SYNTHESIS AND REACTIVITY OF HIGH OXIDATION STATE MOLYBDENUM CATALYSTS FOR RING OPENING METATHESIS POLYMERIZATION OF OLEFINS

by

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B. Sc., University of Ottawa
(1986)

Submitted to the Department of Chemistry in Partial Fulfillment of the Requirements for the degree of

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 1990

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MAR 15 1991
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ABSTRACT

Chapter 1

A series of high oxidation state molybdenum complexes containing the 2,6-diisopropylphenylimido ligand were prepared in order to study their potential use as starting materials to alkylidene complexes. The mono imido derivatives Mo(NAr)(O)Cl₂(py)₂, Mo(NAr)Cl₄(py) and Mo(NAr)(OCMe₃)₄ (NAr = N-2,6-C₆H₃-ᵢ-Pr₂) do not react cleanly with a variety of alkylating reagents. Reaction of the bis imido compound Mo(NAr)₂Cl₂(dme) with two equivalents of Mg(CH₂CM₃)Cl to yield the bis alkyl bis imido compound, Mo(NAr)₂(CH₂CM₃)₂, cleanly. This complex is unreactive towards a variety of nucleophiles but reacts cleanly with three equivalents of triflic acid in dme to yield Mo(CHCM₃)(NAr)(OSO₂CF₃)₂(dme) and ArNH₃OSO₂CF₃ virtually quantitatively. Addition of two equivalents of lithium alkoxide (LiOR, OR = OCMe(CH₃)₂, OCMe₂) to Mo(CHCM₃)(NAr)(OSO₂CF₃)₂(dme) displaces the triflate ligands and coordinated dme to yield four coordinate species of the type Mo(CHCM₃)(NAr)(OR)₂. The overall sequence MoCl₂ + 2 LiOR → Mo(NAr)₂Cl₂(dme) → Mo(CHCM₃)(NAr)(OSO₂CF₃)₂(dme) is a convenient route to the precursor of catalysts of the type Mo(CHCM₃)(NAr)(OR)₂. An X-ray crystal structure determination of Mo(CHCM₃)(NAr)(OSO₂CF₃)₂(dme) showed it to be a pseudo-octahedral species in which the imido and alkylidene ligands are cis to one another, the triflate ligands are mutually trans, and the tert-butyl group points towards the imido ligand (syn orientation).

Chapter 2

Benzonorbornadiene (1), 2,3-dicarbomethoxynorbornadiene (2), and 2,3 bis(trifluoromethyl)norbornadiene (5) can be polymerized by Mo(CHCM₃)(NAr)(OCMe₃)₂ (Mo(CHCM₃)) in a well-behaved living manner to yield essentially monodisperse homopolymers. Poly2 and (especially) poly5 are highly trans, and are believed to be tactic. The rate of polymerization of 2 is approximately 30 times faster than that of 5 at room temperature, a factor of approximately ten of which can be ascribed to the lower reactivity of 5 relative to 2, and the remainder to the lower reactivity of the alkylidene species of living poly5 relative to living poly2. 7-Isopropylidene-2,3-dicarbomethoxynorbornadiene is not polymerized by Mo(CHCM₃), although it does react with Mo(CHCM₃) to give an isolable “mono insertion product” (4) at a rate which is about 500 times slower than the reaction of Mo(CHCM₃) with 2. An X-ray crystal structure determination of 4 shows it to be a pseudo-tetrahedral species containing a syn alkylidene ligand, one face of which is blocked by the
isopropylidene group and the other face of which is blocked by a carbomethoxy group. W(CHCMe3)(NAr)(OCMe3)2 reacts with 5 at low temperatures to yield an isolable square pyramidal metallacycle (6) at a rate that is second order overall. Activation parameters (298 K) calculated for this reaction are ΔH‡ = 6.6 (4) kcal mol⁻¹, and ΔS‡ = -40(1) e.u.. An X-ray structure determination of 6 shows that the metal core is a distorted square pyramid with the imido group in the apical position and with the tert-butyl group in the WC₃ ring pointing toward the imido nitrogen atom. The monomer has added through the exo face to yield a trans metallacyclic ring. This metallacycle rearranges to give the "first insertion product" in a first order manner for which ΔS‡ = -3 (1) e.u.. Consistent with its high stereoregularity, digital scanning calorimetry studies of poly5 prepared with Mo(CHCMe3) as the initiator reveal a well defined Tg at 97 °C and a broad melting endotherm at about 200 °C.

Chapter 3
The norbornadiene dimer, exo-trans-exo pentacyclo [8.2.1.1⁴.⁷.0².⁹.0₃.⁸] tetradeca-5,11-diene (8) can be used in living ring-opening metathesis polymerization as a cross linking reagent for the controlled synthesis of star-shaped polymers. Star polymers are formed when a few equivalents of 8 are added to living polynorbornene initiated with W(CHCMe3)(NAr)(OCMe3)2 or Mo(CHCMe3)(NAr)(OCMe3)2. Addition of 8 to the initiators first followed by addition of norbornene results in the formation of a gel. The reactivity of the alkylidene plays an important role in determining star formation and certain functionalized monomers such as 2,3-dicarbomethoxynorbornadiene can form star polymers only when several equivalents of norbornene are added to the living polymer before 8 is added. Reactive alkylidenes, such as living poly-2-carbonitilenorbornene can be quantitatively converted into living star polymers. Treatment of these star polymers with relatively unreactive monomers such as 2,3-bis(trifluoromethyl)norbornadiene give "heterostar" polymers, since all the sites in the core act as initiators for the polymerization of these second monomers. The number of the two functionalized arms are nearly equivalent as determined by ¹³C NMR spectroscopy of the end groups.

Chapter 4
Norbornenes containing ester, carbonitrile, acetate and related functionalities can be polymerized in a living manner employing Mo(CHCMe3)(NAr)(OCMe3)2 (Mo(CHCM₃)) as the initiator to give polymers with polydispersities as low as 1.04. Functionalities in the exo position are tolerated more easily than in the endo position. The alkylidene resonances in the ¹H NMR spectrum of living polymers are sensitive to the nature and regiochemistry of the functionalities. Reaction of Mo(CHCMe₃) with exo,cis-2,3-dichloro-endo,cis-carbonitonorbornene (10) at low temperature yields a square pyramidal molybdenacycle. The formation of this molybdenacycle is reversible with some of the species rearranging to the propagating alkylidene and some reverting to the original species upon warming. The polymerization of 10 fails due to the slow rate of initiation and propagation. For this monomer propagating species deactivation competes effectively with the rate of polymerization. Poly(exo-cis-2,3-norbornenediacetate) and poly(exo-syn-5-norbornene-2,7-diol diacetate) can be prepared in a controlled fashion and can be quantitatively converted to the polyl derivatives. Pyrolysis of these polymers yields conjugated materials which are highly air sensitive. Block copolymers of poly(2-carbonitilenorbornene) (poly9) and norbornene can be prepared in a controlled fashion (polydispersities of 1.05) using Mo(CHCMe₃) as the initiator. The stress-strain response for poly9 is typical of a glassy polymer or semicrystalline
polymer below Tg, while the breakpoint of poly9-block-polybornene occurs at a much higher strain.

Chapter 5

The reaction of 7-oxa-2,3-bis(trifluoromethyl)-norbornadiene (16) with Mo(CHCMe3)(NAr)(OCMe3)2 (Mo(CHCMe3)) yields a square pyramidal molybdcyclne (17). This metallacycle breaks up in a first order fashion to yield two rotameric isomers of the propagating alkylidene. Activation parameters (298 K) calculated for this reaction are $\Delta H^\ddagger = 18.8 \pm 4$ kcal mol$^{-1}$, and $\Delta S^\ddagger = -17$ (1) e.u. and $k = 4.2 \times 10^{-5}$ sec$^{-1}$ (T = 35 °C). A more reactive catalyst, Mo(CHCMe3)(NAr)[OCMe2(CF3)]2 can polymerize 16 to yield poly16 with a dispersity of 1.07. The reaction of Mo(CHCMe3) with 7-oxa-2,3-dicarbomethoxynorbornadiene (19) also yields a stable square pyramidal metallacycle (20). A preliminary X-ray structure determination of 20 shows the metal core to be square pyramidal with the imido in the apical position and no coordination of the 7-oxygen to the metal center. The rate of breakup of 20 at 35 °C ($k = 4.2 \times 10^{-4}$ sec$^{-1}$) is slower than that of 17. Reaction of Mo(CHCMe3) and 3 equivalents of both 16 and 2,3-bis(trifluoromethyl)norbornadiene yields exclusively the molybdcyclne 17, two equivalents of unreacted and unreacted 2,3 bis(trifluoromethyl)norbornadiene. Reaction of 7-oxanorbornadiene yields an unstable metallacycle and can be polymerized using Mo(CHCMe3). The dispersities of the resulting polymers are very dependent on the method of addition. The polymerization of 7-oxanorbornenes proceeds smoothly to yield polymers with high glass transition temperatures.

Chapter 6

Monomers containing redox active groups were synthesized in order to prepare well-defined redox active polymers for electrode modification. In particular these contained ferrocene and phenothiazene pendant groups. The polymers and oligomers were prepared by ring-opening metathesis polymerization using Mo(CHCMe3)(NAr)(OCMe3)2 (Mo(CHCMe3)) and were fully characterized by a variety of techniques. The electrochemistry of Mo(CHCMe3) shows a one electron reversible reduction at -2.16 Mo(CHCMe3) vs. SCE and therefore no redox chemistry occurs with the monomers or oligomers prepared. The solution electrochemistry of the polymers was characterized by cyclic voltammetry and is governed by solubility. By block-copolymerizing with polybornene the solubility properties of the redox polymers in the oxidized state can be controlled. A ferrocene substituted alkylidene initiator (Mo(CHFc)(NAr)(OCMe3)2, Mo(CHFc), Fe = ferrocene) was prepared by the reaction of vinyl ferrocene with Mo(CHCMe3). Redox active end groups were incorporated by initiation with Mo(CHFc) and termination with octamethylferrocene-carboxaldehyde. Functionalities were introduced, as either monomers or end groups, into the redox polymers in order to bind them to electrode surfaces. Block copolymers made with 2-triethoxyxilinbornene, a silane coupling reagent, and redox active monomers were used to derivatize Pt and In(Sn)O surfaces. Electroactive polymers capped with pyridine carboxaldehyde were reacted with electrode surfaces which had been treated with silane reagents containing the complementary reactant in order to produce a derivatized surface via a unique covalent bond. The solid state properties of the block copolymers comprised of electroactive chains and polybornene segments displayed phase separation at very low molecular weights of the components as determined by digital scanning calorimetry.
Chapter 7

2-Oxametallacyclobutane complexes can be prepared by adding pentafluorobenzaldehyde to M(CHCMe3)(NAr)(OCMe3)2 (M = Mo, W). In each case two isomers are observed that contain tert-butyl and pentafluorophenyl (PhF) substituents trans or cis to each other (the trans isomer predominating) and that decompose to give trans- or cis-PhFCH=CH(CMe3) respectively. An X-ray crystal structure determination of the major isomer of trans-Mo[CH(CMe3)CH(PhF)O](NAr)(OCMe3)2 (29-trans) showed it to be a square pyramid containing an apical imido ligand and pseudo-equatorial α tert-butyl and β PhF groups in a slightly puckered MoOC2 ring. 29-trans is proposed to form in a reaction involving syn-Mo(CHCMe3)(NAr)(OCMe3)2. At 25 °C 29-trans decomposes twice as rapidly as trans-W[CH(CMe3)CH(PhF)O](NAr)(OCMe3)2 (30-trans) and at 5 °C 30-cis decomposes approximately 25 times more rapidly than 30-trans. These findings are all consistent with square pyramidal 2-oxametallacyclobutane complexes being more stable when they contain trans α and β substituents and when electron-withdrawing substituents in the ring. These results are discussed in relation to analogous findings concerning analogous MC3 metallacyclobutane complexes.

Chapter 8

Complexes of the type Mo(CHCMe3)(NAr)(OR)2 (OR = OCMe(CF3)2, OCMe3) form five-coordinate adducts upon addition of PMe3. PMe3 attacks the C/N/O face of the pseudotetrahedral complexes to give chiral trigonal bipyramidal species in which the phosphine is bound in an axial position and the imido and alkylidene ligands lie in the equatorial plane. Both syn and anti forms of the alkylidene ligand are observed. For OR = OCMe(CF3)2 the syn rotamer forms first; with time it is converted to the anti isomer (95%); this isomerization is catalyzed by addition of a small amount of the base free alkylidene. An X-ray crystal structure of syn-Mo(CHCMe3)(NAr)(OCMe(CF3)2)2(PMe3) demonstrates the crowded nature of the product since the tert-butyl ligand points toward the imido ligand and the phenyl ring of the imido ligand lies approximately in the equatorial plane. PMe3 binds weakly when OR = OCMe3 and is readily lost in vacuo. At room temperature an equilibrium mixture of Mo(CHCMe3)(NAr)(OCMe3)2 and anti-Mo(CHCMe3)(NAr)(OCMe3)2(PMe3) are observed.

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<thead>
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<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>2,6-C₆H₃-i-Pr₂</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Cα</td>
<td>carbon bound to the metal</td>
</tr>
<tr>
<td>Cβ</td>
<td>carbon bound to Cα</td>
</tr>
<tr>
<td>Cᵢ</td>
<td>carbon in an aromatic ring that is bound to oxygen or nitrogen</td>
</tr>
<tr>
<td>Cₘ</td>
<td>carbon in the meta position of an aromatic ring</td>
</tr>
<tr>
<td>Cₒ</td>
<td>carbon in the ortho position of an aromatic ring</td>
</tr>
<tr>
<td>Cₚ</td>
<td>carbon in the para position of an aromatic ring</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>dme</td>
<td>dimethoxyethane</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent(s)</td>
</tr>
<tr>
<td>Fc</td>
<td>ferrocenyl</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
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<td>Hα</td>
<td>hydrogen bound to Cα</td>
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<td>Hβ</td>
<td>hydrogen bound to Cβ</td>
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<td>Hₘ</td>
<td>hydrogen in the meta position of an aromatic ring</td>
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<tr>
<td>Hₚ</td>
<td>hydrogen in the para position of an aromatic ring</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant in Hertz</td>
</tr>
<tr>
<td>kᵢ</td>
<td>rate constant for initiation</td>
</tr>
<tr>
<td>kₚ</td>
<td>rate constant for propagation</td>
</tr>
</tbody>
</table>
Me  methyl
min  minutes
mult  multiplet
NBE  norbornene
NMR  nuclear magnetic resonance spectroscopy
$M_n$  number average molecular weight
$M_w$  weight average molecular weight
NAr  NAr
Np  neopentyl
OAr  O-2,6-C$_6$H$_3$-i-Pr$_2$
OTf  OSO$_2$CF$_3$
PDI  polydispersity index
PhF  pentafluorophenyl
Phz  phenothiazine
$i$-Pr  isopropyl
q  quartet
ROMP  ring-opening metathesis polymerization
s  singlet
SP  square pyramidal
t  triplet
TBP  trigonal bipyramidal
Tg  glass transition temperature
THF  tetrahydrofuran
TMS  trimethylsilyl
$\delta$  chemical shift in ppm downfield from tetramethylsilane
GENERAL INTRODUCTION

The central focus of this dissertation is the synthesis, study and application of molybdenum alkylidene complexes which catalyze the ring opening metathesis reaction of cyclic olefins. In order to keep the volume of this work to a reasonable size a minimal amount of background material is provided in the introductory sections of the individual chapters. Sufficient references are cited to facilitate access to the more fundamental reviews available in the literature. These reviews provide a convenient source of information and will not be repeated here. Readers unfamiliar with this area of chemistry should refer to recent reviews which cover the subjects of high oxidation state alkylidene complexes\textsuperscript{1,2,3}, olefin metathesis\textsuperscript{4,5,6,7}, ring opening metathesis polymerization\textsuperscript{6,7,8} and its applications\textsuperscript{9,10}.

This thesis is divided into eight chapters. The chapters concerned with the polymerization of olefins could have been merged but were kept independent so as to emphasize different aspects of the chemistry involved. Chapter 1 reports the development of a facile new synthesis of compounds of composition Mo(NAr)(CHCM\textsubscript{3})(OR)\textsubscript{2} (NAr = 2,6-C\textsubscript{6}H\textsubscript{3}(CHMe\textsubscript{2})\textsubscript{2}). Chapter 2 presents the reactivity of these compounds as initiators for the living polymerization of norbornadiene derivatives and a study of the electronic and steric factors involved in the stereochemistry of this polymerization. The statistical nature of a living polymerization process can be controlled, to a certain extent, to produce polymers with interesting architectures and this is described in Chapter 3. Chapter 4 and Chapter 5 deal with the interaction of the initiator or the propagating species with pendant functionalities on the monomers. These studies have yielded new materials as well as insight into the principles which govern the mechanism of polymerization. Chapter 6 describes how this information can be used to prepare materials with prescribed properties and responses. The same information can be used to synthesize rare organometallic complexes, such as 2-oxametallacyclobutanes, as reported in Chapter 7. Finally the interaction of bases with these initiators is presented in Chapter 8.
CHAPTER 1

A New Synthetic Route to Catalysts of the Type Mo(NAr)(CHCMe₃)(OR)₂.
INTRODUCTION

The first well defined Lewis acid-free, group VI alkylidene complexes which were found to catalyze olefin metathesis are of the form W(NAr)(CHCMe₃)(OR)₂₁¹ (Ar=2,6-C₆H₃(CHMe₂)₂), where the nature of the R group on the alkoxide controls the catalytic activity. For example, W(NAr)(CHCMe₃)(OCMe(CF₃)₂)₂ metathesizes 3700 equivalents of cis-pentene to equilibrium within 5 minutes at room temperature.¹²(a) Changing the alkoxide to one which is more electron donating reduces the catalytic activity dramatically, as is seen in W(NAr)(CHCMe₃)(OCMe₃)₂, which reaches only 30 % of the equilibrium distribution of cis-pentene after 6 days at room temperature. This lack of reactivity towards acyclic olefins can be exploited in the polymerization of cyclic olefins since W(NAr)(CHCMe₃)(OCMe₃)₂ metathesizes the strained double bond of norbornene to yield living polymers.¹³ The resulting polymer is living since the olefinic bonds in the resulting polymer are left unreacted within the time scale of the polymerization.¹⁴,¹⁵

The key to this versatility is the availability of a common precursor, W(NAr)(CHCMe₃)Cl₂(dme), which readily exchanges chloride for alkoxide ligands when treated with the appropriate lithium alkoxide (Equation 1). The precursor was originally

\[
\begin{align*}
\text{Cl} & \quad \text{NAr} \\
\text{O} & \quad \text{W} & \quad \text{Cl} \\
\end{align*}
\]

\[
+ 2 \text{MOR} \xrightarrow{\text{Et₂O, -40 °C}} \xrightarrow{\text{-dme}}
\]

M = Li or K

<table>
<thead>
<tr>
<th>OR = OCMe(CF₃)₂</th>
</tr>
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<tbody>
<tr>
<td>OR = OCMe₂(CF₃)</td>
</tr>
<tr>
<td>OR = OC(CF₃)₂(CF₂CF₂CF₃)</td>
</tr>
<tr>
<td>OR = OCMe₃</td>
</tr>
<tr>
<td>OR = O-2,6-C₆H₃-i-Pr₂</td>
</tr>
</tbody>
</table>

prepared by Schaverian from the alkylidyne complex W(CCMe₃)(CH₂CMe₃)₃ by the sequence of reactions outlined in Scheme 1.
Scheme 1. Preparation of M(NAr)(CHCMe₃)Cl₂(dme) from M(CCMMe₃)(CH₂CMe₃).
The development of Molybdenum (VI) alkylidene chemistry became possible when Murdzek repeated this synthetic procedure starting with Mo(CCMe₃)(CH₂CMe₃)₃.¹⁶ Furthermore, due to its intrinsic lower electrophilicity Mo(NAr)(CHCMe₃)(OCMe₃)₂ was found to polymerize exo,exo-5,6-dicarbomethoxynorbornene without decomposition within the timescale of the polymerization.¹⁷ The importance of this observation cannot be overemphasized since very few living polymerization systems can tolerate functionalities, none of which is transition metal catalyzed.⁹,¹⁰,¹⁵ However the overall yield of the catalyst via this route is low and the preparation and purification tedious, even by the standards of a synthetic organometallic chemist. A new route was then crucial if the potential of this catalyst was to be realized.

The first, and most serious, problem in the synthesis is encountered in the alkylation of MoO₂Cl₂(THF)₂ to yield Mo(CCMe₃)(CH₂CMe₃)₃ (Equation 2).¹⁸ The reaction's overall yield

\[
\text{MoO}_2\text{Cl}_2(\text{THF})_2 + 6 \text{Me}_3\text{CCH}_2\text{MgCl} \xrightarrow{\text{Et}_2\text{O}} (\text{Me}_3\text{CCH}_2)_3\text{Mo} \equiv \text{CCMe}_3
\]

in molybdenum is 30% (at best) and requires six equivalents of valuable Mg(CH₂CMe₃)Cl to yield one alkylidyne ligand. The more reducible nature of molybdenum combined with the rather harsh nature of the alkylationing reagent result in a lower yield than the analogous tungsten reaction. The rest of the reactions are well behaved, with the exception of the reaction between HCl and Mo(CCMe₃)(CH₂CMe₃)₃ which can have yields in the 60% range (Scheme 1). The final yield is approximately 18% with respect to Mo, which corresponds to 3% relative to Mg(CH₂CMe₃)Cl.

Important to mention is the improved procedure for W(NAr)(CHCMe₃)Cl₂(dme) which was developed by Yang and is shown in Scheme 2.¹⁹ Two points are to be noted. The imido ligand is introduced early in order to provide steric and electronic protection. Second, only two equivalents of Mg(CH₂CMe₃)Cl are required in the whole sequence and are added to
\[
\begin{align*}
\text{W(O)Cl}_4 & \xrightarrow{\text{ArNCO, octane}} \text{W(NAr)Cl}_4 \\
\text{W(NAr)(OCMe}_3)_2\text{Cl}_2(\text{THF}) & \xrightarrow{2 \text{ (CH}_3)_3\text{CCH}_2\text{MgCl}} \text{W(NAr)(OCMe}_3)_2\text{Cl}_2(\text{THF}) \rightarrow \text{W(NAr)(OCMe}_3)_2(\text{CH}_2\text{CMe}_3)_2 \\
\end{align*}
\]

**Scheme 2.** Preparation of W(CHCMe}_3)(NAr)Cl}_2(dme) from W(O)Cl}_4.
W(NAr)(OCMe3)2Cl2 where the metal center is adequately protected to survive the alkylation reaction.

In this chapter we describe the development of a new route for the synthesis of catalysts of the general form Mo(NAr)(CHMe3)(OR)2. From analysis of the previously reported routes it was deemed desirable that the imido functionality be introduced at the beginning of the reaction sequence, and that the number of equivalents of Mg(CH2CMe3)Cl be minimized.

RESULTS

Preparation of Mo(NAr)(O)Cl2(py) and Derivatives.

A direct route into a suitable molybdenum imido complex was first investigated. In the study of Mo chemistry it is important to appreciate two points, first the relative reluctance of molybdenum complexes to stay in the highest oxidation state and second their lower electrophilicity relative to their tungsten analogues. In an attempt to imitate the route to tungsten catalysts in Scheme 2, MoOCl4 was reacted with ArNCO in an attempt to introduce the imido group with loss of CO2. However reduction of the metal resulted, yielding uncharacterizable paramagnetic species. Reduction, no reaction or a mixture of products was observed for the reaction of ArNCO with MoO2Cl2, MoO2Cl2(CH3CN)2, MoO2Br2, MoOCl3 under different conditions and in a variety of solvents. This "Wittig-like" (2+2) oxo-isocyanate approach to the introduction of imido groups has been used to prepare [Mo(O)(NMe3)Cl2(CH3CN)]3 and Mo(NMe3)2Cl2.20,21 The faster reactivity of Me3CNCO is probably due to a combination of a more basic lone pair on nitrogen (necessary for prior coordination to the metal center) and less steric congestion. For ArNCO lower reactivity requires harsher reaction conditions, which in turn cause reduction of the metal.

The next approach involved a variation of some syntheses of imido complexes reported by Nugent.22 MoOCl4 was reacted with ArNHTMS in the presence of a variety of bases in an attempt to eliminate TMSCl and the HCl-base adduct. Invariably these reactions resulted in reduction due to the basicity of the ArNHTMS reagent. Reaction of the less reducible
MoO₂Cl₂(THF)₂ in dme with 1/2 equiv of 2,6-lutidine followed by 1/2 equiv of ArNH₂TMS in dme results in the precipitation of lutidinium hydrochloride and the formation of red Mo(NAr)(O)Cl₂(dme) which can be isolated by ether extraction (Equation 3). This material cannot be analytically purified but the bis pyridine adduct, Mo(NAr)(O)Cl₂(py)₂, can be prepared and purified by addition of 10 equiv pyridine to the dme adduct in ether followed by toluene extraction. Attempts to alkylate Mo(NAr)(O)Cl₂(py)₂ resulted in either reduction or a variety of products under a variety of conditions and different reagents (Mg(CH₂CMe₃)Cl, Mg(CH₂CMe₃)₂, Mg(CH₂CMe₃)₂(dioxane), Zn(CH₂CMe₃)₂, LiCH₂CMe₃). Evidently the oxo functionality is reactive enough to compete with the chlorine ligand as a leaving group.

In an effort to address this problem several derivatives of Mo(NAr)(O)Cl₂(py)₂ were prepared in order to either further stabilize the metal or to eliminate the presence of ligands which may compete as leaving groups. Treating Mo(NAr)(O)Cl₂(py)₂ with two equiv of LiOCMe₃, in ether at -30 °C yields Mo(NAr)(O)(OCMe₃)₂ and two equivalents of LiCl (Equation 4). Extraction of the reaction mixture with pentane gave Mo(NAr)(O)(OCMe₃)₂ as a yellow oil. Further efforts at purification were unsuccessful and disproportionation to a mixture of Mo(NAr)(O)(OCMe₃)₂, Mo(NAr)₂(OCMe₃)₂, and presumable MoO₂(OCMe₃)₂ observed. Reaction of aldehydes with Mo(CHCMe₃)(NAr)(OCMe₃)₂ in a
Wittig-like fashion has also been used to prepare Mo(NAr)(O)(OCMe$_3$)$_2$. Further chemistry of this compound was not investigated.

The oxo functionality can be removed from the metal coordination sphere by reaction of one equiv of PCl$_5$ with Mo(NAr)(O)Cl$_2$(py)$_2$, in toluene at -30 °C to yield black Mo(NAr)Cl$_4$(py) which is intensely red in solution (Equation 5). The structure of this complex is probably pseudo-octahedral with the pyridine ligand trans to the imido by analogy with the structurally characterized Mo(N-tolyl)Cl$_4$(py) prepared by Maata and coworkers. Alkylations of Mo(NAr)Cl$_4$(py) invariably led to a mixture of paramagnetic compounds.

Treatment of Mo(NAr)Cl$_4$(py) with 4 equiv of LiOCMe$_3$ in toluene at -30 °C yields 4 equiv of LiCl and Mo(NAr)(OCMe$_3$)$_4$, which can be purified by pentane extraction and subsequent recrystallization as dark yellow crystals (Equation 6). The yield by $^1$H NMR is essentially quantitative, but due to its high solubility the yields of the purified material is substantially lower (65%). Alkylation attempts using a variety of reagents gave either the starting materials (Mg(CH$_2$CMe$_3$)$_2$(TMEDA), Mg(CH$_2$CMe$_3$)$_2$(dioxane), Zn(CH$_2$CMe$_3$)$_2$) or
a mixture of products which contained a variety of alkylidenes and alkylated species (LiCH₂CMe₃, Mg(CH₂CMe₃)Cl). Careful analysis by ¹H NMR of the alkylation mixtures shows that two species, Mo(NAr)(OCMe₃)₂(CH₂CMe₃)₄ and Mo(NAr)(CHCMe₃)(OCMe₃)₂, are not present. The reaction of Mo(NAr)(OCMe₃)₄ with a slight excess of Zn(CH₂CMe₃)₂ in C₆D₆ can be followed over the period of a few days in a sealed NMR tube. After approximately 12 hours the formation of Mo(NAr)(OCMe₃)₃(CH₂CMe₃) is observed and after 36 hours an alkylidene signal appears at 11.60 ppm. This alkylidene species is not Mo(NAr)(CHCMe₃)(OCMe₃)₂, since its Hₓ resonates at 11.24 ppm. The slow rate of alkylation may be attributed to the efficient steric protection which the four tert-butoxide ligands and the imido ligand provide. Furthermore it appears that once the second neopentyl group is introduced it then α eliminates neopentane to yield four coordinate Mo(NAr)(CHCMe₃)(OCMe₃)₂ which is more reactive than the starting material and reacts to yield a distribution of products (Scheme 3).

**Preparation and Alkylation of Mo(NAr)₂Cl₂(dme).**

When MoO₂Cl₂(THF)₂ is reacted with 1 equiv of 2,6-lutidine followed by 1 equiv of ArNHTMS in dme at -30 °C the solution colour changes from colourless to bright red as a white solid precipitates (Equation 7). Filtration of the white solid, removal of solvent and ether extraction yields Mo(NAr)₂Cl₂(dme) in 95 % yield as a brick red solid. The yield is calculated

\[
\text{MoO}_2\text{Cl}_2(\text{thf})_2 \xrightarrow{2,6\text{-lutidine}} \text{ArNH(SiMe}_3)\text{DME} \xrightarrow{- (\text{SiMe}_3)_2\text{O}, \ - [\text{MoO}_3]} \text{Cl} \]

\[
\text{Ar}=2,6\text{-diisopropylphenyl}
\]
Scheme 3. Alkylation of Mo(NAr)(OCMe₃)₄ with Zn(CH₂CMe₃)₂.
with respect to the limiting reagent, ArNHTMS and is therefore close to 50% in molybdenum.
Analysis of the stoichiometry of the reaction suggests that the other 50% of the molybdenum
serves to remove the oxygen atoms and appears as a brown solid which is insoluble in ether.
The composition of this brown material has not been determined but IR analysis shows a
strong band at 870 cm\(^{-1}\) where metal oxo stretches are usually found, suggesting some type of
molybdenum oxide species. This reaction is very dependant on the conditions, either changing
the order of addition of reagents or the nature of the solvent gives a mixture of products.

Unlike Mo(NAr)(O)Cl\(_2\)(dme) or any of its derivatives Mo(NAr)\(_2\)Cl\(_2\)(dme) is sterically
protected by the bulky imido ligands which also give electronic flexibility, and only the
chlorides serve as leaving groups. Mo(NAr)\(_2\)Cl\(_2\)(dme) reacts smoothly with 2 equiv of
Mg(CH\(_2\)CMe\(_3\))Cl in ether at -30 °C to yield orange Mo(NAr)\(_2\)(CH\(_2\)CMe\(_3\))\(_2\) and 2 equiv of
MgCl\(_2\) which precipitate out (Equation 8). This bis-imido bis-alkyl compound is readily

\[
\text{Cl} \quad \text{NAr} \quad \text{Cl} \quad \text{NAr} \\
\text{O-} \quad \text{Mo} = N \text{Ar} \quad \text{O-} \\
\text{Et}_2\text{O} \quad \text{2 NpMgCl} \quad \text{- 2 MgCl}_2 \\
\text{NAr} \quad \text{NAr}
\]

purified by pentane extraction and recrystallization from concentrated pentane solutions to yield
large romohedral brown-orange crystals in excellent yield (70 %). An X-ray study of the
analogous species, Mo(NCMe\(_3\))\(_2\)(2,4,6-C\(_6\)H\(_2\)Me\(_3\)) has been reported by Wilkinson and the
arrangement of the ligands around the metal atom is tetrahedral with little distortion.\(^{24}\)

**Preparation and X-ray Crystal Structure of Mo(NAr)(CHCMe\(_3\))(OSO\(_2\)CF\(_3\))\(_2\)(dme), a Versatile Catalyst Precursor.**

The exchange of an imido ligand for an oxo is a thermodynamically favoured reaction
which has precedent in early transition metal chemistry.\(^{2}\) This reaction is usually carried out by
reaction of an unsaturated nucleophilic oxygen functionality such as aldehydes or dioxygen with the imide. Unfortunately Mo(NAr)$_2$(CH$_2$CMe$_3$)$_2$ is unreactive towards a variety of oxygen sources such as PhCHO, CH$_2$O, H$_2$O, O$_2$ or NEt$_4$OH. This stability is attributed to the steric protection afforded by the isopropyl groups on the imido ligand as well as the neopentyl groups which inhibit attack by nucleophiles. Attempted protonation of the imido nitrogen proved unsuccessful using (CF$_3$)$_2$CHOH or ArOH, while reaction with HCl resulted in a mixture of unidentifiable products. Precedent for the protonation of imido groups was Osborn's observation that Mo(NCCMe$_3$)$_2$(CH$_2$CMe$_3$)$_2$ reacts with (CF$_3$)$_2$CHOH to yield an imido alkylidene complex$^{21}$ (Equation 9), the success of which could be attributed to the more basic nitrogen lone pair. In effect, the same reasons which make the introduction of the imido group difficult are those responsible for its lack of reactivity once on the metal sphere. Efforts then concentrated on the introduction of a more basic imido group.

The mixed imido compound Mo(NAr)(NCMe$_3$)Cl$_2$(py)$_2$ can be prepared by reaction of Mo(NAr)(O)Cl$_2$(py)$_2$ with one equivalent of Me$_3$CNCO in toluene at 80 °C (Equation 10).

\[
\begin{align*}
2 \text{HOCH(CF}_3) \text{CN} & \quad \text{Mo(NtBu)}_2(\text{CHtBu})_2 \\
& \quad \text{\rightarrow Mo(NtBu)(CHtBu)}(\text{OCH(CF}_3)\text{)}_2(\text{H}_2\text{NtBu}) \ (9)
\end{align*}
\]

Care must be taken not to add an excess of isocyanate since this causes isocyanate metathesis to yield Mo(NCMe$_3$)$_2$Cl$_2$(py)$_2$. Alkylation of red Mo(NAr)(NCMe$_3$)Cl$_2$(py)$_2$ with two equiv Mg(CH$_2$CMe$_3$)Cl in ether followed by pentane extraction proceeds smoothly to yield orange
Mo(NAr)(NCMe₃)(CH₂CMe₃)₂ in 65% yield (Equation 11). As expected, this material less crystalline than the bis aryl imido derivative and more difficult to isolate and purify. Mo(NAr)(NCMe₃)(CH₂CMe₃)₂ does react with (CF₃)₂CHOH, but ^1H NMR analysis shows that two resonances appear in the alkylidene proton region, approximately in a 1:1 ratio, as well as a complicated mixture of resonances in the upfield region. Evidently no selectivity for the more basic imido is observed and both are protonated to yield a mixture of alkylidenes. This may be due to thermodynamic reasons, i.e. the lone pair in the tert-butyl imido is protonated first to yield a tert-butyl amido ligand which could intramolecularly transfer the proton to the aryl imido nitrogen before the second protonation takes place to remove the amine. However, the mechanism is not fully understood.

The imido nitrogen in Mo(NAr)₂(CH₂CMe₃)₂ can be protonated by use of a strong acid. Treatement of Mo(NAr)₂(CH₂CMe₃)₂ with three equivalents of triflic acid yields yellow Mo(NAr)(CHCMe₃)(OTf)₂(dme) and ArNH₃OTf virtually quantitatively (Equation 12).
Separation of Mo(NAr)(CHCMe₃)(OTf)₂(dme) from ArNH₃(OTf) is achieved conveniently by extraction with toluene. The most logical intermediate in this reaction is Mo(NAr)(CH₂CMe₃)₂(OTf)₂, formed by multiple protonation of an imido ligand and removal of it as the anilinium salt. The resulting Mo(NAr)(CH₂CMe₃)₂(OTf)₂ should be quite unstable with respect to loss of alkane to generate "Mo(NAr)(CHCMe₃)(OTf)₂" given the ionic nature of the triflate ligand and the instability of dineopentyl complexes towards α elimination of neopentane when electronnegative, poor π bonding ligands are present. It should be noted that Mo(NAr)(CHCMe₃)(OTf)₂(dme) is stable to triflic acid, in spite of the potential for protonation of either the alkylidene or the imido ligand. This stability is perhaps largely due to the still relatively high positive charge on the metal. ¹H NMR studies confirm this electron poor metal proposal since the dimethoxyethane does not exchange on the NMR timescale since different methyl signals are observed at 3.85 ppm and 2.76 ppm, together with different signals for the methylene protons at 3.13 ppm and 2.72 ppm. Although the isopropyl methine protons are equivalent, the methyl groups are not, i.e. the phenyl ring does not rotate rapidly about the N-C bond. The complete ¹H NMR spectrum for Mo(NAr)(CHCMe₃)(OTf)₂(dme) is shown in Figure 1. The room temperature ¹⁹F NMR spectrum in C₆D₆ shows a single peak at -77 ppm, typical for the triflate ligand indicating either equivalent triflate ligands or fast exchange on the NMR timescale in the solution state.
Figure 1. 500 MHz $^1$H NMR spectrum of Mo(CHCMe$_3$)(NAr)(OSO$_2$CF$_3$)$_2$(dme) at 25 °C in C$_6$D$_6$. 
The same property which makes Mo(NAr)(CHCMe3)(OTf)2(dme) relatively stable towards triflic acid makes it reactive towards a variety of nucleophiles. Addition of two equivalents of lithium alkoxide to Mo(NAr)(CHCMe3)(OTf)2(dme) yields Mo(NAr)(CHCMe3)(OR)2 and two equivalents of LiCl quantitatively (Equation 13). The yield of these yellow-orange, crystalline metathesis catalysts is lowered (usually in the range 70-80%) by their extreme solubility in hydrocarbons. None contains dimethoxyethane, either coordinated or as a molecule of crystallization.

An X-ray study of Mo(NAr)(CHCMe3)(OTf)2(dme) confirmed that it is a pseudo-octahedral species in which the imido and alkylidene ligands are cis to each other and the triflate ligands mutually trans. Two views of one of the two independent molecules in the unit cell are shown in Figure 2. Important bond distances and angles for the two independent molecules in the unit cell are listed in Table 1. Since the two molecules do not differ significantly only the second is discussed here.

Several features of Mo(NAr)(CHCMe3)(OTf)2(dme) worth pointing out are analogous to previously structurally characterized pseudo-tetrahedral tungsten complexes. The essentially linear imido and neopentylidene ligands are cis to one another, the tert-butyl group points toward the imido ligands (syn orientation; Mo-C(8)-(C81)=141 (1) Å), and the Mo-N(2) (1.72 (1) Å) and Mo-C(8) (1.93 (1) Å) bond lengths are in the expected range. The
Figure 2. Two views of Mo(CHCMe$_3$)(NAr)(OSO$_2$CF$_3$)$_2$(dme).
Table 1. Selected Bond Distances (Å) and Angles (deg) in Mo(CHCMe₃)(NAr)(OSO₂CF₃)₂(dme).

<table>
<thead>
<tr>
<th>Molecule 1</th>
<th>Molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(1)-N(1)</td>
<td>1.72 (1)</td>
</tr>
<tr>
<td>Mo(1)-C(7)</td>
<td>1.90 (1)</td>
</tr>
<tr>
<td>Mo(1)-O(3)</td>
<td>2.085 (8)</td>
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<tr>
<td>Mo(1)-O(1)</td>
<td>2.101 (8)</td>
</tr>
<tr>
<td>Mo(1)-O(5)</td>
<td>2.299 (8)</td>
</tr>
<tr>
<td>Mo(1)-O(51)</td>
<td>2.325 (8)</td>
</tr>
<tr>
<td>Mo(1)-O(1)-S(1)</td>
<td>135.5 (5)</td>
</tr>
<tr>
<td>Mo(1)-O(3)-S(3)</td>
<td>132.5 (5)</td>
</tr>
<tr>
<td>Mo(1)-N(1)-C(11)</td>
<td>171.0 (8)</td>
</tr>
<tr>
<td>Mo(1)-C(7)-C(71)</td>
<td>142.0 (1)</td>
</tr>
<tr>
<td>N(1)-Mo(1)-C(7)</td>
<td>101.4 (5)</td>
</tr>
<tr>
<td>N(1)-Mo(1)-O(3)</td>
<td>98.4 (4)</td>
</tr>
<tr>
<td>N(1)-Mo(1)-O(1)</td>
<td>96.8 (4)</td>
</tr>
<tr>
<td>N(1)-Mo(1)-O(5)</td>
<td>165.6 (4)</td>
</tr>
<tr>
<td>N(1)-Mo(1)-O(51)</td>
<td>95.2 (4)</td>
</tr>
<tr>
<td>C(7)-Mo(1)-O(3)</td>
<td>97.6 (4)</td>
</tr>
<tr>
<td>C(7)-Mo(1)-O(1)</td>
<td>100.1 (4)</td>
</tr>
<tr>
<td>C(7)-Mo(1)-O(5)</td>
<td>92.9 (4)</td>
</tr>
<tr>
<td>C(7)-Mo(1)-O(51)</td>
<td>163.3 (4)</td>
</tr>
<tr>
<td>O(3)-Mo(1)-O(1)</td>
<td>153.8 (3)</td>
</tr>
<tr>
<td>O(3)-Mo(1)-O(5)</td>
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</tr>
<tr>
<td>O(3)-Mo(1)-O(51)</td>
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<tr>
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<tr>
<td>O(1)-Mo(1)-O(51)</td>
<td>79.5 (3)</td>
</tr>
<tr>
<td>O(5)-Mo(1)-O(51)</td>
<td>70.5 (3)</td>
</tr>
</tbody>
</table>
diisopropylphenyl ring of the imido ligand is oriented perpendicular to the C(21)-N(2)-Mo-C(8)-C(81) plane and it must not be able to rotate past the tert-butyl group of the syn neopentylidene ligand for steric reasons. Note how O(62), O(4), C(8) and O(2) are tipped away from the imido ligand, almost to the point that the structure alternatively could be described as a distorted square pyramid in which the imido ligand occupies the axial position. The two oxygen atoms of the triflate ligands bend away from the two doubly bonded ligands and toward each other (O(4)-Mo-O(2)= 153.8 (3) °), as has been observed in other species that contain two multiply bound ligands cis to each other.\(^4\) The Mo-triflate bond lengths are relatively long (Mo(2)-O(2)=2.105 (8) Å and Mo(2)-O(4)=2.100 (8)) but in the range of covalently bound triflate and the Mo-O-S bond angles relatively small compared to typical alkoxide Mo-O bonds, as it would be expected for relatively ionic ligands with poor π bonding abilities. These bond lengths and bond angles are closely similar to values found in other transition metal triflate complexes, and in two other triflate complexes of Mo. The Mo-OTf bond distance in cis-[Mo\(_2\)(O\(_2\)CM\(_3\))\(_2\)(MeCN)\(_4\)(ax-O\(_3\)SCF\(_3\))](HO\(_3\)SCF\(_3\))\(_2\)(THF) is 2.575(15) Å and is described as ionic.\(^{25}\) Covalently bound triflate can be found in Mo(CO)\(_2\)(L)\(_2\)(OSO\(_2\)CF\(_3\))\(_2\) (L=1,3-diethylimidazolidin-2-ylidene) where the Mo-OTf distance is 2.181 (4) Å.\(^{26}\) Note that the triflate ligands are oriented so that the CF\(_3\) group seem to take up the best compromise position sterically. The position of a given SO\(_2\) unit seems to be determined by a combination of steric factors that includes not only the imido isopropyl group and the tert-butyl group, but also the bulky CF\(_3\) group. Any rotation of the OSO\(_2\)CF\(_3\) group about the Mo-O bond would bring either the SO\(_2\) group or the CF\(_3\) group closer to the imido ligand's isopropyl groups. The solution structure is probably not cationic.

**DISCUSSION**

Relative to tungsten, the development of d\(^0\) molybdenum alkylidene chemistry was hampered in the past by the fact that the Mo(CCM\(_3\))(CH\(_2\)CM\(_3\))\(_3\) precursor cannot be prepared on a large scale nor in high yield. To put it in perspective it should be noted that the
discovery of alkylidene catalysts for olefin metathesis occurred as a result of the development of high oxidation state alkylidyne chemistry.27 This chemistry also led to the discovery of novel organometallic fragments, modes of bonding and well defined catalysts for acetylene metathesis. The series of reactions in Scheme 1 is not a synthetic strategy, rather it is the course of events that the chemistry undertook in the search for well defined metathesis catalysts.

The first development in the thinking of synthetic strategies was the synthesis by Dr D. Yang shown in Scheme 2. This sequence of reactions was specifically tailored to yield complexes of the type W(NAr)(CHMe3)(OR)2. A similar approach was attempted for molybdenum, and it was due to the successful synthesis of Mo(NAr)Cl4(py) that it became obvious that a new methodology was necessary in order to accommodate the lower electrophilicity and facility of reduction of the new metal. The reducibility of MoOCl4 invalidated the direct approach and the oxo functionality in Mo(NAr)OCl2(py)2 served as a protecting group for the placing of the two chloride ligands. The oxo ligand is referred as a protecting group because it stabilizes the metal towards reduction and can be readily removed and exchanged for chlorides by addition of PCl5. It was the critical observation that Mo(NAr)(CH2CMe3)2(OCMe3)2 was unstable towards α elimination which led us to abandon this approach and led to a synthesis which was particular to molybdenum.

The introduction of the imido groups in Mo(NAr)OCl2(dme) as well as in Mo(NAr)2Cl2(dme) deserves special attention since the success of the stabilization of the metal relies on the steric bulk of the ligands as well as on the electronic flexibility of the metal-nitrogen multiple bond. The overall strategy is a variation of some syntheses of imido complexes reported by Nugent. For example, treatment of MoO2Cl2 with four equivalents of (CH3C)NHTMS yields Mo(N(CMe3))2(OTMS)2 and two equivalents of (CH3)3CNH2(TMS)Cl. It appears that the N-Si bond first adds across the oxo double bond to yield a siloxy amido complex which is dehydrohalogenated to yield the imido siloxy compound. Repeat of this sequence then yields the bis imide. Note that the TMS group ends
on the oxygen atom and that the reagent itself acts as a base to catalyze the removal of HCl. Analysis of the stoichiometry of reactions 3 and 8 reveals that there must exist some sort of sink for the removal of the oxygen atoms from the starting material. For reaction 3 it is plausible that it proceeds in a similar sequence to that observed by Nugent, first the addition across the metal oxo bond yields the amido siloxide derivative which is then dehydrohalogenated by lutidene to yield Mo(NAr)OCl(OTMS). This material then reacts with unreacted MoO₂Cl₂ (two equivalents present for each equivalent of ArNHTMS) to disproportionate to MoO₂Cl(OTMS) and Mo(NAr)OCIs. A similar sequence of reactions can account for the formation of Mo(NAr)₂Cl₂(dme) as shown in Equation 7. This (trimethylsilyl)oxo disproportionation has precedent in Nugent's chemistry as well, since treatment of MoO₂Cl₂ with 4 equivalents of (1-adamantyl)NHTMS yields ((1-adamantyl)NH)₂Mo(OTMS)₄ demonstrating that subtle changes in the size of the amine can have a profound effect on the course of the reaction. Modification of reaction 7 by other co-workers resulted in a new preparation which optimizes the yield of molybdenum as shown in Equation 14.²⁹ This reaction can be scaled up to convenient quantities. Although

\[
\text{MoO}_2\text{Cl}_2(\text{THF})_2 \xrightarrow{\text{2,2,6-lutidine}} \text{2 ArNH(SiMe}_3\text{)}_\text{2} \\
\text{4 Me}_3\text{SiCl} \\
\text{DME} \\
\text{- (SiMe}_3\text{)}_2\text{O, - [MoO}_3\text{]x}
\]  

(14)

synthetically important this modification does not solve the mechanistic problem. A plausible hypothesis is that the role of the trimethylchlorosilane is to convert any oxo or OSiMe₃ ligands to hexamethyldisiloxane and replace them with chloride. Consistent with this proposal is the remarkable preparation of the bis imido complex, discovered by Harold Fox, where ammonium molybdate is reacted with the aniline, TMSCl and an appropriate amount of base (Equation 15).
Scheme 4. Preparation of Mo(NAr)(CHMe₂)(OSO₂CF₃)₂(dme) from MoO₂Cl₂(THF)₂.
The successful synthesis of molybdenum catalysts is summarized in the sequence of reactions shown in Scheme 4. This was discovered independent of previous tungsten chemistry but was found to be applicable to this metal once the precursor W(NAr)₂Cl₂(dme) was synthesized. The central synthetic concept is utilization of the imido ligand as a protecting group during the alkylation of the metal center, which upon removal by protonation with triflic acid induces α elimination to yield the alkylidene ligand. Although preparation of the original synthetic target Mo(NAr)(CHMe₃)Cl₂(dme) was not achieved there are several properties of the bis triflate analogue which make it a better catalyst precursor. From a practical point of view HOTf, although a stronger acid, is easier to handle than HCl. The whole procedure can be conveniently carried out in the dry box, although it has been successfully repeated using Schlenk line techniques. The dimethoxyethane ligand is more tightly bound in the triflate derivative eliminating oligomerization and subsequent purification problems which are characteristic of the dichloride analogue. Finally the triflate ligand is a better leaving group and so far every substitution reaction has been successful, including replacement by the addition of alcohols and an appropriate base. The recognition of the value of compounds that have poorly coordinating anions (such as perchlorates, fluorosulfates, tetrafluoroborates and triflates) has increased since they serve as inorganic synthons for a range of derivatives formed by substitution of these relatively labile ligands by ligands of greater nucleophilicity. Replacement of chlorides by triflates was the logical evolution for the precursor in order to fully expand the window of different derivatives of potential catalytic activity.
EXPERIMENTAL

General Details All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from molten sodium. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane, pyridine and 2,6-lutidine were distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina.

Me$_3$SiNHAr (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$) was prepared from Me$_3$SiCl and LiNHAr in ether at room temperature and was distilled prior to use. The lithium alkoxides were prepared by addition of n-butyl lithium to the corresponding alcohol and recrystallized from ether or pentane. The procedure for the preparation of MoO$_2$Cl$_2$ by reaction of MoO$_2$ with Cl$_2$, including the necessary apparatus, has been reported. MoO$_2$Cl$_2$(THF)$_2$ was prepared by adding solid MoO$_2$Cl$_2$ slowly to THF at -30 °C. In our experience, addition of THF to MoO$_2$Cl$_2$ is too exothermic to control. All other reagents were purchased from commercial sources and purified by standard techniques.

NMR data are listed in parts per million downfield from TMS for proton and carbon, and downfield from CCl$_3$F for fluorine. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d$_6$ at 25 °C unless otherwise noted.

Mo[N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]OCl$_2$(dme). A solution of 2,6-lutidine (100 mg, 0.93 mmol) in DME (3 mL) was added dropwise to a solution of MoO$_2$Cl$_2$(THF)$_2$ (690 mg, 2.01 mmol) in DME (20 mL) at -30 °C. Immedately after, a solution of ArNSiH(TMS) (250 mg, 1.0 mmol) in DME (5 mL) was added under vigorous stirring. The solution color changes to reddish orang as an orange precipitate forms. The mixture was allowed to warm up to room
temperature and stirred an additional 90 minutes. The solvent was then removed (in vacuo) and the residue extracted with ether and filtered through Celite. Removal of solvent gave 380 mg (85 %) of the product as an orange powder (the compound was purified as the bis pyridene adduct): $^1$H NMR $\delta$ 7.00 (d, 2, $H_m$), 6.88 (t, 1, $H_p$), 4.59 (sept, 2, $CHMe_2$), 3.40 (s, 6, $CH_3O CH_2CH_2OCH_3$), 3.00 (s, 4, $MeOCH_2CH_2OMe$), 1.36 (d, 12, $CHMe_2$).

$\text{Mo[}N-2,6-C_6H_3(CHMe_2)_2]\text{OCI}_2(\text{py})_2$. A solution of pyridine (5.2 g, 6.6 mmol, 10 equiv) in ether (5 mL) was added dropwise to a red solution of $\text{Mo[}N-2,6-C_6H_3(CHMe_2)_2]\text{OCI}_2(\text{dme})$ (3.00 g, 6.6 mmol) in ether (100 mL, -30 °C), allowed to warm up to room temperature and stirred an additional 30 minutes. During this time the solution darkens and some precipitate may form. The reaction mixture was filtered through Celite and the solvent evaporated in vacuo to yield 2.9 g of $\text{Mo[}N-2,6-C_6H_3(CHMe_2)_2]\text{OCI}_2(\text{py})_2$ as a reddish brown solid (85 %): $^1$H NMR $\delta$ 8.98 (b, 4, $\alpha-[NC_5H_5]$), 7.06 (d, 2, $m-[N-2,6-C_6H_3(CHMe_2)_2]$), 6.9 (m, 3), 6.55 (b, 4, $m-[NC_5H_5]$), 4.68 (b, 2, $N-2,6-C_6H_3(CHMe_2)_2$), 1.27 (d, 12, $N-2,6-C_6H_3(CHMe_2)_2$). $^{13}$C NMR 154.0, 152.3, 138.9, 131.1, 124.7, 123.9, 28.5, 25.2.

$\text{Mo(N-2,6-C_6H_3(CHMe_2)_2)O(OCMe}_3)_2$. Solid Li(OCMe$_3$) (46 mg, 0.58 mmol) was added in small portions to a solution of $\text{Mo(N-2,6-C_6H_3(CHMe_2)_2)OCI}_2(\text{py})_2$ (150 mg, 0.29 mmol) in ether (20 mL, -30 °C). The reaction mixture was allowed to warm up to room temperature and stirred for an additional 2 hours. The colour of the solution changed from red to orange as LiCl precipitated out of solution. Removing the solvent in vacuo yielded a yellow waxy solid. This residue was extracted with pentane, the extracts filtered through Celite, and the filtrate stripped down to a yellow oil (apprx. 50 mg, 40%). Several attempts to crystallize this compound failed: $^1$H NMR $\delta$ 7.07 (d, 2, $m-[N-2,6-C_6H_3(CHMe_2)_2]$), 6.97 (t, 1, $p-[N-2,6-C_6H_3(CHMe_2)_2]$), 4.31 (sept, 2, $N-2,6-C_6H_3(CHMe_2)_2$), 1.34 (d, 12, $N-2,6-C_6H_3(CHMe_2)_2$), consistent with its previous characterization.
Mo(N-2,6-C₆H₃(CHMe₂)₂)Cl₄(py). An orange-red solution of Mo[N-2,6-C₆H₃(CHMe₂)₂]OCl₂(py)₂ (1.00 g, 1.93 mmol) in toluene (30 ml, -30°C) was treated with solid PCl₅ (397 mg, 1.93 mmol). The initial red colour intensifies to a dark red colour as the reaction is allowed to warm up to room temperature and PCl₅ goes into solution. After 3 hours the solution is filtered and the solvent removed in vacuo to yield Mo(N-2,6-C₆H₃(CHMe₂)₂)Cl₄(py) as a black microcrystalline solid (765 mg, 80 %): ¹H NMR δ 9.55 (b, 2, o-[NC₅H₅]), 7.09 (d, 2, m-[N-2,6-C₆H₃(CHMe₂)₂]), 6.98 (t, 1, p-[N-2,6-C₆H₃(CHMe₂)₂]), 6.80 (b, 1, p-[NC₅H₅]), 6.54 (b, 2, m-[NC₅H₅]), 5.14 (b, 2, N-2,6-C₆H₃(CHMe₂)₂), 1.35 (d, 12, N-2,6-C₆H₃(CHMe₂)₂). ¹³C NMR δ 158.5, 152.4, 139.0, 135.5, 124.9, 124.3, 29.13, 26.3. Anal. Calcd for MoC₁₇H₂₂Cl₄N₂: C, 41.49; H, 4.51; N, 5.69. Found: C, 41.52; H, 4.55; N, 5.51.

Mo(N-2,6-C₆H₃(CHMe₂)₂)(OCMe₃)₄. A red solution of Mo(N-2,6-C₆H₃(CHMe₂)₂)Cl₄(py) (500 mg, 1.02 mmol) in toluene (15 mL, -30 °C) was treated with solid LiOCMe₃ (355 mg, 4.43 mmol), allowed to warm to room temperature and stirred overnight. The colour changes to light orange as a precipitate forms. The mixture was filtered though Celite, the solvent removed in vacuo and the resulting solid recrystallized from a minimum amount of pentane to yield 401 mg (70%) of orange Mo(N-2,6-C₆H₃(CHMe₂)₂)(OCMe₃)₄ as orange plates: ¹H NMR δ 6.99 (d, 2, m-[N-2,6-C₆H₃(CHMe₂)₂]), 6.87 (t, 1, p-[N-2,6-C₆H₃(CHMe₂)₂]), 4.45 (sept, 2, N-2,6-C₆H₃(CHMe₂)₂), 1.48 (s, 36, OCMe₃), 1.33(d, 12, N-2,6-C₆H₃(CHMe₂)₂). Anal. Calcd for MoC₂₈H₃₂N₂O₄: C, 59.66; H, 9.48; N, 2.48. Found: C, 60.18; H, 9.39; N, 2.12.

Mo(N-2,6-C₆H₃(CHMe₂)₂)(NCMe₃)Cl₂(py)₂. A slight excess of Me₃NCO (75 mg, 0.755 mmol) was added to a solution of Mo[N-2,6-C₆H₃(CHMe₂)₂]OCl₂(py)₂ (300 mg, 0.581 mmol) in toluene (15 mL) and stirred at 80 °C for 12 hours under an Ar atmosphere
without any noticable colour change. Removal of the solvent *in vacuo* yielded a gummy solid. Recrystallization from a minimum amount of ether at -40 °C gave Mo(N-2,6-C₆H₃(CHMe₂)₂)(NCMe₃)Cl₂(py)₂ (239 mg, 72%) as red crystals: ¹H NMR δ 9.12 (d, 4, o-[NC₅H₅]), 7.15 (d, 2, m-[N-2,6-C₆H₃(CHMe₂)₂]), 6.95 (t, 1, p-[N-2,6-C₆H₃(CHMe₂)₂]), 6.81 (t, 2, p-[NC₅H₅]), 6.53 (dd, 4, m-[NC₅H₅]), 4.35 (sept, 2, N-2,6-C₆H₃(CHMe₂)₂), 1.42 (s, 9, NCMe₃), 1.39 (d, 12, N-2,6-C₆H₃(CHMe₂)₂).

The mixed imido compound can be obtained analytically pure in good yield as Mo(N-2,6-C₆H₃(CHMe₂)₂)(NCMe₃)Cl₂(dme) by recrystallization from a concentrated dme solution layered with pentane at -40 °C. Data for Mo(N-2,6-C₆H₃(CHMe₂)₂)(NCMe₃)Cl₂(dme): ¹H NMR δ 7.15 (d, 2, m-[N-2,6-C₆H₃(CHMe₂)₂]), 6.97 (t, 1, p-[N-2,6-C₆H₃(CHMe₂)₂]), 4.33 (sept, 2, N-2,6-C₆H₃(CHMe₂)₂), 3.38 (s, 6, MeOCH₂CH₂OMe), 3.12 (s, 4, MeOCH₂CH₂OMe), 1.42 (d, 12, N-2,6-C₆H₃(CHMe₂)₂), 1.27 (s, 9, NCMe₃). ¹³C NMR: 143.7, 127.4, 124.1, 123.8, 74.6, 71.24, 62.04, 29.6, 28.3, 25.4, 25.0. Anal. Calcd for MoC₂₀H₃₆NCl₂O₂: C, 47.72; H, 4.51; N, 5.69. Found: C, 47.92; H, 7.60; N, 5.57.

Mo(N-2,6-C₆H₃(CHMe₂)₂)(NCMe₃)(CH₂CMe₃)₂. A stock solution of MgCH₂CMe₃Cl was diluted to 5 ml total volume (2.4 M, 175 µL, 0.42 mmol) and added to a dark red solution of Mo(N-2,6-C₆H₃(CHMe₂)(NCMe₃)Cl₂(py)₂ (120 mg, 0.21 mmol) in ether (10 ml, -30°C) over a period of 10-25 minutes. The colour of the solution changes from red to orange as MgCl₂ precipitates. The solution was allowed to warm to RT and stirred for an additional 3 hours. The resulting mixture was filtered through Celite, the filtrate evaporated *in vacuo* and the resulting orange solid recrystallized from a concentrated pentane solution to yield 65 mg of the product as waxy orange crystals (65 %): ¹H NMR δ 7.08 (d, 2, m-[N-2,6-C₆H₃(CHMe₂)₂]), 7.00 (t, 1, p-[N-2,6-C₆H₃(CHMe₂)₂]), 3.75 (sept, 2, N-2,6-C₆H₃(CHMe₂)₂), 3.05(d, 2, J₁₂=17, CH₂CMe₃), 1.29 (d, 12, N-2,6-C₆H₃(CHMe₂)₂), 1.24 (s, 18, CH₂CMe₃), 1.22 (s, 9, NCMe₃). ¹³C NMR : δ 1.54 (C₁₅os), 141.7 (C₇p), 125.3 (C₈p), 122.9 (C₉m), 78.1 (CH₂CMe₃), 70.2 (NCMe₃), 33.9 (CHMe₂), 33.7 (CH₂CMe₃), 32.3
(NCMe$_3$), 28.4 (CHMe$_2$), 23.8 (CH$_2$CMe$_3$).

**Mo(N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$)$_2$Cl$_2$(dme).** To MoO$_2$Cl$_2$(THF)$_2$ (30.0 g) in DME (350 mL, -30 °C), a solution of 2,6-lutidene (9.3 g, 1 equiv) in DME (25 mL) was added dropwise but quickly over a period of 3-5 minutes. Immediately thereafter, a solution of 2,6-diisopropyl-trimethylsilyl aniline (21.8 g, 1 equiv) in DME (40 mL, -30 °C) was added dropwise over a period of 15 minutes. The solution color changed from slightly yellow to bright red as a precipitate formed. The resulting mixture was allowed to warm up to room temperature over a period of 2 hours and filtered through Celite. The filtrate was evaporated to dryness *in vacuo* and the residue was extracted with ether (~500 mL). The extracts were filtered through Celite and the solvent removed from the filtrate to give 26.0 g (95% based on trimethylsilyl aniline) of deep red Mo(NAr)$_2$(dme)Cl$_2$ that was pure enough for the alkylation step. Alternatively this compound can be prepared using the following procedure: To a rapidly stirred solution of MoO$_2$Cl$_2$(thf)$_2$ (10.0 g, 29.0 mmol) in dme (100 mL, -30°C), the following were added in succession: a solution of 2,6-lutidine (6.2 g, 58 mmol) in dme (5 mL, -30°C) over a period of 3-5 min, a solution of chlorotrimethylsilane (12.6 g, 116 mmol) in dme (25 mL, -30°C) over a period of 5-10 min, and a solution of *N*-trimethylsilyl-2,6-diisopropylaniline (14.6 g, 58 mmol) in dme (25 mL, -30°C) over a period of 5-10 min. The color changed from slightly yellow to bright red-orange to deep red-orange as a precipitate formed. The mixture was allowed to stir and warmed to room temperature over a period of 6 hours. The reaction mixture was then filtered through Celite to remove lutidine hydrochloride, which was then washed with diethyl ether until the washings ran through colorless. Solvents were removed from the filtrate *in vacuo* to yield 16.7 g (27.5 mmol, 95%) of brick-red product which need not be purified further: $^1$H NMR δ 7.01 (d, 4, H$_m$), 6.89 (t, 2, H$_p$), 4.29 (sept, 4, CHMe$_2$), 3.44 (s, 6, MeOCH$_2$CH$_2$OME) 3.18 (s, 4, MeOCH$_2$CH$_2$OME), 1.25 (d, 24, CHMe$_2$); $^{13}$C NMR δ 154.2 (C$_{ipso}$), 145.5 (C$_p$), 128.0 (C$_m$), 123.9 (C$_o$), 71.3 (MeOCH$_2$CH$_2$OME), 62.8 (MeOCH$_2$CH$_2$OME), 28.2 (CHMe$_2$), 25.2 (CHMe$_2$). Anal. Calcd
for MoC$_{28}$H$_{44}$Cl$_4$NO$_2$: C, 55.35; H, 7.30; N, 4.61; Cl, 11.67. Found: C, 55.18; H, 7.23; N, 4.72; Cl, 11.61.

Mo[N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]$_2$(OCMe$_3$)$_2$. To a solution of Mo[N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$]$_2$Cl$_2$(dme) (50 mg, 0.0823 mmole) in ether (15 mL, -30 °C) was added LiOCMe$_3$ (14 mg) as a solid. This caused the colour of the solution to change from red to yellow as LiCl precipitated out of solution. The mixture was allowed to warm up to RT and the mixture stirred for 90 minutes. Solvent was evaporated in vacuo and the resulting solids extracted with pentane. Filtration through Celite gave the product (34 mg, 79%): $^1$H NMR δ 6.98 (d, 4, m-[N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$], J=6.4 Hz), 6.92 (t, 2, p-[N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$], J=6.4 Hz, 3.23 (sept, 4, [N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$], J=6.9 Hz), 1.42 (s, 18, OCCMe$_3$), 1.18 (d, 24, [N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$], J=6.9 Hz). $^{13}$C NMR δ 142.8 (C$_{ipso}$), 125.8 (C$_m$), 122.9 (C$_p$), 32.1 (CHMe$_2$), 28.6 (CHMe$_2$), 23.8 (OCMe$_3$), resonances for quaternary carbons could not be found, probably because of coincidence. Anal. Calcd for MoC$_{32}$H$_{52}$N$_2$O$_2$: C, 64.85; H, 8.84; N, 4.74. Found: C, 66.18; H, 8.78; N, 5.15.

Mo(N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$)$_2$(CH$_2$CMe$_3$)$_2$. An ether solution of neopentyl magnesium chloride (98.7 mL, 1.00 M, 98.7 mmol) was added dropwise to a stirred solution of Mo(NAr)$_2$(dme)Cl$_2$ (30 g, 49.3 mmol) in ether (500 mL) at -30°C. All Mo(NAr)$_2$(dme)Cl$_2$ need not be dissolved. The color of the reaction changes from red to orange as MgCl$_2$ precipitates. The reaction mixture was allowed to warm to 25° and was stirred for 3 h. The resulting mixture was filtered through Celite, and the filtrate was concentrated in vacuo and kept at -40 °C to yield several crops (usually three) of orange crystals; yield 20.2 g (70 %): $^1$H NMR δ 6.96 (m, 6, H$_m$ and H$_p$), 3.72 (sept, 4, CHMe$_2$), 2.28 (s, 4, CH$_2$CMe$_3$), 1.26 (s, 18, CH$_2$CMe$_3$), 1.21 (d, 24, CHMe$_2$); $^{13}$C NMR δ 153.2 (C$_{ipso}$), 141.4 (C$_p$), 124.5 (C$_o$), 122.7 (C$_m$), 79.9 (CH$_2$CMe$_3$), 33.7 (CHMe$_2$), 33.5 (CH$_2$CMe$_3$), 28.3 (CHMe$_2$), 23.3

Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OSO₂CF₃)₂(dme). A pre-chilled solution of triflic acid (3.15 mL, 35.5 mmol, 3 equiv) in dme (20 mL) was added dropwise to a solution of Mo(NAr)₂(CHCMe₃)₂ (7.00 g, 11.8 mmol) in dme (200 mL) at -30 °C over a period of 10 min. It is important in this step that the solution be homogeneous and cold. It is best to grind the Mo(NAr)₂(CHCMe₃)₂ crystals to a fine powder to aid dissolution; some pentane (15-30 mL) may be added. The solution was allowed to warm up to room temperature and stirred for 3 h. During this period the color changed from orange to dark yellow. The solvent was evaporated in vacuo to yield a yellow solid, which was then extracted with cold toluene (100-150 mL). The extract was filtered through a bed of Celite and the toluene removed from the filtrate in vacuo to give 5.9 g (65%) of the product as yellow flakes, which can be used without further purification. The product should be checked by NMR for contamination by anilinium triflate, which is slightly soluble in toluene: ¹H NMR δ 14.29 (s, 1, CH-t-Bu), 6.90 (m, 3, H₃ and H₄), 3.91 (sept, 2, CH₂Me₂), 3.85 (s, 3, MeO(CH₂)₂OMe), 3.13 (m, 2, MeO(CH₂)₂OMe), 2.76 (s, 3, MeO(CH₂)₂OMe), 2.72 (m, 2, MeO(CH₂)₂OMe), 1.44 (s, 9, CH-t-Bu), 1.40 (d, 3, CH₂Me₂), 1.24 (d, 3, CH₂Me₂); ¹³C NMR δ 331.9 (C₁₇, J₇₁₇ = 121), 151.2, 141.6, 130.6, 125.6, 121.4, 115.5, 72.5, 70.1, 65.3, 61.5, 31.0, 28.3, 25.2, 22.7; ¹⁹F δ -77.0. Anal. Calcd for MoC₂₃H₇F₆NO₈S₂: C, 37.86; H, 5.11; N, 1.92. Found: C, 37.99; H, 5.33; N, 1.85.

Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OCMe₃)₂. Lithium tert-butoxide (0.95 g, 11.8 mmol) was slowly added as a solid to a solution of Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OSO₂CF₃)₂(dme) (4.00 g, 5.5 mmol) in a mixture of ether (200 mL, -30 °C) and dme (20 mL, -30 °C) over a period of 10 min. The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and evaporated to dryness. The dark orange solid was
extracted with a minimum amount pentane (~50 mL) and filtered through a bed of Celite. Evaporation of the solvent gave 2.54 g (95%) of the product. Purification can be achieved by recrystallization from a concentrated pentane solution at -40 °C. Spectroscopic data is consistent with its previous characterization: **1H NMR** δ 11.23 (s, 1, CHCMe3), 7.04 (m, 3, NAr), 3.96 (sept, 2, CHMe2), 1.33 (s, 18, OCMMe3), 1.26 (d, 12, CHMe2), 1.23 (s, 9, CHCMMe3); **13C NMR** δ 265.8 (d, J = 117, CHCMe3), 153.2 (Cipso), 146.1 (C0), 127.0 (Cp), 123.1 (Cm), 76.6 (OCMMe3), 46.3 (CHCMe3), 32.5 and 32.1 (OCMMe3 and CHCMMe3), 28.2 (CHMe2), 24.0 (CHMe2).

\[
\text{Mo}((\text{C}H\text{CMe}_3)(\text{N}-2,6-\text{C}_6\text{H}_3(\text{CHMe}_2)_2)(\text{OCMe}_2(\text{CF}_3)))_2.
\]

Solid Li(OCMe2(CF3)) (734 mg, 5.48 mmol) was added in small portions over a period of a minute to a stirring solution of crude Mo(CHCMe3)(N-2,6-C6H3(CHMe2)2)(OSO2CF3)2(dme) (2.00 g, 2.73 mmol) in ether (100 ml) stirring at -30 °C. The solution darkened from light yellow to orange and LiCl precipitated as the reaction was allowed to warm to room temperature over the next three hours. Solvents were then removed in vacuo and the residue extracted with pentane. The extracts were filtered through Celite and the filtrate was evaporated in vacuo. The resulting solid was pure according to its **1H NMR** spectrum. Recrystallization from a minimum amount of pentane at -40 °C gave Mo(CHCMe3)(N-2,6-C6H3(CHMe2)2)(OCMe2(CF3))2 as yellow orange blocks in two crops (~1.02 g, 65%). The spectroscopic data is consistent with its previous characterization: **1H NMR** δ 11.61 (s, 1, CHCMe3), 6.99 (s, 3, N-2,6-C6H3(CHMe2)2), 3.74 (sept, CHMe2), 1.35 and 1.28 (s, 6 each, OCMMe2(CF3)), 1.20 (d, 12, CHMe2), 1.12 (s, 9, CHCMMe3); **13C NMR** δ 276.8 (d, J = 118, CHCMe3), 153.4 (Cipso), 146.9 (C0), 128.3 (Cp), 127.4 (q, 1JCF = 287, OCMMe2(CF3)), 123.3 (Cm), 78.5 (q, 2JCF = 30, OCMMe2(CF3)), 47.7 (CHCMe3), 28.5 (CHCMMe3), 24.8 (CHMe2), 24.7 (CHMe2), 23.7 (OCMMe2(CF3)).

\[
\text{Mo}(\text{CHCMe}_3)(\text{N}-2,6-\text{C}_6\text{H}_3(\text{CHMe}_2)_2)(\text{OCMe}(\text{CF}_3))_2.
\]

To a solution of
Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OSO₂CF₃)₂(dme) (2.00 g, 2.73 mmol) in ether (100 mL, -30°C) was added LiOCMe(CF₃)₂ as a solid (1.03 g, 5.48 mmol). This caused the colour of the solution to darken from yellow to orange and LiCl precipitated out of solution as the mixture was allowed to warm to room temperature and stirred for an additional 3 hours. Solvents were then removed in vacuo and the residue was extracted with pentane. The extracts were filtered through Celite and the filtrate evaporated to dryness in vacuo. Recrystallization from a minimum amount of pentane at -40 °C gave Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OCMe(CF₃)₂)₂ as large yellow romboidal crystals. The spectroscopic data is consistent with its previous characterization: ¹H NMR δ 12.06 (s, 1, CHCMe₃), 6.94 (m, 3, N-2,6-C₆H₃(CHMe₂)₂), 3.54 (sept, 2, CHMe₂), 1.37 (s, 6, OCMe(CF₃)₂), 1.16 (d, 12, CHMe₂), 1.04 (s, 9, CHCMe₃); ¹³C NMR δ 288.2 (d, J = 117, CHCMe₃), 154.0 (Cipso), 147.8 (C₀), 129.5 (Cp), 124.2 (q, ¹JC₆ = 288, OCMe(CF₃)₂), 124.1 (q, ¹JC₆ = 288, OCMe(CF₃)₂), 123.5 (Cm), 81.2 (sept, ²JC₆ = 29, OCMe(CF₃)₂), 49.4 (MoCHCMe₃), 31.3 (MoCHCMe₃), 28.6 (CHMe₂), 23.7 (CHMe₂), 18.9 (OCMe(CF₃)₂).

X-ray Structure of Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OSO₂CF₃)₂(dme). The data was collected by Dr. William Davis and the structure solved and refined by Marie O'Regan. Data were collected at -65 °C on a Rigaku AFC6 diffractometer equipped with a liquid nitrogen low temperature device and using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. A total of 11646 reflections were collected, 11239 of which were unique. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. The structure was solved by direct methods. Refinement was by full matrix least squares using TEXSAN from Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (dC-H = 0.95 Å). Final R = 0.054 and Rw = 0.070. Mo(CHCMe₃)(N-2,6-C₆H₃(CHMe₂)₂)(OSO₂CF₃)₂(dme) crystallizes in the
space group $P1$ with $a = 17.543$ Å, $b = 19.008$ Å, $c = 9.711$ Å, $\alpha = 91.91^\circ$, $\beta = 99.30^\circ$, $\gamma = 87.27^\circ$, $Z = 4$, $M_r$ 729.60, $V = 3191.1$ Å$^3$, $\rho$ (calcd) = 1.518 g cm$^{-3}$. 
CHAPTER 2
Living Ring-Opening Polymerization of 2,3-Difunctionalized
Norbornadienes by Mo(NAr)(CHCMe$_3$)(OCMe$_3$)$_2$. 
INTRODUCTION

The ring-opening metathesis polymerization of cyclic olefins is an important application of the olefin metathesis reaction. The accepted mechanism is similar to that of acyclic olefins and consists of reaction of an olefin with an alkylidene complex to form an unstable metallacyclobutane species in a [2+2] type of addition. If the resulting metallacycle breaks up to yield a new olefin it is termed productive metathesis whereas if the original olefin is obtained then degenerative metathesis takes place. Several recent excellent reviews as well as books exist in the literature which address the different types of catalysts involved, mechanistic aspects and applications; the reader should consult those sources first if unfamiliar with this chemistry.4,5,6,7

The development of direct high yield synthesis to catalyst precursors of the type M(CHCMe3)(NAr)(OTf)2(dme) (Chapter 1) for both molybdenum and tungsten opened the opportunity of studying the reactivity of catalysts of the form M(CHCMe3)(NAr)(OR)2. Complexes of the type M(CHCMe3)(NAr)(OCMe3)2 (M = Mo, W) which contain the relatively electron donating tert-butoxide ligand are relatively unreactive for metathesis of ordinary internal olefins, but will metathesize reactive olefinic bonds in strained cyclic olefins such as norbornene (NBE). The new alkylidene only reacts with other strained olefins and not with the olefinic bonds in the resulting polymer, therefore no back-biting is observed.

The overall ring-opening metathesis polymerization (ROMP) reaction using Mo(CHCMe3)(NAr)(OCMe3)2 as the initiator is shown in Scheme 1 and it points out and summarizes several important concepts. The initiator first reacts with an equivalent of monomer to form a metallacyclobutane intermediate which breaks up to yield a propagating alkylidene at a rate $k_i$ (initiation rate, assuming that the rate determining step is metallacycle formation). Propagation of the polymerization is carried out by reaction of the propagating alkylidene with more monomer with a rate constant $k_p$ (propagation rate). These rates are not necessarily the same. It was observed by Murdzek31 that for NBE, $k_p$ is larger than $k_i$ and this was attributed to the lesser steric congestion in the propagating alkylidene allowing easier
Scheme 1. Overall ring-opening metathesis polymerization initiated with $M(\text{CHCMe}_3)(\text{NAr})(\text{OCHMe}_3)_2$. 
access of the monomer. Since there is no chain transfer, back biting or decomposition during the timescale of the polymerization reaction once the monomer is consumed the result is a living polymer. If more monomer is added then it will be incorporated into the polymer chain with a rate $k_p$. If a different type of monomer is added the living polymer takes the role of the initiator and will react with the second monomer with a rate $k_i'$ to form a new propagating species which will then propagate with a new $k_p'$. This type of reactivity can be exploited to synthesize materials such as block copolymers.

The final reaction for any polymerization system is termination. Addition of aldehydes to the living polymers in Scheme 1 effects a Wittig type reaction$^{32}$ which cleaves the organic polymer fragment by formation of Mo(NAr)O(OCMe$_3$)$_2$ (see Chapter 1).

The study of the individual processes which constitute this polymerization system is logical in order to control the reactivity. This in turn allows the preparation of materials with prescribed properties. The corollary of this idea is that the analysis of the resulting polymers is important to understand the organometallic processes which made them. This two way relationship between organometallic mechanisms and the resulting material is one of the central concepts of this thesis.

The sterochemical arrangement of monomers, or microstructure, within a polymer backbone determines many of the bulk properties. A classic example is the different properties that isotactic and atactic polypropylene possess which differ in the relative orientation of the methyl groups along the polymer backbone. Isotactic polypropylene is commercially more important being less soluble, higher melting, and greater in tensile strength than other forms.$^{33}$ Another example is the intense piezo-electric effects that poly-vinylidene fluoride (PVDF) exhibits when it is polymerized in a head to tail fashion. Randomly polymerized PVDF has a lower net dipole moment and is not used commercially.$^{124}$

Specific aspects of the microstructure of polynorbornene and its derivatives which are of interest include:

a) Double bond isomerism. The substituents on the individual olefinic bonds in the
polymer may have a cis or a trans configuration upon ring-opening.

b) Regiochemistry of monomer addition. Unsymmetrically substituted monomers having C1 symmetry may add to form head-to-tail, head-to-head, or tail-to-tail sequences in the polymer.

c) Tacticity. Since norbornene is prochiral, pairs of adjacent rings (dyads) in the polymer chain may have one of two relationships, meso (m) or racemic (r) depending upon whether the chiral allylic carbons on either side of chain vinylenes have the same configuration (r) or opposite (m). Polymers consisting entirely of m dyads are termed isotactic, while those containing only r dyads would be syndiotactic. Atactic polymers consist of a random distribution.34

2,3-Disubstituted norbornadienes are convenient monomers for a detailed study of the stereochemistry of ring-opening for several reasons. First these monomers posses the same point group of NBE (C8) therefore the above tacticity conditions are similar while regiochemistry of monomer addition is eliminated. Therefore only four possible primary structures for polymers made from symmetric norbornadiene monomers are possible, and are illustrated below. (Analogous relatively simple primary structures can be obtained using pure cis-exo or cis-endo disubstituted norbornenenes, although purification of all endo or all exo monomers is tedious.) Second, several 2,3-disubstituted norbornadienes can be prepared readily by Diels-Alder reaction between acetylenes and cyclopentadiene and electronic and steric properties thereby varied to a significant degree in a family of closely related polymers. Third, the substituted double bond should not be attacked for steric reasons.

\[
\begin{align*}
\text{cis isotactic} & \quad \begin{array}{c}
\text{cis syndiotactic}
\end{array}
\end{align*}
\]
This chapter reports a series of studies aimed at elucidating the reactions of norbornadiene derivatives with Mo(CHCMe₃)(NAr)(OCMe₃)₂. In particular, electronic and steric effects were varied in order to delineate their roles in the metathesis process. When appropriate W(CHCMe₃)(NAr)(OCMe₃)₂ was used in order to explore the differences in reactivity between the two metals. This project was done in collaboration with Prof. James Feast and Vernon Gibson of the University of Durham. Part of this work has appeared in a preliminary communication.³⁵

RESULTS

Reactions of Mo(NAr)(CHCMe₃)(OCMe₃)₂ with Benzonorbornadiene.

Preparation of poly(benzonorbornadiene).

Benzonorbornadiene³⁶ (1) reacts smoothly and rapidly with Mo(CHCMe₃)(NAr)(OCMe₃)₂ to yield the living oligomers shown in Equation 1 (Mo(CHCMe₃) = Mo(CHCMe₃)(NAr)(OCMe₃)₂). When a relatively small amount of

\[
\text{Mo(CHCMe₃)} + x \overset{1}{\text{I}} \longrightarrow \text{Mo} \overset{x}{\text{CHCMe₃}} \tag{1}
\]

monomer is added (e.g. x < 30) the reaction can be followed by proton NMR. Analysis by \(^1\)H NMR shows that after only a few minutes at 25 °C the monomer resonances are absent and are replaced by broad resonances characteristic for a polymer. The alkylidene resonance (H₆₂) at
11.23 ppm in Mo(CHCMe$_3$) is replaced by a relatively complex set of alkylidene resonances further downfield for the living oligomers (Figure 1a). It was not possible to distinguish the resonance(s) for oligomers in which x has a specific value, as in the case for other monomers discussed later in this chapter. The fact that the $H_\alpha$ resonance is complex even when x is large is also peculiar in view of the relative simplicity of the resonance(s) for other living oligomers obtained using monomers of C$_3$ symmetry. A plausible explanation is that when a flat ring is present $H_\alpha$ is sensitive to the cis or trans configurations of at least the next double bond in the chain, and that two different alkylidene rotamers are present.

It is possible to obtain an estimate for the value of the ratio of the propagation rate constant to the initiation rate constant, $k_p/k_i$ (= r) by measuring how much neopentylidene initiator remains upon addition of a few equivalents of monomer (see Experimental Section for details and Appendix 1 for the derivation of the kinetic expressions); r was found to be 7 ± 0.5. It should be noted that a significant error arises from the fact that the reaction is rapid and mixing is not instantaneous. As with norbornene the value for $k_p/k_i$ is expected to be >1 because a complex containing the neopentylidene ligand should be less reactive than that containing the alkylidene ligand formed upon opening the C(5)/C(6) (Figure 2) double bond in benzonorbornadiene. The percentage trans double bonds is 76% judging from the ratio of the resonances for trans and cis olefinic protons (at 5.64 and 5.57 ppm in CDCl$_3$) or methine protons adjacent to trans and cis double bonds (at 5.10 and 5.05 ppm). It should be noted that in C$_6$D$_6$ overlap of resonances does not permit this determination. Figure 3 shows the COSY spectrum of the polymer in CDCl$_3$. Due to the monomer's high reactivity the polymerization is too fast to measure either $k_p$ or $k_i$ directly at 25°C.
Figure 1. 500 MHz $^1$H NMR spectra (alkylidene region) of (a) living polybenzonorbornadiene (20 eq); (b) living poly2 (20 eq); (c) living poly5 (20 eq); $^\ast = \text{Mo(CHCMe}_3\text{)}$. 
Figure 2: Numbering scheme for norbornadienes.

The polymers or oligomers can be cleaved off the metal with benzaldehyde or pivaldehyde in a smooth and quantitative Wittig-like reaction (Equation 2). It is not possible to determine the degree to which the terminal double bond is all trans in this case for experimental reasons, although it is usually mostly trans, and sometimes all trans as in the case of exo-exo-2,3-dicarbomethoxynorbornene, for example (Chapter 4). Gel Permeation Chromatography$^{37,38}$ (GPC) analysis of the polymers prepared in which $x$ is as large as 500 showed them to have polydispersities of $\sim 1.05$ (Table 1). These small polydispersities indicate that the polymer consists of a narrow distribution of molecular weights, for which no chain transfer (back biting) or catalyst decomposition within the timescale of the polymerization are a prerequisite. Such narrow polydispersities are not inconsistent with a value of $k_p/k_i = 7$. Theoretical estimates have shown that the polydispersities for polymers containing several hundred monomer units can be as low as 1.05 even when $k_p/k_i$ is as high as 100.$^{39}$

Carbon NMR studies reveal a complex set of overlapping olefinic carbon resonances
Figure 3. COSY (CDCl₃) spectrum of polybenzonorbornadiene.
Table 1. GPC Characterization of polymers prepared using Mo(CHCMe₃)(NAr)(OCMe₃)₂ as the catalyst at 22 °C.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>equivalents</th>
<th>time (h)</th>
<th>$M_n$ calc</th>
<th>$M_n$ found</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0.5</td>
<td>14,360</td>
<td>23,267</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.5</td>
<td>28,560</td>
<td>44,690</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.5</td>
<td>71,160</td>
<td>132,176</td>
<td>1.09b</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.5</td>
<td>20,980</td>
<td>12,430</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.5</td>
<td>41,800</td>
<td>19,250</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>51</td>
<td>4.5</td>
<td>11,700</td>
<td>7,740</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>4.5</td>
<td>23,220</td>
<td>15,060</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>4.5</td>
<td>46,090</td>
<td>27,130</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>153</td>
<td>18</td>
<td>34,880</td>
<td>32,900</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>24</td>
<td>58,660</td>
<td>56,350</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>24</td>
<td>164,900</td>
<td>152,150</td>
<td>1.04</td>
</tr>
</tbody>
</table>

a Capped with pivaldehyde. $M_n$ values versus polystyrene. bHigh MW shoulder present.
near 134 ppm, consistent with the presence of carbons in cis and trans vinylene units with chemical shifts further affected by the geometry of neighboring double bonds, and possibly also racemic and meso dyads (Figure 4). These data convincingly show that ring-opening of 1 is not stereoselective, as already can be concluded on the basis of proton NMR data.

The organic polymer can be readily isolated from the reaction mixture by precipitation from a non polar aliphatic solvent such as hexane in order to remove the metal oxo species, this contrasts with polynorbornene which needs to be precipitated into polar solvents such as methanol. Polybenzonorbornadiene, with a degree of polymerization of up to 500, is a white powder soluble in toluene or dichloromethane, and except for its expected sensitivity to oxygen, it is well-behaved. (Polybenzonorbornadiene prepared using W(CHCMMe3)(NAr)(OCMe3)2 is similar to that reported here, except that it is only 70 % trans, consistent with what in general seems to be a lower stereoselectivity and higher reactivity of a well-defined W catalyst versus an analogous Mo catalyst.) These properties contrast with those reported by Grubbs for polybenzonorbornadiene prepared with a well defined titanium catalyst, where insolubility became a limiting factor when fewer than 10 equivalents of benzonorbornadiene had been polymerized.40 Benzonorbornadiene also has been polymerized by classical catalysts (e.g., WCl6/SnMe4). However, broad molecular weight distributions and partial solubilities were ascribed (in part) to oxidation of the polymer in air.36 In contrast, the polybenzonorbornadiene made here has a low polydispersity and contains ~99% carbon and hydrogen as determined by Elemental Analysis. Therefore, it would appear that polymerization of 1 by Mo(CHCMMe3) (and W(CHCMMe3)) is the most successful synthesis of polybenzonorbornadiene. In general complications may arise in part from the fact that the tertiary proton in the polymer is both allylic and benzylic and is likely to react with catalysts of high activity which contain more polar bonds. Use of Mo(CHCMMe3), a relatively mild reagent, may minimize such complications.
Figure 4. $^{13}$C NMR spectrum (CDCl$_3$) of polybenzonorbornadiene in the olefinic region.
Reaction of Mo(NAr)(CHCMes)(OCMe$_3$)$_2$ with 2,3-dicarbomethoxy-norbornadiene. Preparation of Poly(2,3-dicarbomethoxynorbornadiene).

The simplicity of the alkylidene proton NMR resonances observed in a reaction between 2,3-dicarbomethoxynorbornadiene$^{41}$ (2) and Mo(CHCMes) in C$_6$D$_6$ contrasts markedly with the complex pattern observed in the reaction involving 1. Only two new alkylidene proton resonances ultimately are observed at a field strength of 500 MHz, two doublets in a ratio of approximately 5:1 at 11.694 and 11.652 ppm (Figure 1b). Another 5:1 set of alkylidene proton doublets appears first when one equivalent of 2 is added and disappears as more monomer is added. They can be ascribed to the first insertion product ($x = 1$ in Equation 3). In general the H$_\alpha$ resonances of the second and higher insertion products overlap and the resonance(s) for the first insertion product is (are) slightly shifted from these.

$$\text{Mo(CHCMes)} + x \xrightarrow{} \text{Mo} + \text{CH(t-Bu)}$$

This is attributed to the alkylidene proton's sensitivity to the nature of the group next to the last inserted monomer. For $x = 2$ or greater, the next group is simply another monomer, whereas for the first insertion product contains a tert-butyl group.

From data like those shown in Figure 1b it can be determined that $k_p/k_i = 3$ for this monomer. The main question is why two resonances are associated with the living oligomer. W(CHCMes)(NAr)(OCMe$_3$)$_2$$^{42}$ and W(CHPh)(NAr)(OCMe(CF$_3$)$_2$$^{43}$ have been shown to be pseudo-tetrahedral species in which the alkylidene substituent points toward the imido nitrogen atom (the syn isomer below), but formation of an anti rotamer would also seem
to be possible. (Formation of a pseudo triple metal-imido bond is known to force the alkyldiene's β carbon atom and α hydrogen atom to lie in the N-M-Cα plane.) In fact, there is evidence for syn and anti rotamers in several systems, especially as the size of R (or the alkoxide) becomes smaller than a t-butyl group. Therefore we ascribe one resonance in the spectra of the living oligomers to the syn rotamer of the living oligomer and the other resonance to the anti rotamer. Unfortunately NOE experiments have not been conclusive, and we therefore cannot tell which is which. The $^{13}$C NMR spectrum of living poly2 shows that $J_{CH} = 130$ Hz for the alkyldiene resonance of the major rotamer and $J_{CH} = 123$ Hz for the minor rotamer. Data for other alkyldiene complexes suggest that $J_{CH}$ for the syn rotamer is lower than that for the anti rotamer, although again the data are not extensive. If this rule holds true then the major rotamer in this case is anti.

Other explanations of the NMR results were considered. One alternative explanation is that the minor resonance is ascribable to a living oligomer in which the configuration about the first C=C bond in the chain (after the Mo=C bond) is cis instead of trans. However, carbon NMR spectra (see below) suggest that double bonds in the polymer are between 90 and 95% trans. Also, formation of exclusively a trans-t-butyl-substituted double bond as a result of the first insertion reaction is a feature of all known ring-opening reactions with catalysts of this type, so two alkyldiene resonances should not be observed in the first insertion product ($x = 1$). Another alternative explanation is that a double bond somewhere in the polymer chain is coordinated to the metal and thereby leads to formation of two isomers. Although interactions of that nature have been proposed for the conventional ROMP initiators, there is no hard evidence that supports such proposals, and in any case such interactions seem unlikely.
in a well-defined "deactivated" catalyst of the type discussed here in which the metal center is sterically congested. The possibility that binding of the carbonyl group of the ester gives rise to isomers also does not seem likely for two reasons. The first is that propagation is fast (see below). One would expect intramolecular coordination via the carbonyl oxygen to block propagation to a significant degree. Secondly, IR spectra of the living oligomers in the v_C=O region show no evidence of any shifted C=O absorption, and in fact are identical to those of a structurally characterized monointersection product (vide infra) in which no carbonyl group is bound to the metal.

After termination with either pivaldehyde or benzaldehyde the polymer can be purified from the oxo species by precipitation into hexanes. The ^13C NMR spectrum of isolated polymer has not been previously reported but is straightforward to assign (Figure 5). The resonance for the carbonyl carbon is assigned to the furthest downfield resonance at 165.2 ppm. A single proton coupled spectrum is sufficient to assign the remaining resonances. The two olefinic carbon resonances can be distinguished since the one at 132.3 ppm is split into a doublet (J_{CH} = 154 Hz) and is assigned to C_1; by elimination the other olefinic resonance at 142.1 then is assigned to C_3. The resonance at 51.9 is split into a quartet (J_{CH} = 144 Hz) and is assigned to the methoxy carbon; the two remaining aliphatic carbons can be differentiated since the peak at 49.0 is split into a doublet (C_2) while the one at 37.6 is split into a triplet (C_4). The major resonances for poly2 are analogous to those observed for all trans poly(2,3-bis(trifluoromethyl)norbornadiene) (vide infra), while other resonances are analogous to those for atactic poly(2,3-bis(trifluoromethyl)norbornadiene) (Figure 9). From these considerations we estimate poly2 to be 90 to 95% trans.

The rate of propagation for the polymerization of 2 was determined by Julie Thomas, although an accurate number cannot be obtained because the reaction is very fast. Several determinations by NMR (two) and gas chromatography (three) indicate that k_p \approx 2 \pm 1 \ M^{-1}s^{-1} \ at \ 22 \ ^\circ \ C. \ Since \ k_p/k_i = 3 \pm 0.3 \ the \ rate \ of \ initiation \ can \ be \ estimated \ to \ be \ 0.7 \ \pm \ 0.3 \ \ M^{-1}s^{-1} \ for \ 2 \ when \ the \ initiator \ is \ Mo(CHCMe_3).
Figure 5. $^{13}$C NMR (CDCl$_3$) spectrum of poly2.
The dispersities of poly2 obtained are shown in Table 1 and show that the polymers are virtually monodisperse. For example for $x_{\text{avg}} = 200$ the dispersity index (PDI) is 1.07 relative to polystyrene standards. This indicates that in effect addition of 400 equivalents of carbomethoxy functionality relative to the propagating species does not interfere with the polymerization process. Solutions of living 20 mer in a sealed NMR tube at room temperature proved to contain the alkylidene without any appreciable decomposition for well over a week.

**Reaction of Mo(NAr)(CHCMe$_3$)(OCMe$_3$)$_2$ with 7-isopropylidene-2,3-dicarbomethoxy-norbornadiene. X-ray Study of a Mono Insertion Product.**

The monomer 7-Isopropylidene-2,3-dicarbomethoxynorbornadiene$^{45}$ (3) was employed in order to explore the influence of substituents at the 7 position while keeping the electronic factors of the monomer similar to 2. The reaction of excess 3 (15-20 equivalents, initiator concentration appx 0.02 M) with Mo(CHCMe$_3$) in C$_6$D$_6$ at 25° is slow. In fact the reaction must be heated to 45-55° in order that all of the initiator is consumed in a few hours. Analysis by $^1$H NMR shows that only one equivalent of monomer was consumed, furthermore only one new alkylidene resonance is observed. This resonance can be assigned to the alkylidene proton of the first insertion product which exists in one rotameric form (4, Equation 4). Since only one equivalent of monomer is consumed, even at 55° over a period of several

\[
\text{Mo(CHCMe$_3$) + x} \rightarrow \text{4}
\]

hours in the presence of excess monomer, $k_p = 0$. Therefore by studying this reaction
the "initiation" process can be studied directly.

The kinetic behavior of this reaction was studied by Julie Thomas who found it to be first order in Mo(CHCMe₃) and 3 with ΔHᵣ = 15.6 (1) kcal mol⁻¹ and ΔSᵣ = -18 e.u. (3) and k_{calc} (22 °C) = 1.3 × 10⁻³ M⁻¹s⁻¹ (Table 2). Therefore 3 reacts ~500 times more slowly than 2 at 22 °, a difference that must be ascribed to steric factors. The "new" alkylidene ligand in 4 must be significantly larger than a neopentyliyden ligand in order that 3 virtually does not react with 4.

It should be noted that 4 is capable of metathesizing reactive small olefins. Norbornene can be initiated to give polynorbornene, but kₚ/kᵢ was found to be ~270 by the NMR method mentioned earlier. This ratio is consistent with the initiator being much less reactive than the propagating alkylidene for steric reasons. Therefore the failure of 3 to polymerize is a combination of 4 being a large alkylidene, which prevents approach of large monomers and the large size of 3.

The "first insertion product" (4) can be isolated and completely characterized. Proton and carbon NMR are consistent with the proposed structure. According to proton and carbon NMR spectra only one rotamer is present (> 98%).

An X-ray study of 4 reveals it to have the structure shown in Figure 6. (Relevant bond distances and angles can be found in Table 3) Its basic structure is pseudo-tetrahedral in which the alkylidene ligand adopts the syn conformation. Bond lengths and angles are similar to the other structurally characterized four coordinate alkylidene complexes, W(CHCMe₃)(NAr)(OCMe₃)₂ and W(CHPh)(NAr)[OCMe(CF₃)₂]₂ previously reported and therefore will not be discussed in detail.¹²

The two tert-butoxide ligands appear to be perfectly normal with identical Mo-O lengths of 1.873 (3) Å and Mo-O-C angles of 147.9 (3) and 154.8 (4). These distances are comparable to the W-O in W(CHCMe₃)(NAr)(OCMe₃)₂ which are in the 1.90 Å range with W-O-C angles of 144-148 °. Note how much shorter these Mo-O distances are compared to the Mo-OTf distances of 2.10 Å in Mo(CHCMe₃)(NAr)(OTf)₂(dme) described in Chapter 1.
Table 2. Rate constants for polymerization at 22 °C.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$k_p/k_i$</th>
<th>$k_p$ ($M^{-1}s^{-1}$)</th>
<th>$k_i$ ($M^{-1}s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.0 (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30 (3)</td>
<td>2 (1)</td>
<td>0.7 (3)</td>
</tr>
<tr>
<td>3</td>
<td>~0</td>
<td>~0</td>
<td>0.0013 (1)</td>
</tr>
<tr>
<td>5</td>
<td>0.72 (5)</td>
<td>0.057 ± 0.0007</td>
<td>0.08 (1)$^a$</td>
</tr>
</tbody>
</table>

$^a$Rate of tungstacycle (6) formation = 0.20 (1).
Figure 6. Two views of the product of the reaction between Mo(CHCMe₃) and 3. (a) Full structure. (b) Carbons on tert-butoxide ligands deleted in order to emphasize how substituents on the C₅ ring block both C/N/O faces.
Table 3. Selected Intramolecular Distances (Å) and Angles (deg) Involving the Nonhydrogen Atoms in the Mono Insertion Product, 4.

<table>
<thead>
<tr>
<th></th>
<th>Distance</th>
<th></th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-N</td>
<td>1.731 (4)</td>
<td>N-Mo-O(1)</td>
<td>114.6(2)</td>
</tr>
<tr>
<td>Mo-O(2)</td>
<td>1.873 (3)</td>
<td>N-Mo-C(1)</td>
<td>100.2(2)</td>
</tr>
<tr>
<td>Mo-O(1)</td>
<td>1.873 (3)</td>
<td>O(2)-Mo-O(1)</td>
<td>107.0(1)</td>
</tr>
<tr>
<td>Mo-C(1)</td>
<td>1.880 (4)</td>
<td>O(2)-Mo-C(1)</td>
<td>108.5(2)</td>
</tr>
<tr>
<td>C(1)-C(11)</td>
<td>1.522 (5)</td>
<td>O(1)-Mo-C(1)</td>
<td>109.4(1)</td>
</tr>
<tr>
<td>C(12)-C(121)</td>
<td>1.326 (6)</td>
<td>Mo-O(1)-C(3)</td>
<td>147.9(3)</td>
</tr>
<tr>
<td>C(131)-C(132)</td>
<td>1.291 (6)</td>
<td>Mo-O(2)-C(4)</td>
<td>154.8(4)</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.336 (6)</td>
<td>Mo-N-C(21)</td>
<td>171.7(3)</td>
</tr>
<tr>
<td>N-Mo-O(2)</td>
<td>116.8 (2)</td>
<td>Mo-C(1)-C(11)</td>
<td>140.0(3)</td>
</tr>
</tbody>
</table>
These shorter distances are expected for a more basic (in both a σ and a π sense) tert-butoxide ligand relative to the loosely coordinated triflate ligand.

The Mo-N bond length (1.731 (4) Å) and Mo-N-C angle (171.3 (3)) are what might be expected for an imido ligand bound to an electron deficient metal as a result of sp hybridization about the nitrogen atom and likely donation of the nitrogen lone pair to the metal. Essentially identical imido characteristics are observed in Mo(CHCMe3)(NAr)(OTf)2(dme) (bond length=172 (1) Å and Mo-N-C angle of 173.7 (8)).

The plane of the phenyl ring of the virtually linear imido ligand orients itself such that it approximately bisects the O(2)-Mo-C(1) angle. This causes alignment of the ring along the Mo-O(1) bond therefore the tert-butyl group containing C(3) is forced down and away from the isopropyl group containing C(261) that points toward it. The isopropyl group containing C(221) occupies the space between and above O(2) and C(1). Therefore the tert-butyl group containing C(4), and C(11) of the alkylidene ligand, can turn up around it. The very bulky substituted C5 ring in the alkylidene ligand turns away from the imido ligand. Consequently the isopropylidene group more or less occupies the region on one side of the Mo=C(1) bond, while a carboxemethoxy group occupies the region on the other side of the Mo=C(1) bond. The configuration about the C(131)-C(132) bond is trans, as determined by 1H NMR analysis.

The solution IR spectrum of 4 shows no indication of carbonyl coordination in the solution state (Figure 7). The absorbance observed at 1640 cm⁻¹ is assigned to the olefinic stretching mode. Comparison of the solution IR spectrum of living poly2 (Figure 7b) indicates that the two spectra are essentially identical. As a comparison note that the carbonyl absorbance in W[CH(CHMe3)CH2CH(CO2Me)](NAr)(OCMe2(CF3)2)2 is strong and occurs at 1585 cm⁻¹. In the above compound the coordination has been confirmed by a structural determination.46 Therefore it is unlikely that the carbonyl in living poly2 is coordinated to the metal center.
Figure 7. Solution IR spectrum of (a) mono insertion product 4; (b) living poly2.
Reaction of Mo(NAr)(CHCMe3)(OCMe3)2 with 2,3-bis(trifluoromethyl)-norbornadiene. Preparation of poly(2,3-bis(trifluoromethyl)norbornadiene).

2,3-Bistrifluoromethylnorbornadiene\(^4\) (5) reacts smoothly with Mo(CHCMe3) to give living oligomers (Equation 5; Figure 1c; see also ref. 35). Only one alkylidene resonance is observed for the first insertion product, although another might be hidden among the complex set of resonances in that region for the \(\alpha\) proton in each living alkylidene complex up to \(x = 4\). In fact, for this monomer the \(H_\alpha\) resonance at a field strength of 500 MHz is sensitive to the first, second, third and fourth and higher insertion products. The general method for assignment of these resonances consists of monitoring the relative intensities of the individual doublets as a function of monomer added and is shown in Figure 8. For \(x > 4\) all alkylidene resonances overlap to give a typical broadened doublet alkylidene resonance (Figure 1c). A shoulder can be observed in the 500 MHz \(^1\)H spectrum on the doublet for \(x \geq 10\) that does not disappear upon addition of more monomer, this was not a shimming effect since the other resonances in the spectrum did not show this shoulder, furthermore this is a reproducible result. Resolution enhancement shows that the ratio of the two resonances is ~1:6. These resonances can be ascribed to the syn and anti rotamers of the living alkylidene complexes, although again we cannot say with certainty which is which. The proton decoupled carbon NMR spectrum of the living oligomer where \(x = 10\) is consistent with this proposal in that two carbon resonances in a ratio of ~1:6 are observed at 253.1 and 252.6 ppm, respectively. Relatively low solubility of poly5 prevented a determination of \(J_{CH}\) for the minor isomer in a proton coupled experiment, so \(J_{CH}\) values could not be correlated with the resonances
Figure 8. 500 MHz $^1$H NMR spectra in the alkyldene proton region of samples containing Mo(CHCMe$_3$) and 1, 3, 5, 10 and 20 equivalents of 5. (Numbers above resonances refer to the number of insertions; * = Mo(CHCMe$_3$); C$_6$D$_6$)
observed.

The ratio of $k_p$ to $k_i$ for polymerization of 5 was shown to be 0.72, i.e., 5 reacts more slowly with the new alkyldiene complex than it does with the neopentylidene initiator. The rate of polymerization of 5 ($k_p = 0.057 \pm 0.007 \text{ M}^{-1} \text{s}^{-1}$) also is between 15 and 50 times slower than that of 2. From these data we conclude that $k_i = 0.08 \pm 0.01 \text{ M}^{-1} \text{s}^{-1}$, about an order of magnitude slower than $k_i$ for 2 ($0.7 \text{ M}^{-1} \text{s}^{-1}$), i.e., 5 is about an order of magnitude less reactive than 2 toward Mo(CHCMe3). If the lower reactivity of 5 can be ascribed to an electronic deactivation of the unsubstituted double bond in 5, then the living alkyldiene made from 5 is also likely to be deactivated as a nucleophile. The difference in the reactivity of the living alkyldienes made from 2 and 5 toward norbornene can be assessed by measuring $k_p/k_i$ for each, where $k_{i2}$ is the rate of reaction of living 2 with norbornene, and $k_{i5}$ is the rate of reaction of living poly5 with norbornene; note that $k_p$ should be the same for both since this represents the reactivity of living polynorbornene with norbornene. We find that $k_p/k_{i2} = 4.8$ and $k_p/k_{i5} = 10.2$ so that $k_{i2}/k_{i5} = 2$, i.e., living poly2 reacts approximately twice as fast with norbornene as living poly5 at 22 °C.

Isolation of poly5 is carried out by cleaving the metal by adding pivaldehyde or benzaldehyde followed by precipitation into methanol to yield a polymer suspension. Centrifugation yields the polymer which by GPC analysis (Table 1) was found to be virtually monodisperse. Note that this polymer, unlike polybenzonorbornadiene or poly2, is soluble in hydrocarbon solvents. $^1$H and $^{13}$C NMR spectra of poly5 prepared with various classical catalysts have been analyzed in detail, and provide a useful comparison with samples prepared using Mo(CHCMe3). Carbon NMR spectra of atactic poly5 (Figure 9a) in which the ratio of cis to trans double bonds is ~1:1 show resonances for two vinylene carbons, two methine carbons, and several methylene carbons. Further splitting of the resonances for trans and cis vinylene carbon atoms has been observed, but it was not possible to determine whether the splitting was caused by the cis or trans configuration of the nearest double bond in each case, or to m and r dyads. The carbon NMR spectrum of poly5 prepared using Mo(CHCMe3)
Figure 9. $^{13}$C NMR spectrum ($d_6$-acetone) of poly5 prepared using (a) WCl$_6$/SnMe$_4$; (b) Mo(CHCMe$_3$)$_3$. 
(Figure 9b) by comparison contains only relatively sharp resonances that can be assigned to an all trans form (~98%) on the basis of previous studies, and the tendency for this catalyst to form predominantly trans polynorbornene. The resonances for residual cis poly5 (~2%) can barely be observed. A melting point is observed in this material (vide infra) which is consistent with its being highly tactic.

**Reaction of W(NAr)(CHCM Me)3)(OCMe3)2 with 2,3-bis(trifluoromethyl)-norborradiene. The Formation, X-ray Structure and Decomposition of a Tungstacyclobutane Complex.**

It was noted in the preliminary communication\(^{35}\) that W(CHCM Me)3)(NAr)(OCMe3)2 would not polymerize 5 to give homopolymers with low PDIs. This reaction was therefore examined in detail in an attempt to elucidate the factors that determine this failure.

Addition of 5 to W(CHCM Me)3)(NAr)(OCMe3)2 at -30 °C in toluene-d8 yields a new species quantitatively that is not an alkylidene complex. All data are consistent with it being a square pyramidal tungstacyclobutane complex (6, Equation 6). Resonances for one Hα proton can be observed at 2.23 ppm and the Hβ proton at 2.77 ppm, while a COSY experiment located the other Hα proton resonance at 1.17 ppm. Square pyramidal metallacycles such as W[CH2CH(CMe3)CH2](NAr)(OCMe2(CF3))2 have been observed;\(^{39}\) its ring proton resonances are found at 1.12 (Hα) and 2.36 ppm (Hα) and 2.62 ppm (Hβ). A structural study showed that Hβ points toward the axial imido ligand, i.e., the tert-butyl group is located in a pseudo-equatorial position. In another structurally characterized square pyramidal tungstacyclobutane complex, W[CH(CMe3)CH2CH(CO2Me)](NAr)(OCMe2(CF3))2, prepared by adding methyl acrylate to W(CHCM Me)3)(NAr)(OCMe2(CF3))2, the α tert-butyl group is in a pseudo-equatorial position and the α carbomethoxy group is in a pseudo-axial position.\(^{46}\) The resonance for the α proton near the tert-butyl group is found at 1.98 ppm, that for the axial β proton is found at 2.71 ppm, and that for the equatorial α proton is found at 2.39 ppm. Therefore the proton NMR data for 6 are consistent with the structure shown in Equation 6 in
Figure 10. Arrhenius plot for the formation of 6.
which the imido ligand is on the same side of the WC₃ ring as the tert-butyl group.

\[ W(\text{CHCMe}_3) + \text{5} \rightarrow \text{6} \]

Resonances for the ring carbon atoms in the carbon NMR spectrum of 6 would have to be assigned using 2D techniques since five doublets are found in the region where one would expect to find resonances for the ring carbon atoms (20-50 ppm). Metallacycles containing norbornene have been observed in other systems.⁴⁸,⁴⁹

The kinetics of the formation of 6 was carefully studied by proton NMR. In these experiments precisely one equivalent of 5 was added to a frozen toluene solution of W(\text{CHCMe}_3) and the two reagents mixed at -78 °C. The rate of the reaction was monitored by measuring the appearance of the metallacycle Hₓ resonance against mesitylene (an internal standard). Several attempts to obtain a linear Arrhenius plot failed due to the experimental difficulties associated with second order kinetics. Finally a linear relation was obtained after carefully making toluene stock solutions of the reactants and calibration of the probe's temperature. The formation of 6 was found to be second order with \( \Delta H^\ddagger = 6.6 \text{ kcal mol}^{-1} \) and \( \Delta S^\ddagger = -40 \text{ e.u.} \) over a temperature range of 40 °C (Figure 10). At 22 °C the rate constant for formation of 6 is calculated to be 0.20 M\(^{-1}\) s\(^{-1}\). This value should be compared to \( k_i = 0.08 \text{ M}^{-1} \text{ s}^{-1} \) for the reaction between \( \text{Mo(\text{CHCMe}_3)} \) and 5. We can conclude that 5 reacts with \( \text{W(\text{CHCMe}_3)} \) approximately 2.5 times faster than it reacts with \( \text{Mo(\text{CHCMe}_3)} \). This is the relative reactivity of W versus Mo complexes that has been suspected on the basis of
qualitative observations, although in general the differences in rates were expected to be larger.

Although it has a half life of approximately 20 minutes at room temperature, X-ray quality crystals of 6 can be obtained by addition of the reagents in a minimum amount of toluene at -40 °C and maintaining the solution cold (-40 °C) for 2-3 days. Isolation of the crystals must also be carried out at low temperatures. An X-ray study of 6 was carried out at low temperature (Figure 11). It is approximately a square pyramid in which the imido ligand occupies an apical position. Bond distances and angles are very similar to those found in W(CH₂CH(CMe₃)CH₂)(NAr)(OCMe₂(CF₃))₂ (see Table 4). Metal-ligand bond lengths and angles around the metal are not unusual, and the virtually identical long C-C bond lengths in the tungstacyclic ring (1.50 and 1.52 Å) are typical of metallacyclobutane rings that contain other d⁰ metals.⁵⁰ As expected, 5 has added to the tungsten-neopentyldene bond in the syn rotamer through the more accessible exo face to give the trans tungstacycle. Exo coordination of the monomer is consistent with previous studies carried out on polymers obtained using classical catalysts.⁶

The ligands in 6 arrange themselves to minimize interactions between the bulky imido group and the substituents in the rigid metallacyclobutane ring. The tert-butyl group containing C(411) forces the phenyl ring of the disisopropylphenylimido ligand to turn so that the plane of the phenyl ring contains the W-O(1) bond. The tert-butyl group of the tert-butoxide ligand containing C(11) is forced down and away from the imido ligand by the isopropyl group containing C(321); this allows the tert-butyl group of the other tert-butoxide ligand (containing C(21)) to bend bend up toward the imido ligand. The isopropyl group containing C(361) occupies a significant amount of space above C(47), a fact that virtually eliminates the possibility of forming an analogous cis tungstacyclobutane ring. This structure study provides good evidence that trans metallacycles are formed most rapidly from syn alkylidenes.

The "decomposition" of 6 consists of rearrangement (ring-opening) to give the alkylidene 7 (Equation 7). By proton NMR the conversion of 6 to 7 is high if the temperature
Figure 11. Two views of the tungstacycle made by treatment of $\text{W(CHCMe}_3\text{)}$ with 5. (a) Full view. (b) View of the molecule with the tert-butoxide ligands omitted highlighting steric interactions between the metallacycle substituents and the imido ligand.
Table 4. Important bond distances (Å) and angles (deg) in 6 (left-hand column) compared with those in W(CH₂CH(CMe₃)CH₂)(NAr)[OCMe₂(CF₃)]₂.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
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<tr>
<td>W-N</td>
<td>1.72 (1)</td>
<td>W-N</td>
<td>1.736 (7)</td>
</tr>
<tr>
<td>W-O(1)</td>
<td>1.862 (9)</td>
<td>W-O(1)</td>
<td>1.869 (7)</td>
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<td>W-O(2)</td>
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</tr>
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<td>W-C(41)</td>
<td>2.25 (1)</td>
<td>W-C(21)</td>
<td>2.17 (1)</td>
</tr>
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<td>W-C(23)</td>
<td>2.14 (1)</td>
</tr>
<tr>
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<td>C(21)-C(22)</td>
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<tr>
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<td>1.50 (2)</td>
<td>C(22)-C(23)</td>
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<tr>
<td>O(1)-W-O(2)</td>
<td>98.4 (5)</td>
<td>O(1)-W-O(2)</td>
<td>99.6 (3)</td>
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<td>W-C(41)-C(42)</td>
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<td>W-C(21)-C(22)</td>
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<td>W-C(23)-C(22)</td>
<td>97</td>
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<td>C(21)-C(22)-C(23)</td>
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<td>W-C(47)-C(46)</td>
<td>118 (1)</td>
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<td>C(47)-W-O(1)</td>
<td></td>
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<td>144.4 (5)</td>
</tr>
<tr>
<td>C(41)-W-O(2)</td>
<td></td>
<td></td>
<td>136.1 (4)</td>
</tr>
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is kept below ~40 °C (in order to prevent decomposition of 7). The rate of consumption of 6 is cleanly first order as determined by following the decrease in the resonance of the β proton in the WC₃ ring. Figure 12 shows typical data from which rates were measured, note the clean conversion of the metallacycle resonance at 2.77 ppm to olefinic resonances at 5.45 and 5.31 ppm. Activation parameters were ΔH‡ = 22 kcal mol⁻¹ and ΔS‡ = -3 e.u., as determined by the Arrhenius plot (Figure 13). The thermal instability of 7 provides a rationale for the failure of W(CHCMe₃) to smoothly polymerize 5.

In the downfield region of the proton NMR spectrum of 7 an alkylidene Hₓ resonance first grows in at 8.35 ppm. Another then appears at 9.28 ppm, apparently as a result of conversion of the complex giving rise to the first resonance into the complex giving rise to the second. The two resonances appear to reach an equilibrium ratio for which the upfield (initial) alkylidene resonance dominates (91%). We propose that the two alkylidene resonances can be ascribed to rotamers of 7, and that the rotamer which gives rise to the resonance at 9.28 ppm forms first from 6.

When two equivalents of 5 are added at low temperature 6 forms and an equivalent of 5 remains unreacted. The progress of the reaction was followed by ¹H NMR at 0°C with the metallacycle breaking up at the expected rate. However the leftover equivalent of monomer was consumed very quickly when the majority of the metal existed in the form of the metallacycle. At the end only the alkylidene resonances for 7 are observed at the end of the
Figure 12. Typical $^1$H NMR data for determination of the rate of breakup of 6 to 7.
\[ y = 29.026 - 11.079x \quad R^2 = 0.997 \]

Figure 13. Arrhenius plot for the breakup of 6.
reaction with complete consumption of the monomer. We propose that the monomer was consumed by a small amount of 7 which appeared at the beginning of the reaction with a rate much faster than that of the formation or breakup of 6.

Experiments aimed at the detection of the Mo analogues of 6 proved unsuccessful. The reaction of Mo(CHCMe₃) with 5 at low temperature only shows unreacted monomer and initiator going directly to propagating alkylidene without observation of any metallacycles.

**Polymer Properties.**

Since polymerization using Mo(CHCMe₃) is novel, the physical properties of the resulting polynorbornadienes were studied in order to ascertain how they compared to those made using classical catalysts. In particular poly5 was studied in more detail due to the interest in fluorinated polymers.

Poly5 prepared using classical catalysts displays a range of stereoregularity depending on the catalyst system. The trans content in the polymer backbone has been shown to vary from 54 % using WCl₆/SnMe₄ to 87 % when MoCl₅/SnMe₄ is used to catalyze the reaction, but as is typical of these classical catalysts results are irreproducible.⁴⁷ Consistent with its high stereoregularity DSC studies of poly5 prepared using Mo(CHCMe₃) as the initiator reveal a well defined Tₛ at 97 °C and a broad melting endotherm at about 200 °C (Figure 14), the shape and area of which is dependent on sample history. In samples precipitated from solution the Tₛ transition is not particularly marked and the melting peak shape is consistent with the presence of multiple melting points. In melt-quenched samples the Tₛ transition is marked and the melting peak area is small. The melting peak area increases on prolonged annealing at 180 °C, a slow ordering process that is consistent with low chain mobility in the solid state.

X-ray diffraction studies on fibres drawn from the melt of stereoregular poly5 show evidence of crystalline order and orientation on stretching,⁵¹ whereas fibres drawn from the melt of samples of atactic poly5 are weak, cannot be stretched, and show no evidence of order by X-ray diffraction. Therefore poly5 prepared here shows behavior expected of a
Figure 14. DSC study of stereoregular poly5 ($M_n = 34880$ versus polystyrene; PDI = 1.05): (a) as precipitated; (b) melted, quenched, annealed 2 h at 180 °C; (c) melted, quenched, annealed 16 h at 180 °C.
semicrystalline thermoplastic, whereas all earlier atactic samples were amorphous.

The properties of poly2 were studied since this polymer has not been reported previously, and in general show that this polymer is rather thermally unstable in air. The glass transition temperature, estimated at approximately 140 °C does not appear to be reversible. This instability is confirmed by TGA analysis. The TGA trace displays beginning of decomposition at approximately 200 °C with rapid degradation at 300 °C. A plausible decomposition mode is reaction of the doubly allylic protons in the polymer chain with oxygen, this oxidation has previously been reported for polybenzonorbornadiene.36

DISCUSSION

Control over both structure and molecular weight distribution is a prerequisite for the development of detailed structure/property correlations in any polymerization reaction. The original classical, multicomponent metathesis initiators have suffered from disadvantages that include limited tolerance of functional groups, lack of molecular weight control, and an element of irreproducibility.6 Furthermore, these ill-defined catalysts only rarely produce stereoregular polymers.52 The work described in this Chapter has shown that it is possible to control the polymerization of norbornadiene derivatives by using Mo(CHCMe3)(NAr)(OCMe3)2 as the initiator.

The most important result which was not anticipated was the high stereoregularity of the polymerization of 2,3-bis(trifluoromethyl)norbornadiene (5), even though it has yet to be determined whether the polymer is isotactic or syndiotactic. The narrow molecular weight distributions of the resulting polymers tends to rule out secondary metathesis since this would invariably increase the polydispersities by making shorter and longer chains than expected from a Poisson distribution. Therefore analysis of the polymer microstructure reveals the intimate mechanism which occurred at the metal center during the ring opening metathesis reaction. Another important question is why other monomers of Cs symmetry (such as benzonorbornadiene and norbornene) do not yield stereoregular polymers. The importance of
the electronic factors which determine the reactivity of the monomers and the propagating species will be addressed as well as the steric factors which determine the stereoregulation.

The stereoselectivity analysis begins by assessing the importance of electronic factors. The first question to answer is why the rate of polymerization of 2,3-dicarbomethoxy-norbornadiene (2) is approximately 30 times faster than that of 5. Note that the rates of both norbornene and benzonorbornadiene at the same time are faster than that of 2. In order to quantitate the relative reactivities of the monomers the rate of initiation must be compared. For 2 $k_i$ was found to be approximately an order of magnitude larger than for 5 (Table 2). Since for both measurements the initiator was the same this reactivity difference is a result of differences in intrinsic monomer reactivity.

This difference in reactivity is largely controlled by electronic factors. Norbornadiene is a classic example of a molecule in which a through space interaction between the two double bonds is operative. Significant overlap between the two degenerate orbitals beneath the carbon skeleton results in two new orbitals. This interaction affects the energy of the HOMO, consistent with this proposal is the observation that the ionization potential of norbornadiene is indeed smaller than that of norbornene. Therefore a perturbation on the nature of the C$_2$-C$_3$ olefin is expected to have an influence on the reactive C$_5$-C$_6$ π bond. Another point to consider is the linear relation that exists between the gas-phase ionization potential and the solution-phase half-wave oxidation potential in these molecules (Table 5). Inspection of Table 5 reveals that the incorporation of electronegative groups on the C$_2$-C$_3$ bond results in an increase in the half-wave oxidation potential. One would expect that the ability of the olefin to coordinate to the metal would depend on the electron density of the C$_5$-C$_6$ therefore one can anticipate 2 being a better nucleophile than 5 towards the molybdenum atom on the basis of oxidation potentials. If nucleophillic attack by the alkylidene C$_\alpha$ to the olefin controlled the reactivity then the reactivities would have to be reversed since 5 would be more electrophilic.
Table 5. Half-wave potentials (V) for some norbornadiene derivatives.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structure 1]</td>
<td>1.56</td>
</tr>
<tr>
<td>![Structure 2]</td>
<td>1.95</td>
</tr>
<tr>
<td>![Structure 3]</td>
<td>2.06</td>
</tr>
<tr>
<td>![Structure 4]</td>
<td>2.26</td>
</tr>
<tr>
<td>![Structure 5]</td>
<td>2.51</td>
</tr>
</tbody>
</table>
In short, electron withdrawing groups on the ring have a strong influence on the intrinsic monomer reactivity as one would expect for coordination of the monomer being the rate determining step. These effects appear to effect the reactivity of norbornadiene derivatives more than norbornenes perhaps due to the through space interaction of the olefinic bonds.

Recall that the reactivity of 2 was shown to be 10 times that of 5 towards Mo(CHCMMe₃), while the rates of propagation differ by a factor of approximately 30, this tends to indicate that the reactivity of the propagating alkylidenes must also be different. The determination of k⁺/k⁻ for the polymerization of NBE using living poly2 (k⁺/k⁻) and living poly5 (k⁺/k⁻) allows the indirect measurement of their relative reactivities. Since k⁺ is simply the rate of polynorbornene reacting with norbornene the ratio of the propagation ratios yields k⁺/k⁻ = 2, therefore living poly2 reacts with norbornene approximately twice as fast as living poly5. This difference in reactivity would probably be accentuated in a reaction involving a larger and less reactive monomer (i.e. 2 or 5), so a difference in the rate of polymerization of 2 and 5 of greater than 20 would be expected, as found.
We propose that the difference of alkylidene reactivity is due to deactivation of the nucleophilic alkylidene carbon by electronegative groups located at the γ position. The CF₃ group is somewhat more electron withdrawing than the CO₂Me group and therefore deactivates the alkylidene to a greater extent. Consistent with this proposal is the observation that kₚ/kᵢ = 0.75 for the polymerization of 5, therefore the propagating alkylidene is less reactive towards 5 than Mo(CHCMe₃). Evidently living poly5 is deactivated for electronic reasons, but Mo(CHCMe₃) is relatively unreactive for steric reasons; the two effects are approximately equal.

\[
\begin{align*}
\text{Mo}^+ & \quad \text{δ}^- \\
\alpha & \quad \beta \\
\text{R} & \quad \gamma \\
\end{align*}
\]

The electronic nature of the metal center has profound implications on the mechanism of polymerization. Because of the Lanthanide Contraction both W and Mo have similar radii, therefore Mo(CHCMe₃) and W(CHCMe₃) provide essentially the same steric environment to an incoming monomer. Two main reasons may account for the empirical observation that poly5 prepared with W(CHCMe₃) has a wider range of molecular weights. First, the thermal stability of W based living poly5 is lower than that based in Mo, in particular the possibility of protonation by the acidic doubly allylic protons in the polymer chain is higher for the more reactive W based alkylidenes. The second reason is the observation that the first metallacycle, 6 in Equation 6, is much more stable than the subsequent ones involved in the propagation steps. This introduces the complication of two different intimate mechanisms being the rate determining steps for different steps of the polymerization, a problem which will be encountered with monomers with oxygen at the 7 position (Chapter 5). For the initiation it is the unimolecular breakup of the metallacycle, while for propagation it is the second order
reaction of the monomer with the propagating alkylidene. The first order process is much slower relative to the bimolecular propagation resulting in broader polydispersities.

To our knowledge, the reaction of W(CHCMe₃) with 5 to give 6 (Equation 6) is the first time that the kinetics for formation of a metallacyclobutane complex from a norbornene has been determined. It is interesting also to note that the value for $\Delta S^\ddagger$ (-3 e.u.) for transformation of 6 into 7 (Equation 7) is virtually identical to the $\Delta S^\ddagger$ value found for loss of olefin from square pyramidal W[CH₂CH(CMe₃)CH₂](NAr)(OAr)₂ ($\Delta H^\ddagger = 19.7$ (4) kcal mol⁻¹, $\Delta S^\ddagger = -6$ (1) e.u.) $\Delta S^\ddagger$ values for loss of olefin from three W[CH₂CH(TMS)CH₂] TBP metallacycles have been found to be 11 e.u. (OR = DIPP), 13 e.u. (OR = OCMe(CF₃)₂), and 23 e.u. (OR = OC(CF₃)₂(CF₂CF₂CF₃)). Therefore $\Delta S^\ddagger$ appears to correlate with the geometry of the metallacyclobutane complex. There is another measurement of the rate of rearrangement of a tungstacyclobutane complex, that made by adding norbornene to W(CHCMe₃)(OCH₂CMe₃)₂Br₂ in the presence of GaBr₃. NMR studies suggest that this initial trans tungstacycle has a TBP geometry, but $\Delta S^\ddagger = -6$ e.u. Therefore any correlation between $\Delta S^\ddagger$ and metallacycle geometry may be valid only within a given class of compounds.

The X-ray structures study of 6 serves as a starting point for the analysis of the steric effects which govern the polymerization. The most immediate observation is the preference of the system for a trans arrangement of substituents on the metallacycle ring which upon breakup yields a trans olefinic bond. This agrees with the observed higher ratio of trans double bonds in the resulting polymers resulting from the less reactive monomers. It is important to realize that because the propagation steps are much faster this metallacycle must be involved in the metathesis reaction. If the olefin was to somehow dissociate and react via a different mechanism one would obtain unreacted W(CHCMe₃) when observing the metallacycle breakup kinetics. Furthermore it is interesting to note that the metallacycles involving norbornenes are not unlike those previously characterized which involve acyclic olefins.

Further information regarding the steric factors involved is obtained from analysis of the X-ray structure of the monoinsertion product obtained in Equation 4, (4). The remarkable
lack of reactivity is attributed to the disposition of the isopropylidene and carbomethoxy substituents in the alkylidene ligand, which block both N/C/O faces (Figure 6b). A large monomer, such as 7-isopropylene-2,3-dicarbomethoxy-norbornadiene, is not expected to react since an incoming monomer is expected to coordinate via one of these faces. Smaller monomers such as norbornene do react but with a rate of propagation much larger than that of initiation.

A monomer could approach two other faces of the catalyst, the O/O/N face, which places the monomer opposite the alkylidene and cannot lead to formation of a metallocycle, and the C/O/O face, which can yield a metallocycle if the alkylidene rotates by 90°C about the Mo=C bond. It is always possible that a given monomer can attack either a C/N/O face or the C/O/O face, i.e. that it can be polymerized by two subtly different mechanisms. Such a circumstance would complicate our attempt to understand and control polymerization reactions in detail. In view of the fact that bulky ligands are present in these catalysts and the homogenous arrangement of monomers along the polymer we favour the hypothesis that only one mechanism is operative (attack on the C/N/O) face, especially for monomers of low reactivity.

Having established the importance which substituents on the C5 ring have in determining the propagating alkylidene’s reactivity allows us to postulate a mechanism for stereoselectivity. Consider the syn rotamer first. In Scheme 2 is shown one enantiomer of the living polymer in the syn conformation. The conformation and orientation of the cyclopentene
Scheme 2. Monomer attack on the N/O/C face and away from CF₃ substituents to yield trans-isotactic polymer.
ring in the alkylidene ligand in the syn rotamer is assumed to be the same as found in the X-ray structure of 4. The plane of the imido phenyl ring should be oriented so that it contains the M-O\text{rear} bond in order to minimize interaction between an isopropyl group and the trifluoromethyl groups. (The plane of the phenyl ring in 4 contains the Mo-O\text{front} bond, presumably because both Mo=C faces are approximately equally congested.) Under these circumstances a molecule of 5 can approach only the front side of the M=C bond, the back side being blocked by the trifluoromethyl groups. In addition, an isopropyl group on the imido ligand forces 5 to add so as to give the trans metallacycle. If this metallacycle opens before a rearrangement of the core can "flip" the metallacycle relative to the nitrogen atom of the imido ligand, then the anti alkylidene complex shown must be formed. Although it is not known how rapidly the anti rotamer is converted into the syn rotamer, it now seems that the barrier to rotation about the M=C bond in complexes of this sort will be relatively low (15 - 18 kcal mol\(^{-1}\)). The fact that the product of reaction between Mo(CH\text{CHMe}_3) and one equiv of 2 (x = 1; Equation 3) consists of both syn and anti rotamers is consistent with formation of one rotamer initially (presumably anti) followed by equilibration of it with the other. If one postulates that the propagating alkylidene converts to the syn conformation before reacting, then this sequence of reactions would yield all trans-isotactic polymer. The main point to consider is that addition of monomer to the syn rotamer yields a product in which the carbon atoms bound to the olefinic carbon atoms of the new C=C bond have opposite configurations, indicative of isotactic chain growth.

How the chain would grow from the anti rotamer (Scheme 3, top right) is not as clear, in part because there is no structural evidence that suggests how the cyclopentene ring is oriented. Let's assume for the moment that the orientation that is shown is approximately correct. One could argue that the plane of the phenyl ring in the imido ligand could contain either the M-O\text{rear} bond (in order to allow the tert-butyl group on the front tert-butoxide to bend up out of the way of the CF\(_3\) groups) or the M-O\text{front} bond (in order to place the isopropyl groups as far from the alkylidene CF\(_3\) groups as possible). However, this latter circumstance
probably also would force the tert-butyl group of the front tert-butoxide ligand to bend down so that it would interact more with the CF₃ groups. If we assume that the conformer in which the plane of the phenyl ring contains the M-O_rear bond is the more favored and most reactive, and that 5 must approach the rear face of the M=C bond in this anti rotamer to give a trans metallacycle, then chain growth is again trans and isotactic, as shown.

In this scenario it does not matter which rotamer reacts with monomer, as long as the monomer adds to give the (trans) metallacycle intermediate, and the trifluoromethyl groups force the monomer to add selectively to the less hindered face of the M=C bond. Consequently, it may not matter whether the rotamers interconvert readily, in which case the monomer might react selectively with the more reactive rotamer, or whether the rotamers do not interconvert at all on the time scale of the reaction. Indications are that they do interconvert readily, and therefore that the ratio observed by NMR (approximately 6:1) is a measure of their relative energies. If they did not interconvert readily then the ratio observed by NMR would be a measure of their relative reactivities at equilibrium.

So far the discussion has focused on the mechanism of formation of trans-isotactic poly5. Trans-syndiotactic formation can be rationalized if attack of 5 occurs always via the N/O/C face where the CF₃ substituents are located (Scheme 4). Note that unlike trans-isotactic formation the chirality of ζ alternates after each monomer insertion. The same electronic factors would be involved as well as the formation of a trans metallacyclobutane intermediate analogous to 6. Note that the different reactivities of rotamers are not a factor in this mechanism as long as the monomer always approaches the alkylidene in the same fashion. These arguments would be more definite if the stereochemistry of the polymer was known unequivocally.

It has been assumed up to now that square pyramidal metallacycles are part of the catalytic cycle, that a square pyramid is close to the transition state, and that steric interactions in such metallacycles are therefore a good approximation of those in the transition state. However, that need not be the case. A square pyramidal metallacycle is the only one that can
Scheme 4. Monomer attack on the N/O/C face and towards CF₃ substituents to yield trans-syndiotactic polymer.
be observed. It is perhaps more sensible to propose that the first metallaclycle is a trigonal bipyramid formed by addition of the olefin to a C/N/O face of the pseudo-tetrahedral catalyst. A series of Berry-type pseudo rotations would lead to the observed square pyramidal metallacycles and to further trigonal pyramidal metallacycles from which the olefin can be extruded from the metal coordination sphere (see Chapter 7 for more discussion on the rearrangement of related oxymetallacylclobutanes). Although intermediate TBP and SP metallacycles species should be significantly distorted from ideality, and pseudorotations therefore not definable as precisely as in ideal systems, it is at least sensible to propose that the SP like metallacycles are not those first formed in a reaction between the alkyldiene complex and the olefin, and do not open directly to an alkyldiene complex. It is conceivable that an evaluation of the steric interactions in intermediates closer to the transition state would lead to entirely different conclusions concerning the stereoselectivity of ring-opening than those based on square pyramidal metallacycles.

EXPERIMENTAL

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from molten sodium and kept over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina except for deuterated THF which was vacuum transferred from a purple sodium ketyl solution and kept under nitrogen. Toluene-\textit{d}_8 used in kinetics experiments was distilled from sodium sand and subjected to three freeze-pump-thaw de-gas cycles prior to use. Benzonorbornadiene\textsuperscript{36}, 2,3-dicarbethoxynorbornadiene\textsuperscript{41}, 2-3-bis(trifluoromethyl)-norbornadiene\textsuperscript{47} and 7-isopropylidene-2,3-dicarbethoxynorbornadiene\textsuperscript{05} were prepared as
described in the literature. Norbornene was doubly distilled from molten sodium, in order to achieve this it has to be carried out under a slight positive pressure (mercury bubbler in Schlenck line is adequate). In general more rigorous exclusion of oxygen and moisture, relative to, for example, the reactions described in Chapter 1, is necessary due to the low concentration of catalyst in these polymerizations. Monomer purification must be rigorous as well in order to obtain narrow polydispersities and monomodal GPC traces of the prepared polymers.

NMR data are listed in parts per million downfield from TMS for proton and carbon and downfield from CClF₃ for fluorine. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d₆ at 25 °C unless otherwise noted. Gel Permeation Chromatographic (GPC) analysis were carried out using Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on polymer samples 0.1-0.3% w/v in dichloromethane which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03×10⁶ MW. Thermal analysis (TGA) was done on a Perkin Elmer TGS-2 thermogravimetric analyzer. Elemental analysis were performed using a Perkin Elmer CHN 2400 Elemental Analyzer.

**Determination of the ratio of $k_p$ to $k_i$.** For a reaction in which $M$ is the concentration of monomer, $M_0$ the initial concentration of monomer, $I$ the concentration of initiator ($M$(CCMe₃)), and $I_0$ the initial concentration of initiator, $M - M_0 = (1 - r)(I - I_0) + r I_0 \ln (I/I_0)$ if $I \neq 0$ and $r = k_p/k_i$. If a given quantity of monomer is added to and polymerized by the initiator then $M \rightarrow 0$ and $M_0/I_0 + r \ln (I/I_0) + (1 - r)(I/I_0 - 1) = 0$. By measuring the amount of remaining initiator ($I$), $r$ can be determined. Accurate values for $k_p/k_i$ can be determined only when $I$ is significantly less than $I_0$, but greater than zero (see Appendix 1). All experiments were carried out at room temperature.
As an example, details of the determination of \( k_p/k_i \) for 5 are the following. Approximately 4 mg of 5 (1.9 \( \times \) 10\(^{-5} \) mol) in C\(_6\)D\(_6\) (400 \( \mu \)L) was added at room temperature to a rapidly stirred solution of Mo(CHCM\(_3\)) \(_3\) (10 mg, 2.1 \( \times \) 10\(^{-5} \) mol) in C\(_6\)D\(_6\) (400 \( \mu \)L). After 30 minutes the number of equivalents of monomer added was determined by integrating the bridgehead methylene proton resonance in the ring opened monomers (1.8-2.2 ppm) versus the methine proton resonance in the imido ligand (3.8-4.1 ppm). The ratio of \( I/I_0 \) was obtained by measuring the ratio of the unreacted neopentylidene to total alkylidene proton resonances. Three determinations gave \( M_0/I_0 = 1.11, 1.45, 1.07 \); \( I/I_0 = 0.283, 0.186, 0.293 \); and \( k_p/k_i = 0.72, 0.73, 0.71 \) respectively.

**Typical Polymerization of benzonorbornadiene (1).** A solution of benzonorbornadiene (291 mg, 2.05 mmol) in toluene (3.0 mL) was added dropwise to a rapidly stirred solution of Mo(CHCM\(_3\))(NAr)(OCMe\(_3\))\(_2\) (10 mg, 0.0205 mmol) in toluene (3.0 mL) and the solution was stirred for 20 min. The polymerization was quenched by addition of 25 \( \mu \)L of pivaldehyde. After 20 min the solution was added to 250 mL of hexane, and the precipitated polymer was isolated by centrifugation, washed with hexane, and placed under vacuum overnight (yield 280 mg, 94 % white powder). Anal. Calcd for C\(_{1110}\)H\(_{1020}\): C, 92.84; H, 7.16. Found: C, 91.42; H, 7.33. Proton and carbon NMR are the same as those reported previously.\(^8\)

**Typical Polymerization of 2,3-dicarbomethoxynorbornadiene (2).** A solution of 2 (427 mg, 2.05 mmol) in toluene (5 mL) was added dropwise to a rapidly stirred solution of Mo(CHCM\(_3\))(NAr)(OCMe\(_3\))\(_2\) (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1 min. The color of the solution changed from yellow-orange to red. The living polymer was capped by adding of 25 \( \mu \)L of pivaldehyde and isolated as described above (yield 390 mg; 91%): \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 5.45 (br, H\(_{a}\)), 3.71 (s, CO\(_2\)Me), 3.52 (br, H\(_c\)), 2.43 (m, H\(_b\) or H\(_b\)'), 1.47 (m, H\(_b\) or H\(_b\)'), 0.92 (s, CHMe\(_3\)); \(^{13}\)C NMR \( \delta \) 165.2 (CO\(_2\)CH\(_3\)), 142.1
Polymerization of 2,3-bis(trifluoromethyl)norbordiene (5). A solution of 5 (7.71 g, 33.8 mmol) in toluene (10 mL) was added dropwise to a rapidly stirred solution of Mo(CHCMe₃)(NAr)(OCMe₃)₂ (23 mg, 0.047 mmol) in toluene (15 mL) over a period of 50 min. The reaction was stirred for up to 24 h and analyzed by ¹⁹F NMR to confirm that no monomer remained. Pivaldehyde (50 μL) was then added. After 30 min the volume of the mixture was reduced to 1/3 of the original and was added dropwise to large volume of vigorous stirred methanol. The polymer precipitated as a white powder which was washed several times with methanol and dried under vacuum for 48 h (yield 7.25 g, 94%): ¹H NMR (acetone-d₆; 400 MHz) δ 5.67 and 5.72 (apparent AB quartet, J_{AB} = 14.9), 3.80 (br, allylic H), 2.65 and 2.72 (apparent AB quartet, J_{AB} = 13.6; Hₐ, t, J_{HH} = 9.38; Hₜ, t, J_{HH} = 2.67, methylene protons); ¹³C NMR (acetone-d₆) δ 140.20 (=C-CF₃), 133.50 (=CH), 122.00 (CF₃), 49.80 (CH), 37.20 (CH₂); see Figure 4b.

Determination of k_p for 2. This measurement was carried out by Julie Thomas. The monomer (0.430 g, 100 eq) in 3.30 mL of C₆D₆ was added to a rapidly stirred solution of Mo(CHCMe₃)(NAr)(OCMe₃)₂ (10 mg) in 3.30 mL of C₆D₆. Aliquots (400 μL) were taken at regular intervals, quenched with benzaldehyde (25 μL), and examined by proton NMR; the
resonances at 2.18 and 2.02 ppm were monitored. Alternatively the monomer (0.105 g, 25 eq), toluene (50 µL as a reference), and Mo(CHCMe₃)(NAr)(OCMe₃)₂ (10 mg) were added to 25 mL of benzene. Aliquots were withdrawn, quenched with 25 µL of benzaldehyde, and examined by GC. The consumption of 2 was evaluated assuming pseudo-first-order kinetics.

**Determination of kₚ for 5.** This measurement was carried out by Ezat Khosravi at the University of Durham, England. The monomer (0.24 g, 1.07 mmol) in toluene (5 mL) was added dropwise over a period of 35 min to a rapidly stirred solution prepared by mixing a solution of Mo(CHCMe₃)(NAr)(OCMe₃)₂ (10 mg, 0.021 mmol) in toluene (3 mL) and trifluorotoluene (as a reference; 308 mg, 2.11 mmol) in toluene (2 mL). Aliquots (100 µL) were taken at intervals and benzaldehyde (25 µL) in toluene was added. The samples were analyzed by fluorine NMR, which displayed a singlet at 59.64 ppm for the polymer, a singlet at 62.50 ppm for the monomer, and a singlet at 63.03 ppm for the reference (external CFCl₃). The reaction was followed by monitoring the loss of monomer with time. The data were evaluated by pseudo-first-order kinetics. Four determinations were made: [Mo]₀ = 0.0008, 0.0019, 0.0039, 0.0041 M; [monomer]₀ = 0.0417, 0.1975, 0.1038, 0.1037 M; kₚ = 0.054, 0.065, 0.061, 0.048 M⁻¹, all respectively. Therefore kₚ = 0.057 (0.007), and since kₚ/kᵢ = 0.72, kᵢ = 0.079 (0.010).

**Synthesis of 4.** A solution of 2 (101 mg, 0.41 mmol) in toluene (3.0 mL) was added to a stirred solution of Mo(CHCMe₃)(NAr)(OCMe₃)₂ (290 mg, 0.41 mmol) in toluene (3.0 mL). After 8 h the toluene was removed in vacuo to yield the product as a dark orange oil (300 mg) which was shown by ¹H NMR to be 90-95 % 4. Diffraction quality crystals were obtained by slow crystallization from a minimum amount of toluene at -30 °C over a period of two months: ¹H NMR (C₆D₆) δ 11.03 (d, 1, J = 8, H₆), 7.09 (d, 2, H₃), 7.05 (t, 1, H₆), 6.40 (d, 1, J = 8, H₃), 5.55 (d, 1, CH-t-Bu), 5.44 (dd, 1, CHCH-t-Bu), 4.23 (sept, 2, CHMe₂), 4.01 (d, 1, CHCHCHCMe₃), 3.46 (s, 3, CO₂Me), 3.41 (s, 3, CO₂Me), 1.40 (d, 6,
CHMe₂), 1.35 (s, 9, OCMé₃), 1.34 (d, 6, CHMe₂), 1.33 (s, 9, OCMé₃), 1.02 (s, 9, CHCMé₃); ¹³C NMR δ 250.4 (Cₓ, JCH = 128), 165.4, 165.1, 153.0, 145.1, 144.2, 142.8, 139.6, 135.2, 126.8, 124.3, 123.0, 78.2, 77.7, 66.5, 52.7, 51.6, 51.3, 33.2, 32.5, 32.1, 31.9, 29.8, 28.5, 24.6, 24.1, 21.6, 20.2; IR (C₆D₆) cm⁻¹ 1725, 1720 (s, C=O), 1640 (m, C=C).

**Determination of k_p/k_i₂.** Living poly2 was made by addition of 2 (52 mg, 0.245 mmol) in C₆D₆ (300 µL) to a solution of Mo(CHCMé₃)(NAr)(OCMé₃)₂ (12 mg, 0.0246 mmol) in C₆D₆ (300 µL) under vigorous stirring and allowed to react for 15 minutes in order to ensure monomer consumption. The polymerization of norbornene was initiated using the above solution by addition of a solution of norbornene (10 mg, 0.106 mmol, 4.3 equiv) in C₆D₆ (300 µL). The ratio of I/I₀ was determined to be 0.282 by ¹H NMR measurement of the ratio of unreacted poly2 (11.67 and 11.63 ppm) versus total alkylidene concentration. Due to resonance overlap the amount of monomer versus initiator could not by quantified by ¹H NMR.

**Determination of k_p/k_i₅.** Living poly5 was made by addition of 5 (47 mg, 0.206 mmol) in C₆D₆ (300 µL) to a solution of Mo(CHCMé₃)(NAr)(OCMé₃)₂ (10 mg, 0.0205 mmol) in C₆D₆ (300 µL) under vigorous stirring. The color of the solution turned orange from the original yellow and back to yellow over a period of 45 minutes. The resulting solution was used to initiate the polymerization of norbornene by addition of a solution of norbornene (19 mg, 0.201 mmol) in C₆D₆ (300 µL). The ratio of I/I₀ was determined to be 0.183 by measurement of the ratio of unreacted poly5 (11.34 ppm) to total alkylidene concentration. The amount of norbornene added relative to total living alkylidene was determined to be 9.84 equivalents by ¹H NMR integration of polymer peaks versus the living alkylidenes Hₓ resonance.
Rate of formation of 4. This measurement was carried out by Julie Thomas. Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (10 mg) was dissolved in 700 µL of benzene-d$_6$ and the solution was transferred to an NMR tube. The solution was frozen at -30 °C and 65 µg (13 eq) of 3 was added as a solid. The sample was thawed and placed in a preset and calibrated NMR probe and allowed to equilibrate for 5 min. Spectra were collected over at least three half-lives at 12.7 °C, 21.7 °C, 22.0 °C, and 27.5 °C. The propagating and initial alkylidene resonances were followed and the data treated assuming pseudo-first-order conditions. At 40.5 °C data were collected on a sample consisting of 6 mg of Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ and 16 mg of 3 in 600 µL of benzene-d$_6$. Data were fit to a second order rate law. Thermodynamic parameters from an Arrhenius plot were found to be ΔH$^\ddagger$ = 15.6 (1.0) kcal mol$^{-1}$ ΔS$^\ddagger$ = -18(3) e.u., and ΔG$^\ddagger$(298) = 21.0 (1.3) kcal mol$^{-1}$.

Synthesis of 6. Solutions of W(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (100 mg, 0.17 mmol) and 5 (35 mg, 0.15 mmol) were made up using a minimum amount of toluene (~500 µL for each) and were cooled to -35 °C. (It is important that the compounds stay in solution.) The solutions were mixed at -35 °C and stored at -35°C for 4 days. Yellow X-ray quality crystals formed. The solvent was removed and the crystals stored at -78°C: $^1$H NMR (toluene-d$_8$, -25 °C, 500 MHz) δ 7.01 (t, 1, H$_p$), 6.97 (d, 2, H$_m$), 3.98 (septet, 2, CHMe$_2$), 3.73 (s, 1, bridgehead H), 2.98 (s, 1, bridgehead H), 2.77 (dd, 1, J$_{H\alpha H\beta}$ = 9, H$_\beta$), 2.23 (d, 1, J$_{H\alpha H\beta}$ = 9, H$_\alpha$), 1.45 (d, 1, CH$_2$ bridgehead), 1.32 (s, 9, OCMe$_3$), 1.30 (CH$_2$ bridgehead by COSY), 1.27 (s, 9, OCMe$_3$), 1.24 (d, 6, CHMe$_2$), 1.20 (d, 6, CHMe$_2$), 1.17 (H$_\alpha$, by COSY), 1.08 (s, 9, CMe$_3$); $^{13}$C NMR (toluene-d$_8$, -25 °C) δ 149.5, 146.5, 145.3, 143.0, 127.6, 123.1, 83.13, 82.69, 72.30, 52.81, 50.22, 48.96, 42.70, 37.94, 32.18, 32.10, 30.95, 28.4, 27.2, 23.6.

Rate of formation of 6. The reaction was too fast to study by pseudo-first-order kinetics. A solution of W(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (10 mg in 400 µL of toluene-d$_8$, 4.38
(0.05) x 10^{-2} \text{ M} \) was placed in a 5 mm NMR tube equipped with a 24/40 ground glass joint and stoppered with a rubber septum. The catalyst solution was frozen at 77K and a solution of 4 mg of 5 in 400 \mu L of toluene-\text{d}_8 (4.38 (0.05) x 10^{-2} \text{ M}) was added via syringe. The contents of the NMR tube were frozen and the NMR tube was evacuated and sealed. The two solutions were mixed at -80 °C and kept frozen at 77K until kinetic measurements were done. The reaction was followed by measuring the disappearance of the H\textsubscript{\alpha} resonance in the neopentylidene complex against the appearance of metallacycle resonances at four different temperatures (227.4, 238.2, 248.2, and 258.2 K) with a sample equilibration time in the NMR probe of 5 min. Observed rate constants were 4.14, 9.30, 17.4, and 30.2 x 10^{-3} \text{ M}^{-1}\text{s}^{-1}, respectively. The Arrhenius plot had \rho = 0.999. Consistent results were obtained only when stock solutions of the reactants were prepared in volumetric flasks and reaction temperatures were measured carefully.

**Ring-opening of 6 to give 7.** The metallacycle was made in situ by allowing W(CHCMe\textsubscript{3})(NAr)(OCMe\textsubscript{3})\textsubscript{2} (63 mg, 0.11 mmol) in toluene-\text{d}_8 (1.20 mL) to react with 5 (23 mg, 0.10 mmol) in toluene-\text{d}_8 (1.20 mL) at -35 °C for 12 h. In order to monitor the reaction by \textsuperscript{1}H NMR mesitylene was added as an internal standard (15 mg, 0.12 mmol). The metallacycle solution (800 \mu L) was placed into 5 mm NMR tubes and quickly frozen until the kinetic measurements. First order behavior was monitored at three different temperatures (288.5, 298.5, and 308.4 K). Observed rate constants were 0.766, 3.10, and 9.29 x 10^{-4} \text{ s}^{-1}, respectively. The Arrhenius plot had \rho = 0.998: \textsuperscript{1}H NMR (toluene-\text{d}_8, -25 °C) \delta 8.35 (d, 1, J_{H\alpha H\beta} = 9, H\alpha), 7.09 (t, 1, H\text{p}), 7.05 (d, 2, H\text{m}), 5.52 (b, 1, H\beta), 5.45 (d, 1, CHCMe\textsubscript{3}), 5.31 (dd, 1, CHCHCMe\textsubscript{3}), 3.89 (sept, 2, CHMe\textsubscript{2}), 3.13 (b, 1, CHCHCMe\textsubscript{3}), 2.31 (m, 1, CHH), 1.68 (m, 1, CHH), 1.314 (s, 18, O-t-Bu), 1.28 (d, 6, CHMeMe), 1.24 (d, 6, CHMeMe), 0.96 (s, 9, CH-t-Bu).

**X-ray Study of 4.** Data for this structure was carried out by Dr. William Davis of
the MIT Chemistry Department and solved and refined by Marie O'Regan. Data were collected at -65 °C on a Rigaku AFC6 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069) and a 12KW rotating anode generator. A total of 10212 reflections were collected, 9813 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. No decay correction was applied. The structure was solved by a combination of the Patterson method and direct methods. Refinement was by full matrix least squares using using the TExSAn crystallographic package of Molecular Structure Corporation. Hydrogen atoms were included in calculated positions (dC-H = 0.95 Å). Final R₁ = 0.047 and R₂ = 0.064. Crystal data for 4 are a = 13.64 (1) Å, b = 17.414 (5) Å, c = 17.64 (1) Å, V = 4130 (5) Å³, β = 99.84 (6)°, space group = P2₁/n, Z = 4, Mr = 735.85, ρ = 1.183 g/cm³, μ = 3.48 cm⁻¹, R₁ = 0.047, and R₂ = 0.064.

X-ray Study of 6. The data collection and structure solution and refinement were carried out by Dr William Davies of the MIT Chemistry Department. An orange prism of C₃₄H₅₁NO₂F₆W having approximate dimensions of 0.330 × 0.300 × 0.300 was mounted on a glass fiber. Data were collected at -78° C on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 8944 reflections were collected, 8505 of which were unique. Equivalent reflections were merged. The final refinement was based on 4708 reflections (I>3σ(I)). The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects and a correction for secondary extinction was applied. The structure was solved by the Patterson method and subsequent difference Fourier maps. The refinement was by full matrix least squares using the TExSAn crystallographic package of Molecular Structure Corporation.
Carbon atoms and the nitrogen atom were refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 \AA). Final R_1 = 0.067 and R_2 = 0.074. Crystal data for 6 are a = 12.268(8) \AA, b = 18.436(3) \AA, c = 16.08(1) \AA, \beta = 94.63(3)^\circ, V = 3624(5) \AA^3, space group = P2_1/n, Z = 4, M_r = 803.62, \rho = 1.473 \text{ g/cm}^3, \mu = 33.12 \text{ cm}^{-1}, R_1 = 0.067, \text{ and } R_2 = 0.074.
CHAPTER 3

The Synthesis of Star Block Copolymers by Controlled
Ring-Opening Metathesis Polymerization.
INTRODUCTION

The development of particular macromolecular structures and architectures has been heavily influenced by the development of living polymerization systems.\textsuperscript{59,60} So far these have been transition metal-free polymerizations, i.e., anionic, cationic, and group transfer systems. The relatively recent discovery of well-defined transition metal catalysts for the controlled ring-opening metathesis polymerization (ROMP) of mono and polycyclic olefins has permitted the synthesis of interesting materials such as functionalized block copolymers (Chapter 4), polyacetylene\textsuperscript{9,61,62}, polyenes\textsuperscript{63,64}, and stereoregular fluorinated polymers (Chapter 2). Therefore we set out to determine whether living ROMP technology could be employed in a way that imitates some of the previous living systems, but one which offers advantages characteristic of living ROMP with well-characterized complexes. In particular it was decided whether ROMP could be utilized in order to prepare star shaped polymers.

In this chapter the reactivity of exo-trans-exo pentacyclo [8.2.1.1\textsuperscript{4,7}.0\textsuperscript{3,8}] tetradeca-5,11-diene\textsuperscript{65} (8), as a cross-linking agent for ROMP by M(CHMe\textsubscript{3})(NAr)(OCHMe\textsubscript{3})\textsubscript{2} (M=Mo, W) complexes is reported. This norbornadiene dimer is analogous to the monomers described in Chapter 2 in that it has C\textsubscript{5} symmetry, minimizing the possible stereochemical modes of addition. Other properties of 8 which were taken into account for its choice were the two reactive norbornene-like double bonds which make its ring opening irreversible, its rigid backbone that prevents metathesis of both olefins by the same metal centre and its availability

\[ \text{8} \]

by the catalytic dimerization of norbornadiene. 8 also has been used to prepare a titanium-based bifunctional telechelic ROMP initiator used in the preparation of block copolymers.\textsuperscript{66} Tricyclooctadiene also has been reported as a cross linking reagent in ROMP using classical
catalysts, but the synthesis of tricyclooctadiene is relatively difficult and of low yield compared to 8. 8 could be viewed as the ROMP analog of divinyl benzene in living anionic polymerizations.

RESULTS

Reaction of 1 with Living Polynorbornene.

Norbornene (NBE; 50 eq) is quickly polymerized by W(CHMe3)(NAr)(OCMe3)2 (W(CHCMe3)) in toluene in ~5 min. Addition of benzaldehyde followed by precipitation of the polymer in methanol yields polynorbornene with a polydispersity index (PDI) of 1.05. If 0.5 equiv of 8 is added before benzaldehyde then the mixture of polymers shown in Figure 1 is obtained, this polymer material is noticeably less soluble in methanol than the linear precursor. Because the polydispersity of the initial living 50 mer is so low it is possible to observe GPC peaks for the "dimer" and "trimer" in the final mixture, in addition to the linear 50 mer and higher oligomers. The "dimer" consists of a distribution of chain lengths centered around twice the average molecular weight of the initial polymer and is formed when two living chains are joined by a single molecule of 8 (Equation 1). Formation of the trimer can be rationalized

\[ M = P + 8 \rightarrow M = P \]

(1)
Figure 1. GPC trace of the mixture of polymers resulting from the addition of 0.5 eq. of 8 to a 50 mer of living polynorbornene followed by benzaldehyde quench.
Scheme 1. Formation of "trimer" by reaction of 8 with living polynorbornene.
by steps similar to those shown in Scheme 1. Permutations of such cross linking reactions would account for the higher molecular weight species.

The fact that a distribution of cross-linked polymer chains is observed suggests that the cross-linking process is statistical, i.e., that unreacted 8 and a pendant norbornene on a living alkylidene have similar reactivities, and that alkylidenes A, living poly8, B, and living polynorbornene, have similar reactivities. If the GPC eluent is monitored by UV at 254 nm

(where only the phenyl end cap absorbs in polymers quenched with benzaldehyde) the result is identical to that obtained using the refractometer (which is sensitive to the concentration of the polymer backbone), a result that suggests that all chains were living at the time of termination. Identical results were obtained using Mo(CHCMMe3)(NAr)(OCMe3)2 (Mo(CHCMMe3)) as the initiator.

Addition of 4 equiv of 8 to the living 50 mer followed by benzaldehyde yields a soluble polymer. GPC analysis shows that the complex mixture of polymer chains disappears and only a peak with a narrow dispersity of 1.24 is observed (Figure 2a) and a molecular weight that is approximately 10 times that of the 50 mer (as determined by GPC calibrations relative to polystyrene). Similarly, addition of 3 equiv of 8 to a living 25 mer yields a polymer with a dispersity of 1.11 (Figure 2b). GPC results employing the UV detector again are identical to
Figure 2. GPC trace (refractometer data) of the polymers obtained by (a) treatment of a 50 mer of living polynorbornene with 4 equivalents of 8; (b) treatment of a 25 mer of living polynorbornene with 3 equivalents of 8. Both quenched with benzaldehyde. A slight "raggedness" in the traces is due to the output device, more data points are taken as a function of time and used in the calculation of molecular weights and polydispersities.
those using the refractometer, implying that all the previously observed lower molecular weight peaks were living and were converted quantitatively to the high molecular weight species obtained upon addition of excess 8.

The relatively high molecular weight species observed upon addition of 3-4 equiv of 8 to living polynorbornene fall into the class of "star" polymers, species that are characterized by a relatively localized core from which a number of polymer chains or 'arms' emanate. In this case the number of arms and their lengths are not fixed, but are relatively narrow distributions about the number average. Two methods that have been used extensively for synthesizing star polymers are the reaction of a polyfunctional electrophile (i.e. SiCl₄) with monocarbanionic chains, and polymerization of styrene followed by the addition of divinyl benzene (DVB). In the latter approach the coupling process is self-limiting, since once several chains have been coupled, the reactive sites become buried in the central nodule. Reactions within the same structure then become more favorable than reactions between active sites in separate structures.

Star polymers synthesized from living polynorbornene and 8 can be found in Table 1. Note that the larger the initial living oligomer of norbornene the more 8 is required for complete conversion to star polymer. (Similar results were found in anionic polymerization systems) Care must be exercised in interpreting GPC results, since the hydrodynamic volume of molecules, not their molecular weight nor extended length, determines GPC retention times. With star polymers polydispersity can originate solely as a result of a fluctuation of the number of arms (assuming monodisperse initiator arms). Therefore, GPC cannot accurately determine polydispersities. However, it is the standard technique used to determine if unreacted linear polymer remains. The distribution of the number of arms within the star polymers prepared by block copolymerization of styrene and DVB using sec-butyllithium as initiator have been analyzed by the complex technique of precipitation gel permeation chromatography. In these it was found that the distribution of arms per star polymer approached a Poisson like distribution,
Table 1. GPC characterization of the polynorbornene star polymers.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>equivalents NBE</th>
<th>PDI(arm)</th>
<th>equivalents 8</th>
<th>$M_w$</th>
<th>PDI(star)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(CHCMe₃)</td>
<td>100</td>
<td>1.04</td>
<td>5</td>
<td>173251</td>
<td>1.25</td>
</tr>
<tr>
<td>W(CHCMe₃)</td>
<td>50</td>
<td>1.05</td>
<td>4</td>
<td>77213</td>
<td>1.24</td>
</tr>
<tr>
<td>W(CHCMe₃)</td>
<td>25</td>
<td>1.07</td>
<td>3</td>
<td>60240</td>
<td>1.18</td>
</tr>
<tr>
<td>Mo(CHCMe₃)</td>
<td>100</td>
<td>1.04</td>
<td>4</td>
<td>151134</td>
<td>1.10ᵃ</td>
</tr>
</tbody>
</table>

ᵃSmall amount of linear precursor observed. All reactions capped with benzaldehyde. GPC values are obtained versus polystyrene calibration.
consistent with a random process of combination of chain ends.\textsuperscript{72} It is reasonable to expect the same result for the stars prepared by ROMP methods.

Since there is no mechanism for deactivation on the time scale of forming the star, it is possible to use living stars (the result of adding 8 to living norbornene) to initiate further polymerization of norbornene. Addition of 25 eq of NBE to the star polymer shown in Figure 2b consumes the monomer and results in a new soluble polymer, the GP of which (Figure 3) shows that although the molecular weight is higher than the original star polymer the curve is bimodal. Different reaction conditions result in similar distributions. We attribute this result to a slower initiation at the core of the star and faster propagation as the reacting alkylidene centers move away from the sterically crowded core environment. Under these conditions one might expect some of the original star to remain, depending upon the rate of propagation versus initiation. The UV trace is identical to the refractometer trace shown in Figure 3.

**Reaction of 8 with W(CHCMe\textsubscript{3}) or Mo(CHCMe\textsubscript{3})**

In a variation of the method employing DVB as the coupling agent of living polystyrene, DVB can be polymerized first by butyllithium in dilute benzene solution to give soluble microgels which bear a large number of anionic end groups. These microgels bear a number of carbanionic groups capable of initiating the polymerization of styrene or other monomers yielding star molecules.\textsuperscript{73,74}

In order to test this approach in ROMP 0.5 eq. of 8 was added to W(CHCMe\textsubscript{3}) in C\textsubscript{6}D\textsubscript{6} and the reaction was followed by \textsuperscript{1}H NMR. The neopentylidene resonance at 8.03 ppm decreased little relative to an internal standard, but careful integration showed that new alkylidene resonances were buried in the baseline in the region between 8.35 to 8.50 ppm and equally broad olefinic resonances were found between 5.3 to 5.6 ppm, all assigned to propagating alkylidenes were 8 has been ring opened, poly8. The spectrum did not change upon cooling or heating the sample. The breadth of the signals can be attributed to a crowded steric environment where many different conformations are present. To this mixture of
Figure 3. GPC trace (refractometer data) of the isolated polymers obtained from the reaction of 25 equivalents of norbornene with living polymer prepared from 25 equivalents of norbornene and 3 equivalents of 8 (Figure 2b) followed by benzaldehyde quench.
alkylidenes 50 eq of NBE were added followed by excess benzaldehyde with no observable precipitation. GPC analysis (Figure 4) shows that the molecular weight distribution is complex. The low molecular weight polymer must result from reaction of NBE with leftover initiator, while the broad, high molecular weight fraction probably results from reaction of NBE with the distribution of alkylidenes formed upon reaction of W(CHCMe₃) with 8. A peak corresponding to approximately a 100 mer, which appears at 32.54 min, also can be observed. The "double" molecular weight peak probably arises from a bifunctional initiator which polymerizes the monomer in a telechelic fashion.

A yellow gel precipitates quickly when 3 or 4 eq of 8 are added to W(CHCMe₃) in toluene at -30°C or 25°C. Addition of more (25 eq) of norbornene does not take the polymer into solution, but all the norbornene is consumed. Termination with benzaldehyde followed by stirring the gel in pentane gives an insoluble white solid. Addition of 2 eq of 8 to W(CHCMe₃) at -30°C followed by 25 eq of NBE gave a soluble polymer, which was shown by GPC to be approximately a 1:1 mixture of a high molecular weight polymer and linear oligomers that result from reaction of NBE with W(CHCMe₃). Evidently for complete consumption of W(CHCMe₃) to give poly8, the amount required of 8 is such that the cross-linked polymer becomes insoluble.

The above results are consistent with 8 reacting with A at a rate that is much larger than the rate of reaction of 8 with W(CHCMe₃). The ratio of kₚ to kᵢ (where kᵢ is the rate constant for reaction of 8 with W(CHCMe₃)) can be determined by measuring how much initiator remains after addition of x eq of 8 to W(CHCMe₃) (x is small, see Experimental in Chapter 2). The value of kₚ/kᵢ was found to be 9 (±1) (Table 2), i.e., the propagating alkylidene is more reactive by approximately an order of magnitude. Consequently it appears that addition of 8 to W(CHCMe₃) or Mo(CHCMe₃) first is not a good method for preparing star polymers or the preparation of difunctional telechelic initiators. Note that these gels are living, and therefore potentially could serve as a means of preparing partially soluble or relatively insoluble supported (immobilized) functionalities or catalysts.
Figure 4. GPC trace (UV/VIS detector data) of the mixture of polymers obtained by treatment of $W$(CHCMe$_3$) with 0.5 equivalents of 8 followed by 50 equiv of norbornene and benzaldehyde quench.
Formation of Functionalized Star Polymers.

Addition of 25 eq of 2,3-dicarbomethoxynorbornadiene (2) (see Chapter 2) to Mo(CHCMe3) completely consumes the monomer and produces oligomers with a narrow molecular weight distribution (PDI = 1.08). Reaction of 3 eq of 8 with these living 25 mers results in the formation of star polymers, but some of the original 25 mers of 2 remain (10-20 %; Figure 5). This result contrasts with living polynorbornene where only 3 eq of 8 are needed for complete consumption of the linear precursor. This result can be attributed to a lower reactivity of C relative to A, which causes 8 to react preferentially with more reactive A formed in the initial stages of the reaction. In order to circumvent this propagation/initiation problem 25 eq of NBE were added to a living 25-mer of poly2, C, followed by 6 eq of 8. This strategy, which is summarized in Scheme 2, allows soluble functionalized star polymers to be prepared. The final structure of this star is interesting since it contains a more polar "shell" around a less polar interior and may have interesting physical properties. This experiment illustrates the importance of the reactivity of the living alkylidene in determining conversion. If the propagating alkylidene is not reactive enough then initiator remains and homopolymer is formed in the final mixture. A cross-linking agent that has a low rate of propagation would seem to be ideal, but that would mean that it also would not efficiently cross-link living oligomers. A compromise is inevitable.

![Chemical Structure](image)

Values of $k_p/k_i$ for different monomers roughly measure the reactivity of the propagating alkylidene (see Discussion section). A quantitative measure of the reactivity of
Figure 5. GPC trace (refractomer data) of the polymer mixture resulting from addition of 6 equiv. of 8 to a living 25 mer of poly2 followed by benzaldehyde quench.
Scheme 2. Strategy for the formation of star polymers containing poly2 segments.
different monomers would require that the absolute rates of initiation or propagation also be determined. Unfortunately, these rates are too fast to measure by routine techniques. Values for r are listed in Table 2. The rather low value of $k_p/k_i$ for poly2 is consistent with the poor conversion observed (see above). Conversely $k_p/k_i$ for 2-carbonitrile norbornene (60:40 mixture of endo and exo isomers; 9; $k_p/k_i = 7.0$ (0.5)) compares favorably with that for 8 ($k_p/k_i = 9$ (1)) and would be a better choice for a monomer which would form a functionalized star. 2,3-bis(trifluoromethyl)norbornadiene (5; $k_p/k_i = 0.72$ (0.05) is the poorest choice, since $k_p$ (0.057(0.007) M$^{-1}$s$^{-1}$ at 22$^\circ$C) is small. However, 6 would be an ideal candidate for quantitative propagation from a living star center where one would like the polymerization rate of the linear polymer to be as low as possible in order to counteract the steric problems encountered inside the core of the star.

Polymerization of 50 eq of 9 in THF followed by quenching with excess p-trimethylsilyl-benzaldehyde$^{75}$ yields a polymer with dispersity of 1.05 which can be isolated by precipitation into hexanes. (The properties of this and related functionalized homopolymers will be reported in Chapter 4.) Reaction of this living 50 mer with 5 eq of 8 followed by termination with p-trimethylsilylbenzaldehyde results in quantitative formation of a star polymer (Figure 6). The two end groups of these polymers have resonances in the $^1$H NMR spectrum that are well-separated from the rest of the polymer resonances and can be used to probe the environment surrounding them. In linear poly9 capped with p-trimethylsilyl-benzaldehyde two sharp TMS resonances are observed at 0.232 and 0.217 ppm (major) that can be assigned to TMS groups in cis and trans double bonds, while the tert-butyl group
Table 2. Ratio of rate of propagation to rate of initiation for selected monomers in C\textsubscript{6}D\textsubscript{6}.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( r = \frac{k_p}{k_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="image" /></td>
<td>12.1 (5)</td>
</tr>
<tr>
<td><img src="image2.png" alt="image" /></td>
<td>9 (1)</td>
</tr>
<tr>
<td><img src="image3.png" alt="image" /></td>
<td>7.0 (5)\textsuperscript{a}</td>
</tr>
<tr>
<td><img src="image4.png" alt="image" /></td>
<td>3.0 (3)</td>
</tr>
<tr>
<td><img src="image5.png" alt="image" /></td>
<td>0.72 (5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction carried out in d\textsuperscript{8} THF. All polymerizations used 3 at a concentration of 0.02 M at RT.
Figure 6. GPC trace (refractometer data) of a poly9 star prepared from a living 50 mer of poly9.
resonance is split into four singlets at 1.004, 0.981, 0.963 and 0.956 ppm as a result of sensitivity to exo/endo and head/tail isomerism in an all-trans terminal double bond. (Initiation using Mo(CHCMe₃) appears to always yield a trans olefin.) The ratio of initiator (t-butyl) to terminator (TMS) in poly9 is 1:1 according to integration of the respective resonances in the proton NMR spectrum. For a star polymer prepared from living poly9 the tert-butyl resonances are unchanged but the TMS resonances are unusually broad, consistent with the broad alkylidene resonances previously observed for poly8. The TMS resonances integrate as 70% of the tert-butyl resonance, a result that indicates that sites inside the core of the star were not all initiated, probably for steric reasons. (We assume that the unreacted living sites are deactivated by dioxygen when the samples are exposed to air.)

50 equivalents of 6 are completely consumed by the living poly9-star. Quenching with trimethylsilylbenzaldehyde yields a white fluffy polymer. GPC analysis showed that the molecular weight has increased from that of the original poly9-star and the molecular weight distribution was monomodal. Integration of the allylic proton resonances in the polymer
backbone versus the total olefin resonance area indicates that the stoicheometry is that expected. The resonance for the TMS cap is now sharp and integrates to 90% of the tert-butyl resonance (Figure 7), a result that suggests that the propagating alkylidenes most of the time were in a less crowded and accessible environment, i.e., outside the inner core of the star. This result also implies that the number of arms in poly9 is approximately the same as the number in poly6 within the same star. The $^{13}$C NMR spectrum consists of a superimposition of the spectra of poly9 and poly6. A single olefinic resonance for poly6 is observed at 132.30 ppm; it is characteristic of the stereoselective polymerization of 6 by Mo-based poly6 (Chapter 2).

**DISCUSSION**

Analogous behaviour is observed between the reactivity of 8 in living controlled ROMP and DVB in the living anionic system especially with regards to the formation of star shaped polymers. The focus of this chapter has centered around the synthesis of these materials and not on the potentially interesting properties these may display. To note is the rather simple experimental procedures which ROMP (22-26 °C, drlbox) required which contrasts with the high vacuum, low temperature setup necessary for anionic polymerization. The reactivity of the precursor arm propagating alkylidene is critical and it should be maximized relative to poly8; an outcome of this is the formation of gels if 8 is added to the initiator.

It is important to point out here why the ratios of $k_p/k_i$ using the same initiator for different monomers is a good approximation for the relative reactivities of the respective propagating alkylidenes. The initiation reaction depends on the reactivities of the initiator and the monomer:

\[
M=\text{initiator} + \text{monomer} \rightarrow M=\text{polymerization}
\]
Figure 7. $^1$H NMR spectrum (TMS and tert-butyl end groups region) of (a) poly9; (b) poly9-star; (c) poly9-star-poly6.
The rate of the propagation reaction is dependent on the reactivities of the monomer (as in \( k_i \)) and the propagating alkyldene:

\[
\begin{align*}
M &= \text{alkylidene} \\
n &> 0
\end{align*}
\]

If the propagating alkyldene is more reactive for steric or electronic reasons than the initiator then this ratio will be greater than one, if less reactive then it will be less than one. This can be viewed as a competition experiment between initiator and propagating alkyldene since monomer reactivity is included in both rates. Comparing the ratios of \( k_p/k_i \) for different monomers allows one to measure the relative reactivities of the different propagating alkyldenes if the same initiator is utilized. Therefore, to a first order approximation, the ratio of the ratios of \( k_p/k_i \) allows one to estimate the relative reactivities of the different propagating alkyldenes if the same initiator is used for both monomers.

The control required in the preparation of star polymers contrasts with that required for the preparation of stereoregular polymers (Chapter 2). In the former, architectural control is achieved by a statistical method of cross-linking chains which works because the polymerization system is living. In order to build a particular structure the reactivity of the reactants have to be chosen for each different operation (i.e. star formation versus double star formation). Stereoregulation is a consequence of well matched reactivity between a monomer and its propagating alkyldene such that monomers enter the linear polymer chain in the same fashion.

The ability of Mo(CHMe\(_3\))(NAr)(OCMe\(_3\))\(_2\) to tolerate a wide range of functionalities (see Chapter 4) allows the preparation of star polymers with pendant functionalities. Star polymers where the arms are block-copolymers of different polarities have been prepared as well as star polymers where the composition of the arms are different and again of very
different solubility characteristics and stereochemical regularity; these materials may exhibit interesting intramolecular phase separation. In these latter stars the number of the different arms should be approximately equal. This "double star" synthesis has not been achieved successfully using anionic systems due to gelation of the reaction medium.\textsuperscript{77}

**EXPERIMENTAL.**

**General Details.** All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres dribox or by using standard Schlenk techniques. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina. Norbornene was doubly distilled from molten sodium. Commercially available 2-carbonitrile norbornene (60:40 mixture of exo and endo isomers) was distilled under nitrogen, passed through a column of activated alumina and stored under nitrogen. 2,3-dicarboxmethoxynorbornadiene\textsuperscript{41}, 2,3-bis(trifluoromethyl)norbornadiene\textsuperscript{47}, p-trimethylsilyl-benzaldehyde\textsuperscript{75}, W(CHMe\textsubscript{3})(NAr)(OCMe\textsubscript{3})\textsubscript{2}\textsuperscript{42} and Mo(CHMe\textsubscript{3})(NAr)(OCMe\textsubscript{3})\textsubscript{2}\textsuperscript{29} were prepared as described in the literature.

NMR data are listed in parts per million downfield from TMS for both proton and carbon. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Gel Permeation Chromatographic (GPC) analysis were carried out using Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1-0.3 % w/v in dichloromethane which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03×10\textsuperscript{6} MW. Thermal analysis (TGA) was done on a Perkin Elmer TGS-2 thermogravimetric analyzer.
**Determination of the ratio of k_p to k_i.** For a given reaction in which M is the concentration of monomer, M_0 the initial concentration of monomer, I the concentration of initiator (in this case either 2 or 3), and I_0 the initial concentration of initiator, M - M_0 = (1 - r)(I - I_0) + rI_0 ln(I/I_0) as long as I ≠ 0 and where r = k_p/k_i. If a given quantity of monomer is added to and polymerized by the initiator then M approaches 0 and M_0/I_0 + rln(I/I_0) + (1 - r)(I/I_0 - 1) = 0. Note that M_0/I_0 is the amount monomer added to the initiator, by measuring the amount of remaining initiator (I), r can be determined. This technique is very sensitive to the rate of stirring which should be maximized. For x eq. of I 2x eq. of monomer are considered and no correction is made for the fact that the second strained olefin is not available to the propagating species which reacted the first.

**Preparation of 8.** The procedure is identical to that described in the literature, except for purification. After distillation, the resulting isomeric mixture was found to be 89% exo-trans-exo, and the rest exo-trans-endo and endo-trans-endo isomers. Double recrystallization from toluene gave the major isomer in good yield which by ¹H NMR was found to be free of impurities. The ¹H NMR is the same as that reported previously.

**Typical preparation of polynorbornene star polymer.** A solution of norbornene (41 mg, 0.43 mmol, 25 eq.) in toluene (5.0 mL) was added quickly but dropwise over a period of 1-2 minutes to a solution of W(CHCMe₃)(NAr)(OCMe₃)₂ (10 mg, 0.017 mmol) in toluene (10.0 mL) and stirred and additional 5 minutes. To the resulting solution 8 (10 mg, 0.05 mmol, 3.1 eq.) in toluene (1.0 mL) was added dropwise and stirred for 10 minutes. The resulting solution was divided into two 8.0 ml portions, one of which was immediately quenched with excess benzaldehyde (10 μL, 0.094 mmol) and stirred for 30 min (final yield 22 mg, 84%, GPC trace shown in Figure 2b). To the second solution norbornene (20 mg, 0.21 mmol, 25 eq.) in toluene (2.0 mL) was added dropwise, stirred for 10 minutes, the polymerization was quenched with benzaldehyde (10 μL, 0.094 mmol) and stirred for 30
min (final yield 36 mg, 78 %, GPC trace shown in Figure 3). The polymers were isolated by precipitation into 100 ml of methanol and centrifugation and dried under vacuum for several hours. For both polymers the $^1$H and $^{13}$C NMR are identical to those of polynorbornene prepared with W(CH-t-Bu)(NAr)(O-t-Bu)$_2$, no signals derived from ring opened 8 were found.

**Typical reaction of 8 with initiator.** A solution of 8 (1.6 mg, $8.7 \times 10^{-6}$ mol, from a stock solution) in C$_6$D$_6$ (350 µL) was added under vigorous stirring to a solution of W(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ in C$_6$D$_6$ and stirred for an additional 5 minutes, placed inside an NMR tube and analyzed by $^1$H NMR. $^1$H NMR of living poly8 are extremely broad and can be found by baseline integration: δ 8.4-8.5 (H$_2$), 5.3-5.6 (olefinic), 2.1-2.6 (aliphatic), 1.0-1.1 (tert-butyl cap). The NMR tube was brought inside the glove box, the contents removed, and diluted with an additional 5 mL of toluene. Norbornene (82 mg, ) in toluene (5 mL) was added dropwise but fast to the above solution under vigorous stirring, stirred for 10 minutes, the reaction was terminated by addition of benzaldehyde (15 µL, 0.14 mmol) and stirred for 30 minutes. The solvent was removed in vacuo to yield a gummy yellow solid which was dissolved in a minimum amount of CH$_2$Cl$_2$, precipitated into MeOH (150 mL), filtered and placed under vacuum for several hours. Only signals from polynorbornene were observed in the $^1$H NMR spectrum, signals from ring opened 8 could not found, GPC trace is shown in Figure 3.

**Preparation of poly4-block-polynorbornene star polymer.** A solution of 2,3-dicarbomethoxynorbornadiene (106 mg, 0.509 mmol, 24.8 eq.) in THF (2.00 ml) was added to a rapidly stirring solution of Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (10 mg, 0.0205 mmol) in THF (2.00 ml) at RT and stirred for 20 minutes. The colour of the solution changed from yellow orange to dark orange and back to yellow orange over this period of time. Norbornene (48 mg, 0.051 mmol, 24.9 eq.) in THF was then added dropwise and stirred for 5 minutes.
The solution was divided into two 3 ml fractions, one of which was immediately quenched with excess benzaldehyde (10 μL, 0.094 mmol), stirred for 30 minutes, and saved as a standard for the block copolymer. GPC data for diblock: $M_n=118/0$, PDI=1.09. To the second solution 8 was added (13 mg, 6 eq.) in THF (2 mL), stirred for 5 minutes, and capped with benzaldehyde (10 μL) and stirred for 30 minutes (final yield 82 mg, 91 %). GPC data for star polymer: $M_n=98542$, PDI=1.16. Both fractions were purified by precipitation into 500 ml hexane, solids recovered by centrifugation and placed under vacuum for several hours.

**Preparation of poly9.** A solution of 2-carbonitrile norbornene (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (10 mg, 2.05 × 10$^{-5}$ mol) in THF (1.0 mL) and stirred for 15 minutes. Termination was carried out by addition of 15 μL of p-trimethylsilylbenzaldehyde (8.4 × 10$^{-5}$ mol). The polymer was purified by precipitation of the polymer from the reaction mixture into 250 ml hexane. Final product is obtained as a white-cream powded; yield 103 mg 85 %. $^1$H NMR (CDCl$_3$) δ 5.70, 5.55, 5.37, 5.32, 5.20, 3.0, 2.73, 2.55, 2.30, 2.18, 2.03, 1.75, 1.43, (1.004, 0.981, 0.963, 0.956 )C(CH$_3$)$_3$, (0.232, 0.217)Si(CH$_3$)$_3$; the spectrum is too broad for integration within polymer peaks, however integration of tert-butyl cap versus the olefinic signal is consistent with assigned stoichiometry as well as 1:1 against TMS cap; $^{13}$C NMR (CDCl$_3$) 135.3, 134.6, 132.3, 131.7, 129.7, 129.2, (CN), 120.9 (CN), 58.5, 44.8, 41.8, 41.2, 39.8, 39.2, 37.0, 36.9, 36.2, 33.8, 29.6 C(CH$_3$)$_3$, 1.3 Si(CH$_3$)$_3$; GPC: $M_n=24869$, PDI=1.05.

**Preparation of poly5 star and poly9 star poly6.** A solution of 2-carbonitrile norbornene (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (10 mg, 2.05 × 10$^{-5}$ mol) in THF (1.0 mL) and stirred for 15 minutes. To the resulting solution 8 (20 mg, 1.08 × 10$^{-4}$ mol, appx. 5 eq.) in THF (2.0 mL) was added dropwise but quickly and stirred for 15 minutes. The resulting solution was then
divided into two 2.0 mL portions. One of these was immediately quenched with p-trimethylsilylbenzaldehyde (15 μL, 8.4 \times 10^{-5} \text{ mol}) (final yield of isolated polymer 65 mg, 85 %). GPC data: M_w=259875, PDI=1.27; NMR data identical to poly9. To the second solution 2,3-bis(trifluoromethyl)norbornadiene (117 mg, 5.08 \times 10^{-4} \text{ moles}, 49.6 eq. relative to reactive alkylidene assuming that no termination occurs during timescale of the polymerization), stirred for 90 minutes, and quenched with p-trimethylsilylbenzaldehyde (final polymer yield 150 mg, 79 %). GPC data: M_w=536994, PDI=1.32. Both quenching reactions were stirred for 2 hours. Purification was carried out by precipitation of the reaction solution into 150 mL hexane, the resulting solids were isolated by centrifugation and placed under vacuum for several hours. NMR data are identical to a superposition of poly9 and poly6.
CHAPTER 4

Polymerization of Functionalized Norbornenes with
Mo(CHCMe_3)(NAr)(OCMe_3)_2.
INTRODUCTION

Polymers having a variety of pendant functional groups are finding use in a variety of applications such as supports for solid phase synthesis, precursors to conductive materials, polymer bound catalysts and polymer bound drugs to name only a few. The preparation of such materials using organometallic catalysts has been hampered in the past owing to the sensitivity of such complexes towards the heteroatoms in the monomers. The development of living ROMP catalysts which tolerate functionalities has opened up the possibilities of the preparation of such polymers, with greater control over the polymer structure than has traditionally been available via cationic and anionic polymerization systems.

This chapter reports a survey of functionalities which can be placed on the norbornene skeleton and do not interfere in the polymerization using Mo(CHCMe\(_3\))(NAr)(OCMe\(_3\))\(_2\) (Mo(CHCMe\(_3\))). Such a study was undertaken not only because the resulting organic polymers may have potentially interesting properties, but also because the interaction of functionalities with the metal center sometimes gives insight into the polymerization mechanism. A more subtle reward is the freedom that the presence such functionalities allows for the synthesis of monomers for particular applications (Chapter 5). Focus was placed on the analysis of end groups and the backbone of the polymers, either living or isolated, in order to delineate how the metal complex reacted in the different stages of the polymerization.

The polymerization of certain monomers was sought after in order to prepare materials with particular properties. For example exo,cis-2,3-dichloro-endo,cis-2,3-carbonatonorbornene (endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one) \(10\) has been polymerized using classical catalysts to yield a precursor for conjugated material (Equation 1) but with a polydispersity of 76. Attempts to polymerize 10 using
Mo(CHCMMe₃) were not successful and the reaction was studied in order to understand what factors were involved in this failure. Successful synthesis of precursors to conjugated polymers was achieved and those results are presented here.

RESULTS
An Overview of Functionalized Monomers Polymerized by Mo(CHCMMe₃)(NAr)(OCMe₃)₂.

Monomers which have been successfully polymerized with Mo(CHCMMe₃) are shown in Chart 1, along the polydispersities of the resulting polymers. A polymerization is termed successful if the monomer consumption is quantitative by ¹H NMR and the resulting polymer is soluble, can be isolated and has a narrow polydispersity (PDI). The conditions for all polymerizations are room temperature under a nitrogen atmosphere with a typical catalyst concentration of 0.005 to 0.01 M.

The choice of solvent is important and is illustrated by the successful polymerization of a mixture of exo and endo 2-carbonitrile norbornene (9) in THF and its failure in less polar aromatic solvents such as toluene or benzene. The same effect is observed in the case of
Chart 1. Monomers polymerized using Mo(CHCMe₃).

\[
\begin{array}{cccc}
\text{50}^{a}/1.07^{b} & \text{50/1.06} & \text{50/1.05} & \text{50/1.11} \\
\text{100/1.06} & \text{100/1.04} & \text{100/1.12} & \\
\text{200/1.04} & \text{200/1.04} & \text{200/1.22} & \\
\text{50/1.06} & \text{50/1.14} & \text{50/1.13} & \text{50/1.12} \\
\text{100/1.07} & \text{100/1.19} & \text{100/1.11} & \text{100/1.07} \\
\text{200/1.07} & & & \\
\text{50/1.05} & \text{100/1.07} & \text{100/1.06} & \text{100/1.16}^{c} \\
\end{array}
\]

\(^{a}\)Equivalents of monomer added. \(^{b}\)Polydispersity index. \(^{c}\)Bimodal GPC trace. For reaction conditions refer to experimental section.
exo,exo-2,3-norbornene diacetate for which the polymerization of 200 equivalents yields a polymer with PDI = 1.09 in THF and 2.17 in chlorobenzene (vide infra).

Each propagating alkylidene arising from these monomers has a characteristic NMR signal for H_α which probably depends on subtle changes in electronic and steric factors near the metal center. For example the alkylidene region of the ^1H NMR of living poly9 is shown in Figure 1. Three main envelopes of resonances are observed and can be rationalized in terms of the three main isomers resulting from the ring opening of this unsymmetric monomer (Equation 2). The resonance at 11.53 ppm is assigned to the alkylidene signal which bears

\[
\text{Mo(CHCMe}_3\text{)} + \begin{array}{c}
\text{CN} \\
(9)
\end{array} \xrightarrow{\text{THF}} 
\]

more resemblance to living polynorbornene (11.53 ppm) while the two others at 11.63 and 11.75 ppm are assigned to the propagating alkylidenes in which the carbonitrile group is γ to the metal center, which in turn may be exo or endo in the monomer (the same analysis is true for the tert-butyl cap of the polymer which has previously been discussed in Chapter 3). The complexity within each envelope may arise from sensitivity to the orientation of the second monomer away from the metal as well as from the possible presence of rotamers. The utility of the propagating alkylidene resonances for the calculation of the ratio of the rate of propagation (k_p) to the rate of initiation (k_i) has already been discussed in Chapters 2 and 3.
Figure 1. 500 MHz $^1$H NMR spectrum ($d^6$-THF) in the alkyldiene region of a living 20 mer of poly9.
**Effect of Regiochemistry.**

If certain functionalities are desired in the target polymer one will have to consider the effect of the location where these are placed on the norbornene skeleton. In general it is favorable to place functionalities on the 5 and 6 positions where intramolecular interaction or deactivation is least likely to occur since they are furthest away from the metal center. The 7 position appears to be less innocent. Placing the functionalities in the exo position favours the polymerization, in accordance with empirical observations made with classical systems. For example the exo isomer of cis-(N-phenyl)-5-norbornene-2,3-dicarboximide can be polymerized (PDI = 1.07 (100 equivalents), Equation 3) while the corresponding endo isomer fails to polymerize.

\[ \text{Mo(CHCMMe}_3) + n \text{ exo} \rightarrow \text{polymer} \]  

\[ (3) \]

Comparison of the PDIs of the polymers from cis-exo (PDI = 1.07, 100 equiv)\textsuperscript{82}, cis-endo (PDI = 1.12, 100 equiv) and trans 2,3-dicarbomethoxy-norbornene (PDI = 1.04, 100 equiv) again shows the exo preference although the narrower dispersities and more favorable ratio of \( k_p \) to \( k_i \) for the trans isomer was unexpected. This is the first successful report of the polymerization of the cis-exo and trans dicarbomethoxy norbornenes.

The most striking feature of the \(^1\text{H} \) NMR spectrum of poly(2,3-cis,exo-dicarbomethoxynorbornene) is the similarity to the spectra of 2-3 disubstituted polynorbornadienes which are polymerized in a stereoregular fashion. Propagation has an experimentally observed trans to cis ratio of approximately 95:5, which does not change on a
living polymer after days of ring opening. Analysis of the $^1$H NMR spectrum of an oligomer made by the addition of 19.7 equivalents to Mo(CHCMe$_3$) followed by capping with benzaldehyde yields information regarding the stereospecificity of the individual polymerization steps (Figure 2). The first insertion product occurs with formation of trans olefin exclusively (the error in these determinations by NMR spectroscopy can be estimated at 1-2 %) characterized by two resonances at 5.29 ppm (dd, $J_{HH}$ = 15 Hz and 7 Hz) and 5.53 ppm (d, $J_{HH}$ = 15 Hz). Finally the termination reaction, "quenching" with benzaldehyde, is also all trans with olefinic resonances at 6.02 ppm (dd, $J_{HH}$ = 16 Hz and 7.5 Hz) and 6.42 ppm (d, $J_{HH}$ = 16 Hz). Integration of the four olefinic protons on the two terminal monomers against the tert-butyl cap at 0.97 ppm yields approximately a 9:1:1:1:1 ratio, consistent with the proposed formulation of the polymer. If the polymerization is terminated by addition of pivaldehyde then only the resonances due to the $\alpha$ (5.53 ppm) and $\beta$ (5.28 ppm) olefinic protons near the tert-butyl end group are observed. The assignment of the $^1$H and $^{13}$C NMR spectra can be achieved by a combination of homonuclear and heteronuclear correlation experiments. Assignment of resonances from H$_2$, H$_3$ and H$_4$ along with C$_2$, C$_3$ and C$_4$ is ambiguous on chemical shift arguments alone. H$_2$ is assigned to the resonance at 2.93 ppm since it couples with H$_1$ (5.37 ppm). C$_2$ (39.1 ppm) is split into a triplet in a gated $^{13}$C experiment which allows the assignment of H$_4$ and H$_4'$ ($J_{C2H4} = J_{C2H4'}$) to the resonances at 1.25 and 2.06 ppm since both are shown to be coupled in a HETCOR ($^{13}$C-$^1$H correlation) experiment to C$_2$. The same experiment shows that the resonance at 45.1 ppm is coupled to H$_2$ and therefore belongs to C$_3$. By elimination, C$_4$ (52.4 ppm) and H$_3$ (2.79 ppm) can be assigned.
Figure 2. 500 MHz $^1$H NMR spectrum (CDCl$_3$, 40 °C) in the olefinic region of the organic products resulting from the reaction of appx 20 equiv. of 2,3-cis,exo-dicarbomethoxy norbornene with Mo(CHCMe$_2$) followed by benzaldehyde quench.
The cis-endo isomer does not show such propagation selectivity and the polymer olefin resonances are too broad to distinguish the resonances arising from initiation or termination steps.

For 2,3-trans-dicarbomethoxynorbornene, a monomer of C₃ symmetry, one must also consider the regiochemistry of monomer addition, i.e. head-to-tail, tail-to-tail or head-to-head sequences. The ¹H and ¹³C NMR spectra of the isolated polymers are broad and complex from which little information can be obtained and are indicative of a complex and random microstructure. The ¹H NMR resonances in the alkylidene region are shown in Figure 3. They are also complex and are divided into two main envelopes. By comparison to the living cis-exo and cis-endo homopolymer the two main envelopes can be assigned to isomers where the carbomethoxy functionality on the γ carbon is either exo (11.52 ppm) or endo (11.62 ppm) (see Discussion). Two resonances for the tert-butyl cap are observed at 0.964 and 0.935 ppm, corresponding to transoid or cisoid configurations of the carbomethoxy group relative to the olefinic bond. Addition of 10 equivalents norbornene (NBE) to the above living poly(2,3-trans-dicarbomethoxynorbornene) consumes the norbornene and the alkylidene resonances in the ¹H NMR spectrum are simplified to a doublet typical of living norbornene at 11.53 ppm. The two resonances for the tert-butyl group are unchanged and furthermore, these solutions are stable for days with the only alkylidene resonance observed being the one of living polynorbornene, i.e. no secondary metathesis has occurred with the polymer chain ("back biting").
Figure 3. 500 MHz $^1$H NMR spectrum (C$_6$D$_6$) in the alkyldiene region of a living 20 mer of poly(2,3-trans-dicarbomethoxynorbornene).
Reversible Formation of a Square Pyramidal Molybdocylle with exo,cis-2,3-dichloro-endo,cis-2,3-carbonatonorbornene.

Reaction of 10 equivalents of exo,cis-2,3-dichloro-endo,cis-2,3-carbonatonorbornene (10) with a solution of Mo(CHCMe3) in C6D6 at room temperature for approximately 60 min results in the formation of oligomers and a new alkylidene, but unreacted monomer remains. Complete consumption of the monomer was observed if the reaction is allowed to proceed for 24 h at room temperature (Equation 4). Although the total intensity of the alkylidene signals in

\[
\text{Mo(CHCMe}_3\text{)} + \text{Cl} \text{Cl} \text{O} \text{O} \text{O} \xrightarrow{\text{Mo}} \text{Cl} \text{Cl} \text{O} \text{O} \text{O} \text{Me}_3
\]

(10)

the $^1$H NMR spectrum appears to have decreased by a small amount relative to an internal standard, the new alkylidene signal for the propagating alkylidenes is observed at 11.57 ppm as a broad doublet. Attempts to polymerize 100 equivalents of 10 in toluene in the standard fashion failed and only a small amount of oligomers was obtained as well as unreacted monomer. Increasing the reaction time at a catalyst concentration of 0.02 M up to 24 hours at room temperature gave similar results.

Rate studies by $^1$H NMR showed that the polymerization of 10 at room temperature was very slow. Approximately two equivalents of 10 were consumed over a 2 hour period ([Mo(CHCMe3)] = 0.02 M, 4 equivalents 10, RT). During one of the low temperature investigations (T = -30 °C) it was observed that the intensities of the neopentylidene and the olefin signals decreased without the appearance of any propagating alkylidenes. Concurrently, broad resonances due to a new species could be observed appearing (see Experimental) which
resembled those of previously characterized square pyramidal tungstacyclobutane complexes. This new compound is presumed to be a square pyramidal molybdatecyle (11) resulting from the addition of 10 to Mo(CHCMe₃). Complete conversion of Mo(CHCMe₃) and 10 to 11 was not achieved at -30 °C.

(11)

In order to isolate the metallacycle Mo(CHCMe₃) was added to 10 at -30°C and stored at -40°C for 2-3 days from which bright red crystals formed. This material was dissolved in d⁸-toluene and spectra taken at different temperatures. At -45 °C the metallacycle is observed along with some Mo(CHCMe₃) and 10, the ratio of 11 to Mo(CHCMe₃) is 4:1 while that of Mo(CHCMe₃) to 10 is 1:1 and only trace amounts of the propagating alkyldene (the product of the breakup of 11 in a productive fashion) could be observed (see Table 1). As the temperature is raised the amount of propagating alkyldene increases as well as the amount of Mo(CHCMe₃) or 10 relative to the metallacycle. At 0 °C the ratio of metallacycle to Mo(CHCMe₃) has decreased to 2:1. Finally at 25 °C only traces of 11 are observed and the monomer is regenerated to give approximately 60 % of Mo(CHCMe₃). These results indicate that the metallacycle is unstable at 25 °C but it "decomposes" in two different ways, it can ring open to yield a new propagating alkyldene or degeneratively to yield the original reactants (Equation 5). At low temperatures an equilibrium exists between metallacycle and starting alkyldene and olefin which can be estimated at K = k₁/k₋₁ = 4 at -45 °C while formation of
Table 1. Distribution of products as a function of temperature after dissolving 11 in d⁸-toluene.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Mo(CHCMe₃)</th>
<th>11</th>
<th>10</th>
<th>MIPᵃ</th>
<th>SIPᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0.9</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0.1</td>
<td>0.9</td>
<td>0.3</td>
<td>0.06</td>
</tr>
</tbody>
</table>

ᵃAlkylidene due to first insertion product. ᵇSecond insertion product. Equilibration time at each temperature of 20 minutes.
new alkylidene is negligible ($k_2$ is small). At 0 °C $K$ is approximately 2. Finally at 25 °C $K$ is small and the limit for $k_2$ is set by the polymerization rate of 10.

![Chemical reaction diagram]

**Polymer Reactivity.**

Polymerization of exo-cis-2,3-norbornenediacetate (12) proceeds quantitatively (Equation 6). The polydisperisities of the resulting polymers depend on the choice of

![Polymerization reaction diagram]
solvent for the polymerization reaction. Best results are obtained using THF where, for a 100mer, the resulting polydispersity is 1.19. The use of aromatic solvents (toluene, chlorobenzene or benzene) tends to give polymers with broader polydispersities (1.3-2), with incomplete monomer consumption (85%). The IR spectrum of poly12 shows the characteristic absorption band of the ester carbonyl group at 1740 cm\(^{-1}\) which serves as a probe for the reactivity of the polymer (vide infra). From the \(^1\)H NMR spectrum the trans to cis ratio is determined to be 60:40 by integration of the olefinic and methine protons.

Once isolated poly12 is a white powder which is methanol insoluble and can be cast into flexible transparent films which allowed the examination of the mechanical and thermal properties of the polymer. The value for the tensile strength at break point for this film is 370 kg/cm\(^2\), which is comparable to that of acrylonitrile-butadiene-styrene (ABS) resin (380 kg/cm\(^2\)).\(^{83}\) This polymer was found to be amorphous by DSC analysis which displayed a glass transition temperature (Tg) at 102 °C with no melting point and is relatively stable up to 300 °C as determined by TGA (thermogravimetric analysis).

The TGA thermogram curve shows a two stage degradation pattern (Figure 4). The first degradation stage begins at approximately 300 °C and is attributed to the loss of acetic acid within the polymer backbone (Equation 7). The second stage at higher temperatures is attributed to degradation of the polymer chains. Isothermal pyrolysis was carried out in order to quantify the amount of mass lost at a fixed temperature. At 300 °C for 2 hrs the loss was 55.7 % while heating at 350 °C for 1 hr resulted in 60.9 % loss. This is consistent with the loss of two equivalents of acetic acid from the backbone which would theoretically correspond
Figure 4. TGA analysis of poly12.
to a 57.2% mass loss. In order to analyze the pyrolysis product a strip of poly12 was heated at 300 °C for two hours in a temperature programmable furnace to yield a red-black insoluble film. The IR spectrum of this material shows that the carbonyl absorption characteristic of the precursor polymer has decreased but is still observable and the 1600 cm⁻¹ band due to olefinic linkages increased. We conclude that pyrolysis is incomplete under these conditions with residual ester groups still present in the polymer. The conductivity and the dielectric constant of the materials are the subject of ongoing investigations by other members of the group.84 This unsaturated polymer is unstable in the presence of air as demonstrated by the appearance of an absorption band at 1730 cm⁻¹ in the IR spectrum of samples left exposed to air, due to an undetermined oxidation process.

Hydrolysis of poly12 by NaOMe in MeOH/THF can be carried out to give a newly functionalized polydiol in almost quantitative yield (Equation 8). The alcohol functionality

\[ \text{OAc} \quad \text{OAc} \quad \xrightarrow{\text{NaOMe}} \quad \text{MeOH/THF} \quad \text{OH} \quad \text{OH} \]  

(8)

is an example of one that is likely to be incompatible with the catalyst when present in the monomer but one that can be incorporated readily into a polymer backbone. The polydiol is insoluble in standard solvents (THF, CHCl₃, aromatics, MeOH or H₂O) but can be analyzed in acidic chloroform (CF₃CO₂H/CDCl₃). The IR spectrum of the solid polymer displays a strong absorption in the region between 3100 and 3500 cm⁻¹ due to the presence of the hydroxy groups and the absorption at 1740 cm⁻¹ in the parent polymer is completely absent. The thermal behavior of this polymer was studied and no glass transition temperature was found by DSC up to 220 °C, at which temperature some degradation could be detected. The TGA trace displays a two stage degradation curve the first of which is attributed to a
dehydration to yield a conjugated polymer similar to the one obtained by pyrolyzing poly12 (Equation 9).

\[
\text{OH} \quad \text{OH}
\xrightarrow{T=300 \, ^\circ\text{C}} \quad -2 \text{H}_2\text{O}
\]

The exo-syn-5-norbornene-2,7-diol diacetate (13) isomer behaves similarly to 12 and serves as a good example for the comparison of the resulting changes in the material from a permutation in the location of the functionalities. The monomer is readily synthesized by a one step reaction of norbornadiene with lead acetate in good yield and can be quantitatively polymerized (Equation 10). The resulting polymers are purified by precipitation into methanol and can be cast into flexible, transparent thin films. The tensile strength at break point for these films is 420 Kgr/cm², higher than that found for ABS resins. The DSC analysis indicates that the material is amorphous with a Tg at 110 °C and is stable up to 300 °C. The TGA thermogram has two prominent processes and resembles that of poly11, the first degradation is attributed to the loss of acetic acid from the polymer backbone (Equation 11). Of the two
isomers that are expected to form structure A is expected to be more favorable due to formation of cross conjugation. Isothermal pyrolysis mass loss is consistent with the proposed loss of two equivalents of acetic acid in each monomer unit. The resulting materials are insoluble, brittle and oxidize readily in air.

The hydrolysis of poly13 is carried out in a similar fashion to that of poly11 to yield poly(exo-syn-5-norbornene-2,7-diol) quantitatively (Equation 12). Infrared spectroscopy supports the formation of the polydiol with the expected broad hydroxy absorption band (3100-3500 cm⁻¹), vinyl stretch (1590 cm⁻¹) and complete absence of the the carbonyl absorption. The ¹H NMR spectrum was taken in a 1:1 mixture of CF₃CO₂H:CDCl₃ due to solubility restrictions but it clearly shows the hydroxy protons as a broad signal at δ 2.8 ppm. This polymer also displays the remarkable property of being soluble in aqueous acidic media, the first example of such a material obtained by ROMP technology. The TGA thermogram is similar to that of the cis-exo polydiol with a two stage degradation pattern, with the first stage attributed to the loss of two equivalents of water from the polymer backbone (Equation 13). This dehydration stage begins at 270 °C, and isothermal pyrolysis at 270°C for 2 hours
shows an actual mass loss of 25.8% (theoretical mass loss for dehydration: 28.6%). Isomer A is again expected to be favoured.

A different route to these polydiols begins with the polymerization of exo-cis-5-norbornene-2,3-diol di-O-isopropylidene (14) followed by hydrolysis of the acetanide functionality. The polymerization step is straightforward in THF to yield the expected poly14 quantitatively (Equation 14). $^1$H NMR spectroscopy reveals 60% trans olefinic linkages in the polymer chain by integration of the vinyl and methine protons while analysis of the thermal behavior reveals the Tg at 108 °C and decomposition starting at 300 °C.

**Block Copolymers**

Analysis by $^1$H NMR shows that the addition of 15 equivalents of norbornene (NBE) to a solution of living poly9 consumes the norbornene and the complex set of alkylidene signals characteristic of poly9 (Figure 1) is replaced by the doublet characteristic of Mo based living polyNBE. This implies that poly9 initiates the polymerization of norbornene (Equation
15) the result of which is the block copolymerization of the two monomers into a single polymer chain. Reversing the order of monomer addition yields consistent results, i.e. polymerization of 9 by living polyNBE replaces the alkylidene doublet of polyNBE and yields the signals of poly9.

This reactivity, followed by quenching with an appropriate aldehyde, can be exploited to prepare block copolymers (x = y = 100). The order of addition of the two monomers is not important in this case once the consumption of the first monomer added is complete. The GPC trace of the resulting polymer is shown in Figure 5, similar results are obtained when the order of monomer addition is reversed. Note the narrow polydispersity (PDI = 1.05) and symmetric shape of the peak is indicative of a process in which there is no chain transfer or termination in the timescale of the polymerization.

The spectral properties of the block copolymer are essentially a superimposition of those of polyNBE and pcly9 homopolymers. The olefinic region of the $^{13}$C NMR spectra of both polyNBE-block-poly9 and poly9 is shown in Figure 6. The complexity of the olefinic signals in poly9 can be accounted for by the many types of isomers possible for this material (head-head/head-tail/tail-tail, cis/trans and exo/endo), these signals are broad since they are likely to be sensitive to the stereochemistry of the monomers on both sides of the olefinic bond.
Figure 5. GPC trace of poly-1-block-polybornene.
Figure 6. 125 MHz $^{13}$C NMR spectra (CDCl$_3$) in the olefinic region of (a) poly9; (b) poly9-block-polynorbornene.
In the block copolymer the sharp signals at 133.8 (cis olefin) and 132.9 (trans olefin) ppm are due to the polyNBE block.

The stress-strain responses for polyNBE-\textit{block}-poly9 and poly9 are shown in Figure 7. The behavior of poly9 (Tg = 123 °C) is typical of what one would expect for either a glassy polymer or a semicrystalline polymer at a temperature below Tg with catastrophic collapse occurring at 7.9 % strain. PolyNBE-\textit{block}-poly9 has a dramatically different behavior (Figure 7a) with the break point occurring at 54.5 % strain (see Discussion).

DISCUSSION

The variety of functionalities present in Chart 1 demonstrates the ability of Mo(CHCMe₃) to initiate the polymerization of norbornenes with a variety of heteroatoms present. The narrow dispersities indicate that a high degree of control has been achieved. For example the preparation of a 200 mer of poly(2,3-trans-dicarbomethoxynorbornene) indicates that the polymerization proceeds without significant termination even in the presence of 400 equivalents of ester functionality. The solvent plays an important role in expanding this repertoire of functionalities. In particular the failure to polymerize 2-carbonitrilenorbornene in noncoordinating solvents and its polymerization using THF is noteworthy. The intimate role of the solvent which seems to determine this outcome remains to be elucidated. THF may successfully compete with the functionality for the metal and thereby inhibit a reaction between it and the metal. Another possibility is a bulk solvent effect that keeps the polar groups pointed away from the metal and into the solution. A third possibility is that THF is intimately involved in opening the intermediate metallacycles formed in these reactions.

An array of different bulk properties can be expected from these different polymers and are potentially quite interesting. For example the films obtained from the acetate derivatives are particularly strong and transparent, a combination of properties which is quite desirable. A thorough investigation of these properties was not pursued but may be a profitable endeavor. It is clear that this tolerance allows one to build monomers which can be transformed into
Figure 7. Stress-strain curves (10 mm/min) of (a) poly9; (b) poly9-block-polynorbornene.
materials with specific properties as reported in Chapter 6 (polymers tailored for the modification of electrodes) without the problem of catalyst deactivation.

Because of the variety of isomers available and the different electronic properties of the functionalities a variety of different alkylidene signals can be expected when studied by $^1$H NMR spectroscopy when exploring new monomers. Since the two envelopes of signals for living poly(trans-2,3-dicarbomethoxynorbornene) integrate differently they are interesting since they point out some type of energy difference. The fine structure within the main groupings is again attributed to sensitivity to the next monomer, presence of rotamers as well as diastereomeric pairs. These signals, unlike rotamers, cannot interconvert and therefore are not due to the thermodynamic equilibrium of the two species. This difference then can be accounted for by either an intrinsic alkylidene reactivity difference or a preferred orientation of monomer insertion. The minor envelope centered at 11.65 ppm is assigned to the alkylidene proton which has the ester group endo (or cisoid, Equation 16) relative to the alkylidene carbon, because of its similarity to the resonance of living poly(2,3-cis,endo-dicarbomethoxynorbornene). The two tert-butyl end group signals are also in a skewed ratio,
the major (60%) at 0.964 ppm is tentatively assigned to the one with the carbomethoxy group exo (in the cis-exo homopolymer the tert-butyl group resonates at 0.975 ppm and in cis-endo homopolymer at 0.948 ppm) while the minor resonance at 0.935 has an endo (transoid) carbomethoxy group. This last ratio is due exclusively to a preference in the mode of insertion of the first monomer. It is important to note that a preference for a cisoid tert-butyl group leads to a preference for transoid alkylidene since the carbomethoxy groups are mutually trans. Therefore one would expect to see more of the transoid alkylidene, the fact that this is not the case suggests that after the first insertion the ratio of the two alkylidenes is determined by their relative reactivity. Consistent with this hypothesis is the fact that the cis-exo monomer is polymerized more stereoselectively than the endo isomer, as one would expect for a less reactive and therefore more selective alkylidene.

The failure to polymerize 10 is attributed to the slow rate of its reaction with the alkylidene complex, either Mo(CHCMe3) or its propagating alkylidene. In this case the rate of catalyst deactivation, most likely with the carbonyl bond in the carbonate functionality, competes effectively with the rate of polymerization. Note that the alkylidene complexes appear to tolerate the carbonate functionality for hours, a result that suggests that if it were to be present in a more reactive monomer (such as 10 but without the bulky and electron withdrawing chlorines) it could potentially be placed in a polymer backbone.

It is noteworthy that liberation of 10 from 11 represents the first example where the formation of a metallacyclobutane ring is reversible for a norbornene. This situation is likely to be rare and probably encountered when the monomer is bulky and relatively electron poor. The rate determining step for the ring opening of 10 to propagating alkylidene is difficult to determine and likely to be a function of temperature. The formation of 11 at -30 °C indicates that it is the rate of metallacycle breakup (k2 in Equation 5) which is slow. At higher temperatures this need not be the case, as is expected on consideration of entropy effects, k1 is likely to decrease relative to k-1 and k2. This is reflected by the decrease of K = k1/k-1 upon warming from -45 °C to 0°C, temperatures where k2 is negligible. A complicated system
which is dependant on concentration and temperature effects is therefore expected and encountered in cases where the rate of polymerization is slow.

Thermal treatment of polymers to yield conjugated segments with the loss of small volatile molecules is a fairly mature subject in polymer chemistry. Poly(vinyl acetate), poly(vinyl chloride) and poly(vinyl alcohol) lose acetic acid, HCl and water respectively to yield conjugated polyene sequences when subjected to high temperatures. The pyrolysis of poly12, poly13 and their diol derivatives are the first reports of such reactivity for polymers prepared by metathesis reactions. This is probably due to the previous lack of available catalyst systems for the preparation of such highly functionalized polymers. Similar reaction conditions are required for elimination from the ROMP polymers (poly(vinyl acetate) yields polyenes when heated to 300°C) suggesting that the mechanisms might be related. Further studies are required to determine the extent of conjugation and the dielectric or conduction properties of the resulting conjugated polymers.

Transformation of poly12, poly13, and poly14 to the polyl derivatives is interesting because of the unusual solubility properties of these materials. Poly(exo-5-hydroxynorbornene) has been prepared via the polymerization of an organoborane derivative of norbornene using classical catalysts and alkaline oxidation of the resulting polymer. This latter polymer displays bulk characteristics similar to the ones reported here but the polydispersity was 2.3 and only 65 % of the monomer was consumed. More importantly an attempt to dehydrate the polymer was unsuccessful and it was attributed to the unfavorable introduction of ring strain. It appears that if two hydroxy groups are present the dehydration occurs.

The change in mechanical properties observed when poly9 is block copolymerized with norbornene is a typical example of the control over the physical properties possible when the primary structure of the polymer can be dictated. The two parameters involved in the description of mechanical behavior are stress and strain. Stress is the force applied on a material divided by the cross-sectional area and strain is the change in length divided by the
original length. The small strain for poly9 indicates that the material is brittle and is typical of a
glassy polymer (no melting temperature was observed by DSC analysis). When this material is
block copolymerized with norbornene (an elastomer) the stress at maximum load is adequately
maintained (and under these conditions occurs at approximately the same strain) but the
breakpoint of the material occurs at a much larger strain. It should be noted that the production
of polymers which are both strong (ability to maintain a high load) and tough (a large amount
of energy is absorbed upon fracture) is recognized as a critical step for plastics becoming more
widely accepted as engineering materials. It is not known at this point the mechanism by
which the norbornene block toughens the material. Also it is unclear whether higher molecular
weight poly9 would exhibit stronger behavior.

EXPERIMENTAL SECTION

General Details. All polymerizations were performed under a nitrogen atmosphere
in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran
was predried over calcium chloride and distilled from sodium benzophenone ketyl under
nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored
over sodium potassium alloy. All deuterated NMR solvents were passed through a column of
activated alumina. Norbornene was doubly distilled from molten sodium. Commercially
available 2-carbonitrile norbornene (60:40 mixture of exo and endo isomers) was distilled
under nitrogen, passed through a column of activated alumina and stored under nitrogen.
Commercially available aldehydes were purified by distillation under nitrogen. The monomers
exo-cis-2,3-dichloro-endocis-2,3-carbonatonorbornene, exo-cis-2,3-norbornenediaacetate,91
exo-syn-2,7-norbornenediacetate92 and exo-cis-2,3-norbornenediol di-O-isopropylidene93
were prepared using literature procedures. Trans-2,3-dicarbomethoxynorbornadiene was
prepared by the trivial reaction of freshly cracked cyclopentadiene and dimethylfumarate.

NMR data are listed in parts per million downfield from TMS for both proton and
carbon. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling
constants usually are not listed. Gel Permeation Chromatographic (GPC) analysis were carried out at room temperature employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1-0.3 % w/v in dichloromethane which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03 × 10^6 MW. Thermal analysis (TGA) was done on a Perkin Elmer TGS-2 thermogravimetric analyzer. Differential scanning calorimetry was performed on a Perkin-Elmer instrument at a heating rate of 30 °C/min. Tensile strengths of polymer films (0.35 mm × 3 mm: thickness × width) were measured by use of an Instron 4201 at an extension rate of 10 mm/min.

**Typical Polymerization of exo,cis-2,3-dicarbomethoxynorbornene.** A solution of the monomer (431 mg, 2.05 mmol, 100 equiv) in toluene (10 mL) was added dropwise but quickly to a rapidly stirring solution of Mo(CHMe3)(NR)(OCMe3)2 (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1-2 minutes. The solution was allowed to stir for an additional 20-30 minutes, quenched by addition of excess benzaldehyde (10 μL, appx 0.1 mmol) (or pivaldehyde) and stirred for an additional 20 minutes. The solution was brought out of the box and added dropwise to 500 mL of hexane under vigorous stirring, the resulting precipitate was isolated by centrifugation, washed with hexane or pentane and placed under vacuum overnight. The final appearance of the product was a white powder (380 mg, 88%) soluble in a variety of solvents (toluene, CH2Cl2, benzene): 1H NMR (CDCl3) δ 5.37 (b, 2, H1), 3.62 (s, 6, CO2Me), 2.93 (b, 2, H2), 2.79 (b, 2, H3), 2.06 (b, 1, H4 or H4'), 1.25 (b, 1, H4 or H4'), 0.96 (s, CCMe3 end group); 13C NMR δ 173.1 (CO2Me), 132.0 (C1, d(1H)), 52.4 (C4, d(1H)), 51.7 (CO2Me, q(1H)), 45.1 (C3, d(1H)), 39.1 (C2, t(1H, JH4C = JH4'C), 29.5 (CMe3 end group, q(1H)). GPC data are found in Chart 1.
Living oligomers were prepared by addition of the monomer (65 mg, 0.31 mmol, 15 equiv) in C₆D₆ (300 μL) to a rapidly stirring solution of Mo(CHMe₃)(NAr)(OCMe₃)₂ (10 mg, 0.0205 mmol) in C₆D₆; ¹H NMR δ 11.51 and 11.45 (H₂, J_HαHβ = 7 Hz), 4.61 (H₂, J_HαHβ = 7 Hz), 3.97 (CHMe₂), resonances due to the oligomer protons are similar to those of the polymer, other resonances due to the ligands on the metal centre could not be assigned due to overlap with oligomer signals.

**Typical Polymerization of trans-2,3-dicarbomethoxynorbornene.** A solution of the monomer (431 mg, 2.05 mmol, 100 equiv) in toluene (10 mL) was added dropwise but quickly to a rapidly stirring solution of Mo(CHMe₃)(NAr)(OCMe₃)₂ (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1-2 minutes. The solution was allowed to stir for an additional 20-30 minutes, quenched by addition of excess benzaldehyde (10 μL, appx 0.1 mmol) (or pivaldehyde) and stirred for an additional 20 minutes. The solution was brought out of the box and added dropwise to 500 mL of hexane under vigorous stirring, the resulting precipitate was isolated by centrifugation, washed with hexane or pentane and placed under vacuum overnight. The polymer was obtained as white flakes (405 mg, 94%); ¹H NMR δ (CDCl₃, 500 MHz) 5.08 and 5.25 (b, 2, H₁ and Hʻ₁), 3.43 (s, 3, CO₂Me), 3.40 (s, 3, CO₂Me), 3.00 (b, 1, H₂ or H₂ʻ or H₃ or H₃ʻ), 2.73 (b, 2, H₂ or H₂ʻ or H₃ or H₃ʻ), 2.46 (b, 1, H₂ or H₂ʻ or H₃ or H₃ʻ), 1.76 (b, 1, H₄ or H₄ʻ), 1.27 (b, 1, H₄ or H₄ʻ), 0.935 and 0.962 (s, CMe₃ end group); ¹³C 174.3 (CO₂Me), 173.5 (CO₂Me), 132.2 (C₁), 131.2 (C₁), 129-131.2 (C₁), 51-53 (C₄ and CO₂Me), 44.5 (C₃ or C₃ʻ), 46.7 (C₃ or C₃ʻ), 29.5 (CMe₃ end group), all resonances are extremely broad consistent with the many stereochemical configurations possible. GPC data are found in Chart 1.
Living oligomers were prepared by addition of the monomer (65 mg, 0.31 mmol, 15 equiv) in C₆D₆ (300 µL) to a rapidly stirring solution of Mo(CHMe₃)(NAr)(OCMe₃)₂ (10 mg, 0.0205 mmol) in C₆D₆. Oligomer resonances are similar to the polymer, for signals due to H₆ see Figure 3.

**Polymerization of exo-cis-(N-phenyl)-5-norbornene-2,3-dicarboximide.**
A solution of the monomer (239 mg, 1.03 mmol, 50 equiv) in THF (15 mL) was added dropwise over a period of 2-3 minutes to a rapidly stirring solution of Mo(CHCMe₃) (10 mg, × 10⁻⁵ mol) in THF (4 mL) and stirred an additional 30 minutes. The polymer was quenched with benzaldehyde and isolated as described above. The product was obtained as a gummy solid (213 mg, 90 %): ¹H NMR δ (CDCl₃) 6.9-7.2 (b, 5, HAr), 5.55 (b, 2, CH=CH), 2.87 (b, 2, CHCO or allylic CH), 2.55 (b, 2, CHCO or allylic CH), 1.90 (b, 1, CHH), 1.41 (B, 1, CHH). GPC data: Mn = 21000, PDI = 1.06.

**Polymerization of endo-cis(N-pentafluorophenyl)-5-norbornene-2,3-dicarboximide.** Prepared as described above for the protio analogue using 329 mg of monomer. The product was obtained as a white powder: ¹H NMR δ 5.61 (b, 2, CH=CH), 2.6-2.8 (b, 4, CHO and allylic CH), 1.82 (b, 1, CHH), 1.30 (b, 1, CHH).
Determination of the rate of consumption of 10 by Mo(CHCMe$_3$). A solution of 10 (18 mg, 8.2 \times 10^{-5} \text{ mol}) in $d^8$-toluene (300 \mu L) was added to a solution of Mo(CHCMe$_3$) (10 mg, 2 \times 10^{-5} \text{ mol}) and mesitylene (5 mg, 4.2 \times 10^{-5} \text{ mol}) in $d^8$-toluene (350 \mu L) quickly mixed and immediately frozen until kinetic measurements. Disappearance of the monomer was monitored by following the decrease of its olefinic signals versus the internal standard. After a period of 120 minutes 2 equivalents were consumed, this includes consumption by initiation and propagation processes.

Preparation of 11 and observation of its decomposition. A solution of 10 (68 mg, 0.31 mmol) in ether (2 mL, -30 °C) was layered over a solution of Mo(CHCMe$_3$) (150 mg, 0.31 mmol) in pentane (2.0 mL, -30 °C) and immediately stored at -40 °C for 48 hours. The resulting bright red crystals (98 mg, 45%) were isolated by decanting the solution and briefly placed under vacuum. Analysis by $^1$H NMR was done by dissolving 20 mg of the product in $d^8$-toluene (800 \mu L, [11] = 3.5 \times 10^{-5} \text{ M}) at low temperature: $^1$H NMR (-45 °C) 7.02 (m, 3, H$_{Ar}$), 4.02 (b, 1, CHMe$_2$), 3.83 (b, 1, CHMe$_2$), 3.55 (s, 1, bridgehead H), 3.41 (dd, 1, H$_\beta$, J$_{H\alpha'H\beta}$ = 8, J$_{H\alpha'H\beta}$ = 8), 2.62 (s, 1, bridgehead H), 1.85 (d, 1, CHH bridgehead (H$_\gamma$)), 1.68 (d, 1, CHH bridgehead (H$_\gamma$)), 1.32 (b, 12, CHMe$_2$), 1.29 (s, 9, OCM$_{Me_3}$), 1.17 (s, 9, OCM$_{Me_3}$), 0.92 (s, 9, CHCMe$_3$). GPC data are found in Chart 1.

Typical polymerization of exo-cis-2,3-norbornenediacetate (12). A solution of the monomer (12) (431 mg, 2.05 mmol) in THF (10 mL) was added dropwise but quickly to a vigorously stirring solution of Mo(CHCMe$_3$) (10 mg, 2 \times 10^{-5} \text{ mol}) in THF (5 mL) over a period of 1-2 minutes. The resulting solution was allowed to stir for 1 hour, quenched with benzaldehyde (15 \mu L, approx 0.15 mmol) and allowed to stir for an additional 30 minutes. The polymer was purified by dropwise addition of the resulting solution into a large excess of methanol, filtration, a subsequent precipitation from chloroform into methanol and placing under vacuum for 24 hours. The yield of isolated polymer (410 mg, 95%) was
essentially quantitative: $^1$H NMR (CDCl$_3$) δ 5.42 (b, CH=CH, trans), 5.33 (b, CH=CH, cis), 4.96 (b, CHOAc), 4.87 (b, CHOAc), 3.03 (b, allylic CH), 2.66 (b, allylic CH), 2.08 (b, CHH bridgehead), 2.01(s, OMe), 1.98 (s, OMe), 1.17 (b, CHH bridgehead); $^{13}$C NMR (CDCl$_3$) 170.9, 170.6, 133.0, 132.2, 76.8, 76.5, 45.3, 40.6, 35.2, 34.3, 33.4, 20.9; IR (nujol) 1750 cm$^{-1}$ (strong, C=O stretch). DSC analysis reveals a reversible Tg at 102 °C. TGA is shown in Figure 4; isothermal pyrolysis determined the amount loss to be 55.7 % (300 °C, 2 hours). GPC data are found in Chart 1.

**Typical polymerization of exo-syn-2,7-norbornenediace tate (13).** A solution of the monomer (13) (431 mg, 2.05 mmol) in THF (10 mL) was added dropwise but quickly to a vigorously stirring solution of Mo(CHCMe$_3$) (10 mg, 2 × 10$^{-5}$ mol) in THF (5 mL) over a period of 1-2 minutes. The resulting solution was allowed to stir for 1 hour, quenched with benzaldehyde (15 µL, appx. 0.15 mmol) and allowed to stir for and additional 20 minutes. The polymer was purified by dropwise addition of the resulting solution into a large excess of methanol, filtration, a subsequent precipitation from chloroform into methanol and placing under vaccum for 24 hours. The polymer was obtained as a white powder (388 mg, 90%): $^1$H NMR (CDCl$_3$) δ 5.2-5.4 (broad multiplets, 2, CHCH), 4.6-4.8 (broad multiplets, 2, CHOAc), 2.6 (b, 1, allylic CH), 2.5 (b, 1, allylic CH), 1.95 (s, 3, OMe), 1.77 (m, 3, OMe); $^{13}$C NMR (CDCl$_3$) 171.3 and 171.0 (C=O), 133.1 and 132.0 and 131.3 and 130.2 (CHCH, signals are split due to cis and trans isomers (aprx 50:50) and their relation to the acetate group in the 2 position), 79.3, 76.7, 54.2, 46.1, 36.3, 21.3, 21.0; IR (nujol): 1730 cm$^{-1}$ (strong, C=O stretch). DSC analysis shows a Tg at 110 °C. TGA thermogram is similar to Figure 4 with 56.2 % mass loss observed on heating at 300 °C for 2 hours (calculated for loss of 2 equivalents of acetic acid: 57.2 %). GPC data are found in Chart 1.

**Typical polymerization of exo-cis-2,3-norbornenediol di-O-isopropylidene (14).** A solution of the monomer (344 mg, 2.05 mmol) in THF (5 mL)
was added quickly but dropwise to a solution of Mo(CHCMe$_3$) (10 mg, 2.05 × 10^{-5} mol) in THF (3 mL) over a period of 1-2 minutes. The colour of the solution changed immediately from light yellow to red. The solution was allowed to stir for an additional 30 minutes, quenched with benzaldehyde (15 μL) and stirred for an additional 30 minutes to yield a yellow solution. The polymer was obtained free of impurities by precipitation from the above solution into a large excess of methanol followed by three consequent precipitations from chloroform into methanol and removal of solvent in vacuo for 24 hours. The polymer was obtained as a white flaky solid (327 mg, 95%): $^1$H NMR (CDCl$_3$) δ 5.51 (b, trans-CH=CH), 5.28 (b, cis-CHCH), 5.2-5.3 (broad multiplets, CHO), 2.95 (b, allylic CH), 2.55 (b, allylic CH), 2.94 (b, CHH bridgehead), 1.45 (s, CMe), 1.32 (b, CHH bridgehead), 1.23 (s, CMe), integration of signals consistent with the proposed formulation; $^{13}$C (CDCl$_3$) 133.0, 131.9, 113.4, 87.1, 86.0, 48.3, 44.3, 38.2, 27.7, 25.2. DSC: Tg = 102 °C; TGA polymer degradation begins at 300 °C. GPC data are found in Chart 1.

**Typical base hydrolysis procedure of polyacetate polymers: conversion of poly(exo-syn-2,3-norbornenediacetate) to poly(exo-syn-2,3-norbornenediols):** Poly(exo-syn-2,3-norbornenediacetate) (1.0 g) was dissolved in dry THF (150 mL) and added dropwise to a solution of dry THF (150 mL) and 20 mL of a 10% solution of sodium methoxide in methanol under vigorous stirring under reflux. The resulting solution was refluxed for 12 hours, cooled and neutralized with glacial acetic acid. The resulting fine suspension was filtered or centrifuged, washed with methanol and placed under vacuum for 24 hours to give the product as a light yellow powder (0.5 g, 83%) which sparingly soluble in a variety of solvents: $^1$H NMR δ (CF$_3$CO$_2$H:CDCl$_3$, 1:1) 5.6 (b, 2, CH=CH), 4.21 (b, 1,CHOH), 3.75 (b, 1,CHOH), 2.5-3 (b, 3, OH and allylic CH), 2.05 (b, 3, allylic CH and CH$_2$); IR: 3350 cm$^{-1}$ (b, OH stretch), 1600 cm$^{-1}$ (C=C stretch) no absorption observed in the carbonyl region.
Typical acid hydrolysis procedure for poly(exo-cis-2,3-norbornenediol di-O-isopropylidene). Poly(exo-cis-2,3-norbornenediol di-O-isopropylidene) (0.3 g) was dissolved in 10 mL of 80% aqueous trifluoroacetic acid and stirred for 3 hours at room temperature. The resulting solution was cooled to 0°C and slowly neutralized with aqueous KOH (5 M). During the neutralization procedure the colour changes from light red to nearly colorless at which time polymer began to precipitate. The resulting product was isolated by filtration or centrifugation, washed several times with water and methanol and placed under vacuum for 24 hours to yield the hydrolyzed polymer as a cream powder (0.2 g, 75%): $^1$H NMR δ (MeOD) 5.6 (broad multiplets, 2, CH=CH), 3.55 (b, 2, COH or CHO), 2.9 (b, 2, COH or CHOH), 2.5 (b, 2, allylic CH), 2.0 (b, 1, CHH), 1.1 (b, 1, CHH); IR: 3350 cm$^{-1}$ (b, OH stretch), 1590 cm$^{-1}$ (C=C stretch).

Thermal reaction of acetate polymers. Thermal treatment of poly12 and poly13 was carried out by thermogravimetric analysis (TGA) and temperature programmable pyrolysis oven under a nitrogen atmosphere. Weight loss of the polymers in the powder state was monitored as a function of temperature at a fixed heating rate (10 °C/min) or isothermally as a function of time at a given temperature. Polymers in the film state were heated at the same rate and kept isothermally for 2 hours at a given temperature resulting in insoluble black red films.

Typical polymerization of 2-carbonitrile norbornene. A solution of 2-carbonitrile norbornene (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CHCMe3)(NAr)(OCHMe3)$_2$ (10 mg, 2.05 × 10$^{-5}$ mol) in THF (1.0 mL) and stirred for 15 minutes. Termination was carried out by addition of 15 μL of p-trimethylsilylbenzaldehyde (8.4 × 10$^{-5}$ mol). The polymer was purified by precipitation of the polymer from the reaction mixture into 250 ml hexane. Final product is obtained as a white-cream powder; yield 103 mg 85 %: $^1$H NMR (CDCl$_3$) δ 5.70, 5.55, 5.37, 5.32, 5.20, 3.0, 2.73, 2.55, 2.30,
2.18, 2.03, 1.75, 1.43, (1.004, 0.981, 0.963, 0.956 )C(CH$_3$_3)$_3$, (0.232, 0.217)(Si(CH$_3$_3)$_3$); the spectrum is too broad for integration within polymer peaks, however integration of tert-butyl cap versus olefinic signal is consistent with assigned stoicheometry as well as 1:1 against TMS cap; $^{13}$C NMR (CDCl$_3$) δ 135.3, 134.6, 132.3, 131.7, 129.7, 129.2, (CN), 120.9 (CN), 58.5, 44.8, 41.8, 41.2, 39.8, 39.2, 37.0, 36.9, 36.2, 33.8, 29.6 (C(CH$_3$_3)$_3$), 1.3 (Si(CH$_3$_3)$_3$).

Mechanical behavior is shown in Figure 7; Tg = 123°C by DSC analysis. GPC: $M_n = 24869$, PDI = 1.05.

**Preparation of polyNBE-block-poly9.** A solution of norbornene (NBE) (193 mg, 2.05 mmol) in THF (2 mL) was added dropwise but quickly to a light yellow solution of Mo(CHCMMe$_3$) (10 mg, 2.05 x 10$^{-5}$ mol) in THF (2 mL) under vigorous stirring. After stirring for 15 minutes a solution of 2-carbonitrilenorbornene (9) (244 mg, 2.05 mmol) in THF (2µL) was added in the same fashion and allowed to stir for 25 minutes to yield a light yellow, slightly viscous solution. The polymerization was quenched by addition of benzaldehyde (15 µL) and stirred for an additional 30 minutes. The polymer was isolated by precipitation into a large excess of hexane and centrifugation. The resulting white powder was washed several times with hexane or methanol and placed under vacuum for 24 hours to yield 381 mg (87 %) of the product. The $^1$H and $^{13}$C NMR spectra were identical to the superposition of spectra for polyNBE and poly9. GPC: $M_n = 55780$, PDI = 1.05.
CHAPTER 5

INTRODUCTION

7-oxa substituted norbornene and norbornadiene derivatives represent a family of monomers which have only recently been polymerized using classical catalysts. The resulting polymers are potentially useful for a variety of applications. These have been shown to act as acyclic ionophores and can coordinate a variety of cations such as Na⁺, K⁺ and Cs⁺. In addition, the polymers can be cast into films which can be used as ion permeable membranes. This property has been explained by suggesting the presence of oxygen rich ionophoric channels. The 7-oxa norbornadiene polymers have been claimed to serve as polyene precursors. This reaction involves the removal of the doubly allylic protons in the polymer chain using a dehydrogenative reagent such as DDQ. Since Mo(NAr)(CHCMe₃)(OCMe₃)₂ (Mo(CHCMe₃)) has been shown to initiate the polymerization of functionalized monomers to yield materials of interesting properties (Chapters 2 and 4), it would be of interest to compare the properties of these materials with the 7-oxa counterparts. In particular the glass transition temperature of the 7-oxa analogues is expected to be higher if larger dipolar interactions are present in the bulk material. However stability towards oxidation is likely to decrease due to the labilizing presence of the oxygen atom α to the allylic protons.

Mechanistic aspects are of interest as well since these monomers are capable of being polymerized by Ru and Os based classical catalysts in water. Both the nature of the initiator or propagating species as well as the exact nature of the polymerization mechanism are poorly understood. It should be noted that the polymerization of norbornene derivatives cannot be initiated to the same extent, indicating that the 7-oxa functionality plays an important role in the polymerization. The reaction of these monomers with a well defined alkylidene initiator such as Mo(CHCMe₃) is interesting since the initiation and propagation steps can be studied separately and clear comparisons with the reactivity of norbornenes can be done. Although the findings of such an investigation would be particular to this catalyst general reactivity differences can be obtained which may help decipher the chemistry involved in the complex classical systems.
7-Oxa monomers are well suited for mechanistic studies since they are readily available through the Diels-Alder reaction of furan with a variety of dienophiles. The norbornadiene derivatives provide a family of compounds in which the substituents have different electronic properties. The reactivity of these can be compared with the results of stereoregularity obtained with the norbornadiene derivatives (Chapter 3).

RESULTS
Reactivity of 7-oxa Norbornadiene Derivatives.

Polymerization of 100 equivalents of 7-oxa-2,3-bis(trifluoromethyl)-norbornadiene (16) (7-oxa-2,3-bis(trifluoromethyl)[2.2.1]hepta-2,5-diene) was attempted in the usual manner using a variety of solvents and conditions. Workup of the reaction mixtures, in all cases, gave unreacted monomer without any oligomer or polymer present. Addition of 5 equivalents of 16 to Mo(CHCMe3) changes the solution color from light orange to bright red. Analysis of the \(^{1}\text{H}\) NMR spectrum of the resulting solution (Figure 1) reveals that 4 equivalents of monomer remain unreacted while all of Mo(CHCMe3) has been consumed to yield a species characterized by inequivalent isopropyl methyl groups and tert-butoxide ligands and 3 signals at 2.88, 1.68 and 1.57 ppm. These latter resonances are reminiscent of the resonances of previously characterized square pyramidal tungstacycle resulting from the addition of the norbornadiene analogue (2,3-bis(trifluoromethyl)-norbornadiene, 5) to W(NAr)(CHCMe3)(OCMe3)\(_2\) (W(CHCMe3)) described in Chapter 2. From this observation the product of 16 with Mo(CHCMe3) (17) is presumed to be a square pyramidal metallacycle (Equation 1), this material can be isolated, purified with elemental analysis consistent with its
Figure 1. 500 MHz $^1$H NMR spectrum (CD$\textsubscript{3}$OD) of the products resulting from addition of 5 equivalents of 16 to Mo(CHOCHMe)$_3$; * resonances are due to 16; inset: COSY spectrum of 17.
formulation. Attempts to obtain X-ray quality crystals of 17 failed since it crystallizes as plates from commonly available solvents.

The most remarkable feature of 17 is its stability. After 24 hours in solution at room temperature approximately 75% of the metallacycle is still present. When the metallacycle breaks up two new alkylidene signals appear at 11.233 (major) and 11.072 (minor) ppm in a 9:1 ratio; this ratio remains constant over time. These two signals are assigned to the two rotameric forms of the ring-opened product (Equation 2, see also Chapter 2 for analysis of the 7-methylene analogue). In both rotamers (syn and anti 18) the resulting olefin is trans suggesting that both arise from the same trans metallacycle and quickly isomerize to a thermodynamic syn and anti mixture. Note that as the concentration of the metallacycle decreases the color of the solution lightens to orange from the original bright red. The decomposition of 17 to 18 is quantitative by $^1$H NMR and is cleanly first order as determined
by following the decrease in the resonance of the β proton in the MoC₃ ring relative to an internal standard. The activation parameters were ΔH° = 18.8 kcal mol⁻¹ and ΔS° = -17 e.u., as determined by the Arrhenius plot (see Experimental section for details).

¹H NMR experiments determined that 16 could be polymerized using more reactive catalysts Mo(NAr)(CHCMe₃)[OCMe(CF₃)₂]₂ and Mo(NAr)(CHCMe₃)[OCMe₂(CF₃)]₂. Analysis of the ratio of propagating alkylidene to initiator for the former revealed that the kₚ/kᵢ ratio was very large (30-50) and further reactions were not pursued. John Oskam has shown that using Mo(NAr)(CHCMe₃)[OCMe₂(CF₃)]₂ poly16 was obtained with a polydispersity of 1.07.

The carbomethoxy derivative 7-oxa-2,3-dicarbomethoxynorbornadiene (19) reacts with Mo(CHCMe₃) in a similar fashion as 16. The resulting metallacycle (20, Equation 3) can be

\[ \text{Mo(CHCMe₃)} + \text{19} \rightarrow \text{20} \]

fully characterized. X-ray quality crystals of 20 were obtained by vapor diffusion of pentane into a concentrated ether solution. Unfortunately the structure could not be fully refined due to severe disorder of the carbomethoxy groups making the bond angles and distances unreliable. However, the overall geometry (Figure 2) of the structure that was obtained has the same relative orientation of atoms as the square metallacycle resulting from the reaction of W(CHCMe₃) with 2-3-bis(trifluoromethyl)norbornadiene (Chapter 2). The core distances and angles are similar to an analogous 2-oxymetallacyclobutane derivative described in Chapter 7.
Figure 2. X-ray structure of 20.
The most important point is that the oxygen from the 7 position does not appear to be coordinated to the metal center (3.2 Å).

As is the case for 17 two alkyldene rotamers, again in a 9:1 ratio, are observed when 20 ring opens to yield the new propagating alkyldene (Equation 4). The $^1$H NMR spectra of

![Chemical Structure](image)

the two isomers of 21 can be fully assigned by a COSY experiment (Figure 3). The $J_{\alpha\beta}$ values are different for the two alkyldene isomers with $J_{\alpha\beta} = 7.0$ Hz (major) and $J_{\alpha\beta} = 3.5$ Hz (minor). Note that the two doubly allylic protons are also coupled to each other with $J = 1$ Hz unlike any previously observed single insertion alkyldene complex. A single rate determination showed that 20 breaks cleanly in a first order fashion and completely to the two isomers of 21 ($k = 4.5 \times 10^{-4}$ sec$^{-1}$, $T = 35$ °C).

Attempts to polymerize 19 by increasing the reaction time with Mo(CHCMe$_3$), or by using Mo(NAr)(CHCMe$_3$)[OCMe$_2$(CF$_3$)$_2$] as the initiator resulted in polymers with bimodal molecular weight distributions and broad dispersities.

The nature of the α substituent in the metallacycle and the alkoxide ligands was varied, and the rates of their breakup measured. In all cases first order behavior was observed by monitoring the disappearance of molybdacycle resonances versus an internal standard. Changing the α substituent from tert-butyl to dimethylphenylmethyl (prepared by addition of either 16 or 19 to Mo(NAr)[CHCMe$_2$(Ph)](OCMe$_3$)$_2$) yields more stable
Figure 3. COSY spectrum of 21.
metallacycles. The observed rates at 35 °C were 8.6 × 10⁻⁶ sec⁻¹ (CF₃ derivative) and 2.7 × 10⁻⁴ sec⁻¹ (CO₂Me derivative). Changing the alkoxide from (CH₃)₃CO to (CH₃CH₂)₃CO also slows the rate of breakup (4.2 × 10⁻⁵ sec⁻¹ at 35 °C, dimethylphenylmethyl and CO₂Me substituents), see Table 1.

Competition experiments suggest that the 7-oxa monomers are more reactive than their norbornadiene counterparts. Reaction of Mo(CHCMe₃) with 3 equivalents of both 16 and 5 yields exclusively the molybdacycle 17, two equivalents of unreacted 16 and unreacted 5 by ¹H NMR (Equation 5). If the sensitivity of the NMR technique is assumed to be 1 %, the limiting value for the difference in activation energies can be estimated to be 3 kcal mol⁻¹ at 298 K. A similar experiment was carried out between 16 and 19 by adding equimolar quantities of both to Mo(CHCMe₃). ¹H NMR analysis of the latter experiment showed that 17 and 20 were formed in approximately a 1:1 ratio indicating that both monomers are approximately equally reactive towards the initiator.

Addition of 100 equivalents of 7-oxabenzonorbornadiene (1,4-dihydronaphthalene 1,4-endo-oxide, 22) to Mo(CHCMe₃) results in quantitative formation of poly(7oxabenzonorbornadiene) (poly22). The solution turns red upon addition of monomer and slowly fades back to orange over a period of 45 minutes, suggesting the presence of stable metallacycles during the initial stages of the polymerization. The organic polymers can be isolated free of metal species by first termination with benzaldehyde (or pivaldehyde) and
Table 1. First order breakup rates for decomposition of molybdacycles.

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<th>Structure</th>
<th>Rate Constant</th>
<th>Temperature (°C)</th>
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<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>$k = 8.6 \times 10^{-6}$ sec$^{-1}$</td>
<td>$T = 35$ °C</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>$k = 4.2 \times 10^{-5}$ sec$^{-1}$</td>
<td>$T = 35$ °C</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>$k = 1.3 \times 10^{-4}$ sec$^{-1}$</td>
<td>$T = 0$ °C</td>
</tr>
</tbody>
</table>
precipitation into hexane or methanol. The polydispersities of the isolated polymers are dependent on both the solvent of polymerization and the concentration of propagating species. Polar solvents such as THF tend to yield the narrower dispersities (PDI = 1.34-1.51 for 100 mer) but the GPC traces show tailing toward lower molecular weight species, aromatic solvents such as benzene yield materials with a broader molecular weigh distribution (PDI = 1.80 for 100 mer). Qualitative observations indicate that the more dilute solutions tend to yield the narrower polydispersities.

Analysis by $^1$H NMR at -30 °C of the product resulting from addition of one equivalent of 22 to Mo(CHCMMe$_3$) revealed the presence of a square metallacyclic species (23, Equation 6) analogous to 17 and 20. Qualitatively this new metallacycle is much more unstable than the two previously observed species with approximately 60 % of metallacycle converted to alkylidene species after one hour at 0 °C. Again two rotameric isomers of the propagating alkylidene (24, Equation 7) are observed at 11.69 (major, $J_{\alpha H\beta} = 7.5$ Hz) and 11.47 ppm (minor, $J_{\alpha H\beta} = 4.0$ Hz) in a 8.5:1.5 ratio. Two equivalents of 22 were added to Mo(CHCMMe$_3$) at room temperature and the solution immediately frozen. The $^1$H NMR spectrum (- 30 °C) of the resulting mixture revealed that a small amount of 23 had ring opened to yield syn and anti 24, the extra equivalent of monomer had been consumed and a different alkylidene signal at 11.69 ($J_{\alpha H\beta} = 6.8$ Hz) was present. As the rest of 23 ring-opened over time only the intensities of syn and anti 24 increased. No signals which could be due to the second insertion metallacycle were observed. These results are consistent with 24 reacting with 22 quickly to yield an unstable metallacycle which would result in fast propagation and consumption of the monomer before the majority of 23 has ring opened.

This complication in initiation and propagation is confirmed by $^1$H NMR analysis. Figure 4 a shows the $^1$H NMR spectrum in the propagating alkylidene region of the reaction of 3 equivalents 22 with Mo(CHCMMe$_3$), note that the majority of the alkylidene is present as the two rotamers of 24, with a small amount of the second and higher insertion products observed as an ill defined broad hump centered around 11.65 ppm. If one equivalent of 22 is added to
Figure 4. 500 MHz $^1$H NMR spectrum ($C_6D_6$) in the alkylidene region of the product of (a) addition of 3 equivalents of 22 to Mo(CHCMe$_3$); (b) addition of 1 equivalent of 22, reacting for 20 minutes followed by addition of 2 equivalents of 22.
Mo(CHCMe$_3$), reacted for 30 minutes followed by addition of another 2 equivalents the spectrum (shown in Figure 4b) changes considerably. In the latter case the propagating alkylidene resulting from higher insertion products is predominant. Note that the syn and anti rotamers are also observed with the fine structure in each probably due to sensitivity of the alkylidene signal to the number of inserted monomers. Attempts to isolate pure 24 failed due to the oily nature of the product, which in turn is likely to be a consequence of the two isomers present.

In view of the NMR analysis of the propagating species the polymerization reaction was modified. Instead of adding the monomer all at once, only 2-3 equivalents were added. The reaction turned red. After 20-30 minutes the color turned back to orange (characteristic of alkylidenes) and the rest of 22 (98 equivalents) were then added to the solution and the
reaction was worked up in the usual fashion. The GPC trace of the resulting polymer along
with one obtained by adding the monomer in one portion is shown in Figure 5. The former
method yields polymer which has a narrow molecular distribution (PDI = 1.06) and a
symmetric peak shape.

The above procedure represents the first report of the polymerization of 7-oxa
benzonorbornadiene. This material is obtained as a white powder, is soluble in a variety of
solvents (CHCl₃, CH₂Cl₂ and toluene) and has good thermal properties with a DSC
determined Tg of 167 °C and is thermally stable up to 320 °C under a nitrogen atmosphere as
determined by TGA. As is the case for poly(benzenorbornadiene), poly22 is not stable
toward oxidation with the color turning orange when exposed to air, IR analysis reveals the
appearance of a strong OH absorption around 3420 cm⁻¹ which increases over time.

Polymerization of 7-oxanorbornenes.

Unlike 7-oxanorbornadiene derivatives the polymerization of 7-oxanorbornenes
proceeds without complications. For example 7-oxa-2,3-endo,cis-diacetatonorbornene (25)
reacts with Mo(CHCMe₃) quantitatively to yield polymers with good polydispersities (1.17 for
100 mer) and a 60:40 cis:trans stereoselectivity (Equation 8). The resulting polymers are

soluble in a variety of solvents and can be cast into flexible transparent films. The thermal
behavior of the material shows a two stage degradation pattern by TGA, although the features
are less pronounced than those observed for poly(2,3-endo,cis-diacetatonorbornene)
Figure 5. GPC traces of (a) poly23 100 mer prepared by addition of the monomer in one portion; (b) poly23 prepared by addition of 2-3 equiv of 23, reacting for 20-30 minutes followed by addition of 98 equivalents of 23.
(Chapter 4). The weight loss during the first degradation (300 °C) is 60.2 % and suggests that it is due to the loss of two equivalents of acetic acid in each monomer (57 % theoretical). At slightly higher temperatures further degradation is observed. Tg was determined to be 132 °C by DSC analysis.

Similarly 7-oxa-2,3-endo,cis-norbornenediol di-O-isopropylidene is polymerized smoothly using Mo(CHCMe₃) in THF (Equation 9) to give polymers with a narrow molecular weight distribution (PDI = 1.09 for 150 mer). Analysis by DSC reveals a Tg at 171 °C but decomposition begins at 200 °C by TGA.

**DISCUSSION**

Several conclusions and observations can be drawn from the data presented in this chapter, the most striking of which is the remarkable stability of molybdacycles 17, 20 and their neophysical analogues. This contrasts the previously held view that high oxidation state metallacyclobutane derivatives of molybdenum are unstable. This is mainly due to molybdenum’s preference for the doubly bonded alkylidene ligand over two σ bonds, its ease of reduction and the slower rate of formation with faster breakup of metallacycles relative to tungsten. No other MoC₃ ring derivatives have been observed when either cyclic or acyclic olefins are added to Mo(NAr)(CHCMe₃)(OCMe₃)₂, or its neophysical analogue. What sets these monomers apart from previously reacted olefins is the nature of the substituent on the 7 position. The small steric difference between O and CH₂ and the fact that these substituents are
far from the metal center upon metallacycle formation suggests that this unexpected stability is not induced by steric factors. X-ray data suggests that the 7-oxygen is not likely to be within bonding distance to interact with its lone pairs to the metal. Therefore induction differences between oxygen and carbon (from electronegativity arguments) appear to be implicated in stabilizing the metallacyclobutane ring.

Comparison of the breakup rates between the members of the family of 7-oxanorbornadiene metallacycle derivatives also supports the postulate of electronic control. From the single measurement of 23 at 0 °C (60 % metallacycle consumed in 60 minutes) the rate constant can be crudely estimated to be close to $1.3 \times 10^{-4}$ sec$^{-1}$, assuming first order behavior. From the kinetic measurements on the breakup of 17 the rate constant from breakup at 0°C can be calculated to be $7.3 \ (2) \times 10^{-7}$ sec$^{-1}$. Therefore, by changing the nature of the functionalities from two trifluoromethyls to a benzo derivative the rate of breakup of the ring at 0 °C increases by two orders of magnitude. Similarly, the calculated rate of breakup for 17 at 35 °C ($4.2 \ (2) \times 10^{-5}$ sec$^{-1}$) is an order of magnitude slower than that of 20 ($4.5 \ (1) \times 10^{-4}$ sec$^{-1}$, T=35 °C). Steric differences between the substituents in these metallacycles (benzo, CO$_2$Me, and CF$_3$) are again likely to be a minor contribution to their effects on reactivity. Therefore the energetics of metallacycle breakup are acutely sensitive to the electronic nature of the substituents 4 bonds away from the metal.

Steric effects of groups near the metal center are also implicated in the stability of these metallacycles. By changing the substituent on the α carbon from tert-butyl to the more bulky dimethylphenylmethyl group the rate of breakup decreases by a factor of approximately 5 (Table 1). Similarly increasing the size of the alkoxide from tert-butoxide to triethylcarbinol results in the rate of breakup decreasing by approximately an order of magnitude. Assuming that the change in the electronic nature of these substituents is negligible, the trend indicates that larger groups stabilize the metallacycles. Note that stable metallacycles of a second insertion product, i.e. resulting from monomer addition to either 18, 21, or 24, have not been observed. This suggests that the size of the substituent in the α position, essentially an
isopropyl group, is too small to stabilize the metallacycle and any that forms breaks up quickly to yield the alkyldene complex.

Exactly how these electronic and steric effects are involved in the stabilization of these square pyramidal metallacycles is poorly understood. The entropies of activation for the breakup of the metallacycles are consistent with a considerable amount of rearrangement necessary before the transition state is reached. This is in agreement with previous studies which have suggested that these metallacycles are likely to rearrange to ones of the trigonal bipyramidal type before the olefin can be lost. Since the arrangement of ligands when the olefin leaves must resemble the geometry when the olefin first enters the coordination sphere, then it is plausible that this is a trigonal bipyramidal metallacycle such as C. This geometry is chosen because of the similarities to the structurally characterized base adduct Mo(NAr)(CHCMe₃)[OCMe(CF₃)₂]₂(PMe₃). (For structural details and spectroscopic characterization of Mo(CHCMe₃) adducts see Chapter 8.) If olefins bind in the same mode then they are likely to have a structure such as A. If this adduct yields a metallacycle without further ligand rearrangement then this first species is likely to resemble B. The departing olefin then is likely to have the same geometry except that the α carbons have switched axial and equatorial positions (the alkoxides have also exchanged positions) which yields geometry C. This interconversion is carried out by a single Berry type pseudorotation about the N=Mo bond. Note that the stable square pyramidal metallacycles experimentally observed are the required intermediates for this process. A metallacycle such as C is likely to be closer to the transition state. In theory there are many other possible intermediates with the different ligands permuted in axial an equatorial positions, the interconversion shown here represents the interconversion of B to C with the least motion required. For further discussion on these interconversions see Chapter 7.
It is proposed here that the metallacycles resulting from addition of 7-oxanorbornadienes to Mo(CHCMe₃) are stable because the rate of rearrangement from the square pyramidal geometry to the next is reduced by electron withdrawing substituents on the metallacycle and by bulky groups near the metal center. Note that the negative $\Delta S^\dagger$ implies a more crowded transition state and bulky groups are likely to hinder such a process; furthermore in C an $\alpha$-syn substituent on the metallacycle comes closest to the bulky imido ligand. The larger the magnitude of this steric interaction the higher the energy of the transition state. This could account for the observed dependance on steric size of the reacting alkylidene on the resulting metallacycle stability. If the energetics of olefin binding in the incipient olefin complex are important in stabilizing the transition state then electron poor olefins are likely to raise the transition state energy and the metallacycle would be stabilized.

The preparation of poly22 with a narrow range of molecular weights was achieved using the information obtained from the rates of polymerization. The standard polymerization technique of adding all of the monomer at once assumes that there is no significant difference between the rates of initiation and propagation. For 22 initiation involves the addition of the olefin to form 23, followed by its breakup to propagating alkylidene. Propagation is much
faster, to the point where an effect is observed in the resulting dispersities (Figure 5). Modification of the addition method circumvents this problem. The addition of a few equivalents of monomer traps the initiator as 23, which as it breaks up consumes only the small number of equivalents added. The second batch of monomer is added (97 equivalents) once the metal species is present as the propagating alkylidene 24. The narrow dispersities of the resulting polymer are consistent with no decomposition of the propagating species and with a rate of propagation which is closer to that of initiation. Ideally one would like to isolate pure 24 for initiation of 22.

The successful polymerization of 16 requires a different approach. For this monomer the time required for the metallacycle breakup at room temperature is such that it competes with alkylidene decomposition. The choice of Mo(NAr)(CHCM\text{e}_3)(\text{OCMe}_2\text{CF}_3)_2 as the initiator was based on the fact that electron withdrawing alkoxides tend to form trigonal bipyramidal metallacycles over the square pyramidal type. These catalysts are also more reactive, favoring metal-substrate interactions and therefore are likely to have faster polymerization rates.

This latter property of the catalyst is also likely to be responsible for the difficulties encountered when trying to polymerize 19 in a controlled fashion. Due to the higher reactivity, a Wittig-like reaction with the ester groups seems plausible, which would destroy the propagating species. The functionalities in poly16 do not appear to interact with the polymerization process and furthermore these also would tend to deactivate the olefinic bonds in the polymer. This might be important in preventing secondary metathesis (reaction between alkylidenes and the olefins in the polymer), which would result in chain transfer and consequently in higher dispersities than those predicted for a living polymerization system.

It is interesting that stable metallacycles are not formed using the 7-oxanorbornadiene monomers and the more electron withdrawing alkoxides. If square pyramidal metallacycles are stabilized by the inductive effect of the 7-oxygen in the tert-butoxide system because the energy of the transition state is raised when the departing olefin is electron poor it may seem counterintuitive that this is not the case when the metal center is more electrophilic. However,
the nature of the alkoxides appears to determine the geometry of metallasycles formed. For the more electron withdrawing alkoxides the preferred geometry is trigonal bipyramidal. Therefore it appears that the choice of alkoxide determines the relative energies of the possible geometries of metallasycles. The substituents on the metallasycle in turn may have a stabilizing or destabilizing effect on the geometry dictated by the alkoxide.

The polymers obtained from 7-oxanorbornene and 7-oxanorbornadiene derivatives have the highest glass transition temperatures observed of all the polynorbornene derivatives prepared so far. This is an important property for a variety of applications and is likely to be a result of the higher polarity of the oxygen atom versus the methyldiene counterpart. A drawback which may limit their usefulness is their poorer thermal stability. Comparison of the cis/trans ratio of poly22 (50:50) with polybenzonorbornadiene (24:76, Chapter 2) reveals that the 7-oxa derivative is polymerized less stereoselectively when initiated with Mo(CHCHMe3). This is consistent with either the propagating species of living poly22 being more reactive than living polybenzonorbornadiene or 22 being more reactive than benzonorbornadiene.

Competition experiments (Equation 5) reveal that the 7-oxa monomers are more reactive than their 7-CH2 counterparts. This is particularly surprising since the olefin bond in the former monomers is likely to be less electron rich. The latter suggestion is made on grounds of ionization and oxidation potentials. Therefore if coordination of the olefin determined monomer reactivity these would be expected to be less reactive. The enhanced reactivity could be due to an interaction of the oxygen lone pairs with the metal center which would increase the basicity of the monomer. Note that the lone pairs are on the exo face via which the metal is bound to coordinate as determined by the X-ray structure of 20. Whether the oxygen electrons coordinate first, i.e. formation of an oxygen adduct followed by olefin
coordination and insertion, or they simply overlap with the olefin π system aiding in coordination has not been determined. An alternate explanation rests on the higher electrophilic nature of the olefin carbons once coordinated to the metal. This may aid in the transformation from base adduct to metallacycle and would be consistent with the observation that electron poor alkylidenes tend to be less reactive. If the olefin adduct to metallacycle transformation is aided by a nucleophillic like attack of the alkylidene Cα carbon to the coordinated olefin, then electron withdrawing groups on the olefin would increase the rates of reaction. It is interesting to note that the reactivities of 16 and 19 were approximately the same while the reactivities of their 7-CH₂ counterparts were found to differ by an order of magnitude (CO₂Me substituted reacting faster). In this latter class of monomers there was a correlation of reactivity with ionization potential of the olefin (Chapter 2). This could mean that the oxygen coordinates first, reducing the importance of the olefin in determining reactivity, or that for 19 the higher reactivity expected due to the presence of a more basic olefin is concurrently reduced since this disfavors the approach of Cα for metallacycle formation. Since a reactivity difference is observed for the 7-CH₂ monomers when the olefin becomes more electron poor we prefer arguments based on the oxygen atom aiding in monomer coordination. The data presented argues against the smaller steric field of O vs CH₂ being responsible for the reactivity differences. If this was the case and the 7-O derivatives would be simply more reactive then a reactivity difference between 16 and 19 would be expected. This could be a minor component but it does not appear to be the major source of reactivity control.
Precedent exists in the literature for both aspects of 7-oxanorbornadienes. Irradiation of a solution of Fe(CO)$_5$ and 22 results in the formation of Fe(7-oxanorbornadiene)(CO)$_4$ while the same reaction fails when benzonorbornadiene is used.$^{100}$ In general only olefins having strongly electron withdrawing substituents directly attached to the double bond form stable Fe(CO)$_4$(olefin) complexes.$^{101}$ This suggests that the olefin in 22 is more electron poor than in benzonorbornadiene. Participation of the oxygen lone pairs in 22 in controlling stereochemistry of reactions$^{102}$ and coordination to metal complexes$^{103}$ has been suggested previously but not conclusively proven.

**EXPERIMENTAL**

**General Details.** All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina except for deuterated THF which was vacuum transferred from benzophenone ketyl. Norbornene was doubly distilled from molten sodium. Commercially available aldehydes were purified by distillation under nitrogen. The monomers 7-oxa-,2,3-bis(trifluoromethyl)norbornadiene$^{104}$, 7-oxa-2,3-dicarbomethoxynorbornadiene$^{105}$, 7-oxabenzonorbornadiene$^{106}$ and 7-oxa-2,3-endo,cis-diacetatonorbornene$^{107}$ were prepared using literature procedures.

NMR data are listed in parts per million downfield from TMS for both proton and carbon. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Gel Permeation Chromatographic (GPC) analysis were carried out at room temperature employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1-0.3 %
w/v in dichloromethane which were filtered through a Milllex-SR 0.5 μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03 × 10^6 MW. Thermal analysis (TGA) was done on a Perkin Elmer TGS-2 thermogravimetric analyzer. Differential scanning calorimetry was performed on a Perkin-Elmer instrument at a heating rate of 30 °C/min.

**Synthesis of 17.** A solution of 7-oxa-2,3-bis(trifluoromethyl)norbornadiene (47 mg, 0.2 mmol) in ether (500 μL) was added to a light orange solution of Mo(NAr)(CHCMMe3)(OCMe3)2 (100 mg, 0.2 mmol) in ether (1.0 mL) and stirred for 20 minutes. During this time the color of the solution changes to deep red. Cooling the resulting solution to -40 °C for 48 hours yields the product as red plate like crystals (105 mg, 72 %): 1H NMR δ 6.91 (m, 3, HAr), 5.91 (s, 1, CH bridgehead), 4.82 (s, 1, CH bridgehead), 3.93 (sept, 2, CHMe2), 2.88 (dd, 1, J_HαHβ = 8, Hβ), 1.68 (d, 1, J_HαHβ = 8, Hα), 1.57 (d, 1, J_HαHβ = 8, Hα), 1.38 (s, 9, OCMe3), 1.25 (s, 9, OCMe3), 1.22 (d, 6, CHMeMe), 1.18 (d, 6, CHMeMe), 1.05 (s, 9, CHCMMe3); 1H NMR(d8-THF) δ 7.13 (m, 3, HAr), 5.71 (s, 1, CH bridgehead), 4.89 (s, 1, CH bridgehead), 3.87 (sept, 2, CHMe2), 2.70 (dd, 1, Hβ), 1.53 (d, 1, Hβ), 1.49 (d, 1, Hβ), 1.48 (s, 9, OCMe3), 1.38 (s, 9, OCMe3), 1.22 (d, 6, CHMeMe), 1.23 (d, 6, CHMeMe), 1.07 (s, 9, CHCMMe3); 13C NMR (d8-THF) δ 153.0 (C1 or C0, NAr), 147.6 (C1 or C0, NAr), 141.5 (b, CF3C=CCF3), 140.0 (b, CF3C=CCF3), 129.0 (Cp, NAr), 124.4 (Cm, NAr), 85.7 (CH bridgehead), 86.6 (CH bridgehead), 85.2 (OCMe3), 83.8 (OCMe3), 62.3 (Cβ), 41.2 (Cα), 38.1 (Cα), 32.8 (CHCMMe3), 31.7 (OCMe3), 31.2 (OCMe3), 28.7 (CHMe2), 23.8 (CHMeMe), 23.6 (CMeMe). Anal. Calcd for MoC35H49NO3F6: C, 55.23; H, 6.88; N, 1.95. Found: C, 55.24; H, 7.10; N, 1.82.

**Rate of decomposition of 17.** Solutions of 17 (12 mg, 1.7 × 10^-5 mol) and mesitylene (~2 mg, 1.7 × 10^-5 mol) in C6D6 were prepared from stock solutions, placed in 5
mm NMR tubes and frozen in liquid N₂ until the kinetic measurements. First order behavior was observed by monitoring the disappearance of the metallacycle α or β resonances versus the internal standard in the ¹H NMR spectra. Rates were determined at 3 different temperatures over a 20 °C range (40, 50, 60 °C) with a sample equilibration time in the NMR probe of 10-15 min. Observed rate constants were 0.681, 1.95, 4.37 × 10⁻⁴ sec⁻¹ respectively. The Arrhenius plot had ρ = 0.996. Data for ring opened product (18) ¹H NMR δ (major isomer, 90 %) 11.233 (d, 1, J_HαHβ = 8.5, Hα), 7.23 (d, 1, J_HαHβ = 8.5, Hβ), 7.02 (m, 3, H_Ar), 5.56 (d, 1, J_HH = 14.5, CHCHCMe₃), 5.30 (dd, 1, CHCHCMe₃), 4.99 (d, 1, CH allylic), 3.97 (sept, 2, CHMe₂), 1.34 (s, 9, OCMe₃), 1.28 (d, 6, CHMeMe), 1.23 (d, 6, CHMeMe), 1.24 (s, 9, OCMe₃), 0.87 (s, 9, CHCMes); ¹H NMR (minor isomer, 10 %, partially assigned) δ 11.072 (m, Hα), 5.67 (d, CHCHCMes), 3.87 (sept, CHMe₂).

**Synthesis of 20.** A solution of 7-oxa-2,3-dicarbomethoxynorbornadiene (43 mg, 0.2 mmol) in ether (500 µL) was added to a light orange solution of Mo(NAr)(CHCMes)(OCMe₃)₂ (100 mg, 0.2 mmol) in ether (1.0 mL) and stirred for 15 minutes. The resulting solution was placed inside an open 5 mL vial and this in turn placed inside a 20 mL vial containing pentane. This apparatus was cooled to -40 °C for 1 week from which red crystals of the product were obtained (45 mg, 31 %): ¹H NMR δ 6.82 (m, 3, H_Ar), 6.03 (s, 1, CH bridgehead), 5.07 (s, 1, CH bridgehead), 4.06 (sept, 2, CHMe₂), 3.07 (dd, 1, J_HαHβ = 8, Hβ), 1.98 (d, 1, J_HαHβ = 8, Hα), 1.73 (d, 1, J_HαHβ = 8, Hα), 1.42 (s, 9, OCMe₃), 1.35 (s, 9, OCMe₃), 1.26 (d, 6, CHMeMe), 1.19 (d, 6, CHMeMe), 1.17 (s, 9, CHCMes); ¹³C NMR (d⁸-toluene, 0°C) δ 164.0 (C=O), 163.3 (C=O), 152.0 (C₁ or C₀, NAr), 144.8 (C₁ or C₀, NAr), 139.5 (C=C(CO₂Me)), 123.6 (Cₚ or Cₗ, these are coincident or one of them is buried under solvent peaks), 87.5 (CH bridgehead), 87.0 (CH bridgehead), 82.9 (OCMe₃), 82.6 (OCMe₃), 62.4 (Cₚ), 51.4 (CO₂Me), 41.6 (C₀), 37.8 (C₀), 32.7 (CHMe₂ or CHCMes), 31.4 (OCMe₃), 31.2 (OCMe₃), 23.8 (CHCMes or CHMe₂). Anal. Calcd for MoC₃₅H₅₅NO₇: C, 60.25; H, 7.94; N, 2.01. Found: C, 60.31; H, 7.82; N, 1.68.
Rate of decomposition of 20. A single rate was determined using $^1$H NMR analysis by measuring the disappearane of the $H_\beta$ resonance of $^{20}$ (12 mg in 750 $\mu$L C$_6$D$_6$) versus an internal standard (mesitylene) at 35 °C. First order behavior was observed with a rate of 4.5 (1) $\times$ 10$^{-4}$ sec$^{-1}$. $^1$H NMR (determined by COSY, see Figure 3) of the ring opened product (20): (major isomer, T = 35 °C) $\delta$ 11.565 (d, 1, $J_{H\alpha H\beta}$ = 7.5, $H_\alpha$), 7.424 (dd, 1, $J_{H\alpha H\beta}$ = 7.5, $J_{H\beta H\alpha}$ = 3.5, $H_\beta$), 7.05 (m, 3, $H_Ar$), 5.571 (d, 1, $J_{HH} = 15$, CHCMMe$_3$), 5.564 (dd, 1, CH=CHCMMe$_3$), 5.267 (dd, 1, CH allylic), 4.07 (sept, 2, CHMe$_2$), 1.42 (s, 9, OCMMe$_3$), 1.33 (s, 9, OCMMe$_3$), 1.31 (d, 6, CHMeMe), 1.29 (d, 6, CHMeMe), 0.96 (s, 9, CHCMMe$_3$); (minor isomer is partially assigned, T = 35 °C) 11.414 (d, $J_{H\alpha H\beta}$ = 4.5, $H_\alpha$), 6.64 (dd, $J_{H\alpha H\beta}$ = 4.5, $H_\beta$), 6.9 (M, $H_Ar$), 6.27 (dd, CH=CHCMMe$_3$), 5.80 (d, $J_{HH} = 15$ Hz, CHCMMe$_3$), 4.30 (sept, CHMe$_2$), 1.05 (s, CHCMMe$_3$).

Observation of 23. A solution of 7-oxabenzenonorbornadiene (6 mg, 4 $\times$ 10$^{-5}$ mol) in $d^8$-toluene (300 $\mu$L) was added to a solution of Mo(NAr)(CHCMMe$_3$)(OCMMe$_3$)$_2$ (20 mg, 4$\times$ 10$^{-5}$ mol) in $d^8$-toluene (350 $\mu$L) and the solution immediatly frozen until $^1$H NMR analysis. $^1$H NMR ($d^8$-toluene, -32 °C) $\delta$ 7.01 (m, 3, $H_Ar$), 6.13 (s, 1, CH bridgehead), 5.01 (s, 1, CH bridgehead), 3.98 (sept, 2, CHMe$_2$), 2.87 (dd, 1, H$_\beta$), 1.85 (d, 2, $H_\alpha$ and $H_\alpha$' coincident), 1.53 (s, 9, OCMMe$_3$), 1.37 (s, 9, OCMMe$_3$), 1.20 (broad, 12, CHMe$_2$), 1.17 (s, 9, CHCMMe$_3$). Warming of the solution to 0 °C results in 60 % consumption of the metallacycle to yield two rotamers of the propagating species 24: $^1$H NMR ($d^8$-toluene, 0 °C) major isomer (90 %) $\delta$ 11.69 (d, 1, $J_{H\alpha H\beta}$ = 7.5, $H_\alpha$), 7.61 (d, 1, $J_{H\alpha H\beta}$ = 7.5 Hz), 7.37 (d, 1, $H_1$), 7.08 (dd, 1, H$_2$), 7.0 (m, 4, H$_3$ and H$_{Ar}$), 6.97 (d, 1, H$_4$), 5.71 (d, 1, $J_{HH} = 14.5$, CHCMMe$_3$), 5.53 (dd, 1, CHCHCMMe$_3$), 5.37 (d, 1, CH allylic), 4.13 (sept, 2, CHMe$_2$), 1.38 (s, 9, OCMMe$_3$), 1.32 (d, CHMeMe), 1.30 (s, OCMMe$_3$), 1.29 (d, CHMeMe), 0.98 (s, 9, CHCMMe$_3$); minor isomer (partially assigned) $\delta$ 11.47 (d, $J_{H\alpha H\beta} = 4.0$, $H_\alpha$), 6.80 (dd, $J_{H\alpha HB} = 4$, $H_\beta$),
Polymerization of 7-oxabenzonorbornadiene. Stock solutions (2000 µL) of both Mo(NAr)(CHCMe3)(OCMe3)2 (10 mg, 2.05 × 10⁻⁵ mol) and 7-oxa-benzonorbornadiene (296 mg, 2.05 mmol) in THF were split into 2.0 × 1000 µL portions each. The first polymerization was carried out by adding the monomer to the catalyst all at once under vigorous stirring and was allowed to stir for 45 minutes. The second procedure was carried out by first adding 40 µL (4 × 10⁻⁵ mol, apprx. 4 equivalents) of the monomer solution to the catalyst under vigorous conditions all at once causing the color of the solution to turn from orange to red. The resulting solution was allowed to stir approximately 20 minutes until the color turned back to orange and the rest of the monomer solution added dropwise over a period of 5 minutes and stirred an additional 20 minutes. Both polymerizations were terminated by the addition of excess benzaldehyde (15 µL, approx. 0.15 mmol) and allowed to stir for an additional 30 minutes. The polymers were purified by precipitation from the resulting solution into a large excess of hexane or methanol (200 mL), centrifugation, a subsequent precipitation from chloroform solution into hexane and trapped solvent removed by placing under vacuum for 24 hours. GPC analysis showed that the maxima of both peaks appeared at approximately the same retention time (see Figure 4) with the polymer prepared by the second method having a polydispersity index of 1.06: ¹H NMR (CDCl₃) δ 7.29 (b, 4, HAᵣ), 6.16 (b, 0.5, cis or trans CH=CH), 6.06 (b, 0.5, cis or trans CH=CH), 5.76 (b, 0.5, OCH), 5.66 (b, 0.5, OCH), 0.9 (b, CMe₃ end group); ¹³C NMR (CDCl₃) δ 141.6 (CH aromatic), 133.9 (CH aromatic),
130.02 (C quaternary aromatic), 128.8 (CH=CH), 122.8 (CH=CH), 84.3 (CH allylic), 79.7 (CH, allylic).

**Polymerization of 7-oxa-2,3-endo,cis-diacetatonorbornene.** A solution of the monomer (435 mg, 2.05 mmol) in THF (5 mL) was added dropwise but quickly to a rapidly stirring solution of Mo(NAr(CHMe3)(OCMe3)2 (10 mg, 2.05 × 10^{-5} mol) in THF (5 mL) and allowed to stir for an additional 30 minutes. The polymerization was quenched with benzaldehyde (15 µL, approx 0.15 mmol) and stirred an additional 30 minutes. The polymer was isolated by precipitation from the above solution into a large excess of methanol followed by three subsequent precipitations from a chloroform solution into methanol and finally was placed under vacuum for 24 hours. The product was obtained as a white powder almost quantitatively (400 mg, 92 %) ¹H NMR (CDCl₃) δ 5.73 (b, 0.4, cis or trans CH=CH), 5.65 (b, 0.6, cis or trans CH=CH), 5.42 (b, 1, OCH), 4.78 (b, 0.6, CH allylic), 4.50 (b, 0.4, CH allylic), 2.03 (b, 3, OCMMe), 0.98 (s, CMe₃ end group); ¹³C NMR (CDCl₃) δ 169.5 (s, C=O), 129.1 (m, CH=CH), 79.1 (s, OCH allylic), 62.6 (s, OCH allylic), 73.5 (s, OCH), 20.5 (s, Me).

**Polymerization of 7-oxa-2,3-endo,cis-norbornenedioli di-O-isopropylidene.** This polymer was prepared using a procedure analogous to the one described above. The yield in all cases was in the 85-95% range: ¹H NMR (CDCl₃) δ 6.00 (broad multiplet, 2, CH=CH), 4.67 (b, 2, OCH), 4.32 (b, 1.6, CH allylic), 4.01 (b, 0.8, CH allylic), 1.48 (s, 3, CH₃), 1.22 (s, 3, CH₃), 0.98 (s, CMe₃ end group); ¹³C NMR (d₆-DMSO) δ 131.6 (b, CH=CH), 130.8 (b, CH=CH), 76.8, 75.7, 72.8, 26.0 (CH₃), 25.2 (CH₃), 25.1 (CH₃), 22.2 (C(CH₃)₂).

**X-Ray Crystal Structure of 20.** The data was collected by Dr. William Davis and the structure solved by Marie O'Regan. Data were collected at -73 °C on a Rigaku AFC6
differatometer with graphite monochromated Mo Kα radiation (λ = 0.71069) and a 12 KW rotating anode generator. A total of 9414 reflections were collected, 9222 of which were unique. Equivalent reflections were merged. One set of reflections (h+I) had very large errors, which did not improve with refinement. This may have been caused by poor crystal quality or by misalignment of the diffractometer. As a consequence of the bad set of reflections refinement of the structure did not result in convergence. Hydrogen atoms were included in calculated positions (dCH = 0.95 Å). All non-hydrogen atoms were refined anisotropically, except the carbomethoxy groups. The carbomethoxy groups and the tert-butyl groups of the t-butoxide ligands were highly disordered and were refined as rigid groups. The carbomethoxy groups were badly disordered and did not respond well to modelling. As a result of the aforementioned problems, only the gross structure may be trusted, and not the bond distances and angles. Crystal data are: a = 9.741, b = 20.582, c = 19.015, α = 90, β = 103.7, space group = #14.
CHAPTER 6
Preparation of Redox Active Polymers via
Ring Opening Metathesis Polymerization with
Mo(NAr)(CHMe₃)(OCMe₃)₂.
INTRODUCTION

The focus of the work reported in previous chapters has been the study of the principles which govern the ring opening metathesis polymerization (ROMP) of norbornenes and disubstituted norbornadienes using initiators of the type $M(CHCMe_3)(NAr)(OCMe_3)_2$ ($M = Mo, W$). As mentioned in Chapter 4, the ability to make block copolymers and the tolerance of functionalities when $M = Mo$ sets this technology apart from the more established living polymerization systems. The principles learned can be used to prepare materials with particular functions and properties, via control of the polymer's primary structure (arrangement of monomers along the polymer backbone). This Chapter reports the preparation of electroactive polymers and oligomers designed for the modification of electrode surfaces.

The binding of chemical reagents to electrodes in order to manipulate the properties of the surface is an area of research with many potential applications. The general concept is illustrated schematically in Figure 1.108,109 By placing the reagents on the surface, either covalently or by adsorption, the chemist tries to overcome or counteract some of the phenomena which reduce the applicability of electrodes in analytical or synthetic schemes. Two of the most undesired effects are the fouling of the electrode by precipitation or adsorption of redox species on the electrode surface and the kinetic barrier of some species which require the application of an overpotential for the electron transfer to occur. If the proper reagent is added, properties such as control of the rates and selectivity of electrochemical reactions (electrocatalysis), or elimination of adsorptive and coating effects might be obtained. In particular, applications such as corrosion suppression of semiconductors, electrocatalysis, controlled release of chemically active reagents and microelectrochemical devices have been reviewed.110,111,112

Electroactive polymer films are beginning to replace molecular monolayers bonded to the electrode surface as the reagents of choice.113,114 This is due to a combination of longer stability, ease of preparation and greater diversity of immobilized chemical substances. A
Figure 1. Schematic illustration of the modification of an electrode via reagent functionalization of the surface.
drawback of some of these polymers is their synthesis *in situ* from monomers by
electrochemical polymerization which precludes a thorough characterization. Other approaches
involve the making of polymer films from preformed polymers or by ion-exchange. In these
latter two methods the polymers can be characterized but it is not possible to control the process
as much as would be desirable. For example block copolymers with narrow polydispersities
cannot be made. One of the better introductions into this field is R. W. Murray’s review\textsuperscript{115}
which covers the literature extensively up to 1984.

In this Chapter the synthesis of redox active polymers and oligomers using ROMP
technology is reported. Especial emphasis was placed in the exploitation of the individual
polymerization steps (initiation, propagation and termination) in order to obtain a particular
electrochemical response or property. This project provides the synthetic chemist with the
challenge of making materials with certain properties that are determined by their structure.
These materials can be fully characterized prior to electrochemical measurements.

This work was done in collaboration with Dr. David Albagli and Professor Mark S.
Wrighton. Some of these results have been published in Dr. Albagli’s thesis\textsuperscript{116} but are
presented in this chapter from the point of view of the synthetic chemist. This work could not
have been accomplished without his ideas, experience and enthusiasm.

**RESULTS AND DISCUSSION**

**Synthesis of Norbornene Derivatives Containing Redox Groups.**

It is clear that if redox active polymers are to be designed in a controlled fashion it is
convenient to choose the redox groups to be incorporated in the monomer such that the
polymerization process is unaffected. In order to ascertain the range of redox potentials of
groups which could be placed on the norbornene skeleton without interactions with the
catalyst, the cyclic voltammetry (CV) of Mo(CHCM\textsubscript{3}) was obtained and is shown in
Figure 2. The initiator has a reversible one electron reduction process with a half wave
potential of -2.16 V vs SCE and no oxidation could be observed up to approximately 1 V.
Figure 2. Cyclic voltammogram of Mo(CHClMe₃) at 25 mV/sec in THF/0.1 M [n-Bu₄N]PF₆ at a 25 μm Pt disk electrode.
Note that the molybdenum metal in Mo(CHCMe3) is formally in its highest oxidation state (VI). It is somewhat surprising that a reversible reduction would occur at such a negative potential however this property allows the initiator to be stable towards reduction or oxidation when in the presence of a large number of common redox functionalities.

There are few molecules which are stable in both reduced and oxidized forms. This fact presents the first challenge to monomer construction. Ferrocene, a classic example of a stable redox couple, was found to be unreactive towards Mo(CHCMe3) even when present in large excess. A preliminary standard method of determining whether a functionality can be tolerated by Mo(CHCMe3) consists of polymerizing norbornene (NBE) in the presence of a large amount (30-50 equivalents) of that functionality. Ferrocene did not affect the polymerization. Conversely benzoquinone destroyed the polynorbornene propagating species and was abandoned as a potential redox group. The incorporation of ferrocene into the norbornene skeleton was achieved by the synthesis of trans-2-carbomethoxy-3-ferrocenylnorbornene (26) as shown in Equation 1. Ideally only the redox groups would be

\[
\text{HO}_2\text{C} \quad \text{C}_6\text{H}_6 \quad \text{CO}_2\text{H} \\
\text{Fe} \quad \text{Fe} \\
\text{CH}_2\text{N}_2 \quad \text{Et}_2\text{O} \\
\text{CO}_2\text{Me} \\
\text{Fe} \\
\text{Et}_2\text{O} \\
\text{Et}_2\text{O} \\
(26)
\]

attached to norbornene, but for synthetic reasons (activation of the Diels-Alder reaction) a carbomethoxy group is present in the monomer. As discussed in Chapter IV a carbomethoxy
group is not expected to interfere in the polymerizations. The presence of polar groups such as
carbomethoxy increases the polarity of these monomers as well as the resulting polymers,
aiding solubility in electrolyte media.

A variation of the method for inclusion of ferrocene into monomers is shown in
Equation 2. The monomer is obtained as a mixture of exo and endo isomers as a result of the

\[ \text{CO}_2\text{H} \quad \overset{\text{PCl}_5}{\longrightarrow} \quad \text{COCl} \quad \begin{array}{c} \text{Fe} \\ \text{Fe} \end{array} \quad \overset{\text{CH}_2\text{OH}}{\longrightarrow} \quad \begin{array}{c} \text{CH}_2\text{O(O)C} \\ \text{Fe} \end{array} \]

\( (26') \)

isomer mixture in commercially available norbornene-2-methanol. The properties of the
mixture of endo and exo-2-(methoxycarbonyl)ferrocenyl-5-norbornene \((26')\) are identical to
those of 26. The polymers obtained, poly26 and poly26', are also similar (vide infra).

In order to obtain redox monomers with different oxidation/reduction potentials, the
phenothiazine (Phz) functionality was introduced via the synthetic route shown in Equation 3.
This straightforward preparation can be readily scaled up to give gram quantities of trans-2,3-
\((10'-(2'\text{-ethyl})\text{-phenothiazine})\text{dicarboxylatonorbornene} \((27)\) in good yield.
Preparation and Properties of Redox Polymers and Oligomers.

Monomer 26 can be polymerized quantitatively with Mo(CHCMe₃) and the resulting materials are readily purified by precipitation from non-polar solvents such as hexane, pentane or petroleum ether. GPC analysis shows that the resulting molecular weights are within the narrow range expected for polymers prepared by living systems. The GPC trace of the poly26₁₅ (for ease of presentation the subscript refers to the average degree of polymerization, i.e. the average number of monomers per chain) and poly26₃₀ are shown in Figure 3 and the data presented in Table 1. These polydispersities are indeed quite narrow, especially when the small number of equivalents of monomer which have been added is considered. Deviations of these dispersities from those estimated by the Poisson equation (applicable where \( k_p = k_i \) or \( k_p > k_i \)) are probably due to the slower rate of initiation relative to propagation (\( k_p/k_i = 10 \) for 26) but indicate that termination of propagating species within the timescale of the polymerization reaction is negligible. For cases where \( k_p \gg k_i \) broader dispersities are expected as well as tailing in the GPC traces toward lower molecular weight species (higher retention times in the GPC columns). \(^1\)H and \(^{13}\)C NMR spectra are broad and complex, as is expected in polymers.
Figure 3. GPC trace (refractometer data) of (a) poly26_{15} and (b) poly26_{30}. 
Table I. Gel Permeation Chromatography Data of Redox Polymers and Block Copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PDI&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;0&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>MW&lt;sub&gt;calc&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
<td>Poly26&lt;sub&gt;15&lt;/sub&gt;</td>
<td>1.13</td>
<td>5090</td>
<td>5250</td>
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<tr>
<td>Poly26&lt;sub&gt;30&lt;/sub&gt;</td>
<td>1.13</td>
<td>9030</td>
<td>10290</td>
</tr>
<tr>
<td>Poly26&lt;sub&gt;15&lt;/sub&gt;-block-polyNBE&lt;sub&gt;15&lt;/sub&gt;</td>
<td>1.05</td>
<td>10460</td>
<td>6688</td>
</tr>
<tr>
<td>Poly26&lt;sub&gt;15&lt;/sub&gt;-block-polyNBE&lt;sub&gt;60&lt;/sub&gt;</td>
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<td>16190</td>
<td>10930</td>
</tr>
<tr>
<td>Fc-poly27&lt;sub&gt;5&lt;/sub&gt;-FcMe8</td>
<td>1.22</td>
<td>2700</td>
<td>3430</td>
</tr>
<tr>
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<td>6461</td>
<td>7260</td>
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<td>8360</td>
<td>9630</td>
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<td>Poly27&lt;sub&gt;30&lt;/sub&gt;</td>
<td>1.10</td>
<td>14750</td>
<td>19190</td>
</tr>
<tr>
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<td>26740</td>
<td>23830</td>
</tr>
<tr>
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<td>1.08</td>
<td>35860</td>
<td>13060</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values obtained by GPC calibrated vs. polystyrene standards. <sup>b</sup>Molecular weight calculated for the number of equivalents added to the initiator.
Figure 4. $^1$H NMR spectrum (CDCl$_3$) of poly2615 (residual hexane from precipitation).
with cis/trans, endo/exo and head to tail isomerism: (see Chapter 4). The \(^1\)H NMR of poly\textsubscript{26\textsubscript{15}} is shown in Figure 4.

Termination of the polymerization with para-trimethylsilylbenzaldehyde selectively places a trimethylsilyl (TMS) tag as an end group on poly\textsubscript{26}. Integration by \(^1\)H NMR of the TMS group versus the tert-butyl group leftover from the initiation step allows the determination of the relative amount of initiation and termination events (see Chapter 3 and Equation 4). If some of the propagating species have decomposed during the time of the polymerization then the ratio of TMS : tert-butyl would be less than one. Furthermore, comparison with the integration values of the olefinic region of the polymers (2 protons for each monomer) allows the determination of monomer consumed versus the initiator or terminator. This procedure has been performed with all the monomers whose polymerizations are described in this Chapter and the results have been consistent with the stoichiometry proposed. The combination of the \(^1\)H NMR data for end group determination together with GPC data strongly supports the formulation of the polymers as a narrow distribution with the most abundant chain length having a degree of polymerization equal to the number of equivalents of monomer added.

A technique which can determine both the number of equivalents per chain and the distribution of chain lengths is field desorption mass spectroscopy (FD-MS). This technique has recently been applied to the analysis of synthetic and biological polymer materials.\textsuperscript{117} The mass spectrum obtained from poly\textsubscript{26\textsubscript{15}} is shown in Figure 5. This spectrum shows the
Figure 5. Field desorption mass spectrum of poly26,5. Shown here is the doubly charged manifold of peaks.
Figure 6. Solvent dependence on the solution electrochemistry of poly2615. (a) Cyclic voltammogram in 1:1 THF:CH₃CN and (b) 1:6 THF:CH₃CN. The supporting electrolyte was 0.1 M [n-Bu]₄N BF₄.
doubly charged manifold of peaks where the number of monomers in each ranges from \( x = 8 \) to \( x = 26 \). Similar manifolds were obtained for the singly and triply charged species, which show a similar range of molecular weights. In all these spectra the most abundant peak corresponds to either the 14-mer or the 15-mer, consistent with the proposed average degree of polymerization. Assuming that the relative abundance of the peaks corresponds to the relative concentration of chain lengths the polydispersity can be calculated from data such as shown in Figure 5 to be 1.06. This value is in the range obtained by GPC. FD-MS of higher oligomers could not be obtained, probably do to their large molecular mass.

Solubility has a strong influence on the solution electrochemistry of poly26. In the reduced (neutral) state the polymer is soluble in benzene, toluene, \( \text{CH}_2\text{Cl}_2 \), and dimethylformamide (DMF). When oxidized, poly26 is slightly soluble only in more polar solvents such as \( \text{CH}_3\text{CN} \) and DMF. The effect of solvent on the cyclic voltammetric behavior of poly26_{15} is shown in Figure 6. In 1:1 THF to \( \text{CH}_3\text{CN} \) (Figure 6a) the peak cathodic current is larger than the peak anodic current, rather than being equal as one would expect. Precipitation of the oxidized polymer on the electrode surface accounts for the observed distortion in peak shape. As the neutral polymer is oxidized the current increases quickly, due to the presence of polymer near the electrode, and approaches diffusion controlled current. The reduction process is faster, since the material is precipitated on the surface and the result is a sharp peak as the material is returned back to the neutral state and back into solution (stripping current). When the ratio of \( \text{CH}_3\text{CN} \) is increased in the solvent (Figure 6b) the solubility of the oxidized poly26_{15} increases and the cathodic stripping current disappears resulting in a more symmetric CV wave.

Increasing the chain length augments this solubility effect, as shown in Figure 7 where the cyclic voltammetry of poly26_{15} and poly26_{30} are compared. The stripping current becomes more pronounced for larger polymers as is to be expected based on solubility principles. Note that in the two CV experiment in Figure 7 the concentration of ferrocene is the same (approximately 3mM). The anodic current for the larger polymer is smaller as one would
Figure 7 Comparison of the cyclic voltammetric behavior in CH$_2$Cl$_2$ of (a) poly26$_{15}$ and (b) poly26$_{30}$. The concentration of ferrocene centers is the same in both solutions (3.0 mM).
expect for a slower rate of diffusion. We conclude that increasing the chain length reduces the solubility in the oxidized state and slows diffusion rates.

Phenothiazine-containing polymers are readily prepared by polymerizing 27 using Mo(CHCMe3). The resulting polymers have narrow molecular weight distributions which are listed in Table 1. The GPC trace of poly2710 (shown in Figure 8) is symmetric and has a calculated polydispersity of 1.23. This value should be compared with the theoretical dispersity for 10-mer expected from a Poisson distribution which is 1.08 (PDI = 1 + x/2(x + 1)2, where x is the degree of polymerization). The expansion of the lower molecular weight region shows the presence of individual peaks, which appear to be due to the one-mer, dimer and trimer with the resolution diminishing for higher oligomers. This observation is important since it confirms that the GPC columns chosen are capable of resolving these oligomers at such a low molecular weight regime. This separation is probably due to the large size of the monomer itself (MW = 726). The accuracy of the polydispersities obtained by GPC is dependant on this discrimination since the lower the resolution the lower the precision in the calculations. Attempts to obtain FD-MS data for poly2710 failed, perhaps due to the large molecular masses involved; note that the average molecular weight of a 10 mer of poly27 corresponds to that of a 22 mer of poly26.

Analysis by 1H and 13C NMR of poly27 confirms the formulation of the polymers by utilizing the end group analysis technique previously described. These spectra are broad and complex, as would be expected for polymers made from monomers of C1 symmetry (Chapter 4). As an example the 13C NMR spectrum of poly2715, which can be fully assigned (see Experimental), is shown in Figure 9.

Solubility effects, as was seen for poly26, have a profound effect on the solution electrochemistry of poly27. The sweep rate dependance of poly2715 at moderate sweep rates is shown in Figure 10. The anodic wave maintains the qualities for linear diffusion of the electroactive species and on the reverse scan the reductive stripping wave characteristic of precipitated polymer is observed. Peak potential values are independent of sweep rate which is
Figure 8. Complete GPC trace and expansion of poly27₁₀.
Figure 10. Scan rate dependence in $\text{CH}_2\text{Cl}_2/0.1\text{ M}[\text{n-Bu}_4\text{N}]\text{PF}_6$ of poly27$_{15}$. 
consistent with a chemically and electrochemically reversible process. The peak current increases linearly with the square root of the sweep rate up to the limit of these measurements (500 mV/sec).

Due to the living nature of the polymerization system it is possible to alter the solubility of the oxidized polymers. Block copolymers of poly27 and polynorbornene (polyNBE) were prepared using standard methods (see Chapter 3 and Chapter 4) and characterized by GPC, $^1$H and $^{13}$C NMR spectroscopy and differential scanning calorimetry. Norbornene was chosen because it is the least polar monomer readily available and therefore most likely to solubilize the highly polar oxidized species. The cyclic voltammetry behaviors of two block copolymers of different poly27:polyNBE ratio and the monomer (27) are shown in Figure 11. The monomer exhibits features characteristic of a reversible Nernstian redox couple, with a potential $E^* = 0.75$ vs SCE. For poly27$_{30}$-block-polyNBE$_{50}$ (Figure 11a) the anodic current is similar to that of poly27$_{15}$. However, two features which can be observed in the cathodic current are a small amount of stripping current as well as current from oxidized material diffusing from the solution. It appears that at this particular 27 : NBE ratio some of the oxidized polymer precipitates but is in equilibrium with some solubilized material. It is possible that the precipitated material contains the extremes of the longer poly27 chains or shorter polyNBE chains which are expected to be present due to the statistical nature of the polymerization. An interesting experiment would consist of removing the electrode at a positive potential when it contains the precipitated material, placing it into fresh CH$_2$Cl$_2$, reducing the material and analyzing it by GPC or NMR spectroscopy to see if it is a representative sample of the original range of chain lengths. Poly27$_{10}$-block-polyNBE$_{70}$ (Figure 11b) is more soluble in the oxidized state to the extent that the anodic current no longer shows stripping behavior. At this latter 27 : NBE ratio the oxidized polymer is essentially soluble in CH$_2$Cl$_2$ and the CV is similar to that of the monomer (Figure 11c). In summary then by block copolymerizing poly27 with polyNBE the charge to mass ratio is lowered resulting in a polymer whose
Figure 11. Scan rate dependence in CH$_2$Cl$_2$/0.1 M [n-Bu$_4$N]$^+$PF$_6^-$ of (a) poly27$_{30}$-block-polyNBE$_{30}$; (b) poly27$_{10}$-block-polyNBE$_{70}$; and (c) 27.
solubility is less affected by the state of charge. Thus it is possible then to fine tune the solubility of these polymers via controlled polymerization of different monomers.

**Synthesis and Reactivity of Ferrocenyl-methyldiene Initiator.**

So far, both propagation and termination have been exploited in order to either affect the properties of the resulting polymers or to aid polymer characterization. Since the only step remaining to exploit was initiation, efforts were concentrated on the modification of the initiator in such a way that it would yield useful electrochemical information. The making of an initiator with a redox active alkylidene was an attractive proposition since it would leave an electrochemical "tag" which could serve as an internal standard within the chain.

This "dream" molecule was made by the reaction of one equivalent of vinyl-ferrocene with Mo(CHCMe₃) to yield molybdenum (2,6-diisopropylphenylimido)bis(tert-butoxide)ferrocenyl methyldiene (Mo(CHFc)) as shown in Equation 5. This new initiator can

\[
\begin{align*}
\text{BuO}^\prime\text{Mo} & + \text{Fe} & \rightarrow & \text{BuO}^\prime\text{Mo} \\
\text{BuO} & & & \text{BuO}
\end{align*}
\]

\[\text{Mo(CHFc)}\]

be isolated as a bright red crystalline solid in 50-60% yield. It is important that the two starting materials be present in a 1:1 ratio and they must be added together as solids, with the solvent added dropwise until solution is achieved. Several factors contribute to the success of this reaction, which is the first reported isolation of a modified molybdenum alkylidene by a metathetical reaction. The nature of the olefin used in the reaction is crucial since it is likely to be more electron rich than other primary olefins, such as styrene, which have failed. The side product, tert-butylethylene (neohexene), is a low boiling liquid which probably evaporates
preventing back reaction and eliminating the formation of some type of equilibrium. The concentration is also maximized in order to favour the bimolecular process.

Substitution of the tert-butyl group for a ferrocenyl group has a dramatic effect on the electrochemistry of the initiator. The cyclic voltammograms of Mo(CHFc) in THF/0.1 M [n-Bu$_4$N][AsF$_6$] and in CH$_2$Cl$_2$/0.1 M [n-Bu$_4$N][AsF$_6$] are shown in Figure 12. No reduction wave is observed out to -2.40 V vs SCE. This information suggests that ferrocene is a better electron donor than the tert-butyl group making the addition of the reduction electron more difficult (recall that a reversible one electron reduction wave is observed for Mo(CHCMe$_3$) at -2.16 V vs SCE). It is also known that for catalysts of the type M(CHCMe$_3$)(NAr)(OR)$_2$ (M = Mo, W) alkoxide substitution occurs when a more electron donating alkoxide is added. For example, M(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ can be prepared by addition of two equivalents LiOCMe$_3$ to M(CHCMe$_3$)(NAr)(OCMe(CF$_3$)$_2$)$_2$. Therefore it appears that the reaction in Equation 5 also proceeds for thermodynamic reasons since a more electron donating substituent would stabilize the high oxidation state of the metal.

The oxidation of Mo(CHFc) (Figure 12) was expected to be a ferrocene based single electron reversible wave in the absence of any interactions between the molybdenum metal and ferrocene. Instead, two overlapping oxidation waves are observed at approximately 370 and 550 mV vs SCE. Why two waves are observed is not yet known. A possible explanation is the presence of two isomers (syn and anti rotamers) with different r-ox potentials. Note that when the ferrocene group is oxidized it is likely to weaken the Mo=C bond, resulting in an increase in the rate of rotamer interconversion. Another possibility is that Mo(CHFc) has reacted with itself or with impurities in the electrolyte solution. However, there is no change in the cyclic voltammetric wave shown in Figure 12 over a 2 h period. It would be interesting to obtain more information regarding the nature of Mo(CHFc) in the oxidized state.

Mo(CHFc) initiates the polymerization of 27 to yield polymers or oligomers of low polydispersity (Equation 6, Figure 13). For this reaction $k_o/k_i = 2$ and when Mo(CHCMe$_3$)
Figure 12. Cyclic voltammetry of Mo(CHFc) in (a) THF/0.1 M [n-Bu4N]AsF6 at 100 mV/sec at a 25 µm Pt disk electrode and (b) in CH2Cl2/0.1 M [n-Bu4N]AsF6 at 50 and 500 mV/sec at a 500 µm Pt disk electrode.
Figure 13. Gel permeation chromatogram of Fc-poly2710.
is the initiator this ratio is 6. In both reactions the value of $k_p$ must be the same, therefore it is possible to estimate that $\text{Mo(CHFc)}$ reacts approximately three times faster than $\text{Mo(CHCMe}_3$ towards 27. This enhanced reactivity is most likely due to the smaller size of the alkylidene substituent near the metal center. The electronic factors involved are more difficult to assess since it is not known whether the ferrocenyl group is in conjugation with the alkylidene double bond.

Electrochemical studies of isolated Fc-poly27$_{10}$ capped with pyrene (by addition of pyrene carboxaldehyde to the living polymer, vide infra) reveal two redox waves, as shown in Figure 14 a. The first oxidation at approximately 410 mV vs SCE is in the range for vinyl substituted ferrocenes and is assigned to the ferrocene end group (unlike the initiator only one wave is observed). The second wave at approximately 750 mV vs SCE corresponds to the pendant Phz groups on the oligomer backbone. The ratio obtained from the peak currents is close to 20:1, as expected from the stoichiometry of the polymerization reaction. The peak shape for the Phz groups is consistent with precipitation of the polymer as previously observed. Reduction of the ferrocene end group however does not show stripping characteristics, indicating that selective oxidation of the end group does not appear to cause a sufficient change in solubility to induce precipitation of the polymer.
Precipitation of the oxidized polymer can be used to coat the electrode with electroactive material. Consider the electrode shown in Figure 14a. This electrode was held at a potential of 1.0 V vs SCE, causing precipitation of the polymer onto the surface of the electrode. It was then removed at this potential and placed into a CH$_3$CN/0.1 M [n-Bu$_4$N][PF$_6$] electrolyte solution where both the oxidized and reduced forms of the polymer are insoluble and the resulting cyclic voltammetry is shown in Figure 14b. Note that the lineshape is characteristic of surface bound material with no diffusion controlled current present in either the cathodic or anodic currents. Therefore, once the material on the surface is reduced or oxidized no more current flows. The ratio of the current from the ferrocene end group to the Phz groups is again approximately 20:1.

**Surface Confinement of Redox Active Polymers and Oligomers.**

Covalent binding of molecules to surfaces is a method by which the properties of the surface are modified. One of the most versatile methods is the coupling of silane reagents with an acid treated surface oxide layer resulting in siloxide bond formation. This is particularly well suited for electrodes because of the presence of oxide layers on many electrode materials such as Pt, In(Sn)O$_2$ (ITO), Si, and C, as well as the durability of the siloxide linkages.$^{119}$

The silane functionality can be introduced into redox polymers by block copolymerizing 2-triethoxysilylnorbomene (28). Living poly28$_{10}$ can be characterized by $^1$H and $^{13}$C NMR spectroscopy from which it is possible to determine that the alkylidene signal does not decrease relative to an internal standard even after a few days (Equation 7). Unfortunately these

$$\text{Mo(CHCMe}_3\text{)} + \quad \begin{array}{c}
\text{(28)} \\
\end{array} \xrightarrow{\text{THF}} \quad \text{Mo-CHCMe}_3 \quad \begin{array}{c}
\text{Si(OEt)}_3 \\
\text{10} \\
\text{Si(OEt)}_3 \\
\end{array}$$

(7)
Figure 14. (a) Cyclic voltammetry of Fc-poly2710 in CH$_2$Cl$_2$/[n-Bu$_4$N]PF$_6$; and (b) cyclic voltammetry of the electrode in Figure 14a after being held at a potential of approx. 1 Volt, taken out at that potential and placed in a CH$_3$CN/[n-Bu$_4$N]PF$_6$ electrolyte solution.
polymers are likely to hydrolyze or crosslink and precipitate upon exposure to air ruling out GPC analysis. This element of uncertainty remains in all of these Si(OEt)₃ derivatized polynorbornenes. The $k_p/k_i$ ratio for polymerization of 28 with Mo(CHCMe₃) was determined to be 13, which is in the same range observed for norbornene (see Chapter 3).

In order to explore the binding properties of poly28 blocks a polymer consisting of polyNBE₃₀-block-poly26₃₀-block-poly28₁₀ was made in order to assure that the redox active groups were close to the functionalities binding to the electrode. Functionalized electrodes were prepared by soaking pretreated Pt electrodes in a benzene solution of this polymer for 12 hrs. The electrodes were then removed from the solution and rinsed. The electrochemical behavior of the resulting electrode is shown in Figure 15a. The observed redox process is characteristic of poly26 and from the waveshape it is possible to determine that it is due to surface confined material. No current is observed in electrodes after soaking in solutions of poly26₁₅ or poly26₁₅-block-polyNBE₃₀.

Varying the relative positions of electroactive poly26 and polyNBE does not change the electrochemistry significantly. The cyclic voltammogram of poly26₃₀-block-polyNBE₃₀-block-poly28₁₀ is shown in Figure 15b. Apparently, even though the polyNBE block is closer to the surface it does not, at this chainlength, insulate the electrode from the poly26 block.

Phenothiazine containing polymers can also be bound to electrode surfaces by block copolymerizing poly28 even when only a few equivalents of 28 are present. The cyclic voltammogram of an ITO electrode treated with poly27₃₀-block-poly28₂ in a similar fashion as the Pt electrodes (in Figure 15) is shown in Figure 16a. It is clear that when only two equivalents of 28 are added to living poly27₃₀ not all chains will include this monomer. However, those that do contain it bind to the electrode while the others remain in solution. Since the number of Si(OEt)₃ groups is small the GPC of poly27₃₀-block-poly28₂ using CaCl₂ dried CH₂Cl₂ was carried out, from which the polydispersity was calculated to be 1.11.
Figure 15. Cyclic voltammetric behavior of Pt electrodes derivatized with (a) polyNBE$_{30}$-block-poly26$_{30}$-block-poly28$_{10}$ and (b) poly26-block-polyNBE$_{30}$-block-poly28$_{10}$. 

$\text{CH}_3\text{CN/0.1 M (n-Bu)}_4\text{N PF}_6$ 

$20 \mu\text{A}$ 

$100 \text{ mV/sec}$ 

Potential, $U \text{ vs Ag wire}$
Figure 16. (a) Scan rate dependence of ITO electrodes derivatized with poly27_{30}-block-poly28_{2} in CH_{2}Cl_{2} 0.1 M [n-Bu_4N]PF_6; (b) GPC trace of poly27_{30}-block-poly28_{2}. 

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The small high molecular weight shoulder observed (Figure 16b) is perhaps due to siloxane cross linking.

Quenching of the polymerizations with octamethylferrocenecarboxaldehyde (FcMe₈CHO) introduces selectively a unique redox end group. Using this aldehyde two oligomers were prepared, as shown in Scheme 1, which contained unique oxidation potentials arising from each individual polymerization step. The scan dependance of Fc-poly27₅-FcMe₈ (Scheme 1) is shown in Figure 17 and clearly shows the presence of the end groups in the polymer in a ratio of Fc to FcMe₈ of about 1.06. The reduction wave of the Phz groups is consistent with polymer precipitation on the electrode although it is not as pronounced as previously observed probably due to the small size of the poly27 block. The ratio of peak currents from the Phz groups to end groups is approximately 12:1. Normal pulse voltammetry studies of Fc-poly27₅-FcMe₈ determined the ratio of the components to be 1.0:9.6:0.92 with observed potentials of 0.25 for FcMe₈, 0.55 for Fc and 0.90 for poly27₅. This latter technique eliminates problems of adsorption and precipitation on the electrode and for this reason is considered more accurate than cyclic voltammetry for quantitative measurements of this type.¹²⁰,¹²¹

Pretreated Pt electrodes were soaked in solutions of Fc-poly27₅-block-poly28₂-FcMe₈ and Fc-poly27₅-FcMe₈ for 12 hours, taken out and rinsed in order to compare the binding abilities of the two different oligomers. The electrode treated with the latter material showed no electrochemical response, while the solution containing Fc-poly27₅-block-poly28₂-FcMe₈ yielded a derivatized electrode whose cyclic voltammetry is shown in Figure 18. Note that the three signals observed are characteristic of surface-bound species and are in the same ratio as those observed in the solution electrochemistry of Fc-poly27₅-FcMe₈. These experiments illustrate the ability to obtain a particular electrochemical response from each polymerization step. Furthermore, it is possible to choose between solution or surface bound behavior via controlled block copolymerization of a small amount of monomer containing surface binding functionalities.
Figure 17. Scan rate dependence of Fc-poly27,5-FcMe8 in CH₂Cl₂/0.1 M [n-Bu₄N]PF₆.
Figure 18. Scan rate dependence of a Pt electrode derivatized with Fc-poly275-block-poly282-FcMe8 in CH₂Cl₂/0.1 M [n-Bu₄N]PF₆.
Having succeeded in binding polymers using functionalities present in a block, the focus of the research turned towards the incorporation of a single functionality in the polymer which would form a covalent bond or adsorb onto the surface. It was decided that this functionality would be best introduced either in the initiation or termination step since, unlike propagation, they are not statistical processes. The accessibility to a large number of functionalized aldehydes made termination the preferred choice. Ideally a trialkoxysilyl substituted aldehyde would have been chosen, in order to compare with the previous binding data. Unfortunately the two functionalities are difficult to place on a single molecule due to synthetic considerations.

Pyrene has a strong affinity for carbon surfaces and in small molecules the addition of a pyrene group causes them to attach to carbon surfaces which they would otherwise would not adsorb onto.\textsuperscript{122} This functionality can be readily incorporated as an end group by quenching the polymerization with commercially available pyrenecarboxaldehyde as shown in Equation 8.

\[
\text{Mo}(\text{CHCMe}_3) + 10 \text{ CHO} \rightarrow \text{PhzCH}_2\text{CH}_2\text{O}_2\text{C} \quad \text{CO}_2\text{CHCH}_2\text{Phz}
\]

The pyrene cap can serve as an internal standard in \textsuperscript{1}H NMR (9 H) since it can be integrated versus the tert-butyl end group (9 H) in order to quantify the number of initiation versus termination groups. In all the polymers with a pyrene end group the ratio was found to be 1:1. Soaking of glassy carbon electrodes in solutions of pyrene-poly\textsuperscript{27}\textsubscript{10} resulted in adsorption of the polymer onto the surface. The control experiments showed that pivaldehyde capped poly\textsuperscript{27}\textsubscript{10} also was adsorbed onto the surface, indicating that the polymer itself has some affinity for carbon. Competition experiments between t-Bu-poly\textsuperscript{26}\textsubscript{12} vs pyrene-poly\textsuperscript{215} and pyrene-poly\textsuperscript{26}\textsubscript{12} vs. t-Bu-poly\textsuperscript{215} showed no discrimination by the electrode surface toward
those chains containing pyrene end groups. Evidently the affinity of pyrene for the carbon surface did not overcome the adsorption of either polymer.

An interesting application of the pyrene end group is its use as a luminescent probe, the emission properties of which depend on the primary structure of the polymer. These results are described in Dr. Albagni’s thesis and are not repeated here.\textsuperscript{123}

Reaction between a nucleophile and an electrophile, where one is bound to the electrode and the other is an end group of a polymer can also provide a covalent bond between the polymer and the surface. Such a surface linking reaction is shown schematically in Scheme 2. The two reagents in Scheme 2 are provided by the treatment of ITO electrodes with p-(chloromethyl)phenyltrichlorosilane and by quenching of polymerizations with pyridinecarboxaldehyde. The treated ITO electrodes were exposed to CH$_2$Cl$_2$ solutions of poly27\textsubscript{10} and pyridine-poly27\textsubscript{10} for 24 hrs and then rinsed. The CV of the resulting electrodes is shown in Figure 19. Comparison of Figures 19a (treatment with poly27) and 19b (treatment with pyridene-poly2) demonstrates that the pyridene end group is crucial for the successful binding of the polymer. Also shown in Figure 19c is the response from an ITO electrode exposed to a solution of p-(chloromethyl)phenyltrichlorosilane and pyridene-poly27\textsubscript{10} which had reacted for 24 hours. This reactivity represents the first example of the selective binding of a polymer to a surface via a single functionality present in the chain.

**Solid State Properties of Redox Polymers.**

So far the materials discussed in this chapter may not qualify for what may be considered true polymers, i. e. do not contain an average degree of polymerization of over 100. In general, the minimum molecular weight for polymeric material properties is usually in the range of 5000-10000 depending on the polymer and the particular property.\textsuperscript{124} In these experiments the number of redox monomers in the chains was kept at a minimum, since this makes characterization more straightforward and makes the trial and error nature of exploratory synthetic research less intensive in terms of monomer consumed. One of the characteristics of
Scheme 2. Strategy for formation of a covalent bond between a surface and a polymer via reaction between a surface-bound reagent and a polymer end group functionality.
Figure 19. Cyclic voltammogram at 100 mV/sec for (a) an ITO electrode treated with p-(chloromethyl) phenyltrichlorosilane, followed by a 24 h soak in a CH$_2$Cl$_2$ solution of poly27$_{10}$; (b) an ITO electrode treated with p-(chloromethyl)-phenyltrichlorosilane, followed by a 24 h soak in a CH$_2$Cl$_2$ solution of poly27$_{10}$-pyridine; and (c) an ITO electrode soaked for 10 minutes in a solution of p-(chloromethyl) phenyltrichlorosilane and poly27$_{10}$-pyridine that had reacted for 24 h.
polymeric materials is the glass transition temperature (Tg) at which the amorphous domains of a polymer take the characteristic properties of the glassy state such as brittleness, stiffness and rigidity.

The differential scanning calorimetry (DSC) curves of poly26 polymers and block copolymers are shown in Figure 20 and data are presented in Table 2. For poly26\textsubscript{15} a reversible Tg is observed, even at this short chainlength. Increasing the number of repeat units from poly26\textsubscript{15} to poly26\textsubscript{30} causes an increase in the Tg of 7 °C to 150 °C, a remarkably high temperature for a polynorbornene derivative. Such an increase in Tg is expected as the molecular weight of a homopolymer is increased, until a molecular weight in the range of 10,000 is reached. Both poly26\textsubscript{15}-block-polyNBE\textsubscript{15} and poly26\textsubscript{15}-block-polyNBE\textsubscript{60} show Tg values corresponding to each of the block copolymer component chains. Since these are block copolymers and not blends of the two homopolymers this behavior is most likely to arise from microdomain formation of the two blocks in a heterogeneous phase. Note that the Tg transition arising from the poly26\textsubscript{15} block in these diblocks is comparatively low. This anomalous decrease in Tg for the hard domains has been previously observed in styrene-isoprene block copolymers and has been explained by premature molecular motions in the higher Tg domains, induced by the more labile chains in the lower Tg phase.\textsuperscript{125}

DSC analysis of poly27 polymers and block copolymers is shown in Figure 21 and the data are presented in Table 2. For poly27 the Tg value has stabilized at poly27\textsubscript{15} (calculated molecular weight of 9630). Even for a degree of polymerization as low as 5, a Tg at 80 °C is observed. The block copolymers show Tg's for each of the component chains, indicative of microdomain formation.

Block copolymers will show microdomain formation when the block size is small if the two chains are highly immiscible with each other. The presence of two sharp glass transition temperatures in the DSC curve of poly26\textsubscript{15}-block-polyNBE\textsubscript{60} should be compared with previous studies aimed at obtaining microphase separation with polyNBE and other monomers. These studies indicated that chainlengths on the order of 1000 monomers were required.\textsuperscript{126}
Table 2. Glass transition temperatures obtained by DSC of redox polymers and block copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly26_{15}</td>
<td>143</td>
</tr>
<tr>
<td>Poly26_{30}</td>
<td>150</td>
</tr>
<tr>
<td>Poly26_{15}-block-polyNBE_{15}</td>
<td>60, 123</td>
</tr>
<tr>
<td>Poly26_{15}-block-polyNBE_{60}</td>
<td>43, 107</td>
</tr>
<tr>
<td>Fc-poly27_{5}-FcMe_{8}</td>
<td>81</td>
</tr>
<tr>
<td>Poly27_{15}</td>
<td>88</td>
</tr>
<tr>
<td>Poly27_{30}</td>
<td>88</td>
</tr>
<tr>
<td>Poly27_{30}-block-polyNBE_{50}</td>
<td>45, 91</td>
</tr>
<tr>
<td>Poly27_{10}-block-polyNBE_{70}</td>
<td>50, 80</td>
</tr>
</tbody>
</table>

aScan rate of 20 °C/min, under N₂ atmosphere.
Figure 20. Differential scanning calorimetry (scan rate of 20 °C/min) of (a) poly2615; (b) poly2630; (c) poly2615-block-polyNBE15; and (d) poly2615-block-polyNBE60.
Figure 21. Differential scanning calorimetry (scan rate of 20 °C/min) of (a) Fe-poly27; (b) poly27; (c) poly27; (d) poly27-block-polyNBE; (e) poly27-block-polyNBE.
Therefore, the miscibility of poly26 in polyNBE is very low and can be attributed to the presence of the polar carbomethoxy groups and metal containing ferrocene groups which prefer not to associate with polynorbornene chains. This remarkable ability of metal-containing polynorbornene blocks to separate from unsubstituted polynorbornene blocks has opened up opportunities in the preparation of semiconductor particles using ROMP technology.127

CONCLUSION

Redox active polymers and oligomers have been synthesized by ring opening metathesis polymerization using Mo(CHCMe3)(NAr)(OCMe3)2 (Mo(CHCMe3)) as the initiator. These polymers can be fully characterized before being placed on an electrode surface. The ability to control the order of different monomers on the polymer backbone allows the control of the solubility of these materials by block copolymerizing more soluble monomers such as norbornene. This has dramatic effects on the solution electrochemistry of the polymers.

Mo(CHCFc)(NAr)(OCMe3)2 (Mo(CHCFc), Fc = ferrocenyl) was synthesized in order to introduce a single redox molecule during the initiation reaction. Mo(CHCFc) is more reactive than the parent Mo(CHCMe3), probably for steric reasons. Initiation as well as termination can be utilized in order to introduce redox end groups which serve as internal standards in electrochemical measurements.

These polymers can be placed on electrode surfaces either by oxidative precipitation, siloxane bond formation on pretreated surfaces with triethoxysilyl containing blocks or by a single covalent attachment of an end group. Pyrene cannot be used as a selective adsorbant on carbon surfaces since it cannot compete with the affinity of the surface toward the polymer chain.

Microdomain formation appears to occur with block copolymers containing polynorbornene and metal containing polynorbornene derivatives. This occurs at remarkably small degrees of polymerizations.
Finally, the work detailed here essentially describes the synthetic methodology developed for synthesis of redox active materials. This opens up the possibility of achieving particular electrochemical responses via control of the primary structure of the polymer. It is up to the imagination of future workers to bring this technology up to the application stage. In particular, by making larger block copolymers \((x = 50-100)\) and attaching them at a predetermined location, interesting functions such as rectification and supramolecular rearrangement of the polymer chain may be obtained.

**EXPERIMENTAL**

**General Details.** All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina. Norbornene was doubly distilled from molten sodium. Commercially available aldehydes (4-fluorobenzaldehyde, pivaldehyde, benzaldehyde, 1-pyrenecarboxaldehyde, 4-pyridinecarboxaldehyde) were purified by distillation under nitrogen or recrystallization. 4-Pyridinecarboxaldehyde yellows after a few days of storage and is passed through a 3 cm plug of alumina prior to usage. Octamethylferrocenecarboxaldehyde\(^{128}\), p-(trimethylsilyl)benzaldehyde\(^{75}\) and were prepared according to literature procedures. 2-triethoxysilylnorbornene was obtained from Petarch Systems, Inc. and used as received.

NMR data are listed in parts per million downfield from TMS for both proton and carbon. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in \(C_6D_6\) at 25 °C unless otherwise noted.
Gel Permeation Chromatographic (GPC) analysis were carried out at room temperature employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1-0.3 % w/v in dichloromethane which were filtered through a Milllex-SR 0.5 μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03 × 10^6 MW.

Differential scanning calorimetry (DSC) were done using a Perkin-Elmer DSC-4 interfaced with the Perkin-Elmer Thermal Analysis Data Station. For experiments requiring subambient temperature operation the unit was cooled with dry ice under an N₂ atmosphere (required for Tg determination of polynorbornene blocks). Measurements were made at a rate of 20 °C/min.

Field desorption mass spectrometry (FD-MS) was carried out on a JEOL HX110/HX110 instrument by Cathy Costello.

**Electrochemistry.** Electrochemical experiments were done using conventional 3-electrode cells. The electrolyte was purged with Ar or N₂ before use. In the case of Mo alkylidene compounds, electrochemical experiments were done in a dry box in cells which had been heated to 110 °C under vacuum. Cyclic voltammetric experiments were performed using a Pine Instruments RDE 4 biopotentiostat modified for low current sensitivity. Traces were recorded on a Kipp and Zonen BD 91 X-Y recorder. Pt working electrodes were prepared and pretreated as previously described.¹²⁹ The counter electrode was a large piece of Pt gauze. Indium (tin) oxide (ITO) electrodes were made from 50 × 7 mm slabs of ITO coated on glass. Glassy carbon electrodes were obtained from BAS, and the electrodes were polished before each experiment. The Ag quasi-reference was prepared by dipping a Ag wire in concentrated HNO₃, rinsing with water and methanol and drying. The reference potential was calibrated
with ferrocene (0.380 V vs SCE, 5 mM in CH₃CN/0.1 M [n-Bu₄N]PF₆ and converted to V vs SCE.

**trans-5-Norbornene-3-ferrocenyl-2-carboxylic acid.** This procedure was adapted from the literature. Freshly cracked cyclopentadiene (stored at -80 °C under Ar) was added in 1 mL (15 mmol) portions to a refluxing solution of β-ferrocenylacrylic acid (1.6 g, 6.2 mmol) and p-hydroquinone (25 mg, 0.2 mmol) in benzene (25 mL). The cyclopentadiene addition was performed five times a day over a period of seven days after which the solution was cooled to room temperature, transferred to a separatory funnel and washed three times with 10 % NaHCO₃. The orange aqueous solution was neutralized with 10 % HCl and the resulting precipitate was extracted with Et₂O until the aqueous phase was colorless. The Et₂O extracts were dried over MgSO₄, filtered and the solvent removed *in vacuo* to give an orange solid. The reaction was run twice to 80 % and 90 % conversion of the β-ferrocenylacrylic acid. Two diastereomers (i.e. with the ferrocenyl group either endo or exo and trans to the carboxylic group) of the norbornene product are present in a 2:3 ratio both times. This product was used in the preparation of the carbomethoxy derivative (26) without any further purification: ¹H NMR (CDCl₃) δ 6.39 (m, 0.6), 6.26 (m, 0.4), 6.08 (m, 0.6), 5.94 (m, 0.4), 4.08 (m, 9), 3.49 (m, 0.4), 3.23 (m, 0.6), 3.10 (m, 0.4), 2.90-2.75 (m, 2.2), 2.32 (m, 0.4), 1.84 (m, 0.4), 1.66 (m, 0.6), 1.48 (m, 1).

**trans-(endo, exo)-2-Carbomethoxy-(exo, endo)-3-ferrocenyl-5-norbornene (26).** Diazomethane was generated by adding N-nitroso-N-methyl urea in small portions to Et₂O and 50 % aqueous KOH in a test tube cooled to 0 °C. The yellow-green ether layer was transferred to an ice cooled, stirred ethereal solution of trans-5-norbornene-3-ferrocenyl-2-carboxylic acid. The progress of the reaction was monitored by thin layer chromatograophy (1:19 ethyl acetate:hexane). The ether was removed by rotary evaporation and the yellow solid obtained was purified by chromatography (1:19 ethyl acetate:hexane).
The two resulting isomer were separable and on the basis of $^1$H NMR spectroscopy assigned to be 26a, exo-2-carbomethoxy-endo-3-ferrocenyl-5-norbornene and 26b, endo-2-carbomethoxy-exo-3-ferrocenyl-5-norbornene. Polymerizations were done on a mixture of diastereomers. $R_f$ 26a, 0.33; 26b, 0.39; $^1$H NMR $\delta$ 26a 6.00 (m, 1), 5.81 (m, 1), 4.06 (s, 5), 3.94 (m,1), 3.92 (m, 2), 3.71 (m, 1), 3.62 (m, 1), 3.44 (s, 3), 2.91 (m, 1), 2.67 (m, 1), 2.36 (m, 1), 2.01 (m, 1), 1.42 (m, 1); 26b: 6.26 (m, 1), 6.04 (m, 1), 4.06 (s, 5), 3.96 (m, 4), 3.38 (s, 3), 3.11 (m, 1), 3.05 (m, 1), 2.80 (m, 1), 2.61 (m, 1), 1.51 (m, 1), 1.36 (m, 1); $^{13}$C 26a: 176.02, 136.63, 136.22, 90.67, 68.75, 67.74, 67.64, 66.92, 51.52, 50.9, 49.68, 49.04, 47.89, 43.96; 26b: 174.36, 138.84, 133.77, 92.15, 69.01, 67.89, 67.83, 67.34, 51.66, 51.21, 51.02, 47.56, 46.42, 43.16. Anal. Calcd for C$_{19}$H$_{20}$FeO$_2$: C, 67.88; H, 6.00; Fe, 16.61. Found: C, 68.34; H, 6.12; Fe, 16.51.

**5-Norbornene-2-(methoxycarbonyl)ferrocene.** Ferrocenylcarboxylic acid (2.1 g, 9.1 mmol) was added to a suspension of PCl$_5$ (2.2 g, 10.0 mmol) in benzene (30 mL) and the resulting red solution was stirred for 2 hours at room temperature. The reaction mixture was then filtered and the filtrate concentrated in vacuo. The residue was taken up in hexane, washed with H$_2$O, dried over MgSO$_4$, filtered and the solvent was removed in vacuo. The acid chloride was dissolved in a small amount of THF and added to a solution of 5-norbornene-2-methanol (1.2 mL, 10 mmol) and pyridine (1.5 mL, 20 mmol) in THF (30 mL). The solution was stirred at reflux for 20 h, then worked up with CHCl$_3$ and H$_2$O. Chromatography (1:19 ethyl acetate:hexane) yielded 1.60 g, (52 %) of product which could be recrystallized from ether as orange prisms. The product was a 9:1 mixture of endo and exo isomers; $^1$H NMR $\delta$ 5.98 (m, 1, $CH=CH$), 5.95 (m, 1, $CH=CH$), 4.90 (m, 2, CC$_5$H$_2$H$_2$), 4.04 (m, 8, $CHHO$ and CC$_5$H$_5$ and CC$_5$H$_2$H$_2$), 3.87 (m, 1, $CHHO$), 2.87 (m, 1), 2.57 (m, 1), 2.38 (m, 1), 1.62 (m, 1), 1.42 (m, 1), 1.05 (m, 1, $CHH$ bridgehead), 0.45 (m, 1, $CHH$, bridgehead); $^{13}$C NMR $\delta$ 171.10, 137.7, 132.4, 80.2, 71.1, 70.3, 69.7, 67.4, 49.3, 44.1,
42.2, 38.2, 28.8. Anal. Calcd for C\textsubscript{19}H\textsubscript{20}FeO\textsubscript{2}: C, 67.88; H, 6.00; Fe, 16.61. Found: C, 68.97; H, 6.10; Fe, 16.83.

**Bis(10-(2-ethyl)-phenothiazine)-trans-2,3-dicarboxylatonorbornene**

(27). Under a nitrogen atmosphere a solution of trans-2,3-(dicarbonyl chloride)-5-norbornene (1.65 mL, 10 mmol) in THF (10 mL) was added dropwise to a solution of 10-(2-hydroxyethyl)-phenothiazine (5.32 g, 22 mmol) and pyridine (1.83 mL, 22 mmol) in THF (80 mL) to yield a purple solution. After stirring for 9 hours, the solvents were removed *in vacuo*, and the residue taken up in chloroform and H\textsubscript{2}O. The aqueous phase was extracted twice with CHCl\textsubscript{3} and the combined organic solutions were then dried over MgSO\textsubscript{4}. The crude product was chromatographed with a graded elution solvent, from 3:7 to 3:1 ethyl acetate:hexane and the fractions containing 27 collected and the solvent removed *in vacuo*. The resulting white solid was recrystallized from EtOH/CHCl\textsubscript{3} to yield 3.03 g (48%) of the product: \textsuperscript{1}H NMR δ (CDCl\textsubscript{3}) 7.12 (m, 8, H\textsubscript{Ar}), 6.90 (m, 8, H\textsubscript{Ar}), 6.14 (m, 1, CH=CH\textsubscript{2}), 5.85 (m, 1, CH=CH\textsubscript{2}), 4.41 (t, 2,CH\textsubscript{2}CH\textsubscript{2}), 4.33 (t, 2,CH\textsubscript{2}CH\textsubscript{2}), 4.14 (t, 2,CH\textsubscript{2}CH\textsubscript{2}), 4.07 (t, 2,CH\textsubscript{2}CH\textsubscript{2}), 3.32 (m, 1), 3.17 (m, 1), 3.04 (m, 1), 2.64 (m, 1), 1.44 (m, 1, CHH bridgehead), 1.33 (m, 1, CHH bridgehead); \textsuperscript{13}C: 173.1, 173.2, 144.7, 137.6, 135.0, 127.6, 127.4, 125.4, 125.3, 122.9, 115.4, 115.3, 61.3, 61.0, 47.9, 47.6, 47.4, 47.1, 46.0, 45.8. Anal. Calcd. for C\textsubscript{37}H\textsubscript{32}N\textsubscript{2}O\textsubscript{4}S\textsubscript{2}: C, 70.23; H, 5.10; N, 4.43; S, 10.23. Found: C, 70.22; H, 5.12; N, 4.42; S, 10.24.

**Typical polymerization procedures:**

**Preparation of poly26\textsubscript{15}**. A solution of the monomer (103 mg, 3.1 × 10\textsuperscript{-4} mol) in THF (1 mL) was added quickly to a rapidly stirring solution of Mo(CH\textsubscript{3}CMe\textsubscript{3}) (10 mg, 2.05 × 10\textsuperscript{-5} mol) in THF (1.0 mL) and stirred an additional 15-20 minutes. The polymerization was quenched with an excess of neat pivaldehyde (20 µL) and stirred for 30 minutes. The polymer was collected by precipitation into a 200 mL of hexane and centrifugation. It can be further
purified by reprecipitation from chloroform solution and placing under vacuum for several hours. The polymer is obtained as a light orange powder (95 mg, 92 %). The $^1$H NMR spectrum is shown in Figure 4; $^{13}$C NMR (CDCl$_3$) δ 174.6, 175.0, 129-134 (olefinic region), 91.8, 89.9, 70, 68.4, 67.2, 66.7, 65.1, 55.1, 51.8, 51.4, 47.5, 45.5, 41, 39, 29.8.

**Preparation of Poly27$_{10}$.** A solution of the monomer (128 mg, 2.05 mmol) in THF (1 mL) was added dropwise but quickly to a rapidly stirring solution of Mo(CHCMe$_3$)$_2$ (10 mg, $2.05 \times 10^{-5}$ mol) in THF (1 mL) and the solution was stirred for 20 minutes. The polymerization was terminated by addition of excess pivaldehyde (20 µL) and was stirred for an additional 30 minutes. The polymer was isolated by precipitation into excess hexane (250 mL), centrifugation and placing under vacuum for several hours. The polymer was obtained as a cream powder (120 mg, 94 %). When capped with less volatile aldehydes, such as pyrene or octamethylferrocenecarboxaldehyde, the polymer needs to be purified further by dissolving in toluene or CHCl$_3$ and reprecipitation. The samples for NMR analysis were prepared by dissolving the polymer in CDCl$_3$, removal of the solvent *in vacuo*, and redissolving in CDCl$_3$ in order to remove traces of solvent trapped in the polymer: $^1$H NMR (CDCl$_3$) δ 7.02 (b, 8, H$_{Ar}$), 6.78 (b, 8, H$_{Ar}$), 5.19 (b, 2, CH=CH), 4.22 (b, 4, NCH$_2$), 3.93 (b, 4, OCH$_2$), 3.2-2.4 (b, 4), 1.66 (b, 1, CHH bridgehead), 1.34 (b, 1, CHH bridgehead), 0.94 and 0.91 and 0.89 (s, 0.9, CMe$_3$ end cap); $^{13}$C NMR (CDCl$_3$, see Figure 9) δ 173.2 (C=O), 172.5 (C=O), 144.5 (C$_6$), 133.5 and 132.3 and 130.8 and 129.9 (CH=CH), 127.6 (C$_2$ and C$_3$), 125 (C$_5$), 123 (C$_3$), 115 (C$_1$), 60.5 (CH$_2$N), 52.3 (CH$_2$O), 51.2 (CH$_2$O), 46 and 44.5 and 39 (CH$_2$ bridgehead, CH allylic, CHCO), 32.6 (CMe$_3$), 29.5 (CMe$_3$). The $^{13}$C NMR spectrum was determined using the data from previously characterized$^{130}$ 10-ethylphenothiazine as shown below.
Preparation of poly26_{15}-block-polyNBE_{60}. A solution of norbornene (116 mg, 1.23 mmol) in THF (1.0 mL) was added quickly over a period of 1-2 minutes to a well-stirred solution of Mo(CHCMe₃) (10 mg, 2.05 × 10⁻⁵ mol) in THF (1.0 mL) and stirred an additional 10 minutes. To the above solution the second monomer, 26, (104 mg, 3.1 mmol) in THF (1-2 mL) was added quickly and stirred for 15-20 minutes. The polymerization was quenched by addition of excess neat trimethylsilylbenzaldehyde (20 μL, appx. 0.1 mmol) and stirred for 20-30 minutes. The polymer was isolated as a light yellow powder by precipitation into hexane (200 mL) and centrifugation. The polymer was then reprecipitated into hexane from CHCl₃ solution and placed under vacuum to yield 195 mg (90%) of the product. The ¹H and ¹³C NMR spectra are identical to the superposition of the two blocks in the appropriate ratio. The ratio of TMS to tert-butyl end groups was 1:1.

Observation of living poly28. 2-Triethoxysilyl-5-norbornene (28) (52 mg, 2.0 × 10⁻⁴ mol) was dissolved in C₆D₆ (350 μL) and added all at once to a rapidly stirring solution of Mo(CHCMe₃) (10 mg, 2.05 × 10⁻⁵ mol) in C₆D₆ (350 μL). No signals due to unreacted monomer are observed in the ¹H NMR spectrum after 30 minutes: ¹H NMR δ 12.4 and 11.9 and 11.65 (H₂), 6-5.2 (b, olefinic H), 3.8 (b, OCH₂CH₃), 3.1, 2.8, 2.4, 2.3, 2.1, 1.7, 1.6, 1.2 (b, OCH₂CH₃); the signals are too broad to obtain accurate integrals.

Mo(CH(C₁₀H₉Fe))(N-2,6-C₆H₃(CHMe₂)₂)(OCMe₃)₂ (Mo(CHFc). The two reagents, vinyl ferrocene (65 mg, 0.31 mmol) and Mo(CHCMe₃)(NAr)(OCMe₃)₂ (150
mg, 0.31 mmol) were placed together as solids and a minimum amount of toluene added (apprx. 1-2 mL, room temperature) in order to bring the reagents into solution. The solution color changed from dark orange to bright red as a light red solid precipitated out of solution. The mixture was stirred for 48 hours after which the solvents were removed in vacuo. The red residue was extracted with pentane (1-2 mL) and the extracts filtered through Celite. Recrystallization from a minimum amount of pentane at -40 °C gave the product as bright red needles in two crops (82 mg, 43 %): $^1$H NMR δ 11.90 (s, 1, H$_\alpha$), 7.05 (m, 3, Ar-N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$), 4.21 (dd, 2, C$_\alpha$C$_5$H$_4$Fe), 4.09 (s, 5, C$_5$H$_5$Fe), 4.00 (sept, 2, N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$), 3.97 (dd, 2, C$_\alpha$C$_5$H$_4$Fe), 1.35 (s, 18, OCM$e_3$), 1.08 (d, 12, N-2,6-C$_6$H$_3$(CHMe$_2$)$_2$). $^{13}$C NMR 2.74 (C$_\alpha$, J$_{CH}$=127 Hz), 155.5 (C$_{ipso}$), 146.3 (C$_\alpha$), 127.2 (C$_p$), 123.1 (C$_m$), 95.1 (C$_\beta$), 77.2 (OCMe$_3$), 69.3 (C$_\alpha$C$_\beta$(CH$_2$)$_4$Fe), 69.3 (C$_5$H$_5$Fe), 68.2 ((C$_c$C$_\beta$(CH$_2$)$_4$Fe), 32.0 (OCMe$_3$), 28.4 (CHMe$_2$), 27.8 (CHMe$_2$). Anal. Calc'd for MoC$_{31}$H$_{45}$FeNO$_2$: C, 60.50; H, 7.37; N, 2.28. Found: C, 60.28; H, 7.44; N, 2.07.

**Typical polymerization using Mo(CHFc).**

**Preparation of Fc-poly275-FcM$_{e8}$ and Fc-poly275-block-poly282-FcM$_{e8}$.** The phenothiazine containing monomer (27) (127 mg, 2.0 × 10$^{-4}$ mol) was dissolved in 900 µL of C$_6$D$_6$ and added quickly to a solution of Mo(CHCFc) (25 mg, 4.1 × 10$^{-5}$ mol) in C$_6$D$_6$ (900 µL) and stirred for 15-20 minutes. The resulting solution was split into 3 × 600 µL portions, the first was immediately quenched by addition of 15 µL of pivaldehyde and served as a standard for the polymerization of 2. Octamethylferrocene carboxaldehyde (11 mg, 3.3 × 10$^{-5}$ mol) in C$_6$D$_6$ (100 µL) was added to another portion. To the last portion a solution of 2-triethoxysilyl-5-norbornene (7 mg, 2.7 × 10$^{-5}$ mol, 2 equivalents relative to concentration of propagating alkylidene) in C$_6$D$_6$ (200 µL) was added under vigorous stirring, stirred for an additional 10 minutes and finally quenched with octamethylferrocene carboxaldehyde (11 mg, 3.3 × 10$^{-5}$ mol) in C$_6$D$_6$ (100 µL). The termination of the polymerization was followed by $^1$H NMR by monitoring the disappearance
of the alkylidene and aldehyde signals. Reaction with pivaldehyde is essentially complete after 30-45 minutes while the reaction of octaethylferrocenecarboxaldehyde requires several hours to reach completion. The oligomers were obtained in the usual fashion by precipitating into hexane and twice reprecipitated from chloroform solution. The $^1$H NMR spectra of these oligomers are identical to a superposition of the poly27 and poly3 spectra in the appropriate ratio.
CHAPTER 7

The Synthesis and Kinetics of Decomposition of a Molybdenum (VI)
and an Analogous Tungsten (VI) 2-Oxymetallcyclobutane complex.
INTRODUCTION

2-Oxometallacyclobutane (metallaoxetane) complexes are plausible intermediates in transition metal-catalyzed olefin epoxidation reactions\textsuperscript{131} and Wittig-like reactions between high oxidation state alkylidene complexes and the carbonyl functionality.\textsuperscript{132,133} However, stable examples usually can be prepared only by indirect methods.\textsuperscript{134} An exception in the former category is the synthesis of an oxairidacyclobutane complex from a reaction between a cyclooctadiene complex and oxygen.\textsuperscript{135} Two exceptions in the latter category are β-alkylidene-titana-2-oxacyclobutane complexes prepared by adding ketenes to "TiCp\textsubscript{2}(CH\textsubscript{2})"\textsuperscript{136} and oxatantalacyclobutane complexes prepared by adding aldehydes to TaCp\textsuperscript{+}\textsubscript{2}Me(CH\textsubscript{2}).\textsuperscript{137} Both types are relatively stable, the titanium species perhaps in part because of the nature of the olefin (an allene) that is generated when a metallacycle cleaves to give "TiCp\textsubscript{2}(O)". Only a few X-ray structures of 2-oxometallacycles have been reported.\textsuperscript{4a,5,7}

The work described in Chapters 2 and 5, as well as that of others\textsuperscript{8}, has shown that metallacyclobutane complexes are intermediates in reactions between olefins and alkylidene complexes of the type M(CHCMe\textsubscript{3})(NAr)(OR)\textsubscript{2} (M = Mo, W; Ar = 2,6-C\textsubscript{6}H\textsubscript{3}-i-Pr\textsubscript{2}), and that in some cases they can be isolated and structurally characterized. Square pyramidal metallacycles form when OR = OCM\textsubscript{e}3, and are much more stable than trigonal bipyramidal metallacycles, which form when OR is more electron-withdrawing.\textsuperscript{138} The work described in Chapter 5 suggests that SP metallacycles containing tert-butoxide ligands are more stable when a bulky group such as a tert-butyl group is in the pseudo-equatorial α position or when electron-withdrawing substituents are present on the metallacyclic ring. Since Wittig-like reactions with tert-butoxide complexes have been used routinely to cleave the polymer or oligomer from the metal, we felt that if there is a close similarity between reactions of olefins with alkylidene complexes and reactions of organic carbonyl groups with alkylidene complexes, it may be possible to stabilize and observe an intermediate 2-oxometallacyclobutane complex prepared by treating M(CHCMe\textsubscript{3})(NAr)(OCMe\textsubscript{3})\textsubscript{2} with the appropriate aldehyde. This has now been accomplished and the results are reported in this Chapter. Kinetic and
mechanistic studies confirm that these 2-oxametallacyclobutane complexes and metallacyclobutane complexes of the same type are indeed closely related.

RESULTS

Synthesis and Breakup Rates of 2-oxometallacyclobutane Complexes Derived from $M(\text{CHCMe}_3)(\text{NAr})(\text{OCMe}_3)_2$ ($M = W, \text{Mo}$). X-ray Structure of trans-Mo[CH(\text{CMe}_3)\text{CH}(\text{C}_6\text{F}_5)\text{O}](\text{NAr})(\text{OCMe}_3)_2$.

Two aldehydes that have been used routinely to cleave polymers from Mo or W in living polymers are pivaldehyde and benzaldehyde. Other more specialized aldehydes can be used in order to modify the end group of the polymer for a particular application or response (see Chapter 5). In general, some cis olefin product is formed in reactions involving living alkylidenes (propagating species) as determined by $^1\text{H}$ NMR analysis of the olefinic end group, while trans olefin is formed in reactions involving less reactive neopentyldiene complexes. For example, pivaldehyde reacts smoothly with $M(\text{CHCMe}_3)(\text{NAr})(\text{OCMe}_3)_2$ ($M = W$ or Mo) to yield exclusively trans-di-tert-butylethylene and $M(\text{O})(\text{NAr})(\text{OCMe}_3)_2$ (Equation 1). The reaction is fast and quantitative by $^1\text{H}$ NMR. $M(\text{O})(\text{NAr})(\text{OCMe}_3)_2$ has not yet been isolated in pure form since it appears to disproportionate to $M(\text{NAr})_2(\text{OCMe}_3)_2$ as described in Chapter 1. Addition of benzaldehyde to $M(\text{CHCMe}_3)(\text{NAr})(\text{OCMe}_3)_2$ proceeds similarly except that cis-PhCH=CH(CMe$_3$) appears in 2% yield when $M = W$. No intermediates have been observed by $^1\text{H}$ NMR in these reactions at room or low temperature.

Analogous reactions between $M(\text{CHCMe}_3)(\text{NAr})(\text{OCMe}_3)_2$ and pentafluorobenzaldehyde (Ph$_F$CHO) require up to 3 h to reach completion (Equation 2).
Inspection of the reaction involving Mo(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ (Mo(CHCMe$_3$)) in C$_6$D$_6$ by $^1$H NMR immediately after addition of the aldehyde shows that two intermediates form rapidly in high yield and only relatively slowly decompose to give the observed olefins. They are proposed to be 2-oxametallacyclobutane precursors to those olefins. Since

\[
\text{Me}_3\text{CO}_\text{M}=\text{CHCMe}_3 \quad \text{Ph}_2\text{CHO} \quad \text{M(NAr)}(\text{O})(\text{OCMe})_2 \quad \text{Ph}_2\text{C} \quad \text{CMe}_3
\]

\[ M = \text{Mo or W} \]

96% trans (M=Mo)

74% trans (M=W)

M(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$ complexes have been shown to contain a syn neopentylidene ligand (that with the tert-butyl group pointing toward the imido ligand),$^8$a,c the major intermediate is proposed to contain the $\alpha$ tert-butyl and $\beta$ Ph$_2$C groups in pseudo-equatorial positions in a bent metallacyclobutane ring (Equation 3). This proposal is consistent with the

\[
\text{Me}_3\text{CO}_\text{M}=\text{C}_\text{CMe}_3 \quad \text{Ph}_2\text{CHO} \quad \text{Me}_3\text{CO}_{\text{M}=\text{C}} \quad \text{F} \quad \text{CMe}_3 \quad \text{Ar} \quad \text{N} \quad \text{O} \quad \text{CMe}_3 \quad \text{Me}_3\text{CO} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}
\]

\[ M = \text{Mo or W} \]

29 (M = Mo)

30 (M = W)

fact that when $M = \text{Mo}$ the major intermediate (29-trans) is formed to the extent of 94%, and when $M = \text{W}$ it (30-trans) comprises 74% of the mixture, percentages that match the amount of trans-Ph$_2$CH=CH(CMe$_3$) ultimately formed in each case. Proton and carbon NMR spectra of 29-trans and 30-trans are reminiscent of those for square pyramidal metallacyclobutane complexes that result upon addition of olefins to these same alkylidene complexes.$^{139}$ For
example, in 29-trans the α and β proton resonances appear at 2.45 and 6.62 ppm (Figure 1), and the α and β carbon resonances at 69.98 and 72.53 ppm. The minor isomer (6%; 29-cis) has a similar spectrum with α and β proton resonances at 2.64 and 6.86 ppm. The β resonances are shifted downfield, compared to previously known metallacyclobutane complexes, due to the presence of the oxygen atom and the electron withdrawing C₆F₅ group. We are confident that the structure of 29-trans is as depicted in Equation 3 on the basis of the x-ray results reported below, but cannot be certain that 29-cis also contains a pseudo-equatorial α tert-butyl group, i.e., that it is formed from syn-Mo(CHCMe₃)(NAr)(OCMe₃)₂. Conceivably it could be formed from anti-Mo(CHCMe₃)(NAr)(OCMe₃)₂.

Crystals of pure 29-trans suitable for X-ray analysis were obtained at -30 °C from a concentrated octane solution (see Experimental). Attempts to grow crystals of 30-trans failed, perhaps due to the higher percentage of the cis isomer. The results of a low temperature X-ray analysis of 29-trans are shown in Figure 2. Relevant bond distances and angles are listed in Table 1. The overall geometry of the metal core is square pyramidal. The imido ligand occupies the apical position with the oxametallacycle ring and the two tert-butoxide ligands located in the basal plane; angles between the axial and basal ligands vary from 99.4 (2) to 111.1 (2)°. The Mo-N-C(51) angle of 167.2 (3)° is fairly typical of diisopropylphenylimido ligands in high oxidation state complexes in which the metal is relatively electron-deficient and some π bonding between the imido nitrogen atom and the metal is likely. ⑧-12 (If these electrons are donated the formal electron count at the metal is 18.) The phenyl group of the imido ligand is aligned so that its plane approximately contains the Mo-O(4) and Mo-O(1) bonds, an orientation that minimizes steric interactions between the tert-butyl group on the ring and the isopropyl groups on the imido ligand. The tert-butoxide ligand that contains C(41) consequently is turned away from the imido ligand's isopropyl group. The other tert-butoxide ligand is also turned away from the imido ligand, even though there is no obvious intramolecular steric reason for it to do so. (The α tert-butyl group in a neighboring molecule appears most likely to induce this orientation) The Mo-O(3) bond length (1.860 (3) Å) and
Figure 1. $^1$H NMR spectrum ($d^8$-toluene) of 29-trans.
Figure 2. Two views of trans-Mo[CH(CMe₃)CH(C₆F₅)O](NAr)(OCMe₃)₂ (29-trans).
Table 1. Selected Intramolecular Distances (Å) and Angles (deg) Involving the Nonhydrogen Atoms in \textit{trans}-Mo(CH(CMe₃)CH(C₆F₅)O)(NAr)(OCMe₃)₂ (29-trans).

<table>
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<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (deg)</th>
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<tbody>
<tr>
<td>Mo-N</td>
<td>1.722 (3)</td>
<td>Mo-O(1)-C(1) 100.5 (2)</td>
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<tr>
<td>Mo-O(1)</td>
<td>1.995 (3)</td>
<td>O(1)-C(1)-C(2) 99.9 (3)</td>
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<tr>
<td>Mo-O(3)</td>
<td>1.860 (3)</td>
<td>O(1)-Mo-C(2) 65.4 (1)</td>
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<td>Mo-O(4)</td>
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<td>O(1)-Mo-O(4) 82.4 (1)</td>
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<td>O(3)-Mo-O(4) 101.3 (1)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
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<td>O(3)-Mo-C(2) 93.2 (1)</td>
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</tr>
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<td>Mo-O(3)-C(31)</td>
<td>148.9 (3)</td>
<td>O(4)-Mo-N 111.1 (2)</td>
</tr>
<tr>
<td>Mo-O(4)-C(41)</td>
<td>148.7 (3)</td>
<td>C(2)-Mo-N 99.4 (2)</td>
</tr>
<tr>
<td>Mo-C(2)-C(1)</td>
<td>88.9 (2)</td>
<td>O(3)-Mo-O(1) 144.4 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(4)-Mo-C(2) 140.4 (1)</td>
</tr>
</tbody>
</table>
Mo-O(4) bond length (1.882 (3) Å) and the large Mo-O-C angles (Mo-O(3)-C(31) = 148.9 (3)° and Mo-O(4)-C(41) = 148.7 (3)°) are both typical of alkoxide ligands in complexes of this type in which there is some π bonding between the metal and the alkoxide oxygen atom. The MoOC₂ ring is slightly puckered (21.3°) with the pentafluorophenyl and tert-butyl groups consequently in positions that are approximately halfway between equatorial and axial. The Mo-C(1) bond length (1.995 (3) Å) is consistent with a Mo-O single bond in which there is little π bonding between Mo and O, while the C(1)-O(1) bond length (1.428 (5) Å) is what one would expect on the basis of the structures of other 2-oxametallacyclobutane complexes and the structures of analogous all-carbon square pyramidal tungstacycles (see Discussion Section).

The decomposition of pure 29-trans to yield what we assign as trans-PhFCH=CH(CMe₃) (on the basis of JHH =17 Hz) takes place quantitatively versus an internal standard. No cis-PhFCH=CH(CMe₃) is observed. The decomposition of 29-trans can be followed by observing the decrease in the resonance for the β proton in the MoOC₂ ring, and/or the rate of appearance of trans-PhFCH=CH(CMe₃) (Figure 3). The reaction is cleanly first order with ΔHᵗ = 17.5 (9) kcal mol⁻¹ and ΔSᵗ = -16 (3) e.u. The rate of decomposition of 29-trans in mixtures of 29-trans and 29-cis is the same as for pure 29-trans, and as mentioned earlier, the amount of trans-PhFCH=CH(CMe₃) that is formed is within experimental error of the amount of 29-trans in the mixture. The rate of decomposition of 29-cis could not be measured because of the small amount that is present. Once 29-cis disappears from the mixture no more cis-PhFCH=CH(CMe₃) is formed. All these data suggest that 29-trans decomposes to trans-PhFCH=CH(CMe₃) and 29-cis to cis-PhFCH=CH(CMe₃) without a significant amount of PhFCHO being lost from the metallacyclic ring of either isomer.

Mo(CHCMe₂Ph)(NAr)(OCM₃)₂ reacts with PhFCHO to give primarily (89 %) trans-Mo[CH(CMe₂Ph)CH(PhF)O](NAr)(OCM₃)₂ (31-trans, Equation 4). Decomposition of 31-trans and 31-cis in such mixtures yield trans-PhFCH=CH(CMe₃) (89 %) and cis-
Figure 3. Representative kinetic data for the decomposition of 29-trans at 25 °C. Displayed spectra were taken every 1041 seconds; two additional spectra were acquired between each shown.
PhFCH=CH(CMe3) (11%). The rate of decomposition of isolated 31-trans at 35 °C is ~30 times slower than decomposition of 29-trans (2.5 × 10^{-5} sec^{-1}) at that temperature.

\[ \text{Me}_3\text{CO} \text{Mo} \equiv \text{C} - \text{Me}_2\text{Ph} + \text{PhFCHO} \rightarrow \text{Me}_3\text{CO} \text{Mo} \equiv \text{C} - \text{Me}_2\text{Ph} \quad (4) \]

\text{31-trans}

Mixtures of 30-trans (~75%) and 30-cis (~25%) can be prepared in situ at low temperature. The characteristics of their decomposition were found to be the same as those for mixtures of 29-trans and 29-cis with activation parameters for 30-trans of \( \Delta H^\ddagger = 21.5 \) (6) kcal and \( \Delta S^\ddagger = -7 \) (2) e.u. (see Experimental). In this case the decomposition of 30-cis could be determined; at 5.0 °C the rate is \( k = 1.9 \times 10^{-4} \) sec^{-1}. Comparison with the calculated rate of decomposition of 30-trans at that temperature (7.6 × 10^{-6} s^{-1}) suggests that 30-cis decomposes approximately 25 times faster than 30-trans. A comparison of the decomposition of 30-trans with that of 29-trans leads to the conclusion that trans-molybdacycles decompose approximately twice as fast as trans-tungstacycles at 25 °C (Table 2).

Competition experiments were carried out in order to ascertain the relative reactivities of the alkylidene complexes. The result of a reaction between a 1:1 mixture of Mo(CHRMe3) and W(CHRMe3) and one equivalent of 29 (twofold excess of total alkylidene concentration) at 25 °C is shown in Equation 5. The percentage trans-PhFCH=CH(CMe3) that is produced is inconsistent with what is superficially a selective reaction between W(CHRMe3) and PhFCHO, so the question arises as to whether Mo(O) is stable in the presence of W(CHRMe3). The result shown in Equation 6 reveals that it isn't; at 25° an oxo ligand on
Table 2. Rate constants and kinetic parameters for decomposition of 2-oxametallacycles.

<table>
<thead>
<tr>
<th>Metallacycle</th>
<th>T(°C)</th>
<th>k(x10^4 s^-1)</th>
<th>ΔH‡(kcal mol^-1)</th>
<th>ΔS‡ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-trans</td>
<td>35.1</td>
<td>6.71</td>
<td>17.5</td>
<td>-16</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>4.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>2.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.1</td>
<td>0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-trans</td>
<td>35.1</td>
<td>3.82</td>
<td>21.0</td>
<td>-7</td>
</tr>
<tr>
<td></td>
<td>25.1</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.076 (calcd)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-cis</td>
<td>5.0</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31-trans</td>
<td>35.0</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[
W(\text{CHCMe}_3) + \text{Mo(CHCMe}_3) + F_5C_6\text{CHO} \rightarrow \text{Mo(CHCMe}_3) + W(0) + F_5C_6
\]

\(\sim 80\% \text{ trans}\) 

\[
\begin{align*}
\text{Me}_3\text{CO} &\rightarrow W=\text{CHCMe}_3 + \text{Me}_3\text{CO} \rightarrow \text{Mo} \rightarrow \text{O} & \text{Me}_3\text{CO} &\rightarrow W=O + \text{Me}_3\text{CO} \rightarrow \text{Mo} \rightarrow \text{CHCMe}_3 \\
\text{Me}_3\text{CO} &\rightarrow W=\text{CHCMe}_3 + \text{Me}_3\text{CO} \rightarrow \text{Mo} \rightarrow \text{O} & \text{Me}_3\text{CO} &\rightarrow W=O + \text{Me}_3\text{CO} \rightarrow \text{Mo} \rightarrow \text{CHCMe}_3
\end{align*}
\]

Mo exchanges quantitatively with a neopentylidene ligand on W, presumably via a dimeric intermediate that at some point contains bridging oxo and bridging neopentylidene ligands. (\(\text{Mo(O)}\) was generated in situ from \(\text{Mo(\text{CHCMe}_2\text{Ph})}\) and 1 equiv of benzaldehyde.) The reaction shown in Equation 5 can be explained if both \(\text{Mo(\text{CHCMe}_3)}\) and \(W(\text{CHCMe}_3)\) react with PhFCHO, but \(W(\text{CHCMe}_3)\) reacts approximately three times faster than \(\text{Mo(\text{CHCMe}_3)}\).

The result shown in Equation 7 can be explained on the basis of the findings so far; \(29\text{-trans}\) decomposes quantitatively to \(\text{Mo(O)}\) and \(\text{trans-PhFCH=CH(CMe}_3\) and \(\text{Mo(O)}\) then reacts quantitatively with \(W(\text{CHCMe}_3)\). Note that no \(\text{cis-PhFCH=CH(CMe}_3\) is formed (not detectable by 500 MHz NMR), as one would expect if some PhFCHO were lost from \(29\text{-trans}\) and would then react (three times faster) with \(W(\text{CHCMe}_3)\) than it would back react with \(\text{Mo(\text{CHCMe}_3)}\). If we propose that 1% \(\text{cis-PhFCH=CH(CMe}_3\) could have been observed, we can then estimate that no more than \(\sim 5\%\) PhFCHO could have been lost from \(29\text{-trans}\).
DISCUSSION

It is informative to compare the ring structure in 29-trans to that in three published structures of square pyramidal tungstacyclobutane complexes (Figure 4). The bond lengths and angles in the slightly puckered MoC₂O rings are remarkably similar, as are the angles at the metal (average 65°), Cα (average 95°), and Cβ (average 100°). The Mo-O bond (2.00 Å) and C-O bond (1.43 Å) are shorter than analogous W-Cα and Cα-Cβ bonds, respectively, as one would expect on the basis of the greater electronegativity of oxygen versus carbon, but there are no grounds for claiming that the MoC₂O ring is any less symmetric than the WC₃ rings. One cannot help but conclude that the 2-oxametallacycles must be closely related structurally to the all-carbon tungstacycles, and that perhaps the mechanism of formation and decomposition of 2-oxametallacycles are also closely related to the mechanism of formation and decomposition of all-carbon metallacycles.

The 2-oxametallacycle closest to that described here whose structure is known is Cp²Ta[OC(Ph)CH₂](CH₃).137 The internal angles and bond distances in the slightly puckered TaC₂O ring are virtually identical to those in 29-trans. This fact is further evidence that the MoC₂O ring in 29-trans is not unusual in any significant way.

There are several features of MC₃ complexes of the square pyramidal type that are worth highlighting. Two particular features have already been mentioned, the stability of metallacycles that contain electron-withdrawing substituents, and the stability of metallacycles that contain a pseudo-equatorial α tert-butyl group (Chapter 2 and 5). As far as decomposition of MC₃ complexes is concerned it has been postulated that the incipient olefin in the ring must be drawn toward the metal, and must leave the coordination sphere only after binding to the metal to a significant degree, probably via a metallacycle that has never, and may never, be observed, e.g., one the contains an axial/equatorial ring and an equatorial imido ligand (structure A in Scheme 1). This proposal is consistent with the view that the olefin adds to the metal, probably in an axial position, in order to form a metallacyclic ring, and with the fact that ΔS‡ is usually substantially negative for loss of olefin from the ring (~15 e.u.) in complexes
of this type.\textsuperscript{8} It is proposed that the presence of a tert-butyl group in the pseudo-equatorial $\alpha$ position stabilizes the metallacycle primarily for steric reasons, i.e., the metallacycle cannot rearrange as readily to the required intermediate from which an olefin can be lost (structure B in Scheme 1), and it is more difficult to lose the olefin that contains a bulky $\alpha$ substituent. If the energetics of olefin binding contribute to a significant degree to transition state energies, then an olefin that contains a bulky substituent would bind more poorly in the transition state, and the metallacycle would be stabilized (Scheme 1). Likewise an olefin with an electron-withdrawing substituent also would bind relatively poorly to a relatively electropositive metal center, again stabilizing the metallacycle. The fact that 29 and 30 are relatively stable is good evidence that these principles extend to 2-oxametallacycles also. Comparison of the breakup rates of 29-trans and 31-trans (Table 2) shows that substituting the $\alpha$ tert-butyl group with the larger dimethylphenylmethyl group stabilizes the metallacycle. A similar stabilization effect was observed in the MoC\textsubscript{3} metallacycles described in Chapter 5. The importance of ground state electronic effects is not known, but in a carbon system that is likely to be polarized M($\delta^+$)C\textsubscript{\alpha}($\delta^-$)C\textsubscript{\beta}($\delta^+$), the presence of an electron-donating substituent on the $\alpha$ carbon atom and an electron-withdrawing substituent on the $\beta$ carbon atom would appear to raise the ground state energy rather than lower it.

Two findings reported here do not yet have counterparts in MC\textsubscript{3} chemistry. One is that an oxamolybdacyle rearranges more rapidly than an oxatungstacycle by a factor of 2 (Table 2). This fact plus the documented slower reactivity rates observed for molybdenum compounds relative to their tungsten counterparts\textsuperscript{10} are the main reasons why molybdacycles are much less common than tungstacycles. The work presented here confirms previous speculations that molybdacycles rearrange more rapidly. Secondly, it has been shown that a cis-2-oxametallacycle (presumably that formed from the syn-alkylidene complex) rearranges $\sim$25 times more rapidly than a trans-2-oxametallacycle. No cis MC\textsubscript{3} species has ever been observed in systems of this type (if a trans analog can form), a fact that is consistent with accumulating evidence that cis-metallacyclobutane complexes rearrange much more readily than
Scheme 1. Proposed least motion metallacycle interconversion for olefin metathesis.
trans-metallacycles.¹⁴⁰ (Cis metallacycles must be present in living ROMP reactions since a significant percentage of the double bonds in the polymer chain of (e.g.) polynorbornene are cis and no secondary metathesis is observed¹⁴¹) The findings reported here could be used as evidence that the proposal is correct.

It is important to note that electron-withdrawing groups also stabilize oxaphosphetane intermediates in the Wittig reaction, e.g., Ph₂[(CF₃)₂HCO]P[OC(CF₃)₁(Me)]¹⁴² is stable up to 150 °C. The ring distances in the oxaphosphetane and 29-trans (Figure 4) are virtually identical once the larger radius of Mo relative to P is taken into account. The trend in the cis/trans distribution of olefins in the ylide reaction follows that in the W and Mo alkylidene reactions presented here. The more reactive ylides tend to yield more cis olefin; more reactive W(CHCMe₃)(NAr)(OCMe₃)₂ also yields more cis olefin than Mo(CHCMe₃)(NAr)(OCMe₃)₂. It has been shown that the cis/trans ratio in the olefin product differs from the ratio of the initially formed oxaphosphetanes in the case of Ph₃P[OCH(Ph)CH(Pr)]¹⁴³ implying that the POCC ring breaks up to ylide and aldehyde. The corresponding reaction has not been observed for the Mo and W oxametallacycles reported here. In all systems (P, Mo, W) the cis substituted rings break up faster than trans substituted rings.

The reaction shown in Equation 5 probably proceeds via the formation of a MoOWC dimetallacyclobutane intermediate. The fact that the reaction proceeds to completion is not unexpected since only a 3-4 kcal mol⁻¹ for ΔG°,rxn is required, a relatively small quantity compared to the likely large energies of the bonds involved. A related alkylidene transfer between high oxidation state metal centers (Ta to W) has been reported previously.¹⁴⁴ Disproportionation of M(O)(NAr)(OCMe₃)₂ to M(NAr)₂(OCMe₃)₂ (and presumably initially MoO₂(OCMe₃)₂) probably proceeds via a MOMN metallacycle.

So far we have concentrated on the analogy between loss of an olefin from 2-oxametallacycles and loss of an olefin from all-carbon metallacyclobutane complexes. An interesting question is whether the analogy holds to the extent that a π bound aldehyde is required when it is lost from a 2-oxametallacycle or adds to an alkylidene. Little is known at
Figure 4. Comparison of bond lengths and angles in the metallacyclic rings in three tungstacyclobutane complexes and an oxaphosphetane with the MoC₂O ring in trans-Mo[CH(CMe₃)CH(PhF)O](NAr)(OCMe₃)₂.
this stage. In this context it is interesting to note that the rate of reaction of PhCHO with W(CHCMe3) to give 30 is approximately three times the rate of reaction of PhFCHO with Mo(CHCMe3) to give 29 and it is known that 2,3-bis(trifluoromethyl)norbornadiene reacts 2.5 times more rapidly with W(CHCMe3) than with Mo(CHCMe3). These data could be circumstantial, but they could be used as evidence that the mechanism of addition of a carbonyl group to an alkylidene is closely related to the mechanism of addition of an olefin to an alkylidene, and therefore that π bonding of the aldehyde C=O bond is required to form a 2-oxametallacyclobutane complex. These and related questions concerning the details of the mechanism of reactions involving the carbonyl group and an alkylidene remain to be answered.

EXPERIMENTAL

General Details. All reactions were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether and pentane were distilled from sodium benzophenone ketyl under nitrogen. Tetrahydrofuran was dried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. Dichloromethane was distilled from calcium hydride under nitrogen. Pentane and octane were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride and then distilled from sodium benzophenone ketyl under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina. Aldehydes were purchased commercially and were purified by distillation.

NMR data are listed in parts per million downfield from TMS from proton and carbon, and downfield from CCl3 for fluorine. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d6 at 25 °C unless otherwise noted.
Synthesis of trans-Mo[CH(CMe₃)CH(C₆F₅)O](NaR)(OCMe₃)₂ (29-trans). A solution of C₆F₅CHO (60 mg, 3.06 × 10⁻⁴ mol) in octane (150 μL) was added to a chilled solution (-30 °C) of Mo(CHCMMe₃)(NaR)(OCMe₃)₂ (150 mg, 3.07 × 10⁻⁴ mol) in octane (500 μL). The solution was kept at -40 °C for approximately 48 h to give the product as bright orange crystals (96 mg, 46%) suitable for X-ray analysis: ¹H NMR (toluene-d₈, 263 K) δ 6.96 (m, 3, HAr), 6.62 (d, 1, JHH = 8.5, Cβ), 4.41 (sept, 2, CHMe₂), 2.45 (d, 1, JHH = 8.5), 1.55 (s, 9, OCMe₃), 1.45 (s, 9, OCMe₃), 1.38 (d, 6, CHMe₂), 1.32 (d, 6, CHMe₂), 1.08 (s, 9, CHCMMe₃); ¹³C (125.7 MHz, toluene-d₈, 250 K) δ 152.5 (Ci or Co (NaR)), 147.3 (Ci or Cp (NaR)), 140.0 (CF, JCF = 251), 137.5 (CF, JCF = 245), 128.36 (Cm (NaR)), 122.1 (CF, JCF could not be determined due to overlap), 84.82 (OCMe₃), 84.60 (OCMe₃), 72.53 (Cβ, JCF = 4, JCH=147), 69.98 (Cα, JCH = 127), 31.51 (OCMe₃), 30.72 (CHMe₂), 27.97 (CHCMMe₃), 23.52 (CHCMMe₃). The complex was not stable enough for elemental analysis.

Observation of cis-Mo[CH(CMe₃)CH(C₆F₅)O](NaR)(OCMe₃)₂ (29-cis). The metallacycle could be observed as a minor product (6%) from the reaction of Mo(CHCMMe₃)(NaR)(OCMe₃)₂ (15 mg, 3.1 × 10⁻⁴ mol) in C₆D₆ (350 μL) and pentafluorobenzaldehyde (9 mg, 4.6 × 10⁻⁴ mol) in C₆D₆ (350 μL). The sample was immediately frozen after addition of the aldehyde to Mo(CHCMMe₃) until the spectrum was taken. The major product for this reaction is 29-trans (94 %): ¹H NMR for 29-cis δ 6.95 (m, 3, HAr), 6.82 (d, 1, Hβ), 2.64 (d, 1, Hα, JHαHβ = 8), 1.57 (s, 9, OCCMe₃), 1.38 (s, 9, OCMe₃), CHMe₂ nor CHMe₂ could not be located, 1.09 (s, 9, CHCMMe₃).

Rate of decomposition of trans-Mo[CH(CMe₃)CH(C₆F₅)O](NaR)(OCMe₃)₂. A solution of pure 29-trans (45 mg, 6.6 × 10⁻⁵ mol) and mesitylene (~6 mg, 5 × 10⁻⁵ mol, internal standard) in C₆D₆ (3.00 mL) was split into 4 × 750 μL portions and loaded into 5 mm NMR tubes. The solutions were
frozen in liquid N₂. First order behavior was observed by monitoring the disappearance of the metallaclave β resonances versus the internal standard. Rates were determined at 4 different temperatures over a 30 °C range (35.1, 30.0, 25.0, 15.1 °C) with a sample equilibration time in the NMR probe of 10-15 min. Observed rate constants were 6.71, 4.72, 2.52 and 0.894 \times 10^{-4} \text{ sec}^{-1} respectively. The Arrhenius plot had \( \rho = 0.995 \). ¹H NMR for trans-(Me₃C)CHCH(C₆F₅) δ 6.44 (d, 1, olefinic, JHH = 17), 6.03 (d, 1, olefinic, JHH = 17), 0.94 (s, 9, CMe₃).

**Synthesis of trans-Mo(CH(CMe₂Ph)CH(C₆F₅)O)(NAr)(OCMe₃)₂.** A solution of Mo(CHMe₂Ph)(NAr)(OCMe₃)₂ (150 mg, 2.7 \times 10^{-4} \text{ mol}) in octane (500 µL) was cooled to -40 °C. To the above solution C₆F₅CHO (53 mg, 2.7 \times 10^{-4} \text{ mol}) in octane (500 µL) at RT was added all at once and the solution was stirred for 10 min. A precipitate appeared upon cooling the reaction solution to -40 °C overnight. The product was filtered off and washed with cold (-40 °C) pentane to yield 106 mg (53%) as an orange powder: ¹H NMR δ 7.16 (d, 2, H₀ (C₆H₅)), 7.03 (m, 3, HAr (NAr)), 6.81 (t, 2, Hm (C₆H₅)), 6.61 (t, 1, Hp (C₆H₅)), 6.40 (d, 1, JHH = 8, H₈), 4.17 (sept, 2, CHMe₂), 2.93 (d, 1, JHH = 8, H₉), 1.58 (s, 3, CMe₂(C₆H₅)), (1.53 (s, 9, OCMe₃), 1.51 (s, 3, CMe₂ (C₆H₅)), 1.49 (s, 9, OCMe₃), 1.41 (d, 6, CHMe₂), 1.32 (d, 6, CHMe₂).

**Rate of decomposition of trans-W[CH(CMe₃)CH(C₆F₅)O](NAr)(OCMe₃)₂ (30-trans).** The metallaclave was made in situ [W(CHCMe₃)(NAr)(OCMe₃)₂ (45 mg, 7.02 \times 10^{-5} \text{ mol}) and mesitylene (~10 mg, 8.3 \times 10^{-5} \text{ mol}) in C₆D₆ (1500 µL), C₆F₅CHO (20 mg, 1.01 \times 10^{-4} \text{ mol}, 1.3 equiv) in C₆D₆ (750 µL), 10 min at 22°]. The resulting solution was divided into 3 × 750 µL portions. The rates of metallaclave breakup were determined by monitoring the disappearance of the β proton versus the internal standard. First order behavior was observed at three different temperatures (15.0, 25.1, 35.1 °C) with a sample equilibration time in the NMR probe of 10-15 min.
Observed rate constants were 0.334, 1.11 and $3.82 \times 10^{-4} \text{ sec}^{-1}$ respectively. The Arrhenius plot had $\rho = 0.999$. $^1\text{H NMR of 30-trans}$ $\delta$ 7.04 (d, 2, H\text{m}), 6.96 (t, 1, C\text{p}), 6.53 (d, 1, H\text{p}), 4.15 (septet, 2, CHMe\text{2}), 2.27 (d, 1, H\text{a}, $J_{\text{H}a\text{H}p} = 8$), 1.46 (s, 9, OCMe\text{3}), 1.41 (s, 9, OCMe\text{3}), 1.40 (d, 6, CHMe\text{2}), 1.34 (d, 6, CHMe\text{2}), 1.08 (s, 9, CHCMMe\text{3}).

**Rate of decomposition of cis-W[CH(CMe\text{3})CH(C\text{6}F\text{5})O](NAr)(OCMe\text{3})\text{2} (30-cis).** The sample was made in a similar fashion to the method described above except that toluene-d\text{8} was used as solvent. First order behavior was observed at 5 °C ($7.6 \times 10^{-4} \text{ sec}^{-1}$) by monitoring the appearance of the cis olefin versus an internal standard. $^1\text{H NMR for 30-cis}$ (toluene-d\text{8}, 5 °C) $\delta$ 7.02 (m, 3, H\text{Ar}), 6.95 (d, 1, H\text{p}), 4.14 (b, 2, CHMe\text{2}), 3.05 (d, 1, H\text{a}, $J_{\text{H}a\text{H}p} = 7.5$), 1.51 (s, 9, OCMe\text{3}), 1.46 (s, 9, OCMe\text{3}), resonances for CHMe\text{2} could not be found probably due to overlap with 30-trans, 1.03 (s, 9, CHCMMe\text{3}). $^1\text{H NMR for cis-(Me\text{3}C)CHCH(C\text{6}F\text{5})}$: $\delta$ 5.64 (d, 1, $J_{\text{HH}} = 12$, (Me\text{3}C)CHCH(C\text{6}F\text{5})), 5.41 (d, 1, slightly broad, $J_{\text{HH}} = 11$, (Me\text{3}C)CHCH(C\text{6}F\text{5})), 0.77 (s, 9, CMe\text{3}).

**X-ray Crystal Structure of trans-Mo[CH(CMe\text{3})CH(C\text{6}F\text{5})O](NAr)(OCMe\text{3})\text{2} (29-trans).** The data was collected by Dr. William Davis and the structure solved and refined by Marie O'Regan. Data were collected at -72 °C on a Rigaku AFC6R diffractometer equipped with a liquid nitrogen low temperature device and using graphite monochromated Mo K\text{\alpha} radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. A total of 8469 reflections were collected, 8219 of which were unique. Equivalent reflections were merged. The intensities of two representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability. The structure was solved by direct methods. Refinement was by full matrix least squares using the TEXSAN crystallographic package from Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions ($d_{\text{C-H}} = 0.95$ Å). Crystal data are: $a =$
18.08 (1) Å, b = 10.471 (7) Å, c = 18.072 (4) Å, β = 96.26 (3)°, space group = P21/c. Z = 4, 
Mr = 683.65, V = 3401 (3) Å³, \( \rho(\text{calcd}) = 1.335 \text{ g cm}^{-3} \), \( \mu = 4.31 \text{ cm}^{-1} \). Final R₁ = 0.040 
and R₂ = 0.053.
CHAPTER 8

Preparation and Characterization of PMe₃ Adducts of

Mo(CHCMe₃)(NAr)(OCMe₃)₂ and Mo(CHCMe₃)(NAr)[OCMe(CF₃)₂]₂.
INTRODUCTION

An important question to be addressed is how an olefin attacks an alkylidene complex of the type M(CHR')(NAr)(OR)\textsubscript{2}. It has been proposed that the olefin adds to the metal by approaching the C/N/O face trans to one OR to give an initial "axial/equatorial" metallacyclobutane complex, and that this initial complex then undergoes several "pseudorotations" to yield a new metallacycle of the same type in order to lose the metathesis product (Chapters 5 and 7). Only TBP metallacycles (equatorial ring) or SP metallacycles (basal ring) have been observed, not the proposed TBP metallacycle containing the ring in axial and equatorial positions (see Chapter 7). It seems unlikely that an olefin/alkylidene "intermediate" will ever be observed, since the olefin probably is only weakly bound through primarily a dative $\sigma$ interaction, and such species therefore either form a metallacyclobutane complex or lose the olefin and revert to an alkylidene complex. A study of base adducts would therefore be valuable since they are models for the unobservable olefin/alkylidene intermediate or transition state. It also should be noted that living polymerization of acetylene is only possible in the presence of quinuclidine, possibly because quinuclidine slows the rate of propagation relative to initiation by coordinating to the metal in the sterically more accessible vinylalkylidene intermediates.\textsuperscript{146} Finally, coordinating solvents also play an important role in ROMP, either decreasing the reactivity of the more active catalysts, or allowing some functionalities such as the carbonitrile group in 2-carbonitrilenorbornene to be tolerated (Chapter 4). Some base adducts such as W(CHSiMe\textsubscript{3})(NAr)(OCMe(CF\textsubscript{3})\textsubscript{2})\textsubscript{2}(PMe\textsubscript{3}) and W(CH\textsubscript{2})(NAr)(OCMe(CF\textsubscript{3})\textsubscript{2})\textsubscript{2}(PMe\textsubscript{3}) already have been previously reported, but have not been studied in detail.\textsuperscript{147}

This Chapter reports and discusses findings concerning the formation, structures and interconversion of PMe\textsubscript{3} adducts of syn and anti rotamers of Mo(CHCMe\textsubscript{3})(NAr)(OCMe\textsubscript{3})\textsubscript{2} and Mo(CHCMe\textsubscript{3})(NAr)(OCMe(CF\textsubscript{3}))\textsubscript{2}.
RESULTS

Adducts of Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2. X-ray Structure of syn-Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2(PMe_3).

Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2 reacts with a slight excess of PMe_3 to yield Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2(PMe_3) quantitatively. The PMe_3 ligand seems to be strongly bound to the metal since coupling to phosphorus is maintained on the NMR time scale at 25 °C (δ H_α = 11.90 ppm, 3J_{HP} = 5.4 Hz; δ C_α = 293.2 ppm, J_{CH} = 110 Hz, 2J_{CP} = 26 Hz). The two alkoxide ligands are inequivalent. With time solutions of this initial isomer equilibrate into another isomer, which again possesses no symmetry (δ H_α = 13.25 ppm, 3J_{HP} = 7 Hz; δ C_α = 313.9 ppm, J_{CH} = 138 Hz, 2J_{CP} = 18 Hz). Note the dramatically higher J_{CH} for this second (thermodynamic) isomer. The ratio of the two isomers at equilibrium is 95:5 (thermodynamic:kinetic).

\[
\text{Me}_3\text{P} \quad \text{Me}_3\text{P} \\
\text{Mo(Ch-t-Bu)(NAr)(OR)}_2 + \text{PMe}_3 \quad \text{RO-Mo-CH-C-t-Bu} \quad \text{RO-Mo-CH-C-H} \\
\quad \text{[ OR = OC(CF}_3)_2\text{Me }]} \\
\text{kinetic isomer (syn)} \quad \text{thermodynamic isomer (anti)}
\]

An X-ray study of the kinetic isomer showed it to be the distorted trigonal bipyramidal species shown in Equation 1 and Figure 1 in which the tert-butyl group is syn to the nitrogen atom of the imido ligand. (Relevant distances and angles are listed in Table 1.) Trimethylphoshpine appears to have added to the C/N/O face of syn-Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2 to give a trigonal bipyramid in which the trimethylphosphine ligand occupies an axial position. The structure of Mo(CHCMe_3)(NAr)[OCMe(CF_3)_2]_2 in solution is likely to be syn on the basis of the fact that the alkylidene ligands in W(CHPh)(NAr)[OCMe(CF_3)_2]_2^{12(a)}, W(CCMMe_3)(NAr)(OCMe_3)_2^{12(b)}, and the "first insertion product" made by adding 7-
Figure 1. Two views of Mo(CHCMe$_3$)(NAr)[OCMe(CF$_3$)$_2$](PMe$_3$).
Table 1. Selected bond lengths (Å) and angles (deg) in syn-Mo(CHCMe$_3$)(NAr)[OC(CF$_3$)$_2$Me]$_2$(PMe$_3$).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-N(3)</td>
<td>1.767 (6)</td>
<td>N(3)-Mo-C(1) 110.6 (4)</td>
</tr>
<tr>
<td>Mo-C(1)</td>
<td>1.878 (9)</td>
<td>N(3)-Mo-O(2) 133.7 (3)</td>
</tr>
<tr>
<td>Mo-O(2)</td>
<td>2.014 (5)</td>
<td>N(3)-Mo-O(4) 101.6 (3)</td>
</tr>
<tr>
<td>Mo-O(4)</td>
<td>2.038 (7)</td>
<td>N(3)-Mo-P(5) 87.4 (2)</td>
</tr>
<tr>
<td>Mo-P(5)</td>
<td>2.520 (3)</td>
<td>O(2)-Mo-C(1) 112.2 (4)</td>
</tr>
<tr>
<td>Mo-O(4)-C(4)</td>
<td>134.2 (6)</td>
<td>O(4)-Mo-C(1) 103.0 (4)</td>
</tr>
<tr>
<td>Mo-O(2)-C(2)</td>
<td>146.8 (6)</td>
<td>C(1)-Mo-P(5) 88.0 (3)</td>
</tr>
<tr>
<td>Mo-N(3)-C(31)</td>
<td>158.2 (6)</td>
<td>O(4)-Mo-O(2) 85.3 (2)</td>
</tr>
<tr>
<td>Mo-C(1)-C(11)</td>
<td>156.3 (8)</td>
<td>O(2)-Mo-P(5) 77.3 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O(4)-Mo-P(5) 162.1 (2)</td>
</tr>
</tbody>
</table>
isopropylidene-2,3-dicarbomethoxynorbornadiene to Mo(CHCMes)(NAr)(OCMe$_3$)$_2$ (4, Chapter 2) are all syn. The tert-butyl group of the neopentylidene ligand in the kinetic product therefore still points toward the imido nitrogen atom. The largest angle between equatorial ligands (133.7 (3)$^\circ$) is that between the imido and a hexafluoro-t-butoxide ligand. The Mo-C$_\alpha$-C$_\beta$ angle in the neopentylidene ligand (156.3 (8)$^\circ$) is relatively large compared to the Mo-C$_\alpha$-C$_\beta$ angles of 144-145$^\circ$ in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$$_{3a}^3$ and W(CHCMes)(NAr)(OCMe$_3$)$_2$$_{12}^b$, 141$^\circ$ in trigonal bipyramidal W(O)(CHCMes)Cl$_2$(PET$_3$)$_1^{147}$ and 140$^\circ$ in 4. Note that the Mo-N-C angle is not much larger than the Mo-C$_\alpha$-C$_\beta$ angle since the phenyl ring is forced to lie in the equatorial plane in order to avoid steric interaction between the isopropyl groups and the axial ligands, but the ring must then bend away from the t-butyl group of the neopentylidene ligand. The imido and alkylidene ligands are tipped away from the axial alkoxide (102$^\circ$, 103$^\circ$) toward the smaller axial PMe$_3$ ligand (87$^\circ$, 88$^\circ$). The P-Mo-O$_{ax}$ angle is only 162$^\circ$ with O(4) and P(5) pointing toward O$_{eq}$ (85$^\circ$ and 77$^\circ$, respectively). The Mo=C, Mo=N, and Mo-P bond lengths are all normal.

An X-ray study of the thermodynamic isomer showed it to be a related trigonal bipyramidal species in which the neopentylidene ligand is in the anti conformation. Unfortunately, this structure could not be solved completely because of a disorder problem involving one hexafluoro-t-butoxide ligand, but there is no doubt that the core geometry is basically the same as that of the kinetic isomer except for the orientation of the neopentylidene ligand. It is proposed that the thermodynamic product arises when PMe$_3$ adds to the C/N/O face in anti-Mo(CHCMes)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (see Discussion)

The conversion of syn isomer to anti can be followed by $^1$H NMR by dissolving the syn isomer (analytically pure) in $d^8$-toluene and monitoring the relative percentage of the two H$_\alpha$ resonances. Figure 2 shows the temperature dependance of this interconversion as well as the effect of the addition of 10 % Mo(CHCMes)(NAr)[OCMe(CF$_3$)$_2$]$_2$. In all cases the final anti: syn ratio is approximately 95:5.
Figure 2. Percentage Anti rotamer as a function of time at three different temperatures: (a) 40 °C; (b) 50 °C; (c) 60 °C and (d) in the presence of 10 % base free alkylidene at 40 °C.
Adducts of Mo(CHCMe₃)(NAr)(OCMe₃)₂.

Changing the alkoxide to one which renders the metal center less electrophilic dramatically changes the stability of these PMe₃ adducts. Analysis by ¹H NMR of a sample made by addition of excess PMe₃ (10 equivalents) to Mo(CHCMe₃) reveals the presence of base free alkylidene at room temperature. Pure Mo(CHCMe₃)(NAr)(OCMe₃)₂(PMe₃) (Mo(CHCMe₃)(PMe₃)) can be isolated as orange crystals from concentrated pentane solutions of Mo(CHCMe₃) and PMe₃ due to the generally lower solubility of base adducts. A sample made by dissolving some of this material in d⁸-toluene shows the variable temperature ¹H NMR behavior shown in Figure 3. The room temperature spectrum shows two alkylidene α-proton resonances, one sharp singlet at 12.72 ppm accounting for 40-45% of the total that is ascribed to Mo(CHCMe₃)(PMe₃) and the second at 11.26 ppm for Mo(CHCMe₃). As the sample is cooled an increase in the percentage of the base adduct is observed as well as a decrease in the rate of PMe₃ exchange, to the point where coupling of Hα to phosphorous can be observed. As the sample is cooled further a second doublet appears downfield of the first with both adducts growing at the expense of Mo(CHCMe₃). Finally after cooling the sample to -85 °C for 30-45 minutes the amount of Mo(CHCMe₃) is 2-3% of the total alkylidene concentration and equal amounts of the two base adduct isomers are observed. At this last temperature the coupling between Hα and phosphorous is not observed probably due to shimming broadening or viscosity problems. Carbon NMR spectra of low temperature mixtures reveal that the lower field proton resonance has a relatively high value for JCH (136 Hz) compared to that which gives rise to the higher field resonance (JCH = 110 Hz), consistent with their formulation as anti and syn forms, respectively. Only the thermodynamically more stable anti isomer is observed at room temperature. At relatively high temperatures (70 °C) only Mo(CHCMe₃) is observed with the ratio of free PMe₃ to tert-butyl group being approximately 95:100 as determined by integration (consistent with a small amount of base evaporating to the empty volume above the solution). This VT NMR behavior is completely reversible.
Figure 3. $^1$H NMR study of the binding of PMe$_3$ to Mo(CHCMe$_3$).
The VT NMR analysis of the mixture of products resulting from addition of excess PMe₃ (10 equivalents) to 4 proceeds in a similar fashion. The low temperature limit shows three clearly assigned doublet of doublets with a poorly defined fourth resonance due to the Hₓ in alkylidene complexes which are not due to 4, as shown in Figure 4. By analogy to the behavior of Mo(CHCMe₃)(PMe₃) resonances A and A' are assigned to two diastereomers of the anti base adduct while B and B' to the syn isomer. Note that Hₓ is coupled to both Hᵧ and the phosphorous atom. The sample shows resonances only due to 4 at higher temperatures (80 °C).

4

DISCUSSION

Rotamers are a consequence of the fact that an imido ligand (or the isoelectronic oxo ligand) can form two π bonds to a transition metal, leaving only a metal orbital which is approximately of δ symmetry in relation to the imido nitrogen atom available for forming a π bond to the carbon atom. The relative energies of syn and anti isomers are different for the two observed geometries, with the tetrahedral core prefering the syn arrangement while the five coordinate trigonal bipyramidal geometry has the anti rotamer as the thermodynamic product. The reasons for this difference are likely to be a subtle interplay of steric and orbital overlap factors. The difference in values of Jₓᵧ in syn and anti isomers, especially in five-coordinate adducts, are often significant, and could be viewed as the result of interaction of a C-H bond with the metal. "Distortions" of alkylidene ligands in this manner in high oxidation state complexes (larger than expected M-Cₓ-R angles) have been observed for years. Any
Figure 4. $^1$H NMR spectrum ($d^8$-toluene, -75 °C) in the alkylidene region of the mixture of compounds resulting from addition of 10 equivalents of PMe$_3$ to 4.
interaction between the metal and the C-H electron pair is likely to be disfavored when the alkylidene is anti since this configuration places the C-H bond in competition with the imido ligand which is a strong donor.\textsuperscript{150}

The crystallographic determination of syn-Mo(CHCMe_3)(NAr)[OCMe(CF_3)]_2(PMe_3) suggests that the base adds to the C/N/O face of the syn isomer. It is conceivable that the base adds on another face and quickly rearranges to the geometry observed although there is no evidence for such a process. The unusual angles of the alkylidene and imido ligands seem to be a consequence of the large steric hindrance present on the equatorial plane. A simple polynomial expression relates the J_{C\alpha H\alpha} and M-C_{\alpha-C\beta} angles of structurally characterized "distorted" alkylidene complexes.\textsuperscript{151} The data of J_{CH} = 112 Hz with Mo-C_{\alpha-C\beta} angle of 156 ° is consistent with this relation demonstrating this distortion is not unusual. The higher J_{C\alpha H\alpha} observed in the anti isomer (138 Hz) is consistent with an angle closer to 120 ° and suggests that it is the thermodynamic isomer since it is relieved of some of the steric strain present on the trigonal plane.

Base attack on the C/N/O face is preferred for a variety of reasons. Statistically, there are two C/N/O faces as compared to one of each C/O/O and N/O/O. Secondly, approach on this face places the base trans to the ligand which is expected to have the weakest trans effect. Both the imido and the alkylidene ligand can be considered dianionic and are likely to labilize a base trans to them more than an alkoxide will. A third isomer of achiral syn adduct (equivalent alkoxide ligands) has been observed when a larger base such as quinuclidine is used, leaving open the possibility of attack on the C/O/O or N/O/O faces. It is interesting to note that disubstituted acetylenes have been observed\textsuperscript{148} to add to the C/N/O face in Re(CHCMe_3)(NAr)[OCMe(CF_3)]_2 most easily to give rhenacyclobutadiene complexes that are relatively stable towards loss of acetylene from the ring, but when the acetylene contains relatively bulky substituents then it adds to the C/O/O face to give rhenacycles which readily lose acetylene.\textsuperscript{152} These data suggest that coordination to the face which is favoured by electronic considerations may not be sterically the most accommodating site. In the case of the
rhenacycles small acetylenes prefer to approach the metal transoid to the least labilizing ligand, this being the alkoxide. As the size of the acetylene increases a sterically more accommodating site is attacked and the base prefers the C/O/O face. This last face places the imido ligand trans to the base which is likely to have a weaker trans effect than the alkylidyne ligand. Qualitative orbital arguments also are consistent with the experimental results since the orbital that is oriented perpendicular to the M/N/C plane is still likely to be the LUMO.\textsuperscript{153}

Exactly how these pentacoordinate rotamers interconvert remains to be elucidated. The possible isomerization routes to be considered are shown in Scheme 1. A single Mo=C bond rotation in \textit{Syn}:PMe\textsubscript{3} could potentially yield \textit{Anti}:PMe\textsubscript{3}. However, this intramolecular process cannot account for the faster appearance of \textit{Anti}:PMe\textsubscript{3} when a small amount of Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}]\textsubscript{2} is added. The steric crowding observed in syn-Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}](PMe\textsubscript{3}) also argues against this process since rotation of the neopentyldiene is likely to be hindered by the two axial ligands. Interconversion via \(k_2\) also cannot account for the observed base free catalysis. The following can be assigned: \(k_{\text{Syn}} > k_{\text{Syn}}\) and \(k_{\text{Anti}} > k_{\text{Anti}}\) (since no Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}]\textsubscript{2} is observed even when only one equivalent of PMe\textsubscript{3} is added to Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}]). \(k_{\text{Rot}} > k_{\text{Rot}}\) (only \textit{Syn} is observed for Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}], as determined by \textsuperscript{1}H NMR) and finally \(k_{\text{Anti}} > k_{\text{Anti}} > k_{\text{Syn}} > k_{\text{Syn}}\) (95\% of thermodynamic mixture is \textit{Anti}:PMe\textsubscript{3} and \(k_{\text{Rot}} > k_{\text{Rot}}\)). If \(k_{\text{Syn}} > k_{\text{Rot}}\) then whenever a phosphine dissociates (via \(k_{\text{Syn}}\)) and recombines, the alkylidyne is likely to still be in the syn configuration. A slight excess of Mo(CHCMe\textsubscript{3})(NAr)[OCMe(CF\textsubscript{3})\textsubscript{2}]\textsubscript{2} would dramatically increase the amount of \textit{Anti} present, since it does not come from \textit{Syn}:PMe\textsubscript{3}. Recall that the interconversion starts from \textit{Syn}:PMe\textsubscript{3} and not \textit{Syn} + PMe\textsubscript{3}. This offers a plausible explanation for the observed base free catalysis and strongly suggests the presence, in small concentration, of unobserved \textit{Anti}. Note that if one starts with \textit{Syn}:PMe\textsubscript{3} and \(k_{\text{Syn}} > k_{\text{Rot}}\) to the point where alkylidyne rotation essentially does not happen before PMe\textsubscript{3} recombination then a mechanism via \(k_i\) cannot be ruled out as a competing pathway. Clearly there will be a complicated dependence
Scheme 1. Plausible routes of pentacoordinate rotamer interconversion.
on temperature and concentration since the isomerization could proceed via different first and second order processes.

Changing the alkoxide to tert-butoxide renders the metal center less electrophilic and therefore is likely to decrease $k_{\text{Syn}}$ and $k_{\text{Anti}}$ relative to $k_{\text{-Syn}}$ and $k_{\text{-Anti}}$, respectively. At room temperature only $\text{Syn}$ and $\text{Anti:PMMe}_3$ (in which $J_{\text{PHg}}$ is absent, consistent with the statement in the previous sentence) are observed for both 4 and Mo(CHCMMe$_3$) indicating that $k_{\text{Anti}}/k_{\text{-Anti}} > k_{\text{Syn}}/k_{\text{-Syn}}$. As the temperature is lowered, the effects of the negative entropies of activation decrease and the equilibrium is shifted to the base adducts, as observed experimentally (Figure 3). The ratio of the products observed in Figure 3 at -85 °C need not be the thermodynamic distribution since at this temperature $k_{\text{Syn}}$ could be larger than $k_{\text{-rot}}$ with $k_{\text{Anti}}/k_{\text{-Anti}} > k_{\text{Syn}}/k_{\text{-Syn}}$ which would yield a similar situation as for Mo(CHCMMe$_3$)(NAr)[OCMe(CF$_3$)$_2$)$_2$. Four isomers are expected for the PMe$_3$ adducts of 4 since the two C/N/O faces are inequivalent due the chiral $\beta$ carbon in the alkylidene ligand.

The findings discussed here have some potentially important implications for metathesis of olefins by complexes of the type M(CHCMMe$_3$)(NAr)(OR)$_2$. First, as has been proposed elsewhere, an olefin, which can be regarded as a $\sigma$ base in these systems, would now appear to add most readily to the C/N/O face to yield an initial metallacyclobutane complex in which the ring spans axial and equatorial sites. If the alkylidene contains a chiral center, then the two C/N/O faces are diastereotopic, a circumstance that has been used to explain how selectivity can arise in the ring opening metathesis polymerization reactions discussed in Chapter 2. Finally a reactivity difference between a base and the two possible rotamers has been observed. This may have some implications regarding the rates of reaction of olefins with the two rotamers implying that the rate of rotamer interconversion may be an important factor in some circumstances.
EXPERIMENTAL

**General Details.** All reactions were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether and pentane were distilled from sodium benzophenone ketyl under nitrogen. Tetrahydrofuran was dried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. Dichloromethane was distilled from calcium hydride under nitrogen. Pentane and octane were washed with 5% nitric acid in sulfuric acid, stored over calcium chloride and then distilled from sodium benzophenone ketyl under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina.

NMR data are listed in parts per million downfield from TMS from proton and carbon, and downfield from CFCl₃ for fluorine. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-ᴅ₆ at 25 °C unless otherwise noted.

**Mo(CHCMe₃)(NAr)[OCHMe(CF₃)₂]₂(PMe₃).** PMe₃ (55 µL, 0.54 mmol) was added all at once to a pentane solution (20 mL) of Mo(CHCMe₃)(NAr)[OCHMe(CF₃)₂]₂ (0.35 g, 0.50 mmol) stirring at -30 °C. The solution was allowed to warm to room temperature over the next 60 minutes then solvents were removed in vacuo. The yellow-orange solid thus obtained was virtually pure by ¹H NMR spectroscopy. Recrystallization from a minimum amount of pentane at -40 °C yielded 0.31 g (80%) of yellow-orange crystals in two crops: ¹H NMR δ 11.90 (d, ³JHP = 5.4, 1, MoCH-t-Bu), 6.93 (m, 3, NAr), 4.56 (br, 1, CHMe₂), 3.24 (br sept, 1, CH₂Me₂), 2.14 (s, 3, OCHMe(CF₃)₂), 1.53 (s, 3, OCHMe(CF₃)₂), 1.28 (br, 6, CHMe₂), 1.20 (d, 6, CH₂Me₂), 1.13 (s, 9, MoCH₂Me₃), 0.88 (d, ²JHP = 9.4, 9, PMe₃); ¹³C NMR δ 293.2 (dd, ¹JCH = 110, ²JCP = 26, MoCH-t-Bu), 150.6 (Cipso), 149.7 and 142.7 (C₀), 128.4 (Cₘ), 126.2, 125.7, and 125.5 (q, ¹JCₜF = 290, 289, and 290, respectively,
OCMe(CF3)2, 123.7 (Cp), 82.1 and 80.4 (sept, 2JC_F = 28 for each, OCMe(CF3)2), 48.5 (MoCHCM3), 31.5 (MoCHCM3) 30.3, 27.5, 25.8, and 24.1 (br, CHMe2 and CHMe2), 20.0 and 17.6 (OCMe(CF3)2), 15.2 (dq, 1JC_P = 24, 1JCH = 130, PMe3); 19F NMR δ -75.0, -75.6, -76.5, and -77.7 (s, 3 each, OCMe(CF3)2); 31P{1H} NMR δ 0.45 (PMe3). Anal. Calcd for MoC28H42F12O2NP: C, 43.14; H, 5.43. Found: C, 43.08; H, 5.61.

anti-Mo(CHCM3)(NAr)[OCMe(CF3)2]2(PMe3). Heating a solution of the syn isomer (15 mg) in C6D6 (800 µL) at 60 °C for 12 hours yields 95% anti product cleanly by 1H NMR analysis. Alternatively the product can be isolated by stirring a solution of the syn isomer (250 mg, 0.32 mmol) and base free Mo(CHCM3)(NAr)[OCMe(CF3)2]2 (22 mg, 3 × 10^-5 mol) in 7:1 pentane and toluene (apprx 3 mL) for 12 hours. Storing the resulting solution for 48 hours at -40 °C gave the anti product as yellow needles (160 mg, 64%): 1H NMR δ 13.25 (d, 3JHP = 7.8, 1, MoCH-t-Bu), 6.90 (m, 3, NAr), 4.23 (sept, 1, CHMe2), 3.58 (sept, 1, CHMe2), 2.07 (s, 3, OCMe(CF3)2), 1.53 (s, 3, OCMe(CF3)2), 1.37 (d, 3, CHMe2), 1.28 (d, 3, CHZMe2), 1.20 (s, 9, MoCH-t-Bu), 0.84 (d, JHP = 9, 9, PMe3); 13C NMR 313.9 (dd, 1JCH = 138, 2JCP = 18, MoCH-t-Bu).

Mo(CHCM3)(NAr)(OCMe3)2(PMe3). Trimethylphosphine (100 µL, 1 mmol) in pentane (500 µL) was added all at once to a solution of Mo(CHCM3)(NAr)(OCMe3)2 (150 mg, 0.3 mmol) in pentane (apprx. 1 mL). The resulting solution was stored at -40 °C overnight from which bright orange crystals were obtained, these were quickly filtered, placed under vacuum for 5-10 minutes and kept cold (-40 °C). The VT NMR of this material in d8 toluene is shown in Figure 2, the ratio of trimethylphosphine to alkylidene was determined to be approximately 1:1. Due to the lability of the phosphine ligand and the presence of isomers the NMR spectra is broad and complex, however the alkylidene Cα signals are sufficiently removed from other resonances to be assigned: 1H NMR (d8 toluene, -25 °C) δ 12.73 (d, 3JHP = 7, Hα anti rotamer), 11.80 (d, 3JHP = 5, Hα syn rotamer); 13C NMR (d8 toluene, -25 °C) δ
293.4 (\(^3\)J\(_{CP} = 18, \ J_{CH} = 136, \ C_\alpha \) anti rotamer), 281.1 (\(^3\)J\(_{CP} = 18, \ J_{CH} = 110, \ C_\alpha \) syn rotamer); \(^{31}\)P \(^1\)H) NMR δ -6.0 (PMe\(_3\), anti rotamer), -7.3 (PMe\(_3\), syn rotamer).

X-Ray Crystal Structure of Mo(CH-t-Bu)(NAr)(OCMe(CF\(_3\))\(_2\))\(_2\)(PMe\(_3\)). The data was collected by Dr. Willian Davis and the structure solved and refined by Marie O’Regan. Data were collected at -72 °C on a Rigaku AFC6R diffractometer with graphite monochromated Mo K\(_\alpha\) radiation (\(\lambda=0.71069 \ \AA\)) and a 12 KW rotating anode generator. A total of 4346 reflections were collected, 4344 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. Therefore, no decay correction was applied. The structure was solved by direct methods\(^1\). Refinement was by full-matrix least squares using TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d\(_{C-H} = 0.95 \ \AA\)). Crystal data are a=10.979 (4) \(\AA\), b=17.945 (7) \(\AA\), c=18.375 (8) \(\AA\), \(\beta=106.34 (3) ^\circ\), \(V=3474 (4) \ \AA^3\), space group=Cc (no. 9), Z=4, \(M_r=779.54\), \(\rho=1.490 \ \text{g/cm}^3\), \(\mu=5.00 \ \text{cm}^{-1}\). Final R\(_1\) = 0.037 and R\(_2\) = 0.045.
Appendix 1.

Kinetic Formulation for Determination of $k_p/k_i$. 
The ratio of the rates of propagation to initiation has proven to be useful in cases where the individual rates are too fast to measure. The kinetic formulation presented here follows closely that of Gold (Chapter 2):

Kinetic Derivation for the Calculation of $\frac{k_p}{k_i}$

**Kinetic Formulation:** The polymerization process can be described by the following set of equations.

$$
egin{align*}
M + I \xrightarrow{k_i} & MI, N_1 \\
MI + M \xrightarrow{k_p} & M_2I, N_2 \\
MI_2 + M \xrightarrow{k_p} & M_3I, N_3 \\
M_{n-1}I + M \xrightarrow{k_p} & M_nI, N_n
\end{align*}
$$

Where:

- $k_i$: Rate constant for initiation reaction
- $k_p$: Rate constant for propagation reaction
- $[I]_0$: Initial concentration of initiator
- $[M]_0$: Initial concentration of monomer
- $[M]$: Instantaneous value for the concentration of monomer
- $[I]$: Instantaneous value for the concentration of initiator
- $N_i$: Concentration of the propagating species with the $i^{th}$ degree of polymerization
For a living polymerization system the following constraints and conservation conditions are set:

\[ \sum_{x=1}^{n} N_x = [I]_0 - [I] \]

i.e. no termination or transfer of the propagating species

\[ \sum_{x=1}^{n} x N_x = [M]_0 - [M] \]

i.e. The concentration of monomer consumed equals the concentration times chain length of propagating species.

From polymerization process:

\[ \frac{-d[I]}{dt} = k_i [M][I] \]

\[ \frac{-d[M]}{dt} = k_i [M][I] + k_p [M] \sum_{x=1}^{n} N_x \]

\[ \frac{d[M]}{d[I]} = \frac{k_i[I] + k_p \sum_{x=1}^{n} N_x}{k_i[I]} \]

(Note that this is valid for \([M] = 0\) but not \([I] = 0\))

\[ \therefore \sum_{x=1}^{n} N_x = [I]_0 - [I] \]

\[ \therefore \frac{d[M]}{d[I]} = \frac{k_i[I] + k_p ([I]_0 - [I])}{k_i[I]} \]
= 1 - \frac{k_p}{k_i} + \frac{k_p}{k_i} [I]_0

Let \gamma = \frac{k_p}{k_i}

\int_{[M]_0}^{[M]} \frac{d[M]}{[M]} = \int_{[I]_0}^{[I]} \left(1 - \gamma + \gamma \frac{[I]}{[I]_0}\right) d[I]

[M] = [M]_0 + (1 - \gamma) ([I]_0 - [I]) + \gamma [I]_0 \ln \left(\frac{[I]}{[I]_0}\right)

When the polymerization ends:

[M] \longrightarrow 0

\therefore 0 = [M]_0 + (1 - \gamma) ([I]_0 - [I]) + \gamma [I]_0 \ln \left(\frac{[I]}{[I]_0}\right)

0 = \frac{[M]_0}{[I]_0} + \gamma \ln \left(\frac{[I]}{[I]_0}\right) + (1 - \gamma) \left(\frac{[I]}{[I]_0} - 1\right)

\frac{[M]_0}{[I]_0} : \text{Number of equivalents added to initiator}

\frac{[I]}{[I]_0} : \text{Ratio of unreacted initiator to total reactive species, in our case the ratio of neopentylidene to total alkylidine species.}

Both quantities can be obtained from NMR experiments, therefore can solve for \gamma = \frac{k_p}{k_i}

Due to the logarithmic nature of the formula and the small numbers involved the numbers obtained are extremely sensitive to the variables. Other factors which may also contribute to difficulties in obtaining reproducible \gamma values are:
a) The values of $k_\text{p}$ may not be the same for all the propagation steps. This is especially true when a catalyst as discriminating as Mo(CHCMe$_3$) is used which is sensitive to subtle steric and electronic differences.

(b) In cases where the polymerization is very fast and $\gamma$ is large the distribution of species will depend heavily on the stirring rate and method of addition. This may be the most difficult step to standardize.

(c) Integration values from the NMR analysis are crucial. The quantity of monomer added has to be determined by integration with suitably long delay times.

(d) The kinetic formulation assumes that all the steps are second order. In some cases the rate determining step for initiation could be the breakup of the metallacycle which is first order. In such circumstances the value of $\gamma$ would depend on the concentration of the metal species in a given experiment.
Appendix 2.

X-ray Structure of and Spectroscopic Data for [Mo(NAr)(OCMe₃)]₂.
During an attempt to obtain the x-ray structure of the ferrocenyl-methylidene initiator described in Chapter 6 (Mo(CHFc)) a crystal was mounted on the diffractometer which proved to be a minor impurity from the synthesis of the initiator. The structure was solved and refined and the compound was determined to be the homobimetallic dimer [Mo(NAr)(OCMe₃)₂]₂. Two views of this molecule are shown in Figure 1 with some bond distances and angles shown in Table 1. Note that the crystallographic software package has determined that there is a Mo-Mo bond based on covalent radii considerations. However this need not be the case and the proximity of the metals could be due to steric constraints arising from the bridging nature of the imido ligands. There is a crystallographically imposed plane of symmetry which relates the two halves of the molecule. A plausible route for the formation of [Mo(NAr)(OCMe₃)₂]₂ is via the coupling of two methylidene fragments (Equation 1). The methylidene fragments in turn

\[
\begin{align*}
\text{Me}_3\text{CO}_\text{II,Mo} & \quad \text{Me}_3\text{CO}_\text{Mo} \\
\text{O} & \quad \text{Me}_3\text{CO}_\text{Mo} \\
\text{CH}_2 & \quad \text{Me}_3\text{CO}_\text{Mo}
\end{align*}
\]

are likely to arise by either insertion of vinyl ferrocene or neohexene to yield an α, β disubstituted metallacycle, followed by elimination of the resulting dissubstituted olefin. Note that [Mo(NAr)(OCMe₃)₂]₂ is only minimally soluble in pentane such that separation from the Mo(CHFc) initiator is straightforward.

\[ [\text{Mo(NAr)(OCMe₃)₂}]₂ \textbf{(NMR data).} \] A small amount of the dimer was obtained from a large scale synthesis of Mo(CHFc) which was sufficient for NMR characterization: \(^1\text{H NMR (C}_6\text{D}_6) \delta 7.30 \text{ (t, 1, H}_p\text{), 7.23 \text{ (d, 2, H}_m\text{), 2.25 \text{ (sept, 2, CHMe}_2\text{), 1.27 \text{ (d, 12,}}


Figure 1. (a) Two views of \([\text{Mo(NAr)(OCMe}_3\text{)}_2]\)_2 and (b) three views of the bimetallic coordination sphere.
Table 1. Selected bond lengths (Å) and angles (deg) in [Mo(NAr)(OCMe$_3$)$_2$]$_2$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(1)-Mo(2)</td>
<td>2.654 (1)</td>
<td>Mo(1)-N(1)-Mo(2)</td>
<td>85.6 (2)</td>
</tr>
<tr>
<td>Mo(1)-O(3)</td>
<td>1.887 (3)</td>
<td>O(4)-Mo(2)-O(4)'</td>
<td>111.6 (2)</td>
</tr>
<tr>
<td>Mo(2)-O(4)</td>
<td>1.892 (3)</td>
<td>O(3)-Mo(2)-O(3)'</td>
<td>111.1 (2)</td>
</tr>
<tr>
<td>Mo(1)-N(1)</td>
<td>1.955 (4)</td>
<td>O(4)-Mo(2)-N(1)</td>
<td>117.4 (1)</td>
</tr>
<tr>
<td>Mo(2)-N(1)</td>
<td>1.952 (4)</td>
<td>O(3)-Mo(1)-N(1)</td>
<td>118.2 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo(1)-N(1)-C(11)</td>
<td>137.4 (3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo(2)-N(1)-C(11)</td>
<td>137.0 (3)</td>
</tr>
</tbody>
</table>
CHMe₂), 1.27 (s, 18, OCMε₃), ¹³C NMR (125.7 MHz, C₆D₆) δ 160.4 (C₁), 141.4 (C₀), 126.7 (Cₚ), 125.0 (Cₘ), 79.6 (OCMe₃), 32.6 (OCMe₃), 27.1 (CHMe₂), 26.3 (CHMe₂).

X-ray crystal structure of [Mo(NAr)(OCMe₃)₂]₂. The data was collected by Dr. William Davis and the structure solved and refined by Marie O'Regan. Data were collected at -72 °C on a Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å) and a 12 KW rotating anode generator. A total of 4944 reflections were collected, 4646 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. Therefore, no decay correction was applied. The structure was solved by direct methods¹. Refinement was by full-matrix least squares using TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (dC-H = 0.95 Å). Crystal data are a = 14.772 (6) Å, b = 15.470 (4) Å, c = 19.625 (8) Å, β = 104.62 (3) °, V = 4346 (3) Å³, space group = C2/c (no. 15), Z=4, Mᵣ = 834.88, ρ = 1.276 g/cm³, μ = 5.99 cm⁻¹. Final R₁ = 0.035 and R₂ = 0.047.
REFERENCES


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84. Randy Saunders, personal communication.


98. The rates of metathesis of cis-2-pentene with Mo(NAr)(CHCMe₃)(OCMe₂(CF₃))₂ is approximately 5 turnovers per hour while that of Mo(CHCMe₃) is approximately 1-2 turnovers per day. When the alkoxide is changed to OCMe₂(CF₃)₂ the rate increases to about 5000 turnovers per hour, as determined by approach to equilibrium kinetics.


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126. These estimates are for blocks of polynorbornene and poly(7,8-bis(trifluoromethyl)tricyclo[4.2.2.02,5]deca-3,7,9-triene) or polyacetylene which can also be prepared using the ROMP technology described here, Sankaran V; Schrock, R. R., personal communication.


133. (a) 3-Oxaplatinacyclobutane complexes have been reported. So far there is no evidence that 3-heteroatom metallacycles are formed in reactions between alkylidene complexes and the carbonyl function. (b) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* 1989, 111, 6466.


140. Observation of cis WC₃ metallacycles was claimed in ring opening metathesis reactions involving norbornenes, but later they were shown to be diastereomeric trans


148. Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M; O'Regan, M.; Davis, W. M. (manuscript in preparation)


150. A much more elegant explanation based on orbital considerations of trigonal bipyramidal systems has been put forth by Dr. W. Crowe.\textsuperscript{148} His perception of the symmetry requirements of these C-H interactions stimulated much of the work presented in this Chapter.

152. Weinstock, I. A.; Schrock, R. R.; Davis, W. M. in press.

153. These arguments are based on the isolobal analogy between M(NR)2 fragments and Cp2MX2 complexes. This analogy has been put forth by Dr. W. Crowe and it can account for the observed site selectivity of base attack as well as the reactivity of the complexes of the type M(NAr)2(PR3)2.

ACKNOWLEDGEMENTS

Upon my arrival to MIT I decided to change from the organic division to the inorganic one. The reason for my decision was not complicated; I simply thought organometallic molecules were beautiful. Four years later I still think so.

The work in this thesis fairly well describes what I did during these last four years and I am sure that it could not have been achieved without the help and collaboration of a fair number of individuals:

I am grateful to Professor Richard R. Schrock for the support and mentorship provided during my graduate student career. Many times I would report an “interesting” new molecule only to have Dick ask what it could do. Perhaps that will be the most enduring thing I have learned from him; to appreciate that chemistry which leads to more chemistry. The freedom that I have had to pursue that which I was interested in and his constant interest in my work were the best things that could have happened to me.

Professor James Feast and Dr. Vernon Gibson from the University of Durham pointed out the importance of stereoregulation which led to the investigations described in Chapter 2. I would also like to thank Vernon for his hospitality during my visit to the U. K.

Hyun-Nam Cho brought much appreciated experience for monomer synthesis. Although his English was not perfect (neither is mine) his abilities at the bench were substantial.

The work in Chapter 6 originated from a series of casual conversations with David Albargli. As I mentioned in the text this work would not have happened had it not been for his enthusiasm and experience. Thanks are due to his advisor Professor Mark S. Wrighton for his support for the project.

I owe a lot to Jim Simms who taught me about practical NMR spectroscopy. In a fast moving place such as MIT his uncommon patience and concern for students have made him stand out above others.

I have to thank Marie O'Regan for dealing with the science of X-ray crystallography and other intangibles for me. All the molecules whose structures were determined were air sensitive and some thermally unstable; it was reassuring to know that at least Marie would try her best every time. I would also like to thank her for a lot more than that.

Dr. William Crowe taught me the power of chemical theories that can be explained with pencil and paper alone.

Although Kimo Yap has terrorized me during the last few weeks (months?) his expert management of the Schrock Group Computing Facility is appreciated.

Especial thanks go to Eve Diana for smoothing things out around here and providing expert advice on a wide range of subjects.

Mike Vale reminded me of how wrong things can get when the fundamentals are not mastered.

Schrock group members like Kevin Wallace (past) and Rob Toreki (present) have kept the lab machinery running smoothly so that experiments were easier to carry out, their efforts are appreciated.

Thanks go to Kit Cummins, Amjad Farook, Harold Fox, John Oskam and Darryl Williams for proofreading of the thesis.

The support and good times provided by my friends (Ken C., Mark R., John B., Lea A., Denise C., Tim O. and Ludwig V. B.) were also badly needed.

Finally, and most importantly, I would like to acknowledge the unconditional love of my family throughout so many years.