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SYNTHESIS, STRUCTURE, AND APPLICATIONS OF METALLACYCLIC ALKYLIDENE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

presented by

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of the requirements for the

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Major Professor's Signature

4/10/09

Date

SYNTHESIS, STRUCTURE, AND APPLICATIONS OF METALLACYCLIC ALKYLIDENE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

By

Kapil Shyam Lokare

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ABSTRACT

SYNTHESIS, STRUCTURE, AND APPLICATIONS OF METALLACYCLIC ALKYLIDENE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

By

Kapil Shyam Lokare

Several molybdenum and tungsten metal complexes have been synthesized and characterized by single-crystal X-ray diffraction. The research has been focused primarily on two important aspects.

The first aspect involves the synthesis of the imido-tethered alkylidenes, which is an analogue of the Schrock olefin metathesis system and has been characterized by single-crystal X-ray diffraction. To increase the stability, the complex was prepared with no β-hydrogens in the structure, and the tether long enough to prevent any ring-strain effects. Furthermore, the catalyst system has been applied to the study involving ring-closing metathesis (RCM) as well as ring-opening metathesis polymerization (ROMP).

The second aspect involves the synthesis and study of metallacycles, generated by the addition of cyclooctyne to molybdenum and tungsten bis(imido) complexes. The complexes show a large amount of alkylidene character as suggested by X-ray diffraction and NMR studies. The synthesis of various derivatives of these metallacycles and their application for the carbonyl-olefination reaction have been scrutinized. The cationic derivatives generated by addition of Lewis acids to the above complexes were found to be quite active.

Dedicated to my parents.

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I would also like to thank Dr. Richard J. Staples for his input and help with the crystallography of many complexes. My sincere thanks to Dr. Erin Vogel for her help and thoughtful insights with polymer chemistry study and her patience in helping me with collecting relevant data. I appreciate the help of Dr. David Szymanski and Mathew Parsons from the Department of Geological Sciences for their help in analyzing the resins synthesized in Chapter 6 for molybdenum content using ICP-MS. Much thanks goes to Daniel Holmes, who helped me in understanding and collecting data for various NMR experiments. Lab members Supriyo and Steve have been there to listen and share thoughts over the last couple of years.

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LIST OF ABBREVIATIONS

Ar	2,6-diisopropyl unless mentioned
COD	cycloocta-1,5-diene
DME(dme)	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphinoethane)
h	hours
HB(Pin)	4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane)
HOTf	trifluoromethanesulfonic acid (triflic acid)
Ind	indenyl
Pr^i	isopropyl
M	metal complex unless mentioned
m.p.	melting point
min	minutes
NMR	nuclear magnetic resonance
Nph	neophyl
R	alkyl
RCM	ring-closing metathesis
ROMP	ring-opening metathesis polymerization
RT(rt)	room temperature
THF(thf)	tetrahydrofuran

CHAPTER 1

OLEFIN METATHESIS

Introduction

Olefin metathesis among many others has developed into an important tool commonly used for the formation of carbon-carbon bonds.[1] Many simultaneous discoveries were made in the early 60s. Since then, there has been substantial progress in the development of catalysts for the olefin metathesis reaction.[2] A few recent articles discuss the ingenious applications of metathesis.[3]

$$R_1HC{=}CHR_2 + R_3HC{=}CHR_4 \rightleftharpoons R_1HC{=}CHR_3 + R_2HC{=}CHR_4 \qquad 1.1$$

Heckelsberg, Banks and Bailey at the Philips Petroleum Company discovered the olefin metathesis reaction in the early 60s.[4] The process, however, involved ill-defined heterogeneous catalysts consisting of metal salts and metal oxides; further, the activity of the catalyst varied with the proportion of the components and order in which the components were mixed.[2a] These ill defined, "black-box" type catalyst systems often suffered from a limited substrate scope and harsh reaction conditions.[2a,4] The name "Olefin Metathesis" was coined first by Calderon in 1967 at the Goodyear Tire and Rubber Company as represented in Equation 1.1.[5]

The development of homogeneous, well-defined catalyst systems for target-oriented application of the olefin metathesis reaction has been a key for the wide popularity of the reaction.[6] Indeed, by a rational choice of catalyst and planning of

reaction conditions it is possible to select exactly *which* functional groups will react in the given metathesis reaction.[1a]

A modification of Tebbe's reagent to form the titanacyclobutane complex (Chart 1.1) was studied extensively by Grubbs and coworkers was capable of polymerizing norbornene in a living fashion.[7] However, the catalyst was not functional group tolerant. Acids, Esters, ketones, and aldehydes reacted with the complex preferentially over olefins. Single component tantalum-based catalyst systems were developed by Schrock and coworkers and found to display similar activities in mediating olefin metathesis as the titanocyclobutane.[8] Five-coordinate tungsten complexes studied by Osborn and coworkers were also found to be efficient metathesis catalysts in the presence of a Lewis acid such as aluminium trichloride or gallium tribromide.[9]

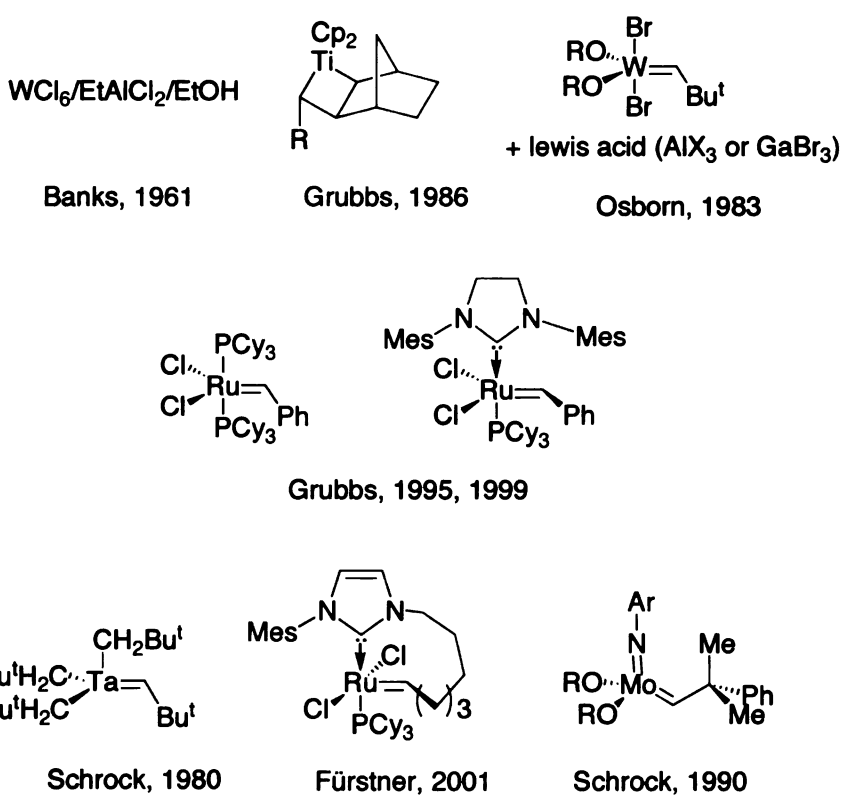


Chart 1.1 Some catalyst systems developed in the last 50 years.

Isolation of various catalytic systems eventually led to the development of well-defined metal complexes containing the M=CHR unit based on tungsten and molybdenum by Schrock and co-workers. Although the catalyst systems based on molybdenum and tungsten were highly active, the oxophilic nature and sensitivity to air and moisture limited their use.[1a]

Catalysts based on late transition metals such as ruthenium developed by Grubbs and co-workers were tuned to react exclusively with olefins and were perhaps the first well-defined air stable metathesis catalysts. These ruthenium-based Grubbs olefin metathesis systems gained wide acceptance among synthetic organic chemists due to ease of handling. Although the catalyst stability was significantly improved as compared to the early transition metal alkylidenes, the relative activity was reduced significantly. Transition metals in-group later than ruthenium give largely cyclopropanation and/or C-H activation products, i.e., moving towards the right in the periodic table does not seem to solve the problem.[10] Therefore, it is important to understand the present catalyst systems and, if necessary, alter the ancillary ligands around the metal center in order to tune the system for target-oriented reactions.

Olefin metathesis can be described as scrambling carbon atoms between a pair of double bonds. Depending on the nature of the starting olefin(s), (Figure 1.1) various interesting products may arise.[11]

Exchange/Cross Metathesis (CM)

Ring-Closing Metathesis (RCM)

Ring-Opening Metathesis Polymerization (ROMP)

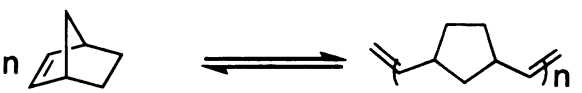
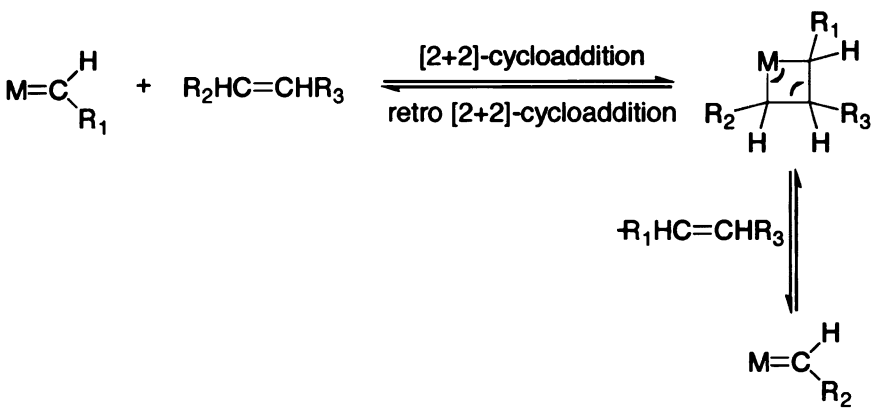


Figure 1.1 Schematic representations of some metathesis reactions.

The transformations shown above have the following common features:

(a) They involve an unprecedented mode of activation of the olefinic double bond. A series of elegant mechanistic studies in the late 60s and early 70s by Hérisson and Chauvin and Grubbs among many others provide evidence that the catalytic process involves a metathetic exchange of the alkylidene of the moieties of the olefin with an $M{=}CHR_1$ species (Scheme 1.1):



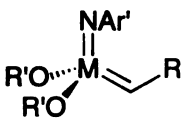
Scheme 1.1 The Chauvin Mechanism

(b) There is no change in the nature and number of the chemical bonds present before and after the transformation. Thus, common strategies for controlling the distribution of products include: relief of ring strain, relief of steric hindrance, and loss of a volatile olefin.

(c) The reactions are generally reversible, and with the right reaction conditions, equilibrium can be attained in a matter of seconds with extremely low catalyst to substrate ratios.

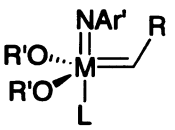
Thesis research

The general formula for Schrock-type catalyst systems is M(CHR')(NAr)$(X)_2$(L).(Figure 1.3) These complexes are d^0, 16 or 14 electron species depending on the presence or absence of donor ligands, which may be employed to avoid bimolecular decomposition.[1a]



M / R / Ar' / R'

Mo, W / CMe_2Ph / 2,6-Pr^i-C_6H_3 / $CMe(CF_3)_2$
Mo, W / CMe_2Ph / 2,6-Pr^i-C_6H_3 / CMe_3
Mo, W / CMe_3 / Ad / $CMe(CF_3)_2$
Mo, W / CMe_2Ph / Ad / CMe_3
Mo, W / CMe_3 / 2,6-Me-C_6H_3 / $CMe(CF_3)_2$
Mo, W / CMe_2Ph / 2,6-Me-C_6H_3 / CMe_3

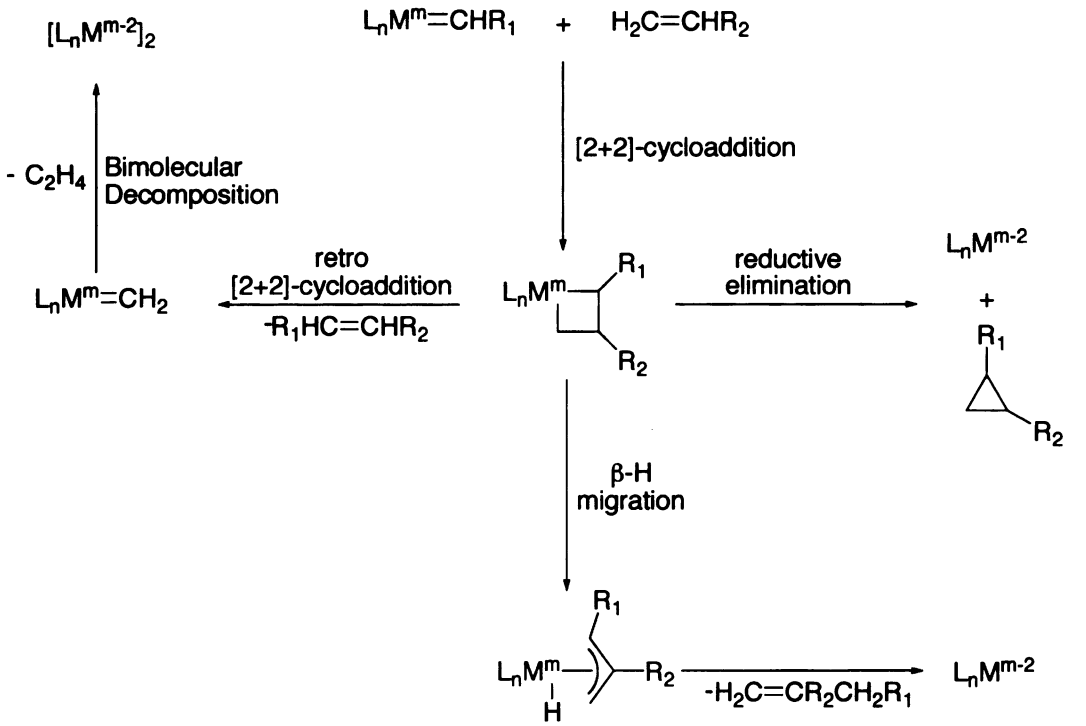


L = THF, quinuclidene, pyridine.

Figure 1.2 Schrock catalyst systems.

The Schrock-type olefin-metathesis systems (especially catalysts of the type M(CHBu^t)(NAr)$(OBu^t)_2$, M = Mo, W) discussed above have successfully been applied to ring-opening metathesis polymerization and (catalysts of the type M(CHBu^t)(NAr)$(OBu^t_{F6})_2$, M = Mo, W) to ring-closing metathesis/cross-metathesis reactions. However, there can be a significant amount of catalyst deactivation due to:

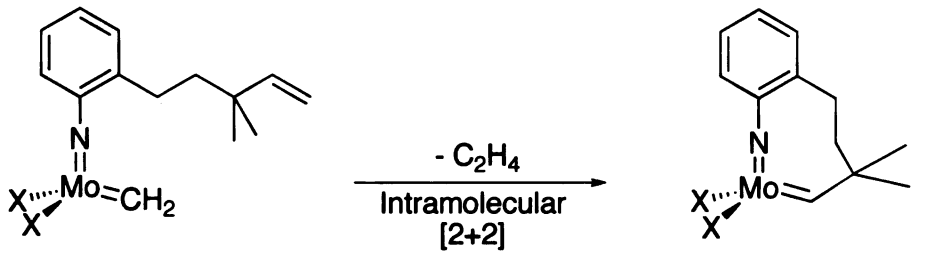
bimolecular decomposition of the methylidene, rearrangement of metallacyclobutane rings via β-H migration to olefins, and reductive elimination of the metallacyclobutane ring to afford cyclopropanation products.[12] Although the latter two decomposition pathways cannot be definitively avoided, it is perhaps trivial to circumvent the bimolecular decomposition of the active methylidene that is formed in an olefin metathesis reaction. (Scheme 1.2)



Scheme 1.2 Decomposition pathways of the metallacyclobutane and the active methylidene complex.

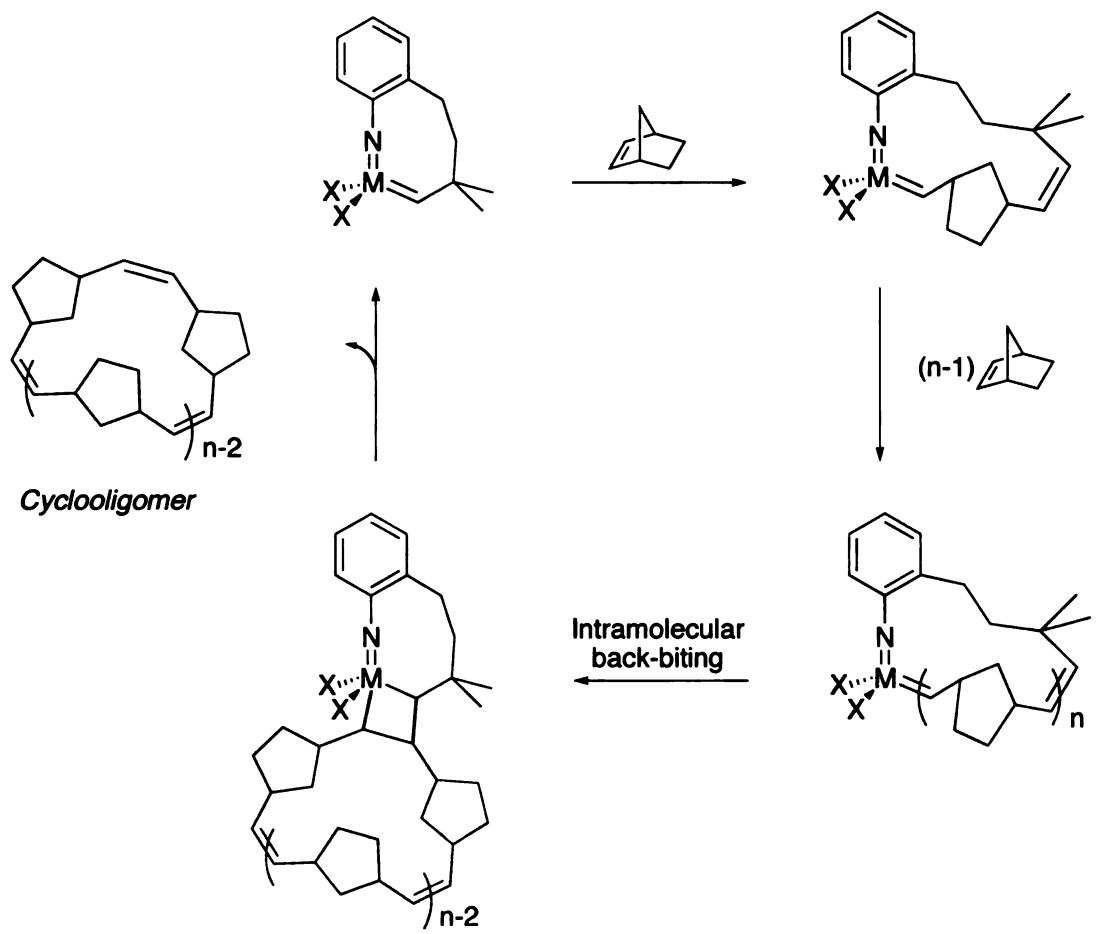
Given the above discussion and the inherent problems involved, one can in principle redesign the existing catalyst systems by tuning or modifying the ancillary ligands bound to the metal center. One of the ways of overcoming the above problems would be to incorporate a tether such that the intramolecular olefin metathesis is favored

over bimolecular decomposition. The tether would produce a stable catalyst that would regenerate after the consumption of the substrate as shown in Equation 1.2.



1.2

In addition a rather interesting application would involve the formation of cyclic polymers via "intramolecular backbiting" of the growing polymer chain as shown in Scheme 1.3.



Scheme 1.3. Formation of cyclo-oligomers using imido-tethered alkylidenes.

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Chapter 2 of this thesis describes the preparation of imido-tethered alkylidenes. These easily synthesized imido-tethered alkylidenes are rare examples of metallacycles with two different metal-ligand multiple bonds. Chapter 3 discusses the synthesis of a close isomer of the tethered-catalyst system that is not a metallacycle. This chapter also discusses the structural and spectroscopic differences between the imido-tethered alkylidenes and their untethered counterparts. Chapter 4 discusses the synthesis and applications of mixed alkoxide of the tethered alkylidenes and the Schrock olefin metathesis system in the ring-closing metathesis reaction of diethyl diallylmalonate and 4,4-dimethyl-1,6-heptadiene. The tethered alkylidene complex has excellent activity in the presence of $HOBu^{t}_{F6}$ and somewhat better stability over complexes without the tether. Chapter 5 discusses the studies toward the synthesis of an imido-tethered tungsten alkylidene. Chapter 6 discusses the synthesis of a scavenger based on the Merrifield's peptide resin for molybdenum based metathesis catalysts, which uses a salicylimine as the site of attachment. The resin is reusable and removes catalyst to the 30-50 ppb level. Chapter 7 discusses the application of these tethered alkylidenes in the synthesis and characterization of novel cyclic polymers. This involves using the scavenger system developed in Chapter 6 to remove the potential linear poly(norbornene) fractions from the reaction mixture to afford pure samples of cyclic poly(norbornene). Chapter 7 discusses the application of the [2π+2π]-reaction for the synthesis of an interesting class of complexes with a large amount of alkylidene character, which can be made readily through reaction of a ring-strained alkyne with an imido. These compounds offer a simplified route to compounds with alkylidene reactivity. This Chapter also discusses the synthesis of various derivatives of the metallacycles and their application for the

carbonyl-olefination reaction. The cationic derivatives generated by addition of Lewis acids to the above complexes were found to be quite active.

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CHAPTER 2

SYNTHESIS OF IMIDO-TETHERED ALKYLIDENES OF MOLYBDENUM

Introduction

Olefin metathesis continues to grow as an important methodology for the generation of new carbon-carbon bonds with applications to synthesis of small molecules and polymers as described in detail in Chapter 1.[1] Two important catalysts types have risen to preferred status for this important reaction (Chart 2.1): one based on ruthenium developed by the Grubbs Group and one based on molybdenum by the Schrock Group. Extensive synthetic effort has gone into the elaboration of both catalyst types from the groups of the catalyst's progenitors and others. At present there is a wide selection of derivatives available for specialized applications, e.g., asymmetric ring closing reactions.[2]

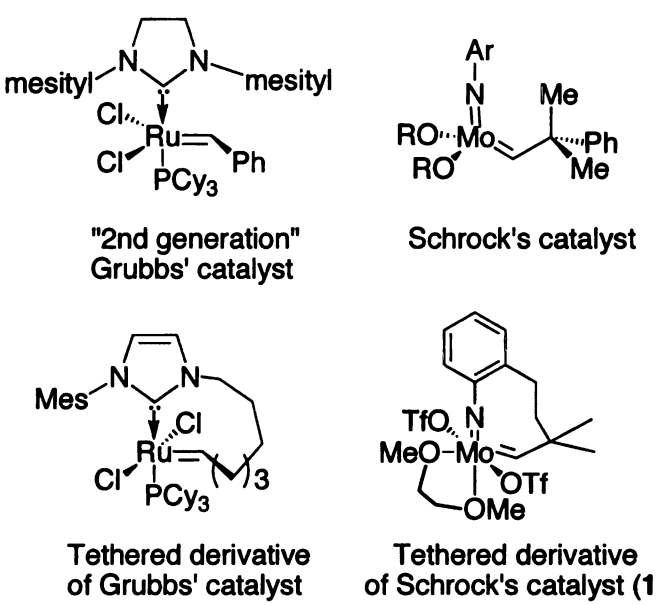
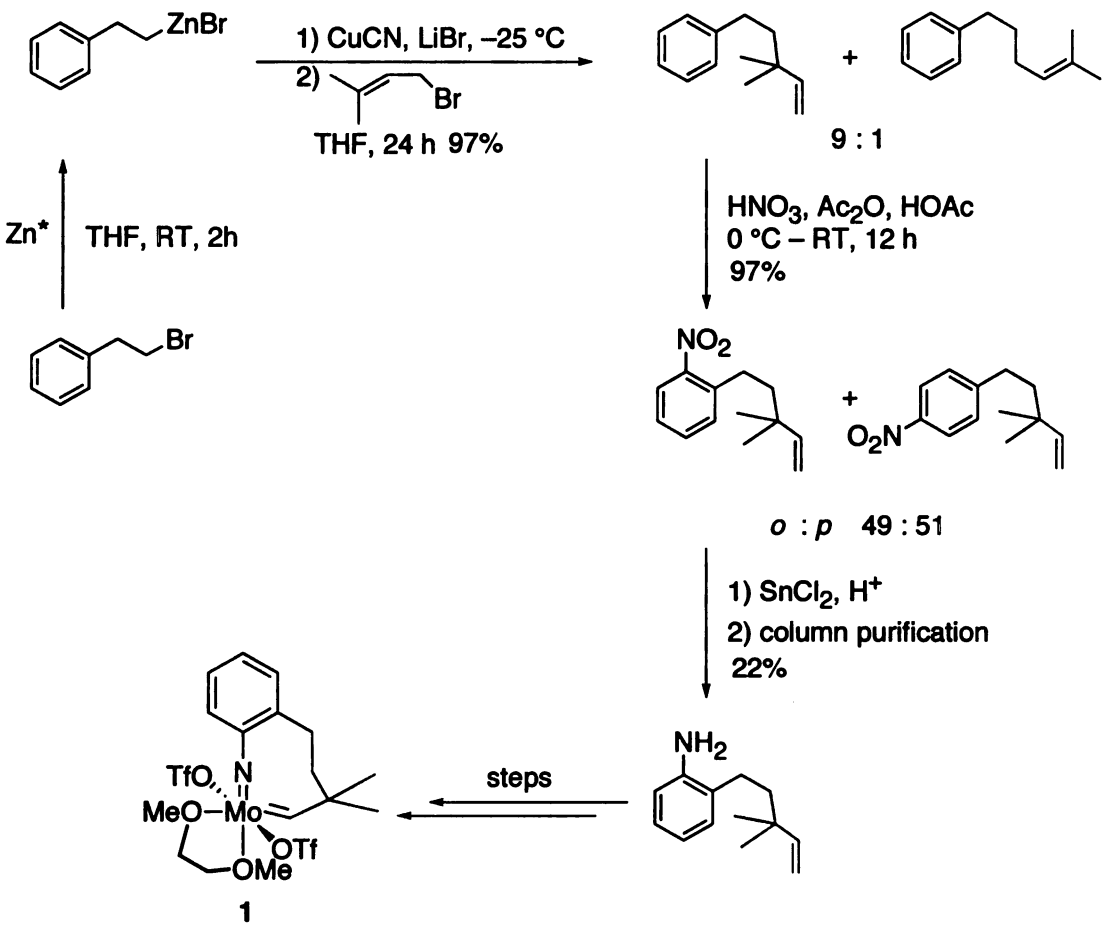


Chart 2.1. Structures of "Generation II" Grubbs' catalyst, Schrock's catalyst, and tethered derivatives.

The R group in Schrock's catalyst is often varied in this system for various applications with R = Bu^t often used for ring-opening metathesis polymerization (ROMP)[3] and R = Bu^t_{F6} often used for ring-closing metathesis (RCM), but many others are of utility. The affect of imido substituents on molybdenum alkylidene reactivity has also been extensively examined.[1]

Our group has been developing catalysts based on the Schrock framework for selective cyclooligomerization of cyclic olefins. In those efforts, we sought to develop a synthesis for covalent attachment of the alkylidene C_α-carbon to an ancillary ligand on the metal center.



Scheme 2.1. Previous tethered alkylidene synthesis.

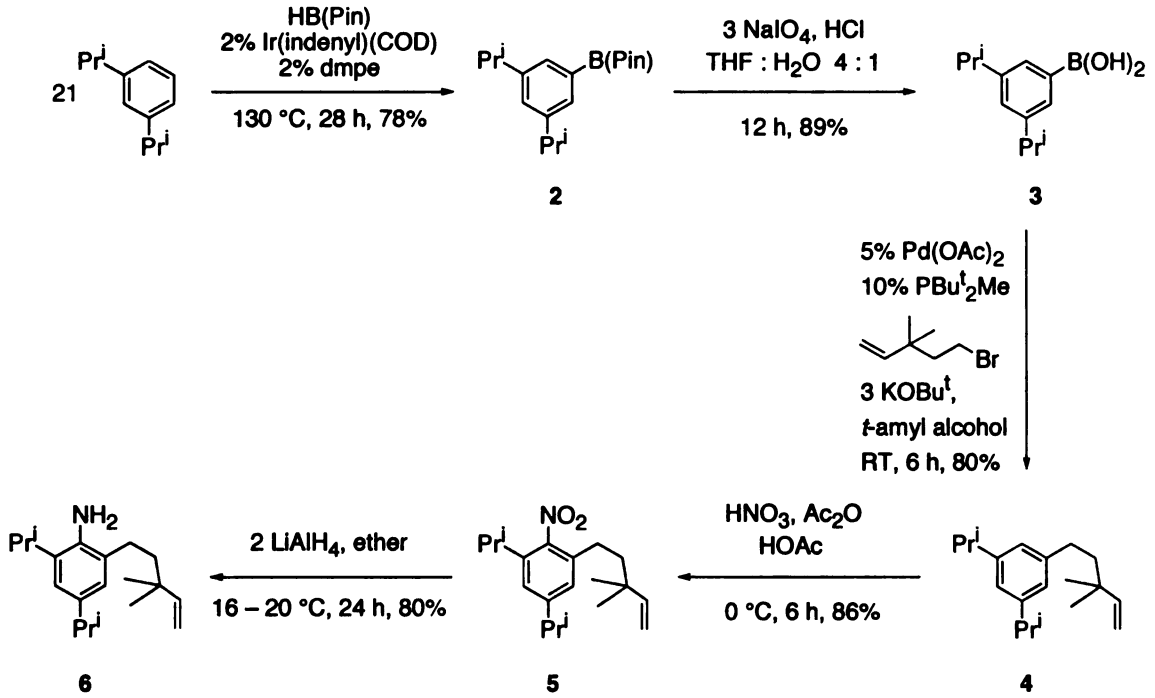
The position of attachment decided upon was through the imido ancillary ligand. During these efforts, a catalyst was reported by Fürstner and coworkers having a tethered alkylidene to an *N*-heterocyclic carbene.[4] This catalyst was employed by Grubbs and coworkers in cyclooligomerization of cyclooctene.[5] Our group reported a tethered carbene of molybdenum based on Schrock's catalyst.[6] In this chapter, we will discuss the synthesis, and structure of these tethered alkylidenes. These complexes are unusual metallacycles bearing two different metal-ligand multiple bonds in a ring. The tethered molybdenum catalyst architecture shown in Chart 2.1 was successful in the sense that it was stable and polymerization active as the bis(triflate) (**1**). However, the bis(triflate) (**1**) was quite a slow catalyst for ROMP, but this does begin to highlight the differences made by the tether considering the untethered versions of the bis(triflate) do not seem to be as active for polymerization of norbornene.

The usual method for increasing catalyst activity in the Schrock system is to generate the alkoxide.[7] However, replacement of the triflates with alkoxides using several different techniques led to uncharacterized paramagnetic products due to decomposition. Coupled with this, the previously designed synthesis was plagued with several regiochemical issues regarding the aromatic ring and the synthesis of the tether containing a quaternary center adjacent to an olefin (Scheme 2.1). The result was an amine that could be prepared on multigram scales but required careful column chromatography for purification. The tethered bis(triflate) complex **1** is prepared using the Schrock protocol with an intramolecular olefin metathesis to generate the metallacycle.[6]

Results and Discussion

In order in increase the stability of the resulting complex, we sought to develop a new synthetic protocol for the tethering amine with more steric protection on the aromatic ring. In addition, we sought to redesign the synthesis so that no tedious column separations were necessary and larger scales were possible.

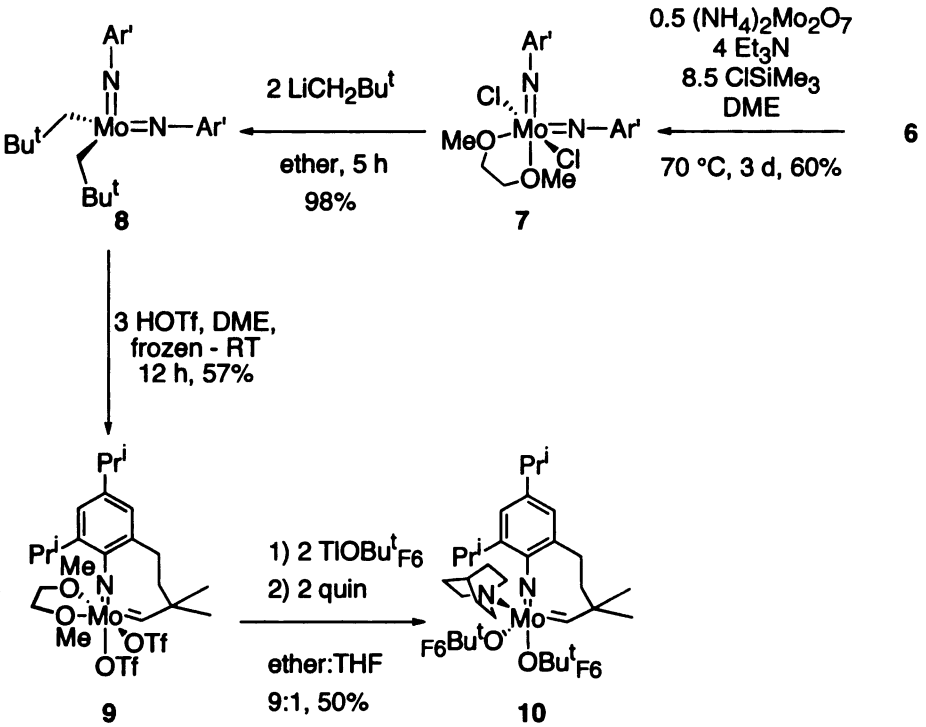
The new synthetic sequence is shown in Scheme 2.2, which takes advantage of recent developments in transition metal catalysis. The first step is selective Smith borylation[8] of 1,3-diisopropylbenzene catalyzed by iridium to generate arene boryl **2**; no other regioisomers of the product are observed. After conversion to the boronic acid **3**, Suzuki coupling using the protocol developed by Fu and coworkers installs the tethering olefin.[9] The new coupling conditions allow high yields of the hydrocarbon **4** using what might otherwise be a problematic alkylbromide containing β-hydrogens. Due to the position and size of the sterics on the aromatic ring, nitration proceeds to give a single observed product **5** with the nitro group *ortho* to the olefinic tethering group as desired. Lithium aluminum hydride reduction of nitro to amine provides the desired aniline derivative **6** in 38% overall yield for the 5 steps. The amino-olefin **6** has been prepared on multigram scales using this protocol, and the purification procedure is essentially a flush through a plug of silica gel. Aniline derivative **6** was installed on the metal to generate bis(imido)dichloro(DME)molybdenum(VI) **7**, which was synthesized from $(NH_4)_2Mo_2O_7$ using the procedure of Schrock and coworkers (Scheme 2.3).[10] Replacement of the chlorides with neopentyl occurs in high yield to provide $Mo(NAr)_2(Np)_2$ (**8**).



Scheme 2.2. Redesigned amine synthesis used to generate the tethering amino-olefin.

Reaction of **8** with triflic acid (HOTf) presumably produces an unobserved intermediate neopentylidene bis(triflate) complex. Formation of the metallacycle occurs by intramolecular olefin metathesis on the neopentylidene providing **9**. In other words, triflic acid addition can be seen as initiating imido protolytic cleavage, α-abstraction of neopentyl to form neopentylidene, and intramolecular olefin metathesis in a single step.

Currently, there are two molybdenum imido alkylidene bis(triflate) derivatives in the Cambridge Structural[11] database: one untethered derivative reported by Schrock and coworkers[10a] and our previously reported tethered derivative 1.[6] Both of these complexes have the two triflate ligands mutually *trans*. Often, these molybdenum bis(triflates) exhibit spectra indicative of several isomers being present in solution. X-ray diffraction on bis(triflate) **9** revealed a different isomer from previous structural studies with *cis* triflate ligands.[6,10]



Scheme 2.3. Synthesis of the tethered carbene alkoxide catalyst **10**.

The distances and angles for the metal-ligand multiple bonds in **9** are quite similar to the two other reported molybdenum bis(triflate) structures. For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **9** see Table 2.1. The differences between the structure of **9** and these previously reported derivatives largely reside in the triflate and DME ligands. In the previously reported complexes the triflates are mutually *trans*, with O(triflate)–Mo–O(triflate) angles of 152.3(4) and 153.8(3)°. In **9**, the two triflates are in *cis*-positions in the pseudo-octahedral compound with an O(triflate)–Mo–O(triflate) angle of 84.0(5)°. One of the triflates is *trans* to the imido, and the other is *trans* to a DME oxygen. As would be expected, the strongly *trans*-influencing imido provides an Mo–O(11) distance of 2.226(11) Å, and the triflate oxygen *trans* to a DME oxygen is significantly shorter at 2.101(11) Å. Likewise, the DME oxygen

coordinated *trans* to the alkylidene has a much longer Mo–O bond, 2.313(12) Å, relative to the one *trans* to triflate, 2.143(12) Å.

In solution, bis(triflate) **9** has access to several different isomers as judged by its NMR spectroscopy. For example, at –60 °C in the ^{19}F NMR spectrum there are 3 pairs of resonances with each pair of near equal integration, which suggests the presence of 3 different isomers with inequivalent triflates. The other nuclei examined show similar behavior with ^{1}H and ^{13}C NMR showing two different alkylidene resonances at room temperature, for example.

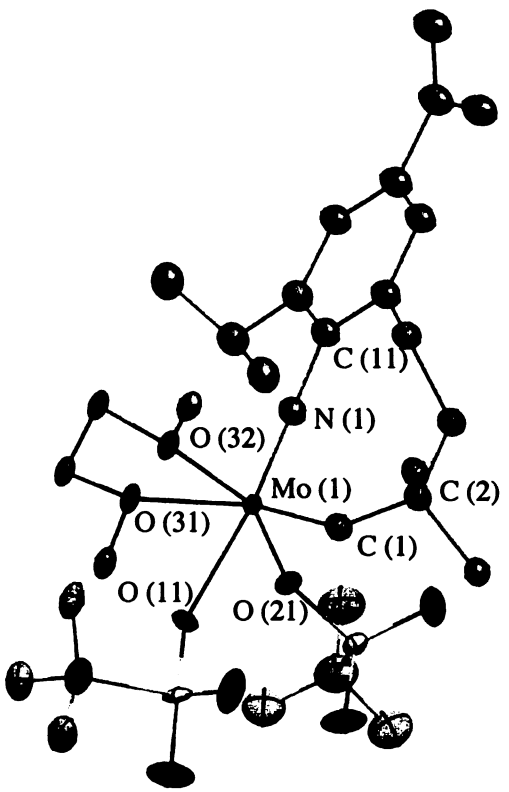


Figure 2.1. ORTEP representation for the structure of **9** from X-ray diffraction with hydrogens and ether solvent omitted.

Contrary to imido alkylidenes of molybdenum not containing the tether, on replacement of the triflates in **9** by hexafluoro-*tert*-butoxide (OBu^t_{F6}) using $TlOBu^t_{F6}$ we were unable to isolate a stable product. However, $TlOBu^t_{F6}$ triflate metathesis (Scheme 2.3) in the presence of quinuclidine (quin) provides isolable $Mo(OBu^t_{F6})_2$(quin)(N-2,4-$Pr^i_2C_6H_2$-6-$CH_2CH_2CMe_2CH$=) (**10**).[12] For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **10** see Table 2.2.

Table 2.1 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **9**.

Mo (1)–N (1)	1.706 (16)	Mo (1)–O (32)	2.143 (12)
Mo (1)–C (1)	1.94 (2)	Mo (1)–O (11)	2.226 (11)
Mo (1)–O (21)	2.101 (11)	Mo (1)–O (31)	2.313 (12)

N (1)–Mo (1)–C (1)	96.1 (8)	N (1)–Mo (1)–O (11)	172.2 (7)
N (1)–Mo (1)–O (21)	96.2 (7)	C (1)–Mo (1)–O (11)	91.5 (7)
C (1)–Mo (1)–O (21)	101.0 (7)	O (21)–Mo (1)–O (11)	84.0 (5)
N (1)–Mo (1)–O (32)	98.3 (7)	O (32)–Mo (1)–O (11)	80.6 (5)
C (1)–Mo (1)–O (32)	155.5 (5)	N (1)–Mo (1)–O (31)	97.5 (7)
C (1)–Mo (1)–O (31)	164.8 (7)	O (32)–Mo (1)–O (31)	73.3 (4)
O (21)–Mo (1)–O (31)	84.4 (5)	O (11)–Mo (1)–O (31)	74.8 (4)

Complex **10** has been structurally characterized, and an ORTEP representation is shown in Figure 2.2. The 5-coordinate complex is best described as a pseudo-square pyramid, $\tau = 0.13$ where $\tau = 0$ is square pyramidal and $\tau = 1$ is trigonal bipyramidal.[13] The alkylidene carbon occupies the pseudo-axial site with angles to the remaining ligands

ranging from 96–109°. This largest angle to the alkylidene is with the alkoxide ligand *trans* to the imido nitrogen, and the angle may be opened slightly to allow this orbital interaction with the alkylidene in an α-agostic interaction. The Mo–O distances are not significantly different despite one being *trans* to imido and the other *trans* to quin. The Mo=N and Mo=C distances are typical at 1.743(4) and 1.870(5) Å, respectively. The angle subtended at N(1) is essentially linear at 175.9(4) Å.

Table 2.2 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **10**.

Mo–N (1)	1.743 (4)	Mo–O (2)	2.010 (3)
Mo–C (1")	1.879 (5)	Mo–N (2)	2.265 (4)
Mo–O (1)	2.008 (3)		

N (1)–Mo–C (1")	97.2 (2)	O (1)–Mo–O (2)	83.62 (13)
N (1)–Mo–O (1)	98.12 (15)	N (1)–Mo–N (2)	90.28 (16)
C (1")–Mo–O (1)	108.51 (17)	C (1")–Mo–N (2)	96.31 (17)
N (1)–Mo–O (2)	160.07 (15)	O (1)–Mo–N (2)	152.44 (14)
C (1")–Mo–O (2)	101.10 (18)	O (2)–Mo–N (2)	79.91 (13)

Conclusion

The synthesis of tethered molybdenum alkylidenes has been improved to the point where these specialized catalysts can be made on relatively large scales. The required tethering aniline can be prepared as a single isomer with work-up procedures not involving rigorous column chromatography separations. The synthesis of the bis(imido)bis(neopentyl)molybdenum(VI) proceeded through the usual route. On

addition of triflic acid, an imido was protolytically cleaved with concomitant α-abstraction to form an unobserved neopentylidene, which was trapped by the pendant olefin to generate the metallacyclic bis(triflate). Metathesis of the triflates to alkoxides was best accomplished with the thallium salts or with an alcohol in the presence of an excess of triethylamine. This occurred to give an isolable hexafluoro-*tert*-butoxide complex **10** in the presence of quinuclidine. Complex **10** is active for ring-opening metathesis polymerization of strained olefins and inactive for ring-closing metathesis of dienes.

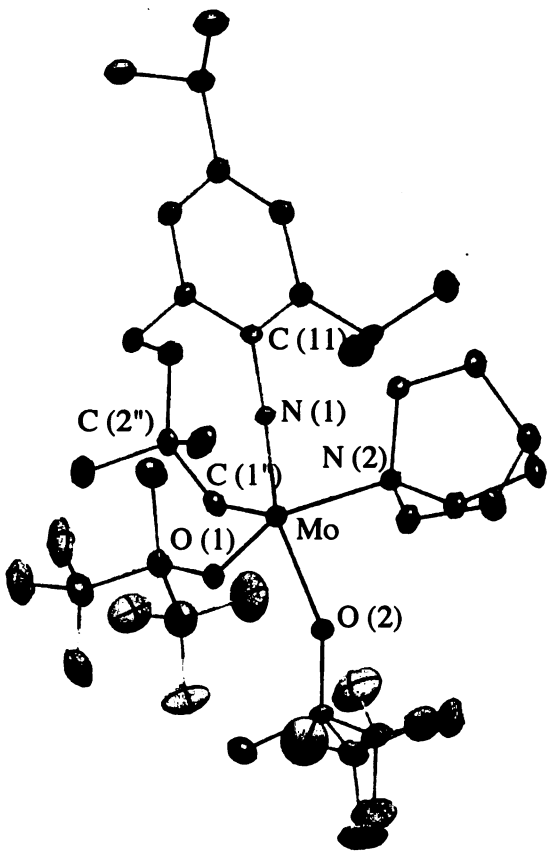


Figure 2.2. ORTEP representation for the structure of **10** from X-ray diffraction with hydrogens omitted.

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. The ^{13}C NMR assignments are based on decoupled ^{13}C, peak heights for overlapping signals, and DEPT experiments. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Alumina, Celite, and silica were dried at a temperature >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. HB(Pin)[14] and Ir(Indenyl)(COD)[15] were prepared as described in the literature. Most conveniently, HB(Pin) supplied by BASF in NEt_3-stabilized form was also employed, which can be used without purification. 1,3-diisopropylbenzene was purchased from Aldrich Chemical Co. and was distilled from purple sodium benzophenone ketyl. Sodium metaperiodate, acetic acid, acetic anhydride, triethylamine, and aluminum chloride were purchased from Spectrum Chemical Co. and used without purification. 5-bromo-3,3-dimethyl-pent-1-ene was prepared as described in literature.[16] Potassium *tert*-butoxide, $Pd(OAc)_2$, $P(Bu^t)_2Me$, fuming nitric acid, triflic acid, $LiAlH_4$,

and dmpe were purchased from Aldrich Chemical Co. and used without purification. *Tert*-amyl alcohol was purchased from TCI Chemical Co., distilled over magnesium turnings, stored over molecular sieves (3 Å, 1/16 inch pellets), and degassed under nitrogen prior to use. Thallium ethoxide was purchased from Strem Chemical Co. and was degassed before use. Quinuclidine hydrochloride was purchased from Aldrich Chemical Co., was basified using K_2CO_3, and crystallized from ether/pentane at –35 °C. Neopentyllithium was prepared as described in literature.[17]

Preparation of hexafluoro-tert-butoxide thallium. In a 120 mL Erlenmeyer flask was loaded $HOBu^t_{F6}$ (1.50 g, 8.24 mmol), a stir bar, and pentane (8 mL). To the stirring solution of the alcohol was added TlOEt (2.055 g, 8.24 mmol) in pentane (10 mL). The reaction mixture was capped with a septum and stirred for 14 h. Volatiles were removed under vacuum. The resulting white solid was crystallized from ether:pentane 1:1 at –35 °C, which provided 2.54 g (80%) of purified thallium alkoxide.[18] ^{1}H NMR (300 MHz, acetone-d_6): 1.60 (sept, CH_3, J_{HF} = 1.2 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, acetone-d_6): 128 (q, CF_3, J_{CF} = 288.45 Hz), 77.18 (sept, CMe$(CF_3)_2$, J_{CF} = 27.55 Hz). ^{19}F NMR (282 MHz, acetone-d_6): –78.06. M.p. = 155-157 °C.

Preparation of 3,5-diisopropylphenylborane pinacolate (2). In a glove box, Ir(Indenyl)(COD) (416 mg, 1 mmol, 2 mol%), dmpe (146 mg, 1 mmol, 2 mol%), HBPin (6.4 g, 0.05 mol), and 1,3-diisopropylbenzene (170.4 g, 1.05 mol) were placed in a 1 L Schlenk flask equipped with a stir bar. The flask was closed with a septum, taken outside the glove box, and stirred at room temperature for 20 min. The flask was purged with a continuous flow of purified N_2 and heated in an oil bath at 130 °C for 28 h. The reaction

mixture was cooled to room temperature, poured into CH_2Cl_2 (200 mL), filtered through a short pad of silica with copious washings (CH_2Cl_2, 250 mL), and concentrated in vacuo. 1,3-Diisopropylbenzene was removed by distillation in vacuo leaving essentially pure product, which could be crystallized from ether at 0 °C as colorless crystals (11.3 g, 0.039 mol, 78.4%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (s, 2 H, *o-H*), 7.17 (s, 1 H, *p-H*), 2.89 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 1.33 (s, 12 H, $C(CH_3)_2$), 1.24 (d, 12 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 148.11, 130.42, 127.65, 83.57, 34.18, 24.84, 24.06. One aryl carbon, which we believe to be the one adjacent to boron, was not located. ^{11}B NMR (96.2 MHz, $CDCl_3$): 31.15. Elemental Analysis Calc. for $C_{18}H_{29}BO_2$: C, 74.99; H, 10.16. Found: C, 74.65; H, 10.01. M.p. = 120–122 °C. MS (EI) m/z = 288(M^+). R_f = 0.84 (SiO_2, CH_2Cl_2).

Preparation of 3,5-diisopropylphenylboronic acid (3). In a 250 mL round bottom flask equipped with a stir bar, was added B (11.0 g, 0.038 mol), THF:H_2O (4:1, 80:20 mL), and $NaIO_4$ (25 g, 0.117 mol, 3 equiv). The mixture was stirred until homogeneous, and then 2 N HCl (2 mL) was added. The reaction mixture was stirred at room temperature for 12 h. After 12 h, the reaction mixture was extracted with ethyl acetate (5 × 30 mL), and the combined organic extracts were washed with water and brine. The solution was dried with Na_2SO_4, and concentrated in vacuo to give a white solid. The solid was washed with ice-cold pentane to give the desired product as white flakes (6.97 g, 0.034 mol, 89%). The compound was used without further purification. ^{1}H NMR (300 MHz, CD_3CN): 7.46 (s, 1 H, *ortho-H*), 7.45 (s, 1 H, *ortho-H*), 7.20 (s, 1 H,

para-H), 6.04 (s, 2 H, O*H*), 2.89 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 1.23 (d, 6 H $CH(CH_3)_2$, J_{CH} = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_3CN): 149.02, 130.39, 128.23, 118.31, 34.95, 24.39. ^{11}B NMR (96.2 MHz, CD_3CN): 29.60. M.p. = 142–144 °C.

Preparation of 1-(3,3-dimethylpent-4-enyl)-3,5-diisopropylbenzene (4). In a glove box, $Pd(OAc)_2$ (316 mg, 1.41 mmol, 5 mol%), and PBu^t_2Me (452 mg, 2.82 mmol, 10 mol%) were placed in a 250 mL Schlenk flask equipped with a stir bar. The flask was closed with a septum and taken outside the glove box. To this was added *t*-amyl alcohol (20 mL), **3** (6.97 g, 0.034 mmol, 1.2 equiv), and $KOBu^t$ (9.48 g, 0.084 mmol, 3 equiv). The reaction mixture was stirred at room temperature for 10 min. To this was added 5-bromo-3,3-dimethylpent-1-ene[18] (4.99 g, 0.028 mmol), and the resulting heterogeneous reaction mixture was stirred vigorously for 6 h at room temperature. The reaction was poured into hexanes (200 mL), filtered through a short pad of Celite with copious washings (hexanes, 200 mL combined), concentrated, and passed though a plug of silica gel (250-400 mesh, 400 g) to afford the desired product as a colorless oil (5.8 g, 0.022 mol, 80%). ^1H NMR (300 MHz, $CDCl_3$): 6.97 (s, 1 H, *p-H*), 6.93 (s, 2 H, *o-H*), 5.96 (dd, 1 H, C*H*=CH_2, J_{CH} = 10.4 Hz, J_{CH} = 17.7 Hz), 5.06-5.09 (m, 1 H, CH=CH_2), 5.02-5.05 (m, 1 H, CH=CH_2), 2.93 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.9 Hz), 2.60-2.54 (m, 2 H, CH_2), 1.71-1.65 (m, 2 H, CH_2), 1.32 (d, 12 H, CH_3, J_{CH} = 6.9 Hz), 1.15 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 149.07, 148.53, 143.31, 124.15, 122.23, 110.9, 45.10, 37.02, 34.45, 31.58, 27.01, 24.39. Elemental Analysis. Calc. for $C_{19}H_{30}$: C, 88.28; H, 11.72.

Found: C, 88.35; H, 12.10. MS (EI) m/z = 258(M^+). R_f = 0.82 (SiO_2, hexane:ethyl acetate 8:2).

Preparation of 1-(3,3-dimethylpent-4-enyl)-3,5-diisopropyl-2-nitro benzene (5). To a flask was added fuming HNO_3 (1.6 mL, 90%, d = 1.5), HOAc (1.5 mL), and Ac_2O (1.2 mL), and the solution was cooled to room temperature before proceeding. This solution was added dropwise to 4 (5.8 g, 0.022 mol) in 2 mL Ac_2O. The reaction was maintained at 0 °C during the addition. After the addition was complete, the mixture was stirred at 0 °C for 6 h. The reaction mixture was poured in ice-cold water (50 mL). The product was extracted with diethyl ether (4 × 25 mL), and the combined organic layers were washed with portions of $NaHCO_3$ (250 mL) until no gas formed on addition of the basic aqueous solution. The organic solution was filtered, and the separated solids washed with ether (5 × 40 mL). The combined ether solutions were dried with $MgSO_4$. The volatiles were removed in vacuum providing the product as a yellow oil (5.85 g, 0.019 mol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.01 (s, 1 H, *aromatic-H*), 6.95 (s, 1 H, *aromatic-H*), 5.93 (dd, 1 H, C*H*=CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 5.03-5.00 (m, 1 H, CH=CH_2), 4.96-4.99 (m, 1 H, CH=CH_2), 2.93 (sept, 2 H, C$H(CH_3)_2$, J_{CH} = 6.9 Hz), 2.66-2.59 (m, 2 H, CH_2), 1.70-1.65 (m, 2 H, CH_2), 1.28 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.22 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.08 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 150.99, 147.44, 139.46, 133.64, 125.71, 123.86, 122.12, 111.22, 44.13, 36.69, 34.16, 29.02, 27.08, 26.68, 26.48, 23.81. Elemental Analysis Calc. for $C_{19}H_{29}NO_2$: C, 75.18; H, 9.65;

N, 4.62. Found: C, 75.09; H, 10.03; N, 4.99. MS (EI) m/z = 302(M^+). R_f = 0.73 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of 2-(3,3-dimethylpent-4-enyl)-4,6-diisopropylaniline (6). In a glove box, $LiAlH_4$ (2.93 g, 0.077 mol, 4 equiv) and diethyl ether (100 mL) were placed in a 250 mL Schlenk flask equipped with a stir bar. The flask was closed with a rubber septum, taken outside the glove box, and kept in a water bath to maintain the temperature between 16-25 °C. To the slurry, was slowly added **5** (5.85 g, 0.019 mol) over a period of 1 h. After the addition was complete, the water bath was removed, and the reaction mixture was stirred overnight at room temperature. The mixture was cooled to 0 °C using an ice bath, and the excess hydride was quenched by the dropwise addition of a saturated solution of $MgSO_4$ solution. The precipitated salts were removed by filtration through Celite, washing with chloroform (200 mL). The filter cake was washed again with chloroform (3 × 50 mL). The combined organic solutions were dried to afford the desired product as a red oil (4.23 g, 0.015 mol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.86 (s, 1 H, *aromatic-H*), 6.75 (s, 1 H, *aromatic-H*), 5.93 (dd, 1 H, C*H*=CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 5.02-5.00 (m, 1 H, CH=CH_2), 4.95-4.97 (m, 1 H, CH=CH_2), 3.49 (br s, 2 H, NH_2), 2.88 (sept, 1 H, CH(CH_3)$_2$, J_{CH} = 6.9 Hz), 2.77 (sept, 1 H, CH(CH_3)$_2$, J_{CH} = 6.9 Hz), 2.41-2.35 (m, 2 H, CH_2), 1.59-1.53 (m, 2 H, CH_2), 1.23 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.19 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.06 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 147.86, 138.77, 138.64, 132.39, 126.95, 124.59, 121.05, 111.17, 41.84, 36.74, 33.58, 27.95, 27.18, 26.62, 24.35, 22.47. Elemental Analysis. Calc. for $C_{19}H_{31}N$: C, 83.45; H,

11.43; N, 5.12. Found: C, 83.35; H, 11.18; N, 4.98. MS (EI) m/z = 273(M^+). R_f = 0.35 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of $Mo(NAr)_2Cl_2(DME)$ (7). In a glove box, in a 250 mL Schlenk flask was loaded $(NH_4)_2Mo_2O_7$ (0.621 g, 1.827 mmol), DME (20 mL), and a stir bar. To the suspension was added NEt_3 (1.48 g, 0.015 mol), $ClSiMe_3$ (3.37 g, 0.031 mmol), and **6** (2 g, 0.0073 mmol). The mixture was stirred at room temperature inside the glove box for 1 h. After 1 h, the flask was closed with a septum, partially evacuated, and heated in an oil bath at 70 °C for 3 d. The reaction was monitored periodically by cooling the reaction mixture to room temperature, evacuating the head-space of the Schlenk flask and taking it inside the glove box. An aliquot was taken, filtered, solvent removed, and an NMR recorded to follow the $ArNHSiMe_3$/$ArN(SiMe_3)_2$ peaks formed during the reaction. The reaction was allowed to proceed until these silyl amine peaks all but disappeared from the spectrum. After cooling to room temperature, the flask was partially evacuated and taken inside the glove box. The solution was filtered though Celite. The volatiles of the filtrate were removed in vacuum to give a dark-red viscous oil, which can be crystallized from hexamethyldisiloxane to give a brick-red powder of the desired product (1.73 g, 2.17 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.85 (s, 2 H, *aromatic-H*), 6.77 (s, 2 H, *aromatic-H*), 5.81 (dd, 2 H, C*H*=CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 4.91-4.82 (m, 4 H, CH=CH_2), 3.92 (s, 4 H, OCH_2), 3.80 (s, 6 H, OCH_3), 3.83 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.6 Hz), 2.89-2.84 (m, 4 H, CH_2), 2.79 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.6 Hz), 1.57-1.51 (m, 4 H, CH_2), 1.16 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.97 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.94 (s,

12 CH_3). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 152.80, 148.87, 147.85, 145.28, 138.99, 122.86, 120.76, 110.05, 71.15, 63.07, 42.57, 36.65, 34.23, 27.35, 26.54, 26.04, 24.65, 23.97. Elemental Analysis. calc. for $C_{42}H_{68}N_2O_2Cl_2Mo$: C, 63.07; H, 8.57; N, 3.50 Found: C, 63.35; H, 8.41; N, 3.72. M.p. = 145-147 °C (dec).

Preparation of $Mo(NAr)_2(Np)_2$ (8). In a glove box, to a –90 °C solution of **7** (1.73 g, 2.169 mmol) in 5 mL ether was added 8.7 mL of 0.5 M solution of neopentyl lithium (4.77 mmol, 2.2 equiv). The solution was allowed to reach room temperature and stirred for 6 h. An aliquot of the reaction mixture was filtered through Celite to remove LiCl and added to dilute nitric acid (0.25 M) solution. This solution was added to a 20 mL vial containing 50 mg of silver nitrate in 1 mL distilled water. The absence of a white precipitate corresponding to AgCl indicated the completion of the reaction. The volatiles were removed in vacuum, and the product was redissolved in pentane and filtered through Celite to remove the lithium chloride. The volatiles of the filtrate were removed in vacuum, to give a bright red viscous oil (1.93 g, 2.131 mmol, 98%). The oil was used without further purification. ^1H NMR (300 MHz, $CDCl_3$): 6.79 (s, 2 H, *aromatic-H*), 6.74 (s, 2 H, *aromatic-H*), 5.65 (dd, 2 H, C*H*=CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 4.77-4.85 (m, 4 H, CH=CH_2), 3.44 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.6 Hz), 2.77 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.6 Hz), 2.48-2.36 (m, 4 H, CH_2), 2.02 (s, 4 H, CH_2), 1.45-1.42 (m, 4 H, CH_2), 1.16 (d, 12 CH_3, J_{CH} = 6.6 Hz), 1.12 (s, 18 H, CH_3), 0.97 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.82 (s, 12 CH_3). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 152.19, 148.38, 145.37, 142.24, 136.60, 123.14, 120.25, 110.46, 79.17, 42.55, 36.50, 34.18, 33.47, 33.34, 27.91, 26.89, 26.53, 24.06, 23.27.

Preparation of Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](DME)$(OTf)_2$ (9). In a glove box, a –90 °C solution of triflic acid (225 mg, 1.50 mmol, 3 equiv) in DME (2 mL) was added dropwise to a –90 °C orange solution of **8** (453 mg, 0.5 mmol) in DME (10 mL). This solution was stirred for 24 h, and then volatiles were removed in vacuum to give a dark yellow oil. The oil was then extracted with about 15 mL of chilled toluene and filtered through Celite. The filtrate was concentrated in vacuum, and the resulting dark yellow oil was dissolved in ether and layered with pentane to obtain a bright yellow precipitate. This bright yellow precipitate was dissolved again in a minimum amount of ether and layered with an equal amount of pentane to obtain essentially pure product (190 mg, 0.256 mmol, 51%). The NMR spectroscopic data are consistent with an approximately 1.8:1 mixture of two major isomers in $CDCl_3$. The spectra are further complicated due to the broadening of some resonances. As a result, the spectra are more complex than expected, and the assignments are difficult due to the multitude of overlapping peaks. ^1H NMR (500 MHz, $CDCl_3$): 14.49 (s, J_{CH} = 126 Hz), 13.74 (s, J_{CH} = 121 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 333 (CH), 324 (CH). ^{19}F NMR (470 MHz, $CDCl_3$): –76.77 (major isomer), –77.88 (minor isomer). Elemental Analysis. calc. for $C_{24}H_{37}NO_8S_2F_6Mo$: C, 38.87; H, 5.03; N, 1.89 Found: C, 38.74; H, 5.23; N, 2.21. M.p. = 110-112 °C (dec).

Preparation of Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](quin)$(OBu^t_{F6})_2$ (10). In a glove box, to a frozen solution of 4 (100 mg, 0.135 mmol) in ether:THF (9:1, 1 mL) was added a solution of quinuclidine (30 mg, 0.269 mmol) in ether:THF (9:1, 1 mL). The reaction mixture stirred for 10 min. After 10 min, $TlO(CF_3)_2CH_3$ (104 mg, 2 equiv,

0.269 mmol) solution was added and stirring continued for 3 h. The solvent then was removed, and the product was dissolved in pentane. The salts were removed by filtration through Celite. The product was crystallized at –35 °C from pentane as yellow crystals (56 mg, 0.07 mmol, 50.2%). Due to fluxionality of the resulting tether and multiple isomers[15b] in solution, the NMR spectrum is broad and complex. The alkylidene resonance for the quinuclidine adduct is sufficiently separated from other resonances to be assigned definitively. The assignable peaks due to the alkylidene in the major isomer are provided here. ^{1}H NMR (500 MHz, C_6D_6): 13.10 (J_{CH} = 125 Hz). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): 294.43. Elemental Analysis. calc. for $C_{33}H_{46}N_2O_2F_{12}Mo$: C, 47.98; H, 5.62; N, 3.39 Found: C, 48.50; H, 5.90; N, 3.42. M.p. = 152-154 °C (dec).

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CHAPTER 3

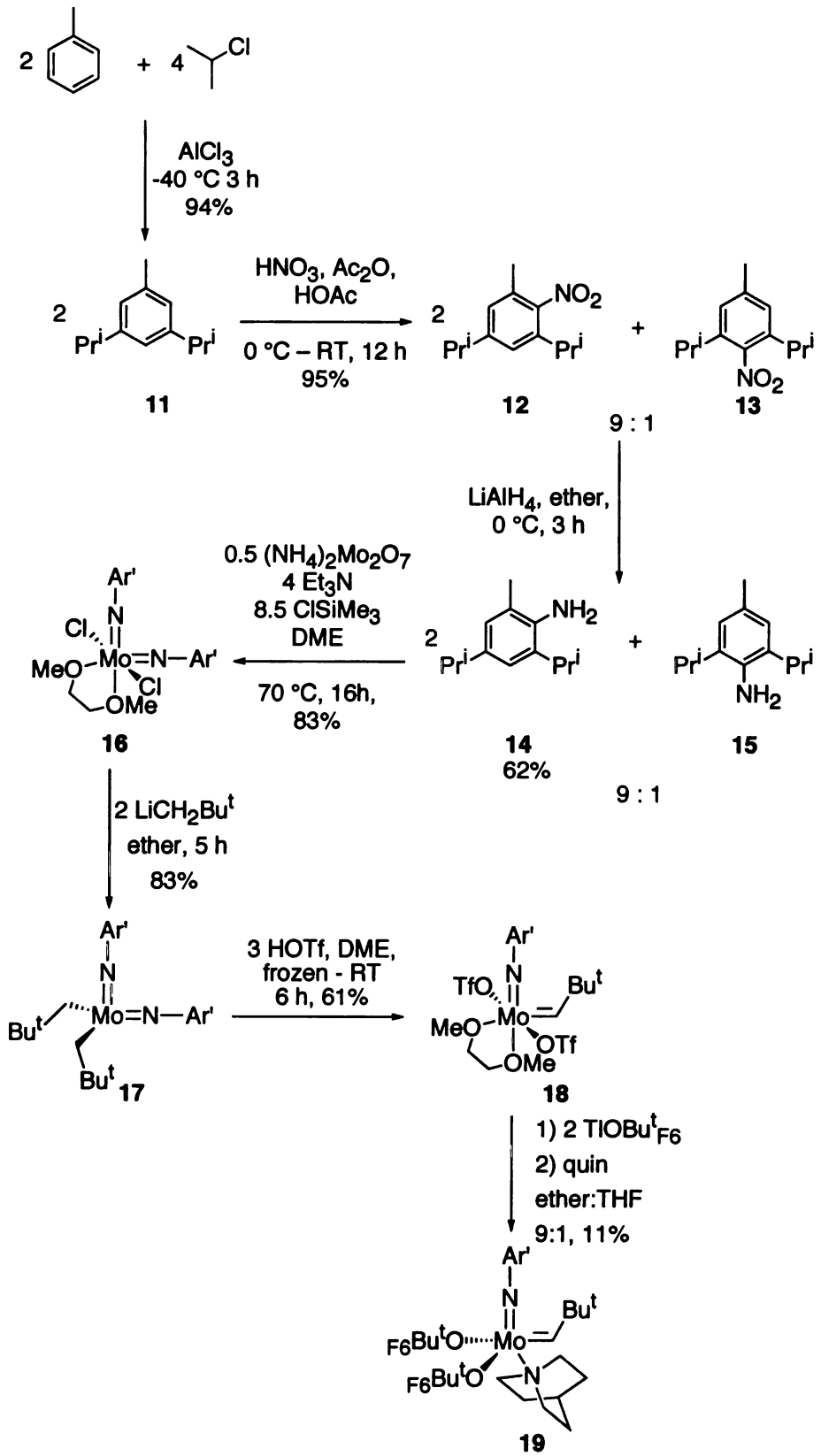
STRUCTURAL AND SPECTROSCOPIC COMPARISON OF TETHERED AND UNTETHERED ALKYLIDENES OF MOLYBDENUM

Introduction

The synthesis of the imido-tethered molybdenum catalyst architecture discussed in Chapter 2 was successful and led to the stable complex $Mo(OBu^t_{F6})_2$(quin)[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=] (**10**).[1] Replacement of the triflates with alkoxides using several standard techniques such as triflate metathesis with MOR, where M = Li, Na, or K, led to uncharacterized paramagnetic products due to decomposition. The substitution of the triflates for alkoxides required relatively mild conditions such as reaction with TlOR or HOR/Et_3N. The electronic difference between tethered and untethered systems is underlined in their reactivity with olefins as well. The tethered bis(triflate) complex **8**, Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](DME)$(OTf)_2$, is an active catalyst for ring-opening metathesis polymerization of norbornene unlike untethered analogues [Mo(NAr")$(CHCMe_2Ph)(OTf)_2$(DME) and Mo(NAr")$(CHBu^t)(OTf)_2$(DME), where Ar" = 2,6-diisopropylphenyl.[2]

Results and Discussion

For comparison with the imido-tethered complex **10**, we prepared a close isomer not bearing the tether, $Mo(OBu^t_{F6})_2$(quin)(NAr')[=C(H)Bu^t] (**19**), where Ar' = C_6H_2-2,4-Pr^i_2-6-Me, using the protocol shown in Scheme 3.1. The first step is the Friedel-Craft alkylation of toluene with 2-chloropropane to generate **11** in 94% yield.



Scheme 3.1. Synthesis of $Mo(OBu^t_{F6})_2(NAr')(=CHBu^t)(quin)$ (**19**).

Nitration of the aromatic ring affords isomers **12** and **13** in a combined 95% yield. The two isomers were not separated at this stage. Lithium aluminium hydride reduction of the mixture provides the desired amine **14**, which was isolated by column chromatography in 55% overall yield from toluene. The amine **14** was installed on the metal using the standard protocol developed by Schrock and co-workers. The pseudotetrahedral, bis(neopentyl) intermediate **17** was also structurally characterized. For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **17** see Table 3.1. The Mo=N distances are typical at 1.755(5) and 1.747(5) Å, respectively. The angle subtended at N(1) and N(2) are essentially linear at 158.7(4) and 160.0(4) Å, respectively.

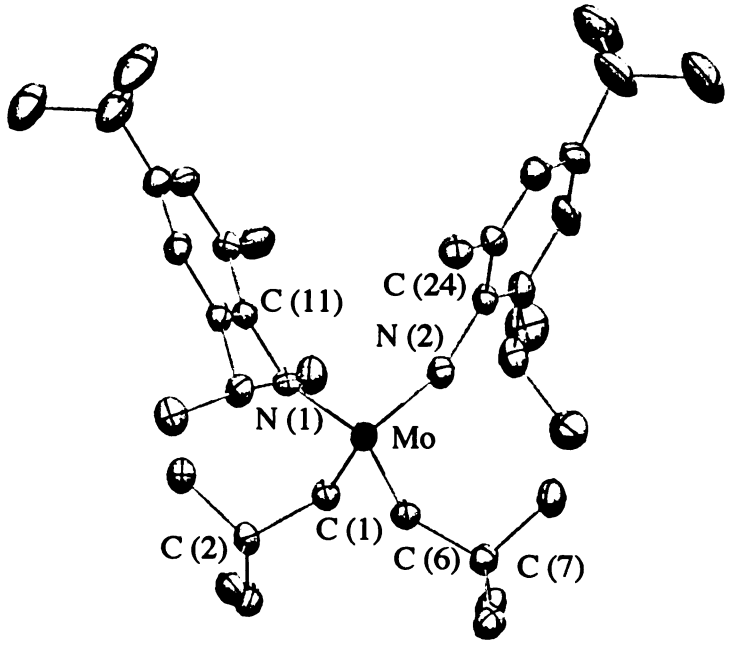


Figure 3.1 ORTEP Diagram of $Mo(NAr')_2(CH_2Bu^t)_2$ (**17**). Hydrogens and pentane solvent excluded for clarity.

Table 3.1 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on $Mo(NAr')_2(CH_2Bu^t)_2$ (**17**).

Mo–C (1)	2.134 (6)	Mo–C (6)	2.138 (6)
Mo–N (1)	1.755 (5)	Mo–N (2)	1.747 (5)
N (1)–Mo–N (2)	113.5 (2)	C (1)–Mo–C (6)	117.6 (2)
N (2)–Mo–C (1)	108.3 (2)	C (11)–N (1)–Mo	158.7 (4)
N (1)–Mo–C (1)	103.7 (2)	C (24)–N (2)–Mo	160.0 (4)
N (2)–Mo–C (6)	103.9 (2)	C (2)–C (1)–Mo	122.2 (4)
N (1)–Mo–C (6)	110.2 (2)	C (7)–C (6)–Mo	120.9 (4)

While **19** only differs in formula from **10** by two hydrogens, its structure is different in the solid state in several ways. The 5-coordinate complex is best described as a pseudo-trigonal bipyramid, $\tau = 0.47$ versus 0.13 for **10**. For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **19** see Table 3.2.

The alkylidene carbon occupies one of the pseudo-equatorial sites, and the axis is the quinuclidine nitrogen and an alkoxide with an angle subtended at Mo of 162°. The imido bends somewhat from essentially linear in **10** to 156.6(4)° in **19**. The aryl ring of the imido rotates to place the larger group towards the *syn*-alkylidene; the bending of the imido is away from this unfavorable steric interaction between imido aryl and alkylidene *tert*-butyl. However, it has been well documented that imido angles, especially of heavier congeners like molybdenum and tungsten, often have very flat potential energy surfaces

associated with imido bending,[3] and it is unlikely that this imido bending results in a large energetic change relative to the linear variety found in the tethered complex.

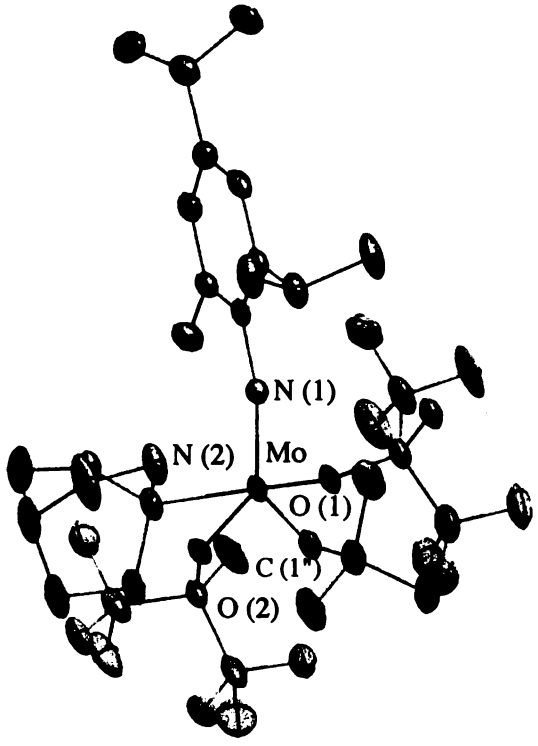
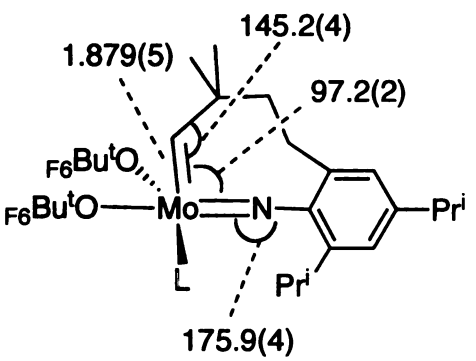


Figure 3.2 ORTEP Diagram of $Mo(OBu^t_{F6})_2(quin)(NAr')[=C(H)Bu^t]$ (**19**)

Of greater possible consequence are the angles associated with the alkylidene (Figure 3.3). The alkylidene CH in Schrock's catalyst has an α-agostic interaction leading to larger than normal Mo–C_α–R angles and depressed J_{CH} couplings relative to common sp^2-hybridized carbons. The tether appears to reduce the Mo–C_α–R angle by about 8° relative to the untethered derivative. In addition, there is an 11° change in the N(imido)-Mo-C(alkylidene) angle, with this parameter for cyclic derivative being significantly smaller. This leads to a rise in the alkylidene J_{CH} coupling of about 4 Hz presumably due to a slightly reduced α-agostic interaction in the tethered complex.[4]

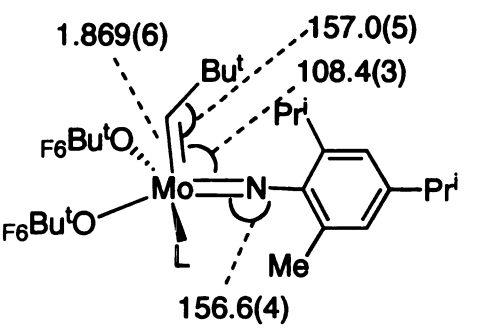
Table 3.2. Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **19**.

Mo–N (1)	1.729 (5)	Mo–O (2)	1.977 (4)
Mo–C (1")	1.869 (6)	Mo–N (2)	2.292 (4)
Mo–O (1)	2.028 (4)		
N (1)–Mo–C (1")	108.4 (3)	O (1)–Mo–O (2)	85.03 (15)
N (1)–Mo–O (1)	97.03 (17)	N (1)–Mo–N (2)	88.77 (19)
C (1")–Mo–O (1)	101.7 (2)	C (1")–Mo–N (2)	92.2 (2)
N (1)–Mo–O (2)	134.34 (18)	O (1)–Mo–N (2)	162.37 (15)
C (1")–Mo–O (2)	115.8 (2)	O (2)–Mo–N (2)	79.08 (16)



Alkylidene J_{CH} = 125 Hz

10



Alkylidene J_{CH} = 121 Hz

19

Figure 3.3. Structural comparisons between tethered **10** and untethered **19**. L = quinuclidine.

Conclusion

Structurally characterized examples of electronically similar tethered and untethered hexafluoro-*tert*-butoxide complexes provided evidence, supported by J_{CH}

couplings from NMR, that the tethered derivative has a slightly attenuated α-agostic interaction. The alternative architecture of the imido-tethered alkylidenes provide interesting differences with untethered analogs and, hence, provide new opportunities to study the effects of these structure types on reactivity and electronic structure.

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. The ^{13}C NMR assignments are based on decoupled ^{13}C, peak heights for overlapping signals, and DEPT experiments. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Alumina, Celite, and silica were dried at a temperature >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. Acetic acid, acetic anhydride, triethylamine, and aluminum chloride were purchased from Spectrum Chemical Co. and used without purification. Fuming nitric acid, triflic acid, and $LiAlH_4$ were purchased from Aldrich Chemical Co. and used without purification. Thallium ethoxide was purchased from Strem Chemical Co. and

was degassed before use. Quinuclidine was purchased from Aldrich Chemical Co., and crystallized from ether/pentane at –35 °C prior to use. 2-Chloropropane was purchased from Acros Chemical Co. and was used without purification. Neopentyllithium was prepared as described in literature.[5]

Preparation of 1-methyl-3,5-diisopropylbenzene (11). A 2-necked flask was loaded with toluene (9.21 g, 0.1 mol) and $AlCl_3$ (26.27 g, 0.2 mol, 2 equiv). This mixture was chilled to –40 °C in a dry ice/acetonitrile bath and stirred vigorously using a mechanical stirrer. To this slurry was slowly added 2-chloropropane (31.42 g, 0.4 mol, 4 equiv), and the mixture was further stirred vigorously for another 3 h. The slurry was added to ice-cold water (500 mL), and this mixture was stirred vigorously for 2 h. The product was extracted with ether (5 × 120 mL). The combined ether extracts were washed with water (2 × 100 mL), brine (2 × 75 mL), and dried over anhydrous $MgSO_4$. After filtration, the volatiles were removed in vacuum to afford the desired product as a yellow oil (16.7 g, 0.094 mol, 94%).[6] ^{1}H NMR (300 MHz, $CDCl_3$): 6.90 (s, 3 H, *aromatic-H*), 2.86 (sept, 2 H, C*H*$(CH_3)_2$, J_{CH} = 6.9 Hz), 2.34 (s, 3 H, C*H*$_3$), 1.26 (d, 12 H, C*H*$_3$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 148.81, 137.62, 124.64, 121.78, 34.11, 24.07, 21.51. Elemental Analysis Calc. For $C_{13}H_{20}$: C, 88.54; H, 11.45. Found: C, 88.95; H, 11.80. MS (EI) *m/z* = 176(M^+). R_f = 0.65 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of 2-methyl-4,6-diisopropyl-1-nitrobenzene (12). To a flask, was added fuming nitric acid (3.6 mL, 90%, d = 1.5), acetic acid (3.5 mL), and acetic anhydride (2.7 mL). The solution was cooled to room temperature. This solution was added dropwise to 1-methyl-3,5-diisopropylbenzene (8.9 g, 0.05 mol) in 4 mL acetic

anhydride. The reaction was maintained at 0 °C during the addition using an ice water bath. After the addition was complete, the mixture was stirred at 0 °C for 12 h. The reaction mixture was poured in ice-cold water (100 mL). The product was extracted with diethyl ether (5 × 50 mL), and the combined organic layers were washed with a saturated solution of $NaHCO_3$ (500 mL) until no gas formed on addition of the solution. The organic solution was filtered, and the separated solids washed with ether (5 × 50 mL). The combined ether solutions were dried with anhydrous $MgSO_4$. The volatiles were removed in vacuum providing the product as a light yellow oil. The compound was used without further purification (10.5 g, 0.047 mol, 95%). The compound was isolated as a mixture of two isomers with the desired isomer favored 9:1. ^1H NMR (300 MHz, $CDCl_3$): 7.02 (s, 1 H, *aromatic-H*), 6.92 (s, 1 H, *aromatic-H*), 2.86 (overlapping sept, 2 H, $CH(CH_3)_2$), 2.24 (s, 3 CH_3), 1.22 (d, 6 CH_3, J_{CH} = 6.9 Hz), 1.21 (d, 6 CH_3, J_{CH} = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 151.02, 139.61, 128.69, 126.53, 124.66, 122.23, 34.12, 28.99, 23.79, 23.77, 17.41. MS (EI) m/z = 221(M^+). R_f = 0.73 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of 2-methyl-4,6-diisopropylaniline (14). In a glove box, $LiAlH_4$ (3.6 g, 0.094 mol, 2 equiv) and diethyl ether (300 mL) were placed in a 500 mL Schlenk flask equipped with a stir bar. The flask was closed with a rubber septum, taken outside the glove box, and kept in a water bath to maintain the temperature between 16-25 °C. To the slurry, was slowly added 2-methyl-4,6-diisopropyl-1-nitrobenzene (10.5 g, 0.047 mol, 9:1 mixture of isomers from previous step) over a period of 1 h. After the addition was completed the water bath was removed, and the reaction mixture was stirred overnight at

room temperature. The mixture was cooled to 0 °C using an ice bath, and the excess lithium aluminum hydride was quenched by the drop-wise addition of a saturated solution of $MgSO_4$ solution. The precipitated salts were removed by filtration through Celite, washing with chloroform (400 mL). The filter cake was again washed with chloroform (5 × 50 mL). The combined organic solutions were dried to afford the mixture as an orange oil. Column chromatography (silica gel, 250–400 mesh, 8:2 hexane:ethyl acetate) afforded the desired product as a yellow oil (5.5 g, 0.029 mol, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.92 (s, 1 H, *aromatic-H*), 6.84 (s, 1 H, *aromatic-H*), 3.55 (s, 2 H, NH_2), 2.93 (sept, 1 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.81 (sept, 1 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.20 (s, 3 CH_3), 1.29 (d, 6 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 1.24 (d, 6 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 139.25, 138.68, 131.94, 125.72, 122.17, 121.15, 33.52, 27.93, 24.35, 22.40, 18.07. MS (EI) *m/z* = 191(M^+). R_f = 0.70 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of Mo(NAr')$_2$Cl$_2$(DME) (16). In a glove box, a 250 mL Schlenk flask was loaded with $(NH_4)_2Mo_2O_7$ (2.44 g, 7.18 mmol), 100 mL DME, and a stir bar. To the suspension was added NEt_3 (5.8 g, 57 mmol), $ClSiMe_3$ (13.25 g, 122 mmol), and Ar'NH_2 (5.5 g, 29 mmol). The mixture was stirred at room temperature inside the glove box for 1 h. The flask was closed with a septum, partially evacuated, and heated in an oil bath at 70 °C for 12 h. The reaction mixture gradually changes color from light yellow to orange to dark red in the first couple of hours. The reaction was monitored in a similar fashion as discussed previously for **7** in Chapter 2. After cooling to room temperature, the flask was evacuated and taken inside the glove box. The solution was filtered though

Celite. The volatiles of the filtrate were removed in vacuum to give a dark-red viscous oil, which can be crystallized from ether/pentane to give a brick-red powder of $Mo(NAr')_2(DME)Cl_2$ (7.6 g, 11.96 mmol, 83%). ^1H NMR (300 MHz, $CDCl_3$): 6.86 (s, 2 H, *aromatic-H*), 6.76 (s, 2 H, *aromatic-H*), 3.96 (s, 4 H, OCH_2), 3.85 (s, 6 H, OCH_3), 3.78 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.79 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.41 (s, 6 CH_3), 1.17 (d, 12 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 1.03 (d, 12 $CH(CH_3)_2$, J_{CH} = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 153.31, 147.79, 144.46, 134.72, 125.38, 120.83, 71.12, 63.11, 33.94, 27.61, 24.45, 23.87, 18.97. Elemental Analysis. Calc. for $C_{30}H_{48}N_2O_2Cl_2Mo$: C, 56.68; H, 7.63; N, 4.41. Found: C, 56.70; H, 7.29; N, 4.41. M.p. = 175-177 °C (dec).

Preparation of $Mo(NAr')_2(CH_2Bu^t)_2$ (17). In a glove box, to a –90 °C solution of $Mo(NAr')_2(DME)Cl_2$ (2.2 g, 3.46 mmol) in 50 mL ether was added neopentyllithium (0.541 g, 6.92 mmol, 2 equiv). The solution was allowed to reach room temperature and stirred for 5 h. The reaction was monitored in a similar fashion as discussed previously for **8** in Chapter 2. The reaction mixture was filtered through Celite to remove LiCl. The volatiles of the filtrate were removed in vacuo to give a red viscous oil, which was crystallized from ether/pentane to afford $Mo(NAr')_2CH_2Bu^t)_2$ as orange microcrystals (1.78 g, 2.88 mmol, 83%). ^1H NMR (300 MHz, $CDCl_3$): 6.83 (s, 2 H, *aromatic-H*), 6.76 (s, 2 H, *aromatic-H*), 3.47 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.78 (sept, 2 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 2.09 (s, 6 H, CH_3), 2.01 (s, 4 H, CH_2), 1.18 (d, 12 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz), 1.11 (s, 18 H, CH_3), 1.03 (d, 12 H, $CH(CH_3)_2$, J_{CH} = 6.9 Hz).

$^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 152.84, 145.09, 141.61, 132.37, 125.01, 120.52, 78.89, 33.92, 33.47, 33.44, 28.00, 23.99, 23.27, 19.48. Elemental Analysis. Calc. for $C_{36}H_{60}N_2Mo$: C, 70.08; H, 9.82; N, 4.54. Found: C, 70.27; H, 9.88; N, 4.55. M.p. = 153-155 °C (dec).

Preparation of Mo(NAr')(CHBu^t)(DME)(OTf)$_2$ (18). In a glove box, a –90 °C solution of triflic acid (1.3 g, 8.64 mmol, 3 equiv) in DME (8 mL) was added to a –90 °C solution of Mo(NAr')$_2$(CH$_2$Bu^t)$_2$ (1.8 g, 2.88 mmol) in DME (30 mL). The reaction was stirred for 12 h. During this period, the color changed from bright orange to dark yellow. The volatiles were removed in vacuo to give dark yellow oil. The resulting oil was extracted with cold toluene, and the extract filtered through a plug of Celite. The filtrate was concentrated in vacuo. The resulting dark yellow oil was dissolved in ether, layered with pentane, and allowed to stand at –35 °C until a bright yellow powder was obtained. The powder was collected by filtration and recrystallized from layered 1:1 ether:pentane to obtain the pure product (1.3 g, 1.75 mmol, 61%). By NMR spectroscopy there were 2 isomers visible. However, one isomer was in much higher concentration than the other. The spectral resonances for the major isomer are given. ^1H NMR (300 MHz, $CDCl_3$): 14.08 (s, 1 H, Mo=C*H*, J_{CH} = 121 Hz), 6.97 (s, 1 H, *aromatic-H*), 6.84 (s, 1 H, *aromatic-H*), 4.28 (br s, 3 H, OC*H*$_3$), 4.07 (br s, 2 H, OCH$_2$), 3.84 (br s, 2 H, OCH$_2$), 3.68 (sept, 1 H, *CH*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 3.52 (br s, 3 H, OC*H*$_3$), 2.84 (sept, 1 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.43 (s, 3 H, C*H*$_3$), 1.26 (s, 9 H, CMe$_3$), 1.21 (d, 12 H, CH(CH$_3$)$_2$, J_{CH}= 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 327.88, 151.98, 147.95, 142.26, 130.43, 130.04, 128.28, 128.22, 126.32, 126.12, 124.68, 124.03, 121.30, 73.18, 70.55, 66.07, 62.67,

58.56, 30.56, 28.10, 27.93, 25.26, 23.47, 22.49. ^{19}F NMR ($CDCl_3$): –76.77. Elemental Analysis. Calc. for $C_{24}H_{39}NO_8S_2F_6Mo$: C, 38.75; H, 5.30; N, 1.88. Found: C, 38.32; H, 5.18; N, 2.09. M.p. = 126-128 °C (dec).

Preparation of Mo(NAr')(CHBu^t)(quin)(OBu$^t_{F6}$)$_2$ (19). In a glove box, to a frozen solution of Mo(NAr')(CHBu^t)(dme)(OTf)$_2$ (700 mg, 0.942 mmol) in ether:THF (9:1, 1 mL) was added a solution of TlOBu$^t_{F6}$ (726 mg, 2 equiv, 1.883 mmol) in ether:THF (9:1, 1 mL). The reaction mixture stirred for 3 h. Then, the solvent was removed, and the product was dissolved in pentane. The salts were filtered away through Celite, and the solvent was removed in vacuo. The product was redissolved in pentane (2 mL). To this was added a solution of quinuclidine (105 mg, 0.0941 mmol) in pentane (1 mL), and the reaction mixture was stirred for 40 min. After 40 min, the solution was concentrated to 1 mL and 3-4 drops of THF were added. The solution was kept in the freezer at –35 °C to afford Mo(NAr')(CHBu^t)(quin)OBu$^t_{F6}$)$_2$ as yellow-orange crystals in 11% isolated yield (78 mg, 0.094 mmol). The NMR spectroscopic data are consistent with an approximately 1:1 mixture of two major isomers in $CDCl_3$; there are at least 3 minor isomers present. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): 13.10 (s, Mo=C*H*, J_{CH} = 139.06 Hz, *anti*), 12.40 (s, Mo=C*H*, J_{CH} = 121 Hz, *syn*), 7.26-7.12 (m, aromatic), 4.46 (sept, 1 H, J_{CH} = 7.2 Hz, *CH*(CH_3)$_2$), 3.51 (sept, J_{CH} = 6.9 Hz, *CH*(CH_3)$_2$), 3.14 (t, J_{CH} = 8.1 Hz, CH_2), 2.85 (t, J_{CH} = 7.5 Hz, CH_2), 1.80 (s, C*H*), 1.46-1.60 (m, CH_2), 1.44 (br s, CH_2), 1.35-1.32 (m, CH_2), 1.30 (s, CH_3), 1.26 (s, CH_2), 1.24 (s, CH_2), 1.22-1.21 (m, CH_2), 1.19 (s, CH_3), 1.16 (s, CH_3). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): 311.04 (*anti*),

298.75 (*syn*), 153.32, 151.97, 148.15, 147.57, 146.07, 128.84, 127.85, 124.30, 123.63, 123.57, 65.88, 52.67, 49.54, 46.45, 46.40, 32.39, 31.50, 29.16, 28.61, 27.92, 26.14, 26.02, 25.58, 24.66, 24.26, 24.06, 23.94, 20.60, 19.83, 19.14, 18.60, 16.48, 15.28. Elemental Analysis. Calc. for $C_{33}H_{48}N_2O_2F_{12}Mo$: C, 47.83; H, 5.84; N, 3.38. Found: C, 47.72; H, 5.72; N, 3.39. M.p. = 168-170 °C.

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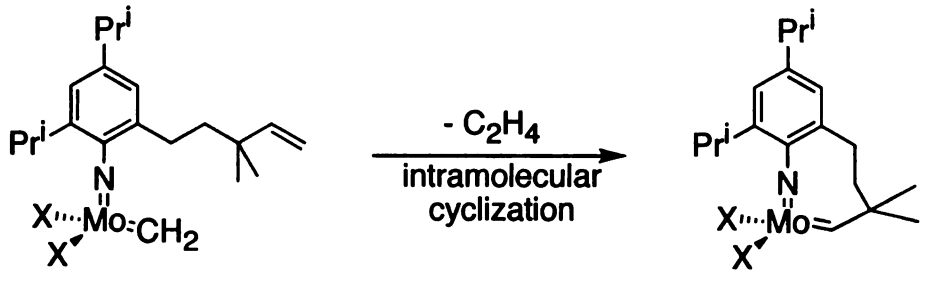
CHAPTER 4

STABILITY AND REACTIVITY OF IMIDO-TETHERED COMPLEXES OF MOLYBDENUM

Introduction

The development of homogeneous, well-defined catalyst systems for target-oriented application of the olefin metathesis reaction has been a key for the wide popularity of the reaction.[1] Complexes of the type $M(CHR)(NAr)(OR')_2$, where M = Mo or W, Ar = 2,6-diisopropylphenyl, R = neopentyl or neophyl, and R' = Bu^t, Bu^t_{F6} developed and well studied by Schrock and coworkers have proven to be useful olefin metathesis catalysts.[2] Chapter 2 discusses the detailed synthesis of an analogous class of Mo-alkylidene complexes.[3] The imido-tethered alkylidene complexes have opened doors for studying reactions of these unique class of complexes.

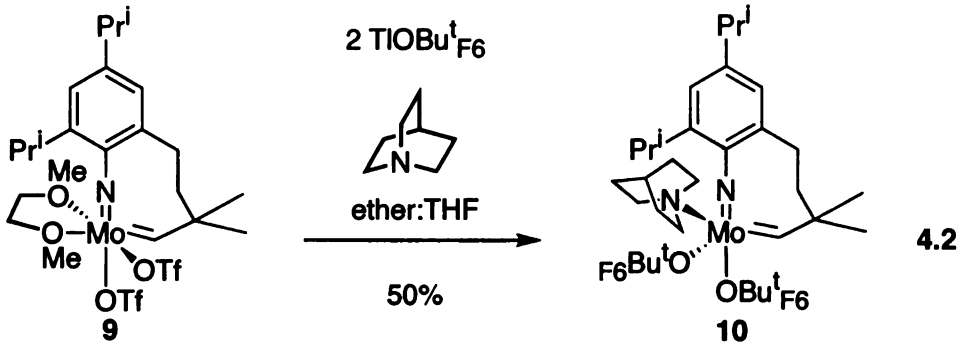
These unique tethered systems can be applied to prevent or slow down the bimolecular decomposition of the active methylidene [$Mo=CH_2$] formed during the course of a ring-closing metathesis reaction.[4] The tether would produce a stable catalyst that would regenerate after the consumption of the substrate (Equation 4.1) via intramolecular cyclization of active methylidene.



4.1

The tethered molybdenum catalyst previously reported by our group was conveniently synthesized as a quinuclidene adduct (Equation 4.2). However, this tethered

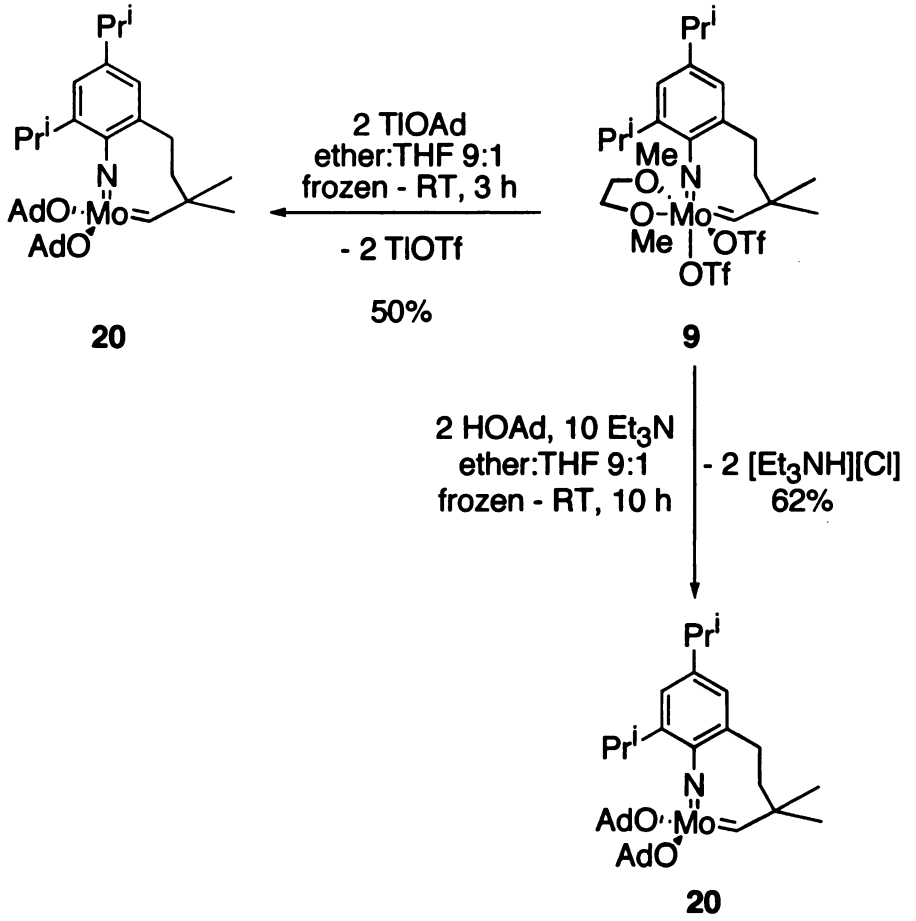
quinuclidene adduct was inactive for the initial test ring-closing metathesis reaction of diethyl diallylmalonate perhaps due to strongly co-ordinated quinuclidene on the metal center. Replacement of the triflate ligands with hexafluoro-*tert*-butoxide ligands in the absence of a donor ligand led to the formation of uncharacterized paramagnetic products.



Results and Discussion

Synthesis and Structure of Catalysts

Herein, we report the synthesis, structure and utility of a stable bis(adamantoxide) complex; $Mo(OAd)_2(N\text{-}2,4\text{-}Pr^i_2C_6H_2\text{-}6\text{-}CH_2CH_2CMe_2CH{=})$ (**20**). By replacement of the triflates in **9** by adamantoxide (OAd) using TlOAd, we were able to isolate a stable product $Mo(OAd)_2(N\text{-}2,4\text{-}Pr^i_2C_6H_2\text{-}6\text{-}CH_2CH_2CMe_2CH{=})$ (**20**). X-ray quality crystals can be easily obtained by triflate metathesis with two equivalents of 1-adamantanol in the presence of excess triethylamine (Scheme 4.1), and an ORTEP representation is shown in Figure 4.1. A molecule of hexane was found disordered in the asymmetric unit. For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **20** see Table 4.1. The complex is pseudo-tetrahedral. The Mo=N and Mo=C distances are typical for this class of molecule at 1.732(6) and 1.877(7) Å, respectively. The angle subtended at N(1) is essentially linear at 172.5(5) Å. The angle subtended at C(1) is 142.5(5) Å.



Scheme 4.1. Synthesis of the tethered carbene alkoxide catalyst **20**

Table 4.1 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **20**.

Mo(1)–N (1)	1.732 (6)	Mo(1)–O (2)	1.901 (5)
Mo(1)–C (1)	1.877 (7)	Mo(1)–O (1)	1.890 (5)
N (1)–Mo (1)–C (1)	99.0 (3)	O (1)–Mo–O (2)	111.5 (2)
N (1)–Mo (1)–O (1)	114.8 (3)	Mo (1)–N (1)–C (11)	172.5 (5)
C (1)–Mo (1)–O (1)	108.1 (3)	Mo (1)–C (1)–C (2)	142.5 (5)
N (1)–Mo (1)–O (2)	113.5 (3)	C (1)–Mo (1)–O (2)	108.9 (3)

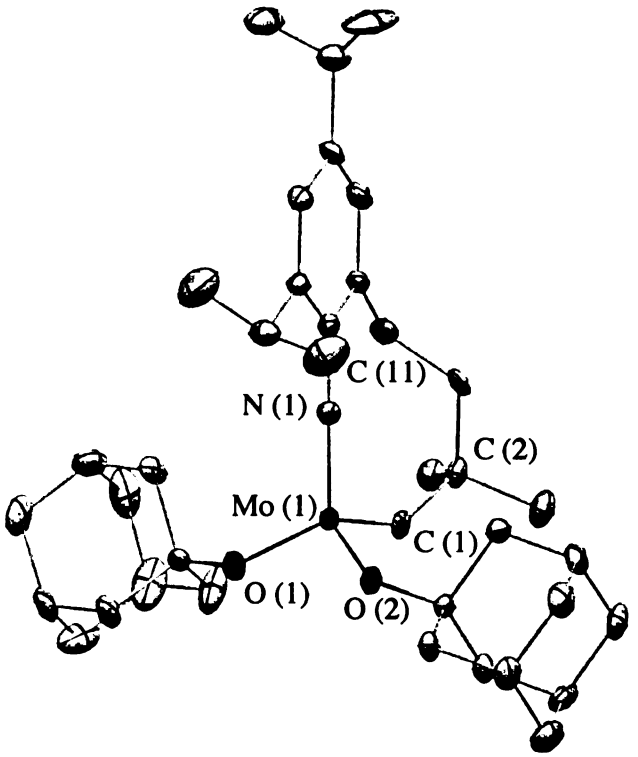
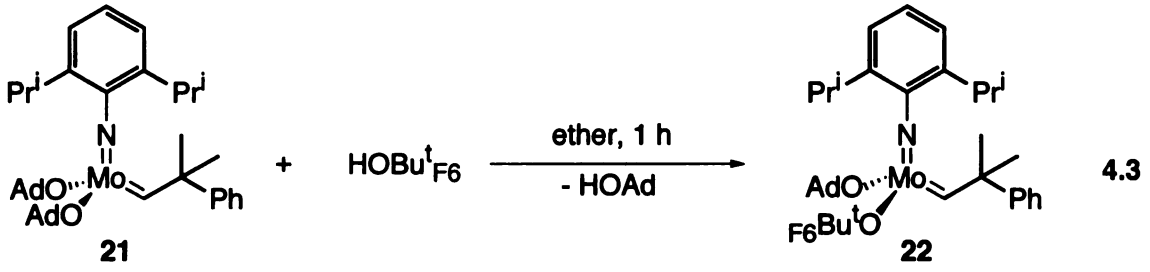


Figure 4.1. ORTEP representation for the structure of **20** from X-ray diffraction. Solvent and hydrogens are excluded for clarity.

In the early 90s, a mixed catalyst system was reported by Gibson and coworkers consisting of the formula $Mo(NAr)(CHCMe_2Ph)(OBu^t)(OBu^t_{F6})$.[5] This catalyst was employed in the polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene. In solution the complex was proposed to be in equilibrium with $Mo(NAr)(CHCMe_2Ph)(OBu^t)_2$ and $Mo(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$; however, no structural data corresponding to the mixed species was presented. Further, Grubbs and Fu reported the in situ synthesis of $Mo(NAr)(CHCMe_2Ph)(OBu^t)(OBu^t_{F6})$ via the addition of $LiOBu^t_{F6}$ to $Mo(NAr)(CHCMe_2Ph)(OBu^t)_2$.[6] In this chapter, we will discuss the synthesis

and structure of this mixed alkoxide species and use this strategy for a comparative study of the imido-tethered and untethered olefin metathesis systems.

By ligand exchange in $Mo(NAr)(CHCMe_2Ph)(OAd)_2$ (**21**) using $HOBu^t_{F6}$, we were able to isolate the stable product $Mo(NAr)(CHCMe_2Ph)(OAd)(OBu^t_{F6})$ (**22**). X-ray quality crystals can be easily obtained by crystallization of the product from pentane at –35 °C as yellow micro-crystals (Equation 4.3), and an ORTEP representation is shown in Figure 4.2.



4.3

For selected bond distances (Å) and angles (°) from the X-ray diffraction study on **22** see Table 4.2. The adamantoxide was found to be disordered over two sites. Tying the occupancies together and refining the ratio modeled this disorder. Unfortunately, the model required the use of restraints in the bond distances and only isotropic refinement. Anisotropic refinement of these carbon atoms was unsuccessful so they were left isotropic and all other non-hydrogen atoms were refined anisotropic. The ratio of the two disordered ligand sites refined to 0.66: 0.44. The complex is pseudo-tetrahedral.

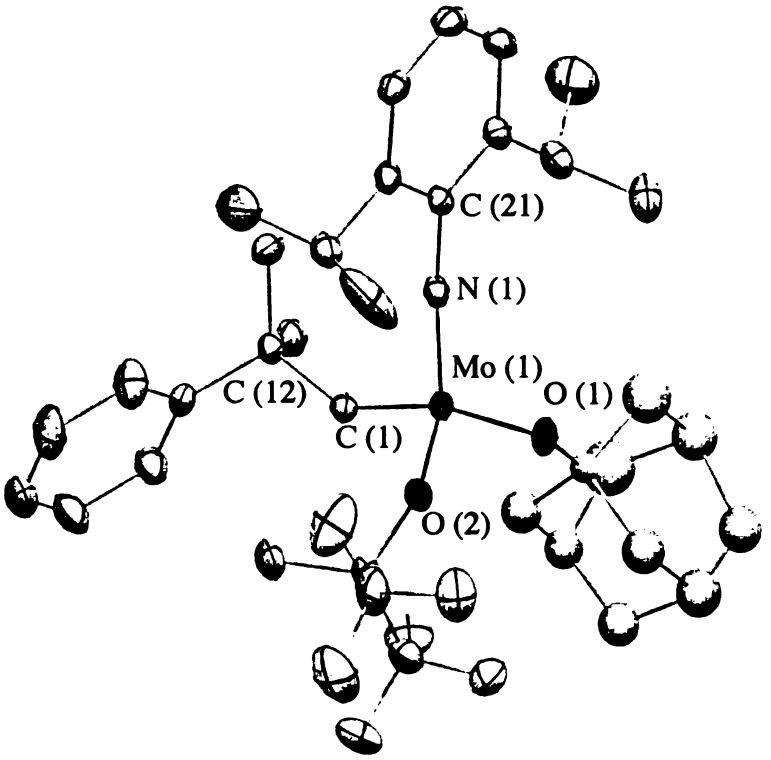


Figure 4.2 ORTEP representation for the structure of **22** from X-ray diffraction with hydrogens and disorder omitted.

Table 4.2 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **22**.

Mo(1)–N (1)	1.729 (3)	Mo(1)–O (2)	1.953 (3)
Mo(1)–C (1)	1.893 (3)	Mo(1)–O (1)	1.877 (2)
N (1)–Mo (1)–C (1)	101.16 (15)	O (1)–Mo–O (2)	111.54 (11)
N (1)–Mo (1)–O (1)	115.27 (13)	Mo (1)–N (1)–C (21)	174.6 (2)
C (1)–Mo (1)–O (1)	109.30 (14)	Mo (1)–C (1)–C (12)	144.2 (3)
N (1)–Mo (1)–O (2)	110.73 (13)	C (1)–Mo (1)–O (2)	108.15 (13)

The Mo=N and Mo=C distances are typical at 1.729(3) and 1.893(3) Å, respectively. The angle subtended at N(1) is essentially linear at 174.6(2) Å. The angle subtended at C(1) is 144.2(3) Å. The Mo-O(Ad) and Mo-O(Bu^t_{F6}) distances are typical at 1.877(2) and 1.953(3) Å, respectively.

At room temperature in C_6D_6, a 0.065 M solution of **22** gives a mixture of **21**, **22** and **23** with an equilibrium constant (K_{eq}) of 116 as shown in Figure 4.3.

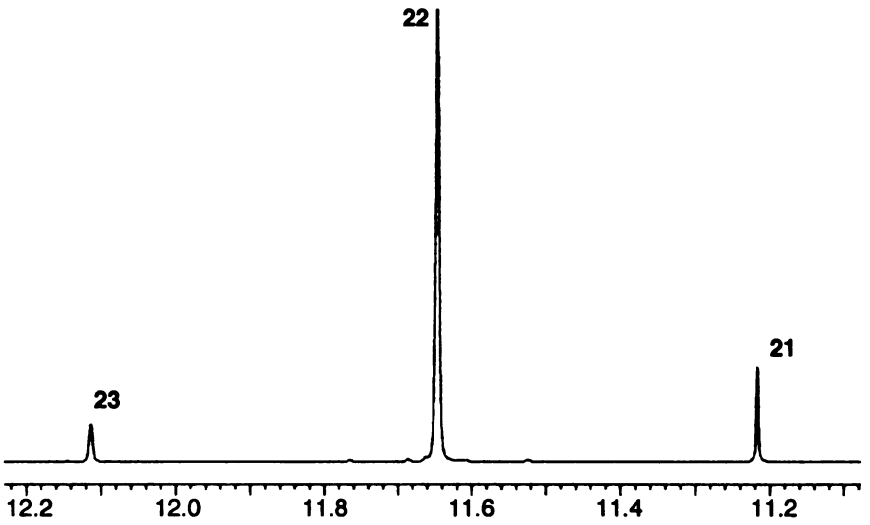


Figure 4.3 Alkylidene region of **22** in C_6D_6 at 500 MHz.

For comparison, we mixed an equimolar (0.065 M) solution of complexes **21** and **23** in C_6D_6. The K_{eq} for the 1:1 mixture is 115 with the equilibrium strongly favoring the product **22**. The equilibrium constant does not vary with additional HOAd (115) or $HOBu^t_{F6}$ (116). Along similar lines, the equilibrium constant for the tethered system was found to be 125 at room temperature in C_6D_6 as shown in Figure 4.4.

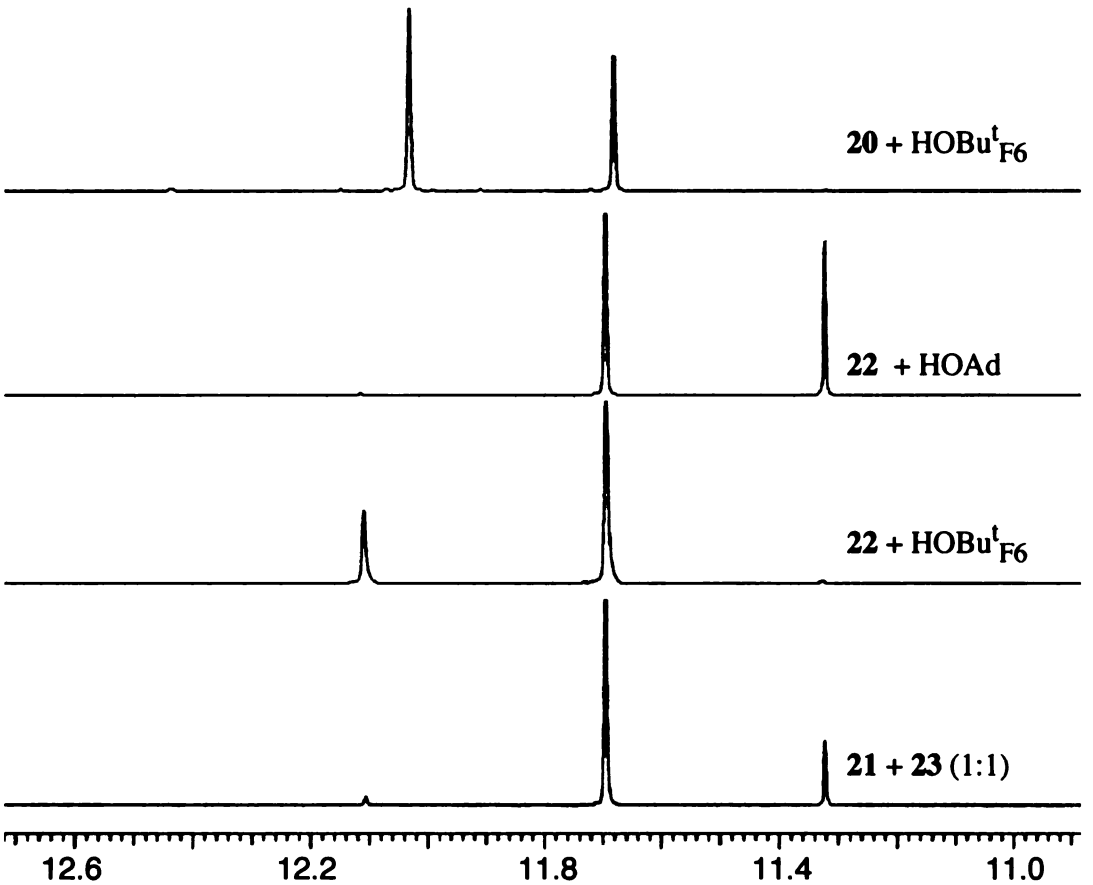


Figure 4.4 Alkylidene regions showing equilibrium mixtures of complexes.

Addition of 50 equivalents of HOBu$^t_{F6}$ to **22** afforded **23** as the major product, with a ratio of **23/22** = 3.8. This ratio was constant over 24 h at room temperature. When the volatiles of the above reaction were removed in vacuo and the product was redissolved in C_6D_6, the ratio of the isomers **22/21** was found to be 0.83 with **21** as the major product. (Figure 4.5)

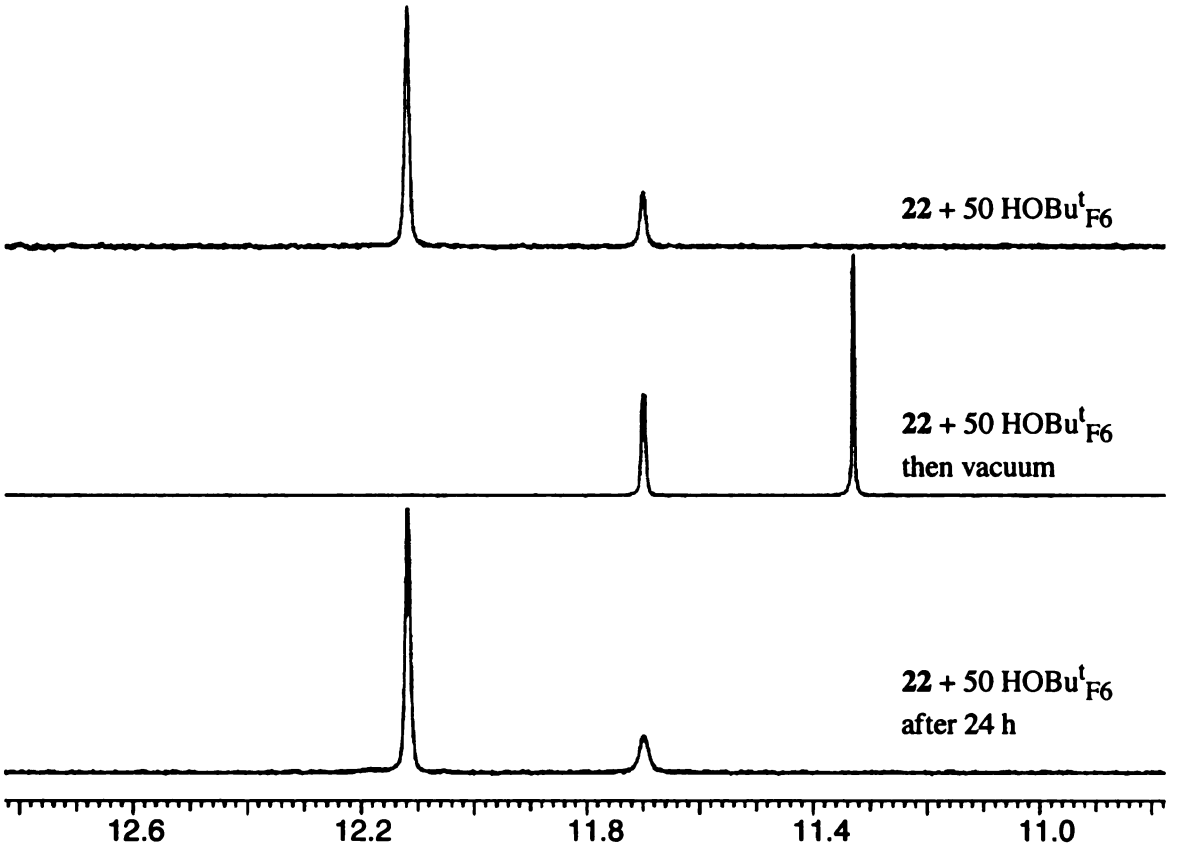
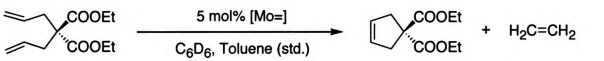


Figure 4.5 Alkylidene regions showing effect of large excess of $HOBu^t_{F6}$ on K_{eq}.

Ring-Closing Metathesis Studies Using Imido-Tethered Alkylidenes

Attempt to carry out catalytic ring-closing metathesis involved the strategy discussed above for a comparative study of the imido-tethered and untethered olefin metathesis systems. The study was carried out in two different ways. First, the consecutive addition of substrate to a solution of catalyst in C_6D_6 was used. The solution was stirred at room temperature for 12 h. An aliquot of the reaction was taken and a ^1H NMR recorded. To the reaction mixture was then added another batch of substrate and toluene (as internal standard) and the process repeated. The plot of % yield versus cycle is shown in Figure 4.6. The data indicates that the Schrock metathesis system is stable for an extended time period. This perhaps could be due to the fact that the methylidene

complex formed at the end of the first cycle is stabilized by the formation of a complex $Mo(NAr)(CH_2)(OAd)(OBu^t_{F6})(L)$, where L = olefin or coordination of oxygen from the substrate.[7]



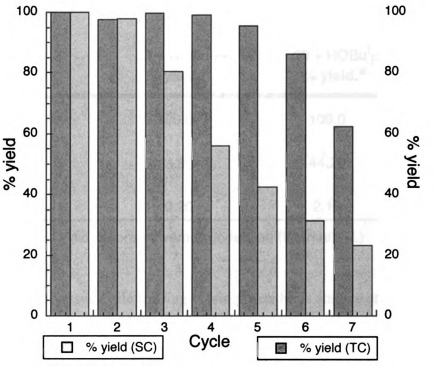
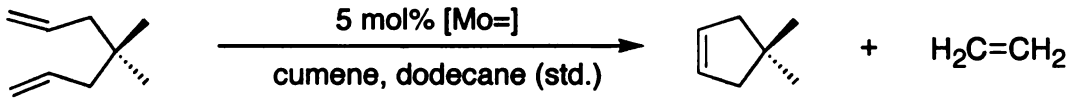


Figure 4.6 % yield versus cycle for ring-closing metathesis studies of diethyl diallylmalonate, where SC = **21** + $HOBu^t_{F6}$ and TC = **20** + $HOBu^t_{F6}$.

In the second method, substrate was added to a solution of catalyst in dichloromethane, and the solution was stirred at room temperature for 2.5 h. A sample of the reaction was taken and a GC-FID was recorded. The volatiles of the reaction mixture were then removed in vacuo, and the residue was redissolved in CH_2Cl_2. To the reaction mixture was then added another batch of substrate, and the process was repeated. The

data of % yield versus cycle is shown in Figure 4.7. In this case the tethered catalyst system decomposes similarly to the untethered system. This could be attributed to the fact that the intramolecular cyclization of the active methylidene is slower than olefin-coordination to the metal center.



Cycle	21 + $HOBu^t_{F6}$ % yield.[a]	20 + $HOBu^t_{F6}$ % yield.[a]
1	100.0	100.0
2	3.80	44.20
3	0.20	2.10

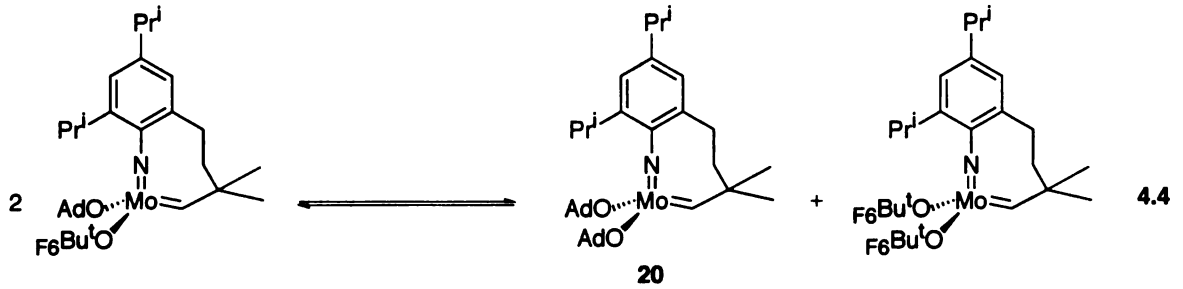
[a] GC-FID % yield calibrated versus dodecane (internal std.)
1 Cycle : 2.5 h

Figure 4.7. % yield versus cycle for ring-closing metathesis studies of 4,4-dimethyl-1,6-heptadiene.

Conclusion

We have synthesized and demonstrated the application of imido-tethered alkylidenes in ring-closing metathesis and structurally characterized the first example of a mixed alkoxide species. The tethered alkylidene complex (**20**) has excellent activity in the presence of $HOBu^t_{F6}$ and somewhat better stability over complexes without the tether. The observations could be explained on the basis of a relatively simple equilibrium reaction as shown in Equation 4.4.[8] For the equilibrium to be maintained as written in Equation 4.4 all complexes should be stable under given conditions. However, the bis-

hexafluoro-*tert*-butoxide complex was found to be highly unstable and decomposed at room temperature. Thus the equilibrium would favor the formation of **20** as a major product and hence the decrease in activity for the given ring-closing metathesis reaction.



Experimental

General Considerations All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Some of the assignments are tentative due to the large number of overlapping peaks. The ^{13}C NMR assignments are based on decoupled ^{13}C, peak heights for overlapping signals and DEPT experiments. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Alumina, Celite, and silica were dried at a temperature >200 °C under dynamic vaccum

for at least 16 h, then stored under inert atmosphere. Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](DME)$(OTf)_2$ (**9**) was prepared as described in the literature.[3a] Mo[=N-2,6-$Pr^i_2C_6H_3$](CHCMe$_2$Ph)$(OAd)_2$ (**21**) was prepared as described in the literature.[9] Thallium ethoxide was purchased from Strem Chemical Co. and was degassed before use. 1-adamantanol was purchased from Aldrich Chemical Co., and was used without purification. Triethylamine was purchased from Spectrum Chemical Co., distilled over anhydrous KOH under dry N_2 prior to use. Diethyldiallyl malonate was purchased from Aldrich Chemical Co., and was distilled over molecular sieves (3 Å, 1/16 inch pellets) under dry N_2. Diethyldiallyl malonate was stored in sealed vials in a dry box prior to use. 4,4-dimethyl-1,6-heptadiene was prepared as described in the literature.[10] 4,4-dimethyl-1,6-heptadiene distilled under dry N_2, stored in a sealed vial in a dry box at –35 °C prior to use.

Preparation of 1-adamantoxide thallium(I) [TlOAd]. In the glove box, in a 125 mL Erlenmeyer flask was loaded 1-adamantanol (1.0 g, 6.57 mmol), a stir bar, and ether (30 mL). To the stirring solution of the alcohol was added TlOEt (1.64 g, 6.57 mmol) in ether (10 mL). The reaction was capped with a septum and stirred for 6 h at room temperature. The product was collected by filtration on a frit and washed with cold pentane (5 × 20 mL) to remove EtOH and residual TlOEt. The volatiles were removed in vacuo to afford 1.89 g (81%) of product as a white powder. The compound is insoluble in C_6D_6, acetone-d_6, $CDCl_3$, and is sparingly soluble in THF-d_8. Hence ^1H and ^{12}C NMR data for the compound are not reported. M.p. = >400 °C.

Preparation of Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](OAd)$_2$ (20).

Method A. In a glove box, to a near frozen solution of **9** (350 mg, 0.472 mmol) in ether:THF (9:1, 10 mL) was added TlOAd (336 mg, 2 equiv, 0.944 mmol). The solution was allowed to reach room temperature and stir for 3 h. The solvent then was removed in vacuo, and the product was dissolved in pentane. The salts were removed by filtration though Celite. The volatiles of the filtrate were removed in vacuo to afford a dark orange powder. The desired product was crystallized from ether:pentane 1:2 at –35 °C, as yellow-orange powder (162 mg, 0.247 mmol, 52%).

Method B. In a glove box, to a chilled solution of **9** (100 mg, 0.135 mmol) in THF (2 mL) was added a solution of Et_3N (136 mg, 10 equiv, 1.348 mmol) and 1-adamantanol (41 mg, 2 equiv, 0.269 mmol) in THF:hexanes (2:8, 5 mL). The resulting mixture was allowed to reach room temperature and stir for 10 h. The solvent then was removed, and the product was dissolved in hexane. The salts were removed by filtration though Celite. The volatiles of the filtrate were removed under vacuum to afford a dark orange powder. The desired product crystallized from ether:hexane 1:4 at –35 °C as yellow-orange micro-crystals (56 mg, 0.0853 mmol, 63%). X-ray quality crystals of the above compound were obtained from Method B. A molecule of hexane was found disordered in the asymmetric cell. Due to fluxionality of the resulting tether and resonances due to the adamantyl ligands, the NMR spectrum is broad and complex. Assignments are made where possible. ^{1}H NMR (500 MHz, $CDCl_3$): 10.82 (J_{CH} = 121 Hz), 6.90 (d, 1H, *aromatic-H*, J_{CH} = 1.2 Hz), 6.88 (d, 1 H, *aromatic-H*, J_{CH} = 1.2 Hz), 3.55 (sept, 1 H, J_{CH} = 7.0 Hz), 2.83 (sept, 1 H, J_{CH} = 7.0 Hz), 2.19 (br s, 2 H), 2.07 (br s, 6 H), 1.67 (br s, 9 H), 1.54 (br s, 18 H), 1.22

(t, 12 CH_3, J_{CH} = 6.5 Hz), 1.02 (s, 6 CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 261.33, 152.35, 144.37, 140.39, 139.56, 123.43, 120.31, 54.67, 46.40, 46.09, 45.96, 36.20, 34.04, 31.13, 30.75, 29.07, 24.12, 23.19, 22.32, 14.04. Satisfactory elemental analysis could not be obtained for the complex. This could perhaps be due to a molecule of hexane trapped in the unit cell. Elemental Analysis Calc. for $[C_{38}H_{57}NO_2Mo]_2$.hexane ($C_{82}H_{128}N_2O_4Mo_2$): C, 70.44; H, 9.25; N, 2.00. Found: C, 71.50; H, 9.01; N, 1.87. M.p. = 150-152 °C.

Attempted Preparation of Mo(NAr)(CHMe$_2$Ph)(OAd)(OBu$^t_{F6}$) (22). In a glove box, to a near frozen solution of Mo(NAr)(CHCMe$_2$Ph)(OAd)$_2$ (**21**) (100 mg, 0.142 mmol) in ether (5 mL) was added HOBu$^t_{F6}$ (26 mg, 1 equiv, 0.142 mmol). The solution was allowed to reach room temperature and stirred for 1 h. The volatiles were then removed in vacuo. The product was redissolved in hexanes and filtered though Celite to remove residual 1-adamantanol. The volatiles of the filtrate were removed in vacuo to give a yellow powder. The desired product was crystallized from pentane at –35 °C as yellow micro-crystals. The NMR spectroscopic data in $CDCl_3$ are consistent with an approximately 1.00: 11.00: 1.44 mixture of the three complexes: Mo(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$ (**23**), Mo(NAr)(CHCMe$_2$Ph)(OAd)(OBu$^t_{F6}$) (**22**) and Mo(NAr)(CHCMe$_2$Ph)(OAd)$_2$ (**21**). The spectra are further complicated due to overlapping broad adamantoxide peaks and overlapping aromatic peaks. The assignable peaks due to the alkylidene are listed here. ^1H NMR (500 MHz, $CDCl_3$): 11.78 (J_{CH} = 121.7 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 273.47. ^{19}F NMR (282 MHz, $CDCl_3$): -77.88 (q, 3F), -78.30 (q, 3F).

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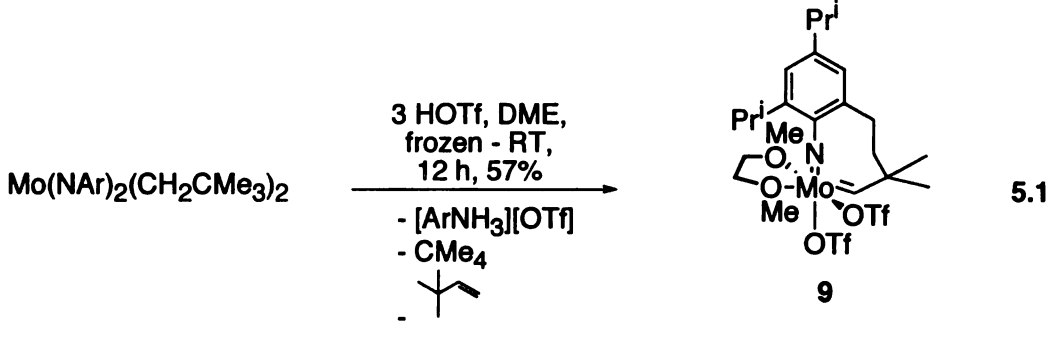
CHAPTER 5

STUDIES TOWARD THE SYNTHESIS OF AN IMIDO-TETHERED TUNGSTEN ALKYLIDENE

Introduction

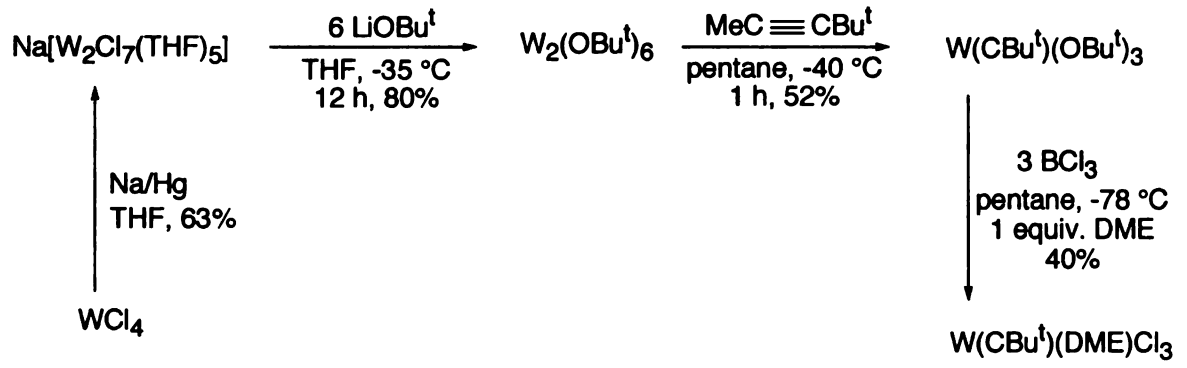
The synthesis of the imido-tethered molybdenum catalyst architecture discussed in Chapter 2 was successful and led to the stable complexes $Mo(OBu^t_{F6})_2$(quin)[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=] (**10**), and $Mo(OAd)_2$[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=] (**20**).[1] Formation of Mo[=N-2,4-$Pr^i_2C_6H_2$-2-$CH_2CH_2CMe_2CH$=](DME)$(OTf)_2$ (**9**) in the synthesis described in Chapter 2 involves the loss of one equivalent of the expensive amine moiety as the anilinium salt as shown in Equation 5.1. As part of the ongoing research involved around the synthesis of imido-tethered alkylidenes, we evaluated the viability of an imido-tethered tungsten alkylidene. The tungsten analogue would provide a complementary handle for the applications of these unique class of compounds.



5.1

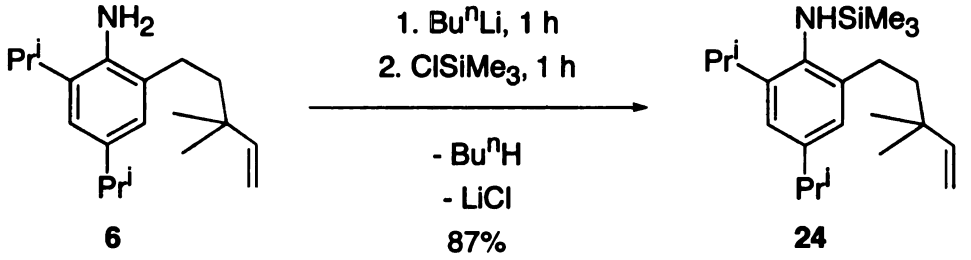
Results and Discussion

To avoid this loss of a relatively expensive amine, an alternative route for the synthesis of a tethered alkylidene was sought. The procedure involves the synthesis of $W(CBu^t)(DME)Cl_3$ using the protocol shown in Scheme 5.1.[2]



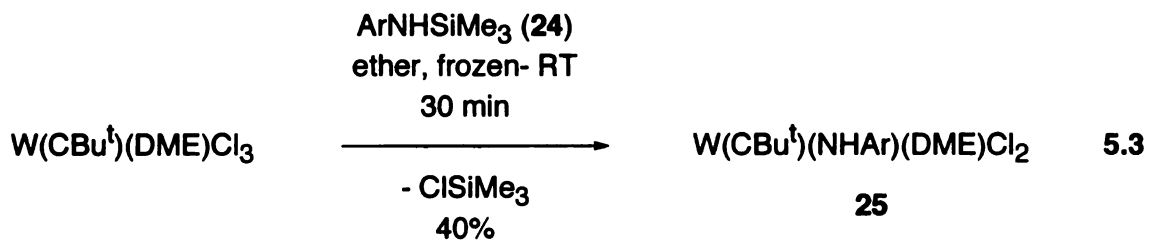
Scheme 5.1 Synthesis of $W(CBu^t)(DME)Cl_3$

$ArNHSiMe_3$ can be readily made by reaction of $ArNH_2$ (**6**) with 1 equivalent of *n*-butyllithium followed by addition of one equivalent of $ClSiMe_3$ as shown in Equation 5.2. The product **24** was not purified at this stage.



5.2

The reaction between $W(CBu^t)(DME)Cl_3$ and $ArNHSiMe_3$ (**24**) proceeds smoothly in diethylether to afford $W(CBu^t)(NHAr)(DME)Cl_2$ (**25**) as yellow micro-crystals in 40% yield as shown in Equation 5.3. X-ray crystallographic studies were carried out on single crystals of $W(CBu^t)(NHAr)(DME)(Cl)_2$. Selected bond lengths and angles for **25** are given in Table 5.1. The complex is pseudo-octahedral with the neopentylidyne and amido ligands *cis* to each other. The two chlorides are *trans* to each other [Cl(1)–W–Cl(2) = 155.91(7)°], and the coordinated DME completes the octahedral coordination sphere.



5.3

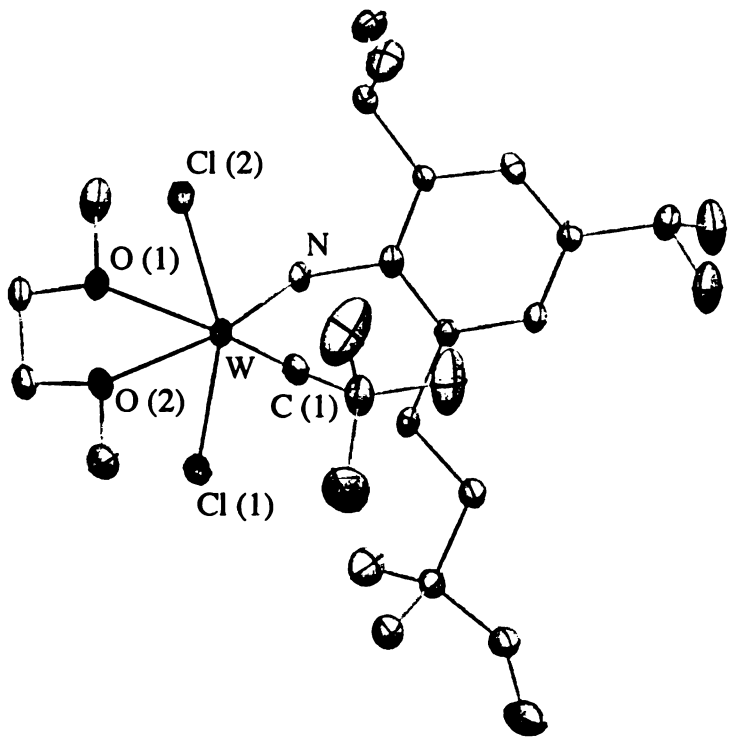


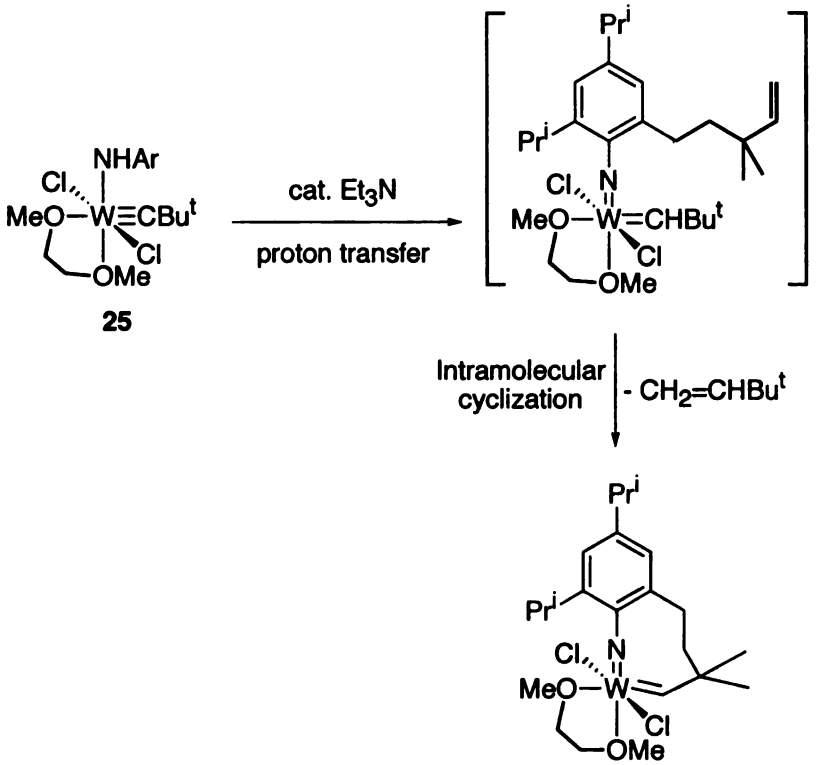
Figure 5.1 ORTEP Diagram of **25** from X-ray diffraction. Hydrogens are excluded for clarity.

The tungsten-neopentylidyne bond length [W–C(1) = 1.719(8) Å] is slightly shorter than the tungsten-neopentylidyne bond length values of $W(CBu^t)(PHPh)(PEt_3)_2(Cl)_2$ [1.808(6)Å], and $W(CBu^t)(CHBu^t)(CH_2Bu^t)(dmpe)$ [1.785(8)Å].[3] The neopentylidyne α-carbon resonance was found at 304 ppm, which is analogous to the diisopropyl derivative $W(NHAr')(CBu^t)(DME)(Cl)_2$, where Ar' = 2,6-diisopropylphenyl made by Schrock and co-workers.[2]

Table 5.1 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **25**.

W–C (1)	1.719 (8)	W–Cl (2)	2.380 (19)
W–N	1.902 (5)	W–Cl (1)	2.396 (18)
W–O (1)	2.257 (4)	W–O (2)	2.454 (5)
C (1)–W–N	96.2 (3)	C (1)–W–O (1)	99.6 (2)
N–W–O (1)	164.18 (19)	C (1)–W–Cl (2)	100.8 (2)
N–W–Cl (2)	97.91 (15)	O (1)–W–Cl (2)	79.92 (13)
C (1)–W–Cl (1)	96.2 (2)	N–W–Cl (1)	97.08 (16)
O (1)–W–Cl (1)	80.52 (13)	Cl (2)–W–Cl (1)	155.91 (7)
C (1)–W–O (2)	170.6 (2)	N–W–O (2)	92.68 (18)
O (1)–W–O (2)	71.50 (17)	Cl (2)–W–O (2)	80.89 (12)
Cl (1)–W–O (2)	79.67 (12)		

Although this procedure for the synthesis of a tethered alkylidene is potentially more convergent, the migration the α hydrogen from nitrogen to carbon in the presence of catalytic amount of Et_3N followed by an intramolecular cyclization to generate the tethered alkylidene (Scheme 5.2) has been unsuccessful. The proton transfer reaction gives multiple unisolable products in the presence of catalytic amounts of acids, such as HCl and HOTf. Catalytic amounts of bases such as pyridine, 2,6-lutidine, $LiOBu^t$, and $KO(C_6H_3\text{-}2,6\text{-}Pr^i_2)$ did not lead to alkylidene either.



Scheme 5.2 Attempted formation of an imido-tethered alkylidene.

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. C_6D_6 was purchased from Cambridge Isotopes Laboratories, Inc. distilled from sodium under dry N_2 and stored under a sealed container equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Celite was dried at a temperature >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. W(CBu^t)(DME)Cl_3 was prepared as described in the literature.[2]

Preparation of $ArNHSiMe_3$ (24). In a glove box, to a near frozen solution of **6** (500 mg, 1.82 mmol) and pentane (10 mL) in a 20 mL vial was slowly added *n*-BuLi (1.3 mL, 1.6 M, 1.1 equiv) over a period of 10 min. The reaction mixture was stirred for 1 h and allowed to come to room temperature. Me_3SiCl (197 mg, 1.82 mmol) in diethylether (2 mL) was slowly added to the reaction mixture. The reaction mixture was stirred for 1 h and allowed to come to room temperature. The volatiles of the reaction mixture were removed in vacuo, and the product was dissolved in pentane. The LiCl was removed by filtration through Celite, and the volatiles were removed in vacuo to give **24** (550 mg, 1.59 mmol, 87%), which was used without further purification. ^1H NMR (C_6D_6, 300 MHz): 7.11 (s, 1 H, *aromatic-H*), 7.02 (s, 1 H, *aromatic-H*), 5.79-5.88 (m, 1 H, -C*H*=CH_2), 4.98-5.04 (m, 2 H, -CH=CH_2), 3.55 (sept, 1 H, -C*H*$(CH_3)_2$, J_{CH} = 6.9 Hz), 2.82 (sept, 1 H, -C*H*$(CH_3)_2$, J_{CH} = 7.2 Hz), 2.63-2.69 (m, 2 H, -C$H_2$$CH_2$-), 1.99 (s, 1 H, -N*H*), 1.55-1.61 (m, 2 H, -CH_2CH_2-), 1.28 (d, 6 CH_3, J_{CH} = 6.9 Hz) 1.25 (d, 6 CH_3, J_{CH} = 7.2 Hz), 1.06 (s, 6 CH_3), 0.14 (s, 9 H, -Si(CH_3)$_3$. $^{13}C\{^1H\}$ NMR (C_6D_6): 148.39, 144.47, 143.73, 138.95, 138.44, 124.73, 123.11, 121.34, 111.01, 44.26, 36.96, 34.31, 28.64, 28.29, 26.90, 24.48, 24.04, 1.032.

Preparation of $W(CBu^t)(NHAr)(DME)Cl_2$ (25). In a glove box, a solution of $W(CBu^t)(DME)Cl_3$ (200 mg, 0.45 mmol) in diethyl ether (10 mL) was cooled to –35 °C. To this was slowly added a solution of **24** (154 mg, 0.45 mmol) in diethyl ether (2 mL). The reaction changed color from purple to dark orange over 30 min. After 30 min, the solvent was removed in vacuo to give a dark brown paste, which was recrystallized from ether/pentane at –35 °C to give yellow cubes of **25** (120 mg, 0.17 mmol, 40%) that

decomposes at 145 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): 10.43 (s, 1 H, N*H*), 7.20 (s, 2 H, aromatic-*H*), 6.05-6.15 (m, 1 H, -C*H*=CH_2), 5.03-5.17 (m, 2 H, -CH=C*H*$_2$), 4.20 (sept, 1 H, -C*H*$(CH_3)_2$, J_{CH} = 7.2 Hz), 3.23 (s, 6 H, MeOC*H*$_2$C*H*$_2$OMe), 3.10 (s, 4 H, C*H*$_3$OCH$_2$CH$_2$OC*H*$_3$), 2.87 (sept, 1 H, -C*H*$(CH_3)_2$, J_{CH} = 7.2 Hz), 2.78-2.84 (m, 2 H, -C*H*$_2$CH$_2$-), 1.60-1.65 (m, 2 H, -CH$_2$C*H*$_2$-), 1.28 (s, 12 C*H*$_3$), 1.26 (d, 6 C*H*$_3$, J_{CH} = 7.2 Hz) 0.93 (s, 9 C*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 300 MHz): 304.38, 152.07, 149.16, 146.69, 143.64, 138.84, 123.78, 120.86, 110.55, 72.05, 50.00, 43.85, 37.27, 34.43, 33.60, 31.15, 28.61, 27.73, 27.18, 24.67.

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CHAPTER 6

SOLID SUPPORTED SCAVENGER FOR MOLYBDENUM ALKOXIDES

Introduction

During the last decade the olefin metathesis reaction has been used extensively in the synthesis of complex natural products.[1] Chapters 1 through 3 give a very elaborate and detailed picture of the olefin metathesis reaction. Also, as discussed in Chapter 1, at the end of a olefin metathesis reaction, the reaction mixture consists of dark colored Mo(IV) species formed due to the bimolecular decomposition of the methylidene complex.[2] Removal of the metal catalysts or residual Mo species from solution can be an important step in producing useful products.[3] In many cases, if the catalyst can be removed using a selective scavenger, time-consuming chromatography can be avoided.[4] In addition, clean removal of catalysts without quenching of the entire reaction mixture, which usually means addition of aqueous solutions, avoids aqueous waste streams and can leave the product ready for further reactions. Also, removal of metal-residues from polymers generated is sometimes essential for the stability and properties of the material.[5]

In principle one could have two different approaches to addressing the above problem. First, one could have the alkylidene released into solution and then recaptured by a support upon reaction completion, known as 'boomerang' catalyst system first studied by Barrett and co-workers. Second, one could scavenge the alkylidene upon completion of the metathesis reaction followed by filtration to remove the metal complex.[6] For use in our laboratories, we chose the second method for removal of the residual Mo species from the reaction mixture. Another parameter was that the resin used

needed to simply replace the ancillary ligands, e.g. chloride or alkoxide, and not lead to complete decomposition of the catalyst and contamination of the reaction mixtures by all of the ligands on the metal. This removal of all the ligands on the metal might be expected from supports like alumina and silica bearing terminal hydroxyls, and we chose to use a relatively inert polystyrene support. The ideal sequestering agent would contain all it needs to remove the metal from solution with no external reagents, e.g. base, that would add contaminates to the products. Lastly, the ideal quenching agent would be prepared in only a few steps using inexpensive reagents and would be reusable after some method of removing the metal from the resin.

Results and Discussion

For this study, a simple bidentate salicylimine seemed well suited as these ligands are commonly employed across the transition series, and salicylimine derivatives have been incorporated onto solid supports for various applications.[7]

The design settled upon started with Merrifield Resin due to its relative affordability and ready availability from numerous commercial sources. In this work, a sample of 3.5-4.5 mmol of Cl^-/g of polystyrene (PS) resin **26** was purchased from Aldrich with a 200-400 mesh size. In all of the steps, an internal standard, dodecane, was added, and the disappearance of the reagent from solution was monitored by GC-FID. The reactions were run until the reagent concentration in solution leveled. For all three steps, the loading of reagent as measured by loss of starting material was ~3.5 mmol/g of resin.

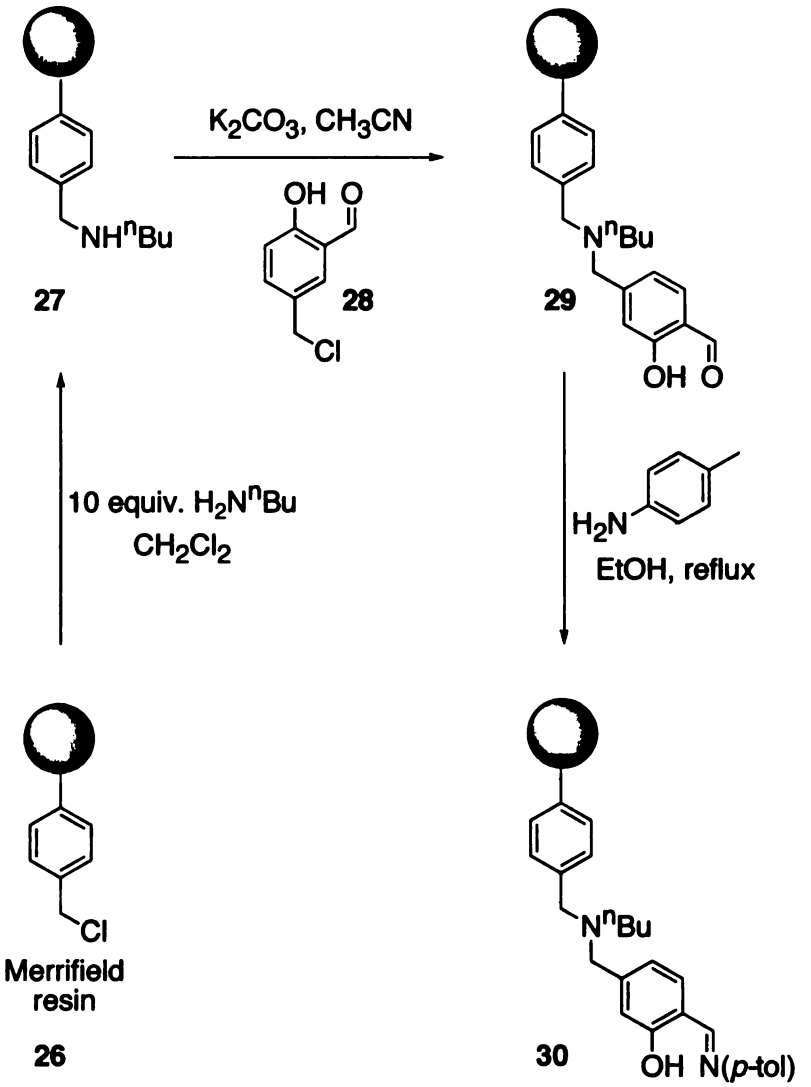
The initial step was the addition of excess *n*-butylamine (Scheme 6.1). In principle, almost any primary amine could be used, but this basic amine is small with a

substantial enough boiling point to make it easy to use. After treatment with amine, poly(styrene)-tethered secondary amine **27** should result.

Secondary amines are known to react[8] cleanly with 5-(chloromethyl)salicylaldehyde, which is readily prepared on large scales from salicylaldehyde, paraformaldehyde, and HCl.[9] The PS-tethered secondary amine **27** was treated with 5-(chloromethyl)salicylaldehyde **28** in the presence of K_2CO_3 in acetonitrile to provide salicylaldehyde attached to poly(styrene) **29**. Finally, treatment of the PS-tethered salicylaldehyde **29** with *p*-toluidine in EtOH resulted in the bright yellow salicylimine scavenger **30**. Here also, a large variety of aniline derivatives are likely as applicable as *p*-toluidine.

Characterization of resins during reaction sequences was done using several techniques. The starting resin was reacted with H_2NBu^n. The amine loss was observed by GC/FID versus dodecane internal standard, which is likely a rough gauge at best due to likely absorption of amine and standard by the resin. In all cases the loss of reagent from solution was higher than that expected for the amount of resin present using this technique. The beads were washed to remove as much of the physisorbed reagent as possible. The beads after reaction to form **27** and basic workup had a negative halide test indicating that all the choromethyl groups of the starting Merrifield Resin had been consumed. In the next step, resin **29** showed a strong O=C stretch in the IR. After production of **30**, the resonance in the IR ascribed to the carbonyl stretch had disappeared. A new resonance at 1640 cm^{-1} assigned to the C=N stretch was found. Swelling the polymer with C_6D_6 and using MAS ^1H NMR led to an easily observed

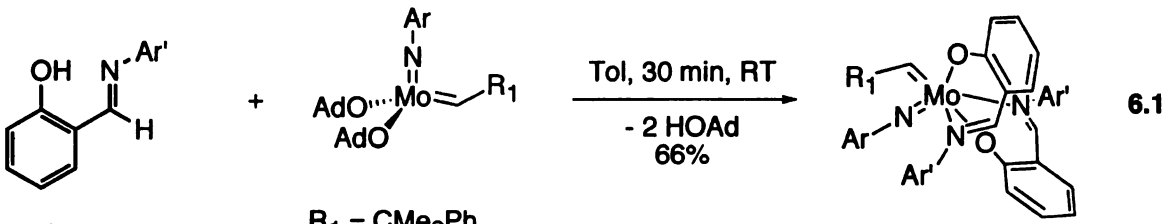
imine hydrogen resonance at 8.6 ppm, where expected for the surface bound imine as judged from the spectrum of molecular 2-(*p*-tolylimino)phenol.



Scheme 6.1. Synthesis of the polystyrene (PS) scavenger **30**.

Before reactions with material **30**, we tested replacement of alkoxides with a salicylimine derivative H-DIB (**31**) (Equation 6.1) in homogeneous solution on a derivative of Schrock's catalyst, Mo(NAr)(OAd)$_2$(CHR) (Mo_{Ad}) where Ar = 2,6-diisopropylphenyl, R = dimethylphenylmethyl, and Ad = 1-adamantyl. A salicylimine was prepared from salicylaldehyde and 2,6-dimethylaniline by refluxing in ethanol. The

protio ligand 2-hydroxy-1-(2,6-dimethylphenyl)iminobenzaldehyde (H-DIB, **31**) crystallized readily as yellow plates. Reaction of Mo_{Ad} with 2 equiv of 4 resulted in formation of $Mo(CHR)(NAr)(DIB)_2$ (**32**). The reaction was complete in minutes at room temperature and appeared quantitative by NMR spectroscopy.



31 **32** **6.1**

$R_1 = CMe_2Ph$
Ar = 2,6-diisopropylphenyl
Ar' = 2,6-dimethylphenyl

Separation of the complex from generated HOAd by crystallization afforded pure **32** as a red solid. The compound has been examined by X-ray diffraction, and an ORTEP diagram from the model is shown in Figure 6.1. As might be expected, the two metal-ligand multiple bonds are *cis* to avoid electronic competition between these strong *trans*-influencing ligands. Opposite these two strong donors are the relatively weakly donating imine groups. The Mo(1)–N(2) distance *trans* to the imido is longer at 2.432(4) Å than the Mo(1)-N(3) distance of 2.389(4) Å *trans* to the alkylidene. The Mo(1)–N(1) imido and Mo(1)–C(1) alkylidene distances are fairly typical at 1.731(4) and 1.932(4) Å. The aryloxide oxygens are mutually *trans* in the solid-state structure and have distances from molybdenum of 2.006(3) and 2.032(3) Å. Selected bond lengths, and angles for the complex **32** are given in Table 6.1.

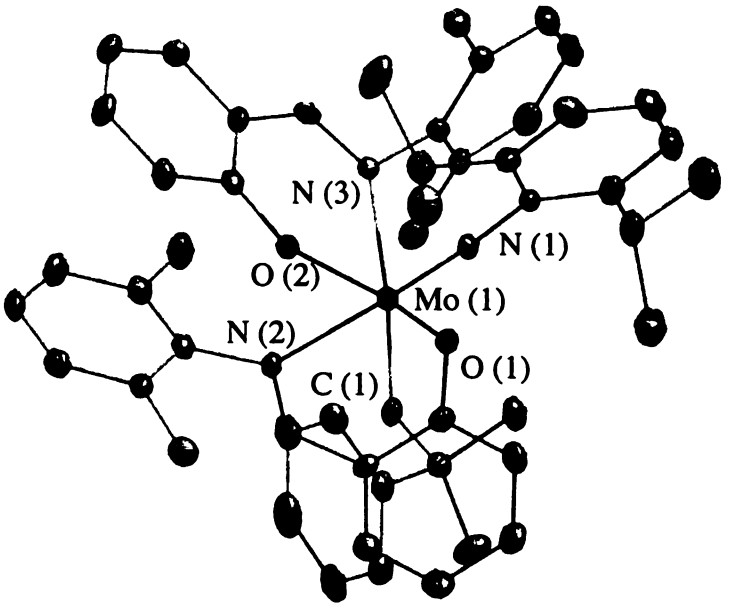


Figure 6.1. ORTEP diagram of the model of complex **32** from the X-ray diffraction experiment.

Table 6.1 Selected Bond Distances (Å) and Angles (deg) from the X-ray Diffraction Study on **32**

Mo (1)–O (1)	2.006 (3)	Mo (1)–N (1)	1.731 (4)
Mo (1)–O (2)	2.032 (3)	Mo (1)–N (3)	2.389 (4)
Mo (1)–C (1)	1.932 (4)	Mo (1)–N (2)	2.432 (4)

N (1)–Mo (1)–C (1)	97.69 (18)	N (1)–Mo (1)–O (2)	100.15 (14)
O (1)–Mo (1)–N (1)	101.14 (14)	C (1)–Mo (1)–O (2)	198.04 (15)
O (1)–Mo (1)–C (1)	94.68 (15)		

In solution, **32** has several different isomers available with 1 major compound and 5 minor isomers judging from the alkylidene region of the ^{1}H and ^{13}C NMR spectra. In the solid state, the observed isomer has the donor imines *trans* to the mutually *cis* metal ligand multiple bonds. The alkylidene substituent is *syn* to the imido nitrogen. Presumably, the other available isomers involve various combinations of alkoxides *trans* to metal ligand multiple bonds in combination with alkylidene rotations.

The compound was also investigated by ^{95}Mo NMR spectroscopy, and a single peak was observed at 548 ppm ($\nu_{1/2}$ = 2050 Hz), which was somewhat broad due to the quadrupolar nature of the nucleus and perhaps the number of isomers in solution. For comparison, the ^{95}Mo NMR spectrum of Mo(NAr)($CHCMe_2Ph$)$(OAd)_2$ (Mo_{Ad}) was also measured; a single resonance at 284 ppm ($\nu_{1/2}$ = 1632 Hz) was found.

The salicylimine-PS system **30** was tested as a scavenger for imido alkylidenes of molybdenum. Here, we used Mo[$C(H)CMe_2Ph$](NAr)$(OBu^{t}_{F6})_2$ (Mo_{F6}) and Mo[$C(H)CMe_2Ph$](NAr)$(OAd)_2$ (Mo_{Ad}), where Ar = 2,6-diisopropylphenyl and Ad = 1-adamantyl. The hexafluoro-*tert*-butoxide derivative Mo_{F6} is one of the most commonly used metathesis catalysts and is commercially available. Nonfluorinated alkoxides are often used in ring-opening metathesis polymerizations; the most commonly employed of these being *tert*-butoxide. However, the *tert*-butoxide complex is quite lipophilic, and we have preferred to use the more crystalline but otherwise similar 1-adamantoxide complex Mo_{Ad}.[10]

Table 6.2 Scavenger **30** test results for molybdenum catalysts.

		[$Mo(CHCMe_2Ph)(NAr)(OAd)_2$] (ppm)	[$Mo(CHCMe_2Ph)(NAr)(OBu^t_{F6})_2$] (ppm)
First Cycle	**Solution**	0.046	0.042
	Resin	113.16	130.10
Second Cycle (Recycled)	**Solution**	0.050	0.036
	Resin	92.82	101.80

Toluene solutions of Mo_{F6} and Mo_{Ad} were stirred for 1 h with the salicylimine-PS beads at room temperature. The yellow solutions of the complex quickly became colorless after the beads were added, and the light yellow beads darkened somewhat. The concentration of molybdenum[11] was measured using ICP-MS calibrated using an internal standard (Table 6.2). The concentration of molybdenum that remained in solution and on the beads was measured.[12] As shown in Table 6.2, this readily prepared scavenger removed the molybdenum complex from solution down to the 30-50 parts per billion range. By comparison, the concentration on the beads was 90-130 parts per million depending on the concentration of catalyst solution treated.

The beads were recycled by refluxing the molybdenum-loaded material in methanol under air for 6 h. After vacuum drying, the recycled beads were treated with solutions similar to those used previously. The recycled beads provided very similar results to the first use material and also removed molybdenum from solution down to the 30-50 ppb range according to ICP-MS (Table 6.2).

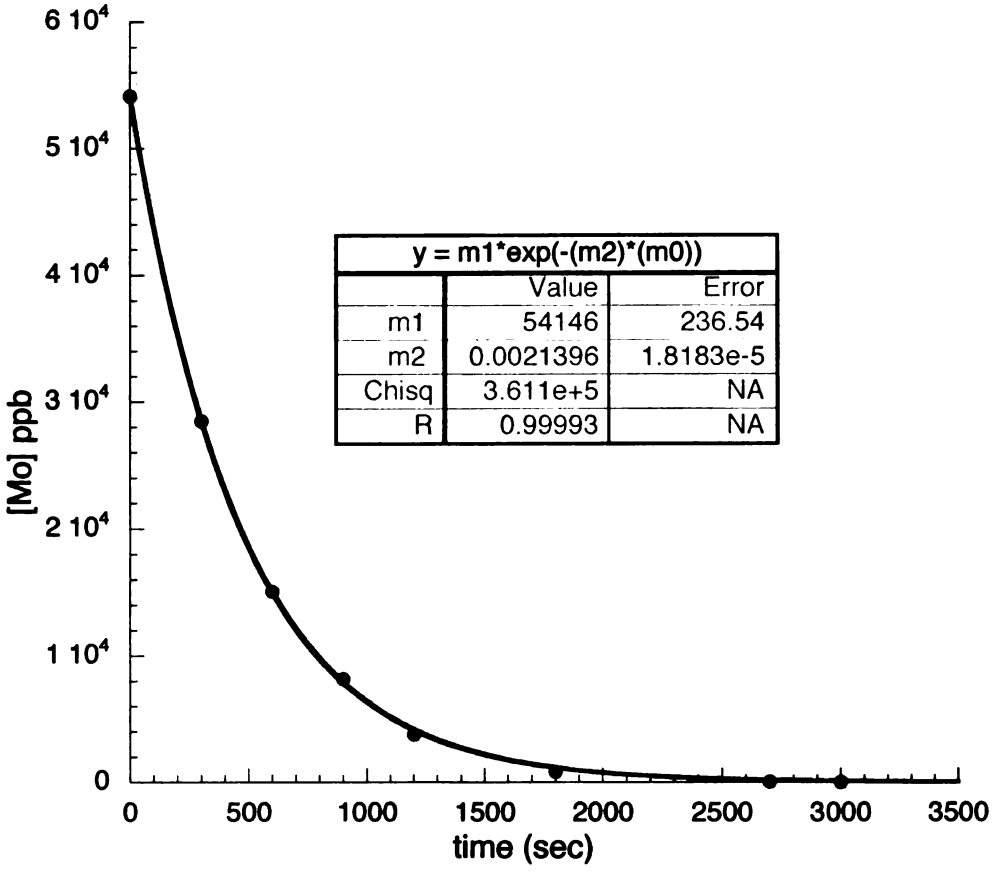


Figure 6.2. Plot of molybdenum concentration versus time after addition of scavenger to an RCM reaction.

We also tested the new scavenger's ability to remove molybdenum from a ring closing metathesis (RCM) reaction. For this test reaction, diethyl diallylmalonate (DEDAM) was used with 3.3 mol% Mo_{F6} (Figure 6.2). The RCM reaction was allowed to run for 2 h; when, it was found to be complete by GC FID. To the crude reaction mixture was added the scavenger. Aliquots were taken periodically from the DEDAM RCM reaction after the scavenger was added. The aliquots were tested by ICP-MS to track the decrease in molybdenum concentration over time. The detected concentration of the metal dropped in an apparent first order process from 54000 ppb to 15 ppb over the course of about 50 min using an excess of the scavenger (Figure 6.2). The fit to the plot

of [Mo] versus time was done with the equation $[Mo]=[Mo]_0\exp[-k_{obs}t]$, which gave $[Mo]_0$ = 54146 ppm and k = 0.00214 s^{-1}. While the exponential plot gave an R = 0.9993 as shown in Figure 6.2, there were noticeable deviations from linearity in a ln[Mo] versus time plot. The loss of molybdenum from solution in this heterogeneous reaction is likely to be sensitive to such factors as the stir rate.

Conclusion

The scavenger production employed here simply involves sequential addition of *n*-butylamine, 5-(chloromethyl)salicylaldehyde, and *p*-toluidine to Merrifield resin. Using this simple resin, aqueous work up can be avoided and little waste is generated while employing the reusable material.

From the model study it appeared that $Mo(OR)_2(NAr)(=CHR)$ complexes treated with salicylimine ligands only reacted at the alkoxide ligands, and reaction with either the imido or alkylidene was not observed. In one further test for the site of reactivity for the resin, we added resin to a 1:1 d_7-toluene solution of Mo_{OAd} and ferrocene as an internal standard. As expected from the model study, NMR of the resin-treated solution only shows 1 equivalent of HOAd, relative to the standard, being generated; no other products were visible. In other words, consistent with the model system, the site of reaction on the molybdenum catalyst appears to be the alkoxide ligands. Unlike the model system, only one alkoxide is replaced, presumably due to ligand localization on the polystyrene beads.

We have developed a very simple and reusable resin to remove the catalyst down to the part per billion range. Consequently in cases where ring-closing metathesis provides clean products, treating with the scavenger and filtering would provide solutions ready for the next step of the synthesis.

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. The ^{95}Mo NMR spectra are reported relative to external 0.147 M $(NH_4)_2Mo_2O_7$ in D_2O as 0 ppm. KBr was dried at 130 °C under dynamic vacuum for at least 3 d, then stored under inert atmosphere. Celite was dried at >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. $Mo(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$ and $Mo(NAr)(CHCMe_2Ph)(OAd)_2$ were prepared as reported in literature.[10] Merrifield peptide resin (200-400 mesh, 3.5-4.5 mmol Cl/g), 2-hydroxybenzaldehyde, and paraformaldehyde were purchased from Aldrich Chemical Co. and were used without further purification. *n*-Butylamine was purchased from Aldrich Chemical Co. and distilled from potassium hydroxide prior to use. 5-(Chloromethyl)-2-hydroxybenzaldehyde was prepared as reported in literature.[13] The Schiff bases 2-[(2,6-dimethyl-phenylimino)-methyl]-phenol (H-DIB, **31**) and 2-(*p*-tolylimino)phenol were

prepared as reported in literature.[14] Molybdenum-containing samples were analyzed on a Micromass (now Thermo Electron Corporation) Platform quadrupole ICP-MS with Hexapole collision cell using a CECTAC ASX-500 autosampler at Michigan State University. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Tune conditions were optimized using a 10 mg/L (ppb) solution of Be, Co, In, Ce, Bi, and U. The final nebulizer gas flow rate was 0.75 L/min. Samples were scanned for 1.0 min using a dwell time of 0.1 s. The instrument response was corrected using ^{115}In as an internal standard for the Mo samples. Final sample concentrations were quantified using a set of multi-element external calibration standards ranging from 0-1000 ppb.

Preparation of secondary amine resin (27). In a 500 mL round bottom flask was loaded Merrifield peptide resin (5.0 g, 200-400 mesh, 3.5-4.5 mmol Cl^-/g). To this was added 200 mL CH_2Cl_2, *n*-$BuNH_2$ (13.31 g, 182 mmol), and dodecane (3.835 g, 22.5 mmol). This reaction mixture was then refluxed for 2 d. After 2 d, the reaction mixture was cooled to room temperature and another batch of *n*-$BuNH_2$ (2.5 mL) was added, and the reaction mixture was refluxed for 2 h to ensure complete conversion. Finally, the volatiles were removed, and the resulting resin was washed with 2% NaOH solution (3 × 100 mL). The resin was washed again with hexanes (5 × 50 mL), and dried under vacuum at 40 °C for 24 h to afford a white solid (5.683 g). This mass suggests ~3.7 mmol amine/g. The resin had a negative halide test using $AgNO_3$. FT-IR (KBr): 3000 (str br, NH) cm^{-1}.

Preparation of tethered salicylaldehyde resin (29) This synthesis was adapted from that reported by Wei.[8d] In a 500 mL round bottom flask was taken 1 (5.5 g), K_2CO_3 (8.55 g, 62 mmol), and acetonitrile (250 mL). To this was added 2-hydroxy-5-(chloromethyl)benzaldehyde **28** (8.445 g, 50 mmol) in acetonitrile (50 mL) over a period of 1 h. This mixture was refluxed for 36 h. After 36 h, the solvent was evaporated, and distilled water (250 mL) was added to the reaction mixture. Stirring was continued for 6 h, and the mixture was filtered. The resin was then washed with ethanol (5 × 100 mL) and dried under vacuum at 35 °C for 48 h to afford an off-white solid. This solid was transferred in a 250 mL round bottom flask with CH_2Cl_2 (200 mL). The slurry was refluxed for 24 h. The reaction mixture was cooled to room temperature and filtered. The resin was washed with CH_2Cl_2 (3 × 100 mL) until the washings were colorless to afford an off-white solid. The resin was dried under vacuum at 50 °C to a constant weight. This process of swelling and drying of the resin was repeated twice to remove any trace contaminants from the resulting resin (7.510 g). Using 3.7 mmol amine/g from previous step, the weight suggests 74% of the available amine sites reacted or ~2.7 mmol salicylaldehyde groups/g of resin. FT-IR (KBr): 3227 (br str, OH), 2878 (str Fermi d, CH stretch), 1859 (str, C=O) cm^{-1}.

Preparation of tethered salicylimine scavenger resin (30). In a 500 mL round bottom flask was taken **29** (6.0 g) in EtOH (150 mL). To this was added *p*-toluidine (11.57 g, 108.0 mmol) and formic acid (0.100 mL). The reaction mixture was heated at 80 °C for 48 h. After 48 h, the reaction mixture was cooled to room temperature and washed with ethanol (5 × 100 mL) to remove the excess *p*-toluidine. The final solid was washed with hexanes (5 × 50 mL) and dried under vacuum at 35 °C for 24 h to afford a

bright yellow solid. This solid was transferred in a 250 mL round bottom flask with CH_2Cl_2 (200 mL). The slurry was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered. The resin was washed with CH_2Cl_2 (3 × 100 mL) until the washings were colorless to afford a bright yellow solid. The resin was dried under vacuum at 65 °C to a constant weight. This process of swelling and drying of the resin was repeated 3 times to remove any trace contaminants from the resulting resin each time drying to constant weight. The final weight was 7.121 g, which suggests ~78% yield for this step. However, loss of colored compound in the washings, which is likely unbound salicylimine, suggests that there was trapped aldehyde in the resin. In other words, it is likely that there is little salicylaldehyde on the resin after *p*-toluidine addition. Instead, the yield of substituted sites in the production of **29** is probably not as high as calculated from the mass. Consistent with this, the C=O stretch in the FT-IR is completely quenched during this step. FT-IR (KBr): 3200 (br str, OH), 1640 (w, C=N) cm^{-1}.

Preparation of Mo(NAr)(CHCMe$_2$Ph)(DIB)$_2$ (32). In a glove box, a 20 mL vial was loaded with Mo(NAr)(CHCMe$_2$Ph)(OAd)$_2$ (70 mg, 0.099 mmol) in toluene (5 mL). To this was added a solution of 2-[(2,6-dimethylphenylimino)methyl]phenol (H-DIB (**31**), 45 mg, 0.198 mmol, 2 equiv) in toluene (2 mL). The reaction mixture was stirred for 30 min. The solvent was removed, and the crude product was dissolved in hexanes. The liberated 1-adamantanol was removed by filtration through Celite. The solvent was removed in vacuo, and the desired product was crystallized from a minimum amount of ether/pentane (1:10) as orange-red microcrystals (56 mg, 0.066 mmol, 66%). The NMR spectroscopic data are consistent with a mixture of at least six isomers in $CDCl_3$. As a

result, the spectra are more complex than expected, and the assignments are difficult due to the multitude of overlapping peaks. Assignments are made where possible. ^{1}H NMR (500 MHz, $CDCl_3$): 14.09 (Major isomer alkylidene, J_{CH} = 122 Hz), 13.86, 13.11, 13.00, 12.04, 7.89 (2 H, J_{CH} = 2.5 Hz, C*H*=N), 7.34-7.38 (m, 1 H), 6.89-7.21 (m, 18 H), 6.82-6.78 (m, 3 H), 6.59-6.69 (m, 5 H), 6.44-6.48 (m, 2 H), 3.97 (sept, J_{CH} = 7 Hz, 1 H), 3.56 (sept, J_{CH} = 7 Hz, 1 H), 2.85 (s, 3H), 2.41 (s, 3 H), 1.76 (s, 3H), 1.27 (d, J_{CH} = 7 Hz, 3 H), 1.19 (s, 3 H), 0.81 (d, J_{CH} = 7 Hz, 3 H), 0.79 (d, J_{CH} = 7Hz, 3 H), 0.73 (d, J_{CH} = 7Hz, 3H), 0.4 (s, 3 H). ^{13}C NMR (C_6D_6): 326.58, 326.48, 309.46, 298.47, 172.12, 170.71, 167.89, 165.04, 159.68, 154.89, 152.37, 151.59, 149.68, 148.45, 136.35, 135.82, 135.49, 132.18, 132.01, 131.26, 130.47, 129.79, 129.50, 128.75, 128.35, 128.12, 128.03, 127.86, 127.66, 127.33, 126.27, 125.90, 125.81, 125.32, 125.05, 124.96, 122.89, 122.76, 121.94, 121.81, 120.75, 119.60, 115.21, 113.54, 55.7, 30.45, 27.81, 27.71, 27.51, 26.89, 26.34, 23.73, 23.43, 22.28, 20.09, 19.68, 19.41, 18.69, 18.11. ^{95}Mo NMR ($CDCl_3$): 548 ppm. Elemental Analysis Calc. for $C_{52}H_{57}N_3O_2Mo$: C, 73.29; H, 6.76; N, 4.93. Found: C, 73.12; H, 6.64; N, 4.89. M. p. = 138-140 °C.

Procedure for the scavenging experiments with 30. The solution of metal complex was prepared by dissolving ~10 mg of $Mo(NAr)(CHCMe_2Ph)(OR)_2$ [OR = OAd, OBu^t_{F6}] in toluene (see Table 1). To this solution was added 550 mg of **30**, and the resulting mixture was stirred vigorously for 1 h. After 1 h, the beads were filtered and dried under vacuum (Sample A). The volatiles from the resulting mother liquor were removed under vacuum (Sample B). Both Sample A and B were analyzed by ICP-MS for their molybdenum content.

Recycling procedure for scavenger 30. A 100 mL round bottom flask was loaded with 1.00 g of beads, a magnetic stir bar, and methanol (30 mL). The resulting slurry was refluxed in air for 6 h. The mixture was cooled to room temperature, and the beads were filtered through a frit. The beads were washed with 100 mL of methanol and dried at 45 °C for 24 h. These beads were tested using the scavenging procedure (vide supra). See Table 6.2.

Procedure for scavenging from crude ring closing metathesis reaction. Ring-closing metathesis followed by scavenging was performed inside a well-purged drybox. To a solution of $Mo(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$ (Mo_{F6}, 12 mg, 0.0157 mmol) and toluene (5 mL) in a 20 mL vial was added diethyl diallylmalonate (30 equiv, 113 mg, 0.470 mmol) in toluene (1 mL). The solution was stirred at room temperature for 2 h, and 600 mg of the scavenger resin **30** was added to the reaction mixture. The resulting slurry was stirred vigorously. Samples (200 μL) were withdrawn from the reaction mixture at regular intervals and filtered. The volatiles from the samples were removed in vacuo, and the samples were analyzed by ICP-MS for their residual molybdenum contents. The concentration versus time data are shown in Figure 6.2.

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11. We attempted to measure the solid-state MAS ^{95}Mo NMR spectrum of the beads for comparison with our solution spectra of isolated Mo_{Ad} and **29**. Unfortunately, no signal was observed.

12. During calibration, the ICPMS technique provided results within 1 part per billion of standards.

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CHAPTER 7

APPLICATION OF IMIDO-TETHERED COMPLEXES OF MOLYBDENUM TO THE SYNTHESIS OF CYCLIC POLY(NORBORNENE)

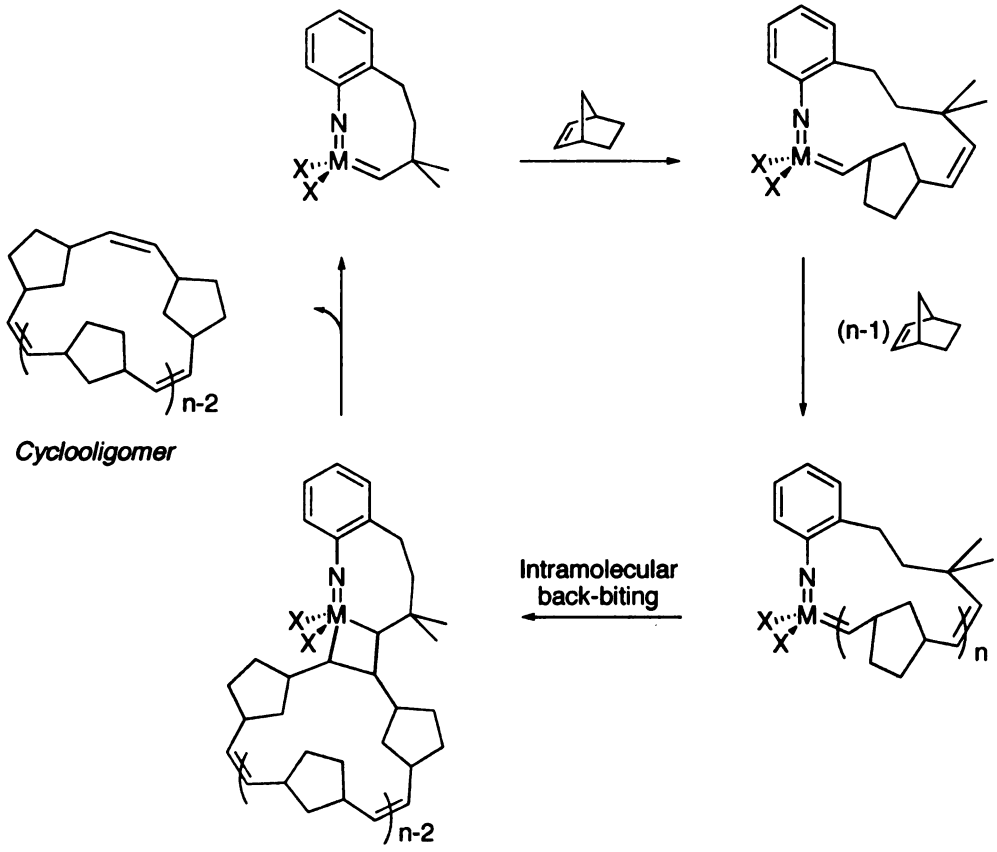
Introduction

The imido-tethered alkylidene complexes discussed in Chapters 2 and 4 have opened doors for studying reactions of this unique class of complexes. Complexes of the type $M(CHBu^t)(NAr)(OBu^t)_2$ and $M(CHCMe_2Ph)(NAr)(OBu^t)_2$, where M = Mo or W and Ar = 2,6-diisopropylphenyl developed and well studied by Schrock and coworkers have been applied extensively to the synthesis of monodisperse polyolefins.[1] Chapters 1 and 2 discuss the detailed picture of Mo-alkylidene complexes. A rather interesting application involving the imido-tethered alkylidenes would be the formation of cyclic polymers via "intramolecular backbiting" of the polymer chain as shown in Scheme 7.1.

Fürstner and co-workers first reported a ruthenium-based complex very similar to the above thought process.[2] Soon, Grubbs and co-workers used the catalyst to study the cyclooligomerization of cyclooctene.[3] Synthesis of large quantities of pure cyclooligomers using the olefin metathesis strategy has been a topic of debate and interest for quite sometime. Further, applications of the novel cyclooligomers, so far, have been unexplored.

It should be noted at this point that the approach discussed above is not the only method for the synthesis of cyclic polymers and that the untethered Schrock-type olefin metathesis systems can also be used for the synthesis of "cyclic polymers" under dilute conditions such that the probability of the two ends of a polymer chain reacting is fairly high. However, the "dilution method" is not the ideal for the synthesis of cyclic polymers

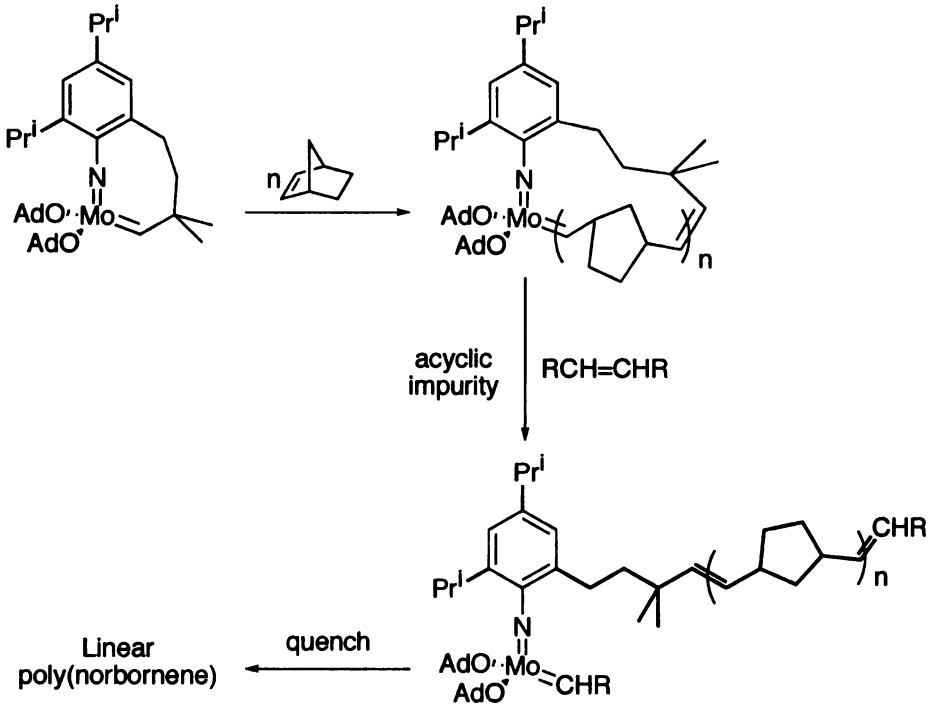
and will be contaminated with the linear analogs, rotaxanes, catenanes, or mixtures of all of the above. The resultant mixture could be prepared on large scales but would require careful fractionation to obtain pure samples for further study and analysis.



Scheme 7.1 Formation of cyclo-oligomers using imido-tethered alkylidenes.

Results and Discussion

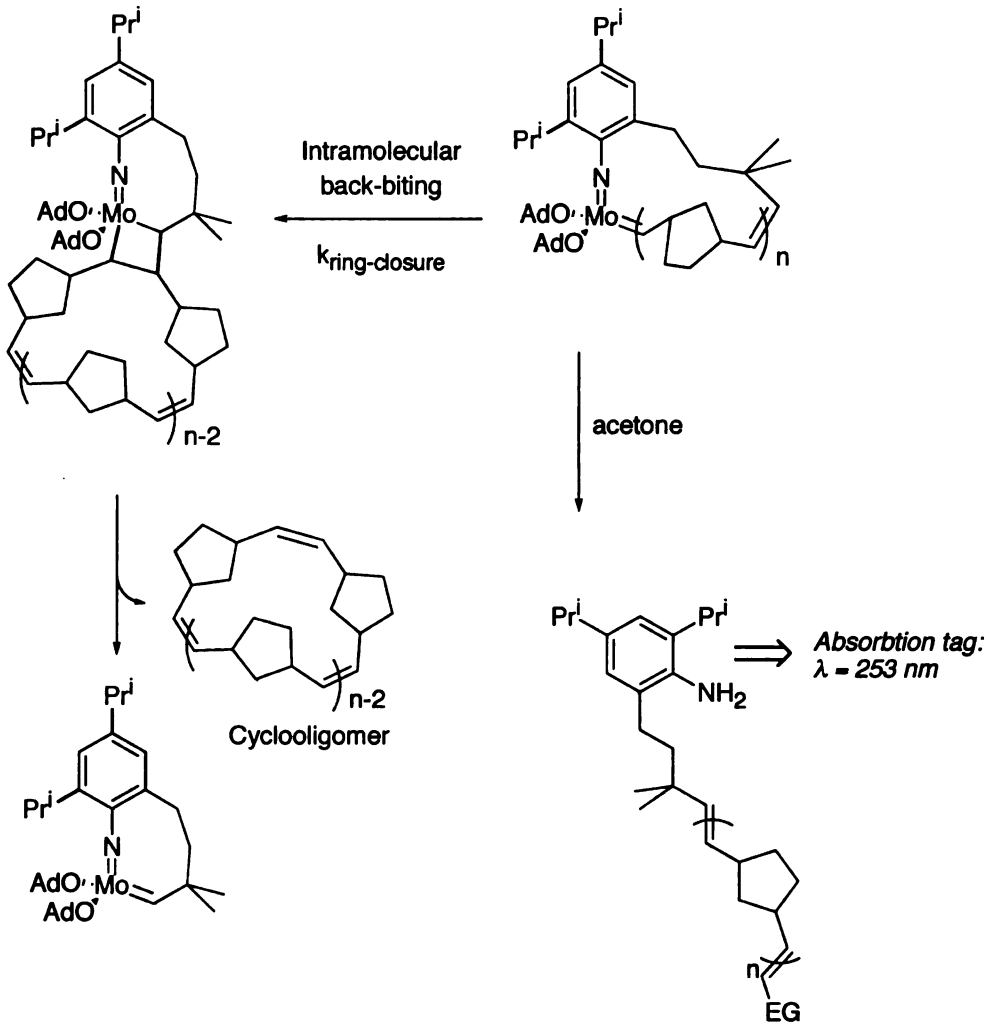
In order to facilitate the formation of cycloligomers it is important that the catalyst, substrate and solvents be extremely pure and free of acyclic impurities. (Scheme 7.2)



Scheme 7.2 Formation of linear poly(norbornene) due to acyclic impurities.

Another potential problem would be high linear-polymer contamination if the reaction were to be quenched before the intramolecular back-biting reaction. This problem however, can be used to study the kinetics of back-biting reaction by quenching the reaction mixture at regular intervals and measuring the concentration of the tagged polymer that would result at the end of the reaction as shown in Scheme 7.3. For this test reaction, norbornene was treated with $Mo(OAd)_2(N\text{-}2,4\text{-}Pr^i_2C_6H_2\text{-}6\text{-}CH_2CH_2CMe_2CH=)$ in toluene. The ROMP reaction was found to be complete i.e. norbornene had been consumed, in the first couple minutes as judged by GC-FID. Suggesting the formation of the macro-metallacycle was complete. Aliquots were taken periodically from the reaction. The aliquots were quenched in acetone and examined by UV-Vis. The absorption spectra were used to track the decrease in concentration of polymer tagged with amine (λ_{max} = 253 nm) cleaved from Mo if the cyclization was not complete over

time. The concentration of the tagged polymer dropped in an apparent first order process from 7.5×10^{-3} mM to 2.5×10^{-3} mM over the course of about 240 min. (Figure 7.1)



Scheme 7.3 Formation of cyclic and linear poly(norbornene), where EG = end group.

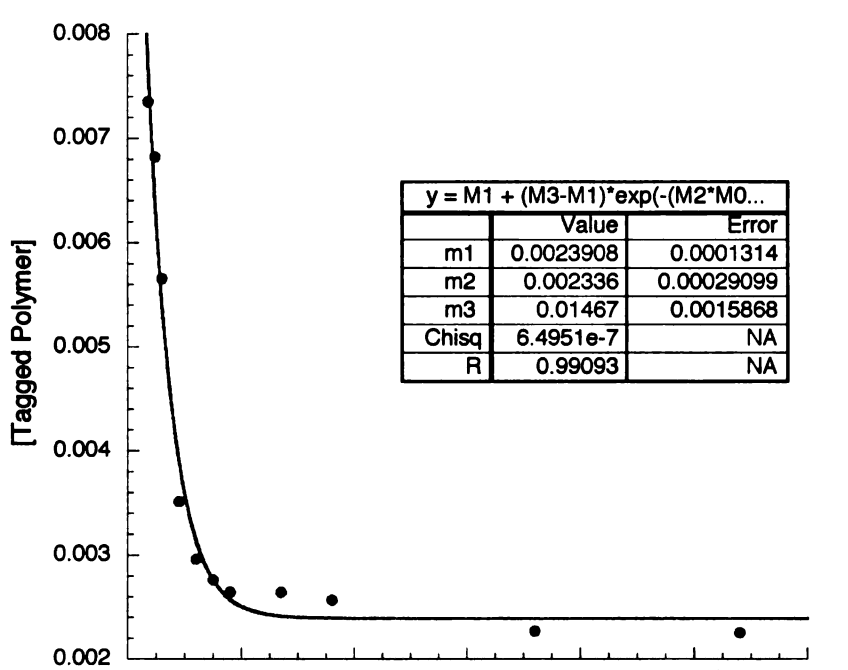
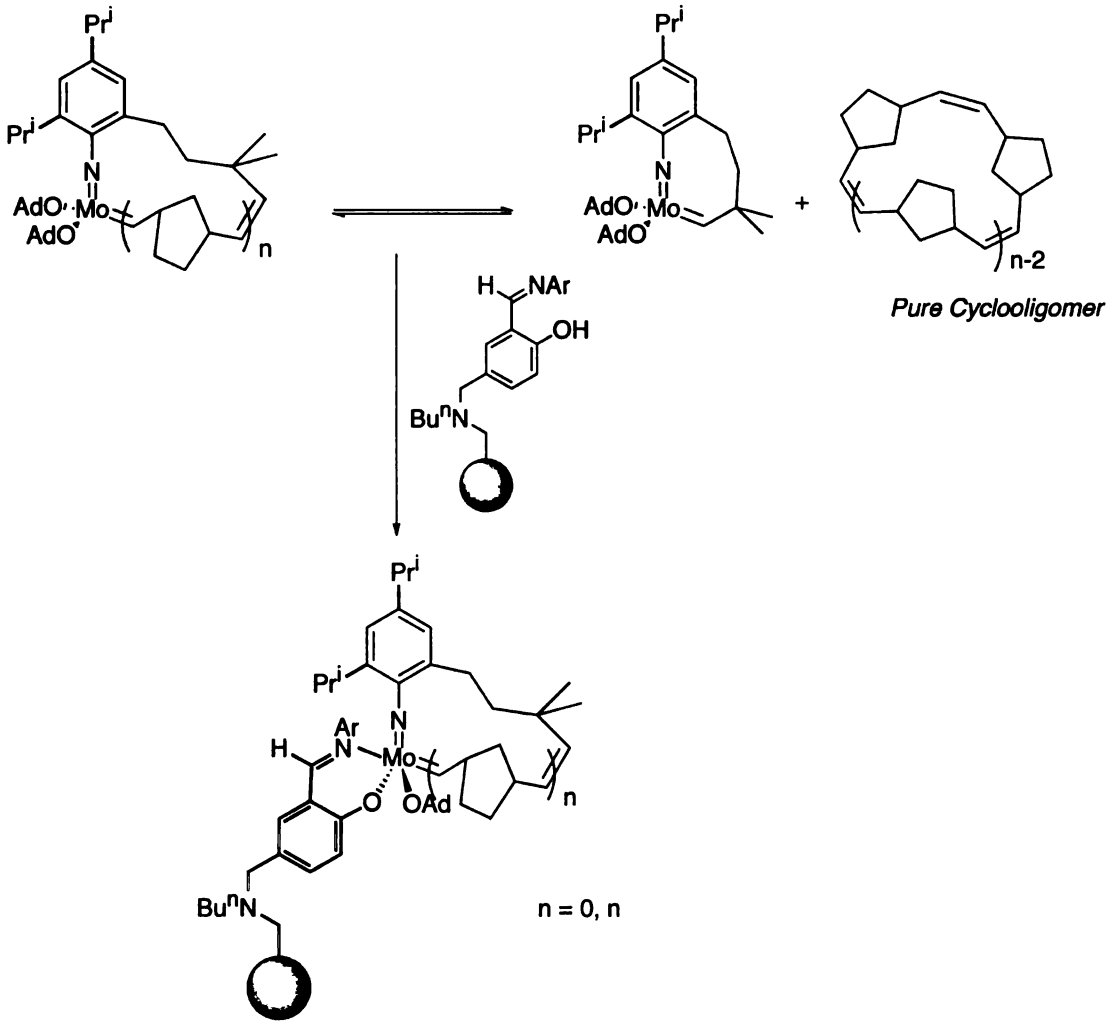


Figure 7.1 Plot of tagged polymer concentration versus time of a polymerization reaction.

The second aspect of the process involves the removal of the residual metal-complex from the reaction mixture to avoid traces of linear impurities. This involves using the scavenger system developed in Chapter 6 to afford pure samples of cyclic poly(norbornene) as shown in Scheme 7.4.



Scheme 7.4 Removal of metal complex from reaction mixture.

Using the above strategy we prepared samples of cyclic poly(norbornene), and a ^{13}C NMR spectrum for the resulting polymer is shown in Figure 7.2 (a). For comparison we also prepared a linear sample with a similar catalyst/monomer ratio. [Figure 7.2 (b)] As can be seen from the NMR there are no aromatic peaks present in the cyclic sample.

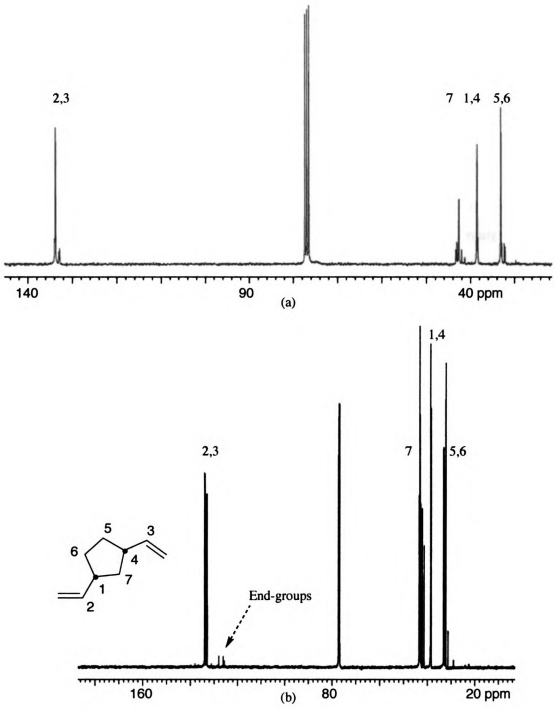


Figure 7.2 ^{13}C NMR ($CDCl_3$, 125 MHz) for (a) cyclic and (b) linear poly(norbornene).[4]

Conclusion

The tethered molybdenum alkylidenes have been applied to the synthesis of novel cyclic polymers based on norbornene. The required tethered alkylidene along with the

substrate and solvents used for the synthesis have to be rigorously pure to avoid formation of potential linear contaminants. NMR studies indicate that there are no end groups present in the samples prepared via this strategy for the study. However, the preliminary studies do not confirm the exact nature of the resulting polymer samples and detailed studies are required to confirm the nature of the polymer rheology.[5]

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Norbornene was purchased from Aldrich Chemical Co., and sublimed twice before use. Linear poly(norbornene) samples were prepared as described in literature.[6]

Procedure for studying kinetics of ring-closure from a ring-opening metathesis reaction. In a glove box, in a 250 mL Schlenk flask was loaded norbornene (745 mg, 7.930 mmol), toluene (17 mL), and a stir bar. The Schlenk flask was taken outside the glove box. To this was added a solution of $Mo(OAd)_2(N\text{-}2,4\text{-}Pr^i_2C_6H_2\text{-}6\text{-}$

$CH_2CH_2CMe_2CH$=) (13 mg, 0.0198 mmol) and toluene (4 mL). The solution was stirred vigorously at room temperature. Samples of about 200 μL were withdrawn from the reaction mixture at regular intervals and precipitated in methanol (10 mL). The samples were then filtered, and dried in vacuo for 24-48 h until constant weight. The samples were analyzed by UV-Vis for their residual amine content. The concentration versus time data are shown in Figure 7.1.

Procedure for polymerization of norbornene using $Mo(OAd)_2$(N-2,4-$Pr^i_2C_6H_2$-6-$CH_2CH_2CMe_2CH$=). In a glove box, in a 20 mL vial was loaded norbornene (180 mg, 1.9114 mmol), toluene (2.5 mL), and a stir bar. To this was added a solution of $Mo(OAd)_2$(N-2,4-$Pr^i_2C_6H_2$-6-$CH_2CH_2CMe_2CH$=) (5 mg, 7.625 mmol) in toluene (0.2 mL). The solution was stirred vigorously at room temperature for 45 min. To this solution was then added **29** (250 mg) and the slurry was stirred for 1 h. After 1 h, the sample filtered to remove the catalyst bound to **29** and precipitated in ice-cold acetone. The polymer sample was filtered, and dried in vacuo until constant weight (160 mg). The resulting resin was not analyzed further.

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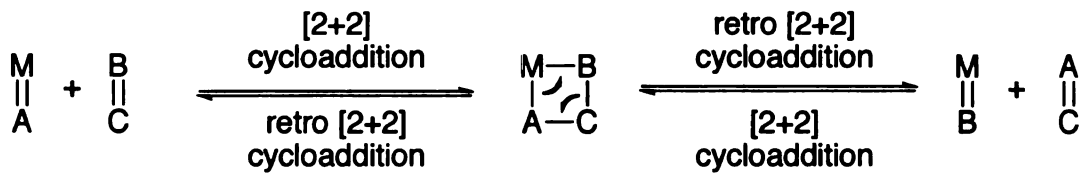
CHAPTER 8

SYNTHESIS, STRUCTURE, AND REACTIVITY OF METALLACYCLIC COMPLEXES OF TUNGSTEN AND MOLYBDENUM BASED ON CYCLOOCTYNE

Introduction

The chemistry of metal alkylidene complexes has undergone very rapid development since the 60s as described in detail in Chapter 1, and the olefin metathesis reaction can be thought of as a subset of a much larger family of [2 + 2]-cycloaddition reactions.[1] The reaction in its most general form can be given as shown in Scheme 8.1, where M = transition metal; A, B, and C = carbon, nitrogen, or oxygen.



Scheme 8.1 [2+2]-cycloaddition reaction

The [2 + 2]-cycloaddition reaction has been well studied and applied to many useful reactions.[2] Cycloaddition between an imido and an alkyne forms an azametallacyclobutene. This reaction between a metal-imido and an alkyne may be of utility in the synthesis of compounds with alkylidene character, under the appropriate circumstances.[3] There is an important question to attend; how can the alkylidene/imine (Figure 8.1) form be made dominant?

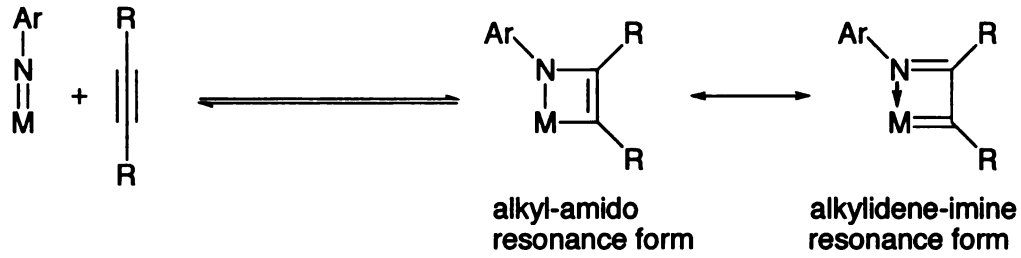


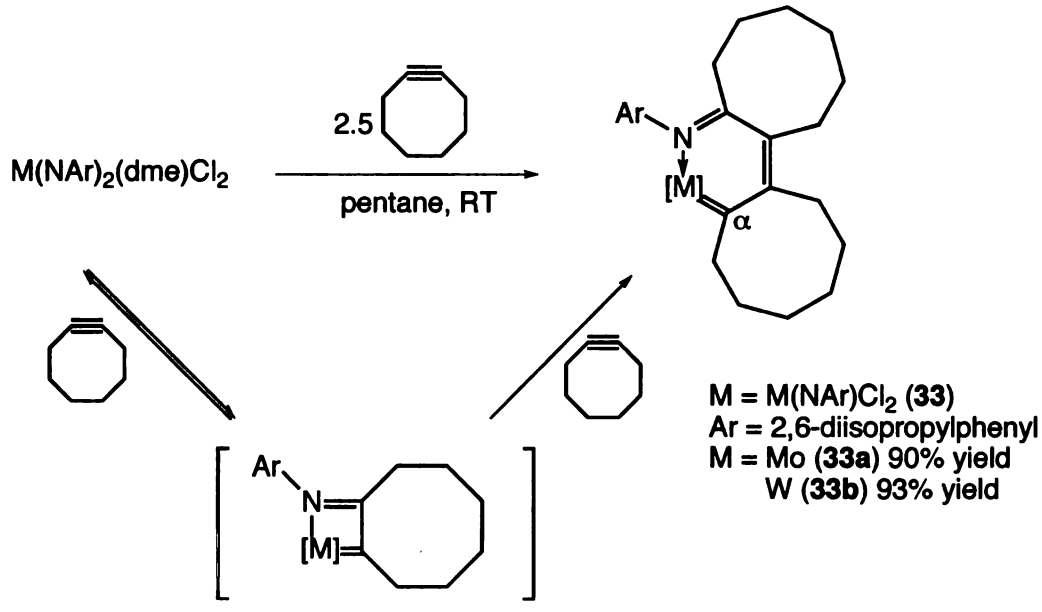
Figure 8.1 Alkyl-amido and alkylidene-imine resonance forms

The alkylidene-imine resonance form (Figure 8.1) is most likely to be observed for metal complexes where converting the imido to an alkylidene yields a system known to have stable M=C linkages. To stabilize a multiple-bond over a two single-bond system, it would be advantageous to choose a metal center and oxidation state where $d\pi$-$p\pi$ bonding is prevalent. The most metal-ligand multiple bond complexes are known for Group VI metals, molybdenum especially. In addition, a large number of stable imido alkylidene complexes of molybdenum and tungsten have been reported by Schrock and co-workers.[4] Therefore, molybdenum and tungsten imido alkylidenes were thought to be an excellent place to begin when trying to encourage alkylidene bonding.

Results and Discussion

In an initial experiment, reaction of $Mo(NAr)_2(DME)Cl_2$, where Ar= 2,6-diisopropylphenyl,[5] with ~500 equivalents of 3-hexyne at 75 °C over several hours gave no reaction. To induce reactivity with the alkyne, ring strain was added to the alkyne substrate. The smallest ring alkyne that is stable at room temperature is cyclooctyne, which is readily prepared on 15 g scales using Brandsma's procedure starting from cyclooctene.[6] The reaction between cyclooctyne and $Mo(NAr)_2(DME)Cl_2$ in pentane proceeds smoothly to give a bright yellow precipitate over the course of a few hours at room temperature. The product was identified as $M(NAr)(=C_8H_{12}=C_8H_{12}=NAr)(Cl)_2$,

perhaps from a [2 + 2]-cycloaddition followed by insertion of alkyne into the 4-membered ring metallacyclic intermediate.



Scheme 8.2 Reaction of cyclooctyne with $M(NAr)_2(DME)Cl_2$.

The complexes **33a** and **33b** were available in 90% and 93% yield respectively as bright yellow micro-crystals. Both complexes are insoluble in pentane and analytically pure crystals were obtained by layering pentane on solutions of **33a** and **33b** dissolved in a minimal volume of diethyl ether. Single crystal X-ray diffraction confirmed that instead of the carbene-imine drawn above, a second equivalent of cyclooctyne had inserted to give the product as shown in Scheme 8.2.

Selected bond lengths, and angles for the complexes are given in Table 8.1. The central metal atom of complexes **33a** and **33b** is in a distorted square-pyramidal coordination environment. The two electronegative chloride ligands are *cis* to each other [Cl(1)–Mo–Cl(2) = 84.65(6)° and Cl(1)–W–Cl(2) = 84.24(3)°]. The molybdenum-alkylidene bond length [Mo–C(1A) = 1.932(6) Å] is somewhat longer than in

$Mo[CHCMe_2Ph](NAr)[OBu^t_{F6}]_2(PMe_3)$[7] [Mo–C = 1.878(9) Å] made by Schrock and co-workers. Furthermore, the molybdenum and tungsten metallacycles are identical within error by X-ray diffraction. The metallacycle can be represented in two resonance forms and shown in Figure 8.3. For the carbene-imine resonance, the bond order between C(2A) and C(2B) should be 2; the bond length is 1.404(5) Å, somewhat longer than the C=C distance of 1.336 Å in butadiene. The C(1A)–C(2A) and C(1B)–C(2B) distances average 1.449(6) Å, and the C–C single bond distance in butadiene is 1.465 Å.[8] The W–N(2) distance is 2.120(3) Å.

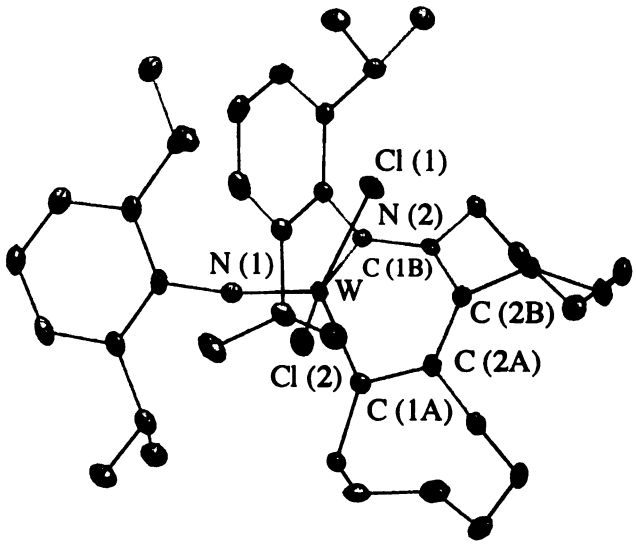


Figure 8.2 ORTEP diagram of $W(Cl)_2(=C_8H_{12}C_8H_{12}=NAr)(=NAr)$ **(33b)** from X-ray diffraction.

Thus, the metric parameters are more consistent with a favored carbene-imine resonance form than the potential alkyl-amido form as opposed to the alkyl-amido resonance form observed for a similar class of compounds studied by Wigley and co-workers.[9] Wolczanski and co-workers have suggested similar resonance forms for

titanium-based complexes as shown in Figure 8.3. In addition to the structural evidence, the ^{13}C NMR spectroscopy is also indicative of alkylidene character.[10] The resonance for C_α of the metallacycle has a chemical shift above 270 ppm, (309 ppm when M = W and 278 ppm when M = Mo).

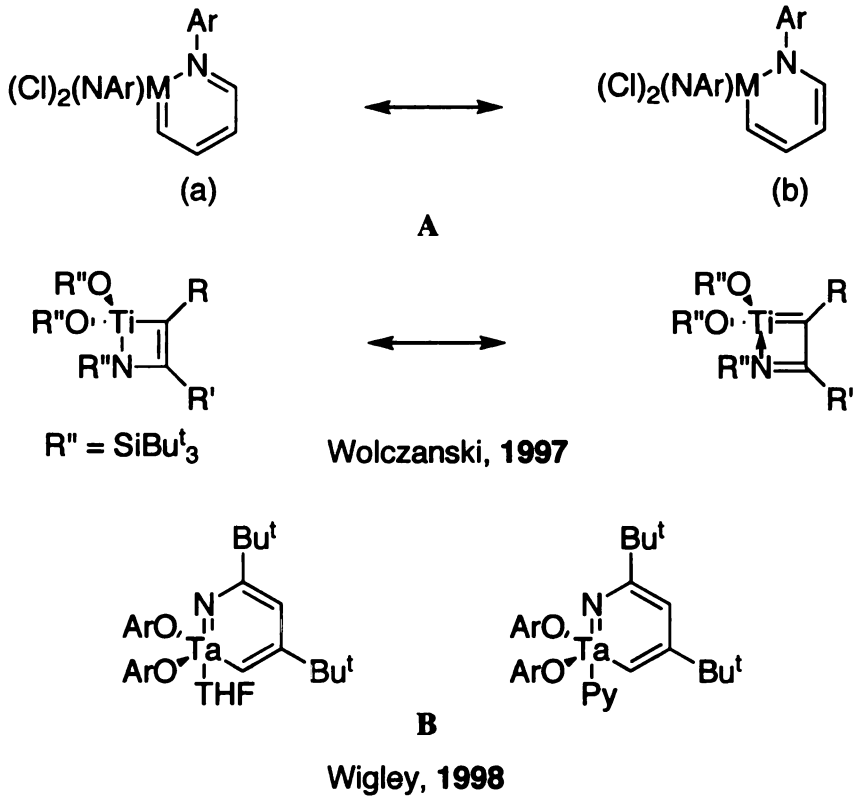


Figure 8.3 A. Alkylidene-imine (a) and alkyl-amido (b) resonance forms for complexes **33a** and **33b**. **B.** Similar resonance forms suggested/observed by Wolczanski and Wigley.

The complexes **33a** and **33b** have displayed several interesting reactions so far. For example, the metallacycles undergo an unusual decomposition reaction that results in the formation of pyrrole **34** in high yield. The product formation may be regarded as reductive elimination from the alkyl-amido or intramolecular nucleophilic attack of the imine on the carbene in the alkylidene-imine. The process involves a net reduction of the metal center. Decomposition of the tungsten derivative occurs more slowly than for the

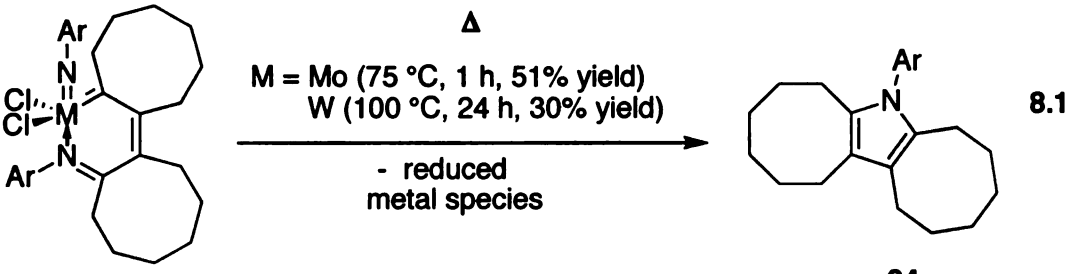
corresponding molybdenum complex. (Equation 8.1) To avoid decomposition the complexes **33a** and **33b** are best stored at –35 °C in a dry box.

Table 8.1 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **33a, 33b**

	33a	**33b**
M–N (1)	1.736 (5)	1.736 (3)
M–C (1A)	1.932 (6)	1.944 (4)
M–N (2)	2.154 (5)	2.120 (3)
M–Cl (1)	2.449(18)	2.412 (10)
M–Cl (2)	2.419 (18)	2.409 (10)
N (1)–M–C (1A)	104.9 (2)	107.30 (14)
N (1)–M–N (2)	106.1 (2)	100.81 (12)
C (1A)–M–N (2)	84.4 (2)	86.94 (13)
N (1)–M–Cl (2)	94.63 (16)	94.70 (9)
C (1A)–M–Cl (2)	91.85 (18)	93.04 (11)
N (2)–M–Cl (2)	159.23 (13)	163.77 (8)
N (1)–M–Cl (1)	119.40 (15)	122.11(10)
C (1A)–M–Cl (1)	135.70 (19)	130.59 (11)
N (2)–M–Cl (1)	83.83 (13)	83.49 (8)
Cl (2)–M–Cl (1)	84.65 (6)	84.24 (3)
N (1)–M–C (2A)	140.2 (2)	140.57 (12)
C(1A)–M–C (2A)	35.3 (2)	33.73 (13)
N (2)–M–C (2A)	77.43 (18)	77.40 (11)
Cl (2)–M–C (2A)	87.75 (14)	93.64 (8)
Cl (1)–M–C (2A)	100.43 (15)	97.04 (8)

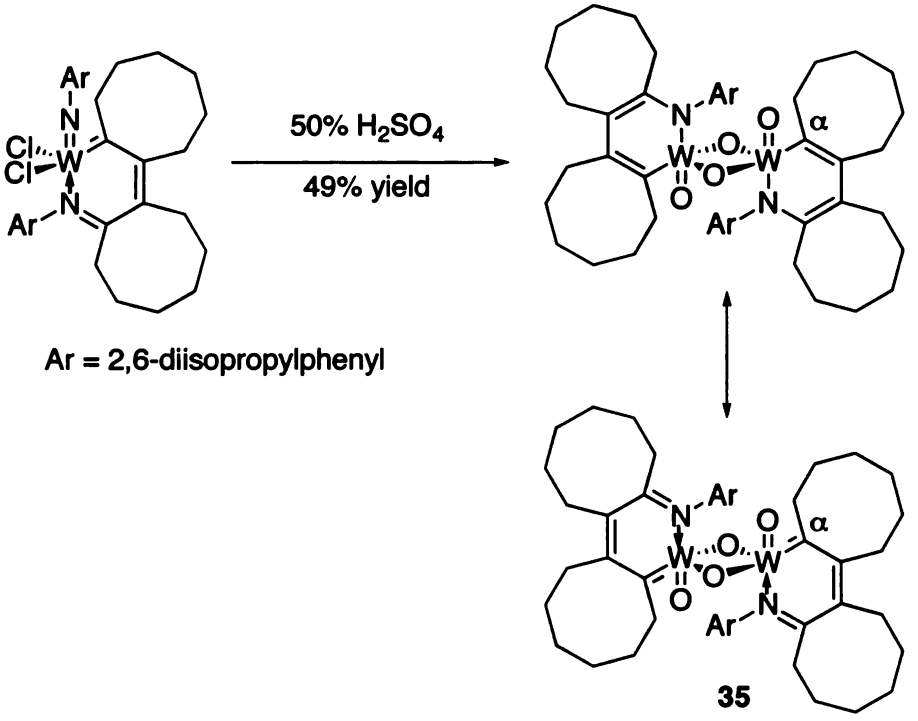
While **33a** and **33b** are thermally sensitive due to pyrrole elimination, they are quite chemically robust for molybdenum (VI) and tungsten (VI) complexes with

alkylidene character, which is perhaps due to resonance stabilization of the metallacycle. The tungsten derivative can be taken into the air in toluene solution and shaken with 50% aqueous H_2SO_4, and the metallocycle is retained in the product!



34 8.1

The reaction replaces all the ligands on tungsten except those associated with the metallacycle, which are retained in the μ-oxo (**35**). (Scheme 8.3) The tungsten μ-oxo complex is apparently less alkylidene-like in its properties than its imido precursor as determined by its X-ray diffraction metric parameters. The W–C(1A) distance increases from 1.944(4) Å in the imido complex to 2.010(4) Å in the oxo.



Scheme 8.3 Formation of μ-oxo (**35**)

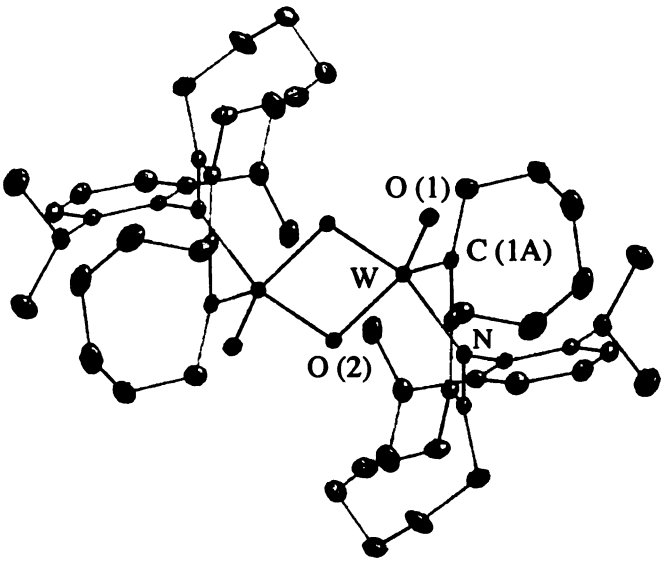


Figure 8.4 ORTEP diagram of $[W(O)(\mu\text{–}O)(=C_8H_{12}CH_{12}=NAr)]_2$ (**35**) from X-ray diffraction.

Table 8.2 Selected Bond Distances (Å) and Angles (°) from the X-ray Diffraction Study on **35.**

W–O (1)	1.696 (3)
W–O (2)	1.940 (2)
W–C (1A)	2.010 (4)
W–N	2.021 (3)
O (1)–W–O (2)	124.84 (12)
O (1)–W–O (2)	99.07 (11)
O (2)–W–O (2)	77.15 (11)
O (1)–W–C (1A)	111.38 (14)
O (2)–W–C (1A)	123.69 (13)
O (1)–W–N	100.55 (12)
O (2)–W–N	85.54 (11)

Indeed, all the distances in the metallocycle are consistent with greater participation of the amido-alkyl resonance form than in the imido derivative. For example, the W–N distance in the metallacycle of the oxo shrinks to 2.021(3) Å from 2.120(3) Å in the imido, consistent with increased alkyl-amido resonance form participation. Consistent with this assertion, the ^{13}C NMR resonance for the C_α carbon is shielded significantly to 222 ppm in the oxo from 278 ppm in the imido derivative.

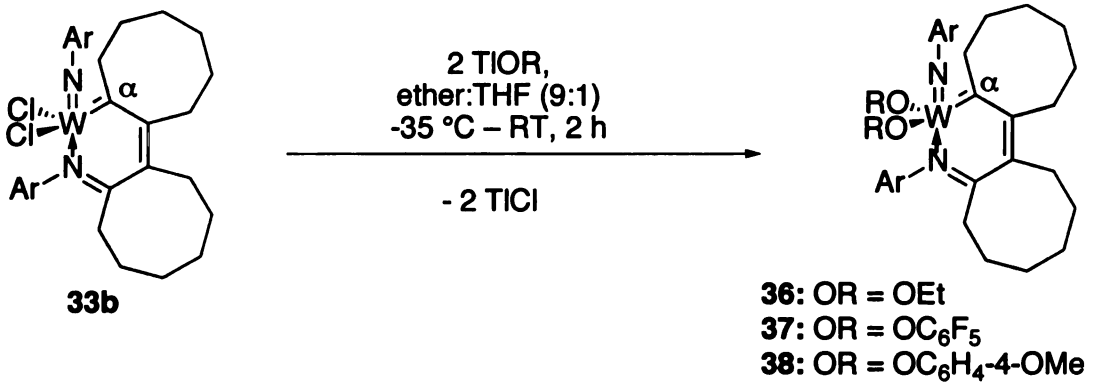
The complex **33b** has a structure very similar to the Schrock olefin metathesis system as described in Chapter 1. These metallacycles should provide a general route to reactive alkylidene complexes that have similar reactivity patterns as the Schrock alkylidenes. Carbonyl olefination in combination with ring closing metathesis has been extensively used in the synthesis of olefinic rings. Originally, carbonyl olefination[11] with ring closing by Group-VI metals was reported by Grubbs and Fu using derivatives of Schrock's catalyst, $M(=NAr)(=CHR)(OBu^t_{F6})_2$, where M = W or Mo and Ar = 2,6-diisopropylphenyl.[12] However, the complexes require several steps to access, are quite expensive, and are used stiochiometrically in this application.

There is a long history of using titanium alkylidenes or their surrogates, e.g., Tebbe's reagent, in carbonyl olefination.[13] In addition, several in situ and isolable complexes based on titanium have been used and even applied to complex organic syntheses.[14] A very useful system is prepared by a combination of $TiCl_4$, TMEDA, Zn, $PbCl_2$, and CH_2Br_2. The drawbacks of this system are the $PbCl_2$ additive and the very high reactivity with lack of tunability of the proposed titanium alkylidene reagent, which

will react with most carbonyl substituents present. Even so, these "modified Takai" systems have proven very useful.[15]

Because of ready access to $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2$ (**33b**), we thought it potentially appropriate for carbonyl olefination where it would be used stoichiometrically in reactions with substrates containing carbonyl groups (e.g. ketones or esters) with pendant olefins (vide infra). Dichloride **33b** itself was not active for these reactions. Consequently, we examined the synthesis of various derivatives of **33b**, and their activity in carbonyl olefination reactions.

One set of derivatives of **33b** that were of interest required replacement of the chlorides with alkoxides similar to the well-known Schrock metathesis catalyst system. Fortunately, thallium alkoxides led to clean replacement of chloride in **33b**, and a series of complexes was generated. The alkoxide complexes are summarized in Scheme 8.4. For this study, we prepared complexes bearing alkoxide (OEt, **36**), electron-deficient aryloxide (OC_6F_5, **37**), and electron-rich aryloxide (OC_6H_4-*p*-OMe, **38**) ligands.

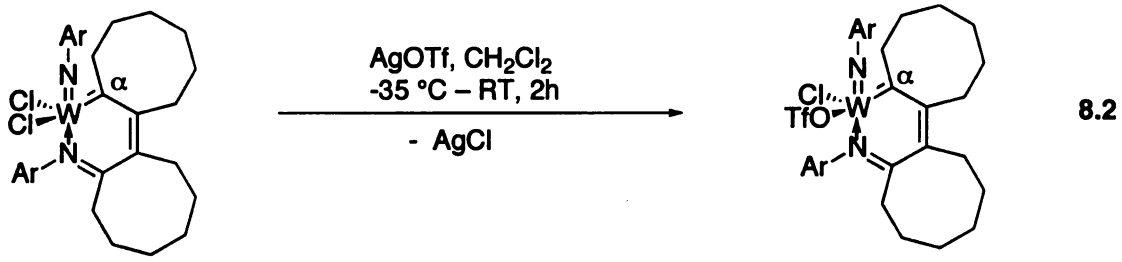


33b

36: OR = OEt
37: OR = OC_6F_5
38: OR = OC_6H_4-4-OMe

Scheme 8.4 Synthesis of tungsten alkoxide complexes **36**-**38**.

Also, we replaced one of the chloride ligands with a triflate by reaction with AgOTf (Equation 8.2). The resulting compound was a mixed triflate chloride metallacycle **39**.



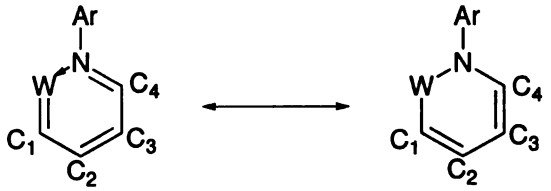
33b **39** **8.2**

The solid-state structures for compounds **33b**, **36**, **37**, **38** and **39** are summarized in Table 8.3 with emphasis on the metallacyclic fragment. The W–C distances vary from 1.944(4) to 2.039(4) Å in this set of compounds. The 4-carbon backbone in the metallacycle can be examined relative to butadiene as a conjugated 4-carbon system for reference. The C–C and C=C bonds in butadiene have bond lengths of 1.465(5) and 1.336(5) Å, respectively. The C1-C2 distances vary over much of this range for this series, 1.372(5) to 1.438(5) Å. In addition, the C1-C2 and C3-C4 distances vary together and are the same within error in all the complexes. The C4–N distance ranges from 1.315(4) to 1.408(5) Å, which can be compared to typical C–N and C=N distances of 1.472 and 1.276 Å.[16] The W–N distances are not particularly sensitive to changes in ligands on W and, excluding dichloride **33b** (vide infra), only vary from 1.991(3) to 2.006(3) Å.

The most noticeable deviation in the data when explaining the structures using only these two resonance forms is the C2-C3 distances. These distances are the same within error for all the compounds prepared except the dichloride **33b**, which seems to exhibit more double bond character. While some possible trends can be picked out among

the alkoxides like the favoring of resonance form **A** for more electron-withdrawing ligands, c.f. compound **37** and **38**, there is no discernable pattern for all the ligands used in the study.

Table 8.3 Bond distances (Å) for the metallacycles in compounds **33b**, **36**, **37**, **38** and **39** from X-ray diffraction.



W = $W(NAr)(X)_2$

[W]	*W–C1*	*C1-C2*	*C2-C3*	*C3-C4*	*C4-N*	*N–W*	^{13}C *NMR*[a]
WCl_2 (**33b**)	1.944(4)	1.438(5)	1.404(5)	1.458(5)	1.315(4)	2.120(3)	278
$W(OEt)_2$ (**36**)	2.030(5)	1.371(7)	1.449(8)	1.384(7)	1.390(6)	2.004(4)	235
$W[OC_6F_5)_2$ (**37**)	1.983(4)	1.404(5)	1.452(5)	1.409(5)	1.370(5)	2.003(3)	268
$W[OC_6H_4(OMe)]_2$ (**38**)	2.039(4)	1.372(5)	1.463(5)	1.381(5)	1.408(5)	1.991(3)	247
W(Cl)(OTf) (**39**)	1.960(5)	1.420(7)	1.433(7)	1.414(6)	1.361(6)	1.999(4)	278

[a] ^{13}C NMR chemical shift in ppm for the resonance assigned to the alkylidene carbon.

It is currently unknown exactly what is leading to the structural deviations from these two expected resonance forms. However, two observations can be made that are affecting the structure and likely leading to the deviations from this simple bonding model. Both of these observations are effects (steric and electronic) resulting from the fact that the structures are not flat, as might be expected for a metallapyridinium. First,

the structure has an "envelope" conformation with W forming the "flap". The C3 carbon is curled slightly toward a monoanionic ligand on the metal, e.g. Cl, in most cases, and sterics in that position may be greatly affecting the structure of the metallacycle.

In the case of bis(perfluorophenyl) **37**, the metallacycle curls away from these large ligands. Second, the imido may be competing with π-type orbitals within the metallacycle; filling of these orbitals has been postulated to lead to similar ring distortions in metallabenzene complexes.[17] What is known is that the electronic structure of these complexes appears quite complex and a variety of factors seem to influence their structure. In Figure 8.5 is a representation of the solid state structure for W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)(Cl)(OTf) (**39**) to illustrate the conformation of the metallacycle.

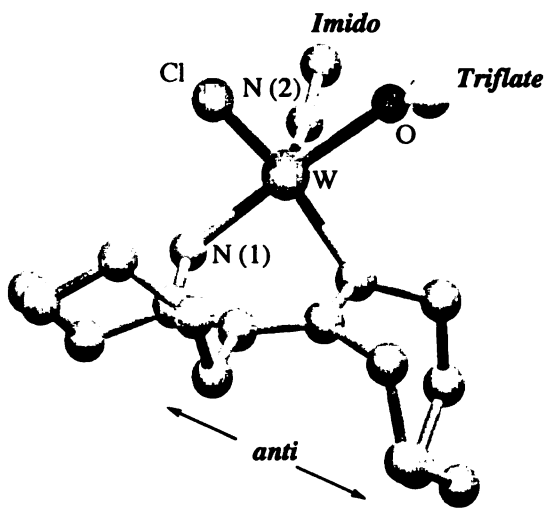


Figure 8.5 Ball and stick structure from X-ray diffraction for W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)(Cl)(OTf) (**39**). Hydrogens and all but the *ipso*-carbon of the 2,6-diisopropylphenyl groups and CF_3 group excluded for clarity.

In derivatives **36**, **37**, **38**, and **39**, the two cyclooctyne rings are *anti* across the 6-membered metallacycle (Figure 8.5). In dichloride **33b**, however, the two rings are *syn* across this metallacycle (Figure 8.6), and the cyclooctyne-derived rings are both *anti* to the tungsten "flap" of the 6-membered ring envelope. Considering the largest deviations in the bond distances for the metallacycles also occur in **33b**, one can surmise that the cyclooctyne conformations are strongly affecting the structure of the metallacycle. In addition, the NMR spectra of all these metallacycles are quite complex and temperature dependant; it seems several conformers are accessible in solution.

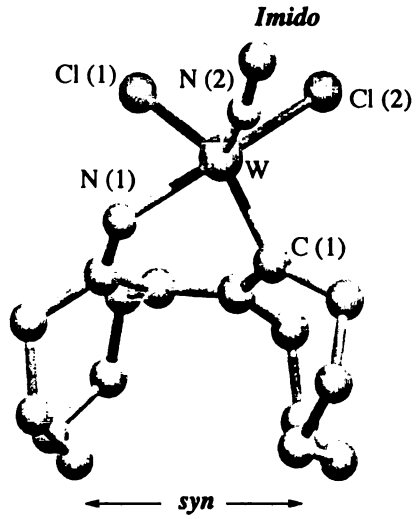
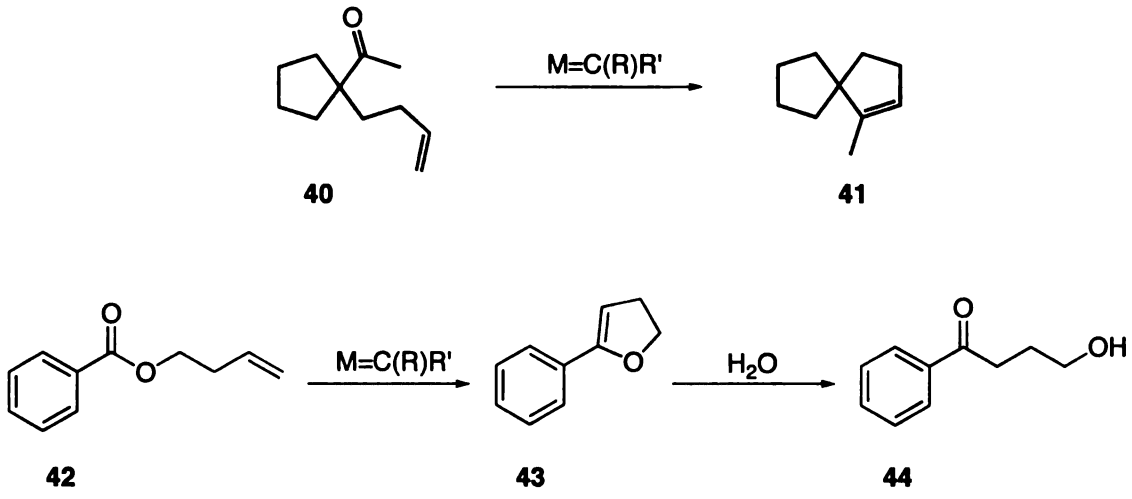


Figure 8.6 Ball and Stick structure from X-ray diffraction for $W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)Cl_2$ (**33b**). Hydrogens and all but the *ipso*-carbon of the 2,6-diisopropylphenyl groups excluded for clarity.

In Table 8.3 are also collected the chemical shifts for the alkylidene carbons of the complexes from the ^{13}C NMR spectra. The trends are fairly consistent with what might be expected. For example, within the class of alkoxides, the chemical shift

increases from OEt to OC_6H_4-*p*-OMe to OC_6F_5, i.e., the chemical shift increases from electron-rich to electron-deficient alkoxides.



40 41 42 43 44

Scheme 8.5 Substrates tested in this exploratory study and the products of carbonyl olefination.

In addition to the complexes described in detail above, we attempted to isolate and characterize the cation $[W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)Cl]^+$ by reaction of **33b** with 1 equiv of sodium tetrakis[(3,5-bis(trifluoromethyl)phenyl]borate ($Na[B(Ar_F)_4]$). However, the product was an oil that was not induced to provide a solid on repeated attempts at crystallization. The amount of NaCl produced suggested that all the $Na[B(Ar_F)_4]$ added had reacted. Two new resonances appeared in the ^{13}C NMR spectrum at 254 and 234 ppm. The generated complex(es) was active for carbonyl olefination (vide infra).

For this study we examined two different substrates for carbonyl olefination, one a ketone (**40**) and the other an ester (**42**). Their structures along with the expected ring-closed products are shown in Scheme 8.5. Carbonyl olefination of ketone **40** should generate the spiro-olefin product **41**. Similarly, carbonyl olefination of **42** derived from

esterification of benzoic acid with 3-butenol should result in the 4,5-dihydrofuran **43**.[18] The cyclic vinyl ether **43** was readily observed by GC-FID and GC-MS of crude reaction mixtures. However, the compound hydrolyzed during attempted purification by column chromatography. As a result, the hydrolysis product, 4-hydroxyl-1-phenyl-1-butanone (**44**), was isolated.[19]

The isolated and fully characterized derivatives **33b**, **36**, **37**, **38**, and **39** were found to be extremely slow or inactive for carbonyl olefination with both of the substrates **40** and **42**. Consequently, we turned to reagents that could potentially generate cationic metallacycles to examine their reactivity. Four different additives were tested ($AlCl_3$, $ZnCl_2$, $Ag[SbF_6]$, and $Na[B(Ar_F)_4]$), and the results are summarized in Table 8.4.

Table 8.4 Results of Carbonyl Olefination and Ring Closing Metathesis Reactions

Mediator	Additive	**40 – 41** % yield[a]	**42 – 44** % yield[b]
33b	$AlCl_3$	81	52
33b	$ZnCl_2$	—	NR[c]
33b	$Ag[SbF_6]$	—	NR[c]
33b	$Na[B(Ar_F)_4]$	84	37[d]
$W(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$	—	75	50[d]
$Mo(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$	—	86	NR[c]

[a] GC-FID %yield versus dodecane internal standard with 1 equiv of mediator and 1 equiv of additive in CH_2Cl_2 for 30 min. [b] GC-FID %yield versus dodecane internal standard with 1 equiv of mediator and 1 equiv of additive in toluene for 30 min. [c] No cyclization observed. [d] Reaction run in CH_2Cl_2.

With the additives examined, $AlCl_3$ and $Na[B(Ar_F)_4]$ were both found to be effective and both had comparable activity to $W(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$ with these substrates. Several attempts were made to isolate and identify the cyclooctyne-derived by-product resulting from carbonyl olefination with the metallacycle, but we were unable to identify the fate of this fragment. However, the by-product did not offer difficulties with isolation of the desired organic products in these cases.

Conclusion

The isolated metallacycles **33a**, **33b**, and **35** are not olefin metathesis active. However, addition of $AlCl_3$ to **33a** or **33b** results in mixtures that polymerize norbornene.[20] From the readily-prepared $W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)Cl_2$ (**33b**) we were able to generate a series with alternative monoanionic ligands. All members of this series were structurally characterized, and the differences in the metallacyclic fragment are shown in Table 8.3. It is apparent from the structures that there are large steric and electronic components to the structure within the metallacycle. It is also surmised from the structures that the conformation of the cyclooctyl rings is both flexible and affects the metallacycle.

The members of this series were tested for their activity in carbonyl olefination with two different substrates, and it was found that these isolable and fully characterized complexes were of only moderate to low activity. Generating cationic derivatives with $AlCl_3$ and $Na[B(Ar_F)_4]$ was found to give compounds with excellent reactivity for carbonyl olefination comparable to $W(NAr)(CHCMe_2Ph)(OBu^t_{F6})_2$.

These tungsten metallacycles offer very good thermal stability and are only mildly water sensitive, generating a μ-oxo metallacyclic complex on hydrolysis. Even though the behavior of the metallacycle is complex and seems to depend heavily on the steric and electronic nature of the other ligands, these systems can have reactivity similar to alkylidenes, especially when cationic.

Experimental

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Celite was dried at >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. $W(NAr)_2(DME)Cl_2$ and $Mo(NAr)_2(DME)Cl_2$ were prepared as reported in literature. $W(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$[21] and $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$[22] were prepared as reported in literature. Thallium ethoxide was purchased from Strem

Chemical Co. and was used without purification. Thallium alkoxide salts were prepared as reported in the literature.[23] Silver triflate was purchased from Aldrich Chemical Co. and was used without further purification. $Na[B(Ar_F)_4]$ was prepared using the literature procedure.[24]

Preparation of $Mo(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2$ (33a). To a stirred solution of $Mo(NAr)_2(DME)Cl_2$ (250 mg, 0.411 mmol, 1 equiv) in 5 mL pentane was added cyclooctyne (112 mg, 1.03 mmol, 2.5 equiv). After 3 h, the yellow precipitate was isolated by decanting the liquid, washing with pentane, and drying in vacuum to give pure **33a** (271 mg, 0.369 mmol, 90%). ^1H NMR ($CDCl_3$): 7.27 (dd, 1 H), 7.16 (t, 1 H), 7.03 (m, 1 H), 6.93 (m, 3 H), 4.85 (m, 1 H), 4.16 (m, 1 H), 3.53 (sept, 2 H), 3.37 (sept, 1 H), 3.10 (m, 1 H), 2.5–2.9 (m, 6 H), 1.9–2.2 (m, 6 H), 1.5–1.9 (m, 10 H), 1.35 (d, 3 H), 1.23 (d, 3 H), 1.20 (d, 6 H), 0.93 (d, 6 H), 0.90 (d, 3 H), 0.78 (d, 3 H). ^{13}C NMR ($CDCl_3$): 309.31 (C_α), 177.14 (N=*C*), 153.75 (*C*), 147.32 (2 overlapping *C*), 143.71 (*C*), 141.87 (*C*), 139.74 (*C*), 133.91 (*C*), 130.96 (*C*), 128.69 (*C*H), 128.13 (*C*H), 125.44 (*C*H), 124.10 (*C*H), 122.55 (2 overlapping *C*H), 44.21 (CH_2), 32.38 (CH_2), 31.06 (CH_2), 28.72 (^{i}Pr-*C*H), 28.59 (2 overlapping ^{i}Pr-*C*H and overlapping CH_2), 28.34 (^{i}Pr-*C*H), 28.15 (CH_2), 28.03 (CH_2), 27.38 (CH_2), 26.30 (CH_2), 26.02 (^{i}Pr-CH_3), 25.98 (CH_2), 25.44 (^{i}Pr-CH_3), 25.20 (CH_2), 25.13 (CH_2), 24.80 (CH_2), 24.51(^{i}Pr-CH_3), 24.38 (^{i}Pr-CH_3), 24.29 (^{i}Pr-CH_3), 22.80 (^{i}Pr-CH_3). Anal. Calcd. for $C_{40}H_{58}Cl_2N_2Mo$: C, 65.48; H, 7.97; N, 3.82. Found: C, 65.59; H, 8.20; N, 3.87. Decomposition temp. 95-97 °C.

Preparation of $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2$ (33b). To a stirred solution of $W(NAr)_2(DME)Cl_2$ (1.00 g, 1.44 mmol, 1 equiv) in 10 mL pentane was added cyclooctyne (389 mg, 3.595 mmol, 2.5 equiv). After 12 h, the green-yellow precipitate was collected on a frit, washed with cold pentane, and dried *in* vacuum to give pure **33b** (1.1 g, 1.34 mmol, 93%). ^1H NMR (C_6D_6): 7.07 (dd, 1 H), 7.03 (t, 1 H), 6.94 (m, 1 H), 6.85 (m, 3 H), 4.82 (m, 1 H), 4.61 (m, 1 H), 4.31 (sept, 2 H), 3.98 (sept, 1 H), 2.72 (m, 1 H), 2.65 – 2.21 (m, 6 H), 1.69 – 1.87 (m, 6 H), 1.43 – 1.68 (m, 10 H), 1.37 (d, 3 H), 0.1.26 (d, 3 H), 1.24 (d, 6 H), 1.20 (d, 6 H), 0.97 (d, 3 H), 0.73 (d, 3 H). ^{13}C NMR ($CDCl_3$): 280.89 (C_α), 169.19 (N=*C*), 150.80 (*C*), 146.85 (2 overlapping *C*), 144.68 (*C*), 143.44 (*C*), 140.68 (*C*), 137.76 (*C*), 128.45 (*C*H), 127.76 (*C*H), 127.35 (*C*), 125.30 (*C*H), 124.22 (*C*H), 122.35 (2 overlapping *C*H), 122.35 (2 overlapping *C*H), 41.88 (CH_2), 31.34 (CH_2), 30.92 (CH_2), 29.73 (CH_2), 29.44 (CH_2), 29.35 (CH_2), 29.12 (CH_2), 28.59 (2 overlapping *C*H), 27.94 (2 overlapping *C*H and one overlapping CH_2), 26.30 (CH_2), 25.84 (CH_3), 25.64 (CH_2), 25.59 (CH_2), 25.50 (2 overlapping CH_3), 25.27 (CH_3), 25.05 (CH_2), 24.88 (2 overlapping CH_3), 24.72 (CH_3), 23.52 (CH_3). Anal. Calcd. for $C_{40}H_{58}Cl_2N_2W$: C, 58.46; H, 7.13; N, 3.41. Found: C, 58.40; H, 7.06; N, 3.46. Decomposition temp. 138-140 °C.

Preparation of Pyrrole (34). From 33a. In a pressure tube, $Mo(NAr)(=C_8H_{12}=C_8H_{12}=NAr)Cl_2$ (0.100 g, 0.136 mmol) was dissolved in toluene (20 mL). The sealed pressure tube was heated at 75 °C in an oil bath for 90 min. The volatiles were removed *in vacuo*, and the black solid was dissolved in 5 mL diethyl ether and

passed through a short column of silica gel. Removal of the volatiles in vacuo yielded a yellow solid. Recrystallization from pentane gave 27 mg (0.0702 mmol, 51.6%) of the pyrrole decomposition product as light yellow crystals. **From 33b.** In a pressure tube, W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)Cl_2 (0.100 g, 0.122 mmol) was dissolved in toluene (20 mL). The sealed pressure tube was heated at 100 °C in an oil bath for 24 h. The volatiles were removed *in vacuo*, and the black solid was dissolved in 5 mL diethyl ether and passed through a short column of silica gel. Removal of the volatiles in vacuo yielded a solid, which was recrystallized from pentane giving 14 mg (0.0357 mmol, 30%) of the pyrrole as light yellow crystals. ^{1}H NMR ($CDCl_3$): 7.35 (dd, 1 H, *p-H*), 7.18 (app dd, 2 H, *m-H*), 2.62-2.57 (m, 4 H), 2.39 (sept, J = 6.9 Hz, 2 H, C*H*Me_2), 2.26-2.32 (m, 4 H), 1.56-1.66 (m, 4 H), 1.45-1.38 (m, 12 H), 1.10 (d, 12 H, J = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): 148.27 (*C*–^{i}Pr), 134.34 (*ipso-C*), 128.59 (*p-C*), 128.40 (pyrrole-2-*C*), 123.63 (*m-C*), 116.96 (pyrrole-3-*C*), 29.82 (*C*H_2), 29.49 (*C*H_2), 27.42 (*C*HMe_2), 26.33 (*C*H_2), 25.46 (*C*H_2), 25.17 (*C*H_2), 24.61 (CH(*C*H_3)$_2$), 22.31 (*C*H_2). Anal. Calcd. for $C_{28}H_{41}N$: C, 85.87; H, 10.55; N, 3.58. Found: C, 85.97; H, 10.88; N, 3.71. M.p. = 116-118 °C.

Synthesis of [W(=C_8H_{12}=C_8H_{12}=NAr)(O)(μ-O)]$_2$ (35). From 33b and 50% H_2SO_4: In a separatory funnel, W(Ndip)(=C_8H_{12}=C_8H_{12}=Ndip)Cl_2 (400 mg, 0.487 mmol) was dissolved in 200 mL toluene outside the glovebox. To this, 400 mL of 50% H_2SO_4 was added, and the mixture was shaken for 5 min. The toluene layer was separated and dried with K_2CO_3. The volatiles were removed in vacuo to yield an orange-red solid. Recrystallization from pentane gave 223 mg of pure **35** (0.1835 mmol, 38%).

Anal. Calcd. for $C_{56}H_{82}N_2O_4W_2$: C, 55.35; H, 6.82; N, 2.31. Found: C, 55.67; H, 6.83; N, 2.61. M.p. = 208-210 °C (dec).

General procedure for the preparation of W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OR)$_2$. In a glove box, to a near frozen solution of W(C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2 (**33b**) (1 mmol, 1 equiv) in 2 mL ether:THF (9:1) was added TlOR (2 mmol, 2 equiv). The solution was allowed to reach room temperature and stirred for 2 h. In order to check for reaction completion, an aliquot of the reaction mixture was filtered through Celite to remove TlCl and removed from the box. The aliquot was added to dilute nitric acid (0.25 M) and treated with 50 mg of $AgNO_3$ in 1 mL distilled water. The absence of a white precipitate corresponding to AgCl indicated reaction completion. Volatiles then were removed from the reaction in vacuo. The product was redissolved in a small amount of pentane, and the solution was filtered through Celite to remove TlCl. The product was crystallized from a minimum amount of pentane at –35 °C.

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OEt)$_2$ (36). The compound was recrystallized as bright orange crystals from pentane in 80% isolated yield. ^{1}H NMR (500 MHz, C_6D_6): 6.83-7.07 (m, 6 H), 4.56-4.64 (m, 3 H), 4.38-4.48 (m, 4 H), 4.22-4.27 (m, 3 H), 3.73-3.84 (m, 5 H), 3.58-3.64 (m, 6 H), 2.73-2.86 (m, 6 H), 2.55-2.67 (m, 6 H), 2.19-2.26 (m, 6 H), 1.52-1.94 (m, 6 H), 1.24-1.34 (m, 6 H), 1.16-1.19 (m, 4 H), 1.05 (d, 4 H, J_{CH} = 7.0 Hz), 0.95 (d, 3 H, J_{CH} = 7.0 Hz). ^{13}C NMR (125 MHz, C_6D_6): 234.94 (C_α), 150.99, 150.67, 148.6, 146.60, 143.71, 141.60, 128.29, 127.08, 126.03, 125.48, 124.75, 124.26, 122.75, 67.32, 65.09, 41.72, 34.35, 31.81, 30.17, 30.80, 29.43, 28.32, 28.09, 27.98, 27.92, 27.78, 27.12, 25.66, 25.62, 25.23, 24.45, 24.01, 23.58, 20.62, 20.17. Anal. Calcd. for

$C_{44}H_{68}N_2O_2W$: C, 62.85; H, 8.15; N, 3.33. Found: C, 63.08; H, 8.28; N, 3.30. M.p. = 196-198 °C (dec).

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OC_6F_5)$_2$ (37). The compound was recrystallized as light orange crystals from pentane in 78% isolated yield. ^{1}H NMR (300 MHz, C_6D_6): 6.77-7.04 (m, 6 H), 4.41-4.46 (m, 1 H), 4.16-4.46 (m, 1 H), 3.89-4.00 (m, 1 H), 3.54-3.69 (m, 3 H), 2.64-3.01 (m, 2 H), 2.43-2.49 (m, 1 H), 2.27 (sept, 2 H, J_{CH} = 6.9 Hz), 1.91-1.98 (m, 1 H), 1.60-1.98 (m, 6 H), 1.41-1.53 (m, 6 H), 1.34-1.39 (m, 10 H), 1.23 (d, 3 H, J_{CH} = 6.9 Hz), 0.95-1.22 (m, 3 H), 0.88 (d, 6 H, J_{CH} = 6.9 Hz), 0.76 (d, 6 H, J_{CH} = 6.6 Hz). ^{13}C NMR (75 MHz, C_6D_6): 268.17 (C_α), 164.19, 148.99, 147.59, 146.51, 145.21, 140.89, 130.72, 128.59, 128.55, 125.46, 124.51, 123.12, 38.87, 35.51, 34.39, 32.00, 31.51, 30.25, 30.13, 30.07, 29.80, 28.77, 28.33, 27.38, 27.06, 26.07, 25.92, 25.58, 25.50, 25.46, 25.21, 25.07, 24.99, 24.59, 22.67, 14.21. ^{19}F NMR (282 MHz, $CDCl_3$): –160.0 (quar, J_{FF} = 9.87 Hz), –167.47 (t, J_{FF} = 21.71 Hz), –181.58 to –181.81 (m, J_{FF} = 9.87 Hz). Anal. Calcd. for $C_{52}H_{58}N_2O_2F_{10}W$: C, 55.92; H, 5.23; N, 2.51. Found: C, 55.82; H, 5.38; N, 2.43. M.p. = 210-212 °C (dec).

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OC_6H_4-p-OMe)$_2$ (38). The compound was recrystallized as dark orange crystals from pentane in 83% isolated yield. ^{1}H NMR (300 MHz, C_6D_6): 7.00-7.10 (m, 7 H), 6.68-6.86 (m, 7 H), 4.37-4.53 (m, 2 H), 3.41-3.65 (m, 3 H), 3.74 (s, 3 H), 3.26 (s, 3 H), 2.93-2.81 (m, 1 H), 2.62-2.77 (m, 2 H), 2.00-2.35 (m, 4 H), 1.34-1.83 (m, 16 H), 1.14 (d, 12 H, J_{CH} = 6.6 Hz), 1.08 (d, 12 H, J_{CH} = 6.9 Hz). ^{13}C NMR (75 MHz, C_6D_6): 246.67 (C_α), 158.67, 158.59, 153.81, 153.46, 152.89, 150.72,

148.58, 146.02, 145.80, 143.79, 143.14, 127.14, 125.14, 124.87, 124.47, 123.05, 121.67, 120.47, 114.16, 113.99, 55.21, 55.10, 42.06, 34.97, 32.20, 30.63, 30.57, 29.99, 29.23, 28.61, 28.57, 28.23, 28.12, 28.02, 27.39, 27.15, 26.25, 25.82, 25.61, 25.46, 25.08, 24.45, 24.15, 23.77, 22.66, 22.55. Anal. Calcd. for $C_{54}H_{72}N_2O_4W$: C, 65.05; H, 7.28; N, 2.81. Found: C, 65.30; H, 7.92; N, 2.53. M.p. 118-120 °C.

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(Cl)(OTf) (39). In a glove box, to a near frozen solution of W(C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2 (**33b**) (100 mg, 0.1217 mmol, 1 equiv) in 2 mL CH_2Cl_2 was added AgOTf (30.3 mg, 0.1217 mmol, 1 equiv). The solution was allowed to reach room temperature and stirr for 2 h. The volatiles were removed in vacuo, and the product was redissolved in ether. The AgCl precipitate was removed by filtration through Celite. The volatiles of the filtrate were removed in vacuo to give a viscous oil. The resulting oil was crystallized from ether at –35 °C to give **39** (93.3 mg, 0.0994 mmol, 82%). ^{1}H NMR (300 MHz, C_6D_6): 7.07 (1 H), 7.03 (1 H), 6.89-7.00 (m, 1 H), 6.69-6.88 (m, 3 H), 4.80 (s, 1 H), 4.31 (sept, 2 H, J_{CH} = 6.9 Hz), 3.98 (sept, 2 H, J_{CH} = 6.9 Hz), 2.84-2.96 (m, 1 H), 2.29-2.50 (m, 6 H), 1.61-1.96 (m, 6 H), 1.40-1.59 (m, 10 H), 1.32 (d, 3 H, J_{CH} = 6.9 Hz), 1.26 (d, 3 H, J_{CH} = 6.9 Hz), 1.24 (d, 6 H, J_{CH} = 6.9 Hz), 1.20 (d, 6 H, J_{CH} = 6.9 Hz), 0.97 (d, 3 H, J_{CH} = 6.6 Hz), 0.73 (d, 3 H, J_{CH} = 6.6 Hz). ^{13}C NMR (74.5 MHz, $CDCl_3$): 277.93 (C_α), 147.04, 142.32, 140.53, 129.68, 129.04, 128.19, 125.33, 124.49, 124.32, 124.01, 122.66, 65.82, 41.93, 30.46, 30.33, 29.70, 29.55, 29.12, 28.53, 27.89, 27.56, 26.47, 25.99, 25.68, 25.22, 24.96, 24.84, 24.70, 24.40, 24.03, 23.38, 15.23. ^{19}F NMR (282 MHz, $CDCl_3$): –77.83 (s). M.p. = 155-157 °C (dec).

Representative carbonyl olefination procedure to produce 1-methylspiro[4.4]non-1-ene (41). In a glove box, W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)$(Cl)_2$ (**33b**) (200 mg, 0.246 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added to a solution of $AlCl_3$ (33 mg, 0.246 mmol, 1 equiv) and 1-acetyl-1-(3-butenyl)cyclopentane (**40**, 40 mg, 0.240 mmol, 1 equiv) in CH_2Cl_2 (3 mL). The resulting mixture was stirred vigorously. After 30 min, the reaction mixture was taken outside the glove box, quenched with distilled water (0.2 mL), and concentrated in vacuo. The product **41** can be purified by column chromatography (silica gel, 250-400 mesh, pentane) as a light yellow oil (21 mg, 0.154 mmol, 64%). R_f = 0.80 (SiO_2, hexanes). ^1H NMR ($CDCl_3$, 500 MHz): 5.28-5.29 (m, C*H*, 1H), 2.15-2.28 (m, CH_2, 2H), 1.69-1.72 (m, 2 H), 1.59-1.64 (m, 6 H), 1.54-1.58 (m, CH_2, 2 H), 1.31-1.36 (m, CH_2, 2 H), 1.25 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): 145.60, 123.78, 57.20, 39.89, 36.07, 29.45, 25.06, 12.42. MS (EI) *m/z* = 136 (M^+). Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30; H, 11.62.

Representative carbonyl olefination procedure to produce 4-hydroxy-1-phenylbutanone (44). In a glove box, W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)$(Cl)_2$ (**33b**) (200 mg, 0.246 mmol, 1 equiv) in toluene (2 mL) was added to a solution of $AlCl_3$ (33 mg, 0.246 mmol, 1 equiv) and 4-benzoyloxybut-1-ene (**42**, 42 mg, 0.241 mmol, 1 equiv) in toluene (3 mL). The resulting mixture was stirred vigorously. After 3.5 h, the reaction mixture was taken outside the glove box, quenched with distilled water (0.2 mL), and concentrated in vacuo. The product **44** can be purified by column chromatography (silica gel, 250-400 mesh, hexanes then acetone:hexane 1:9 to 2:8) as a colorless oil (18 mg, 0.11 mmol, 45.5%).[25] R_f = 0.70 (SiO_2, acetone:hexane, 2:8). ^1H NMR ($CDCl_3$, 300 MHz)

: 7.94-7.97 (m, *o*-Ph, 2 H), 7.51-7.56 (m, *p*-Ph, 1H), 7.41-7.46 (m, *m*-Ph, 2 H), 3.72 (t, C(O)CH_2, 2 H, J_{CH} = 6 Hz), 3.11 (t, HOCH_2, 2 H, J_{CH} = 6.9 Hz), 2.00 (pent, $CH_2CH_2CH_2$, 2 H, J_{CH} = 6.6 Hz), 1.91 (br s, O*H*, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 200.52, 136.85, 133.11, 128.58, 128.07, 62.29, 35.26, 26.90. MS (EI) m/z = 164 (M^+).

Reaction of W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2 (33b) with Na[B(Ar_F)$_4$]. In a glove box, to a near frozen solution of W(C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2 (**33b**) (100 mg, 0.122 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added sodium tetrakis[(3,5-bis(trifluoromethyl)phenyl]borate (Na[B(Ar_F)$_4$]) (119 mg, 0.134 mmol, 1.1 equiv). The solution was allowed to reach room temperature and stir for 2 h. The NaCl precipitate was filtered through a weighed pipette with glass filter paper and Celite. The Celite was washed with CH_2Cl_2 (4 mL). The pipette with its contents was dried to a constant weight, and the amount of NaCl formed during the reaction was recorded (6.5 mg, 91% yield). The volatiles of the filtrate were removed in vacuo to give a viscous oil. The resulting oil was dissolved in $CDCl_3$, and NMR spectra were recorded. Conversion was complete after 2 h according to ^{13}C NMR spectroscopy. There were two new C_α resonances in the ^{13}C NMR. ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 254 (C_α) and 234 (C_α). ^{19}F NMR (282 MHz, $CDCl_3$): –63.10.

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