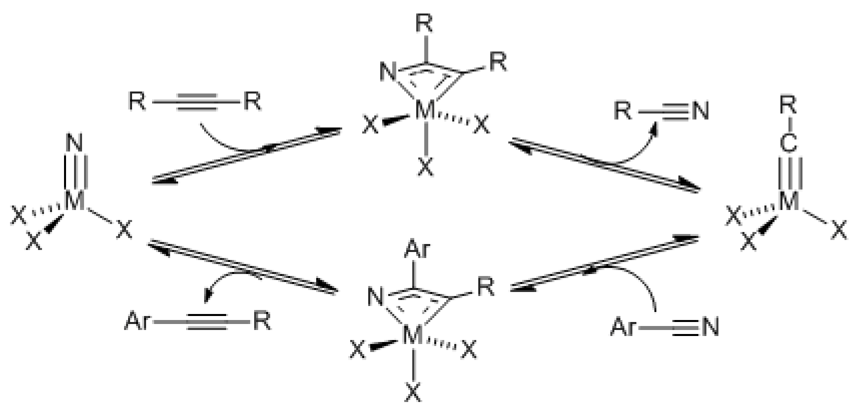
Chapter Two:

Development of Nitrile-Alkyne Cross-Metathesis

2.1 Introduction

As discussed in Chapter 1, the major disadvantage of alkyne metathesis is the need for pre-existing alkyne moieties in both substrates. Extension of metathesis to include nitriles would avoid the necessity of an alkyne moiety in one of the substrates. Such a system, nitrile-alkyne cross-metathesis (NACM), would require the reversible conversion of metal nitride and alkylidyne species as outlined in Scheme 2.1.



Scheme 2.1. Reversible conversion of nitride and alkylidyne moieties.

Since molybdenum and tungsten-based alkylidyne complexes have clearly demonstrated triple-bond metathesis activity, these group 6 metal centers are optimal initial choices for catalyst development. As Robyn Gdula in our lab demonstrated, selected molybdenum nitride complexes *irreversibly* convert to their alkylidyne counterparts.[1] Combining this with higher barriers to metalacycle formation with molybdenum relative to tungsten,[2,3] design and development was centered initially on tungsten-based complexes.

Tungsten alkylidyne complexes with *t*-butoxide ligands have already been demonstrated to *completely* convert to their nitride complexes via metathesis with nitriles.[4] This indicates that there is likely a thermodynamic preference for the nitride complex over that of the alkylidyne complex with these ancillary ligands. Since the nitride moiety is more oxidizing than the alkylidyne moiety, the relative stability of the complexes should be shifted by decreasing the electron donating ability of the ancillary ligands, i.e. increasing the fluorination of the alkoxides (Figure 2.1).[5]

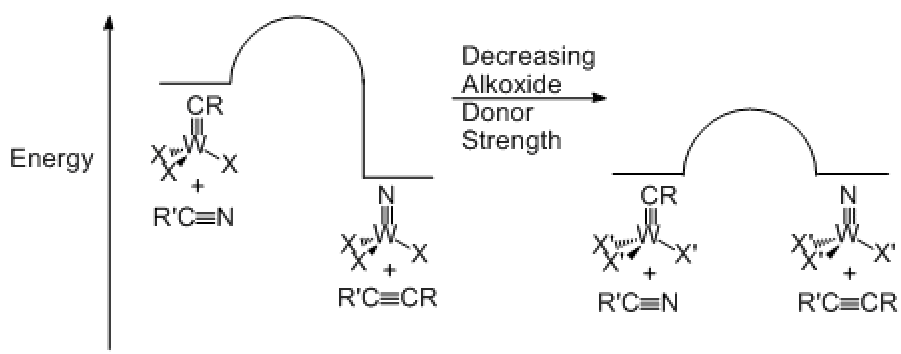


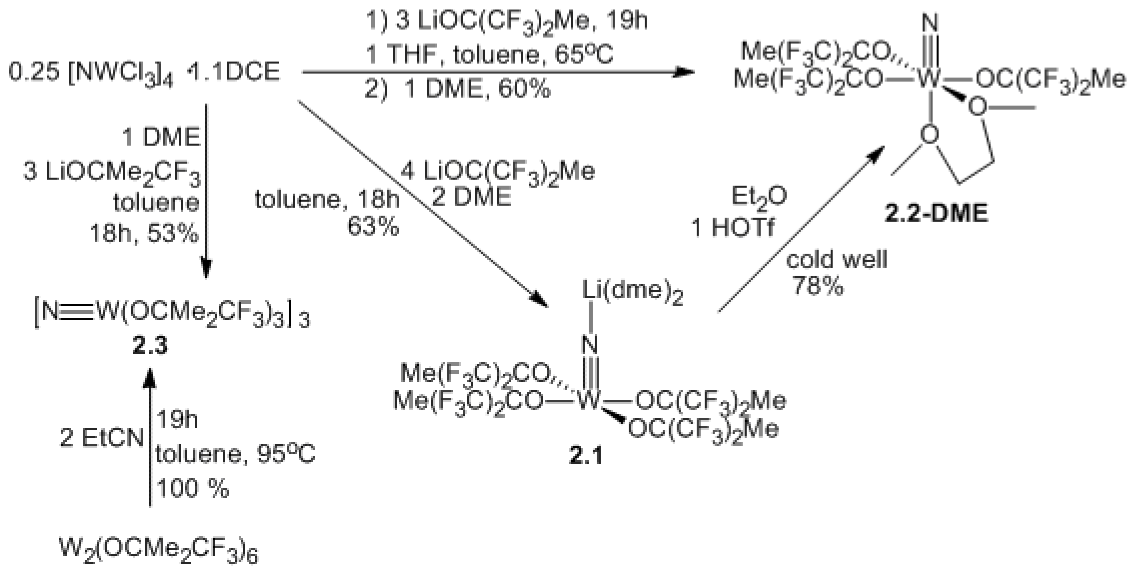
Figure 2.1. Influence of alkoxide donating strength on relative stability of nitride and alkylidyne complexes.

2.2 Synthesis of Tungsten Nitride Complexes

$N{\equiv}W(OR)_3$ complexes (R=CMe_2CF_3 and $CMe(CF_3)_2$) were selected as candidates for development of catalysts for NACM. Both alkoxides were selected in order to examine the influence that the increased fluorination has on the relative stability of the tungsten nitride and alkylidyne species. Furthermore, when R=$CMe(CF_3)_2$ enhanced rates of metathesis relative to R=CMe_2CF_3 were anticipated as a result of known electronic trends in alkyne metathesis.[6]

2.2.1 Synthesis of [Li(DME)$_2$][N≡W(OC(CF_3)$_2$Me)$_4$] and N≡W(OC(CF_3)$_2$Me)$_3$(DME)

[Li(DME)$_2$][N≡W(OC(CF_3)$_2$Me)$_4$] (**2.1**) was prepared in a 63% yield via salt metathesis of (N≡WCl_3)$_4$•1.1DCE with 16 equivalents of LiOCMe(CF_3)$_2$ in the presence of 8 equivalents of DME in toluene at room temperature (Scheme 2.2). The neutral complex N≡W(OC(CF_3)$_2$Me)$_3$(DME) (**2.2-DME**) was formed via treatment of **2.1** with trifluoromethanesulfonic acid (HOTf) in just-thawed Et_2O. This reaction could be successfully completed with only ≤500 mg of **2.1**; further scaling led to decomposition and unreliability. Attempted direct synthesis of **2.2-DME** via salt elimination with 12 equivalents of LiOCMe(CF_3)$_2$ resulted in inseparable mixtures of **2.1** and **2.2-DME**. Alternatively, preliminary formation of a THF adduct at 65 °C followed by filtration of the reaction mixture and subsequent treatment of the filtrate with DME yielded solely **2.2-DME** (Scheme 2.2). Attempted isolation of the THF adduct, which initially is a bis-THF adduct that upon attempted workup loses 1 equivalent of THF, was unsuccessful due to decomposition of the material.



Scheme 2.2. Syntheses of tungsten nitride complexes.

Colorless crystals of **2.1** and **2.2-DME** can be isolated from Et_2O/pentane at -35 °C. Single crystal X-ray diffraction indicates that both **2.1** and **2.2-DME** are monomeric in the solid state. A thermal ellipsoid plot (Figure 2.2) of **2.2-DME** reveals a short W≡N bond length of 1.680 Å, consistent with other known terminal tungsten nitride complexes.[7] An approximately octahedral coordination is present, with the O atom of the DME ligand binding trans to the nitride and the other trans to the alkoxide. The large trans influence of the nitride ligand versus that of the alkoxide ligand is evident in the substantially elongated W-O bond (2.483 Å) of DME bound trans to the nitride.[8]

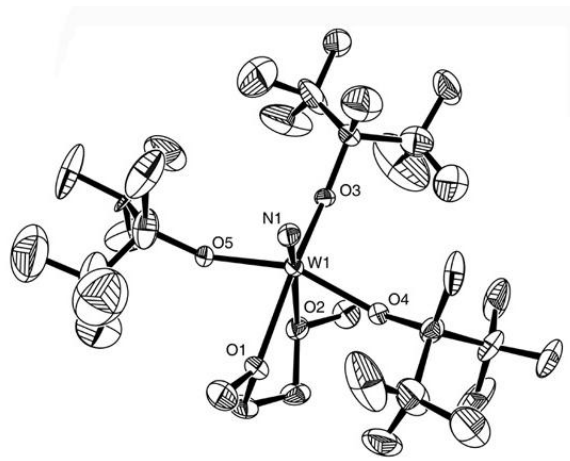


Figure 2.2. 50% thermal ellipsoid plot of **2.2-DME**.

Single crystal X-ray diffraction reveals four crystallographically independent molecules in each asymmetrical unit of **2.1**. The thermal ellipsoid plot (Figure 2.3) indicates that lithium is directly bonded to the nitride ligand with two DME molecules coordinated to lithium. Selected bond distances and bond angles are reported in Table 2.1 for both **2.1** and **2.2-DME**.

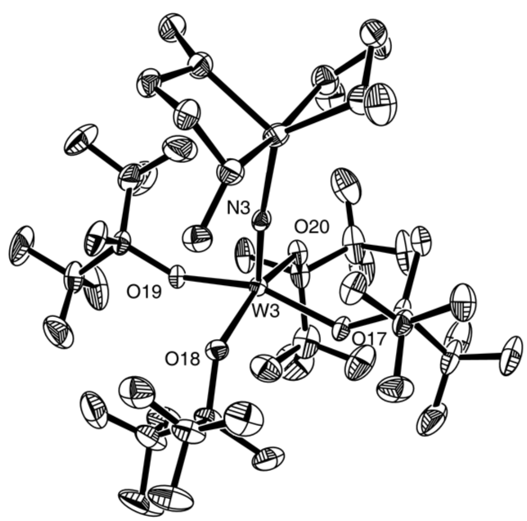


Figure 2.3. 50% thermal ellipsoid plot of **2.1**.

Table 2.1. Selected bond distances and bond angles of **2.1** and **2.2-DME**. (Complete data for single crystal XRD experiments can be found in Appendices 1 and 2)

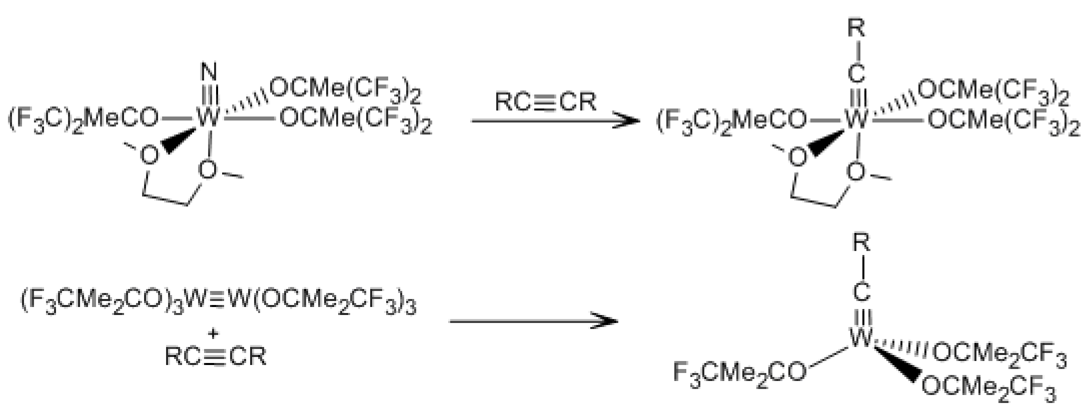
Complex **2.2-DME**		Complex **2.1**	
	Bond distances (Å)		
W-N	1.680(5)	W-N	1.672(1)
W-O(3)	1.906(3)	W-O(17)	1.9703(10)
W-O(5)	1.954(3)	W-O(18)	1.9569(10)
W-O(4)	1.949(3)	W-O(19)	1.9665(10)
W-O(1)	2.192(4)	W-O(20)	1.9640(10)
W-O(2) *trans to nitride*	2.483(4)	N-Li	2.063(3)
	Bond Angles (deg)		
N-W-O(3)	105.20(14)	N-W-O(17)	102.23(5)
N-W-O(5)	102.00(14)	N-W-O(18)	100.17(5)
N-W-O(4)	100.70(14)	N-W-O(19)	102.18(5)
N-W-O(1)	97.85(14)	N-W-O(20)	100.31(5)
O(3)-W-O(5)	93.21(13)	O(18)-W-O(17)	87.81(4)
O(3)-W-O(4)	94.92(12)	O(18)-W-O(19)	88.10(4)
O(1)-W-O(4)	81.37(12)	O(20)-W-O(19)	87.96(4)
O(1)-W-O(5)	81.39(12)	O(20)-W-O(17)	87.53(4)
		W-N-Li	173.60(10)

2.2.2 Synthesis of [N≡W(OCMe$_2$CF$_3$)$_3$]$_3$

Chisholm originally synthesized [N≡W(OCMe$_2$CF$_3$)$_3$]$_3$ (**2.3**) via metathetical tungsten-tungsten triple bond scission of W$_2$(OCMe$_2$CF$_3$)$_6$ by an aryl nitrile at room temperature.[9] Under similar conditions, Schrock reported that scission of the W≡W with acetonitrile does not take place.[10] Analogous results were found with propionitrile; however, upon heating the reaction mixture to 95 °C, complete conversion to the nitride complex occurred. The preferred method for formation of **2.3** in relatively few steps and moderate yields was developed by Gdula. She was able to access **2.3** in 46% yield via treatment of $(N{\equiv}WCl_3)_4{\bullet}1.1DCE$ with 12 equivalents of $LiOCMe_2CF_3$ at room temperature (Scheme 2.2).[11]

2.3 Synthesis of Tungsten Alkylidyne Complexes

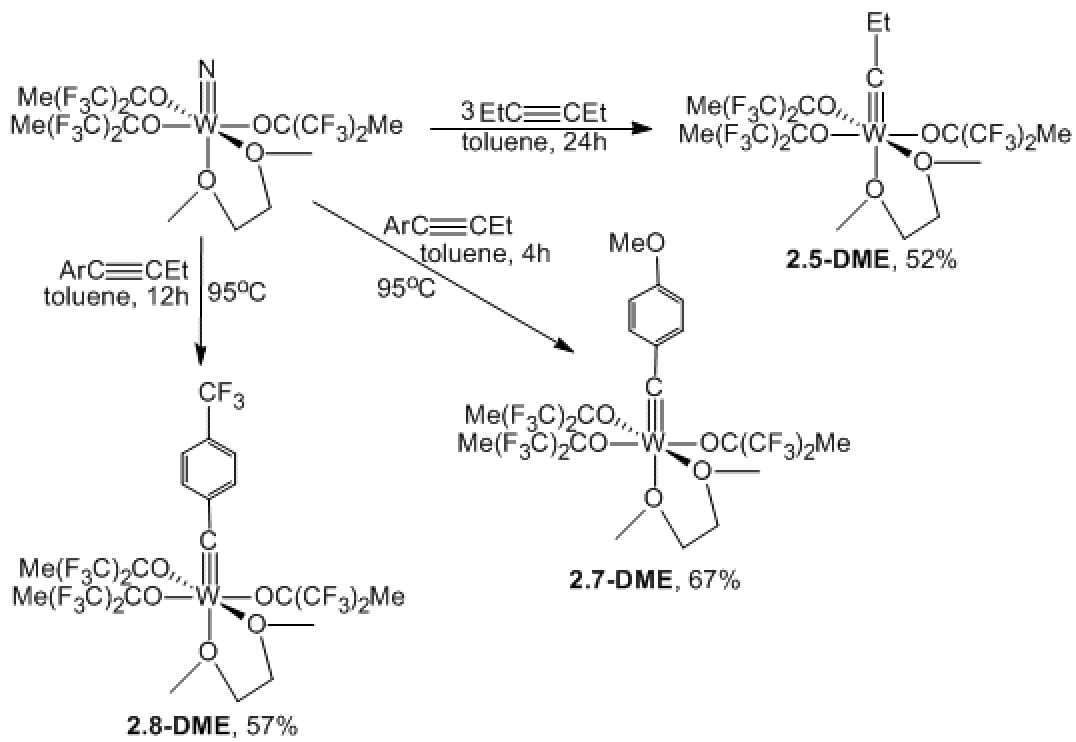
Two different methods (Scheme 2.3) were used for synthesizing the desired metalacycle and propylidyne complexes $(C_3Et_3)W(OC(CF_3)_2Me)_3$ (**2.4**), $EtC{\equiv}W(OC(CF_3)_2Me)_3(DME)$ (**2.5-DME**) and $EtC{\equiv}W(OCMe_2CF_3)_3$ (**2.6**). For $RC{\equiv}W(OCMe(CF_3)_2)_3(DME)$ complexes conversion of the tungsten nitride ligand to an alkylidyne moiety is achieved via metathesis. $RC{\equiv}W(OCMe_2CF_3)_3$ complexes may be accessed via W-W triple bond scission of $W_2(OR)_6$ complexes with internal alkynes. Desired benzylidyne complexes can then be afforded through alkyne metathesis with the alkylidyne complexes or where feasible from direct metathesis with nitride precursors.



Scheme 2.3. General syntheses of tungsten alkylidyne complexes.

2.3.1 Synthesis of Tungsten Alkylidyne Complexes: RC≡W(OC(CF_3)$_2$Me)$_3$(DME)

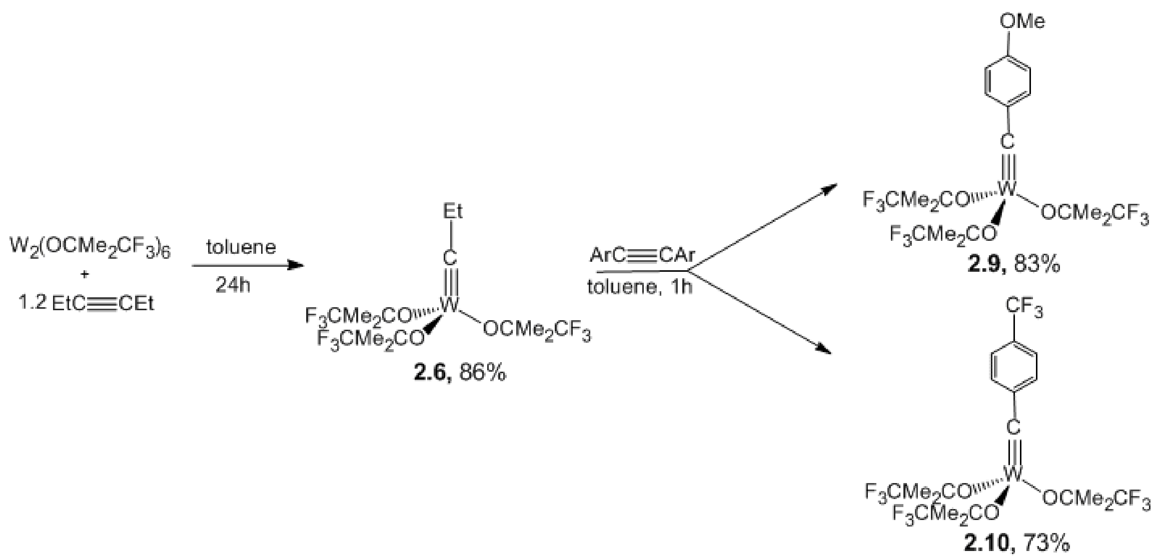
Investigation of the relative stability of **2.2-DME** and the corresponding alkylidyne complexes revealed that alkylidyne complexes are more thermodynamically favored. Successful conversion of **2.2-DME** with 3-hexyne to a mixture of **2.4** (5 mol%) and **2.5-DME** (95 mol%) was achieved at room temperature. This is the first example of the conversion of a tungsten nitride complex to an alkylidyne complex. Several benzylidyne complexes were afforded via treatment of **2.2-DME** with unsymmetrical alkynes [Ar=4-MeOC_6H_4 (**2.7-DME**), 4-$CF_3C_6H_4$ (**2.8-DME**)] as outline in Scheme 2.4. These reactions were completed at elevated temperatures in order to drive the product mixture towards benzylidyne complexes.



Scheme 2.4. Synthesis of tungsten alkylidyne complexes with OR=OCMe(CF_3)$_2$.

2.3.2 Synthesis of Tungsten Alkylidyne Complexes: RC≡W($OCMe_2CF_3$)$_3$(DME)

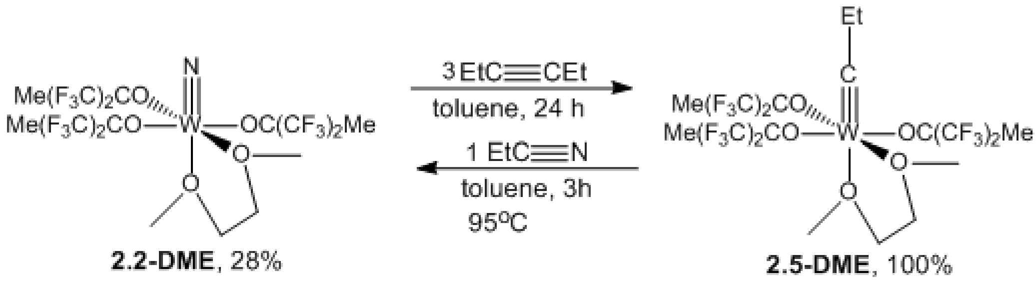
Unlike **2.2-DME**, the relative stability of **2.3** and the corresponding alkylidyne complexes was found to rest towards that of the nitride complex. As a result, alkylidyne complexes could not be readily synthesized from **2.3**. Instead **2.6** was accessed via triple bond scission of $W_2(OCMe_2CF_3)_6$ as previously alluded to by Schrock.[10] Then alkyne metathesis of symmetrical alkynes with **2.6** at room temperature afforded benzylidyne complexes [Ar=4-$MeOC_6H_4$ (**2.9**), 4-$CF_3C_6H_4$ (**2.10**)] in good yields as outlined in Scheme 2.5**.**



Scheme 2.5. Synthesis of tungsten alkylidyne complexes with OR=$OCMe_2CF_3$.

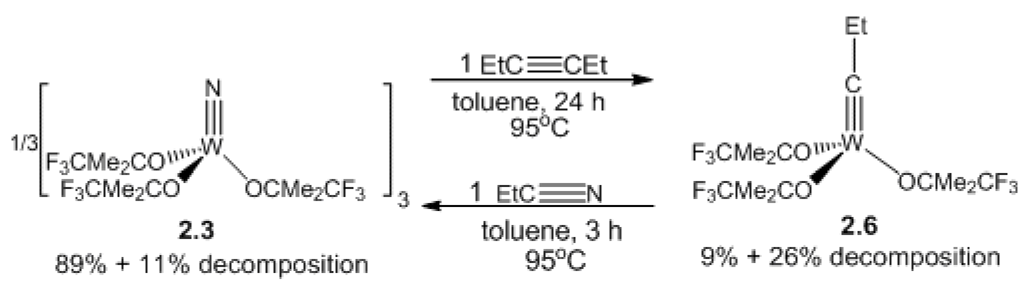
2.4 Reversible Alkylidyne and Nitride Complex Formation

As revealed in the syntheses of the alkylidyne complexes, the choice of alkoxide ligand causes large differences in the relative stabilities of the nitride and alkylidyne complexes. The *ideal* catalyst system for NACM would lead to an equilibrium mixture of nitride and alkylidyne complexes at room temperature. In section 2.3.1 it was noted that **2.2-DME** completely converts to **2.5-DME** at room temperature. Although the reverse reaction does not take place at room temperature, heating **2.5-DME** in the presence of propionitrile at 95 °C results in the formation of the alkylidyne complex in a 28% conversion over 3 hours (Scheme 2.6).



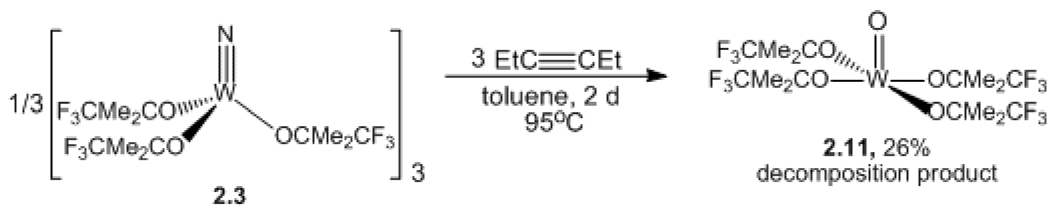
Scheme 2.6. Reversible alkylidyne and nitride complex formation with OR=OCMe(CF_3)$_2$.

Examining the same relationship with **2.3**, it is found that the reaction mixture lies towards the nitride complex (Scheme 2.7). Subjection of **2.3** to 3-hexyne at 95 °C results in 9% conversion to **2.6** along with some decomposition to O=W($OCMe_2CF_3$)$_4$ (**2.11**). The reverse reaction results in complete conversion to **2.3** along with formation of 11 mol% **2.11**.



Scheme 2.7. Reversible formation of nitride and alkylidyne complexes with OR=$OCMe_2CF_3$.

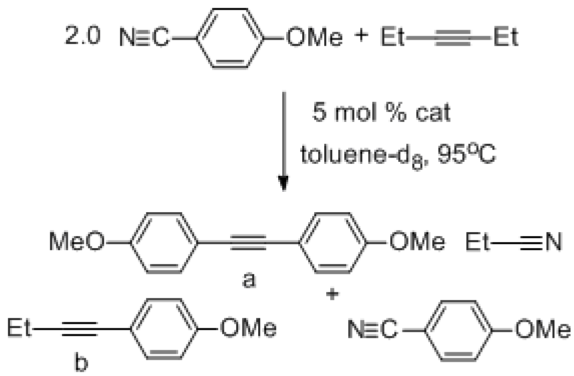
A sample of **2.11** (26%) was isolated from the reaction of **2.3** and 3 equivalents of 3-hexyne after heating at 95 °C for two days (Scheme 2.8). C-O bond scission of the alkoxide ligands, known to afford terminal oxo complexes in other cases, is a plausible method for the formation of **2.11**.[12] Vacuum transfer of an unidentified fluorine-containing volatile material from this reaction mixture provides further evidence of C-O bond scission. The lack of C-O bond scission with **2.2-DME** under the reaction conditions can be accounted for by the increased C-O bond strength in $OCMe(CF_3)_2$ relative to $OCMe_2CF_3$ ligands when bound to the metal center.



Scheme 2.8. Isolation of the decomposition product of **2.3**.

2.5 Initial Discovery of Nitrile-Alkyne Cross-Metathesis

The reversibility tests performed in Section 2.4 revealed the potential for NACM at 95 °C with **2.1**, **2.2-DME,** and **2.3**. Accordingly, NACM with 20 equivalents of anisonitrile and 10 equivalents of 3-hexyne in toluene was examined for each of the catalysts (Scheme 2.9). Catalysis with **2.2-DME** resulted in the formation of 1-(4-methoxyphenyl)-1-butyne (15%) and bis(4-methoxyphenyl)acetylene (77%) along with remaining anisonitrile. Successful production of 1-(4-methoxyphenyl)-1-butyne (19%) and bis(4-methoxyphenyl)acetylene (65%) was achieved with **2.1**. Although **2.3** only showed slight conversion to **2.6** in the reversibility studies, successful NACM was also observed under similar conditions, forming 1-(4-methoxyphenyl)-1-butyne (18%) and bis(4-methoxyphenyl)acetylene (61%).



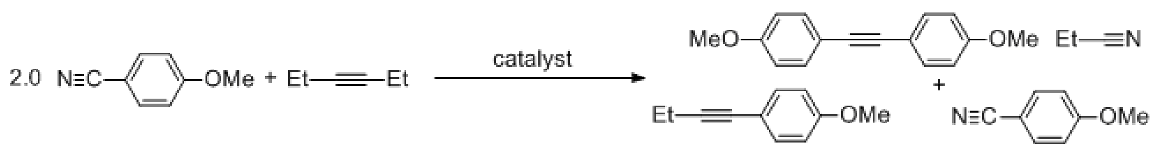
catalyst	yield a (%)	yield b (%)
2.1	65%	19%
2.2-DME	77%	15%
2.3	61%	18%

Scheme 2.9. Successful NACM with **2.1, 2.2-DME**, and **2.3**.

Complex **2.2-DME** is the most active catalyst for NACM in terms of both yield and reaction time, as **2.2-DME** requires only 8 h to reach completion, whereas **2.1** and **2.3** require 10 h and 31 h, respectively. The increased rate of reaction with **2.2-DME** relative to **2.3** is consistent with known trends in alkyne metathesis, where the rate of metathesis decreases as the pK_a of the parent alcohol of the alkoxide ligands increases.[6] Also, since **2.3** exists as a trimer in solution, metathesis could be slowed due to the additional tungsten-nitrogen interactions that are present.[9] The slower metathesis rate with **2.1** in comparison to **2.2-DME** is unsurprising, as more species must dissociate from **2.1** in order to access the active catalyst. It is worth noting that trace amounts of **2.2-DME** and free alkoxide are always present as determined by ^{19}F NMR spectroscopy even in elementally pure samples of **2.1**. This indicates that some ligand dissociation from **2.1** occurs at room temperature in solution.

2.6 Optimization of Nitrile-Alkyne Cross-Metathesis

After the initial discovery of NACM, we sought to optimize the system, based on NACM with anisontrile and 3-hexyne as the test reaction (Scheme 2.10). Reaction solvent, concentration, catalyst and 3-hexyne loadings, and temperature investigations were completed.

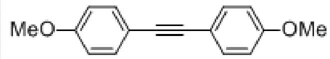
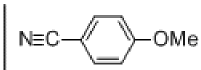


Scheme 2.10. NACM test reaction with anisonitrile and 3-hexyne.

2.6.1 Solvent Studies

A survey of solvents was completed at 95 ºC with 5 mol% **2.2-DME** in the reaction depicted in Scheme 2.10 (Table 2.2). These studies revealed that the highest ratio of symmetrical to unsymmetrical alkyne is observed in toluene. The reaction is also most rapid in toluene. Extension to similar solvents, such as benzene and bromobenzene, results in a decreased ratio of alkyne products and increased alkyne polymerization. Chloroform and 1,2-dichloroethane lead to rapid catalyst destruction, resulting in low conversion of anisontrile to alkyne products. Although reactions in dichloromethane require lower operating temperatures, no significant catalyst decomposition is observed. As in toluene, high conversion of anisontrile is achieved; however, in dichloromethane the selectivity for diaryl alkyne formation is weak. Coordinating solvents such as THF severely hinder metathesis rates.

Table 2.2. Solvent optimization studies with **2.2-DME**.

Solvent (equiv)	Time (h)	 (%)	 (%)	 (%)
toluene	8	81	11	8
bromobenzene	12	64	11	26
benzene	16	55	20	25
dichloromethane	42	46	42	12
1,2-dichloroethane	6	49	20	32
chloroform	2	33	31	36
tetrahydrofuran	62	1	14	85

2.6.2 Concentration Studies

The complete consumption of 3-hexyne under conditions in which some anisonitrile remains suggests that poly(3-hexyne) is forming with all three catalysts. As introduced in Chapter 1, alkyne polymerization and alkyne metathesis are known to compete in some systems.[13] Investigation of the test reaction (Scheme 2.10) at 95 °C in toluene indicates that as the concentration of **2.2-DME** is increased, the rate of metathesis decreases relative to alkyne polymerization (Figure 2.4). A catalyst concentration of 6.0 mM maximizes alkyne metathesis and minimizes alkyne polymerization.

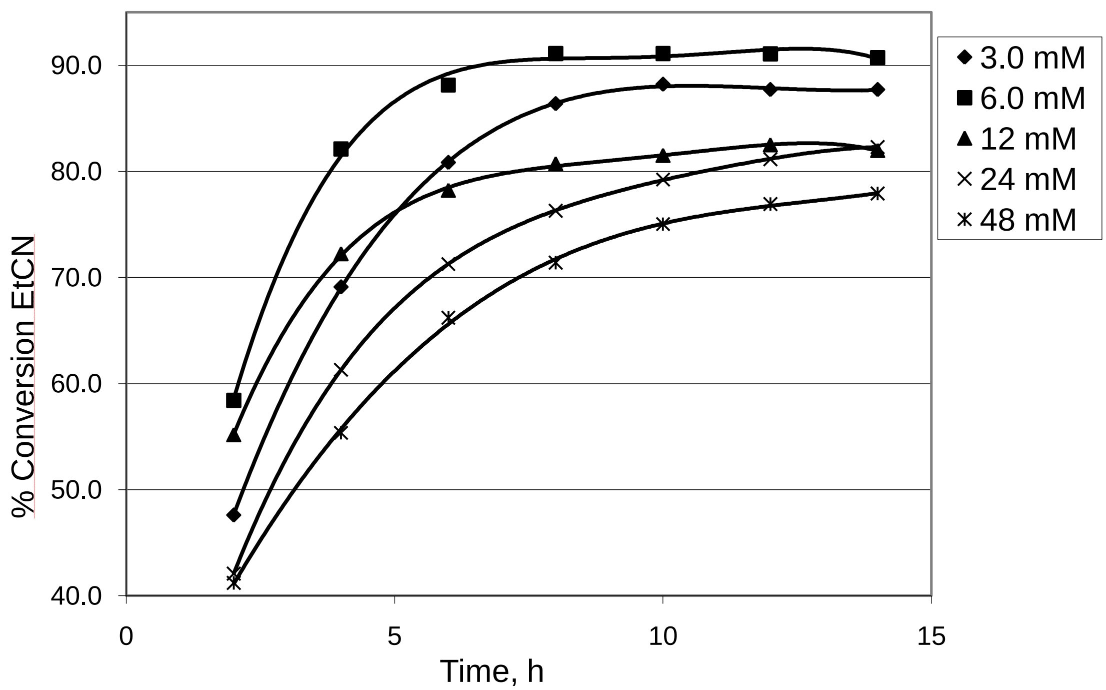


Figure 2.4. Catalyst concentration optimization studies with **2.2-DME**.

Interestingly, the optimum concentration of **2.3** is much higher, namely 34 mM. This contrast in optimal catalyst concentration is likely due to the difference in catalyst resting states (Figure 2.5). As noted in section 1.4.4, a resting state consisting of a metalacycle in preference to an alkylidyne complex appears to favor alkyne polymerization. Therefore, conditions that favor an alkylidyne resting state should somewhat suppress alkyne polymerization. Moreover, a catalyst resting state consisting of the benzylidyne or nitride complex should even further discourage alkyne polymerization. Further investigations of catalyst resting state are pursued in Chapter 3. Reactions were completed in triplicate with both catalysts to verify that the rate differences are significant.

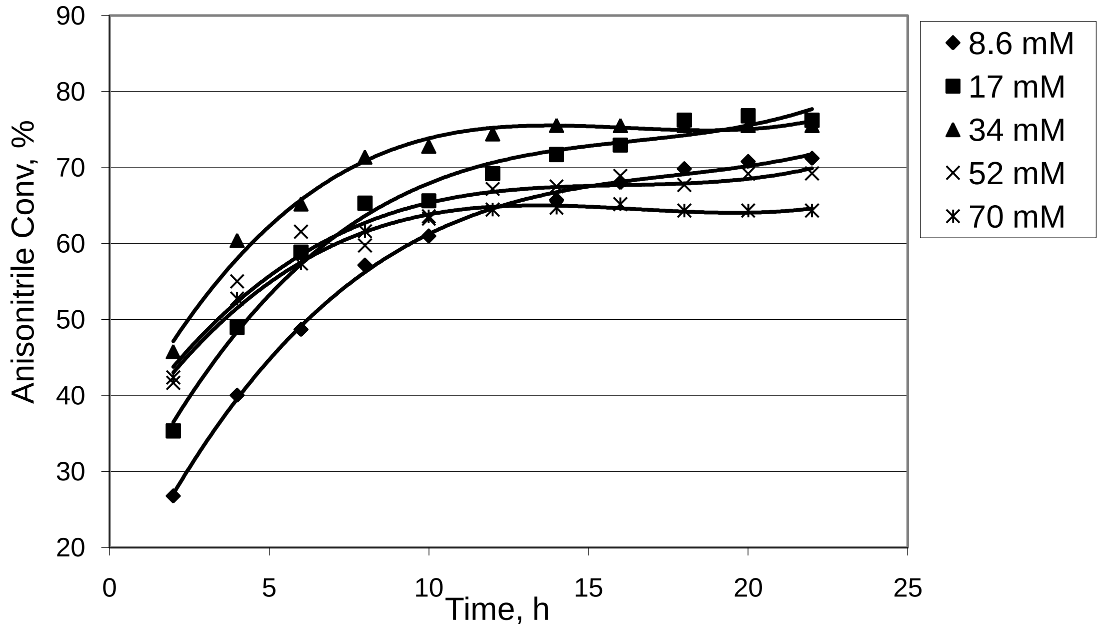
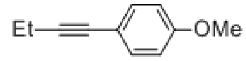
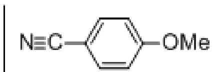


Figure 2.5. Concentration optimization studies with **2.3**.

2.6.3 Catalyst Loading Studies

After establishing optimal solvent and concentration conditions, catalyst loading studies were completed with **2.2-DME** at 95 °C in the presence of 2 equivalents of anisonitrile and 1 equivalent of 3-hexyne (Scheme 2.10). As anticipated, increasing catalyst loading resulted in increased reaction rates with no influence on product yields (Table 2.3).

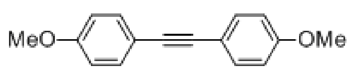
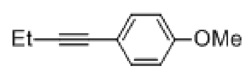
Table 2.3. Catalyst loading studies with **2.2-DME**.

Catalyst Loading (%)	Time (h)	 (%)	 (%)	 (%)
3.75	8	79	12	9
5	8	81	11	7
10	6	77	15	8
20	4	81	12	6

2.6.4 Influence of Temperature

Temperature studies were completed with 5 mol% 6 mM **2.2-DME** in toluene-d_8 with 2 equivalents of anisonitrile and 1 equivalent of 3-hexyne (Scheme 2.10, Table 2.4). As the reaction temperature was decreased, the rate of alkyne polymerization increased relative to alkyne metathesis. This can be seen in the decreased yields of alkyne products at lower temperatures despite complete consumption of 3-hexyne. The reaction at 75 °C was very sluggish, and displayed slowed mass transport due to the large amount of insoluble polymer present. As a result, reaction monitoring was discontinued after 10 h.

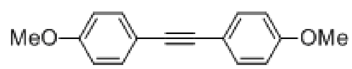
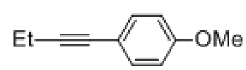
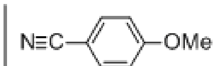
Table 2.4. Temperature studies with **2.2-DME**.

Temp (°C)	Time (h)	 (%)	 (%)	 (%)
95	8	81	11	7
85	20	64	13	23
75	10	23	22	55

2.6.5 Influence of 3-hexyne

Next the influence of the quantity of 3-hexyne on the ratio of alkyne products in the presence of 5 mol% 6 mM **2.2-DME** and anisonitrile in toluene was examined (Scheme 2.9, Table 2.5). An increase in the number of equivalents of 3-hexyne in the system shifts the ratio of reaction products; ultimately, the unsymmetrical alkyne becomes favored. This is consistent with the presence of an alkyne metathesis equilibrium. Although the whole NACM/ACM system is not at equilibrium because of the concurrent alkyne polymerization reaction, a similar trend is expected. The rate of consumption of NCAr also increases in the presence of excess 3-hexyne.

Table 2.5. Influence of 3-hexyne on NACM with **2.2-DME**.

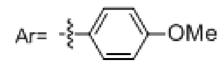
3-hexyne (equiv)	Time (h)	 (%)	 (%)	 (%)
1	8	81	11	7
2	6	48	49	3
3	6	40	55	5

2.6.6 Multivariable Studies

One of the drawbacks of the current NACM catalyst systems is that high temperatures are required. In order to allow the system to function at decreased reaction temperatures, several variables were altered in order to optimize NACM with **2.2-DME** as the catalyst (Scheme 2.10, Table 2.6). For instance, addition of more catalyst (10 mol% **2.2-DME**) and excess 3-hexyne (2 equivalents) drastically improves alkyne formation; only 14 hours are required (Entry 2). As expected, the product ratio of alkynes is shifted towards production of unsymmetrical alkyne. Successful NACM can even be achieved at 65 °C with high catalyst loading and excess 3-hexyne (Entries 4-5).

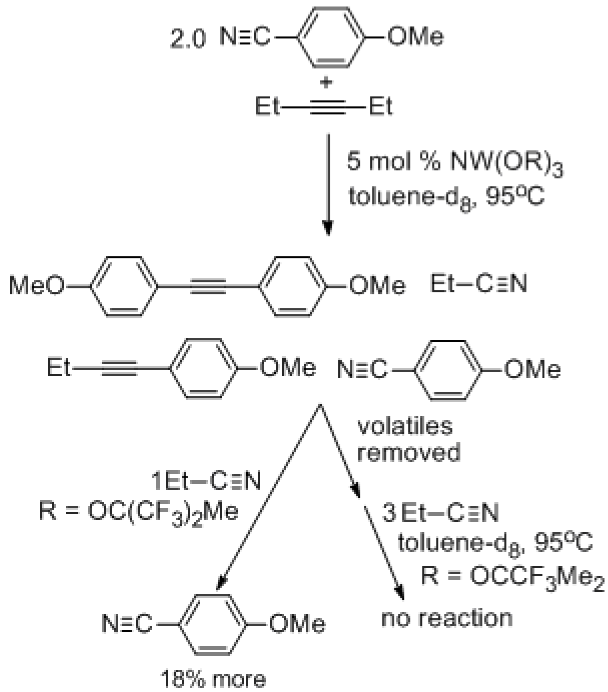
Table 2.6. Multivariable studies of NACM with **2.2-DME**.

Entry	Temp (°C)	3-hexyne (equiv)	**2.2** (mol %)	Time (h)	Ar—≡—Ar (%)	Et—≡—Ar (%)	N≡C–Ar (%)
1	85	2	10	8	28	69	3
2	75	2	10	14	35	57	8
3	65	2	10	69	44	33	23
4	65	4	10	82	28	61	11
5	65	4	20	56	20	64	16



2.7 Catalyst Activity

A comparison of the optimization studies completed with **2.2-DME** and **2.3** reveals significant differences in alkyne product ratios and alkyne polymerization. In order to probe the activity of the catalysts at the end of NACM (after complete consumption of 3-hexyne), an excess of anisonitrile was introduced into the system in order to test whether the product ratio could be shifted (Scheme 2.11). With **2.2-DME**, the reaction mixture was shifted towards that of reactants. In contrast, no back-reaction was observed with **2.3**.



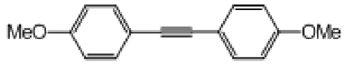
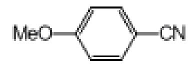
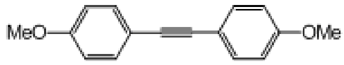
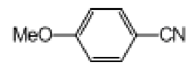
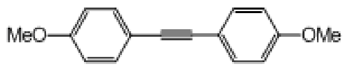
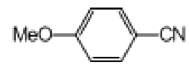
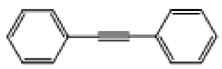
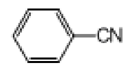
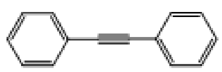
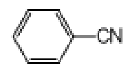
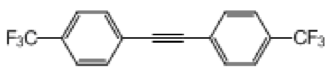
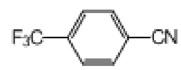
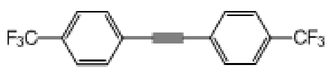
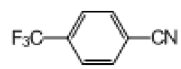
Scheme 2.11. Reversibility studies with **2.2-DME** and **2.3**.

2.8 Nitrile-Alkyne Cross-Metathesis to Afford Nitriles

The studies in Section 2.7 with **2.2-DME** suggest that there is a potential to develop NACM for the synthesis of nitriles from alkynes in cases where the desired nitrile is less readily available than the alkyne. Several aryl alkynes and alkyl nitriles were surveyed for reactivity in the presence of **2.2-DME** (Scheme 2.12) as indicated in Table 2.7.

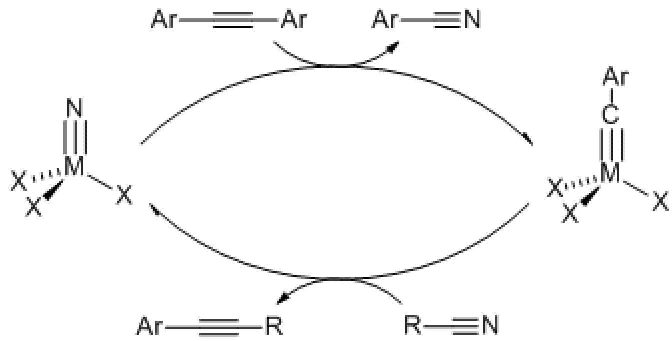
Scheme 2.12. NACM to afford aryl nitriles with **2.2-DME**.

Table 2.7. NACM to afford aryl nitriles from alkyl nitriles.

Entry	Starting Material	Nitrile	Product (% Yield)		Time (hr)
1		EtCN		22	36
2		Cl_3CCN		45	21
3		MeCN		37	19
4		MeCN		10	20
5		Cl_3CCN		35	15
6		MeCN		5	48
7		Cl_3CCN		15	15

From Table 2.7, variations in reactivity as a result of the electronic nature of the alkyne and nitrile were apparent in the studies with diphenylacetylene (entries 4-5) and bis(4-trifluoromethylphenyl)acetylene (entries 6-7). In general, trichloroacetonitrile afforded larger quantities of aryl nitrile than do the other alkyl nitriles. Several other halogenated alkyl nitriles including bromoacetonitrile, dichloroacetonitrile, and chloroacetonirile were surveyed. Unfortunately, these nitrile substrates result in largely catalyst decomposition. Additional system optimization is necessary in order to generate synthetically useful amounts of nitrile-containing products.

The yields of aryl nitrile products in Table 2.7 are somewhat deceptive (Scheme 2.13). The stoichiometric conversion of **2.2-DME** to form a benzylidyne complex, the first step of NACM, would account for 20% formation of aryl nitrile in the reaction mixture. The alkyl nitrile could then react with the benzylidyne complex to regenerate the nitride catalyst and form unsymmetrical alkyne, completing one complete NACM cycle. It is evident from Table 2.7, that only entries 2, 3, and 5, produced yields of aryl nitrile that reflected greater than stoichoimetric conversion of the catalyst. For entries 2 and 5, no evidence of $Cl_3CC{\equiv}CAr$ was found via ^{1}H NMR or mass spectroscopies due to decomposition of the unsymmetrical alkyne under the reaction conditions.



Scheme 2.13. Accounting for ArCN formation with **2.2-DME**.

2.9 Conclusions

Through systematic catalyst design, the first examples of the *reversible* formation of $N{\equiv}W(OR)_3$ and $R'C{\equiv}W(OR)_3$ ($R{=}CMe_2CF_3$ and $CMe(CF_3)_2$) were accessed. A novel method for synthesizing several new alkyne-metathesis-active tungsten alkylidyne complexes from tungsten nitride precursors was developed. By harnessing the *reversibility* of the conversion, the first example of NACM was achieved. This system overcomes constraints of alkyne metathesis, where a pre-existing alkyne moiety must be present in both substrates.

Pre-catalysts **2.1**, **2.2-DME**, and **2.3** serve as sources of $N{\equiv}W(OR)_3$ in NACM. These complexes can be readily accessed in moderate to good yields via salt metathesis of $[N{\equiv}WCl_3]_4{\cdot}1.1DCE$ with the appropriate lithium alkoxide. Complex **2.2-DME** serves as an excellent precursor to alkylidyne formation via metathesis with the desired

R′C≡CR′ or R′C≡CEt moiety. In contrast with **2.2-DME**, **2.3** does not readily undergo conversion to alkylidyne complexes in synthetically useful yields. Therefore, R'C≡W($OCMe_2CF_3$)$_3$ was obtained via triple bond scission of $W_2(OR)_6$ with 3-hexyne. The ethyl unit could then be displaced through alkyne metathesis with ArC≡CAr to install benzylidyne moieties.

Catalyst comparison studies with NACM revealed relative catalyst activities of **2.2-DME** > **2.1** > **2.3**. This difference in reactivity is due to the relative alkoxide donating strength and the number of species that must dissociate to access the active catalyst. Additionally, **2.2-DME** was found to maximize alkyne metathesis and minimize alkyne polymerization at a concentration of 6 mM, while the optimal concentration of **2.3** was 34 mM. The source of varying ratios of alkyne products and the relative rates of alkyne metathesis and alkyne polymerization is likely the catalyst resting state, which will be addressed in Chapter 3.

Further catalyst optimization studies found that toluene is the preferred medium for NACM. Although reaction temperatures of 95 °C result in high product yields in short time periods, the slower reaction rate at decreased temperatures can be countered by introducing excess 3-hexyne and/or increasing the catalyst loading. One drawback of introducing excess 3-hexyne into the system is that the product ratio is shifted towards unsymmetrical alkynes. Methods to circumvent this effect of excess 3-hexyne will be discussed in Chapter 3.

The ability to conduct NACM to afford aryl nitriles from diarylacetylenes and alkyl nitriles was surveyed. Although greater than one entire NACM cycle turnover was observed in general, low yields were achieved. Alkyl nitrile identity influences the overall yields of aryl nitriles. Further system optimization will be needed in order to make these transformations useful.

2.10 Experimental

2.10.1 General Procedures

All reactions were performed in an atmosphere of dinitrogen, either in a nitrogen-filled MBRAUN Labmaster 130 glove box or by using standard air-free techniques. ^{1}H NMR spectra were recorded at 499.909 MHz on a Varian Inova 500 spectrometer, 399.967 MHz on a Varian Inova 400 spectrometer, or 300.075 MHz on a Varian Inova 300 spectrometer and referenced to the residual protons in C_6D_6 (7.15 ppm), toluene-d_8 (2.09 ppm), CD_2Cl_2 (5.32 ppm), THF-d_8 (3.58 ppm), $CDCl_3$ (7.26 ppm), C_6D_5Br (7.18 ppm). "No D" ^{1}H NMR spectra were recorded at 499.909 MHz on a Varian Inova 500 spectrometer and referenced to the protons in 1,2 DCE (3.63 ppm). ^{19}F NMR spectra were recorded at 282.384 MHz on a Varian Inova 300 spectrometer or 282.314 MHz on a Varian Inova 400 spectrometer and were referenced to an external standard of $CFCl_3$ in $CDCl_3$ (0.00 ppm). ^{13}C NMR spectra were recorded at 100.587 MHz on a Varian Inova 400 spectrometer or at 100.596 MHz on a Varian Inova 300 spectrometer and were referenced to naturally abundant ^{13}C nuclei in C_6D_6 (128.00 ppm), $CDCl_3$ (77.16 ppm), or CD_2Cl_2 (54.00 ppm). GC/MS data were collected on a Shimadzu GCMS-QP5000 with a Restek XTI-5 phase column (30m, 0.25 I.D., 0.25 D. F.).

2.10.2 Materials

All solvents used were dried and deoxygenated by the method of Grubbs. 1-(4-methoxyphenyl)-1-butyne, bis(4-trifluoromethylphenyl)acetylene, 1-(4-trifluoromethylphenyl)-1-butyne, bis(4-methoxyphenyl)acetylene, $[N{\equiv}W(OCMe_2CF_3)_3]_3$ (**2.3**), $[N{\equiv}WCl_3]_4{\cdot}1.1DCE$, $LiOC(CF_3)_2Me$ and $W_2(OCMe_2CF_3)_6$ were prepared according to literature procedures. $LiOCMe_2CF_3$ was prepared in a manner analogous to that used for the preparation of $LiOC(CF_3)_2Me$. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried over 4Å molecular sieves for at least 24 hours. 1,2-dichloroethane and 1,2-dimethoxyethane were obtained anhydrous from Aldrich and were further dried over 4Å molecular sieves for 48 hours and run through a plug of alumina before use. Anisonitrile and 3-hexyne were obtained from Acros. Propionitrile and 1,3,5-trimethoxybenzene were obtained from Aldrich. Propionitrile and 3-hexyne were dried for 24 hours using 4Å molecular sieves. All other reagents were used as received.

2.10.3 Catalyst Syntheses

$[Li(DME)_2][N{\equiv}W(OC(CF_3)_2Me_3)_4]$ (2.1): $[N{\equiv}WCl_3]_4{\cdot}1.1DCE$ (1.50 g, 1.13 mmol) was added to a 250 mL round bottom flask and was slurried in 30 mL of toluene. DME (965 μL, 9.28 mmol, 8.20 equiv) was added to the solution via syringe and the mixture was stirred for 1 hour. $LiOC(CF_3)_2Me_3$ (3.40 g, 18.1 mmol, 16.0 equiv) was washed into the dark red mixture using additional toluene (10 mL) and the reaction was stirred for 17 h at room temperature. The solution was then heated and washed through a plug of celite using hot toluene (60 mL). The filtrate was reduced *in vacuo*. The resulting residue was slurried in toluene (15 mL) and DME (500 μL) overnight. The solution was filtered to yield 2.67 g of **2.1** as a white microcrystalline powder. An additional 3 crops were collected at −35 ºC, resulting in a total yield of 3.15 g (62.7%, 2.95 mmol) of **2.1**. ^{1}H NMR (300 MHz, THF-d_8): δ 3.43 (s, 11H, *Me*OCH_2*C*H_2O*Me*), 3.27 (s, 7H, MeOCH_2CH_2OMe), 1.72 (s, 12H, OC(CF_3)$_2$CH_3). ^{19}F NMR (THF-d_8): δ –76.88 (s). ^{13}C{^{1}H} NMR (THF-d_8): δ 125.69 (q) (OC(CF_3)$_2$CH_3, J_{C-F} = 289.87 Hz), 82.38 (m) (O*C*(CF_3)$_2$CH_3), 72.64 (s) (DME), 58.82 (s) (DME), 17.25 (s) (OC(CF_3)$_2$*C*H_3). ^{1}H NMR (300 MHz, C_6D_6): δ 2.99 (s, 11H, *Me*OCH_2*C*H_2O*Me*), 2.68 (s, 7H, MeOCH_2CH_2OMe), 1.86 (s, 12H, OC(CF_3)$_2$CH_3). ^{19}F NMR (300 MHz, C_6D_6): δ –76.18 (s). ^{13}C{^{1}H} NMR (400 MHz, C_6D_6): δ 125.64 (q) (OC(CF_3)$_2$CH_3, J_{C-F} = 289.52 Hz), 82.84 (m) (O*C*(CF_3)$_2$CH_3), 70.41 (s) (DME), 59.12 (s) (DME), 17.39 (s) (OC(CF_3)$_2$*C*H_3). Anal. Calcd for $LiNWO_8C_{24}H_{32}F_{24}$: C, 25.99; H, 2.91; N, 1.26. Found: C, 25.67; H, 2.85; N, 1.36.

NW(OC(CF_3)$_2$Me)$_3$(DME) (2.2-DME). Method A. [N≡WCl_3]$_4$·1.1DCE (4.00 g, 3.02 mmol) and LiOC(CF_3)$_2$Me (6.81 g, 36.2 mmol, 12.0 equiv) were slurried in toluene (40 mL) in a bomb flask. THF (982 μL, 12.1 mmol, 4 equiv) was added via syringe and the bomb flask was sealed. The reaction mixture was heated with stirring for 19.5 h at 65 °C. The reaction mixture was heated to nearly boiling and filtered through celite. The celite was washed with hot toluene (40 mL). The volatiles were removed *in vacuo* from filtrate. The resulting residue was taken up in Et_2O (12 mL) and DME (1.25 mL, 12.07 mmol, 4 equiv). Pentane (8 mL) was added and the solution was cooled to −35 °C. Complex **2.2-DME** was collected as yellow crystals via filtration (6.01 g, 7.23 mmol, 60% yield). **Method B.** A mixture of **2.1** (1.43 g, 1.29 mmol) and **2.2-DME** (124.2 mg, 0.149 mmol, 0.12 equiv) was dissolved in 30 mL Et_2O and frozen in the cold well. A solution of HOTf (114 μL, 1.29 mmol, 1 equiv) in Et_2O (10 mL) at −35 ºC was added via pipet to the former just thawed solution with stirring. The reaction mixture was allowed to warm to 28 ºC, and after 12 h incomplete conversion was indicated by ^{19}F NMR spectroscopy. The reaction mixture was then re-frozen in the cold well. A solution of HOTf (6 μL, 0.067 mmol, 0.05 equiv) in Et_2O (10 mL) at −35 ºC was added via pipet into the just thawed reaction mixture with stirring. After 2 h the volatiles were removed *in vacuo.* The residue was extracted with 30 mL hot toluene and filtered. The precipitate was washed with 20 mL hot toluene. The rinsings and filtrate were reduced to dryness *in vacuo*. The resulting brown residue was dissolved in a 50/50 mixture of Et_2O/pentane (20 mL) and cooled to −35 ºC. A dark brown powder was isolated via filtration and washed with 10 mL cold Et_2O to afford the product, a light yellow powder (837.7 mg). A second crop was collected (87.7 mg) to give a total yield of 925.4 mg (1.11 mmol, 78%). ^{1}H NMR (300 MHz, C_6D_6): δ 3.21(v. br. s, 6H, *Me*OCH_2CH_2O*Me*), 2.76 (br s, 4H, MeO$\mathit{CH_2CH_2}$OMe), 1.97 (s, 9H, $OC(CF_3)_2C\mathit{H}_3$). ^{19}F NMR (C_6D_6): δ -77.19 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 124.46 (q, $OC(\mathit{C}F_3)_2CH_3$, $J_{C\text{-}F}$ = 287.96 Hz), 82.56 (m, $O\mathit{C}(CF_3)_2CH_3$, ~71 (v br s, $MeOCH_2CH_2OMe$), ~59 (v br s, $MeOCH_2CH_2OMe$), 15.6 (s, $OC(CF_3)_2\mathit{C}H_3$). Anal. Calcd for $LiNWO_5C_{16}H_{19}F_{18}$: C, 23.12; H, 2.30; N, 1.69. Found: C, 23.38; H, 2.43; N, 1.67.

$[NW(OCMe_2CF_3)_3]_3$ (2.3). $W_2(OCMe_2CF_3)_6$ (10.0 mg, 0.00885 mmol) was dissolved in toluene-*d_8* (0.5 mL). EtCN (1.2 μL, 0.0173 mmol, 2.0 equiv) was introduced via syringe and the resulting reaction mixture was heated at 95 °C for 18.5h. At this point ^{1}H NMR and ^{19}F NMR spectroscopies indicated complete conversion to **2.3**. Spectroscopy data agreed with the literature.[9]

$CH_3CH_2C{\equiv}W(OC(CF_3)_2Me)_3(DME)$ (2.5-DME). Complex **2.2-DME** (450 mg, 0.541 mmol) was dissolved in toluene (10 mL) and the solution was transferred to a bomb flask. To this solution 3-hexyne (61.5 μL, 0.541 mmol, 1 equiv) was added via syringe. The bomb flask was sealed and heated at 95 °C for 16 h. ^{1}H NMR spectroscopy indicated incomplete conversion to the alkylidyne. Additional 3-hexyne (20.0 μL, 0.176 mmol, 0.325 equiv) was syringed into the reaction mixture. This was then heated at 95 °C for 2 h. The resulting mixture was then filtered through celite to remove poly-3-hexyne. The volatiles were removed *in vacuo* from the filtrate. The red residue was then taken up in 5 mL pentane and cooled to −35 °C. A red powder, **2.5-DME**, was collected via filtration (242.8 mg, 0.283 mmol, 52%). Characterization data agreed with the literature.[3]

$CH_3CH_2C{\equiv}W(OCMe_2CF_3)_3$ (2.6). $W_2(OCMe_2CF_3)_6$ (570.4 mg, 0.505 mmol) was dissolved in toluene (10 mL). 3-hexyne (68.8 μL, 0.605 mmol, 1.2 equiv) was added via syringe and reaction mixture was stirred for 1 hr. The volatiles were removed *in vacuo* and the resulting residue was taken up in 10 mL pentane. The pentane solution was filtered and the filtrate was reduced in volume to 2 mL. The resulting solution was cooled to −35 °C. A powder of **2.6** was collected via filtration (528.2 mg, 0.871 mmol, 86%). ^{1}H NMR (300 MHz, tol-d_8): δ 3.40 (q, 2H, ≡CCH_2CH$_3$, J=8.2 Hz), 1.31 (d, 2H, ArH, J=8.4 Hz), 1.65 (s, 18H, OC(CH_3)$_2$CF$_3$) ^{19}F NMR (400 MHz, C_6D_6): δ −82.59(OC(CH$_3$)$_2$CF_3). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 274.18 (t, W≡*C*, $J_{W\text{-}C}$=148.1 Hz), 127.39 (q, OC(CH$_3$)$_2$*C*F$_3$, $J_{C\text{-}F}$=284.0 Hz), 82.29 (q, O*C*CF$_3$(CH$_3$)$_2$, $J_{C\text{-}F}$=28.8 Hz), 40.71 (s, C*C*H$_2$CH$_3$), 25.62 (s, OC(*C*H$_3$)$_2$CF$_3$), 16.89 (s, CCH$_2$*C*H$_3$).

4-MeO(C_6H_4)C≡W(OC(CF$_3$)$_2$Me)$_3$(DME) (2.7-DME). Complex **2.2-DME** (200 mg, 0.241 mmol) and 1-(4-methoxyphenyl)-1-butyne (38.8 mg, 0.241 mmol, 1 equiv) were slurried in toluene-d_8 (1 mL) in a J. Young tube. This mixture was heated at 95 °C for 2.5 h. The volatiles were removed *in vacuo*. The resulting residue was reconstituted in toluene-d_8 (1 mL) and heated at 95°C for 2 h. The volatiles were removed *in vacuo.* The remaining material was dissolved in a total of 4 mL 1:1 Et_2O/pentane and cooled to −35 °C. The product (**2.7-DME**), a deep red-orange powder, was collected via filtration (124.2 mg, 0.133 mmol, 67%). ^{1}H NMR (500 MHz, C_6D_6): δ 6.81 (d, 2H, ArH, J=6.8 Hz), 6.71 (d, 2H, ArH, J=6.8 Hz), 3.65 (br s, 3H, DME), 3.25 (s, 3H, OCH_3), 3.20 (br s, 4H, DME), 2.92 (br s, 3H, DME), 1.88 (s, 9H, OC(CF$_3$)$_2$CH_3). ^{1}H NMR (300 MHz, toluene-d_8, −20°C): δ 6.80 (d, 2H, ArH, J=9.0 Hz), 6.65 (d, 2H, ArH, J=9.0 Hz), 3.65 (s, 3H, DME), 3.21 (s, 3H, OCH_3), 3.10 (s, 3H, DME), 3.07 (t, 2H, DME, J=4.3 Hz), 2.86 (t, 2H, DME, J=4.3 Hz), 1.89 (s, 9H, OC(CF$_3$)$_2$CH_3). ^{19}F NMR (400 MHz, CD_2Cl_2): δ −77.05 (s). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 278.26 (s) (W≡*C*), 160.05 (s) (MeO*C*Ar), 137.84 (s) (CAr), 135.47 (s) (CAr), 124.7 (q) (OC(*C*F$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 289.00 Hz), 112.76 (s) (CAr), 83.11 (m) (O*C*(CF$_3$)$_2$CH$_3$), 75.34 (s) (DME), 73.00 (s)

(DME), 70.60 (s) (DME), 59.50 (s) (DME), 55.64 (s) (O*C*H_3), 18.97 (s) (OC(CF_3)$_2$*C*H_3). Anal. Calcd for $WO_6C_{24}H_{26}F_{18}$: C, 30.79; H, 2.80. Found: C, 30.97; H, 2.96.

4-$F_3C(C_6H_4)C{\equiv}W(OC(CF_3)_2Me)_3$(DME) (2.8-DME). 2.2-DME (250 mg, 0.301 mmol) and 1-(4-trifluoromethylphenyl)-1-butyne (59.9 mg, 0.301 mmol, 1 equiv) were slurried in toluene-d_8 (1 mL) in a J. Young tube. The reaction mixture was heated at 95 °C for 12 h. The volatiles were removed *in vacuo*. The resulting residue was dissolved in 5 mL pentane and cooled to −35 °C. The product, a deep yellow powder, was collected via filtration (95.0 mg, 0.0975 mmol, 32%). A second crop of 71.2 mg was collected to give a total yield of 57% (0.171 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ 7.33 (d, 2H, ArH, J=8.2 Hz), 6.70 (d, 2H, ArH, J=8.2 Hz), 3.57 (br s, 3H, DME), 3.05 (s, 4H, OC*H_3*), 3.78 (br s, 2H, DME), 3.44 (br s, 3H, DME), 1.83 (s, 9H, OC(CF_3)$_2$C*H_3*). ^{1}H NMR (300 MHz, toluene-d_8, −20°C): δ 7.25 (d, 2H, ArH, J=8.1 Hz), 6.68 (d, 2H, ArH, J=8.1 Hz), 3.56 (s, 3H, DME), 3.07 (s, 3H, DME), 3.04 (t, 2H, DME, J=4.3 Hz), 2.82 (t, 2H, DME, J=4.3 Hz), 1.89 (s, 9H, OC(CF_3)$_2$C*H_3*). ^{19}F NMR (400 MHz, CD_2Cl_2): δ -63.21 (s, CF_3) −77.61 (s, OC(CF_3)$_2$$CH_3$). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 276.41 (s, W≡*C*), 146.44 (s, CAr), 134.13 (s, CAr), 129.13 (q, *C*Ar, $J_{C\text{-}F}$ = 65.3 Hz), 124.50 (q, OC(*C*F_3)$_2$$CH_3$, $J_{C\text{-}F}$ =289.0 Hz), 123.86 (q, CAr, $J_{C\text{-}F}$ = 272.1 Hz), 124.66 (q, ArCF_3, $J_{C\text{-}F}$ = 4.4 Hz), 83.28 (m, O*C*(CF_3)$_2$$CH_3$), 75.71 (s, DME), 73.55 (s, DME), 69.96 (s, DME), 59.94 (s, DME), 18.87 (s, OC(CF_3)$_2$*C*H_3). Anal. Calcd for $WO_5C_{24}H_{23}F_{21}$: C, 29.59; H, 2.38. Found: C, 29.38; H, 2.19.

$MeO(C_6H_4)C{\equiv}W(OCMe_2CF_3)_3$ (2.9). Complex **2.6** (200 mg, 0.330 mmol) was dissolved in toluene (5 mL). To this solution, solid bis(4-methoxyphenyl)acetylene (39.3 mg, 0.165 mmol) was added. The solution was diluted with toluene (5 mL). The reaction mixture was stirred for one hour. Then the volatiles were removed *in vacuo*. The resulting mixture was dissolved in pentane (15 mL) and filtered. The volume of the filtrate was reduced to 6 mL and the solution was cooled to −35 °C. Deep yellow-orange crystals of **2.9** were isolated via filtration and washed with 2 mL cold pentane (188 mg, 0.274 mmol, 83% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.00 (d, 2H, ArH, J=8.8 Hz), 6.87 (d, 2H, ArH, J=8.6 Hz), 3.79 (s, 3H, OCH_3), 1.64 (s, 18H, OC(CH_3)$_2$CF$_3$). ^{19}F NMR (400 MHz, CD_2Cl_2): δ −83.17 (s, OC(CH$_3$)$_2$CF_3). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 264.99 (s, W≡*C*), 158.34 (s, *C*Ar), 138.94 (s, CAr), 132.83 (s, CAr), 125.94 (q, OC(CH$_3$)$_2$*C*F$_3$, $J_{C\text{-}F}$=284.4 Hz), 112.23 (s, CAr), 81.83 (q, O*C*CF$_3$(CH$_3$)$_2$, $J_{C\text{-}F}$=28.8 Hz), 54.76 (s, OMe), 24.36 (s, OC(*C*H$_3$)$_2$CF$_3$). Anal. Calcd for $WO_4C_{20}H_{25}F_9$: C, 35.11; H, 3.68. Found: C, 34.86; H, 3.43.

$4\text{-}F_3C(C_6H_4)C{\equiv}W(OCMe_2CF_3)_3)$ (2.10). Complex **2.6** (200 mg, 0.330 mmol) was dissolved in toluene (5 mL). Then 1,2-bis(4-trifluoromethylphenyl)acetylene (51.8 mg, 0.165 mmol) was dissolved in toluene (5 mL) and added to the solution of **2.6**. The reaction mixture was stirred for 1 h. The volatiles were removed *in vacuo*. The resulting mixture was dissolved in pentane (10 mL) and filtered. The volume of the filtrate was reduced to 3 mL and the solution was cooled to -35 °C. Light yellow feathers of **2.10** were collected via filtration and washed with 2 mL cold pentane (175 mg, 0.242 mmol, 73% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.62 (d, 2H, ArH, J=8.2 Hz), 7.13 (d, 2H, ArH, J=8.4 Hz), 1.65 (s, 18H, OC(CH_3)$_2$CF$_3$) . ^{19}F NMR (400 MHz, CD_2Cl_2): δ −83.18 (s, 9F, OC(CH$_3$)$_2$CF_3), −62.99 (s, 3F, ArCF_3). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 265.11 (t, W≡*C*, $J_{C\text{-}W}$=152.0 Hz), 148.95 (s, *C*Ar), 133.06 (s, CAr), 127.16 (q, OC(CH$_3$)$_2$*C*F$_3$, $J_{C\text{-}F}$=268.2 Hz), 124.56 (q, CAr, $J_{C\text{-}F}$=271.4 Hz), 125.32 (q, ArCF$_3$, $J_{C\text{-}F}$=4.0 Hz), 83.74 (q, O*C*CF$_3$(CH$_3$)$_2$, $J_{C\text{-}F}$=29.2 Hz), 25.71 (s, OC(*C*H$_3$)$_2$CF$_3$). Anal. Calcd for $WO_3C_{20}H_{22}F_{12}$: C, 33.26; H, 3.07. Found: C, 33.15; H, 3.13.

O=W(OCMe$_2$CF$_3$)$_4$ (2.11). Complex **2.3** (500 mg, 0.863 mmol) was dissolved in toluene (10 mL) in a bomb flask. 3-hexyne (294 μL, 2.59 mmol, 3 equiv) was added via syringe to the solution and the bomb flask was sealed and heated at 95 °C for 2 days. The reaction mixture was filtered thru celite with Et_2O (40 mL). The filtrate was dried *in vacuo* and taken up in pentane (20 mL). The mixture was again filtered and the resulting filtrate was reduced to 5 mL and cooled to −35 °C. Deep orange crystals of **2.11** were collected via filtration and washed with 3 mL cold pentane (111.6 mg, 0.158 mmol, 27% yield). ^{1}H NMR (400 MHz, tol-*d$_8$*): δ 1.43 (s, OC(CH$_3$)$_2$CF$_3$). ^{19}F NMR (400 MHz, tol-*d$_8$*): δ −81.4 (s, OC(CH$_3$)$_2$CF$_3$). ^{13}C{^{1}H} NMR (400 MHz, C_6D_6): δ 127.67 (q, OC(*C*F$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ =285.4 Hz), 84.60 (q, CAr, $J_{C\text{-}F}$ =29.9 Hz), 22.10 (s, OC(CF$_3$)$_2$*C*H$_3$). Anal. Calcd for $WO_5C_{16}H_{24}F_{12}$: C, 27.14; H, 3.42. Found: C, 27.13; H, 3.32.

2.10.4 Reversible Alkylidyne and Nitride Complex Formation Reactions

2.2-DME + 3-hexyne. **2.2-DME** (10 mg, 0.012 mmol) was dissolved in toluene-*d$_8$* (2.0 mL) and was transferred to a NMR tube. 3-hexyne (2.7 μL, 0.024 mmol, 2.0 equiv) was added to the tube via syringe. The mixture was allowed to react for 20 h at 28

°C. By integration of a ^{1}H NMR spectrum, the solution was determined to contain EtC≡W(OC(CF_3)$_2$$CH_3$)$_3$(DME) (**2.5-DME**) (95.2%) and Et_3C_3W(OC(CF_3)$_2$$CH_3$)$_3$ (**2.4**) (4.8%) at equilibrium. ^{1}H NMR data were consistent with the literature data.

2.5-DME + **Propionitrile.** Complex **2.5-DME** (20.0 mg, 0.0233 mmol) was dissolved in toluene-d_8 (1 mL) and placed in a J. Young tube. EtCN (1.6 μL, 0.023 mmol, 1 equiv) was added to this solution via syringe. An internal standard of 1,3,5-trimethoxybenzene was also added. No reaction was observed at room temperature over 21 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. The reaction endpoint was achieved after 3 h with the W-containing species remaining including a combination of **2.4** and **2.5-DME** (72%) and **2.2-DME** (28%).

2.3 + 3-hexyne. Complex **2.3** (10.0 mg, 0.0173 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, 3-hexyne (2.0 μL, 0.017 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. No reaction was observed at room temperature. The reaction mixture was heated at 95 °C and monitored by ^{1}H and ^{19}F NMR spectroscopy. After 16 h all 3-hexyne had been consumed and the catalyst resting state consisted of **2.6** (9%), **2.11** (26%), and remaining **2.3** (63%). Additionally, an unidentified volatile F-containing species was present in the reaction mixture. This is likely a by-product of the decomposition of **2.3** under these reaction conditions.

2.6 + **Propionitrile.** Complex **2.6** (10.0 mg, 0.0165 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, propionitrile (1.2 μL, 0.017 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. After 20 h the reaction mixture consisted of 80% unidentified F-containing products, **2.11** (10%), and **2.6** (9%). The reaction mixture was then heated at 95 °C and monitored by ^{1}H and ^{19}F NMR spectroscopy for 36 h. At this point all of **2.6** had been converted to **2.3** (89%) and **2.11** (11%).

2.10.5 Catalyst Comparison Reactions

NACM with **2.2-DME**. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.12 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.061 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 8 h at 95 ºC, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (80.6%) and 1-(4-methoxyphenyl)-1-butyne (10.9%) with anisonitrile remaining (8.5%). ^{1}H NMR (400 MHz, toluene-d_8): δ 7.44 (d, 4H, *o*-ArH, J = 9.2 Hz), 6.61 (d, 4H, *m*-ArH, J = 8 Hz), 3.23 (s, ArO*Me*, 6H).

NACM with **2.1**. Complex **2.1** (5.0 mg, 0.0086 mmol) and anisonitrile (23.0 mg, 0.173 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (9.8 μL, 0.086 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was heated at 95 ºC for 31 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-

methoxyphenyl)acetylene (60.9%) and 1-(4-methoxyphenyl)-1-butyne (17.5%) with anisonitrile remaining (21.6%).

NACM with **2.3.** Complex **2.3 (**5.0 mg, 0.0045 mmol) and anisonitrile (12.0 mg, 0.090 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (5.1 μL, 0.045 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was heated at 95 ºC for 10 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (64.9%) and 1-(4-methoxyphenyl)-1-butyne (19.4%) with anisonitrile remaining (15.7%).

2.10.6 Solvent Study Reactions

Toluene-*d*$_8$. See section 2.9.5.

$CDCl_3$. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in $CDCl_3$ (1 mL). Then 3-hexyne (6.8 μL, 0.062 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was frozen and the headspace was evacuated. After 2 h of heating at 95 ºC, ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (33%) and 1-(4-methoxyphenyl)-1-butyne (31%) with anisonitrile remaining (36%). Additional heating resulted in no further reaction due to catalyst destruction.

C_6D_6. Complex **2.2-DME (**10.2 mg, 0.0126 mmol) and anisonitrile (32.9 mg, 0.247 mmol, 20 equiv) were added to a J. Young tube and dissolved in C_6D_6 (1 mL, [**2.2-DME**] = 10 mg/mL). Then 3-hexyne (13.6 μL, 0.120 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was frozen and the headspace was evacuated. After 16 h of heating at 95 ºC, ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (55%) and 1-(4-methoxyphenyl)-1-butyne (20%) with anisonitrile remaining (25%). At this point, 3-hexyne had been completely consumed.

THF-d_8. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in THF-d_8 (1 mL). Then 3-hexyne (6.8 μL, 0.062 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was frozen and the headspace was evacuated. After 61.5 h of heating at 95 ºC, ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (1%) and 1-(4-methoxyphenyl)-1-butyne (14%) with anisonitrile remaining (85%). Reaction monitoring was discontinued due to slow conversion.

CD_2Cl_2. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (8.0 mg, 0.060 mmol, 10 equiv) were added to a J. Young tube and dissolved in CD_2Cl_2 (1 mL). Then 3-hexyne (6.8 μL, 0.062 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was frozen and the headspace was evacuated. After 41.5 h of heating at 75 ºC, ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (46%) and 1-(4-methoxyphenyl)-1-butyne (42%) with anisonitrile remaining (12%). At this point, 3-hexyne had been completely consumed.

1,2-dichloroethane. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in $C_2H_4Cl_2$ (1 mL). Then 3-hexyne (6.8 μL, 0.62 mmol, 20 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was frozen and the headspace was evacuated. After 6 h of heating at 95 ºC, ^{1}H NMR ("No D")[14] spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (49%) and 1-(4-methoxyphenyl)-1-butyne (20%) with anisonitrile remaining (31%). Additional heating resulted in no further reaction due to catalyst destruction.

bromobenzene-*d*$_5$. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in bromobenzene-*d*$_5$ (1 mL). Then 3-hexyne (6.8 μL, 0.62 mmol, 20 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. After 11.5 h of heating at 95 ºC, ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (64%) and 1-(4-methoxyphenyl)-1-butyne (11.0%) with anisonitrile remaining (26%). Additional heating resulted in no further reaction due to complete consumption of 3-hexyne.

2.10.7 Concentration Study Reactions

General Procedure 1. Complex **2.2-DME** and anisonitrile (20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 at the desired concentration of **2.2-DME**. Then 3-hexyne (10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 95 ºC and monitored by ^{1}H NMR spectroscopy. The results are reported in Table 2.8.

Following General Procedure 1 for a concentration of 40 mg/mL (48 mM): Complex **2.2-DME (**30.0 mg, 0.037 mmol), anisonitrile (98.5 mg, 0.74 mmol), 3-hexyne (42.0 μL, 0.37 mmol), and toluene-d_8 (0.75 mL).

Following General Procedure 1 for a concentration of 20 mg/mL (24 mM): Complex **2.2-DME (**15.0 mg, 0.019 mmol), anisonitrile (49.3 mg, 0.37 mmol), 3-hexyne (21.0 μL, 0.19 mmol), and toluene-d_8 (0.75 mL).

Following General Procedure 1 for a concentration of 10 mg/mL (12 mM): Complex **2.2-DME (**10.0 mg, 0.012 mmol), anisonitrile (33.0 mg, 0.25 mmol), 3-hexyne (13.6 μL, 0.12 mmol), and toluene-d_8 (1.0 mL).

Following General Procedure 1 for a concentration of 5 mg/mL (6 mM): Complex **2.2-DME (**10.0 mg, 0.012 mmol), anisonitrile (16.0 mg, 0.12 mmol), 3-hexyne (6.8 μL, 0.061 mmol), and toluene-d_8 (1.0 mL).

For a concentration of 2.5 mg/mL (3 mM): Complex **2.2-DME** from a stock solution at 2.5 mg/mL (1 mL, 0.0030 mmol) was added to a J. Young tube containing anisonitrile (8.2 mg, 0.062 mmol). Then 3-hexyne (3.5 μL, 0.031 mmol) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 95 ºC and monitored by ^{1}H NMR spectroscopy.

Table 2.8. Concentration studies with **2.2-DME**.

Time (h)	**3.0 mM (%)**	**6.0 mM (%)**	**12 mM (%)**	**24 mM (%)**	**48 mM (%)**
2	47.6 ±8.4	58.4 ± 1.3	55.2 ± 7.4	42.1 ± 2.2	41.2 ± 3.9
4	69.1 ± 5.9	82.1 ± 4.1	72.2 ± 6.4	61.3 ± 2.3	55.3 ± 4.0
6	80.8 ± 5.2	88.1 ± 3.7	78.2 ± 4.9	71.3 ± 2.3	66.2 ± 2.4
8	86.4 ± 5.0	91.1 ± 3.7	80.7 ± 3.8	76.3 ± 2.4	71.4 ± 2.6
10	88.2 ± 3.7	91.1 ± 3.8	81.5 ± 2.6	79.2 ± 2.5	75.0 ± 3.0
12	88.2 ± 3.7	91.1 ± 3.3	82.5 ± 3.4	81.1 ± 1.6	76.9 ± 4.4
14	88.2 ± 3.7	90.7 ± 2.7	82.0 ± 2.3	82.4 ± 2.3	77.9 ± 4.3

General Procedure 2. Complex **2.3** and anisonitrile (20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 at the desired concentration of **2.3**. Then 3-hexyne (10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 95 ºC and monitored by ^{1}H NMR spectroscopy. The results are reported in Table 2.9.

Following General Procedure 2 for a concentration of 40 mg/mL (70 mM). Complex **2.3 (**20.0 mg, 0.035 mmol), anisonitrile (92.0 mg, 0.69 mmol), 3-hexyne (39.2 μL, 0.35 mmol), and toluene-d_8 (0.50 mL).

Following General Procedure 2 for a concentration of 30 mg/mL (52 mM). Complex **2.3 (**15.0 mg, 0.026 mmol), anisonitrile (69.0 mg, 0.52 mmol), 3-hexyne (29.4 μL, 0.26 mmol), and toluene-d_8 (0.50 mL).

Following General Procedure 2 for a concentration of 20 mg/mL (35 mM). Complex **2.3 (**10.0 mg, 0.017 mmol), anisonitrile (46.0 mg, 0.35 mmol), 3-hexyne (19.6 μL, 0.17 mmol), and toluene-d_8 (0.50 mL).

Following General Procedure 2 for a concentration of 10 mg/mL (17 mM). Complex **2.3 (**5.0 mg, 0.0086 mmol), anisonitrile (23.0 mg, 0.17 mmol), 3-hexyne (9.8 μL, 0.086 mmol), and toluene-d_8 (0.50 mL).

Following General Procedure 2 for a concentration of 5 mg/mL (8.6 mM). Complex **2.3 (**5.0 mg, 0.0086 mmol), anisonitrile (23.0 mg, 0.17 mmol), 3-hexyne (9.8 μL, 0.086 mmol), and toluene-d_8 (1.0 mL).

Table 2.9. Concentration studies with **2.3**.

Time (h)	8.6 mM (%)	17 mM (%)	35 mM (%)	52 mM (%)	70 mM (%)
2	26.8 ± 6.8	35.3 ± 4.1	45.8 ± 0.0	41.7 ± 3.9	42.4 ± 2.0
4	40.0 ± 8.1	49.0 ± 1.7	60.4 ± 1.3	55.0 ± 1.1	52.7 ± 0.7
6	48.7 ± 10.2	58.9 ± 2.3	65.2 ± 2.6	61.6 ± 4.4	57.4 ± 1.9
8	57.1 ± 5.4	65.3 ± 1.3	71.4 ± 1.5	59.7 ± 3.9	61.6 ± 2.2
10	61.0 ± 5.8	65.6 ± 2.5	72.8 ± 0.2	63.3 ± 3.1	63.6 ± 2.1
12		69.2 ± 3.2	74.4 ± 0.7	67.2 ± 2.4	64.5 ± 0.8
14	65.7 ± 9.9	71.7 ± 3.7	75.5 ± 0.9	67.5 ± 3.1	64.7 ± 1.5
16	68.0 ± 4.1	73.0 ± 0.3	75.5 ± 1.1	68.9 ± 1.5	65.2 ± 4.2
18	69.8 ± 4.7	76.2 ± 0.1		67.7 ± 1.6	64.3 ± 3.0
20		76.8 ± 1.7		69.2 ± 0.3	
22	71.2 ± 6.0	76.2 ± 0.9			

2.10.8 Catalyst Loading Reactions

3.75 mol% catalyst loading. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (21.3 mg, 0.165 mmol, 27 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (9.1 μL, 0.082 mmol, 13 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 8 h at 95 ºC, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (78.7%) and 1-(4-methoxyphenyl)-1-butyne (12.5%) with anisonitrile remaining (8.8%).

5.0 mol% catalyst loading. See section 2.9.5.

10.0 mol% catalyst loading. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (8.2 mg, 0.062 mmol, 10 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (3.5 μL, 0.031 mmol, 5 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 6 h at 95 ºC, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (58.3%) and 1-(4-methoxyphenyl)-1-butyne (32.8%) with anisonitrile remaining (8.9%).

20.0 mol% catalyst loading. Complex **2.2-DME (**10.0 mg, 0.060 mmol) and anisonitrile (8.2 mg, 0.062 mmol, 5 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (1.8 μL, 0.015 mmol, 2.5 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 4 h at 95 ºC, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (81.2%) and 1-(4-methoxyphenyl)-1-butyne (12.1%) with anisonitrile remaining (6.7%).

2.10.9 Temperature Study Reactions

At 95 ºC. See section 2.9.5

At 85 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.061 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 20 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-

methoxyphenyl)acetylene (64.0%) and 1-(4-methoxyphenyl)-1-butyne (13.4%) with anisonitrile remaining (22.6%). At this point, 3-hexyne had been completely consumed.

At 75 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.061 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 10 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (23.3%) and 1-(4-methoxyphenyl)-1-butyne (22.1%) with anisonitrile remaining (54.6%). Reaction monitoring was discontinued due to slow conversion.

2.10.10 Influence of 3-hexyne Reactions

10 equivalents 3-hexyne relative to catalyst. See section 2.9.5.

20 equivalents 3-hexyne relative to catalyst. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.12 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (13.7 μL, 0.12 mmol, 20 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 95 ºC for 6 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (47.6%) and 1-(4-methoxyphenyl)-1-butyne (49.0%) with anisonitrile remaining (3.4%).

30 equivalents 3-hexyne relative to catalyst. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.12 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (20.5 μL, 0.18 mmol, 30 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated for 6 h at 95 ºC, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (40.2%) and 1-(4-methoxyphenyl)-1-butyne (54.6%) with anisonitrile remaining (5.2%).

2.10.11 Multivariable Study Reactions

10 equivalents 3-hexyne and 10 mol% catalyst loading at 85 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 10 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 85 ºC for 8 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (27.4%) and 1-(4-methoxyphenyl)-1-butyne (68.8%) with anisonitrile remaining (3.8%).

10 equivalents 3-hexyne and 10 mol% catalyst loading at 75 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (8.2 mg, 0.062 mmol, 10 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 75 ºC for 14 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (35.2%) and 1-(4-methoxyphenyl)-1-butyne (56.8%) with anisonitrile remaining (8.0%).

10 equivalents 3-hexyne and 10 mol% catalyst loading at 65 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (8.2 mg, 0.062 mmol, 10 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 65 ºC for 68.5 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (44.1%) and 1-(4-methoxyphenyl)-1-butyne (33.4%) with anisonitrile remaining (22.5%). Heating the reaction for an additional 19 h resulted in a further 4.5% conversion of anisonitrile to bis(4-methoxyphenyl)acetylene (49.7%) and 1-(4-methoxyphenyl)-1-butyne (32.3%). Reaction monitoring was discontinued due to slow conversion.

20 equivalents 3-hexyne and 10 mol% catalyst loading at 65 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (8.2 mg, 0.062 mmol, 10 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (13.7 μL, 0.120 mmol, 20 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 65 ºC for 62.5 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (23.5%) and 1-(4-methoxyphenyl)-1-butyne (58.1%) with anisonitrile remaining (18.4%). Heating the reaction for an additional 19 h resulted in a further 6.6% conversion of anisonitrile to bis(4-methoxyphenyl)acetylene (27.9%) and 1-(4-methoxyphenyl)-1-butyne (60.3%). Reaction monitoring was discontinued due to slow conversion as a result of increased viscosity.

20 equivalents 3-hexyne and 20 mol% catalyst loading at 65 ºC. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (4.0 mg, 0.031 mmol, 5 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (13.7 μL, 0.120 mmol, 20 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction was heated at 65 ºC for 56 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (19.7%) and 1-(4-methoxyphenyl)-1-butyne (64.2%) with anisonitrile remaining (16.1%). Reaction monitoring was discontinued due to slow conversion as a result of increased viscosity.

2.10.12 Catalyst Activity Studies

With 2.2-DME. Complex **2.2-DME (**5.0 mg, 0.0060 mmol) and anisonitrile (16.0 mg, 0.124 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1 mL). Then 3-hexyne (6.8 μL, 0.062 mmol, 10 equiv) and an internal standard of 1,3,5-

trimethoxybenzene were introduced via syringe. The reaction mixture was heated overnight at 95 ºC. To the resulting reaction mixture was added propionitrile (4.2 μL, 0.062 mmol, 10 equiv). The reaction was heated at 95 ºC for 23 h at which point an additional 18% of anisonitrile was present as indicated by ^{1}H NMR spectroscopy. Further heating of the reaction mixture resulted in no additional conversion to anisonitrile.

With 2.3. Complex **2.3 (**10.0 mg, 0.0173 mmol) and anisonitrile (46.0 mg, 0.345 mmol, 20 equiv) were added to a J. Young tube and dissolved in tolene-d_8 (0.5 mL). Then 3-hexyne (19.6 μL, 0.0173 mmol, 10 equiv) and an internal standard of 1,3,5-trimethoxybenzene were introduced via syringe. The reaction mixture was heated overnight at 95 ºC. To the resulting reaction mixture was added propionitrile (12.2 μL, 0.173 mmol, 10 equiv). The reaction was heated at 95 ºC for 5 h at which point the ^{1}H NMR spectrum was too broadened to interpret accurately due to the presence of insoluble polymer. The resulting reaction mixture was filtered through celite with toluene (5 mL) to remove poly-3-hexyne. The filtrate was reduced *in vacuo* to dryness. The resulting residue was taken up in toluene-d_8. To this solution was added propionitrile (36.6 μL, 0.519 mmol, 30 equiv) via syringe. The reaction mixture was heated at 95 ºC for 24 h with no conversion to anisonitrile indicated by ^{1}H NMR spectroscopy.

2.10.13 Nitrile-Alkyne Cross-Metathesis to Afford Nitriles Studies

General Procedure. Complex **2.2-DME** (5.0 mg, 0.0060 mmol) and diarylacetylene were dissolved in toluene-d_8 (0.5 mL). Then a nitrile was added via syringe. An internal standard of 1,3,5-trimethoxybenzene or mesitylene was added. The reaction mixture was heated at 95 °C and monitored via ^{1}H NMR spectroscopy.

Bis(4-methoxyphenyl)acetylene and acetonitrile. Following the general procedure: **2.2-DME**, bis(4-methoxyphenyl)acetylene (7.2 mg, 0.030 mmol, 5 equiv), and acetonitrile (3.2 μL, 0.060 mmol, 10 equiv) were heated for 19 h. Further heating resulted in no additional conversion to anisonitrile. At this point the reaction mixture consisted of 37% anisonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: C_8H_7ON (133, R_t 5.080 min), $C_{16}H_{14}O$ (238, R_t 14.080 min)

Bis(4-methoxyphenyl)acetylene and propionitrile. Following the general procedure: **2.2-DME**, bis(4-methoxyphenyl)acetylene (7.2 mg, 0.030 mmol, 5 equiv), and propionitrile (4.2 μL, 0.060 mmol, 10 equiv) were heated for 36 h. Further heating resulted in no additional conversion to anisonitrile. At this point the reaction mixture consisted of 22% anisonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: C_8H_7ON (133, R_t 5.050 min), $C_{16}H_{14}O$ (238, R_t 14.063 min)

Bis(4-methoxyphenyl)acetylene and trichloroacetonitrile. Following the general procedure: **2.2-DME**, bis(4-methoxyphenyl)acetylene (7.2 mg, 0.030 mmol, 5 equiv), and trichloroacetonitrile (6.0 μL, 0.060 mmol, 10 equiv) were heated for 21 h. Further heating resulted in no additional conversion to anisonitrile. At this point the reaction mixture consisted of 45% anisonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: C_8H_7ON (133, R_t 5.073 min), $C_{16}H_{14}O$ (238, R_t 14.113 min)

Diphenylacetylene and acetonitrile. Following the general procedure: **2.2-DME**, diphenylacetylene (21.4 mg, 0.0602 mmol, 10 equiv), and acetonitrile (6.3 μL, 0.12 mmol, 20 equiv) were heated for 20 h. Further heating resulted in no additional conversion to benzonitrile. At this point the reaction mixture consisted of only 10% benzonitrile. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: C_7H_5N (103, R_t 12.080 min), $C_{14}H_{10}$ (178, R_t 18.277 min)

Diphenylacetylene and trichloroacetonitrile. Following the general procedure: **2.2-DME**, diphenylacetylene (5.4 mg, 0.030 mmol, 5 equiv), and trichloroacetonitrile (6.0 μL, 0.060 mmol, 10 equiv) were heated for 15 h. Further heating resulted in no additional conversion to benzonitrile. At this point the reaction mixture consisted of 35% benzonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: C_7H_5N (103, R_t 11.883 min), $C_{14}H_{10}$ (178, R_t 18.117 min)

Diphenylacetylene and bromoacetonitrile. Following the general procedure: **2.2-DME**, diphenylacetylene (5.4 mg, 0.030 mmol, 5 equiv), and bromoacetonitrile (4.2 μL, 0.060 mmol, 10 equiv) were heated for 20 h. At this point the catalyst had completely decomposed and no conversion to benzonitrile was observed.

Diphenylacetylene and chloroacetonitrile. Following the general procedure: **2.2-DME**, diphenylacetylene (5.4 mg, 0.030 mmol, 5 equiv), and chloroacetonitrile (3.8 μL, 0.060 mmol, 10 equiv) were heated for 30 h. At this point the catalyst had completely decomposed and trace conversion to benzonitrile was observed.

Diphenylacetylene and dichloroacetonitrile. Following the general procedure: **2.2-DME**, diphenylacetylene (5.4 mg, 0.030 mmol, 5 equiv), and dichloroacetonitrile (4.8 μL, 0.060 mmol, 10 equiv) were heated for 17 h. At this point the catalyst had completely decomposed and no conversion to benzonitrile was observed.

Bis(4-trifluoromethylphenyl)acetylene and acetonitrile. Following the general procedure: **2.2-DME**, bis(4-trifluoromethylphenyl)acetylene (9.5 mg, 0.030 mmol, 5 equiv), and acetonitrile (6.3 μL, 0.060 mmol, 10 equiv) were heated for 48 h. Further heating resulted in no additional conversion to 4-trifluoromethylbenzonitrile. At this point the reaction mixture consisted of 5% 4-trifluoromethylbenzonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: $C_8H_4NF_3$ (171, R_t 11.943 min), $C_{16}H_8F_6$ (314, R_t 17.913 min)

Bis(4-trifluoromethylphenyl)acetylene and trichloroacetonitrile. Following the general procedure: **2.2-DME**, bis(4-trifluoromethylphenyl)acetylene (9.5 mg, 0.030 mmol, 5 equiv), and trichloroacetonitrile (6.0 μL, 0.060 mmol, 10 equiv) were heated for 15 h. Further heating resulted in no additional conversion to 4-trifluoromethylbenzonitrile. At this point the reaction mixture consisted of 15% 4-trifluoromethylbenzonitrile with respect to internal standard. The reaction mixture was filtered through silica gel with dichloromethane. GC/MS $[M/Z]^+$: $C_8H_4NF_3$ (171, R_t 11.646 min), $C_{16}H_8F_6$ (314, R_t 17.667 min)

2.11 References

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Chapter Three:

Mechanistic Investigations and Applications of Nitrile-Alkyne Cross-Metathesis

3.1 Introduction

Nitrile-alkyne cross-metathesis (NACM) broadens the field of triple bond metathesis to encompass not only carbon-carbon triple bonds, but also carbon-nitrogen triple bonds. In Chapter 2, NACM catalyst design, synthesis, and system optimization studies were detailed. In the process of completing these studies several questions regarding the influence of the alkoxide ligands on catalyst resting state, alkyne product ratios, and competing alkyne polymerization with NACM arose.

In order to probe questions of catalyst resting state, this chapter includes detailed experimental and theoretical investigations of the mechanism of NACM. From the proposed mechanism of alkyne formation, the influence of the catalyst on alkyne product ratios is addressed along with further system developments including tandem alkyne cross-metathesis (ACM)-alkyne polymerization reactions. Finally, the utility of NACM is evaluated through investigations of substrate tolerance, deactivation modes of the catalysts, and application in the synthesis of large macrocycles.

3.2 ^{19}F NMR Investigations

The catalyst activity studies in Section 2.5 revealed that a large difference in alkyne product ratios is observed when working with $N{\equiv}W(OCMe(CF_3)_2)_3(DME)$ (**3.1-**

DME) and [N≡W(OCMe$_2$CF$_3$)$_3$]$_3$ (**3.2**). Initial investigations with both catalysts focused on directly monitoring the formation of symmetrical and unsymmetrical alkynes. The metathesis of 2 equivalents of 4-trifluoromethylbenzonitrile with 1 equivalent of 3-hexyne in the presence of 5 mol% catalyst in toluene-d_8 was monitored over 2 h at 95 °C via ^{19}F NMR spectroscopy.

From Figure 3.1, the slower conversion of 4-trifluoromethylbenzonitrile to alkyne products with **3.2** is evident. As seen in previous studies, a large difference in the relative proportions of symmetrical and unsymmetrical alkynes is found. With **3.2** there is a build-up of unsymmetrical alkyne prior to symmetrical alkyne formation, whereas with **3.1-DME** symmetrical alkyne formation is rapid with a nearly statistical mixture of alkynes being present at all times.

One potential source of alkyne ratio variance is the presence of different catalyst resting states, a fact that is apparent in the ^{19}F NMR spectra. The gradual transformation of **3.1-DME** into its corresponding benzylidyne catalyst is observed. Unlike **3.1-DME**, the resting state of catalyst **3.2** is not a benzylidyne complex (Figure 3.1). The ^{19}F NMR chemical shift of the alkoxide ligands of the possible catalyst resting states overlap, but ^{1}H NMR spectroscopy provides additional information on the likely catalyst resting state. Following the reaction with **3.1-DME**, a gradual transformation of **3.1-DME** into a mixture of alkylidyne and benzylidyne species with subsequent funneling towards the benzylidyne complex is observed. An alkylidyne/benzylidyne catalyst resting state would favor rapid alkyne metathesis, accounting for a statistical mixture of symmetrical and unsymmetrical alkynes at all times. In comparison, **3.2** does not exhibit a resting state of benzylidyne or alkylidyne complexes. Instead, the catalyst resting state appears to be a non-trimeric form of **3.2**, likely due to coordination of nitriles and/or alkynes to the metal center. A nitride resting state would account for an accumulation of unsymmetrical alkyne relative to symmetrical alkyne, as secondary alkyne metathesis to form the symmetrical alkyne would be suppressed.

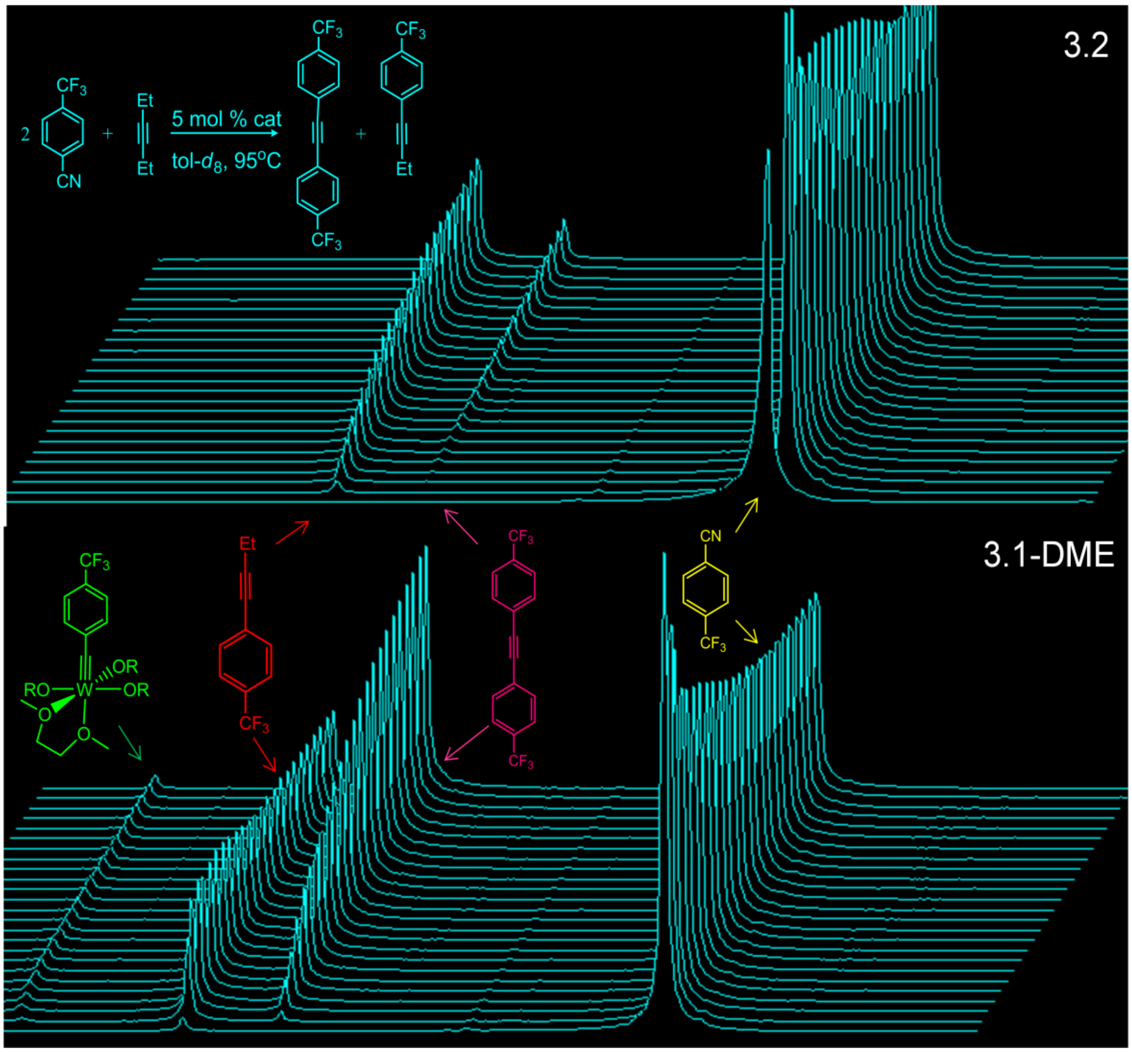
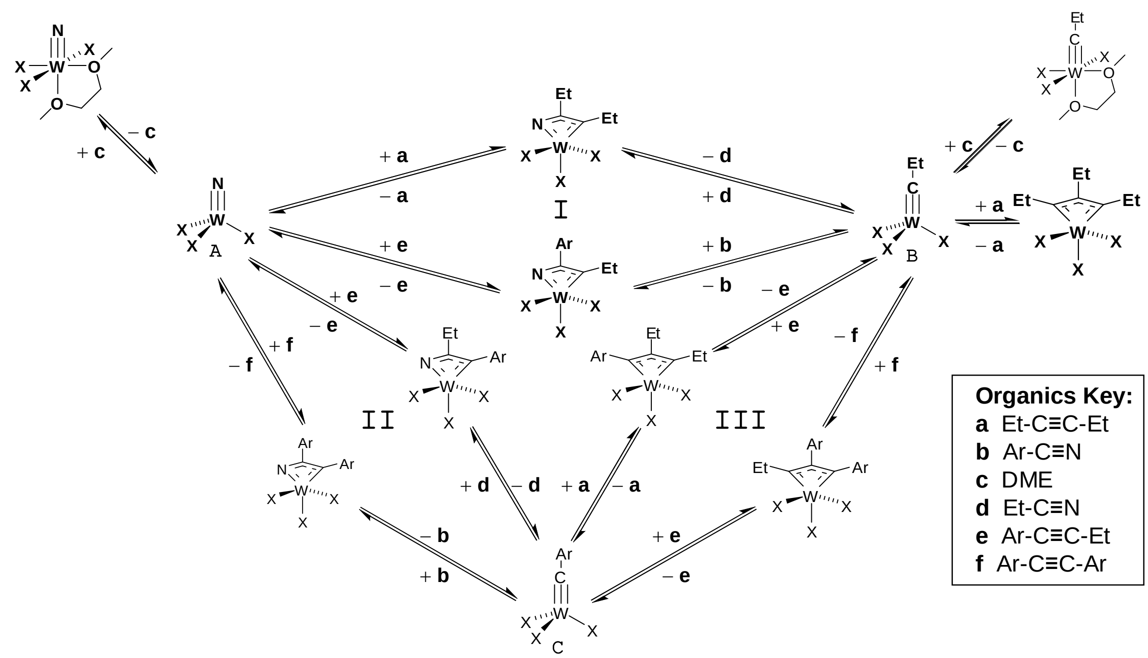


Figure 3.1. ^{19}F NMR studies of **3.1-DME** and **3.2**.

3.3 Pathway Studies

While the pathway for formation of the unsymmetrical alkyne is apparent, the method of formation of the symmetrical alkyne has yet to be determined. Three cycles (I, II, and III) that account for the production of the unsymmetrical alkyne and subsequent generation of the symmetrical alkyne are depicted in Scheme 3.1. The metal complexes are labeled with capital letters (**A-C**) and the organic substrates are indicated by lower case letters (**a-f**).



Scheme 3.1. Possible cycles for symmetrical alkyne formation.

Initial formation of the unsymmetrical alkyne *must* occur through NACM as the only aryl unit source is the aryl nitrile (**b**). This cycle (I) involves the metathesis of 3-hexyne (**a**) with **A** to form **B** with concomitant release of propionitrile (**d**). Then **B** can undergo metathesis with the aryl nitrile (**b**) to produce the desired unsymmetrical alkyne (**e**) and regenerate **A.** At this point, two pathways (Cycles II and III) could account for formation of the symmetrical alkyne (**f**). The most obvious pathway, Cycle III, is simpley ACM via **B** and **C** to produce symmetrical alkynes (**f**) and (**a**) from two unsymmetrical alkynes (**e**). An alternative method of symmetrical alkyne (**f**) formation, Cycle II, involves NACM. In this cycle, **A** interacts with the unsymmetrical alkyne (**e**) to form **C** and release propionitrile (**d**). Then subsequent reaction of an equivalent of aryl nitrile (**b**) with **C** affords the symmetrical alkyne (**f**) and regenerates **A**.

These cycles were studied in detail to establish the pathway(s) by which the symmetrical alkyne is likely forming. As all of these cycles could in principle operate simultaneously, studies were undertaken with each individual pathway to examine catalyst resting state, reversibility, substrate influence, reaction time, and whether an equilibrium is established. Catalysts ligated by $OCMe_2CF_3$ or $OCMe(CF_3)_2$ ligands were applied in the studies (See Figure 3.2 for the catalyst numbering scheme). Aryl groups substituted in the *para* position by methoxy or trifluoromethyl groups were selected for the substrate studies to investigate the electronic influence of the substrate on NACM.

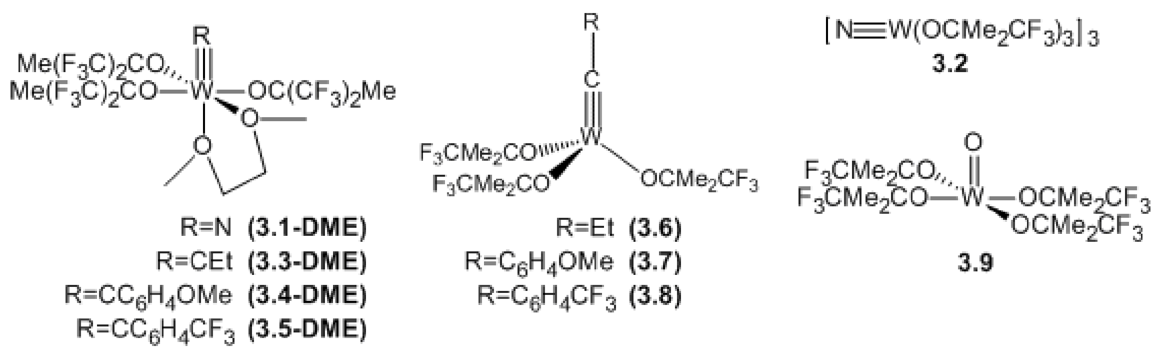
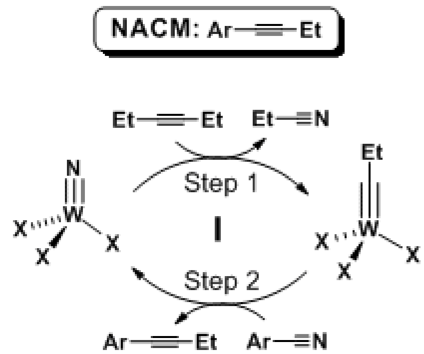


Figure 3.2. Catalyst numbering scheme.

3.3.1 Nitrile-Alkyne Cross-Metathesis to Form Unsymmetrical Alkynes



Scheme 3.2. Cycle I: NACM to produce an unsymmetrical alkyne.

Scheme 3.2 depicts Cycle I of NACM, where the first step involves the transformation of the tungsten nitride complex via metathesis with 3-hexyne into a propylidyne species with release of propionitrile. The second portion of the cycle comprises triple bond metathesis of a propylidyne species with an aryl nitrile substrate to afford an unsymmetrical alkyne and regenerate the tungsten nitride catalyst. Tables 3.1a-d summarize the results obtained with these reactions at 95°C.

Table 3.1a. N≡[W] + EtC≡CEt → EtC≡[W] + EtC≡N.

Entry	Catalyst	W≡N, %	W=O, %	W≡CR, W(C_3R_3), %
1	**3.2**	63	26	9
2	**3.1-DME**[a]	0	0	100

[a]Conducted at room temperature.

Table 3.1b. N≡[W] + EtC≡CEt ← EtC≡[W] + EtC≡N.

Entry	Catalyst	W≡N, %	W=O, %	W≡CEt,W(C_3Et_3), %
1	**3.6**	89	11	0
2	**3.3-DME**	28	0	72

Tables 3.1a-b detail the reversible formation of alkylidyne and nitride complexes in step 1 of Cycle I. From these studies it is apparent that catalyst formation is indeed reversible with E≡W(OC(CF_3)$_2$Me)$_3$(DME) and E≡W(OCMe$_2$CF$_3$)$_3$ (E=CR or N), although an unperturbed equilibrium is not established. The lack of an equilibrium is due to competing alkyne polymerization, which operates in all of the pathway studies where ethyl units are present. The varying amounts of **3.9** formed in the reactions with E≡W(OCMe$_2$CF$_3$)$_3$ (E=CR or N) are due to differences in reaction rates. Longer reaction times result in greater quantities of decomposition because of extended exposure to heat. With OC(CF_3)$_2$Me ligands, the catalyst resting state lies towards that of the propylidyne complex (Table 3.1a, entry 2; Table 3.1b, entry 2) as expected from the ^{19}F NMR studies. In contrast, use of more electron-donating OCMe$_2$CF$_3$ ligands results in preferential formation of the nitride species (Table 3.2a, entry 1; Table 3.2b, entry 1).

Table 3.1c. N≡[W] + *p*-XC_6H_4C≡CEt → EtC≡[W] + *p*-XC_6H_4C≡N.

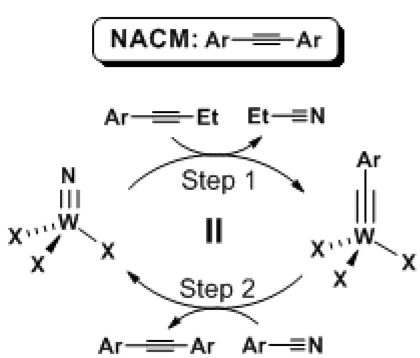
Entry	Catalyst	X	W≡N, %	W=O, %	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.2**	OMe	75	14	0	9
2	**3.1-DME**	OMe	6	0	14	80
3	**3.2**	CF_3	42	33	0	25
4	**3.1-DME**	CF_3	13	0	0	87

Table 3.1d. N≡[W] + *p*-XC_6H_4C≡CEt ← EtC≡[W] + *p*-C_6H_4C≡N.

Entry	Catalyst	X	W≡N, %	W=O, %	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.6**	OMe	60	9	0	25
2	**3.3-DME**	OMe	12	0	10	78
3	**3.6**	CF_3	64	5	4	19
4	**3.3-DME**	CF_3	13	0	0	87

Tables 3.1c-d highlight the reversible formation of alkylidyne and nitride complexes in step 2 of Cycle I. Once again, reversible formation of all species is observed. The presence of alkyne polymerization leads to the absence of a single equilibrium state. The benzylidyne complex is favored over the alkylidyne complex, regardless of alkoxide ligand. However, the relative preference for benzylidyne versus nitride complex is dependent on alkoxide ligation. Similar to the first step of Cycle I, the nitride species is favored with $OCMe_2CF_3$ ligands, while the benzylidyne complex is favored for $OCMe(CF_3)_2$ ligands. No significant electronic influence on catalyst resting state as a function of aryl nitrile is observed.

3.3.2 Nitrile-Alkyne Cross-Metathesis to Form Symmetrical Alkynes



Scheme 3.3. Cycle II: NACM to produce a symmetrical alkyne.

The formation of a symmetrical alkyne via NACM (Cycle II) is detailed in Scheme 3.3. The first step involves nitride ligand conversion via metathesis with an unsymmetrical alkyne to form the benzylidyne complex with simultaneous release of propionitrile. The second step of the cycle results in the regeneration of the nitride catalyst from the benzylidyne complex through triple bond metathesis with an aryl nitrile. A summary of the results of these reactions at 95 °C is reported in Tables 3.2a-d.

Table 3.2a. N≡[W] + *p*-XC_6H_4C≡CEt → *p*-XC_6H_4C≡[W] + EtC≡N.

Entry	Catalyst	X	W≡N, %	W=O, %	W≡CAr, %	W≡CEt, W(C_3Et_3), %
1	**3.2**	OMe	75	14	9	0
2	**3.1-DME**	OMe	6	0	80	14
3	**3.2**	CF_3	42	33	25	0
4	**3.1-DME**	CF_3	13	0	87	0

Table 3.2b. N≡[W] + *p*-XC_6H_4C≡CEt ← *p*-XC_6H_4C≡[W] + EtC≡N.

Entry	Catalyst	X	W≡N, %	W=O, %	W≡CAr, %	W≡CEt, W(C_3Et_3), %
1	**3.7**	OMe	70	7	14	0
2	**3.4-DME**	OMe	42	0	39	19
3	**3.8**	CF_3	61	11	21	0
4	**3.5-DME**	CF_3	17	0	83	0

Tables 3.2a-d show that the catalyst resting state lies largely towards the benzylidyne complex with $OCMe(CF_3)_2$-ligated complexes and towards the nitride complex with $OCMe_2CF_3$-ligated complexes. Alkyne polymerization continues to influence the equilibrium as described in Section 3.3.1. Interestingly, not all conversions were found to be reversible for both aryl nitriles. Entry 3 in Table 3.2c reveals no

formation of **3.8** from **3.2** upon treatment with bis(4-trifluoromethylphenyl)acetylene. The reverse reaction, Entry 3 in Table 3.2d, is consistent with the lack of formation of **3.8** in the forward reaction as the catalyst resting state consists entirely of **3.2** with some decomposition to **3.9**. In Tables 3.2c-d, replacement of the para-substituent with a methoxy group (Entry 1) results in slight catalyst conversion, allowing for the reversible formation of **3.2** and **3.9**. In summary, the operative mechanistic pathways and resulting alkyne ratio obtained by NACM are not only influenced by the ancillary ligands, but also by the electronic nature of the substrates.

Table 3.2c. N≡[W] + *p*-C_6H_4XC≡C-*p*-*p*-C_6H_4X → *p*-C_6H_4XC≡[W] + *p*-C_6H_4XC≡N.

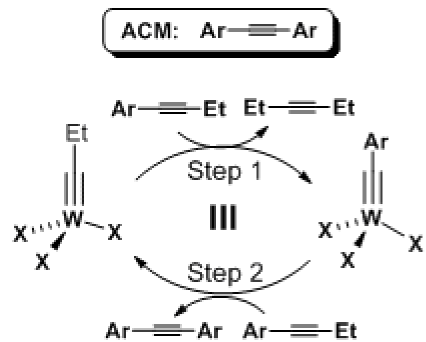
Entry	Catalyst	X	W≡N, %	W=O, %	W≡CAr, %
1	**3.2**	OMe	76	17	7
2	**3.1-DME**[a]	OMe	46	0	54
3	**3.2**	CF_3	100	0	0
4	**3.1-DME**	CF_3	67	0	33

[a]Conducted at room temperature.

Table 3.2d. N≡[W] + *p*-XC_6H_4C≡C-*p*-*p*-C_6H_4X ← *p*-C_6H_4XC≡[W] + *p*-C_6H_4XC≡N.

Entry	Catalyst	X	W≡N, %	W=O, %	W≡CAr, %
1	**3.7**	OMe	90	10	0
2	**3.4-DME**	OMe	49	0	51
3	**3.8**	CF_3	86	14	0
4	**3.5-DME**	CF_3	65	0	35

3.3.3 Alkyne Cross-Metathesis to Form Symmetrical Alkynes



Scheme 3.4. Cycle III: ACM to produce a symmetrical alkyne.

Scheme 3.4 highlights the use of ACM (Cycle III) to afford a symmetrical alkyne. This cycle invokes the well-established interconversion of alkylidyne and benzylidyne species via metathesis with an unsymmetrical alkyne. In contrast to the NACM studies, all ACM reactions were completed at room temperature. A summary of the results of these reactions is reported in Tables 3.3a-d.

Table 3.3a. EtC≡[W] + *p*-C_6H_4XC≡CEt → *p*-C_6H_4XC≡[W] + EtC≡CEt.

Entry	Catalyst	X	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.6**	OMe	present	present
2	**3.3-DME**	OMe	31	69
3	**3.6**	CF_3	35	65
4	**3.3-DME**	CF_3	21	79

Table 3.3b. EtC≡[W] + *p*-C_6H_4XC≡CEt ← *p*-C_6H_4XC≡[W] + EtC≡CEt.

Entry	Catalyst	X	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.7**	OMe	present	present
2	**3.4-DME**	OMe	52	48
3	**3.8**	CF_3	33	67
4	**3.5-DME**	CF_3	49	51

As seen in Tables 3.3a-d all steps are reversible. Evidence of alkyne polymerization is present. No strong influence of alkoxide ligation or substrate substitution on the catalyst resting state is evident. Some catalyst resting state ratios were not reported due to overlapping resonances in the ^{1}H and ^{19}F NMR spectra. In general, the overall resting state with both catalysts is the benzylidyne complex.

Table 3.3c. EtC≡[W] + *p*-C_6H_4XC≡C-*p*-C_6H_4X → *p*-C_6H_4XC≡[W] + *p*-C_6H_4XC≡CEt.

Entry	Catalyst	X	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.6**	OMe	trace	100
2	**3.3-DME**	OMe	6	93
3	**3.6**	CF_3	0	100
4	**3.3-DME**	CF_3	16	84

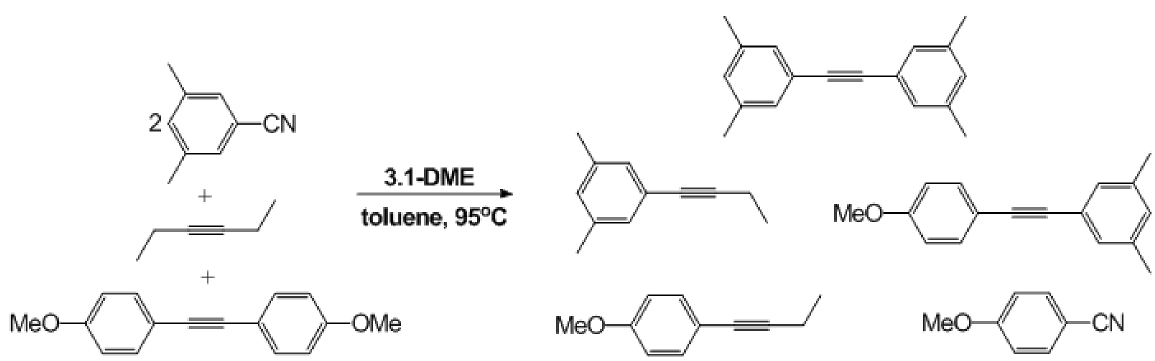
Table 3.3d. EtC≡[W] + *p*-C_6H_4XC≡C-*p*-C_6H_4X ← *p*-C_6H_4XC≡[W] + *p*-C_6H_4XC≡CEt.

Entry	Catalyst	X	W≡CEt, W(C_3Et_3), %	W≡CAr, %
1	**3.7**	OMe	present	present
2	**3.4-DME**	OMe	20	80
3	**3.8**	CF_3	trace	100
4	**3.5-DME**	CF_3	0	100

3.4 Nitrile-Alkyne Cross-Metathesis versus Alkyne Cross-Metathesis for Symmetrical Alkyne Formation

The pathway studies lead to three major conclusions. First, although the catalyst resting states were largely uninfluenced by the aryl nitrile, some reaction pathways were shutdown as a function of aryl nitrile. This reveals that subtle effects due to substrate electronic structure can influence NACM. Hammett studies were attempted with **3.1-DME** to further investigate the influence of substrate electronic structure; however, concurrent alkyne polymerization prevented the attainment of meaningful data.

Second, since ACM occurs at room temperature and NACM requires elevated temperatures, ACM is largely responsible for the production of symmetrical alkyne. The difference in ACM and NACM rates was also investigated through ^{1}H NMR studies of the interaction of 2 equivalents of 3,5-dimethylbenzonitrile with 1 equivalent of bis(4-methoxyphenyl)acetylene and 1 equivalent of 3-hexyne in the presence of **3.1-DME** in toluene at 95 °C. This system was selected because of the presence of well-defined spectral features for each of the possible products listed in Scheme 3.5. The product 1-(4-methoxyphenyl)-1-butyne can form only via ACM. All other products require NACM.



Scheme 3.5. ACM vs NACM with all possible products shown.

As illustrated in Spectrum A of Figure 3.2, the first 10 min of reaction results in only the formation of 1-(4-methoxyphenyl)-1-butyne. This indicates that the rapidly established statistical equilibrium of 1-(4-methoxyphenyl)-1-butyne and bis(4-methoxyphenyl)acetylene is solely due to ACM. Evidence of some NACM product formation is present after 3 h at 95 °C, as highlighted in the Spectrum B of Figure 3.3. Similar results were obtained with **3.2** as the catalyst, except that an extended amount of time was required in order to achieve an equilibrium mixture of 1-(4-methoxyphenyl)-1-butyne and bis(4-methoxyphenyl)acetylene.

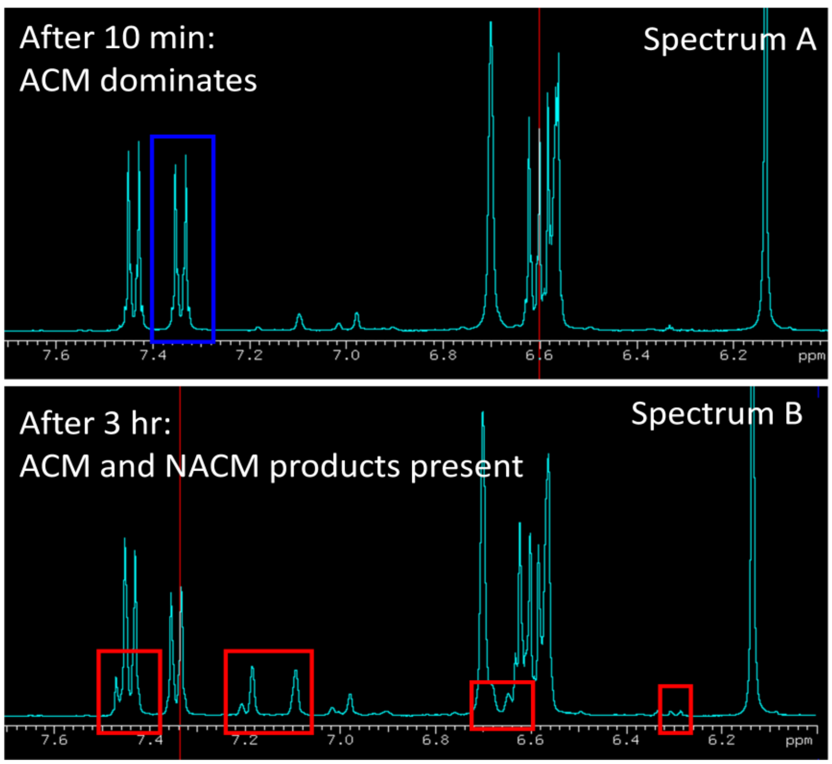
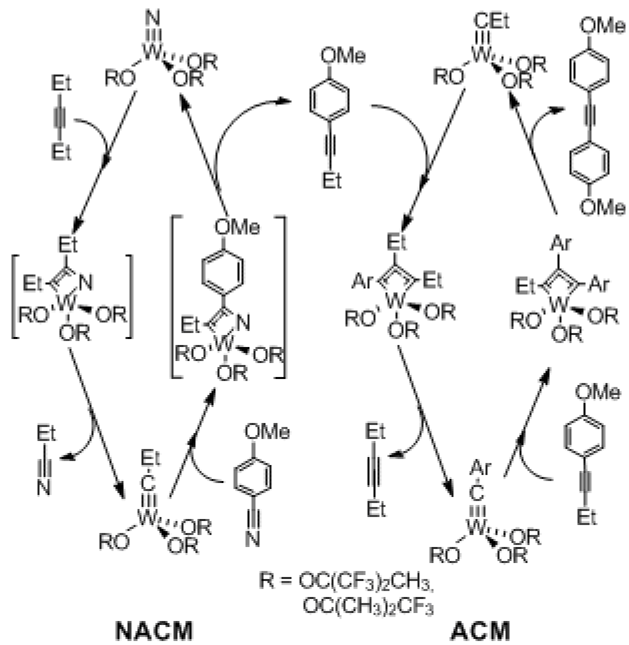


Figure 3.3. ^{1}H NMR studies of NACM vs ACM with **3.1-DME**.

From the pathway studies, it was noted that the alkoxide ligands do not significantly influence the rates of ACM. Instead, the difference in rate of equilibration of alkynes arises from differences in catalyst resting states. Thus, the smaller symmetrical-to-unsymmetrical alkyne ratios from NACM when $OCMe_2CF_3$ ligands are present is due to the suppression of ACM as a result of a tungsten nitride resting state. The increased symmetrical-to-unsymmetrical alkyne ratio when $OC(CF_3)_2Me$ ligands are employed is a result of a benzylidyne resting state, which favors rapid ACM.

Therefore, the formation of a symmetrical alkyne is best accounted for by initial NACM to generate an unsymmetrical alkyne followed by rapid ACM to afford the symmetrical alkyne in both catalyst systems (Scheme 3.6).



Scheme 3.6. Preferred pathways for formation of symmetrical alkynes.

3.5 DFT Calculations of Nitrile-Alkyne Cross-Metathesis Mechanism

Prof. Barry Dunietz and coworkers investigated the mechanism of NACM using a model system composed of $N{\equiv}W(OCMe_3)_3$ and 2-butyne to form $MeC{\equiv}W(OCMe_3)_3$ and acetonitrile. Although the specific findings and related discussion of the computational methods have been reported elsewhere, pertinent mechanistic details will be briefly summarized here.[1]

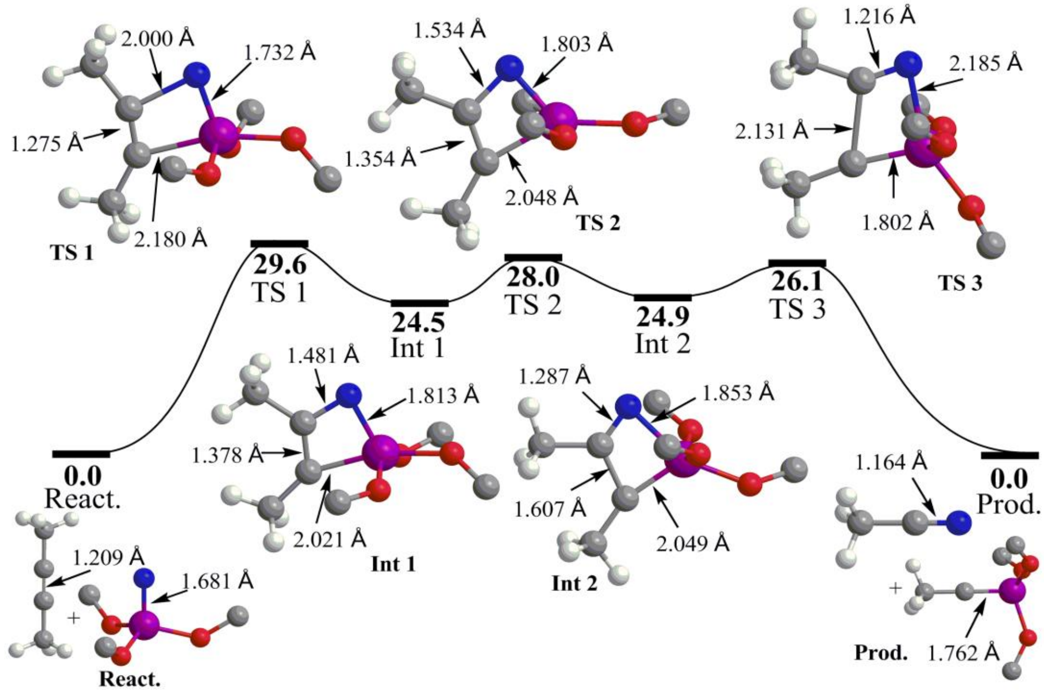
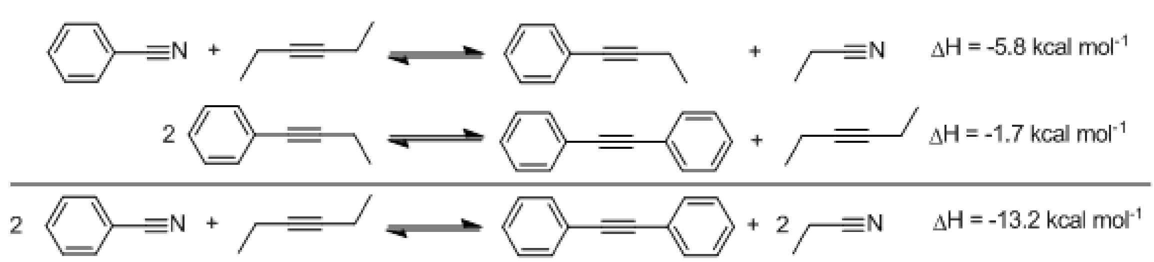


Figure 3.4. Calculated structures and relative Gibbs energies (kcal mol^{-1}) for nitride-alkylidyne complex interconversion in a model system. Hydrogen atoms have been removed from the methoxy groups for clarity.[1]

In this model system (Figure 3.4), the reactants and products are nearly isoenergetic with moderate barriers to metalacycle formation, thus accounting for the reversibility of NACM. This is achieved via a [2 + 2] cycloaddition-cycloreversion mechanism involving two azatungstenacyclobutadiene intermediates with significant bond localization in the W-N-C-C rings. The experimental $OCMe_2CF_3$ and $OCMe(CF_3)_2$ ligands are not quite accurately modeled by OMe. Decreased barriers to cyclobutadiene intermediate formation and stabilization of the alkylidyne complex with respect to the corresponding nitride complex would occur upon accounting for the increased fluorination in the experimental systems. This agrees with the experimental results, where the more fluorinated $OCMe(CF_3)_2$-ligated complex favors alkylidyne formation and the nitride catalyst is favored by $OCMe_2CF_3$ ligation. Comparison of this theoretical system with calculations on the analogous ACM system reveals lower barriers to metalacycle formation with ACM than NACM, 22.3 kcal mol^{-1} and 29.6 $kcal^{-1}$ mol, respectively.[2] This agrees with our pathway studies, which revealed that while ACM occurs rapidly at room temperature, NACM requires elevated temperatures.

3.6 Preferential Alkyne Formation

ACM should give rise to a statistical mixture of unsymmetrical and symmetrical alkynes. However, in these NACM systems a large preference for symmetrical alkyne formation is present. Thus, rapid ACM cannot solely account for the alkyne selectivity. Turning to thermodynamics (Scheme 3.7), it can be noted that the formation of an unsymmetrical alkyne from benzonitrile and 3-hexyne is favored in the gas phase ($\Delta H°$= -5.8 kcal mol^{-1}.)[3] Even more favored is the conversion of benzonitrile and 3-hexyne into a symmetrical alkyne, for which $\Delta H°$= -13.2 kcal mol^{-1}.[3] Therefore, symmetrical alkyne formation is enthalpically favored relative to unsymmetrical alkyne formation.

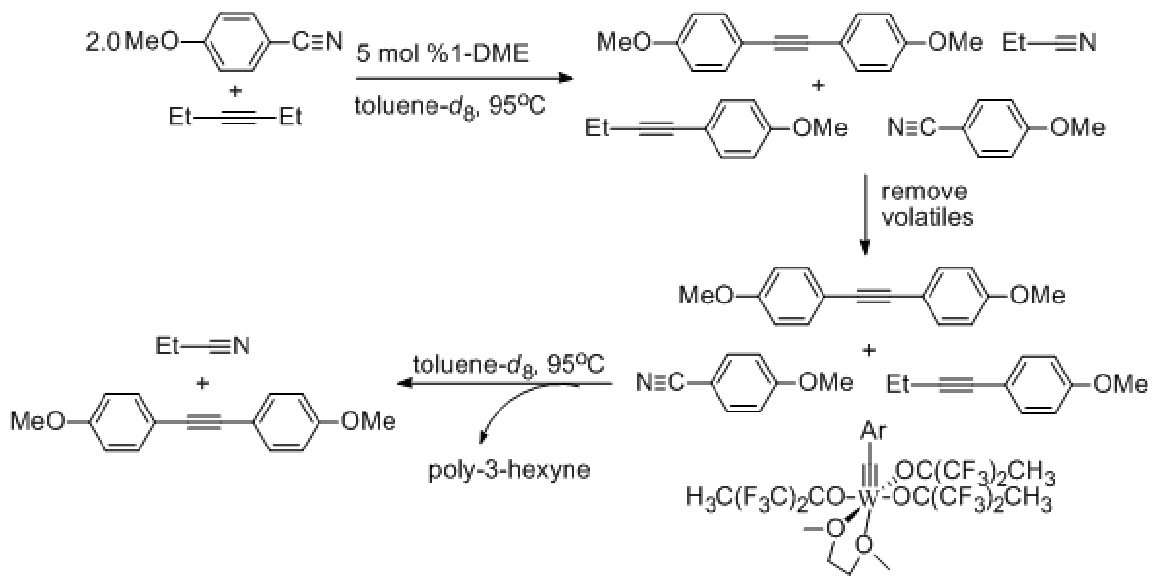


Scheme 3.7. Thermodynamically favored formation of a symmetrical alkyne.

In addition to thermodynamically driven alkyne formation, the simultaneous side reaction of alkyne polymerization shifts the reaction mixture towards production of symmetrical alkyne. This is accomplished through the removal of 3-hexyne from the system via polymerization to form insoluble poly(3-hexyne). In addition to direct observation of the insoluble polymer in reaction mixtures, the incomplete conversion of starting nitrile into alkyne products with complete consumption of 3-hexyne serves as indirect evidence of alkyne polymerization.

3.6.1 Selective Formation of Symmetrical Alkynes

Harnessing alkyne polymerization in conjunction with ACM allows one to purposely drive the NACM reaction towards symmetrical alkyne formation (Scheme 3.8). This is accomplished by allowing the NACM system to completely convert the nitrile to a mixture of alkyne products followed by removal of the volatile components from the reaction system. The resulting residue, consisting of unsymmetrical and symmetrical alkyne along with the catalyst in its final resting state is then reconstituted in toluene. At this point, the reaction mixture is heated to 95 °C to remove 3-hexyne from the system and shift the reaction mixture towards symmetrical alkyne via tandem ACM-alkyne polymerization of the unsymmetrical alkyne

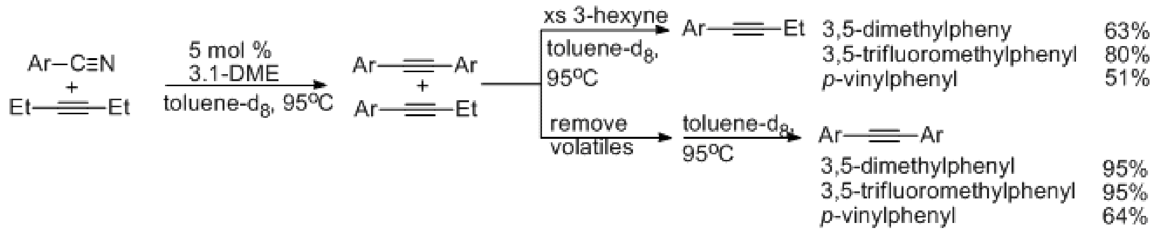


Scheme 3.8. Harnessing alkyne polymerization to form symmetrical alkynes.

Tandem ACM-alkyne polymerization can be achieved with **3.1-DME** as depicted in Scheme 3.9. Interestingly, when **3.2** is used there is no evidence of symmetrical alkyne formation. Since **3.2** has a catalyst resting state of the nitride complex, the low concentration of alkylidyne catalyst appears to preclude alkyne polymerization under the reaction conditions tested.

3.6.2 Selective Formation of Unsymmetrical Alkynes

In addition to selective formation of symmetrical alkynes, NACM can be applied to afford unsymmetrical alkynes preferentially. This is accomplished by introducing excess 3-hexyne into the NACM system. Scheme 3.9 highlights the ability to preferentially form symmetrical or unsymmetrical alkynes from the same starting materials by altering reaction conditions and relative ratios of the starting materials.

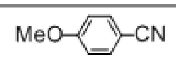
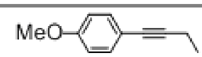
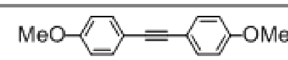
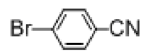
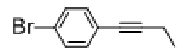
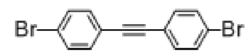
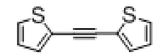
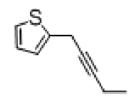
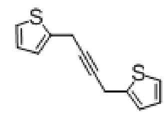
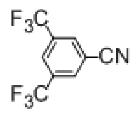
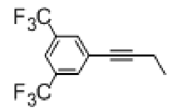
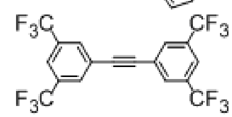
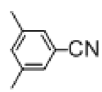
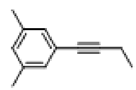
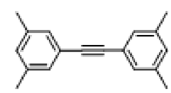
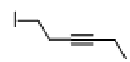
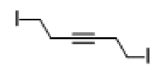
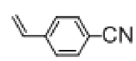
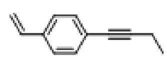
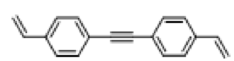
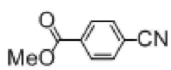
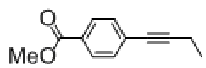
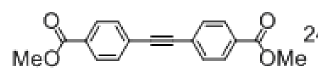
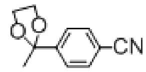
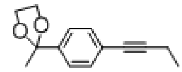
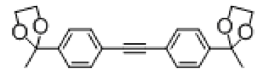
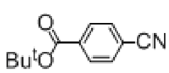
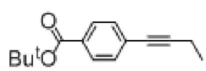
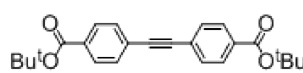
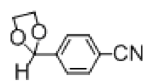
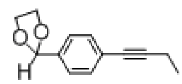
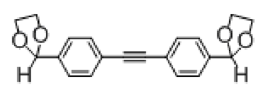
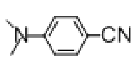
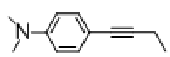
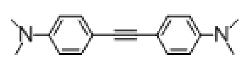


Scheme 3.9. Selective formation of symmetrical or unsymmetrical alkynes.

3.7 Substrate Scope

A survey of substrates was completed with the assistance of Eric Wiedner to analyze the functional group compatibility of **3.1-DME** and **3.2** (Table 3.4). Both aryl and alkyl-based nitriles are tolerated. Substituted nitriles possessing halide, alkyl, tertiary aniline, and vinyl groups are compatible with the catalysts. Although many Lewis basic substrates are not tolerated - including pyridines, amines, amides, anilines, ketones, aldehydes, nitroarenes, and alcohols - some are surprisingly compatible. Thiophenes, which have previously been reported to be incompatible with tungsten-based catalysts,[4,5] are one such substrate.

Table 3.4. Substrate survey with **3.1-DME** and **3.2**.

Entry	Starting Nitrile	Products (% Yield) Unsymmetrical Alkyne		Symmetrical Alkyne		Time (h)	3-hexyne (equiv)
1			11 18[a]		81 61[a]	8 31[a]	1.0 1.0[a]
2			0		100	15	2.0
3			19		41	11	2.0
4			0		75	22	2.0
5			5		95	25	2.0
6			<5		>95	24	2.0
7			40		33	6	2.0
8			34		64	13	1.6
9			76		24	24	3.0
10			19 58[a]		23 12[a]	11 25[a]	1.0 1.0[a]
11			43[a]		6[a]	20[a]	2.0[a]
12			4 25[a]		0 0[a]	12 25[a]	1.0 1.0[a]
13			69		13	18	2.0

95°C, toluene. NMR yields. [a] catalyst = **3.2**

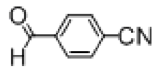
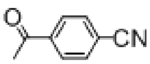
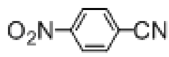
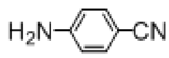
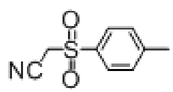
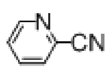
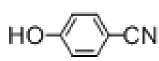
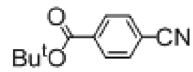
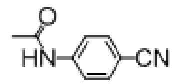
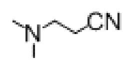
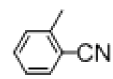
In order to overcome intolerance of ketones and aldehydes, acetals and ketals may be used in the system. Catalyst **3.2** is tolerant of a broader range of substrates than **3.1-DME**. The increased substrate tolerance of **3.2** likely stems from the reduced Lewis acidity of the metal center. Deactivation of **3.1-DME** by acetals and ketals occurs over time as the protecting groups are cleaved by the electrophilic tungsten center. Likewise, **3.1-DME** is incompatible with t-butyl esters, but the more acid-resistant methyl esters are tolerated. Other likely modes of catalyst deactivation include strong coordination by Lewis bases and protonolysis reactions.

Overall, this study demonstrates that some substrate incompatibilities with NACM catalysts can be overcome by adjusting the Lewis acidity of the metal center. Unfortunately, functional group tolerance of the first generation of NACM catalysts is more limited than that of the alkyne metathesis catalyst $Me_3CC{\equiv}W(OCMe_3)_3$.[6] However, NACM would be impossible in the current system without the relatively Lewis acidic metal centers that bring about substrate incompatibility.

3.7.1 Catalyst Deactivation Modes

In many cases the form of the catalyst that undergoes deactivation varied (Table 3.5). ^{1}H NMR spectroscopy indicated either complete conversion of **3.1-DME** to **3.3-DME** (Table 3.5: entries 1, 3, 5, 8, 12) prior to catalyst deactivation or immediate catalyst deactivation (Table 3.5: entries 2, 4, 6-7, and 9-11). Catalyst deactivation was detected through the addition of anisonitrile to the reaction mixtures. The absence of metathesis with anisonitrile indicated complete catalyst deactivation. When working with bulky substrates such as *t*-butyl nitriles and ortho-substituted benzonitriles, no catalyst deactivation was detected (Table 3.5: entries 13-14). However, with these bulky substrates, NACM was prevented and only alkyne polymerization was observed.

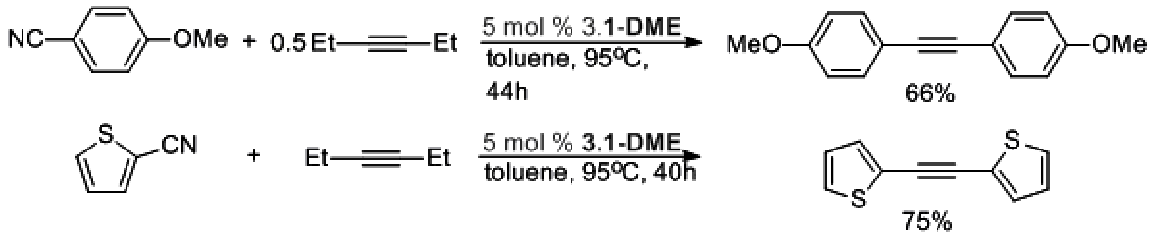
Table 3.5. Catalyst deactivation (indicated by Y) modes with incompatible substrates.

Entry	Starting Nitrile	Cat. Decomp. 3.1-DME	Cat. Decomp. 3.3-DME
1		N	Y
2		Y	
3		N	Y
4		Y	
5		N	Y
6		Y	
7		Y	
8		N	Y
9		Y	
10		Y	
11		Y	
12		N	Y
13		N	N
14		N	N

3.8 Applications

3.8.1 Preparative Scale Reactions

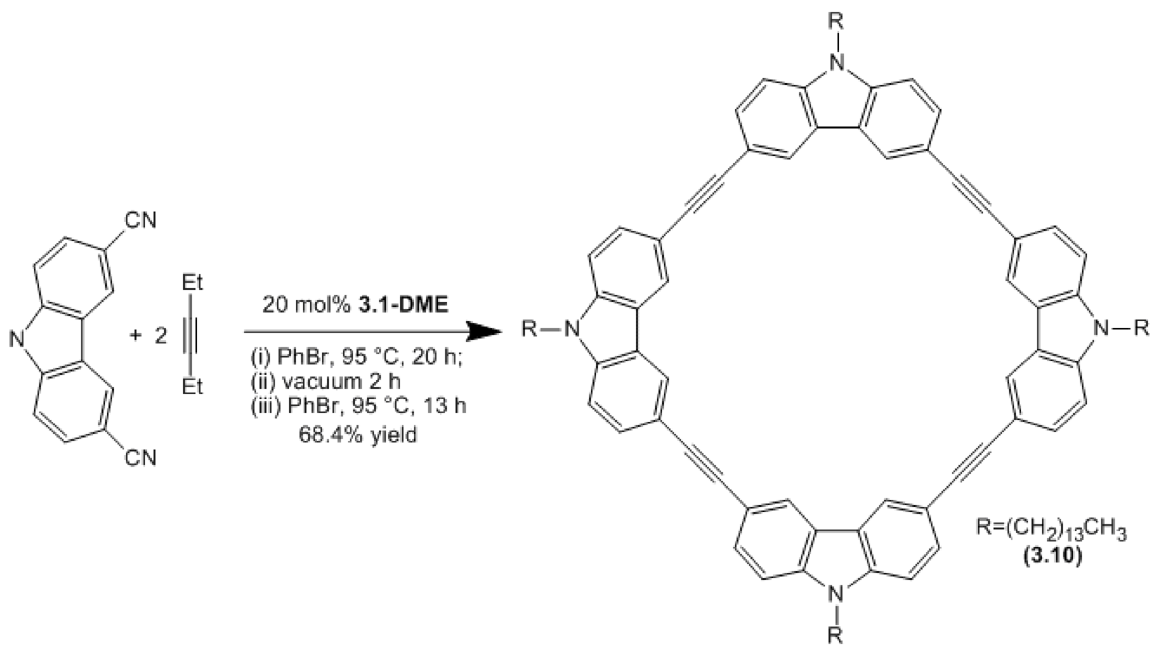
Following substrate compatibility analysis, we wanted to reveal the synthetic utility of NACM. This was accomplished by demonstrating the scalability of these reactions. Two reactions were selected for scale-up as depicted in Scheme 3.10, with both symmetrical alkynes being isolated in good yield.



Scheme 3.10. Preparative scale NACM reactions to afford symmetrical alkynes.

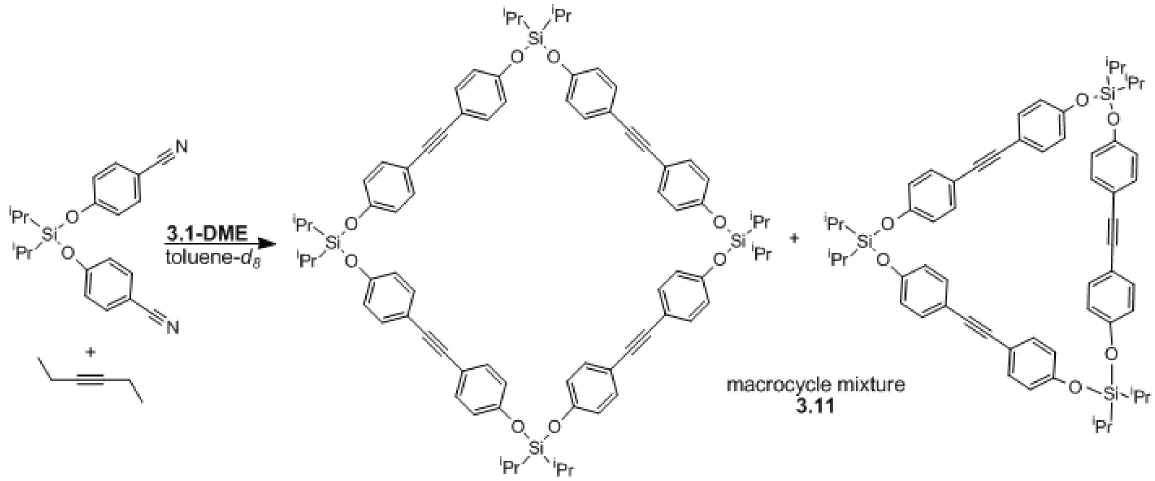
3.8.2 Macrocycle Formation

Extension of NACM to more complicated systems is desired. As proof of concept, we pursued the synthesis of large arylene-ethynylene macrocycles. Interest in these materials stems from their potential for applications in nanomaterials and nanodevices.[7] The macrocycle (**3.10**) shown in Scheme 3.11, originally developed by Moore, has been used as a component to detect explosive materials.[7] Eric Wiedner was able to successfully synthesize **3.10** via a shorter pathway than current syntheses. It consisted of two fewer steps and avoids a palladium cross-coupling reaction.[1] The pure product was obtained in similar yields to the best alternative route.[8] During the course of the preparation of **3.10**, ^{1}H NMR spectroscopy revealed initial oligomerization prior to ring closing, which is known to occur in ring-closing metathesis reactions.[9,10]



Scheme 3.11. NACM to afford an isolable arylene-ethynylene macrocycle.

The synthesis of other macrocycles was attempted using NACM (Scheme 3.12). Unfortunately, selective ring formation was not observed. Instead, multiple ring species were formed as a result of the lack of rigidity in the macrocycle (mixture **3.11**). Heating the reaction to a variety of temperatures did not appear to increase selectivity, as additional ring sizes appeared to form at elevated temperatures. Despite the lack of ring selectivity, the ability to form other macrocycles via NACM has been illustrated.



Scheme 3.12. NACM to afford a mixture of macrocycles.

3.9 Conclusions

Pathway studies revealed that the ancillary ligands greatly influence the catalyst resting states in NACM. Ligation with $OCMe_2CF_3$ results in **3.2** as a resting state, while the resting state with $OC(CF_3)_2Me$ is the benzylidyne species. Slight system perturbations are observed as a result of the electronic influence of the aryl nitrile. For instance, one cycle of NACM is no longer reversible with **3.2** in the presence of a benzonitrile with a *p*-substituted strongly electron-withdrawing group. In spite of the subtle electronic influences of the substrates, all steps of NACM are reversible with **3.1-DME**. Furthermore, the proposed mechanism of NACM, involving a [2 + 2] cycloaddition-cycloreversion, is supported by DFT calculations.

The variation in catalyst resting state as a function of alkoxide ligands influences the production of symmetrical alkyne. An alkylidyne/benzylidyne resting state favors rapid ACM, while a nitride resting state suppresses ACM. Consequently, more symmetrical alkyne is formed in reactions catalyzed by **3.1-DME** than by **3.2**. The general method for formation of the symmetrical alkyne involves NACM to produce an unsymmetrical alkyne followed by ACM to produce the symmetrical alkyne. A large preference for symmetrical alkyne formation can be achieved by means of tandem ACM-alkyne polymerization. Conversely, the unsymmetrical alkyne can be favored by addition of excess 3-hexyne to the reaction system.

Substrate compatibility was broadest with **3.2**, although **3.1-DME** was most active. A variety of functional groups were tolerated with the exception of several Lewis basic substrates. Previously observed tungsten-alkylidyne incompatibility with thiophenes was not observed with our system. The catalyst deactivation mode was substrate-dependent, with **3.1-DME** occasionally converting to **3.3-DME** prior to deactivation. The synthetic utility of NACM was demonstrated through the successful synthesis of an arylene-ethynylene macrocycle and two reactions completed on a preparative scale.

3.10 Experimental

3.10.1 General Procedures

All reactions were performed in an atmosphere of dinitrogen, either in a nitrogen-filled MBRAUN Labmaster 130 glove box or by using standard air-free techniques.[11] ^{1}H NMR spectra were recorded at 499.909 MHz, 399.967 MHz on a Varian Inova 400 spectrometer or 300.075 MHz on a Varian Inova 300 spectrometer and referenced to the residual protons in toluene-d_8 (2.09 ppm). ^{19}F NMR spectra were recorded at 282.384

MHz on a Varian Inova 300 spectrometer or 376.326 MHz on a Varian Inova 400 spectrometer and were referenced to an external standard of $CFCl_3$ in $CDCl_3$ (0.00 ppm). ^{13}C NMR spectra were recorded at 75.465 MHz on a Varian Inova 300 spectrometer and were referenced to naturally abundant ^{13}C nuclei in CD_2Cl_2 (54.00 ppm). GC/MS data were collected on a Shimadzu GCMS-QP5000 with a Restek XTI-5 phase column (30m, 0.25 I.D., 0.25 D. F.). Trace GC/MS data were collected on a Finnigan Trace GCMS 2000 with a DB-1 capillary column (25m, 0.2 I.D., 0.33 D. F.).

3.10.2 Materials

All solvents used were dried and deoxygenated by the method of Grubbs.[12] 1-(4-methoxyphenyl)-1-butyne,[13] 1-(4-trifluoromethylphenyl)-1-butyne,[13] 3,5-dimethylbenzonitrile,[15] bis(4-trifluoromethylphenyl)acetylene,[14] 4-(1-(ethylenedioxy)ethyl)benzonitrile,[16] 4-(1,3-dioxolan-2-yl)benzonitrile,[17] 4,4′-(diisopropylsilanediyl)bis(oxy)dibenzonitrile,[19] *t*-butyl-4-cyanobenzoate,[18] 4-butynylbenzaldehyde,[13] and $[N{\equiv}W(OCMe_2CF_3)_3]_3$ (**3.2**)[20] were prepared according to literature procedures. $N{\equiv}W(OCMe(CF_3)_2)_3(DME)$ (**3.1-DME**), $EtC{\equiv}W(OCMe(CF_3)_2)_3(DME)$ (**3.3-DME**), *4*-$MeOC_6H_4C{\equiv}W(OCMe(CF_3)_2)_3(DME)$ (**3.4-DME**), *4*-$F_3CC_6H_4C{\equiv}W(OCMe(CF_3)_2)_3(DME)$ (**3.5-DME**), $EtC{\equiv}W(OCMe_2CF_3)_3$ (**3.6**), *4*-$MeOC_6H_4C{\equiv}W(OCMe_2CF_3)_3$ (**3.7**), and *4*-$F_3CC_6H_4C{\equiv}W(OCMe_2CF_3)_3$ (**3.8**) were prepared according to Section 2.9.3. $(Et_3C_3)W(OCMe(CF_3)_2)_3$ (**3.12**) was made *in situ* as described in Section 2.9.3. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried over 4Å molecular sieves for at least 24 hours. Anisonitrile, 3-aminopropionitrile, *p*-aminobenzonitrile, *p*-dimethylaminobenzontrile, *p*-

nitrobenzonitrile, trimethylacetonitrile, *p*-hydroxybenzonitrile, 2-cyanopyridine, trichloroacetonitrile, *p*-toluenesulfonic acid monohydrate, 4-cyanostyrene, 4-bromostyrene, 4-nitrobenzonitrile, 3-(dimethylamino)propionitrile, 4-acetylbenzonitrile, N-methyl-β-alaninenitrile, *p*-tolunitrile, and 3-hexyne were obtained from Acros. 3,5-bis(trifluoromethyl)benzonitrile was obtained from Matrix Scientific. Pentanenitrile was obtained from GFS Chemicals. 2-thiophenecarbonitrile was obtained from Oakwood Chemicals. Propionitrile, *p*-bromobenzonitrile, 4-cyano-benzoic acid methyl ester, 2-thiopheneacetonitrile and 1,3,5-trimethoxybenzene were obtained from Aldrich. 4-cyanobenzaldehyde and *p*-toluenesulfonyl acetonitrile were obtained from Alfa Aesar. 2-hydroxybenzonitrile was obtained from Fluka. 4-trifluoromethylbenzonitrile was obtained from TCI. All liquid nitriles and 3-hexyne were dried for 24 hours using 4Å molecular sieves. 2-thiopheneacetonitrile was distilled prior to use. All other reagents were used as received.

3.10.3 High Temperature ^{19}F NMR Studies

The reactions were monitored at 95 °C via ^{19}F NMR spectroscopy on the 300 MHz NMR instrument. Spectra were acquired every 5 min over 2 h.

With 3.1-DME. 4-trifluoromethylbenzonitrile (20.6 mg, 0.120 mmol, 20 equiv) and **3.1-DME** (5.0 mg, 0.0060 mmol) were combined and dissolved in toluene-d_8 (1 mL). To this solution was added 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) via syringe.

With 3.2. 4-trifluoromethylbenzonitrile (59.0 mg, 0.345 mmol, 20 equiv) and **3.2** (10.0 mg, 0.0172 mmol) were combined and dissolved in toluene-d_8 (0.5 mL). To this solution was added 3-hexyne (19.6 μL, 0.172 mmol, 10 equiv) via syringe.

3.10.4 Metalacycle Formation Reaction for Pathway Study Reference

$(Et_3C_3)W(OCMe_2CF_3)_3$ (3.13). Complex **3.6** (160.0 mg, 0.264 mmol) was dissolved in CD_2Cl_2 (500 μL). 3-hexyne (33.0 μL, 0.290 mmol, 1.1 equiv) was introduced to the solution via syringe. The resulting ^{1}H NMR spectrum was observed at −60 °C. The complete removal of volatiles resulted in conversion to **3.6**. ^{1}H NMR (300 MHz, tol-d_8, −60 °C): δ 3.56 (q, 4H, $C_\alpha CH_2CH_3$, J=7.0 Hz), 2.62 (q, 2H, $C_\beta CH_2CH_3$, J=7.0 Hz), 1.81 (s, 6H, $OC(CH_3)_2CF_3$), 1.37 (t, 6H, $C_\alpha CH_2CH_3$, J=7.0 Hz), 1.65 (s, 18H, $OC(CH_3)_2CF_3$), 0.95 (s, 18H, $OC(CH_3)_2CF_3$), 0.76 (t, 3H, $C_\beta CH_2CH_3$, J=7.0 Hz). ^{19}F NMR (300 MHz, tol-d_8, −60 °C): δ −81.30 (s, 6F, $OC(CH_3)_2CF_3$ *ax*), −81.55 (s, 3F, $OC(CH_3)_2CF_3$ *eq*). $^{13}C\{^1H\}$ NMR (300 MHz, CD_2Cl_2, −60 °C): δ 238.19 (t, W−C_α, $J_{W\text{-}C}$=61.7 Hz), 130.47 (s, W−C_β), 127.92 (q, $OC(CH_3)_2CF_3$ *eq*, $J_{C\text{-}F}$=286.2 Hz), 27.60 (q, $OC(CH_3)_2CF_3$ *ax*, $J_{C\text{-}F}$=287.4 Hz), 81.25 (q, $OCCF_3(CH_3)_2$ *eq*, $J_{C\text{-}F}$=28.5 Hz), 76.34 (q, $OCCF_3(CH_3)_2$ *ax*, $J_{C\text{-}F}$=27.3 Hz), 29.97 (s, $OC(CH_3)_2CF_3$ *eq*), 25.08 (s, $C_\alpha CH_2CH_3$), 25.62 (s, $OC(CH_3)_2CF_3$), 20.02 (s, $C_\beta CH_2CH_3$), 14.26 (s, CH_3), 12.30 (s, CH_3).

3.10.5 Pathway Study Reactions with $N{\equiv}W(OCMe(CF_3)_2)_3(DME)$

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (3.9 mg, 0.024 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.1-DME** (20.0 mg, 0.0241 mmol) and an internal standard of 1,3,5-

trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 24 mM in toluene-d_8 (based on **3.1-DME**). The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. After 20 min the reaction mixture was composed of the following W-containing species: **3.4-DME** (80%), **3.1-DME** (6%), and **3.3-DME** (14%). The aryl moiety was distributed as follows: **3.4-DME** (82%), anisonitrile (4%), bis(4-methoxyphenyl)acetylene (6%), 1-(4-methoxyphenyl)-1-butyne (8%). After this point, polymerization of the ethyl unit to form poly-3-hexyne shifted the reaction mixture towards formation of the nitride. After 8 h the W-containing complex distribution was **3.4-DME** (82%), **3.1-DME** (7%), **3.3-DME** (11%). The aryl moiety was distributed as follows: **3.4-DME** (85%), anisonitrile (4%), bis(4-methoxyphenyl)acetylene (9%), 1-(4-methoxyphenyl)-1-butyne (2%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 7.60 min), 162 ($C_{11}H_{12}O$, R_t 8.30 min), 238 ($C_{16}H_{14}O_2$, R_t 15.08 min)

1,2-bis(4-methoxyphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-methoxyphenyl)acetylene (2.9 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.1-DME** (10.0 mg, 0.0120 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 24 mM in toluene-d_8 (based on **3.1-DME**). The reaction progress was monitored at room temperature via ^{1}H NMR spectroscopy. After 46 h the distribution of W-containing species was **3.1-DME** (54%) and **3.4-DME** (46%). The aryl moiety was distributed as follows: bis(4-methoxyphenyl)acetylene (50%), **3.4-DME** (27%), and anisonitrile (23%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 7.61 min), 238 ($C_{16}H_{14}O_2$, R_t 15.74 min)

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-trifluoromethylphenyl)-1-butyne (2.0 mg, 0.0099 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.1-DME** (8.3 mg, 0.0099 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 10 mM in toluene-d_8 (based on **3.1-DME**). No reaction was observed at room temperature over 4 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. An equilibrium mixture was achieved after 20 min consisting of W-containing species **3.1-DME** (13%) and **3.5-DME** (87%). The aryl moiety was distributed as follows: bis(4-trifluoromethylphenyl)acetylene (6%), **3.5-DME** (89%), and 1-(4-trifluoromethylphenyl)-1-butyne (5%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 314 ($C_{16}H_8F_6$, R_t 8.59 min)

bis(4-trifluoromethylphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-trifluoromethylphenyl)acetylene (7.6 mg, 0.024 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.1-DME** (20.0 mg, 0.0241 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 24 mM in toluene-d_8 (based on **3.1-DME**). No reaction was observed at room temperature over 3 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. An equilibrium mixture was achieved after 3.7 h consisting of W-containing complexes **3.1-DME** (67%) and **3.5-DME** (33%). The aryl moiety was distributed as follows: bis(4-trifluoromethylphenyl)acetylene (38%), **3.5-DME** (33%), and 4-trifluoromethylbenzonitrile (29%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 12.247 min), (314 ($C_{16}H_8F_6$, R_t 18.127 min)

3.10.6 Pathway Study Reactions with EtC≡W(OCMe(CF$_3$)$_2$)$_3$(DME)

Propionitrile. Complex **3.3-DME** (20.0 mg, 0.0233 mmol) was dissolved in toluene-d_8 (1 mL) and placed in a J. Young tube. EtCN (1.6 μL, 0.023 mmol, 1 equiv) was added to this solution via syringe. An internal standard of 1,3,5-trimethoxybenzene was also added. No reaction was observed at room temperature over 21 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. The reaction endpoint was achieved after 3 h with the W-containing species remaining including a combination of **3.12** and **3.3-DME** (72%) and **3.1-DME** (28%).

Anisonitrile. From a stock solution in toluene-d_8, anisonitrile (3.1 mg, 0.023 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (20.0 mg, 0.023 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 12 mM in toluene-d_8 (based on **3.3-DME**). Only slight reaction was observed at room temperature after 21.5 h with the following W-containing species being present in solution: **3.10** and **3.3-DME** (80%), **3.1-DME** (10%), **3.4-DME** (10%). The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. After 20 min the reaction mixture contained **3.4-DME** (78%), **3.1-DME** (12%), and **3.3-DME** (10%). The aryl moiety was distributed as follows: **3.4-**

DME (71%), anisonitrile (23%), bis(4-methoxyphenyl)acetylene (3%), and 1-(4-methoxyphenyl)-1-butyne (3%). After this point, polymerization of the ethyl unit to form poly-3-hexyne shifted the reaction mixture towards formation of **3.4-DME**. After 43 h the W-containing complex distribution was **3.4-DME** (73%) and **3.1-DME** (27%). The aryl moiety was distributed as follows: **3.4-DME** (71%), anisonitrile (26%), and bis(4-methoxyphenyl)acetylene (3%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 5.657 min).

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (1.9 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (10.0 mg, 0.0117 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 22 mM in toluene-d_8 (based on **3.3-DME**). The reaction progress was monitored at room temperature via ^{1}H NMR spectroscopy. After 10 min the W-containing species included **3.4-DME** (69%), **3.3-DME** (22%), and **3.12** (9%). The aryl moiety was distributed as follows: **3.4-DME** (72%), 1-(4-methoxyphenyl)-1-butyne (26%), and bis(4-methoxyphenyl)acetylene (2%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 162 ($C_{11}H_{12}O$, R_t 8.30 min), 238 ($C_{16}H_{14}O_2$, R_t 15.06 min)

bis(4-methoxyphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-methoxyphenyl)acetylene (2.8 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (10.0 mg, 0.0117 mmol) and an internal standard of 1,3,5-

trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 22 mM in toluene-d_8 (based on **3.3-DME**). The reaction progress was monitored at room temperature via ^{1}H NMR spectroscopy. After 9.5 h the W-containing species included **3.4-DME** (93%) and **3.3-DME** (6%). The aryl moiety was distributed as follows: **3.4-DME** (63%), 1-(4-methoxyphenyl)-1-butyne (9%), and bis(4-methoxyphenyl)acetylene (28%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 162 ($C_{11}H_{12}O$, R_t 8.29 min), 238 ($C_{16}H_{14}O_2$, R_t 15.07 min)

***p*-trifluoromethylbenzonitrile.** From a stock solution in toluene-d_8, *p*-trifluoromethylbenzonitrile (2.0 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (10.0 mg, 0.0117 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 22 mM in toluene-d_8 (based on **3.3-DME**). No reaction was observed at room temperature. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. An equilibrium mixture was achieved after 20 min consisting of W-containing complexes **3.1-DME** (13%) and **3.5-DME** (87%). The aryl moiety was distributed as follows: bis(4-trifluoromethylphenyl)acetylene (10%), **3.5-DME** (78%), *p*-trifluoromethylbenzonitrile (6%), and 1-(4-trifluoromethylphenyl)-1-butyne (6%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 3.66 min), 198 ($C_{11}H_9F_3$, R_t 6.04 min), 314 ($C_{16}H_8F_6$, R_t 10.61 min).

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-trifluoromethylphenyl)-1-butyne (2.3 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (10.0 mg, 0.0117 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 12 mM in toluene-d_8 (based on **3.3-DME**). No reaction was observed at room temperature. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. The reaction endpoint was achieved after 8 h with the W-containing species including **3.5-DME** (79%), **3.3-DME** (21%), and trace **3.12**. The aryl moiety was distributed as follows: **3.5-DME** (76%), 1-(4-trifluoromethylphenyl)-1-butyne (22%), and bis(4-trifluoromethylphenyl)acetylene (2%). The volatiles were removed *in vacuo* (including unsymmerical alkyne). The resulting mixture was dissolved in dichloromethane and filtered through silica. Trace GC/MS $[M/Z]^+$: 314 ($C_{16}H_8F_6$, R_t 10.61 min).

bis(4-trifluoromethylphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-trifluoromethylphenyl)acetylene (3.7 mg, 0.012 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.3-DME** (10.0 mg, 0.0117 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 12 mM in toluene-d_8 (based on **3.3-DME**). No reaction was observed at room temperature. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. The reaction endpoint was achieved after 8 h with the W-containing complexes including **3.5-DME** (84%), **3.3-DME** (10%), and **3.10** (6%). The aryl moiety was distributed as follows: **3.5-DME** (45%), 1-(4-trifluoromethylphenyl)-1-butyne

(26%), and bis(4-trifluoromethylphenyl)acetylene (29%). Removed volatiles *in vacuo* (including unsymmerical alkyne). Took up resulting mixture in dichloromethane and filtered through silica. GC/MS $[M/Z]^+$: 314 ($C_{16}H_8F_6$, R_t 18.123 min).

3.10.7 Pathway Study Reactions with *4*-MeOC$_6$H$_4$C≡W(OCMe(CF$_3$)$_2$)$_3$(DME)

3-hexyne. Complex **3.4-DME** (10.0 mg, 0.0107 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, 3-hexyne (1.2 μL, 0.010 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. The reaction progress was monitored at room temperature via ^{1}H NMR spectroscopy. After 1.25 h the reaction mixture contained **3.4-DME** (48%), **3.12** (14%), and **3.3-DME** (38%). The aryl moiety was distributed as follows: **3.4-DME** (53%), 1-(4-methoxyphenyl)-1-butyne (6%), bis(4-methoxyphenyl)acetylene (41%). After this point, polymerization of the ethyl unit to form poly-3-hexyne shifted the reaction mixture towards formation of **3.4-DME**. After 29 h the W-containing complex distribution was **3.4-DME** (73%) and combination of **3.10** and **3.3-DME** (27%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 162 ($C_{11}H_{12}O$, R_t 8.30 min), 238 ($C_{16}H_{14}O_2$, R_t 15.07 min).

Propionitrile. Complex **3.4-DME** (20.0 mg, 0.0214 mmol) was dissolved in toluene-d_8 (1.0 mL) and transferred to a J. Young tube. To this solution, EtCN (1.5 μL, 0.021 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. No reaction occurred after 20.5 h at room temperature. The reaction mixture was heated at 95 °C and progress was monitored via ^{1}H NMR spectroscopy. After 59 h the reaction mixture contained **3.1-DME** (42%), **3.4-DME** (39%), and **3.3-DME** (19%). The aryl moiety was distributed as follows: **3.4-DME** (56%), anisonitrile (38%), and bis(4-methoxyphenyl)acetylene (6%). After the point, reaction monitoring was discontinued due to the slow rate of polymerization of the ethyl units to form poly-3-hexyne. The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 5.653 min).

Anisonitrile. From a stock solution in toluene-d_8, anisonitrile (2.8 mg, 0.021 mmol, 1 equiv) was placed in a J. Young tube. To this solution **3.4-DME** (20 mg, 0.021 mmol) and internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 21 mM in toluene-d_8 (based on **3.4-DME**). No reaction was observed at room temperature over 21 h. The reaction mixture was heated at 95 °C and monitored by ^1H NMR spectroscopy. An equilibrium mixture was achieved after 6 h consisting of tungsten containing complexes **3.1-DME** (49%) and **3.4-DME** (51%). The aryl moiety was distributed as follows: anisonitrile (51%), **3.4-DME** (38%), and bis(4-methoxyphenyl)acetylene (11.4%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 7.59 min).

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (1.7 mg, 0.010 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.4-DME** (10 mg, 0.010 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 20 mM in toluene-d_8 (based on **3.4-DME**). The reaction endpoint was achieved in 2 h at room temperature with the W-containing complex distribution as follows: **3.4-DME** (80%) and a combination of **3.12** and **3.3-DME** (20%). The aryl moiety was distributed as follows: **3.4-DME** (69%), 1-(4-methoxyphenyl)-1-butyne (18%), bis(4-methoxyphenyl)acetylene (13%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 162 ($C_{11}H_{12}O$, R_t 8.90 min), 238 ($C_{16}H_{14}O_2$, R_t 15.07 min)

3.10.8 Pathway Study Reactions with *4*-$F_3CC_6H_4C{\equiv}W(OCMe(CF_3)_2)_3(DME)$

3-hexyne. Complex **3.5-DME** (10.0 mg, 0.0103 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, 3-hexyne (1.2 μL, 0.010 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. The reaction progress was monitored at room temperature via ^1H NMR spectroscopy. After 3 h the reaction mixture contained **3.5-DME** (51%), **3.10** (16%), and **3.3-DME** (33%). The aryl moiety was distributed as follows: **3.5-DME** (49%) and 1-(4-trifluoromethylphenyl)-1-butyne (51%). After this point, polymerization of the ethyl unit to form poly-3-hexyne shifted the reaction mixture towards formation of **3.5-DME**. After 72 h the W-containing complex distribution was **3.5-DME** (86%) and a combination of **3.12** and **3.3-DME** (14%). The aryl moiety was distributed as follows: **3.5-DME** (79%), 1-(4-trifluoromethylphenyl)-1-butyne (18%), and bis(4-trifluoromethylphenyl)acetylene (3%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 198 ($C_{11}H_9F_3$, R_t 6.04 min), 314 ($C_{16}H_8F_6$, R_t 10.63 min)

Propionitrile. Complex **3.5-DME** (10.0 mg, 0.0103 mmol) was dissolved in toluene-d_8 (500 µL) and placed in a J. Young tube. EtCN (0.7 µL, 0.01 mmol, 1 equiv) was added to this solution via syringe. An internal standard of 1,3,5-trimethoxybenzene was added. No reaction was observed at room temperature over 4 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. The reaction endpoint was achieved after 30 min with the W-containing species remaining including: **3.5-DME** (83%) and **3.1-DME** (17%). The aryl moiety was distributed as follows: **3.5-DME** (83%), 1-(4-trifluoromethylphenyl)-1-butyne (9%), bis(4-trifluoromethylphenyl)acetylene (7%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 3.63 min), 198 ($C_{11}H_9F_3$, R_t 6.02 min), 314 ($C_{16}H_8F_6$, R_t 10.63 min)

***p*-trifluoromethylbenzonitrile.** From a stock solution in toluene-d_8, *p*-trifluoromethylbenzonitrile (1.8 mg, 0.010 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.5-DME** (10.0 mg, 0.0103 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 21 mM in toluene-d_8 (based on **3.5-DME**). No reaction was observed at room temperature over 5.5 h. The reaction mixture was heated at 95 °C and monitored by ^{1}H NMR spectroscopy. An equilibrium mixture was achieved after 3.5 h consisting of W-containing species **3.1-DME** (65%) and **3.5-DME** (35%). The aryl moiety was distributed as follows: bis(4-trifluoromethylphenyl)acetylene (27%), **3.5-DME** (35%), *p*-trifluoromethylbenzonitrile (38%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 12.247 min), 314 ($C_{16}H_8F_6$, R_t 18.127 min)

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-trifluoromethylphenyl)-1-butyne (2.0 mg, 0.010 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.5-DME** (10.0 mg, 0.0103 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 21 mM in toluene-d_8 (based on **3.5-DME**). The reaction progress was monitored at room temperature via ^{1}H NMR spectroscopy. Throughout the reaction **3.5-DME** was the only W-containing species observed. After 68.5 h the aryl moiety was distributed as follows: **3.5-DME** (59%), 1-(4-trifluoromethylphenyl)-1-butyne (19%), bis(4-trifluoromethylphenyl)acetylene (22%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 198 ($C_{11}H_9F_3$, R_t 6.03 min), 314 ($C_{16}H_8F_6$, R_t 10.63 min)

3.10.9 Pathway Study Reactions with $[N{\equiv}W(OCMe_2CF_3)_3]_3$

3-hexyne. Complex **3.2** (10.0 mg, 0.0173 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, 3-hexyne (2.0 μL, 0.017 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. No reaction was observed at room temperature. The reaction mixture was heated at 95 °C and monitored by ^{1}H and ^{19}F NMR spectroscopy. After 16 h all 3-hexyne had been consumed and the catalyst resting state consisted of **3.6** (9%), **3.9** (26%), and remaining **3.2** (63%). Additionally, an unidentified volatile F-containing species was present in the reaction mixture. This is likely a by-product of the decomposition of **3.2** under these reaction conditions.

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (2.8 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.2** (10.0 mg, 0.0173 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 35 mM in toluene-d_8 (based on **3.2**). The reaction mixture was monitored by ^{1}H and ^{19}F NMR spectroscopy at 95 °C, since no reaction occurred at room temperature. After 3 h no further conversion of the reaction mixture, containing **3.7** (11%), **3.9** (14%), and **3.2** (75%), was observed. The reaction mixture, largely bis(4-methoxyphenyl)acetylene with traces of anisonitrile, 1-(4-methoxyphenyl)-1-butyne, and propionitrile was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 7.62 min), 162 ($C_{11}H_{12}O$, R_t 11.08 min), 238 ($C_{16}H_{14}O_2$, R_t 15.06 min).

1,2-bis(4-methoxyphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-methoxyphenyl)acetylene (4.1 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.2** (10.0 mg, 0.0173 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 35 mM in toluene-d_8 (based on **3.2**). Only slight catalyst degradation to **3.9** was observed at room temperature over 16 hr. The reaction mixture was then heated at 95 °C for 21 h to afford 9% conversion to anisonitrile with a W-containing species distribution of **3.7** (7%), **3.9** (17%), and **3.2** (76%). Additional heating only resulted in further formation of **3.9**. The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 133 (C_8H_7ON, R_t 7.26 min), 238 ($C_{16}H_{14}O_2$, R_t 15.05 min).

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-*d*$_8$, 1-(4-trifluoromethylphenyl)-1-butyne (6.9 mg, 0.035 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.2** (20.0 mg, 0.0345 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 35 mM in toluene-*d*$_8$ (based on **3.2**). No reaction was observed at room temperature. The reaction progress was then monitored at 95 °C via ^{1}H NMR spectroscopy. After 10 hr the W-containing species were **3.8** (25%), **3.9** (33%) and remaining **3.2** (42%). The aryl moiety was distributed as follows: **3.8** (29%), 1-(4-trifluoromethylphenyl)-1-butyne (48%), and bis(4-trifluoromethylphenyl)acetylene (23%). No further conversion of 1-(4-trifluoromethylphenyl)-1-butyne was evident upon additional heating. The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 198 ($C_{11}H_9F_3$, R_t 14.37 min), 314 ($C_{16}H_8F_6$, R_t 18.13 min).

1,2-bis(4-trifluoromethylphenyl)acetylene. From a stock solution in toluene-*d*$_8$, bis(4-trifluoromethylphenyl)acetylene (5.4 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.2** (10.0 mg, 0.0173 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 35 mM in toluene-*d*$_8$ (based on **3.2**). No metathesis was observed at room temperature or 95 °C via ^{1}H NMR spectroscopy. Took up resulting mixture in dichloromethane and filtered through silica. GC/MS $[M/Z]^+$: trace 171 ($C_8H_4NF_3$, R_t 11.633 min), 314 ($C_{16}H_8F_6$, R_t 17.630 min).

3.10.10 Pathway Study Reactions with EtC≡W($OCMe_2CF_3$)$_3$

Propionitrile. Complex **3.6** (10.0 mg, 0.0165 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, propionitrile (1.2 μL, 0.017 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. After 20 h the reaction mixture consisted of 80% unidentified F-containing products, **3.9** (10%), and **3.6** (9%). The reaction mixture was then heated at 95 °C and monitored by ^1H and ^{19}F NMR spectroscopy for 36 h. At this point all of **3.6** had been converted to **3.2** (89%) and **3.9** (11%).

Anisonitrile. From a stock solution in toluene-d_8, anisonitrile (2.2 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). After 24 h the reaction mixture consisted of 71% unidentified F-containing products, **3.9** (7%), and **3.6** (22%). The reaction mixture was then heated at 95 °C and monitored by ^1H and ^{19}F NMR spectroscopy for 4 h. The W-containing species included- **3.2** (60%), **3.7** (25%), **3.9** (9%), and unidentified material (6%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 238 ($C_{16}H_{14}O_2$, R_t 15.33 min).

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (2.7 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). After 10 min the reaction mixture exhibited very broad peaks in the ^{1}H NMR spectrum. Cooling the reaction mixture to −40 °C revealed the presence of **3.6**, **3.7**, and **3.13**. Relative ratios were undetermined due to broadening of peaks in the spectrum. Further cooling of the reaction mixture resulted in the formation of additional unidentified peaks in the ^{1}H NMR spectrum.

bis(4-methoxyphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-methoxyphenyl)acetylene (3.9 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). After 15 min at room temperature broadening of the ^{1}H NMR spectrum was seen. Lowering temperature to −40 °C revealed the presence of largely **3.7** with trace **3.6** remaining. Further decreasing the temperature revealed **3.13** along with additional unknown peaks. Due to broadening of the spectrum exact ratios of catalyst resting-states could not be determined.

***p*-trifluoromethylbenzonitrile.** From a stock solution in toluene-d_8, *p*-trifluoromethylbenzonitrile (2.8 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-

trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). After 72 h the W-containing species were distributed as follows: **3.8** (19%), **3.6** (4%), **3.9** (5%), **3.2** (64%), and one unknown (8%). The aryl-containing units were distributed as follows: **3.8** (19%), *p*-trifluoromethylbenzonitrile (35%), 1-(4-trifluoromethylphenyl)-1-butyne (38%), and bis(4-trifluoromethylphenyl)acetylene (8%). The reaction mixture was filtered through silica gel with CH_2Cl_2. GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 11.367 min), 314 ($C_{16}H_8F_6$, R_t 17.410 min), 198 ($C_{11}H_9F_3$, R_t 13.663 min)

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-trifluoromethylphenyl)-1-butyne (3.3 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). Within 10 min the reaction was complete. Room temperature ^{1}H NMR spectra were severely broadened. The temperature was reduced to −40 °C revealing the presence of **3.8** (65%) and a combination of **3.6** and **3.13** (35%).

bis(4-trifluoromethylphenyl)acetylene. From a stock solution in toluene-d_8, bis(4-trifluoromethylphenyl)acetylene (5.2 mg, 0.017 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.6** (10.0 mg, 0.0165 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 33 mM in toluene-d_8 (based on **3.6**). Complete conversion to **3.8** was observed within 15 min by ^{1}H NMR spectroscopy. The aryl group was distributed as follows: **3.8** (46%), 1-(4-trifluoromethylphenyl)-1-butyne (38%), and bis(4-trifluoromethylphenyl)acetylene (16%).

3.10.11 Pathway Study Reactions with *4*-$MeOC_6H_4C{\equiv}W(OCMe_2CF_3)_3$

3-hexyne. Complex **3.7** (10.0 mg, 0.0146 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, 3-hexyne (1.7 μL, 0.015 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. The ^{1}H NMR spectrum was broadened at room temperature. Cooling to below −30 °C revealed a mixture of **3.7**, **3.13**, and **3.6** with relative integrations being undetermined due to broadening.

Propionitrile. Complex **3.7** (10.0 mg, 0.0146 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution, propionitrile (1.0 μL, 0.015 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. The slow reaction was monitored at room temperature for 7 days. At this point, the W-containing materials were distributed as **3.2** (21%), **3.9** (5%), a combination of **3.7** and **3.6** (30%), and unknown materials (44%). The reaction mixture was then heated at 95 °C for 5 h with the W-containing materials being distributed as **3.2** (70%), **3.7** (14%), **3.9** (7%), and unknown materials (9%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^{+}$: 238 ($C_{16}H_{14}O_2$, R_t 15.31 min).

Anisonitrile. From a stock solution in toluene-d_8, anisonitrile (1.9 mg, 0.015 mmol, 1 equiv) was placed in a J. Young tube. To this solution, **3.7** (10.0 mg, 0.0146 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 29 mM in toluene-d_8 (based on **3.7**). The reaction was monitored at room temperature. Slow conversion to **3.2** was observed. After 4 days the distribution of W-containing materials was **3.7** (29%), **3.2** (23%), **3.9** (8%), and unknown (40%). The reaction mixture was then heated at 95 °C for 8 h with complete conversion to **3.2** along with 10% decomposition to **3.9**.

1-(4-methoxyphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-methoxyphenyl)-1-butyne (2.4 mg, 0.015 mmol, 1 equiv) was placed in a J. Young tube. To this solution **3.7** (10.0 mg, 0.0146 mmol) and an internal standard of 1,3,5-trimethoxybenzene were added. The total concentration of the reaction mixture was diluted to 29 mM in toluene-d_8 (based on **3.7**). The reaction mixture exhibited very broad peaks in the ^{1}H NMR spectrum. Cooling the reaction mixture to −40 °C revealed the presence of **3.6**, **3.7**, and **3.13**. Relative ratios were undetermined due to broadening of peaks in the spectrum. Further cooling of the reaction mixture resulted in the formation of additional unidentified peaks in the ^{1}H NMR spectrum. The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 238 ($C_{16}H_{14}O_2$, R_t 15.30 min).

3.10.12 Pathway Study Reactions with *4*-$CF_3C_6H_4C{\equiv}W(OCMe_2CF_3)_3$

3-hexyne. Complex **3.8** (10.0 mg, 0.0138 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution 3-hexyne (1.6 μL, 0.0138 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. After 10 min the aryl-containing moieties were distributed as follows: **3.8** (67%), 1-(4-trifluoromethylphenyl)-1-butyne (31%), and bis(4-trifluoromethylphenyl)acetylene (2%). The W-containing material was **3.8** (67%) and **3.9** (33%) (^{1}H NMR at −40 °C).

Propionitrile. Complex **3.8** (10.0 mg, 0.0138 mmol) was dissolved in toluene-d_8 (500 μL) and transferred to a J. Young tube. To this solution propionitrile (1.0 μL, 0.014 mmol, 1 equiv) and an internal standard of 1,3,5-trimethoxybenzene were added. No reaction was observed at room temperature. The reaction mixture was then heated at 95°C for 88 h at which point no further conversion of **3.8** was observed. The W-containing materials were distributed as follows: **3.8** (21%), **3.2** (61%), **3.9** (11%), and unknown materials (7%). The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 314 ($C_{16}H_8F_6$, R_t 10.69 min)

***p*-trifluoromethylbenzonitrile.** From a stock solution in toluene-d_8, *p*-trifluoromethylbenzonitrile (2.4 mg, 0.014 mmol, 1 equiv) was placed in a J. Young tube. To this solution **3.8** (10.0 mg, 0.0138 mmol) and an internal standard of 1,3,5-trimethoxybenzene was added. The total concentration of the reaction mixture was diluted to 28 mM in toluene-d_8 (based on **3.8**). After 7 days at room temperature the W-containing species were distributed as follows: **3.8** (58%), **3.9** (7%), and **3.2** (34%). The aryl-containing units were distributed as follows: **3.8** (23%), *p*-trifluoromethylbenzonitrile (56%), and bis(4-trifluoromethylphenyl)acetylene (21%). The mixture was then heated at 95 °C for 18 h at which point **3.8** was completely converted to

3.2 with 14% decomposition to **3.9**. The reaction mixture was filtered through silica gel with CH_2Cl_2. Trace GC/MS $[M/Z]^+$: 171 ($C_8H_4NF_3$, R_t 3.66 min), 314 ($C_{16}H_8F_6$, R_t 10.60 min)

1-(4-trifluoromethylphenyl)-1-butyne. From a stock solution in toluene-d_8, 1-(4-trifluoromethylphenyl)-1-butyne (2.8 mg, 0.014 mmol, 1 equiv) was placed in a J. Young tube. To this solution **3.8** (10.0 mg, 0.038 mmol) and an internal standard of 1,3,5-trimethoxybenzene was added. The total concentration of the reaction mixture was diluted to 28 mM in toluene-d_8 (based on **3.8**). Within 10 min the reaction was complete. Room temperature ^{1}H NMR spectra were slightly broadened. The temperature was reduced to −40 °C revealing largely the presence of **3.8** with trace **3.6** present.

3.10.13 Attempted Hammett Studies

General Procedure. Complex **3.1-DME** (5.0 mg, 0.0060 mmol) and all solid substrates (0.120 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL). Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and liquid substrates (0.120 mmol, 20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by ^{1}H NMR spectroscopy over 540 min, with spectra being recorded every 10 min. All reactions were completed in triplicate. The data is summarized in Table 3.6. The following subtrates were analyzed: *p*-bromobenzonitrile, *p*-trifluoromethylbenzonitrile, *p*-*t*-butylbenzonitrile, benzonitrile, *p*-tolunitrile, *p*-methoxybenzonitrile, *p*-methyl ester benzonitrile, and *p*-dimethylaminobenzonitrile.

Table 3.6. Hammett studies data summary.

Time, min	% Conversion of Anisonitrile into Alkyne Products Substrates *p*-Br	*p*-CF_3	*p*-^{t}Bu	H	*p*-Me	*p*-OMe	*p*-OAc	*p*-NMe_2
0	0.0	0.0	0.0	0.0	0	0.0	0.0	0.0
10	5.8	8.1	5.7	0.7	2.9	8.6	4.6	0.9
20	14.2	15.5	12.7	9.2	7.4	16.2	8.5	4.0
30	22.2	25.1	18.9	15.1	11.9	21.4	10.7	6.8
40	27.6	30.7	23.7	18.4	15.6	26.3	13.6	10.2
50	32.5	35.3	27.4	23.6	20.5	31.4	15.4	11.5
60	36.4	38.5	30.4	28.1	25.0	35.2	16.7	14.1
70	40.0	41.4	33.4	30.5	27.6	38.5	19.8	15.9
80	42.0	43.0	36.5	33.5	30.7	41.8	21.6	17.4
90	44.9	45.6	39.3	35.4	33.7	44.4	21.9	20.9
100	46.7	46.8	40.8	36.9	35.9	46.7	23.6	21.7
110	48.6	48.3	42.9	38.6	38.1	49.0	23.7	22.5
120	50.4	50.0	43.9	41.1	39.7	51.3	24.1	24.0
140	53.3	52.2	47.8	43.9	44.2	55.0	25.7	27.6
160	56.0	54.3	50.1	46.4	46.6	58.7	27.7	28.3
180	58.1	55.8	52.4	49.6	49.5	61.4	29.1	30.7
210	60.4	58.0	55.8	52.1	52.7	64.7	30.4	31.9
240	62.7	59.6	57.9	54.3	55.8	67.0	32.0	34.6
300	65.3	61.9	61.4	57.2	59.2	69.4	33.5	37.1
420	69.9	66.5	65.7	61.8	64.7	72.9	35.9	41.5
540	72.7	66.5	65.7	61.8	68.1	72.9	36.6	41.5

3.10.14 Alkyne Metathesis versus Nitrile-Alkyne Cross-Metathesis for Formation of Symmetrical Alkyne

With 3.1-DME. Bis(4-methoxyphenyl)acetylene (14.4 mg, 0.060 mmol, 10 equiv), 3,5-dimethylbenzonitrile (15.8 mg, 9.129 mmol, 20 equiv) and **3.1-DME** (5.0 mg, 0.0060 mmol) were dissolved in toluene-d_8 (0.5 mL) in a J-Young tube. Then 3-hexyne (6.8 μL, 0.061 mmol, 10 equiv) was added via syringe. The reaction mixture was heated to 95 °C and monitored via ^{1}HNMR spectroscopy. Within 10 min evidence of 1-(4-methoxyphenyl)-1-butyne was found, whereas no evidence was found for NACM products. Within 30 min a small amount of nitrile containing products had formed

(Relative integrations were undetermined due to resonance overlap in the ^{1}H NMR spectrum). After 46 h, 3-hexyne was completely consumed.

With 3.2. Bis(4-methoxyphenyl)acetylene (41.1 mg, 0.173 mmol, 10 equiv), 3,5-dimethylbenzonitrile (45.3 mg, 0.345, 20 equiv) and **3.2** (10.0 mg, 0.0173 mmol) were dissolved in toluene-d_8 (0.5 mL) in a J-Young tube. Then 3-hexyne (19.6 μL, 0.173 mmol, 10 equiv) was added via syringe. The reaction mixture was heated to 95 °C and monitored via ^{1}HNMR spectroscopy. Within 10 min evidence of 1-(4-methoxyphenyl)-1-butyne was found, whereas no evidence was found for NACM products. After 40 min a small amount of nitrile containing products had formed (Relative intergrations were undetermined due to resonance overlap in the ^{1}H NMR spectrum). After 100 min the reaction mixture was removed from heat and filtered through celite with CH_2Cl_2. GC/MS $[M/Z]^+$: 131 (C_9H_9N, R_t 4.773 min), 133 (C_8H_7NO, R_t 5.430), 158 ($C_{12}H_8$, R_t 6.103), 160 ($C_{11}H_{12}O$, R_t 6.633), 236 ($C_{17}H_{16}O$, R_t 14.077 min), 238 ($C_{16}H_{14}O_2$, R_t 15.203 min)

3.10.15 Preferential Formation of Symmetrical Alkynes

Preferential symmetrical alkyne formation with the 3,5-dimethylbenzonitrile and 3,5-bis(trifluoromethyl)benzonitrile were completed by Eric Wiedner and are reported elsewhere.[20]

4-cyanostyrene. Complex **3.1-DME** (5.0 mg, 0.0060 mmol), was added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL) to give a concentration of 5 mg/mL based on **3.1-DME**. Then 3-hexyne (11.1 μL, 0.092 mmol, 10 equiv) and 4-cyanostyrene (9.9 μL, 0.120 mmol, 20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. After 8 h of heating, conversion to asymmetric alkyne, 4-(1-butynyl)styrene (50.6%), and symmetric alkyne, 4,4'-divinyltolan (39.2%), with starting material remaining (10.2%) was indicated by ^{1}H NMR spectroscopy. The volatiles were removed *in vacuo* and the resulting residue was dissolved in toluene-d_8 (0.50 mL) and heated for 4.5 h, at which point ^{1}H NMR spectroscopy indicated conversion to 4-(1-butynyl)styrene (33.9%) and 4,4'-divinyltolan (64.2%) with starting material remaining (1.9%). The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. The resulting residue was dissolved in $CDCl_3$ and filtered through a plug of silica. ^{1}H NMR spectroscopy indicated only the presence of 4,4'-divinyltolan. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, Ar*H*, J = 8.2 Hz), 7.39 (d, 2H, Ar*H*, J = 8.4 Hz), 6.72 (dd, 1H, ArC*H*CH$_2$, J^1_{HH} = 17.5 Hz, J^2_{HH} = 10.7 Hz), 5.79 (d, 1H, ArCHC*H*$_2$, J = 17.5 Hz), 5.30 (d, 1H, ArCHC*H*$_2$, J = 10.7 Hz) ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.59, 136.40, 131.92, 126.33, 122.69, 114.92 (*C*H$_2$), 90.27 (Ar*CC*Ar) GC/MS $[M/Z]^+$: 230 ($C_{18}H_{14}$, R_t 14.793 min).

3.10.16 Preferential Formation of Unsymmetrical Alkynes

3,5-bis(trifluoromethyl)benzonitrile. Complex **3.1-DME** (5.0 mg, 0.0060 mmol) was added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL) to give a concentration of 5 mg/mL based on **3.1-DME**. Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and 3,5-bis(trifluoromethyl)benzonitrile (20.0 μL, 0.120 mmol, 20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. After 10 h of heating, more 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) was added. The reaction mixture was then heated for an additional 22 h. At this point ^{1}H NMR spectroscopy indicated conversion to 4-(3,5-bis(trifluoromethyl)phenyl)-1-butyne (45%), bis(3,5-bis(trifluoromethylphenyl))acetylene (30%), with remaining 3,5-bis(trifluoromethyl)benzonitrile. At this point the reaction mixture was filtered through alumina to remove polymer. The volatiles were removed *in vacuo* from the reaction mixture. The resulting residue was taken up in toluene-d_8 (1.0 mL). Additional **3.1-DME** (5.0 mg, 0.0060 mmol) was introduced along with 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv). The resulting mixture was heated for 30 min, at which point ^{1}H NMR spectroscopy indicated conversion to 4-(3,5-bis(trifluoromethyl)phenyl)-1-butyne (80%), bis(3,5-bis(trifluoromethylphenyl))acetylene (10%), with remaining 3,5-bis(trifluoromethyl)benzonitrile. The resulting reaction mixture was washed through a plug of silica with methylene chloride. GCMS: 266 ($C_{12}H_8F_6$, R_t 3.287 min), 450 ($C_{18}H_6F_{12}$, R_t 6.133 min)

3,5-dimethylbenzonitrile. Complex **3.1-DME** (5.0 mg, 0.0060 mmol) and 3,5-dimethylbenzonitrile (16.1 mg, 0.120 mmol, 20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL) to give a concentration of 5 mg/mL based on **3.1-DME**. Then 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) was added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. After 6 h of heating, more 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) was added. The reaction mixture was then heated for an additional 19 h. At this point ^{1}H NMR spectroscopy indicated conversion to 4-(3,5-dimethylphenyl)-1-butyne (48%), bis(3,5-dimethylphenyl)acetylene (41%), with remaining 3,5-dimethylbenzonitrile. At this point the reaction mixture was filtered through alumina to remove polymer. The volatiles were removed *in vacuo* from the reaction mixture. The resulting residue was taken up in toluene-d_8 (1.0 mL). Additional **3.1-DME** (5.0 mg, 0.0060 mmol) was introduced along with 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv). The resulting mixture was heated for 30 min, at which point ^{1}H NMR spectroscopy indicated conversion to 4-(3,5-dimethylphenyl)-1-butyne (63%), bis(3,5-dimethylphenyl)acetylene (26%), with remaining 3,5-bis(trifluoromethyl)benzonitrile. The resulting reaction mixture was washed through a plug of silica with methylene chloride. GCMS: 131 (C_9H_6N, R_t 4.527), 143 ($C_{12}H_{11}$, R_t 5.867 min), 234 ($C_{18}H_{12}$, R_t 12.667 min)

4-cyanostyrene. Complex **3.1-DME** (5.0 mg, 0.0060 mmol), was added to a J. Young tube and dissolved in toluene-d_8 (1.0 mL) to give a concentration of 5 mg/mL based on **3.1-DME**. Then 3-hexyne (11.1 μL, 0.092 mmol, 10 equiv) and 4-cyanostyrene (9.9 μL, 0.120 mmol, 20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. After 8 h of heating, conversion to asymmetric alkyne, 4-(1-butynyl)styrene (50.6%), and symmetrical alkyne, 4,4’-divinyltolan (39.2%), with starting material remaining (10.2%) was indicated by ^{1}H NMR spectroscopy.

3.10.17 Substrate Compatibility Studies with N≡W(OCMe(CF_3)$_2$)$_3$(DME)

General Procedure. Complex **3.1-DME** and all solid substrates (20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 to give a concentration of 5 mg/mL based on **3.1-DME**. Then 3-hexyne (10 equiv) and liquid substrates (20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. Additional 3-hexyne and/or **3.1-DME** were added as necessary to each reaction.

4-cyanostyrene. See Section 3.10.15.

***p*-aminobenzonitrile**. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), *p*-aminobenzonitrile (14.2 mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 4 h of heating the catalyst had decomposed with no evidence of production of propionitrile as indicated by ^{1}H NMR spectroscopy. No NACM was observed.

***p*-dimethylaminobenzonitrile.** Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), *p*-dimethylaminobenzonitrile (17.6 mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 10 h of heating, 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) and **3.1-DME (**5.0 mg, 0.0060 mmol, 1.0 equiv) were added to the reaction mixture. The reaction mixture was heated for an additional 18 hrs at which point the mixture was composed of 4-butynyl-N,Ndimethylaniline (69%), di-*p*-dimethylaminophenylacetylene (13%), and remaining *p*-dimethylaminobenzonitrile (18%). GC/MS $[M/Z]^+$: 336 ($C_{14}H_8Br_2$, R_t 16.687 min). The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. ^1H NMR was consistent with the literature data.[21] GC/MS $[M/Z]^+$: 145 ($C_9H_{10}N_2$, R_t 8.373 min), 173 ($C_{12}H_{15}N$, R_t 8.853 min), 264 ($C_{18}H_{20}N_2$, R_t 26.280 min).

***p*-tolunitrile.** Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), *p*-tolunitrile (14.2 μL, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After heating for 2 h propionitrile (5%) was observed, however no evidence for conversion of *p*-tolunitrile was found. Further heating only resulted in polymerization of 3-hexyne.

4-bromobenzonitrile. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), 4-bromobenzonitrile (21.9 mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 8 h of heating, additional 3-hexyne (6.8 μL, 0.060 mmol, 10 equiv) was added. The reaction was further heated for 2.5 h, to give a 97% conversion of 4-bromobenzonitrile to symmetric alkyne, bis(4-bromphenyl)acetylene (79.3%), and asymmetric alkyne, 1-(4-bromphenyl)-1-butyne (17.7%), by ^1H NMR spectroscopy. The volatiles were removed *in vacuo* and the resulting residue was dissolved in toluene-d_8 (0.50 mL) and heated for 2.5 h, at which point ^1H NMR spectroscopy indicated conversion to bis(4-bromophenyl)acetylene (100%). The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. ^{1}H NMR was consistent with the literature data.[14] GC/MS $[M/Z]^+$: 336 ($C_{14}H_8Br_2$, R_t 16.687 min).

4-cyanobenzaldehyde. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), 4-cyano-benzaldehyde (15.8 mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). An internal standard of CH_2Cl_2 was introduced instead of 1,3,5-trimethoxybenzene. After 21 h of heating, no metathesis products were observed by ^{1}H NMR spectroscopy.

4-(1,3-dioxolan-2-yl)benzonitrile. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), 4-(1,3-dioxolan-2-yl)benzonitrile (21.1 mg, .120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 11.5 h of heating ^{1}H NMR spectroscopy indicated conversion to asymmetric alkyne, 2-(4-But-1-ynyl-phenyl)-[1,3]dioxolane (3.4%), with starting material remaining. The volatiles were removed *in vacuo* and the resulting residue was dissolved in toluene-d_8 (1.0 mL) and heated for 12.5 h. No further reaction was observed. The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. GC/MS $[(M-1)/Z]^+$: 201 ($C_{13}H_{14}O_2$, R_t = 9.807 min), 175 ($C_{10}H_9O_2N$, R_t = 8.323 min)

4-(1-(ethylenedioxy)ethyl)benzonitrile. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), 4-(1-(ethylenedioxy)ethyl)benzonitrile (22.8

mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 11 h of heating ^{1}H NMR spectroscopy indicated conversion to symmetric alkyne, 1,2-bis[(4-(1-ethylenedioxy)ethyl)phenyl]acetylene (23.2%), and asymmetric alkyne, 2-(4-But-1-ynyl-phenyl)2-methyl-[1,3]dioxolane (18.8%), with starting material remaining (58.0%). The volatiles were removed *in vacuo* and the resulting residue was dissolved in toluene-d_8 (1.0 mL) and heated for 12.5 h. No further reaction was observed. The reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. The identity of the asymmetric product was further verified by independent synthesis as shown in Section 3.10.19. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 4H, sym, ArH, J = 8.4 Hz), 7.46 (d, 4H, sym, ArH, J = 8.4 Hz), 7.39 (d, 2H, asym, ArH, J = 8.6 Hz), 7.36 (d, 2H, asym, ArH, J = 8.6 Hz), 4.00-4.06 (m, 4H, sym & asym, OCH_2CH_2O), 3.73-3.80 (m, 4H, asym & sym, OCH_2CH_2O), 2.41 (q, 2H, asym, RCH_2CH_3, J = 7.4 Hz), 1.65 (s, 3H, sym, $Ar(OCH_2CH_2)CCH_3$), 1.63 (s, 3H, asym, $Ar(OCH_2CH_2)CCH_3$), 1.25 (t, 3H, asym, RCH_2CH_3, J = 7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.58 (sym, $HCCOCH_2CH_2OC$), 142.67 (asym, $H_3CCCOCH_2CH_2OC$), 131.62 (sym, *C*Ar), 131.50 (asym, *C*Ar), 125.49 (sym, *C*Ar), 125.31 (asym, *C*Ar), 123.67 (asym, *C*Ar), 122.88 (sym, *C*Ar), 108.73 (sym & asym overlap, $CH_3COCH_2CH_2OC$), 91.94 (asym, CH_3CH_2C) 89.39 (sym, Ar*CC*Ar), 79.74 (asym, $CCCH_2CH_3$), 64.61 (sym, OCH_2CH_2O), 64.55 (asym, OCH_2CH_2O), 29.83 (sym, CCH_3), 27.56 (asym, CCH_3), 14.04 (asym, CH_2CH_3), 13.22 (asym, CH_2CH_3). GC/MS $[M/Z]^+$: 350 ($C_{22}H_{25}O_4$, R_t 28.250 min), 216 ($C_{14}H_{16}O_2$, R_t = 9.447 min), 172 ($C_{12}H_{12}O$, R_t = 8.187), 145 (C_9H_7NO, R_t = 8.320) $[(M-15)/Z]^+$:174 ($C_{11}H_{11}O_2N$, R_t = 8.020 min)

4-cyano-benzoic acid methyl ester. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), 4-cyano-benzoic acid methyl ester (19.4 mg, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 6 h of heating, additional 3-hexyne (6.8 μL, 0.060 mmol) was added. Following 15 h of heating, 3-hexyne (6.8 μL, 0.060 mmol) was added. The reaction was further heated for 2.5 h, at which point ^{1}H NMR spectroscopy indicated conversion to symmetric alkyne, 1,2-bis(4-carbomethoxyphenyl)ethyne (24.4%), and asymmetric alkyne, methyl 4-(1-butynyl)benzoate (75.6%). The volatiles were removed *in vacuo* and the resulting residue was dissolved in toluene-d_8 (1.0 mL) and heated for 6 h. No further reaction was observed. The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. ^{1}H NMR data were consistent with the literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$, asym.): δ 8.13 (d, 2H, ArH, J=8.0 Hz), 7.61 (d, 2H, Ar*H*, 2H), 4.04 (s, 3H, OCH_3), 2.59 (q, 2H, C$H_2$$CH_3$, J=7.4 Hz), 1.41 (t, 2H, CH_2CH_3, J=7.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$, asym.): δ 166.49 (C=0), 132.02 (CAr), 131.34 (CAr), 129.29 (CAr), 128.79 (CAr), 94.96 (C*C*CH_2CH_3), 79.4 (*C*CCH_2CH_3), 52.07 (O*C*H_3), 20.17 (CH_2CH_3), 13.08 (CH_2CH_3) GC/MS $[M/Z]^+$: 294 ($C_{18}H_{14}O_4$, R_t = 22.557 min), 188 ($C_{12}H_{12}O_2$, R_t = 8.397 min), 161 ($C_9H_7O_2N$, 6.520 min).

Pentanenitrile. Following the general procedure: Complex **3.1-DME (**5.0 mg, 0.0060 mmol), pentanenitrile (12.6 μL, 0.120 mmol), and 3-hexyne (6.8 μL, 0.060 mmol) were dissolved in toluene-d_8 (1.0 mL). After 4 h of heating, ^{1}H NMR spectroscopy indicated conversion from pentanenitrile (70.6% remaining). At this point, the reaction mixture had become viscous, thus preventing further reaction. The products were filtered through a plug of alumina. All peaks in ^{1}H NMR (300 MHz, C_6D_6) were overlapping, however GC/MS indicated presence of 3-octyne, 5-decyne, and pentanenitrile. GC/MS $[M/Z]^+$: 138 ($C_{10}H_{18}$, R_t = 6.577 min), 84 (C_5H_9N, R_t = 6.063 min) 110 ($C_{12}H_{14}$, R_t = 4.293 min).

Substrate studies with the following nitriles were completed by Eric Wiedner and are reported elsewhere:[20] trimethylacetonitrile, 4-hydroxybenzonitrile, 4-nitrobenzonitrile, 4-acetylbenzonitrile, p-toluenesulfonyl acetonitrile, 2-cyanopyridine, 3-aminopropionitrile, N-methyl-β-alaninenitrile, 3-dimethylaminopropionitrile, t-butyl-4-cyanobenzoate, 3,5-dimethylbenzonitrile, 2-thiophenecarbonitrile, 3,5-bis(trifluoromethyl)benzonitrile, 3-iodopropionitrile.

3.10.18 Substrate Compatibility Studies with $[N{\equiv}W(OCMe_2CF_3)_3]_3$

General Procedure. Complex **3.2** (5.0 mg, 0.0086 mmol) and all solid substrates (20 equiv) were added to a J. Young tube and dissolved in toluene-d_8 to give a concentration of 5 mg/mL based on **3.2**. Then 3-hexyne (10 equiv) and liquid substrates (20 equiv) were added to the reaction mixture. An internal standard of 1,3,5-trimethoxybenzene was introduced. The J. Young tube was placed in an oil bath at 95 ºC and the reaction was monitored by NMR spectroscopy. Additional 3-hexyne and/or **3.2** were added as necessary to each reaction.

Tert-butyl-4-cyanobenzoate. Following the general procedure: Complex **3.2**, *tert*-butyl-4-cyanobenzoate (35.0 mg, 0.173 mmol), and 3-hexyne (9.8 μL, 0.086 mmol) were dissolved in toluene-d_8 (1.0 mL). After 15.5 h of heating, ^{1}H NMR spectroscopy indicated conversion to asymmetric alkyne, 4-but-1-ynyl-benzoic acid *tert* -butyl ester (32.3%), and symmetric alkyne, bis[4-(*tert* -butylbenzoate)]acetylene (13.8%), with starting material remaining (54%). Then 3-hexyne (9.8 μL, 0.086 mmol) was added and the reaction was heated for an additional 5 h. At this point ^{1}H NMR spectroscopy indicated conversion to 4-but-1-ynyl-benzoic acid *tert* -butyl ester (42.6%) and bis[4-(*tert* -butylbenzoate)]acetylene (5.5%) with starting material remaining (51.9%). The volatiles were removed *in vacuo*. The resulting residue was taken up in toluene-d_8 (1.0 mL) and 3-hexyne (9.8 μL, 0.086 mmol) was added. This mixture was heated for an additional 3 h without further conversion to metathesis products. The volatiles were removed *in vacuo*. The resulting residue was dissolved in toluene-d_8 (1.0 mL) and heated for and additional 2 h with no further conversion. This reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 4H, sym, ArH, J = 8.2 Hz), 7.80 (d, 2H, asym, ArH, J = 8.2 Hz), 7.58 (d, 4H, sym, ArH, J = 8.2 Hz), 7.41 (d, 2H, asym, ArH, J = 8.2 Hz), 2.44 (q, 2H, asym, CH_2, J = 7.4 Hz), 1.58 ($C(CH_3)_3$, 1.24 (t, 3H, asym, CH_2CH_3, J =7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 165.52 (asym, *C*=O), 165.3 (sym, *C*=O), 131.98 (sym, *C*Ar), 131.66 (sym, *C*Ar), 131.46 (asym, *C*Ar), 129.60 (sym, *C*Ar), 129.42 (asym, *C*Ar), 128.47 (asym, *C*Ar), 127.07 (sym, *C*Ar), 94.88 (asym, CCH_2CH_3), 91.45 (sym, -*C*≡*C*-), 81.58 (sym, $C(CH_3)_3$), 81.30 (asym,

$C(CH_3)_3$), 79.74 (asym, -C≡CCH_2CH_3), 13.94 (overlapping sym & asym, $C(CH_3)_3$), 13.94 (CH_2CH_3), 13.40 (CH_2CH_3). EI (M^+): 378.18 ($C_{24}H_{26}O_4$), 230.13 ($C_{15}H_{18}O_2$)

4-(1-(ethylenedioxy)ethyl)benzonitrile. Following the general procedure: Complex **3.2,** 4-(1-(ethylenedioxy)ethyl)benzonitrile (32.7 mg, .173 mmol), and 3-hexyne (9.8 μL, 0.086 mmol) were dissolved in toluene-d_8 (1.0 mL). After 12.5 h of heating ^{1}H NMR spectroscopy indicated conversion to symmetric alkyne, bis[(4-(1-ethylenedioxy)ethyl)phenyl]acetylene (4.7%), and asymmetric alkyne, 2-(4-But-1-ynyl-phenyl)2-methyl-[1,3]dioxolane (45.2%), with starting material remaining (50.1%). Additional **3.2** (5.0 mg, 0.0086 mmol) was added and the reaction was heated for a further 12 h, at which point ^{1}H NMR spectroscopy indicated conversion to bis[(4-(1-ethylenedioxy)ethyl)phenyl]acetylene (11.7%) and 1-(4-(1-ethylenedioxy)ethylphenyl)-1-butyne (57.9%) with starting material remaining (30.4%). The reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. GC/MS $[M/Z]^+$: 350 ($C_{22}H_{25}O_4$, R_t 28.187 min), 216 ($C_{14}H_{16}O_2$, R_t = 9.413 min), $[(M-15)/Z]^+$:174 ($C_{11}H_{11}O_2N$, R_t = 7.977 min)

4-(1,3-dioxolan-2-yl)benzonitrile. Following the general procedure: Complex **3.2**, 4-(1,3-*d*ioxolan-2-yl)benzonitrile (30.3 mg, .173 mmol), and 3-hexyne (9.8 μL, 0.086 mmol) were dissolved in toluene-d_8 (1.0 mL). After 6 h of heating, ^{1}H NMR spectroscopy indicated conversion to asymmetric alkyne, 2-(4-but-1-ynyl-phenyl)-[1,3]dioxolane (18.9%), with starting material remaining (81.1%). Additional **3.2** (5.0

mg, 0.0086 mmol) was added and the reaction was heated for a further 4 h, at which point ^{1}H NMR spectroscopy indicated conversion to 2-(4-but-1-ynyl-phenyl)-[1,3]dioxolane (24.9%) with starting material remaining (75.1%). The resulting reaction mixture was washed through a plug of alumina with chloroform and concentrated *in vacuo*. The identity of the asymmetric product was further verified by independent synthesis as shown Section 3.10.19. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 2H, Ar*H*, J = 8.6 Hz), 7.39 (d, 2H, Ar*H*, J= 8.6 Hz), 5.78 (s, COC*H*), 4.05-4.09 (m, 2H, OCH_2CH_2O), 3.99-4.02 (m, 2H, OCH_2CH_2O), 2.41 (q, 2H, CH_2CH_3, J = 7.4 Hz), 1.23 (t, 3H, CH_2CH_3, J = 7.4 Hz) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.24 (CCH_3), 131.69 (*C*Ar), 126.51 (*C*Ar), 125.08 (*C*Ar), 102.61 (CCH_3), 92.46 (CCH_2CH_3),79.80 (-*C*≡CCH_2-), 65.47 (OCH_2CH_2O), 14.03 (CH_2CH_3), 13.29 (CH_2CH_3). GC/MS $[(M-1)/Z]^+$: 201 ($C_{13}H_{14}O_2$, R_t = 9.780 min), 175 ($C_{10}H_9O_2N$, R_t = 8.303 min), 7.163 ($C_{11}H_{10}O$, R_t = 7.163 min).

4-acetylbenzonitrile. Following the general procedure: Complex **3.2,** 4-acetylbenzonitrile (25.0 mg, 0.173 mmol), and 3-hexyne (9.8 μL, 0.086 mmol) were dissolved in toluene-d_8 (1.0 mL). After 4.5 h of heating, no metathesis products were observed by ^{1}H NMR spectroscopy. At this point the catalyst had been destroyed.

4-cyanobenzaldehyde. Following the general procedure: Complex **3.2**, 4-cyano-benzaldehyde (22.6 mg, 0.173 mmol), and 3-hexyne (9.8 μL, 0.086 mmol) were dissolved in toluene-d_8 (1.0 mL). After 17.5 h of heating, no metathesis products were observed by ^{1}H NMR spectroscopy. The catalyst had been deactivated at this point.

3.10.19 Independent Syntheses of Unsymmetrical Alkynes

2-(4-But-1-ynyl-phenyl)-2-methyl-[1,3]dioxolane. 4-(1-butynyl)acetophenone (519.9 mg, 3.02 mmol) was dissolved in dry C_6H_6 (30 mL) under a flow of N_2. To this was added ethylene glycol (506 μL, 9.05 mmol, 3 equiv) and *p*-toluenesulfonic acid monohydrate (28.7 mg, 0.151 mmol, 0.050 equiv). The reaction mixture was heated to reflux in the presence of a Dean-Stark trap. After refluxing for 17 h, the mixture was cooled to room temperature and washed with saturated aqueous sodium bicarbonate solution (20 mL). The layers were separated and the aqueous layer was washed with C_6H_6 (10 mL). The organic layers were combined, dried with anhydrous $MgSO_4$, and reduced to dryness *in vacuo*. A crude yield of 464.4 mg material was collected. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H, ArH, J = 8.6 Hz), 7.36 (d, 2H, ArH, J = 8.6 Hz), 4.00-4.04 (m, 4H, OCH_2CH_2O), 3.73-3.79 (m, 4H, OCH_2CH_2O), 2.41 (q, 2H, RCH_2CH_3, J = 7.4 Hz), 1.63 (s, 3H, CCH_3), 1.23 (t, 3H, RCH_2CH_3, J = 7.4 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.67 ($H_3CCCOCH_2CH_2OC$), 131.45 (*C*Ar), 125.28 (*C*Ar), 123.65 (*C*Ar), 108.73 ($CH_3COCH_2CH_2OC$), 91.86 (CH_3CH_2C), 79.73 ($CCCH_2CH_3$), 64.50 (OCH_2CH_2O), 27.51 (CCH_3), 14.00 (CH_2CH_3), 13.18 (CH_2CH_3). GC/MS $[M/Z]^+$: 216 ($C_{14}H_{16}O_2$, R_t 9.453 min).

2-(4-But-1-ynyl-phneyl)-[1,3]dioxolane. *4*-But-1-ynyl-benzaldehyde (293.1 mg, 1.85 mmol) was dissolved in dry C_6H_6 under a flow of N_2. To this was added ethylene glycol (155 μL, 2.78 mmol, 1.5 equiv) and para-toluenesulfonic acid monohydrate (17.6 mg, 0.093 mmol, 0.050 equiv). The reaction mixture was heated to reflux in the presence of a Dean-Stark trap. After refluxing for 22 h, additional ethylene glycol (75 μL, 1.39 mmol, 0.75 equiv) was added with C_6H_6 (20 mL). After 14 h of heating, the mixture was cooled to room temperature and washed with 20 mL saturated aqueous sodium bicarbonate solution. The layers were separated and the aqueous layer was washed with 10 mL C_6H_6. The organic layers were combined, dried with anhydrous $MgSO_4$, and reduced to dryness *in vacuo*. A crude yield of 334 mg material was collected. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 2H, Ar*H*, J = 8.6 Hz), 7.39 (d, 2H, Ar*H*, J= 8.6 Hz), 5.78 (s, COC*H*), 4.05-4.09 (m, 2H, OC*H*$_2$C*H*$_2$O), 3.99-4.02 (m, 2H, OC*H*$_2$C*H*$_2$O), 2.41 (q, 2H, C*H*$_2$CH$_3$, J = 7.4 Hz), 1.23 (t, 3H, CH$_2$C*H*$_3$, J = 7.4 Hz) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.87 (*C*H$_3$C), 131.35 (*C*Ar), 126.15 (*C*Ar), 124.74 (*C*Ar), 103.23 (H$_3$C*C*), 92.10 (H$_3$CH$_2$C*C*), 79.45 (*C*CCH$_2$CH$_3$), 65.13 (O*C*H$_2$*C*H$_2$O), 13.69 (CH$_2$CH$_3$), 12.94 (CH$_2$CH$_3$) GC/MS $[M/Z]^+$: 201 ($C_{14}H_{16}O_2$, R_t 9.453 min).

3.10.20 Large Scale Reactions

Bis(4-methoxyphenyl)acetylene. Complex **3.1-DME (**78.0 mg, 0.094 mmol) and anisonitrile (250.0 mg, 1.88 mmol, 20 equiv) were added to a bomb flask and dissolved in toluene (16 mL). Then 3-hexyne (213.3 μL, 1.88 mmol, 20 equiv) was introduced via syringe. The reaction was heated for 18.5 h at 95 ºC, and then the volatiles were removed *in vacuo*. The resulting residue was dissolved in toluene (8 mL) and heated for an additional 25 h. Upon cooling to room temperature, the mixture was filtered through alumina and rinsed with THF (20 mL). The filtrate was reduced to dryness via rotary evaporation, at which point ^1H NMR spectroscopy indicated conversion to bis(4-methoxyphenyl)acetylene (80.6%) and 1-(4-methoxyphenyl)-1-

butyne (10.9%) with anisonitrile remaining (8.5%). The crude product was purified by silica gel chromatography (10:1 hexanes/ethyl acetate) to afford 147.4 mg (0.619 mmol, 66.0%) of bis(4-methoxyphenyl)acetylene as a white powder. ^{1}H NMR data were consistent with the literature.[14] GC/MS $[M/Z]^+$: 238 ($C_{16}H_{14}O_2$, R_t 16.047 min).

1,4-dithiophen-2-yl-but-2-yne. Complex **3.1-DME** (84.3 mg, 0.101 mmol) and 2-thiopheneacetonitrile (250 mg, 2.02 mmol, 20 equiv) were combined in a bomb flask with toluene (18 mL). Then 3-hexyne (230.6 μL, 2.02 mmol, 20 equiv) was added via syringe. The reaction was heated for 35.5 h at 95 ºC, then the volatiles were removed *in vacuo*. The resulting residue was dissolved in toluene (10 mL) and heated for an additional 5 h. The reaction mixture was filtered through silica with chloroform (10 mL) and dried via rotary evaporation. The by-products were then vacuum distilled from the remaining red material. The remaining red-orange liquid was identified as the symmetric alkyne, 1,4-dithiophen-2-yl-but-2-yne (164.9 mg, 0.756 mmol, 74.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, 1H, 4-Ar*H*, J^1_{HH} = 1.2 Hz, J^2_{HH} = 5.1 Hz), 6.98 (dd, 1H, Ar*H*, J^1_{HH} = 1.2 Hz, J^2_{HH} = 3.5 Hz), 6.94 (dd, 1H, Ar*H*, J^1_{HH} = 5.1 Hz, J^2_{HH} = 8.5 Hz) 3.81 (s, 2H, CH_2) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140. 10 (1-*C*Ar), 126.97 (*C*Ar), 125.08 (*C*Ar), 124.14 (*C*Ar), 79.29 (CH_2CCCH_2), 20.21 (CH_2) GC/MS $[M/Z]^+$: 218 ($C_{12}H_{10}S_2$, R_t 10.957 min)

Macrocycle 3.10. See references.[1]

Macrocycles 3.11. Prep A: Dissolved 4,4′-(diisopropylsilanediyl)bis(oxy)dibenzonitrile (21.9 mg, 0.0625 mmol, 10 equiv) in toluene-d_8 (1.0 mL). Then **3.1-DME** (5.2 mg, 0.0062 mmol) and 3-hexyne (14.2 μL, 0.125 mmol, 20 equiv) were added. An internal standard of 1,3,5-trimethoxybenzene was added and the reaction mixture was heated at 95 °C. After 12 h a 96% conversion of starting materials to a mixture of products was observed. At this point volatiles were removed *in vacuo* and the reaction mixture was taken up in toluene-d_8 (1.0 mL). The reaction mixture was heated for 16 h at which point volatiles were again removed *in vacuo* and the reaction mixture was taken up in toluene-d_8 (1.0 mL). Further heating (3 h) resulted in the formation of 2 major products identified by ^{1}H NMR, ^{13}C NMR, and MALDI as the trimeric and tetrameric macrocycles **3.11**. **Prep B:** Dissolved 4,4′-(diisopropylsilanediyl)bis(oxy)dibenzonitrile (12.6 mg, 0.0359 mmol, 10 equiv) in toluene-d_8 (1.0 mL). Then **3.1-DME** (3.0 mg, 0.0036 mmol) and 3-hexyne (8.2 μL, 00722 mmol, 20 equiv) were added. An internal standard of 1,3,5-trimethoxybenzene was added and the reaction mixture was heated at 100 °C for 21 h. At that point the volatiles were removed *in vacuo* and the reaction mixture was taken up in toluene-d_8 (1.0 mL). The reaction mixture was returned to the oil bath for another 20 h. No selective macrocycle formation was observed. The volatiles were removed *in vacuo* and the resulting residue was taken up in bromobenzene-d_5 (1.0 mL). The reaction mixture was heated at 150 °C for 15 h. No selective macrocycle formation was observed. Then the reaction mixture was heated at 170 °C for 5 d. At this point the volatiles were removed *in vacuo*. The resulting mixture was taken up in $CDCl_3$. ^{1}H NMR spectroscopy indicated trimeric (33%) and tetrameric (33%) macrocycles along with a third unidentified product. NMR data agreed with the literature.[22,23]

3.11 References

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Chapter Four:

Interconversion of $Mo_2(OR)_6$ and $RC{\equiv}Mo(OR)_3$ Complexes

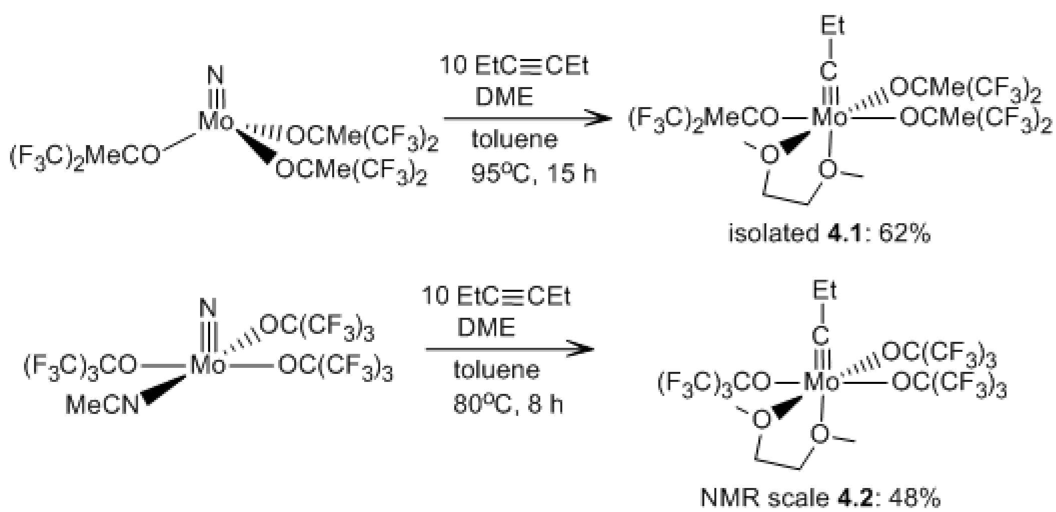
4.1 Introduction

With successful tungsten-based nitrile-alkyne cross-metathesis (NACM) in hand we turned to the development of an analogous molybdenum-based system. The broader functional group tolerance and decreased alkyne polymerization activity of molybdenum-based relative to tungsten-based alkylidyne catalysts would increase the utility of NACM. In approaching the design and development of molybdenum alkylidyne catalysts for NACM, alkylidyne complexes that can be readily synthesized are desired. As discussed in Chapter 1, one of the biggest limitations of molybdenum-based alkyne metathesis is the difficult syntheses of the catalysts.

An ideal method for accessing molybdenum alkylidyne complexes would involve Mo-Mo triple bond scission of $Mo_2(OR)_6$ complexes with *internal* alkynes. Unfortunately, this type of triple bond scission, while well-known with tungsten, has yet to be demonstrated with molybdenum.[1] Previous scissions of $Mo_2(OCMe_3)_6$ were only successful with terminal alkynes, affording low isolated yields of alkylidyne complexes due to decomposition and competing alkyne polymerization.[2,3] In this chapter, alternative methods for the synthesis of molybdenum alkylidyne complexes including their formation from the interaction of internal alkynes with $Mo_2(OR)_6$ complexes is addressed.

4.2 Molybdenum Alkylidyne Syntheses

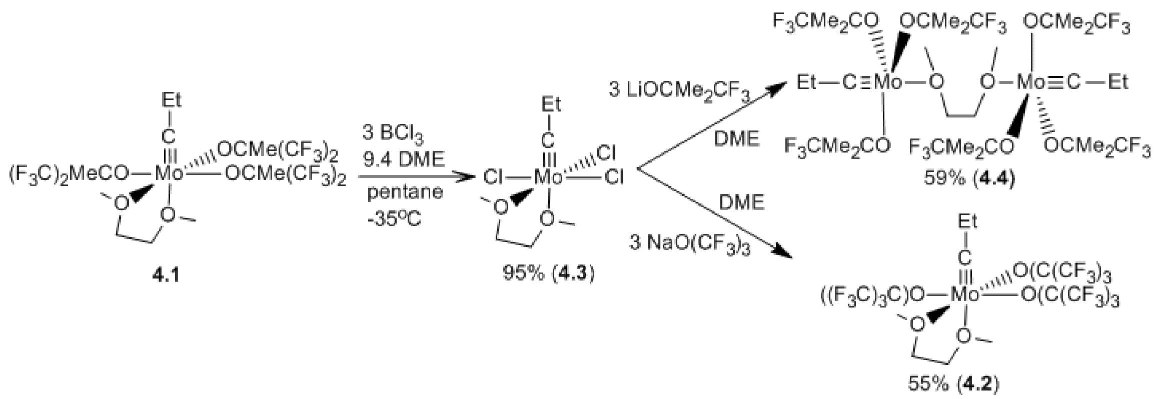
This section will focus on the synthesis of RC≡Mo(OR)$_3$ complexes with ancillary alkoxides varying from $OCMe_3$, $OCMe_2CF_3$, $OCMe(CF_3)_2$, to $OC(CF_3)_3$. As illustrated with tungsten-based NACM, the alkoxide ligands exert a large influence on catalyst activity and resting state, so a broad range of alkylidyne complexes will be investigated. One method to readily access EtC≡Mo(OR)$_3$(DME) when OR= $OCMe(CF_3)_2$ (**4.1**) or $OC(CF_3)_3$ (**4.2**) is via metathesis of N≡Mo(OR)$_3$ with 3-hexyne in the presence of DME (Scheme 4.1).[4] Complex **4.1** can be readily isolated, while **4.2** is difficult to isolate due to decomposition as discussed in Chapter 5.



Scheme 4.1. Formation of **4.1** and **4.2** from N≡Mo(OR)$_3$ complexes.

4.2.1 Syntheses of RC≡Mo(OCMe$_2$CF$_3$)$_3$(DME) (R=alky, aryl) Complexes and EtC≡Mo(OC(CF$_3$)$_3$)$_3$(DME) (4.2)

Since the formation of isolable alkylidyne complexes via metathesis of a molybdenum nitride complex with 3-hexyne is largely limited to $OCMe(CF_3)_2$ ligands, an alternative approach needed to be developed for the installation of other ancillary alkoxides. Coupling of Gdula's facile synthesis of **4.1** and Hopkins's[5] high-yielding conversion of RC≡W(OCMe$_3$)$_3$ complexes to RC≡WX$_3$(DME) complexes results in successful formation RC≡MoX$_3$(DME) species. Specifically, treatment of **4.1** with BCl$_3$ at -35 °C in pentane affords EtC≡MoCl$_3$(DME) (**4.3**) in 95% yield. Subsequent salt elimination of **4.3** with NaOC(CF$_3$)$_3$ or LiOCMe$_2$CF$_3$ yields EtC≡Mo(OC(CF$_3$)$_3$)$_3$(DME) (**4.2**) or [EtC≡Mo(OCMe$_2$CF$_3$)$_3$]$_2$[μ–$\kappa^1\kappa^1$–DME] (**4.4**), respectively (Scheme 4.2).



Scheme 4.2. Formation of **4.2** and **4.4** from **4.3**.

Complex **4.4** can be isolated in crystalline form from pentane. The thermal ellipsoid plot reveals a bridging DME ligand, which is an atypical binding mode for DME in alkylidyne complexes (Figure 4.1).[6] Furthermore, DME is bound trans to the strongest trans influence ligand in the alkylidyne complex, which is also unexpected.[7] The molybdenum centers are related by a center of inversion; the DME ligand is disordered. Complete data for single crystal XRD can be found in Appendix 3.

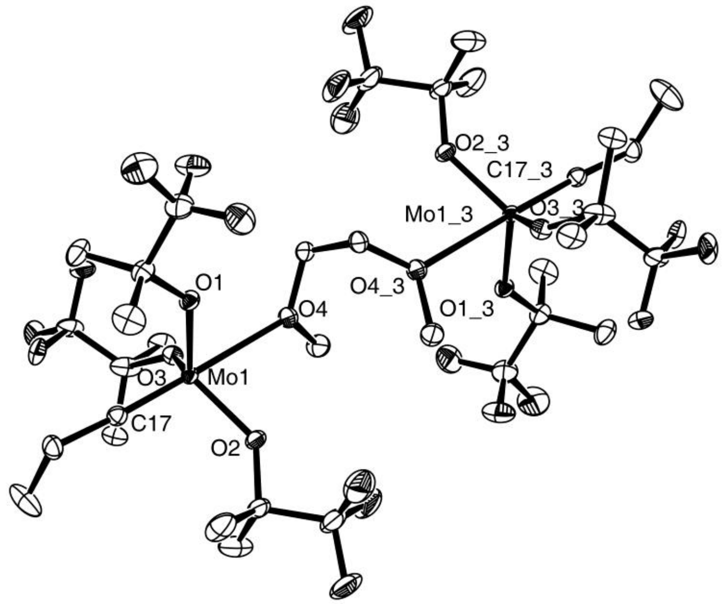
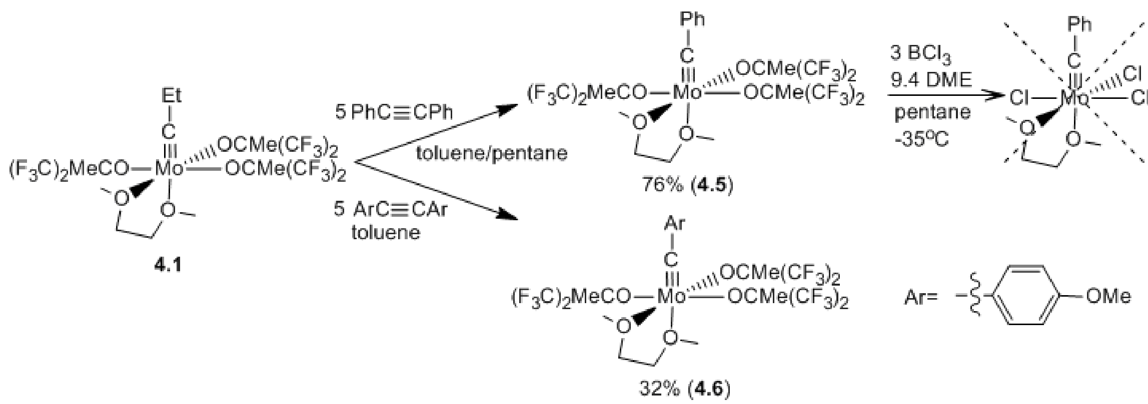


Figure 4.1. 50% thermal ellipsoid plot of **4.4**.

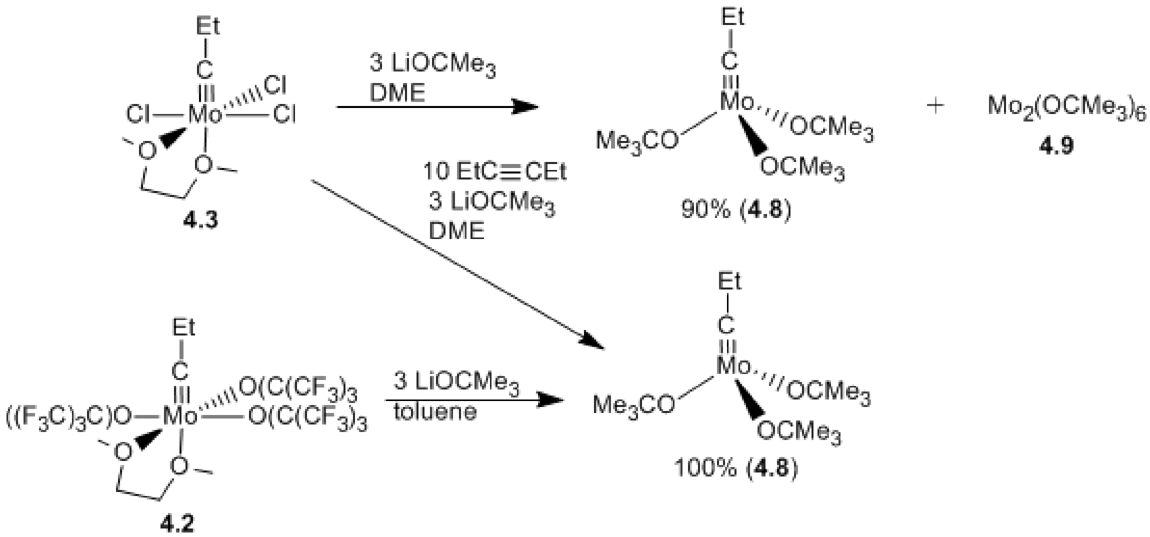
Several benzylidyne complexes were also desired in order to study the relative reactivity of the propylidyne and benzylidyne complexes. PhC≡Mo(OC(CF_3)$_2$Me)$_3$(DME) (**4.5**) and 4-MeOC_6H_5C≡Mo(OC(CF_3)$_2$Me)$_3$(DME) (**4.6**) are readily synthesized via alkyne metathesis of **4.1** with diphenylacetylene and bis(4-methoxyphenyl)acetylene, respectively (Scheme 4.3). Direct conversion of **4.4** to PhC≡Mo(OCMe_2CF_3)$_3$(DME) (**4.7**) through metathesis with diphenylacetylene was achieved; however, separation of the excess diphenylacetylene from **4.7** was unsuccessful. As a result, an alternative approach to the synthesis of **4.7** from PhC≡MoCl_3(DME) was desired. A synthetic pathway similar to that for the synthesis of **4.3** was attempted. Unfortunately, treatment of **4.5** with BCl_3 under a variety of conditions resulted in the formation of intractable product mixtures (Scheme 4.3). Similar results were obtained for the reaction of **4.5** with trimethylsilylchloride and HCl.



Scheme 4.3. Synthesis of **4.6** and **4.7** and subsequent treatment with BCl_3.

4.2.2 Synthesis of EtC≡Mo(OCMe$_3$)$_3$

Addition of lithium *t*-butoxide to **4.3** affords a mixture of EtC≡Mo(OCMe$_3$)$_3$ (**4.8**) and $Mo_2(OCMe_3)_6$ (**4.9**) (Scheme 4.4). The formation of **4.9** can be minimized via the dropwise addition of **4.3** to lithium *t*-butoxide in DME. This suggests that **4.9** is likely being formed through the interaction of two incompletely substituted alkylidyne complexes. Selective formation of **4.8** can be achieved via dropwise addition of **4.3** to a mixture of 3-hexyne and lithium *t*-butoxide. This implies that addition of 3-hexyne helps prevent alkylidyne complex decomposition to **4.9**.



Scheme 4.4. Syntheses of **4.8**.

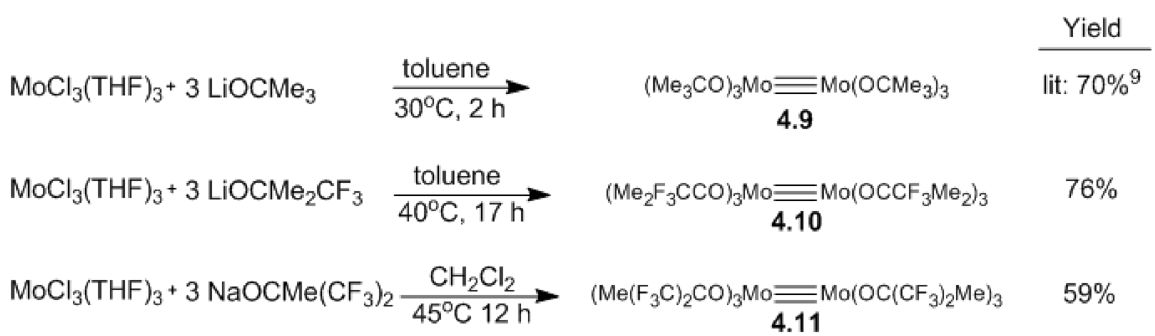
It was also found that treatment of **4.2** with 3 equivalents of lithium *t*-butoxide resulted in complete conversion to **4.8** with no evidence of **4.9** (Scheme 4.4). Isolation of **4.8** from $LiOC(CF_3)_3$ was unsuccessful due to the similar solubility properties of the materials. Attempted salt metathesis with sodium *t*-butoxide resulted in a mixture of products consisting of only a small amount of **4.8**. Repeated recrystallization attempts of **4.8** result in slow bimolecular decomposition to form **4.9**.

4.3 Syntheses of $Mo_2(OR)_6$ Complexes

A simple synthesis of **4.9** from $MoCl_3(THF)_3$ and $LiOCMe_3$ was reported by the Cummins group in 1996 (Scheme 4.5).[8] Extension of this method to the synthesis of other $Mo_2(OR)_6$ complexes is discussed in the following sections.

4.3.1 Syntheses of $Mo_2(OCMe_2CF_3)_6$ and $Mo_2(OCMe(CF_3)_2)_6$

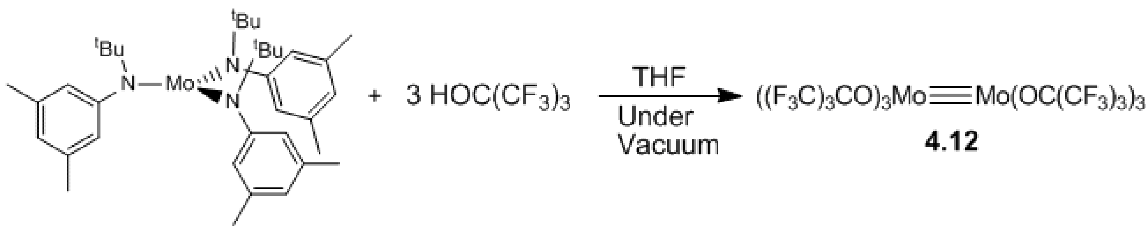
Previous syntheses of $Mo_2(OCMe_2CF_3)_6$ (**4.10**) and $Mo_2(OCMe(CF_3)_2)_6$ (**4.11**) require that the Mo-Mo triple bond is present in the precursor molecule.[9] By using Cummins's method with $LiOCMe_2CF_3$, **4.10** can be isolated readily in a 76% yield (Figure 4.6). Successful formation of **4.11** can be achieved in a 59% yield (compared to 29% from previous methods)[9] via treatment of $MoCl_3(THF)_3$ with 3 equivalents of $NaOCMe(CF_3)_2$ in CH_2Cl_2 at elevated temperatures. Employment of the sodium salt is crucial as the corresponding lithium salt does not lead to the desired reactivity.



Scheme 4.5. Syntheses of $Mo_2(OR)_6$ complexes.

4.3.2 Attempted Syntheses of $Mo_2(OC(CF_3)_3)_6$

Several attempts at synthesizing $Mo_2(OC(CF_3)_3)_6$ (**4.12**) via Cummins's method as described in Section 4.3 resulted in mixtures of materials, but there was no direct evidence of product formation. As a result, the synthesis of **4.12** was approached through treatment of $Mo(N[^tBu]Ar)_3$ (Ar= 3,5-$C_6H_3Me_2$) with $HOC(CF_3)_3$ under vacuum (Scheme 4.6). This reaction must be completed under vacuum as there appears to be N_2 cleavage when the reaction is completed under a dinitrogen atmostphere. This is indicated by the formation of a blue-purple reaction mixture similar to that associated with known μ-N_2 compounds formed from $Mo(NRAr)_3$ precursors.[10] In the absence of N_2, a yellow solution results from the protonolysis reaction with evidence of HN[^{t}Bu]Ar and a single fluorine-containing product indicated by NMR spectroscopy.

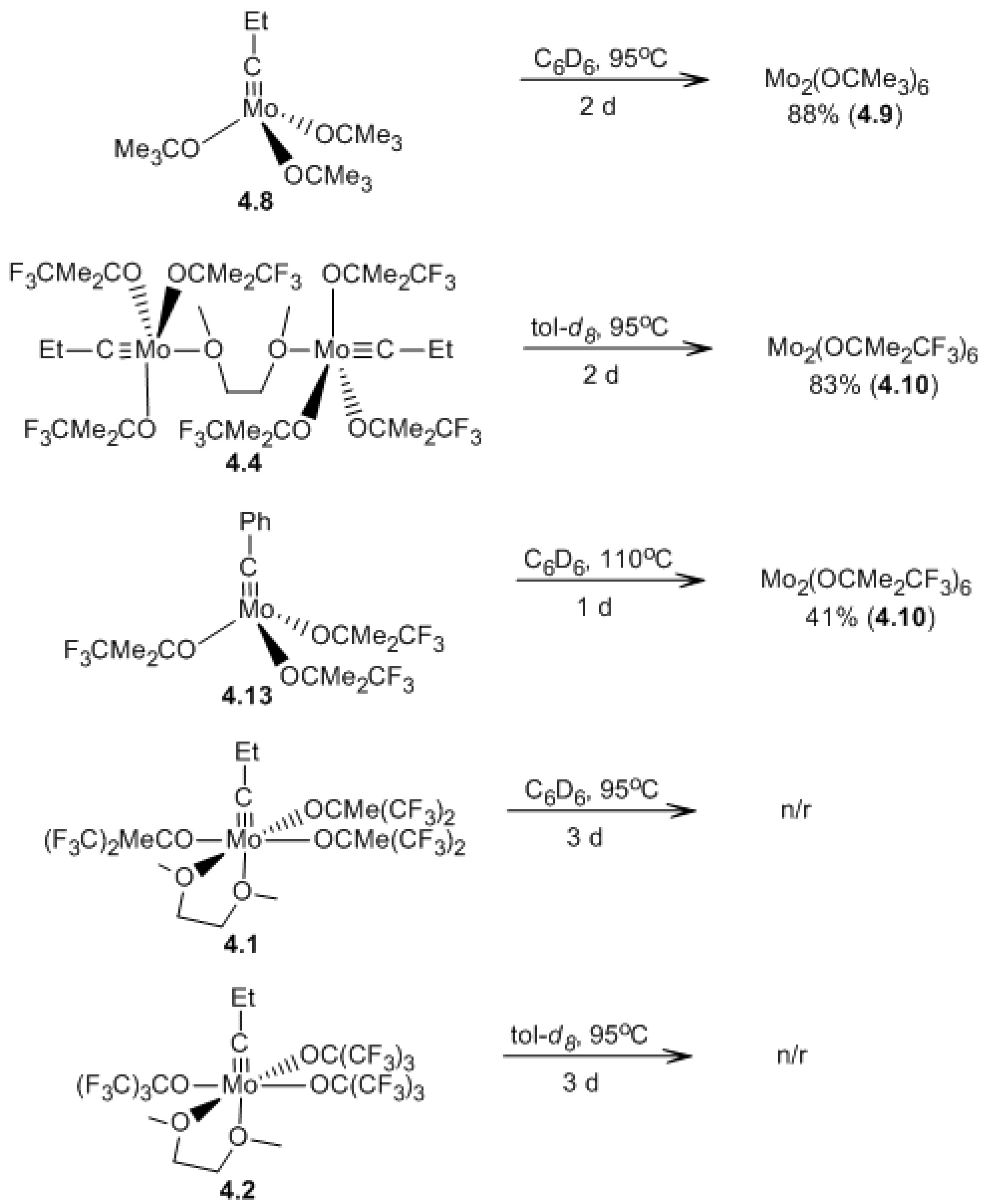


Scheme 4.6. Synthesis of **4.12**.

4.4 Formation of $Mo_2(OR)_6$ Complexes from RC≡Mo(OR)$_3$

An interesting reaction dichotomy exists between molybdenum and tungsten-based alkylidyne and nitride complexes. In molybdenum and tungsten nitride species with $OCMe(CF_3)_2$ ancillary ligands, the alkylidyne complexes are thermodynamically favored relative to the nitride complexes. However, in the molybdenum-based system the nitride complex does not form reversibly, while with tungsten it does. Since $W_2(OR)_6$ complexes are known to undergo metathesis with alkynes to form alkylidyne complexes and $Mo_2(OR)_6$ complexes had previously demonstrated an inability to cleave internal alkynes, we proposed that molybdenum-based complexes might favor the reverse reaction. Additional support for the proposed bimolecular reaction of the alkylidyne complexes to form $M_2(OR)_6$ is found in Chisholm's strong evidence for an equilibrium between "HC≡W(OCMe$_3$)$_3$" and $W_2(\mu\text{-}C_2H_2)(py)(OCMe_3)_5(\mu\text{-}OCMe_3)$.[11]

This hypothesis was tested by heating several molybdenum-based alkylidyne and benzylidyne complexes as depicted in Scheme 4.7. Compounds **4.4** and **4.8** readily convert to $Mo_2(OR)_6$ complexes upon prolonged heating at 95 °C. In comparison to **4.4**, PhC≡Mo($OCMe_2CF_3$)$_3$ (**4.13**) requires harsher conditions for formation of **4.10** (110 °C); no conversion to **4.10** is observed at 95 °C. Higher yields of **4.10** from **4.4** than from **4.13** result from more C-O bond scission at the higher temperatures used.

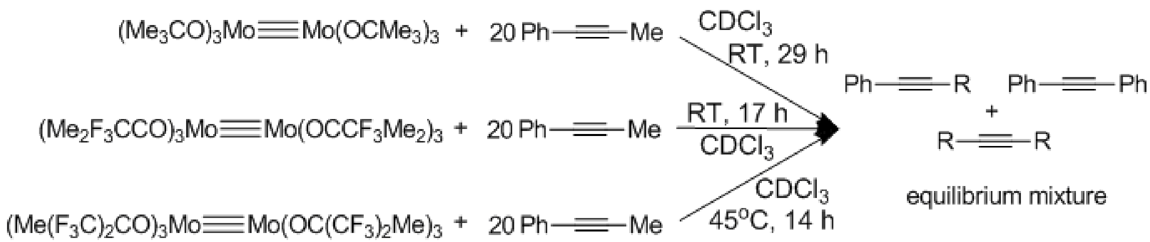


Scheme 4.7. Formation of $Mo_2(OR)_6$ from alkylidyne precursors.

Unlike the alkylidyne complexes that have $OCMe_2CF_3$ and $OCMe_3$ ancillary ligands, those with $OCMe(CF_3)_2$ and $OC(CF_3)_3$ ligands display no conversion to $Mo_2(OR)_6$ complexes (Scheme 4.7). This lack of reactivity was unexpected, as these weaker donor ligands should favor Mo^{3+} relative to Mo^{6+}. In these cases, the strongly bound DME ligand likely prevents the bimolecular reaction. Attempts to isolate $EtC{\equiv}Mo(OCMe(CF_3)_2)_3$ (**4.14**), via sublimation of **4.1** result in isolation of DME-bound **4.1**. Alternative attempts to synthesize and isolate **4.14** are detailed in Chapter 5.

4.5 Alkyne Metathesis with $Mo_2(OR)_6$ Complexes

Based on Schrock's statement, "$Mo_2(OCMe_3)_6$ did not react with disubstituted acetylenes or nitriles,"[2] we set out to establish the ability to form alkylidyne complexes from $Mo_2(OR)_6$ complexes and internal alkynes. An analysis of the work previously performed revealed that all tests for Mo-Mo triple bond scission of **4.9** with internal acetylenes involved symmetrical alkynes such as 4-octyne.[1] In order to probe the potential for alkylidyne formation from **4.9**, unsymmetrical alkynes were employed for two reasons. First, symmetrical alkynes do not react as readily with $W_2(OR)_6$ complexes as unsymmetrical alkynes do.[12] Second, the formation of a symmetrical alkyne from an unsymmetrical alkyne would indicate that an alkylidyne species must have formed at some point in the reaction even if it is not evident by NMR spectroscopy.



Scheme 4.8. Alkyne metathesis with $Mo_2(OR)_6$.

Treatment of **4.9** and **4.10** with 1-phenyl-1-propyne in $CDCl_3$ at room temperature results in an equilibrium mixture of diphenylacetylene, 2-butyne, and unsymmetrical alkyne (Scheme 4.8). Complex **4.11** behaves similarly, except that mild heating of 45 °C is required in order to observe alkyne metathesis (Scheme 4.8). Although no direct evidence of benzylidyne or alkylidyne formation is observed via NMR spectroscopy, alkyne metathesis serves as indirect evidence of the formation of these complexes.

4.5.1 Solvent Studies

The alkyne metathesis activity of **4.9**, **4.10**, and **4.11** with 1-phenyl-1-propyne were investigated in $CDCl_3$, CD_2Cl_2, and C_6D_6. The amount of time required to achieve an equilibrium mixture using each of the catalysts is shown in Table 4.1. Since no alkyne polymerization is observed under the reaction conditions, an equilibrium is established with K_{eq}= 0.27 (±0.01) based on the calculations shown in Figure 4.2.

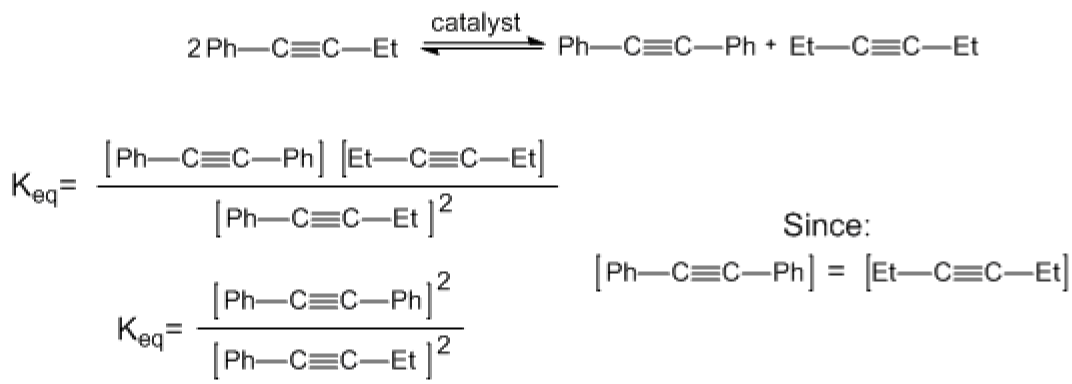


Figure 4.2. Equilibrium calculations.

Alkyne metathesis at room temperature with **4.9** is only observed in $CDCl_3$. Both C_6D_6 and CD_2Cl_2 can serve as media for alkyne metathesis at elevated temperatures with **4.9**. Unlike **4.9**, **4.10** displays alkyne metathesis activity in all tested solvents at room temperature, but $CDCl_3$ is the optimal medium (Table 4.1). Complex **4.11** is active for alkyne metathesis at elevated temperatures in all tested solvents, but only incomplete conversion is observed in CD_2Cl_2. One possible reason that $CDCl_3$ yields the most rapid formation of alkyne metathesis products is that trace amounts of DCl may be present. The ability for acids to increase alkyne metathesis rates is demonstrated in Chapter 5.

Table 4.1. Time in h to equilibrium mixture of symmetrical and unsymmetrical alkynes in various solvents with $Mo_2(OR)_6$ complexes.

Solvent	4.9	4.10	4.11
C_6D_6	n/r[a]	33	25
CD_2Cl_2	n/r	47	6 (IC[b])
$CDCl_3$	29	17	14
Temp	RT	RT	45°C

[a] n/r = no reaction [b]IC = incomplete reaction

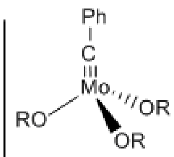
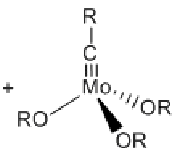
4.6 Formation of RC≡Mo(OR)$_3$ from $Mo_2(OR)_6$ Complexes

As previously noted, formation of alkylidyne complexes from $Mo_2(OR)_6$ and 1-phenyl-1-propyne was not observed by NMR spectroscopy under the tested reaction conditions. Since this is a potentially facile method for formation of molybdenum alkylidyne complexes on a large scale, it is desirable to be able to readily form and isolate the alkylidyne complexes from this system. The following sections focus on altering the reaction conditions and alkyne substrates to facilitate alkylidyne complex formation and isolation from $Mo_2(OR)_6$ complexes.

4.6.1 $Mo_2(OCMe_3)_6$ as a Precursor to RC≡Mo(OR)$_3$

The interaction of several alkynes with **4.9** was initially examined at 85 °C in C_6D_6 as shown in Table 4.2 (Entries 1-4). The use of aryl and alkyl-based symmetrical alkynes highlighted in Entries 3-5 result in little to no conversion to the desired alkylidyne species. In the case of 3-hexyne, the formation of insoluble polymer provides evidence of alkyne polymerization. Use of an unsymmetrical alkyne, 1-phenyl-1-butyne, results in moderate conversion to the benzylidyne complex after 2 days, with further heating resulting in the formation of an unidentified material (Entries 1-2). Completion of the same reaction at a lower temperature (50 °C) results in slower conversion, but higher overall yield as formation of undesired materials and decomposition is avoided. Comparison of 1-phenyl-1-butyne (Entry 6) and 1-phenyl-1-propyne (Entry 7) reveals a surprising difference in reaction rate. Despite operating at slightly elevated temperatures relative to 1-phenyl-1-butyne, 1-phenyl-1-propyne displays much slower conversion to the benzylidyne complex.

Table 4.2. Composition of reaction mixtures from the interaction of **4.9** with alkynes at the time of maximum yield.

Entry	OR=OCMe$_3$			+ 	+ $Mo_2(OR)_6$	+ ROH
1	$Mo_2(OR)_6$ + 5 PhC≡CEt	C_6D_6, 85^oC, 4 d	26%	0%	0%	52%
2	$Mo_2(OR)_6$ + 5 PhC≡CEt	C_6D_6, 85^oC, 2 d	43%	13%	0%	34%
3	$Mo_2(OR)_6$ + 2.5 PhC≡CPh	C_6D_6, 85^oC, 2 d	10%	n/a[a]	0%	55%
4	$Mo_2(OR)_6$ + 5 EtC≡CEt	C_6D_6, 85^oC, 2 d	n/a	0%	38%	42%
5	$Mo_2(OR)_6$ + 5 ^{n}BuC≡C^{n}Bu	1. C_6D_6, 65^oC, 2 d; 2. C_6D_6, 100^oC, 3 d	n/a[a]	0%	100%	0%
6	$Mo_2(OR)_6$ + 5 PhC≡CEt	C_6D_6, 50^oC, 4 d	62%	4%	3%	31%
7	$Mo_2(OR)_6$ + 5 PhC≡CMe	C_6D_6, 60^oC, 4 d	24%	0%	71%	5%

Since the presence of DME was postulated to prevent $Mo_2(OR)_6$ formation with **4.1** and **4.2**, the influence of DME on the relative proportions of $Mo_2(OR)_6$ and RC≡$Mo(OR)_3$(DME) was investigated (Table 4.3). This Lewis base's influence on RC≡$Mo(OR)_3$(DME) formation was found to be substrate-dependent. For instance, with 1-phenyl-1-butyne and diphenylacetylene the overall rate of reaction was suppressed in the presence of DME (Entries 1-4). This could be due to coordination of the DME to **4.9** slowing reaction with the alkynes. In contrast, with 3-hexyne formation of the alkylidyne complex was favored in the presence of DME, although alkyne polymerization was still present (entries 5-6). In this case, the presence of DME may be suppressing the reverse reaction of the alkylidyne complex to form **4.9** at a greater rate than the forward reaction. Form a thermodynamic perspective, stronger coordination of DME to RC≡$Mo(OR)_3$ than

$Mo_2(OR)_6$ could account for the preferential formation of $RC{\equiv}Mo(OR)_3(DME)$. Examination of a slightly longer alkyl alkyne, 4-octyne, revealed no influence on activity by DME (Entries 7-8) and in fact no net reaction, in accordance with Schrock's report.[1]

Table 4.3. Influence of DME on composition of reaction mixtures from the interaction of **4.9** and alkynes at maximum conversion.

Entry	OR=OCMe$_3$	Conditions	$PhC{\equiv}Mo(OR)_3$ +	$RC{\equiv}Mo(OR)_3$ +	$Mo_2(OR)_6$ +	ROH
1	$Mo_2(OR)_6$ + 5 PhC≡CEt	C_6D_6, 50 °C, 4 d	62%	4%	3%	31%
2	$Mo_2(OR)_6$ + 5 PhC≡CEt + DME	C_6D_6, 50 °C, 4 d	55%	0%	29%	16%
3	$Mo_2(OR)_6$ + 2.5 PhC≡CPh	C_6D_6, 85 °C, 2 d	10%	n/a[a]	0%	55%
4	$Mo_2(OR)_6$ + 2.5 PhC≡CPh + DME	C_6D_6, 85 °C, 2 d	trace	n/a		
5	$Mo_2(OR)_6$ + 5 EtC≡CEt	C_6D_6, 60 °C, 4 d	n/a	trace	100%	trace
6	$Mo_2(OR)_6$ + 5 EtC≡CEt + DME	C_6D_6, 50 °C, 4 d	n/a	31%	46%	23%
7	$Mo_2(OR)_6$ + 5 $^nBuC{\equiv}C^nBu$	1. C_6D_6, 65 °C, 2 d; 2. C_6D_6, 100 °C, 3 d	n/a	0%	100%	0%
8	$Mo_2(OR)_6$ + 5 $^nBuC{\equiv}C^nBu$ + DME	1. C_6D_6, 65 °C, 2 d; 2. C_6D_6, 100 °C, 3 d	n/a	0%	100%	0%

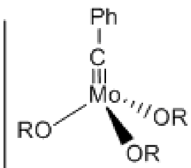
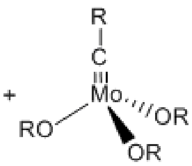
After establishing that 1-phenyl-1-butyne is the optimal substrate for the conversion of **4.9** to $PhC{\equiv}Mo(OCMe_3)_3$ (**4.15**) the reaction was completed on a preparative scale. Unfortunately, separation of 1-phenyl-1-butyne, diphenylacetylene, **4.9**, and **4.15** proved difficult. Removal of 1-phenyl-1-butyne from the reaction mixture can be achieved through slight heating (31 °C) under vacuum. Separation of diphenylacetylene and **4.15** is more difficult as their solubility properties are very similar.

Sublimation of the materials results in isolation of a mixture of all materials, since they all sublime at relatively low temperatures. In order to overcome isolation difficulties, 1-(4-biphenyl)-1-buyne was synthesized and employed in place of 1-phenyl-1-butyne, since bis(4-biphenyl)acetylene is much more insoluble in nonpolar solvents relative to diphenylacetylene. Unfortunately, much lower conversions to benzylidyne species (35% versus 62%) are observed with 1-(4-biphenyl)-1-butyne in comparison to 1-phenyl-1-butyne. This could be due to the steric interaction of the *p*-phenyl group with the alkoxide ligands of **4.9**.

4.6.2 $Mo_2(OCMe_2CF_3)_6$ as a Precursor to $RC{\equiv}Mo(OR)_3$

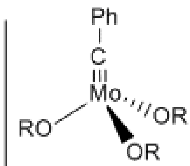
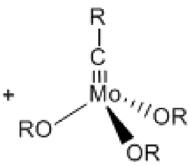
The effectiveness of **4.10** as a precursor to $RC{\equiv}Mo(OR)_3$ complex formation was evaluated with several alkyne sources as shown in Table 4.4. Initial investigations were completed with 5 equivalents of alkyne relative to **4.10** at 85 °C; little to no production of benzylidyne complex was observed (Entries 1-2). Increasing the ratio of alkyne to **4.10** and decreasing the temperature improves the rate of conversion of the 1-phenyl-1-butyne and the overall yield of the benzylidyne complex (Entries 2 vs 3). As with **4.9**, 1-phenyl-1-butyne is superior to 1-phenyl-1-propyne for benzylidyne production from **4.10** (Entries 3-4). Symmetrical alkynes afforded decreased or no conversion to alkylidyne products relative to unsymmetrical alkynes even at elevated temperatures and after prolonged reaction times (entries 5-6).

Table 4.4. Composition of reaction mixtures at maximum conversion from the interaction of **4.10** with alkynes.

Entry	OR=$OCMe_2CF_3$		 +	 +	$Mo_2(OR)_6$
1	$Mo_2(OR)_6$ + 5 PhC≡CPh	C_6D_6, 85°C, 2 d	0%	0%	100%
2	$Mo_2(OR)_6$ + 5 PhC≡CEt	C_6D_6, 85°C, 4 d	15%	1%	84%
3	$Mo_2(OR)_6$ + 20 PhC≡CEt	C_6D_6, 70°C, 1 d	78%	0%	22%
4	$Mo_2(OR)_6$ + 20 PhC≡CMe	C_6D_6, 70°C, 1 d	27%	0%	73%
5	$Mo_2(OR)_6$ + 20 $^nBuC≡C^nBu$	C_6D_6, 70°C, 5 d	0%	0%	100%
6	$Mo_2(OR)_6$ + 20 PhC≡CPh	C_6D_6, 110°C, 8 d	42%	0%	58%

Next the influence of DME on the relative ratios of alkylidyne complexes and **4.10** was examined as indicated in Table 4.5. Addition of DME to the reactions with symmetrical alkynes did not encourage alkylidyne complex formation (Entries 1-2, 7-8). However, benzylidyne complex formation was facilitated upon addition of DME to the reactions with unsymmetrical alkynes (Entries 3-6). As mentioned for **4.9**, DME ligation to the benzylidyne complex could slow the reformation of **4.10** at elevated temperatures, thus allowing for a greater accumulation of the benzylidyne complex.

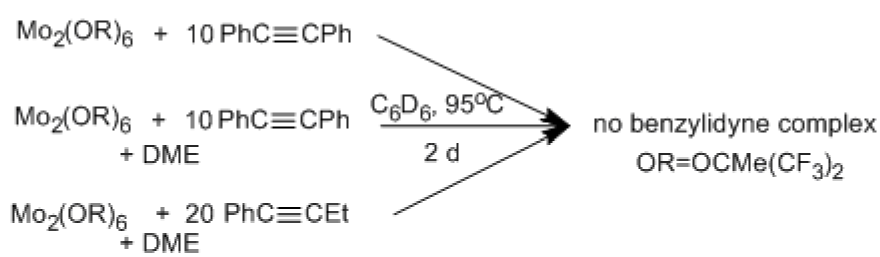
Table 4.5. Influence of DME on composition of reaction mixtures at maximum conversion from the interaction of **4.10** with alkynes.

Entry	OR=OCMe$_2$CF$_3$		+ 	+ Mo$_2$(OR)$_6$
1	Mo$_2$(OR)$_6$ + 5 PhC≡CPh $\xrightarrow[2\ d]{C_6D_6,\ 85^oC}$	0%	0%	100%
2	Mo$_2$(OR)$_6$ + 5 PhC≡CPh + DME $\xrightarrow[2\ d]{C_6D_6,\ 85^oC}$	trace	0%	100%
3	Mo$_2$(OR)$_6$ + 5 PhC≡CEt $\xrightarrow[4\ d]{C_6D_6,\ 85^oC}$	15%	1%	84%
4	Mo$_2$(OR)$_6$ + 5 PhC≡CEt + DME $\xrightarrow[4\ d]{C_6D_6,\ 85^oC}$	46%	15%	39%
5	Mo$_2$(OR)$_6$ + 20 PhC≡CMe $\xrightarrow[2\ d]{C_6D_6,\ 70^oC}$	30%	0%	70%
6	Mo$_2$(OR)$_6$ + 20 PhC≡CMe + DME $\xrightarrow[2\ d]{C_6D_6,\ 70^oC}$	38%	0%	62%
7	Mo$_2$(OR)$_6$ + 20 ^{n}BuC≡C^{n}Bu $\xrightarrow[2\ d]{C_6D_6,\ 70^oC}$	0%	0%	100%
8	Mo$_2$(OR)$_6$ + 20 ^{n}BuC≡C^{n}Bu + DME $\xrightarrow[2\ d]{C_6D_6,\ 70^oC}$	0%	0%	100%

From the combined data in Tables 4.4 and 4.5 the optimal conditions for the conversion of **4.10** to the benzylidyne complex employ 20 equivalents of 1-phenyl-1-butyne and DME at 70 °C. After 2 days, the reaction exhibits 83% conversion of Mo$_2$(OR)$_6$ to a mixture of alkylidyne and benzylidyne complexes. In order to drive formation of the benzylidyne complex, 10 equivalents of diphenylacetylene was introduced into the reaction mixture at this time resulting in 90% conversion to the benzylidyne complex over 2 additional days at 70 °C. Upon increasing to a preparative scale, complete separation of diphenylacetylene and the **4.13** could not be achieved. A sample composed largely of **4.13** (> 95%) was isolated and examined by ^{13}C NMR spectroscopy, verifying the presence of an alkylidyne complex. In order to overcome isolation difficulties, 1-(4-biphenyl)-1-butyne and 1-(4-benzonitrile)-1-butyne were sampled for activity. Unfortunately, no benzylidyne complexes formed under the standard reaction conditions of 70 °C in the presence of DME over 3 days.

4.6.3 $Mo_2(OCMe(CF_3)_2)_6$ as a Precursor to $RC{\equiv}Mo(OR)_3$

The ability of **4.11** to undergo triple bond metathesis with internal alkynes to produce isolable $RC{\equiv}Mo(OR)_3$ complexes was investigated at 95 °C in C_6D_6. As described in Scheme 4.9, neither symmetrical nor unsymmetrical alkynes resulted in appreciable formation of the benzylidyne complex from **4.11** even upon addition of DME. The preference for a dimeric molybdenum species over an alkylidyne complex is not surprising, as the weakly electron donating ligands would favor the 3+ oxidation state relative to the 6+ oxidation state.



Scheme 4.9. Attempted formation of $RC{\equiv}Mo(OR)_3$ complexes from **4.11** with internal alkynes.

4.7 $N{\equiv}Mo(OR)_3$ Complexes as Precursors to $Mo_2(OR)_6$

Since $Mo_2(OR)_6$ complexes are readily accessed from the propylidyne complexes **4.4** and **4.8**, $N{\equiv}Mo(OR)_3$ complexes ligated with $OCMe_3$, $OCMe_2CF_3$, $OCMe(CF_3)_2$, and $OC(CF_3)_3$ were examined for similar bimolecular decomposition behavior at 95 °C in toluene-d_8. No evidence of $Mo_2(OR)_6$ complex formation is observed with any of the nitride complexes.

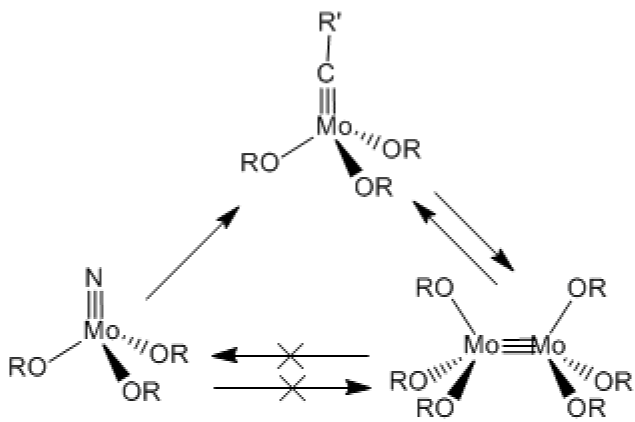
4.8 Conclusions

Molybdenum-based alkylidyne complexes are attractive alkyne metathesis catalysts because of their functional group tolerance and activity. Unfortunately, they are not widely used as a result of the laborious syntheses of the catalysts. This chapter introduced two new, facile methods for the synthesis of alkylidyne complexes. One method involves the conversion of $N{\equiv}Mo(OC(CF_3)_2Me)_3$ to **4.1** followed by treatment with BCl_3 to afford **4.3** in a 95 % yield. This complex can then serve as a precursor to several alkylidyne species. Alternatively, $Mo_2(OR)_6$ complexes ligated with $OCMe_3$ and $OCMe_2CF_3$ alkoxides were found to undergo Mo-Mo triple bond scission in the presence of internal alkynes to afford alkylidyne complexes.

The successful formation of alkylidyne complexes from $Mo_2(OR)_6$ precursors is substrate-dependent; unsymmetrical internal alkynes displayed the greatest conversion of $Mo_2(OR)_6$ species to benzylidyne complexes. A comparison of simple unsymmetrical alkynes revealed increased conversions to the benzylidyne complex upon treatment with 1-phenyl-1-butyne relative to 1-phenyl-1-propyne. The influence of a Lewis base, DME, depends on the alkoxide: $OCMe_2CF_3$ ligands in general favor benzylidyne complex formation in the presence of DME and $OCMe_3$ ligands show suppressed conversion to the benzylidyne complex. Although $Mo_2(OCMe(CF_3)_2)_6$ displayed alkyne metathesis activity, thus indicating that trace amounts of benzylidyne complex form in the presence of alkynes, no accumulation of benzylidyne complex was observed by NMR spectroscopy. Future work will focus on isolating the benzylidyne complexes from these reaction mixtures.

An interesting complication to the formation of alkylidyne complexes from $Mo_2(OR)_6$ species is the presence of the reverse reaction under similar reaction conditions depending on the nature of the alkylidyne complex. Propylidyne complexes ligated with either $OCMe_3$ or $OCMe_2CF_3$ ancillary alkoxides readily undergo conversion to $Mo_2(OR)_6$ species. The benzylidyne complex, **4.13**, displays similar reactivity at elevated temperatures. Unexpectedly, propylidyne complexes ligated by $OCMe(CF_3)_2$ and $OC(CF_3)_3$ do not form $Mo_2(OR)_6$ species under the reaction conditions tested. This is likely due to strong adduct formation with DME preventing the bimolecular interaction.

From the overall objective of developing NACM with molybdenum-based alkyne metathesis catalysts, the system grows more complicated. Unlike tungsten, an extra interconversion between alkylidyne and dimeric molybdenum complexes must now either be included or avoided in order to achieve successful NACM as demonstrated in Scheme 4.10. This then brings about the question of the interconversion of $Mo_2(OR)_6$ complexes and $N{\equiv}Mo(OR)_3$, which has not yet been fully investigated.[2] The formation of $Mo_2(OR)_6$ complexes from $N{\equiv}Mo(OR)_3$ currently has no precedent.



Scheme 4.10. Known interconversions of N≡[Mo], RC≡[Mo], and [Mo]≡[Mo] species.

4.9 Experimental

4.9.1 General Procedures

All reactions were performed in an atmosphere of dinitrogen, either in a nitrogen-filled MBRAUN Labmaster 130 glove box or by using standard air-free techniques.[13] ^{1}H NMR spectra were recorded at 499.909 MHz, 399.967 MHz on a Varian Inova 400 spectrometer or 300.075 MHz on a Varian Inova 300 spectrometer and referenced to the residual protons in toluene-d_8 (2.09 ppm), $CDCl_3$ (7.26 ppm), CD_2Cl_2 (5.33 ppm), THF-d_8 (3.58 ppm), and C_6D_6 (7.15 ppm). ^{19}F NMR spectra were recorded at 282.384 MHz on a Varian Inova 300 spectrometer or 376.326 MHz on a Varian Inova 400 spectrometer and were referenced to an external standard of $CFCl_3$ in $CDCl_3$ (0.00 ppm). ^{13}C NMR spectra were recorded at75.465 MHz on a Varian Inova 300 spectrometer and were referenced to naturally abundant ^{13}C nuclei in CD_2Cl_2 (54.00 ppm) and THF-d_8 (67.57 ppm). GC/MS data were collected on a Shimadzu GCMS-QP5000 with a Restek XTI-5 phase column (30m, 0.25 I.D., 0.25 D. F.). EI MS data were collected on a VG (Micromass) 70-250-S Magnetic sector mass spectrometer.

4.9.2 Materials

All solvents used were dried and deoxygenated by the method of Grubbs.[14] Bis(4-methoxyphenyl)acetylene,[15] N≡Mo($OCMe_3$)$_3$,[16] N≡Mo($OCMe_2CF_3$)$_3$,[17] EtC≡Mo(OCMe(CF_3)$_2$)$_3$ (**4.1**),[18] N≡Mo(OC(CF_3)$_3$)$_3$(MeCN),[18] $MoCl_3$(thf)$_3$,[19] 1-butynyllithium,[20] LiOC(CF_3)$_2$Me,[21] NaOC(CF_3)$_3$,[22] N≡Mo(N^tBuAr) (Ar=$C_6H_3Me_2$),[23] 1-(4-cyanophenyl)-1-butyne,[24] and Mo_2($OCMe_3$)$_6$[8] were prepared according to literature procedures. $LiOCMe_2CF_3$ and LiOC(CF_3)$_3$ were prepared in a manner analogous to that used for the preparations of LiOC(CF_3)$_2$. NaOCMe(CF_3)$_2$ were prepared in a manner analogous to that used for the preparation of NaOC(CF_3)$_3$. $LiOCMe_3$ was obtained from Strem. BCl_3 (1M in heptane) and HCl (3M in Et_2O) were obtained from Aldrich. HOC(CF_3)$_3$ was obtained from Apollo Scientific Ltd. Trimethylsilyl chloride (TMSCl), mesitylene, diphenylacetylene, zinc chloride, and 1,3,5-trimethoxybenzene were obtained from Acros. 3-hexyne, 1-phenyl-1-butyne, 1-phenyl-1-propyne, and 4-octyne were obtained from GFS Chemicals and dried over 4 Å molecular sieves for at least 24 hours. Magnesium sulfate was obtained from Fischer Scientific. Pd(PPh_3)$_4$ was obtained from Pressure Chemical Company. 4-bromobiphenyl was obtained from TCI Organic Chemicals. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried over 4 Å molecular sieves for at least 24 hours. Anhydrous 1,2-dimethoxyethane (DME) was obtained from Aldrich and further dried over sodium benzophenone/ketal. All reagents were used as received unless otherwise noted.

4.9.3 Alkylidyne Complex Syntheses

EtC≡MoCl$_3$(DME) (4.3). **4.1** (2.00 g, 2.60 mmol) was slurried in pentane (100 mL) and DME (2.54 mL, 24.4 mmol, 9.4 equiv). The reaction mixture was frozen in the cold well. To the just thawed slurry boron trichloride (7.76 mL, 7.76 mmol, 2.99 equiv) at -35 °C was added via syringe with stirring and allowed to warm to room temperature. The reaction mixture went through a series of precipitations, ultimately forming a dark blue precipitate. After 15 h the reaction mixture was filtered to collect a powder that was washed with 50 mL pentane. A blue powder was isolated (812.7 mg, 2.44 mmol, 95%). ^{1}H NMR (300 MHz, THF-d_8): δ 3.76 (q, 2H, CH_2 , J=7.6 Hz), 3.43 (s, 4H, DME), 3.28 (s, 6H, DME), 1.18 (d, 2H, CH_3, J=7.6 Hz). ^{13}C{^{1}H} NMR (400 MHz, THF-d_8): δ 337.91 (s, Mo≡*C*), 72.82 (s, DME) 59.08 (s, DME), 43.88 (s, C*C*H$_2$CH$_3$), 11.60 (s, CCH$_2$*C*H$_3$). Anal. Calcd for $MoO_2C_7H_{15}Cl_3$: C, 25.21; H, 4.53. Found: C, 25.17; H, 4.58.

EtC≡Mo(OC(CF$_3$)$_3$)$_3$(DME) (4.2). **4.3** (250.0 mg, 0.7507 mmol) was dissolved in DME (10 mL). Sodium nonafluoro-*t*-butoxide (581.0 mg, 2.252 mmol, 3 equiv) was dissolved in Et$_2$O (5 mL). The former solution was added to the latter solution with stirring. The reaction mixture immediately turned pink. After stirring for 10 min the volatiles were removed *in vacuo*. The resulting residue was taken up in Et$_2$O (40 mL) and filtered through celite. The filtrate volume was reduced to 10 mL and the solution was cooled to -35 °C. Pink crystals of **4.2** were collected via filtration (381.6 mg, 55.0%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 3.10 (v br s, 4H, DME), 2.88 (q, 2H, ≡CCH_2CH$_3$, J=7.4 Hz), 2.79 (v br s, 6H, DME), 0.43 (t, 3H, ≡CCH$_2$CH_3, J=7.4 Hz). ^{19}F NMR (300 MHz, C$_6$D$_6$): –72.45 (s, CF_3). ^{13}C{^{19}F} NMR (400 MHz, CD$_3$CN): δ 334.73 (s, br, Mo≡*C*), 122.42 (s, OC(*C*F_3)$_3$), 86.18 (s, O*C*(CF_3)$_3$), 72.45 (t, DME, $J_{C\text{-}H}$=141.4 Hz), 58.90 (q, DME, $J_{C\text{-}H}$=141.4 Hz), 43.54 (t, C*C*H_2CH_3, $J_{C\text{-}H}$=129.5 Hz), 10.97 (q, CH_2*C*H_3, $J_{C\text{-}H}$=129.5 Hz). $^{13}C\{^1H\}$ NMR (400 MHz, CD_3CN): δ 334.59 (s, br, Mo≡*C*), 122.34 (q, OC(*C*F_3)$_3$, $J_{C\text{-}F}$=295.4 Hz), 86.36 (m, O*C*(CF_3)$_3$, $J_{C\text{-}F}$=29.6 Hz), 72.38 (s, DME), 58.84 (s, DME), 43.45 (s, C*C*H_2CH_3), 10.88 (s, CCH_2*C*H_3). Anal. Calcd for $MoO_5C_{19}H_{15}F_{27}$: C, 24.48; H, 1.62. Found: C, 24.30; H, 1.70.

[EtC≡Mo(OCMe$_2$CF$_3$)$_3$]$_2$[*μ–κ^{1}κ^1*–DME] (4.4). **4.3** (300.0 mg, 0.9004 mmol) was dissolved in DME (10 mL). Lithium trifluoro-*t*-butoxide (362.0 mg, 2.701 mmol, 3 equiv) was dissolved in DME (3 mL). The solution of lithium trifluoro-*t*-butoxide was added to the former solution was stirring. The reaction mixture immediately turned red-brown. After stirring for 15 min the volatiles were removed *in vacuo*. The resulting residue was taken up in pentane (40 mL) and filtered through celite. The filtrate volume was reduced to 10 mL and the solution was cooled to -35 °C. Deep red brown crystals of **4.4** were collected via filtration (298.1 mg, 58.7%). ^1H NMR (300 MHz, C_6D_6): δ 3.37 (s, 2H, DME), 3.15 (s, 3H, DME), 2.56 (q, 2H, ≡CC*H*$_2$CH$_3$, J=7.3 Hz), 1.38 (s, 18, OC(C*H*$_3$)$_2$CF$_3$, 0.740 (t, 3H, ≡CCH$_2$C*H*$_3$, J=7.3 Hz) ^{19}F NMR (300 MHz, C_6D_6): –82.56 (OC(CH$_3$)$_2$C*F*$_3$). $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): δ 300.20 (s, Mo≡*C*), 126.90 (q, OC(CH$_3$)$_2$*C*F$_3$, $J_{C\text{-}F}$=285.2 Hz), 81.43 (q, O*C*CF$_3$(CH$_3$)$_2$, $J_{C\text{-}F}$=28.4 Hz), 72.00 (s, DME) 58.96 (s, DME), 44.34 (s, C*C*H$_2$CH$_3$), 25.64 (s, OC(*C*H$_3$)$_2$CF$_3$), 13.67 (s, CCH$_2$*C*H$_3$). Anal. Calcd for $Mo_2O_8C_{35}H_{59}F_{18}$: C, 36.25; H, 5.01. Found: C, 36.25; H, 5.10.

4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_2$Me)$_3$(DME) (4.6). **4.1** (250.0 mg, 0.3245 mmol) and bis(4-methoxyphenyl)acetylene (386.6 mg, 1.623 mmol, 5.0 equiv) were dissolved in toluene (10 mL). After stirring for 15 min, the volatiles were removed *in vacuo*. Then the resulting residue was extracted with pentane (45 mL). The pentane was removed *in vacuo* and the material was dissolved in Et_2O (5 mL) and cooled to −35 °C. The resulting precipitate was filtered and taken up in 1:1 Et_2O/pentane (5 mL) and cooled to −35 °C. Red-orange crystals of **4.6** were isolated from the reaction mixture. An additional crop of crystals were collected for a total 87.5 mg (0.103 mmol, 31.8%) product. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.14 (d, 2H, ArH, J=6.8 Hz), 6.81 (d, 2H, ArH, J=6.8 Hz), 3.78 (s, 3H, OMe), 3.71 (s, 4H, DME), 3.58 (s, 6H, DME), 1.86 (s, 9H, OCCH_3(CF$_3$)$_2$). ^{19}F NMR (400 MHz, CD_2Cl_2): –77.51 (OCMe(CF_3)$_2$). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 296.40 (s, Mo≡*C*), 160.73 (s, Ar), 138.23 (s, Ar), 132.51 (s, Ar), 124.31 (q, OC(*C*F$_3$)$_2$Me, $J_{C\text{-}F}$=288.9 Hz), 113.79 (s, Ar), 84.1 (m, O*C*Me(CF$_3$)$_2$), 72.26 (s, DME), 63.76 (s, OMe), 55.84 (s, DME), 19.42 (s, OC*C*H$_3$(CF$_3$)$_2$).

EtC≡Mo(OCMe$_3$)$_3$ (4.8). **Method 1.** **4.3** (10.0 mg, 0.0300 mmol) was slurried in DME (8 mL) and placed in an addition funnel. Lithium *t*-butoxide (7.2 mg, 0.090 mmol, 3 equiv) was dissolved in DME (6 mL). **4.3** was added dropwise with stirring to the solution of lithium *t*-butoxide. The reaction was allowed to stir overnight. ^{1}H NMR spectroscopy indicated formation of **4.8** (89%) and $Mo_2(OCMe_3)_6$ (11%). **Method 2.** **4.3** (200.0 mg, 0.5997 mmol) was slurried in DME (10 mL). Lithium *t*-butoxide (144.0 mg, 1.799 mmol, 3 equiv) and 3-hexyne (681 μL, 6.00 mmol, 10 equiv) were dissolved in

DME (8 mL). The solution of **4.3** was added dropwise with stirring to the solution of 3-hexyne and lithium t-butoxide over 30 min. The reaction mixture was stirred for an additional 30 min. The volatiles were then removed *in vacuo* to afford a red ppt. ^{1}H NMR spectroscopy indicated complete conversion to **4.8**. At this point, the reaction mixture was taken up in pentane and filtered. The filtrate was reduced to 5 mL and then Et_2O (3.0 mL) was added. The mixture was then cooled to -35 °C. A mixture f **4.8** and the decomposition product **4.9** was isolated. **Method 3.** **4.2** (215.0 mg, 0.2306 mmol) and lithium *t*-butoxide (55.4 mg, 0.692 mmol, 3 equiv) were slurried in toluene (10 mL). The reaction mixture was heated to 60 °C for 1.5 h. The reaction mixture was filtered and the white precipitate was washed with pentane (5 mL). The volatiles were removed *in vacuo* from the filtrate. The residue was dissolved in Et_2O (5 mL) and cooled -35 °C. The resulting precipitate was filtered. However, ^{19}F and ^{1}H NMR spectroscopy indicated a mixture of $LiOC(CF_3)_3$ and **4.8**. Attempted recrystallizations from toluene, toluene/pentane, pentane/Et_2O did not lead to selective isolation of the product. Decomposition to **4.9** was becoming evident after repeated recrystallization attempts. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.08 (q, 2H, $\equiv CCH_2CH_3$, J=7.6 Hz), 1.39 (s, 27, $OC(CH_3)_3$, 1.16 (t, 3H, $\equiv CCH_2CH_3$, J=7.6 Hz). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 289.61 (s, Mo≡*C*), 78.9 (s, O*C*Me$_3$), 43.16 (s, *C*H$_2$CH$_3$) , 32.73 (s, OC(*C*H$_3$)$_3$), 14.27 (s, CH$_2$*C*H$_3$). EI MS [*m/z*]$^+$: 358.141.

Reaction of 4.5 with BCl_3. Method 1. 4.5 (30.0 mg, 0.0367 mmol) was slurried in a mixture of pentane (7 mL), toluene (1 mL), and DME (35.8 μL, 0.345 mmol, 9.4 equiv). The mixture was cooled to -35 °C. Then BCl_3 (110.0 μL, 0.110 mmol, 3 equiv) was added to the reaction mixture with stirring. No obvious color change occurred as the reaction mixture warmed to room temperature. After 5 min, additional toluene (2 mL) was added to increase the solubility of the materials. Within 1 h, the reaction mixture had turned from orange-red to pink with a brown ppt forming. After 12 h a tan/orange ppt was isolated via filtration. ^{1}H NMR spectroscopy of the material indicated the presence of a mixture of products. **Method 2.** **4.5** (30.0 mg, 0.0367 mmol) was dissolved in CH_2Cl_2 (8 mL) and DME (35.8 μL, 0.345 mmol, 9.4 equiv). The mixture was cooled to -35 °C. Then BCl_3 (110.0 μL, 0.110 mmol, 3 equiv) was added to the reaction mixture with stirring. Within 20 min, the reaction mixture had turned from orange-red to yellow and then to a marigold color. After 2.5 h the volatiles were removed *in vacuo*. The resulting oily residue was dissolved in CD_2Cl_2; however, a lot of materials precipitated upon addition of CD_2Cl_2. Pentane was added to the reaction mixture and the material was filtered. The resulting precipitate was extracted with MeCN. The volatiles were removed from the extract and the resulting material was reconstituted in CD_3CN. ^{1}H NMR spectroscopy of the material indicated the presence of a mixture of products.

Reaction of 4.5 with HCl. **4.5** (30.0 mg, 0.0367 mmol) was dissolved in CH_2Cl_2 (8 mL) and DME (35.8 μL, 0.345 mmol, 9.4 equiv). The mixture was cooled to -35 °C. Then HCl (54.9 μL, 0.110 mmol, 3 equiv) was added to the reaction mixture with stirring. The reaction mixture turned from deep orange to yellow within 20 min. After 2.5 h the volatiles were removed *in vacuo*. The resulting residue was dissolved in CD_2Cl_2; however, a lot of materials precipitated upon addition of CD_2Cl_2. Pentane was added to the reaction mixture and the material was filtered. The resulting precipitate was extracted with MeCN. The volatiles were removed from the extract and the resulting material was reconstituted in CD_3CN. ^1H NMR spectroscopy of the material indicated the presence of a mixture of products.

Reaction of 4.5 with TMSCl. 4.5 (30.0 mg, 0.0367 mmol) was dissolved in CH_2Cl_2 (8 mL) and DME (35.8 μL, 0.345 mmol, 9.4 equiv). The mixture was cooled to -35 °C. Then TMSCl (35.8 μL, 0.110 mmol, 3 equiv) was added to the reaction mixture with stirring. No color change occurred over 20 min. The reaction mixture stirred for 2 d. Pentane was added to the reaction mixture and the resulting precipitate was filtered. This solid was extracted with MeCN. After 2.5 h the volatiles were removed *in vacuo*. The resulting residue was dissolved in CD_2Cl_2; however, a lot of materials precipitated upon addition of CD_2Cl_2. Pentane was added to the reaction mixture and the material was filtered. The resulting precipitate was extracted with MeCN. The volatiles were removed from the extract and the resulting material was reconstituted in CD_3CN. ^1H NMR spectroscopy of the material indicated the presence of a mixture of products.

4.9.4 $Mo_2(OR)_6$ Syntheses

$Mo_2(OCMe_2CF_3)_6$ (4.10). $MoCl_3(thf)_3$ (3.155 g, 7.536 mmol) was slurried in toluene (25 mL). $LiOCMe_2CF_3$ (3.03 g, 22.6 mmol, 3 equiv) was added to the slurry with toluene (25 mL). The reaction mixture was sealed and heated at 45 °C for 14 h. The reaction mixture was filtered through celite and the celite was washed with toluene (60 mL). The filtrate was reduced to 15 mL *in vacuo* and the resulting solution was cooled to -35 °C. Three crops of red powder were collected via filtration (2.722 g, 2.852 mmol, 76%). Spectroscopic data agree with the literature.[9] ^{19}F NMR (400 MHz, C_6D_6): –82.53 (s, $OCMe_2CF_3$).

$Mo_2(OCMe(CF_3)_2)_6$ (4.11). $MoCl_3(thf)_3$ (500 mg, 1.19 mmol) was slurried in CH_2Cl_2 (10 mL). $NaOCMe(CF_3)_2$ (731 mg, 3.58 mmol, 3 equiv) was added to the slurry with CH_2Cl_2 (10 mL). The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction mixture was sealed and heated at 45 °C for 21 h. The reaction mixture was filtered. The filtrate was reduced to 15 mL *in vacuo* and the resulting mixture was cooled to -35 °C. A bright orange-red powder was collected via filtration (453.3 mg, 0.354 mmol, 59%). Spectroscopic data agree with the literature.[9] ^{19}F NMR (400 MHz, $CDCl_3$): –77.85 (s, $OCMe(CF_3)_2$). EI/MS $[M/Z]^+$: 1281.86

Reaction of $MoCl_3(thf)_3$ and $MOC(CF_3)_3$. $MoCl_3(thf)_3$ was slurried in the desired solvent. Then $MOC(CF_3)_3$ (M= Li, Na) was added to the reaction mixture. The reaction was monitored at the desired temperature via ^{19}F NMR spectroscopy. A summary of the attempts are shown in Table 4.6.

Table 4.6. Attempted syntheses of **4.11**.

$MOC(CF_3)_3$	Solvent	Temp	Time	^{19}F NMR Data
Li	CD_2Cl_2	RT	24 h	-70.7 (2%), -72.2 (8%), -75.2 (86%), SM (4%)
Li	CD_2Cl_2	42°C	17 h	Mixture- all new products volatile
Na	CD_2Cl_2	RT	24 h	largely SM

Na	CD_2Cl_2	42°C	17 h	No reaction
Na	$CDCl_3$	80°C	16 h	No reaction
Na	CD_3CN	RT	26 h	No reaction
Na	CD_3CN	70°C	18 h	multiple products
Li	CD_3CN	70°C	24 h	No reaction
Na	Toluene	RT	15 h	No new pks

Reaction of Mo(NRAr)$_3$ and HOC(CF$_3$)$_3$. N≡Mo(N^{t}BuAr)$_3$ (Ar=3,5-C_6H_3Me) (100.0 mg, 0.1601 mmol) was placed in a J. Young tube. Then THF (1.0 mL) and HOC(CF$_3$)$_3$ (133.9 μL, 0.9604 mmol, 6 equiv) were placed in a separate J. Young tube. The solution was frozen and the overlying volatiles were removed *in vacuo*. The solution was then allowed to thaw and vacuum transferred into the J. Young tube containing N≡Mo(N^{t}BuAr)$_3$. After complete vacuum transfer the reaction mixture was allowed to warm to room temperature overnight. The voltailes were then removed *in vacuo* and the resulting residue was taken up in C_6D_6. ^{19}F NMR spectroscopy indicated the presence of only one species at -74.1 ppm.

4.9.5 Formation of Mo$_2$(OR)$_6$ Complexes from RC≡Mo(OR)$_3$ Precursors

Formation of 4.9. **4.3** (10.0 mg, 0.0300 mmol) was dissolved in DME (3 mL). To this solution was added solid LiOCMe$_3$ (7.2 mg, 0.090 mmol, 3 equiv) with stirring. After stirring for 19 h, the volatiles were removed *in vacuo* to afford **4.8** (82%) and **4.9** (18%) as indicated by ^{1}H NMR spectroscopy. The material was taken up in C_6D_6 and heated at 60°C for 17 h. At this point the reaction mixture consisted of **4.8** (68%) and **4.9** (32%). The reaction mixture was frozen and the overlying volatiles were removed *in* *vacuo*. The reaction mixture was then heated to 90 °C for 4 d. At this point the reaction mixture consisted of 88% **4.9**.

Formation of (4.10). Method 1. 4.4 was dissolved in toluene-d_8 (0.5 mL). The solution was heated at 95 °C for 2 d. At this point ^{19}F NMR spectroscopy indicated 80% conversion to **4.10** with the remaining material being composed of unknown decomposition products. **Method 2. 4.7** was dissolved in C_6D_6 and heated at 90 °C for 22 h. No reaction was observed. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 110 °C for 23 h at which point ^{1}H and ^{19}F NMR spectroscopy indicated the formation of **4.10** (43%). Additional heating resulted in decomposition of the reaction mixture. GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 16.877 min).

Attempted formation of 4.11 from 4.1. Attempt 1. 4.1 (5.0 mg, 0.0065 mmol) was dissolved in C_6D_6 (750 μL). The reaction mixture was frozen and the overlying volatiles were evacuated. The solution was placed in an oil bath at 80 °C. No evidence of **4.11** formation was found by ^{1}H NMR spectroscopy over 2 d. **Attempt 2. 4.1** (5.0 mg, 0.0065 mmol) was dissolved in $CDCl_3$ (750 μL). The reaction mixture was frozen and the overlying volatiles were evacuated. The solution was placed in an oil bath at 80 °C. No evidence of **4.11** formation was found by ^{1}H NMR spectroscopy over 3 d, however several decomposition products were present.

Attempted formation of 4.12 from 4.2. **4.2** (5.0 mg, 0.0065 mmol) was dissolved in $CDCl_3$ (750 μL). The reaction mixture was frozen and the overlying volatiles were evacuated. The solution was placed in an oil bath at 80 °C. No evidence of the formation of a new product or decomposition of the starting material was found by ^1H NMR spectroscopy over 3 d.

4.9.6 Alkyne Metathesis Solvent Studies with $Mo_2(OR)_6$ Complexes

General Procedure. $Mo_2(OR)_6$ was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added via syringe. The reaction was monitored at the desired temperature.

Reaction with 4.10. Following the general procedure at room temperature: **4.10** (5.0 mg, 0.0052 mmol), 1-phenyl-1-propyne (12.9 μL, 0.105 mmol). GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.173 min), 115 (C_9H_8, R_t 3.040 min).

Reaction with 4.9. Following the general procedure at room temperature: **4.9** (5.0 mg, 0.0079 mmol), 1-phenyl-1-propyne (19.6 μL, 0.159 mmol). GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.180 min), 115 (C_9H_8, R_t 3.043 min).

Reaction with 4.11. Following the general procedure at room temperature: **4.11** (5.0 mg, 0.0039 mmol), 1-phenyl-1-propyne (9.7 μL, 0.078 mmol). GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 16.897 min), 115 (C_9H_8, R_t 11.737 min).

4.9.7 Formation of RC≡Mo(OCMe$_3$)$_3$ from Mo$_2$(OCMe$_3$)$_6$.

Reaction of 4.9 with 4-octyne. 4.9 (5.0 mg, 0.0079 mmol) was dissolved in C_6D_6 (0.5 mL). Then 4-octyne (5.8 μL, 0.034 mmol, 5 equiv) and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 65 °C for 41 h with no observed reaction. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 100 °C for 3 d with no observed alkylidyne formation.

Reaction of 4.9 with 3-hexyne. Method 1. 4.9 (5.0 mg, 0.0079 mmol) was dissolved in C_6D_6 (0.5 mL). Then 3-hexyne (4.5 μL, 0.040 mmol, 5 equiv) was added via syringe to the solution. The reaction mixture was then heated at 85 °C for 2 d. At this point ^{1}H NMR spectroscopy did not indicate the presence of EtC≡Mo(OCMe$_3$)$_3$ (**4.16**); however, a large portion of polymer had formed. **Method 2. 4.9** (5.0 mg, 0.0079 mmol) and an internal standard of 1,3,5-trimethoxybenzene were dissolved in C_6D_6 (0.5 mL). Then 3-hexyne (4.5 μL, 0.040 mmol, 5 equiv) was added via syringe to the solution. The reaction mixture was then heated at 60 °C for 5 d. At this point ^{1}H NMR spectroscopy indicated only trace **4.16**; however, a large portion of polymer had formed.

Formation of 4.15. Method 1. **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-butyne (11.3 μL, 0.792 mmol, 5 equiv) was added via syringe to the solution. The reaction mixture was then heated at 50 °C for 4 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.15** (62%), **4.16** (4%), **4.9** (3%), and ^{t}BuOH (31%).

Method 2. **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (1.0 mL). Then 1-phenyl-1-butyne (11.3 μL, 0.792 mmol, 5 equiv) was added via syringe to the solution. The reaction mixture was then heated at 85 °C for 2 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.15** (43%), **4.16** (13%), ^{t}BuOH (34%), and unknown (10%). Further heating for 2 d resulted in additional decomposition with the reaction mixture being composed of **4.15** (26%), ^{t}BuOH (52%), and unidentified material (22%).

Method 3. **4.9** (5.0 mg, 0.0079 mmol) was dissolved in toluene-d_8 (0.5 mL). Then 1-phenyl-1-propyne (4.9 μL, 0.040 mmol, 5 equiv) was added via syringe to the solution. The reaction mixture was then heated at 60 °C for 3 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.15** (24%), **4.9** (71%), and ^{t}BuOH (5%). Heating for an additional 3 d resulted in no further conversion to **4.15**.

Method 4. **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (1.0 mL). Then diphenylacetylene (7.1 mg, 0.040 mmol, 2.5 equiv) was added to the solution. The reaction mixture was then heated at 85 °C for 2 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.15** (10%), ^{t}BuOH (55%), and unidentified material (35%).

Preparative Scale. **4.9**. (410.0 mg, 0.650 mmol) was dissolved in toluene (10 mL). Then 1-phenyl-1-butyne (1.85 mL, 13.0 mmol, 20 equiv) was added via syringe to the solution. The reaction mixture was then heated at 60 °C for 6 d. An aliquot of the reaction mixture was composed of **4.15** (90%) and **4.9** (10%). The reaction mixture was filtered through celite and the celite was washed with toluene (60 mL). The volatiles were removed *in vacuo* from the filtrate. The resulting residue was taken up in pentane (5 mL) and cooled to -35 °C. Repeated recrystallization attempts in a variety of solvents did not result in clean isolation of **4.15**.

4-biphenyl-C≡Mo(OCMe$_3$)$_3$ (4.18). **4.9** (5.0 mg, 0.0079 mmol) was dissolved in C_6D_6 (0.5 mL). Then 4-(but-1-ynyl)biphenyl (32.7 mg, 0.159 mmol, 20 equiv) was added via syringe to the solution. The reaction mixture was then heated at 60 °C for 3 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.18** (21%), **4.16** (0%), and **4.9** (79%). Heating for an additional 24 h resulted in no further conversion. At this point the reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated to 95 °C for 2 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.18** (35%), **4.9** (49%), and ^{t}BuOH (16%).

4.9.8 Formation of RC≡Mo(OCMe$_3$)$_3$ from Mo$_2$(OCMe$_3$)$_6$ and DME.

Reaction of 4.9 with 4-octyne and DME. **4.9** (5.0 mg, 0.0079 mmol) was dissolved in C_6D_6 (0.5 mL). Then 4-octyne (5.8 μL, 0.034 mmol, 5 equiv), DME (1.6

μL, 0.016 mmol, 2 equiv), and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 65 °C for 41 h with no observed reaction. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 100°C for 3 d with no observed alkylidyne formation.

Formation of 4.8. **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (0.5 mL). Then 3-hexyne (9.0 μL, 0.079 mmol, 5 equiv) and DME (1.6 μL, 0.016 mmol, 1 equiv) were added via syringe to the solution. The reaction mixture was then heated at 50 °C for 4 d. At this point ^{1}H NMR spectroscopy indicated the presence of **4.8** (31 %), **4.9** (46 %), and ^{t}BuOH (23 %).

PhC≡Mo(OCMe$_3$)$_3$(DME) (4.17). **Method 1.** **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (1.0 mL). Then 1-phenyl-1-butyne (11.3 μL, 0.792 mmol, 5 equiv) and DME (1.6 μL, 0.016 mmol, 1 equiv) were added via syringe to the solution. The reaction mixture was then heated at 50 °C for 4 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.17** (55%), **4.8** (0%), **4.9** (29%), and ^{t}BuOH (16%).

Method 2. **4.9** (10.0 mg, 0.0159 mmol) was dissolved in C_6D_6 (1.0 mL). Then diphenylacetylene (9.3 mg, 0.052 mmol, 5 equiv) and DME (2.2 μL, 0.021 mmol, 2 equiv) were added to the solution. The reaction mixture was then heated at 85 °C for 2 d.

At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of trace **4.17**.

4.9.9 Formation of RC≡Mo($OCMe_2CF_3$)$_3$ from $Mo_2(OCMe_2CF_3)_6$.

Reaction of 4.10 with 4-octyne. **4.10** (5.0 mg, 0.0052 mmol) was dissolved in C_6D_6 (0.5 mL). Then 4-octyne (15.4 μL, 0.105 mmol, 20 equiv) and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 65 °C for 41 h with no observed alkylidyne complex formation, but some polymerization is present. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 100 °C for 3 d with no observed alkylidyne formation and more polymer formation.

Formation of 4.13. Method 1. **4.10** (10.0 mg, 0.0105 mmol) was dissolved in C_6D_6 (1.0 mL). Then 1-phenyl-1-butyne (7.4 μL, 0.052 mmol, 5 equiv) and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 85 °C for 4 d. At this point the reaction mixture was composed of **4.13** (15%), EtC≡Mo($OCMe_2CF_3$)$_3$ **4.19** (1%), and **4.10** (84%).

Method 2. **4.10** (10.0 mg, 0.0105 mmol) was dissolved in C_6D_6 (1.0 mL). Then diphenylacetylene (9.3 mg, 0.052 mmol, 5 equiv) was introduced to the solution. The solution was heated at 85 °C for 3 d with no evidence of benzylidyne complex formation. Heating for an additional 3 d led to trace **4.13**.

Method 3. **4.10** (5.0 mg, 0.0052 mmol) was dissolved in C_6D_6 (1.0 mL). Then diphenylacetylene (18.7 mg, 0.105 mmol, 20 equiv) was introduced to the solution. The solution was heated at 110 °C for 8 d. At this point the reaction mixture consisted of **4.13** (42%).

Method 4. **4.10** (20.0 mg, 0.0210 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-propyne (51.8 μL, 0.419 mmol, 20 equiv) was introduced via syringe to the solution. The solution was heated at 70 °C for 2 d. At this point the reaction mixture was composed of **4.13** (30%), **4.19** (0%), and **4.10** (70%).

Method 5. **4.10** (20.0 mg, 0.0210 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-butyne (59.6 μL, 0.419 mmol, 20 equiv) was added via syringe to the solution. The reaction mixture was then heated at 70 °C for 1 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.13** (78%) and **4.10** (22%).

Method 6. **4.10** (20.0 mg, 0.0210 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-propyne (51.8 μL, 0.419 mmol, 20 equiv) was added via syringe to the solution. The reaction mixture was then heated at 70 °C for 1 d. At this point ^{1}H NMR spectroscopy indicated that the reaction mixture was composed of **4.13** (27%) and **4.10** (73%). Heating for an additional 24 h only resulted in 3% further conversion to **4.13**.

Reaction of 4.10 and 4-(but-1-ynyl)biphenyl. **4.10** (5.0 mg, 0.0052 mmol) and 4-(but-1-ynyl)biphenyl (21.6 mg, 0.105 mmol, 20 equiv) were dissolved in C_6D_6 (0.5

mL). An internal standard of mesitylene was introduced to the reaction. The solution was heated at 70 °C for 4 d. No evidence of benzylidyne complex formation was present.

4.9.10 Formation of RC≡Mo($OCMe_2CF_3$)$_3$ from Mo_2($OCMe_2CF_3$)$_6$ and DME.

Reaction of 4.10 with 4-octyne and DME. **4.10** (5.0 mg, 0.0052 mmol) was dissolved in C_6D_6 (0.5 mL). Then 4-octyne (15.4 μL, 0.105 mmol, 20 equiv), DME (1.1 μL, 0.010 mmol, 2 equiv), and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 65 °C for 41 h with no observed alkylidyne complex formation, but some polymerization is present. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 100 °C for 3 d with no observed alkylidyne complex formation and more polymer formation.

Reaction of 4.10 with 3-hexyne and DME. **4.10** (10.0 mg, 0.0105 mmol) was dissolved in C_6D_6 (1.0 mL). Then 3-hexyne (6.0 μL, 0.052 mmol, 5 equiv) and DME (1.1 μL, 0.011 mmol, 1 equiv) were introduced via syringe to the solution. The solution was heated at 85 °C for 3 d with only trace alkylidyne complex formation, but some polymerization was present.

Formation of 4.13. Method 1. **4.10** (10.0 mg, 0.0105 mmol) was dissolved in C_6D_6 (1.0 mL). Then 1-phenyl-1-butyne (7.4 μL, 0.052 mmol, 5 equiv), DME (1.1 μL, 0.011 mmol, 1 equiv), and an internal standard of mesitylene were introduced via syringe to the solution. The solution was heated at 85 °C for 4 d. At this point the reaction mixture was composed of **4.13** (46%), **4.4** (15%), and **4.10** (39%).

Method 2. 4.10 (20.0 mg, 0.0210 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-propyne (51.8 μL, 0.419 mmol, 20 equiv) and DME (2.2 μL, 0.021 mmol, 1 equiv) were introduced via syringe to the solution. The solution was heated at 70 °C for 3 d. At this point the reaction mixture was composed of a mixture of **4.13** and $MeC{\equiv}Mo(OCMe_2CF_3)_3(DME)$ (38%). Reaction monitoring was discontinued due to slow conversion.

Method 3. 4.10 (10.0 mg, 0.0105 mmol) was dissolved in C_6D_6 (1.0 mL). Then diphenylacetylene (9.3 mg, 0.052 mmol, 5 equiv) and DME (2.2 μL, 0.021 mmol, 2 equiv) were introduced to the solution. The solution was heated at 85 °C for 2 d. At this point the reaction mixture only consisted of trace **4.13**.

Method 4. **4.10** (20.0 mg, 0.0210 mmol) was dissolved in C_6D_6 (0.5 mL). Then 1-phenyl-1-butyne (59.6 μL, 0.419 mmol, 20 equiv) and DME (2.2 μL, 0.021 mmol, 1 equiv) were introduced to the solution. The solution was heated at 70 °C for 2 d. At this point the reaction mixture only consisted of a mixture of **4.13** and **4.4** (83%). Further heating resulted in no additional conversion. Then diphenylacetylene (37.3 mg, 0.210 mmol, 10 equiv) was introduced into the reaction mixture and heated at 70 °C for 2 d. At this point the reaction mixture shifted towards production of benzylidyne complex being composed of **4.13** (90%), **4.4** (3%), and **4.10** (7%).

Preparative Scale. **4.10** (410.0 mg, 0.430 mmol) was dissolved in toluene (10 mL). To this solution were added 1-phenyl-1-butyne (1.22 mL, 8.59 mmol, 20 equiv) and DME (44.7 μL, 0.430 mmol, 1 equiv). The solution was heated at 70 °C for 3 d. At this point diphenylacetylene (765.7 mg, 4.30 mmol, 10 equiv) was added to the reaction mixture. The material was then heated for an additional 1 d. The reaction mixture was filtered through celite. The celite was washed with pentane (30 mL). The volatiles were removed *in vacuo* and the resulting residue was taken up in 50/50 toluene/pentane (5 mL) and cooled to -35 °C. After repeated recrystallizations a sample still slightly contaminated with side-products and starting material was pure enough for spectroscopy analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34 (dd, $^{3}J_{HH}$ =7.3 Hz, $^{3}J_{HH}$ =7.3 Hz), 7.30 (d, J= 7.3 Hz), 7.22 (t, J=7.3 Hz) 1.63 (s, 18, $OC(CH_3)_2CF_3$) ^{19}F NMR (300 MHz, CD_2Cl_2): –83.16 ($OC(CH_3)_2CF_3$). $^{13}C\{^{1}H\}$ NMR (400 MHz, CD_2Cl_2): δ 287.38 (s, Mo≡*C*), 145.54 (s, ArC), 129.94 (s, ArC), 129.06 (s, ArC), 128.69 (s, ArC), 126.72 (q, $OC(CH_3)_2CF_3$, $J_{C\text{-}F}$=284.6 Hz), 82.57 (q, $OCCF_3(CH_3)_2$, $J_{C\text{-}F}$=29.3 Hz), 25.68 (s, $OC(CH_3)_2CF_3$).

Reaction of 4.10, 4-(but-1-ynyl)biphenyl, and DME. **4.10** (10.0 mg, 0.105 mmol) and 4-(but-1-ynyl)biphenyl (43.2 mg, 0.210 mmol, 20 equiv) were dissolved in C_6D_6 (1.0 mL). DME (1.1 μL, 0.010 mmol, 1 equiv) and mesitylene were introduced via syringe into the reaction mixture. The solution was heated at 70 °C for 4 d. No evidence of benzylidyne complex formation was present.

Reaction of 4.10, 1-(4-cyanophenyl)-1-butyne, and DME. 4.10 (5.0 mg, 0.052 mmol) and 1-(4-cyanophenyl)-1-butyne (16.3 mg, 0.105 mmol, 20 equiv) were dissolved in C_6D_6 (1.0 mL). DME (0.5 μL, 0.05 mmol, 1 equiv) was introduced via syringe into the reaction mixture. The solution was heated at 70 °C for 2 d. No evidence of benzylidyne complex formation was present.

4.9.11 Attempted Formation of RC≡Mo(OCMe(CF$_3$)$_2$)$_3$ from Mo$_2$(OCMe(CF$_3$)$_2$)$_6$.

Reaction of 4.11 and diphenylacetylene. 4.11 (5.0 mg, 0.0039 mmol) and diphenylacetylene (7.0 mg, 0.039 mmol, 10 equiv) were dissolved in C_6D_6 (0.5 mL). An internal standard of mesitylene was introduced into the reaction mixture and heated at 65 °C for 3 d. No evidence of benzylidyne complex formation was indicated by ^{1}H NMR spectroscopy. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 95 °C for 3 d with no evidence of benzylidyne complex formation.

Reaction of 4.11, DME, and diphenylacetylene. 4.11 (10.0 mg, 0.00782 mmol) and diphenylacetylene (13.9 mg, 0.0782 mmol, 10 equiv) were dissolved in C_6D_6 (1.0 mL). DME (1.6 μL, 0.016 mmol, 2 equiv) and an internal standard of mesitylene were introduced into the reaction mixture and heated at 65 °C for 3 d. No evidence of benzylidyne complex formation was indicated by ^{19}F NMR spectroscopy. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 95 °C for 2 d with no evidence of benzylidyne complex formation.

Reaction of 4.11, DME, and 1-phenyl-1-butyne. **4.11** (10.0 mg, 0.00782 mmol) was dissolved in C_6D_6 (1.0 mL). 1-phenyl-1-butyne (22.2 μL, 0.156 mmol, 20 equiv), DME (1.6 μL, 0.016 mmol, 2 equiv), and an internal standard of mesitylene were introduced into the reaction mixture and heated at 65 °C for 3 d. No evidence of benzylidyne complex formation was indicated by ^{19}F NMR spectroscopy. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated at 95 °C for 2 d with no evidence of benzylidyne complex formation. Evidence of polymer formation was present.

4.9.12 Decomposition Studies of N≡Mo(OR)$_3$ Complexes

N≡Mo(OCMe$_3$)$_3$. N≡Mo(OCMe$_3$)$_3$ (5.0 mg, 0.015 mmol) was dissolved in toluene-d_8 (0.5 mL) and heated at 95 °C. No reaction was observed over 3 d.

N≡Mo(OCMe$_2$CF$_3$)$_3$. N≡Mo(OCMe$_2$CF$_3$)$_3$ (5.0 mg, 0.010 mmol) was dissolved in toluene-d_8 (0.5 mL) and heated at 95 °C. No reaction was observed over 3 d.

4.1. **4.1** was dissolved in toluene-d_8 (0.5 mL) and heated at 95 °C. No evidence of **4.**11 formation was observed over 5 d.

N≡Mo(OC(CF$_3$)$_3$)$_3$(MeCN). N≡Mo(OC(CF$_3$)$_3$)$_3$(MeCN) (5.0 mg, 0.0058 mmol) was dissolved in toluene-d_8 (0.5 mL) and heated at 95 °C. No reaction was observed over 3 d.

4.9.13 Synthesis of 1-(4-biphenyl)-1-butyne.

1-(4-biphenyl)-1-butyne. $ZnCl_2$ (9.84 g, 72.2 mmol, 1.08 equiv) was slurried in THF (50 mL). To this slurry was slowly added 1-butynyllithium (4.62 g, 77.0 mmol, 1.15 equiv). The mixture was stirred for 10 m. Then 4-bromobiphenyl (15.54 g, 66.67 mmol) was added to the reaction mixture with stirring. Then $Pd(PPh_3)_4$ (4.17 g, 5 mol %) was added to the reaction mixture with THF (80 mL). The reaction mixture was heated to 60 °C for 22 h. Then HCl (150 mL) was added to the reaction mixture. The material was extracted with Et_2O (50 ml) twice. The resulting organic layers were combined and dried with magnesium sulfate. The volatiles were removed *in vacuo*. Separation was completed via silica gel chromatography with pentane. A white powder (9.092 g, 44.1 mmol, 66%) was isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H, ArH, J=7.2 Hz), 7.60 (d, 2H, ArH, J=7.6 Hz), 7.56 (d, 2H, ArH, J=7.6 Hz), 7.50 (t, 2H, ArH, J=7.6 Hz), 7.41 (t, 1H, ArH, J=7.2 Hz), 2.53 (q, 2H, CH_2CH_3, J=7.6 Hz), 1.34 (t, CH_2CH_3, J=7.6 Hz). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 140.43 (s, ArC), 140.15 (s, ArC), 131.92 (s, ArC), 128.76 (s, ArC), 127.40 (s, ArC), 126.91 (s, ArC), 126.82 (s, ArC), 122.98 (s, ArC), 92.34 (s, C≡C), 79.77 (s, C≡C), 13.92 (s, CH_2CH_3), 13.17 (s, CH_2CH_3). GC/MS $[M/Z]^+$: 206 ($C_{16}H_{14}$, R_t 8.950 min).

4.10 References

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Chapter Five:

Lewis Acid-Assisted Alkyne Metathesis Using N≡Mo(OR)$_3$ and Mo$_2$(OR)$_6$ Complexes as Precatalysts

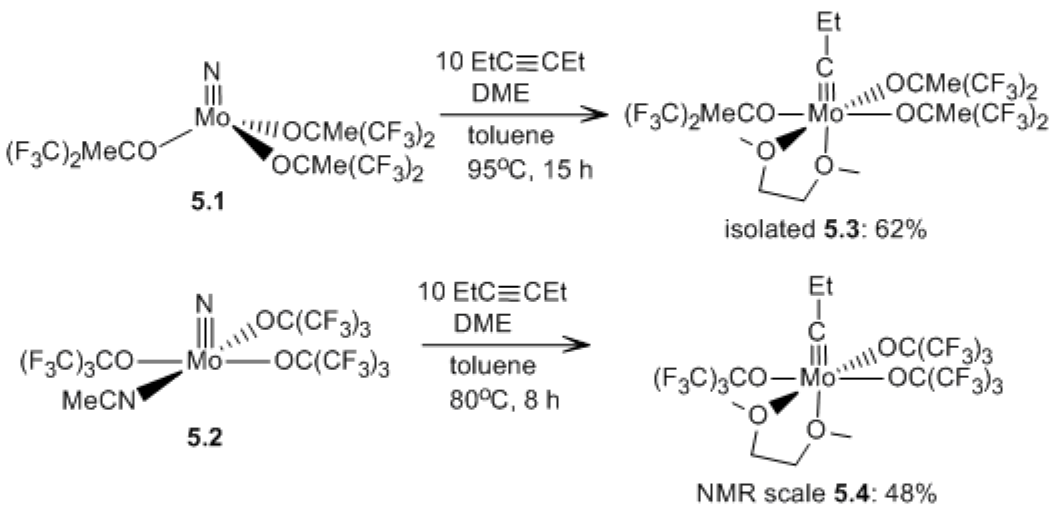
5.1 Introduction

The development of molybdenum-based nitrile-alkyne cross-metathesis (NACM) will require the reversible formation of molybdenum nitride and alkylidyne complexes. The formation of a molybdenum nitride complex from a molybdenum alkylidyne complex has not been established. The *irreversible* formation of propylidyne complexes from the interaction of N≡Mo(OCMe(CF$_3$)$_2$)$_3$ (**5.1**) or N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) (**5.2**) with 3-hexyne at elevated temperatures has been demonstrated by Johnson and coworkers.[1] Although NACM is not feasible with **5.1** or **5.2** the facile formation of alkylidyne complexes from nitride precursors is a useful method for synthesizing molybdenum-based alkyne metathesis (AM) catalysts. The molybdenum-nitride-to-alkylidyne transformation has only been reported with 3-hexyne. The ability to broaden the scope of this reaction to include other alkynes for the facile synthesis of several alkylidyne species will be discussed.

Previous work by the Grela, Mori, and Bunz groups has demonstrated the value of introducing acids into molybdenum precatalyst systems of Mo(CO)$_6$ to encourage AM.[2-5] Although the active species in these homogenous systems are presently unknown, the influence of the added phenols is substantial. AM activity is dependent on the phenol and alkyne substrate introduced. Realizing the potential implications that an acid could have on NACM, the impact of Lewis acids (LAs) on the conversion of molybdenum-nitride to -alkylidyne complexes is detailed. The influence of LAs on *in situ* AM activity with $Mo_2(OR)_6$ complexes is also included.

5.2 Formation of RC≡Mo(OR)$_3$ Complexes from N≡Mo(OR)$_3$ Complexes

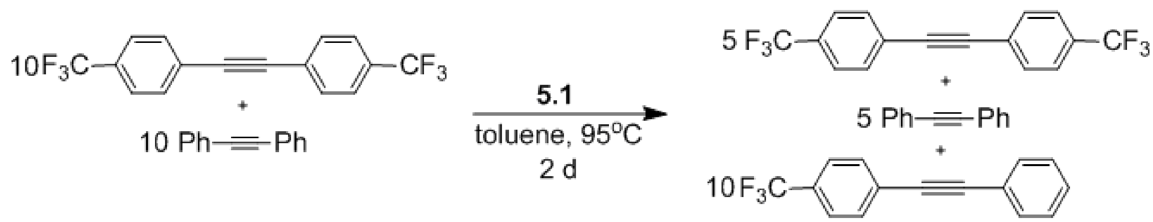
As reviewed in Chapter 4, Gdula and coworkers developed a method to readily access EtC≡Mo(OR)$_3$(DME) complexes when OR= OCMe(CF_3)$_2$ (**5.3**) and OC(CF_3)$_3$ (**5.4**) from the corresponding nitride precursors (Scheme 5.1).[1] The original synthesis of **5.4** reported by Robyn Gdula, was conducted at 90 °C resulting in complete decomposition of **5.4** to an unknown product instead of **5.4**. If the reaction is conducted at decreased reaction temperatures for a shortened reaction time, successful conversion to **5.4** with some decomposition can be effected (Scheme 5.1). This section will focus on expanding this reaction to include the synthesis of benzylidyne complexes.



Scheme 5.1. Synthesis of **5.3** and **5.4** from N≡[Mo] precursors.

5.2.1 Synthesis of RC≡Mo(OCMe(CF_3)$_2$)$_3$ Complexes

Following the successful synthesis of **5.3** from **5.1**, direct conversion of **5.1** to benzylidyne catalysts was of interest. Initial conversion attempts at 95 °C using diphenylacetylene provided no evidence of PhC≡Mo(OCMe(CF_3)$_2$)$_3$ (**5.5**) formation by ^{1}H and ^{19}F NMR spectroscopies. Introduction of a second symmetrical alkyne, bis(4-trifluoromethylphenyl)acetylene, into the reaction mixture resulted in the formation of unsymmetrical alkyne (Scheme 5.2). The presence of AM products indicates that a trace quantity of benzylidyne complex is formed under the reaction conditions, despite the lack of direct spectral evidence for the benzylidyne complex itself.

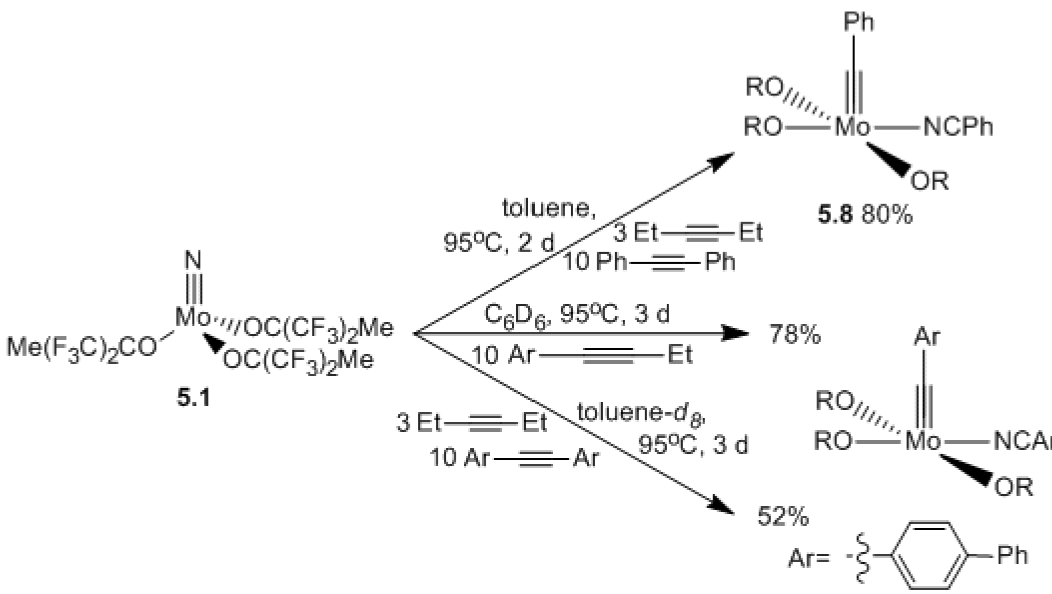


Scheme 5.2. AM of two diarylalkynes with **5.1**.

If an equilibrium that rests heavily towards the nitride complex exists, then introduction of DME could potentially perturb this equilibrium towards alkylidyne complex formation. This shift towards product formation is observed in the conversion of some $Mo_2(OR)_6$ precursors to benzylidyne complexes as discussed in Chapter 4. Furthermore, addition of DME to the reaction mixture of **5.1** with 3-hexyne increases the ability to isolate the produced propylidyne complex.[1] Although formation of EtC≡Mo(OCMe(CF_3)$_2$)$_3$(NCEt) (**5.6**) from **5.1** in the absence of DME is indicated by ^{1}H and ^{19}F NMR spectroscopies, isolation of this compound cannot be effected as it decomposes upon concentration of the reaction mixture.

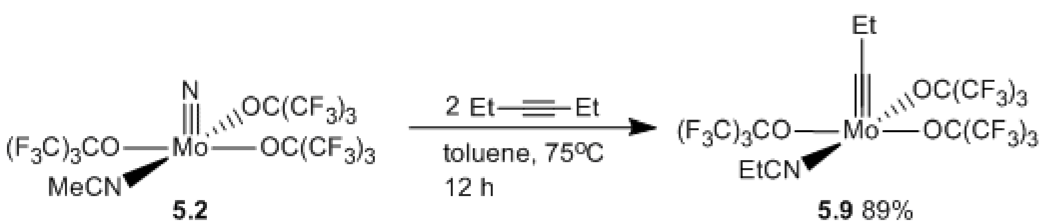
A bimolecular decomposition pathway is more likely to occur with **5.6** than with **5.3** due to the absence of a chelating ligand. The formation of $Mo_2(OR)_6$ species via bimolecular decomposition from propylidyne complexes is precedented with $OCMe_3$ and $OCMe_2CF_3$ ancillary ligands as detailed in Chapter 4. Identification of Mo_2(OCMe(CF_3)$_2$)$_6$ (**5.7**) has been unsuccessful, as multiple species are formed upon decomposition of **5.3** and **5.6**. The formation of multiple products is unsurprising, as the synthesis of **5.7** is very sensitive to the reaction conditions.[6]

Unfortunately, no accumulation of **5.5** was found upon addition of DME into a mixture of diphenylacetylene and **5.1** at 95 °C. Since conversion of **5.1** to a propylidyne complex required dialkyl alkynes, initial alkylidyne complex formation was accomplished by introducing 3 equivalents of 3-hexyne into a mixture of 10 equivalents of diphenylacetylene and **5.1** (Scheme 5.3). In this case, formation of what is likely PhC≡Mo(OCMe(CF_3)$_2$)$_3$(NCPh) (**5.8**) was indicated by ^{1}H and ^{19}F NMR spectroscopies. Difficulty in separating diphenylacetylene and **5.8** due to similar solubility properties has prevented isolation of **5.8**. In order to readily separate the benzylidyne species from the symmetrical alkynes, 1-(4-biphenyl)-1-butyne was synthesized, since bis(4-biphenyl)acetylene is rather insoluble in hydrocarbon solvents. As highlighted in Figure 5.3, treatment of **5.1** with 1-(4-biphenyl)-1-butyne resulted in successful conversion to the benzylidyne complex (78%). Although bis(4-biphenyl)acetylene can be readily removed from the reaction mixture, the similar solubility properties of the benzylidyne complex and the unsymmetrical alkyne have prevented isolation of the desired complex. Direct treatment of **5.1** with 3 equivalents of 3-hexyne and 10 equivalents of bis(4-biphenyl)acetylene results in decreased conversions to the benzylidyne complex (52%) relative to 1-(4-biphenyl)-1-butyne (78%).



Scheme 5.3. Formation of benzylidyne complexes from **5.1**.

5.2.2 Synthesis of RC≡Mo(OC(CF$_3$)$_3$)$_3$ Complexes



Scheme 5.4. Formation of **5.9** from **5.2**.

Unlike with **5.3**, addition of DME to a mixture of **5.1** and 3-hexyne does not result in the formation of readily isolable **5.4**. However, crystalline EtC≡Mo(OC(CF$_3$)$_3$)$_3$(NCEt) (**5.9**) can be isolated via crystallization of the material during removal of solvent from the reaction mixture (Scheme 5.4). The thermal ellipsoid plot of **5.9** reveals that propionitrile is bound trans to an alkoxide ligand (Figure 5.1). This is anticipated, since the alkoxide ligand is a weaker trans influence ligand than the alkylidyne moiety.[7] Data for the single crystal XRD experiment can be found in Appendix 4. Since **5.9** readily decomposes upon concentration of the reaction mixture, only a few crystals of **5.9** were isolated. Several materials form upon decomposition; there was no spectroscopic evidence of the formation of $Mo_2(OC(CF_3)_3)_6$.

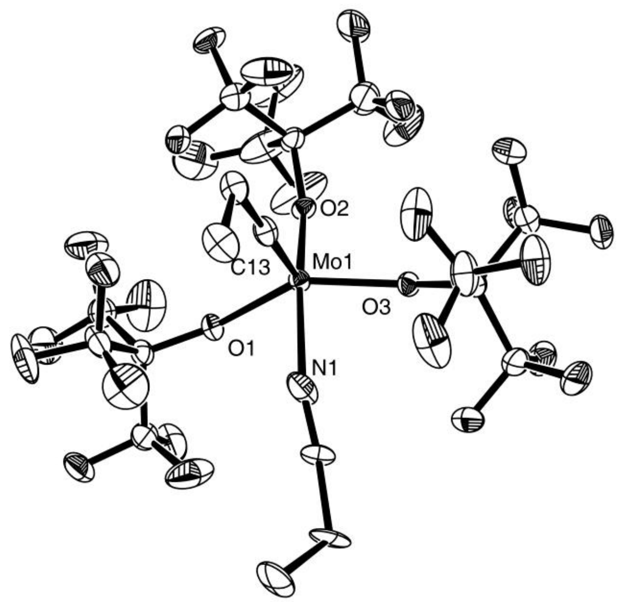
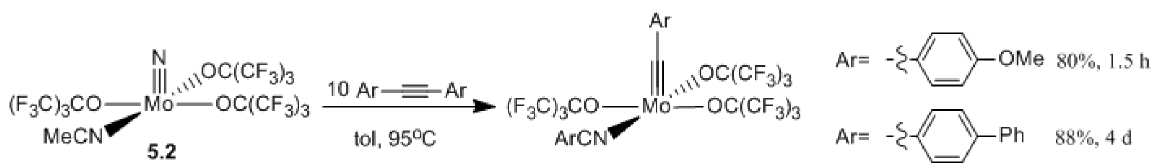


Figure 5.1. 50% thermal ellipsoid plot of **5.9**.

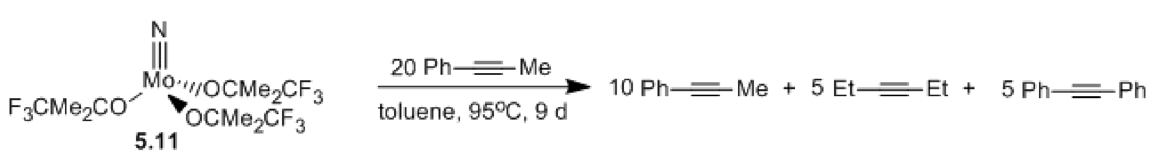
Since isolation of **5.4** and **5.9** from **5.2** had proven difficult thus far, the formation of stable benzylidyne complexes from other alkyne substrates was investigated. Conversion of **5.2** to a benzylidyne complex with no evidence of decomposition was achieved with bis(4-methoxyphenyl)acetylene (Scheme 5.5). The increased Lewis acidity of **5.2** relative to **5.1** was likely responsible for the direct cleavage of symmetrical diarylalkynes, which is not observed with **5.1**. Isolation of the benzylidyne complex proved fruitless, as the symmetrical alkyne was difficult to separate by solubility properties. Extension of this method to bis(4-biphenyl)acetylene results in benzylidyne complex formation in a 88% yield (Scheme 5.5). The increased amount of time required for conversion of **5.2** to the benzylidyne complex with bis(4-biphenyl)acetylene (4 days) relative to bis(4-methoxyphenyl)acetylene (1.5 hours) under the same reaction conditions is likely due to the poor solubility and increased steric bulk of bis(4-biphenyl)acetylene.



Scheme 5.5. Formation of benzylidyne complexes from **5.2**.

5.3 Alkyne Metathesis with N≡Mo(OR)$_3$ Complexes Assisted by Lewis Acids

N≡Mo(OR)$_3$ complexes ligated by OCMe$_3$ (**5.10**) or OCMe$_2$CF$_3$ (**5.11**) would serve as excellent precursors to alkylidyne complexes, as these ligands are much more economical than the OC(CF$_3$)$_2$Me and OC(CF$_3$)$_3$ ligands that currently allow for alkylidyne catalyst formation. However, no alkylidyne complex formation from **5.10** or **5.11** has been observed by ^{1}H or ^{19}F NMR spectroscopies under the standard reaction conditions.[1]



Scheme 5.6. AM with **5.11**.

Complexes **5.10** and **5.11** were treated with an unsymmetrical alkyne at elevated temperatures to probe for AM activity. While only trace conversion to diphenylacetylene (likely due to a decomposition product) is observed with **5.10**, an equilibrium mixture of unsymmetrical and symmetrical alkynes is observed with **5.9** after 9 days at 95 °C (Scheme 5.6). No direct evidence of alkylidyne complex formation is observed under the reaction conditions by NMR spectroscopy. Although *in situ* AM with **5.11** lacks synthetic utility because of slow conversion, the ability to form an alkylidyne complex from **5.11** is implicated.

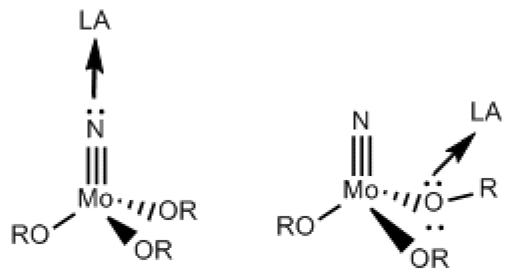


Figure 5.2. Potential binding modes of LAs with molybdenum nitride complexes.

As the pK_a of the conjugate acid of the ancillary alkoxides increases, the conversion of $N{\equiv}Mo(OR)_3$ to $RC{\equiv}Mo(OR)_3$ is inhibited.[1] We propose that the conversion of a nitride moiety into an alkylidyne moiety could be catalyzed by a Lewis acid (LA). The LA would bind directly to the nitride ligand or the oxygen of the alkoxide ligands, decreasing electron donation to the metal center (Figure 5.2). This in turn would create a more reactive molybdenum center. Thus, binding of a LA to the alkylidyne complex should influence the conversion of a metal nitride complex to an alkylidyne complex in a manner similar to that observed when less electron-rich ancillary alkoxides are present in the system (Figure 5.3). The effect on the conversion will then depend on the LA selected.

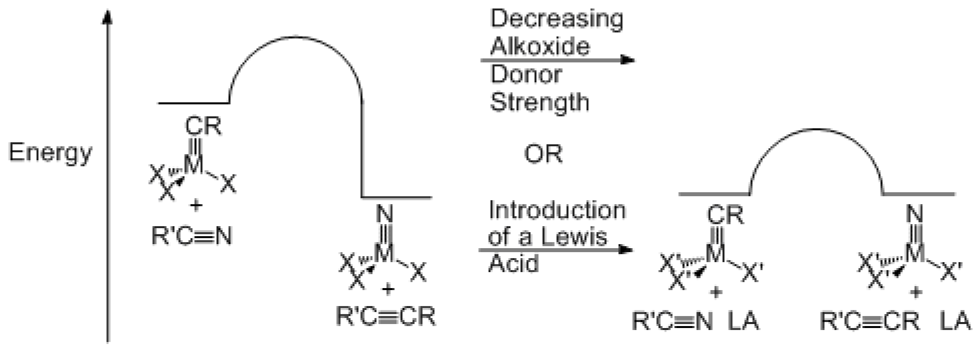


Figure 5.3. Influence of alkoxides and LAs on nitride and alkylidyne complex stability.

5.3.1 Solvent Effects in Alkyne Metathesis with N≡Mo(OR)$_3$ Assisted by Lewis Acids

Preliminary LA studies with 2 equivalents of magnesium bromide and 20 equivalents of Ph-C≡C-R (R=Et or Me) with **5.10** or **5.11** reveal AM activity as shown in Table 5.1. The reactions were monitored until no further reaction was observed. The theoretical K_{eq}= 0.25. These values are calculated based on Figure 5.4.

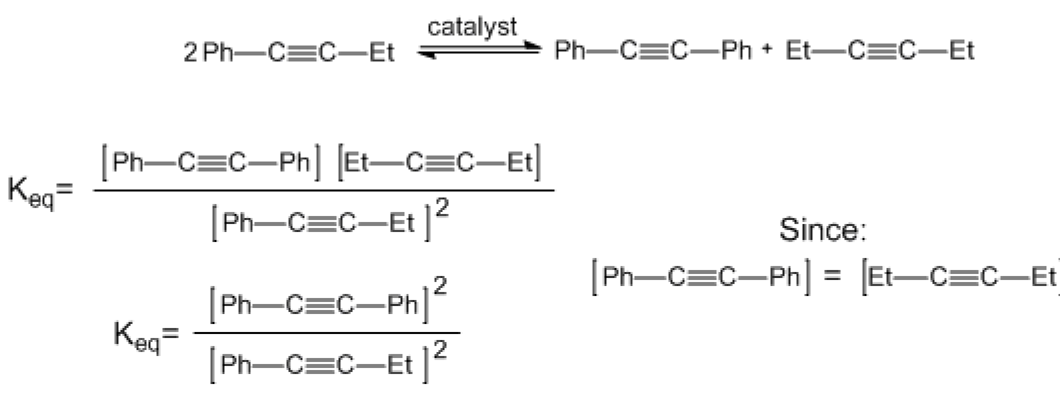


Figure 5.4. Equilibrium calculations.

All reactions achieved within 5% conversion to equilibrium (K_{eq}=0.25, 33% diphenylacetylene/66% 1-phenyl-1-butyne considering only the aryl-containing materials) with the corresponding reaction quotients (Q values) being reported in Table 5.1. For **5.11**, solvent optimization was completed with 1-phenyl-1-butyne instead of 1-phenyl-1-propyne in order to avoid overlapping resonances in the ^{1}H NMR spectrum. The increased solubility of magnesium bromide in CD_2Cl_2 relative to other surveyed solvents results in it serving as the preferred medium for reactions with **5.11** at 60 °C. Operating at the same temperature, the activity of **5.10** is highest in $CDCl_3$: a greater conversion to diphenylacetylene was observed under these reaction conditions. The formation of an equilibrium mixture of diphenylacetylene and 1-phenyl-1-propyne can be achieved with **5.10** by increasing the reaction temperature to 80 °C. As a result, AM studies with **5.10** are conducted in C_6D_6.

Table 5.1. Solvent studies in AM with N≡Mo(OR)$_3$ and Ph-C≡C-R (R=Et, Me) assisted by LAs: Time to reaction endpoint (Q).[a]

Catalyst	C_6D_6 (h)	CD_2Cl_2 (h)	$CDCl_3$ (h)	R	Temp (°C)	Q
5.11/$MgBr_2$	14[b]	4	11	Et	60	0.20±0.01[c]
5.10/$MgBr_2$	43[d]	NR[e]	43[f]	Me	60	-
5.1	4	6	8	Me	RT[g]	0.25±0.01[h]
5.2	9	13	7	Me	RT	0.24±0.02[h]

[a]NMR scale reactions with 5 mol% catalyst [b]toluene-d_8 [c]31% diphenylacetylene/69% 1-phenyl-1-butyne [d] 15% diphenylacetylene/85% 1-phenyl-1-propyne (Q=0.03) [e]NR = no reaction [f] 24% diphenylacetylene/76% 1-phenyl-1-propyne (Q=0.11) [g]RT = room temperature [h]33% diphenylacetylene/67% 1-phenyl-1-propyne

In the absence of LAs, optimal solvents for AM with **5.1** and **5.2** are C_6D_6 and $CDCl_3$, respectively. Comparison of the two catalysts reveals more rapid AM with **5.1** relative to **5.2**. The slower rate of metathesis with **5.2** is likely due to adduct formation hindering access to the active alkylidyne catalyst. Similar results are found when comparing $Me_3CC{\equiv}Mo(OC(CF_3)_2Me)_3(DME)$ (**5.12**) and $Me_3CC{\equiv}Mo(OC(CF_3)_3)_3(DME)$ (**5.13**). According to Schrock, the slower rate of activity with is due to the presence of a more strongly bound DME in **5.13** relative to **5.12**.[8]

5.3.2 Alkyne Metathesis with $N{\equiv}Mo(OCMe_3)_3$ Assisted by Lewis Acids

As the least likely catalyst to display AM activity in the presence of a LA (2 equivalents), the observation of conversion of 1-phenyl-1-propyne to diphenylacetylene at 80 °C with 5 mol% **5.10** was surprising. The time required to achieve a reaction composition of 20% diphenylacetylene and 80% 1-phenyl-1-propyne (Q=0.07) is reported in Table 5.2. Only seven of the sampled LAs promote AM with **5.10**. Additional heating of the reaction mixtures results in no further conversion towards equilibrium, except in the case of $MgBr_2$. In this case, a nearly equilibrium mixture of unsymmetrical and symmetrical alkynes (Q=0.21) is achieved. Unlike the other LAs, triphenylboron induces alkyne polymerization, as indicated by the formation of insoluble gelatinous material. There is presently no apparent trend in the LAs that promote AM with **5.10**. An induction period corresponding to the time necessary to convert the nitride catalyst to trace amounts of the alkylidyne species prior to any evidence of alkyne metathesis is present. The length of this activation period is dependent on the Lewis acid introduced into the reaction. Under the reaction conditions, no alkylidyne complexes are observed by ^1H NMR spectroscopy.

Table 5.2. AM studies with **5.10** and 1-phenyl-1-propyne assisted by LAs: Time to 20% diphenylacetylene/80% 1-phenyl-1-propyne (Q= 0.07±0.01).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	NR[b]	12	$CoCl_2{\bullet}6H_2O$	Dec.
2	$MgCl_2$	NR	13	$PdCl_2$	NR
3	$MgBr_2$	23[c]	14	CuCl	NR
4	MgI_2	19[d]	15	$CuCl_2$	27
5	CaI_2	NR	16	$CuBr_2$	27
6	$TiCl(O^iPr)_3$	88	17	$ZnCl_2$	NR
7	$ZrCl_4$	11	18	BPh_3	polymer[f]
8	$CrCl_2$	NR	19	$GaCl_3$	Dec.
9	$MnCl_2$	NR	20	HCl	NR
10	$FeCl_2$	NR	21	NBu_4Br	NR
11	$FeBr_3$	Dec.[e]	22	None	NR

[a]NMR scale reactions in C_6D_6 at 80 °C with 5 mol% **5.10** [b]NR = no reaction [c]Q=0.21 [d]13% diphenylacetylene/87% 1-phenyl-1-propyne [e]Dec. = catalyst decomposition [f]poly(3-hexyne) present

5.3.3 Alkyne Metathesis with N≡Mo(OCMe$_2$CF$_3$)$_3$ Assisted by Lewis Acids

The influence of 2 equivalents of LA on the activity of **5.11** with 20 equivalents of 1-phenyl-1-propyne in CD_2Cl_2 at 40 °C was investigated next. A subset of LAs that promote AM activity with **5.10** also do so with **5.11** (Table 5.3). An equilibrium mixture of materials is not achieved under the reaction conditions (K_{eq}=0.25). Instead, the reaction mixtures consist of 20% diphenylacetylene and 80% 1-phenyl-1-propyne (Q=0.06). As with **5.10**, an induction period for catalyst conversion is present and there is no direct evidence of alkylidyne complex formation under the reaction conditions.

Table 5.3. AM studies with **5.11** and 1-phenyl-1-propyne assisted by LAs: Time to 20% diphenylacetylene/80% 1-phenyl-1-propyne (Q=0.06±0.01).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	NR[b]	13	$FeBr_3$	Dec.
2	MgF_2	NR	14	$CoCl_2 \cdot 6H_2O$	Dec.
3	$MgCl_2$	NR	15	$PdCl_2$	NR
4	$MgBr_2$	93	16	CuCl	NR
5	MgI_2	59	17	CuI	NR
6	$CaCl_2$	NR	18	$CuCl_2$	99
7	$CaBr_2$	NR	19	$CuBr_2$	59
8	CaI_2	NR	20	$ZnCl_2$	NR
9	$TiCl(O^iPr)_3$	Dec.[c]	21	BPh_3	NR
10	$ZrCl_4$	Dec.	22	HCl	Dec.
11	$CrCl_2$	NR	23	None	NR
12	$CrCl_3$	NR			

[a]NMR scale reactions in CD_2Cl_2 at 40 °C with 5 mol% **5.11** [b]NR = no reaction [c]Dec. = catalyst decomposition

5.3.4 Alkyne Metathesis with $N{\equiv}Mo(OCMe(CF_3)_2)_3$ Assisted by Lewis Acids

Since LAs assist in AM with nitride complexes that previously displayed little to no activity, the ability of LAs to increase the rate of metathesis with **5.1** was investigated. In order to observe the greatest impact on the rate of metathesis, the solvent that results in the slowest rate of AM in the absence of a LA, $CDCl_3$, was selected as the medium for the reaction. Upon surveying several LAs (2 equivalents) in $CDCl_3$ at room temperature, only two are found to enhance the rate of metathesis of 20 equivalents of 1-phenyl-1-propyne by **5.1** (Table 5.4). The reactions were monitored to a composition of 31% diphenylacetylene and 69% 1-phenyl-1-propyne. As observed with **5.10** a pre-incubation period was present.

Table 5.4. AM studies with **5.1** and 1-phenyl-1-propyne assisted by LAs: Time to 31% diphenylacetylene/69% 1-phenyl-1-propyne (Q=0.20±0.01).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	NRE[b]	10	$PdCl_2$	NRE
2	$MgBr_2$	NRE	11	CuCl	NRE
3	MgI_2	NRE	12	$CuCl_2$	NRE
4	$CaBr_2$	NRE	13	$CuBr_2$	NRE
5	CaI_2	NRE	14	$ZnCl_2$	NRE
6	$TiCl(O^iPr)_3$	Dec.[c]	15	BPh_3	NRE
7	$ZrCl_4$	6	16	HCl	6
8	$CrCl_2$	NRE	17	None	8
9	$FeBr_3$	NRE			

[a]NMR scale reaction in $CDCl_3$ with 5 mol% **5.1** at room temperature [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition

5.3.5 Alkyne Metathesis with N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) Assisted by Lewis Acids

The influence of 2 equivalents of LA on the AM activity of **5.2** was investigated with 20 equivalents of 1-phenyl-1-propyne at room temperature (Table 5.5). As in the studies with **5.1**, C_6D_6 was selected as the reaction medium in order to observe the greatest affect on the rate of metathesis. Of the surveyed LAs, only triphenylboron was found to increase the rate of AM with **5.2**. The interaction of triphenylboron and **5.2** was monitored closely to produce a reaction curve with the reaction slowing as equilibrium was approached (Figure 5.5). In this system, no extended incubation period was required for catalyst conversion. Compared to the other nitride catalysts, one additional mode of LA interaction with the metal center is present. The LA could bind to the acetonitrile, thereby facilitating metathesis by causing the active precursor N≡Mo(OC(CF$_3$)$_3$)$_3$ to alkylidyne complex formation to be more readily accessed.

Table 5.5. AM studies with **5.2** and 1-phenyl-1-propyne assisted by LAs: Time to 31% diphenylacetylene/69% 1-phenyl-1-propyne (Q=0.20±0.01).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	NRE[b]	9	$PdCl_2$	NRE
2	$MgBr_2$	NRE	10	CuCl	NRE
3	MgI_2	NRE	11	$CuCl_2$	NRE
3	$CaBr_2$	NRE	12	$CuBr_2$	NRE
4	CaI_2	NRE	13	$ZnCl_2$	NRE
5	$TiCl(O^iPr)_3$	Dec.[c]	14	BPh_3	5
6	$ZrCl_4$	NRE	15	HCl	NRE
7	$CrCl_2$	NRE	16	None	9
8	$FeBr_3$	NRE			

[a]NMR scale reaction in C_6D_6 with 5 mol% **5.2** at room temperature [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition

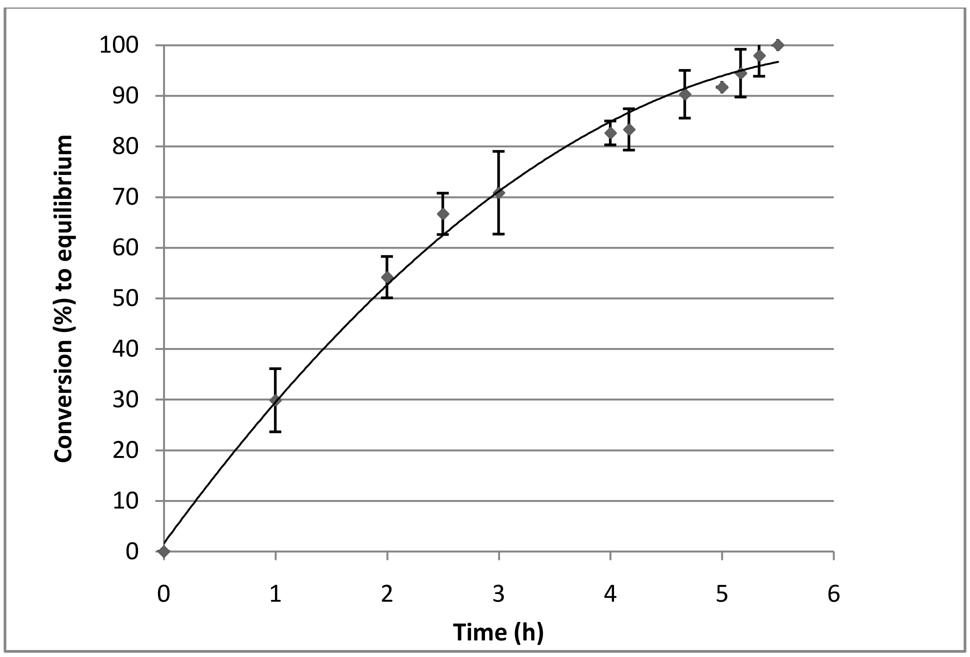


Figure 5.5. Conversion towards equilibrium: AM with **5.2** and BPh_3.

5.3.6 Alkyne Dependence

Close examination of nitride-complex-catalyzed AM reveals that the metathesis activity depends on the R-group in R-C≡C-Ph. (Table 5.6). For instance, metathesis of 1-

phenyl-1-propyne and 1-phenyl-1-butyne by **5.11** reveals that when R=Et increased rates of metathesis and overall yields of diphenylacetylene are observed relative to R=Me under the same reaction conditions. Although a difference in alkyne polymerization rates of 2-butyne and 3-hexyne could potentially account for the variation in metathesis rates, alkyne polymerization does not appear to occur to a large extent under the reaction conditions. Furthermore, if the difference in metathesis rates were attributed to the relative rates of alkyne polymerization of the byproducts (3-hexyne or 2-butyne) then metathesis with 1-phenyl-1-propyne should be more rapid than 1-phenyl-1-butyne. This is demonstrated by previous work with AM catalysts, in which increased alkyl-chain length decreases the rate of alkyne polymerization in these reaction systems.[9] As there are no significant electronic or steric differences in the unsymmetrical alkynes, the source of the varied metathesis rates and yields has yet to be determined.

Table 5.6. AM alkyne dependence studies with **5.11** and Ph-C≡C-R (R=Et,Me) assisted by LAs.[a]

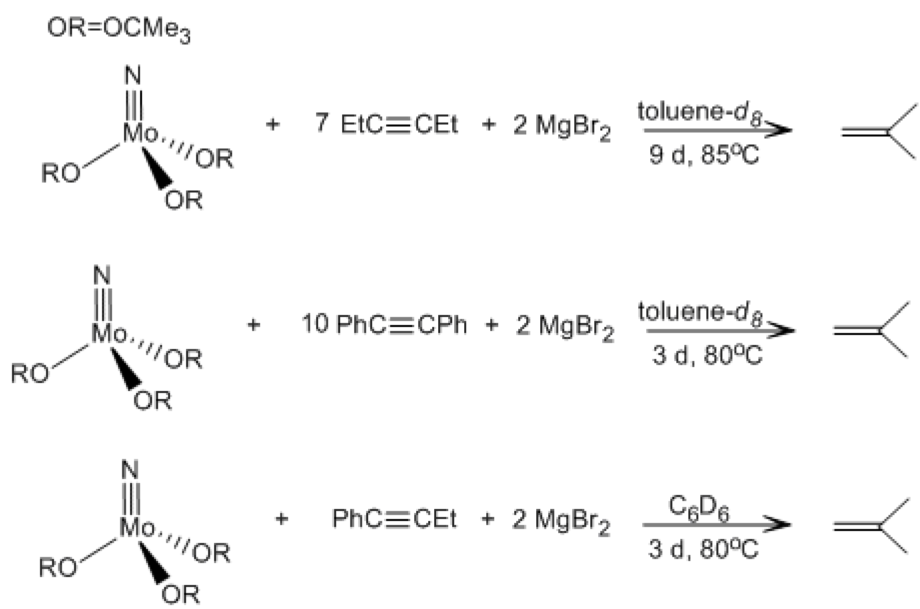
Lewis Acid	Et (Time, h)	Me (Time, h)
$MgBr_2$	18	93
MgI_2	5.5	59
$CuCl_2$	44	99
$CuBr_2$	8[b]	59[b]
BPh_3	45 (polymer)	NR
None	NR[c]	NR
Q	0.22±0.3[d]	0.07[b]

[a]NMR scale reactions with 5 mol% **5.11** at 40°C in CD_2Cl_2 [b]20% diphenylacetylene/80% 1-phenyl-1-propyne (Q=0.07±0.02) [c]NR = no reaction [d]33% diphenylacetylene/67% 1-phenyl-1-butyne

5.4 Attempted Isolation of RC≡Mo(OR)$_3$ Complexes from N≡Mo(OR)$_3$ Complexes in the Presence of Lewis Acids

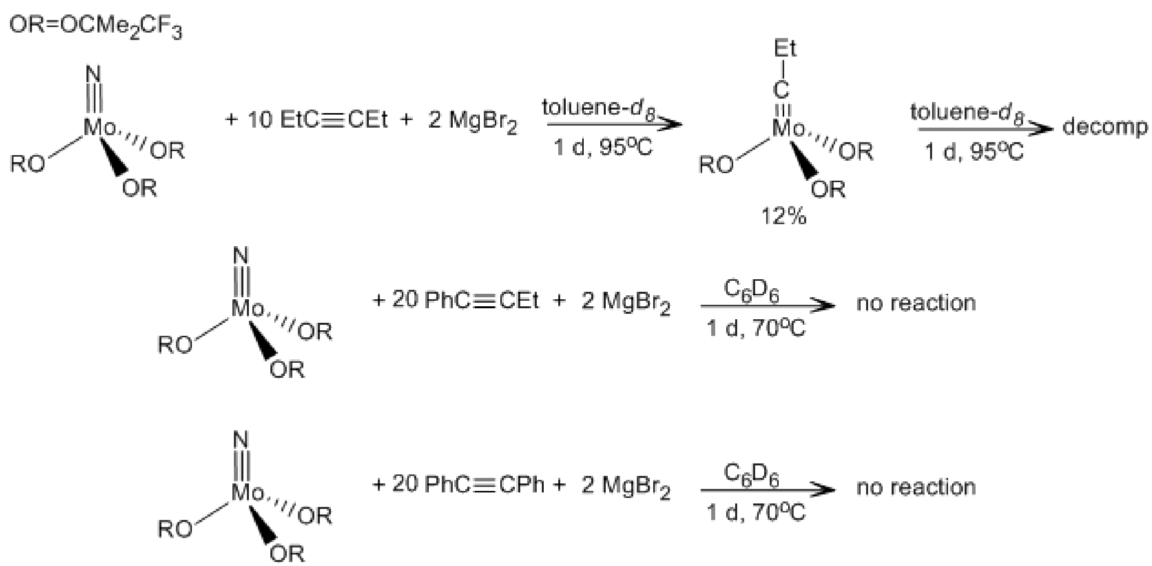
The formation of readily isolable alkylidyne complexes via LA-assisted conversions of **5.10** and **5.11** would provide ready access to molybdenum-based AM catalysts. Reaction conditions and alkyne substrates were varied with both **5.10** and **5.11** in order to encourage formation of the alkylidyne complexes. Since magnesium bromide was found to readily promote *in situ* AM with **5.10** and **5.11**, it was selected as the LA for the studies of alkylidyne complex formation.

Studies with **5.10** and symmetrical alkyl- and aryl-based alkynes in aromatic solvents yield no evidence of alkylidyne complex formation by ^{1}H or ^{19}F NMR spectroscopies (Scheme 5.7). Similar results are found with unsymmetrical alkyne substrates. In all cases, the only readily identifiable material formed is isobutylene, which likely results from C-O bond scission of the alkoxides.



Scheme 5.7. Attempted isolation of RC≡Mo(OCMe$_3$)$_3$ in the presence of LAs.

The formation of alkylidyne complexes from **5.10** and several alkynes in the presence of magnesium bromide was examined as depicted in Scheme 5.8. Unlike **5.9**, evidence of alkylidyne formation is observed with **5.10** and 3-hexyne by ^{1}H and ^{19}F NMR spectroscopies. Attempts to drive the formation of the alkylidyne complex to completion result in decomposition of the alkylidyne complex. This is because the alkylidyne complex is unstable in the presence of a LA for extended time at elevated temperatures. Subjection of **5.10** to diphenylacetylene or 1-phenyl-1-butyne does not provide evidence for alkylidyne complex formation via ^{1}H and ^{19}F NMR spectroscopies, even when operating at lower temperatures to deter alkylidyne complex decomposition.



Scheme 5.8. Attempted isolation of RC≡Mo($OCMe_2CF_3$)$_3$ in the presence of LAs.

5.5 Alkyne Metathesis with $Mo_2(OR)_6$ Complexes Assisted by Lewis Acids

With the discovery of LA-assisted AM with N≡Mo(OR)$_3$ complexes, the potential to increase the rate of metathesis with $Mo_2(OR)_6$ complexes was also investigated. Unlike N≡Mo(OR)$_3$ complexes, the only binding mode for LAs with $Mo_2(OR)_6$

complexes is through the oxygen of the alkoxides. The presence of LA-assisted AM with $Mo_2(OR)_6$ would then validate the potential of an alkoxide binding mode of LAs with $N\equiv Mo(OR)_3$.

5.5.1 Alkyne Metathesis with $Mo_2(OCMe_3)_6$ Assisted by Lewis Acids

The influence of 2 equivalents of LA on the rate of AM of 20 equivalents of 1-phenyl-1-butyne with $Mo_2(OCMe_3)_6$ (**5.14**) was examined at room temperature in $CDCl_3$. As shown in Table 5.7, several LAs enhance the rate of metathesis with **5.14**. Although there is some overlap in the LAs that co-catalyze AM with **5.11** and **5.14**, several additional LAs enhance metathesis with **5.14**. Magnesium bromide and magnesium iodide exhibit the largest influence on the rate of AM. As observed with the nitride catalysts, an induction period is observed.

Table 5.7. AM equilibrium studies with **5.14** and 1-phenyl-1-butyne assisted by LAs: Time to 33% diphenylacetylene/67% 1-phenyl-1-butyne (Q = 0.22±0.03).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiCl	NRE[b]	15	$FeCl_2$	NRE
2	LiBr	25	16	$VCl_3(thf)_3$	Dec.
3	LiI	NRE	17	$FeBr_3$	Dec.
4	KBr	NRE	18	$PdCl_2$	NRE
5	$MgCl_2$	NRE	19	CuCl	NRE
6	$MgBr_2$	2	20	$CuCl_2$	NRE
7	MgI_2	4	21	AgOTf	NRE
8	$Mg(OTf)_2$	NRE	22	$ZnCl_2$	NRE
9	$CaCl_2$	23	23	BPh_3	NRE
10	$CaBr_2$	25	24	$GaCl_3$	Dec.
11	CaI_2	28	25	HCl	48[d]
12	$TiCl(O^iPr)_3$	Dec.[c]	26	NBu_4Br	NRE
13	$TiCl_4$	Dec.	27	$AlCl_3$	NRE
14	$ZrCl_4$	22	28	none	44

[a]NMR scale reaction with 5 mol% **5.14** in $CDCl_3$ at room temperature [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition [d]C_6D_6

The interaction of 20 equivalents of 1-phenyl-1-propyne and 2 equivalents of LA in the presence of 5 mol% **5.14** was examined. Only the LAs that enhanced the rate of metathesis with 1-phenyl-1-butyne were surveyed (Table 5.8). As observed with the molybdenum nitride catalysts, the rate of metathesis with 1-phenyl-1-propyne is slower than that observed with 1-phenyl-1-butyne. The number of LAs that enhance the rate of metathesis with 1-phenyl-1-propyne is smaller than for 1-phenyl-1-butyne. This may be related to the decrease in enhanced metathesis rate; however, as discussed for the molybdenum nitride catalysts, the source of this deviation in metathesis activity has not been determined. The interaction of **5.14** with 1-phenyl-1-propyne and magnesium iodide was followed closely by ^1H NMR spectroscopy to produce a reaction curve (Figure 5.6). As observed with several of the catalyst, an induction period is present during the reaction.

Table 5.8. AM equilibrium studies with **5.14** and 1-phenyl-1-propyne assisted by LAs: Time to 31% diphenylacetylene/69% 1-phenyl-1-propyne (Q = 0.20).[a]

Entry	Lewis Acid	Time (h)
1	LiBr	NRE[b]
3	$MgBr_2$	8
4	MgI_2	4
5	$CaCl_2$	NRE
6	$CaBr_2$	NRE
7	CaI_2	NRE
8	$ZrCl_4$	Dec.[c]
9	HCl	NRE
10	None	76

[a]NMR scale reaction with 5 mol% **5.14** in $CDCl_3$ at room temperature [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition

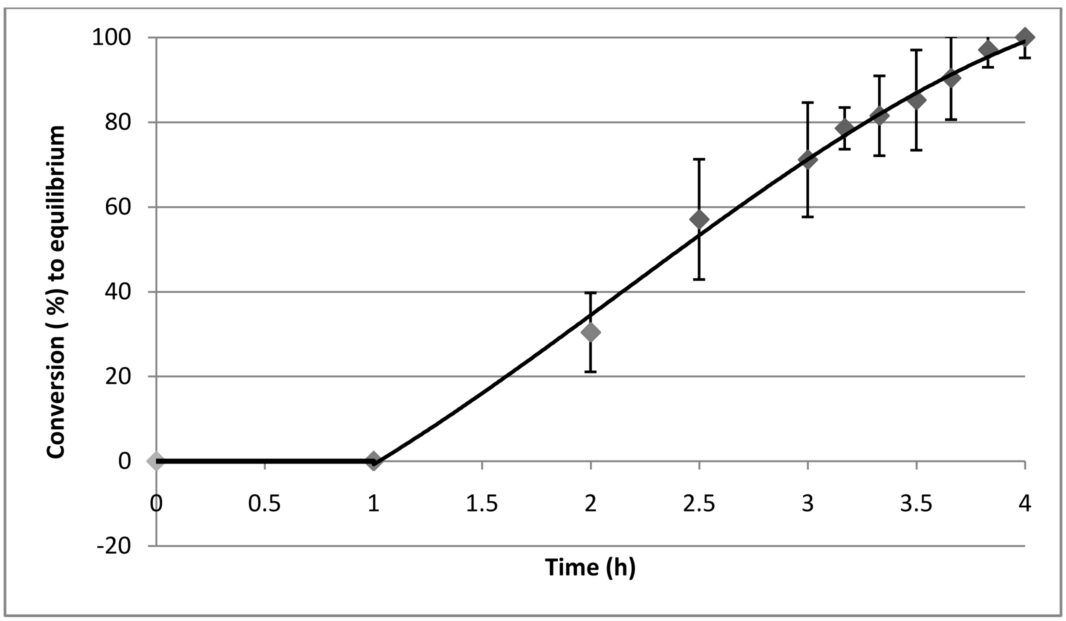


Figure 5.6. Conversion to equilibrium with MgI_2 and 1-phenyl-1-propyne catalyzed by **5.14**.

5.5.2 Alkyne Metathesis with $Mo_2(OCMe_2CF_3)_6$ Assisted by Lewis Acids

LA-assisted AM studies with $Mo_2(OCMe_2CF_3)_6$ (**5.15**) were completed with 20 equivalents of 1-phenyl-1-propyne in CD_2Cl_2 at room temperature. The reaction medium that results in the slowest rate of AM in the absence of a LA was selected in order to measure changes in AM rates. The LAs that enhance AM activity with **5.15** are listed in Table 5.9. A greater number of LAs co-catalyze AM with **5.15** than **5.14** or **5.11**. Magnesium bromide, magnesium iodide, iron (III) bromide, and triphenylboron most greatly improve the rate of metathesis. An induction period is also present in this system.

Table 5.9. AM equilibrium studies with **5.15** and 1-phenyl-1-propyne assisted by LAs: Time to 31% diphenylacetylene/69% 1-phenyl-1-propyne (Q=0.20).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	43	12	$CoCl_2$•$6H_2O$	Dec.
2	$MgCl_2$	NRE[b]	13	$PdCl_2$	18
3	$MgBr_2$	13	14	CuCl	43
4	MgI_2	13	15	$CuCl_2$	15
5	CaI_2	37	16	$CuBr_2$	15
6	$TiCl(O^iPr)_3$	Dec.[c]	17	$ZnCl_2$	NRE
7	$ZrCl_4$	Dec.	18	BPh_3	13
8	$CrCl_2$	NRE	19	HCl	18
9	$MnCl_2$	NRE	20	NBu_4Br	NRE
10	$FeCl_2$	NRE	21	None	47
11	$FeBr_3$	13			

[a]NMR scale reaction with 5 mol% **5.15** in CD_2Cl_2 at room temperature [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition

5.5.3 Alkyne Metathesis with $Mo_2(OCMe(CF_3)_2)_6$ Assisted by Lewis Acids

The influence of two equivalents of LA on the AM activity of **5.7** with 20 equivalents of 1-pheny-1-propyne was investigated in C_6D_6 at 45 °C. As shown in Table 5.10, the only surveyed LA that increases the rate of AM with **5.7** is CuCl.

Table 5.10. AM equilibrium studies with **5.7** and 1-phenyl-1-propyne assisted by LAs: Time to 31% diphenylacetylene/69% 1-phenyl-1-propyne (Q=0.20).[a]

Entry	Lewis Acid	Time (h)	Entry	Lewis Acid	Time (h)
1	LiI	NRE[b]	8	$PdCl_2$	NRE
2	$MgBr_2$	NRE	9	CuCl	15
3	MgI_2	NRE	10	$CuCl_2$	NRE
4	CaI_2	NRE	11	BPh_3	NRE
5	$TiCl(O^iPr)_3$	Dec.[c]	12	HCl	NRE
6	$ZrCl_4$	Dec.	13	None	25
7	$FeBr_3$	NRE			

[a]NMR scale reactions with 5 mol% **5.7** in C_6D_6 at 45°C [b]NRE = no rate enhancement [c]Dec. = catalyst decomposition

5.6 Attempted Formation of N≡Mo(OR)$_3$ from EtC≡Mo(OR)$_3$

As reported by Gdula et. al, the reformation of **5.1** and **5.2** from **5.3** and **5.4**, respectively, is not observed.[1] Attempted formation of **5.10** and **5.11** from their corresponding alkylidyne precursors and propionitrile at elevated temperatures results in the formation of only $Mo_2(OR)_6$ species.

5.7 Conclusions

Further development of a facile method to synthesize molybdenum alkylidyne complexes from molybdenum nitride precursors via metathesis has been developed. The ability to transform the nitride moiety into a propylidyne moiety depends on the alkoxide; $OCMe(CF_3)_2$ and $OC(CF_3)_3$-based complexes readily undergo the conversion.[1] Formation of the corresponding benzylidyne complexes through metathesis with symmetrical diarylalkynes is only successful with **5.2**. Benzylidyne complexes can be obtained through treatment of **5.1** with unsymmetrical alkynes.

Although **5.10** and **5.11** do not readily undergo metathesis to form alkylidyne complexes, introduction of a LA into the reaction system permits *in situ* AM. This indicates that under the reaction conditions, some amount of alkylidyne complex is being generated. Isolation of the desired alkylidyne complexes was unsuccessful due to decomposition of the alkylidyne species upon extended heating in the presence of the LA. The identity of the catalyst, substrate, and LA all affect AM.

Several LAs were also found to co-catalyze AM with AM precatalysts, **5.1**, **5.2**, and $Mo_2(OR)_6$ complexes. The binding mode of the LA with the catalyst has not been identified. However, the ability for the LAs to promote AM with $Mo_2(OR)_6$ complexes provides evidence that binding through the oxygen of the alkoxide is one mode of interaction. A secondary mode of interaction through the nitride of the catalyst has not yet been probed and as a result cannot be excluded. Additionally, the influence of mechanical stirring on the rate of alkyne metathesis and the potential of trace Lewis acid contamination are currently being explored.

5.8 Experimental

5.8.1 General Procedures

All reactions were performed in an atmosphere of dinitrogen, either in a nitrogen-filled MBRAUN Labmaster 130 glove box or by using standard air-free techniques. ^{1}H NMR spectra were recorded at 499.909 MHz, 399.967 MHz on a Varian Inova 400 spectrometer or 300.075 MHz on a Varian Inova 300 spectrometer and referenced to the residual protons in toluene-d_8 (2.09 ppm), $CDCl_3$ (7.26 ppm), CD_2Cl_2 (5.33 ppm), and C_6D_6 (7.15 ppm). ^{19}F NMR spectra were recorded at 282.384 MHz on a Varian Inova 300 spectrometer or 282.314 MHz on a Varian Inova 400 spectrometer and were referenced to an external standard of $CFCl_3$ in $CDCl_3$ (0.00 ppm). ^{13}C NMR spectra were recorded at 100.596 MHz on a Varian Inova 300 spectrometer and were referenced to naturally abundant ^{13}C nuclei in CD_2Cl_2 (54.00 ppm). GC/MS data were collected on a Shimadzu GCMS-QP5000 with a Restek XTI-5 phase column (30m, 0.25 I.D., 0.25 D. F.). EI MS data were collected on a VG (Micromass) 70-250-S Magnetic sector mass spectrometer.

5.8.2 Materials

All solvents used were dried and deoxygenated by the method of Grubbs. Bis(4-methoxyphenyl)acetylene,[10] $VCl_3(thf)_3$,[11] $N{\equiv}Mo(OCMe_3)_3$ (**5.10**),[12] $N{\equiv}Mo(OCMe_2CF_3)_3$ (**5.11**),[13] $N{\equiv}Mo(OCMe(CF_3)_2)_3$ (**5.1**),[14] $N{\equiv}Mo(OC(CF_3)_3)_3(NCMe)$ (**5.2**),[14] and $Mo_2(OCMe_3)_6$ (**5.14**)[15] were prepared according to literature procedures. 1-(4-biphenyl)-1-butyne, $Mo_2(OCMe_2CF_3)_6$ (**5.15**), and $Mo_2(OCMe(CF_3)_2)_6$ (**5.7**) were synthesized as detailed in Chapter 4. Mesitylene, diphenylacetylene, zinc chloride, silver trifluoromethansulfonate, chlorotitanium trisisopropoxide, tetrabutylammonium bromide, anhydrous lithium bromide, lithium chloride, anhydrous lithium iodide, aluminum chloride, and magnesium trifluoromethanesulfonate were obtained from Acros. 3-hexyne, 1-phenyl-1-butyne, and 1-phenyl-1-propyne were obtained from GFS Chemicals and dried over 4Å molecular sieves for at least 24 hours. Anhydrous calcium iodide, ultra dry calcium chloride, anhydrous calcium bromide, iron (II) chloride, and anhydrous magnesium chloride were obtained from Alfa Aesar. Palladium chloride, copper (II) bromide, copper (I) iodide, magnesium bromide, magnesium iodide, magnesium fluoride, gallium chloride, iron (III) bromide, titanium (IV) chloride, potassium bromide, and hydrochloric acid (2.0 M) in Et_2O were obtained from Aldrich. Chromium (III) chloride was obtained from Johnson Matthey. Copper (I) chloride, zirconium (IV) chloride, and copper (II) chloride were obtained from Strem Chemicals, Inc. Cobalt (II) chloride hexahydrate was obtained from Matheson Coleman and Bell. Manganese (II) chloride was obtained from Apache Chemicals Inc. NMR solvents were obtained from Cambridge Isotope Laboratories and were dried over 4Å molecular sieves for at least 24 hours. All reagents were used as received unless otherwise noted.

5.8.3 RC≡Mo(OR)$_3$ Syntheses with OR=CMe(CF$_3$)$_2$

EtC≡Mo(OCMe(CF$_3$)$_2$)$_3$(NCEt). **5.1** (10.0 mg, 0.0153 mmol) was dissolved in C_6D_6 (0.5 mL). Then 3-hexyne (17.4 μL, 0.153 mmol, 10 equiv) was added to the solution via syringe. The solution was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated to 95 °C for 29 h. At this point the reaction mixture consisted of EtC≡Mo(OMe(CF$_3$)$_2$)$_3$(EtCN) (80%) and a decomposition product. The volatiles were removed *in vacuo* from the reaction mixture. The resulting residue was then reconstituted in C_6D_6. At this point insoluble material was present in the reaction mixture along with increased evidence of decomposition with EtC≡Mo(OMe(CF$_3$)$_2$)$_3$(EtCN) only accounting for 63% of the ^{19}F NMR spectrum. ^{1}H NMR (400 MHz, C_6D_6): δ 2.44 (q, 2H, ≡CH_2CH$_3$, J=7.6 Hz), 1.55 (s, 9H, OC(CH$_3$)$_2$CF$_3$), 1.10 (s br, 2H, N≡CH_2CH$_3$), 0.56 (t, 3H, ≡CH$_2$CH_3, J=7.6 Hz), 0.34 (t, 3H, N≡CH$_2$CH_3, J=7.6 Hz) ^{1}H NMR (400 MHz, CD_2Cl_2, -40°C): δ 3.15 (q br, 2H, ≡CH_2CH$_3$, J=7.5 Hz), 2.62 (q br, 2H, N≡CH_2CH$_3$, J=7.5 Hz), 1.81 (s, 9H, OC(CH$_3$)$_2$CF$_3$), 1.32 (t br, 3H, N≡CH$_2$CH_3, J=7.5 Hz), 1.02 (t br, 3H, ≡CH$_2$CH_3, J=7.5

Hz). ^{19}F NMR (300 MHz, C_6D_6): δ -77.67 (s, CF_3). EI/MS $[M/Z]^+$: 730.0 (EtC≡Mo(OCMe(CF_3)$_2$)$_3$)

Attempted PhC≡Mo(OCMe(CF_3)$_2$)$_3$ Synthesis. **Method A. 5.1** (20.0 mg, 0.0306 mmol) and diphenylacetylene (5.5 mg, 0.031 mmol) was dissolved in C_6D_6 (0.5 mL). The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The solution was then heated to 90 °C for 2 d. No reaction was observed. **Method B. 5.1** (5.0 mg, 0.0077 mmol), diphenylacetylene (27.3 mg, 0.153 mmol, 20 equiv), and bis(4-trifluoromethylphenyl)acetylene (48.1 mg, 0.153 mmol, 20 equiv) were dissolved in C_6D_6 (0.5 mL). The reaction mixture was then heated at 70 °C for 2 d. Evidence of alkyne cross metathesis was present at this point. No direct evidence of benzylidyne complex formation was observed by ^{1}H or ^{19}F NMR spectroscopies.

PhC≡Mo(OCMe(CF_3)$_2$)$_3$(DME). **5.1** (1.00 g, 1.53 mmol) and diphenylacetylene (2.73 g, 15.3 mmol, 10 equiv) were dissolved in toluene (50 mL). Then 3-hexyne (522 μL, 4.59 mmol, 3 equiv) was added to the reaction mixture via syringe. The mixture was sealed and heated at 95 °C for 24 h. The reaction mixture was filtered through celite and the celite was washed with pentane (40 mL). The volatiles were then removed *in vacuo*. The reaction mixture was taken up in toluene/pentane (16 mL) and DME (159 μL, 1.53 mmol, 1 equiv) was added. The mixture was then cooled in the freezer. Following repeated recrystallizations PhC≡Mo(OCMe(CF_3)$_2$)$_3$(DME) (158 mg, 0.205 mmol, 20%)

was isolated. Further isolation could not be achieved through recrystallization. Characterization data agreed with the literature.[8]

4-PhC$_6$H$_4$C≡Mo(OCMe(CF$_3$)$_2$)$_3$(4-PhC$_6$H$_4$CN). **5.1** (5.0 mg, 0.0077 mmol) and bis(4-biphenyl)acetylene (25.3 mg, 0.0766 mmol, 10 equiv) were slurried in toluene-d_8 (0.5 mL). Then 3-hexyne (1.9 μL, 0.023 mmol, 3 equiv) was added via syringe. The reaction mixture was heated to 95 °C for 3 d. At this point the reaction mixture consisted of 4-PhC$_6$H$_4$C≡Mo(OC(CF$_3$)$_2$)$_3$(4-PhC$_6$H$_4$CN) (51%) and **5.1** (39%). Further heating of the reaction mixture for 1 d only resulted in an additional 1 % formation of 4-PhC$_6$H$_4$C≡Mo(OC(CF$_3$)$_2$)$_3$(4-PhC$_6$H$_4$CN) (51%).

5.8.4 RC≡Mo(OR)$_3$ Syntheses with OR=C(CF$_3$)$_3$

EtC≡Mo(OC(CF$_3$)$_3$)$_3$(NCEt). **5.2** (100.0 mg, 0.117 mmol) was dissolved in toluene (3 mL). 3-hexyne (26.5 μL, 0.234 mmol, 2 equiv) was added via syringe. The solution was then heated at 75 °C for 12 h. Upon removal of volatiles *in vacuo* red crystals of **5.4** crystallized on the side of the reaction vial. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 2.79 (q, 2H, ≡CH_2CH$_3$, J=7.6 Hz), 0.62 (t, 3H, ≡CH$_2$CH_3, J=7.6 Hz), 0.35 (t, 3H, N≡CH$_2$CH_3, J=7.6 Hz). ^{1}H NMR (400 MHz, toluene-d_8, -20°C): 2.83 (q br, 2H, ≡CH_2CH$_3$, J=7.0 Hz), 1.08 (q br, 2H, N≡CH_2CH$_3$, J=7.6 Hz), 0.67 (t, 3H, ≡CHCH_3, J=7.0 Hz), 0.39 (t, 3H, N≡CH$_2$CH_3, J=7.4 Hz). ^{19}F NMR (300 MHz, C$_6$D$_6$): -72.44 (s, CF$_3$). EI/MS [M/Z]$^+$: 843.9 (EtC≡Mo(OC(CF$_3$)$_3$)$_3$)

4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-MeOC$_6$H$_4$CN). **5.2** (500.0 mg, 0.5840 mmol) and bis(4-methoxyphenyl)acetylene (339.2 mg, 1.424 mmol, 2.438 equiv) were dissolved in toluene (25 mL). The reaction mixture was heated at 60 °C for 6 d. The reaction volume was reduced by half and the mixture was heated at 60 °C for 2 d. At this point, the reaction mixture was 84% 4-MeOC$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-MeOC$_6$H$_4$CN), 7% N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe), and 9% decomposition. The volatiles were removed *in vacuo* and the reaction mixture was extracted with pentane (30 mL) and filtered. The resulting filtrate was extracted with pentane (10 mL) and the volatiles were removed *in vacuo*. The resulting material was dissolved in Et$_2$O/pentane (5 mL) and cooled to −35 °C. A purple powder was isolated via filtration (133.2 mg, 0.1075 mmol, 21.6%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.23 (d, 2H, ArH, J=9.0 Hz), 7.06 (d, 2H, ArH, J=9.0 Hz), 6.35 (d, 2H, ArH, J=9.0 Hz), 6.15 (d, 2H, ArH, J=9.0 Hz), 3.04 (s, 3H, OMe), 2.95 (s, 3H, OMe). ^{19}F NMR (300 MHz, C$_6$D$_6$): –72.48 (s, C*F*$_3$). ^{13}C{^{1}H} NMR (400 MHz, CD$_2$Cl$_2$): δ 321.94 (s, Mo≡*C*), 165.95 (s, ArC), 162.20 (s, ArC), 137.52 (s, ArC), 135.54 (s, ArC), 133.23 (s, ArC), 133.14 (s, ArC), 121.60 (q, OC(*C*F$_3$)$_3$, J$_{C\text{-}F}$=293.2 Hz), 116.15 (s, ArC), 113.22 (s, ArC), 101.83 (s, ArC) 99.38 (s, CN), 87.02 (m, O*C*(CF$_3$)$_3$), 56.44 (s, OMe), 55.86 (s, OMe).

4-Ph-C$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-PhC$_6$H$_4$CN). **5.2** (5.0 mg, 0.0058 mmol) and bis(4-biphenyl)acetylene (19.3 mg, 0.0584 mmol, 10 equiv) were slurried in C$_6$D$_6$ (0.5 mL). The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The mixture was then heated at 95 °C for 3 d. At this point the reaction mixture consisted of 88% 4-Ph-C$_6$H$_4$C≡Mo(OC(CF$_3$)$_3$)$_3$(4-PhC$_6$H$_4$CN). **Scale-Up**. **5.2** (1.0 g, 1.17

mmol) and bis(4-biphenyl)acetylene (2.88 g, 8.76 mmol, 7.5 equiv) were slurried in toluene (50 mL). The reaction mixture was then heated at 95 °C for 3 d. The mixture and the resulting white precipitate were washed with toluene (40 mL) and then pentane (10 mL). The volatiles were removed *in vacuo* from the filtrate. The resulting material was extracted with pentane and filtered. The resulting filtrate was reduced to 15 mL and cooled to -35 °C. ^{19}F NMR (400 MHz, C_6D_6): −72.3 (s, CF_3). ^{1}H NMR (400 MHz, C_6D_6): 7.40 (d, J=8.2 Hz), 7.00-7.278 (m), 7.01 (d, J= 7.0 Hz). EI/MS $[M/Z]^+$: 968.0, 4-$PhC_6H_4C{\equiv}Mo(OCMe(CF_3)_2)_3$.

5.8.5 Alkyne Metathesis Solvent Studies with $N{\equiv}Mo(OR)_3$ Complexes

General Procedure with 5.1. Complex **5.1** (5.0 mg, 0.0077 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (18.9 μL, 0.153 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. The reaction was monitored at room temperature.

General Procedure with 5.2. Complex **5.2** (5.0 mg, 0.0058 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (14.4 μL, 0.117 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. The reaction was monitored at room temperature.

General Procedure with 5.10. Complex **5.10** (5.0 mg, 0.015 mmol) was dissolved in an appropriate solvent (500 μL). Then 1-phenyl-1-propyne (37.5 μL, 0.304 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. This solution was transferred to a vial containing magnesium iodide (5.6 mg, 0.030 mmol, 2 equiv). The resulting reaction mixture was then placed in a J. Young tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was then monitored at 60 °C.

General Procedure with 5.11. Complex **5.11** (10.0 mg, 0.0204 mmol) was dissolved in an appropriate solvent (1 mL). Then 1-phenyl-1-butyne (57.9 μL, 0.407 mmol, 20 equiv) and an internal standard of mesitylene were added via syringe. This solution was transferred to a vial containing magnesium bromide (7.5 mg, 0.041 mmol, 2 equiv). The resulting reaction mixture was then placed in a J. Young tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was then monitored at 60 °C.

5.8.6 Alkyne Metathesis Studies with $N{\equiv}Mo(OCMe)_3$ Assisted by Lewis Acids

General Procedure. Complex **5.10** was dissolved in C_6D_6 (30.4 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 80 °C.

Calcium iodide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), calcium iodide (8.9 mg, 0.030 mmol). No metathesis was observed after 62 h.

Chlorotitanium trisisopropoxide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), chlorotitanium trisisopropoxide (7.9 μL, 0.030 mmol). After 88 h, 80% 1-phenyl-1-propyne and 20% diphenylacetylene was present (Q= 0.06). GC/MS $[M/Z]^{+}$: 178 ($C_{14}H_{10}$, R_t 8.00 min).

Cobalt (II) chloride hexahydrate. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), cobalt (II) chloride hexahydrate (7.2 mg, 0.030 mmol). Immediate catalysts decomposition was observed.

Copper (I) chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), copper (I) chloride (8.1 mg, 0.061 mmol). This reaction was conducted in the dark. No metathesis was observed after 42 h.

Copper (II) bromide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), copper (II) bromide (6.8 mg, 0.030 mmol). After 27 h, the reaction mixture was composed of 19% 1-phenyl-1-propyne and 81% diphenylacetylene (Q=0.06). GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.05 min).

Copper (II) chloride. Following the general procedure: **5.10** (7.5 mg, 0.023 mmol), 1-phenyl-1-propyne (56.3 μL, 0.455 mmol), copper (II) chloride (6.1 mg, 0.046 mmol). This reaction was conducted in the dark. After 27 h, the reaction mixture was composed of 22% 1-phenyl-1-propyne and 78% diphenylacetylene (Q=0.08). GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.08 min).

Chromium (II) chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), chromium (II) chloride (7.5 mg, 0.061 mmol). No metathesis was observed after 62 h.

Gallium trichloride. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), gallium trichloride (5.3 mg, 0.030 mmol). Immediate catalysts decomposition was observed.

Hydrochloric acid. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), hydrochloric acid (1.9 μL, 0.0038 mmol). No metathesis was observed after 40 h.

Iron (III) bromide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), iron (III) bromide (9.0 mg, 0.030 mmol). No metathesis was observed after 42 h.

Iron (II) chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), iron (II) chloride (7.7 mg, 0.061 mmol). No metathesis was observed after 62 h.

Lithium iodide. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), lithium iodide (8.1 mg, 0.061 mmol). This reaction was conducted in the dark. No metathesis was observed after 62 h.

Magnesium bromide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), magnesium bromide (5.6 mg, 0.030 mmol). After 23 h an equilibrium mixture was achieved (Q=0.21). GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.08 min).

Magnesium chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), magnesium chloride (5.8 mg, 0.061 mmol). No metathesis was observed after 62 h.

Magnesium iodide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), magnesium iodide (8.4 mg, 0.030 mmol). After 19 h, the reaction mixture was composed of 15% 1-phenyl-1-propyne and 85% diphenylacetylene (Q=0.03). GC/MS $[M/Z]^{+}$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.06 min).

Manganese (II) chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), manganese (II) chloride (7.6 mg, 0.061 mmol). No metathesis was observed after 47 h.

Palladium (II) chloride. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), palladium (II) chloride (5.4 mg, 0.030 mmol). No metathesis was observed after 42 h.

Tetrabutylammoniumbromide. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), tetrabutylammoniumbromide (9.8 mg, 0.030 mmol). No metathesis was observed after 42 h.

Triphenylboron. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), triphenylboron (7.4 mg, 0.030 mmol). A large polymeric residue was observed after 18 h.

Zinc chloride. Following the general procedure: **5.10** (10.0 mg, 0.0304 mmol), 1-phenyl-1-propyne (75.1 μL, 0.607 mmol), zinc chloride (8.3 mg, 0.061 mmol). No metathesis was observed after 62 h.

Zirconium (IV) chloride. Following the general procedure: **5.10** (5.0 mg, 0.015 mmol), 1-phenyl-1-propyne (37.5 μL, 0.304 mmol), zirconium (IV) chloride (7.1 mg, 0.030 mmol). After 11 h, the reaction mixture was composed of 21% 1-phenyl-1-propyne and 79% diphenylacetylene (Q=0.07). GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.05 min).

5.8.7 Alkyne Metathesis Studies with $N{\equiv}Mo(OCMe_2CF_3)_3$ Assisted by Lewis Acids

General procedure. Complex **5.11** was dissolved in CD_2Cl_2 (20.4 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 40 °C.

Calcium bromide. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), calcium bromide (8.1 mg, 0.041 mmol). No alkyne metathesis was observed after 3 d. Some catalyst decomposition had occurred (31%).

Calcium chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), calcium chloride (4.5 mg, 0.041 mmol). No alkyne metathesis was observed after 4 d. Some catalyst decomposition had occurred (4%).

Calcium iodide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), calcium iodide (6.0 mg, 0.020 mmol). After 4 d no alkyne metathesis was observed. Some catalyst decomposition had occurred (5%).

Chlorotitanium trisisopropoxide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), chlorotitanium trisisopropoxide (4.2 μL, 0.020 mmol). After 13 h no metathesis had occurred and the catalyst had completely decomposed.

Chromium (II) chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), chromium (II) chloride (5.0 mg, 0.041 mmol). After 3 d no metathesis had occurred and 11% of the catalyst had decomposed.

Chromium (III) chloride. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), chromium (III) chloride (3.2 mg, 0.020 mmol). After 38 h no metathesis had occurred and 11% of the catalyst had decomposed.

Cobalt (II) chloride hexahydrate. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), cobalt (II) chloride hexahydrate (4.8 mg, 0.020 mmol). After 28 h no metathesis had occurred and the catalyst had decomposed.

Copper (II) bromide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), copper (II) bromide (4.5 mg, 0.020

mmol). After 59 h, the reaction mixture is composed of 82% 1-phenyl-1-propyne and 18% diphenyacetylene with Q=0.06.

Copper (I) chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), copper (I) chloride (4.0 mg, 0.041 mmol). After 4 d no metathesis had occurred.

Copper (II) chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), copper (II) chloride (5.5 mg, 0.041 mmol). After 99 h the reaction mixture was composed of 80% 1-phenyl-1-propyne and 20% diphenylacetylene (Q=0.06). No further reaction was observed over the next 24 h.

Copper (I) iodide. Following the general procedure: **5.11** (7.5 mg, 0.015 mmol), 1-phenyl-1-propyne (37.7 μL, 0.305 mmol), copper (I) iodide (5.4 mg, 0.031 mmol). This reaction was conducted in the dark. After 40 h no metathesis had occurred.

Hydrochloric acid. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), hydrochloric acid (2.5 μL, 0.0051 mmol). After 51 h trace metathesis had occurred and 39% of the catalyst had decomposed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.09 min)

Iron (III) bromide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), iron (III) bromide (6.0 mg, 0.020 mmol). After 51 h no metathesis had occurred and the catalyst had completely decomposed.

Lithium iodide. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), lithium iodide (5.4 mg, 0.041 mmol). After 45 hr no metathesis had occurred.

Magnesium bromide. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), magnesium bromide (7.5 mg, 0.041 mmol). After 93 h the reaction mixture was composed of 80% 1-phenyl-1-propyne and 20% diphenylacetylene. No further reaction was observed over the next 24 h (Q=0.06).

Magnesium chloride. Following the general procedure: **5.11** (15.0 mg, 0.0305 mmol), 1-phenyl-1-propyne (75.5 μL, 0.611 mmol), magnesium chloride (5.8 mg, 0.061 mmol). After 4 d no metathesis had occurred. Some catalyst decomposition was present (4%).

Magnesium fluoride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-butyne (50.3 μL, 0.407 mmol), magnesium fluoride (2.5 mg, 0.041 mmol). After 31 h no metathesis had occurred.

Magnesium iodide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), magnesium iodide (5.7 mg, 0.020 mmol). After 59 h the reaction mixture was composed of 80% 1-phenyl-1-propyne and 20% diphenylacetylene (Q=0.06). No further reaction was observed over the next 24 h.

Palladium (II) chloride. Following the general procedure: **5.11** (7.5 mg, 0.015 mmol), 1-phenyl-1-propyne (37.7 μL, 0.305 mmol), palladium (II) chloride (5.4 mg, 0.031 mmol). After 4 d no metathesis had occurred and 5% of the catalyst had decomposed.

Triphenylboron. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), triphenylboron (4.9 mg, 0.020 mmol). No alkyne metathesis was observed after 4 d. Some catalyst decomposition had occurred (22%).

Zinc (II) chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-propyne (50.3 μL, 0.407 mmol), zinc (II) chloride (5.5 mg, 0.041 mmol). No alkyne metathesis was observed after 3 d. Some catalyst decomposition had occurred (6%).

Zirconium (IV) chloride. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-propyne (25.2 μL, 0.204 mmol), zirconium (IV) chloride (4.7 mg, 0.020 mmol). After 51 h trace metathesis had occurred and 22% of the catalyst had decomposed.

5.8.8 Alkyne Metathesis Studies with $N{\equiv}Mo(OCMe(CF_3)_2)_3$ Assisted by Lewis Acids

General Procedure. Complex **5.1** was dissolved in $CDCl_3$ (1.0 mL). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^1H NMR spectroscopy at room temperature.

Calcium bromide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), calcium bromide (6.1 mg, 0.031 mmol). No metathesis rate enhancement was observed.

Calcium iodide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), calcium iodide (9.0 mg, 0.031 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (4%).

Chlorotitanium trisisopropoxide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), chlorotitanium trisisopropoxide (8.0 mg, 0.031 mmol). No metathesis rate enhancement was observed due to complete catalyst decomposition.

Chromium (II) chloride. Following the general procedure: **5.1** (15.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), zinc (II) chloride (4.2 mg, 0.031 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Copper (II) bromide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), copper (II) bromide (6.8 mg, 0.031 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Copper (I) chloride. Following the general procedure: **5.1** (15.0 mg, 0.0230 mmol), 1-phenyl-1-propyne (56.8 μL, 0.459 mmol), copper (I) chloride (4.5 mg, 0.046 mmol). The reaction mixture was covered with aluminum foil. No metathesis rate enhancement was observed. Some catalyst decomposition was observed (3%).

Copper (II) chloride. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), copper (II) chloride (4.1 mg, 0.031 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Hydrochloric acid. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), hydrochloric acid (15.3 μL, 0.0306 mmol). An equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was achieved after 6 h. Some catalyst decomposition was observed (49%).

Iron (III) bromide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), iron (III) bromide (9.1 mg, 0.031 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (42%).

Lithium iodide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), lithium iodide (54.1 mg, 0.031 mmol). The reaction mixture was covered in aluminum foil. No metathesis rate enhancement was observed. Some catalyst decomposition was observed (18%).

Magnesium bromide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), magnesium bromide (5.6 mg, 0.031 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (7%).

Magnesium iodide. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), magnesium iodide (8.5 mg, 0.031 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (26%).

Palladium (II) chloride. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), palladium (II) chloride (5.4 mg, 0.031 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Triphenylboron. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), triphenylboron (7.4 mg, 0.031 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (16%).

Zinc (II) chloride. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), zinc (II) chloride (4.2 mg, 0.031 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Zirconium (IV) chloride. Following the general procedure: **5.1** (10.0 mg, 0.0153 mmol), 1-phenyl-1-propyne (37.8 μL, 0.306 mmol), zirconium (IV) chloride (7.1 mg, 0.031 mmol). An equilibrium mixture of 1-phnenyl-1-propyne and diphenylacetylene was observed after 6 h with Q=0.21. Some catalyst decomposition was observed (30%).

5.8.9 Alkyne Metathesis Studies with $N{\equiv}Mo(OC(CF_3)_3)_3(NCMe)$ Assisted by Lewis Acids

General Procedure. Complex **5.2** was dissolved in C_6D_6 (1.0 mL). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^1H NMR spectroscopy at room temperature.

Calcium bromide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), calcium bromide (4.7 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (38%).

Calcium iodide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), calcium iodide (6.9 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (27%).

Chlorotitanium trisisopropoxide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), chlorotitanium trisisopropoxide (6.1 mg, 0.023 mmol). No metathesis rate enhancement was observed due to complete catalyst decomposition.

Chromium (II) chloride. Following the general procedure: **5.2** (15.0 mg, 0.0175 mmol), 1-phenyl-1-propyne (43.3 μL, 0.350 mmol), chromium (II) chloride (4.3 mg, 0.035 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (12%).

Copper (II) bromide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), copper (II) bromide (5.2 mg, 0.023 mmol). No metathesis rate enhancement was observed. Trace catalyst decomposition was observed.

Copper (I) chloride. Following the general procedure: **5.2** (15.0 mg, 0.0175 mmol), 1-phenyl-1-propyne (43.3 μL, 0.350 mmol), copper (I) chloride (3.5 mg, 0.035 mmol). The reaction mixture was covered with aluminum foil. No metathesis rate enhancement was observed. Some catalyst decomposition was observed (27%).

Copper (II) chloride. Following the general procedure: **5.2** (15.0 mg, 0.0175 mmol), 1-phenyl-1-propyne (43.3 μL, 0.350 mmol), copper (II) chloride (4.7 mg, 0.035 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (29%).

Hydrochloric acid. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), hydrochloric acid (11.7 μL, 0.0234 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (64%).

Iron (III) bromide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), iron (III) bromide (6.9 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (58%).

Lithium iodide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), lithium iodide (3.1 mg, 0.023 mmol). The reaction mixture was wrapped with aluminum foil. No metathesis rate enhancement was observed. Some catalyst decomposition was observed (16%).

Magnesium bromide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), magnesium bromide (4.3 mg, 0.023 mmol). No metathesis rate enhancement was observed.

Magnesium iodide. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), magnesium iodide (6.5 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (32%).

Palladium (II) chloride. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), palladium (II) chloride (4.1 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (32%).

Triphenylboron. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), triphenylboron (5.7 mg, 0.023 mmol). An equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was obtained in 4.7±0.6 h for three replicate samples. Some catalyst decomposition was observed (20%). GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 11.71 min), 178 ($C_{14}H_{10}$, R_t 16.92 min).

Zinc (II) chloride. Following the general procedure: **5.2** (15.0 mg, 0.0175 mmol), 1-phenyl-1-propyne (43.3 μL, 0.350 mmol), zinc (II) chloride (4.8 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (23%).

Zirconium (IV) chloride. Following the general procedure: **5.2** (10.0 mg, 0.0117 mmol), 1-phenyl-1-propyne (28.9 μL, 0.234 mmol), zirconium (IV) chloride (5.4 mg, 0.023 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was observed (25%).

5.8.10 Alkyne Metathesis Alkyne Dependence Studies with N≡Mo($OCMe_2CF_3$)$_3$ Assisted by Lewis Acids

General procedure. Complex **5.11** was dissolved in CD_2Cl_2 (20.4 mM). 1-phenyl-1-butyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction mixture was frozen and the overlying volatiles were removed *in vacuo*. The reaction was monitored via ^{1}H NMR spectroscopy at 40 °C.

Copper (II) bromide. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-butyne (57.9 μL, 0.407 mmol), copper (II) bromide (9.1 mg, 0.041 mmol). After 8 h the reaction mixture was composed of 18% diphenylacetylene and 82% 1-phenyl-1-butyne. Some catalyst decomposition had occurred (55%).

Copper (II) chloride. Following the general procedure: **5.11** (10.0 mg, 0.0204 mmol), 1-phenyl-1-butyne (57.9 μL, 0.407 mmol), copper (II) chloride (5.5 mg, 0.041 mmol). After 44 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.25). Some catalyst decomposition had occurred (55%). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.61 min), 178 ($C_{14}H_{10}$, R_t 8.17 min)

Magnesium bromide. Following the general procedure: **5.11** (7.5 mg, 0.015 mmol), 1-phenyl-1-butyne (43.4 μL, 0.305 mmol), magnesium bromide (5.6 mg, 0.031 mmol). After 18 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.23). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.59 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Magnesium iodide. Following the general procedure: **5.11** (5.0 mg, 0.010 mmol), 1-phenyl-1-butyne (28.9 μL, 0.204 mmol), magnesium iodide (5.7 mg, 0.020 mmol). After 5.5 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.19). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.56 min), 178 ($C_{14}H_{10}$, R_t 8.15 min)

5.8.11 Isolation Attempts of RC≡Mo(OR)$_3$ Complexes from N≡Mo(OCMe$_3$)$_3$ in the Presence of $MgBr_2$

5.10 and 3-hexyne. **5.10** (10.0 mg, 0.0304 mmol) was dissolved in toluene-d_8 (1.0 mL). 3-hexyne (25.0 μL, 0.220 mmol, 7 equiv) was added to the solution via syringe. Then magnesium bromide (11.2 mg, 0.0608 mmol, 2 equiv) was added to the solution. The reaction mixture was then monitored at 85 °C by ^{1}H NMR spectroscopy. After 3 d no further changes were observed. The volatiles were vacuum transferred. ^{1}H NMR spectroscopy of the volatiles revealed the presence of isobutylene. The non-volatile residue had no evidence of **5.14** or EtC≡Mo(OCMe$_3$)$_3$.

5.10 and diphenylacetylene. **5.10** (5.0 mg, 0.015 mmol) was dissolved in toluene-d_8 (0.5 mL). Diphenylacetylene (27.1 mg, 0.152 mmol, 10 equiv) was added to the solution. Then magnesium bromide (5.6 mg, 0.030 mmol, 2 equiv) was added to the solution. The reaction mixture was heated at 80 °C for 3 d with no evidence of metathesis. Formation of isobutylene was indicated by ^{1}H NMR spectroscopy.

5.10 and 1-phenyl-1-butyne. **5.10** (10.0 mg, 0.0304 mmol) was dissolved in toluene-d_8 (0.5 mL). 1-phenyl-1-butyne (4.3 µL, 0.041 mmol, 1.0 equiv) was added to the solution. Then magnesium bromide (5.6 mg, 0.041 mmol, 1 equiv) was added to the solution. The reaction mixture was heated at 80 °C for 3 d with no evidence of metathesis. Formation of isobutylene was indicated by ^{1}H NMR spectroscopy.

5.8.12 Isolation Attempts of RC≡Mo(OR)$_3$ Complexes from N≡Mo(OCMe$_2$CF$_3$)$_3$ in the Presence of MgBr$_2$

5.11 and 3-hexyne. **5.11** (5.0 mg, 0.010 mmol) was dissolved in toluene-d_8 (0.5 mL). Then 3-hexyne (11.6 µL, 0.102 mmol, 10 equiv) was added via syringe to the solution. Then magnesium bromide (3.7 mg, 0.020, 2 equiv) was added to the solution. The reaction mixture was heated at 95 °C for 1 d. At this point evidence of alkylidyne formation (12 %) was present by ^{1}H NMR spectroscopy. Further heating resulted in decomposition of the reaction mixture.

5.11 and diphenylacetylene. **5.11** (5.0 mg, 0.010 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to a vial containing diphenylacetylene (9.1 mg, 0.051 mmol, 5 equiv). Magnesium bromide (3.7 mg, 0.020 mmol, 2 equiv) was then added to the solution. The reaction mixture was heated at 60 °C for 2 d without evidence of metathesis. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The mixture was then heated at 95 °C for 1 d with no evidence of metathesis.

5.11 and 1-phenyl-1-propyne. **5.11** (10.0 mg, 0.0204 mmol) was dissolved in C_6D_6 (0.5 mL). 1-phenyl-1-propyne (50.3 μL, 0.407 mmol, 20 equiv) was added to the solution. Then magnesium bromide (7.5 mg, 0.041 mmol, 2 equiv) was added to the solution. The reaction mixture was heated at 70 °C for 2 d with no evidence of alkylidyne complex formation. The reaction mixture was then frozen and the overlying volatiles were removed *in vacuo*. The reaction mixture was heated at 95 °C for 1 d with no clear evidence of alkylidyne complex formation.

5.11 and 1-phenyl-1-butyne. **5.11** (10.0 mg, 0.0204 mmol) was dissolved in C_6D_6 (0.5 mL). 1-phenyl-1-butyne (57.9 μL, 0.407 mmol, 20 equiv) was added to the solution. Then magnesium bromide (7.5 mg, 0.041 mmol, 2 equiv) was added to the solution. The reaction mixture was heated at 70 °C for 1 d with no evidence of alkylidyne complex formation.

5.8.13 Alkyne Metathesis Studies with $Mo_2(OCMe_3)_6$ Assisted by Lewis Acids

General Procedure A. Complex **5.14** was dissolved in $CDCl_3$ (15.8 mM). 1-phenyl-1-butyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0

equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^{1}H NMR spectroscopy.

General Procedure B. Complex **5.14** was dissolved in $CDCl_3$ (15.8 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^{1}H NMR spectroscopy.

Aluminium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), aluminum chloride (4.2 mg, 0.032 mmol). The reaction was monitored at room temperature. After 1 h the reaction mixture was composed of 9% 1-phenyl-1-propyne and 91% diphenylacetylene. No further reaction was observed over 24 h. GC/MS $[M/Z]^{+}$: 130 ($C_{10}H_{10}$, R_t 3.59 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Calcium bromide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), calcium bromide (6.3 mg, 0.032 mmol). The reaction was monitored at room temperature. After 25 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.25). GC/MS $[M/Z]^{+}$: 130 ($C_{10}H_{10}$, R_t 3.49 min), 178 ($C_{14}H_{10}$, R_t 8.03 min)

Calcium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), calcium chloride (3.5 mg, 0.032 mmol). The reaction was monitored at room temperature. After 23 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.25). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.51 min), 178 ($C_{14}H_{10}$, R_t 8.03 min)

Calcium iodide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), calcium iodide (4.2 mg, 0.032 mmol). The reaction was monitored at room temperature. After 28 h and equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.25). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.51 min), 178 ($C_{14}H_{10}$, R_t 8.02 min)

Chlorotitanium trisisopropoxide. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), chlorotitanium trisisopropoxide (3.3 μL, 0.016 mmol). The reaction was monitored at room temperature. After 22 h the reaction mixture was composed of 12% 1-phenyl-1-butyne and 88% diphenylacetylene.

Copper (I) chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), copper (I) chloride (3.1 mg, 0.032 mmol). The reaction was monitored at room temperature in the dark. After 24 h no metathesis was observed. The reaction mixture was heated to 40 °C and after 21 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present.

Copper (II) chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), copper (II) chloride (4.3 mg, 0.032 mmol). The reaction was monitored at room temperature. After 20 h the reaction mixture was composed of 25% 1-phenyl-1-butyne and 75% diphenylacetylene. No further reaction was seen over 48 h.

Gallium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), gallium chloride (5.6 mg, 0.032 mmol). The reaction was monitored at room temperature. Immediate catalyst decomposition occurred.

Hydrochloric acid. **5.14** (5.0 mg, 0.0079 mmol) was dissolved in C_6D_6 (500 μL). Then 1-phenyl-1-butyne (22.5 μL, 0.0159 mmol, 20 equiv) and hydrochloric acid (1.0 μL, 0.0020 mmol, 0.25 equiv) were added to the reaction mixture. The reaction was monitored at room temperature. After 44 h an equilibrium mixture of 1-phenyl-1-buyne and diphenylacetylene was present (Q=0.25). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.59 min), 178 ($C_{14}H_{10}$, R_t 8.18 min)

Iron (III) bromide. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), iron (III) bromide (4.7 mg, 0.016 mmol). The reaction was monitored at room temperature. After 2 h the reaction mixture was composed of 12% 1-phenyl-1-butyne and 88% diphenylacetylene at this point the catalyst had completely decomposed. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.59 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Iron (II) chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), iron (II) chloride (4.0 mg, 0.032 mmol). No reaction was observed at room temperature over 23 h. The reaction mixture was heated at 40 °C for 20 h and no reaction was observed. The mixture was then frozen and the overlying atmosphere was removed under vacuum. The mixture was then heat at 60 °C for 12 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.13 min).

Lithium bromide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), lithium bromide (2.8 mg, 0.032 mmol). The reaction was monitored at room temperature. After 25 h an equilibrium mixture of 1-phenyl-1-buyne and diphenylacetylene was present (Q=0.20). GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.50 min), 178 ($C_{14}H_{10}$, R_t 8.04 min)

Lithium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), lithium chloride (1.3 mg, 0.032 mmol). The reaction was monitored at room temperature. After 22 h no metathesis reactivity was observed. The reaction mixture was then heated at 40 °C for 12 h at which point only trace metathesis was present.

Lithium iodide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), lithium iodide (4.2 mg, 0.032 mmol). The reaction was monitored at room temperature in the dark. No rate enhancement was observed.

Magnesium bromide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), magnesium bromide (5.8 mg, 0.032 mmol). The reaction was monitored at room temperature and completed in triplicate. After 2.3±0.6 hr the reaction was composed of an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene where Q=0.20±0. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.60 min), 178 ($C_{14}H_{10}$, R_t 8.16 min)

Magnesium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), magnesium chloride (3.0 mg, 0.032 mmol). No reaction was observed at room temperature over 19 h. The reaction mixture was heated at 40°C for 21 h and no reaction was observed. The mixture was then frozen and the overlying atmosphere was removed under vacuum. The mixture was then heat at 60 °C for 20 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.60 min), 178 ($C_{14}H_{10}$, R_t 8.15 min)

Magnesium iodide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), magnesium iodide (8.8 mg, 0.032 mmol). The reaction was monitored at room temperature. After 3.7±0.6 hr the reaction was composed of an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene (Q=0.20±0).

Magnesium trifluoromethanesulfonate. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), magnesium trifluoromethanesulfonate (5.1 mg, 0.016 mmol). No reaction was observed at room temperature over 18 h. The reaction mixture was heated at 40 °C for 31 h and no reaction was observed. The mixture was then frozen and the overlying atmosphere was removed under vacuum. The mixture was then heat at 60 °C for 5 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present.

Palladium chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), palladium chloride (5.6 mg, 0.032 mmol). No reaction was observed at room temperature over 23 h. The reaction mixture was heated at 40 °C for 20 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.60 min), 178 ($C_{14}H_{10}$, R_t 8.17 min).

Potassium bromide. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), potassium bromide (3.8 mg, 0.032 mmol). No reaction was observed at room temperature over 19 h. The reaction mixture was heated at 40 °C for 19 h and no reaction was observed. The mixture was then frozen and the overlying atmosphere was removed under vacuum. The mixture was then heat at 60 °C for 20 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.61 min), 178 ($C_{14}H_{10}$, R_t 8.16 min)

Silver trifluoromethanesulfonate. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), silver trifluoromethanesulfonate (4.1 mg, 0.016 mmol). The reaction was monitored at room temperature in the dark. After 8 h the reaction mixture was composed of 13% 1-phenyl-1-butyne and 87% diphenylacetylene. No further reaction was observed over 24 h.

Tetrabutylammonium bromide. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), tetrabutylammonium bromide (5.1 mg, 0.016 mmol). No reaction was observed at room temperature over 23 h. The reaction mixture was heated at 40 °C for 25 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.58 min), 178 ($C_{14}H_{10}$, R_t 8.13 min).

Triphenylboron. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), triphenylboron (3.8 mg, 0.016 mmol). The reaction was monitored at room temperature. After 22 h no metathesis was observed. The reaction mixture was heated at 40 °C for 13 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present.

Titanium (IV) chloride. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), titanium (IV) chloride (3.3 μL, 0.016 mmol). The reaction was monitored at room temperature. After 48 h no metathesis had occurred and the catalyst had decomposed.

Vanadium (III) chloride tristetrahydrofuran. Following General Procedure A: **5.14** (5.0 mg, 0.0079 mmol), 1-phenyl-1-butyne (22.5 μL, 0.159 mmol), vanadium (III) chloride tritetrahydrofuran (5.9 mg, 0.016 mmol). The reaction was monitored at room temperature. After 1 h, the reaction mixture was composed of 14% 1-phenyl-1-propyne and 86% diphenylacetylene. No further reaction was observed over 24 h. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.59 min), 178 ($C_{14}H_{10}$, R_t 8.13 min).

Zinc chloride. Following General Procedure A: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-butyne (45.1 μL, 0.317 mmol), zinc chloride (4.3 mg, 0.032 mmol). No reaction was observed at room temperature over 19 h. The reaction mixture was heated at 40 °C for 22 h at which point an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.60 min), 178 ($C_{14}H_{10}$, R_t 8.16 min).

Zirconium (IV) chloride. Following General Procedure A: **5.14** (7.5 mg, 0.0119 mmol), 1-phenyl-1-butyne (33.8 μL, 0.238 mmol), zirconium (IV) chloride (5.5 mg, 0.024 mmol). The reaction was monitored at room temperature. After 7 h, a statistical mixture of 1-phenyl-1-butyne and diphenylacetylene was present (Q=0.19).

Calcium bromide. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), calcium bromide (6.3 mg, 0.032 mmol). The reaction was monitored at room temperature. No AM rate enhancement was observed.

Calcium chloride. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), calcium chloride (3.5 mg, 0.032 mmol). The reaction was monitored at room temperature. No AM rate enhancement was observed.

Calcium iodide. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), calcium iodide (9.3 mg, 0.032 mmol). The reaction was monitored at room temperature. No AM rate enhancement was observed.

Lithium bromide. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), lithium bromide (2.8 mg, 0.032 mmol). The reaction was monitored at room temperature. No AM rate enhancement was observed.

Magnesium bromide. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), magnesium bromide (5.8 mg, 0.032 mmol). The reaction was monitored at room temperature and completed in triplicate. After 7.7±0.6 hr the reaction was composed of an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene where Q=0.20±0. GC/MS $[M/Z]^+$: 130 ($C_{10}H_{10}$, R_t 3.60 min), 178 ($C_{14}H_{10}$, R_t 8.16 min)

Magnesium iodide. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), magnesium iodide (8.8 mg, 0.032

mmol). The reaction was monitored at room temperature. The reaction was completed in triplicate- requiring 5±0.3 h.

Zirconium (IV) chloride. Following General Procedure B: **5.14** (10.0 mg, 0.0159 mmol), 1-phenyl-1-propyne (39.2 μL, 0.317 mmol), zirconium (IV) chloride (7.4 mg, 0.032 mmol). The reaction was monitored at room temperature. No AM rate enhancement was observed. Complete catalyst decomposition was observed.

5.8.14 Alkyne Metathesis Studies with $Mo_2(OCMe_2CF_3)_6$ Assisted by Lewis Acids

General Procedure. Complex **5.15** was dissolved in CD_2Cl_2 (10.5 mM). 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^{1}H NMR spectroscopy at room temperature.

Calcium iodide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), calcium iodide (6.2 mg, 0.021 mmol). After 37 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present (Q=0.25). GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.13 min).

Chlorotitanium isopropoxide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), chlorotitanium isopropoxide (4.4 μL, 0.021 mmol). No reaction was observed due to complete catalyst decomposition.

Chromium (II) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), chromium (II) chloride (2.6 mg, 0.021 mmol). No enhanced rate of metathesis was observed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.15 min)

Cobalt (II) chloride hexahydrate. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), cobalt (II) chloride hexahydrate (5.0 mg, 0.021 mmol). No enhanced rate of metathesis was observed. Catalyst decomposition of 53% was present. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.03 min), 178 ($C_{14}H_{10}$, R_t 8.14 min)

Copper (II) bromide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), copper (II) bromide (4.7 mg, 0.021 mmol). After 15 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.15 min).

Copper (I) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), copper (I) chloride (2.1 mg, 0.021 mmol). This reaction was conducted in the dark. After 43 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.08 min).

Hydrochloric acid. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), hydrochloric acid (1.3 μL, 0.0026 mmol). After 18 h an equilibrium mixture of 1-phenyl-1-butyne and diphenylacetylene was present. The catalyst had decomposed by 11%. GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.08 min).

Iron (III) bromide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), iron (III) bromide (6.2 mg, 0.021 mmol). After 13 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was observed. Also, 24% catalyst decomposition has occurred. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.03 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Iron (II) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), iron (II) chloride (2.7 mg, 0.021

mmol). No enhanced rate of metathesis was observed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.09 min).

Lithium iodide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), copper (I) chloride (2.1 mg, 0.021 mmol). This reaction was conducted in the dark. No AM rate enhancement was observed.

Magnesium bromide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), magnesium bromide (3.9 mg, 0.021 mmol). After 13 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.09 min).

Magnesium chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), magnesium chloride (2.0 mg, 0.021 mmol). No metathesis rate enhancement was observed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Magnesium iodide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), magnesium iodide (5.8 mg, 0.021

mmol). After 13 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.01 min), 178 ($C_{14}H_{10}$, R_t 8.13 min).

Manganese (II) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), manganese (II) chloride (2.6 mg, 0.021 mmol). No enhanced rate of metathesis was observed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

Palladium (II) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), palladium (II) chloride (3.7 mg, 0.021 mmol). After 18 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. The catalyst had decomposed by 7%.

Tetrabutylammoniumbromide. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), tetrabutylammoniumbromide (6.8 mg, 0.021 mmol). No enhanced rate of metathesis was observed.

Triphenylboron. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), triphenylboron (5.1 mg, 0.021 mmol). After

13 h an equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was present. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.15 min).

Zinc chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), zinc chloride (2.9 mg, 0.021 mmol). No enhanced rate of metathesis was observed. GC/MS $[M/Z]^+$: 178 ($C_{14}H_{10}$, R_t 8.07 min).

Zirconium (IV) chloride. Following the general procedure: **5.15** (10.0 mg, 0.0105 mmol), 1-phenyl-1-propyne (25.9 μL, 0.210 mmol), zirconium (IV) chloride (4.9 mg, 0.021 mmol). No enhanced rate of metathesis was observed. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 3.02 min), 178 ($C_{14}H_{10}$, R_t 8.14 min).

5.8.15 Alkyne Metathesis Studies with $Mo_2(OCMe(CF_3)_2)_6$ Assisted by Lewis Acids

General procedure. Complex **5.7** was slurried in C_6D_6. 1-phenyl-1-propyne (20 equiv) and an internal standard of mesitylene were added to the solution via syringe. This solution was placed in a vial containing the Lewis acid (2.0 equiv). The resulting slurry was transferred to a J. Young Tube. The reaction was monitored via ^1H NMR spectroscopy at 45 °C.

Calcium iodide. Following the general procedure: **5.7** (10.0 mg, 0.00782 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (19.3 μL, 0.156 mmol), calcium iodide (4.6 mg, 0.016 mmol). No metathesis rate enhancement was observed.

Chlorotitanium trisisopropoxide. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), chlorotitanium trisisopropoxide (6.1 mg, 0.023 mmol). No metathesis rate enhancement was observed due to catalyst decomposition.

Copper (I) chloride. Following the general procedure: **5.7** (20.0 mg, 0.0156 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (38.7 μL, 0.313 mmol), copper (I) chloride (3.1 mg, 0.031 mmol). The reaction mixture was wrapped in aluminum foil. An equilibrium mixture of 1-phenyl-1-propyne and diphenylacetylene was obtained in 15 h. GC/MS $[M/Z]^+$: 115 (C_9H_8, R_t 11.71 min), 178 ($C_{14}H_{10}$, R_t 16.92 min).

Copper (II) chloride. Following the general procedure: **5.7** (20.0 mg, 0.0156 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (38.7 μL, 0.313 mmol), copper (II) chloride (4.2 mg, 0.031 mmol). The reaction mixture was wrapped in aluminum foil. No metathesis rate enhancement was observed.

Hydrochloric acid. Following the general procedure: **5.7** (5.0 mg, 0.0039 mmol), C_6D_6 (500 μL), 1-phenyl-1-propyne (9.7 μL, 0.078 mmol), triphenylboron (2.0 μL, 0.0078 mmol). No metathesis rate enhancement was observed.

Iron (III) bromide. Following the general procedure: **5.7** (10.0 mg, 0.00782 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (19.3 μL, 0.156 mmol), iron (III) bromide (4.6 mg, 0.016 mmol). No metathesis rate enhancement was observed. Some catalyst decomposition was present.

Lithium iodide. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), lithium iodide (3.1 mg, 0.023 mmol). The reaction mixture was wrapped with aluminum foil. No metathesis rate enhancement was observed.

Magnesium bromide. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), magnesium bromide (4.3 mg, 0.023 mmol). No metathesis rate enhancement was observed.

Magnesium iodide. Following the general procedure: **5.7** (10.0 mg, 0.00782 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (19.3 μL, 0.156 mmol), magnesium iodide (4.4 mg, 0.016 mmol). No metathesis rate enhancement was observed.

Palladium (II) chloride. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), palladium (II) chloride (5.5 mg, 0.023 mmol). No metathesis rate enhancement was observed.

Triphenylboron. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), triphenylboron (5.7 mg, 0.023 mmol). No metathesis rate enhancement was observed.

Zirconium (IV) chloride. Following the general procedure: **5.7** (15.0 mg, 0.0117 mmol), C_6D_6 (1.0 mL), 1-phenyl-1-propyne (29.0 μL, 0.235 mmol), zirconium (IV) chloride (5.5 mg, 0.023 mmol). No metathesis rate enhancement was observed due to catalyst decomposition.

5.8.16 Symmetrical Alkyne Formation

Bis(4-biphenyl)acetylene. **5.2** (467 mg, 0.545 mmol) and 1-(4-biphenyl)-1-butyne (4.5 g, 21.8 mmol, 40 equiv) was slurried in toluene (50 mL). The reaction mixture was stirred for 4 h and then filtered. 2.881 g of the white powder, bis(4-

biphenyl)acetylene, (8.72 mmol, 80%) was collected. Spectroscopic data agreed with the literature.[16]

5.9 Reference

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Chapter Six:

Conclusions and Future Directions

6.1 Conclusions

This work has focused on the development of triple-bond metathesis with alkynes and nitriles. The systematic design and development of tungsten-based catalysts allowed for the successful development of nitrile-alkyne cross-metathesis (NACM). Initial studies to extend NACM to molybdenum-based catalysts resulted in the development of a new method to synthesize molybdenum alkylidyne complexes from $Mo_2(OR)_6$ complexes and internal alkynes. Furthermore, the previously inaccessible formation of some molybdenum alkylidyne catalysts from nitride precursors and alkynes was achieved *in situ* through the addition of simple Lewis acids. Lewis acid addition was also found to increase the rate of alkyne cross-metathesis (ACM) with alkyne metathesis (AM)-active $N{\equiv}Mo(OR)_3$ and $Mo_2(OR)_6$ complexes.

6.1.1 Nitrile-Alkyne Cross-Metathesis

Previous work with tungsten-based catalysts revealed the ability to completely transform the alkylidyne moiety into a nitride moiety through metathesis with propionitrile.[1] Upon systematic examination of the influence of increasingly fluorinated alkoxides on the relative stability of nitride and alkylidyne complexes, the development of the reversible transformation of nitride ligands into alkylidyne ligands was achieved. By harnessing the *reversible* formation of $N\equiv W(OR)_3$ and $EtC\equiv W(OR)_3$ ($OR=OCMe_2CF_3$ or $OCMe(CF_3)_2$), NACM was successfully developed. Optimization of NACM reaction conditions including reaction medium, temperature, catalyst loading, concentration, and the influence of 3-hexyne was completed. Through these studies a large difference in the behavior of the three NACM-active catalysts, including a difference in relative rates and yields of unsymmetrical and symmetrical alkyne formation, was revealed.

Mechanistic investigations of $N\equiv W(OCMe(CF_3)_2)_3(DME)$ (**6.1**) and $[N\equiv W(OCMe_2CF_3)_3]_3$ (**6.2**) were undertaken to identify their underlying differences in NACM. These mechanistic studies indicated that both NACM and ACM are feasible pathways for the formation of unsymmetrical and symmetrical alkynes. NACM and ACM pathways are in general reversible with some substrate-dependent irreversibility. Differences in catalyst resting states were observed, with $OCMe_2CF_3$-ligated species preferring the nitride complex and $OCMe(CF_3)_2$-ligated complexes favoring the benzylidyne complex. Further comparison of the catalysts revealed that **6.1** is the most active NACM catalyst; however, the less Lewis acidic **6.2** is more tolerant of functional groups. A previously unobserved tolerance of thiophene-based substrates with tungsten-based AM catalysts was found with **6.1**. Incompatible substrates included Lewis basic substrates; in those cases, initial conversion to the alkylidyne complex was sometimes observed prior to complete catalyst deactivation.

Alkyne metathesis (AM) and NACM competition studies indicated that the unsymmetrical alkyne is afforded via NACM; subsequent rapid AM accounts for the formation of the symmetrical alkyne. Alteration of the reaction conditions allowed for the selective formation of unsymmetrical or symmetrical alkynes. This methodology was extended to several scale-up reactions including the formation of large arylene-ethynylene macrocycles.

6.1.2 Reversible Formation of $Mo_2(OR)_6$ and $RC{\equiv}Mo(OR)_3$

Simple methods for synthesizing molybdenum alkylidyne complexes have been desired since the early 1980s. The related tungsten-based complexes can be readily accessed via reaction of $W_2(OR)_6$ complexes with internal alkynes. Similar attempts with the corresponding molybdenum species had proven fruitless until this work. Under the appropriate reaction conditions, $Mo_2(OR)_6$ complexes can be cleaved with internal alkynes to form alkylidyne complexes. The reaction conditions vary depending on the alkoxide present; successful ACM was observed with $OCMe_3$, $OCMe_2CF_3$, and $OCMe(CF_3)_2$ ancillary ligands. Optimization of the reaction conditions for various alkyne substrates resulted in the formation of molybdenum alkylidyne complexes with $OCMe_3$ and $OCMe_2CF_3$ supporting ligands. No accumulation of alkylidyne complexes was observed when $OC(CF_3)_2Me$ ligands are employed.

The reverse reaction, involving the bimolecular decomposition of the molybdenum alkylidyne complexes ligated with $OCMe_3$ and $OCMe_2CF_3$, was observed upon heating. The corresponding $RC{\equiv}Mo(OR)_3$ ($OCMe(CF_3)_2$ and $OC(CF_3)_3$) species did not display similar behavior, likely due to the presence of a strongly bound DME adduct. Bimolecular decomposition was not found in the tungsten-based alkylidyne complexes applied in NACM. As a result, extension of NACM to include molybdenum-based catalysts will require that the formation of $Mo_2(OR)_6$ species is avoided. Additionally, examination of N≡Mo(OC(CF$_3$)$_x$Me$_{(3-x)}$)$_3$ (X=0-3) complexes revealed no bimolecular decomposition activity to form the corresponding $Mo_2(OR)_6$ complexes.

6.1.3 Alkyne Metathesis Assisted by Lewis Acids

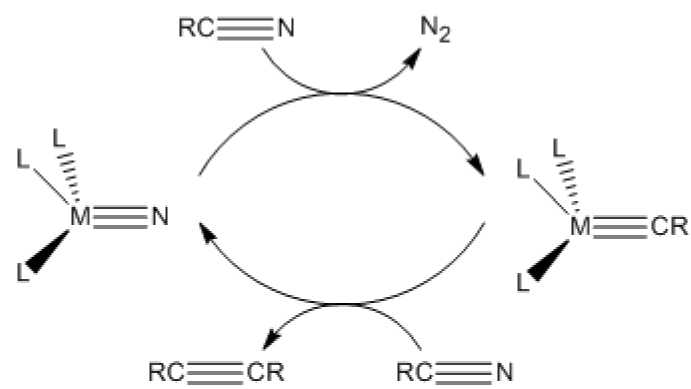
Exploration of the reactivity of N≡Mo(OR)$_3$ complexes by Gdula in our lab revealed that when OR=OCMe(CF$_3$)$_2$ and OC(CF$_3$)$_3$ the nitride moiety can be *irreversibly* transformed into the alkylidyne moiety in the presence of 3-hexyne at elevated temperatures.[2] Extension of this methodology to include other alkyne substrates was achieved. Interestingly, the difference in Lewis acidity of the metal center due to alkoxide identity dictated whether or not an accumulation of a benzylidyne complex was observed upon introduction of a diarylalkyne. The more Lewis acidic N≡Mo(OC(CF$_3$)$_3$)$_3$(NCMe) (**6.3**) readily cleaved diarylalkynes to afford benzylidyne complexes. On the other hand, direct conversion of N≡Mo(OCMe(CF$_3$)$_2$)$_3$ (**6.4**) with diarylalkynes to afford benzylidyne complexes was slow, circumventing direct synthetic application of this method to the formation of benzylidyne complexes. Indirect synthesis of benzylidyne complexes from **6.4** can be achieved via *in situ* formation of the propylidyne complex in the presence of the symmetrical alkyne; AM then affords the desired benzylidyne complex.

Similar studies were completed with N≡Mo(OR)$_3$ (OCMe$_3$ and OCMe$_2$CF$_3$). Unfortunately, no formation of the desired alkylidyne complexes was observed. However, addition of a Lewis acid into a reaction mixture consisting of one of the nitride complexes and an unsymmetrical alkyne resulted in successful ACM under mild conditions. Several Lewis acids were surveyed with no obvious trend in the influence on ACM activity being observed. Activity depended on substrate identity: 1-phenyl-1-butyne required much shorter reaction times to achieve equilibrium alkyne mixtures than did 1-phenyl-1-propyne. Unfortunately, alkylidyne complexes could not be isolated from these reactions because the alkylidyne species appear to decompose upon extended heating in the presence of the Lewis acids.

The introduction of a Lewis acid into mixtures of known AM-active precursors **6.3**, **6.4**, or $Mo_2(OR)_6$ and unsymmetrical alkynes resulted in enhanced rates of ACM in the case of some Lewis acids. The ability of the Lewis acid to influence the rate of catalysis with $Mo_2(OR)_6$ revealed that the interaction of a Lewis acid with the alkoxide oxygen could account for the enhanced metathesis activity with the nitride complexes. However, the possibility of the Lewis acid binding to the nitride ligand and increasing the rate of metathesis cannot be discounted at this point.

6.2 Future Directions

With the success of NACM using tungsten-based catalysts, the design and synthesis of a second generation of catalysts based on molybdenum is our lab's next objective. A molybdenum-based system would offer increased functional group tolerance, a necessity in order to extend NACM to a broad range of applications. In order to achieve NACM with molybdenum, the formation of a metal nitride complex from a metal alkylidyne species and/or Mo_2X_6 complexes must be established. In addition to furthering NACM, expansion of metal nitride catalysis to include triple-bond metathesis of two nitriles to produce an alkyne and nitrogen gas is of interest to our lab (Scheme 6.1).



Scheme 6.1. Nitrile metathesis.

6.2.1 Tridentate Ligand Motif

Theoretical calculations on tungsten- and molybdenum-based NACM reveal that higher kinetic barriers are present in the proposed molybdenum systems relative to that of tungsten. In order to overcome this activation barrier, a catalyst design that would enforce a geometry similar to that of the transition state is desired. Metal nitride or alkylidyne complexes with tridentate ligands would provide access to such a molecule as illustrated in Figure 6.1 with metal nitride complexes. A few examples of trianionic ligands of this type were recently reported by Veige and Bercaw (Figure 6.1).[3,4]

Furthermore, this ligand motif should enhance the stability of the catalyst as ligand decomposition should be suppressed. A variety of tridentate ligands could be synthesized in order to investigate the influence of various substituents on NACM. The ligands should also be designed to readily allow for electronic and steric tuning through backbone substitution, since the electronic and steric nature of the ligands greatly influences the rate of NACM, AM, and alkyne polymerization as highlighted in this work and others.[5] Additionally, the flexibility of the tridentate ligand can be adjusted through backbone design.

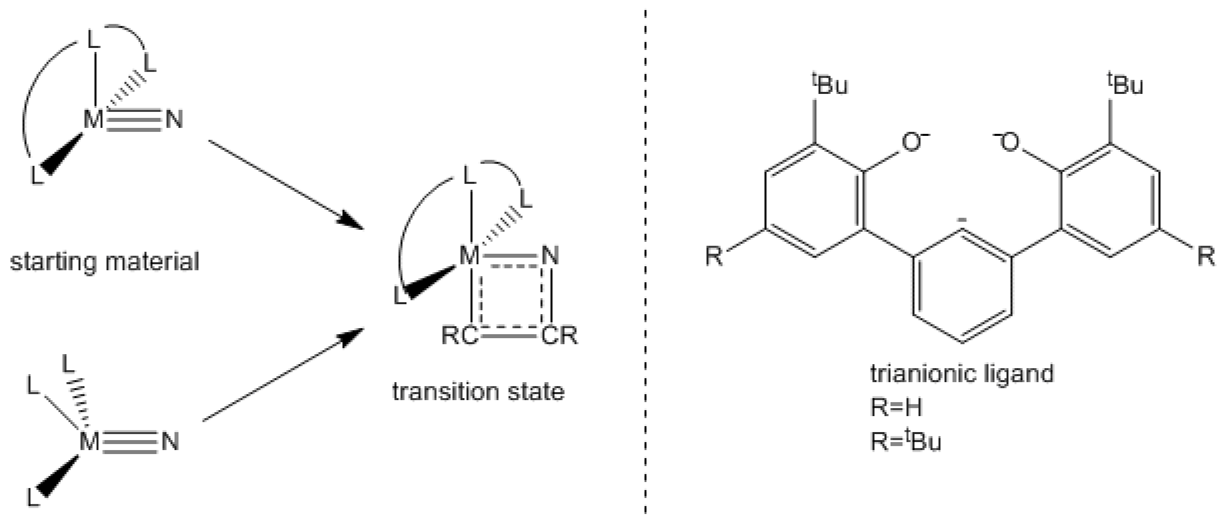


Figure 6.1. Comparison of starting material distortions of tridentate and monodentate-nitride complexes required for NACM with examples of trianionic ligands.

6.2.2 Mo_2X_6 Interactions with Alkynes and Nitriles

In addition to adjusting the ligand motif to encourage reversible formation of metal nitride and alkylidyne species, further exploration of the reactivity of Mo_2X_6 species with nitriles and alkynes should be pursued for the development of NACM. This work has focused on the interaction of $Mo_2(OR)_6$ species with internal alkynes and nitriles, expansion to $Mo_2(OR)_4R'_2$[6] complexes and other species should be addressed. These complexes could allow for more rapid formation of alkylidyne complexes, since $RC{\equiv}MR'X_2$ complexes have been shown to display fast AM activity.[7] Given the increased rate of metathesis that was found with $Mo_2(OR)_6$ complexes with alkynes in the presence of a Lewis acid, the influence of Lewis acids on the interaction of nitriles and $Mo_2(OR)_6$ species should also be investigated.

6.2.3 Lewis Acid-Assisted Nitrile Metathesis

The development of nitrile metathesis (NM) would serve as an-atom economical method for synthesizing alkynes from nitrile precursors. Since nitriles are in general more readily installed in molecules than are alkynes, NM is even more appealing than NACM for the synthesis of alkynes.[8,9] Preliminary theoretical calculations indicate that a higher activation barrier is present for NM relative to NACM. As a result, the use of tridentate ligands would help to lower the activation barrier as discussed in Section 6.2.1.

Currently, interactions of metal nitride complexes and nitriles involve degenerate N-atom exchange (NAX) as detailed in Chapter 1.[10,11] In order to reduce the charge distribution across the triple-bond in the metal nitride and/or nitrile, Lewis acids will be introduced into the reaction system (Figure 6.2). Binding of the Lewis acid to the nitride ligand and/or the nitrile should reduce the preference for NAX over NM. Chelating Lewis acids would further increase the likelihood of NM by reducing the charge polarization across the triple bond and bringing the substrates into close proximity with one another. Alignment of the nitrile and nitride complex in the appropriate regiochemistry could also be assisted through the use of sterically encumbering Lewis acids. The hindered Lewis acid would then be less likely to align with the bulky alkoxides of the nitride complexes due to steric constraints; thus, NM should be favored over NAX.

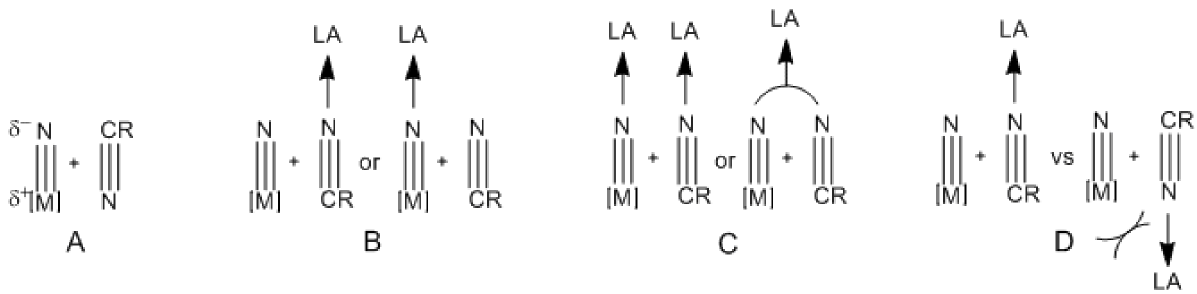


Figure 6.2. Metal nitride complex and nitrile interactions. **A.** NAX. **B.** Monodentate Lewis acid interaction. **C.** Two Lewis acids interacting or bidentate Lewis acid interaction. **D.** Steric interference of Lewis acids.

6.3 References

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Appendix 1:

Crystallographic Data for N≡W(OCMe(CF$_3$)$_2$)$_3$(DME)

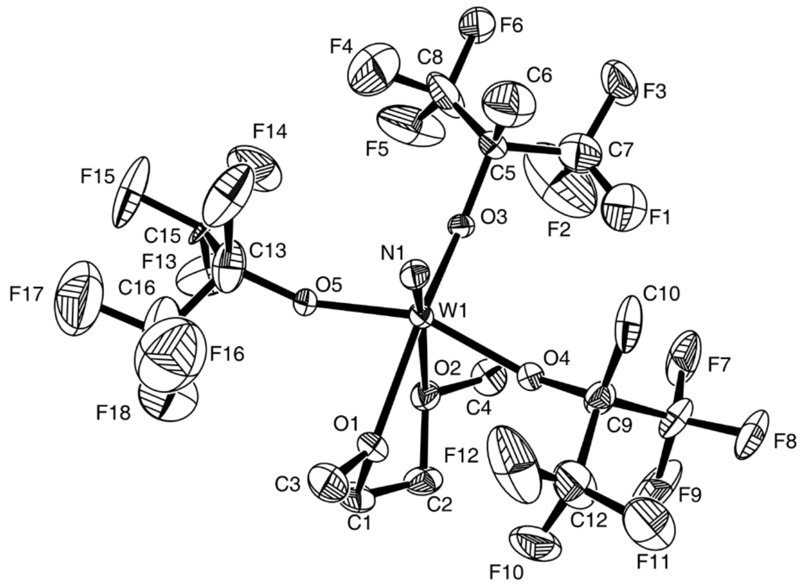

Figure A1.1 50% thermal ellipsoid plot of N≡W(OCMe(CF$_3$)$_2$)$_3$(DME) view A.

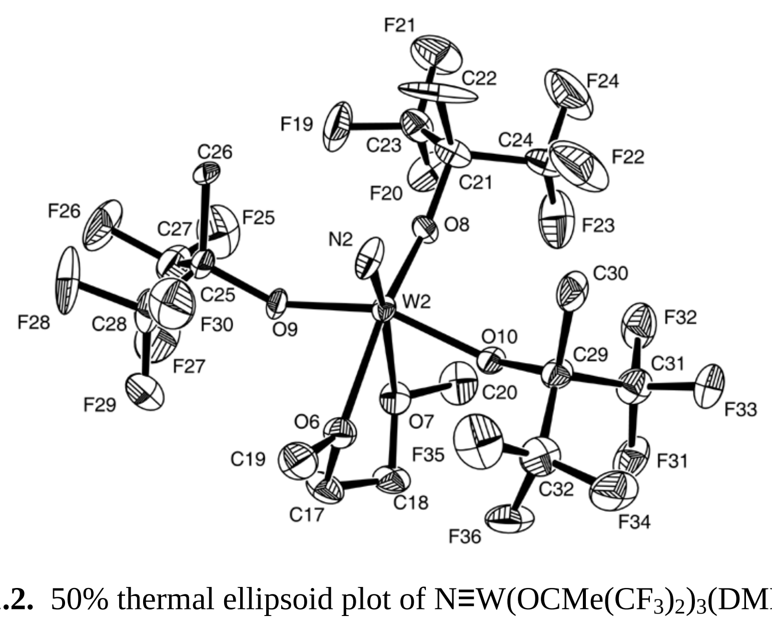

Figure A1.2. 50% thermal ellipsoid plot of N≡W(OCMe(CF$_3$)$_2$)$_3$(DME) view B.

Structure Determination.

Colorless needles of N≡W(OCMe(CF_3)$_2$)$_3$(DME) **(ag551)** were grown from a pentane/diethyl ether solution at -35 °C. A crystal of dimensions 0.44 x 0.42 x 0.16 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 3000 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 111329 reflections to a maximum 2θ value of 56.82° of which 12760 were independent and 12059 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 8931 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The compound crystallized as a pseudo-merohedral twin, twin law (1 0 0, 0 –1 0, 0 0 –1) and twin scale factor 0.3732(8). The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 8 for the formula $C_{16}H_{19}F_{18}NO_5W$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0533 and wR2 = 0.1384 [based on I > 2sigma(I)], R1 = 0.0569 and wR2 = 0.1411 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

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Table A1.1. Crystal data and structure refinement for ag551.

Identification code	ag551
Empirical formula	C16 H19 F18 N O5 W
Formula weight	831.17
Temperature	108(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.7803(12) Å alpha = 90 deg. b = 21.2002(18) Å beta = 90.260(2) deg. c = 17.4958(15) Å gamma = 90 deg.
Volume	5111.3(8) Å ^3
Z, Calculated density	8, 2.160 Mg/m^3
Absorption coefficient	4.681 mm^-1
F(000)	3184
Crystal size	0.44 x 0.42 x 0.16 mm
Theta range for data collection	1.88 to 28.41 deg.
Limiting indices	-18<=h<=18, -28<=k<=28, -23<=l<=23
Reflections collected / unique	111329 / 12760 [R(int) = 0.0615]
Completeness to theta = 28.41	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5213 and 0.2325
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	12760 / 0 / 740
Goodness-of-fit on F^2	1.122
Final R indices [I>2sigma(I)]	R1 = 0.0533, wR2 = 0.1384
R indices (all data)	R1 = 0.0569, wR2 = 0.1411
Largest diff. peak and hole	3.421 and -2.375 e. Å ^-3

Table A1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ag551. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	6287(1)	1696(1)	1384(1)	18(1)
W(2)	8690(1)	8390(1)	6488(1)	17(1)
O(1)	5232(3)	2028(2)	2231(3)	27(1)
O(2)	4621(3)	1606(2)	822(3)	27(1)
O(3)	6723(3)	1391(2)	423(2)	18(1)
O(4)	5808(3)	880(2)	1742(2)	22(1)
O(5)	6094(3)	2556(2)	1004(3)	25(1)
O(6)	9640(3)	8027(2)	7390(3)	27(1)
O(7)	10351(3)	8320(2)	5981(3)	28(1)
O(8)	8339(3)	8695(2)	5496(3)	23(1)
O(9)	8757(3)	7516(2)	6144(2)	23(1)
O(10)	9254(3)	9186(2)	6813(3)	22(1)
N(1)	7298(4)	1775(2)	1917(3)	21(1)
N(2)	7651(4)	8395(2)	6995(3)	28(1)
C(1)	4239(5)	2135(4)	1982(5)	34(2)
C(2)	3947(5)	1614(3)	1440(4)	34(2)
C(3)	5452(6)	2344(4)	2949(4)	42(2)
C(4)	4437(5)	1086(3)	312(4)	34(2)
C(5)	7537(4)	1168(3)	35(4)	24(1)
C(6)	8436(7)	1105(6)	521(7)	64(3)
C(7)	7297(8)	480(5)	-184(6)	60(2)
C(8)	7649(8)	1516(4)	-711(6)	69(3)
C(9)	6047(5)	419(3)	2283(4)	26(1)
C(10)	7114(7)	285(3)	2359(5)	43(2)
C(11)	5524(6)	-191(3)	2005(4)	37(2)
C(12)	5625(8)	622(4)	3064(5)	54(2)

C(13)	6525(4)	3126(4)	962(5)	48(2)
C(14)	7613(5)	3120(5)	1136(7)	78(3)
C(15)	6351(5)	3366(3)	136(4)	33(2)
C(16)	5969(10)	3597(5)	1420(8)	83(4)
C(17)	10591(5)	7809(4)	7161(4)	34(2)
C(19)	9347(6)	7799(4)	8145(4)	40(2)
C(20)	10626(5)	8801(4)	5439(5)	44(2)
C(21)	7623(5)	8956(4)	5033(4)	32(2)
C(22)	6615(6)	8919(7)	5367(6)	80(4)
C(23)	7668(6)	8626(4)	4266(4)	35(2)
C(24)	7945(5)	9676(4)	4900(4)	33(2)
C(25)	8149(5)	6984(3)	6115(5)	31(2)
C(26)	7051(4)	7120(3)	5965(4)	27(2)
C(27)	8573(6)	6623(3)	5443(5)	42(2)
C(28)	8185(7)	6650(4)	6892(8)	65(3)
C(29)	9108(4)	9693(3)	7309(4)	25(1)
C(30)	7990(5)	9863(3)	7395(5)	35(2)
C(31)	9645(6)	10250(4)	6947(4)	33(2)
C(32)	9564(6)	9541(4)	8076(4)	36(2)
F(1)	6924(6)	150(3)	273(5)	101(3)
F(2)	6467(7)	557(5)	-768(5)	136(3)
F(3)	8014(5)	191(3)	-529(4)	89(2)
F(4)	8130(6)	2086(4)	-471(5)	105(3)
F(5)	6989(5)	1765(4)	-1014(4)	94(2)
F(6)	8282(4)	1281(2)	-1185(3)	56(1)
F(7)	5710(5)	-299(2)	1297(3)	57(2)
F(8)	5724(4)	-687(2)	2418(3)	50(1)
F(9)	4536(4)	-106(3)	2041(4)	81(2)
F(10)	4738(4)	854(3)	3021(3)	73(2)
F(11)	5636(5)	143(3)	3563(3)	84(2)
F(12)	6178(6)	1082(3)	3358(3)	84(2)
F(14)	6835(6)	2987(3)	-333(4)	98(2)
F(15)	6702(5)	3924(2)	-21(4)	80(2)
F(16)	6356(9)	3485(5)	2150(6)	123(3)
F(17)	6310(8)	4213(3)	1287(6)	119(3)
F(18)	5110(7)	3567(4)	1421(6)	115(3)
F(19)	7545(5)	7980(2)	4338(3)	61(2)
F(20)	8523(3)	8657(2)	3951(3)	49(1)
F(21)	7002(4)	8821(3)	3753(3)	64(2)
F(22)	7645(5)	9954(3)	5518(4)	95(2)
F(23)	8838(5)	9717(2)	4756(4)	70(2)
F(24)	7381(6)	9898(3)	4328(4)	86(2)
F(25)	8585(5)	6917(3)	4823(3)	67(2)
F(26)	8042(4)	6077(2)	5313(4)	73(2)
F(27)	9488(4)	6399(3)	5605(5)	78(2)
F(28)	7755(6)	6073(3)	6813(5)	93(2)

F(29)	9124(4)	6542(3)	7091(4)	74(2)
F(30)	7739(4)	6958(3)	7419(3)	56(2)
F(31)	10619(3)	10185(2)	6978(3)	44(1)
F(32)	9401(4)	10319(2)	6199(3)	46(1)
F(33)	9433(4)	10798(2)	7296(3)	49(1)
F(34)	9692(4)	10054(2)	8521(3)	50(1)
F(35)	8972(4)	9143(2)	8477(3)	53(1)
F(36)	10446(3)	9266(2)	8004(3)	44(1)

Table A1.3. Bond lengths [Å] and angles [deg] for ag551.

W(1)-N(1)	1.680(5)
W(1)-O(3)	1.901(4)
W(1)-O(4)	1.955(4)
W(1)-O(5)	1.958(4)
W(1)-O(1)	2.197(5)
W(1)-O(2)	2.502(5)
W(2)-N(2)	1.687(6)
W(2)-O(8)	1.912(4)
W(2)-O(10)	1.942(4)
W(2)-O(9)	1.951(4)
W(2)-O(6)	2.187(5)
W(2)-O(7)	2.464(5)
O(1)-C(1)	1.452(8)
O(1)-C(3)	1.454(9)
O(2)-C(2)	1.429(8)
O(2)-C(4)	1.440(8)
O(3)-C(5)	1.397(7)
O(4)-C(9)	1.399(8)
O(5)-C(13)	1.349(8)
O(6)-C(17)	1.448(8)
O(6)-C(19)	1.464(9)
O(7)-C(18)	1.433(9)
O(7)-C(20)	1.444(9)
O(8)-C(21)	1.389(8)
O(9)-C(25)	1.405(7)
O(10)-C(29)	1.398(8)
C(1)-C(2)	1.509(11)
C(5)-C(8)	1.507(12)
C(5)-C(6)	1.506(12)
C(5)-C(7)	1.542(12)
C(7)-F(1)	1.183(13)
C(7)-F(3)	1.312(12)

C(7)-F(2)	1.539(14)
C(8)-F(5)	1.176(12)
C(8)-F(6)	1.305(11)
C(8)-F(4)	1.440(13)
C(9)-C(10)	1.503(11)
C(9)-C(12)	1.547(11)
C(9)-C(11)	1.559(10)
C(11)-F(7)	1.286(9)
C(11)-F(8)	1.303(9)
C(11)-F(9)	1.375(10)
C(12)-F(10)	1.320(11)
C(12)-F(12)	1.339(12)
C(12)-F(11)	1.340(10)
C(13)-C(16)	1.495(15)
C(13)-C(14)	1.528(7)
C(13)-C(15)	1.551(11)
C(15)-F(13)	1.295(9)
C(15)-F(15)	1.308(7)
C(15)-F(14)	1.329(9)
C(16)-F(18)	1.186(16)
C(16)-F(16)	1.401(17)
C(16)-F(17)	1.406(13)
C(17)-C(18)	1.495(11)
C(21)-C(22)	1.512(11)
C(21)-C(23)	1.514(10)
C(21)-C(24)	1.607(11)
C(23)-F(20)	1.305(9)
C(23)-F(21)	1.345(9)
C(23)-F(19)	1.385(9)
C(24)-F(23)	1.260(10)
C(24)-F(22)	1.302(10)
C(24)-F(24)	1.350(10)
C(25)-C(27)	1.521(11)
C(25)-C(28)	1.534(14)
C(25)-C(26)	1.561(9)
C(27)-F(25)	1.250(10)
C(27)-F(27)	1.377(10)
C(27)-F(26)	1.389(9)
C(28)-F(30)	1.290(13)
C(28)-F(29)	1.358(11)
C(28)-F(28)	1.366(10)
C(29)-C(32)	1.513(10)
C(29)-C(31)	1.533(10)
C(29)-C(30)	1.591(9)
C(31)-F(33)	1.345(9)
C(31)-F(31)	1.350(9)

C(31)-F(32)	1.357(9)
C(32)-F(34)	1.350(9)
C(32)-F(36)	1.354(9)
C(32)-F(35)	1.370(9)

N(1)-W(1)-O(3)	105.1(2)
N(1)-W(1)-O(4)	101.0(2)
O(3)-W(1)-O(4)	95.17(17)
N(1)-W(1)-O(5)	101.9(2)
O(3)-W(1)-O(5)	93.38(18)
O(4)-W(1)-O(5)	152.46(17)
N(1)-W(1)-O(1)	98.2(2)
O(3)-W(1)-O(1)	156.65(17)
O(4)-W(1)-O(1)	80.96(17)
O(5)-W(1)-O(1)	80.87(17)
N(1)-W(1)-O(2)	169.3(2)
O(3)-W(1)-O(2)	85.34(16)
O(4)-W(1)-O(2)	75.40(16)
O(5)-W(1)-O(2)	79.27(16)
O(1)-W(1)-O(2)	71.37(17)
N(2)-W(2)-O(8)	105.3(2)
N(2)-W(2)-O(10)	100.4(2)
O(8)-W(2)-O(10)	94.06(18)
N(2)-W(2)-O(9)	102.1(2)
O(8)-W(2)-O(9)	93.04(18)
O(10)-W(2)-O(9)	153.64(17)
N(2)-W(2)-O(6)	97.5(2)
O(8)-W(2)-O(6)	157.25(18)
O(10)-W(2)-O(6)	81.77(18)
O(9)-W(2)-O(6)	81.91(18)
N(2)-W(2)-O(7)	169.0(2)
O(8)-W(2)-O(7)	85.67(17)
O(10)-W(2)-O(7)	77.61(16)
O(9)-W(2)-O(7)	77.65(17)
O(6)-W(2)-O(7)	71.59(17)
C(1)-O(1)-C(3)	112.4(5)
C(1)-O(1)-W(1)	118.3(4)
C(3)-O(1)-W(1)	126.5(4)
C(2)-O(2)-C(4)	111.4(5)
C(2)-O(2)-W(1)	107.5(4)
C(4)-O(2)-W(1)	117.4(4)
C(5)-O(3)-W(1)	143.4(4)
C(9)-O(4)-W(1)	139.1(4)
C(13)-O(5)-W(1)	142.5(4)
C(17)-O(6)-C(19)	113.5(5)
C(17)-O(6)-W(2)	116.9(4)

C(19)-O(6)-W(2)	126.9(4)
C(18)-O(7)-C(20)	112.8(5)
C(18)-O(7)-W(2)	108.8(4)
C(20)-O(7)-W(2)	116.2(4)
C(21)-O(8)-W(2)	147.2(4)
C(25)-O(9)-W(2)	138.1(4)
C(29)-O(10)-W(2)	142.3(4)
O(1)-C(1)-C(2)	108.9(5)
O(2)-C(2)-C(1)	108.2(5)
O(3)-C(5)-C(8)	109.9(6)
O(3)-C(5)-C(6)	114.6(6)
C(8)-C(5)-C(6)	116.4(7)
O(3)-C(5)-C(7)	105.6(6)
C(8)-C(5)-C(7)	105.7(7)
C(6)-C(5)-C(7)	103.3(7)
F(1)-C(7)-F(3)	111.4(9)
F(1)-C(7)-F(2)	100.8(9)
F(3)-C(7)-F(2)	107.6(8)
F(1)-C(7)-C(5)	118.9(9)
F(3)-C(7)-C(5)	113.3(8)
F(2)-C(7)-C(5)	102.9(8)
F(5)-C(8)-F(6)	113.7(9)
F(5)-C(8)-F(4)	96.3(8)
F(6)-C(8)-F(4)	101.4(8)
F(5)-C(8)-C(5)	121.9(9)
F(6)-C(8)-C(5)	115.7(7)
F(4)-C(8)-C(5)	102.0(8)
O(4)-C(9)-C(10)	114.7(5)
O(4)-C(9)-C(12)	108.4(5)
C(10)-C(9)-C(12)	110.3(7)
O(4)-C(9)-C(11)	105.1(5)
C(10)-C(9)-C(11)	108.8(6)
C(12)-C(9)-C(11)	109.4(6)
F(7)-C(11)-F(8)	110.4(6)
F(7)-C(11)-F(9)	105.6(7)
F(8)-C(11)-F(9)	106.6(6)
F(7)-C(11)-C(9)	110.8(6)
F(8)-C(11)-C(9)	113.5(6)
F(9)-C(11)-C(9)	109.4(6)
F(10)-C(12)-F(12)	106.0(7)
F(10)-C(12)-F(11)	109.1(8)
F(12)-C(12)-F(11)	107.2(7)
F(10)-C(12)-C(9)	114.0(7)
F(12)-C(12)-C(9)	109.0(8)
F(11)-C(12)-C(9)	111.2(7)
O(5)-C(13)-C(16)	110.1(7)

O(5)-C(13)-C(14)	114.5(7)
C(16)-C(13)-C(14)	113.8(9)
O(5)-C(13)-C(15)	106.1(6)
C(16)-C(13)-C(15)	101.7(7)
C(14)-C(13)-C(15)	109.6(7)
F(13)-C(15)-F(15)	107.7(6)
F(13)-C(15)-F(14)	103.9(7)
F(15)-C(15)-F(14)	103.4(6)
F(13)-C(15)-C(13)	116.9(6)
F(15)-C(15)-C(13)	115.9(6)
F(14)-C(15)-C(13)	107.5(6)
F(18)-C(16)-F(16)	111.4(13)
F(18)-C(16)-F(17)	112.7(11)
F(16)-C(16)-F(17)	100.5(10)
F(18)-C(16)-C(13)	118.6(11)
F(16)-C(16)-C(13)	100.4(9)
F(17)-C(16)-C(13)	111.1(11)
O(6)-C(17)-C(18)	109.3(6)
O(7)-C(18)-C(17)	107.0(6)
O(8)-C(21)-C(22)	113.9(7)
O(8)-C(21)-C(23)	107.6(6)
C(22)-C(21)-C(23)	111.1(7)
O(8)-C(21)-C(24)	105.4(5)
C(22)-C(21)-C(24)	111.1(8)
C(23)-C(21)-C(24)	107.3(6)
F(20)-C(23)-F(21)	108.5(6)
F(20)-C(23)-F(19)	101.5(6)
F(21)-C(23)-F(19)	106.3(6)
F(20)-C(23)-C(21)	113.1(6)
F(21)-C(23)-C(21)	114.8(6)
F(19)-C(23)-C(21)	111.7(6)
F(23)-C(24)-F(22)	116.7(7)
F(23)-C(24)-F(24)	112.8(7)
F(22)-C(24)-F(24)	105.9(7)
F(23)-C(24)-C(21)	111.5(6)
F(22)-C(24)-C(21)	102.8(6)
F(24)-C(24)-C(21)	106.2(6)
O(9)-C(25)-C(27)	101.5(6)
O(9)-C(25)-C(28)	108.7(6)
C(27)-C(25)-C(28)	116.2(6)
O(9)-C(25)-C(26)	115.9(5)
C(27)-C(25)-C(26)	109.8(6)
C(28)-C(25)-C(26)	105.2(6)
F(25)-C(27)-F(27)	109.6(8)
F(25)-C(27)-F(26)	106.5(7)
F(27)-C(27)-F(26)	103.1(6)

F(25)-C(27)-C(25)	115.2(7)
F(27)-C(27)-C(25)	111.7(7)
F(26)-C(27)-C(25)	110.0(7)
F(30)-C(28)-F(29)	110.9(10)
F(30)-C(28)-F(28)	108.5(9)
F(29)-C(28)-F(28)	106.7(7)
F(30)-C(28)-C(25)	112.8(7)
F(29)-C(28)-C(25)	109.5(8)
F(28)-C(28)-C(25)	108.2(9)
O(10)-C(29)-C(32)	109.1(5)
O(10)-C(29)-C(31)	105.3(5)
C(32)-C(29)-C(31)	109.4(6)
O(10)-C(29)-C(30)	112.1(5)
C(32)-C(29)-C(30)	111.3(6)
C(31)-C(29)-C(30)	109.5(6)
F(33)-C(31)-F(31)	106.8(6)
F(33)-C(31)-F(32)	107.0(6)
F(31)-C(31)-F(32)	107.0(6)
F(33)-C(31)-C(29)	111.7(6)
F(31)-C(31)-C(29)	112.7(6)
F(32)-C(31)-C(29)	111.3(6)
F(34)-C(32)-F(36)	106.6(6)
F(34)-C(32)-F(35)	106.1(6)
F(36)-C(32)-F(35)	108.6(6)
F(34)-C(32)-C(29)	113.1(6)
F(36)-C(32)-C(29)	112.3(6)
F(35)-C(32)-C(29)	109.8(6)

Symmetry transformations used to generate equivalent atoms:

Table A1.4. Anisotropic displacement parameters (Å^2 x 10^3) for ag551. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W(1)	16(1)	16(1)	23(1)	-2(1)	2(1)	1(1)
W(2)	14(1)	17(1)	21(1)	0(1)	4(1)	-2(1)
O(1)	26(2)	24(2)	32(2)	-3(2)	7(2)	4(2)
O(2)	23(2)	25(2)	33(2)	1(2)	1(2)	-2(2)
O(3)	16(2)	19(2)	20(2)	-2(2)	3(2)	-2(2)

O(4)	21(2)	19(2)	24(2)	1(2)	3(2)	2(2)
O(5)	22(2)	15(2)	37(2)	-2(2)	9(2)	-2(2)
O(6)	25(2)	29(2)	28(2)	1(2)	-1(2)	0(2)
O(7)	21(2)	29(2)	35(2)	-2(2)	10(2)	2(2)
O(8)	24(2)	19(2)	27(2)	4(2)	-2(2)	4(2)
O(9)	24(2)	14(2)	31(2)	0(1)	0(2)	-7(2)
O(10)	11(2)	22(2)	32(2)	-6(2)	3(2)	2(2)
N(1)	14(2)	20(2)	30(3)	-1(2)	-2(2)	-3(2)
N(2)	34(3)	23(2)	27(3)	-7(2)	12(2)	-13(2)
C(1)	15(3)	39(4)	46(4)	-2(3)	4(3)	6(3)
C(2)	16(3)	44(4)	43(4)	11(3)	4(3)	5(2)
C(3)	55(5)	38(4)	33(3)	-10(3)	12(3)	1(4)
C(4)	25(3)	37(3)	40(4)	-9(3)	-11(3)	-7(3)
C(5)	23(3)	22(3)	26(3)	-3(2)	4(2)	3(2)
C(6)	51(4)	73(4)	68(4)	1(4)	3(3)	4(3)
C(7)	69(4)	54(4)	57(4)	0(3)	26(3)	7(3)
C(8)	105(6)	46(4)	58(5)	17(4)	43(5)	46(4)
C(9)	33(3)	24(3)	22(2)	4(2)	2(2)	-2(2)
C(10)	60(5)	18(3)	50(4)	11(3)	-20(4)	-1(3)
C(11)	42(4)	28(3)	40(4)	13(3)	0(3)	-14(3)
C(12)	83(6)	51(4)	29(4)	15(3)	9(4)	32(4)
C(13)	67(4)	28(3)	49(3)	10(3)	-12(3)	0(3)
C(14)	88(5)	63(4)	81(5)	13(4)	-14(4)	-42(4)
C(15)	17(2)	20(2)	62(4)	16(2)	3(3)	-12(2)
C(16)	108(8)	39(4)	101(7)	14(5)	-39(6)	-1(5)
C(17)	24(3)	39(4)	40(4)	8(3)	1(3)	10(3)
C(18)	18(3)	39(3)	47(4)	-7(3)	-4(3)	12(2)
C(19)	45(4)	44(4)	29(3)	14(3)	-6(3)	-9(3)
C(20)	31(3)	49(4)	51(4)	3(4)	27(3)	-3(3)
C(21)	29(3)	38(3)	27(3)	3(3)	-2(3)	11(3)
C(22)	21(3)	172(11)	48(5)	1(6)	-12(3)	39(5)
C(23)	41(4)	34(3)	30(3)	5(3)	-2(3)	6(3)
C(24)	25(3)	49(4)	24(3)	2(3)	1(2)	14(3)
C(25)	26(3)	16(3)	52(4)	-3(3)	-9(3)	-4(2)
C(26)	9(2)	21(3)	50(4)	3(3)	-4(2)	-3(2)
C(27)	33(4)	35(3)	59(4)	-13(3)	1(4)	-4(3)
C(28)	48(5)	31(4)	114(8)	31(4)	-14(5)	-20(3)
C(29)	17(3)	26(3)	32(3)	-5(3)	2(2)	0(2)
C(30)	29(3)	24(3)	51(4)	-18(3)	5(3)	2(3)
C(31)	38(4)	35(3)	26(3)	-2(3)	0(3)	-3(3)
C(32)	33(3)	40(4)	37(4)	-9(3)	4(3)	5(3)
F(1)	100(5)	51(3)	153(6)	-9(4)	59(4)	-8(3)
F(2)	125(6)	158(6)	125(5)	-88(4)	-44(5)	42(5)
F(3)	131(4)	46(3)	90(3)	24(3)	78(3)	40(3)
F(4)	125(5)	73(4)	118(5)	19(4)	57(4)	-10(4)
F(5)	79(4)	147(5)	58(3)	53(3)	29(3)	63(3)

F(6)	81(3)	38(2)	50(2)	6(2)	46(2)	4(2)
F(7)	96(4)	25(2)	49(3)	-5(2)	-2(3)	-22(2)
F(8)	58(3)	29(2)	61(3)	23(2)	-1(2)	-13(2)
F(9)	38(2)	78(3)	127(5)	59(3)	-17(3)	-34(2)
F(10)	91(3)	74(3)	54(3)	27(2)	47(3)	43(3)
F(11)	137(5)	77(3)	39(2)	32(2)	37(3)	57(3)
F(12)	149(6)	68(3)	35(2)	-22(2)	-25(3)	45(4)
F(13)	39(3)	120(5)	50(3)	15(3)	-15(2)	-19(3)
F(14)	140(5)	81(4)	73(3)	35(3)	72(3)	48(4)
F(15)	114(4)	33(2)	93(4)	31(2)	-39(3)	-36(3)
F(16)	143(5)	120(4)	107(4)	10(4)	-1(4)	-17(4)
F(17)	161(7)	64(4)	133(6)	-18(4)	11(6)	-34(5)
F(18)	122(6)	96(5)	128(6)	-21(5)	52(5)	-10(5)
F(19)	93(4)	31(2)	59(3)	-4(2)	-15(3)	-26(2)
F(20)	38(2)	65(3)	45(2)	-23(2)	14(2)	-7(2)
F(21)	73(3)	82(4)	36(2)	0(3)	-21(2)	20(3)
F(22)	114(4)	89(4)	80(4)	-28(3)	-33(4)	68(3)
F(23)	92(4)	41(3)	77(4)	9(3)	24(4)	-8(3)
F(24)	113(5)	65(3)	80(4)	21(3)	-27(4)	35(4)
F(25)	96(4)	51(3)	55(3)	-18(2)	8(3)	8(3)
F(26)	53(3)	32(2)	133(5)	-42(3)	6(3)	-10(2)
F(27)	35(2)	52(3)	148(6)	-28(4)	22(3)	10(2)
F(28)	116(5)	33(2)	129(6)	29(3)	3(5)	-37(3)
F(29)	57(3)	50(3)	115(5)	39(3)	-38(3)	-6(3)
F(30)	51(3)	64(3)	53(3)	23(2)	16(2)	-8(3)
F(31)	31(2)	39(2)	60(3)	-8(2)	10(2)	-15(2)
F(32)	61(3)	35(2)	44(2)	8(2)	4(2)	-12(2)
F(33)	57(3)	25(2)	64(3)	-13(2)	-12(3)	-4(2)
F(34)	52(3)	55(3)	43(2)	-27(2)	14(2)	13(2)
F(35)	72(3)	56(3)	32(2)	2(2)	12(2)	4(3)
F(36)	28(2)	59(3)	46(2)	-16(2)	-14(2)	14(2)

Table A1.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ag551.

	x	y	z	U(eq)
H(1C)	4188	2548	1722	40
H(1D)	3802	2138	2429	40
H(2C)	3954	1203	1708	41
H(2D)	3282	1691	1243	41

H(3A)	4847	2438	3218	63
H(3B)	5800	2738	2846	63
H(3C)	5858	2068	3267	63
H(4A)	3763	1103	132	51
H(4B)	4548	688	584	51
H(4C)	4876	1112	-126	51
H(6A)	8286	859	980	96
H(6B)	8666	1525	670	96
H(6C)	8943	889	229	96
H(10A)	7450	666	2536	64
H(10B)	7373	158	1862	64
H(10C)	7215	-55	2730	64
H(14A)	7723	2960	1654	116
H(14B)	7870	3550	1097	116
H(14C)	7945	2848	768	116
H(17A)	10536	7388	6918	41
H(17B)	11018	7770	7615	41
H(18A)	11110	8684	6856	42
H(18B)	11656	8116	6428	42
H(19A)	9922	7663	8432	59
H(19B)	8901	7443	8085	59
H(19C)	9021	8140	8423	59
H(20A)	11298	8730	5277	65
H(20B)	10573	9217	5679	65
H(20C)	10195	8781	4993	65
H(22A)	6436	8476	5441	120
H(22B)	6151	9118	5016	120
H(22C)	6604	9138	5860	120
H(26A)	6976	7345	5479	40
H(26B)	6793	7379	6381	40
H(26C)	6694	6720	5941	40
H(30A)	7648	9508	7630	52
H(30B)	7711	9949	6890	52
H(30C)	7922	10238	7720	52

Appendix 2:

Crystallographic Data for [N≡W(OCMe(CF_3)$_2$)$_4$][Li(DME)$_2$]

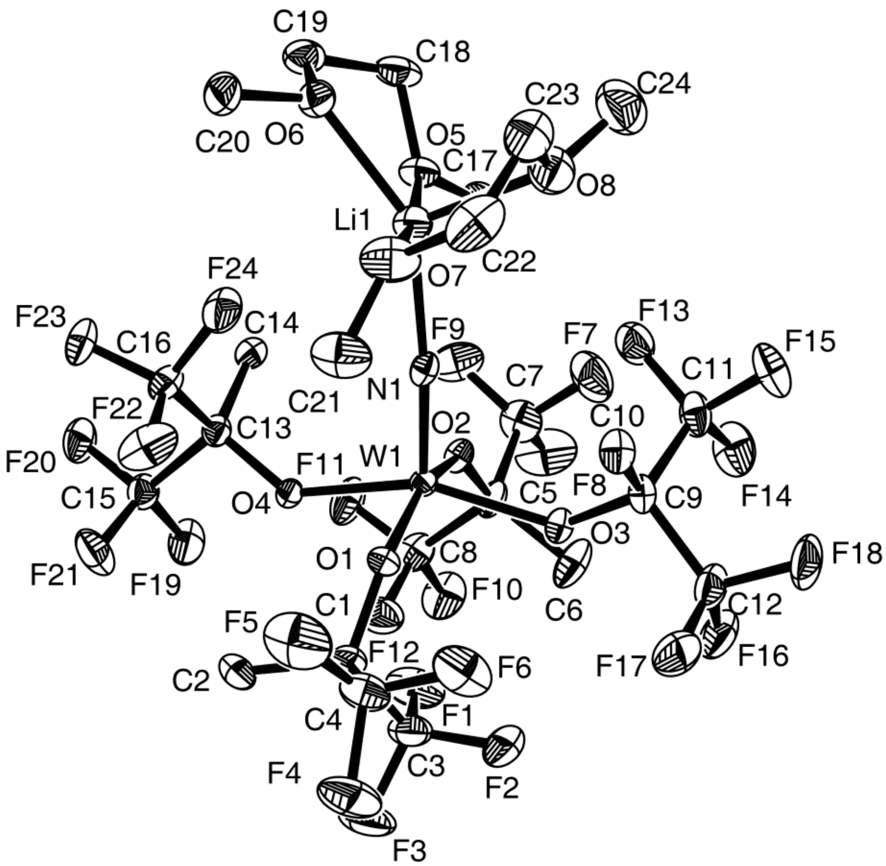

Figure A2.1. 50% Thermal ellipsoid plot of [N≡W(OCMe(CF_3)$_2$)$_4$][Li(DME)$_2$] view A.

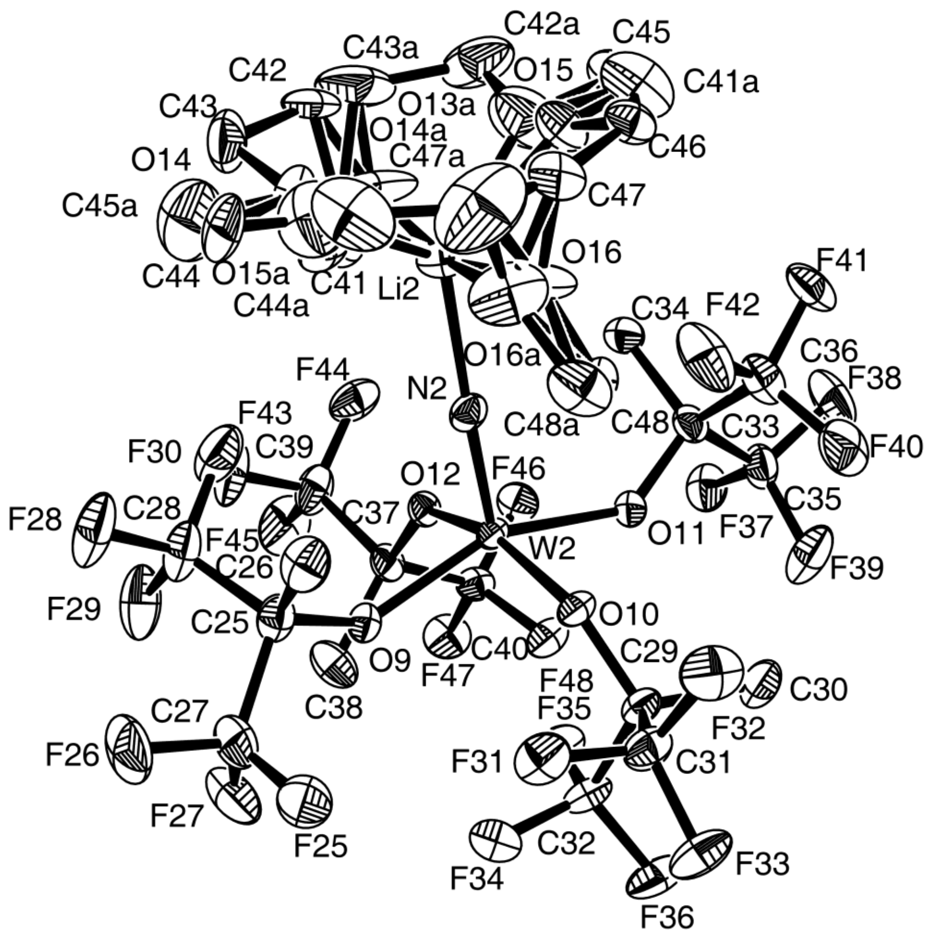

Figure A2.2. 50% Thermal ellipsoid plot of [N≡W(OCMe(CF_3)$_2$)$_4$][Li(DME)$_2$] view B.

Structure Determination

Colorless needles of [N≡W(OCMe(CF_3)$_2$)$_4$][Li(DME)$_2$] **(ag 679)** were grown from a toluene/pentane solution at -35 °C. A crystal of dimensions 0.46 x 0.26 x 0.22 mm was mounted on a Bruker SMART-1K CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.912 cm from the crystal. A total of

2342 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 20 s/frame. The integration of the data yielded a total of 298848 reflections to a maximum 2θ value of 56.64° of which 37755 were independent and 34774 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9771 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 16 for the formula $C_{24}H_{32}NLiO_8F_{24}W$. There are four crystallographically independent complexes in the asymmetric unit. The structure is a pseudo-orthorhombic twin with twin law (1 0 0, -1 0 0, 0 0 –1). The refined twin fraction is 0.3915(2). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The dimethoxyethane ligands are disordered on one complex. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0236 and wR2 = 0.0486 [based on I > 2sigma(I)], R1 = 0.0292 and wR2 = 0.0504 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table A2.1. Crystal data and structure refinement for ag679.

Identification code	ag679
Empirical formula	C24 H32 F24 Li N O8 W
Formula weight	1109.30
Temperature	108(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 22.880(5) Å alpha = 90 deg. b = 18.040(4) Å beta = 90.034(3) deg. c = 36.791(7) Å gamma = 90 deg.
Volume	15185(5) Å ^3
Z, Calculated density	16, 1.941 Mg/m^3
Absorption coefficient	3.205 mm^-1
F(000)	8640
Crystal size	0.40 x 0.26 x 0.22 mm
Theta range for data collection	1.81 to 28.32 deg.
Limiting indices	-30<=h<=30, -24<=k<=24, -49<=l<=49
Reflections collected / unique	298848 / 37755 [R(int) = 0.0500]
Completeness to theta = 28.32	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4941 and 0.3833
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	37755 / 373 / 2271
Goodness-of-fit on F^2	1.036

Final R indices [I>2sigma(I)] R1 = 0.0236, wR2 = 0.0486

R indices (all data) R1 = 0.0292, wR2 = 0.0504

Largest diff. peak and hole 1.290 and -1.337 e. Å ^-3

Table A2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^2 x 10^3) for ag679. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	2426(1)	4044(1)	3677(1)	14(1)
F(1)	1216(1)	4389(1)	3772(1)	44(1)
F(2)	1152(1)	4395(1)	4352(1)	46(1)
F(3)	720(1)	5242(1)	4042(1)	48(1)
F(4)	1361(1)	5991(1)	4563(1)	47(1)
F(5)	2277(1)	6148(1)	4445(1)	56(1)
F(6)	1989(1)	5154(1)	4700(1)	46(1)
F(7)	2478(1)	1758(1)	3217(1)	52(1)
F(8)	1786(1)	1707(1)	2819(1)	58(1)
F(9)	2528(1)	2420(1)	2734(1)	44(1)
F(10)	1000(1)	2827(1)	2810(1)	42(1)
F(11)	1736(1)	3476(1)	2641(1)	36(1)
F(12)	1230(1)	3817(1)	3102(1)	39(1)
F(13)	3101(1)	2418(1)	3966(1)	36(1)
F(14)	2359(1)	1772(1)	4128(1)	43(1)
F(15)	3052(1)	1989(1)	4509(1)	40(1)
F(16)	1471(1)	2518(1)	4454(1)	41(1)
F(17)	1733(1)	3431(1)	4791(1)	45(1)
F(18)	2097(1)	2352(1)	4884(1)	45(1)
F(19)	1798(1)	5028(1)	2658(1)	38(1)
F(20)	2509(1)	5632(1)	2422(1)	33(1)
F(21)	2065(1)	6072(1)	2889(1)	40(1)
F(22)	2945(1)	6032(1)	3384(1)	44(1)
F(23)	3387(1)	5964(1)	2871(1)	32(1)
F(24)	3592(1)	5200(1)	3297(1)	38(1)
O(1)	2255(1)	4864(1)	4009(1)	19(1)
O(2)	2288(1)	3246(1)	3325(1)	19(1)
O(3)	2172(1)	3356(1)	4060(1)	19(1)
O(4)	2338(1)	4757(1)	3278(1)	18(1)
C(1)	1767(1)	5308(2)	4070(1)	21(1)
C(2)	1699(2)	5925(2)	3789(1)	36(1)

C(3)	1206(1)	4831(2)	4067(1)	31(1)
C(4)	1851(2)	5649(2)	4445(1)	33(1)
C(5)	1845(1)	2789(2)	3195(1)	22(1)
C(6)	1462(2)	2452(2)	3488(1)	37(1)
C(7)	2164(2)	2167(2)	2986(1)	34(1)
C(8)	1456(2)	3227(2)	2935(1)	29(1)
C(9)	2432(1)	3017(2)	4360(1)	21(1)
C(10)	2876(1)	3502(2)	4553(1)	25(1)
C(11)	2733(2)	2297(2)	4238(1)	28(1)
C(12)	1928(2)	2829(2)	4623(1)	31(1)
C(13)	2681(1)	5020(2)	2993(1)	19(1)
C(14)	2985(1)	4407(2)	2780(1)	23(1)
C(15)	2261(1)	5445(2)	2737(1)	24(1)
C(16)	3150(1)	5566(2)	3136(1)	24(1)
N(1)	3154(1)	4008(1)	3719(1)	18(1)
Li(1)	4058(2)	4035(2)	3739(1)	25(1)
O(5)	4127(1)	3365(1)	3294(1)	26(1)
O(6)	4805(1)	4462(1)	3494(1)	27(1)
O(7)	4116(1)	4796(2)	4170(1)	42(1)
O(8)	4389(1)	3365(1)	4162(1)	39(1)
C(17)	3805(2)	2708(2)	3220(1)	34(1)
C(18)	4717(1)	3335(2)	3176(1)	33(1)
C(19)	4920(2)	4127(2)	3154(1)	33(1)
C(20)	4951(2)	5232(2)	3489(1)	38(1)
C(21)	3694(2)	5358(2)	4248(1)	41(1)
C(22)	4366(2)	4485(2)	4483(1)	45(1)
C(23)	4724(2)	3842(2)	4378(1)	41(1)
C(24)	4637(2)	2659(2)	4127(1)	56(1)
W(2)	4805(1)	4064(1)	1287(1)	16(1)
F(25)	4152(1)	3390(1)	164(1)	47(1)
F(26)	4431(1)	2256(1)	122(1)	54(1)
F(27)	3800(1)	2570(1)	525(1)	51(1)
F(28)	5346(1)	1852(1)	520(1)	55(1)
F(29)	4618(1)	1749(1)	888(1)	54(1)
F(30)	5396(1)	2331(1)	1053(1)	47(1)
F(31)	4449(1)	4992(1)	211(1)	35(1)
F(32)	4793(1)	6007(1)	426(1)	42(1)
F(33)	3878(1)	5919(1)	296(1)	40(1)
F(34)	3580(1)	4356(1)	582(1)	36(1)
F(35)	3627(1)	4476(1)	1164(1)	31(1)
F(36)	3169(1)	5286(1)	840(1)	41(1)
F(37)	4274(1)	4997(1)	2384(1)	34(1)
F(38)	4816(1)	5949(1)	2447(1)	50(1)
F(39)	4158(1)	5910(1)	2029(1)	48(1)
F(40)	5102(1)	6365(1)	1668(1)	48(1)
F(41)	5780(1)	6034(1)	2038(1)	41(1)

F(42)	5719(1)	5534(1)	1512(1)	53(1)
F(43)	4745(1)	1797(1)	1740(1)	50(1)
F(44)	4875(1)	2433(1)	2224(1)	39(1)
F(45)	4087(1)	1801(1)	2158(1)	53(1)
F(46)	4150(1)	3537(1)	2357(1)	29(1)
F(47)	3363(1)	2979(1)	2193(1)	35(1)
F(48)	3637(1)	3966(1)	1912(1)	30(1)
O(9)	4541(1)	3348(1)	916(1)	20(1)
O(10)	4686(1)	4846(1)	922(1)	20(1)
O(11)	4690(1)	4830(1)	1660(1)	20(1)
O(12)	4640(1)	3314(1)	1656(1)	20(1)
C(25)	4789(2)	2957(2)	631(1)	27(1)
C(26)	5277(2)	3378(2)	436(1)	34(1)
C(27)	4288(2)	2794(2)	359(1)	38(1)
C(28)	5036(2)	2220(2)	773(1)	38(1)
C(29)	4215(1)	5294(2)	826(1)	22(1)
C(30)	4168(2)	5982(2)	1071(1)	32(1)
C(31)	4331(2)	5546(2)	438(1)	30(1)
C(32)	3643(1)	4852(2)	844(1)	27(1)
C(33)	5011(1)	5156(2)	1940(1)	23(1)
C(34)	5389(1)	4600(2)	2148(1)	28(1)
C(35)	4565(2)	5510(2)	2199(1)	30(1)
C(36)	5405(2)	5777(2)	1786(1)	35(1)
C(37)	4180(1)	2884(2)	1789(1)	23(1)
C(38)	3755(2)	2607(2)	1497(1)	36(1)
C(39)	4474(2)	2226(2)	1979(1)	34(1)
C(40)	3833(1)	3341(2)	2068(1)	23(1)
N(2)	5533(1)	3994(1)	1266(1)	22(1)
Li(2)	6423(2)	3948(3)	1240(1)	31(1)
O(13)	6471(3)	3014(5)	1562(2)	30(2)
O(14)	6916(3)	3145(3)	1012(2)	34(2)
O(15)	7017(3)	4694(3)	1480(2)	33(2)
O(16)	6545(3)	4833(4)	885(2)	42(2)
C(41)	6090(4)	2798(5)	1845(2)	28(2)
C(42)	7058(4)	2859(7)	1610(3)	36(2)
C(43)	7072(5)	2549(5)	1219(2)	47(2)
C(44)	6957(5)	2943(6)	641(2)	45(2)
C(45)	7085(5)	4861(6)	1865(2)	38(3)
C(46)	7171(4)	5288(4)	1258(2)	31(2)
C(47)	7107(4)	5010(6)	880(2)	30(2)
C(48)	6142(5)	5271(7)	702(4)	20(3)
O(13A)	6998(2)	4369(3)	1593(1)	68(2)
O(14A)	6545(2)	3182(3)	1662(2)	73(2)
O(15A)	6891(3)	3405(3)	830(1)	73(2)
O(16A)	6532(2)	4670(3)	800(2)	58(2)
C(41A)	7136(4)	5117(4)	1670(3)	86(3)

C(42A)	7148(3)	3891(4)	1872(2)	66(2)
C(43A)	7088(3)	3097(4)	1733(2)	69(2)
C(44A)	6122(4)	2685(5)	1785(3)	45(2)
C(45A)	6929(6)	2638(6)	745(4)	81(3)
C(46A)	7094(5)	3886(5)	556(2)	66(2)
C(47A)	7063(3)	4632(5)	672(3)	94(2)
C(48A)	6140(3)	5174(4)	652(2)	43(2)
W(3)	10116(1)	9186(1)	3690(1)	15(1)
N(3)	9402(1)	9013(1)	3715(1)	18(1)
Li(3)	8535(2)	8753(3)	3799(2)	24(1)
F(49)	11232(1)	7685(1)	4397(1)	52(1)
F(50)	10896(1)	8510(1)	4760(1)	54(1)
F(51)	10645(1)	7374(1)	4826(1)	47(1)
F(52)	9758(1)	6868(1)	4434(1)	37(1)
F(53)	10424(1)	6884(1)	4023(1)	41(1)
F(54)	9598(1)	7400(1)	3923(1)	31(1)
F(55)	11630(1)	8373(1)	2754(1)	64(1)
F(56)	11303(1)	9292(1)	3064(1)	44(1)
F(57)	10798(1)	8863(1)	2614(1)	50(1)
F(58)	11012(1)	7119(1)	2764(1)	52(1)
F(59)	10172(1)	7645(1)	2719(1)	42(1)
F(60)	10371(1)	6983(1)	3186(1)	45(1)
F(61)	10548(1)	10291(1)	2624(1)	51(1)
F(62)	9908(1)	11133(1)	2567(1)	58(1)
F(63)	10553(1)	11209(1)	2986(1)	56(1)
F(64)	8962(1)	11091(1)	3001(1)	51(1)
F(65)	9616(1)	11463(1)	3373(1)	60(1)
F(66)	9081(1)	10535(2)	3511(1)	74(1)
F(67)	11245(1)	9758(1)	3784(1)	41(1)
F(68)	11650(1)	10608(1)	4111(1)	62(1)
F(69)	11371(1)	9592(1)	4356(1)	51(1)
F(70)	10960(1)	11064(1)	4694(1)	56(1)
F(71)	10028(1)	10997(1)	4611(1)	51(1)
F(72)	10505(1)	10035(1)	4781(1)	51(1)
C(49)	10229(1)	8041(2)	4326(1)	22(1)
C(50)	9739(2)	8411(2)	4541(1)	27(1)
C(51)	10756(2)	7901(2)	4580(1)	36(1)
C(52)	10006(1)	7293(2)	4174(1)	25(1)
C(53)	10840(1)	8143(2)	3161(1)	27(1)
C(54)	11282(2)	7885(2)	3444(1)	36(1)
C(55)	10591(2)	7469(2)	2951(1)	33(1)
C(56)	11139(2)	8673(2)	2893(1)	38(1)
C(57)	9799(1)	10303(2)	3066(1)	22(1)
C(58)	9473(2)	9718(2)	2852(1)	35(1)
C(59)	10209(2)	10746(2)	2811(1)	32(1)
C(60)	9366(2)	10850(2)	3241(1)	38(1)

C(61)	10621(2)	10442(2)	4167(1)	26(1)
C(62)	10575(2)	11156(2)	3943(1)	36(1)
C(63)	10530(2)	10630(2)	4566(1)	40(1)
C(64)	11229(2)	10103(2)	4113(1)	39(1)
C(65)	7740(2)	9990(2)	3463(1)	34(1)
C(66)	7852(2)	8867(2)	3142(1)	28(1)
C(67)	7934(2)	8052(2)	3209(1)	28(1)
C(68)	8931(2)	7730(2)	3148(1)	29(1)
C(69)	7962(2)	7300(2)	4120(1)	47(1)
C(70)	7716(2)	8484(2)	4345(1)	33(1)
C(71)	8032(2)	9133(2)	4510(1)	34(1)
C(72)	8714(2)	10061(2)	4371(1)	42(1)
O(17)	10439(1)	8468(1)	4040(1)	21(1)
O(18)	10351(1)	8499(1)	3305(1)	21(1)
O(19)	10158(1)	10002(1)	3334(1)	18(1)
O(20)	10185(1)	9937(1)	4075(1)	20(1)
O(21)	8143(1)	8048(1)	4172(1)	34(1)
O(22)	8364(1)	9469(1)	4236(1)	34(1)
O(23)	7904(1)	9228(1)	3484(1)	29(1)
O(24)	8475(1)	7917(1)	3390(1)	29(1)
W(4)	2486(1)	8845(1)	1220(1)	15(1)
N(4)	1778(1)	9079(1)	1210(1)	19(1)
Li(4)	880(2)	9156(3)	1127(2)	29(1)
F(73)	2796(1)	6657(2)	615(1)	85(1)
F(74)	2979(1)	7513(2)	234(1)	62(1)
F(75)	2266(1)	6780(1)	145(1)	48(1)
F(76)	1304(1)	7708(1)	969(1)	71(1)
F(77)	1306(1)	6955(1)	524(1)	35(1)
F(78)	1814(1)	6722(2)	993(1)	77(1)
F(79)	2742(1)	10365(1)	247(1)	43(1)
F(80)	2926(1)	10969(1)	736(1)	42(1)
F(81)	3603(1)	10811(1)	340(1)	40(1)
F(82)	4094(1)	9473(1)	288(1)	37(1)
F(83)	3244(1)	9046(1)	152(1)	39(1)
F(84)	3726(1)	8580(1)	600(1)	34(1)
F(85)	2216(1)	7205(1)	2207(1)	37(1)
F(86)	3131(1)	7094(1)	2328(1)	36(1)
F(87)	2719(1)	8167(1)	2341(1)	36(1)
F(88)	3904(1)	7356(1)	1743(1)	38(1)
F(89)	3653(1)	8436(1)	1932(1)	34(1)
F(90)	3564(1)	8167(1)	1366(1)	31(1)
F(91)	3181(1)	9613(1)	2309(1)	41(1)
F(92)	2979(1)	10775(1)	2318(1)	44(1)
F(93)	3600(1)	10346(1)	1932(1)	40(1)
F(94)	2151(1)	11265(1)	1863(1)	46(1)
F(95)	2885(1)	11153(1)	1503(1)	41(1)

F(96)	2057(1)	10672(1)	1361(1)	35(1)
C(73)	2162(1)	7701(2)	610(1)	22(1)
C(74)	1925(2)	8280(2)	350(1)	26(1)
C(75)	2554(2)	7156(2)	402(1)	37(1)
C(76)	1644(2)	7265(2)	778(1)	31(1)
C(77)	3320(1)	9760(2)	702(1)	23(1)
C(78)	3769(1)	9943(2)	996(1)	29(1)
C(79)	3148(2)	10482(2)	502(1)	30(1)
C(80)	3593(1)	9214(2)	432(1)	29(1)
C(81)	2874(1)	7615(2)	1754(1)	20(1)
C(82)	2810(2)	6862(2)	1569(1)	29(1)
C(83)	2736(2)	7522(2)	2161(1)	27(1)
C(84)	3502(1)	7894(2)	1705(1)	26(1)
C(85)	2587(1)	10057(2)	1826(1)	23(1)
C(86)	2057(2)	9765(2)	2029(1)	28(1)
C(87)	3092(2)	10203(2)	2097(1)	30(1)
C(88)	2424(2)	10793(2)	1639(1)	32(1)
C(89)	1002(2)	8104(2)	1797(1)	34(1)
C(90)	138(2)	8786(3)	1703(2)	68(2)
C(91)	252(2)	9580(3)	1769(1)	70(2)
C(92)	573(2)	10680(2)	1469(2)	68(2)
C(93)	-37(2)	8025(2)	800(2)	64(1)
C(94)	237(2)	8978(2)	429(1)	39(1)
C(95)	485(2)	9752(2)	427(1)	40(1)
C(96)	1377(2)	10338(2)	570(1)	36(1)
O(25)	2509(1)	7997(1)	885(1)	20(1)
O(26)	2800(1)	9467(1)	829(1)	20(1)
O(27)	2474(1)	8129(1)	1621(1)	19(1)
O(28)	2812(1)	9569(1)	1568(1)	19(1)
O(29)	616(1)	8444(2)	1549(1)	45(1)
O(30)	500(1)	9916(2)	1450(1)	46(1)
O(31)	204(1)	8747(2)	793(1)	45(1)
O(32)	1003(1)	9738(1)	638(1)	33(1)

Table A2.3. Bond lengths [Å] and angles [deg] for ag679.

W(1)-N(1)	1.676(2)
W(1)-O(1)	1.9567(19)
W(1)-O(4)	1.9608(18)
W(1)-O(2)	1.9629(19)
W(1)-O(3)	1.9634(19)
F(1)-C(3)	1.349(4)
F(2)-C(3)	1.317(4)
F(3)-C(3)	1.338(4)

F(4)-C(4)	1.351(4)
F(5)-C(4)	1.327(4)
F(6)-C(4)	1.333(4)
F(7)-C(7)	1.334(4)
F(8)-C(7)	1.347(4)
F(9)-C(7)	1.326(4)
F(10)-C(8)	1.349(4)
F(11)-C(8)	1.335(4)
F(12)-C(8)	1.333(4)
F(13)-C(11)	1.326(4)
F(14)-C(11)	1.340(4)
F(15)-C(11)	1.356(4)
F(16)-C(12)	1.341(4)
F(17)-C(12)	1.328(4)
F(18)-C(12)	1.343(4)
F(19)-C(15)	1.332(4)
F(20)-C(15)	1.333(3)
F(21)-C(15)	1.338(4)
F(22)-C(16)	1.326(4)
F(23)-C(16)	1.326(4)
F(24)-C(16)	1.345(4)
O(1)-C(1)	1.393(3)
O(2)-C(5)	1.391(3)
O(3)-C(9)	1.397(3)
O(4)-C(13)	1.395(3)
C(1)-C(4)	1.523(5)
C(1)-C(2)	1.527(4)
C(1)-C(3)	1.545(4)
C(5)-C(6)	1.516(4)
C(5)-C(8)	1.527(5)
C(5)-C(7)	1.544(5)
C(9)-C(10)	1.517(4)
C(9)-C(11)	1.537(4)
C(9)-C(12)	1.544(5)
C(13)-C(14)	1.524(4)
C(13)-C(16)	1.550(4)
C(13)-C(15)	1.549(4)
N(1)-Li(1)	2.069(5)
Li(1)-O(5)	2.041(5)
Li(1)-O(6)	2.080(5)
Li(1)-O(7)	2.102(5)
Li(1)-O(8)	2.111(5)
O(5)-C(18)	1.418(4)
O(5)-C(17)	1.422(4)
O(6)-C(19)	1.413(4)
O(6)-C(20)	1.430(4)

O(7)-C(22)	1.403(5)
O(7)-C(21)	1.429(4)
O(8)-C(24)	1.401(5)
O(8)-C(23)	1.399(4)
C(18)-C(19)	1.504(5)
C(22)-C(23)	1.471(6)
W(2)-N(2)	1.672(2)
W(2)-O(12)	1.955(2)
W(2)-O(10)	1.966(2)
W(2)-O(11)	1.966(2)
W(2)-O(9)	1.973(2)
F(25)-C(27)	1.330(4)
F(26)-C(27)	1.345(4)
F(27)-C(27)	1.336(5)
F(28)-C(28)	1.346(4)
F(29)-C(28)	1.348(5)
F(30)-C(28)	1.334(5)
F(31)-C(31)	1.330(4)
F(32)-C(31)	1.345(4)
F(33)-C(31)	1.343(4)
F(34)-C(32)	1.323(4)
F(35)-C(32)	1.361(4)
F(36)-C(32)	1.337(4)
F(37)-C(35)	1.328(4)
F(38)-C(35)	1.337(4)
F(39)-C(35)	1.336(4)
F(40)-C(36)	1.340(4)
F(41)-C(36)	1.344(4)
F(42)-C(36)	1.314(4)
F(43)-C(39)	1.327(4)
F(44)-C(39)	1.337(4)
F(45)-C(39)	1.344(4)
F(46)-C(40)	1.335(4)
F(47)-C(40)	1.339(4)
F(48)-C(40)	1.342(3)
O(9)-C(25)	1.387(4)
O(10)-C(29)	1.393(4)
O(11)-C(33)	1.394(4)
O(12)-C(37)	1.396(4)
C(25)-C(26)	1.528(5)
C(25)-C(28)	1.535(5)
C(25)-C(27)	1.549(5)
C(29)-C(31)	1.522(4)
C(29)-C(32)	1.532(5)
C(29)-C(30)	1.540(4)
C(33)-C(34)	1.530(4)

C(33)-C(35)	1.536(5)
C(33)-C(36)	1.545(5)
C(37)-C(38)	1.530(5)
C(37)-C(39)	1.534(5)
C(37)-C(40)	1.538(4)
N(2)-Li(2)	2.040(5)
Li(2)-O(13A)	1.996(7)
Li(2)-O(14)	2.019(7)
Li(2)-O(13)	2.063(9)
Li(2)-O(16)	2.081(8)
Li(2)-O(16A)	2.094(7)
Li(2)-O(15A)	2.094(7)
Li(2)-O(14A)	2.096(7)
Li(2)-O(15)	2.104(7)
O(13)-C(42)	1.382(11)
O(13)-C(41)	1.412(10)
O(14)-C(43)	1.365(9)
O(14)-C(44)	1.416(9)
O(15)-C(46)	1.395(9)
O(15)-C(45)	1.456(9)
O(16)-C(47)	1.324(10)
O(16)-C(48)	1.389(11)
C(42)-C(43)	1.543(12)
C(46)-C(47)	1.484(10)
O(13A)-C(42A)	1.383(7)
O(13A)-C(41A)	1.414(8)
O(14A)-C(43A)	1.279(7)
O(14A)-C(44A)	1.397(9)
O(15A)-C(46A)	1.411(9)
O(15A)-C(45A)	1.421(10)
O(16A)-C(47A)	1.304(8)
O(16A)-C(48A)	1.387(7)
C(42A)-C(43A)	1.526(9)
C(46A)-C(47A)	1.414(11)
W(3)-N(3)	1.667(2)
W(3)-O(18)	1.956(2)
W(3)-O(20)	1.965(2)
W(3)-O(19)	1.9708(19)
W(3)-O(17)	1.971(2)
N(3)-Li(3)	2.061(6)
Li(3)-O(23)	2.039(6)
Li(3)-O(21)	2.075(6)
Li(3)-O(22)	2.102(6)
Li(3)-O(24)	2.133(6)
Li(3)-C(70)	2.790(6)
F(49)-C(51)	1.338(5)

F(50)-C(51)	1.321(4)
F(51)-C(51)	1.337(4)
F(52)-C(52)	1.350(4)
F(53)-C(52)	1.331(4)
F(54)-C(52)	1.326(4)
F(55)-C(56)	1.346(4)
F(56)-C(56)	1.336(4)
F(57)-C(56)	1.333(5)
F(58)-C(55)	1.343(4)
F(59)-C(55)	1.323(4)
F(60)-C(55)	1.330(4)
F(61)-C(59)	1.322(4)
F(62)-C(59)	1.328(4)
F(63)-C(59)	1.315(4)
F(64)-C(60)	1.348(4)
F(65)-C(60)	1.337(5)
F(66)-C(60)	1.318(4)
F(67)-C(64)	1.360(4)
F(68)-C(64)	1.328(4)
F(69)-C(64)	1.325(4)
F(70)-C(63)	1.343(4)
F(71)-C(63)	1.335(5)
F(72)-C(63)	1.334(4)
C(49)-O(17)	1.389(3)
C(49)-C(50)	1.527(5)
C(49)-C(51)	1.547(5)
C(49)-C(52)	1.548(4)
C(53)-O(18)	1.395(4)
C(53)-C(54)	1.523(5)
C(53)-C(56)	1.536(5)
C(53)-C(55)	1.549(5)
C(57)-O(19)	1.394(3)
C(57)-C(58)	1.513(4)
C(57)-C(60)	1.540(5)
C(57)-C(59)	1.551(5)
C(61)-O(20)	1.393(4)
C(61)-C(63)	1.524(5)
C(61)-C(64)	1.531(5)
C(61)-C(62)	1.533(4)
C(65)-O(23)	1.427(4)
C(66)-O(23)	1.422(4)
C(66)-C(67)	1.503(5)
C(67)-O(24)	1.425(4)
C(68)-O(24)	1.413(4)
C(69)-O(21)	1.424(4)
C(70)-O(21)	1.407(4)

C(70)-C(71)	1.504(5)
C(71)-O(22)	1.397(4)
C(72)-O(22)	1.425(4)
W(4)-N(4)	1.675(2)
W(4)-O(27)	1.9600(18)
W(4)-O(26)	1.964(2)
W(4)-O(25)	1.9663(18)
W(4)-O(28)	1.974(2)
N(4)-Li(4)	2.082(6)
Li(4)-O(30)	2.014(6)
Li(4)-O(29)	2.105(6)
Li(4)-O(32)	2.103(6)
Li(4)-O(31)	2.107(6)
F(73)-C(75)	1.316(4)
F(74)-C(75)	1.321(5)
F(75)-C(75)	1.335(4)
F(76)-C(76)	1.318(4)
F(77)-C(76)	1.337(4)
F(78)-C(76)	1.316(4)
F(79)-C(79)	1.336(4)
F(80)-C(79)	1.331(4)
F(81)-C(79)	1.339(4)
F(82)-C(80)	1.348(4)
F(83)-C(80)	1.336(4)
F(84)-C(80)	1.336(4)
F(85)-C(83)	1.331(4)
F(86)-C(83)	1.339(4)
F(87)-C(83)	1.339(4)
F(88)-C(84)	1.343(4)
F(89)-C(84)	1.332(4)
F(90)-C(84)	1.349(4)
F(91)-C(87)	1.336(4)
F(92)-C(87)	1.338(4)
F(93)-C(87)	1.337(4)
F(94)-C(88)	1.340(4)
F(95)-C(88)	1.336(4)
F(96)-C(88)	1.341(4)
C(73)-O(25)	1.390(3)
C(73)-C(74)	1.517(4)
C(73)-C(75)	1.536(5)
C(73)-C(76)	1.551(5)
C(77)-O(26)	1.384(4)
C(77)-C(78)	1.528(4)
C(77)-C(80)	1.531(5)
C(77)-C(79)	1.548(4)
C(81)-O(27)	1.390(3)

C(81)-C(82)	1.527(4)
C(81)-C(84)	1.534(4)
C(81)-C(83)	1.539(4)
C(85)-O(28)	1.395(3)
C(85)-C(86)	1.520(4)
C(85)-C(88)	1.540(4)
C(85)-C(87)	1.549(4)
C(89)-O(29)	1.410(4)
C(90)-O(29)	1.378(5)
C(90)-C(91)	1.477(7)
C(91)-O(30)	1.437(6)
C(92)-O(30)	1.389(5)
C(93)-O(31)	1.416(5)
C(94)-O(31)	1.404(5)
C(94)-C(95)	1.507(6)
C(95)-O(32)	1.415(4)
C(96)-O(32)	1.403(4)
N(1)-W(1)-O(1)	99.84(10)
N(1)-W(1)-O(4)	101.32(10)
O(1)-W(1)-O(4)	87.23(8)
N(1)-W(1)-O(2)	101.07(10)
O(1)-W(1)-O(2)	159.09(8)
O(4)-W(1)-O(2)	88.27(8)
N(1)-W(1)-O(3)	101.77(10)
O(1)-W(1)-O(3)	88.36(8)
O(4)-W(1)-O(3)	156.91(8)
O(2)-W(1)-O(3)	87.82(8)
C(1)-O(1)-W(1)	134.02(18)
C(5)-O(2)-W(1)	141.17(19)
C(9)-O(3)-W(1)	135.89(18)
C(13)-O(4)-W(1)	136.78(18)
O(1)-C(1)-C(4)	106.0(2)
O(1)-C(1)-C(2)	113.0(2)
C(4)-C(1)-C(2)	109.4(3)
O(1)-C(1)-C(3)	110.2(2)
C(4)-C(1)-C(3)	109.6(3)
C(2)-C(1)-C(3)	108.6(3)
F(2)-C(3)-F(3)	107.9(3)
F(2)-C(3)-F(1)	106.8(3)
F(3)-C(3)-F(1)	106.7(3)
F(2)-C(3)-C(1)	114.0(3)
F(3)-C(3)-C(1)	112.4(3)
F(1)-C(3)-C(1)	108.6(3)
F(5)-C(4)-F(6)	106.3(3)
F(5)-C(4)-F(4)	107.4(3)

F(6)-C(4)-F(4)	106.1(3)
F(5)-C(4)-C(1)	111.5(3)
F(6)-C(4)-C(1)	113.4(3)
F(4)-C(4)-C(1)	111.7(3)
O(2)-C(5)-C(6)	114.5(2)
O(2)-C(5)-C(8)	109.4(2)
C(6)-C(5)-C(8)	108.5(3)
O(2)-C(5)-C(7)	104.9(3)
C(6)-C(5)-C(7)	109.7(3)
C(8)-C(5)-C(7)	109.9(3)
F(9)-C(7)-F(7)	107.2(3)
F(9)-C(7)-F(8)	107.3(3)
F(7)-C(7)-F(8)	107.2(3)
F(9)-C(7)-C(5)	113.2(3)
F(7)-C(7)-C(5)	109.9(3)
F(8)-C(7)-C(5)	111.7(3)
F(12)-C(8)-F(11)	106.9(3)
F(12)-C(8)-F(10)	106.4(3)
F(11)-C(8)-F(10)	106.1(3)
F(12)-C(8)-C(5)	110.6(3)
F(11)-C(8)-C(5)	113.7(3)
F(10)-C(8)-C(5)	112.7(3)
O(3)-C(9)-C(10)	113.7(2)
O(3)-C(9)-C(11)	109.2(2)
C(10)-C(9)-C(11)	108.9(3)
O(3)-C(9)-C(12)	106.0(3)
C(10)-C(9)-C(12)	109.5(2)
C(11)-C(9)-C(12)	109.4(2)
F(13)-C(11)-F(14)	107.2(3)
F(13)-C(11)-F(15)	106.4(3)
F(14)-C(11)-F(15)	106.0(2)
F(13)-C(11)-C(9)	111.5(2)
F(14)-C(11)-C(9)	113.5(3)
F(15)-C(11)-C(9)	111.8(3)
F(17)-C(12)-F(16)	107.2(3)
F(17)-C(12)-F(18)	106.9(3)
F(16)-C(12)-F(18)	106.7(3)
F(17)-C(12)-C(9)	111.3(3)
F(16)-C(12)-C(9)	112.6(3)
F(18)-C(12)-C(9)	111.9(3)
O(4)-C(13)-C(14)	113.4(2)
O(4)-C(13)-C(16)	110.6(2)
C(14)-C(13)-C(16)	108.7(2)
O(4)-C(13)-C(15)	106.1(2)
C(14)-C(13)-C(15)	109.2(2)
C(16)-C(13)-C(15)	108.7(2)

F(19)-C(15)-F(20)	106.9(2)
F(19)-C(15)-F(21)	107.6(3)
F(20)-C(15)-F(21)	106.9(2)
F(19)-C(15)-C(13)	110.3(2)
F(20)-C(15)-C(13)	112.9(3)
F(21)-C(15)-C(13)	111.9(2)
F(23)-C(16)-F(22)	108.0(3)
F(23)-C(16)-F(24)	106.3(3)
F(22)-C(16)-F(24)	106.0(3)
F(23)-C(16)-C(13)	112.2(2)
F(22)-C(16)-C(13)	113.1(3)
F(24)-C(16)-C(13)	110.9(3)
W(1)-N(1)-Li(1)	175.16(19)
O(5)-Li(1)-N(1)	92.0(2)
O(5)-Li(1)-O(6)	78.92(19)
N(1)-Li(1)-O(6)	144.5(3)
O(5)-Li(1)-O(7)	170.8(3)
N(1)-Li(1)-O(7)	96.0(2)
O(6)-Li(1)-O(7)	91.9(2)
O(5)-Li(1)-O(8)	103.0(2)
N(1)-Li(1)-O(8)	111.7(2)
O(6)-Li(1)-O(8)	103.8(2)
O(7)-Li(1)-O(8)	78.18(19)
C(18)-O(5)-C(17)	113.7(3)
C(18)-O(5)-Li(1)	109.9(2)
C(17)-O(5)-Li(1)	127.3(2)
C(19)-O(6)-C(20)	111.1(3)
C(19)-O(6)-Li(1)	112.3(2)
C(20)-O(6)-Li(1)	123.9(2)
C(22)-O(7)-C(21)	113.2(3)
C(22)-O(7)-Li(1)	112.6(3)
C(21)-O(7)-Li(1)	124.9(2)
C(24)-O(8)-C(23)	112.9(3)
C(24)-O(8)-Li(1)	126.8(3)
C(23)-O(8)-Li(1)	105.2(2)
O(5)-C(18)-C(19)	105.9(3)
O(6)-C(19)-C(18)	107.5(3)
O(7)-C(22)-C(23)	109.0(3)
O(8)-C(23)-C(22)	109.3(3)
N(2)-W(2)-O(12)	99.98(10)
N(2)-W(2)-O(10)	99.19(10)
O(12)-W(2)-O(10)	160.83(9)
N(2)-W(2)-O(11)	102.65(10)
O(12)-W(2)-O(11)	88.54(8)
O(10)-W(2)-O(11)	87.42(8)
N(2)-W(2)-O(9)	102.89(10)

O(12)-W(2)-O(9)	88.12(8)
O(10)-W(2)-O(9)	87.48(9)
O(11)-W(2)-O(9)	154.44(9)
C(25)-O(9)-W(2)	137.0(2)
C(29)-O(10)-W(2)	134.11(18)
C(33)-O(11)-W(2)	137.97(19)
C(37)-O(12)-W(2	140.72(19)
O(9)-C(25)-C(26)	113.7(3)
O(9)-C(25)-C(28)	109.5(3)
C(26)-C(25)-C(28)	108.8(3)
O(9)-C(25)-C(27)	106.4(3)
C(26)-C(25)-C(27)	109.3(3)
C(28)-C(25)-C(27)	109.0(3)
F(25)-C(27)-F(27)	107.2(3)
F(25)-C(27)-F(26)	106.9(3)
F(27)-C(27)-F(26)	106.4(3)
F(25)-C(27)-C(25)	111.5(3)
F(27)-C(27)-C(25)	112.4(3)
F(26)-C(27)-C(25)	112.1(3)
F(30)-C(28)-F(29)	106.8(3)
F(30)-C(28)-F(28)	106.5(3)
F(29)-C(28)-F(28)	106.5(3)
F(30)-C(28)-C(25)	111.0(3)
F(29)-C(28)-C(25)	113.1(3)
F(28)-C(28)-C(25)	112.6(3)
O(10)-C(29)-C(31)	106.0(2)
O(10)-C(29)-C(32)	110.4(2)
C(31)-C(29)-C(32)	110.3(3)
O(10)-C(29)-C(30)	111.9(2)
C(31)-C(29)-C(30)	108.8(3)
C(32)-C(29)-C(30)	109.5(3)
F(31)-C(31)-F(33)	106.9(3)
F(31)-C(31)-F(32)	106.6(3)
F(33)-C(31)-F(32)	106.5(3)
F(31)-C(31)-C(29)	113.5(3)
F(33)-C(31)-C(29)	112.3(3)
F(32)-C(31)-C(29)	110.7(3)
F(34)-C(32)-F(36)	107.4(3)
F(34)-C(32)-F(35)	106.8(3)
F(36)-C(32)-F(35)	106.3(3)
F(34)-C(32)-C(29)	114.4(3)
F(36)-C(32)-C(29)	112.8(3)
F(35)-C(32)-C(29)	108.7(2)
O(11)-C(33)-C(34)	112.9(2)
O(11)-C(33)-C(35)	106.6(2)
C(34)-C(33)-C(35)	109.7(3)

O(11)-C(33)-C(36)	110.0(3)
C(34)-C(33)-C(36)	109.1(3)
C(35)-C(33)-C(36)	108.4(3)
F(37)-C(35)-F(39)	105.5(3)
F(37)-C(35)-F(38)	106.3(3)
F(39)-C(35)-F(38)	107.5(3)
F(37)-C(35)-C(33)	111.1(3)
F(39)-C(35)-C(33)	113.3(3)
F(38)-C(35)-C(33)	112.7(3)
F(42)-C(36)-F(40)	107.3(3)
F(42)-C(36)-F(41)	107.2(3)
F(40)-C(36)-F(41)	106.2(3)
F(42)-C(36)-C(33)	111.1(3)
F(40)-C(36)-C(33)	112.9(3)
F(41)-C(36)-C(33)	111.8(3)
O(12)-C(37)-C(38)	114.5(3)
O(12)-C(37)-C(39)	105.0(3)
C(38)-C(37)-C(39)	110.3(3)
O(12)-C(37)-C(40)	109.0(2)
C(38)-C(37)-C(40)	108.4(3)
C(39)-C(37)-C(40)	109.7(3)
F(43)-C(39)-F(44)	106.8(3)
F(43)-C(39)-F(45)	107.5(3)
F(44)-C(39)-F(45)	106.4(3)
F(43)-C(39)-C(37)	110.7(3)
F(44)-C(39)-C(37)	113.1(3)
F(45)-C(39)-C(37)	112.0(3)
F(46)-C(40)-F(47)	106.8(2)
F(46)-C(40)-F(48)	107.3(2)
F(47)-C(40)-F(48)	106.8(2)
F(46)-C(40)-C(37)	113.3(3)
F(47)-C(40)-C(37)	112.5(3)
F(48)-C(40)-C(37)	109.7(2)
W(2)-N(2)-Li(2)	178.02(19)
O(13A)-Li(2)-O(14)	100.1(3)
O(13A)-Li(2)-N(2)	127.7(3)
O(14)-Li(2)-N(2)	127.3(3)
O(13A)-Li(2)-O(13)	84.4(3)
O(14)-Li(2)-O(13)	67.9(3)
N(2)-Li(2)-O(13)	93.4(3)
O(13A)-Li(2)-O(16)	91.6(3)
O(14)-Li(2)-O(16)	102.3(3)
N(2)-Li(2)-O(16)	97.6(3)
O(13)-Li(2)-O(16)	168.5(4)
O(13A)-Li(2)-O(16A)	100.9(3)
O(14)-Li(2)-O(16A)	93.3(3)

N(2)-Li(2)-O(16A)	97.4(3)
O(13)-Li(2)-O(16A)	161.1(4)
O(16)-Li(2)-O(16A)	11.8(3)
O(13A)-Li(2)-O(15A)	108.1(3)
O(14)-Li(2)-O(15A)	22.9(2)
N(2)-Li(2)-O(15A)	124.2(3)
O(13)-Li(2)-O(15A)	90.2(3)
O(16)-Li(2)-O(15A)	80.7(3)
O(16A)-Li(2)-O(15A)	70.9(3)
O(13A)-Li(2)-O(14A)	71.5(3)
O(14)-Li(2)-O(14A)	76.1(3)
N(2)-Li(2)-O(14A)	97.2(2)
O(13)-Li(2)-O(14A)	13.9(3)
O(16)-Li(2)-O(14A)	162.2(3)
O(16A)-Li(2)-O(14A)	165.2(3)
O(15A)-Li(2)-O(14A)	99.0(3)
O(13A)-Li(2)-O(15)	20.0(2)
O(14)-Li(2)-O(15)	105.8(3)
N(2)-Li(2)-O(15)	126.8(3)
O(13)-Li(2)-O(15)	104.3(3)
O(16)-Li(2)-O(15)	71.7(3)
O(16A)-Li(2)-O(15)	81.4(3)
O(15A)-Li(2)-O(15)	105.8(3)
O(14A)-Li(2)-O(15)	91.5(3)
C(42)-O(13)-C(41)	116.7(8)
C(42)-O(13)-Li(2)	106.8(7)
C(41)-O(13)-Li(2)	128.0(6)
C(43)-O(14)-C(44)	108.5(7)
C(43)-O(14)-Li(2)	118.6(5)
C(44)-O(14)-Li(2)	128.6(6)
C(46)-O(15)-C(45)	112.6(7)
C(46)-O(15)-Li(2)	114.1(5)
C(45)-O(15)-Li(2)	127.6(6)
C(47)-O(16)-C(48)	120.0(9)
C(47)-O(16)-Li(2)	109.0(6)
C(48)-O(16)-Li(2)	130.7(7)
O(13)-C(42)-C(43)	88.6(7)
O(14)-C(43)-C(42)	103.3(7)
O(15)-C(46)-C(47)	105.3(6)
O(16)-C(47)-C(46)	99.4(7)
C(42A)-O(13A)-C(41A)	113.1(6)
C(42A)-O(13A)-Li(2)	114.1(4)
C(41A)-O(13A)-Li(2)	129.7(5)
C(43A)-O(14A)-C(44A)	122.0(7)
C(43A)-O(14A)-Li(2)	111.1(5)
C(44A)-O(14A)-Li(2)	124.9(5)

C(46A)-O(15A)-C(45A)	114.9(7)
C(46A)-O(15A)-Li(2)	113.3(5)
C(45A)-O(15A)-Li(2)	130.2(7)
C(47A)-O(16A)-C(48A)	119.6(6)
C(47A)-O(16A)-Li(2)	110.9(5)
C(48A)-O(16A)-Li(2)	129.4(5)
O(13A)-C(42A)-C(43A)	108.4(5)
O(14A)-C(43A)-C(42A)	92.5(6)
O(15A)-C(46A)-C(47A)	110.6(7)
O(16A)-C(47A)-C(46A)	101.9(7)
N(3)-W(3)-O(18)	101.06(10)
N(3)-W(3)-O(20)	99.57(10)
O(18)-W(3)-O(20)	159.33(9)
N(3)-W(3)-O(19)	102.96(10)
O(18)-W(3)-O(19)	88.85(8)
O(20)-W(3)-O(19)	87.69(8)
N(3)-W(3)-O(17)	101.95(10)
O(18)-W(3)-O(17)	87.35(8)
O(20)-W(3)-O(17)	87.25(9)
O(19)-W(3)-O(17)	155.06(9)
W(3)-N(3)-Li(3)	174.1(2)
O(23)-Li(3)-N(3)	120.1(3)
O(23)-Li(3)-O(21)	109.1(2)
N(3)-Li(3)-O(21)	130.9(3)
O(23)-Li(3)-O(22)	92.5(2)
N(3)-Li(3)-O(22)	98.9(2)
O(21)-Li(3)-O(22)	77.8(2)
O(23)-Li(3)-O(24)	81.5(2)
N(3)-Li(3)-O(24)	96.8(2)
O(21)-Li(3)-O(24)	90.3(2)
O(22)-Li(3)-O(24)	164.2(3)
O(23)-Li(3)-C(70)	90.4(2)
N(3)-Li(3)-C(70)	142.5(3)
O(21)-Li(3)-C(70)	29.17(12)
O(22)-Li(3)-C(70)	55.21(16)
O(24)-Li(3)-C(70)	109.9(2)
O(17)-C(49)-C(50)	113.9(2)
O(17)-C(49)-C(51)	106.1(3)
C(50)-C(49)-C(51)	109.2(3)
O(17)-C(49)-C(52)	108.9(2)
C(50)-C(49)-C(52)	109.1(3)
C(51)-C(49)-C(52)	109.5(3)
F(50)-C(51)-F(49)	107.4(3)
F(50)-C(51)-F(51)	107.3(3)
F(49)-C(51)-F(51)	106.7(3)
F(50)-C(51)-C(49)	110.9(3)

F(49)-C(51)-C(49)	112.2(3)
F(51)-C(51)-C(49)	112.0(3)
F(54)-C(52)-F(53)	107.2(3)
F(54)-C(52)-F(52)	106.5(3)
F(53)-C(52)-F(52)	106.4(2)
F(54)-C(52)-C(49)	110.9(2)
F(53)-C(52)-C(49)	113.3(3)
F(52)-C(52)-C(49)	112.1(3)
O(18)-C(53)-C(54)	114.4(3)
O(18)-C(53)-C(56)	108.4(3)
C(54)-C(53)-C(56)	109.4(3)
O(18)-C(53)-C(55)	104.9(3)
C(54)-C(53)-C(55)	110.1(3)
C(56)-C(53)-C(55)	109.4(3)
F(59)-C(55)-F(60)	107.6(3)
F(59)-C(55)-F(58)	107.7(3)
F(60)-C(55)-F(58)	107.2(3)
F(59)-C(55)-C(53)	113.5(3)
F(60)-C(55)-C(53)	109.4(3)
F(58)-C(55)-C(53)	111.2(3)
F(57)-C(56)-F(56)	108.1(3)
F(57)-C(56)-F(55)	107.5(3)
F(56)-C(56)-F(55)	106.4(3)
F(57)-C(56)-C(53)	113.2(3)
F(56)-C(56)-C(53)	109.9(3)
F(55)-C(56)-C(53)	111.5(3)
O(19)-C(57)-C(58)	112.8(2)
O(19)-C(57)-C(60)	109.4(3)
C(58)-C(57)-C(60)	110.4(3)
O(19)-C(57)-C(59)	105.9(3)
C(58)-C(57)-C(59)	110.0(3)
C(60)-C(57)-C(59)	108.2(3)
F(63)-C(59)-F(61)	107.3(3)
F(63)-C(59)-F(62)	107.9(3)
F(61)-C(59)-F(62)	106.3(3)
F(63)-C(59)-C(57)	113.1(3)
F(61)-C(59)-C(57)	110.4(3)
F(62)-C(59)-C(57)	111.5(3)
F(66)-C(60)-F(65)	107.1(3)
F(66)-C(60)-F(64)	107.1(3)
F(65)-C(60)-F(64)	105.3(3)
F(66)-C(60)-C(57)	111.0(3)
F(65)-C(60)-C(57)	114.0(3)
F(64)-C(60)-C(57)	112.0(3)
O(20)-C(61)-C(63)	106.4(3)
O(20)-C(61)-C(64)	111.0(3)

C(63)-C(61)-C(64)	109.8(3)
O(20)-C(61)-C(62)	111.8(3)
C(63)-C(61)-C(62)	108.7(3)
C(64)-C(61)-C(62)	109.1(3)
F(72)-C(63)-F(71)	106.8(3)
F(72)-C(63)-F(70)	107.0(3)
F(71)-C(63)-F(70)	107.3(3)
F(72)-C(63)-C(61)	113.4(3)
F(71)-C(63)-C(61)	110.4(3)
F(70)-C(63)-C(61)	111.6(3)
F(69)-C(64)-F(68)	107.7(3)
F(69)-C(64)-F(67)	105.9(3)
F(68)-C(64)-F(67)	106.7(3)
F(69)-C(64)-C(61)	114.4(3)
F(68)-C(64)-C(61)	112.8(3)
F(67)-C(64)-C(61)	108.9(3)
O(23)-C(66)-C(67)	106.9(3)
O(24)-C(67)-C(66)	110.7(3)
O(21)-C(70)-C(71)	106.5(3)
O(21)-C(70)-Li(3)	45.96(18)
C(71)-C(70)-Li(3)	80.3(2)
O(22)-C(71)-C(70)	108.0(3)
C(49)-O(17)-W(3)	136.85(19)
C(53)-O(18)-W(3)	142.0(2)
C(57)-O(19)-W(3)	137.11(18)
C(61)-O(20)-W(3)	133.0(2)
C(70)-O(21)-C(69)	112.9(3)
C(70)-O(21)-Li(3)	104.9(2)
C(69)-O(21)-Li(3)	128.1(3)
C(71)-O(22)-C(72)	112.3(3)
C(71)-O(22)-Li(3)	112.7(3)
C(72)-O(22)-Li(3)	128.5(3)
C(66)-O(23)-C(65)	111.8(2)
C(66)-O(23)-Li(3)	111.7(2)
C(65)-O(23)-Li(3)	128.4(3)
C(68)-O(24)-C(67)	112.8(2)
C(68)-O(24)-Li(3)	124.4(2)
C(67)-O(24)-Li(3)	105.3(2)
N(4)-W(4)-O(27)	99.79(10)
N(4)-W(4)-O(26)	101.14(10)
O(27)-W(4)-O(26)	159.06(9)
N(4)-W(4)-O(25)	102.02(10)
O(27)-W(4)-O(25)	87.78(8)
O(26)-W(4)-O(25)	88.45(8)
N(4)-W(4)-O(28)	102.30(10)
O(27)-W(4)-O(28)	87.42(8)

O(26)-W(4)-O(28)	87.57(8)
O(25)-W(4)-O(28)	155.67(9)
W(4)-N(4)-Li(4)	167.1(2)
O(30)-Li(4)-N(4)	112.6(3)
O(30)-Li(4)-O(29)	81.6(2)
N(4)-Li(4)-O(29)	97.7(3)
O(30)-Li(4)-O(32)	103.0(3)
N(4)-Li(4)-O(32)	91.5(2)
O(29)-Li(4)-O(32)	167.2(3)
O(30)-Li(4)-O(31)	105.5(3)
N(4)-Li(4)-O(31)	141.8(3)
O(29)-Li(4)-O(31)	90.4(2)
O(32)-Li(4)-O(31)	77.0(2)
O(25)-C(73)-C(74)	113.4(2)
O(25)-C(73)-C(75)	106.0(3)
C(74)-C(73)-C(75)	109.6(3)
O(25)-C(73)-C(76)	109.9(2)
C(74)-C(73)-C(76)	109.1(3)
C(75)-C(73)-C(76)	108.7(3)
F(73)-C(75)-F(74)	107.6(3)
F(73)-C(75)-F(75)	106.4(3)
F(74)-C(75)-F(75)	106.3(3)
F(73)-C(75)-C(73)	112.7(3)
F(74)-C(75)-C(73)	110.6(3)
F(75)-C(75)-C(73)	113.0(3)
F(78)-C(76)-F(76)	107.9(3)
F(78)-C(76)-F(77)	106.2(3)
F(76)-C(76)-F(77)	106.5(3)
F(78)-C(76)-C(73)	113.0(3)
F(76)-C(76)-C(73)	110.8(3)
F(77)-C(76)-C(73)	112.1(3)
O(26)-C(77)-C(78)	114.9(2)
O(26)-C(77)-C(80)	108.8(3)
C(78)-C(77)-C(80)	108.9(3)
O(26)-C(77)-C(79)	105.2(3)
C(78)-C(77)-C(79)	109.1(3)
C(80)-C(77)-C(79)	109.6(3)
F(80)-C(79)-F(79)	107.1(3)
F(80)-C(79)-F(81)	106.9(3)
F(79)-C(79)-F(81)	107.5(3)
F(80)-C(79)-C(77)	110.1(3)
F(79)-C(79)-C(77)	112.3(3)
F(81)-C(79)-C(77)	112.7(3)
F(83)-C(80)-F(84)	107.3(3)
F(83)-C(80)-F(82)	106.4(3)
F(84)-C(80)-F(82)	106.6(3)

F(83)-C(80)-C(77)	113.7(3)
F(84)-C(80)-C(77)	110.2(3)
F(82)-C(80)-C(77)	112.3(3)
O(27)-C(81)-C(82)	112.0(2)
O(27)-C(81)-C(84)	110.9(2)
C(82)-C(81)-C(84)	109.2(3)
O(27)-C(81)-C(83)	106.2(2)
C(82)-C(81)-C(83)	108.5(2)
C(84)-C(81)-C(83)	110.0(3)
F(85)-C(83)-F(87)	106.4(3)
F(85)-C(83)-F(86)	107.3(2)
F(87)-C(83)-F(86)	107.0(3)
F(85)-C(83)-C(81)	110.8(3)
F(87)-C(83)-C(81)	113.1(2)
F(86)-C(83)-C(81)	111.9(3)
F(89)-C(84)-F(88)	106.8(3)
F(89)-C(84)-F(90)	106.6(3)
F(88)-C(84)-F(90)	106.7(3)
F(89)-C(84)-C(81)	114.1(3)
F(88)-C(84)-C(81)	113.1(3)
F(90)-C(84)-C(81)	109.1(2)
O(28)-C(85)-C(86)	114.3(2)
O(28)-C(85)-C(88)	109.2(2)
C(86)-C(85)-C(88)	109.1(3)
O(28)-C(85)-C(87)	105.7(3)
C(86)-C(85)-C(87)	109.6(2)
C(88)-C(85)-C(87)	108.7(2)
F(91)-C(87)-F(93)	106.6(3)
F(91)-C(87)-F(92)	106.8(3)
F(93)-C(87)-F(92)	107.1(3)
F(91)-C(87)-C(85)	110.8(3)
F(93)-C(87)-C(85)	112.9(3)
F(92)-C(87)-C(85)	112.2(3)
F(95)-C(88)-F(94)	106.9(3)
F(95)-C(88)-F(96)	106.7(3)
F(94)-C(88)-F(96)	106.2(3)
F(95)-C(88)-C(85)	113.3(3)
F(94)-C(88)-C(85)	112.7(3)
F(96)-C(88)-C(85)	110.6(2)
O(29)-C(90)-C(91)	111.1(4)
O(30)-C(91)-C(90)	110.2(4)
O(31)-C(94)-C(95)	107.4(3)
O(32)-C(95)-C(94)	107.2(3)
C(73)-O(25)-W(4)	137.73(18)
C(77)-O(26)-W(4)	141.36(18)
C(81)-O(27)-W(4)	133.92(18)

C(85)-O(28)-W(4)	135.95(19)
C(90)-O(29)-C(89)	115.2(3)
C(90)-O(29)-Li(4)	105.0(3)
C(89)-O(29)-Li(4)	124.3(3)
C(92)-O(30)-C(91)	115.2(4)
C(92)-O(30)-Li(4)	130.7(3)
C(91)-O(30)-Li(4)	111.4(3)
C(94)-O(31)-C(93)	108.2(3)
C(94)-O(31)-Li(4)	114.4(3)
C(93)-O(31)-Li(4)	126.7(3)
C(96)-O(32)-C(95)	113.6(3)
C(96)-O(32)-Li(4)	128.3(3)
C(95)-O(32)-Li(4)	111.4(3)

Symmetry transformations used to generate equivalent atoms:

Table A2.4. Anisotropic displacement parameters (Å^2 x 10^3) for ag679. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
W(1)	13(1)	14(1)	16(1)	0(1)	0(1)	-2(1)
F(1)	27(1)	43(1)	60(1)	-21(1)	-12(1)	3(1)
F(2)	36(1)	36(1)	64(2)	12(1)	21(1)	-4(1)
F(3)	19(1)	45(1)	79(2)	-8(1)	1(1)	10(1)
F(4)	46(1)	53(1)	43(1)	-18(1)	4(1)	24(1)
F(5)	50(1)	37(1)	82(2)	-29(1)	-7(1)	-4(1)
F(6)	58(1)	60(1)	20(1)	-7(1)	-3(1)	26(1)
F(7)	58(2)	23(1)	76(2)	2(1)	-8(1)	3(1)
F(8)	48(1)	50(1)	76(2)	-39(1)	1(1)	-18(1)
F(9)	37(1)	54(1)	39(1)	-19(1)	7(1)	-5(1)
F(10)	34(1)	52(1)	40(1)	1(1)	-16(1)	-21(1)
F(11)	42(1)	45(1)	22(1)	9(1)	-6(1)	-17(1)
F(12)	25(1)	39(1)	51(1)	-3(1)	-4(1)	1(1)
F(13)	44(1)	29(1)	35(1)	3(1)	6(1)	11(1)
F(14)	55(1)	21(1)	54(1)	-2(1)	-10(1)	-10(1)
F(15)	55(1)	30(1)	36(1)	7(1)	-14(1)	11(1)
F(16)	32(1)	52(1)	39(1)	16(1)	-2(1)	-18(1)

F(17)	50(1)	50(1)	34(1)	2(1)	18(1)	4(1)
F(18)	50(1)	53(1)	33(1)	27(1)	-1(1)	-4(1)
F(19)	29(1)	43(1)	42(1)	17(1)	-16(1)	-10(1)
F(20)	41(1)	36(1)	23(1)	11(1)	-2(1)	-4(1)
F(21)	53(1)	32(1)	37(1)	7(1)	-2(1)	18(1)
F(22)	41(1)	49(1)	43(1)	-26(1)	11(1)	-18(1)
F(23)	37(1)	27(1)	33(1)	8(1)	1(1)	-13(1)
F(24)	25(1)	43(1)	45(1)	15(1)	-12(1)	-14(1)
O(1)	18(1)	17(1)	22(1)	0(1)	2(1)	4(1)
O(2)	21(1)	16(1)	20(1)	-2(1)	0(1)	-8(1)
O(3)	22(1)	17(1)	16(1)	1(1)	-1(1)	-4(1)
O(4)	16(1)	18(1)	19(1)	4(1)	1(1)	-1(1)
C(1)	21(1)	19(1)	23(2)	-3(1)	4(1)	4(1)
C(2)	35(2)	32(2)	43(2)	14(2)	11(2)	17(1)
C(3)	20(2)	32(2)	41(2)	-3(2)	4(1)	4(1)
C(4)	32(2)	31(2)	36(2)	-10(2)	2(2)	9(2)
C(5)	26(2)	22(2)	19(1)	0(1)	0(1)	-12(1)
C(6)	40(2)	46(2)	26(2)	5(2)	0(2)	-25(2)
C(7)	37(2)	24(2)	42(2)	-12(1)	-6(2)	-8(1)
C(8)	26(2)	32(2)	28(2)	-3(1)	-4(1)	-11(1)
C(9)	28(2)	16(1)	19(1)	3(1)	-1(1)	-1(1)
C(10)	31(2)	24(2)	22(2)	1(1)	-6(1)	-5(1)
C(11)	35(2)	18(1)	31(2)	4(1)	-7(1)	-6(1)
C(12)	34(2)	37(2)	23(2)	12(1)	-2(1)	-6(2)
C(13)	19(1)	18(1)	20(1)	2(1)	-1(1)	-3(1)
C(14)	22(2)	24(2)	24(2)	2(1)	5(1)	-1(1)
C(15)	26(2)	25(2)	22(1)	4(1)	-1(1)	-1(1)
C(16)	21(2)	28(2)	23(2)	2(1)	1(1)	-7(1)
N(1)	22(1)	16(1)	16(1)	0(1)	2(1)	-4(1)
Li(1)	23(2)	23(2)	29(3)	-4(2)	0(2)	-2(2)
O(5)	21(1)	28(1)	30(1)	-5(1)	2(1)	4(1)
O(6)	24(1)	29(1)	28(1)	4(1)	-1(1)	-2(1)
O(7)	32(1)	54(2)	40(2)	-13(1)	-6(1)	0(1)
O(8)	38(1)	42(2)	36(1)	2(1)	-6(1)	-1(1)
C(17)	39(2)	25(2)	37(2)	-6(1)	-1(2)	7(2)
C(18)	24(2)	46(2)	31(2)	-3(2)	4(1)	14(2)
C(19)	24(2)	49(2)	26(2)	10(2)	3(1)	7(2)
C(20)	26(2)	31(2)	55(2)	14(2)	-6(2)	-7(1)
C(21)	37(2)	38(2)	48(2)	-22(2)	-1(2)	3(2)
C(22)	43(2)	62(3)	30(2)	-8(2)	-2(2)	-21(2)
C(23)	37(2)	53(2)	33(2)	6(2)	-12(2)	-10(2)
C(24)	60(3)	63(3)	44(2)	12(2)	-2(2)	18(2)
W(2)	14(1)	15(1)	20(1)	3(1)	1(1)	1(1)
F(25)	58(1)	47(1)	36(1)	-5(1)	-14(1)	7(1)
F(26)	77(2)	49(1)	36(1)	-24(1)	0(1)	4(1)
F(27)	48(1)	55(1)	49(1)	-20(1)	-2(1)	-18(1)

F(28)	81(2)	38(1)	46(1)	-6(1)	12(1)	28(1)
F(29)	83(2)	21(1)	57(1)	1(1)	17(1)	1(1)
F(30)	63(1)	41(1)	39(1)	1(1)	-3(1)	25(1)
F(31)	40(1)	44(1)	21(1)	3(1)	2(1)	9(1)
F(32)	38(1)	43(1)	46(1)	22(1)	0(1)	-9(1)
F(33)	39(1)	47(1)	35(1)	18(1)	-2(1)	17(1)
F(34)	31(1)	41(1)	36(1)	-2(1)	-7(1)	-4(1)
F(35)	25(1)	36(1)	32(1)	13(1)	3(1)	2(1)
F(36)	22(1)	50(1)	51(1)	15(1)	2(1)	14(1)
F(37)	34(1)	31(1)	37(1)	-2(1)	10(1)	0(1)
F(38)	60(2)	48(1)	43(1)	-26(1)	6(1)	-18(1)
F(39)	68(2)	41(1)	36(1)	-1(1)	1(1)	30(1)
F(40)	63(2)	30(1)	51(1)	15(1)	-16(1)	-15(1)
F(41)	44(1)	35(1)	45(1)	3(1)	-12(1)	-22(1)
F(42)	56(1)	52(1)	52(1)	-10(1)	22(1)	-33(1)
F(43)	64(2)	20(1)	67(2)	-2(1)	16(1)	11(1)
F(44)	37(1)	37(1)	44(1)	17(1)	-3(1)	9(1)
F(45)	55(1)	30(1)	74(2)	26(1)	15(1)	-8(1)
F(46)	31(1)	34(1)	23(1)	-1(1)	0(1)	-1(1)
F(47)	26(1)	40(1)	39(1)	7(1)	11(1)	-8(1)
F(48)	25(1)	29(1)	35(1)	7(1)	3(1)	6(1)
O(9)	22(1)	18(1)	22(1)	-1(1)	3(1)	1(1)
O(10)	16(1)	19(1)	25(1)	4(1)	1(1)	3(1)
O(11)	21(1)	17(1)	21(1)	0(1)	0(1)	0(1)
O(12)	20(1)	16(1)	24(1)	1(1)	1(1)	-3(1)
C(25)	35(2)	24(2)	23(2)	-2(1)	2(1)	6(1)
C(26)	39(2)	39(2)	26(2)	-2(1)	10(2)	5(2)
C(27)	48(2)	38(2)	28(2)	-14(2)	-2(2)	1(2)
C(28)	53(2)	26(2)	36(2)	-4(2)	9(2)	13(2)
C(29)	23(2)	23(1)	20(1)	3(1)	-2(1)	7(1)
C(30)	41(2)	27(2)	29(2)	0(1)	-3(2)	13(2)
C(31)	30(2)	28(2)	30(2)	10(1)	-2(1)	5(1)
C(32)	20(2)	34(2)	27(2)	9(1)	0(1)	10(1)
C(33)	23(2)	20(1)	27(2)	1(1)	-1(1)	-6(1)
C(34)	26(2)	28(2)	29(2)	1(1)	-6(1)	-1(1)
C(35)	40(2)	22(2)	27(2)	-5(1)	-4(2)	1(1)
C(36)	44(2)	30(2)	31(2)	0(1)	-3(2)	-12(2)
C(37)	23(2)	18(1)	28(2)	2(1)	2(1)	-6(1)
C(38)	36(2)	38(2)	33(2)	-2(2)	3(2)	-17(2)
C(39)	38(2)	20(2)	44(2)	9(1)	10(2)	2(1)
C(40)	18(1)	25(2)	26(2)	5(1)	1(1)	-3(1)
N(2)	26(1)	21(1)	21(1)	3(1)	-3(1)	5(1)
Li(2)	20(2)	42(3)	31(3)	3(3)	-1(2)	2(2)
O(13)	17(3)	42(5)	30(4)	13(3)	-19(3)	-6(3)
O(14)	41(4)	26(3)	35(3)	0(2)	7(3)	8(3)
O(15)	39(4)	39(3)	21(2)	0(2)	-2(3)	-11(3)

O(16)	19(3)	67(5)	41(4)	12(3)	-7(3)	-9(3)
C(41)	30(3)	30(4)	24(3)	0(3)	0(3)	7(3)
C(42)	18(3)	47(6)	45(3)	11(4)	-13(4)	-5(4)
C(43)	66(5)	22(3)	54(3)	-5(3)	-9(4)	7(4)
C(44)	57(6)	39(5)	39(3)	-15(4)	14(4)	18(4)
C(45)	42(5)	52(6)	21(3)	-3(3)	-3(4)	-9(5)
C(46)	27(4)	33(4)	31(3)	4(3)	-1(3)	-9(3)
C(47)	23(3)	36(5)	30(3)	11(4)	10(4)	-13(4)
C(48)	21(4)	20(5)	19(5)	0(4)	15(4)	0(4)
O(13A)	74(3)	77(3)	54(3)	-2(2)	-22(3)	-13(3)
O(14A)	25(2)	104(4)	89(4)	61(3)	-16(2)	-3(2)
O(15A)	78(4)	87(3)	53(3)	-10(3)	9(3)	9(3)
O(16A)	46(3)	78(4)	50(3)	20(3)	12(2)	1(2)
C(41A)	78(5)	85(3)	96(5)	-21(4)	-25(5)	-14(4)
C(42A)	54(4)	104(3)	38(3)	-16(3)	-18(3)	35(3)
C(43A)	45(3)	84(3)	78(5)	28(4)	-36(4)	-6(4)
C(44A)	44(4)	34(4)	56(5)	15(4)	-6(4)	9(3)
C(45A)	82(7)	85(3)	75(7)	-26(4)	18(6)	12(6)
C(46A)	52(4)	107(3)	39(4)	-21(3)	27(3)	-22(4)
C(47A)	71(3)	102(3)	109(6)	26(4)	46(4)	18(4)
C(48A)	51(3)	47(4)	32(4)	12(3)	-9(3)	-13(3)
W(3)	15(1)	14(1)	16(1)	1(1)	-1(1)	-3(1)
N(3)	25(1)	14(1)	17(1)	1(1)	-2(1)	4(1)
Li(3)	20(2)	26(3)	28(3)	-1(2)	-5(2)	-1(2)
F(49)	29(1)	64(2)	64(2)	28(1)	-14(1)	2(1)
F(50)	66(2)	46(1)	50(1)	13(1)	-36(1)	-18(1)
F(51)	54(1)	44(1)	43(1)	25(1)	-17(1)	-5(1)
F(52)	49(1)	27(1)	36(1)	11(1)	0(1)	-12(1)
F(53)	39(1)	23(1)	61(1)	1(1)	11(1)	6(1)
F(54)	39(1)	23(1)	30(1)	1(1)	-11(1)	-3(1)
F(55)	57(1)	50(1)	84(2)	3(1)	54(1)	5(1)
F(56)	39(1)	35(1)	58(1)	0(1)	17(1)	-10(1)
F(57)	74(2)	45(1)	30(1)	5(1)	15(1)	1(1)
F(58)	47(1)	42(1)	66(2)	-24(1)	18(1)	9(1)
F(59)	45(1)	42(1)	40(1)	-19(1)	-1(1)	2(1)
F(60)	50(1)	24(1)	62(2)	-1(1)	11(1)	-6(1)
F(61)	66(2)	45(1)	43(1)	12(1)	26(1)	3(1)
F(62)	63(2)	58(1)	51(1)	40(1)	-12(1)	-5(1)
F(63)	78(2)	57(1)	32(1)	8(1)	-3(1)	-46(1)
F(64)	43(1)	41(1)	70(2)	18(1)	-17(1)	12(1)
F(65)	76(2)	44(1)	60(2)	-16(1)	-20(1)	25(1)
F(66)	67(2)	72(2)	82(2)	46(1)	39(1)	43(1)
F(67)	30(1)	47(1)	46(1)	-5(1)	4(1)	-8(1)
F(68)	42(1)	56(2)	89(2)	0(1)	-10(1)	-31(1)
F(69)	42(1)	52(1)	60(2)	10(1)	-27(1)	-9(1)
F(70)	86(2)	52(1)	30(1)	-3(1)	-17(1)	-45(1)

F(71)	73(2)	47(1)	34(1)	-15(1)	7(1)	-14(1)
F(72)	88(2)	47(1)	18(1)	7(1)	-8(1)	-34(1)
C(49)	26(2)	21(1)	19(1)	8(1)	-7(1)	-2(1)
C(50)	38(2)	26(2)	18(1)	3(1)	0(1)	-5(1)
C(51)	40(2)	35(2)	34(2)	17(2)	-18(2)	-7(2)
C(52)	28(2)	21(2)	26(2)	9(1)	-2(1)	0(1)
C(53)	23(2)	26(2)	32(2)	-1(1)	10(1)	2(1)
C(54)	24(2)	34(2)	51(2)	6(2)	1(2)	7(2)
C(55)	29(2)	31(2)	39(2)	-9(2)	10(2)	2(1)
C(56)	41(2)	33(2)	40(2)	-2(2)	21(2)	3(2)
C(57)	24(2)	23(1)	20(1)	7(1)	-4(1)	-2(1)
C(58)	39(2)	36(2)	31(2)	9(2)	-18(2)	-11(2)
C(59)	45(2)	26(2)	25(2)	10(1)	-5(2)	-7(2)
C(60)	39(2)	33(2)	43(2)	17(2)	1(2)	7(2)
C(61)	36(2)	22(2)	19(1)	2(1)	-4(1)	-16(1)
C(62)	61(2)	22(2)	24(2)	4(1)	-5(2)	-17(2)
C(63)	65(3)	31(2)	25(2)	-1(1)	-9(2)	-27(2)
C(64)	35(2)	38(2)	44(2)	6(2)	-13(2)	-22(2)
C(65)	40(2)	28(2)	35(2)	5(1)	2(2)	9(2)
C(66)	25(2)	35(2)	24(2)	2(1)	-7(1)	-5(1)
C(67)	29(2)	30(2)	26(2)	-2(1)	-8(1)	-3(1)
C(68)	28(2)	29(2)	30(2)	-7(1)	-1(1)	1(1)
C(69)	62(3)	33(2)	45(2)	8(2)	1(2)	-9(2)
C(70)	29(2)	42(2)	29(2)	3(2)	0(1)	-2(2)
C(71)	44(2)	39(2)	20(2)	2(1)	4(1)	7(2)
C(72)	63(3)	27(2)	38(2)	-8(2)	1(2)	-2(2)
O(17)	21(1)	21(1)	21(1)	7(1)	-5(1)	-3(1)
O(18)	21(1)	20(1)	23(1)	0(1)	1(1)	3(1)
O(19)	23(1)	18(1)	14(1)	2(1)	-2(1)	-3(1)
O(20)	26(1)	16(1)	18(1)	1(1)	-1(1)	-9(1)
O(21)	35(1)	28(1)	39(1)	1(1)	1(1)	-1(1)
O(22)	39(1)	33(1)	30(1)	-2(1)	1(1)	0(1)
O(23)	32(1)	31(1)	25(1)	-1(1)	-1(1)	6(1)
O(24)	24(1)	37(1)	25(1)	-3(1)	-2(1)	1(1)
W(4)	14(1)	14(1)	17(1)	2(1)	-2(1)	1(1)
N(4)	19(1)	16(1)	22(1)	0(1)	-1(1)	1(1)
Li(4)	16(2)	35(3)	37(3)	4(2)	1(2)	2(2)
F(73)	135(2)	67(2)	51(2)	-17(1)	-25(2)	76(2)
F(74)	40(1)	68(2)	79(2)	-44(1)	23(1)	-5(1)
F(75)	56(1)	47(1)	41(1)	-28(1)	-1(1)	2(1)
F(76)	63(2)	70(2)	80(2)	-50(1)	41(1)	-46(1)
F(77)	37(1)	33(1)	34(1)	-10(1)	-12(1)	-6(1)
F(78)	86(2)	74(2)	72(2)	49(1)	-50(1)	-52(1)
F(79)	38(1)	48(1)	43(1)	23(1)	-15(1)	-7(1)
F(80)	48(1)	30(1)	49(1)	12(1)	7(1)	8(1)
F(81)	36(1)	38(1)	45(1)	20(1)	8(1)	-9(1)

F(82)	24(1)	52(1)	36(1)	6(1)	9(1)	-3(1)
F(83)	32(1)	59(1)	26(1)	-5(1)	0(1)	-3(1)
F(84)	31(1)	34(1)	38(1)	2(1)	5(1)	3(1)
F(85)	33(1)	42(1)	37(1)	17(1)	4(1)	-4(1)
F(86)	42(1)	36(1)	32(1)	15(1)	-11(1)	2(1)
F(87)	54(1)	31(1)	24(1)	1(1)	2(1)	4(1)
F(88)	24(1)	36(1)	55(1)	10(1)	-3(1)	12(1)
F(89)	27(1)	36(1)	38(1)	-2(1)	-9(1)	-7(1)
F(90)	24(1)	38(1)	32(1)	13(1)	3(1)	0(1)
F(91)	55(1)	40(1)	29(1)	1(1)	-16(1)	-2(1)
F(92)	58(1)	36(1)	38(1)	-18(1)	-6(1)	-9(1)
F(93)	31(1)	52(1)	38(1)	-8(1)	-7(1)	-13(1)
F(94)	64(2)	21(1)	52(1)	-9(1)	1(1)	10(1)
F(95)	51(1)	24(1)	49(1)	6(1)	-1(1)	-15(1)
F(96)	43(1)	20(1)	41(1)	2(1)	-12(1)	2(1)
C(73)	27(2)	17(1)	22(1)	0(1)	-7(1)	3(1)
C(74)	29(2)	29(2)	21(2)	-2(1)	-8(1)	2(1)
C(75)	46(2)	34(2)	32(2)	-12(1)	-8(2)	15(2)
C(76)	38(2)	29(2)	27(2)	-5(1)	-8(2)	-10(2)
C(77)	22(2)	28(2)	19(1)	7(1)	-2(1)	-5(1)
C(78)	22(2)	40(2)	26(2)	5(1)	-4(1)	-9(1)
C(79)	26(2)	30(2)	33(2)	10(1)	-1(1)	-3(1)
C(80)	21(2)	39(2)	26(2)	4(1)	4(1)	-4(1)
C(81)	21(1)	15(1)	24(1)	3(1)	-5(1)	2(1)
C(82)	32(2)	16(1)	39(2)	-1(1)	-11(2)	5(1)
C(83)	31(2)	21(2)	29(2)	8(1)	-2(1)	2(1)
C(84)	23(2)	27(2)	28(2)	5(1)	-7(1)	6(1)
C(85)	29(2)	18(1)	22(1)	-3(1)	0(1)	-4(1)
C(86)	31(2)	27(2)	28(2)	-6(1)	7(1)	1(1)
C(87)	38(2)	28(2)	24(2)	-4(1)	-2(1)	-6(2)
C(88)	44(2)	18(1)	33(2)	-2(1)	-2(2)	-2(2)
C(89)	40(2)	34(2)	27(2)	5(1)	1(2)	-5(2)
C(90)	51(3)	76(3)	77(3)	20(3)	28(3)	15(3)
C(91)	51(3)	96(4)	63(3)	-44(3)	34(2)	-22(3)
C(92)	62(3)	39(2)	104(4)	-17(3)	19(3)	10(2)
C(93)	47(2)	50(3)	93(4)	12(2)	-28(2)	-23(2)
C(94)	29(2)	52(2)	36(2)	-11(2)	-6(2)	6(2)
C(95)	35(2)	55(2)	32(2)	6(2)	-5(2)	6(2)
C(96)	36(2)	33(2)	40(2)	6(2)	-1(2)	-5(2)
O(25)	22(1)	18(1)	19(1)	-4(1)	-4(1)	3(1)
O(26)	18(1)	24(1)	19(1)	4(1)	1(1)	-5(1)
O(27)	19(1)	16(1)	21(1)	4(1)	0(1)	1(1)
O(28)	21(1)	17(1)	19(1)	-1(1)	-2(1)	-2(1)
O(29)	24(1)	66(2)	45(2)	24(1)	5(1)	4(1)
O(30)	47(2)	50(2)	41(2)	-6(1)	4(1)	22(1)
O(31)	44(2)	41(2)	50(2)	5(1)	-9(1)	-5(1)

O(32)	28(1)	35(1)	34(1)	3(1)	-6(1)	1(1)

Table A2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ag679.

	x	y	z	U(eq)
H(2A)	2066	6203	3771	55
H(2B)	1385	6260	3863	55
H(2C)	1605	5708	3552	55
H(6A)	1699	2129	3643	56
H(6B)	1150	2161	3375	56
H(6C)	1290	2848	3635	56
H(10A)	3219	3569	4397	38
H(10B)	2995	3264	4781	38
H(10C)	2701	3986	4606	38
H(14A)	3227	4112	2945	35
H(14B)	3231	4628	2591	35
H(14C)	2690	4087	2667	35
H(17A)	3820	2600	2959	51
H(17B)	3397	2776	3295	51
H(17C)	3976	2293	3356	51
H(18A)	4744	3093	2936	40
H(18B)	4958	3053	3352	40
H(19A)	5344	4145	3101	40
H(19B)	4708	4391	2959	40
H(20A)	5369	5289	3437	56
H(20B)	4863	5452	3726	56
H(20C)	4723	5483	3300	56
H(21A)	3356	5135	4369	61
H(21B)	3569	5593	4021	61
H(21C)	3870	5732	4408	61
H(22A)	4055	4327	4653	54
H(22B)	4613	4858	4608	54
H(23A)	5071	4010	4241	49
H(23B)	4860	3577	4598	49
H(24A)	5012	2698	4000	83
H(24B)	4372	2338	3989	83
H(24C)	4702	2446	4369	83
H(26A)	5135	3870	365	52
H(26B)	5395	3103	219	52
H(26C)	5613	3431	599	52
H(30A)	4053	5829	1317	48

H(30B)	3873	6321	972	48
H(30C)	4547	6233	1081	48
H(34A)	5146	4183	2228	41
H(34B)	5561	4844	2361	41
H(34C)	5701	4418	1990	41
H(38A)	3563	3032	1382	53
H(38B)	3459	2289	1610	53
H(38C)	3970	2324	1314	53
H(41A)	6158	2275	1905	42
H(41B)	5684	2865	1767	42
H(41C)	6165	3104	2061	42
H(42A)	7137	2483	1800	44
H(42B)	7303	3305	1645	44
H(43A)	7468	2371	1155	57
H(43B)	6790	2137	1190	57
H(44A)	7354	2770	589	68
H(44B)	6868	3374	488	68
H(44C)	6677	2546	589	68
H(45A)	7496	4972	1916	58
H(45B)	6961	4433	2010	58
H(45C)	6844	5292	1928	58
H(46A)	7578	5444	1305	37
H(46B)	6908	5716	1300	37
H(47A)	7192	5400	698	36
H(47B)	7358	4573	834	36
H(48A)	6115	5756	822	30
H(48B)	5759	5029	706	30
H(48C)	6268	5338	450	30
H(41D)	6917	5281	1884	129
H(41E)	7031	5427	1461	129
H(41F)	7556	5161	1717	129
H(42C)	6887	3970	2083	79
H(42D)	7555	3985	1950	79
H(43C)	7328	2996	1515	83
H(43D)	7162	2720	1923	83
H(44D)	6204	2190	1688	67
H(44E)	5735	2847	1703	67
H(44F)	6129	2668	2051	67
H(45D)	6688	2531	531	121
H(45E)	6788	2345	952	121
H(45F)	7336	2508	694	121
H(46C)	6854	3822	334	79
H(46D)	7503	3761	495	79
H(47C)	7356	4738	864	113
H(47D)	7120	4980	467	113
H(48D)	6346	5635	593	65

H(48E)	5830	5277	827	65
H(48F)	5969	4965	430	65
H(50A)	9868	8901	4623	41
H(50B)	9642	8105	4753	41
H(50C)	9393	8463	4386	41
H(54A)	11441	8316	3572	54
H(54B)	11601	7618	3322	54
H(54C)	11090	7555	3618	54
H(58A)	9751	9350	2759	53
H(58B)	9270	9952	2647	53
H(58C)	9188	9473	3010	53
H(62A)	10693	11056	3691	54
H(62B)	10833	11534	4047	54
H(62C)	10171	11335	3947	54
H(65A)	8004	10250	3297	52
H(65B)	7765	10214	3705	52
H(65C)	7338	10028	3373	52
H(66A)	8153	9052	2972	34
H(66B)	7461	8962	3035	34
H(67A)	7608	7863	3360	34
H(67B)	7929	7783	2975	34
H(68A)	8848	7248	3037	43
H(68B)	9301	7705	3282	43
H(68C)	8959	8109	2958	43
H(69A)	7909	7061	4356	70
H(69B)	8262	7033	3981	70
H(69C)	7593	7292	3985	70
H(70A)	7515	8194	4536	40
H(70B)	7422	8657	4167	40
H(71A)	7748	9492	4611	41
H(71B)	8290	8963	4709	41
H(72A)	8462	10438	4482	64
H(72B)	8935	10282	4171	64
H(72C)	8986	9870	4555	64
H(74A)	1653	8606	480	39
H(74B)	1719	8034	150	39
H(74C)	2249	8575	253	39
H(78A)	3601	10301	1167	44
H(78B)	4119	10155	884	44
H(78C)	3875	9489	1127	44
H(82A)	2401	6702	1581	43
H(82B)	3057	6498	1693	43
H(82C)	2930	6902	1314	43
H(86A)	1723	9732	1863	43
H(86B)	1961	10102	2229	43
H(86C)	2144	9272	2127	43

H(89A)	1210	8487	1935	50
H(89B)	1284	7799	1664	50
H(89C)	779	7790	1965	50
H(90A)	41	8539	1936	82
H(90B)	-203	8734	1539	82
H(91A)	-117	9833	1833	84
H(91B)	526	9635	1976	84
H(92A)	194	10916	1513	103
H(92B)	735	10861	1240	103
H(92C)	841	10801	1669	103
H(93A)	-447	8045	724	95
H(93B)	-11	7825	1047	95
H(93C)	181	7704	633	95
H(94A)	-156	8975	317	47
H(94B)	493	8641	289	47
H(95A)	572	9910	175	49
H(95B)	200	10105	533	49
H(96A)	1462	10364	309	54
H(96B)	1742	10270	705	54
H(96C)	1188	10799	647	54

Appendix 3:

Crystallographic Data for [EtC≡W$(OCMe_2CF_3)_3]_2[\mu-\kappa^1\kappa^1$–DME]

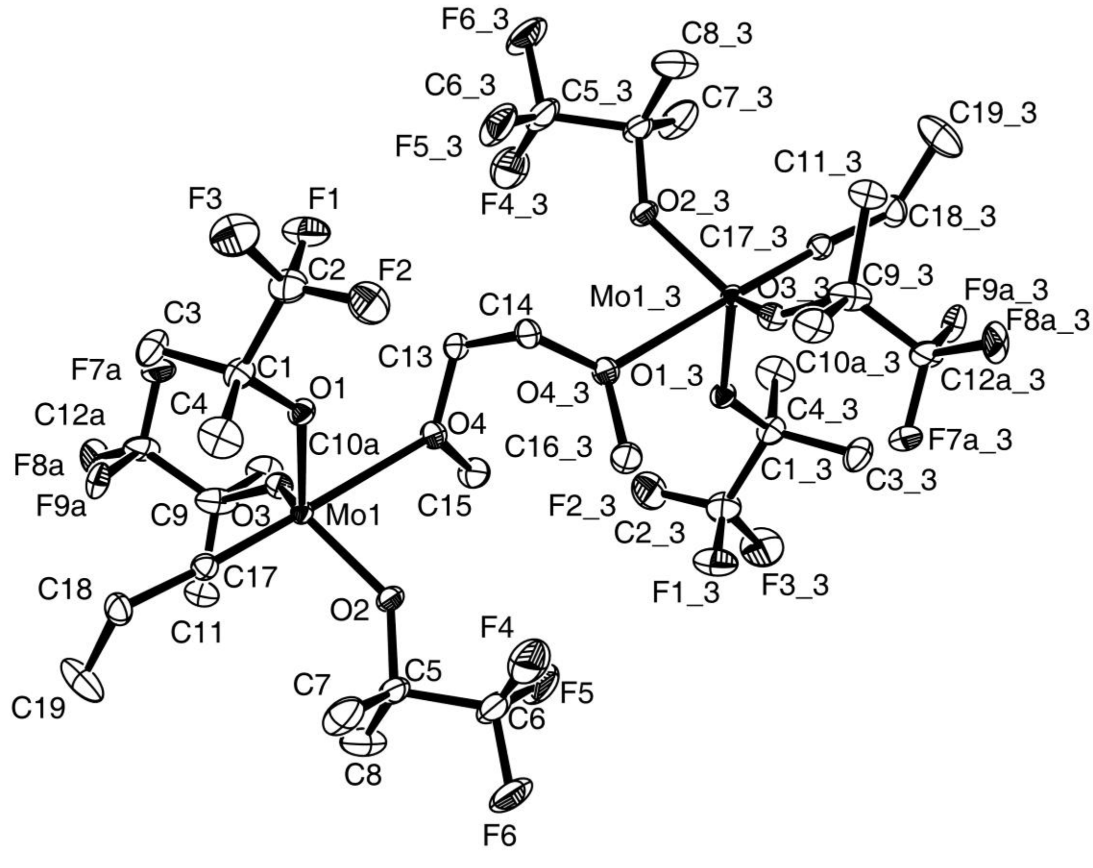

Figure A3.1. 50% Thermal ellipsoid plot of [EtC≡W$(OCMe_2CF_3)_3]_2[\mu-\kappa^1\kappa^1$–DME] view A.

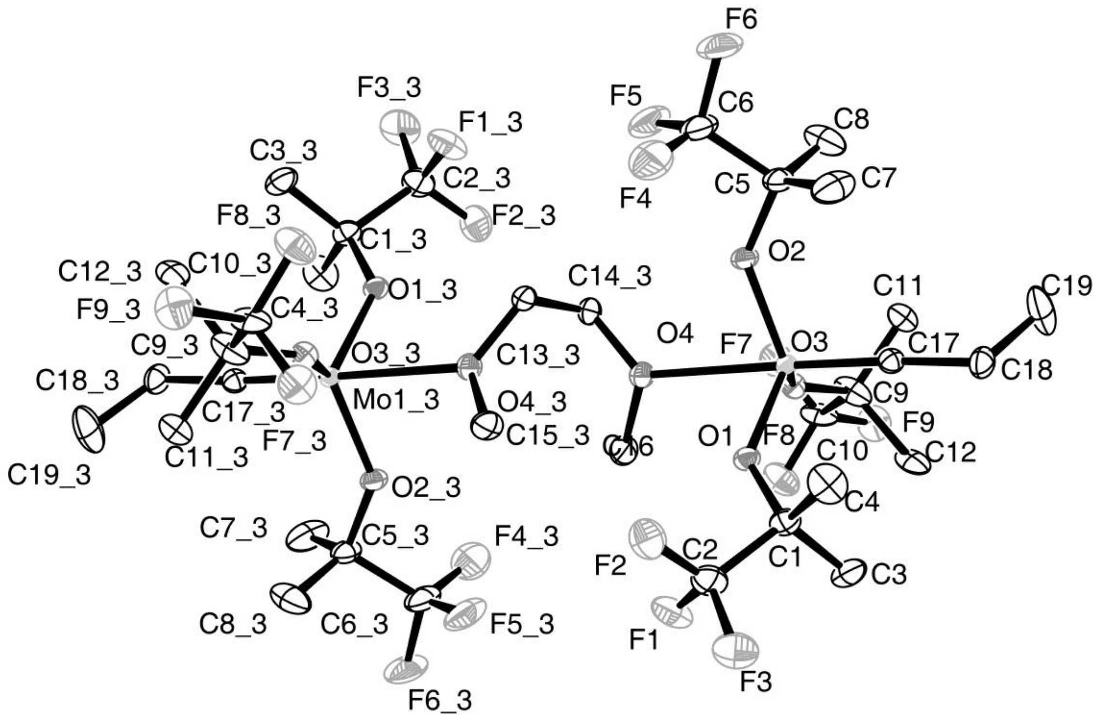

Figure A3.2. 50% Thermal ellipsoid plot of $[EtC{\equiv}W(OCMe_2CF_3)_3]_2[\mu{-}\kappa_1\kappa_1{-}DME]$ view B.

Structure Determination.

Pale yellow to colorless blocks of $[EtC{\equiv}W(OCMe_2CF_3)_3]_2[\mu{-}\kappa_1\kappa_1{-}DME]$ (**ag1572**) were grown from a pentane solution at -35 °C. A crystal of dimensions 0.38 x 0.28 x 0.15 mm mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 5190 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 7 s/frame. The integration of the data yielded a total of 113219 reflections to a maximum 2θ value of 60.26° of which 6513 were independent and 6089 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9996 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package, using the space group P2(1)/n with Z = 2 for the formula $C_{34}H_{56}O_8F_{18}Mo_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The dimeric complex lies on a crystallographic inversion center of the lattice which bisects a bridging dimethoxyethane (DME) ligand. The DME is disordered over two orientations. One of the 2,2,2-trifluoro-t-butoxy ligands and its inversion-related partner are also disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0227 and wR2 = 0.0615 [based on I > 2sigma(I)], R1 = 0.0247 and wR2 = 0.0632 for all data.

Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray, Madison, WI, 2008.

Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Saint Plus, v. 7.53A, Bruker Analytical X-ray, Madison, WI, 2008.

Table A3.1. Crystal data and structure refinement for ag1572.

Identification code	ag1572
Empirical formula	C34 H56 F18 Mo2 O8
Formula weight	1126.67
Temperature	85(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 14.8875(11) Å alpha = 90 deg. b = 9.8968(7) Å beta = 113.9990(10) deg. c = 17.1654(13) Å gamma = 90 deg.
Volume	2310.5(3) Å ^3
Z, Calculated density	2, 1.619 Mg/m^3
Absorption coefficient	0.659 mm^-1
F(000)	1140
Crystal size	0.38 x 0.28 x 0.15 mm
Theta range for data collection	2.35 to 29.63 deg.
Limiting indices	-20<=h<=20, -13<=k<=13, -23<=l<=23
Reflections collected / unique	113219 / 6513 [R(int) = 0.0280]
Completeness to theta = 29.63	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6513 / 42 / 353
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0227, wR2 = 0.0615

R indices (all data)	R1 = 0.0247, wR2 = 0.0632
Largest diff. peak and hole	0.640 and -0.406 e. Å^-3

Table A3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ag1572. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	7289(1)	1482(1)	4959(1)	13(1)
O(1)	6613(1)	515(1)	3926(1)	17(1)
O(2)	7640(1)	491(1)	5989(1)	19(1)
O(3)	6820(1)	3265(1)	4963(1)	17(1)
O(4)	5687(1)	1036(1)	4984(1)	20(1)
F(1)	5079(1)	152(1)	2407(1)	37(1)
F(2)	5745(1)	-1722(1)	2992(1)	39(1)
F(3)	5949(1)	-977(1)	1899(1)	44(1)
F(4)	7742(1)	-2002(1)	6714(1)	49(1)
F(5)	7499(1)	-376(2)	7422(1)	47(1)
F(6)	8911(1)	-1345(2)	7885(1)	48(1)
F(7)	6195(2)	5464(2)	5566(2)	32(1)
F(8)	5593(2)	5416(2)	4200(2)	34(1)
F(9)	6690(2)	6902(2)	4885(2)	34(1)
F(7A)	6340(2)	4721(2)	3519(1)	35(1)
F(8A)	7322(2)	6333(2)	4198(2)	29(1)
F(9A)	7898(2)	4387(2)	4076(1)	23(1)
C(1)	6810(1)	173(2)	3212(1)	20(1)
C(2)	5891(1)	-597(2)	2632(1)	28(1)
C(3)	6921(2)	1442(2)	2757(1)	27(1)
C(4)	7704(1)	-744(2)	3457(1)	31(1)
C(5)	8517(1)	105(2)	6686(1)	23(1)
C(6)	8162(1)	-915(2)	7173(1)	33(1)
C(7)	9231(2)	-615(2)	6399(1)	39(1)
C(8)	8973(2)	1321(2)	7242(1)	40(1)
C(9)	7160(1)	4606(2)	4994(1)	28(1)
C(10)	6379(4)	5624(4)	4904(3)	26(1)
C(10A)	6324(3)	5374(5)	5162(4)	27(1)
C(11)	8111(1)	4842(2)	5772(1)	23(1)
C(12)	7422(4)	4818(5)	4180(3)	28(1)
C(12A)	7147(4)	5018(5)	4159(3)	27(1)

C(13)	4782(2)	707(3)	4294(2)	20(1)
C(14)	4517(2)	-760(4)	4301(2)	21(1)
C(15)	5558(2)	1662(4)	5697(2)	25(1)
C(16)	4872(2)	1702(4)	4289(2)	26(1)
C(17)	8425(1)	1762(1)	4910(1)	17(1)
C(18)	9364(1)	1941(2)	4805(1)	23(1)
C(19)	10085(1)	2939(2)	5396(2)	43(1)

Table A3.3. Bond lengths [Å] and angles [deg] for ag1572.

Mo(1)-C(17)	1.7499(14)
Mo(1)-O(3)	1.8989(10)
Mo(1)-O(2)	1.8994(10)
Mo(1)-O(1)	1.9039(10)
Mo(1)-O(4)	2.4430(10)
O(1)-C(1)	1.4123(17)
O(2)-C(5)	1.4176(17)
O(3)-C(9)	1.4133(19)
O(4)-C(14)#1	1.405(3)
O(4)-C(13)	1.423(3)
O(4)-C(15)	1.453(3)
O(4)-C(16)	1.467(3)
F(1)-C(2)	1.334(2)
F(2)-C(2)	1.334(2)
F(3)-C(2)	1.3490(19)
F(4)-C(6)	1.330(3)
F(5)-C(6)	1.336(2)
F(6)-C(6)	1.344(2)
F(7)-C(10)	1.284(5)
F(8)-C(10)	1.312(6)
F(9)-C(10)	1.351(5)
F(7A)-C(12A)	1.290(5)
F(8A)-C(12A)	1.324(5)
F(9A)-C(12A)	1.337(5)
C(1)-C(4)	1.522(2)
C(1)-C(3)	1.522(2)
C(1)-C(2)	1.528(2)
C(5)-C(8)	1.515(3)
C(5)-C(7)	1.518(2)
C(5)-C(6)	1.536(2)
C(9)-C(12A)	1.482(4)
C(9)-C(10)	1.498(4)
C(9)-C(11)	1.518(2)

C(9)-C(10A)	1.583(4)
C(9)-C(12)	1.610(4)
C(13)-C(14)	1.506(5)
C(14)-O(4)#1	1.405(3)
C(17)-C(18)	1.490(2)
C(18)-C(19)	1.507(3)
C(17)-Mo(1)-O(3)	102.51(6)
C(17)-Mo(1)-O(2)	102.80(6)
O(3)-Mo(1)-O(2)	116.04(5)
C(17)-Mo(1)-O(1)	100.90(6)
O(3)-Mo(1)-O(1)	114.50(4)
O(2)-Mo(1)-O(1)	116.70(5)
C(17)-Mo(1)-O(4)	177.92(5)
O(3)-Mo(1)-O(4)	78.78(4)
O(2)-Mo(1)-O(4)	77.96(4)
O(1)-Mo(1)-O(4)	77.05(4)
C(1)-O(1)-Mo(1)	135.40(9)
C(5)-O(2)-Mo(1)	137.25(9)
C(9)-O(3)-Mo(1)	138.27(10)
C(14)#1-O(4)-C(13)	102.43(18)
C(14)#1-O(4)-C(15)	36.64(19)
C(13)-O(4)-C(15)	113.24(19)
C(14)#1-O(4)-C(16)	113.38(19)
C(13)-O(4)-C(16)	40.23(19)
C(15)-O(4)-C(16)	98.3(2)
C(14)#1-O(4)-Mo(1)	127.54(14)
C(13)-O(4)-Mo(1)	128.82(13)
C(15)-O(4)-Mo(1)	113.71(15)
C(16)-O(4)-Mo(1)	113.23(14)
O(1)-C(1)-C(4)	111.68(13)
O(1)-C(1)-C(3)	110.56(12)
C(4)-C(1)-C(3)	111.61(14)
O(1)-C(1)-C(2)	103.78(12)
C(4)-C(1)-C(2)	109.51(13)
C(3)-C(1)-C(2)	109.40(14)
F(1)-C(2)-F(2)	107.38(15)
F(1)-C(2)-F(3)	106.25(14)
F(2)-C(2)-F(3)	106.53(14)
F(1)-C(2)-C(1)	112.15(14)
F(2)-C(2)-C(1)	112.64(14)
F(3)-C(2)-C(1)	111.49(14)
O(2)-C(5)-C(8)	109.91(14)
O(2)-C(5)-C(7)	112.31(13)
C(8)-C(5)-C(7)	112.52(17)
O(2)-C(5)-C(6)	103.56(13)
C(8)-C(5)-C(6)	110.13(15)

C(7)-C(5)-C(6)	108.01(15)
F(4)-C(6)-F(5)	106.43(17)
F(4)-C(6)-F(6)	107.44(17)
F(5)-C(6)-F(6)	106.51(15)
F(4)-C(6)-C(5)	112.99(15)
F(5)-C(6)-C(5)	111.94(16)
F(6)-C(6)-C(5)	111.16(15)
O(3)-C(9)-C(12A)	111.0(2)
O(3)-C(9)-C(10)	112.1(2)
C(12A)-C(9)-C(10)	90.6(3)
O(3)-C(9)-C(11)	111.66(13)
C(12A)-C(9)-C(11)	116.6(2)
C(10)-C(9)-C(11)	113.2(2)
O(3)-C(9)-C(10A)	99.3(2)
C(12A)-C(9)-C(10A)	110.0(3)
C(10)-C(9)-C(10A)	20.06(16)
C(11)-C(9)-C(10A)	106.7(2)
O(3)-C(9)-C(12)	107.4(2)
C(12A)-C(9)-C(12)	15.8(2)
C(10)-C(9)-C(12)	105.9(3)
C(11)-C(9)-C(12)	105.9(2)
C(10A)-C(9)-C(12)	125.6(3)
F(7)-C(10)-F(8)	111.4(5)
F(7)-C(10)-F(9)	109.6(4)
F(8)-C(10)-F(9)	108.1(3)
F(7)-C(10)-C(9)	105.2(3)
F(8)-C(10)-C(9)	110.7(4)
F(9)-C(10)-C(9)	111.9(4)
F(7A)-C(12A)-F(8A)	111.2(3)
F(7A)-C(12A)-F(9A)	109.4(4)
F(8A)-C(12A)-F(9A)	107.9(4)
F(7A)-C(12A)-C(9)	113.7(4)
F(8A)-C(12A)-C(9)	107.3(4)
F(9A)-C(12A)-C(9)	107.0(3)
O(4)-C(13)-C(14)	112.1(2)
O(4)#1-C(14)-C(13)	110.2(2)
C(18)-C(17)-Mo(1)	175.59(12)
C(17)-C(18)-C(19)	116.31(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Table A3.4. Anisotropic displacement parameters (A^2 x 10^3) for ag1572. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo(1)	13(1)	15(1)	12(1)	1(1)	6(1)	1(1)
O(1)	20(1)	18(1)	14(1)	-1(1)	7(1)	-1(1)
O(2)	17(1)	25(1)	14(1)	5(1)	6(1)	4(1)
O(3)	16(1)	17(1)	19(1)	-1(1)	7(1)	2(1)
O(4)	16(1)	28(1)	19(1)	2(1)	9(1)	1(1)
F(1)	28(1)	48(1)	25(1)	-8(1)	1(1)	1(1)
F(2)	45(1)	29(1)	38(1)	-8(1)	13(1)	-16(1)
F(3)	55(1)	51(1)	26(1)	-22(1)	18(1)	-12(1)
F(4)	56(1)	36(1)	47(1)	17(1)	13(1)	-2(1)
F(5)	40(1)	80(1)	31(1)	23(1)	24(1)	17(1)
F(6)	40(1)	72(1)	28(1)	29(1)	10(1)	18(1)
F(7)	31(1)	33(1)	34(1)	-3(1)	16(1)	3(1)
F(8)	24(1)	34(1)	36(1)	-1(1)	3(1)	6(1)
F(9)	36(1)	21(1)	44(1)	0(1)	16(1)	4(1)
F(7A)	27(1)	41(1)	22(1)	13(1)	-4(1)	-10(1)
F(8A)	31(1)	12(1)	45(1)	12(1)	15(1)	-1(1)
F(9A)	31(1)	20(1)	25(1)	7(1)	18(1)	3(1)
C(1)	26(1)	18(1)	17(1)	-3(1)	10(1)	0(1)
C(2)	34(1)	29(1)	21(1)	-8(1)	10(1)	-4(1)
C(3)	40(1)	27(1)	19(1)	1(1)	15(1)	-3(1)
C(4)	32(1)	25(1)	37(1)	-9(1)	15(1)	6(1)
C(5)	19(1)	33(1)	17(1)	8(1)	7(1)	7(1)
C(6)	31(1)	46(1)	22(1)	16(1)	11(1)	10(1)
C(7)	34(1)	56(1)	33(1)	20(1)	19(1)	27(1)
C(8)	30(1)	46(1)	28(1)	-1(1)	-3(1)	1(1)
C(9)	26(1)	13(1)	29(1)	-4(1)	-3(1)	4(1)
C(10)	33(2)	13(2)	20(2)	6(1)	-2(2)	9(2)
C(10A)	26(2)	12(2)	35(3)	6(2)	3(2)	7(1)
C(11)	19(1)	24(1)	23(1)	-5(1)	5(1)	2(1)
C(12)	28(2)	16(2)	25(2)	11(1)	-6(1)	-1(2)
C(12A)	22(2)	15(2)	29(2)	11(1)	-4(1)	1(1)
C(13)	16(1)	29(2)	17(1)	3(1)	7(1)	-1(1)
C(14)	16(1)	30(2)	20(1)	1(1)	10(1)	-2(1)
C(15)	23(1)	35(2)	20(1)	-3(1)	12(1)	3(1)
C(16)	17(1)	33(2)	29(2)	11(1)	9(1)	7(1)
C(17)	17(1)	17(1)	16(1)	1(1)	7(1)	2(1)
C(18)	18(1)	27(1)	28(1)	6(1)	12(1)	3(1)

C(19)	20(1)	53(1)	60(1)	-18(1)	19(1)	-9(1)

Table A3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ag1572.

	x	y	z	U(eq)
H(3A)	6342	2020	2623	41
H(3B)	6980	1188	2228	41
H(3C)	7512	1934	3127	41
H(4A)	8288	-265	3852	47
H(4B)	7799	-997	2944	47
H(4C)	7601	-1560	3734	47
H(7A)	8892	-1360	6017	58
H(7B)	9781	-973	6899	58
H(7C)	9479	24	6098	58
H(8A)	9171	1983	6917	59
H(8B)	9552	1035	7744	59
H(8C)	8493	1732	7426	59
H(10A)	5688	5215	4685	41
H(10B)	6465	6345	5216	41
H(10C)	6299	5038	5690	41
H(11A)	7997	4714	6290	35
H(11B)	8342	5766	5758	35
H(11C)	8610	4198	5769	35
H(12A)	7969	4223	4229	43
H(12B)	7611	5760	4157	43
H(12C)	6846	4598	3658	43
H(13A)	4833	914	3749	24
H(13B)	4252	1275	4328	24
H(14A)	3934	-976	3774	25
H(14B)	5069	-1334	4317	25
H(15A)	5039	1188	5801	37
H(15B)	5372	2611	5564	37
H(15C)	6175	1608	6208	37
H(16A)	4249	1286	4225	39
H(16B)	4960	1601	3756	39
H(16C)	4863	2664	4420	39
H(18A)	9202	2229	4211	28
H(18B)	9693	1051	4885	28
H(19A)	9797	3846	5284	65
H(19B)	10690	2932	5299	65
H(19C)	10238	2688	5988	65

Appendix Four:

Crystallographic Data for EtC≡Mo(OC(CF_3)$_3$)$_3$(NCEt)

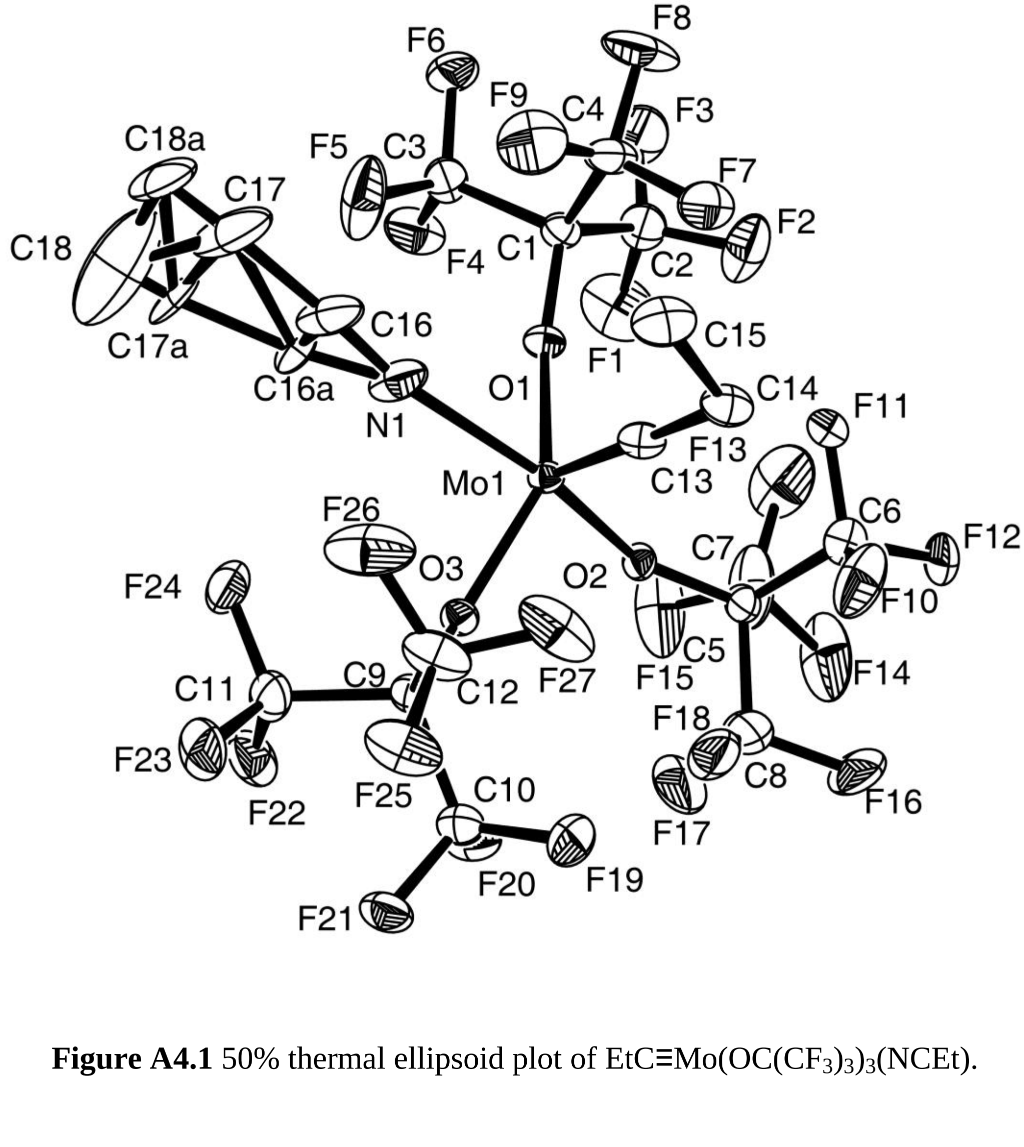

Figure A4.1 50% thermal ellipsoid plot of EtC≡Mo(OC(CF_3)$_3$)$_3$(NCEt).

Structure Determination.

Orange needles of EtC≡Mo(OC(CF_3)$_3$)$_3$(NCEt) (**ag1458**) were grown from a toluene solution at 25 deg. C. A crystal of dimensions 0.32 x 0.14 x 0.11 mm mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3490 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 15 s/frame. The integration of the data yielded a total of 90081 reflections to a maximum 2θ value of 60.20° of which 7850 were independent and 7227 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 9987 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package, using the space group P2(1)/n with Z = 4 for the formula $C_{18}H_{10}F_{27}NO_3Mo$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The propionitrile ligand is disordered over two positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0402 and wR2 = 0.1040 [based on I > 2sigma(I)], R1 = 0.0436 and wR2 = 0.1069 for all data.

Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray, Madison, WI, 2008.

Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Saint Plus, v. 7.53, Bruker Analytical X-ray, Madison, WI, 2006.

Table A4.1. Crystal data and structure refinement for ag1458.

Identification code	ag1458
Empirical formula	C18 H10 F27 Mo N O3
Formula weight	897.21
Temperature	85(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.9445(9) Å alpha = 90 deg. b = 18.1387(15) Å beta = 110.8650(10) deg. c = 15.0623(12) Å gamma = 90 deg.
Volume	2794.1(4) Å ^3
Z, Calculated density	4, 2.133 Mg/m^3
Absorption coefficient	0.676 mm^-1
F(000)	1736
Crystal size	0.32 x 0.14 x 0.11 mm
Theta range for data collection	1.83 to 29.60 deg.
Limiting indices	-15<=h<=15, -25<=k<=25, -20<=l<=20
Reflections collected / unique	90081 / 7850 [R(int) = 0.0433]
Completeness to theta = 29.60	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9294 and 0.8128
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	7850 / 39 / 496
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1040
R indices (all data)	R1 = 0.0436, wR2 = 0.1069
Largest diff. peak and hole	1.328 and -0.840 e. Å ^-3

Table A4.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^2 x 10^3) for ag1458. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	9835(1)	59(1)	7774(1)	16(1)
O(1)	8494(2)	-648(1)	7052(1)	20(1)
O(2)	11202(2)	-680(1)	8058(1)	19(1)
O(3)	10643(2)	582(1)	8974(1)	18(1)
F(1)	8496(3)	-2051(1)	6717(2)	65(1)
F(2)	8773(2)	-1552(1)	5554(2)	52(1)
F(3)	6897(2)	-2011(1)	5393(2)	58(1)
F(4)	6453(2)	-1532(1)	7153(1)	49(1)
F(5)	6016(2)	-401(1)	6949(2)	63(1)
F(6)	5214(2)	-1167(1)	5790(1)	40(1)
F(7)	8251(2)	-138(1)	5260(1)	39(1)
F(8)	6337(2)	-594(2)	4630(1)	61(1)
F(9)	6677(2)	284(1)	5622(2)	55(1)
F(10)	12664(2)	-11(1)	6916(2)	52(1)
F(11)	11064(2)	-770(1)	6228(1)	33(1)
F(12)	13041(2)	-1163(1)	6605(1)	41(1)
F(13)	11329(3)	-2058(1)	7082(2)	70(1)
F(14)	13403(3)	-2093(2)	8095(2)	75(1)
F(15)	11849(3)	-2012(1)	8635(2)	73(1)
F(16)	14564(2)	-764(2)	8384(2)	81(1)
F(17)	13659(2)	-1026(2)	9473(1)	90(1)
F(18)	13444(2)	64(1)	8758(2)	59(1)
F(19)	13281(2)	1300(1)	9613(1)	38(1)
F(20)	12815(2)	448(1)	10422(1)	32(1)
F(21)	12875(2)	1578(1)	10868(1)	30(1)
F(22)	10738(2)	759(1)	10885(1)	39(1)

F(23)	10376(2)	1925(1)	10596(1)	43(1)
F(24)	9025(2)	1121(1)	9752(2)	44(1)
F(25)	11460(2)	2491(1)	9406(1)	40(1)
F(26)	9571(2)	2066(1)	8511(2)	54(1)
F(27)	11283(2)	1828(1)	8192(1)	48(1)
C(1)	7501(2)	-875(1)	6263(2)	21(1)
C(2)	7891(3)	-1627(2)	5947(2)	32(1)
C(3)	6257(3)	-990(2)	6529(2)	29(1)
C(4)	7185(3)	-320(2)	5430(2)	30(1)
C(5)	12253(2)	-944(1)	7876(2)	23(1)
C(6)	12257(3)	-722(2)	6884(2)	35(1)
C(7)	12195(5)	-1807(2)	7929(3)	61(1)
C(8)	13514(3)	-660(3)	8648(3)	58(1)
C(9)	11051(2)	1205(1)	9501(2)	19(1)
C(10)	12537(3)	1129(2)	10120(2)	26(1)
C(11)	10276(3)	1267(2)	10188(2)	32(1)
C(12)	10855(3)	1909(2)	8893(2)	35(1)
C(13)	10083(2)	623(1)	6933(2)	22(1)
C(14)	10269(3)	1114(1)	6209(2)	25(1)
C(15)	9211(3)	1706(2)	5874(2)	33(1)
N(1)	8107(2)	687(1)	7716(2)	36(1)
C(16)	7159(4)	1013(3)	7547(4)	42(1)
C(17)	5906(4)	1374(3)	7402(5)	72(2)
C(18)	5496(8)	1262(4)	8197(8)	108(4)
C(16A)	7241(11)	830(6)	7986(11)	20(3)
C(17A)	6093(10)	1116(7)	8163(10)	33(3)
C(18A)	5032(14)	1405(10)	7388(12)	51(5)

Table A4.3. Bond lengths [Å] and angles [deg] for ag1458.

Mo(1)-C(13)	1.722(2)
Mo(1)-O(2)	1.9390(16)
Mo(1)-O(3)	1.9528(16)
Mo(1)-O(1)	1.9604(16)
Mo(1)-N(1)	2.182(2)
O(1)-C(1)	1.359(3)
O(2)-C(5)	1.360(3)
O(3)-C(9)	1.361(3)
F(1)-C(2)	1.352(4)
F(2)-C(2)	1.306(3)
F(3)-C(2)	1.311(3)
F(4)-C(3)	1.324(3)
F(5)-C(3)	1.315(3)

F(6)-C(3)	1.319(3)
F(7)-C(4)	1.323(3)
F(8)-C(4)	1.328(3)
F(9)-C(4)	1.308(4)
F(10)-C(6)	1.360(4)
F(11)-C(6)	1.330(3)
F(12)-C(6)	1.345(3)
F(13)-C(7)	1.368(6)
F(14)-C(7)	1.357(4)
F(15)-C(7)	1.304(4)
F(16)-C(8)	1.356(4)
F(17)-C(8)	1.368(5)
F(18)-C(8)	1.329(5)
F(19)-C(10)	1.336(3)
F(20)-C(10)	1.314(3)
F(21)-C(10)	1.331(3)
F(22)-C(11)	1.352(4)
F(23)-C(11)	1.329(3)
F(24)-C(11)	1.317(3)
F(25)-C(12)	1.336(3)
F(26)-C(12)	1.345(4)
F(27)-C(12)	1.307(4)
C(1)-C(4)	1.549(3)
C(1)-C(2)	1.553(4)
C(1)-C(3)	1.564(3)
C(5)-C(8)	1.542(4)
C(5)-C(6)	1.550(4)
C(5)-C(7)	1.571(5)
C(9)-C(12)	1.541(4)
C(9)-C(11)	1.557(3)
C(9)-C(10)	1.567(3)
C(13)-C(14)	1.477(3)
C(14)-C(15)	1.528(4)
N(1)-C(16)	1.142(4)
N(1)-C(16A)	1.185(8)
C(16)-C(17)	1.463(5)
C(17)-C(18)	1.435(9)
C(16A)-C(17A)	1.470(9)
C(17A)-C(18A)	1.421(11)

C(13)-Mo(1)-O(2)	105.16(9)
C(13)-Mo(1)-O(3)	104.72(9)
O(2)-Mo(1)-O(3)	94.16(7)
C(13)-Mo(1)-O(1)	105.30(9)
O(2)-Mo(1)-O(1)	92.10(7)
O(3)-Mo(1)-O(1)	146.48(7)

C(13)-Mo(1)-N(1)	91.30(11)
O(2)-Mo(1)-N(1)	163.43(9)
O(3)-Mo(1)-N(1)	83.30(8)
O(1)-Mo(1)-N(1)	81.47(8)
C(1)-O(1)-Mo(1)	153.10(15)
C(5)-O(2)-Mo(1)	147.11(15)
C(9)-O(3)-Mo(1)	152.85(15)
O(1)-C(1)-C(4)	112.91(19)
O(1)-C(1)-C(2)	108.3(2)
C(4)-C(1)-C(2)	109.2(2)
O(1)-C(1)-C(3)	108.30(19)
C(4)-C(1)-C(3)	109.3(2)
C(2)-C(1)-C(3)	108.8(2)
F(2)-C(2)-F(3)	110.3(2)
F(2)-C(2)-F(1)	103.4(3)
F(3)-C(2)-F(1)	106.6(3)
F(2)-C(2)-C(1)	112.1(2)
F(3)-C(2)-C(1)	113.9(2)
F(1)-C(2)-C(1)	109.9(2)
F(5)-C(3)-F(6)	110.1(3)
F(5)-C(3)-F(4)	105.8(3)
F(6)-C(3)-F(4)	106.9(2)
F(5)-C(3)-C(1)	110.9(2)
F(6)-C(3)-C(1)	112.7(2)
F(4)-C(3)-C(1)	110.1(2)
F(9)-C(4)-F(7)	107.8(3)
F(9)-C(4)-F(8)	107.4(3)
F(7)-C(4)-F(8)	107.3(2)
F(9)-C(4)-C(1)	110.9(2)
F(7)-C(4)-C(1)	111.2(2)
F(8)-C(4)-C(1)	111.9(2)
O(2)-C(5)-C(8)	109.0(2)
O(2)-C(5)-C(6)	113.3(2)
C(8)-C(5)-C(6)	109.3(3)
O(2)-C(5)-C(7)	106.8(2)
C(8)-C(5)-C(7)	109.6(3)
C(6)-C(5)-C(7)	108.7(2)
F(11)-C(6)-F(12)	107.2(2)
F(11)-C(6)-F(10)	108.1(3)
F(12)-C(6)-F(10)	109.7(2)
F(11)-C(6)-C(5)	111.1(2)
F(12)-C(6)-C(5)	111.6(2)
F(10)-C(6)-C(5)	109.0(2)
F(15)-C(7)-F(14)	106.7(3)
F(15)-C(7)-F(13)	111.1(4)
F(14)-C(7)-F(13)	110.5(3)

F(15)-C(7)-C(5)	110.7(3)
F(14)-C(7)-C(5)	109.6(4)
F(13)-C(7)-C(5)	108.2(3)
F(18)-C(8)-F(16)	105.5(4)
F(18)-C(8)-F(17)	111.1(3)
F(16)-C(8)-F(17)	111.3(3)
F(18)-C(8)-C(5)	110.3(3)
F(16)-C(8)-C(5)	110.9(3)
F(17)-C(8)-C(5)	107.8(4)
O(3)-C(9)-C(12)	113.16(19)
O(3)-C(9)-C(11)	107.75(19)
C(12)-C(9)-C(11)	110.0(2)
O(3)-C(9)-C(10)	109.20(19)
C(12)-C(9)-C(10)	108.8(2)
C(11)-C(9)-C(10)	107.9(2)
F(20)-C(10)-F(21)	108.9(2)
F(20)-C(10)-F(19)	107.6(2)
F(21)-C(10)-F(19)	107.4(2)
F(20)-C(10)-C(9)	110.6(2)
F(21)-C(10)-C(9)	111.5(2)
F(19)-C(10)-C(9)	110.7(2)
F(24)-C(11)-F(23)	108.1(2)
F(24)-C(11)-F(22)	106.6(2)
F(23)-C(11)-F(22)	107.8(2)
F(24)-C(11)-C(9)	111.7(2)
F(23)-C(11)-C(9)	113.4(2)
F(22)-C(11)-C(9)	109.0(2)
F(27)-C(12)-F(25)	108.0(3)
F(27)-C(12)-F(26)	107.4(2)
F(25)-C(12)-F(26)	107.9(2)
F(27)-C(12)-C(9)	111.9(2)
F(25)-C(12)-C(9)	112.1(2)
F(26)-C(12)-C(9)	109.4(2)
C(14)-C(13)-Mo(1)	178.8(2)
C(13)-C(14)-C(15)	112.4(2)
C(16)-N(1)-C(16A)	35.8(6)
C(16)-N(1)-Mo(1)	170.1(4)
C(16A)-N(1)-Mo(1)	152.6(7)
N(1)-C(16)-C(17)	173.5(8)
C(18)-C(17)-C(16)	111.5(6)
N(1)-C(16A)-C(17A)	168.4(14)
C(18A)-C(17A)-C(16A)	118.9(14)

Symmetry transformations used to generate equivalent atoms:

Table A4.4. Anisotropic displacement parameters (Å ^2 x 10^3) for ag1458. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo(1)	15(1)	14(1)	16(1)	0(1)	3(1)	1(1)
O(1)	20(1)	18(1)	19(1)	-1(1)	3(1)	-2(1)
O(2)	19(1)	20(1)	18(1)	2(1)	7(1)	5(1)
O(3)	19(1)	16(1)	19(1)	-3(1)	6(1)	-1(1)
F(1)	94(2)	29(1)	63(2)	0(1)	17(1)	9(1)
F(2)	42(1)	45(1)	80(2)	-21(1)	38(1)	-8(1)
F(3)	48(1)	57(1)	68(2)	-37(1)	20(1)	-21(1)
F(4)	45(1)	72(1)	29(1)	9(1)	10(1)	-28(1)
F(5)	58(1)	51(1)	105(2)	-39(1)	61(1)	-26(1)
F(6)	21(1)	62(1)	34(1)	-2(1)	5(1)	-12(1)
F(7)	34(1)	50(1)	31(1)	10(1)	9(1)	-14(1)
F(8)	50(1)	95(2)	22(1)	11(1)	-8(1)	-46(1)
F(9)	61(1)	46(1)	54(1)	23(1)	14(1)	25(1)
F(10)	43(1)	51(1)	75(2)	21(1)	38(1)	5(1)
F(11)	25(1)	55(1)	19(1)	-3(1)	6(1)	2(1)
F(12)	32(1)	66(1)	33(1)	-7(1)	20(1)	11(1)
F(13)	64(2)	43(1)	110(2)	-37(1)	40(2)	-7(1)
F(14)	101(2)	68(2)	78(2)	29(1)	58(2)	65(2)
F(15)	124(2)	40(1)	90(2)	37(1)	80(2)	44(1)
F(16)	18(1)	144(3)	74(2)	-61(2)	8(1)	10(1)
F(17)	53(1)	187(3)	21(1)	4(1)	1(1)	64(2)
F(18)	28(1)	84(2)	66(2)	-51(1)	19(1)	-15(1)
F(19)	28(1)	51(1)	41(1)	-7(1)	18(1)	-12(1)
F(20)	27(1)	27(1)	32(1)	-2(1)	0(1)	3(1)
F(21)	30(1)	32(1)	24(1)	-9(1)	4(1)	-7(1)
F(22)	49(1)	45(1)	29(1)	-6(1)	22(1)	-16(1)
F(23)	44(1)	38(1)	52(1)	-26(1)	24(1)	-4(1)
F(24)	23(1)	58(1)	53(1)	-25(1)	18(1)	-6(1)
F(25)	59(1)	18(1)	34(1)	-2(1)	3(1)	-9(1)
F(26)	51(1)	28(1)	56(1)	-2(1)	-14(1)	10(1)
F(27)	83(2)	32(1)	26(1)	1(1)	16(1)	-24(1)
C(1)	20(1)	21(1)	20(1)	-1(1)	6(1)	-6(1)
C(2)	33(1)	28(1)	36(1)	-11(1)	12(1)	-8(1)

C(3)	28(1)	32(1)	31(1)	-8(1)	13(1)	-13(1)
C(4)	23(1)	40(1)	22(1)	5(1)	0(1)	-9(1)
C(5)	21(1)	29(1)	19(1)	-1(1)	7(1)	8(1)
C(6)	28(1)	46(2)	32(1)	-4(1)	13(1)	1(1)
C(7)	82(3)	44(2)	79(3)	23(2)	58(3)	36(2)
C(8)	27(2)	103(3)	37(2)	-19(2)	3(1)	18(2)
C(9)	20(1)	18(1)	19(1)	-3(1)	7(1)	-2(1)
C(10)	24(1)	28(1)	24(1)	-4(1)	6(1)	-4(1)
C(11)	30(1)	33(1)	38(1)	-16(1)	17(1)	-7(1)
C(12)	49(2)	20(1)	27(1)	-1(1)	2(1)	-5(1)
C(13)	22(1)	19(1)	20(1)	1(1)	2(1)	0(1)
C(14)	28(1)	22(1)	22(1)	5(1)	4(1)	-2(1)
C(15)	33(1)	25(1)	34(1)	12(1)	4(1)	2(1)
N(1)	20(1)	29(1)	49(1)	-16(1)	0(1)	3(1)
C(16)	23(2)	33(2)	54(3)	-22(2)	-8(2)	7(2)
C(17)	24(2)	65(3)	99(5)	-53(3)	-13(2)	18(2)
C(18)	77(5)	52(4)	226(11)	20(5)	90(7)	14(4)
C(16A)	15(4)	12(4)	35(6)	9(4)	11(4)	7(3)
C(17A)	10(5)	31(5)	58(7)	3(5)	12(4)	10(4)
C(18A)	19(6)	53(9)	62(9)	-18(7)	-8(6)	18(5)

Table A4.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^2 x 10^3) for ag1458.

	x	y	z	U(eq)
H(14A)	10259	815	5657	30
H(14B)	11135	1354	6478	30
H(15A)	9374	2017	5395	49
H(15B)	9229	2011	6416	49
H(15C)	8352	1471	5596	49
H(17A)	5988	1909	7306	87
H(17B)	5234	1174	6821	87
H(18A)	4665	1518	8082	163
H(18B)	6161	1459	8773	163
H(18C)	5382	734	8278	163
H(17C)	5746	712	8448	39
H(17D)	6398	1509	8648	39
H(18D)	4433	1668	7630	76
H(18E)	4564	1000	6975	76