SYNTHESIS OF MOLYBDENUM OLEFIN METATHESIS CATALYSTS THROUGH PROTONATION REACTIONS

by

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Dedicated to my parents
for their unswerving love and constant encouragement,
and to my teachers for showing the way.

Nullius addictus iurare in verba magistri.

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ABSTRACT

Chapter 1

The attempted syntheses of molybdenum imido alkylidene complexes of the type $Mo(NAr_{Cl})(CH\text{-}t\text{-}Bu)[Biphen]$ and $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_2Ph)[Biphen]$ ($Biphen^{2-}$ = 3,3'-di-t-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) from $Mo(NAr_{Cl})(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ and $[Biphen]K_2$ have sporadically afforded mixtures containing the desired products along with the corresponding amido alkylidyne complexes, $Mo(NHAr_{Cl})(C\text{-}t\text{-}Bu)[Biphen]$ and $Mo(NH\text{-}2\text{-}CF_3C_6H_4)(CCMe_2Ph)[Biphen]$, respectively. The reaction of $[Biphen]K_2$ with $Mo(NAr_{Cl})(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ and 10 equivalents of triethylamine reproducibly gave $Mo(NHAr_{Cl})(C\text{-}t\text{-}Bu)[Biphen]$ in 40% yield. An X-ray crystal structure of a related complex, $Mo(NHAr_{Cl})(CCMe_2Ph)[S\text{-}Biphen]$ confirmed the proposed structure and also revealed that one ortho chloride approaches within 2.93 Å of the metal approximately *trans* to the alkylidyne ligand. Attempts to prepare three other amido alkylidyne complexes in an analogous manner from $Mo(NR'')(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ (NR'' = N-2-$CF_3C_6H_4$, N-2,6-i-$Pr_2C_6H_5$, N-2,6-$Me_2C_6H_5$) with $[Biphen]K_2$ in the presence of 10-20 equivalents of triethylamine failed.

Chapter 2

The reaction between $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$ (Ar = 2,6-i-$Pr_2C_6H_3$) and various alcohols (1-AdamantylOH, t-BuOH, ArOH, $(CF_3)_2CHOH$, $(CF_3)_2MeCOH$, $(CF_3)_3COH$, C_6F_5OH) in pentane or toluene yielded either complexes of the type $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OR)$ through direct addition of ROH across a Mo-C bond, or complexes of the type $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OR)$ through direct addition of ROH across a Mo=C bond. The trineopentyl species appear to be formed when the alcohol has a relatively low pK_a. The outcome also can depend upon whether the alcohol is employed neat, or in benzene, and mixtures are observed in some circumstances. The conversion of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OR)$ into $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OR)$ was shown to be unimolecular in several examples. $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OR)$ complexes have been found to be surprisingly active catalysts for various metathesis reactions. In contrast, $M(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$ species are virtually inactive for metathesis. X-ray structures are reported for $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$, $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)[OSi(O\text{-}t\text{-}Bu)_3]$, $[Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$, and $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)(PMe_3)$.

Chapter 3

Complexes of the type $Mo(NR'')(CHR')(N(R^1)3,5\text{-}C_6H_3Me_2)_2$ (NR'' = N-2,6-i-$Pr_2C_6H_5$, N-2,6-$Me_2C_6H_5$; R' = t-Bu, CMe_2Ph; R^1 = i-Pr, t-Bu) and $Mo(NR'')(CHR')(NR_2)_2$ (NR'' = N-2,6-i-$Pr_2C_6H_5$, N-2,6-$Me_2C_6H_5$; R' = t-Bu, CMe_2Ph; R = Me, Ph) can be isolated as orange-red solids in 30-35% yields or oils by reacting $Mo(NR'')(CHR')(OTf)_2(dme)$ with $LiN(R^1)(3,5\text{-}C_6H_3Me_2)$(ether) or with $LiNR_2$. The synthesis of $Mo(NR'')(CHCMe_2Ph)(NPh_2)_2$ can be improved to 70-90% isolated yields when $Mo(NR'')(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ is used with $LiNPh_2$(ether). $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ has been crystallographically characterized. $Mo(NR'')(CHR')(N(R^1)3,5\text{-}C_6H_3Me_2)_2$ species reacted with t-BuOH and $Me(CF_3)_2COH$ in benzene to give $Mo(NR'')(CHR')(OR)_2$ (OR = O-t-Bu, $OCMe(CF_3)_2$) *in situ*. However, no reactions of $Mo(NR'')(CHR')(N(R^1)3,5\text{-}C_6H_3Me_2)_2$ were observed with enantiomerically pure diols such as [*R*-TRIP]H_2 (3,3'-2,4,6-i-$Pr_3C_6H_2$-binaphthol), [*R*-Ph]H_2 (3,3'-C_6H_5-binaphthol), [*rac*-Mesitylbinap]H_2 (3,3'-2,4,6-$Me_3C_6H_2$-binaphthol) and [*R*-TMSbinap]H_2 (3,3'-$SiMe_3$-binaphthol). Bisamido complexes of the type $Mo(NR'')(CHR')(NPh_2)_2$ were found to react with the aforementioned alcohols and diols to give Mo(NR'')(CHR')(diolate) species *in situ*, which were further reacted in a catalytic fashion with two substrates to give the corresponding ring-closed products. Preliminary results of the *in situ* catalysis demonstrated here compare fairly well with the analogous catalytic reactions reported with isolated catalysts.

Appendix A

$Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$ (Ar = 2,6-i-$Pr_2C_6H_3$) can be reacted with 5-10 equivalents of *trans*-3-hexene to give a crystallographically characterized dimeric complex, $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$ that contains an unbridged Mo=Mo bond (2.410(8) Å) in high yields. The above complex can also be prepared by treating $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$ with 0.5 equivalents of divinylbenzene. $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$ will slowly catalyze the metathesis reactions of simple substrates, although less than 5% of the catalyst seems to be activated in such reactions. It was observed that catalytically active species for metathesis reactions can be generated by another Mo (d^2) species, $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)$(ether) ($NAr_{Cl}$ = N-2,6-$Cl_2C_6H_3$, $Biphen^{2-}$ = 3,3'-di-t-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) that could effect the ring-opening metathesis polymerization of norbornene. A mixture of $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)$(ether) and 20 equivalents of diallylether in benzene-d_6 when treated with 10 equivalents of norbornene gives 54% conversion to dihydrofuran in 10 days.

Thesis Supervisor: Richard R. Schrock
Title: Frederick G. Keyes Professor of Chemistry

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Appendix A

List of Abbreviations

Ad	1-adamantyl
ADMET	Acyclic Diene Metathesis
Anal. Calcd.	elemental analysis calculated
anti	alkylidene rotamer with hydrogen directed towards the imido group
Ar	2,6-diisopropylphenyl
Ar'	2,6-dimethylphenyl
ArCl	2,6-dichlorophenyl
Biphen	*rac*-3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate (racemic, unless otherwise noted)
CM	cross metathesis
conv	conversion
deg	degrees
dme	1,2-dimethoxyethane
dppm	diphenylphosphinomethane
dmpe	dimethylphosphinoethane
ether	diethyl ether
eu	entropy units
G	free energy
H	heat of enthalpy
HMQC	heteronuclear multiple quantum correlation
i-Pr	isopropyl
${}^{n}J_{AB}$	coupling constant between nuclei A and B through n bonds
k	rate constant
K	degrees Kelvin
K_a	acid dissociation constant
K_{eq}	equilibrium constant
M	moles/liter
M_n	number average molecular weight
Mes	mesityl, 2,4,6-trimethylphenyl
mmol	millimole
mol	mole
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	triflate
p-	*para*-
PDI	polydispersity index
ph	phenyl
py	pyridine
PS	polymer supported
R-	*R*-configuration
RCM	ring-closing metathesis
ROMP	ring-opening metathesis polymerization
rt	room temperature

S	entropy
S-	*S*-configuration
Si_{surf}	surface silica
syn	alkylidene rotamer with hydrogen directed away from imido
THF	tetrahydrofuran
TON	turnover number
TMS	trimethylsilyl
TRIP	2,4,6-tri-*iso*-propylphenyl
tol	toluene
triflate	trifluoromethylsulfonate
Ts	tosyl, *para*-tolylsulfonate

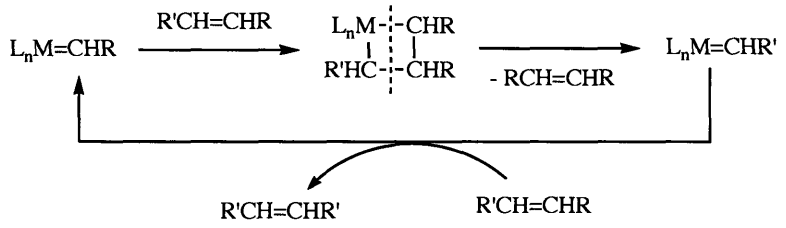
GENERAL INTRODUCTION

Synthetic strategies in organic chemistry have always relied upon the development of facile tools for the manipulation of carbon-carbon bonds.[1] In this regard, olefin metathesis has emerged as a powerful technique for effecting transformations in unsaturated molecules.[2] An olefin metathesis reaction refers to a statistical distribution involving breaking and reforming of C=C bonds (equation I.1).[3]

$$2\ RHC{=}CHR' \rightleftharpoons RHC{=}CHR + R'HC{=}CHR' \qquad (I.1)$$

Early catalyst systems employed in olefin metathesis reactions involved generation of the active species from mixtures of simple inorganic compounds such as MoO_3, WCl_6, $W(O)Cl_4$ and Re_2O_7 in the presence of aluminum/tin-based alkylating agents or alumina in ethanol or chlorobenzene.[4] Although high turn over numbers ($\sim 10^3$ min^{-1}) were achieved utilizing these systems, the catalytic activity was not sustained for more than a few minutes, and poor selectivity and low tolerance to functional groups in the substrates were observed. Moreover, the low percentage of the active species in the above mixtures precluded their characterization.[5]

Development in the area of metal-carbon multiple bond chemistry[6] was instrumental in providing complexes[7], studies on which led to the evolution of well-defined catalysts for olefin metathesis that were later developed.[8,9,10] Based on Chauvin's proposal of the reaction mechanism[11] (Scheme I.1), the key step in a catalytic olefin metathesis reaction is a [2+2] cycloaddition of the olefin to a metal-carbon double bond to form a metallacyclobutane intermediate, which can then undergo cycloreversion to yield the starting materials, or it can undergo a productive metathesis process to generate a new metal-carbon double bond and a different olefin.



Scheme I.1. Chauvin's mechanism for olefin metathesis.

There are two classes of organometallic complexes that are most widely used for catalyzing different variations of olefin metathesis reactions (Figure I.1).[12] Complexes based on molybdenum (or tungsten)[13] are more air- and moisture-sensitive compared to their ruthenium[14] counterparts. However, the molybdenum-based catalysts are more effecient than the ruthenium systems, especially when metathesis is desired in a sterically demanding system.[2] In addition, there is a greater scope for utilizing the modularity[15] of the catalysts in the case of molybdenum complexes (*vide infra*).

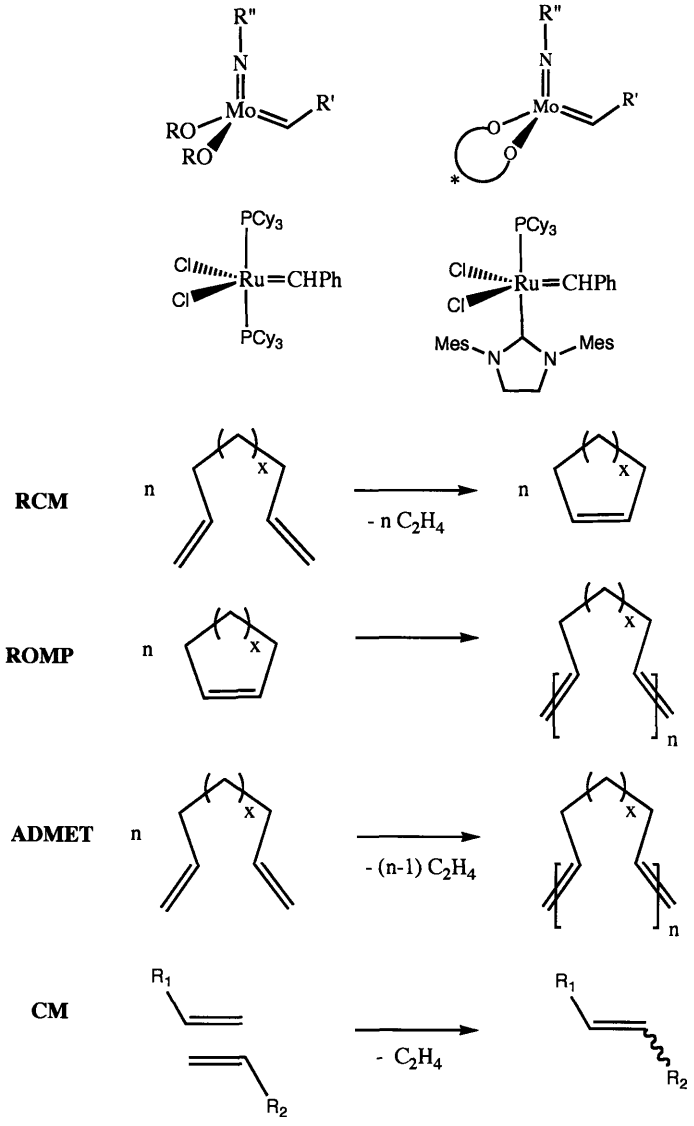
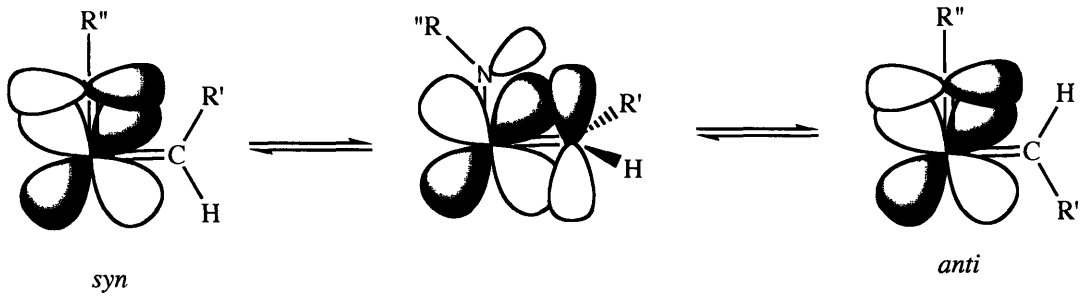


Figure I.1. Mo- and Ru-based catalysts used for different variations of the olefin metathesis reaction.

The basic design of the molybdenum catalysts utilizes the metal in its highest possible oxidation state (+6).[16] This feature allows the stabilization of electrons of the incoming olefin in a metal-based LUMO due to the high positive charge on the metal.[17] The choice of sterically demanding ligands bearing no β-hydrogens is dictated by the principle of protecting an electronically unsaturated four-coordinate metal center towards both inter- as well as intramolecular decomposition reactions.[18]

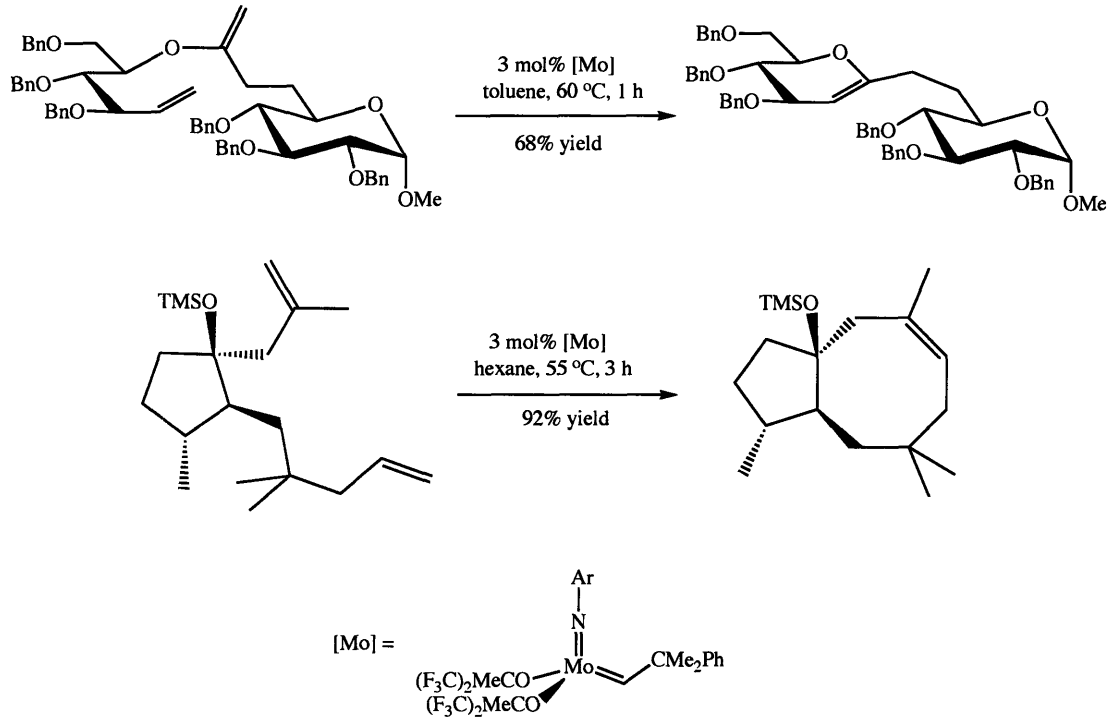
Two rotational isomers are possible for complexes such as Mo(NR″)(CHR′)$(OR)_2$ or Mo(NR″)(CHR′)(diolate) due to the presence of two strong π-bonding groups, viz. the imido and the alkylidene moieties, both of which compete for the d orbital that would allow the free rotation of the Mo=C bond (Scheme I.2)[19]. In case of the *syn* isomer, the alkylidene substituent (R′) is directed towards the imido group (NR″), while R′ and NR″ groups lie on the opposite side of the Mo=C bond for the *anti* isomer. The *syn* isomer is the lower energy species due to stabilization gained through an agostic interaction[20] of the metal with the C-H_α bond.[21] Consequently, the greater electrophilicity (and reactivity) of the *anti* isomer is exhibited in its tighter binding of a Lewis base such as PMe_3. The *syn* isomer is characterized by a lower J_{CH} for the alkylidene carbon and H_α compared to the *anti* isomer due to an increase in the bond order of Mo=C bond in the former which is a direct result of the α-agostic interaction mentioned above. The increase in the s-character of the Mo=C bond for *syn* alkylidene is also evident from a shorter Mo=C bond (by ~0.1 Å) compared to the *anti* form.[13] The two isomers can interconvert at room temperature and the rate for this process ($k_{s/a}$) is most dramatically affected by the nature of the alkoxide ligands. Electron-withdrawing alkoxides such as $OCMe(CF_3)_2$ retard the interconversion of the rotational isomers by a factor of $\sim 10^5$ compared to the electron-donating alkoxide, O-t-Bu. The imido group and the alkylidene ligand also influence the value of $k_{s/a}$, although the effect is not as pronounced as the alkoxides.[19]

Molybdenum-based olefin metathesis has been successfully employed in a myriad of organic transformations[22] as well as synthesis of polymers. Several circuitous organic syntheses have been conveniently simplified by employing such metathesis techniques that serve to shorten the synthetic route and make the route more convergent than would have been possible otherwise.



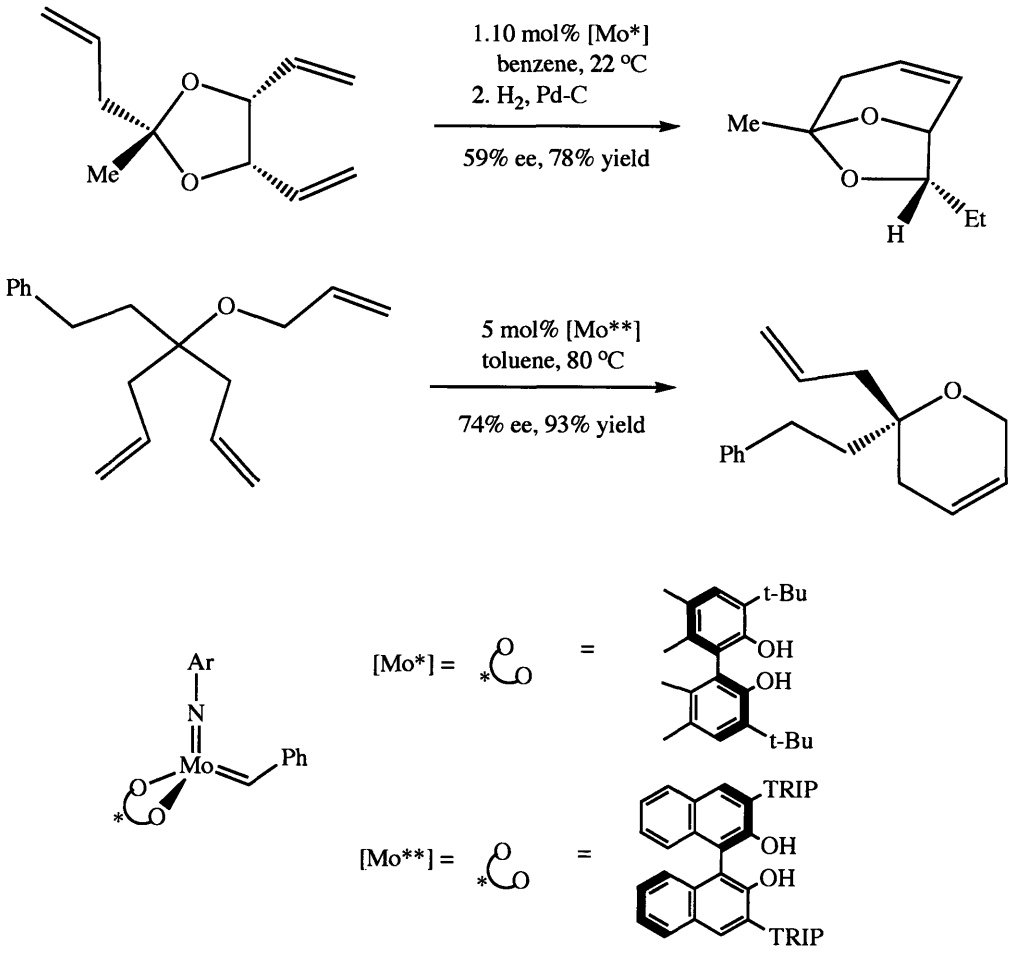
Scheme I.2. Interconversion of rotational isomers.

Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$[23] has been the most utilized complex amongst molybdenum catalysts for carrying out achiral reactions.[24] Two illustrative examples of ring-closing metathesis[25] (RCM) reactions by Postema[26] and Fürstner[27] demonstrate the formation of biologically relevant molecules in good to excellent yields that could not be synthesized efficiently otherwise (Scheme I.3).



Scheme I.3. RCM reactions applied to the synthesis of six- and eight-membered rings.

The availability of enantiomerically pure biphenol-[28] and binaphthol-based[29] ligands has allowed the applications of molybdenum catalysts in asymmetric syntheses. Kinetic resolution or desymmetrization methods[13] with M(NAr)(CHR')(diolate*) type species have been utilized in metathesis reactions to effect chirality at a remote carbon center in an olefinic substrate. Excellent asymmetric induction can be obtained for forming a variety of n-membered heterocyclic rings (n = 5-8). The methodology of asymmetric ring-closing metathesis has been employed in making diverse natural products and pharmaceutically relevant molecules, two examples of which accomplished by Burke[30] and Hoveyda[31] are shown in Scheme I.4.



Scheme I.4. Selected examples of Mo-catalyzed ARCM reaction.

In addition to the examples shown above, Mo-based catalysis has also been used in the other variations of metathesis reactions shown in Figure I.1: ring-opening metathesis polymerization (ROMP)[19,32,33,34], acyclic diene metathesis (ADMET)[35] reactions leading to formation of polymers, and cross-metathesis (CM)[36,37,38].

Currents efforts aimed at improving synthetic schemes to obtain bisalkoxide or diolate based catalysts have looked at three aspects: 1) identifying conditions that lead to catalyst contamination at the preparation stage by amido alkylidyne species (Chapter 1), 2) employing different precursors for making catalysts and modifying the stereo-electronic attributes of the catalyst by using ligands other than alkoxides, for example, dialkyl complexes of the type Mo(NR′′)(CHR′)(CH_2R′)$_2$. While dialkyl complexes have shown poor metathesis activity in RCM reactions, they can be reacted with ROH to afford Mo(NR′′)(CHR′)(CH_2R′)(OR) type complexes, some of which have demonstrated surprisingly high reactivity towards a variety of olefins (Chapter 2). M(NR′′)(CHR′)(CH_2R′)(OR) (M = Mo, W) species bearing smaller alkoxides (e.g., OC_6F_5) have been found to decompose bimolecularly giving rise to bimetallic complexes containing unbridged M=M bonds. The reactivity of M=M complexes shown in Appendix A have lent some credence to the assumption that under certain conditions catalytically active species (most probably complexes containing a M=C bond) may be obtained in small amounts from species such as M=M that are known to be sinks of a catalytic reaction, and 3) exploiting the structural modularity of complexes of the type Mo(NR′′)(CHR′)(OR)$_2$ and Mo(NR′′)(CHR′)(diolate*) via which the reactivity at the metal center can be subtly "fine-tuned" to meet the requirements of a given reaction. This attribute cannot be underestimated considering the fact that minor variations in the structural skeleton of a substrate family can lead to situations where previously known potent catalysts can be rendered ineffective.[39] Therefore, it is desired to gain access to a diverse catalyst library with various electronic and structural modifications. An ongoing direction of research in our group in collaboration with Prof. Amir Hoveyda's group at Boston College has been the synthesis of chiral molybdenum-based catalysts (Figure I.2).[13]

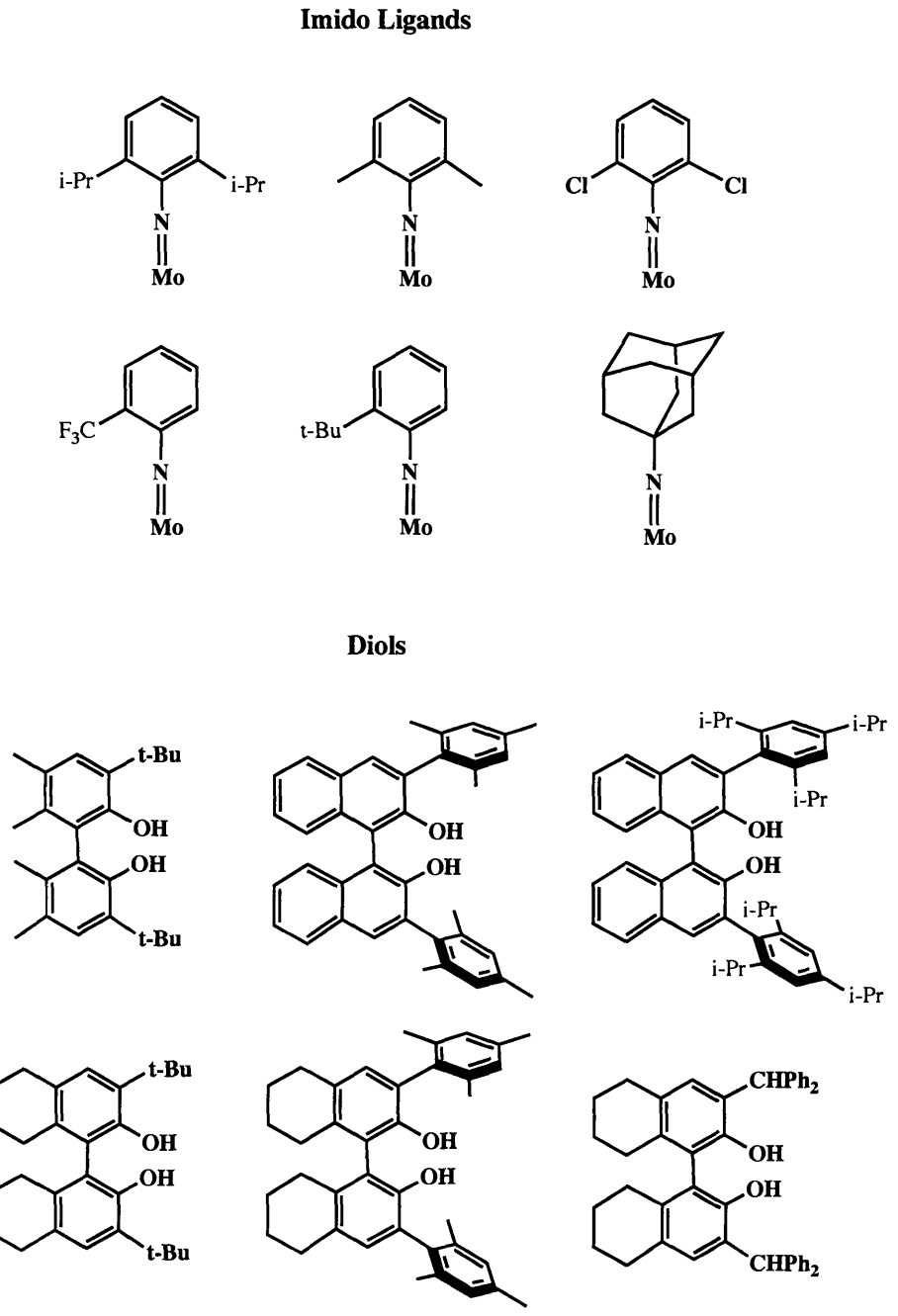


Figure I.2. Modular nature of Mo-based catalysts for ARCM reactions.

As the number of the available catalysts increase, it would be germane to devise ways that could facilitate rapid and high throughput methodologies to synthesize and evaluate the efficacy of various catalysts from one precursor. In addition, the high solubility and stability issues of certain catalysts preclude their availability is an isolable

form. Therefore, it would be convenient to generate such species in solution and screen them with different substrates in an *in situ* mode. The synthesis of bisamido complexes of the type $Mo(NR'')(CHR')(NR_2)_2$ and their reactivity towards alcohols and diols have been explored with an aim to demonstrate the utility of *in situ* catalysis (Chapter 3).

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Chapter 1

SYNTHESIS OF AMIDO ALKYLIDYNE SPECIES

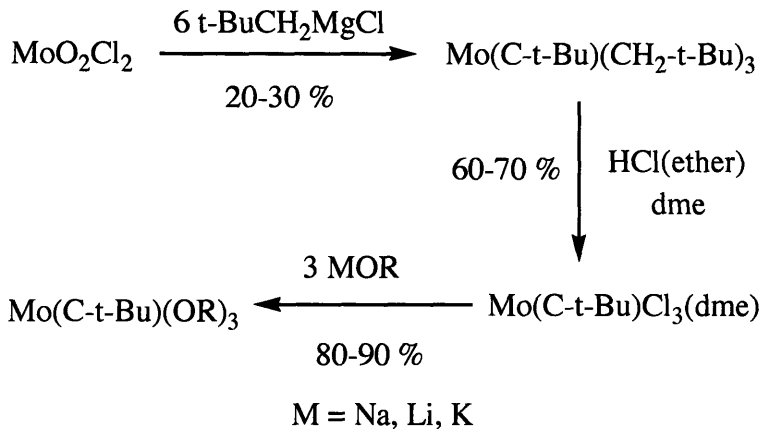
A portion of this chapter has appeared in print:

Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J., Jr.; Sinha, A.; Lopez, L. P. H. "Synthesis of Molybdenum Alkylidyne Complexes that Contain a 3,3'-Di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate ($[Biphen]^{2-}$) Ligand" *J. Organomet. Chem.* **2003**, *684*, 56.

INTRODUCTION

The formation of triple bonds is observed rarely between carbon and other elements besides itself, nitrogen and oxygen. Fischer reported the synthesis of carbyne complexes of the type $L_nM{\equiv}CR$ (M = Cr, Mo, W) containing a triple bond between a low oxidation state transition metal and a monosubstituted carbon atom.[1] However, "Fischer-type" carbyne species had limited sustainability in alkyne metathesis reactions analogous to what was observed regarding low oxidation state carbene complexes in the case of olefin metathesis reactions. The fact that olefin metathesis reactions could be successfully accomplished by high oxidation state alkylidenes led to the development of high oxidation state alkylidynes by Schrock as catalysts for alkyne metathesis reactions.[2] Considering the alkylidyne moiety as a trianion (i.e., isoelectronic with a nitride) renders the metal in its highest possible oxidation state (6+). As in the case of olefin metathesis catalysts, alkoxides were found to be suitable ancillary ligands for promoting alkyne metathesis reactions using alkylidyne complexes of molybdenum or tungsten.[3] Complexes of the type $M(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ (M = Mo or W)[4] react with three equivalents of HCl in ether in the presence of dimethoxyethane to yield the corresponding trichloride complexes, $M(C\text{-}t\text{-}Bu)Cl_3(dme)$, which in turn can be treated with alkali salts of alkoxides to yield $M(C\text{-}t\text{-}Bu)(OR)_3$ complexes as shown in Scheme 1.1.[5] More recently, works of Cummins,[6] Fürstner[7] and Moore[8] have demonstrated the use of three coordinate molybdenum compounds of the type $Mo[N(R)Ar]_3$[9] as precursors for catalyzing alkyne metathesis reactions.

Historically, alkylidyne complexes of molybdenum and tungsten were utilized in developing the synthesis of the first well-defined olefin metathesis catalysts that were isolated and studied.[10] The first synthesis of imido alkylidene bisalkoxide complexes relied on the preparation of an amido neopentylidyne complex such as $Mo(NHAr)(C\text{-}t\text{-}Bu)Cl_2(dme)$ from $Mo(C\text{-}t\text{-}Bu)Cl_3(dme)$ as shown in Scheme 1.2.[11]

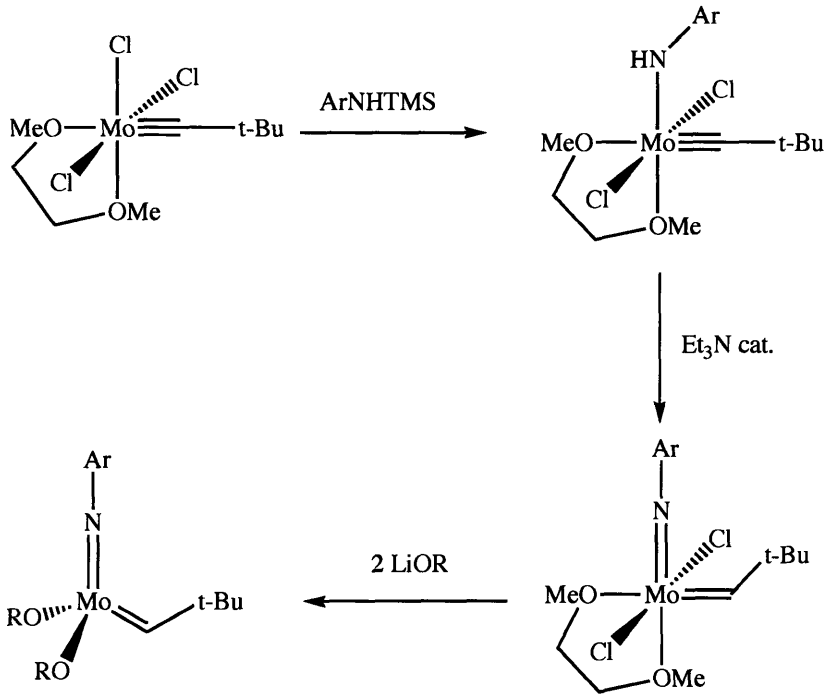


Scheme 1.1. Synthesis of Mo(C-t-Bu)(OR)$_3$.

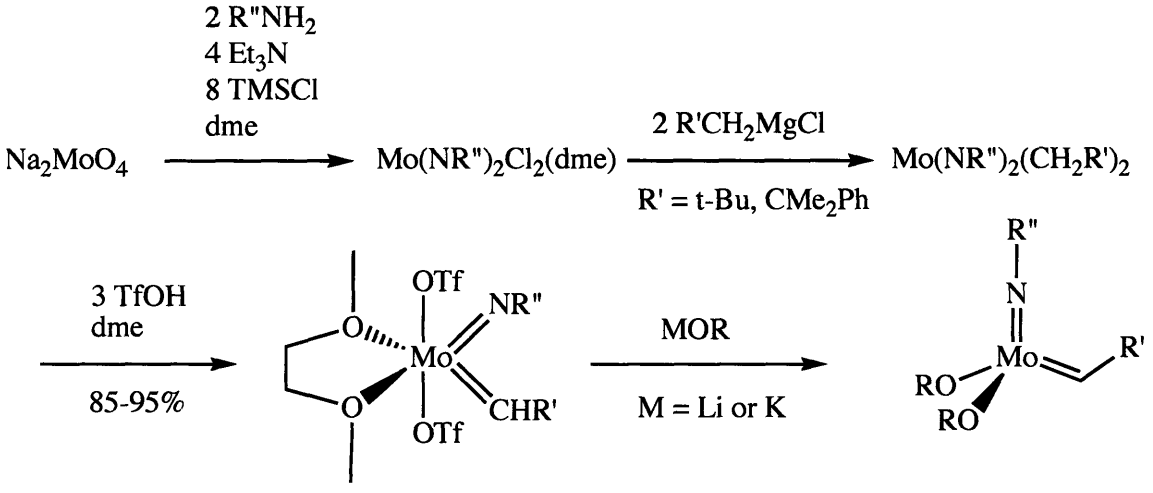
Mo(NHAr)(C-t-Bu)Cl_2(dme) can be converted to Mo(NAr)(CH-t-Bu)Cl_2(dme) by the addition of a catalytic amount of triethylamine. Replacement of the chlorides in Mo(NAr)(CH-t-Bu)Cl_2(dme) with sterically demanding alkoxides then yielded imido neopentylidene complexes Mo(NAr)(CH-t-Bu)$(OR)_2$. The advent of more practical routes to imido alkylidene complexes involved the three step synthesis of bistriflate species such as Mo(NR″)(CHR')$(OTf)_2$(dme) (R' = t-Bu, or CMe_2Ph, NR″ = aryl- or alkylimido).[12] Treatment of Mo(NR″)(CHR')$(OTf)_2$(dme) with MOR or [diolate]M_2 (M = Li, or K) salts produced the desired Mo(NR″)(CHR')$(OR)_2$[12(b)] or Mo(NR″)(CHR')(diolate)[13] type catalysts (Scheme 1.3).

A major problem encountered during the syntheses of the extremely useful olefin metathesis catalysts of the type Mo(NR″)(CHR)(diolate), especially when NR″ = N-2-$CF_3C_6H_5$ was the contamination of the reaction mixture by the corresponding amido-alkylidyne compound, i.e. Mo(NHR″)(CR)(diolate).[13(c)] This is observed in the attempted preparation of Mo(N-2-$CF_3C_6H_5$)($CHCMe_2Ph$)[Biphen] ([Biphen]$^{2-}$ = [3,3'-Di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate]$^{2-}$) where an impurity that appeared to be an alkylidyne species, namely Mo(NH-2-$CF_3C_6H_4$)($CCMe_2Ph$)[Biphen] was present. Although a resonance at 11.7 ppm in the proton NMR spectrum and a singlet resonance at 315.7 ppm in the carbon NMR spectrum of the Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen] samples could be mistaken as resonances for the *anti*

isomer, the broadening of the resonance at 11.7 ppm at higher temperatures unlike a regular base-free *anti* species indicated otherwise.



Scheme 1.2. Synthesis of Mo-based imido alkylidene bisalkoxide catalysts from an amido alkylidyne complex.



Scheme 1.3. A practical route to the synthesis of bisalkoxide catalysts.

It was proposed that the resonance near 11.7 ppm is the NH proton in Mo(NH-2-$CF_3C_6H_5$)(CCMe$_2$Ph)[Biphen], while the resonance at 315.7 ppm is the alkylidyne carbon atom resonance. Once formed, the two isomeric complexes Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[Biphen] and Mo(NH-2-$CF_3C_6H_4$)(CCMe$_2$Ph)[Biphen] did not interconvert by the action of triethylamine or [Biphen]K_2. A similar problem arose during the attempted synthesis of Mo(NAr_{Cl})(CHR')[Biphen][14] (R' = t-Bu, or CMe_2Ph, NAr_{Cl} = N-2,6-$Cl_2C_6H_5$) through the addition of K_2Biphen to Mo(NAr_{Cl})(CHR')$(OTf)_2$(dme). A significant impurity in several preparations appeared to be Mo($NHAr_{Cl}$)(CCMe$_2$R)[Biphen], according to NMR spectra of crude reaction mixtures.[15] However, conditions could not be found where Mo($NHAr_{Cl}$)(CCMe$_2$R)[Biphen] was the sole product.

This chapter deals with examining the conditions under which amido alkylidyne complexes can be formed reproducibly such that complications involving such species as impurities in the synthesis of olefin metathesis catalysts may be avoided.

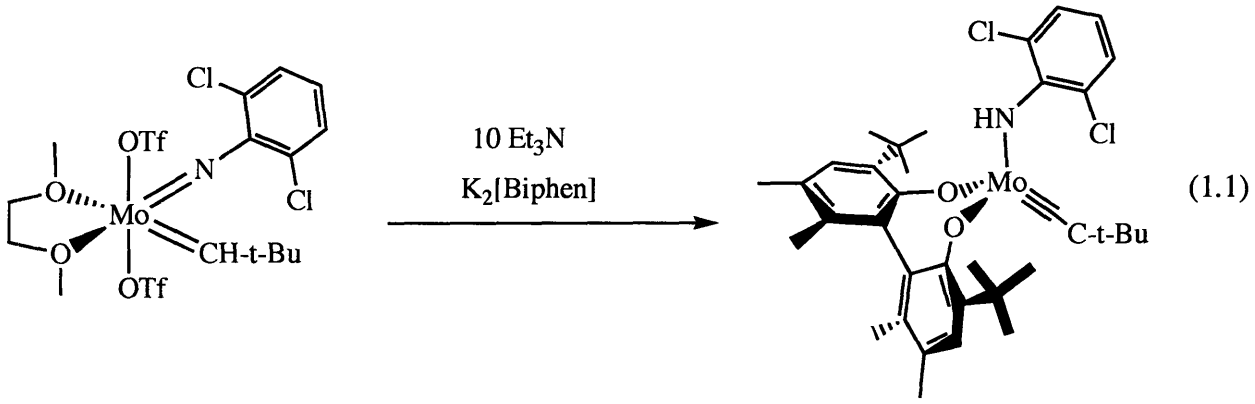
RESULTS AND DISCUSSIONS

1.1 Synthesis of amido alkylidyne biphen complexes

The reported method[14] of synthesizing Mo(NAr_{Cl})(CH-t-Bu)[Biphen] (as a THF adduct) involves a reaction between Mo(NAr_{Cl})(CH-t-Bu)$(OTf)_2$(dme) and [Biphen]K_2. Sporadically, however, the reaction yields mixtures of Mo(NAr_{Cl})(CH-t-Bu)[Biphen] and what was postulated to be Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen]. In one instance a small amount of Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen] could be isolated in 17% yield as a yellow powder.

The imido alkylidene complex Mo(NAr_{Cl})(CH-t-Bu)[Biphen] is isomeric with the amido alkylidyne complex Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen] in the way a proton is attached to carbon in the former, and to nitrogen in the later. Therefore, it was worth investigating if the above two species could be interconverted by a proton-transfer agent. Considering the fact that Mo(NHAr)(C-t-Bu)Cl_2(dme) can be converted to Mo(NAr)(CH-t-Bu)Cl_2(dme) (*vide supra*) by catalytic amounts of a relatively weakly coordinating base such as triethylamine,[11] the investigation of the reverse reactions of this type by using the same base was carried out.

Upon adding a THF solution of [Biphen]K_2 at -20 °C to a stirred solution of Mo(NAr_{Cl})(CH-t-Bu)($OTf)_2$(dme) and 10 equivalents of triethylamine, Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen] was obtained reproducibly as a bright orange crystalline material in 40% isolated yield (equation 1.1). The ^{1}H NMR spectrum (500 MHz, benzene-d_6) of the orange solid showed a singlet resonance at 11.73 ppm that was assigned to the N*H* proton. This is the region where one would expect to find the α hydrogen resonance for an alkylidene in an imido alkylidene complex. In the ^{13}C NMR spectrum a resonance was found at 327.7 ppm for a carbon that has no proton attached to it (confirmed by a ^{1}H coupled ^{13}C NMR experiment). Since the resonance is in the region characteristic of an alkylidyne carbon resonance[2,5], it is assigned to the alkylidyne α carbon resonance in Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen]. The *meta* protons on the arylimido ligand appear as a broad singlet resonance at 6.69 ppm, indicating that the rate of rotation of the imido aryl ring is of the order of the NMR time scale at room temperature. The use of 3-6 equivalents of triethylamine in the reactions of [Biphen]K_2 with Mo(NAr_{Cl})(CH-t-Bu)($OTf)_2$(dme) results in mixtures containing both Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen] as well as Mo(NAr_{Cl})(CH-t-Bu)[Biphen].



(1.1)

Jennifer Jamieson had obtained the solid state structure of the related neophylidyne complex Mo($NHAr_{Cl}$)($CCMe_2Ph$)[*S*-Biphen] (Figure 1.1)[15]. The Mo≡C(1) distance (1.72(7)Å) and Mo≡C-C bond angle (170.5(5)°) are typical of a high oxidation state alkylidyne complex.[5] The Mo-N(1) bond length (1.990(6)Å) is much longer (by ~0.2 Å) than is typically found for a Mo=N pseudo triple bond (e.g., Mo=N = 1.872 Å in

$Mo(NAr_{Cl})$(CH-t-Bu)[*S*-Biphen](THF)[14]) and moreover the Mo-N(1)-C_{ipso} angle is only 133.8(5)°; both are characteristic of an amido ligand. Although the amido α proton was not located, it is likely to lie in the Mo-N-C_{ipso} plane, since amido ligands are typically planar when bound to high oxidation state metals. Interestingly, one ortho chloride (Cl(1)) is pointed toward the metal and approaches within 2.93 Å of the metal approximately *trans* to the alkylidyne ligand. Weak binding of an ortho chloride to the metal was also found in $Mo(NAr_{Cl})$(CH-t-Bu)[*S*-Biphen](THF) where one ortho chloride approaches within ~3.0 Å of the metal.[14]

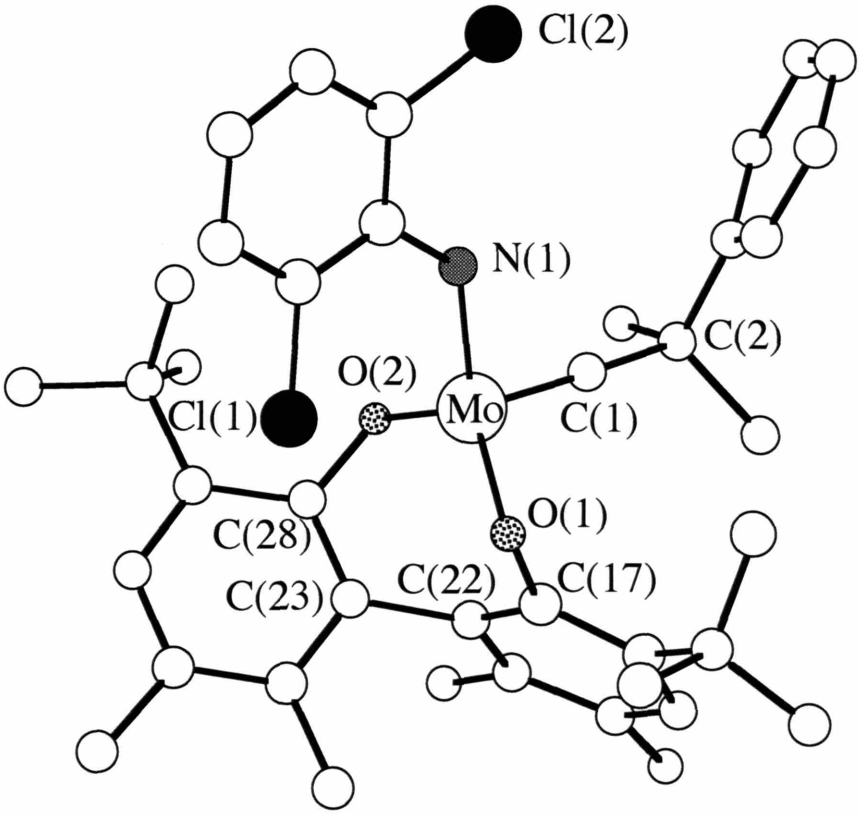
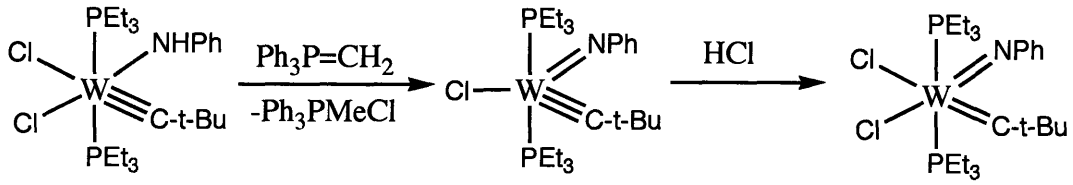


Figure 1.1. Chem 3D drawing of Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)[*S*-Biphen].

When a prechilled mixture (at -20 °C) of $Mo(NAr_{Cl})$(CH-t-Bu)$(OTf)_2$(dme) and 10 equivalents of triethylamine in THF was allowed to react with 2 equivalents of $KOCMe(CF_3)_2$ at -20 °C, the proton NMR of the product mixture showed a resonance at

11.59 ppm (indicating an amido alkylidyne species) along with two other broad resonances in the 10.20-10.70 ppm region. However, this reaction could not be reproduced to give the amido alkylidyne complex as the sole product. Attempts to prepare three other amido alkylidyne complexes in the presence of 10-20 equivalents of triethylamine failed. Addition of [Biphen]K_2 to Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)($OTf)_2$ in the presence of 20 equivalents of triethylamine yielded neither Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen] nor Mo(NH-2-$CF_3C_6H_4$)($CCMe_2Ph$)[Biphen]; the product or products of this reaction could not be identified. As mentioned before, mixtures of Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen] and Mo(NH-2-$CF_3C_6H_4$)($CCMe_2Ph$)[Biphen] were sometimes obtained upon the attempted synthesis of Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[Biphen].[13(c)] Addition of [Biphen]K_2 to Mo(N-2,6-$R_2C_6H_5$)($CHCMe_2Ph$)($OTf)_2$ (R = Me or i-Pr) led only to the known Mo(N-2,6-$R_2C_6H_5$)($CHCMe_2Ph$)[Biphen] species.

Moving a proton from carbon to nitrogen is the reverse of a step in the original syntheses of imido alkylidene dichloride complexes of Mo and W from amido alkylidyne dichloride complexes. Therefore, it is clear that an imido alkylidene and an amido alkylidyne can be close in energy and that a proton can move in either direction (from nitrogen to carbon or the reverse). However, even two decades after the first such reactions were observed,[16] it is not clear exactly what mechanism or mechanisms are responsible for these transformations. It had been earlier reported that W(NHPh)(C-t-Bu)($PEt_3)_2Cl_2$ reacts with $Ph_3P{=}CH_2$ to yield [Ph_3PCH_3]Cl and W(NPh)(C-t-Bu)($PEt_3)_2Cl$, which subsequently can be treated with HCl to yield W(NPh)(CH-t-Bu)($PEt_3)_2Cl_2$ (Scheme 1.4)[16]. In light of this observation, it can be assumed that an imido alkylidyne intermediate like {Mo(NAr_{Cl})(C-t-Bu)[Biphen]}$^-$ is a plausible intermediate for the formation of amido alkylidyne species Mo($NHAr_{Cl}$)(C-t-Bu)[Biphen] from the corresponding imido alkylidene species Mo(NAr_{Cl})(CH-t-Bu)[Biphen]. {Mo(NAr_{Cl})(C-t-Bu)[Biphen]}$^-$ would result when triethylammonium triflate is formed from the reaction of triethylamine and Mo(NAr_{Cl})(CH-t-Bu)$(OTf)_2$(dme).



Scheme 1.4. Precedence for an imido alkylidyne intermediate.

Isolable complexes of the type Mo(NAr)(CH-t-Bu)[OCMe$(CF_3)_2$]$_2$ and Mo(NHAr)(C-t-Bu)[OCMe$(CF_3)_2$]$_2$(dme) can be independently prepared, and they do not interconvert in the presence of a catalytic amount of triethylamine.[11] Addition of 20 equivalents of triethylamine to Mo(NHAr$_{Cl}$)(C-t-Bu)[Biphen] or Mo(NAr$_{Cl}$)(CH-t-Bu)[Biphen] in benzene-d_6 at 22 °C did not lead to conversion of one into the other, i.e., the proton could not be moved by triethylamine once the Biphen ligand was present. Therefore it can be proposed that a good leaving group (e.g., chloride or triflate) must be present so that [BaseH]X (X = chloride or triflate) can be lost from either an imido alkylidene or an amido alkylidyne to yield a neutral imido alkylidyne intermediate, one that is likely to be stabilized by coordination of some donor ligand such as dme (cf. W(NPh)(C-t-Bu)$(PEt_3)_2$Cl). Of course, [BaseH]X must also be acidic enough to reprotonate N or α C in the imido alkylidyne intermediate to facilitate the process of proton transfer. The required loss of [BaseH]X to yield a neutral imido alkylidyne intermediate would account for the failure to interconvert imido alkylidene and amido alkylidyne complexes that contain only alkoxides, at least with triethylamine as the base. Since it is known that W(NHPh)(C-t-Bu)$(PEt_3)_2Cl_2$ is converted into W(NPh)(CH-t-Bu)$(PEt_3)_2Cl_2$ simply through heating,[16] donor ligands (e.g., a phosphine or dme) might dissociate and play the role as a base in certain circumstances. Finally, the possibility that a proton can transfer directly, or via a metal-hydrogen bond from N to C or from C to N in the right circumstances, without an external base being required cannot be excluded. This proton migration reaction would be related to an α hydrogen abstraction, which produces an alkylidene from a dialkyl complex.[10(a)]

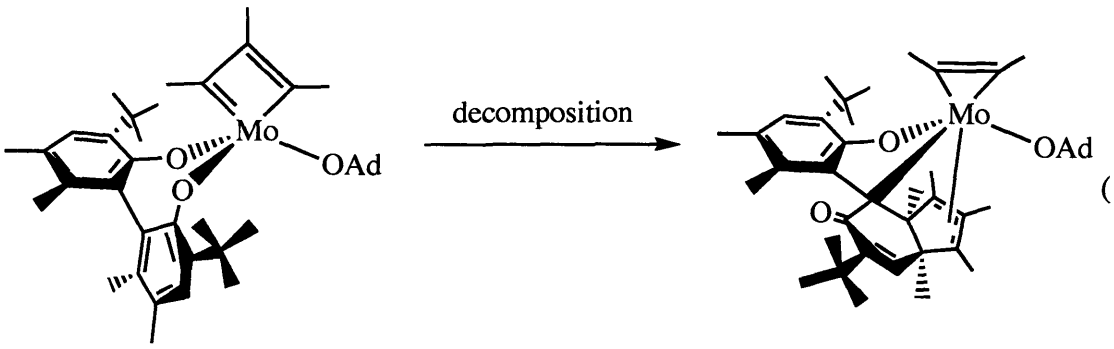
The proton transfer reaction (N to C or vice versa) is likely to be delicately balanced. Therefore the nature of the substituent on nitrogen in the amido or imido group

is likely to be one of several important variables. A proton might be transferred to the $Mo{=}NAr_{Cl}$ group relatively easily because of a weak interaction between an ortho chloride and the metal in the developing bent amido ligand, as shown in the crystal structure of $Mo(NHAr_{Cl})(CCMe_2Ph)$[S-Biphen] (Figure 1.1).

1.2 Reactions of amido alkylidyne biphen complexes

The room temperature reactions of $Mo(NHAr_{Cl})$(C-t-Bu)[Biphen] in benzne-d_6 with 2 equivalents of an alcohols such as 1-adamantanol (AdOH) gives a mixture of that contains the starting material, free [Biphen]H_2 ligand as well as new species that exhibit a broad resonance at 11.60 ppm in the proton NMR spectrum. Conditions could not be optimized such as to get the alkylidyne species cleanly and reproducibly. This observation suggested that this route cannot be undertaken for the synthesis of complexes that could serve as alkyne metathesis catalysts of the type Mo(CR′)[Biphen](OR).

Jennifer Jamieson prepared $Mo(CCH_2SiMe_3)$[Biphen](OAd) in 46% yield by reacting Cummins' $Mo(\eta^2\text{-}H_2CCSiMe_3)[N(i\text{-}Pr)(3,5\text{-}C_6H_3Me_2)]_3$[17] with 1 equivalent each of [Biphen]H_2 and 1-adamantanol in toluene at 80 °C for 12 h. However, treating $Mo(CCH_2SiMe_3)$[Biphen](OAd) with 10 equivalents of 2-butyne resulted in formation of of a metallacyclobutadiene complex $Mo(C_3Me_3)$[Biphen](OAd) that was spectroscopically characterized.[15] Although $Mo(C_3Me_3)$[Biphen](OAd) is stable for days in the solid state, it undergoes slow decomposition in ether/pentane solution over a period of several days to give a species in which the integrity of one ring of the Biphen ligand was destroyed by the metallacyclobutadiene fragment (equation 1.2). It should be noted that $Mo(CCH_2SiMe_3)(OAd)_3$ reacts with 2-butyne to give $Mo(CCH_3)(OAd)_3$ quantitatively.[17]



(1.2)

CONCLUSIONS

This work has demonstrated the synthesis of molybdenum amido alkylidyne species containing a biphenolate-based ligand. A large excess of triethylamine (10 equivalents) is required to effect proton transfer from the alkylidene bistriflate complex to presumably give an imido alkylidyne intermediate that gets reprotonated to give the amido alkylidyne complex. This kind of reaction works reproducibly only when the imido group employed is NAr_{Cl}. The imido alkylidene species and the amido alkylidyne complexes do not interconvert when the metal is ligated by alkoxide ligands. Moreover, given the instability of the biphenolate-based ligand under catalytic conditions, the potential of Mo(CR')[Biphen](OR) type complexes as catalysts for alkyne metathesis reactions does not seem bright.

Two important lessons learned from this study that can be utilized in the synthesis of olefin metathesis catalysts are: one, imido ligands such as N-2,6-$R_2C_6H_5$ (R = Me or i-Pr) are not amenable to the proton transfer reactions that result in alkylidyne impurities when synthesis of Mo(NR'')(CHR')$(OR)_2$ or Mo(NR'')(CHR')(diolate) type catalysts are attempted, and two, the choice of bistriflate complexes of the type Mo(NR'')(CHR')$(OTf)_2$(dme) as precursors for making olefin metathesis catalysts by reactions with Li or K salts of alkoxides should be revisited.

EXPERIMENTAL SECTION

General. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. The glassware, including NMR tubes were flame- and/or oven-dried prior to

use. Ether, pentane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed thrice by freeze-pump-thaw technique. Dichloromethane was distilled from CaH_2 under N_2. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^1H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using a Varian Mercury (^1H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz) or a Varian Inova (^1H 500 MHz, ^{13}C 125 MHz) spectrometers and referenced to the residual protio solvent resonances or external C_6F_6 (-163.0 ppm). Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Neopentylmagnesium chloride and neophylmagnesium chloride were titrated against propanol in a THF solution using 1,10-phenanthroline as an indicator immediately prior to use. The bistriflate complexes Mo(NR″)(CH-t-Bu)$(OTf)_2$(dme) (NR″ = N-2-$CF_3C_6H_4$, N-2,6-i-$Pr_2C_6H_3$, N-2,6-$Me_2C_6H_3$) were prepared according to literature procedures.[12,13] A slightly modified synthesis of the reported complex Mo(NAr_{Cl})(CH-t-Bu)$(OTf)_2$(dme) is given below. The sample obtained by the published procedure[14] gives lower yields (~ 56%) and in many instances is limited in giving the product as a crystalline material. All other chemicals were procured from commercial sources and used as received.

Synthesis of Mo(NAr_{Cl})(CH-t-Bu)$(OTf)_2$(dme). A suspension of Mo$(NAr_{Cl})_2(CH_2$-t-$Bu)_2$ (3.18 g, 5.69 mmol) in 80 ml of pentane and 20 ml of dme was chilled to -20 °C. 4.03 g (3 equivalents) of triflic acid in dme chilled at -20 °C was added to the above suspension dropwise and the reaction mixture was allowed to stir for 12 h. Complete removal of solvents in vacuo afforded a yellow foam that was extracted with cold pentane and filtered over a 2 cm layer of Celite. Removing the volatiles under reduced pressure afforded a yellow-brown solid that was recrystallized with a mixture of ether and pentane to give 3.55 g of Mo(NAr_{Cl})(CH-t-Bu)$(OTf)_2$(dme) as a yellow crystalline solid (87% yield) that was identical in all respects with the sample obtained by the published procedure[14].

Mo(NH-2,6-$Cl_2C_6H_3$)(C-t-Bu)[Biphen][18]. Benzylpotassium (0.740 g, 5.70 mmol) was added in portions to a stirred solution of [Biphen]H_2 (1.010 g, 2.80 mmol) in 40 ml of THF until a slight yellow color persisted. The solution was chilled to -30 °C and added dropwise to a stirred, prechilled solution of Mo(N-2,6-$Cl_2C_6H_3$)(CH-t-Bu)$(OTf)_2$(dme) (2.030 g, 2.84 mmol) and 10 equiv triethylamine (5 ml, 28.4 mmol) in 75 ml THF. The resulting deep red solution was stirred for 2 h at room temperature and the volatile solvents were removed *in vacuo* to give an orange-brown solid. This solid was dissolved in toluene and the solution was filtered through a pad of Celite. The toluene was removed and the product was dissolved in a minimum amount of pentane. Standing the pentane solution at -30 °C produced bright orange crystals in 40 % yield: ^{1}H NMR (500 MHz, C_6D_6) δ 11.73 (s, 1, N*H*), 7.40 (s, 1, Ar*H*), 7.25 (s, 1, Ar*H*), 6.69 (br s, 2, Ar*H*), 6.05 (t, 1, Ar*H*), 2.20 (s, 3, ArCH_3), 2.17 (s, 3, ArCH_3), 1.75 (overlapping peaks, 12, ArCH_3, ArC-t-Bu), 1.67 (s, 3, ArCH_3), 1.39 (s, 9, ArC-t-Bu), 1.01 (s, 9, Mo≡C-t-Bu); ^{13}C NMR (125 MHz, C_6D_6) δ 327.7, 160.6, 155.8, 147.2, 137.1, 135.7, 135.1, 131.2, 130.3, 129.9, 129.8, 129.7, 128.7, 128.3, 127.7, 121.4, 54.9, 36.1, 35.6, 30.9, 30.2, 28.8, 20.8, 20.9, 17.2, 17.0. Anal. Calcd for $MoC_{35}H_{45}Cl_2NO_2$: C, 61.95; H, 6.63; N, 2.06; Mo, 14.14. Found: C, 62.10; H, 6.51; N, 2.10; Mo, 14.20.

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Chapter 2

REACTIONS OF MOLYBDENUM IMIDO ALKYLIDENE DIALKYL COMPLEXES WITH ALCOHOLS TO GIVE OLEFIN METATHESIS CATALYSTS.

Portions of this chapter have appeared in print:

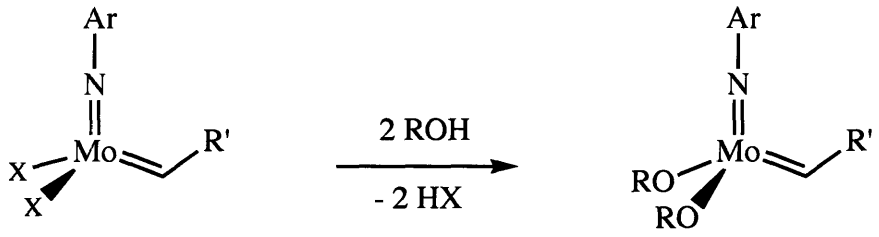
Sinha, A.; Schrock, R. R. "Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ with Alcohols to Give Metathesis Catalysts of the Type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)" *Organometallics* **2004**, *23*, 1643.

Blanc, F.; Copéret, C.; Thiovolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. "Surface vs. Molecular Siloxy Ligands in Well-Defined Olefin Metathesis Catalysts: [{$(RO)_3SiO$}Mo(=NAr)(=CH-t-Bu)(CH_2-t-Bu)]" *Angew. Chem. Int. Ed.* **2006**, *45*, 1216.

Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Müller, P. "Reactions of M(N-2,6-i-$Pr_2C_6H_3$)(CHR)(CH_2R')$_2$ (M = Mo or W) Complexes with Alcohols to Give Olefin Metathesis Catalysts of the Type M(N-2,6-i-$Pr_2C_6H_3$)(CHR)(CH_2R')(OR")" *Organometallics* **2006**, *25*, 1412.

INTRODUCTION

High oxidation state molybdenum or tungsten imido alkylidene complexes of the types M(NAr)(CHR')$(OR)_2$[1] and M(NAr)(CHR')(diolate)[2] developed previously in the Schrock group have been successfully employed in a myriad of olefin metathesis reactions.[3] Recent years have seen a surge in the number of synthetic chemists incorporating olefin metathesis in their general synthetic frameworks.[4] This increase in demand requires an expansion of the catalyst libraries in terms of making subtle variations in the catalyst structure by using different groups (other than alkoxides) on the metal imido alkylidene framework that are already available to the end user. In this regard the preparation of molecules of the type Mo(NAr)(CHR')X_2 (X = carbon-based ligands) was undertaken to test their catalytic activity as well as to study the feasibility of getting the bisalkoxide type catalysts by addition of two equivalents of ROH to Mo(NAr)(CHR')X_2 complexes (equation 2.1).



(2.1)

This chapter reports the reactions of selected alcohols with Mo(NAr)(CH-t-Bu)$(CH_2$-t-$Bu)_2$ and the olefin metathesis reactions catalyzed by the products of above reactions. Some results with silica-supported catalysts of the type Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OSi_{surf}) prepared in collaboration with Dr. Christophe Copéret in the Basset group at CNRS, Lyon will be mentioned. Unless otherwise stated, the imido group (NAr) used in this chapter is N-2,6-diisopropylphenyl which offers maximum steric protection to the metal center compared to the three other widely used imido functionalities in the chemistry of Mo(NR)(CHR')$(OR)_2$ and Mo(NR)(CHR')(diolate) complexes, viz., N-2,6-dimethylphenyl, N-2,6-dichlorophenyl, and N-1-adamantyl.[3]

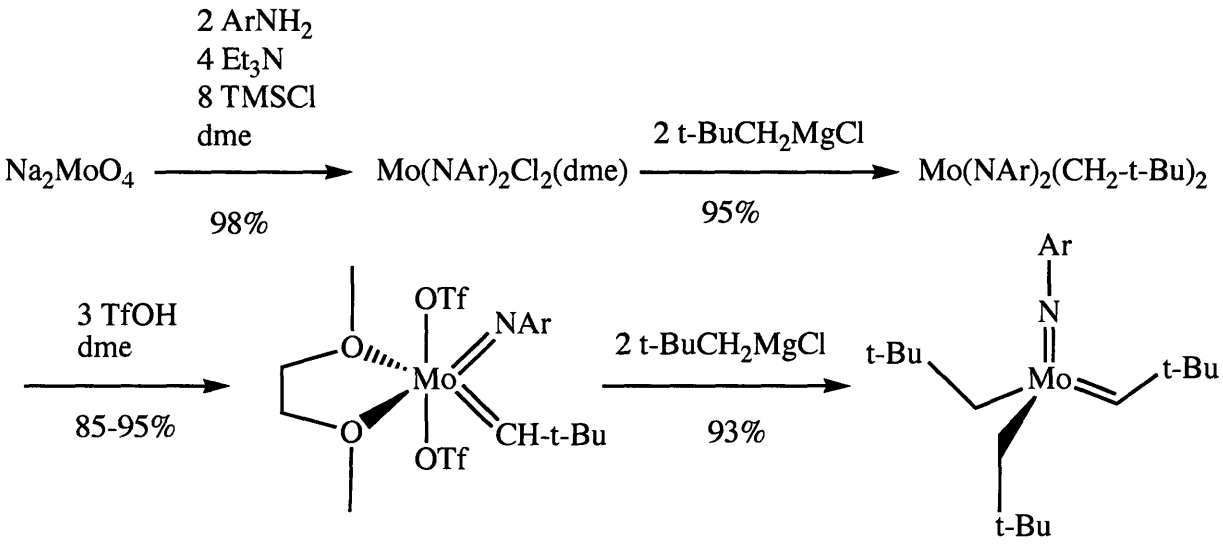
RESULTS AND DISCUSSIONS

It is naturally desired that the by-product of the reaction shown in equation 2.1, HX, be catalytically non-interfering and easy to eliminate. For this reason, reactions between dineopentyl imido alkylidene species of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (Ar = 2,6-i-$Pr_2C_6H_3$) and alcohols were explored such that two equivalents of neopentane would be evolved to give the M(NAr)(CH-t-Bu)(OR)$_2$ species. Such a precursor would also be useful in making well-defined surface-immobilized catalysts upon reaction with an appropriate choice of surface like silica ($Si_{surf}OH$). Similar reactions of silica with molecular precursors containing Ta,[5] W[6] and Re[7] have been employed[8] in the hope of enhancing the lifetime of the catalytically active species on the surface[9] vis-à-vis that in solution by minimizing bimolecular decomposition[10] which can readily occur in the latter case resulting in a loss of reactivity.

During the exploration of the feasibility of the above methodology, it was found out that the addition of alcohols to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ did *not* lead to bisalkoxide species, rather to M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR). Such species that are chiral at the metal center could be an interesting platform to study olefin metathesis reactions considering the fact that possible approaches of an olefin either *trans* to OR or *trans* to a neopentyl ligand could differ significantly in energy. It is imperative for the neopentyl group to survive during metathesis reactions without complications. Prior to this work, only one example of a complex of this general type has been reported by Osborn in which Ph_3SiOH was allowed to react with Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ to give Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)($OSiPh_3$).[11] However, neither extensive characterization nor any catalytic studies were reported for this complex. Alkylimido diolate complexes[12] (such as those involving adamantylimido group), and related dineopentyl species Mo(NAd)(CH-t-Bu)(CH_2-t-Bu)$_2$[13] are unstable with respect to bimolecular decomposition yielding di-t-butylethylene. Based on this, it is believed that the t-butylimido ligand is "too small" to prevent bimolecular decomposition of Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)($OSiPh_3$) and formation of products that prevent crystallization of these already highly soluble compounds. Moreover, the route undertaken to synthesize Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ involved the ill-defined starting material [MoO(N-t-Bu)Cl_2(MeCN)]$_n$ (n = 2 or 3) that further contributed to the oily appearance of the products obtained.[11]

2.1. Synthesis of Mo(NAr)(CHR')$(CH_2R')_2$ and related complexes

Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ can be conveniently prepared on a large scale from readily accessible starting materials. It is obtained as a red-orange solid on a 10 g scale by reacting an ether solution of Mo(NAr)(CH-t-Bu)$(OTf)_2$(dme)[1(c)] with two equivalents of neopentylmagnesium chloride in ether (Scheme 2.1).



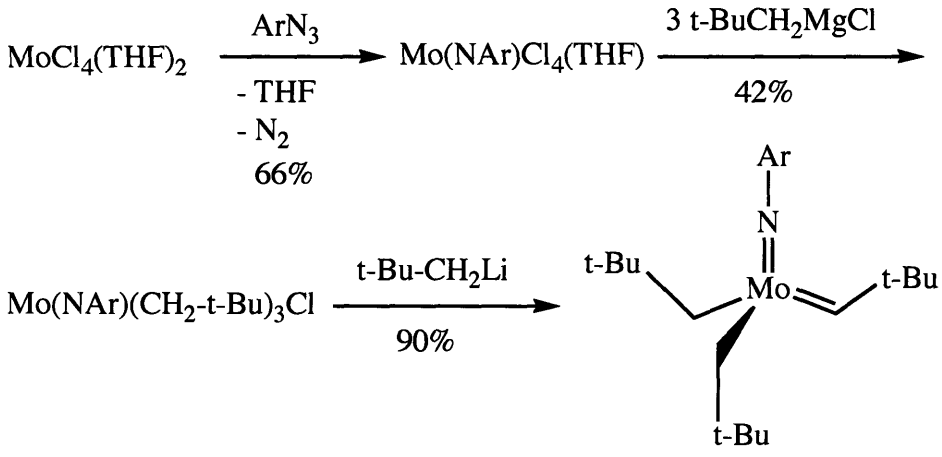
Scheme 2.1. Synthesis of Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ from Na_2MoO_4.

All the isolated intermediates shown in Scheme 2.1 are highly crystalline and can be obtained in high yields. By using t-BuCH_2MgCl that was titrated immediately prior to each use and pure Mo(NAr)(CH-t-Bu)$(OTf)_2$(dme), the highly soluble Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ can be employed in a "crude" form for carrying out further reactions. Proton NMR spectrum of Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ shows a sharp resonance at 9.50 ppm (J_{CH} = 108 Hz) for the neopentylidene ligand and at 2.75 and at 0.65 ppm (δ CHH; J_{HH} = 12 Hz) for the diastereotopic methylene protons in the neopentyl groups (by virtue of a lack of mirror plane of symmetry in the molecule). A proton-coupled carbon NMR confirms the J_{CH} of the alkylidene ligand as a doublet appearing at 255.0 ppm. The through-bond coupling of the two resonances (9.50 ppm in the proton NMR and the 255.0 ppm in the carbon NMR spectra respectively) is also revealed in a ^1H-^{13}C heteronuclear multiple quantum coherence (HMQC) experiment. These chemical shifts are consistent with those observed for high oxidation state *syn* alkylidene complexes[14,15] and are

comparable to δH_α = 9.22 ppm and δC_α = 249.3 ppm (J_{CH} = 106 Hz) in Mo(N-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$[11]. The alkylidene resonance for *anti* isomer of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ could not be observed.

An alternate synthesis of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ as a brown powder starting from $MoCl_4(THF)_2$ (Scheme 2.2) was later reported by Tatiana Pilyugina.[13] This approach was based on the synthetic route utilizing tungsten as the metal center to give W(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$[16] that was demonstrated by Pia Lopez, and W(NPh)(CH-t-Bu)(CH_2-t-Bu)$_2$[17] which was prepared by Steven Pederson. Alkylation of ether or THF adducts of M(NAr)Cl_4 (M = Mo, W) with four equivalents of neopentylmagnesium chloride gives a mixture of M(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and significant amounts of M(NAr)(CH_2-t-Bu)$_3$Cl. The stepwise alkylation of an early transition metal chloride by using Grignard or alkyl zinc reagents followed by alkyl lithium to avoid reduction of the metal center was used to prepare the first example of a high-oxidation state alkylidene complex by Schrock.[18]

Related complexes of the type Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ and Mo(NAr)(CH-t-Bu)(CH_2CMe_2Ph)$_2$ can be prepared in a straightforward manner through alkylation of Mo(NAr)($CHCMe_2Ph$)(OTf)$_2$(dme) with t-BuCH_2MgCl and by alkylation of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) with PhMe_2CCH_2MgCl. Although Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ can be obtained in 65% yield as a red-orange solid, Mo(NAr)(CH-t-Bu)(CH_2CMe_2Ph)$_2$ and Mo(NAr)($CHCMe_2Ph$)(CH_2CMe_2Ph)$_2$ were isolated as red-oils.

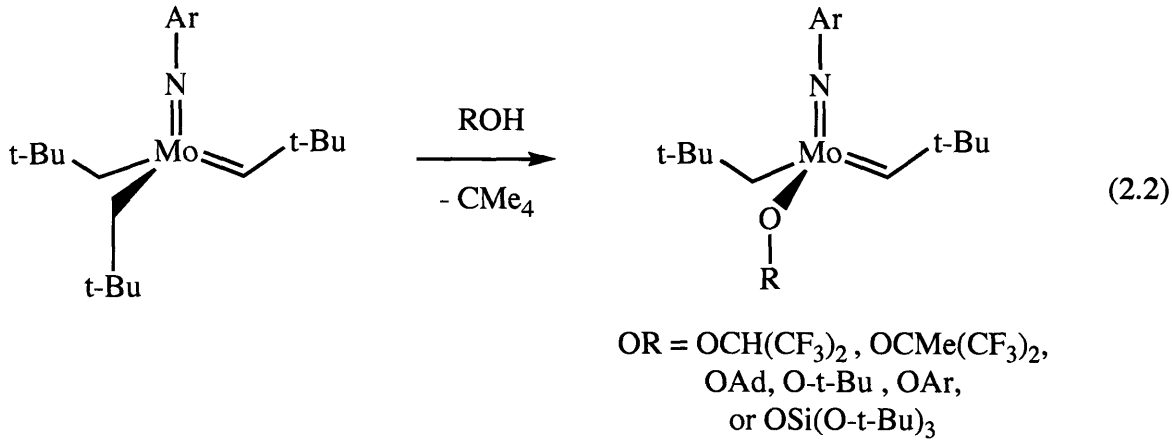


Scheme 2.2. Synthesis of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ from $MoCl_4(THF)_2$.

No evidence was found for an intramolecular proton migration that would lead to alkyl/alkylidene scrambling in any of these mixed alkyl/alkylidene species in solution at room temperature. This type of intramolecular transfer or migration of a proton from the α carbon of an alkyl ligand to an alkylidene α carbon is known to be slow in all high oxidation state systems so far where it has been tested.[14,15] No evidence for a transfer of alkyl or alkylidene ligands between metals could be found.

2.2. Reactions of alcohols with Mo(NAr)(CHR')(CH_2R')$_2$

Reacting Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ with one equivalent of the alcohols listed in equation 2.2 in pentane or toluene at room temperature affords yellow or red-orange colored isolable complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) in high yields. The reaction times for the formation of these complexes increase with an increase in the steric bulk of the alcohol being employed and heating the reaction mixtures can accelerate the reactions rates.



(2.2)

OR = $OCH(CF_3)_2$, $OCMe(CF_3)_2$,
OAd, O-t-Bu , OAr,
or $OSi(O\text{-}t\text{-}Bu)_3$

The characteristic resonances for the alkyl methylene protons appear as doublets (J_{CH} = 13 Hz). The separation between these doublets is far less (0.26-0.39 ppm) in Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes than the value of 2.14 ppm that is observed for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$. The t-butyl substituent of the alkylidene ligand in these compounds has the option of pointing toward the imido ligand or away from it thus giving rise to two isomers, *i.e.*, *syn* and *anti*.[15] Since these isomers can interconvert into one another by rotation along the metal-alkylidene carbon bond, they are also called rotational isomers. These isomers can be distinguished by lower J_{CH} values and an upfield shift (by about 1-3 ppm) for the alkylidene

proton in *syn* compared to those in the *anti* form.[14] The J_{CH} value of approximately 115 Hz for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) type species indicates the alkylidene ligand to be present as the *syn* isomer. At room temperature no corresponding *anti* isomer could be detected. Variable temperature ^{1}H NMR spectroscopic studies were performed on two such complexes (prepared *in situ* in toluene-d_8 (118 mM) at 60 °C over 2-8 h) to obtain the thermodynamic parameters ΔS^o, ΔH^o, ΔG^o and the equilibrium constant K_{eq} for the conversion of *anti* form to *syn*. The results are summarized in Table 2.1.

In the case of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(O-t-Bu), the relative abundance of the *anti* isomer (lower field resonance) increases with increase in temperature, although the *syn* species predominates at room temperature. This observation is supported by the decrease in the value of K_{eq} for *anti* →*syn* with increase in temperature. The negative value of ΔH^o coupled with a positive value of ΔS^o (Table 2.1) is the driving force for the conversion of the *syn* isomer to the *anti* form. However, the Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OCMe(CF_3)$_2$) complex behaves differently. The striking feature of this compound is that the slope of ln(K_{eq}) versus (1/T) is positive, *i.e.*, the ratio of *syn/anti* decreases with an increase in the temperature. The highly positive value of ΔS^o (15.12 eu) offsets the relatively small positive value of ΔH^o (1.92 kcal/mol) such that the change in free energy, ΔG^o at 298 K is -2.58 kcal/mol.

Table 2.1. Thermodynamic parameters for *anti*→*syn* in Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species.

OR	K_{eq}	$\Delta S^{o\,b}$	$\Delta H^{o\,c}$	$\Delta G^{o}_{298}{}^{c}$
O-t-Bu	40.6[a]	3.804	-1.095	-2.23
OCMe(CF_3)$_2$	70.5[a]	15.12	1.92	-2.58

[a] 293K, [b] values in eu, [c] values in kcal/mol.

Single crystals of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$] suitable for X-ray crystallographic studies were grown from a concentrated solution of hexamethyldisiloxane at room temperature, and the structure was determined by Peter Müller. The structure of

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-$Bu)_3$] (Figure 2.1) is typical of pseudo tetrahedral species of this type.[15] The structure shows extensive disorder, in which only the Mo-atom is not involved. Only the major component of the structure is shown in Figure 2.1, although both sets of selected bond lengths and angles are listed in Table 2.2. The neopentylidene ligand in each molecule has a *syn* orientation in which the t-butyl group points toward the imido nitrogen. The Mo-C(1) bond lengths (1.831(3) and 1.860(6) Å) and Mo-C(1)-C(2) bond angles (146.5(4) and 151.5(8)°) are typical for *syn* isomers. The neopentyl ligands appear to be normal with Mo-C(6) distances of 2.144(5) and 2.259(6) Å and Mo-C(6)-C(7) angles of 118.1(5) and 116.6(6)°. Perhaps the largest difference between the two molecules are the Mo-O(1)-Si(1) angles of 134.5(2)° and 148.8(3)°. These variations may be ascribed to subtle differences in steric crowding in the two molecules.

Table 2.2. Selected bond lengths [Å] and angles [°] for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-$Bu)_3$].

	Molecule 1	Molecule 2
Mo-N(1)	1.725(5)	1.753(11)
Mo-C(1)	1.831(3)	1.860(6)
Mo-O(1)	1.973(3)	1.842(4)
Mo-C(6)	2.144(5)	2.259(6)
N(1)-Mo-C(1)	106.8(4)	109.5(8)
N(1)-Mo-O(1)	125.1(4)	126.3(8)
N(1)-Mo-C(6)	103.1(4)	98.1(8)
C(1)-Mo-O(1)	109.13(13)	114.3(3)
C(1)-Mo-C(6)	98.11(17)	92.7(3)
O(1)-Mo-C(6)	111.15(17)	109.0(2)
C(7)-C(6)-Mo	118.1(5)	116.6(6)
Mo-N(1)-C(11)	158.5(9)	165.4(18)
Mo-C(1)-C(2)	146.5(4)	151.5(8)
Mo-O(1)-Si(1)	134.5(2)	148.8(3)

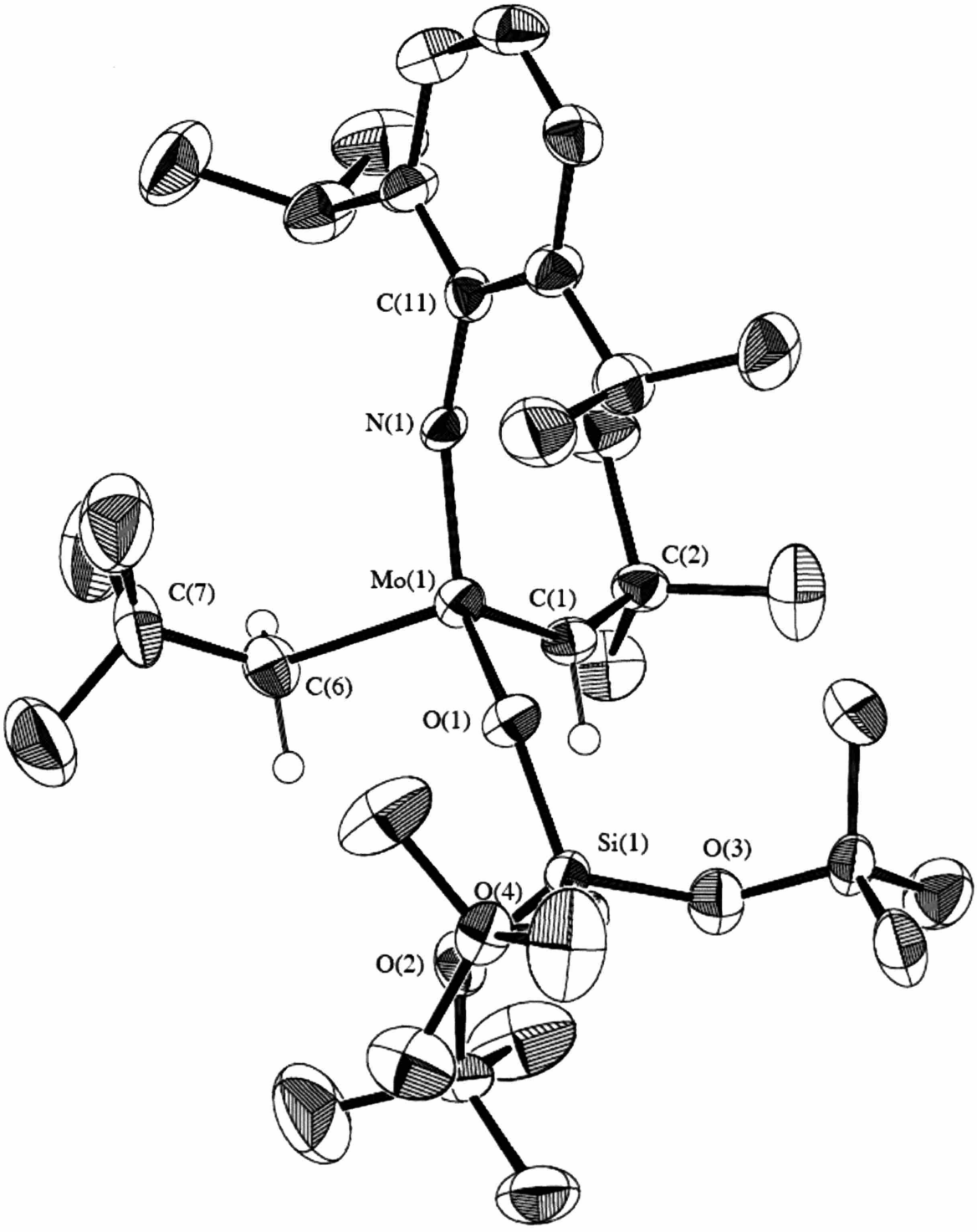
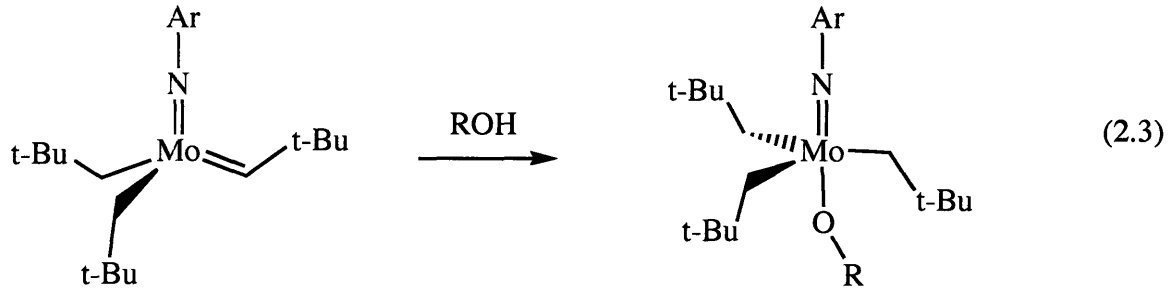


Figure 2.1. ORTEP drawing of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$].

The reaction of more acidic alcohols like C_6F_5OH with $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$ leads to addition of the alcohol –OH across the Mo=C resulting in the formation of the trineopentyl complex $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$. The methylene resonances of the three equivalent neopentyl (27 H) groups appear at 1.14 ppm. The five fluorine atoms of the pentaflurophenoxide group appear as three distinct sets in the ^{19}F NMR spectrum. A similar trineopentyl species $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3[OCH(CF_3)_2]$ is formed when $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_2$ is treated with *neat* $(CF_3)_2CHOH$ (equation 2.3) at ambient temperature.



(2.3)

OR = OC_6F_5 or $OCH(CF_3)_2$
(in *neat* $HOCH(CF_3)_2$)

Yellow crystals of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$ were obtained from a concentrated toluene solution kept at -20 °C. William Davis mounted an appropriate crystal for crystallographic studies and Adam Hock carried out the structure determination results of which are shown in Figure 2.2 and Table 2.3. $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$ is a pseudo-trigonal bipyramid with the imido and phenoxide ligands in the axial positions. The three equatorial neopentyl ligands are approximately 120° apart. All Mo-ligand distances are in the expected range. The Mo-N-C(21) bond angle is 169.9(3)°. It is not clear whether steric factors or π bonding from oxygen to Mo, or both, are responsible for the large Mo-O-C(11) angle (163.0(3)°).

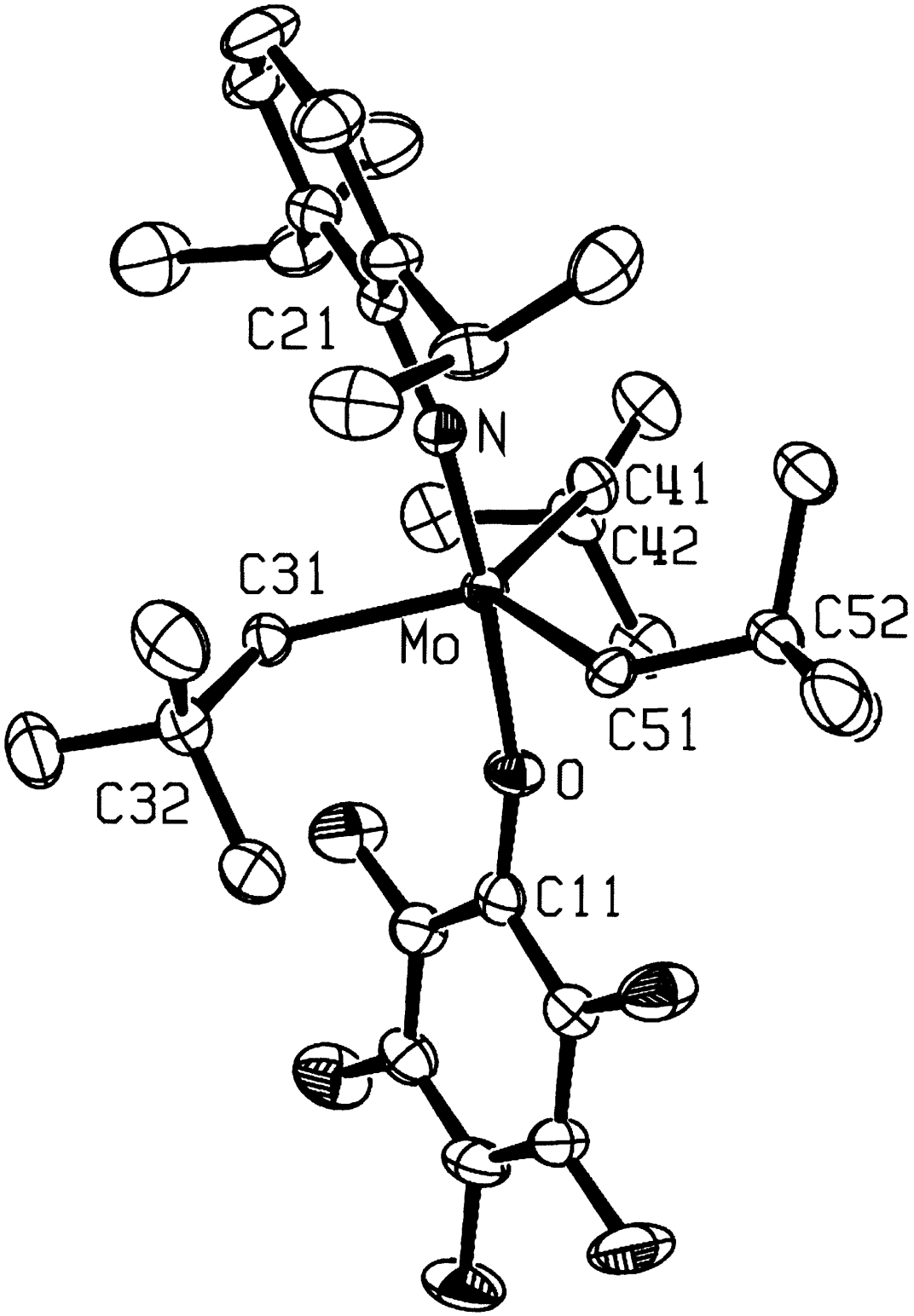


Figure 2.2. Thermal ellipsoid drawing of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$.

Table 2.3. Selected bond lengths [Å] and angles [°] for $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$.

Mo-N(1)	1.747(3)	O(1)-Mo-C(41)	90.91(14)
Mo-O(1)	2.006(2)	O(1)-Mo-C(51)	87.36(14)
Mo-C(31)	2.145(4)	C(41)-Mo-C(31)	121.37(17)
Mo-C(41)	2.140(4)	C(51)-Mo-C(31)	121.33(16)
Mo-C(51)	2.126(4)	C(51)-Mo-C(41)	116.75(17)
N(1)-Mo-O(1)	174.34(14)	Mo-N(1)-C(21)	169.9(3)
N(1)-Mo-C(31)	89.92(16)	Mo-O(1)-C(11)	163.0(2)
N(1)-Mo-C(41)	92.87(16)	Mo-C(31)-C(32)	121.3(3)
N(1)-Mo-C(51)	94.68(16)	Mo-C(41)-C(42)	126.1(3)
O(1)-Mo-C(31)	84.51(14)	Mo-C(51)-C(52)	121.5(3)
		Mo-O(1)-C(11)	162.9(2)

Upon heating solutions of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$ or $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3[OCH(CF_3)_2]$ to 60 °C over a period of hours neopentane evolves smoothly to yield $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OR)$ (OR = OC_6F_5 or $OCH(CF_3)_2$) quantitatively. The conversion of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$ to $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$ was studied by ^1H NMR spectroscopy. The plot of $\ln[Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)]$ versus time was a straight line showing that the reaction followed first order kinetics with $k = 10 \times 10^{-5}$ s^{-1} in benzene-d_6 at 60 °C (Figure 2.3). The above process is slightly accelerated in a polar solvent like methylene chloride where the first order rate constant was 14×10^{-5} s^{-1}.

X-ray quality crystals of $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$ were grown from a concentrated toluene solution at room temperature. Adam Hock mounted the crystals and carried out the crystallographic studies. The solid-state structure (Figure 2.4) shows a centrosymmetric *dimeric* species in which the phenoxide unsymmetrically bridges two metals. Each phenoxide is covalently bound to one metal and behaves as a donor toward the other. The donor interaction takes place roughly *trans* to the alkylidene ligand (C(1)-Mo-O(1A) = 158.76(10)°) (Table 2.4) at a typical distance (Mo-O(1A) = 2.3509(19) Å). Formation of an adduct in which the base is *trans*

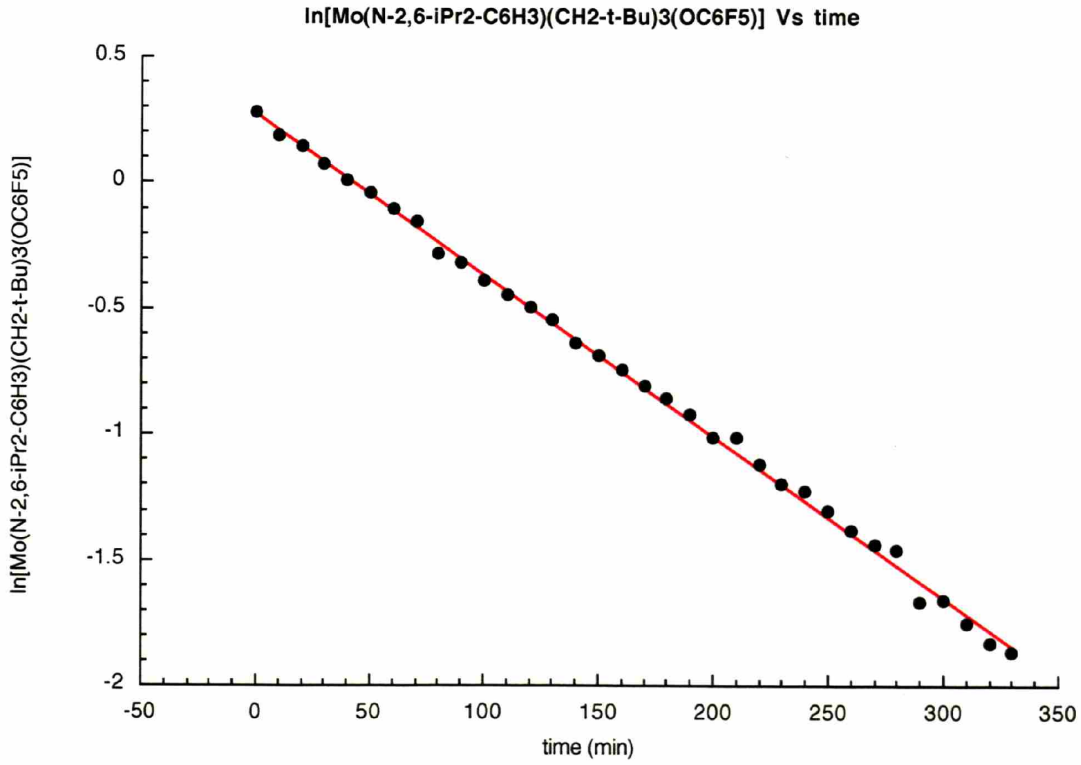


Figure 2.3. First-order kinetics for the conversion of Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in benzene-d_6 at 60 °C.

to the alkylidene ligand has been observed in various base adducts through NMR spectroscopy,[19] although structures of such species have only been elucidated recently.[20] The neopentylidene has the *syn* orientation with regular bond lengths and angles (Mo-C(1) = 1.912(3) Å and Mo-C(1)-C(2) = 143.9(2)°). This is a rare example of a dimeric form of a pseudotetrahedral high oxidation state imido alkylidene species, although other species that contain a relatively small alkoxide and a neopentylidene or neophylidene ligand almost certainly could form analogous dimeric species in the solid state, but simply have not been crystallographically characterized. "Ate" species are also known when the alkoxide is small; for example, addition of three equivalents of $LiOCH(CF_3)_2$ to $Mo(NAd)(CHCMe_2Ph)(OTf)_2(dme)$ (Ad = 1-Adamantyl) in diethyl ether yields off-white, crystalline, pentane-soluble $Li(dme)Mo(NAd)(CHCMe_2Ph)[OCH(CF_3)_2]_3$.[1(d)]

Table 2.4. Selected bond lengths [Å] and angles [°] for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5).

Mo(1)-N(1)	1.727(2)	C(1)-Mo(1)-C(24)	99.69(13)
C(1)-Mo(1)-O(1)	93.42(11)	C(2)-C(1)-Mo(1)	143.9(2)
Mo(1)-C(1)	1.912(3)	N(1)-Mo(1)-O(1)	135.69(10)
Mo(1)-C(24)	2.139(3)	C(6)-O(1)-Mo(1A)	119.31(16)
O(1)-Mo(1)-C(24)	114.79(10)	N(1)-Mo(1)-O(1A)	98.24(9)
Mo(1)-O(1)	2.1112(19)	Mo(1)-O(1)-Mo(1A)	113.89(8)
N(1)-Mo(1)-C(1)	100.63(12)	C(1)-Mo(1)-O(1A)	158.76(10)
C(12)-N(1)-Mo(1)	168.2(2)	O(1A)-Mo(1)-C(24)	85.02(10)
N(1)-Mo(1)-C(24)	104.00(12)	Mo(1)-O(1A)	2.3509(19)
Mo(1)-O(1)-C(6)	126.71(16)	O(1)-Mo(1)-O(1A)	66.11(8)

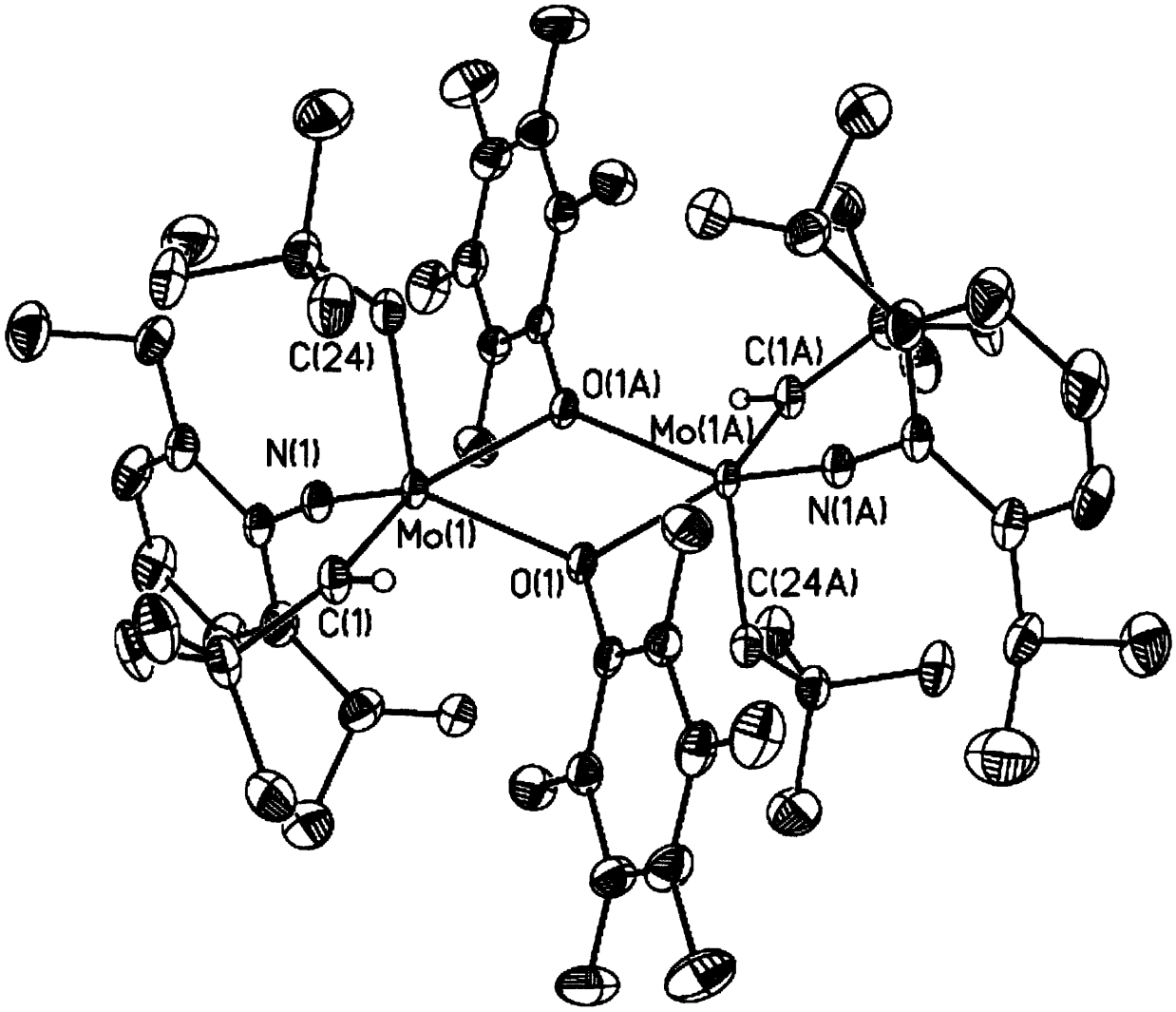


Figure 2.4. Solid state structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5).

Treatment of one equivalent of $(CF_3)_3COH$ with Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ affords both Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)$[OC(CF_3)_3]$ and Mo(NAr)$(CH_2$-t-Bu$)_3[OC(CF_3)_3]$ species in a ratio of 1:1.2. On the other hand, the reaction between Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ and *neat* $(CF_3)_3COH$ yields a mixture containing >95% Mo(NAr)$(CH_2CMe_3)_3[OC(CF_3)_3]$ and <5% Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)$[OC(CF_3)_3]$. Mo(NAr)$(CH_2CMe_3)_3[OC(CF_3)_3]$ can be converted to Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)$[OC(CF_3)_3]$ in benzene-d_6 in a unimolecular fashion with a rate constant of 7.2 x 10^{-4} s^{-1}. This acceleration in the rate of α-abstraction by a factor of ~7 (cf. k = 1.0 x 10^{-4} s^{-1} for conversion of Mo(NAr)$(CH_2$-t-Bu$)_3(OC_6F_5)$ to Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OC_6F_5)) may be attributed to the bulky nature of $OC(CF_3)_3$ vis-à-vis that of OC_6F_5, since the acidities of both these alcohols are very similar (pK_a's of $(CF_3)_3COH$ and C_6F_5OH are 5.4 and 5.5, respectively in water)[23-25]. α-Abstraction processes have previously been known to be accelerated by the virtue of steric effects.[15,21]

The conversion of trialkyl complexes of the type M(NAr)$(CH_2$-t-Bu$)_3$(X) (M = Mo, W) to the corresponding alkylidene species M(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(X) is not limited to X = OR. It has been shown by Pia Lopez (for tungsten)[22] and Tatiyana Pilyugina (for molybdenum)[13] that a benzene or toluene solution of M(NAr)$(CH_2$-t-Bu$)_3$Cl can be heated to evolve neopentane and give the corresponding M(NAr)(CH-t-Bu)$(CH_2$-t-Bu)Cl complex. The rate constants for these unimolecular reactions are consistent with what one would expect based on the steric effects of the X group, i.e., reaction rates decrease in the order X = $OC(CF_3)_3$ > Cl > OC_6F_5 (Table 2.5).

Table 2.5. Rate constants for conversion of M(NAr)$(CH_2$-t-Bu$)_3$X into M(NAr)$(CH_2$-t-Bu)(CH-t-Bu)X.[a]

	Mo	W
M(NAr)$(CH_2$-t-Bu$)_3$Cl	30 x 10^{-5} s^{-1}	11 x 10^{-5} s^{-1}
M(NAr)$(CH_2$-t-Bu$)_3(OR_{F9})$	72 x 10^{-5} s^{-1}	17 x 10^{-5} s^{-1}
M(NAr)$(CH_2$-t-Bu$)_3(OC_6F_5)$	10 x 10^{-5} s^{-1} [b]	7.0 x 10^{-5} s^{-1}

[a] Reactions done in C_6D_6 at 60 °C except otherwise noted, [b] 14 x 10^{-5} s^{-1} in CD_2Cl_2

The alkylidene resonances for Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OR) type complexes appear farther downfield in the range 11.63-12.28 ppm in the ^{1}H NMR spectra (benzene-d_6) than Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ (*cf.* 9.50 ppm) indicating that the metal center is more electron

deficient in the former species. As has been observed in the complexes of the type $Mo(NAr)(CHR')(OR)_2$, there is a reasonable correlation of the chemical shifts[1(b)] observed for the alkylidene proton and carbon in Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) with the magnitude of the negative inductive effect (exerted by the alkoxide group, reflected by the respective pK_a values (Table 2.6)). Two notable exceptions in the trend are for OR = $OSi(O\text{-}t\text{-}Bu)_3$ where the a relatively electropositive element silicon is attached directly to the alkoxide oxygen, and for a bulky alkoxide like OAr. As will be demonstrated later in Section 2.9, the electron-withdrawing or bulky alkoxides exhibit an enhanced reactivity towards various molecules compared to smaller and/or electron-donating alkoxides.

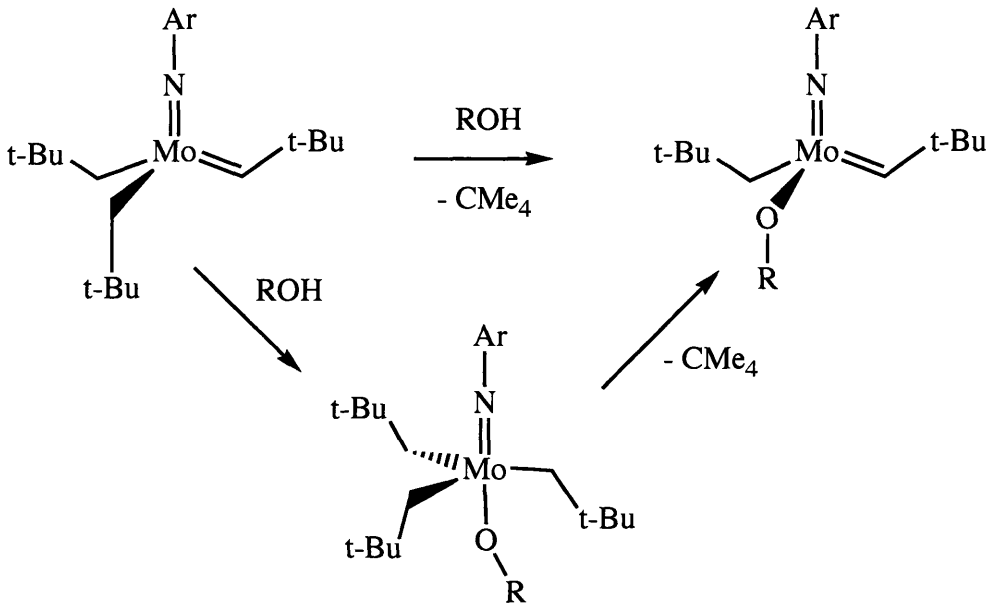
Table 2.6. Correlation of ^1H NMR (C_6D_6) alkylidene resonance δH_α in M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) with the pK_a of ROH in water.

ROH	δH_α	pK_a[23,24,25]
t-BuOH	11.63	19.2
1-Adamantanol	11.71	18
$(t\text{-}BuO)_3SiOH$	12.28	11.78
ArOH	11.99	11
$(CF_3)_2CHOH$	11.80	9.3
C_6F_5OH	12.07	5.5
$(CF_3)_3COH$	12.21	5.4

The complexes Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (OR = OAd, $OCMe_3$, OAr) show reasonable resistance to thermal degradation. For example, less than 0.5 % decomposition is observed when a 0.04 M solution of these complexes in toluene is heated at 60 °C for 11 days. On the other hand, Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) shows 54% decomposition in 11 days when heated to 60 °C. Under identical conditions, a 0.04M solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ in toluene shows 24% decomposition after 1 day, 46% after 3 days and 100% decomposition in 6 days. The nature of the decomposition products is not known.

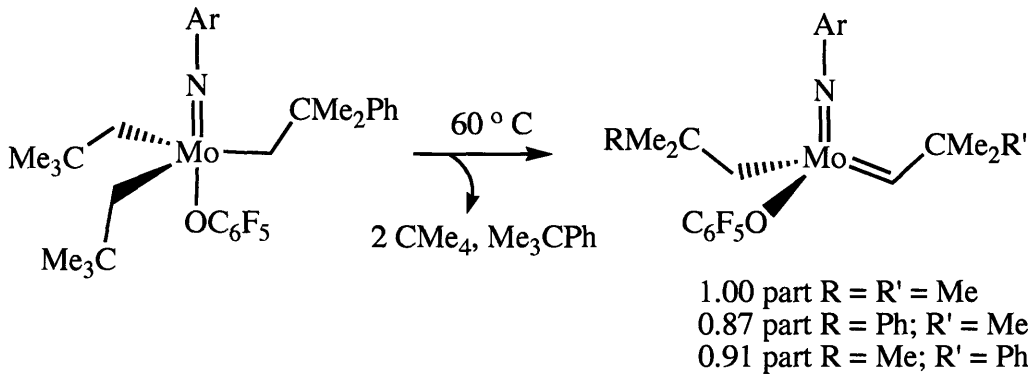
2.3. Pathways leading to the formation of Mo(NAr)(CHR')(CH_2R')(OR)

In principle, a molecule like Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ has three distinct sites that are amenable to protonation by an incoming alcohol, namely the N (imido), C_α (alkylidene) and C_α (alkyls). Although there is no evidence for protonation of the imido group, a fast reversible attachment of the proton to the imido nitrogen cannot be discounted. The reactions shown in Section 2.2 indicate at least two ways by which complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) may be accessed starting from Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$. One of the pathways involves the apparent cleavage of the Mo-C bond where as, in the other case, the alcohol adds across the Mo=C to give a trialkyl complex which gives Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) as the product α-abstraction after (Scheme 2.3). The isolation of the trialkyl species only in certain cases raises the question if the reaction with any alcohol always proceeds via addition across the Mo=C. A fast rate for the formation of Mo(NAr)(CH_2-t-Bu)$_3$(OR) for some alcohols, and a faster rate for its conversion to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) could preclude the observation of the trialkyl species and ostensibly show the Mo-C bond to be involved. This hypothesis can be easily verified by making use of a "mixed" alkyl/alkylidene complex, e.g., Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$.



Scheme 2.3. Two possible pathways for formation of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR).

Addition of C_6F_5OH to $Mo(NAr)(CHCMe_2Ph)(CH_2CMe_3)_2$ in pentane or benzene-d_6 over 6 h at 22 °C gives $Mo(NAr)(CHCMe_2Ph)(CH_2CMe_3)_2(OC_6F_5)$, which upon heating for 12 h at 60 °C in benzene-d_6 is transformed into a mixture of the expected three complexes in an almost statistical ratio with concomitant evolution of neopentane and t-butylbenzene (equation 2.4).



(2.4)

However, alcohols like AdOH or t-BuOH and $(CF_3)_2CHOH$ add across a Mo-C bond directly, since addition of ROH to $Mo(NAr)(CHCMe_2Ph)(CH_2CMe_3)_2$ in benzene-d_6 (74 mM) at room temperature gives $Mo(NAr)(CHCMe_2Ph)(CH_2\text{-t-Bu})(OR)$ exclusively. This confirms the existence of two distinct pathways by which alcohols react with $Mo(NAr)(CHR')(CH_2R')_2$ type of complexes. The reaction of $(CF_3)_3COH$ with $Mo(NAr)(CHCMe_2Ph)(CH_2\text{-t-Bu})_2$ in benzene-d_6 at 22 °C shows that within 1 h the alkylidene that is formed initially (~50% of the mixture) is only $Mo(NAr)(CHCMe_2Ph)(CH_2\text{-t-Bu})[OC(CF_3)_3]$, thus confirming that in this case a Mo-C bond is cleaved directly in competition with addition of $(CF_3)_3COH$ to the Mo=C bond to give $Mo(NAr)(CH_2CMe_2Ph)(CH_2\text{-t-Bu})_2[OC(CF_3)_3]$. When $Mo(NAr)(CH_2CMe_2Ph)(CH_2\text{-t-Bu})_2[OC(CF_3)_3]$ decomposes at 60 °C it yields all possible alkylidenes analogous to those shown in equation 2.4 in approximately a 1:1:1 ratio. Basset and Copéret using deuterium labeled silica support $Si_{surf}OD$ have reported reactions of this sort in the surface chemistry of tantalum and rhenium showing the formation of one product via two separate pathways similar to the ones mentioned above.[8]

2.4. Factors affecting the nature of product(s): ROH and M (Mo vs. W)

As depicted in the previous sections, the reactions between $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ and a given alcohol gives either $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OR)$ or $Mo(NAr)(CH_2\text{-t-}$

$Bu)_3(OR)$ as clean products and the latter can be heated to yield the former. The preference of an alcohol to attack the Mo-C or the Mo=C bond is related not only to the pK_a and the steric bulk of the alcohol employed, but also to the conditions under which the reaction is carried out, as in a solvents like benzene, pentane or under neat conditions. The results obtained during the course of this study indicate that while the weakly acidic alcohols almost certainly cause protonation of the Mo-C bond, small alcohols with lower pK_a's add across the Mo=C bond. The same is true for the treatment of W(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$[22] with these alcohols (Table 2.7). The notable difference between Mo and W systems is the point of crossover in pK_a's of the alcohols when preference for a given type of product takes precedence, $(CF_3)_3COH$ in case of Mo and $(CF_3)_2CHOH$ for W.

Table 2.7. Formation of complexes of the type M(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)$(OR) (A) or M(NAr)$(CH_2$-t-Bu$)_3$(OR) (B).

ROH	p*K*a	Mo	W
t-BuOH	19.2	A	A
1-Adamantanol	18	A	A
ArOH	11	A	A
$Me(CF_3)_2COH$	9.8	A	A
$(CF_3)_2CHOH$	9.3	A or B[a]	A + B
C_6F_5OH	5.5	B	B
$(CF_3)_3COH$	5.4	A + B	B

[a] Neat only.

2.5. Variation of the imido ligand

The complexes enumerated above make use of the bulkiest imido group (NAr) employed in the chemistry of high oxidation state metal-carbon multiple bond complexes of Group 6.[15] The modular nature of the imido ligand used in the bistriflate starting material Mo(NR″)(CH-t-Bu)$(OTf)_2$(dme) provides avenues for preparing complexes of the type Mo(NR″)(CHR′)$(CH_2$R′$)$(OR) with varying substituents on the imido nitrogen. Previous studies with Mo(NAd)(CHR′)$(OR)_2$[1(d)] and Mo(NAd)(CHR′)(diolate)[12] species that utilize 1-

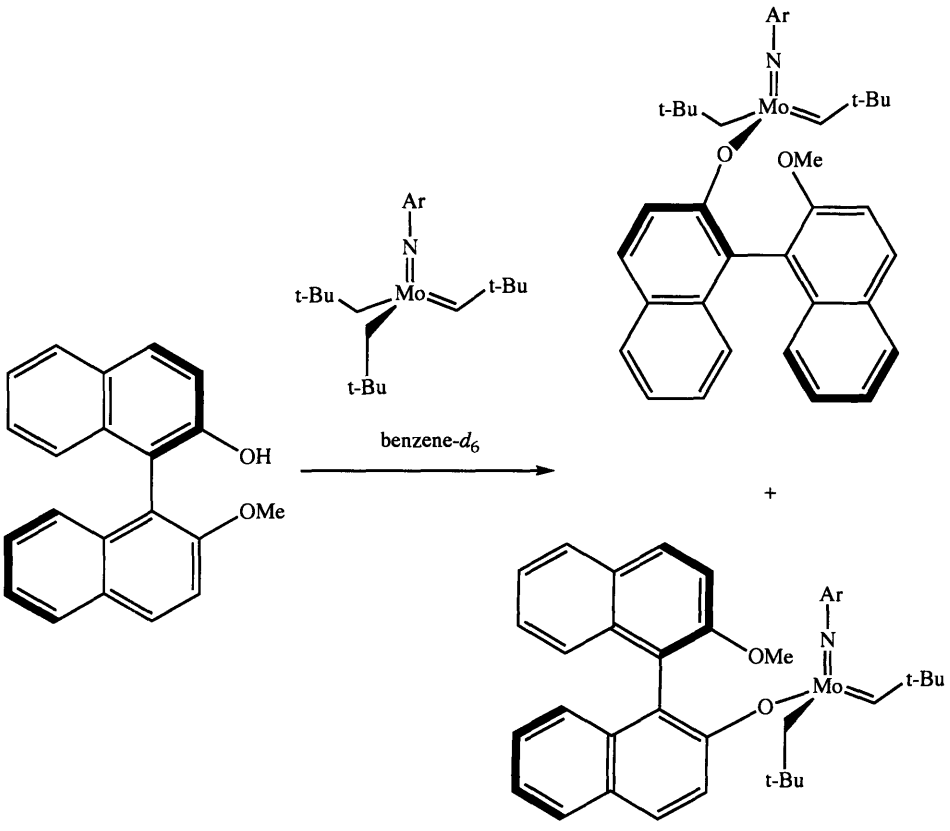
adamantylimido (NAd) ligands have yielded significantly different results in terms of reactivity and selectivity towards olefins compared with that of the 2,6-disubstitued arylimido ligands.[26] This finding served as a motivation to explore the formation and reactivity of Mo(NAd)(CHR′)(CH_2R')$_2$ complexes.

Analogous to the process that has been described in Section 2.1, reactions of Mo(NAd)(CHR′)-(OTf)$_2$(dme) with R′CH_2MgCl (R′ = CMe_3, CMe_2Ph) yielded complexes of the type Mo(NAd)-(CHR′)(CH_2R')$_2$ as oily materials. These experiments were performed in collaboration with Monica Duval who went on to explore the reactions of Mo(NAd)(CHR′)(CH_2R')$_2$ with various alcohols and observed decomposition and scrambling of the alkyl/alkylidene moieties of the starting material in presence of ROH. The instability of these species may be attributed to the smaller size of the adamantylimido substituent compared to the bulky 2,6-diisopropylphenyl imido group, which makes the former susceptible to bimolecular decomposition.[13] This is reminiscent of the oily nature of compounds with N-t-Bu group reported by Osborn.[11] The importance of a sterically encumbering imido group can be ascertained from the fact that when a mono-substituted imido group like N-2-$CF_3C_6H_4$ is used, the formation of Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ (δH_α = 9.33 in C_6D_6) when attempted in an analogous manner as described in Section 2.1 does not occur cleanly.

2.6. Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ with enantiomerically pure alcohols

Mo(NR″)(CHR′)(diolate) complexes containing an enantiomerically pure diolate based on biphenolate and binaphtholate backbones have been employed in the past to carry out organic transformations by making use of asymmetric metathesis techniques. With a view to expand the available library of chiral catalysts[3], the feasibility of making complexes of the type Mo(NR″)(CHR′)(CH_2R')(OR*) (OR* = a chiral alkoxide) was explored. Unlike Mo(NR″)(CHR′)(OR)$_2$ species, the Mo(NR″)(CHR′)(CH_2R')(OR) type complexes are chiral at the metal center. This property adds a complication arising from the possibility for two diastereomeric forms for Mo(NR″)(CHR′)(CH_2R')(OR*) type species. Therefore, for Mo(NR″)(CHR′)(CH_2R')(OR*) to be used in asymmetric reactions, not only must the alkoxide ligand be enantiomerically pure, but also one diastereomer of the complex has to be the only one present or must be vastly more reactive than the other diastereomer.

(R)-Binaphthol can be methylated using MeI in the presence of 2.5 equivalents of K_2CO_3 in acetone to give a mixture of the mono- and di-methylated diol, which can be easily separated by column chromatography. Reacting the monomethyl protected (R)-binaphthol with one equivalent of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ in benzene-d_6 (80 mM) at room temperature gives a mixture of diastereomers in equal proportions (equation 2.5). Heating the above mixture at 65 °C for a period of 48 h did *not* lead to the conversion of one diastereomer into the other. The two diastereomers exhibit non-differential reactivities, which can be confirmed by no enantiomeric excess for the product shown in equation 2.6. Similar results showing a mixture containing equal amounts of both the diastereomers (of equal reactivities towards olefins) were obtained by Monica Duval upon reacting Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ with various secondary and tertiary chiral alcohols. These findings suggest that the preparation of one diastereomer of Mo(NR′′)(CHR′)(CH_2R′)(OR*) species is not feasible by the route currently undertaken.



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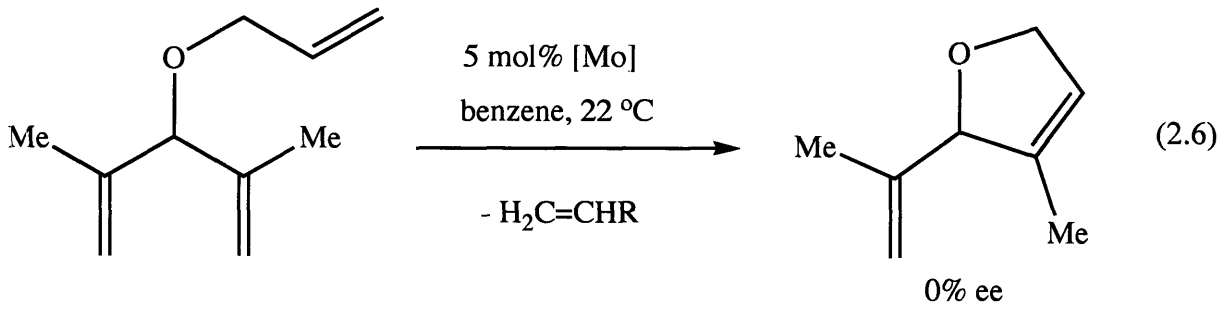


(2.6)

2.7. Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) with neutral Lewis bases

The question of how an olefin a approaches a high oxidation state alkylidene complex is important in effecting better design catalyst systems to meet the required reactivity and selectivity criteria for different types of substrates.[3] The initial interaction of an olefin with the metal center is thought to be a weak dative σ-bond, which leads to formation of a metallacyclobutane and/or causes reversion to an alkylidene complex.[27] Therefore, it is highly unlikely that an olefin-adduct of an alkylidene complex can be isolated and crystallographically examined. The importance of base binding studies is evident in this respect. A neutral Lewis base is a nucleophile similar to an olefin. Therefore, as a very crude approximation, the isolation of a neutral base-adduct with complexes like Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) would come closest to the simulation of the approach of olefins towards such complexes.[19]

Studies on Mo(NAr)(CH-t-Bu)$(OR)_2$ catalysts with neutral bases have shown a preference for the base binding for the C/N/O face[14,19], although a complex having a THF molecule bound on the N/O/O face was recently crystallographically characterized.[20] Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes differ from the Mo(NAr)(CH-t-Bu)$(OR)_2$ species in the way one of the alkoxide group is replaced by a neopentyl ligand. This feature in complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) makes them interesting platforms to study because the approach of an olefin *trans* to the alkyl or the alkoxide ligands would be energetically very different in such chiral (at the metal) complexes.

When 1 equivalent of 2,4-lutidine was added to an *in situ* prepared pentane solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OCH(CF_3)_2$] (by reacting Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and 1 equivalent of $HOCH(CF_3)_2$ at room temperature for 1 day), a yellow-brown material precipitated out. Washing this yellow-brown solid with cold pentane afforded a yellow powder in 90% isolated yield. ^{1}H NMR of this yellow powder showed the predominant species to be the base-

free compound. When the other Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes (OR = O-t-Bu, OAd, OAr, OC_6F_5) in benzene-d_6 (34-42 mM) were allowed to react with 1 equivalent of pyridine at room temperature, the following amounts of the pyridine-adducts were observed (Table 2.8).

Table 2.8. Percentage of pyridine-adducts of M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) in benzene.

OR	% py-adduct
O-t-Bu	21
OAd	30
OAr	<1
OC_6F_5	71

The above findings suggest that an electron withdrawing alkoxide is needed to make the metal electrophilic enough for a base molecule to bind to it. A sterically bulky alkoxide would hinder the approach of the base (cf. OAr, Table 2.8). Based on these observations, one would expect the Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) complex to be the best for isolating the base-adduct for structure determination. It was also hoped that a stronger (more Lewis basic) base like PMe_3 would be a better candidate than pyridine. A benzene-d_6 solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ does not react with Lewis bases like pyridine, 2,4-lutidine and PMe_3 at room temperature over two days.

The room temperature reaction of 1.1 equiv of PMe_3 with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in benzene-d_6 (33 mM) resulted in the total disappearance of the parent alkylidene peak in the proton NMR spectrum. A ^{1}H NMR spectrum of the above solution showed two new alkylidene resonances at 13.3 ppm and 10.8 ppm in approximately a 1:1 ratio. On the basis of the chemical shift and coupling constant values,[19] the peak at 13.3 ppm (J_{CH} = 136 Hz) has been assigned to the *anti* PMe_3-adduct species where as that at 10.8 ppm (J_{CH} = 108 Hz) to the *syn* base-free species. The 13.3 ppm resonance is a doublet due to splitting by ^{31}P nucleus ($^3J_{HP}$ = 3.5 Hz). The ^{31}P NMR shows two peaks at –10.9 ppm and –14.9 ppm corresponding to the phosphines in the *anti* and *syn* base-adducts. In toluene, in the ^{13}C NMR spectrum, the *anti* base-

adduct resonance appaears at 309.7 ppm and the *syn* base-adduct appears at 278.7 ppm. The *anti* to *syn* ratio does not change over a period of 3 days. When only 0.5 equiv of PMe_3 was added to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in benzene a sharp *anti* base-adduct resonance was observed along with broad alkylidene proton resonance for the *syn* adduct and the base-free species at room temperature. Apparently trimethylphosphine is lost more readily from the *syn* adduct than from the *anti* adduct. A weaker coordination of a base to a *syn* isomer is a common finding for bisalkoxide imido alkylidene complexes.[3,14,26] The ready loss of trimethylphosphine from the *syn* isomer suggests that the constant ratio of *anti* to *syn* adducts is the result of ready equilibration of the two through loss of phosphine.

Single crystals of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) were obtained from a saturated solution of the complex in toluene and Adam Hock carried solved the structure. The structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) (Figure 2.5) is a distorted trigonal bipyramid in which trimethylphosphine is approximately *trans* to the neopentyl ligand (C(6)-Mo(1)-P(1) = 154.63(11)°) (Table 2.9); the neopentylidene, imido and alkoxide ligands are all located in "equatorial" positions. The alkylidene ligand was found in two orientations (*syn* and *anti*) in a ratio of ~70:30, a circumstance not encountered in compounds of this type before. This disorder was refined with the help of restraints on the thermal parameters while setting the total occupancy to unity. The hydrogen atom on the major isomer was located in the difference map and refined using distance restraints. The H atom on the minor isomer was included on its geometrically calculated position and refined using a riding model. None of the bond lengths and angles are unusual, with one exception: The Mo(1)-P(1) bond length (2.5680(11) Å) is relatively long, which suggests that trimethylphosphine is relatively weakly bound and should be relatively labile, as found experimentally. In the *syn* form, the Mo-C(1) bond length is 1.881(8) Å and the Mo-C(1)-C(2) bond angle is 149.6(7)°. In the *anti* form the Mo-C(1A) bond length is 1.96(3) Å and the Mo-C(1A)-C(2A) bond angle is 137(2)°. Each is typical of a *syn* or *anti* isomer. The angle between the two α carbon atoms in the two neopentylidene ligands in the two different isomers is 19.6(6)°. Therefore angles at Mo for the two isomers differ slightly, e.g., N(1)-Mo-C(1) = 113.0(3)° (*syn*) while N(1)-Mo-C(1A) = 93.5(6)° (*anti*). It is striking that the structures of two species that differ so little are maintained in solution, i.e., distinct *syn* and *anti* adducts are observed in NMR spectra as noted above.

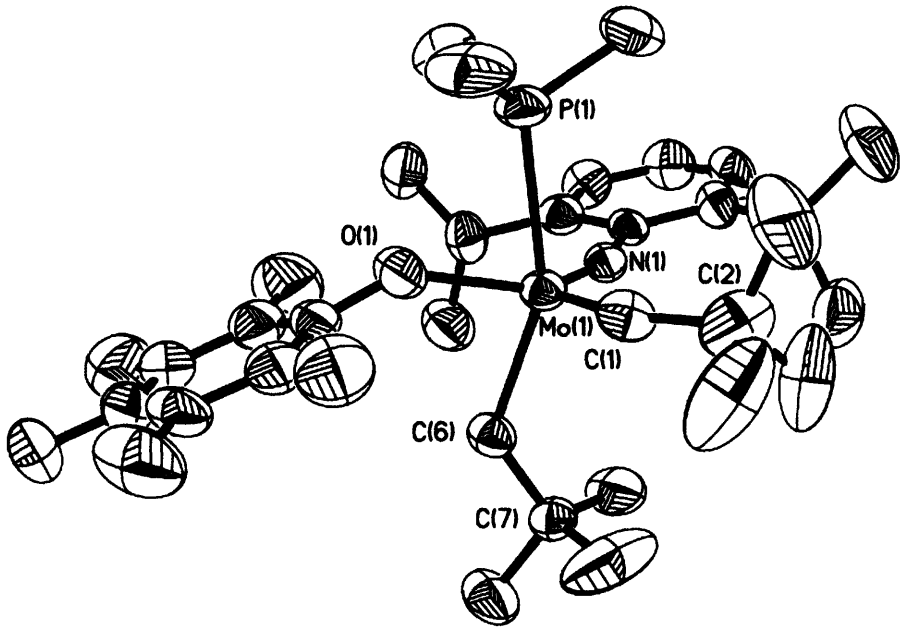


Figure 2.5A. Thermal ellipsoid drawing of *syn*-Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

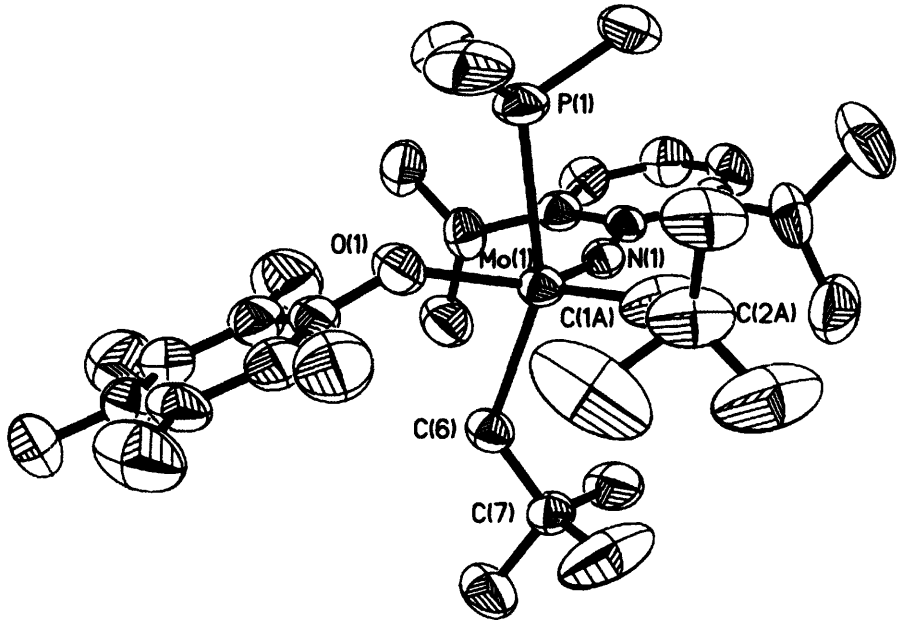


Figure 2.5B. Thermal ellipsoid drawing of *anti*-Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

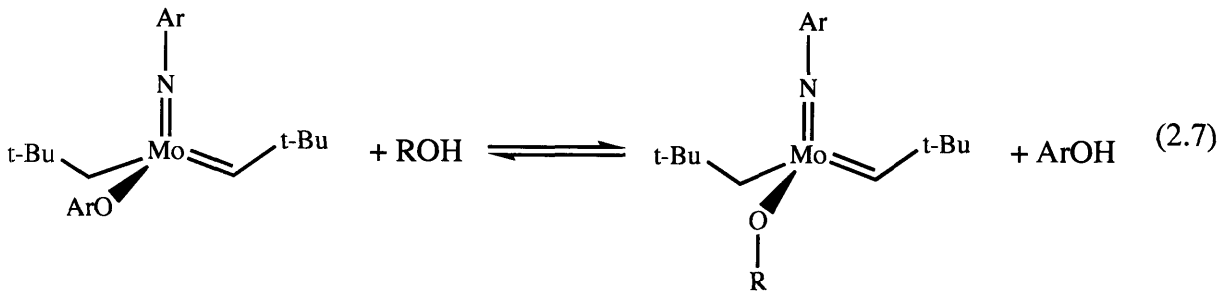
Table 2.9. Selected bond lengths [Å] and angles [°] for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

Mo(1)-N(1)	1.737(3)	C(1A)-Mo(1)-O(1)	128.7(6)
Mo(1)-C(1)	1.881(8)	C(1)-Mo(1)-C(6)	101.0(3)
Mo(1)-C(1A)	1.96(3)	C(1A)-Mo(1)-C(6)	107.0(7)
Mo(1)-O(1)	2.051(3)	C(1)-Mo(1)-P(1)	93.8(3)
Mo(1)-C(6)	2.199(4)	C(1A)-Mo(1)-P(1)	93.8(7)
Mo(1)-P(1)	2.5680(10)	O(1)-Mo(1)-C(6)	81.76(13)
N(1)-Mo(1)-C(1)	113.0(3)	O(1)-Mo(1)-P(1)	73.84(9)
N(1)-Mo(1)-C(1A)	93.5(6)	C(2)-Mo(1)-P(1)	154.63(11)
N(1)-Mo(1)-O(1)	134.93(15)	Mo(1)-N(1)-C(17)	162.5(3)
N(1)-Mo(1)-C(6)	102.37(13)	Mo(1)-O(1)-C(11)	141.7(3)
N(1)-Mo(1)-P(1)	90.34(10)	Mo(1)-C(6)-C(7)	126.1(3)
C(1)-Mo(1)-O(1)	110.0(3)	Mo(1)-C(1)-C(2)	149.6(7)
C(1)-Mo(1)-C(1A)	19.6(6)	Mo(1)-C(1A)-C(2A)	134(2)

2.8. Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) with ROH

The inability to obtain Mo(NAr)(CH-t-Bu)$(OR)_2$ complexes from the reactions between Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ and two equivalents of ROH prompted the investigation of reactions between Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species and ROH. This study would also shed light on the potential tolerance of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) towards alcohol functionality in olefinic substrates for metathesis reactions considering that catalysts of the type Mo(NAr)(CH-t-Bu)$(OR)_2$ undergo decomposition due to protonolysis[3] by compounds containing free –OH group(s).

When Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) in benzene-d_6 (60 mM) is treated with 1 equivalent of ROH (OR = $OCMe_3$, OAd, OC_6F_5) at 22 °C, a mixture containing both Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (and the expected alcohols) is obtained within 30 minutes (equation 2.7).

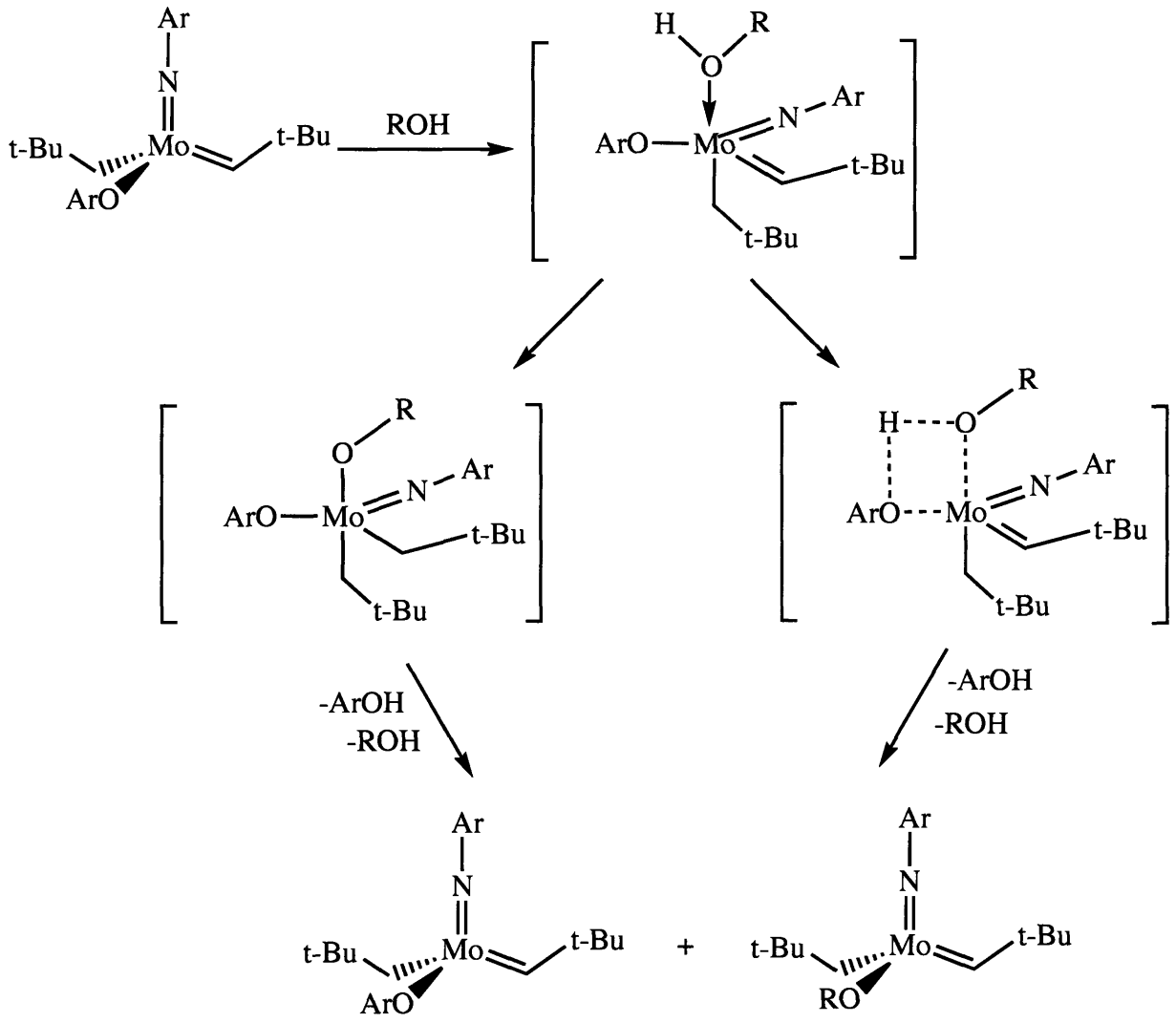


(2.7)

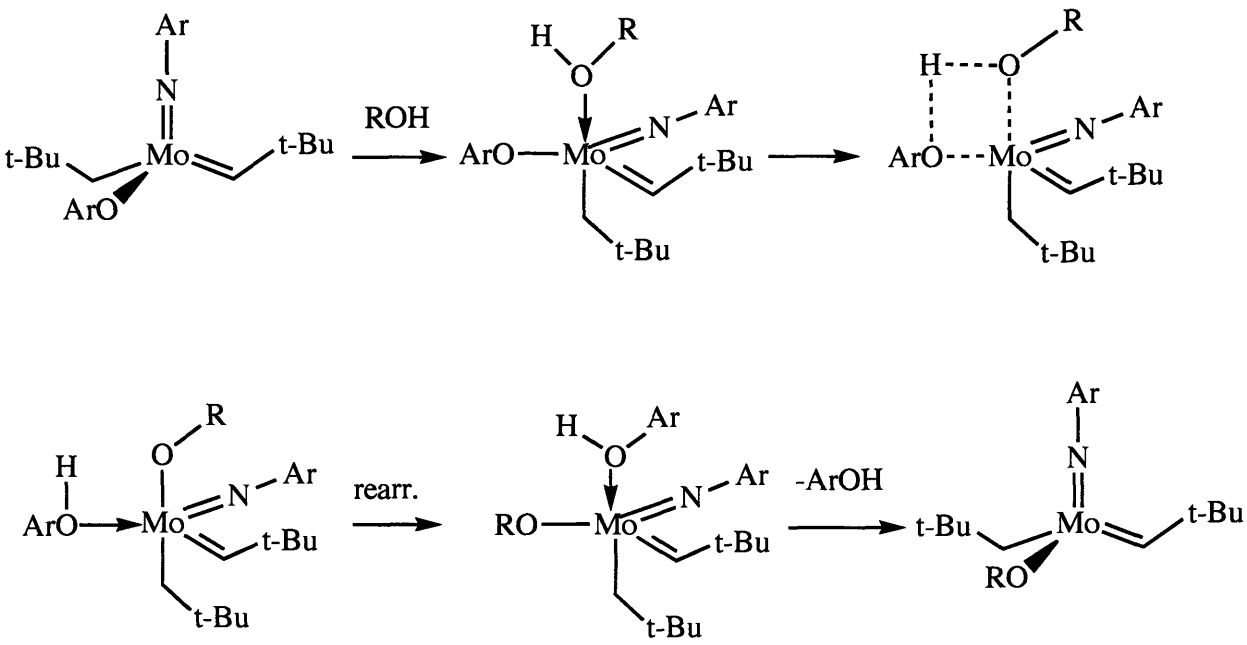
On the basis of the structure obtained for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) (*vide supra*) it is believed that the donor, in this case ROH, initially approaches the electrophilic metal center *trans* to the alkyl group, *i.e.*, on the C_{ene}/N/O face (Scheme 2.4). The proton in theory could then migrate to the imido nitrogen, the alkylidene α carbon atom, or the alkoxide oxygen. Migration of the proton to the imido group at a rate that is faster than migration to the alkoxide or the alkylidene cannot be ruled out, although migration to the imido nitrogen would have to be readily reversible since proton migration to the imido group to give an amido complex has not been observed for NAr = N-2,6-diisopropylphenyl (see Chapter 1). Scheme 2.4 shows two pathways corresponding to the protonation of the alkylidene α carbon and that of the alkoxide oxygen, respectively that would account for the observed products. Evidence in support of one of the pathways can be obtained by employing a "mixed" alkyl/alkylidene complex of the type Mo(NAr)(CHR′)(CH_2R″)(OAr).

Reaction of Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$ in benzene-d_6 (74 mM) with ArOH at 22 °C over 12 h gave Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)(OAr) *in situ*, which was treated with one equivalent of t-BuOH at room temperature to produce a mixture containing Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)(O-t-Bu) and Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)(OAr), exclusively (along with ArOH and t-BuOH) within 10 minutes. If the proton were to migrate to the alkylidene carbon to give Mo(NAr)(CH_2-t-Bu)$_2$(OR)(OAr), that species either would be relatively stable toward loss of neopentane (W(NAr)(O-t-Bu)$_2$(CH_2-t-Bu)$_2$ is known[28]) or it would lose neopentane to yield Mo(NAr)(CHR')(OR)(OAr) in which R' would most likely be either t-Bu or CMe_2Ph. Rearrangement of the new five-coordinate species containing ArOH (Scheme 2.5), e.g., via a turnstile mechanism, would yield a ArOH adduct of the same type that was formed initially (or its enantiomer) from which ArOH would be lost to generate the new monoalkoxide species. The structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3) is highly

distorted from any ideal. Therefore, a discussion of exchange in terms of ideal structures, rearrangements, etc., may not be valid. The fact that even relatively acidic C_6F_5OH simply exchanges with OAr on the metal, suggests that these catalysts may be stable in the presence of an alcohol functionality, at least if any monoalkoxide alkylidene that results from reaction with any alcohol in the system is itself reactive toward olefins.



Scheme 2.4. Proposed pathways for alkoxide exchange at the metal center.



Scheme 2.5. Mechanism of alkoxide exchange at the metal center.

When a 0.05 M benzene-d_6 solution Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) was allowed to react with one equivalent C_6F_5OH at 70 °C for 12 h, a mixture of what appears to be Mo(NAr)(CH_2-t-Bu)(OC_6F_5)$_3$ (based on its proton NMR spectrum) and unreacted Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) was obtained. Reaction of two equivalents of C_6F_5OH with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) resulted in the formation of Mo(NAr)(CH_2-t-Bu)(OC_6F_5)$_3$ exclusively via addition of the alcohol across the Mo=C bond. Therefore it may be inferred that under forcing conditions, at least with a relatively small and acidic alcohol, Mo(NAr)(CH-t-Bu)(OC_6F_5)$_2$ is formed either directly (through addition of C_6F_5OH to Mo-C) or indirectly (through addition of C_6F_5OH to Mo=C followed by α abstraction) and that Mo(NAr)(CH-t-Bu)(OC_6F_5)$_2$ reacts with C_6F_5OH rapidly to yield Mo(NAr)(CH_2-t-Bu)(OC_6F_5)$_3$.

A similar trialkoxide species Mo(NAr)(CH_2-t-Bu)[$OCH(CF_3)_2$]$_3$ that was formed by the reaction between Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and 2.5 equivalents of hexaisopropanol in a methylene chloride was crystallographically characterized with the help of Dmitry Yandulov. X-ray studies performed on the crystals grown from pentane at -20 °C revealed its geometry as a pseudo-trigonal bipyramidal structure with two sets of the three alkoxide groups, two of which lie in the equatorial plane while the third one is disposed *trans* to the imido ligand on the axial

position (N(1)-Mo(1)-O(1) = 173.22(13)°). The bulky neopentyl ligand lies in the equatorial plane (Figure 2.6 and Table 2.10).

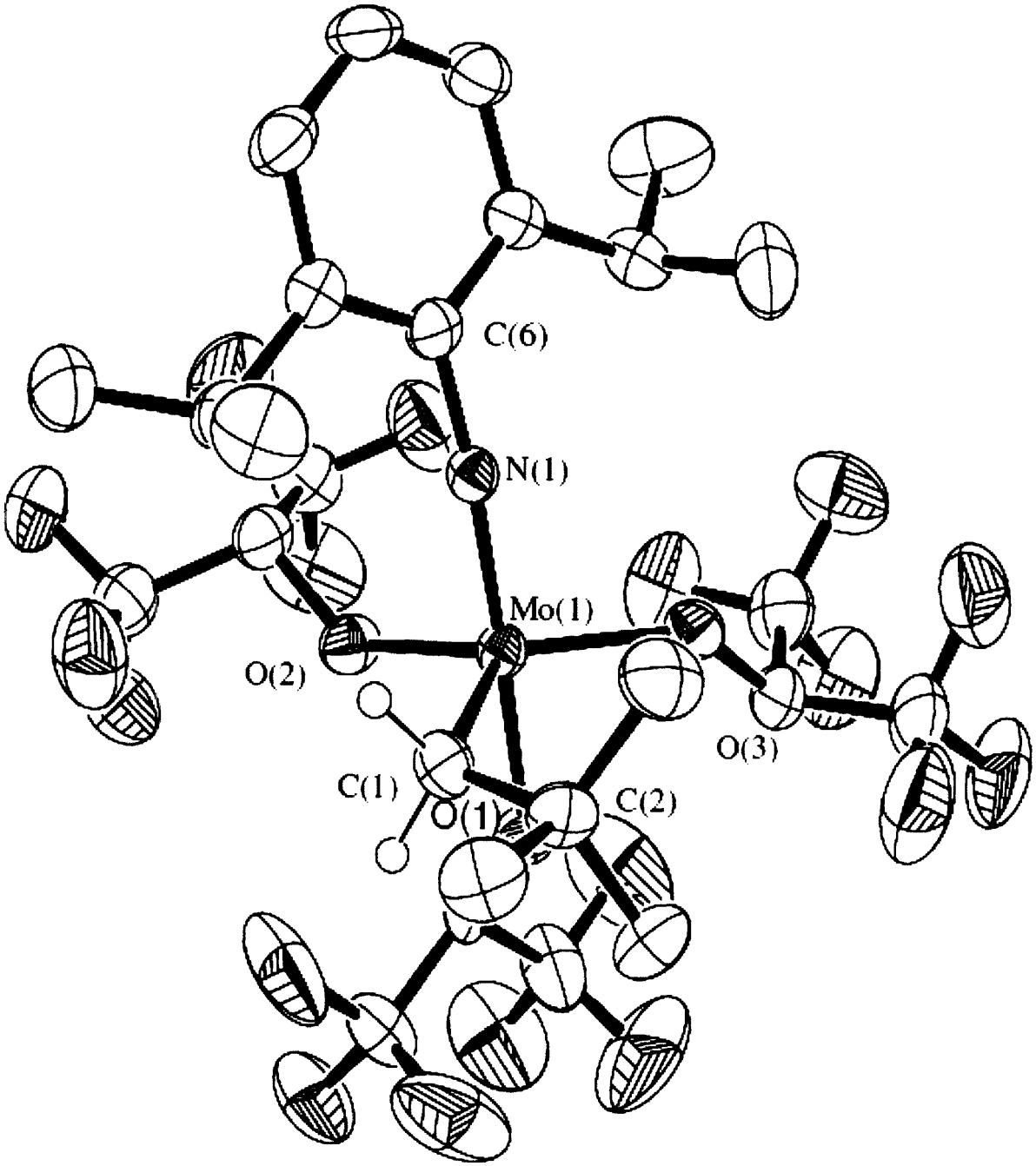


Figure 2.6. Thermal ellipsoid drawing of $Mo(NAr)(CH_2\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3$.

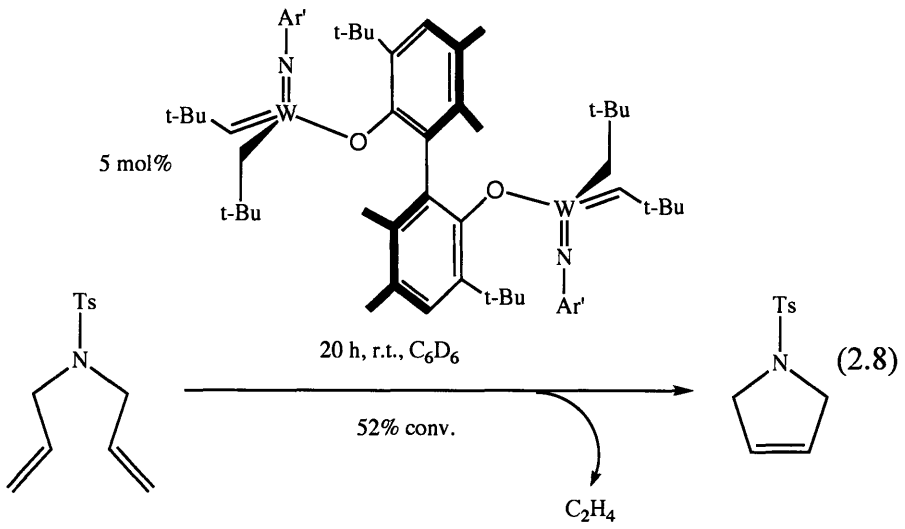
Table 2.10. Selected bond lengths [Å] and angles [°] for Mo(NAr)(CH_2-t-Bu)[$OCH(CF_3)_2$]$_3$.

Mo(1)-N(1)	1.765(3)
Mo(1)-O(2)	1.912(3)
Mo(1)-O(3)	1.920(3)
Mo(1)-O(1)	2.002(3)
Mo(1)-C(1)	2.134(4)
N(1)-Mo(1)-O(2)	93.65(14)
N(1)-Mo(1)-O(3)	95.87(13)
N(1)-Mo(1)-O(1)	173.22(13)
N(1)-Mo(1)-C(1)	94.60(16)
C(6)-N(1)-Mo(1)	169.7(3)
O(1)-Mo(1)-C(1)	90.85(15)
O(2)-Mo(1)-O(1)	80.80(12)
O(3)-Mo(1)-O(1)	85.69(12)
C(2)-C(1)-Mo(1)	119.3(3)

2.9. Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) with olefins: Metathesis activity

The Mo(NAr)(CH-t-Bu)$(OR)_2$ family of complexes have been shown to be excellent metathesis catalysts for a many types of olefins.[3] On the other hand, Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ is metathetically inactive with the exception of its ability to carry out the ring-opening metathesis polymerization of a highly strained olefin like norbornene (*vide infra*). In this respect, it would be interesting to determine the reactivity of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes. Of course, the neopentyl ligand on the metal would have to survive the catalytic cycles.

In an earlier work, Sarah Aielts had shown that 5 mol% of a related dinuclear complex [W(Ar')(CH-t-Bu)(CH_2-t-Bu)]$_2$[μ-Biphen] (Ar' = 2,6-$Me_2C_6H_3$, $Biphen^{2-}$ = 3,3'-di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate) would catalyze the ring-closing metathesis (RCM) reaction of *N,N*-diallyl tosylsulfonamide shown in equation 2.8 at room temperature.[29] No further work was reported with this tungsten complex, especially with regard to asymmetric ring-closing metathesis (ARCM) reactions.

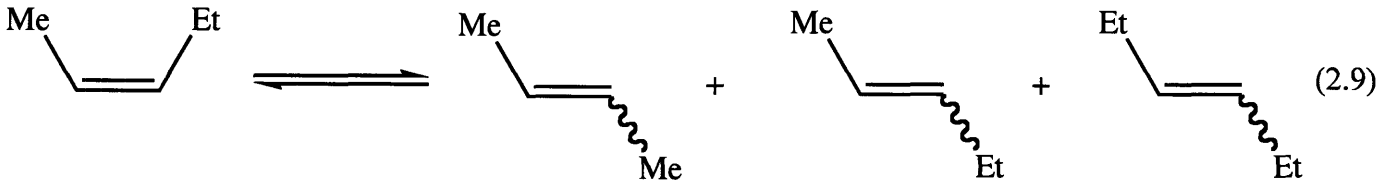


(2.8)

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species were allowed to react with a variety of olefinic substrates to study their utility as metathesis catalysts for simple internal olefins as well as for ring-closing and ring-opening processes. As will be shown below, alkoxides bearing highly electron deficient and/or bulky substituents yield the best results in this study.

2.9.1. Metathesis of *cis*-2-pentene

Reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with an olefin like *cis*-2-pentene was carried out at room temperature with 5 mol% of these complexes in a toluene solution (5 mM) of *cis*-2-pentene. The reaction progress was measured by analyzing aliquots taken out from the reaction mixture at regular time intervals by gas chromatography. The time taken for equilibrating *cis*-2-pentene to a mixture of *cis*- and *trans*-2-butenes, 2-pentenes, and 3-hexenes (equation 2.9) are shown in Table 2.11.



(2.9)

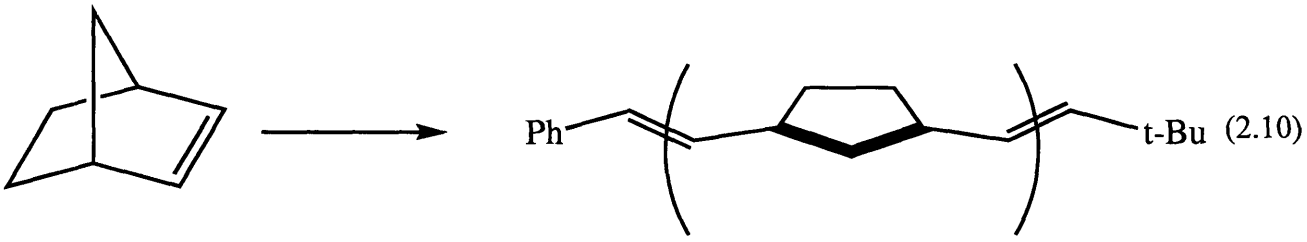
Table 2.11. Metathesis of *cis*-2-pentene by 5 mol% of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (min)
O-t-Bu	720
OAd	720
OAr	1
OC_6F_5	1

It has been previously shown in case of Mo(NAr)(CH-t-Bu)$(OR)_2$ complexes that electron withdrawing groups on the Mo center are pivotal in increasing the rate of olefin metathesis.[1(c)] The high catalytic activity of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) (TON = 20 min^{-1}) can therefore be attributed to the presence of a highly electron withdrawing alkoxide. On the other hand, the rate of olefin metathesis is drastically reduced when electron donating groups like O-t-Bu or OAd are used. The amount of time taken (12 h) by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(O-t-Bu) or Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) corresponds to 1.7 turnovers per hour, which is approximately 10^3 times slower than that for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5). Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) despite having electron donating group metathesizes 20 equiv of *cis*-2-pentene to equilibrium in under 1 min, corresponding to a turnover number of 20 min^{-1}. The high catalytic activity of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) can be explained on the basis of high stability of the new alkylidenes (that are smaller than neopentylidene) formed under catalytic conditions. For example, Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) reacts with 5 equiv of *trans*-3-hexene at to give a mixture containing Mo(NAr)(CH-Et)(CH_2-t-Bu)(OAr) along with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) in a ratio of 0.46:1.00. Mo(NAr)(CH-Et)(CH_2-t-Bu)(OAr) thus generated is stable for more than 10 days at 22 °C in a benzene-d_6 solution in a J-Young NMR tube, i.e., the aforementioned ratio does not change (also see Section A.1). Metathesis reactions on *cis*-2-pentene employing lower catalyst loadings, i.e., less than 5 mol% was not carried out with these complexes.

2.9.2. Ring-opening metathesis polymerization (ROMP) of norbornene

Reaction with a strained olefin such as norbornene (equation 2.10) was carried out to investigate the potential of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes as catalysts for ring-opening metathesis polymerization reactions. NMR scale reactions at room temperature were performed using 5 mol% of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes and 20 equivalents of norbornene in benzene-d_6 (85 mM in substrate) to make 20-mers of polynorbornene. In one case (*vide infra*), a new alkylidene species corresponding to the metal center being directly attached to the polymer chain was observed at 12.43 ppm in the ^{1}H NMR spectrum. The % activation of a catalyst refers to the percentage of the new alkylidene species in the reaction mixture containing the new alkylidene and the parent alkylidene complexes. In cases where no new alkylidene resonance was observed in the proton NMR, which is also reflected in the amount of the parent alkylidene being virtually constant (relative to an internal standard), the % activation was assigned to be less than 1%. Similarly, a >99% activation was noted when no resonance corresponding to the alkylidene α hydrogen atom of the starting complex was observed, i.e., the both the reactants (monomer and the parent alkylidene) were completely consumed. The % activation of each of the catalysts for complete polymerization of the substrate within 10 minutes at 22 °C is listed in Table 2.12. No resonance for any new alkylidene species was observed when the above reaction was carried out using Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) even though the starting materials were completely consumed. When norbornene was added to a 5 mol% solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ under identical conditions, no monomer was observed and the amount of the complex activated was <1%.



(2.10)

Table 2.12. % Activation of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes upon reaction with 20 equivalents of norbornene.

X	% Activation
O-t-Bu	<1
OAd	<1
OAr	7
OC_6F_5	>99
CH_2-t-Bu	<1

100-mers of polynorbornene were prepared on a 50 mg scale by reacting a toluene solution (10.6 mM) of an appropriate Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complex with 100 equivalents of norbornene in toluene (106.2 mM in substrate) for 1 h at 22 °C. The polymer was isolated after quenching the above reaction mixture by stirring for an additional 1 h with 2 ml of benzaldehyde and precipitating the polymer in 65 ml methanol. The polymer samples were analyzed by gel permeation chromatography (GPC). The results are summarized in Table 2.13.

Table 2.13. GPC data for polymers isolated from a 50 mg sample of norbornene upon reaction with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(X) complexes.

X	Polymer Yield (%)	M_n (x 10^3)[a]	PDI[b]	%Activation[c]
O-t-Bu	93.8	175	1.55	5.1
OAd	94.0	205	1.85	4.3
OAr	94.4	255	1.29	3.5
OC_6F_5	96.0	8.88	1.29	100.0
CH_2-t-Bu	94.2	152	1.65	5.9

[a] theoretical M_n=9.6 x 10^3

[b] polydispersity index

[c] relative to Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) assuming it is 100% activated.

For all the cases, polymers are obtained in high yields. The efficient activation of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) relative to the other Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(X) complexes seen from the NMR experiments (Table 2.12) is supported by the data obtained from GPC analysis (Table 2.13). Due to low activation of the complexes with electron donating ligands, the polymer chain lengths are ~17-29 times longer than that obtained by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5). Catalysts with X = OAr, OC_6F_5 offer decent polydispersity indices (PDI) for the polynorbornene obtained.

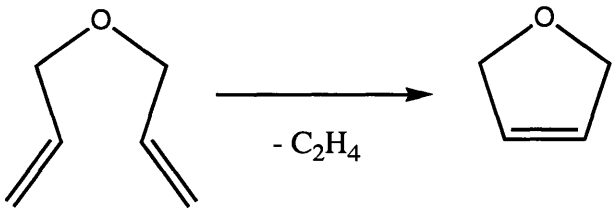
Except for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5), all the other complexes give mainly the *cis*-polymer upon reaction with 100 equivalents of norbornene (85 mM) in benzene-d_6 at room temperature (Table 2.14) . The highest selectivity is observed in case of the monoalkoxide catalysts is for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) which gives ~85% *cis*-polymer. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) reacts completely (100% activation, *vide supra*) with norbornene to yield an almost equal mixture of *cis*- and *trans*- polynorbornene. However, after 6 h, the polymer observed is majorly *trans*-, the *cis*-polymer being only 27% of the mixture. The *cis*:*trans* ratio virtually remains unaltered for complexes containing the other alkoxides. The isomerization of the polymer in case of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) may be attributed to the "back-biting" of the polymer chain by the highly electron withdrawing (and therefore reactive) molybdenum center. The % activation does not change over a period of 24 h for any of these complexes. Interestingly, the amount of *cis*-polymer in the polymer mixture was 90% after 10 min and no isomerization of polynorbornene in solution was observed over a day when Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ was employed as a catalyst.

Table 2.14. Percentage of *cis*-norbornene obtained by reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with 20 equivalents of norbornene.

X	***% cis*-polymer**	
	after 10 min	**after 6 h**
O-t-Bu	64	65
OAd	78	78
OAr	85	84
OC_6F_5	44	27
CH_2-t-Bu	90	90

2.9.3. Ring-closing metathesis (RCM) reactions with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)

The ring-closing metathesis reaction of diallyl ether to dihydrofuran and ethylene (equation 2.11) was the first set of experiments undertaken to test the efficacy of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species as potential catalysts for ether substrates. Preliminary reactions performed at room temperature in a J-Young NMR tube with 13.6 mM concentration in benzene-d_6 showed two of the catalysts Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) to be rather efficient with >90% conversion in relatively small amount of time (< 30 min). Reactions with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(O-t-Bu) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) are relatively slow and do not go to completion, as expected since the metal center is likely to be less electrophilic. It is worth noting that Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ shows poor catalytic activity (27% in 20 h) with no improvement in another 24 h. The reaction profiles depicting percentage conversion to the ring-closed product monitored by ^{1}H NMR as a function of time for the ring-closing of diallyl ether with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(X) species are shown in Figure 2.7.



(2.11)

The effect of catalyst loading in the above reaction is given in Table 2.15. The most notable observation is the superior performance of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) species even at lower catalyst loadings (2.5 and 1.7 mol%) making it the best catalyst in this set of complexes under the conditions employed. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) appears to be relatively short-lived (most likely as a consequence of the significantly lower steric protection against bimolecular decomposition of intermediate alkylidenes than that in case of the bulkier OAr ligand) since a second aliquot of 20 equivalents of diallyl ether was not metathesized rapidly when added to the first reaction mixture. The catalytic performance for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) (OR = O-t-Bu, OAd) species goes down in terms of longer time periods taken to give poorer conversions when the catalyst loading is lowered.

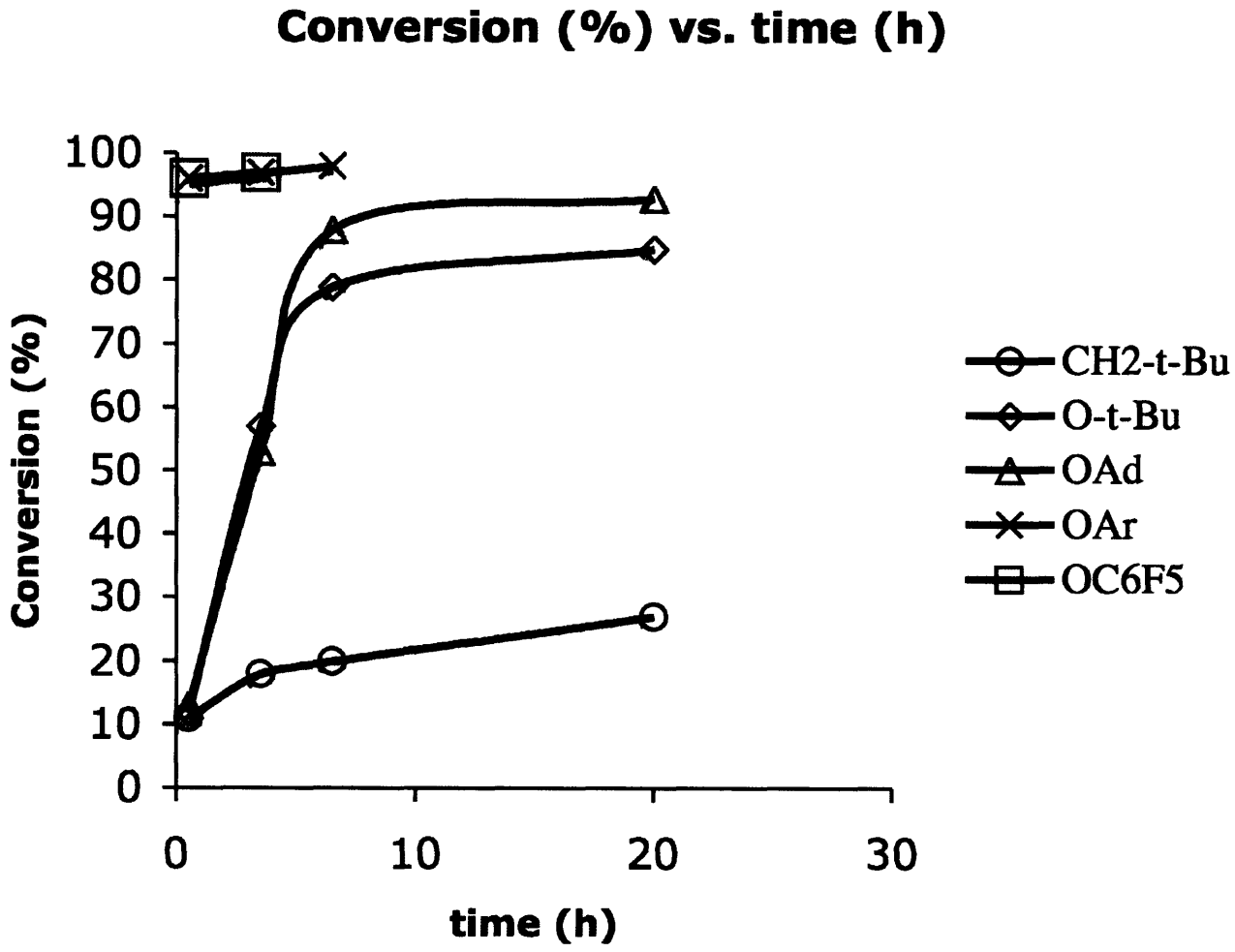


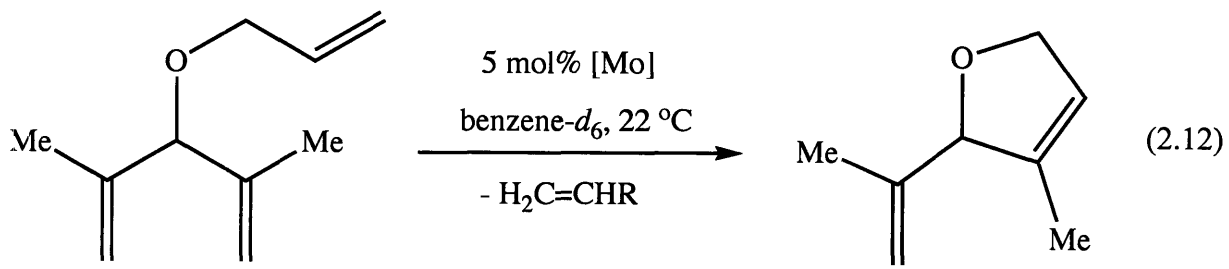
Figure 2.7. Reaction profiles for ring-closing metathesis reactions of diallyl ether with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(X) species.

Table 2.15. Effect of catalyst loading in the ring-closing metathesis of diallyl ether. [a]

OR	loading (%)	time (h)	conv (%)
O-t-Bu	5.0	6.5	79
	2.5	17.5	48
OAd	5	6.5	88
	2.5	17.5	52
OAr	5.0	0.1	92[b]
	2.5	0.2	92
	1.7	0.2	88
OC_6F_5	5.0	0.1	93[c]
	2.5	0.2	85

[a]All reactions were carried out in benzene-d_6 at room temperature using 0.23 M diallyl ether and monitored by proton NMR spectroscopy. The ethylene formed in the reaction was released only if a second aliquot was added. [b] An additional 20 equiv of diallyl ether were converted to product in 91% yield in 1.1 h. [c] An additional 20 equiv of diallyl ether were not metathesized over a period of 2.3 h.

Formation of 5-membered ether rings with increasing number of methyl groups on the resulting olefinic bond was investigated with two of the most reactive catalysts Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5). The products of the reactions shown in equations 2.12-2.14 are important intermediates in the fragrance industry.[30] A trisubstituted olefinic ring-closed product in extremely high conversion can be observed by the use of both the catalysts (equation 2.12, Table 2.16). The reaction done in benzene-d_6 (13 mM) at room temperature proceeds in less than ten minutes with a turnover number of 196 h^{-1}.

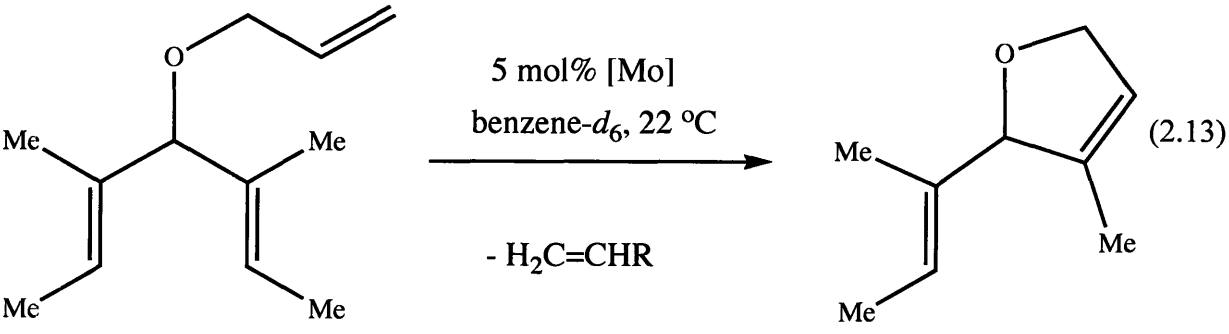


(2.12)

Table 2.16. Catalysis of the ring-closing metathesis reaction shown in equation 2.12 by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
OAr	0.1	93
OC_6F_5	0.1	73

Upon increasing the size of the substrate by introducing two extra methyl groups on the olefinic bond, as in substrate shown in equation 2.13, the bigger, more stable catalyst Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) gives 20% better conversion than Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) under identical conditions as described above for equation 2.12. The latter can be thought to offer better initial reactivity by forming the initial alkylidene. However, it apparently cannot sustain the difference in delay (compared to the substrate in equation 2.12) when a bulkier arm is required to fold in order to give the ring-closed product, and decomposes.

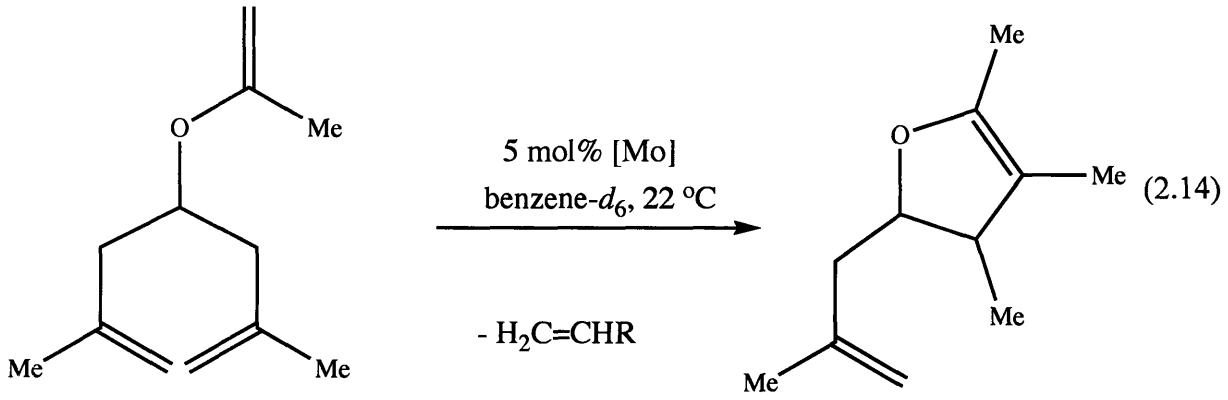


(2.13)

Table 2.17. Catalysis of the ring-closing metathesis reaction shown in equation 2.13 by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
OAr	0.1	98
OC_6F_5	0.1	98

Formation of tetrasubstituted olefins has traditionally been unsuccessfully applied via ring-closing metathesis reactions using molybdenum catalysts. Reaction (13 mM in benzene-d_6 at 22 °C) shown in equation 2.14 with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) proceeds to 30% completion in 1 h presumably due to decomposition of the intermediates. No reactivity was observed with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr), a result somewhat anticipated due to the presence of a bulky alkoxide group.



(2.14)

Table 2.18. Catalysis of the ring-closing metathesis reaction shown in equation 2.14 by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
OAr	24	N.R.
OC_6F_5	0.1	30[a]

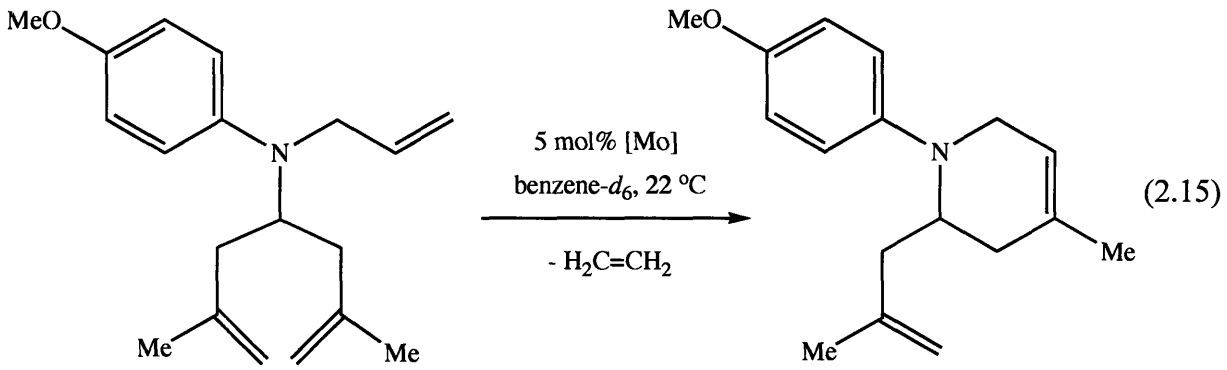
[a] No improvement was seen after 24 h.

The ring-closing metathesis reaction of *N,N*-diallyl tosylsulfonamide (equation 2.8, *vide ante*) is a benchmark experiment to evaluate the potential of a given set of complexes in catalyzing nitrogen containing substrates. All four of the catalysts enumerated before show decent to excellent conversions of *N,N*-diallyl tosylsulfonamide to N-tosyl-2,5-dihydropyrrole and ethylene at room temperature with 5 mol% loading of the catalyst in a 4.2 mM benzene-d_6 solution (Table 2.19).

Table 2.19. Ring-closing metathesis reaction of *N,N*-diallyl tosylsulfonamide by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
O-t-Bu	5.0	78
OAd	4.5	82
OAr	0.1	>99
OC_6F_5	0.1	>99

Carbocyclic amines form an important class of compounds due their ubiquitous availability in biological systems.[31] So far, only a few catalysts from the previous generations, have given excellent conversions (90-98%) with tertiary amines of the type shown in equation 2.15.[32] By including these new catalysts in the catalyst library, decent to excellent conversions have been observed. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) catalyze the reaction (13 mM in benzene-d_6) shown in equation 2.15 in under 10 min at 22 °C (Table 2.20). The less reactive complexes Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(O-t-Bu) also give decent yields under identical conditions, although they are ~10^3 slower than the former two complexes in carrying out the conversion, as been observed in the metathesis reactions of *cis*-2-pentene (*vide supra*).

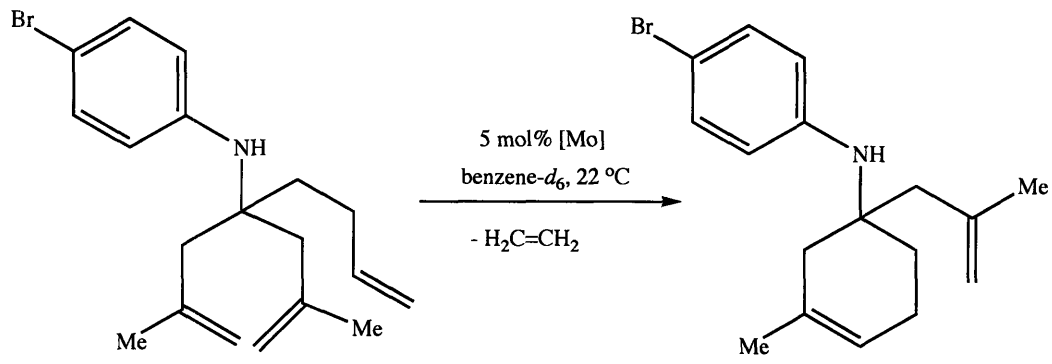


(2.15)

Table 2.20. Catalysis of the ring-closing metathesis reaction shown in equation 2.15 by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
O-t-Bu	40.0	82
OAd	40.0	73
OAr	0.1	>99
OC_6F_5	0.1	>99

Secondary amines containing NH group are have low propensity to undergo ring-closing metathesis by the majority of the catalysts available, primarily due to catalyst decomposition by protonation of the alkoxide group on the catalyst, and by strong coordination of the amine nitrogen atom to the metal, thereby blocking the path of the substrate.[33] Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species yield encouraging results (Table 2.21) for reactions depicted in equation 2.16. While the reaction (performed using 13 mM catalyst concentration in benzene-d_6 at room temperature) with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) proceeds rapidly (under 10 min) to 85% completion, only a marginal improvement is seen over 18 h, with no change thereafter.

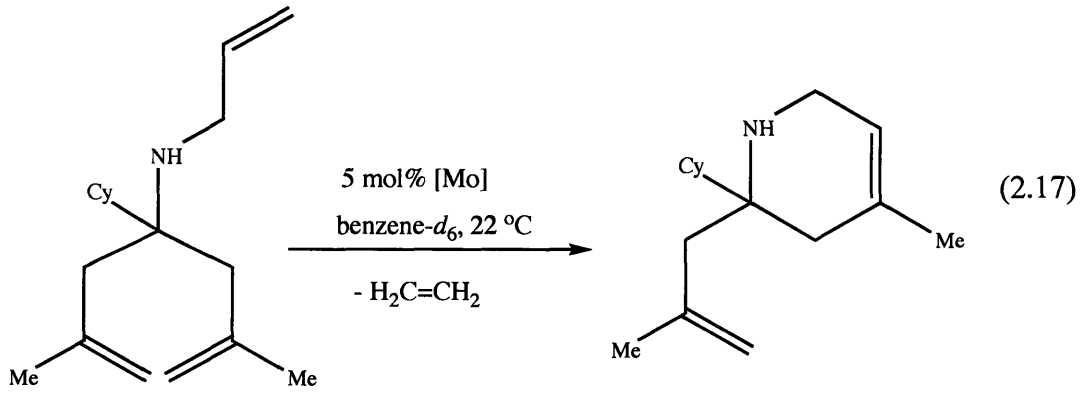


(2.16)

Table 2.21. Catalysis of the ring-closing metathesis reaction shown in equation 2.16 by Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
O-t-Bu	40.0	89
OAd	40.0	66
OAr	0.1, 18	85, 92
OC_6F_5	0.1	>99

Alex Cortez (Hoveyda Group) performed a side by side study of the room temperature reaction in benzene-d_6 (equation 2.17) with two of the catalysts (OR = OAr, OC_6F_5) prepared in course of the current work, and Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2$] complex, which is the most efficient catalyst known in the molybdenum family of catalysts (Table 2.22). The latter gives only 76% of the product in the reaction mixture as opposed to the full conversion achieved by the new complexes of the type Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR).



(2.17)

Table 2.22. Comparison of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$] for the ring-closing metathesis reaction shown in equation 2.17.

[Mo]	Time (h)	% Conversion
Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr)	12	>99
Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)	12	>99
Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]	12	76

2.10. Wittig-type reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)

The alkylidene species Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) undergo Wittig-type reaction[15] to give PhC=CH-t-Bu when they are allowed to react with one equivalent of benzaldehyde in 80 mM solution of benzene-d_6 at room temperature (Table 2.23), although the reaction rates seem to be slower than those observed for the bisalkoxide catalysts[1(c)]. In comparison with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes, the above reaction with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ goes to only 20% completion in 4h.

Table 2.23. Wittig-type reactions of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes.

OR	Time (h)	% Conversion
O-t-Bu	0.1, 1.0, 4.0	49, 60, 100
OAd	0.1, 1.0, 4.0	53, 60, 86
OAr	0.1, 1.0, 4.0	45, 59, 100
OC_6F_5	0.1	100

2.11. Surface-supported catalysis

The bimolecular decomposition of smaller alkylidene (for example, methylidene) intermediates that are formed during a given catalytic cycle provides a major conduit for the loss of catalyst activity[1(c),10(a)] (also see Appendix A). Therefore, a significant amount of work by various research groups has been directed towards improving the practical applications (including those in combinatorial synthesis) of molybdenum-based olefin metathesis catalysts,

more specifically addressing the issues concerning the robustness, efficacy, recyclability, ease of removal from reaction mixtures, and low contamination of the desired products by metal residue.[34]

Initial efforts made in this direction have primarily relied upon site-isolation of the metal center to prevent bimolecular decomposition pathways by immobilizing the catalyst on a polymer support.[35,36,37] Figure 2.8 depicts few of the relevant examples employing various types of polymer support. In several cases of reactions involving ring-closing and ring-opening cross-metathesis processes, the catalyst supported on a polystyrene resin PS-1[35] (Figure 2.8) offered virtually comparable performance in terms of conversion and enantioselectivity of the product obtained. In some instances, increasing the amount of solvent in the reaction mixture improved the activity of the polymer bound catalyst by allowing more diffusion of the substrate molecules to the metal center in the polymer resin. These catalysts were recyclable in some reactions. For example, the reaction shown in equation 2.18 is catalyzed efficiently (98% conversion, 98% ee) with up to 2 cycles. The third cycle although gives decent enantioselectivity (89% ee), the activity considerably goes down (55% conversion) compared to the first two cycles. This has been attributed to the degradation of the solid support, as the filtered reaction mixtures contain increasing amounts of the oligomeric fragments of the resin as well as more loss of the metal after each cycle.

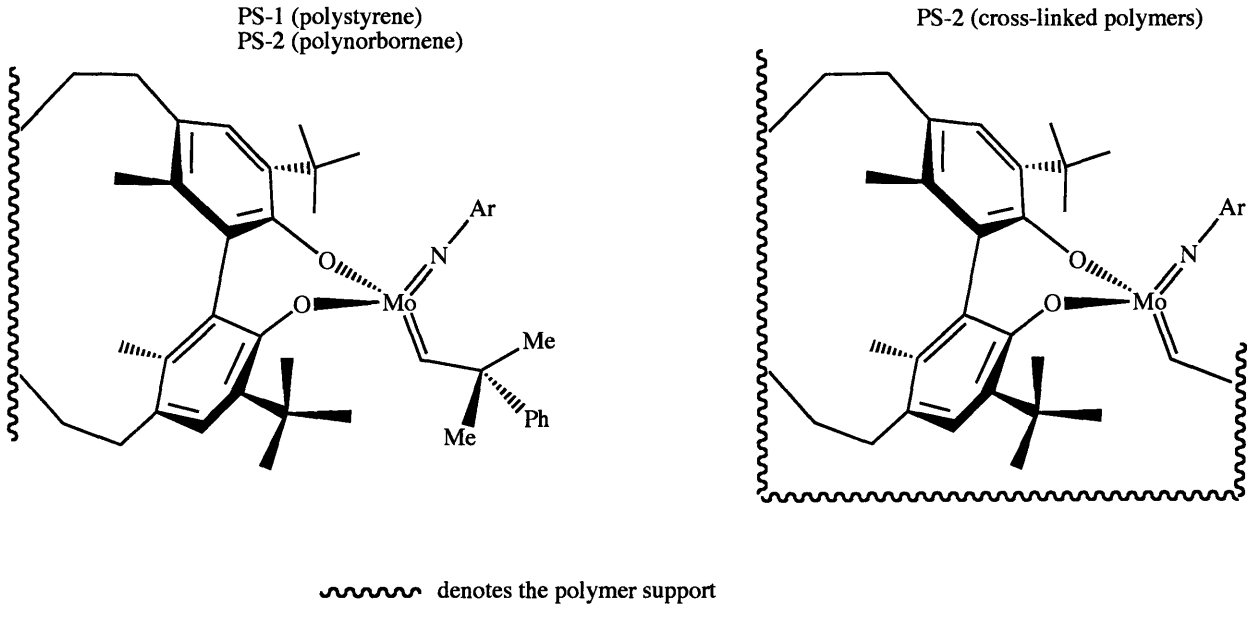
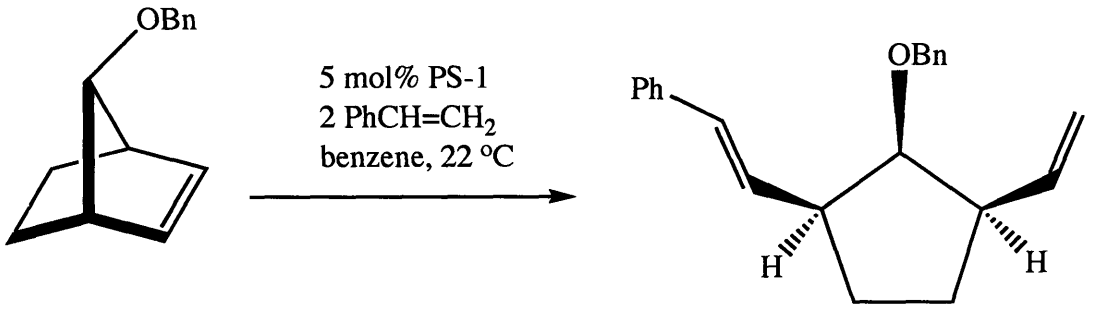


Figure 2.8. Examples of polymer supported catalysts.

The increased activity of the PS-2 system[36] developed by Buchmeiser for several ring-closing reactions is related to the increased swelling and flexibility of the polynorbornene support that allows for higher substrate diffusion. PS-3[37] is an example of a catalyst that is immobilized on a cross-linked polymer backbone via both the diolate as well as the alkylidene groups. The catalyst performance in this case was found to be dependent (*inter alia*) upon the level of cross-linking. When sterically less demanding imido groups such as 1-adamantylimido or 2,6-dichlorophenylimido were used, the resin support was found to be degraded by the metal center.



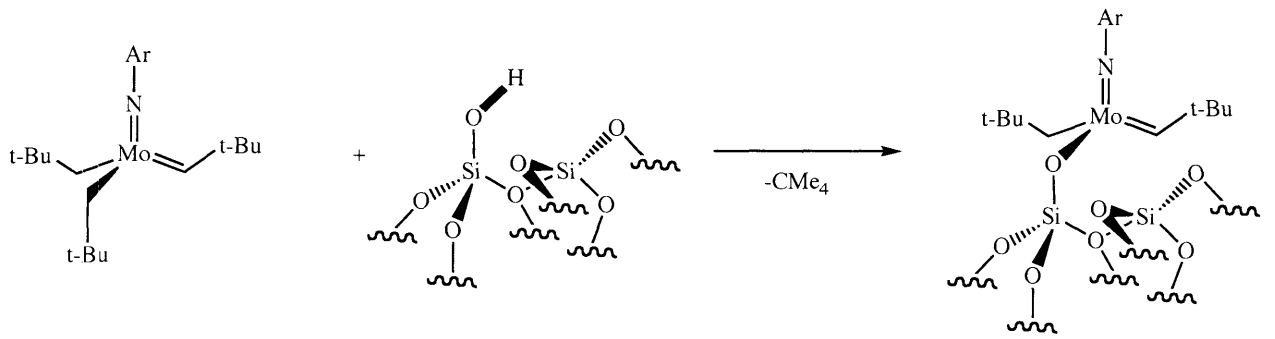
(2.18)

The research on silica-supported catalysis resulted from a search for an alternate solid support that would lead to an enhanced performance of the catalytic system along with providing a better understanding of the principles of heterogeneous catalysis vis-à-vis that observed for the molecular analogs in a homogeneous phase.[8] The choice of silica support is dictated by various factors. One, the number of silanol groups (therefore the surface area available for molecule immobilization) in a given sample of silica can be controlled in a relatively well-defined fashion depending upon the temperature at which the sample is heated under vacuum. For example, dehydroxylation processes employing 200, 500, and 700 °C on commercially available silica under reduced pressures result in the availability of 2.6, 1.2, and 0.7 per nm^2 hydroxyl groups respectively. Compared to other supports (like alumina), silica offers low acidity that is comparable to several alcohols that are commonly used in the molecular catalysts. In addition to being relatively homogenous with respect to the silanol groups that are present on the surface, a decent number of silica-analogs like polyhedral oligomeric silsequioxanes (POSS) and other simpler trialkylsilanols are available to be used as molecular models of the surface-supported

catalysts. Also, there are a number of spectroscopic and crystallographic tools available to probe these surface systems.

The early work concerning silica impregnation by metal complexes was done utilizing tantalum and rhenium. Notably, a surface bound rhenium catalyst [(Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf})] exhibited better activity than all the molecular catalysts of rhenium utilized in homogeneous medium, and comparable activity with respect to molybdenum complexes. Therefore, the better performance of the Mo-based catalysts compared to the Ta and Re complexes in homogeneous catalysis prompted the need to make robust, yet reactive molybdenum catalysts that could be linked to a silica support. The availability of a suitable precursor Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ and partially dehyroxylated silica at 700 °C, $SiO_{2-(700)}$ facilitated a collaboration with Dr. Christophe Copéret's in the Basset group at CNRS, Lyon. Since the surface of $SiO_{2-(700)}$ can be compared to a bulky monodentate ligand, the resulting supported catalyst for olefin metathesis reactions would be expected to be relatively well-defined and well behaved.

The room temperature reaction of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ in pentane with a disk of $SiO_{2-(700)}$ results in the formation of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) along with evolution of 1 equivalent of neopentane (equation 2.19). The surface organometallic species can then be dried under vacuum and analyzed spectroscopically and by combustion analysis. The yellow solid thus obtained contains 1.7-2.1 $\%_{wt}$ of Mo, which corresponds to 0.17-0.21 mmol of $Mo.g^{-1}$ of solids in agreement with the consumption of most surface silanols. Moreover, the materials contain in average 23 ± 3 C and 1.0 ± 0.3 N/grafted Mo, which is consistent with the proposed structure of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) as drawn in equation 2.19, for which 22 C/Mo and 1 N/Mo are expected. An IR experiment showed a complete disappearance of the peaks associated with the surface silanols (3747 cm^{-1}). The unambiguous assignments of resonances for the silica-supported complex in the NMR experiments was made possible by preparing the α-carbon ^{13}C-labeled species Mo(NAr)(*CH-t-Bu)(*CH_2-t-Bu)(OSi_{surf}) from Mo(NAr)(*CH-t-Bu)(*CH_2-t-Bu)$_2$ and $SiO_{2-(700)}$.



(2.19)

Two of the molecular species representing structural models for isolated molybdenum sites on silica are shown in Figure 2.9. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{POSS})(OSi_{POSS} = (*c*-$C_5H_9)_7Si_7O_{12}OSi$) was prepared by Frédéric Blanc at CNRS, Lyon by the treatment of $Si_{POSS}OH$[8] with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ in benzene or pentane.

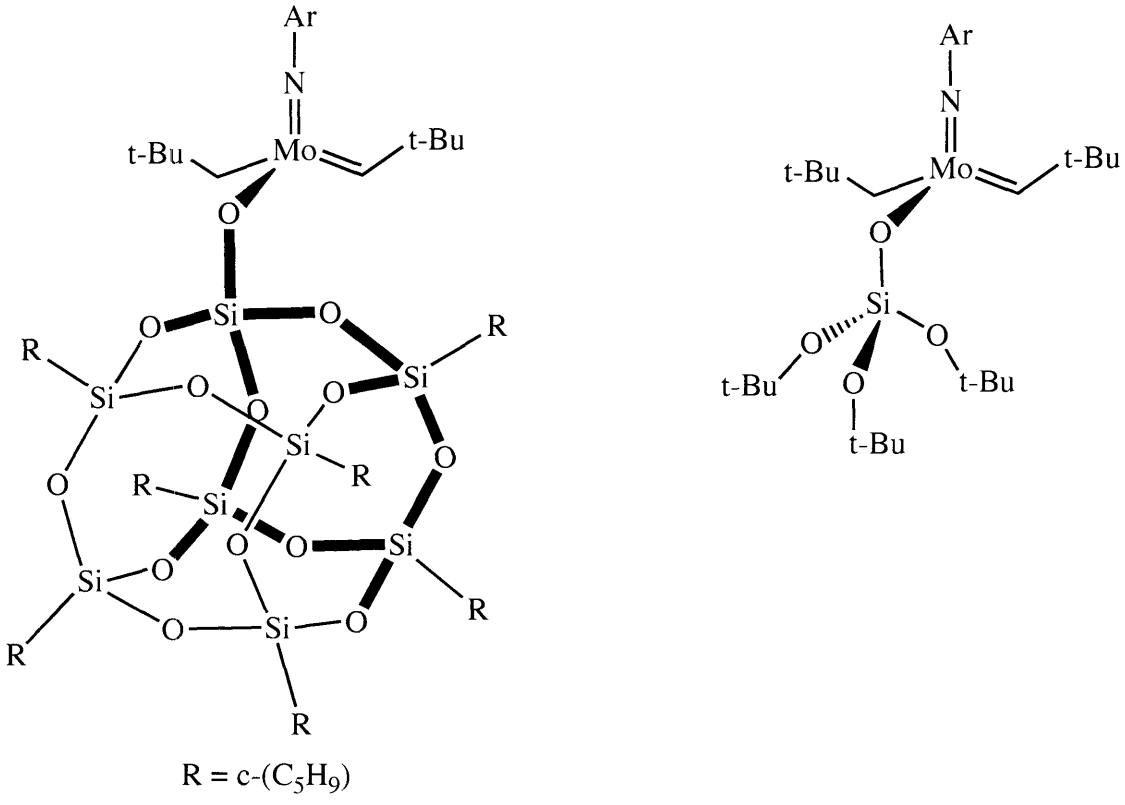


Figure 2.9. Molecular models for silica-supported molybdenum catalysts.

Ring-closing metathesis of diallyl ether with 5 mol% Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) in benzene-d_6 in a J-Young NMR tube at room temperature was very slow compared (96% conversion in 5 h) to two of the most reactive molecular catalysts Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) and Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) (cf. Table 2.15). The sluggishness of the reaction is expected due its heterogeneous nature. However, the performance of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) deteriorated considerably in the second cycle when only 18% conversion to the ring-closed product was seen in 5 h with no improvement over 24 h. The loss of catalytic activity could in principle be attributed to the reaction of the propagating alkylidene fragments on silica with ethylene (generated as a byproduct in the reaction) to give metallacycles similar to what has been observed for the molecular bisalkoxide catalysts[10(c)] that eventually lead to formation of catalytically inactive ethylene adducts of the type Mo(NAr)(CH_2-t-Bu)(OSi_{surf})(H_2C=CH_2). However, this speculation has yet to be verified. The degradation of the catalyst can be visually observed by the change in color from yellow to red. It is generally assumed that the metal site isolation obtained on the silica surface causes the metal centers to be ~ 10 Å apart, thereby preventing bimolecular decomposition processes leading to formation of metallic dimers (this will be discussed in Appendix A).

On the other hand, the molecular analog Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$] shows excellent activity for ring closing a variety of ether- and amine-based substrates (92-99% conversions) at room temperature under condition described in Section 2.9.3. A comparison of the reactivity of the silica-impregnated catalyst Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) with the Mo(NAr)(CH-t-Bu)(CH_2-t-Bu) (OSi_{POSS}) is given in Table 2.24. This work was carried out with Frédéric Blanc at CNRS, Lyon. When Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) is treated with 1350 equiv. of propene at 25 °C in a batch reactor, the equilibrium is reached within 20 min with an initial rate (TOF) of 1.0 mol/mol Mo/s. Moreover, roughly 0.7 equiv of a 2.7:1 mixture of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene is formed, which shows that initiation is almost quantitative in agreement with a well-defined system. The self-metathesis of 0.5 M solutions of 1-octene and ethyl oleate in toluene in the presence of 1% of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) gives the equilibrated mixture in 10 and 60 min at room temperature, respectively. The respective initial rates are 0.06 and 0.04 mol/mol Mo/s, which is very close to those obtained for Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf})[38]. The initial rates with the corresponding molecular complex Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{POSS}) are similar, but the reaction times

needed to reach the same conversion (thermodynamic equilibrium) are much longer, which shows that decomposition is faster in this case.

Table 2.24. Comparison of surface-supported catalysts with a molecular analog.[a]

Olefins	MoNAr(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf})		Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{POSS})	
	TON_{max}[b] (Time/min)	TOF[c]/s^{-1}	TON_{max}[b] (Time/min)	TOF[c]/s^{-1}
Propene[d]	2000 (300)	4.2	-	-
1-octene[e]	47 (10)	0.06	47 (60)	0.06
Ethyl oleate[e]	45 (60)	0.04	47 (1440)	0.03
Diethyl diallylmalonate[e]	50 (20)	0.05	30 (60)	0.03

[a] All reactions were monitered by gas chromatography. [b] Maximum Turn Over Number obtained under those conditions in mol of substrate per mol of Mo. [c] Initial Turn Over Frequency in mol of substrate per mol of Mo per min at 5 min. [d] Experimental conditions : 0.015 % Mo, 25 °C, *neat*. [e] Experimental conditions : 1 % Mo, 25 °C, Toluène, under Ar atmosphere.

The tungsten analogs of the supported catalysts are considerably less active than the molybdenum system, as would be expected from the comparison of Mo- and W-based homogeneous catalysts. For example, the metathesis reaction of propene and ring-closing of diallyl ether with W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) do not go to completion, the conversions being 30% and 57% for the two substrates respectively in longer times than have observed for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf})[22].

CONCLUSIONS

The present work details the synthesis of complexes of the type $Mo(NAr)(CHR')(CH_2R')_2$ and their reactions with alcohols to give either M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) or $M(NAr)(CH_2\text{-t-Bu})_3(OR)$. The latter can be transformed into the former upon heating. The reaction conditions, using alcohols in solvents, or under neat conditions drastically affects the outcome of the reaction depending upon whether the alcohol adds to the M=C or M-C bond. In general, alcohols with higher pK_a's add preferentially across the Mo-C bond, although it is not clear why this should be the case. The role of a bulky imido group like 2,6-diisopropylimido in stabilizing the metal center cannot be underestimated considering that Mo(NR)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with smaller 1-adamantylimido are obtained as oils and are prone to decomposition.

While $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ species are virtually inactive for metathesis, M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes can be highly active. Mo(NR)(CH-t-Bu)(CH_2-t-Bu)(OR) species have demonstrated encouraging reactivity in different types of metathesis reactions towards a variety of substrates. A comparative experiment of a few of these complexes with a $Mo(NAr)(CHR)(OR)_2$ catalyst (Table 2.22) suggests that the new catalysts can offer good results (at least in certain reactions) vis-à-vis the previous generation of catalysts.

Most of the fluxional metallacyclobutane intermediates that can be thought of as intermediates in these reactions are "electronically" unsymmetric at the metal, i.e., unsymmetric as a consequence of different elements being present in α positions, not unsymmetric merely as a consequence of asymmetry in the ligands themselves, as in a chiral diolate derivative. This stands in contrast to both trigonal bipyramidal (TBP) and square pyramidal (SP) metallacyclobutane complexes derived from bisalkoxide species.[14] An electronically unsymmetric metallacyclobutane may more rapidly eject an olefin than one that is not electronically unsymmetric.

Silica-supported catalysts can be facilely prepared from $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})_2$ species. The surface complex M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) and its molecular analogs, are electronically very similar as is indicated both from their comparable NMR data and initial rates in olefin metathesis. Nonetheless, the supported catalyst has greater life time under catalytic conditions, which shows that the effect of site isolation prevents some deactivation pathways such as dimerization of reactive intermediates.

Relevant to the results described here are some recent DFT (B3PW91) calculations on systems of the type Re(C-t-Bu)(CH-t-Bu)(X)(Y), which are isoelectronic with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) species when X = alkyl and Y = alkoxide.[39] A key step in the reaction of Re(CR)(CHR')(alkyl)(alkoxide) species with an olefin is a distortion toward a trigonal monopyramid in which the alkyl ligand is in the axial position. This distortion prepares the metal for a weak interaction with an olefin, and facile formation of a heavily distorted TBP metallacyclobutane intermediate with an "axial" alkylidyne and "axial" alkoxide. When both X and Y are alkoxides, then the barrier for addition of the olefin and conversion to the metallacycle is higher by several kilocalories. When both X and Y are alkyls the barrier is higher still. These calculations help explain why addition of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)$_2$ to silica(700) yielded a well-defined Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(OSi_{surf}) species, which has an unusually high metathesis activity[8], while homogeneous Re(C-t-Bu)(CH-t-Bu)(OR)$_2$ species are relatively poor metathesis catalysts.[40] Although bimolecular decomposition reactions are essentially eliminated on the surface at the mild temperatures employed, it seems plausible that there is not a linear relationship between the electron-withdrawing ability of the two atoms attached to the metal and reactivity, and that "distorted" and, in particular, *unsymmetric* (at the metal) species have shallower energy surfaces leading to and from a metallacyclobutane intermediate. This is potentially an important new insight in olefin metathesis reactions with well-defined species.

EXPERIMENTAL SECTION

General. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. The glassware, including NMR tubes were flame- and/or oven-dried prior to use. Ether, pentane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed thrice by freeze-pump-thaw technique. Dichloromethane was distilled from CaH_2 under N_2. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^1H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using a Varian Mercury (^1H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz) or a Varian Inova (^1H 500 MHz, ^{13}C 125 MHz) spectrometers and referenced to the residual protio

solvent resonances or external C_6F_6 (-163.0 ppm). Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Mo(NAr)(CH-t-Bu)$(OTf)_2$(dme) was prepared as described in the literature.[1(c)] Neopentylmagnesium chloride and neophylmagnesium chloride were titrated against propanol in a THF solution using 1,10-phenanthroline as an indicator immediately prior to use. All other chemicals were procured from commercial sources and used as received.

Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$.[41] A solution (23.5 ml) of 1.85 M neopentylmagnesium chloride solution in ether was added drop-wise to a prechilled solution (at -27 °C)of 15.88 g (21.76 mmol) of Mo(NAr)(CH-*t*-Bu)$(OTf)_2$(dme) in 270 ml ether. The color changed from yellow to deep red-orange as a precipitate formed. The mixture was stirred for 12 h, ether was removed *in vacuo*, and the residue was extracted with pentane. The pentane extract was filtered through Celite and the pentane was removed *in vacuo* to afford 9.75 g of a red powder (93% yield) that was pure enough for further reactions: ^{1}H NMR (C_6D_6) δ 9.50 (s, 1, C*H*CMe_3, J_{CH} = 108 Hz), 7.05 (br s, 3, Ar*H*), 3.99 (sept, 2, C*H*Me_2), 2.76 (d, 2, CH*H*CMe_3), 1.30 (d, 12, CH*Me*$_2$), 1.22 (s, 18, CH_2C*Me*$_3$), 1.17 (s, 9, CHC*Me*$_3$), 0.62 (d, 2, C*H*HCMe_3); ^{13}C NMR (C_6D_6) δ 255.0 (*C*HCMe_3), 154.2 (C_{ipso}), 144.8 (C_{ortho}), 127.2 (C_{para}), 123.5 (C_{meta}), 77.9 (*C*H_2CMe_3), 47.1 (CH*C*Me_3), 34.8 (CH_2C*Me*$_3$), 34.1 (CH_2*C*Me_3), 32.7 (CHC*Me*$_3$), 29.2 (*C*HMe_2), 24.9 (CH*Me*$_2$). Anal. Calcd for $C_{27}H_{49}NMo$: C, 67.05; H, 10.21; N, 2.90; Mo, 19.84. Found: C, 66.79; H, 10.08; N, 3.18; Mo, 20.04.

Mo(NAr)(CHCMe$_2$Ph)$(CH_2$-t-Bu$)_2$.[41] A 4.27 mmol reaction was carried out in a manner virtually identical with that above for Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ to give 1.52 g (65%) of the product as a red-orange powder: ^{1}H NMR (C_6D_6) δ 9.69 (s, 1, C*H*CMe_2Ph), 7.44 (d, 2, CHCMe_2*Ph*), 7.16 (m, 2, CHCMe_2*Ph*), 7.05 (br s, 3, Ar*H*), 3.97 (sept, 2, C*H*Me_2), 2.71 (d, 2, CH*H*CMe_3), 1.54 (s, 6, CHC*Me*$_2$Ph), 1.26 (d, 12, CH*Me*$_2$), 1.14 (s, 18, CH_2C*Me*$_3$), 0.74 (d, 2, C*H*HCMe_3); ^{13}C NMR (C_6D_6) δ 252.8, 154.2, 149.5, 145.0, 128.7, 127.4, 126.6, 126.5, 123.6, 78.3, 52.9, 34.5, 33.9, 32.1, 28.8, 24.5. Anal. Calcd for $C_{32}H_{51}NMo$: C, 70.43; H, 9.42; N, 2.57. Found: C, 70.25; H, 9.27; N, 2.56.

Mo(NAr)(CH-t-Bu)(CH_2CMe_2Ph)$_2$.[41] This complex was obtained as a deep red oil from the reaction between Mo(NAr)(CH-*t*-Bu)(OTf)$_2$(dme) and neophylmagnesium chloride in a procedure analogous to the preparation of Mo(NAr)($CHCMe_2Ph$)(CH_2-t-Bu)$_2$:. ^{1}H NMR (C_6D_6) δ 8.85 (s, 1, C*H*CMe_3), 7.38- 7.16 (overlapping resonances, 10, $CHCMe_2$*Ph*), 7.07 (br s, 3, Ar*H*), 4.00 (sept, 2, C*H*Me_2), 2.65 (d, 2, CH*H*CMe_2Ph), 1.44- 0.99 (33, $CHCMe_2Ph$, $CHMe_2$, CH_2CMe_3), 0.63 (d, 2, C*H*HCMe_2Ph); ^{13}C NMR (C_6D_6) δ 259.4, 154.2, 152.8, 149.7, 145.1, 129.1, 127.3, 126.6, 126.4, 123.7, 77.1, 46.6, 40.6, 34.7, 34.1, 32.9, 32.1, 31.8, 29.6, 28.6, 24.6, 24.1.

Mo(NAr)($CHCMe_2Ph$)(CH_2CMe_2Ph)$_2$. 1.2 g (1.52 mmol) of Mo(NAr)($CHCMe_2Ph$)(OTf)$_2$(dme) in 35 ml ether at -20 °C was treated with 4.5 ml of a 0.67 M solution of neophylmagnesium chloride in ether. After the workup as described above for similar complexes, the desired species was obtained as deep-red oil. ^{1}H NMR (C_6D_6) δ 9.067 (s, 1, C*H*CMe_2Ph), 7.302-7.068 (overlapping resonances, 18, $CHCMe_2$*Ph*, CH_2CMe_2*Ph*, Ar*H*), 3.97 (sept, 2, C*H*Me_2), 2.62 (d, 2, CH*H*CMe_2Ph), 1.40- 1.13 (30, $CHCMe_2Ph$, $CHMe_2$, CH_2CMe_2Ph), 0.67 (d, 2, C*H*HCMe_2Ph)

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[$OCH(CF_3)_2$].[41] Perfluoroisopropanol (97 μl, 0.91 mmol, 2.2 equiv) was added to a solution of 200 mg (0.41 mmol) of Mo(NAr)(CH-t-Bu)(CH_2-*t-Bu*)$_2$ in 5 mL toluene. The reaction mixture was stirred for 16 h at room temperature and stored at -20 °C to afford red-orange crystals in 52% yield (124 mg): ^{1}H NMR (C_6D_6) δ 11.80 (s, 1, C*H*CMe_3, J_{CH} = 116 Hz), 6.99 (m, 3, Ar*H*), 4.55(sept, 1, $(CF_3)_2CHO$), 3.73 (sept, 2, C*H*Me_2), 2.42 (d, 1, CH*H*CMe_3, J_{CH} = 13 Hz), 2.16 (d, 1, C*H*HCMe_3), 1.27 (d, 6, $CHMe_2$)1.24 (d, 6, $CHMe_2$), 1.18 (s, 9, CH_2CMe_3), 1.11 (s, 9, $CHCMe_3$); ^{13}C NMR (C_7D_8) δ 284.5, 153.2, 146.5, 123.7, 58.7, 48.1, 33.7, 32.7, 31.9, 31.4, 30.5, 28.4, 24.6, 23.8; ^{19}F NMR (C_6D_6) δ -74.97 (CF_3), -75.17 (CF_3). Anal. Calcd for $C_{25}H_{39}NOF_6Mo$: C, 51.81; H, 6.78; N, 2.42. Found: C, 51.64; H, 6.79; N, 2.36.

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd).[41] Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (520 mg, 1.07 mmol) was placed in a 25 ml scintillation vial and 1-adamantanol (163 mg, 1.07 mmol) and 6 ml of pentane were added at 22 °C. The reaction mixture was stirred overnight at room temperature.

Removing the volatiles *in vacuo* afforded an orange-yellow powder that could be washed with cold pentane to obtain a fine yellow powder; yield 502 mg (83%): ^{1}H NMR (C_6D_6) δ 11.71 (s, 1, C*H*CMe$_3$, J_{CH} = 115 Hz), 7.07 (br s, 3, Ar*H*), 3.99 (sept, 2, C*H*Me$_2$), 2.38 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.12 (d, 1, C*H*HCMe$_3$), 2.05 (br s, 3, C*H*), 1.92 (m, 6, C*H*$_2$), 1.51 (s, 6, C*H*$_2$), 1.29 (m, 30, CH*Me*$_2$, CH$_2$C*Me*$_3$, CHC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 275.7, 153.2, 145.3, 126.6, 123.6, 79.0, 52.7, 46.7, 36.7, 34.5, 32.2, 31.9, 29.2, 24.9, 24.1. Anal. Calcd for $C_{32}H_{53}NOMo$: C, 68.18; H, 9.48; N, 2.48. Found: C, 68.03; H, 9.32; N, 2.55.

Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OCMe$_3$).[41] Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ (1g, 2.07 mmol) was placed in a 100 ml heavy walled pressure vessel along with a magnetic stirrer and 1.1 equivalents of t-BuOH (169 mg, 2.28 mmol) and 10 ml toluene were added to it at 22 °C. Stirring the reaction mixture at 80 °C for 2 h caused the color of the solution to change from red to dark yellow-orange. Removing toluene *in vacuo* resulted in a dark orange oil that was dissolved in minimum amount of pentane and stored at -20 °C to give 0.97 g (96%) of a yellow-brown powder: ^{1}H NMR (C_6D_6) δ 11.63 (s, 1, C*H*CMe$_3$, J_{CH} = 115 Hz), 7.05 (br s, 3, Ar*H*), 3.96 (sept, 2, C*H*Me$_2$), 2.38 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.09 (d, 1, C*H*HCMe$_3$), 1.35 (s, 9, OC*Me*$_3$), 1.29 (d, 12, CH*Me*$_2$), 1.26 (s, 9, CH$_2$C*Me*$_3$), 1.21 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 275.9, 153.1, 145.3, 126.6, 123.5, 79.8, 52.7, 46.7, 34.5, 32.9, 32.2, 29.2, 24.9, 24.1. Anal. Calcd for $C_{26}H_{47}NOMo$: C, 64.31; H, 9.76; N, 2.88. Found: C, 64.38; H, 9.69; N, 2.81.

Alternatively when a pentane solution of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ and 1.1 equivalent of t-BuOH is stirred for 12 h the product is obtained quantitatively as an orange powder.

Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OAr).[41] To Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ (500 mg, 1.03 mmol) in 5 ml pentane was added 210 µl (203mg, 1.13mmol) of 2,6-diisopropylphenol and the reaction was stirred for 12 h at room temperature. After removing the solvent, a red waxy material was obtained. This waxy material was dissolved in a minimum amount of pentane and the solution was stored at -20 °C; a red orange solid (575mg) was filtered off (95% yield): ^{1}H NMR (C_6D_6) δ 11.99 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 7.07 (d, 2, Ar*H*), 7.00 (t, 1, Ar*H*), 6.97 (br s, 3, Ar*H*), 3.55 (sept, 4, C*H*Me$_2$), 2.72 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.35 (d, 1, C*H*HCMe$_3$), 1.34 - 1.13 (overlapping signals, 42, CH*Me*$_2$, CH$_2$C*Me*$_3$, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 277.7,

159.1, 153.4, 145.6, 137.2, 127.3, 123.8, 123.5, 122.4, 59.5, 47.7, 33.9, 32.2, 30.0, 28.4, 24.7, 24.0, 23.2. Anal. Calcd for $C_{34}H_{55}NOMo$: C, 69.24; H, 9.40; N, 2.37. Found: C, 69.26; H, 9.29; N, 2.32.

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$].[42,43] (t-BuO)$_3$SiOH (437 mg, 1.65 mmol) was added to a solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ (800 mg, 1.65 mmol) in 5 ml pentane at 22 °C. Stirring the resulting brown-yellow solution for 15 h followed by removing volatiles in vacuo afforded a yellow brown solid which could be recrystallized from hexamethyldisiloxane at room temperature (82% yield). ^{1}H NMR : δ 12.28 (s, 1H, C*H*C(CH$_3$)$_3$), 7.06 (s br, 3H, Ar*H*), 3.94 (sept, 2H, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7 Hz), 2.69 (d, 1H, C*H*HC(CH$_3$)$_3$, $^2J_{HH}$ = 13 Hz), 2.26 (d, 1H, CH*H*C(CH$_3$)$_3$, $^2J_{HH}$ = 13 Hz), 1.45 (s, 27H, OSiC(C*H*$_3$)$_3$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7 Hz), 1.31 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7 Hz), 1.30 (s, 9H, CH$_2$C(C*H*$_3$)$_3$), 1.24 (s, 9H, CHC(C*H*$_3$)$_3$). ^{13}C NMR : δ 282.5 (*C*HC(CH$_3$)$_3$, $^1J_{CH}$ = 116 Hz), 153.1 (C$_{ipso}$), 145.8 (C$_{ortho}$), 127.1 (C$_{para}$), 123.7 (C$_{meta}$), 73.0 (OSi*C*(CH$_3$)$_3$), 57.2 (*C*H$_2$C(CH$_3$)$_3$), 47.1 (CH*C*(CH$_3$)$_3$), 34.3 (CH$_2$C(*C*H$_3$)$_3$, 32.3 (OSiC(*C*H$_3$)$_3$), 31.9 (CHC(*C*H$_3$)$_3$, 29.3 (*C*H(CH$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR : δ_{Si} = -101.63 (Q^4). Anal. Calcd for $C_{34}H_{65}NO_4SiMo$: C, 60.42; H, 9.69; N, 2.07. Found: C, 60.86; H, 9.52; N, 2.04.

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OCMe(CF_3)$_2$]. 200 mg (0.41 mmol) of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)$_2$ in 3 ml toluene was treated with 1 equivalent 83 mg of HOCMe(CF_3)$_2$ and the reaction mixture was heated to 60 °C for 8 h in a heavy walled pressure vessel. Complete removal of volatiles in vacuo afforded the desired compound as a red oily material. ^{1}H NMR (C_6D_6) δ 11.90 (s, 1, C*H*CMe$_3$, J_{CH} = 117 Hz), 6.99 (m, 3, Ar*H*), 3.78 (sept, 2, C*H*Me$_2$), 2.43 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.15 (d, 1, C*H*HCMe$_3$), 1.73 (s, 3, OC*Me*(CF$_3$)$_2$), 1.29 (overlapping peaks, 30, CH*Me*$_2$, CH$_2$C*Me*$_3$, CHC*Me*$_3$); ^{13}C NMR (toluene-d_8) δ 283.6, 153.1, 146.4, 128.1, 123.7, 58.6, 48.0, 33.8, 32.7, 31.9, 31.5, 29.4, 28.3, 24.9, 23.8, 20.1; ^{19}F NMR (C_6D_6) δ -78.5, -78.9.

Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5).[41] A solution of Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5) (1.4 g, 2.10 mmol) in 11 ml toluene was stirred and heated at 60 °C for 8 h in a heavy walled pressure vessel. The light yellow color of the solution darkened. Toluene was removed *in vacuo* to leave an orange-yellow solid. Washing this solid with cold pentane over a fine porosity frit

gave 1.01 g (81%) of a pale yellow powder: ^{1}H NMR (C_6D_6) δ 12.07 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 6.99 (m, 3, Ar*H*), 3.75 (sept, 2, C*H*Me$_2$), 2.61 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.22 (d, 1, C*H*HCMe$_3$), 1.24 (d, 12, CH*Me*$_2$), 1.22 (s, 9, CH$_2$C*Me*$_3$), 1.08 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 286.5, 153.3, 146.5, 123.8, 60.4, 48.2, 33.6, 32.8, 31.2, 30.7, 29.9, 24.5, 23.8; ^{19}F NMR (C_6D_6) δ -160.83 (d, 2), -165.07 (t, 2), -169.83 (t, 1). Anal. Calcd for $C_{28}H_{38}NOF_5Mo$: C, 56.47; H, 6.43; N, 2.35. Found: C, 56.28; H, 6.28; N, 2.40.

Mo(NAr)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$].[41] A few drops of neat (CF$_3$)$_2$CHOH were added to 20 mg (0.04 mmol) of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ at 22 °C; a yellow suspension formed immediately. The reaction mixture was stirred for 10 min and the excess alcohol removed in vacuo to yield the product quantitatively: ^{1}H NMR (C_6D_6) δ 6.98 (m, 3, Ar*H*), 5.22 (sept, 1, (CF$_3$)$_2$C*H*O), 4.06 (sept, 2, C*H*Me$_2$), 2.51 (s, 6, C*H*$_2$CMe$_3$), 1.24 (d, 12, CH*Me*$_2$), 1.13 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6): δ 146.4, 124.6, 123.7, 82.9, 58.6, 47.9, 37.1, 33.7, 31.9, 31.3, 30.4, 29.7, 25.6, 24.6, 23.8.

Mo(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$).[41] Pentafluorophenol (761 mg, 4.14 mmol) was added all at once to a solution of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ (2 g, 4.14 mmol) in 10 ml pentane. Stirring the reaction mixture for 6 h and removing the volatile components *in vacuo* afforded an orange-brown solid which was washed with cold pentane to get a bright yellow solid (1.80 g, 66%). Alternatively, the orange-brown solid can be dissolved in minimum amount of pentane and the solution stored at -20 °C for 24 h to afford yellow crystalline material in 75% yield: ^{1}H NMR (C_6D_6) δ 6.99 (br s, 3, Ar*H*), 4.14 (sept, 2, C*H*Me$_2$), 2.73 (s, 6, C*H*$_2$CMe$_3$), 1.28 (d, 12, CH*Me*$_2$), 1.14 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 150.5, 128.7, 124.9, 123.8, 84.5, 36.9, 33.7, 31.9, 29.9, 28.9, 25.7, 24.5, 23.7; ^{19}F NMR (C_6D_6) δ -157.39 (d, 2), -165.53 (t, 2), -171.94 (t, 1). Anal. Calcd for $C_{33}H_{50}NOF_5Mo$: C, 59.36; H, 7.55; N, 2.10; Mo, 14.37; F, 14.23. Found C, 59.40; H, 7.42; N, 2.12; Mo, 14.40; F, 14.16.

Mo(NAr)(CH$_2$-t-Bu)$_3$[OC(CF$_3$)$_3$].[41] Neat (CF$_3$)$_3$COH was added to 20 mg (0.04 mmol) of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ to obtain a yellow-orange suspension immediately. Stirring the reaction mixture for 10 min and removing the excess alcohol yielded a yellow-orange solid almost quantitatively that contains <5% Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OC(CF$_3$)$_3$]: ^{1}H NMR

(C_6D_6) δ 7.03 (m, 3, Ar*H*), 4.21 (sept, 1, C*H*Me$_2$), 2.84 (s, 6, C*H*$_2$CMe$_3$), 1.35 (d, 12, CH*Me*$_2$), 1.24 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6): δ 151.2, 150.3, 128.7, 125.1, 83.9, 37.9, 33.8, 31.1, 28.7, 25.5. 22.9.

Conversion of Mo(NAr)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$] into Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$].[41] Mo(NAr)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$] (20 mg) was dissolved in 0.6 ml C_6D_6 in a JYoung® NMR tube to give a yellow solution. Heating the tube to 60 °C overnight resulted in darkening of the color of solution. The ^{1}H NMR spectrum showed that Mo(NAr)(CH$_2$-t-Bu)$_3$[OCH(CF$_3$)$_2$] had been converted quantitatively into Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$].

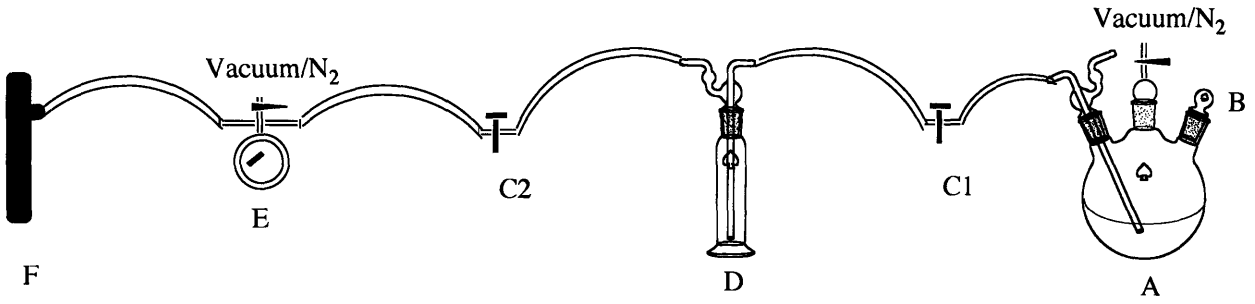
Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OC$_6$F$_5$)(PMe$_3$).[40] Mo(NAr)(CH$_2$-t-Bu)$_3$(OC$_6$F$_5$) (200mg, 0.34 mmol) was taken in 2ml pentane and 5 equiv PMe$_3$ (174 μl, 1.68 mmol) was added to it via a microsyringe. Stirring for 2 h afforded a green suspension from which volatiles were removed *in vacuo* to obtain a lime-lemon (green-yellow) solid in almost quantitative yield. Recrystallization in minimum amount of pentane at -20 °C overnight afforded yellow crystals in 72% yield (162mg). ^{1}H NMR (C_6D_6) δ 13.3 (d, J_{CH} = 136.1 Hz, $^3J_{HP}$ = 3.5 Hz, 1, *anti*-C*H*CMe$_3$), 10.8 (s, J_{CH} = 107.7 Hz, 1, *syn*-C*H*CMe$_3$); ^{13}C NMR (toluene-d_8): δ 309.7, 278.7; ^{31}P NMR (C_6D_6) δ -10.9, -14.9.

Conversion of Mo(NAr)(CH$_2$-t-Bu)$_3$[OC(CF$_3$)$_3$] into Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OC(CF$_3$)$_3$].[41] A yellow solution was obtained when 20 mg of Mo(NAr)(CH$_2$-t-Bu)$_3$[OC(CF$_3$)$_3$] was dissolved in 0.6 ml C_6D_6 in a JYoung® NMR tube. Heating the tube to 60 °C overnight produced a darker solution whose ^{1}H NMR spectrum (C_6D_6) was consistent with the formation of Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)[OC(CF$_3$)$_3$]: δ 12.21 (s, 1, C*H*CMe$_3$, J_{CH} = 116 Hz), 6.98 (m, 3, Ar*H*), 3.71 (sept, 2, C*H*Me$_2$), 2.54 (d, 1, CH*H*CMe$_3$, J_{CH} = 13 Hz), 2.18 (d, 1, C*H*HCMe$_3$), 1.21 (d, 6, CH*Me*$_2$)1.24 (d, 6, CH*Me*$_2$), 1.15 (s, 9, CH$_2$C*Me*$_3$), 1.07 (s, 9, CHC*Me*$_3$).

Mo(NAr)(CH$_2$-t-Bu)[OCH(CF$_3$)$_2$]$_3$. Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)$_2$ (200 mg, 0.414 mmol) was taken in 4 ml dichloromethane to obtain an orange-red solution. 2 equivalents of (CF$_3$)$_2$CHOH (90 μl) was added to the above solution at room temperature and allowed the

reaction mixture to stir overnight. Removed volatiles in vacuo to get a red oily material. Adding minimum amount of pentane to the above to the oil obtained and storing the solution overnight at -20 °C afforded red crystals in 34% yield: ^{1}H NMR (C_6D_6) δ 6.84 (d, 2, Ar*H*), 6.73 (t, 1, Ar*H*), 5.92(br s, 3, $(CF_3)_2CHO$), 4.01 (s, 2, CH_2CMe_3), 3.80 (sept, 2, $CHMe_2$), 1.18 (d, 12, $CHMe_2$), 1.05 (s, 9, CH_2CMe_3); ^{19}F NMR (C_6D_6) δ -73.88, -74.50. Anal. Calcd for $C_{26}H_{31}NO_3F_{18}Mo$: C, 37.02; H, 3.70; N, 1.66. Found C, 37.11; H, 3.74; N, 1.62.

Synthesis of α-labeled Pivalic Acid (t-Bu^{13}CO$_2$H)



The assembly shown above was oven and flame dried, and allowed to cool under vacuum. The flow control valve C1 was closed and the 2 L three-necked round-bottomed flask A equipped with an egg-shaped magnetic stir bar was filled with nitrogen. t-BuMgCl (Aldrich, 150 ml of a 2.0 M solution in ether, 300 mmol) was cannula transferred into A, followed by addition of 60 ml dry diethyl ether. The stopper B was replaced by a nitrogen filled balloon attached to a flow control adapter. A liquid nitrogen bath was used to freeze flask A and the entire assembly was degassed three times. $^{13}CO_2$ (Cambridge Isotope Laboratories 99% ^{13}C, 5 L, 156.8 psi) was introduced by opening up the lecture bottle F fitted with a Matheson control valve such that the pressure gauge E showed greater than1 atm and less than 2 atm pressure. Valves C2 and C1 were opened and the gas was allowed to bubble through a vigorously stirring ether solution of t-BuMgCl. At this point, the gas pressure should be high enough to prevent the solution in A from getting pulled into the trap D. Any excess pressure is indicated by the inflation of the balloon at which point valve C1 should be closed. The gas present in flask A and the balloon should be allowed to react completely before introducing more gas via valve C1. The reaction vessel begins to warm up in ~15 min, after which an ice bath was placed under flask A. Bubbling of the gas ceases in the next 40 min indicating that all of gas from the lecture

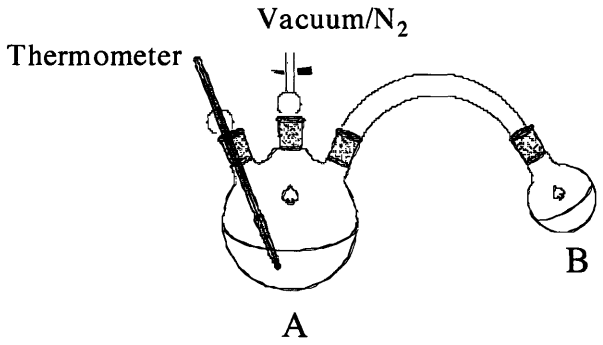
bottle has been consumed (This can be confirmed by weighing the lecture bottle before and after the reaction). After stirring the reaction mixture for another hour, flask A was cooled to approximately -10 °C by employing an NaCl-ice bath. A solution of 40 ml HCl in 200 ml water was added to A via an addition funnel such that the temperature did not exceed 0 °C. The aqueous layer was separated from the ether layer. Washed the former layer with ether, combined the ether extracts and dried over $MgSO_4$. Removing ether by rotary evaporation at room temperature caused needle-shaped crystals to form (Yield = 87% based on $^{13}CO_2$). The yield can be improved by 5-7% if the reaction is allowed to proceed for 10 h before adding HCl. The 10-12% ether present in the sample thus obtained was not distilled off.

^{1}H NMR (300 MHz, C_6D_6): δ 11.44 (br s, 1H, $(CH_3)_3C^{13}CO_2H$), 1.08(d, J_{CH} = 4.2 Hz, 9H, $(CH_3)_3C^{13}CO_2H$); ^{13}C NMR (125 MHz, C_6D_6): δ 186.1($(CH_3)_3C^{13}CO_2H$), 39.4 ($(CH_3)_3C^{13}CO_2H$), 27.3 ($(CH_3)_3C^{13}CO_2H$).

Preparation of Neopentyl Alcohol (t-Bu^{13}CH$_2$OH). An oven-dried 2 L three-necked round-bottomed flask was equipped with a magnetic stir bar, reflux condenser, a stopper and a nitrogen/vacuum flow control adapter attached to a high vacuum line. The above assembly was flame-dried and allowed to cool under a dynamic vacuum. The apparatus is filled with nitrogen and lithium aluminum hydride (Strem 95%, 22.3 g, 587.5 mmol) was added followed by 600 ml of diethyl ether via cannula. An addition funnel containing pivalic acid (235 mmol) is connected and the rate of addition of pivalic acid to the vigorously stirring suspension of lithium aluminum hydride in ether is adjusted to afford a gentle reflux. The reaction continues to reflux without external heating and the complete addition of the pivalic acid is done over a period of 4 h. The reaction soon subsides and external heating is applied in order to maintain a gentle reflux for 12 h. The reaction flask is cooled to 0 °C and 300 ml water followed by 500 ml 10% H_2SO_4 solution are added dropwise by an addition funnel. After separating the aqueous layer from ether layer, extracted the former with 150 ml ether and combined the ether extracts. Drying over $MgSO_4$ and removing ether by rotary evaporation gave 75.3% (177mmol) of neopentyl alcohol.

^{1}H NMR (300 MHz, C_6D_6): δ 3.08 (d, J_{CH} = 139.2 Hz, 2H, $(CH_3)_3C^{13}CH_2OH$), 1.54 (br s, 1H, $(CH_3)_3C^{13}CH_2OH$), 0.84 (d, J_{CH} = 4.8 Hz, 9H, $(CH_3)_3C^{13}CH_2OH$); ^{13}C NMR (125 MHz, C_6D_6): δ 73.5($(CH_3)_3C^{13}CH_2OH$), 33.2 ($(CH_3)_3C^{13}CH_2OH$), 26.5 ($(CH_3)_3C^{13}CH_2OH$).

Synthesis of Vilsmeier Reagent ([Me_2N=CHCl]Cl). An oven-baked 2 L three-necked round-bottomed flask equipped with a magnetic stir bar, a nitrogen inlet, and two stoppers was flame-dried and allowed to cool under vacuum. After filling the apparatus with nitrogen, both the stoppers were replaced with a rubber septum and a thermometer, respectively. 400 ml of DMF (99.94%, dried over 4 Å molecular sieves for five weeks), was cannula transferred into the flask. PCl_5 (Strem 98%, 240 g, 1150 mmol) was taken into a nitrogen filled 250 ml flask B. B was connected to the flask A containing DMF by a Tygon tubing. Flask B was gradually lifted such as to add ~ 5 g of PCl_5 at a time to the DMF vigorously stirring in flask A. Complete addition of PCl_5 was carried out over a period of 5 h ensuring that the temperature in the flask was always below 45 °C. The resulting orange colored reaction mixture was stirred for 12 h at room temperature and then filtered over a swivel frit. Washing the solid with 250 ml of cold DMF (0 °C) and 300 ml of cold diethyl ether (0 °C), and finally drying on a high vacuum line yielded 130 g (88.5%) of Vilsmeier reagent as a white powder.



Preparation of Neopentyl Chloride (t-Bu$^{13}CH_2Cl$). In the dry box, a 250 ml three-necked round-bottomed flask equipped with a magnetic stir bar, a nitrogen inlet, and two stoppers was charged with 35 g (273 mmol) of Vilsmeier reagent. The flask was taken out of the dry box and connected to a high vacuum line. After attaching a water cooled condenser to the flask, 70 ml DMF was transferred into the flask via cannula. Neopentyl alcohol (182 mmol) in 20 ml DMF was added dropwise over a period of 1.5 h to the stirring solution of Vilsmeier reagent by means of an addition funnel. The color of the reaction mixture changes gradually from pale yellow to a clear orange-yellow. The reaction mixture was then heated at 110 °C for 12 h. A short path distillation set up was employed to distill the product (along with ~10%

DMF) from the reaction vessel. Subsequent washings with conc. sulfuric acid, water, saturated sodium bicarbonate solution followed by brine and finally drying over calcium chloride afforded 73% of pure neopentyl chloride.

^{1}H NMR (500 MHz, C_6D_6): δ 2.96 (d, J_{CH} = 148.9 Hz, 2H, $(CH_3)_3C^{13}CH_2Cl$), 0.78 (d, J_{CH} = 5.5 Hz, 9H, $(CH_3)_3C^{13}CH_2Cl$); ^{13}C NMR (125 MHz, C_6D_6): δ 57.4($(CH_3)_3C^{13}CH_2Cl$), 33.1 ($(CH_3)_3C^{13}CH_2Cl$), 27.3 ($(CH_3)_3C^{13}CH_2Cl$).

Preparation of Neopentyl Magnesium Chloride (t-Bu^{13}CH$_2$MgCl). Mg turnings (Mallinckrodt AR grade, washed with dilute HCl, acetone and stored in a 200 °C oven for two days, 10.4 g, 429 mmol) were stirred vigorously for 6 h under nitrogen in a 100 ml three-necked round-bottomed flask equipped with a nitrogen inlet, a water cooled Freidrichs condenser and a stopper. 30 ml diethyl ether was added to the flask followed by 1 ml of t-Bu^{13}CH$_2$MgCl via syringe. The solution was heated by means of a heating gun until it refluxed gently. 5-6 drops of 1, 2-dibromoethane was added to initiate the reaction. The remainder of the neopentyl chloride (10 ml) was slowly added by a syringe and the reaction vessel was heated to cause gentle reflux for another 10 h. The mixture was filtered through a 2 cm layer of Celite in a frit and washed the filter cake with diethyl ether until the supernatant was colorless. Titration of a 100 μl aliquot against propanol using 1, 10-phenanthroline as an indicator suggested the concentration of the Grignard solution prepared to be 1.08 M (71% conversion).

Synthesis of Mo(NAr)$_2$(^{13}CH$_2$-t-Bu)$_2$. Mo(NAr)$_2$Cl$_2$(dme) (3.0 g, 4.94 mmol) in 50 ml ether was chilled at -27 °C in a dry box and t-Bu^{13}CH$_2$MgCl (1.08 M, 9.2 ml, 9.88 mmol) was added dropwise to it via an addition funnel. Stirred the resulting orange-red solution for 6 h at room temperature and filtered through Celite on a frit. Washing the residual salt with ether followed by removing volatiles in vacuo afforded an orange solid that was recrystallized from ether at -27 °C to afford orange crystals (4.75 g, 94%).

^{1}H NMR (500 MHz, C_6D_6): δ 6.97 (m, 6H, Ar*H*), 3.74 (sept, J_{CH} = 7.0 Hz, 4H, C*H*Me$_2$), 2.29 (d, J_{CH} = 119.4 Hz, 4H, $(CH_3)_3C^{13}CH_2$), 1.27 (d, J_{CH} = 4.5 Hz, 18H, $(CH_3)_3C^{13}CH_2$), 1.15 (d, J_{CH} = 7.0 Hz, 24H, CH*Me*$_2$); ^{13}C NMR (125 MHz, C_6D_6) labeled carbon: δ 79.9 ($(CH_3)_3C^{13}CH_2$).

Synthesis of Mo(NAr)(^{13}CH-t-Bu)(OTf)$_2$(dme). Cooled Mo(NAr)$_2$(^{13}CH$_2$-t-Bu)$_2$ (2.65 g, 4.49 mmol) in 70 ml dme and 15 ml pentane at -27 °C. A prechilled solution of 2.03 g triflic acid (13.46 mmol) in 15 ml dme was added dropwise to the stirring solution of Mo(NAr)$_2$(^{13}CH$_2$-t-Bu)$_2$. The solution was allowed to stir at room temperature for 12 h and evaporated the volatiles in vacuo to obtain a dark brown solid, which was then extracted with cold toluene. Filtering the toluene extract through Celite and removing toluene from the filtrate in vacuo gave a yellow-brown solid. Washing this solid with cold ether over a frit yielded 2.20 g of a yellow powder (67%).

^{1}H NMR (500 MHz, C_6D_6): δ 14.30 (d, J_{CH} = 120.1 Hz, 1H, $(CH_3)_3C^{13}CH$), 6.92 (m, 3H, Ar*H*), 3.92 (sept, J_{CH} = 6.5 Hz, 4H, C*H*Me$_2$), 3.86 (s, 3H, $CH_3OCH_2CH_2OCH_3$), 3.13 (m, 2H, $CH_3OCH_2CH_2OCH_3$), 2.77 (s, 3H, $CH_3OCH_2CH_2OCH_3$), 2.72 (m, 2H, $CH_3OCH_2CH_2OCH_3$), 1.45 (d, J_{CH} = 4.0 Hz, 9H, $(CH_3)_3C^{13}CH$), 1.40 (d, J_{CH} = 7.0 Hz, 6H, CH*Me*$_2$), 1.25 (d, J_{CH} = 7.0 Hz, 6H, CH*Me*$_2$); ^{13}C NMR (125 MHz, C_6D_6) labeled carbon: δ 331.1 $(CH_3)_3C^{13}CH$).

Synthesis of Mo(NAr)(^{13}CH-t-Bu)(^{13}CH$_2$-t-Bu)$_2$. Mo(NAr)(^{13}CH-t-Bu)(OTf)$_2$(dme) (1.0 g, 1.37 mmol) was taken in 40 ml ether and chilled at -27 °C. 2.53 ml of t-BuCH$_2$MgCl (1.08 M, 2.74 mmol) was dropwise added to the above solution by a syringe. The color of solution changes from yellow to orange-red. Stirred the reaction mixture overnight, evaporated ether in vacuo and extracted with pentane. Filtering off the pentane extract through Celite and removing the solvent in vacuo afforded an orange-red solid (556 mg, 83.4%).

^{1}H NMR (300 MHz, C_6D_6): δ 9.50 (d, J_{CH} = 108.3 Hz, 1H, $(CH_3)_3C^{13}CH$), 7.05 (m, 3H, Ar*H*), 3.99 (sept, J_{CH} = 6.9 Hz, 2H, C*H*Me$_2$), 2.75 (dd, J_{CH} = 120.6 Hz, J_{HH} = 12.9 Hz, 2H, $(CH_3)_3C^{13}CHH$), 1.29 (d, J_{CH} = 6.9 Hz, 12H, CH*Me*$_2$), 1.21 (d, J_{CH} = 18.0 Hz, 18H, $(CH_3)_3C^{13}CH_2$), 1.16 (d, J_{CH} = 4.8 Hz, 9H, $(CH_3)_3C^{13}CH$), 0.61 (dd, J_{CH} = 120.6 Hz, J_{HH} = 12.9 Hz, 2H, $(CH_3)_3C^{13}CHH$); ^{13}C NMR (125 MHz, C_6D_6) labeled carbons: δ 255.6 ($(CH_3)_3C^{13}CH$), 77.9 ($(CH_3)_3C^{13}CH_2$).

General method employed for metathesis reactions of *cis*-2-pentene. 5 mol% of the Mo(NAr)(CH-t-Bu)(CH$_2$-t-Bu)(OR) complex in 1 ml toluene was added to a 10 ml scintillation vial that was capped with a rubber septa. Added *cis*-2-pentene to the above solution via a syringe and the solution was allowed to stand. Aliquots were taken out of the reaction mixture at regular

time intervals and were diluted with toluene (1:10) and the reaction progress was followed by gas chromatography.

General method employed for ring-opening metathesis polymerization reactions. A 25 ml scintillation via was charged with a magnetic stirrer and 50 mg of norbornene in 5 ml toluene was added to it followed by the addition of 1 mol% of the Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complex in 0.5 ml of toluene. After stirring the reaction mixture for 1 h, 2 ml of benzaldehyde was added. The above solution was allowed to stir for an additional 1 h following which it was treated with excess (65 ml) of methanol. Stirring the resulting suspension overnight gave the polymer which was filtered, dried on a high vacuum line and analyzed by gel permeation chromatography.

General method employed for ring-closing metathesis reactions. A solution of the substrate in C_6D_6 and 10 μl of anisole (an internal standard) were placed in a JYoung® NMR tube and 5 mol% of the catalyst was then added. The tube was capped and the solution was allowed to stand at room temperature. In other cases, 10 mg of the substrate was taken in 0.5 ml C_6D_6 followed by addition of 5 mol% of catalyst. Conversions were determined by ^1H NMR spectroscopy (500 MHz).

Solid State structure determination by X-ray crystallographic studies. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97. All non-hydrogen atoms, were refined anisotropically. All hydrogen atoms (except the hydrogen atoms on carbon that binds directly to molybdenum in the structures of Mo(NAr)(CH_2-t-Bu)$_3$(OC_6F_5), Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) and (NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3), which have been taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times

for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed after references.

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Crystal Data and Structure Refinement for Compounds Reported in Chapter 2

Table 2XR.1. Crystal data and structure refinement for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)[OSi(O-t-Bu)$_3$].

Empirical formula	C34 H65 Mo N O4 Si	
Formula weight	675.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.7654(5) Å	a= 97.7880(10)°.
	b = 11.4342(5) Å	b= 97.465(2)°.
	c = 18.8010(8) Å	g = 108.6840(10)°.
Volume	1936.44(15) Å^3	
Z	2	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	0.402 mm^{-1}	
F(000)	728	
Crystal size	0.20 x 0.20 x 0.07 mm^3	
Theta range for data collection	1.11 to 29.13°.	
Index ranges	-13≤h≤13, -15≤k≤15, -25≤l≤25	
Reflections collected	42470	
Independent reflections	10424 [R(int) = 0.0283]	
Completeness to theta = 29.13°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9724 and 0.9239	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10424 / 1389 / 750	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1133	
R indices (all data)	R1 = 0.0485, wR2 = 0.1165	
Largest diff. peak and hole	1.642 and -0.559 e.Å^{-3}	

Table 2XR.2. Crystal data and structure refinement for $Mo(NAr)(CH_2\text{-}t\text{-}Bu)_3(OC_6F_5)$.

Empirical formula	C33 H50 F5 Mo N O	
Formula weight	667.68	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.2823(7) Å	a= 90°.
	b = 17.4374(11) Å	b= 92.240(2)°.
	c = 18.7360(12) Å	g = 90°.
Volume	3356.7(4) $Å^3$	
Z	4	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	0.443 mm^{-1}	
F(000)	1400	
Crystal size	0.26 x 0.21 x 0.16 mm^3	
Theta range for data collection	1.60 to 27.48°.	
Index ranges	-13≤h≤13, -22≤k≤22, -24≤l≤13	
Reflections collected	20925	
Independent reflections	7666 [R(int) = 0.0689]	
Completeness to theta = 27.48°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9325 and 0.8934	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7666 / 19 / 401	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0722, wR2 = 0.1211	
R indices (all data)	R1 = 0.1122, wR2 = 0.1318	
Largest diff. peak and hole	0.732 and -1.285 $e.Å^{-3}$	

Table 2XR.3. Crystal data and structure refinement for [Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)]$_2$.

Empirical formula	C56 H76 F10 Mo2 N2 O2	
Formula weight	1191.07	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.0135(14) Å	a= 106.623(2)°.
	b = 11.2803(14) Å	b= 98.447(2)°.
	c = 13.7273(17) Å	g = 111.854(2)°.
Volume	1453.8(3) Å^3	
Z	1	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.503 mm^{-1}	
F(000)	616	
Crystal size	0.20 x 0.16 x 0.12 mm^3	
Theta range for data collection	1.62 to 28.26°.	
Index ranges	-13≤h≤14, -14≤k≤12, -14≤l≤18	
Reflections collected	9217	
Independent reflections	6454 [R(int) = 0.0211]	
Completeness to theta = 28.26°	89.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9421 and 0.9061	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6454 / 3 / 344	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1215	
R indices (all data)	R1 = 0.0521, wR2 = 0.1264	
Largest diff. peak and hole	1.965 and -0.807 e.Å^{-3}	

Table 2XR.4. Crystal data and structure refinement for Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)(PMe_3).

Empirical formula	C31 H47 F5 Mo N O P	
Formula weight	671.61	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.0422(6) Å	a= 90°.
	b = 17.2364(9) Å	b= 105.176(2)°.
	c = 18.4223(9) Å	g = 90°.
Volume	3384.0(3) $Å^3$	
Z	4	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.485 mm^{-1}	
F(000)	1400	
Crystal size	0.16 x 0.13 x 0.13 mm^3	
Theta range for data collection	1.65 to 25.68°.	
Index ranges	$-13 \le h \le 12$, $0 \le k \le 21$, $0 \le l \le 22$	
Reflections collected	20039	
Independent reflections	6423 [R(int) = 0.0466]	
Completeness to theta = 25.68°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9396 and 0.9264	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6423 / 126 / 416	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1535	
R indices (all data)	R1 = 0.0703, wR2 = 0.1630	
Largest diff. peak and hole	1.667 and -0.809 $e.Å^{-3}$	

Table 2XR.5. Crystal data and structure refinement for Mo(NAr)(CH_2-t-Bu)[$OCH(CF_3)_2]_3$.

Empirical formula	C26 H31 F18 Mo N O3	
Formula weight	843.46	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.015(4) Å	α= 90.266(7)°.
	b = 10.723(4) Å	β= 101.592(7)°.
	c = 16.708(6) Å	γ = 104.715(6)°.
Volume	1697.1(12) $Å_3$	
Z	2	
Density (calculated)	1.651 Mg/m_3	
Absorption coefficient	0.514 mm_{-1}	
F(000)	844	
Crystal size	0.2 x 0.2 x 0.08 mm_3	
Theta range for data collection	2.15 to 25.00°.	
Index ranges	-11≤h≤11, -12≤k≤8, -16≤l≤19	
Reflections collected	7993	
Independent reflections	5757 [R(int) = 0.0502]	
Completeness to theta = 25.00°	96.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	5757 / 0 / 531	
Goodness-of-fit on F_2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.0963	
R indices (all data)	R1 = 0.0610, wR2 = 0.1068	
Largest diff. peak and hole	0.839 and -0.642 $e.Å^{-3}$	

Chapter 3

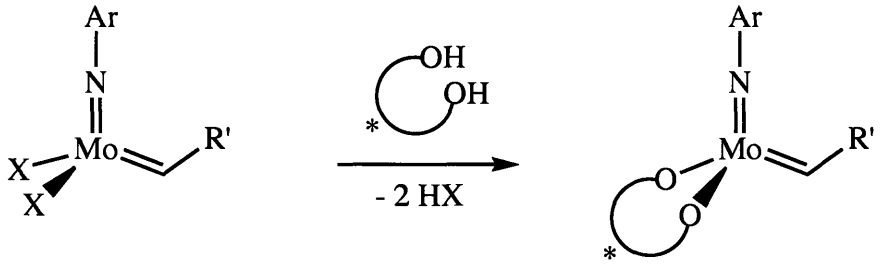
SYNTHESIS OF MOLYBDENUM IMIDO ALKYLIDENE BISAMIDO COMPLEXES AND THEIR USE IN METATHESIS REACTIONS BY *IN SITU* TECHNIQUES: A PRELIMINARY STUDY

A portion of this chapter has been submitted for publication:

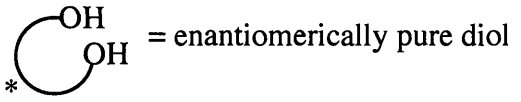
Sinha, A.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. "Amido Precursors to Bis-alkoxide Molybdenum Imido Alkylidene Olefin Metathesis Catalysts" **2006**.

INTRODUCTION

A pragmatic approach to utilizing the modular character of metathesis catalysts of the type Mo(NAr)(CHR′)(diolate)[1] would entail the preparation of several catalysts of an entire given catalyst library from a single common precursor having fixed imido and alkylidene groups. This goal could be accomplished via the protonation of two monoanionic ligands X in an imido alkylidene precursor Mo(NAr)(CHR′)X_2 by a variety of enantiomerically pure diols (equation 3.1). Catalysts prepared this way could be utilized in an *in situ* fashion and the corresponding catalyses with substrates examined by high-throughput or combinatorial methods for activity and selectivity optimization for a given substrate. This route would potentially obviate the occasional occurrence of amido alkylidyne type of species Mo(NHAr)(CR′)(diolate) as an impurity[2,3] in the reactions of Mo(NAr)(CHR′)$(OTf)_2$(dme) with 1 equivalent of [diolate]M_2 (M = Li or K) to give the desired imido alkylidene catalysts as described in Chapter 1.



(3.1)



= enantiomerically pure diol

The results obtained from the work in Chapter 2 demonstrated that imido alkylidene dialkyl complexes of the type Mo(NAr)(CHR′)$(CH_2R')_2$ could *not* be used as precursors for obtaining catalysts with bisalkoxide or diolate ligands, and that the reactions of alcohols with Mo(NAr)(CHR′)$(CH_2R')_2$ instead gave new monoalkoxide type catalysts Mo(NAr)(CHR′)(CH_2R')(OR). The limited reactivity of certain transition metal alkyl complexes towards alcohols[4] may be a reason for not obtaining substitution of both alkyl groups by alkoxide ligands. It had been shown by using a variety of alcohols that the second molecule of ROH approaches the $C_{alkylidene}$-N-O face of

Mo(NAr)(CHR′)(CH_2R′)(OR) (based on the structure of a PMe_3 adduct of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)) and undergoes a non productive concerted sigma bond metathesis with the alkoxide bound to the metal to give back Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) and a molecule of ROH. Moreover, attempts to make complexes like Mo(NAr)(CHR′)(CH_2R′)(OR*) (OR* = chiral alcohol) in their diastereomerically pure form that could be used in asymmetric metathesis reactions were not successful.

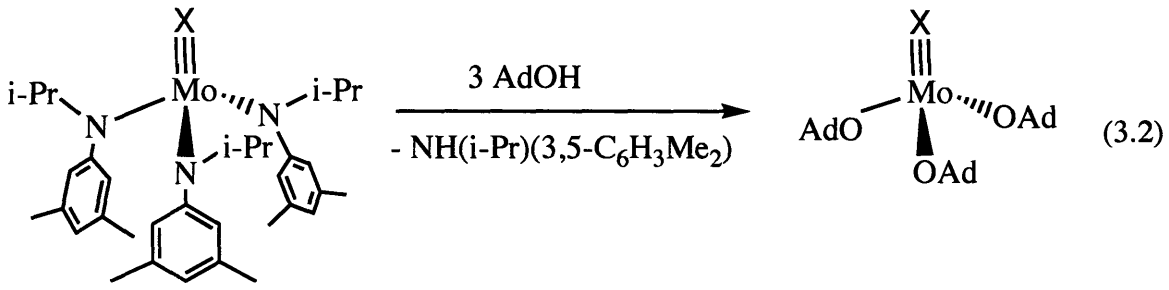
Therefore, we focused our attention on simple nitrogen-donor ligands on a molybdenum imido alkylidene precursor that could be protonated with one equivalent of an enantiomerically pure diol to give catalysts for ARCM reactions. Our choice of amido ligands in this respect was guided by the notion that in addition to nitrogen having a lone pair of electrons that would make it amenable to protonation more readily than carbon-based alkyl ligands[5], the greater polarity of the Mo-N bond compared to Mo-C would also contribute to the success of the reaction shown in equation 3.1. Also, removing an amide group, which is a stronger base than an alkyl anion, would be thermodynamically more favorable to give the bisalkoxide species from bisamide complexes compared to the dialkyl species.

Amido groups have good σ and π donating abilities by virtue of which they are extensively used in forming complexes with transition metals.[6] Despite the donor nature of amides, the metal center in various amido complexes has a significant degree of electrophilic character. This feature has been utilized extensively in the chemistry of group 4 elements to achieve living polymerization of simple olefins.[7] In addition, several ligands incorporating the amido functionality have been used in the activation of relatively inert molecules such as dinitrogen.[8,9]

The protonation of amido ligands has been utilized by the Cummins group to make trisalkoxide complexes of the type Mo(X)($OR)_3$ from the alcoholysis of Mo(X)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_3$ type species. This strategy was used to make several isolable high oxidation state molybdenum complexes with different isolobal fragments (X = CCH_2SiMe_3[10], N[11], P[12]) (equation 3.2) from common Mo(X)(amide)$_3$ precursors.[13]

This chapter concerns the synthesis of molybdenum imido alkylidene bisamido complexes of the type Mo(NR″)(CHR′)($NR_2)_2$ and their reactions with enantiomerically pure diols to give Mo(NR″)(CHR′)(diolate*) species *in situ*. Preliminary work on these

systems has shown that catalysts generated can be successfully employed in carrying out ARCM reactions and that the results obtained in the course of these studies match reasonably well with the activities and selectivities that have been observed for catalysis with the isolated catalysts.



(3.2)

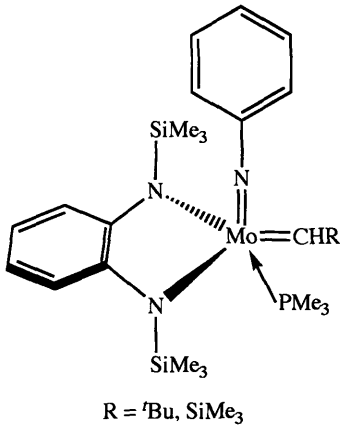
X = CCH_2SiMe_3, N, P

RESULTS AND DISCUSSIONS

Although group 6 elements bearing both diamido and imido ligands are known, there have been relatively few examples of molybdenum or tungsten imido alkylidene complexes having ancillary amido groups.[6] Boncella had isolated M(NPh)(CH-t-Bu)[*o*-$(Me_3SiN)_2C_6H_4$](PMe_3) (M = Mo[14], W[15]) by inducing an α-abstraction of a neopentyl group in M(NPh)(CH_2-t-Bu)$_2$[*o*-$(Me_3SiN)_2C_6H_4$] (M = Mo, W) by heating the dineopentyl species in the presence of 5 equivalents of PMe_3. Jennifer Jamieson in our group had prepared molybdenum imido alkylidene complexes[16] with chelating diamido ligands such as [BINA$(NR)_2$]H_2 ([BINA$(NR)_2$]$^{2-}$ = N,N′-bis(alkyl)-2,2′-diamido-1,1′-binaphthyl) (Figure 3.1).

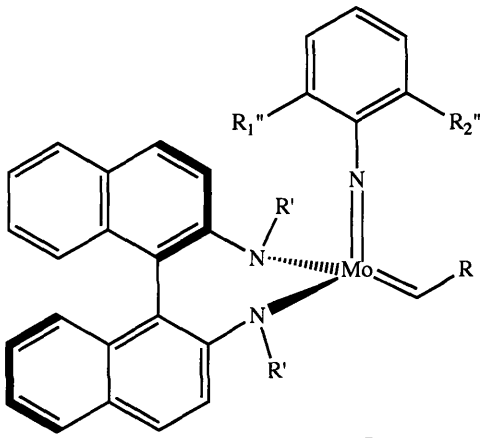
The work presented in this section describes the synthesis of new imido alkylidene complexes of molybdenum with different types of amido ligands.

Boncella *et al.*



R = ^{t}Bu, $SiMe_3$

Schrock *et al.*

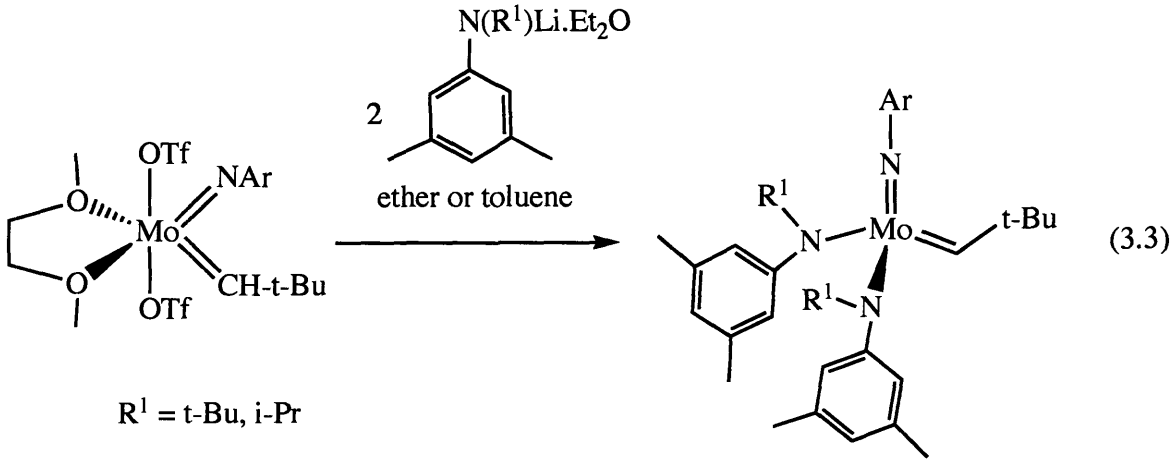


$R_1" = R_2"$ = i-Pr
$R_1" = CF_3$, $R_2" = H$
R' = Ts, $SiMe_3$, i-Pr
R = t-Bu, CMe_2Ph

Figure 3.1. Molybdenum imido alkylidene diamido complexes reported prior to this work.

3.1. Synthesis of $Mo(NR'')(CHR')[N(R^1)(3,5\text{-}C_6H_3Me_2)]_2$ type complexes

$HN(R^1)(3,5\text{-}C_6H_3Me_2)$ (R^1 = t-Bu, i-Pr) prepared by the methods based on the works of Cummins[17] and Micovic[18] can be converted to their respective Li salts by reacting with n-BuLi at -27 °C in pentane. $Mo(NAr)(CH\text{-}t\text{-}Bu)[N(R^1)(3,5\text{-}C_6H_3Me_2)]_2$ (R^1 = t-Bu, i-Pr) can then be synthesized by treating a pre-chilled solution (-27 °C) of $Mo(NAr)(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ in diethyl ether or toluene with two equivalents of the corresponding $LiN(R^1)(3,5\text{-}C_6H_3Me_2)(ether)$ (equation 3.3).



R^1 = t-Bu, i-Pr

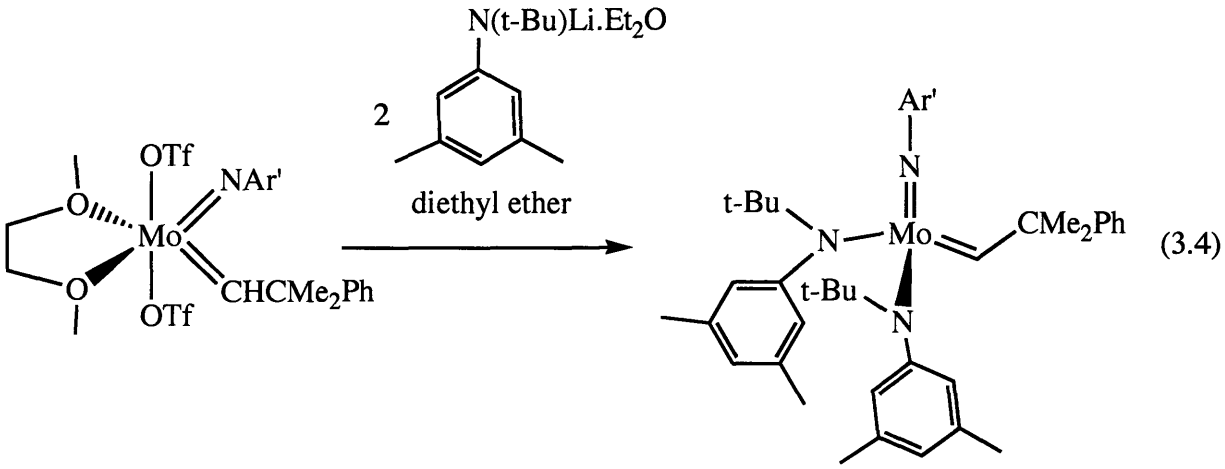
(3.3)

Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$ prepared can be isolated in pure form as an orange-red crystalline solid in 34% yield. The low yield for this reaction is attributed to the presence of the parent amine HN(t-Bu)(3,5-$C_6H_3Me_2$) in the reaction mixture, which is difficult to remove due to its low volatility (b.p. = 104 °C at 3 Torr[19]). Proton and carbon NMR spectra of Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$ in benzene-d_6 show resonances for H_α at 10.71 and for C_α at 293.0 ppm indicating significant electron density on the metal center (cf. H_α = 14.29 ppm, C_α = 331.9 ppm for Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme)). The value for the coupling constant (J_{CH} = 120 Hz) for the alkylidene ligand is in agreement with the observed values for typical high oxidation state *syn* alkylidene complexes.[20,21] No alkylidene resonance for the *anti* isomer of Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$ could be found at 22 °C. The aryl substituent (3,5-$C_6H_3Me_2$) on the amido ligand was found to be freely rotating on the NMR timescale.

Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$ prepared in similar fashion starting from Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) could be isolated as a red oil that was found to be contaminated by 29% of the high boiling amine HN(i-Pr)(3,5-$C_6H_3Me_2$). Repeated attempts at triturating and lyophilizing the above oily material with cold pentane and benzene respectively did not lead to the removal of HN(i-Pr)(3,5-$C_6H_3Me_2$). Heating the samples of above mixture for 8 h at 60-80 °C under reduced pressure initiated the decomposition of Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$ without any change in the composition of the oil. No improvement in the yield and purity of the desired product was observed when the different solvents (toluene, THF) and/or lower temperature (-78 °C) conditions were employed in the above reaction. As shown above for Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$, the alkylidene ligand in Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$ was found to be present exclusively in the *syn* orientation (J_{CH} = 119 Hz) with resonances for H_α and C_α appearing at 11.10 ppm and 285.5 ppm respectively in benzene-d_6. Two sets of methine resonances corresponding to the isopropyl substituents on the amido and the imido ligands appear as septets at 4.25 ppm and 4.01 ppm respectively.

Mo(NAr')(CHCMe$_2$Ph)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$ (NAr' = N-2,6-$Me_2C_6H_3$) bearing a sterically less encumbering imido group can be prepared as an oil from the reaction of

$Mo(NAr')(CHCMe_2Ph)(OTf)_2(dme)$ and $LiN(t\text{-}Bu)(3,5\text{-}C_6H_3Me_2)$ in diethyl ether at -40 °C (equation 3.4). Extensive trituration of the oily substance with pentane gave a dark red solid which was crystallized from cold pentane (-27 °C) to give an orange-red crystalline material in three crops in a total of 33% yield. Similar yield is obtained when the potassium salt of the amine, $KN(t\text{-}Bu)(3,5\text{-}C_6H_3Me_2)$ is employed in the above reaction. The resonances for the *syn* alkylidene ligand (J_{CH} = 120 Hz) appear slightly upfield (H_α = 10.61 ppm, C_α = 289.4 ppm in benzene-d_6) compared to the 2,6-diisopropylphenyl imido complexes shown above.



(3.4)

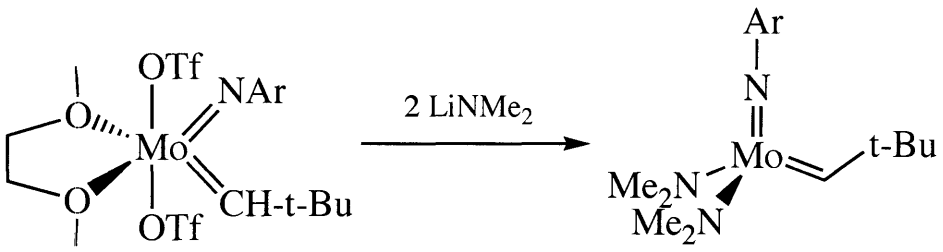
The reaction of $Mo(NAr')(CHCMe_2Ph)(OTf)_2(dme)$ with $LiN(i\text{-}Pr)(3,5\text{-}C_6H_3Me_2)$ in diethyl ether, THF or toluene did not proceed cleanly even at -78 °C. The dark oil obtained showed a major contamination (~ 50%) of the $Mo(NAr')(CHCMe_2Ph)[N(i\text{-}Pr)(3,5\text{-}C_6H_3Me_2)]_2$ species with the free amine $HN(i\text{-}Pr)(3,5\text{-}C_6H_3Me_2)$.

3.2. Synthesis of $Mo(NR'')(CHR')(NR_2)_2$ type complexes

3.2.1. Starting from the bistriflate complex

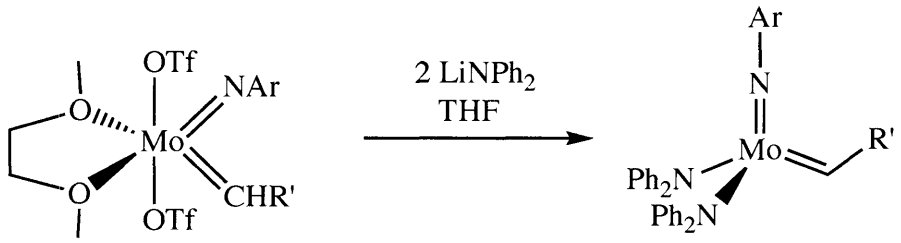
Reacting a pre-chilled solution (-27 °C) of 1.0 g of $Mo(NAr)(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ in diethyl ether with solid $LiNMe_2$ caused the color of the reaction mixture to change from yellow to dark brown. Working up the reaction after allowing the reaction flask to warm up to room temperature afforded a brown oil which according to the proton and carbon NMR studies was found to be a mixture containing the desired

$Mo(NAr)(CH\text{-}t\text{-}Bu)(NMe_2)_2$ complex along with an unidentified material that did not show any resonance downfield of 8 ppm (equation 3.5) . Although the formation of alkylidyne species from the reaction of $Mo(NAr)(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$ with LiOR or KOR in the presence of a base like triethylamine has been well documented (Chapter 1), the ^{13}C NMR spectrum of the above mixture did not show any resonance in the range for alkylidyne species (300-350 ppm[21,22]).



(3.5)

Adding a cold suspension of $LiNPh_2$ in THF or toluene to a stirring suspension of $Mo(NAr)(CHR')(OTf)_2(dme)$ (R' = t-Bu, CMe_2Ph) in THF at -27 °C gave $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ as a red solid in a maximum of 12% yield and $Mo(NAr)(CH\ CMe_2Ph)(NPh_2)_2$ in 35 % yield (equation 3.6). The alkylidene resonances in the proton spectra of for $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ and $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ in benzene-d_6 were located at 10.96 ppm and 11.18 ppm respectively. In the case of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$, a resonance corresponding to the *anti* isomer is seen at 11.78 ppm. The ratio of the two isomers is 100:4 with the *syn* isomer being the dominant species.



(3.6)

R' = t-Bu, CMe_2Ph

Single crystals of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ suitable for X-ray crystallographic studies were obtained by layering a concentrated solution of the complex in dichloromethane with a minimum amount of pentane and storing the resulting solution at -27 °C. The structure determination was carried out by Peter Müller (Figure 3.2 and Table 3.1). The molecular structure of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ in the solid state reveals a pseudo tetrahedral geometry about the molybdenum atom. In agreement with the proton NMR spectrum, the alkylidene ligand is found to exist as the *syn* isomer. Mo(1)-C(37)-C(38) bond angle of 146.2(3)° and Mo(1)-C(37) bond distance of 1.877(3) Å are the values that are expected in a high oxidation state alkylidene ligand which has a *syn* orientation.[20] The imido Mo(1)-N(1) bond distance of 1.739(3) Å is considerably shorter than the amido bond distances of 2.009(3) Å and 2.007(3) Å for the Mo(1)-N(2) and Mo(1)-N(3) bonds respectively. These values for $Mo\text{-}N_{amide}$ bond lengths are in between those for similar bonds in the crystallographically characterized complexes $Mo(NAr)(CHCMe_2Ph)[BINA(N\text{-}i\text{-}Pr)_2]$ ($Mo\text{-}N_{amide}$ = 1.993 Å) and $Mo(NAr)(CHCMe_2Ph)[BINA(NTs)_2]$ ($Mo\text{-}N_{amide}$ = 2.118 Å) that have been earlier reported[16]. The amido nitrogen atoms are both nearly planar since the sum of the angles about each of them approach 360° (359.4° for N(2) and 360° for N(3)).

Table 3.1. Selected bond lengths [Å] and angles [°] for $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$.

Mo(1)-N(1)	1.739(3)	Mo(1)-C(37)	1.877(3)
Mo(1)-N(3)	2.007(3)	Mo(1)-N(2)	2.009(3)
N(1)-C(1)	1.406(4)	N(1)-Mo(1)-C(37)	103.98(13)
N(1)-Mo(1)-N(2)	114.03(11)	N(1)-Mo(1)-N(3)	116.34(11)
N(2)-Mo(1)-N(3)	110.32(10)	N(2)-Mo(1)-C(37)	104.07(12)
N(3)-Mo(1)-C(37)	106.86(12)	Mo(1)-C(37)-C(38)	146.2(3)
Mo(1)-N(1)-C(1)	169.0(2)	C(13)-N(2)-C(19)	115.2(2)
C(13)-N(2)-Mo(1)	118.61(19)	C(19)-N(2)-Mo(1)	125.61(19)
C(31)-N(3)-C(25)	117.6(3)	C(31)-N(3)-Mo(1)	132.3(2)
C(25)-N(3)-Mo(1)	110.1(2)		

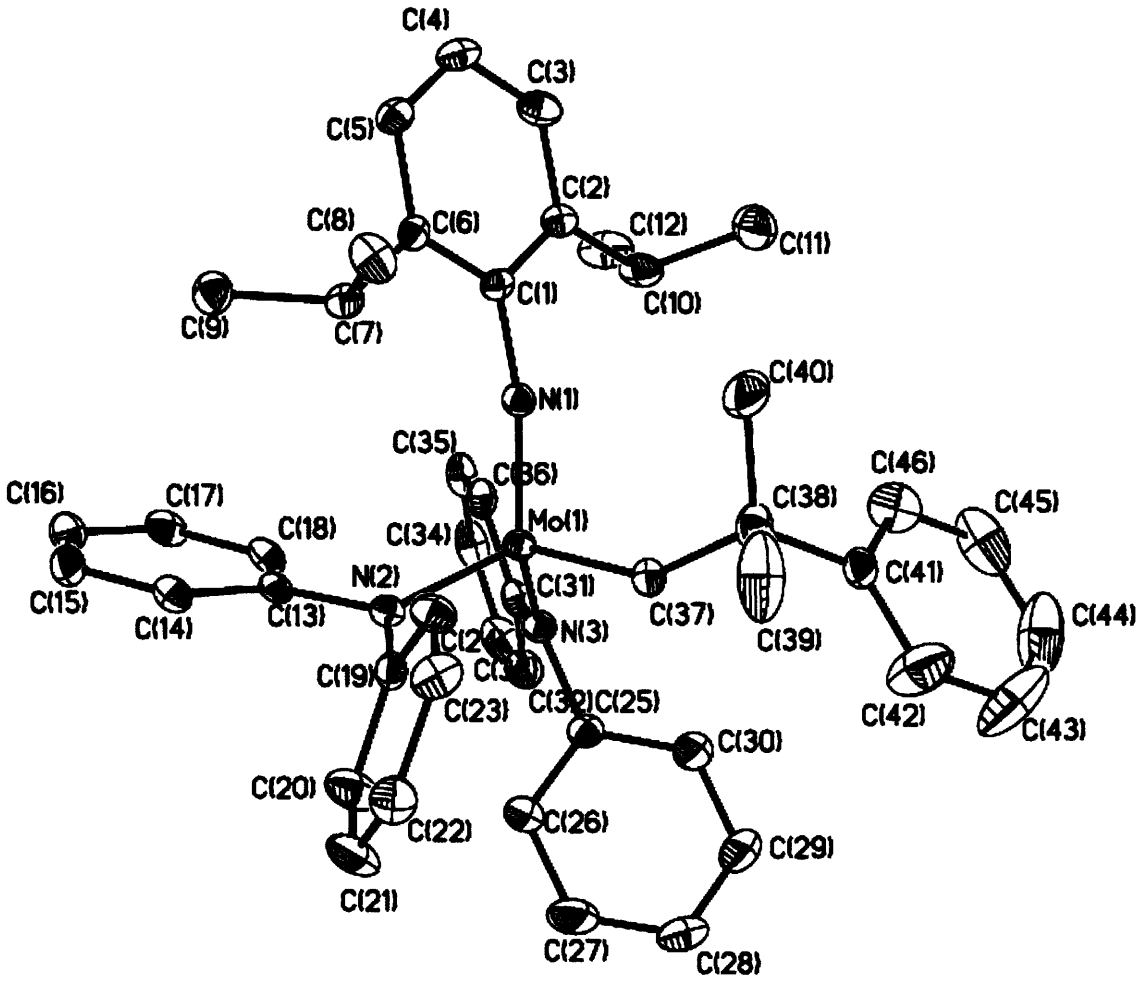


Figure 3.2. Thermal ellipsoid drawing of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$.

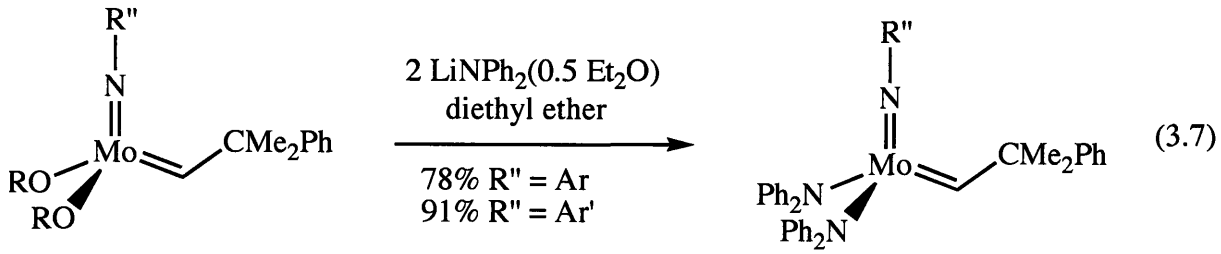
The planes defined by the two amido nitrogen atoms are virtually perpendicular to one another which allows donation of a lone pair of electrons from both the amide ligands. The electron count on the metal center inclusive of the four σ sigma bonds, and π bonds from the alkylidene and imido ligands including the lone pair of electrons on the imido nitrogen is 14. Taking the donation of amide π electrons into account, the total electron count becomes 18. The pseudo 18-electron nature of the complex has significant ramifications in the stability and reactivity of such species.

In all cases so far, the direct synthesis of $Mo(NR'')(CHR')(NR_2)_2$ starting from the bistriflate complex $Mo(NR'')(CHR')(OTf)_2(dme)$ was found to be low yielding. The product sample obtained via this route was found to be contaminated by the free amine HNR_2 which is a result of an adventitious protonation of the lithium amide that was employed in the reaction. Moreover, the use of a strong base in reactions with $Mo(NR'')(CHR')(OTf)_2(dme)$ species have been found to cause deprotonation of the alkylidene carbon to give an alkylidyne species which contributes to the problems concerning the formations as well as isolation of the desired species (Chapter 1). Therefore, an alternate precursor was explored for the synthesis of $Mo(NR'')(CHR')(NR_2)_2$.

3.2.2. Starting from the bisalkoxide complex

As has been discussed in Chapter 1, alkoxide ligands bind strongly to the metal center in four coordinate complexes of the type $M(NR'')(CHR')(OR)_2$ (M = Mo, W) and render them inactive towards intramolecular or bimolecular proton transfer processes that may lead to formation of alkylidyne species. In particular, the relatively high acidity of $Me(CF_3)_2COH$ (pK_a in water = 9.8[23]) compared with other commonly used alcohols (such as t-BuOH, ArOH, 1-adamantanol) in the chemistry of bisalkoxide catalysts allows the facile substitution (via salt metathesis reactions) of $OCMe(CF_3)_2$ group in $M(NR'')(CHR')[OCMe(CF_3)_2]_2$ by electron donating alkoxides. This attribute of $OCMe(CF_3)_2$ group has been exploited in the past to synthesize catalysts that cannot be easily obtained in good purity and/or crystalline form starting from $Mo(NR'')(CHR')(OTf)_2(dme)$.[24]

$Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ can be obtained as a yellow crystalline material in ~ 85% yield from the reaction of $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ with 2 equivalents of $LiOCMe(CF_3)_2$ in diethyl ether.[25] Treating a prechilled solution (-27 °C) of $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ in diethyl ether with two equivalents of $LiNPh_2(0.5\ Et_2O)$ afforded $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ as bright orange crystals in 78% yield (equation 3.7). $Mo(NAr')(CHCMe_2Ph)(NPh_2)_2$ can be similarly prepared as a red-orange crystalline material in 91% yield starting from $Mo(NAr')(CHCMe_2Ph)[OCMe(CF_3)_2]_2$. The complexes thus prepared exhibit identical spectral features to the samples obtained directly from the bistriflate species, but are obtained in higher yields compared to the bistriflate route.



(3.7)

R" = Ar, Ar'; OR = $OCMe(CF_3)_2$

However, $Mo(NAr)(CHCMe_2Ph)(NMe_2)_2$ could be isolated only in 16% yield, albeit in pure from the above synthetic route (cf. equation 3.7). The possible reason for the low yield could be the small size of the amido ligand that could lead to loss of product via some sort of bimolecular decomposition of the alkylidene complex, although a process involving a β-hydrogen resulting in an imine complex eventually causing product degradation cannot be ruled out.

A summary of the spectral values of the bisamido complexes prepared in the course of this work is listed in Table 3.2. In virtually all cases, the alkylidene ligand was found exclusively as the *syn* isomer and the low field resonance of H_α relative to the bisalkoxide or the bistriflate complexes indicates the high electron density on the metal center[21], consequences of which are exhibited in the reactivity of the bisamido species.

Table 3.2. NMR data for bisamido complexes in benzene-d_6 at 22 °C.

Compound	δH_α	δC_α	J_{CH}
Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$	10.71	293.0	120
Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$	11.10	285.5	119
Mo(NAr′)(CHCMe$_2$Ph)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$	10.61	289.4	120
Mo(NAr′)(CHCMe$_2$Ph)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$	11.16	286.1	
Mo(NAr)(CH-t-Bu)(NMe$_2$)$_2$	10.56	273.3	115
Mo(NAr)(CHCMe$_2$Ph)(NMe$_2$)$_2$	10.69	270.1	116
Mo(NAr)(CH-t-Bu)(NPh$_2$)$_2$	10.96	294.8	117
Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$	11.18	292.6	119
Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$	11.08	292.5	122

3.3. Reactions of bisamido complexes with olefins and benzaldehyde

The reactivity of all the above bisamido complexes was tested with simple olefins like ethylene and diallylether. Reacting the Mo(NR″)(CHR′)(NR$_2$)$_2$ or Mo(NR″)(CHR′)[N(R^1)(3,5-$C_6H_3Me_2$)]$_2$ complexes in benzene-d_6 (7.2-11.6 mM) in a J-Young NMR tube with 1 atm of ethylene at room temperature failed to generate the corresponding methylidene species or any metallacycle intermediate. Heating the above reaction mixtures at 60 °C for 24 h did not show any change in the proton NMR spectra of the bisamido complexes. The ability of bisamido species to perform ring-closing metathesis (RCM) reactions was explored by using diallylether as a substrate. Room temperature reactions performed on a NMR scale containing 5 mol% of the bisamido complexes in benzene-d_6 (20 mM) and diallyl ether showed no conversion to 2,4-dihydrofuran and ethylene over 24 h. A complete lack of reactivity was observed even when benzene solutions (~10 mM) of Mo(NR″)(CHR′)(NR$_2$)$_2$ or Mo(NR″)(CHR′)[N(R^1)(3,5-$C_6H_3Me_2$)]$_2$ complexes were treated with benzaldehyde at room temperature over a period of 10 h, which is found to react rapidly in a Wittig-type fashion with complexes of the type Mo(NR″)(CHR′)(OR)$_2$[25] and Mo(NR″)(CHR′)(CH$_2$R′)(OR) (Chapter 2). A similar trend in terms of reactivity towards olefins and benzaldehyde was observed for Mo(NR″)(CHR′)[BINA(NR)$_2$] type

complexes that have been reported[16] prior to this work by Jennifer Jamieson in our group. Although the lack of reactivity of $Mo(NR'')(CHR')[N(R^1)(3,5\text{-}C_6H_3Me_2)]_2$ and $Mo(NR'')(CHR')[BINA(NR)_2]$ species may be attributed to the bulky amide and chelating diimido ligands respectively, the inability of even simple bisamide complexes $Mo(NR'')(CHR')(NR_2)_2$ (R = Ph) to react with olefins is largely due to electronic effects. The π electron donation by the amides in such pseudo 18-electron species shifts the LUMO high in energy, or changes the nature of it so that no favorable interaction with olefins is possible.

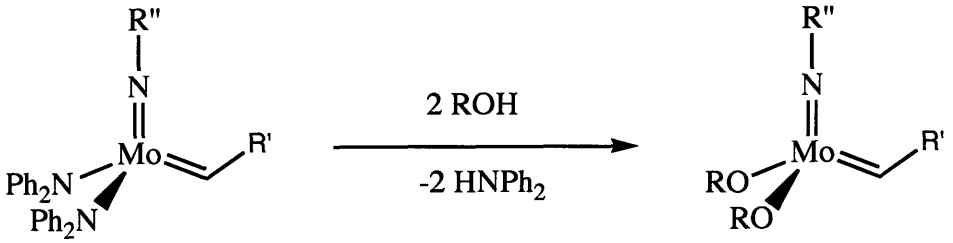
3.4. Alcoholysis reactions of bisamido complexes

It was intended to utilize the amido-based complexes prepared in this work that could be protonated with alcohols to give useful catalysts.

3.4.1. Alcoholysis reactions of $Mo(NR'')(CHR')(NR_2)_2$ complexes

Two representative complexes bearing arylimido ligands with different steric effects, $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ and $Mo(NAr')(CHCMe_2Ph)(NPh_2)_2$ were used as precursors in alcoholysis reactions with simple alcohols like t-BuOH and $Me(CF_3)_2COH$. Upon adding the alcohol to 27-29 mM benzene solutions of the bisamide complexes, the corresponding bisalkoxides species $Mo(NAr)(CH\text{-}t\text{-}Bu)(OR)_2$ and $Mo(NAr')(CHCMe_2Ph)(OR)_2$ (OR = O-t-Bu, $OCMe(CF_3)_2$) were obtained within 10 minutes at room temperature with concomitant appearance of the free amine $HNPh_2$ (equation 3.8).

These initial encouraging results prompted the investigation of the reactions of the bisamide complexes with enantiomerically pure diol in the hope to obtain $Mo(NR'')(CHR')(diolate*)^1$ type catalysts for asymmetric ring-closing metathesis (ARCM) reactions. The initial experiments were designed to quantify the formation of the new alkylidene (of the diolate complex) and the appearance of $HNPh_2$ with respect to the consumption of the bisamido complex.

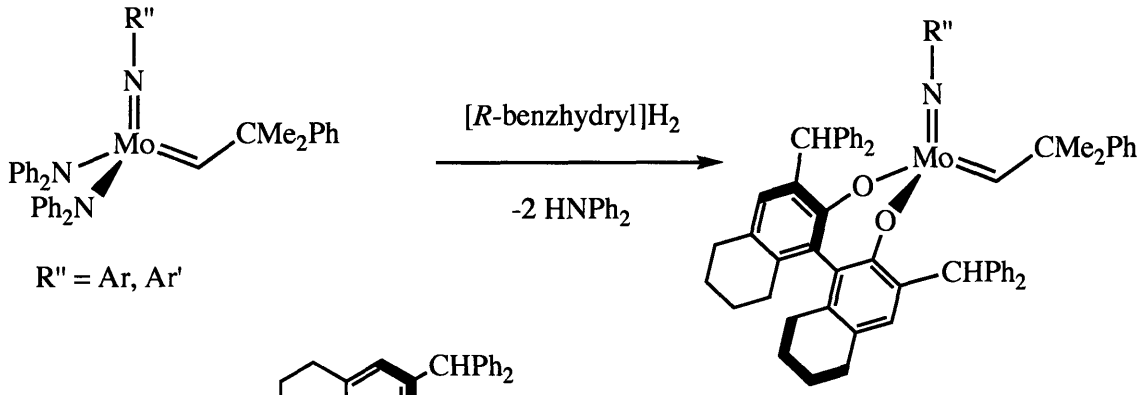


(3.8)

R" = Ar, R' = t-Bu
R" = Ar', R' = CMe_2Ph

ROH = t-BuOH, $Me(CF_3)_2COH$

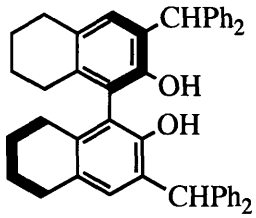
The room temperature reaction of $Mo(NR'')(CHCMe_2Ph)(NPh_2)_2$ (NR'' = NAr, NAr') with one equivalent of [*R*-benzhydril]H_2 was monitored in a 27 mM solution of the bisamido complex in benzene-d_6 using anthracene as an internal standard (equation 3.9).



(3.9)

R" = Ar, Ar'

[*R*-benzhydryl]H_2 =



Figures 3.3 and 3.4 demonstrating the reaction profile (obtained from ^{1}H NMR experiments) indicate a good correlation between the consumption of $Mo(NAr')(CHCMe_2Ph)(NPh_2)_2$ with simultaneous formation of the two products, the diolate complex and $HNPh_2$. The concentration units for the three species involved in the above reaction were determined by integrating the resonances for the two alkylidene protons and the amine proton with respect to an aryl proton of anthracene. The plot of

ln[Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$] versus time was found to be a straight line showing that the initial rate constant for the reaction was k = 13 x 10^{-5} s^{-1} (Figure 3.5). Increasing the size of the *ortho* substituents on the imido group from methyl (NAr′) to isopropyl (NAr) is directly reflected in the sluggishness of the reaction of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ with [*R*-benzhydril]H$_2$ that was performed under identical conditions as in the case of Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$. The reaction profiles depicting the concentrations of the bisamido complex Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ with respect to the formation of Mo(NAr)(CHCMe$_2$Ph)[*R*-benzhydril] and HNPh$_2$ are depicted in Figures 3.6 and 3.7. The initial rate constant for the consumption of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ was found to be k = 5.7 x 10^{-5} s^{-1} (Figure 3.8) at room temperature, which is less than half of the value obtained with the Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ species (*vide supra*). The two reactions proceed to 93% and 85% completion in 15 h at room temperature for NAr′ and NAr imido ligands respectively.

The room temperature reactions of Mo(NR″)(CHCMe$_2$Ph)(NPh$_2$)$_2$ (NR″ = NAr, NAr′) in benzene-d_6 (0.3 M) with enantiomerically pure diols with different substituents on the 3,3′-positions were explored. In general, the bulkier the substituent on the imido and/or the diol, the longer time it took to form the Mo(NR″)(CHCMe$_2$Ph)(diolate*) species (*vide infra*). Also, in most cases, the aforementioned reaction does not go to completion at room temperature, *i.e.*, the 5-10 % of the bisamido species and the diol was found to be present in the reaction shown in equation 3.9 even after 24 h. In case of sterically demanding diols like [Biphen]H$_2$ (Biphen^{2-} = 3,3'-Di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate), no reaction was observed when [Biphen]H$_2$ was added to a benzene-d_6 (0.1 M)solution of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ over a period of 2 days at room temperature. Heating the above solution at 50 °C for 1 day shows 44% conversion to the desired Mo(NAr)(CHCMe$_2$Ph)[Biphen] species along with the starting materials and four new alkylidene resonances in the 11.40-11.80 ppm region (a total of 20% of the mixture)of with no improvement thereafter. The new alkylidene resonances can be thought to correspond to [Mo(Ar)(CHCMe$_2$Ph)(NPh$_2$)]$_2$[μ-Biphen] type species (that are related to the [W(Ar′)(CH-t-Bu)(CH$_2$-t-Bu)]$_2$[μ-Biphen] complex depicted in equation 2.8) purportedly resulting from the monosubstitution of a diphenyl amide ligand

by one hydroxyl group of the diol. However, these bimetallic species bridged by diols have not been prepared and at this stage are mere speculations. Such species can form in the reaction conditions that allows excess of metal centers available to a molecule of a sterically demanding diol. When the metal complex is added to a benzene solution of the diol (reverse addition), the *extra* alkylidene peaks as seen above are present in less than 8% of the reaction mixture. However, complete conversion was not observed. The analogous reaction of [Biphen]H_2 with Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ with gave 64% conversion to Mo(NAr′)(CHCMe$_2$Ph)[Biphen] in 7 days at 50 °C.

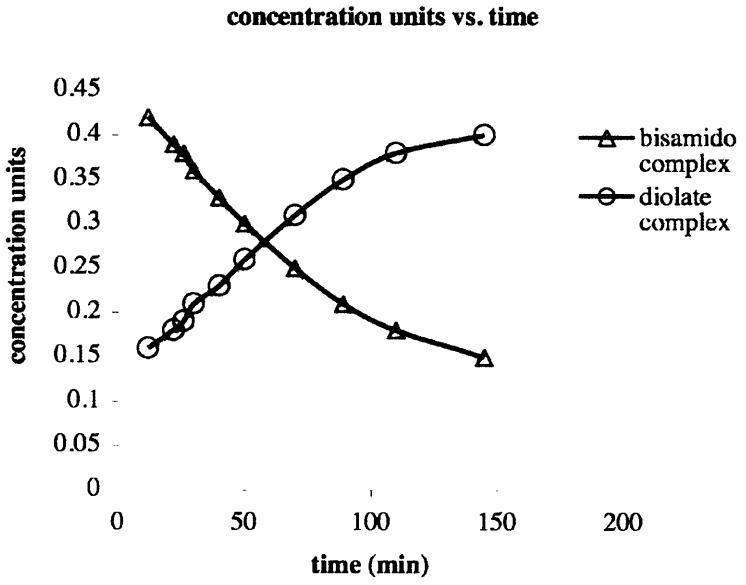


Figure 3.3. Variation of the concentrations of Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and Mo(NAr′)(CHCMe$_2$Ph)[*R*-benzhydril] with time in benzene-d_6 at 22 °C.

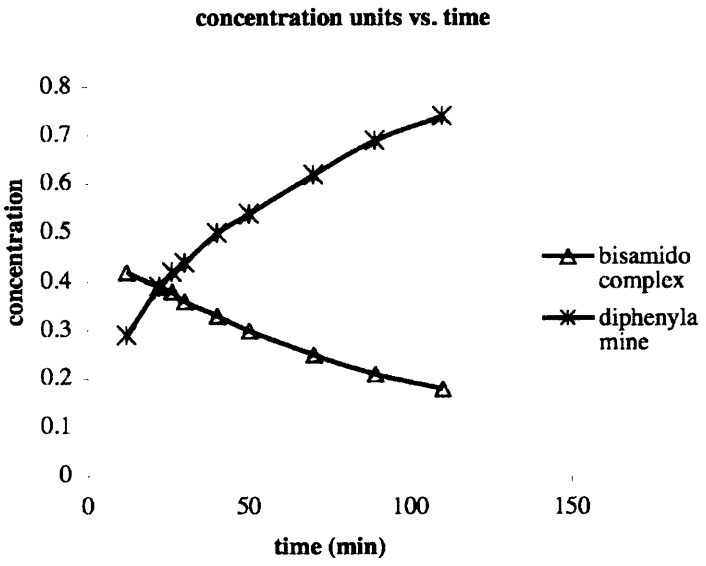


Figure 3.4. Variation of the concentrations of Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and HNPh$_2$ with time in benzene-d_6 at 22 °C.

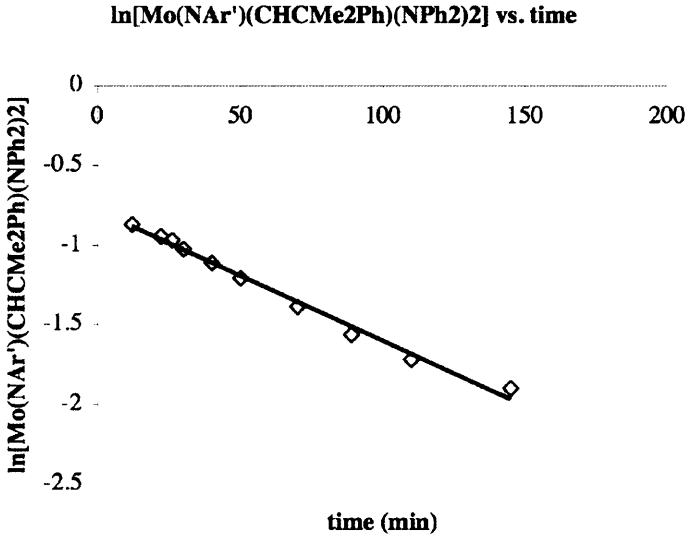


Figure 3.5. Initial kinetics for the consumption of Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ in benzene-d_6 at 22 °C.

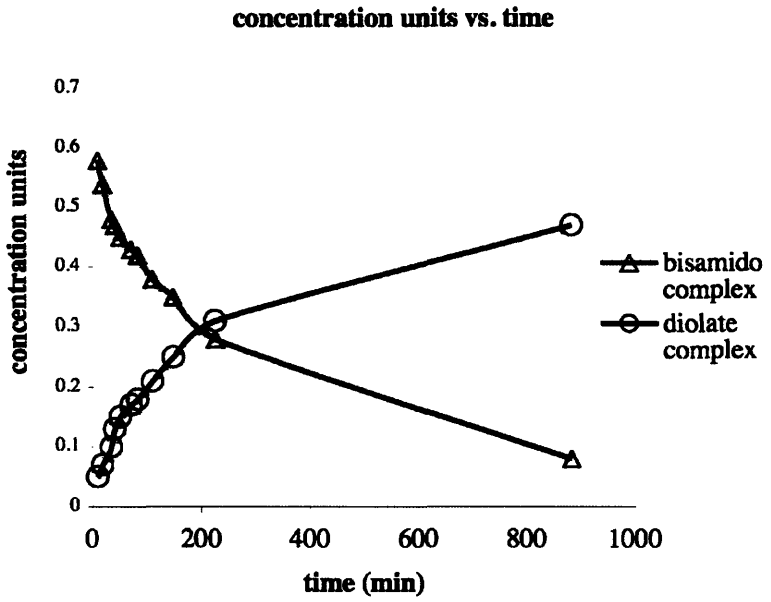


Figure 3.6. Variation of the concentrations of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and Mo(NAr)(CHCMe$_2$Ph)[*R*-benzhydril] with time in benzene-d_6 at 22 °C.

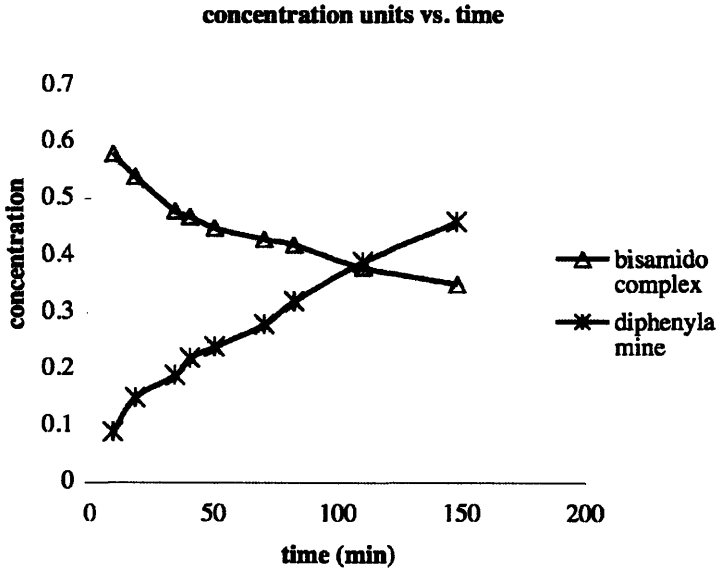


Figure 3.7. Variation of the concentrations of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and HNPh$_2$ with time in benzene-d_6 at 22 °C.

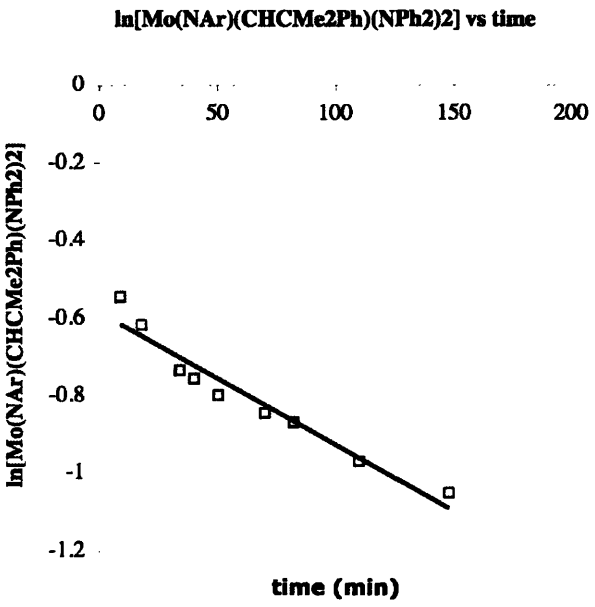


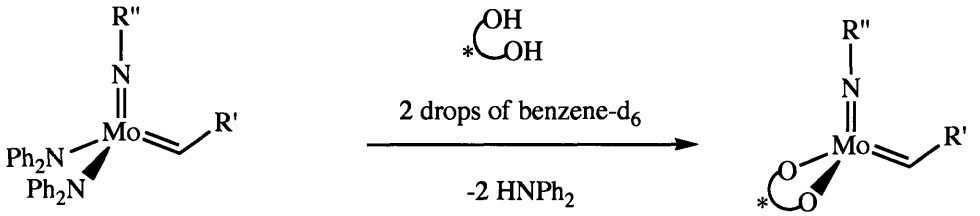
Figure 3.8. Initial kinetics for the consumption of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ in benzene-d_6 at 22 °C.

Binaphtholate-based ligands provide less steric hindrance at the metal center compared to the biphenolate-based diols. This feature is reflected in the less amount of time necessary for the reactions to yield high conversions with ligands such as [*R*-TRIP]H_2 (3,3′-2,4,6-i-Pr$_3$C$_6$H$_2$)[26], [*R*-Ph]H_2 (3,3′-C$_6$H$_5$)[27], [*rac*-Mesitylbinap]H_2 (3,3′-2,4,6-Me$_3$C$_6$H$_2$)[27] and [*R*-TMSbinap]H_2 (3,3′-SiMe$_3$)[28]. Even within the binaphtholate family of ligands, the time and temperature requirements for the reaction to go to completion depend upon the size of the substituent on the 3,3′ positions. No reaction was observed when the bulky Si-i-Pr$_3$ group was placed on 3,3′ position of the biphenolate ligand. The reactions shown in Scheme 3.1 have been carried out by adding the Mo-bisamido complex to the diol in 2 drops of benzene-d_6 (0.3 M) to accelerate the bimolecular interaction between the diol and the bisamido precursor by using minimum amount of solvent. The % conversion refers to the consumption of the starting bisamide complex while the % product refers to the amount of the desired Mo(NR″)(CHCMe$_2$Ph)(diolate*) in the reaction mixture. After heating the reaction mixtures for the stipulated time, more solvent was added and the conversions were

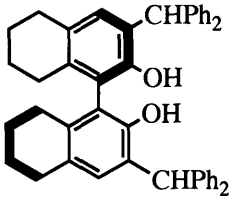
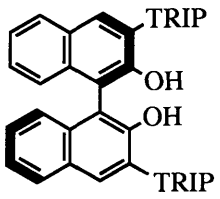
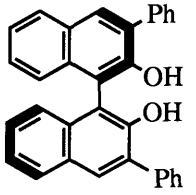
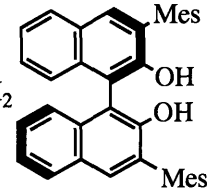
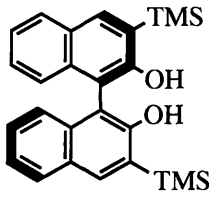
determined by ^{1}H NMR spectroscopy. Decent to excellent conversions were found for virtually all the reactions in Scheme 3.1 and these results fare well with the ~ 30-80% yields observed in the case of isolated Mo(NR″)(CHCMe$_2$Ph)(diolate*) complexes. The product mixture obtained was in some cases found to contain small amounts (< 5-10%) of unidentified new alkylidene peaks along with the desired diolate product (see the discussion for the reaction with [Biphen]H$_2$). The impurity content in the mixture was found in relatively large amounts (26%) when the diol employed was [*R*-TMSbinap]H$_2$, a ligand on which has not been extensively studied in context of the chemistry of Mo(NR″)(CHCMe$_2$Ph)(diolate*) type complexes.[1] The extraneous alkylidene species observed in above reaction would *not* be expected to be totally catalytically inactive. Therefore it would be interesting to know if these unidentified alkylidene peaks cause the *in situ* catalysis to drastically differ from reactivity patterns that have been observed with the isolated catalysts with the simple RCM substrates employed in this study.

3.4.2. Alcoholysis reactions with Mo(NR″)(CHR′)[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ type complexes

The reactions of alcohols with amido complexes bearing bulky substituents Mo(NR″)(CHR′)[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ was observed to proceed slowly (observed by the time taken for a change in color of the solution followed by NMR studies) or not at all compared to similar reactions with Mo(NR″)(CHR′)(NR$_2$)$_2$ type species. Both Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ and Mo(NAr′)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ reacted at room temperature with two equivalents of a relatively acidic alcohol like Me(CF$_3$)$_2$COH in benzene-d_6 (28 mM) to give the corresponding bisalkoxide complexes within 10 minutes. However, the analogous reaction proceeded very slowly (~ 12-15 h) when an electron rich alcohol such as t-BuOH was used. Reducing the steric requirements on the amido ligand by using Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$ and Mo(NAr′)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$ complexes, the reaction with both Me(CF$_3$)$_2$COH as well as t-BuOH were completed in 10 minutes under conditions used as above.



R" = Ar, R' = t-Bu
R" = Ar', R' = CMe_2Ph

OH / OH =		time (h), temp °C		% conversion (product %)
[*R*-benzhydril]H_2		R" = Ar	8.0, 50	100(81)
		R" = Ar'	1.0, 70	100(100)
[*R*-TRIP]H_2		R" = Ar	48.0, 60	100(100)
		R" = Ar'	48.0, 60	100(100)
[*R*-Ph]H_2		R" = Ar	0.5, 50	100(100)
		R" = Ar'	1.0, 70	100(100)
[*rac*-Mesitylbinap]H_2		R" = Ar	14.0, 70	100(100)
		R" = Ar'	14.0, 70	91(86)
[*R*-TMSbinap]H_2		R" = Ar	8.0, 50	82(56)
		R" = Ar'	36.0, 70	90(90)

Scheme 3.1. ***In situ*** **generation of Mo(NR'')(CHCMe$_2$Ph)(diolate*) from bisamides.**

All the Mo(NR′′)(CHR′)[N(R[1])(3,5-$C_6H_3Me_2$)]$_2$ type complexes showed a complete lack of reactivity towards enantiomerically pure diols. This does not come as a surprise upon inspection of the space fill models for these species (Figure 3.9), which shows that the access to the amido nitrogens is severely restricted for both Mo(NAr)(CHCMe$_2$Ph)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$ as well as Mo(NAr)(CHCMe$_2$Ph)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$. However, the reactivities of these complexes are being explored with Si_{surf}OH with a view to make the silica surface-bound analogs of the bisalkoxide catalysts.

3.5. *In situ* ring-closing metathesis reactions using the bisamido precursors

The Mo(NR′′)(CHR′)(diolate*) species that are shown in Scheme 3.1 were used for the *in situ* catalysis of ring-closing metathesis reactions. Reacting diallylether with 5 mol% of the *in situ* generated Mo(NAr′)(CHCMe$_2$Ph)(diolate*) in a 5 mM benzene-d_6 solution at 22 °C afforded dihydrofuran and ethylene (Scheme 3.2).

The synthesis of a five-membered ring via Mo-catalyzed desymmetrization reaction at room temperature using 5 mol% of Mo(NAr)(CH-t-Bu)(diolate*) and Mo(NAr′)(CHCMe$_2$Ph)(diolate*) complexes is shown in Scheme 3.3. Two main points worth mentioning are: firstly, the *in situ* asymmetric ring-closing metathesis reaction works reasonably well vis-à-vis the results obtained for the same reaction using the catalysts that have been prepared and isolated. The enantioselectivity obtained by employing Mo(NAr)(CH-t-Bu)(diolate*) is in the range 68-95%, while the range obtained from the use of Mo(NAr′)(CHCMe$_2$Ph)(diolate*) is 56-97%. Secondly, this approach allows the rapid screening of those catalysts that have not been reacted with the substrate shown in Scheme 3.3 due to problems in isolating those complexes in pure form and/or due to the tremendous manpower that is already being invested in the discovery of new catalysts and optimizing the catalysis with a given catalyst for a particular substrate. Scheme 3.3 clearly depicts the superior performance of 2,6-dimethylphenyl imido complexes with [*R*-benzhydril]$^{2-}$ and [*R*-TRIP]$^{2-}$ diolates, two of the catalysts which were not screened with this particular substrate.

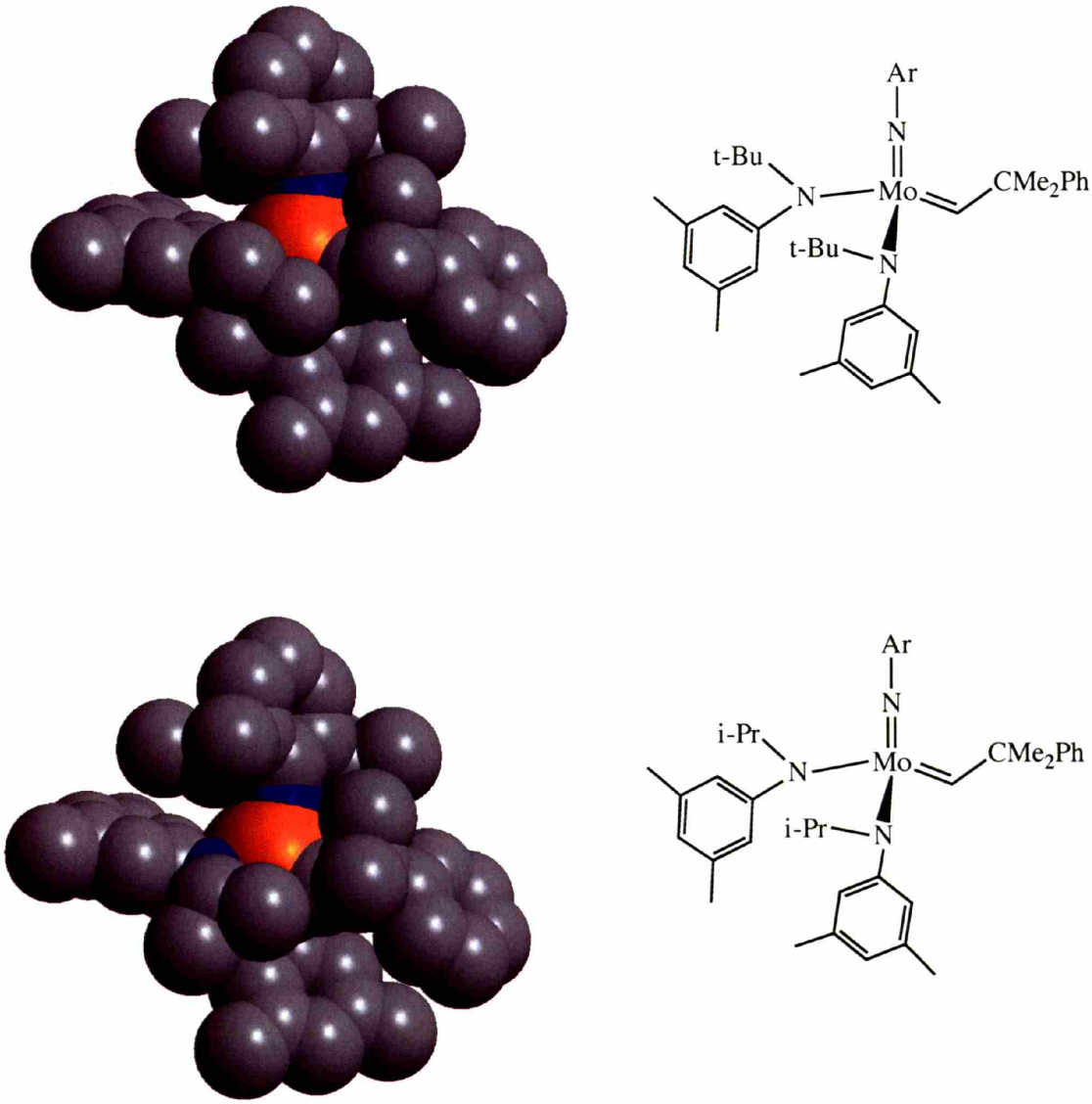
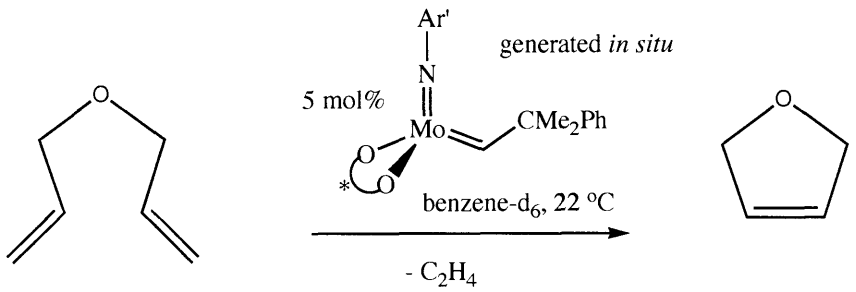
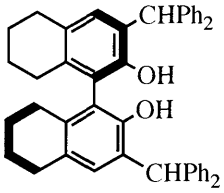
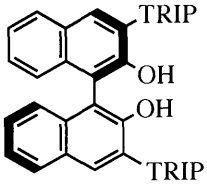
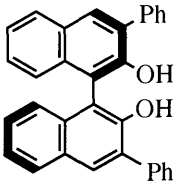
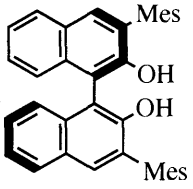
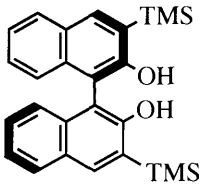
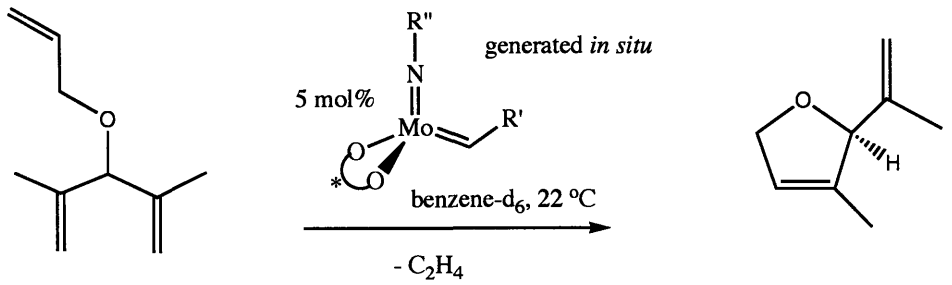


Figure 3.9. Space fill models of Mo(NAr)(CHCMe$_2$Ph)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ and Mo(NAr)(CHCMe$_2$Ph)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$.

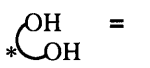


		In situ catalyst % conv, time (h)
[*R*-benzhydril]H_2		95.0, 0.5
[*R*-TRIP]H_2		51.0, 3.0
[*R*-Ph]H_2		44.4, 0.5
[*rac*-Mesitylbinap]H_2		100.0, 0.5
[*R*-TMSbinap]H_2		36.0, 3.0

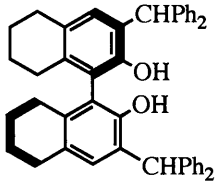
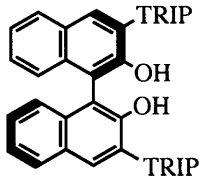
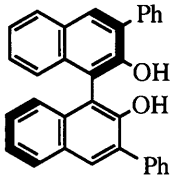
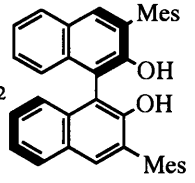
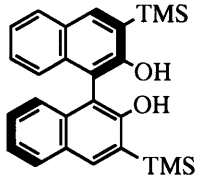
Scheme 3.2. RCM of diallylether by in situ generated Mo(NAr′)(CHCMe$_2$Ph)(diolate*).



R" = Ar, R' = t-Bu
R" = Ar', R' = CMe_2Ph



=

			In situ cat.alyst % conv, % ee	Isolated catalyst % conv, % ee
[*R*-benzhydril]H_2		R" = Ar	77, 94	95, 93[3]
		R" = Ar'	99, 97	N.A.
[*R*-TRIP]H_2		R" = Ar	82, 95	N.A.
		R" = Ar'	99, 96	N.A.
[*R*-Ph]H_2		R" = Ar	90. 68	90, 75[24]
		R" = Ar'	95, 87	N.A.
[*rac*-Mesitylbinap]H_2		R" = Ar	75, N.A.	92, 86[24]
		R" = Ar'	93, N.A.	N.A.
[*R*-TMSbinap]H_2		R" = Ar	92, 72	N.A.
		R" = Ar'	99, 56	N.A.

Scheme 3.3. Comparison of ARCM reactions catalyzed by *in situ* and isolated catalysts.

CONCLUSIONS

The bisamido complexes of the types $Mo(NR'')(CHR')[N(R^1)(3,5\text{-}C_6H_3Me_2)]_2$ and $Mo(NR'')(CHR')(NR_2)_2$ can be prepared starting from the bistriflate complex $Mo(NR'')(CHR')(OTf)_2(dme)$. The yields of the complexes made from this route are low, perhaps due to the propensity of the bistriflate complex to undergo "proton-moving" reactions in the presence of strong bases to give alkylidyne-type species, a process that competes with the formation of the desired imido alkylidene complexes. In certain cases, yields can be improved by making the bisamido complexes from the $Mo(NR'')(CHR')[OCMe(CF_3)_2]_2$ complexes. Alkoxide ligands on the metal have been known to block intra-or intermolecular proton transfer processes that are normally responsible for appearance of the corresponding alkylidyne species.[29]

The bisamido complexes prepared in the course of this work are stable pseudo 18-electron species as a consequence of the perpendicular disposition of the planes defined by the two amido groups. These species have been found to be metathetically inactive, at least in the reactions reported in this chapter. Both the aforementioned complexes react with simple alcohols to give active catalysts of the type $Mo(NR'')(CHR')(OR)_2$. Additionally, $Mo(NR'')(CHR')(NR_2)_2$ species can react with enantiomerically pure diols to give catalytically active Mo(NR'')(CHR')(diolate*) complexes that can be effectively used in both the achiral as well as the asymmetric versions of ring-closing metathesis reactions. Perhaps, the greatest advantage of catalyst screening using this methodology is the freedom experienced by the end user who can generate a wide variety of catalysts bearing a given imido group by using one single precursor and alcohols and diols that are readily available in any synthetic laboratory. The other benefit of this sort of rapid high throughput *in situ* catalysis would be the significant saving of time/manpower that otherwise would go into the extensive work-up and isolation of the metal complexes to be used in catalysis.

Based on the preliminary studies presented here, NAr and NAr′ imido alkylidene complexes with NPh_2 ligands seem to best fit the three quintessential criteria of a suitable precursor: high yields, crystalline form, and most importantly the ability to react with a variety of enantiomerically pure diols to give the desired chiral catalysts. Moreover, the low basicity of $HNPh_2$ prevents it from binding to the metal center that would otherwise

slow the reaction times for catalytic runs. The immediate additional work in this area from an organometallic view point would be two folds: one, deal with developing high yielding and shorter routes to the synthesis of stable bisamido precursors, and two, develop more user-friendly methods for the effective and widespread applications of this form of catalysis.

EXPERIMENTAL SECTION

General. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. The glassware, including NMR tubes were flame- and/or oven-dried prior to use. Ether, pentane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed thrice by freeze-pump-thaw technique. Dichloromethane was distilled from CaH_2 under N_2. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^1H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using a Varian Mercury (^1H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz) or a Varian Inova (^1H 500 MHz, ^{13}C 125 MHz) spectrometers and referenced to the residual protio solvent resonances or external C_6F_6 (-163.0 ppm). Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Mo(NR′′)(CHR′)$(OTf)_2$(dme) complexes and LiN(i-Pr)(3,5-$C_6H_3Me_2$).were prepared as described in the literature. $LiNPh_2$ was prepared by reacting $HNPh_2$ with n-BuLi (1.6 M in hexanes) in toluene. $LiNPh_2$(0.5 ether) was obtained from the crystallization of $LiNPh_2$ from diethyl ether. $LiNMe_2$ was a generous gift from Zachary Tonzetich. Adam Hock is thanked for the gift of LiN(t-Bu)(3,5-$C_6H_3Me_2$). All other chemicals were procured from commercial sources and used as received. Crystal data and structure refinement for Mo(NAr)$(CHCMe_2Ph)(NPh_2)_2$ are given after references.

Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$. To a suspension of Mo(NAr)(CH-t-Bu)$(OTf)_2$(dme) (468 mg, 0.64 mmol) in 30 ml ether at -27 °C was added LiN(t-

Bu)(3,5-$C_6H_3Me_2$)(ether) (330 mg, 1.28 mmol) to obtain a red solution that was stirred at ambient temperature for 1.5 h. Removing volatiles *in vacuo* followed by pentane extraction and filtering the extracts over Celite gave a red oil. Extensive trituration with cold pentane gave a waxy red material. Dissolving this waxy solid in minimum amount of pentane and storing at -27 °C overnight gave 152 mg (34%) of the complex as orange-red crystals: ^{1}H NMR (C_6D_6) δ 10.71 (s, 1, C*H*CMe$_3$, J_{CH} = 120 Hz), 7.17 (br s, 2, Ar*H*), 7.09 (br s, 5, Ar*H*), 6.68 (br s, 2, Ar*H*), 4.58 (sept, 2, C*H*Me$_2$), 2.22 (s, 12, C_6H_3*Me*$_2$), 1.38 (d, 12, CH*Me*$_2$), 1.34 (s, 18, NC*Me*$_3$), 0.98 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 293.0, 157.2, 153.9, 144.9, 137.9, 129.7, 126.6, 126.2, 124.3, 59.5, 48.7, 32.3, 31.5, 27.6, 24.6, 21.7. Anal. Calcd for $C_{41}H_{63}N_3Mo$: C, 70.97; H, 9.15; N, 6.06. Found: C, 71.06; H, 9.06; N, 5.97.

Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_2$. An ether solution of LiN(i-Pr)(3,5-$C_6H_3Me_2$)(ether) (343 mg, 1.41 mmol) was added to a suspension of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (6.00 g, 8.22 mmol) in 40 ml of ether at -27 °C to obtain a deep red solution. Stirring the reaction mixture at room temperature for 1 h was followed by removing solvents under reduced pressure. Extracting with pentane and filtering over Celite afforded a red liquid which was concentrated to obtain a red oil that was found to contain 29% of HN(i-Pr)(3,5-$C_6H_3Me_2$) that could not be removed on a high vacuum line, or by heating the oil under reduced pressure: ^{1}H NMR (C_6D_6) δ 11.10 (s, 1, C*H*CMe$_3$, J_{CH} = 119 Hz), 7.07 (br s, 3, Ar*H*), 6.85 (br s, 4, Ar*H*), 6.56 (br s, 2, Ar*H*), 4.25 (sept, 2, C*H*Me$_2$), 4.01 (sept, 2, C*H*Me$_2$), 2.14 (s, 12, C_6H_3*Me*$_2$), 1.26 (d, 12, CH*Me*$_2$), 1.23 (d, 12, CH*Me*$_2$), 1.19 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 285.2, 154.9, 145.0, 138.5, 126.4, 125.0, 123.7, 123.2, 58.6, 48.4, 32.2, 28.2, 25.4, 25.0, 24.9, 21.9.

Mo(NAr′)(CHCMe$_2$Ph)[N(t-Bu)(3,5-$C_6H_3Me_2$)]$_2$. 1.85 g (7.19 mmol) of LiN(t-Bu)(3,5-$C_6H_3Me_2$)(ether) was added to a stirring solution of Mo(NAr′)(CH-t-Bu)(OTf)$_2$(dme) in ether at -27 °C. Removing volatiles *in vacuo* followed by pentane extraction and filtering the extracts over Celite gave a red oily material. Extensive trituration with cold pentane gave an orange-red crystalline material in 33% yield (827 mg): ^{1}H NMR (C_6D_6) δ 10.61 (s, 1, C*H*CMe$_2$Ph, J_{CH} = 120 Hz), 7.10-6.82 (overlapping

peaks, 12, Ar*H*), 6.43 (br s, 2, Ar*H*), 2.48 (s, 6, CHC*Me*$_2$Ph) 1.93 (s, 12, C_6H_3*Me*$_2$), 1.18 (s, 24, Ar'*Me*$_2$, NC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 289.4, 157.2, 156.7, 150.2, 137.9, 134.2, 129.9, 128.8, 126.7, 126.0, 125.2, 59.7, 54.6, 32.3, 30.7, 21.8, 21.3. Anal. Calcd for $C_{42}H_{57}N_3Mo$: C, 72.08; H, 8.21; N, 6.00. Found: C, 66.80; H, 8.80; N, 5.05.

Mo(NAr')(CHCMe$_2$Ph)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$. Mo(NAr')(CH-t-Bu)(OTf)$_2$(dme) (1.07 g, 1.45 mmol) in 80 ml ether was chilled to -27 °C. 707 mg (2.91 mmol) of LiN(i-Pr)(3,5-$C_6H_3Me_2$)(ether) was added to it and the resulting brownish red solution was allowed to stir to room temperature for 1 h. The reaction mixture was taken to dryness on a high vacuum line and extracted with pentane. Filtration of the pentane extracts over Celite followed by removal of solvents *in vacuo* gave a red oil that was found to be a mixture of the desired product along with HN(i-Pr)(3,5-$C_6H_3Me_2$)(ether): ^{1}H NMR (C_6D_6) δ 11.16 (s, 1, C*H*CMe$_2$Ph); ^{13}C NMR (C_6D_6): δ 286.1.

Mo(NAr)(CH-t-Bu)(NMe$_2$)$_2$. Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (1.00 g, 1.37 mmol) in 80 ml ether was chilled to -27 °C. 140 mg (2.75 mmol) of LiNMe$_2$ was added to it and the resulting brownish red solution was allowed to stir to room temperature for 1 h. The reaction mixture was taken to dryness and extracted with pentane. Filtration of the pentane extracts over Celite followed by removal of solvents *in vacuo* afforded a red-brown oil which contained an unidentified impurity along with the desired product: ^{1}H NMR (C_6D_6) δ 10.56 (s, 1, C*H*CMe$_3$, J_{CH} = 115 Hz), 7.02 (m, 3, Ar*H*), 4.05 (sept, 2, C*H*Me$_2$), 3.27 (s, 12, N*Me*$_2$), 1.37 (d, 12, CH*Me*$_2$), 1.22 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 273.3. Anal. Cald. for $C_{21}H_{39}MoN_3$: C, 58.73; H, 9.15; N, 9.78. Found: C, 58.66; H, 9.06; N, 9.68.

Mo(NAr)(CHCMe$_2$Ph)(NMe$_2$)$_2$. A yellow solution of Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (400 mg, 0.52 mmol) in 50 ml ether was cooled to -27 °C. Gradual addition of 2 equivalents of LiNMe$_2$ (53 mg, 1.05 mmol) as a white powder to the above reaction resulted in a change in color from yellow to orange to red within 5 minutes. The color of the solution continued to change to brownish yellow to eventually greenish yellow showing some possible decomposition as the reaction mixture

was allowed to warm to room temperature. Stirring the reaction mixture for 1 h followed by complete removal of solvents under reduced pressure afforded a green waxy solid. Storing this green material at -27 °C in minimum amount of pentane allowed bright orange material to crystallize out. Washing the orange crystals obtained with a few drops of cold pentane (-27 °C) afforded the desired complex in 16% yield: ^{1}H NMR (C_6D_6) δ 10.56 (s, 1, C*H*CMe$_2$Ph, J_{CH} = 116 Hz), 7.50 (d, 2, Ar*H*), 7.24 (t, 1, Ar*H*), 7.18 (t, 3, Ar*H*), 7.10 (d, 2, Ar*H*), 4.12 (sept, 2, C*H*Me$_2$), 3.29 (s, 12, N*Me*$_2$) 1.70 (s, 6, CHC*Me*$_2$Ph), 1.37 (d, 12, CH*Me*$_2$); ^{13}C NMR (C_6D_6): δ 273.3. Anal. Cald. for $C_{26}H_{41}MoN_3$: C, 63.53; H, 8.41; N, 8.55. Found: C, 57.96; H, 8.59; N, 7.02.

Mo(NAr)(CH-t-Bu)(NPh$_2$)$_2$. A solution of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (6.00 g, 8.22 mmol) in 80 ml THF at -27 °C was treated with a pre-chilled solution of 2.88 g (16.44 mmol) Ph$_2$NLi in 20 ml THF. The color changed from yellow to red immediately. After stirring for 1h while allowing the reaction mixture to warm to room temperature, volatiles were removed i*n vacuo* and the residue extracted with pentane. Filtering the extracts over Celite followed by removal of solvent gave an orange red powder in 12 % yield and a red oily material which was found to be essentially the desired complex by proton NMR: : ^{1}H NMR (C_6D_6) δ 10.96 (s, 1, C*H*CMe$_3$, J_{CH} = 117 Hz), 7.12 -6.83 (overlapping peaks, 23, Ar*H*, N*Ph$_2$*), 3.90 (sept, 2, C*H*Me$_2$), 1.81 (d, 12, CH*Me*$_2$), 0.98 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 294.8. Anal. Cald. for $C_{41}H_{47}MoN_3$: C, 72.66; H, 6.99; N, 6.20. Found: C, 72.52; H 7.08; N 6.11.

Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$. Method A: 500 mg (0.63 mmol) of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) was taken in 8ml of THF and cooled in the box fridge to -27 °C. A pre-chilled solution of Ph$_2$NLi (221 mg, 1.26 mmol) in 2ml THF was added to the above solution in a drop wise fashion to immediately afford a red solution. After stirring for 1h at room temperature, volatiles were removed *in vacuo* to give a red foam which was extracted with pentane and filtered over Celite. The filtrate was concentrated to dryness to obtain an oily red material. Triturating with cold pentane several times followed by dissolving in minimum amount of toluene gave an orange red powder (35%).

Method B: A yellow solution of Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (505 mg, 0.66 mmol) in 50 ml ether was cooled to -27 °C. Gradual addition of 2 equivalents of LiNPh$_2$(Et$_2$O)$_{0.5}$ (280 mg, 1.32 mmol) as a white powder to the above reaction resulted in a change in color from yellow to orange to red as the reaction mixture was allowed to warm to room temperature. Stirring the reaction mixture for 1 h followed by partial removal of solvents and layering the reaction mixture with 5 ml pentane allowed bright orange material to crystallize out. Washing the orange crystals obtained with 5 ml of cold pentane (-27 °C) afforded the desired complex in 78% yield in two crops: ^{1}H NMR (C$_6$D$_6$) δ 11.78 (s, 0.04, *anti* C*H*CMe$_2$Ph), 11.18 (s, 1, *syn* C*H*CMe$_2$Ph, J_{CH} = 119 Hz), 7.10-6.79 (overlapping peaks, 28, Ar*H*, N*Ph*$_2$), 3.86 (sept, 2, C*H*Me$_2$), 1.45 (s, 6, CHC*Me*$_2$Ph), 1.61 (d, 12, CH*Me*$_2$); ^{13}C NMR (C$_6$D$_6$): δ 292.6, 155.5, 154.1, 148.5, 146.3, 129.9, 128.9, 127.8, 126.5, 126.4, 124.6, 123.9, 123.6, 55.7, 31.0, 28.6, 24.7. Anal. Cald. for C$_{46}$H$_{49}$MoN$_3$: C, 74.68; H, 6.68; N, 5.68. Found: C, 74.57; H, 6.62; N, 5.69.

Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$. Mo(NAr′)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (539 mg, 0.76 mmol) in 55 ml ether was chilled to -27 °C. Gradual addition of 2 equivalents of LiNPh$_2$(Et$_2$O)$_{0.5}$ (322 mg, 1.52 mmol) as a white powder to the above reaction resulted in a change in color from yellow to orange to red-orange as the reaction mixture was allowed to warm to room temperature. Stirring the reaction mixture for 1 h followed by partial removal of solvents and layering the reaction mixture with 5 ml pentane allowed bright red-orange solid to crystallize out. Washing the red-orange crystals obtained with 3 ml of cold pentane (-27 °C) afforded the desired complex in 91% yield (475 mg): ^{1}H NMR (C$_6$D$_6$) δ 11.08 (s, 1, C*H*CMe$_2$Ph, J_{CH} = 122 Hz), 7.10-6.81 (overlapping peaks, 28, Ar*H*, N*Ph*$_2$), 2.33 (s, 6, CHC*Me*$_2$Ph), 1.37 (s, 6, Ar′*Me*$_2$); ^{13}C NMR (C$_6$D$_6$): δ 292.5, 157.2, 155.2, 148.4, 135.4, 129.9, 128.8, 126.8, 126.5, 126.4, 124.5, 123.6, 55.3, 30.5, 19.6. Anal. Cald. for C$_{42}$H$_{41}$MoN$_3$: C, 73.78; H, 6.04; N, 6.15. Found: C, 73.59; H, 6.12; N, 6.02.

Representative method for generating Mo(NR′′)(CHCMe$_2$Ph)(diolate*). 10-20 mg of the bisamido precursor was added to a solution of the enantiomerically pure diol in 0.5 ml drops of benzene-d_6 in a J-Young tube. The reaction mixture was heated at 60 °C till the

starting materials were consumed and the progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Representative method for *in situ* catalysis using Mo(NR'')(CHCMe$_2$Ph)(diolate*). To the Mo(NR'')(CHCMe$_2$Ph)(diolate*) species generated in the J-Young tube as shown above, 20 equivalents of the substrate was added and the conversions were determined by ^{1}H NMR spectroscopy. For asymmetric ring-closing metathesis reactions, the enantiomeric excess was determined by injecting 1 μl of the reaction mixture (that was passed through a plug of silica) into a GC equipped with a Chiraldex column.

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Crystal Data and Structure Refinement for Compound Reported in Chapter 3

Table 3XR.1. Crystal data and structure refinement for $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$.

Empirical formula	C46 H49 Mo N3	
Formula weight	739.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.279(3) Å	α= 79.848(6) °.
	b = 20.158(7) Å	β= 89.997(6) °.
	c = 20.739(8) Å	γ = 83.507(6) °.
Volume	3793(2) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.382 mm^{-1}	
F(000)	1552	
Crystal size	0.20 x 0.15 x 0.05 mm^3	
Theta range for data collection	1.00 to 28.49°.	
Index ranges	$-12\leq h\leq 12$, $-26\leq k\leq 27$, $0\leq l\leq 27$	
Reflections collected	23612	
Independent reflections	23612 [non-merohedral twin]	
Completeness to theta = 28.49∞	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9812 and 0.9276	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23612 / 0 / 914	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1032	
R indices (all data)	R1 = 0.0726, wR2 = 0.1119	
Largest diff. peak and hole	0.946 and -0.517 e. $Å^{-3}$	

Appendix A

BIMOLECULAR DECOMPOSITION OF MOLYBDENUM ALKYLIDENE COMPLEXES TO GIVE MO=MO SPECIES

A portion of this chapter has appeared in print:

Schrock, R. R.; Lopez, L. P. H.; Hafer, J.; Singh, R.; Sinha, A.; Müller, P. "Olefin Metathesis Reactions Initiated by d^2 Molybdenum or Tungsten Complexes" *Organometallics* **2005**, 24, 5211.

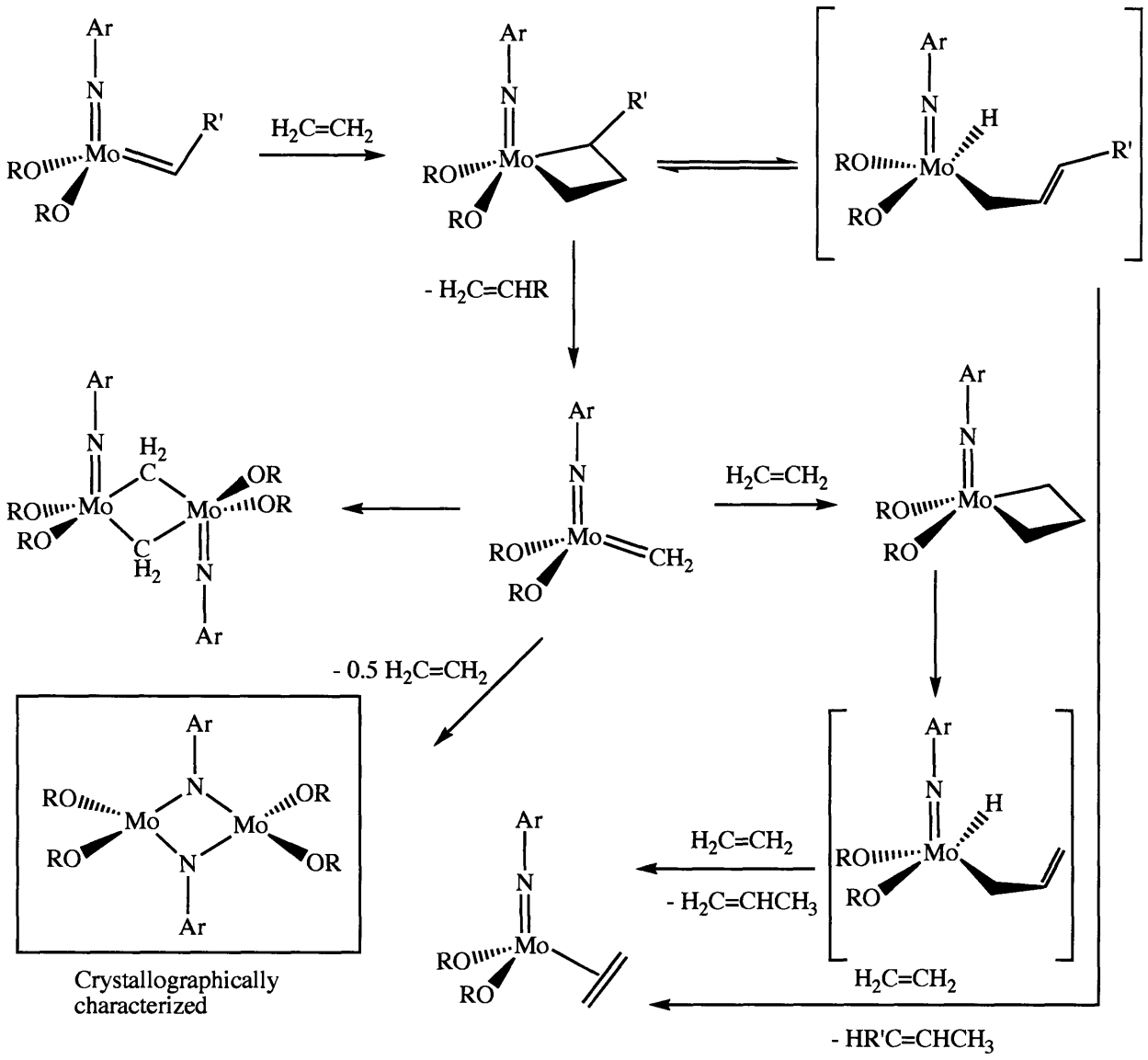
INTRODUCTION

The inherent design of the well-defined tetrahedral complexes Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) provides for the stabilization of a highly electron deficient molybdenum center by sterically demanding imido, alkoxide and alkyl/alkylidene groups.[1] A careful choice of ligands having no β-hydrogen obviates any intramolecular processes such as β-hydrogen elimination that would otherwise lead to decomposition of the complex.[2] However, formation of new alkylidenes that are smaller than the parent neopentylidene group during a catalytic cycle opens up new pathways for formation of catalytically inactive (or at the very least much less reactive) moieties that eventually renders the catalysis inoperable. A few of the species that have been detected by extensive NMR experiments[3,4] for the reactions of Mo(NAr)(CHR')$(OR)_2$ (or Mo(NAr)(CHR')(diolate)) complexes with ethylene are shown in Scheme A.1. The isolation and crystallographic characterization of $[Mo(OR)_2]_2(\mu\text{-}NAr)_2$[5] (OR = O-t-Bu) (obtained in 50% yield from the reaction of ethylene (2 atm) and Mo(NAr)(CH-t-Bu)$(OR)_2$) led to the general precept that such binuclear species bridged by imido ligands would be a major "sink" leading to the deactivation of catalytically relevant molecules during catalysis. Disruption of catalysis processes, especially concerning tungsten, has also been observed via formation of metallacycles that prove too stable to react even with ethylene.[6] It was, therefore, intended to probe the bimolecular decomposition of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes with a view to isolate and study the dimeric species vis-à-vis the imido-bridged complex $[Mo(OR)_2]_2(\mu\text{-}NAr)_2$ that was seen in the bisalkoxide system.

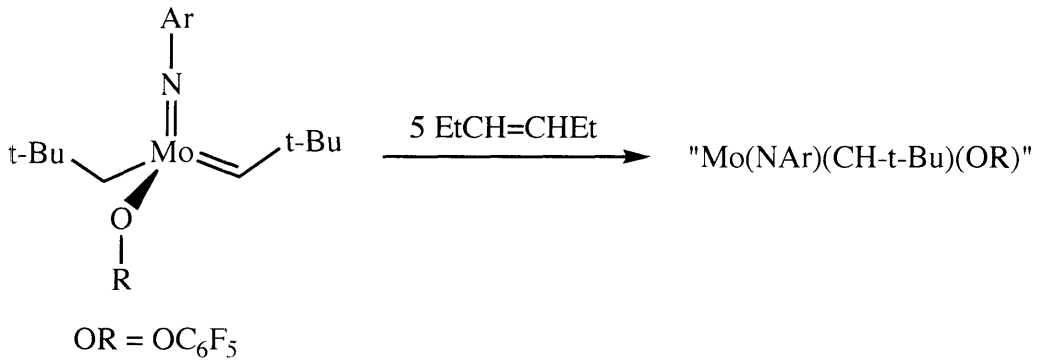
RESULTS AND DISCUSSION

A.1. Formation of unbridged Mo=Mo species

The room temperature reaction of yellow colored Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) in pentane with 5.8 equivalents of *trans*-3-hexene gives a red solid in 78% yield. The absence of any alkylidene resonance in the proton and carbon NMR spectra, and the presence of characteristic resonances for the imido and neopentyl groups[2] indicated a species with the empirical formula Mo(NAr)(CH_2-t-Bu)(OC_6F_5) (equation A.1). This finding was also supported by an elemental analysis performed on the red solid. The ^{19}F NMR exhibited the presence of three sets of fluorine resonances indicating a freely rotating pentaflurophenoxide ligand.



Scheme A.1. Intermediates identified in the reactions of Mo(NAr)(CHR')(OR)$_2$ complexes with ethylene.



(A.1)

OR = OC_6F_5

Single crystals of the red solid were obtained from a mixture of toluene and pentane stored at -20 °C. Adam Hock mounted a suitable crystal and solved the structure with Peter Müller's assistance to reveal a dimeric complex, $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ (Figure A.1). As opposed to $[Mo(OR)_2]_2(\mu\text{-NAr})_2$, the X-ray structure of $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ showed the presence of an "unsupported" Mo=Mo bond (2.410(8) Å) *without* bridging imido or alkoxide ligands that would normally be expected to bridge the two metal centers. This is a homochiral species (*R*, *R*) with a C_2-axis running perpendicular to the Mo=Mo bond. The bulky neopentyl ligands on the two metal atoms are eclipsed with respect to the C_2-axis, the dihedral angle being only 12.5 °. Interestingly, the imido ligand rests virtually perpendicular to the axis defined by the two molybdenum atoms ((N(1)-Mo(1)-Mo(1A) angle is 89.89(5)°) (Table A.1) while the Mo(1)-N(1)-C(12) angle (170.69(12)°) and Mo(1)-N(1) bond length (1.740(15) Å) are within the regular range for similar species.[7] The opening up of the Mo(1)-O(1)-C(6) angle at 156.90(15)° suggests a significant amount of π character in the bonding involved. The neopentyl ligand seems relatively undistorted since the Mo(1)-C(1)-C(2) angle is 114.67(13)°.

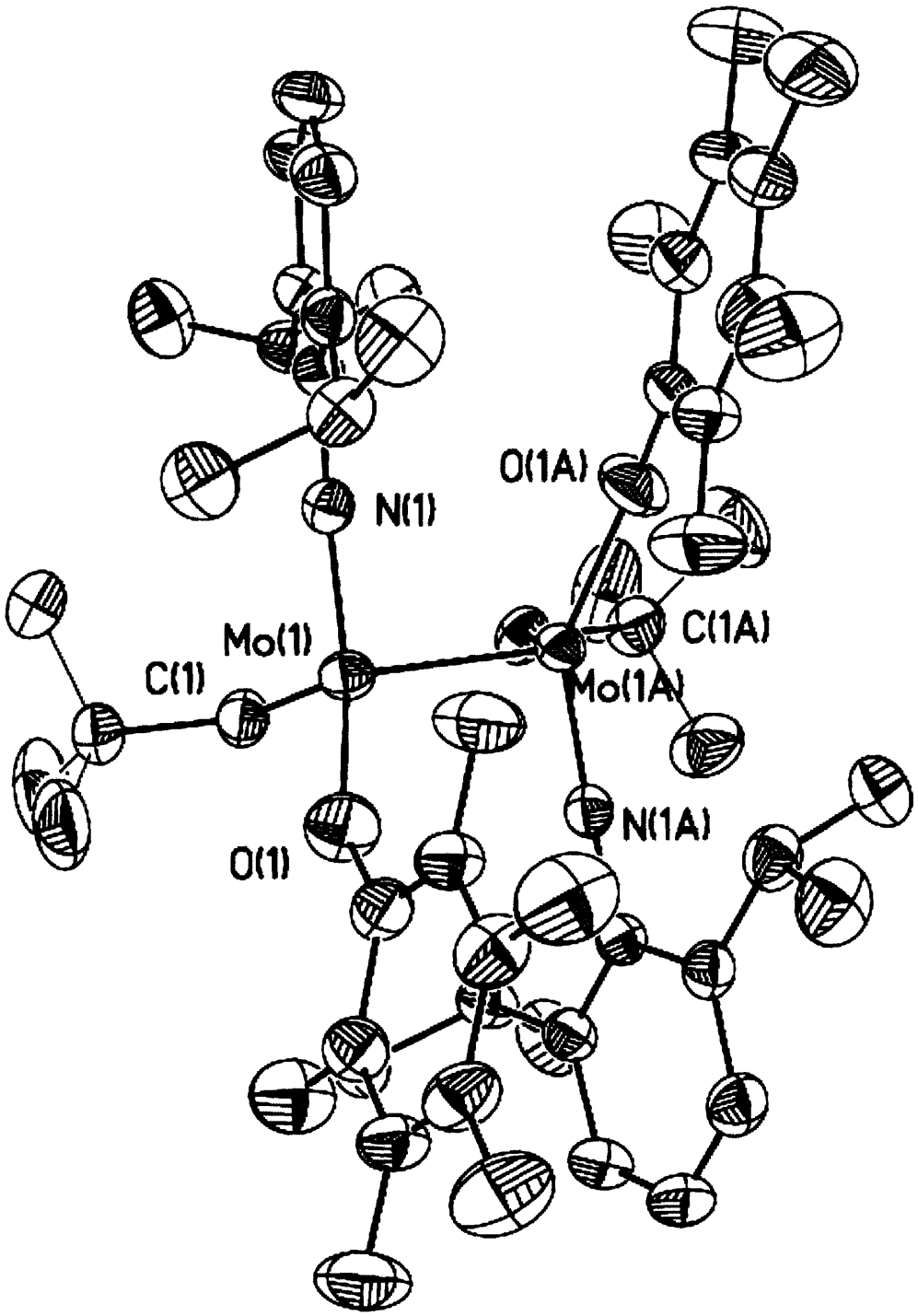
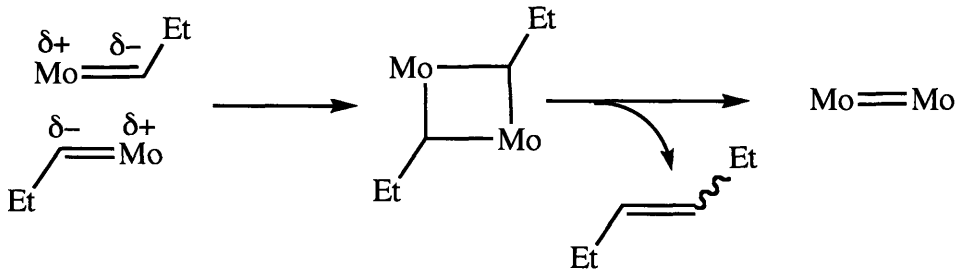


Figure A.1. Thermal ellipsoid drawing of $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$.

Table A.1. Selected bond lengths [Å] and angles [°] for $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$.

Mo(1)-N(1)	1.7397(15)
Mo(1)-O(1)	1.9377(14)
Mo(1)-C(1)	2.1417(19)
Mo(1)-Mo(1A)	2.4104(8)
N(1)-Mo(1)-O(1)	138.22(7)
N(1)-Mo(1)-C(1)	101.13(7)
O(1)-Mo(1)-C(1)	109.69(8)
N(1)-Mo(1)-Mo(1A)	89.89(5)
O(1)-Mo(1)-Mo(1A)	109.43(5)
C(1)-Mo(1)-Mo(1A)	102.61(5)
Mo(1)-N(1)-Mo(12)	170.69(12)
Mo(1)-O(1)-C(6)	156.90(15)
Mo(1)-C(1)-C(2)	114.67(13)

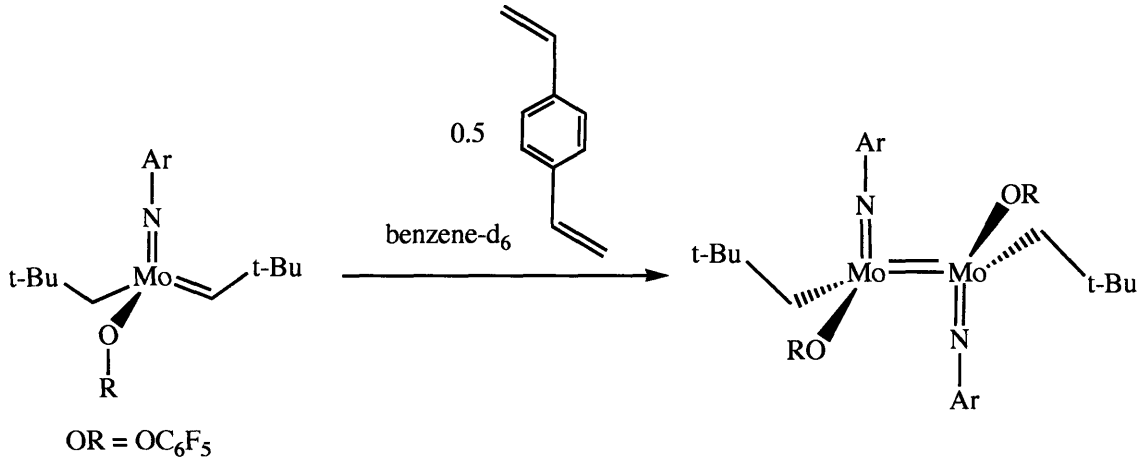
This bimetallic complex presumably forms via a $Mo(NAr)(CHEt)(CH\text{-}t\text{-}Bu)(OC_6F_5)$ intermediate (not observed) that is unstable with respect to bimolecular decomposition due to the replacement of the sterically encumbering neopentylidene group by a propylidene moiety (*vide infra*). The Mo=Mo bond would then result as a consequence of coupling of two $Mo(NAr)(CHEt)(CH\text{-}t\text{-}Bu)(OC_6F_5)$ units via a dimetallacyclobutane species (equation A.2).



(A.2)

$[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$ can also be cleanly observed within 10 minutes when $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$ is treated with 0.5 equivalents of divinylbenzene in a solution of benzene (60mM) at room temperature (equation A.3). A related tungsten complex

$[W(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ obtained in both the homo- as well as the heterochiral forms has been prepared (and crystallographically characterized) by Pia Lopez by treating $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ with an internal olefin like *cis*-2-pentene.[7] The homochiral complexes for both molybdenum and tungsten show minimal differences in the structural parameters. While the heterochiral isomer of $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ can also be synthesized by simply heating a toluene solution of $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ at 80 °C for a few hours, the analogous route to prepare the heterochiral molybdenum complex does not yield the desired species. Heating a solution $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ in toluene for 72 h at even 90 °C gives only the parent alkylidene species along with some decomposition product which was *not* the expected heterochiral complex. It should be noted that the tungsten species $W(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ is so prone to bimolecular decomposition (giving rise to the dimeric complexes) that it can only be prepared cleanly when dilute solutions (< 0.05 M) of $W(NAr)(CH_2\text{-t-Bu})_3(OC_6F_5)$ are employed.



(A.3)

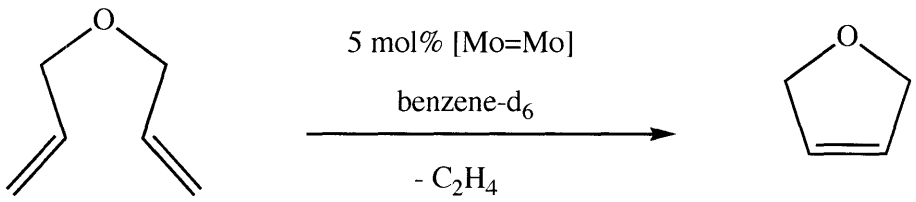
The M=M (M = Mo, W) complexes described above bear a striking resemblance to the two rhenium complexes $[Re(C\text{-t-Bu})(OR)_2]_2$ (OR = O-t-Bu, $OCMe(CF_3)_2$)[8] prepared by Robert Toreki in our group about 15 years ago by reacting $Re(C\text{-t-Bu})(CH\text{-t-Bu})(OR)_2$ (OR = O-t-Bu, $OCMe(CF_3)_2$) complexes in THF with excess vinyl ethers CH_2=CHOR′ (OR′ = OEt, $OSiMe_3$) at room temperature. The alkylidyne group (which is isolobal with an imido ligand) is located perpendicular to the bond defined by the two rhenium atoms, the two C≡Re=Re bond angles being 90.02(2)° and 89.5(1)° respectively. The two d^2, d^2 metal centers exhibit diamagnetic

behavior for the rhenium complexes by virtue of the metal-metal double bond as is found in the case of molybdenum and tungsten complexes (*vide supra*). This observation is supported by the Fenske-Hall molecular orbital calculations performed by Casey *et al.* which suggest a $\sigma^2\pi^2$ configuration of the ground state for the metal-metal bonding configuration in high oxidation state rhenium complexes.[9] By the same analogy, it can be assumed for $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ that three of the d-orbitals (d_{xy}, d_{xz} and d_{yz}) are involved in the π-bonding, whereas the σ-bond framework results from a combination of s orbital with d_z^2, and the three p orbitals.

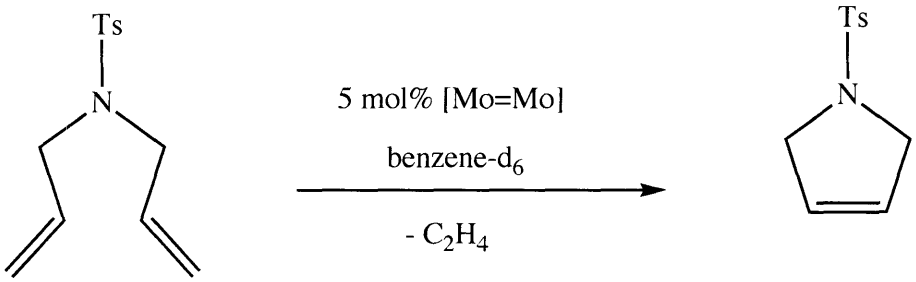
Attempts to synthesize $[Mo(NAr)(CH_2\text{-t-Bu})(OR)]_2$ complexes with two other alkoxides (OR = OAd, OAr) via the aforementioned route of using an internal olefin failed. When a solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) in pentane was treated with 5 equivalents of *trans*-3 hexene, no reaction was observed for a period of 2 days. Adding 10 equivalents of *cis*-2-pentene to the above reaction mixture and heating at 70 °C for 3 days in a heavy walled tubular vessel did not lead to any consumption of the starting material. No reaction was observed when Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd) was treated with 0.5 equivalents of divinylbenzene (cf. equation 2.19). Upon adding 5 equivalents of *trans*-3-hexene to a benzene solution of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) at room temperature, a mixture containing the starting material and a new alkylidene Mo(NAr)(CHEt)(CH_2-t-Bu)(OAr) (triplet at 12.5 ppm, J_{CH} = 8 Hz) in a ratio of 1: 0.46 is obtained. The conversion of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) to Mo(NAr)(CHEt)(CH_2-t-Bu)(OAr) can be maximized to 78% in the reaction mixture containing 22% of the parent alkylidene when 20 equivalents of *trans*-3-hexene is used with Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAr) in benzene, and the reaction heated to 70 °C for 2 days. When the above reaction is allowed to proceed at 70 °C for 4 days, complete decomposition of both the propylidene as well as the neopentylidene moieties is observed. The decomposition product(s) could not be identified.

A.2. Reactions of unbridged Mo=Mo species with olefins

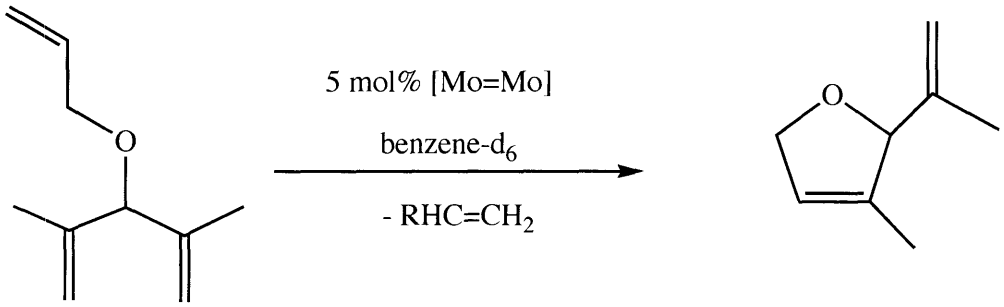
Considering the fact that the dimeric complex $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ is formed through a bimolecular decomposition process involving alkylidene species, the reverse reaction should be feasible in principle. Therefore, reactions of $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ with various olefins amenable to ring-closing metathesis reactions were explored (Scheme A.2).



Temperature (°C)	% conv, % time (h)
22	71, 21
50	86, 3



Temperature (°C)	% conv, % time (h)
55	95, 1



Temperature (°C)	% conv, % time (h)
55	38, 20

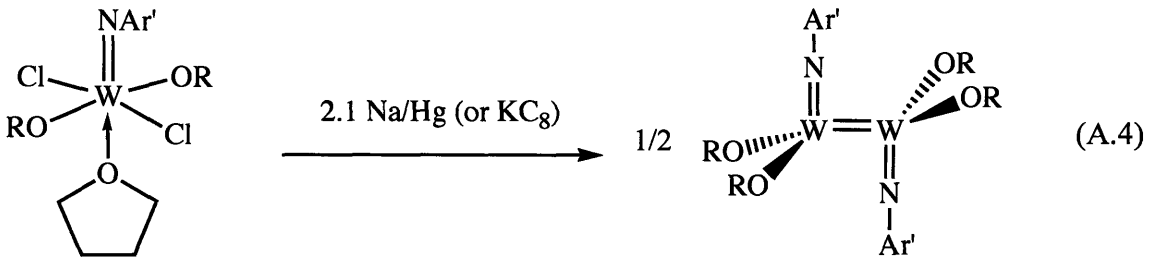
Scheme A.2. Ring-closing metathesis reactions using 5 mol% [Mo(NAr)(CH_2-t-Bu)(OC_6F_5)]$_2$.

5 mol% $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ as a 19 mM benzene-d_6 solution will convert diallylether to dihydrofuran and ethylene with 71% conversion in 20 h at 22 °C. Elevating the temperature to 50 °C causes 86% of the transformation to be complete in 3 h. Similarly, a reaction performed on *N,N*-diallyltosylsulfonamide at 55 °C using a 19 mM solution of 5 mol% of $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ shows 95% conversion to the ring-closed product at room temperature. The reaction of $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ in benzene-d_6 (19 mM) with 20 equivalents of a hindered ether-type substrate 3-(allyloxy)-2,4-dimethylpenta-1,4-diene at 55 °C proceeds to 38% completion in 20 h.

Upon reacting 5 mol% of $[Mo(NAr)(CH_2\text{-t-Bu})(\ OC_6F_5)]_2$ with norbornene at 22 °C, complete polymerization was observed. The activation of $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ relative to the parent alkylidene $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OC_6F_5)$ was found to be <1% by ^1H NMR spectroscopy, i.e., there was no evident change in the amount of $[Mo(NAr)(CH_2\text{-t-Bu})(\ OC_6F_5)]_2$ relative to an internal standard even after 6 h. Upon doing a 50 mg scale polymerization reaction, the chain length of the polynorbonene sample obtained by $[Mo(NAr)(CH_2\text{-t-Bu})(\ OC_6F_5)]_2$ was ~38 times (M_n = 3.430 x 10^5, PDI = 1.25, *cf* Table 2.13) that obtained by the latter. This corresponds to 2.6% activation of $[Mo(NAr)(CH_2\text{-t-Bu})(\ OC_6F_5)]_2$ if it is assumed that the polymerization of norbornene is living. Reaction of a tungsten bimetallic species $[W(NAr')(CH\text{-t-Bu})(OCMe_2(CF_3))]_2$ (Ar' = *N*-2,6-$Me_2C_6H_3$) with norbornene similarly gives a polymer with a molecular weight that is ~50 times that of a sample made by employing $W(NAr')(CH\text{-t-Bu})(OCMe_2(CF_3)_2$ (Ar' = *N*-2,6-$Me_2C_6H_3$) as the catalyst.[10]

The above reactions suggest that catalytic amounts of M=M (M = Mo, W) species can effect slow metathesis reactions. However, the present route undertaken to synthesize such dimeric species utilizes the corresponding alkylidene complexes as the starting material. Therefore, despite repeated crystallization cycles used to purify the M=M species hence obtained, the presence of an extremely tiny amount of residual alkylidene starting material that cannot be observed by NMR spectroscopy cannot be discounted. To resolve this issue, the aforementioned bimetallic tungsten complex $[W(NAr')(CH\text{-t-Bu})(OCMe_2(CF_3))]_2$ was prepared by Jillian Hafer using a route that did *not* involve any alkylidene species at any stage (equation A.4). The sample hence prepared was found to be identical in all respects to that prepared via the bimolecular decomposition of $W(NAr')(CH\text{-t-Bu})(OCMe_2(CF_3)_2$ and it caused the

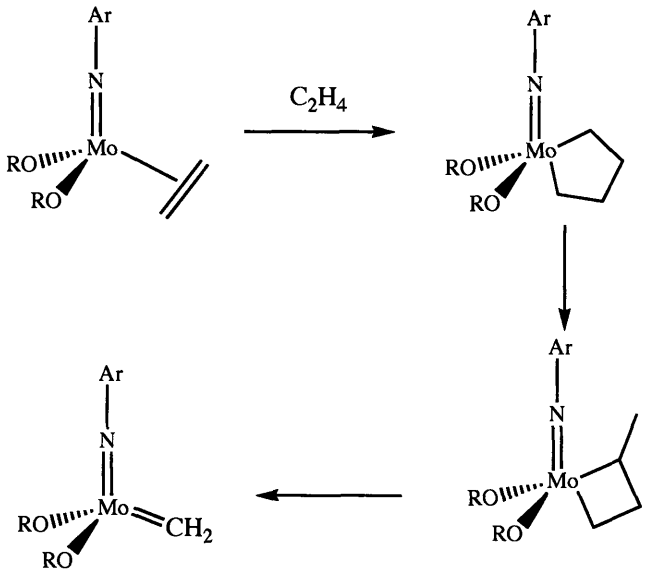
polymerization of norbornene as shown above. Hence, the metathesis ability of M=M species is not necessarily due to the presence of residual alkylidene complexes.



(A.4)

NAr' = *N*-2,6-$Me_2C_6H_3$
OR = $OCMe_2CF_3$

As an extension of the work on Mo=Mo (d^2/d^2) complexes, it was observed that catalytically active species for metathesis reactions can be generated by another Mo (d^2) species, $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$[4] ($NAr_{Cl}$ = *N*-2,6-$Cl_2C_6H_3$, $Biphen^{2-}$ = 3,3'-di-t-butyl-5,5',-6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate). $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ can effect the ring-opening metathesis polymerization (ROMP) of norbornene at room temperature. The molecular weight (M_n) of the sample of polynorbornene hence obtained (in 83% isolated yield) was found to be 8.158×10^5 (PDI = 1.47), which was twice that of a sample synthesized under identical conditions using $Mo(NAr_{Cl})(Biphen)(CH\text{-}t\text{-}Bu)$. The reaction of $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ with 20 equivalents of diallylether at 22 °C fails to give any ring-closed product over a period of 10 days. However, when a mixture of $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ and 20 equivalents of diallylether in benzene-d_6 is treated with 10 equivalents of norbornene, 54% conversion to dihydrofuran is observed in 10 days. This experiment demonstrates that an alkylidene species can be generated in presence of norbornene. Infact $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ has been used in an earlier work in the Schrock group to cause homologation of vinyltin to allyltin species in the presence of ethylene.[11] In this respect, a plausible pathway for formation of an alkylidene species from a Mo-ethylene complex is shown in Scheme A.3. For d^2 species of the type $(t\text{-}Bu_3SiO)_3M(H_2C{=}CHR)$[12] (M = Nb, Ta), Wolczanski has shown that species can rearrange to give the isomeric alkylidene complexes $(t\text{-}Bu_3SiO)_3M(CHCH_2R)$ via intramolecular δ- and α-H abstraction processes. Therefore, the formation of metal alkylidene species from metal olefin complexes is not restricted to Group 6.



Scheme A.3. Formation of alkylidene species from a Mo-ethylene complex.

CONCLUSIONS

This work demonstrates the designed formation of an unbridged bimetallic complex $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ from the decomposition of an alkylidene species containing a small OR group (OR = OC_6F_5). Although complexes containing unbridged bonds of the other types (single, triple and quadruple) are well known[13], there have been few examples of unsupported M=M reported in the literature. In these unsupported M=M species (M = Os, Ru), the porphyrin ligand framework obviates any opportunity for bridging the M=M bond.[14] In this respect, complexes of the type $[Re(C\text{-t-Bu})(OR)_2]_2$[8] (Toreki), $[W(NAr)(CH_2\text{-t-Bu})(OR)]_2$[10] and $[W(NAr)(OR)_2]_2$[7] (Lopez), $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ (this work) are different in the way that they all contain an unbridged M=M bond even in the presence of potentially bridging ligands. Attempts to make similar Mo=Mo complexes from the reactions of olefins such as *cis*-2-pentene, *trans*-3-hexene and divinylbenzene with $Mo(NAr)(CH\text{-t-Bu})(CH_2\text{-t-Bu})(OR)$ species containing bulky alkoxides (OR = OAr, OAd) were unsuccessful. The Mo=Mo species have been shown to slowly catalyze the ring-closing metathesis reactions of simple olefins in decent yields at elevated temperatures. The ring-opening metathesis polymerization of norbornene has been demonstrated by using catalytic amounts of Mo=Mo species, and the high molecular weight polymer obtained through this reaction indicates a low activation of these bimetallic species,

which is certainly expected. In addition to Mo=Mo complexes, another d^2 species, $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$, was shown to polymerize norbornene. Only in the presence of norbornene, $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ was found to catalyze the ring-closing metathesis of diallylether indicating that given proper conditions, catalytically active species can be accessed through Mo-olefin complexes which have been thought of as one of the sinks in a catalytic cycle. Therefore, it may be possible for Mo=Mo species to serve as precursors to metal olefin or metal alkylidene complexes that are actually responsible for the metathesis activity.

EXPERIMENTAL SECTION

General. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. The glassware, including NMR tubes were flame- and/or oven-dried prior to use. Ether, pentane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed thrice by freeze-pump-thaw technique. Dichloromethane was distilled from CaH_2 under N_2. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^1H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using a Varian Mercury (^1H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz) or a Varian Inova (^1H 500 MHz, ^{13}C 125 MHz) spectrometers and referenced to the residual protio solvent resonances or external C_6F_6 (-163.0 ppm). Elemental Analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR) complexes were prepared as described in Chapter 2. $Mo(NAr_{Cl})(Biphen)(H_2C{=}CH_2)(ether)$ was prepared as described in the literature.[4] Crystal data and structure refinement for $[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$ are given after references.

$[Mo(NAr)(CH_2\text{-t-Bu})(OC_6F_5)]_2$. In a 50 ml round bottom flask, 2.50 g (4.20 mmol) of Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5) was dissolved in 35 ml of pentane. To the yellow colored suspension obtained, 3 ml (24.3 mmol) of *trans*-3-hexene was added all at once. The color of the reaction mixture changed immediately to dark red. After stirring overnight, the volatiles were removed in vacuo to obtain a red solid. Washing the red solid with cold pentane

followed by crystallization in toluene to obtain a rust-red crystalline material in 78% yield (1.72 g): ^{1}H NMR (C_6D_6) δ 6.79 (br s, 6, Ar*H*), 4.70 (br s, 2, C*H*Me$_2$), 3.09 (br s, 2, C*H*Me$_2$), 2.33 (d, 2, CH*H*CMe$_3$), 1.58 (d, 2, C*H*HCMe$_3$), 1.82 (br s, 6, CH*Me*$_2$), 1.38 (br s, 6, CH*Me*$_2$), 1.15 (br s, 6, CH*Me*$_2$), 1.03 (s, 18, CH$_2$C*Me*$_3$), 0.81 (br s, 6, CH*Me*$_2$); ^{13}C NMR (C_6D_6) δ 156.3, 139.7,129.3, 128.6, 125.4, 68.7, 65.4, 35.7, 34.6, 33.4, 33.3, 32.3, 31.5, 29.9, 29.3, 25.8, 21.1; ^{19}F NMR (C_6D_6) δ -159.9, -165.3, -170.3. Anal. Calcd for $C_{46}H_{56}N2O_2F_{10}Mo_2$: C, 52.58; H, 5.37; N, 2.67. Found: C, 52.46; H, 5.33; N, 2.55.

Representative method employed for ring-closing metathesis reactions. A solution of the substrate in C_6D_6 and 10 μl of anisole (an internal standard) were placed in a JYoung® NMR tube and 5 mol% of the catalyst was then added. The tube was capped and the solution was allowed to stand at room temperature. In other cases, 10mg of the substrate was taken in 0.5 ml C_6D_6 followed by addition of 5 mol% of catalyst. Conversions were determined by ^{1}H NMR spectroscopy (500 MHz).

Ring-opening metathesis polymerization reaction of norbornene using [Mo(NAr)(CH$_2$-t-Bu)(OC$_6$F$_5$)]$_2$. A 25 ml scintillation via was charged with a magnetic stirrer and 50 mg of norbornene in 5 ml toluene was added to it followed by the addition of 1 mol% (5.6 mg) of the metal complex in 0.5 ml of toluene at room temperature. After stirring the reaction mixture for 1 h, 2 ml of benzaldehyde was added. The above solution was allowed to stir for an additional 1 h following which it was treated with excess (65 ml) of methanol. Stirring the resulting suspension overnight gave the polymer, which was filtered, dried on a high vacuum line and analyzed by gel permeation chromatography.

Ring-opening metathesis polymerization reaction of norbornene using Mo(NAr$_{Cl}$)(Biphen)(H$_2$C=CH$_2$)(ether). A solution of 2.1 mg (2.82 x 10^{-3} mmol) of the Mo-complex in 0.5 ml toluene was added to a stirring solution of 26.6 mg of norbornene and stirred the reaction mixture for 1 h. Adding 1 ml of benzaldehyde followed by addition of 50 ml of methanol caused the precipitation of polynorbornene as a white solid. Drying the solid on a high vacuum line afforded 21 mg (79% yield) of the polymer that was analyzed by gel permeation chromatography.

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Crystal Data and Structure Refinement for Compound Reported in Appendix A

Table AXR.1. Crystal data and structure refinement for $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$.

Empirical formula	C53 H64 F10 Mo2 N2 O2	
Formula weight	1142.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 13.110(3) Å	α= 90°.
	b = 11.176(2) Å	β= 100.21(3)°.
	c = 18.491(4) Å	γ = 90°.
Volume	2666.5(9) $Å^3$	
Z	2	
Density (calculated)	1.424 Mg/m^3	
Absorption Correction Method	Empirical	
Absorption coefficient	0.545 mm^{-1}	
F(000)	1172	
Crystal size	0.26 x 0.16 x 0.02 mm^3	
Theta range for data collection	2.09 to 28.33°.	
Index ranges	$-17\leq h\leq 15$, $-14\leq k\leq 14$, $-24\leq l\leq 24$	
Reflections collected	27986	
Independent reflections	6629 [R(int) = 0.0148]	
Completeness to theta = 28.33°	99.6 %	
Max. and min. transmission	0.9903 and 0.8712	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6629 / 217 / 406	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0716	
R indices (all data)	R1 = 0.0338, wR2 = 0.0771	
Largest diff. peak and hole	0.570 and -0.311 $e.Å^{-3}$	

CURRICULUM VITAE

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HIGHLIGHTS

- Well versed in milligram to multi-gram scale synthesis utilizing glove box and Schlenk techniques
- Extensive experience in the following spectroscopies: NMR, IR, UV, fluorescence
- Hands on experience with X-ray crystallography, chromatographic methods (GC, HPLC, GPC)
- Environmental Health and Safety committee member at MIT involved in inspections and training
- Part of several collaborations in multi-cultural teams.

EDUCATION

DOCTOR OF PHILOSOPHY, ORGANOMETALLIC CHEMISTRY 2001- 2006
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE MA
Thesis: "Synthesis of Molybdenum Olefin Metathesis Catalysts Through Protonation Reactions"
Advisor: Prof. Richard R. Schrock

MASTER OF SCIENCE, INORGANIC CHEMISTRY 1999-2001
INDIAN INSTITUTE OF TECHNOLOGY, BOMBAY, INDIA
Thesis: "Study of Reactivity of Metal Acetylides in Cluster Chemistry"
Advisor: Prof. Pradeep Mathur

BACHELOR OF SCIENCE (HONORS), CHEMISTRY 1996-1999
ST. STEPHEN'S COLLEGE, UNIVERSITY OF DELHI, NEW DELHI, INDIA

RESEARCH EXPERIENCE

RESEARCH ASSISTANT, DEPARTMENT OF CHEMISTRY, MIT, CAMBRIDGE MA 2001-2006
Advisor: Prof. Richard R. Schrock
Collaborators: Prof. Amir H. Hoveyda, Boston College
Prof. Christophe Copéret, CNRS, France

- Designed and developed a new class of molybdenum-based catalysts for ring-closing and ring-opening metathesis reactions
- Discovered the first complex containing an "unsupported" molybdenum-molybdenum double bond in the presence of potentially bridging ligands, and demonstrated its catalytic activity
- Developed an in-situ catalytic system for high throughput screening of pro-chiral substrates
- Studied heterogeneous catalysis promoted by silica-supported molybdenum catalysts.

RESEARCH ASSISTANT, DEPARTMENT OF CHEMISTRY, IIT, BOMBAY 1999-2001
Advisor: Prof. Pradeep Mathur
Collaborator: Dr. Sumit Bhaduri, Reliance Industries Limited

- Synthesized mixed-chalcogen iron clusters and their reactivity with unsaturated organic molecules
- Investigated the enantioselective catalysis of substrates by dehydrogenase enzyme and Chini complexes.

VISITING SCIENTIST, MALARIA GROUP, INTERNATIONAL CENTER FOR GENETIC ENGINEERING AND BIOTECHNOLOGY
NEW DELHI SUMMER AND WINTER 2000
Advisors: Prof. Virander S. Chauhan and Dr. Dinkar Sahal

- Studied the interaction of anti-malaria drugs with histidine-rich proteins produced by the malarial parasite Plasmodium falciparum
- Developed a one-step chemo-detection protocol for detection of histidine-rich proteins.

TEACHING AND MENTORSHIP EXPERIENCE

TEACHING ASSISTANT, DEPARTMENT OF CHEMISTRY, MIT

Courses: Principles of Inorganic Chemistry I, Introductory Chemical Experimentation — 2001-2002
Principles of Inorganic Chemistry II (Group Theory and Spectroscopy) — FALL 2005

RESEARCH SUPERVISOR, SCHROCK GROUP, MIT — SUMMER 2004
Mentored an undergraduate student in experimental organometallic chemistry.

SELECTED AWARDS AND HONORS

German Exchange Program Representative for American Chemical Society	2005
Cambridge Science Foundation Travel Grant	2004
Jawaharlal Nehru Fellowship	2001
First position in Inorganic Chemistry Division, IIT Bombay	2000
Distinction and top 2% of 480 students, University of Delhi	1999
First position in Science Aptitude Test, University of Delhi	1998
Summer Fellow of the Indian Academy of Sciences	1998, 1997

PUBLICATIONS

Sinha, A.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. "Amido Precursors to Bis-alkoxide Molybdenum Imido Alkylidene Olefin Metathesis Catalysts" *Organometallics* **2006**, *Submitted.*

Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Müller, P. "Reactions of M(N-2,6-i-$Pr_2C_6H_3$)(CHR)$(CH_2R')_2$ (M = Mo or W) Complexes with Alcohols to Give Olefin Metathesis Catalysts of the Type M(N-2,6-i-$Pr_2C_6H_3$)(CHR)(CH_2R')(OR")" *Organometallics* **2006**, *25*, 1412.

Blanc, F.; Copéret, C.; Thiovolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. "Surface vs. Molecular Siloxy Ligands in Well-Defined Olefin Metathesis Catalysts: [{$(RO)_3SiO$}Mo(=NAr)(=CH*t*Bu)$(CH_2t$Bu)]" *Angew. Chem. Int. Ed.* **2006**, *45*, 1216.

Schrock, R. R.; Lopez, L. P. H.; Hafer, J.; Singh, R.; Sinha, A.; Müller, P. "Olefin Metathesis Reactions Initiated by d^2 Molybdenum or Tungsten Complexes" *Organometallics* **2005**, 24, 5211.

Sinha, A.; Schrock, R. R. "Reactions of Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ with Alcohols to Give Metathesis Catalysts of the Type Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OR)" *Organometallics* **2004**, *23*, 1643.

Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J., Jr.; Sinha, A.; Lopez, L. P. H. "Synthesis of Molybdenum Alkylidyne Complexes that Contain a 3,3'-Di-t-butyl-5,5',6,6'-tetramethyl-1,1'-Biphenyl-2,2'-diolate ([Biphen]$^{2-}$) Ligand" *J. Organomet. Chem.* **2003**, *684*, 56.

Sahal, D.; Kannan, R.; Sinha, A.; Babbarwal, V.; Prakash, B. G.; Singh G.; Chauhan, V. S. "Specific and instantaneous one-step chemodetection of histidine-rich proteins by Pauly's stain", *Analytical Biochemistry*, **2002**, *308*, 405.

Sinha, A. "Buckyball C_{60}–The Story So Far", *Resonance (Journal of Science Education)*, **2001**, *6*, 55.

REFERENCES

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In the summer of 1997, I came across the webpage of Prof. Richard Schrock whose research attracted my attention to the area of olefin metathesis. He was the major motivating factor for me to come to MIT and has been the same driving force during my time in his group. Many a time, a major reward for me to make brilliantly colored chemicals was Dick's childlike excitement and the glitter in his eyes when he would come over to check them out. Apart from sparing no expenses in making sure that I had whatever I needed for my research, Dick was always enthusiastic about exploring new ideas even if they were of fundamental interest only. He has given me opportunities that have increased my confidence in dealing with, and fixing machines and instruments. He has also been a great help with glass blowing a variety of apparatus that have been used in my work. He and his wife, Nancy have always played wonderful hosts at the group parties at their house. I thank him for all this, as well as leading the group by example.

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