

Recent Advances in the Syntheses and Applications of Molybdenum and Tungsten Alkylidene and Alkylidyne Catalysts for the Metathesis of Alkenes and Alkynes

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Received: September 8, 2006

Abstract: The last several years have produced some key advances in the area of alkene and alkyne metathesis by high oxidation state alkylidene and alkylidyne complexes along with new applications in organic and polymer chemistry. In this review we cover some of these developments and applications. The first part of this review concerns developments in catalyst synthesis and new catalysts. The second part concerns notable applications in organic and polymer chemistry. We discuss only high oxidation state alkylidene and alkylidyne chemistry of relevance to alkene or alkyne metathesis reactions and favor studies in the homogeneous phase.

- 1 Introduction
- 2 Developments in Alkylidene and Alkylidyne Chemistry
 - 2.1 Synthesis and Reactivity of Bisalkoxide (or Dio-late) Alkylidene Catalysts
 - 2.2 Decomposition of Alkylidene Complexes
 - 2.3 Precursors to Bisalkoxides (Dialkyls, Bisamides, Dipyrrolys)
- 3 Generation of Alkylidenes from Olefins

- 4 Well-Defined Catalysts Attached to Organic or Inorganic Supports through Covalent Bonds
 - 4.1 Organic Supports
 - 4.2 Inorganic Supports
- 5 New Alkylidene Complexes as Metathesis Catalysts
- 6 Developments in Alkylidyne Chemistry
- 7 Applications of Metathesis Catalysts in Organic Synthesis
 - 7.1 Alkene Metathesis
 - 7.2 Alkane Metathesis
- 8 Advances in Controlled Polymer Synthesis
 - 8.1 Synthesis of Triblock Copolymers Employing Bi-functional Initiators
 - 8.2 Polyenes Prepared through Polymerization of Diethyl Dipropargylmalonate
 - 8.3 Cyclopropenes
- 9 Stoichiometric Reactions
- 10 Concluding Comments

Keywords: alkenes; alkynes; metathesis; molybdenum; tungsten

1 Introduction

Catalytic alkene and (to a lesser extent) alkyne metathesis and its many variations have emerged as useful catalytic transformations in modern chemical synthesis in the last 15 years. High oxidation state alkylidene^[1] and alkylidyne^[2] complexes of Mo and W comprise a significant class of catalysts for these transformations.^[3,4] In 2003 a review of the discovery and development of imido alkylidene catalysts of Mo and W as efficient olefin metathesis catalysts in organic chemistry was published.^[5] A review of the application of alkyne metathesis in organic chemistry has also appeared recently,^[6] as have reviews of polymerization reactions that involve well-defined transition metal alkylidene catalysts,^[7] polymerization of 1-al-

kyne and 1,6-heptadiynes,^[8] and metathesis polymerization to and from surfaces.^[9] The last several years have produced some key advances in the area of alkene and alkyne metathesis by high oxidation state species along with new applications in organic and polymer chemistry. In this review we cover some of these developments and applications. The first part of this review concerns developments in catalyst synthesis and new catalysts. The second part concerns notable recent applications in organic and polymer chemistry. We intend to discuss only high oxidation state alkylidene and alkylidyne chemistry of relevance to alkene or alkyne metathesis reactions; this review is not intended to be comprehensive.

Constantin Czekelius was born in Germany in 1974. After undergraduate studies in Freiburg i.Br. and Würzburg he obtained a diploma in chemistry in 2000 at the ETH Zurich. Under the supervision of Erick M. Carreira he earned a PhD degree in 2004 working on the enantioselective catalytic reduction of nitroalkenes and the synthesis of chiral bidentate carbene ligands. During his postdoctoral studies at the Massachusetts Institute of Technology in the group of Richard R. Schrock he worked on the synthesis of extended polyenes and ring-opening metathesis polymerization of cyclopropenes. In 2006 he became leader of an independent research group at the Freie Universität Berlin. His interests include enantioselective catalytic methods for facile preparation of synthetically interesting building blocks, the synthesis of new optically active ligands, and research in materials science.



Richard R. Schrock received his PhD in inorganic chemistry from Harvard in 1971. After one year as an NSF postdoctoral fellow at Cambridge University and three years at the Central Research and Development Department of E. I. DuPont de Nemours and Co., he moved to M.I.T. in 1975 where he became full professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the inorganic and organometallic chemistry and catalysis involving high oxidation state, early metal complexes (especially those that contain an alkylidene or alkylidyne ligand), the chemistry of high oxidation state dinitrogen complexes and catalytic dinitrogen reduction, and the controlled polymerization of olefins and acetylenes. In 2005 he shared the Nobel Prize in Chemistry with R. H. Grubbs and Y. Chauvin. (Photo by L. Barry Hetherington.)



2 Developments in Alkylidene and Alkylidyne Chemistry

2.1 Synthesis and Reactivity of Bisalkoxide (or Diolate) Alkylidene Catalysts

This section will review the fundamentals concerning the synthesis and reactivity of tungsten and molybdenum species of the type $M(NR)(CHR')(OR'')_2$. For complete details the reader should refer to recent reviews.^[1,3,5]

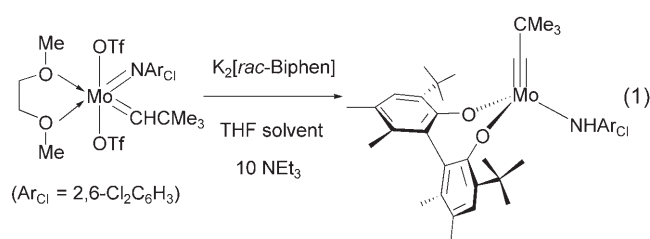
The synthesis of $M(NR)(CHR')(OR'')_2$ ($M=Mo$ or W) species relies on synthesis of a bistriflate species of the type $M(NR)(CHR')(OTf)_2(DME)$ from an $M(NR)_2(CH_2R')_2$ species through addition of three equivalents of triflic acid.^[10,11] The α abstraction reaction that gives rise to the alkylidene is most facile (and the resulting alkylidene most stable) when the alkyl is CH_2CMe_3 or CH_2CMe_2Ph . Addition of a large alkoxide or diolate to $M(NR)(CHR')(OTf)_2(DME)$ then gives the desired $M(NR)(CHR')(OR'')_2$ species. The number of synthetic steps to bisalkoxides overall is four for Mo and five for W . No other general method of synthesizing $M(NR)(CHR')(OR'')_2$ species has been developed.

$M(NR)(CHR')(OR'')_2$ ($M=Mo$ or W) species are electron-deficient (14 electron count), sensitive to air and water, and thermally unstable toward bimolecular

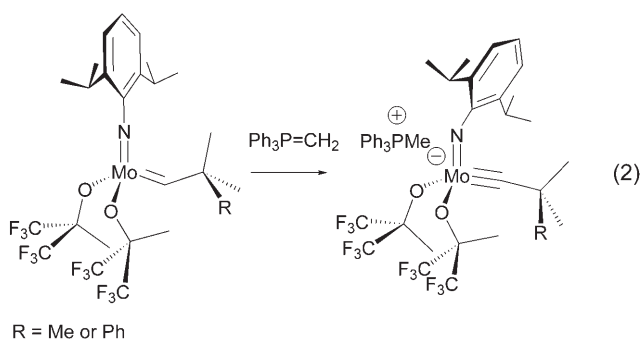
coupling of alkylidenes and consequent “reduction” of the metal when one or more of the four ligands in the pseudotetrahedral complex is not sufficiently sterically demanding. The most stable terminal alkylidene toward bimolecular decomposition is neopentylidene or neophylidene ($CHCMe_2Ph$). [Little is known concerning secondary alkylidenes (disubstituted carbene ligands), although they are likely to be much more stable toward bimolecular decomposition reactions.^[12] Exactly which ligand combinations result in relatively stable but reactive species must be determined through educated trial and error; no quantitative and/or predictive methods have been forthcoming. During metathesis the alkylidene is often transformed into a smaller terminal alkylidene, internal alkylidene, or methylene. Methylene species are especially unstable toward bimolecular decomposition, which is why isolable but reactive (not 18 electron) methylene species are especially rare. One or (rarely) two bases can add to any pseudotetrahedral species when sterically possible to yield much more stable $M(NR)(CHR')(OR'')_2L$ or 18e $M(NR)(CHR')(OR'')_2L_2$ species. Five- and six-coordinate species are dramatically less reactive since $M(NR)(CHR')(OR'')_2$ must be formed through dissociation of L before an olefin can react with the alkylidene. The challenge has been to find $M(NR)(CHR')(OR'')_2$ species that can be isolated and employed as the initial alkylidene species in an alkene metathesis reaction, or $M(NR)-$

(CHR')(OR'')₂L species in which the donor ligand L is labile. Note that a donor functionality present in a metathesis substrate may bind preferentially to the metal and block metathesis reactions, especially if that functionality is close to the M=C bond in an intermediate.^[86] In virtually all M(NR)(CHR')(OR'')₂ species R' is a carbon group. The known exceptions are a silyl group, and recently published derivatives in which R' is a germyl group.^[13]

A potential problem with the synthesis of M(NR)(CHR')(OR'')₂ catalysts from M(NR)(CHR')(OTf)₂ (DME) species has been conversion of an imido/alkylidene species into an amido/alkylidyne species in the process of substituting triflates with alkoxides [Eq. (1)]. At some unknown point during the reaction the



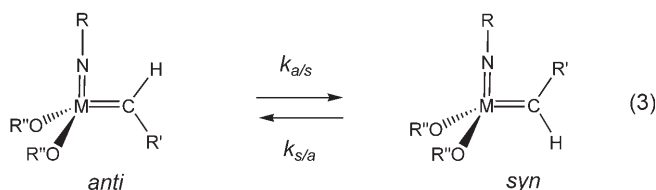
nucleophile attacks the alkylidene's α proton in competition with attack at the metal and the imido nitrogen is subsequently protonated,^[14,15] thereby lowering the yield of the desired imido alkylidene species. Recently an imido/alkylidene complex was completely deprotonated in good yield upon reaction of Ph₃P(CH₂) with Mo(NAr)(CHCMe₃)(OR_{F6})₂ [Ar = 2,6-*i*-Pr₂C₆H₃, OR_{F6} = OCMe(CF₃)₂; Eq. (2)]. The anionic



imido alkylidyne complex contains a "bent" imido ligand [$\text{Mo}-\text{N}_{\text{imido}}-\text{C}_{\text{ipso}} = 141.16(17)^\circ$] as a consequence of only three strong π bonds between the metal and the imido and alkylidyne ligands being possible.

An important feature of M(NR)(CHR')(OR'')₂ species is the possibility of forming two isomers, a *syn* alkylidene, in which the alkylidene substituent points toward the imido ligand, or an *anti* alkylidene, in

which the alkylidene substituent points away from the imido nitrogen [Eq. (3)].^[16] The rates of intercon-



sion of these two isomers depend dramatically on the nature of OR'' and can vary by as many as six orders of magnitude. The *anti* form is believed to be the more reactive of the two forms in general, again by orders of magnitude. In short, an additional variable (*syn* or *anti* isomer) is built into these systems, in addition to variations possible in M (Mo or W), NR, and OR''. *syn* and *anti* isomers interconvert through rotation about the M=C bond in four-coordinate species. Both *syn* and *anti* isomers bind two electron donors to different degrees, a fact that can dramatically alter the degree to which each M(NR)(CHR')(OR'')₂ species is involved in a metathesis reaction. The complexity of an olefin metathesis reaction by M(NR)(CHR')(OR'')₂ species clearly is potentially high. Consequently, an understanding of all details is rare.

M(NR)(CHR')(OR'')₂ species have four pseudotetrahedral faces to which a donor, including an olefin, can add to the metal. Two of the faces correspond to the two faces of the M=C bond; these are the "CNO faces" of the catalyst. Olefins are believed to add to the CNO faces in order to form an intermediate metalacyclobutane ring. Addition of an olefin to the "COO" face *trans* to the imido group could give rise to a metalacycle only if the alkylidene were to rotate by 90°, while addition of an olefin to the NOO face *trans* to the alkylidene could not lead to formation of a metalacyclobutane intermediate without rearrangement of the five-coordinate core.

A wide variety of catalysts has been prepared that contain chiral diolates (either racemic or enantiomerically pure), usually those based on biphenolates or binaphtholates.^[5] Racemic catalysts are sufficient for controlling the structure of a polymer that is prepared with an alkylidene initiator in a living polymerization process, while enantiomerically pure catalysts are required for asymmetric reactions. No example of an M(NR)(CHR')(OR'')₂ complex that contains an enantiomerically pure imido ligand has been published, although there is no reason in principle why this should not be possible. Catalysts that contain a dianionic chiral ligand that is not C₂ symmetrical are also virtually unknown.

Theoretical studies have appeared that concern asymmetric metathesis catalysts,^[17] the ROMP of nor-

bornadiene with Mo catalysts,^[18] and the structural, spectroscopic, and electronic properties of Mo and W imido alkylidene complexes.^[19] DFT and QM/MM calculations have also been carried out on rhenium complexes of the type $\text{Re}(\text{CR})(\text{CHR})(\text{X})(\text{Y})$ (where X and Y are alkyls or alkoxides).^[20]

Alkylidene complexes usually can be observed readily by ^1H NMR spectroscopy. The alkylidene's H_α resonance usually is found between 8 and 14 ppm. The resonance that corresponds to the often minor *anti* isomer typically appears 1–2 ppm downfield of the *syn* H_α resonance. The $J_{\text{C,H}}$ coupling constant for the *syn* isomer is typically smaller (~ 125 Hz) than for the *anti* isomer (~ 140 Hz). A lower value for $J_{\text{C,H}}$ correlates with a smaller $\text{M}-\text{C}_\alpha-\text{H}_\alpha$ angle and consequently a more significant agostic interaction of the CH_α bond with the metal. DFT calculations of NMR $J_{\text{C,H}}$ coupling constants in high oxidation state complexes of Ta, Mo, and Re have been reported recently.^[21]

Tungsten imido alkylidene complexes have been explored less than Mo catalysts since metalacyclobutane complexes, especially unsubstituted $\text{W}(\text{C}_3\text{H}_6)$ species, tend to be more stable toward loss of olefin than molybdacyclobutanes. Therefore it has been possible to crystallize and structurally characterize several tungstacyclobutane complexes.^[3b] Two types of tungstacyclobutanes, each of which has distinctive ^1H and ^{13}C NMR spectra, have been observed under a variety of conditions. Crystallographic studies indicate that these metalacyclobutanes possess either a trigonal bipyramidal geometry, in which the MC_3 ring and an alkoxide oxygen are in the equatorial plane, or a square pyramidal geometry, in which the imido ligand is in an axial position. It has not been determined which geometry, if either, is formed *directly* upon reaction of the alkylidene complex with an olefin, since five-coordinate species can rearrange readily. It is believed that $\text{W}(\text{C}_3\text{H}_6)$ species can be relatively stable catalyst “reservoirs” that limit the amount of metal that is actually involved in the metathesis reaction.

2.2 Decomposition of Alkylidene Complexes

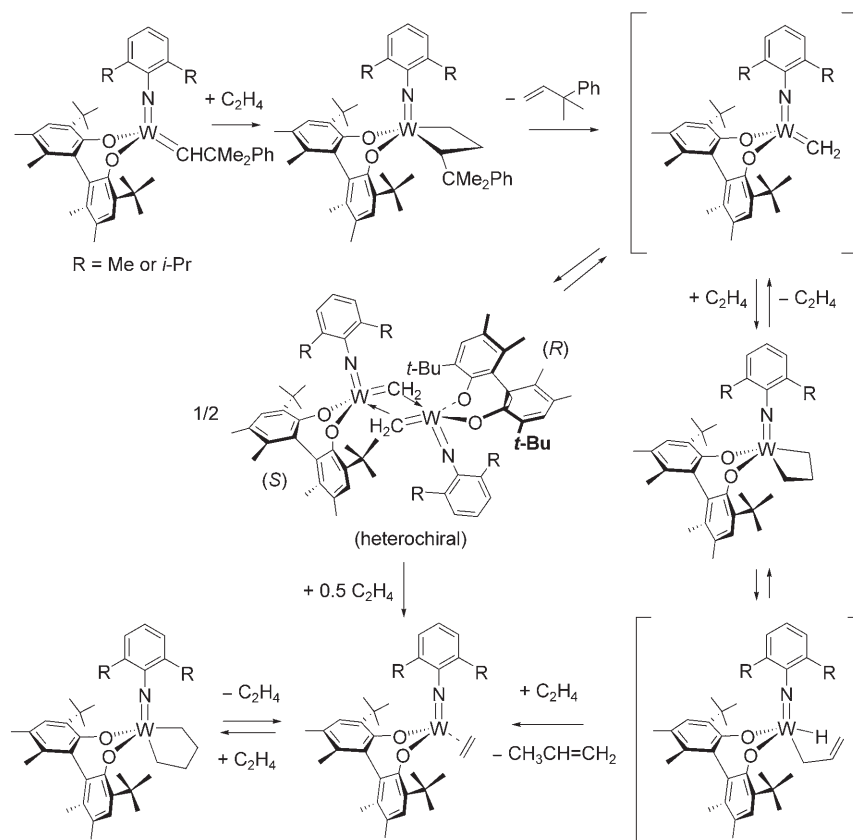
High oxidation state alkylidenes often decompose during a metathesis reaction, a fact that figures heavily in overall metathesis efficiency. Two modes of decomposition have been observed. One is bimolecular coupling of alkylidenes. This pathway is fastest for methylene complexes, the most reactive and therefore the least stable of the alkylidenes. The second is rearrangement of metalacyclobutanes to olefins *via* a β -hydride elimination reaction. Precise details of each reaction are largely unknown.

In a paper devoted to alkylidene complexes of tungsten that contain the chiral biphenoxide Biphen^{2-}

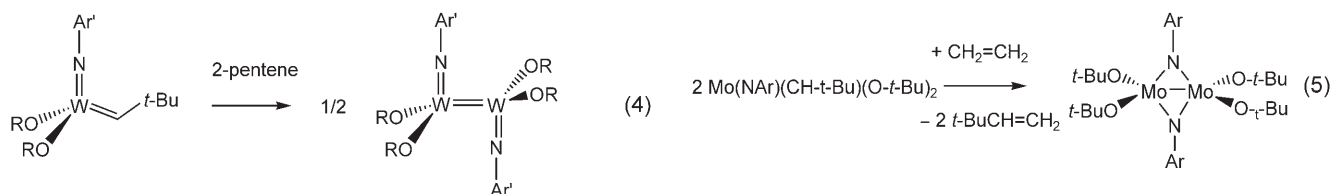
ligand (where $\text{Biphen}^{2-} = 3,3'$ -di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate),^[22] the reaction of the initial neophylidene complex with ethylene could be followed in detail, as shown in Scheme 1, through the use of ^{13}C -labeled ethylene. The most surprising feature was detection of a dimeric methylene complex, the presumed precursor to an ethylene complex in the presence of ethylene. An ethylene complex also was formed through rearrangement of an unsubstituted tungstacyclobutane, as judged by formation of propylene (< 1 equiv.). The final product *via* each pathway is the $\text{W}(\text{IV})$ ethylene complex (in the presence of ethylene). But the $\text{W}(\text{IV})$ ethylene complex also reacts readily and reversibly with ethylene to form a tungstacyclopentane complex, which is a (slow) catalyst for formation of 1-butene *via* β -hydride elimination. Similar observations have been made in the analogous Mo system,^[23] although no dimeric methylene complex was observed and the molybdacyclopentane lost ethylene much more readily than the tungstacyclopentane complex. When the imido ligand was 2,6-dichlorophenylimido an Mo ethylene complex could be isolated (as a diethyl ether adduct) and crystallographically characterized. Olefin complexes and metalacyclopentane species have also been observed by Boncella in systems that contain a chelating diamido ligand in place of two alkoxides or a diolate ligand.^[24]

Recently, tungsten alkylidene complexes that contain the 2,6-dichlorophenylimido (NAr_{Cl}) ligand, $\text{W}(\text{NAr}_{\text{Cl}})(\text{CHCMe}_3)(\text{OR}_{\text{F}_6})_2$ and $\text{W}(\text{NAr}_{\text{Cl}})(\text{CHCMe}_3)(\text{Biphen})(\text{THP})$ (THP = tetrahydropyran), were prepared.^[25] Compounds analogous to those shown in Scheme 1 could be isolated and crystallographically characterized, including heterochiral $[\text{W}(\text{NAr}_{\text{Cl}})(\text{Biphen})(\mu\text{-CH}_2)]_2$, and the homochiral “1,2-ditungstacyclobutane” species, $[\text{W}(\mu\text{-NAr}_{\text{Cl}})(\text{Biphen})]_2(\mu\text{-CH}_2\text{CH}_2)$, which is believed to be the precursor to $[\text{W}(\mu\text{-NAr}_{\text{Cl}})(\text{Biphen})]_2$. $\{[\text{W}(\mu\text{-NAr}_{\text{Cl}})(\text{Biphen})]_2(\mu\text{-CH}_2\text{CH}_2)\}$ is related to a species shown in Eq. (6) below.} The fact that $[\text{W}(\text{NAr}_{\text{Cl}})(\text{Biphen})(\mu\text{-CH}_2)]_2$ is heterochiral and $[\text{W}(\mu\text{-NAr}_{\text{Cl}})(\text{Biphen})]_2(\mu\text{-CH}_2\text{CH}_2)$ is homochiral suggests that the C–C bond is not formed through rearrangement of $[\text{W}(\text{NAr}_{\text{Cl}})(\text{Biphen})(\mu\text{-CH}_2)]_2$, but through dissociation and recombination of homochiral $\text{W}(\text{NAr}_{\text{Cl}})(\text{Biphen})(\mu\text{-CH}_2)$ intermediates. The tungsten NAr_{Cl} system has provided the most complete series of complexes formed when a neopentylidene species reacts with ethylene.

When tungsten bisalkoxide complexes react with an *internal* olefin such as 2-pentene unusual compounds are formed that contain *unbridged* $\text{W}=\text{W}$ bonds and *terminal* imido ligands [Eq. (4)].^[26] It had been known in the literature that unstable $\text{W}(\text{NAr}')(\text{CHet})[\text{OCMe}(\text{CF}_3)_2]_2$ ($\text{Ar}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) decomposes to yield “ $\text{W}(\text{NAr}')[\text{OCMe}(\text{CF}_3)_2]_2$ ”, which was proposed



Scheme 1.

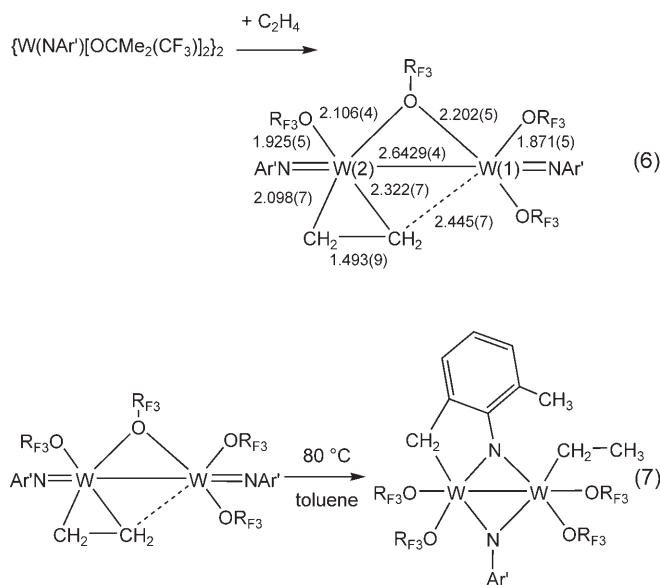


to contain a bridging imido group, i.e., $\{W(\mu-NAr')-[OCMe(CF_3)_2]_2\}_2$.^[11] However, an X-ray study showed that this species is actually $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$ in which the $W=W$ bond [2.4751(4) Å] is unsupported by bridging ligands. $[W(NAr')(OCMe_2CF_3)_2]_2$ and $[W(NAr')(OCMe_2CF_3)_2]_2$ were prepared in a similar manner and confirmed through X-ray diffraction studies to contain unbridged $W=W$ bonds.

It should be noted that a reaction between $Mo(NAr)(CH-t-Bu)(O-t-Bu)_2$ and ethylene yields a dimer that has bridging imido groups and approximately a tetrahedral arrangement of ligands about each metal [Eq. (5)].^[27] Since no propylene was observed as a product of this reaction, it was proposed that $[Mo(\mu-NAr)(O-t-Bu)_2]_2$ formed exclusively *via* bimolecular decomposition of intermediate $Mo(NAr)(CH_2)(O-t-Bu)_2$ species. It is now known that, in general, as described for the system shown in Scheme 1,

bimolecular decomposition of methylenes and rearrangement of a metalacyclobutane often are both operative in a given system.

Dimeric species, with or without bridging imido groups, are well along the pathway of decomposition of imido alkylidene bisalkoxides. However, when and how bridging or non-bridging complexes are formed, versus olefin complexes and metalacyclopentanes, is still a subject of current research. Such species are of significant interest in view of the finding that they can themselves behave as olefin metathesis catalysts in certain circumstances,^[28] although the alkylidene that is formed could not be observed or identified. In this context it is interesting to note that $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ will react with ethylene reversibly to yield the adduct shown in Eq. (6), which upon heating is converted into the ethyl complex shown in Eq. (7) as a consequence of CH activation in the *ortho* methyl group of the NAr' ligand. More can be found about



the possibility of reforming alkylidenes from olefins in a later section.

An important remaining challenge in high oxidation state metathesis chemistry is to limit, or possibly even prevent, decomposition of alkylidenes, *via* either bimolecular decomposition or rearrangement of metalacyclobutanes. In a later section we show how to prepare well-defined catalysts attached to silica surfaces, an approach that prevents bimolecular decomposition of intermediate alkylidenes in a metathesis reaction. However, catalyst activity still decreases with time in the heterogeneous catalyst system, which suggests that unimolecular metalacyclobutane rearrangement is still a viable pathway of decomposition.

2.3 Precursors to Bisalkoxides (Dialkyls, Bisamides, Dipyrrolys)

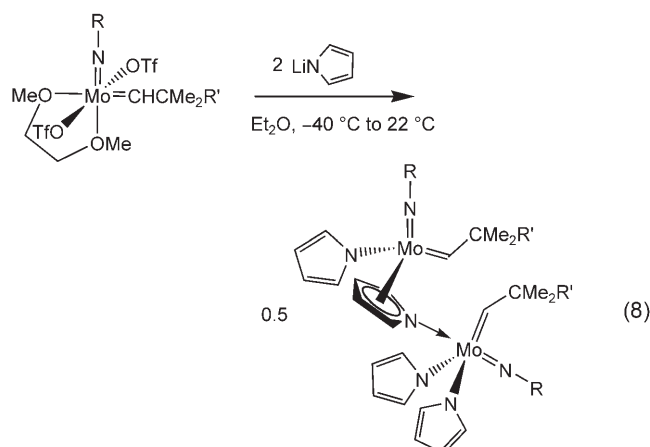
The dramatic increase in the number of possible catalysts and the extreme sensitivity of the outcome of a given metathesis reaction to subtle changes in the catalyst require that catalysts ultimately be generated *in situ*, at least for screening purposes. Therefore we have been searching for methods of synthesizing $Mo(NR)(CHCMe_2R')(OR'')_2$ ($R' = Me$ or Ph) species (or species that contain enantiomerically pure biphenolate or binaphtholate ligands^[51]) by treating an appropriate $M(NR)(CHCMe_2R')X_2$ species with two equivalents of a monoalcohol or one of a diol. Of course, the synthesis of $M(NR)(CHCMe_2R')(OR'')_2$ species from $M(NR)(CHCMe_2R')X_2$ species requires that both X groups be protonated and replaced readily, that the HX product of this reaction does not interfere to any significant degree with subsequent reactions that involve $M(NR)(CHCMe_2R')(OR'')_2$, and

that the HX product does not react with any organic species in the reaction.

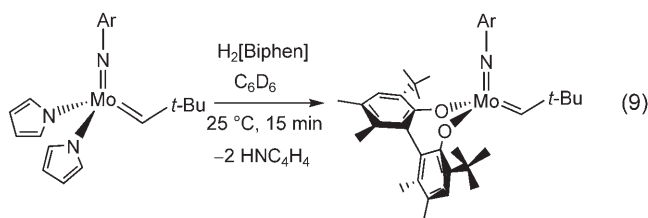
The first investigations involved $M(NR)(CHCMe_2R')(CH_2-t-Bu)_2$ species. The reaction between $M(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ ($M = Mo$ or W) and various alcohols [1-adamantylOH, *t*-BuOH, ArOH, $(CF_3)_2CHOH$, $(CF_3)_2MeCOH$, CF_3Me_2COH , $(CF_3)_3COH$, C_6F_5OH] in pentane or toluene yields either complexes of the type $M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)$ through direct addition of ROH across an $Mo-C$ bond, or complexes of the type $M(NAr)(CH_2-t-Bu)_3(OR)$ through direct addition of ROH across an $Mo=C$ bond.^[29,30] The trineopentyl species appear to be formed when the alcohol has a relatively low pK_a . The outcome also can depend upon whether the alcohol is employed neat, or in benzene, and mixtures are observed in some circumstances. Conversion of $M(NAr)(CH_2-t-Bu)_3(OR)$ into $M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)$ was shown to be unimolecular in several examples. Preliminary experiments showed that $M(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)$ complexes are surprisingly active catalysts for various metathesis reactions, although conversion is sometimes limited by decomposition of intermediate alkylidenes to yield dimeric species that contain $M=M$ bonds.^[26] The reasons are discussed in a later section.

A second approach is to employ bisamido complexes, $Mo(NR)(CHR')(NR'')_2$ as precursors.^[31] We found that $Mo(NAr)(CHR')(NPh_2)_2$ ($R' = t-Bu$ or CMe_2Ph) and $Mo(NAr')(CHCMe_2Ph)(NPh_2)_2$ ($Ar' = 2,6-Me_2C_6H_3$) can be prepared through addition of two equivalents of $LiNPh_2$ to $Mo(NR'')(CHR')(OTf)_2$ (DME) species ($R'' = Ar$ or Ar' , DME = 1,2-dimethoxyethane). Yields are low as a consequence of competitive deprotonation of the alkylidene. A high yield route consists of addition of $LiNPh_2$ to bishexafluoro-*tert*-butoxide species. The diphenylamido complexes react readily with *t*-BuOH and $(CF_3)_2MeCOH$, but not readily with the sterically demanding biphenol $H_2[Biphen]$ ($Biphen^{2-} = 3,3'$ -di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate). The diphenylamido complexes do react with various 3,3'-disubstituted binaphthols to yield binaphtholate catalysts. These catalysts can be prepared *in situ* and employed for a simple asymmetric ring-closing metathesis reaction. In several cases conversions and enantioselectivities were comparable to those of reactions in which isolated catalysts were employed.

Recently a variety of dipyrrolyl complexes, $Mo(NR)(CHCMe_2R')(NC_4H_4)_2$, were prepared in good yield directly from bistriflate precursors, $Mo(NR)(CHCMe_2R')(OTf)_2$ (DME) [$R = 2,6$ -*i*-Pr₂C₆H₃, 1-adamantyl, or 2,6-Br₂-4-MeC₆H₂; Eq. (8)].^[32] No sign of competitive deprotonation of the alkylidene to give an alkylidyne complex was observed. The dipyrrolyl species react rapidly with sterically demanding biphenols and binaphthols, even with



$\text{H}_2[\text{Biphen}]$ when $\text{NR}=\text{NAr}$, to yield two equivalents of pyrrole and bisalkoxide or biphenolate or binaphtholate species [Eq. (9)]. All dipyrrolyl complexes are

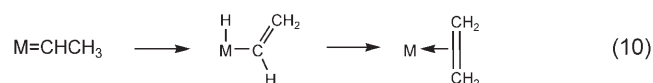


dimers [as shown in Eq. (8)] which are fluxional on the NMR time scale as a consequence of dissociation into monomeric units and interconversion of η^1 and η^5 pyrrolyl ligands. Preliminary results suggest that the pyrrole that is generated binds more weakly to the resulting bisalkoxide or diolate complex than does THF. In the case where $\text{NR}=\text{N}-2,6\text{-Br}_2\text{-4-MeC}_6\text{H}_2$ a catalyst was prepared *in situ* that could not be isolated in good yield through the traditional route.^[33] The catalytic activity of $\text{Mo}(\text{N}-2,6\text{-Br}_2\text{-4-MeC}_6\text{H}_2)(\text{CHCMe}_3)(\text{rac-Biphen})$ was confirmed through the ring-closing metathesis of ~ 80 equivalents of diallyl ether to dihydrofuran in 15 min at room temperature in C_6D_6 . On the basis of these preliminary findings it seems likely that other catalysts that have been isolated only as THF adducts, or that have not been isolated before, may be prepared from dipyrrolyl precursors. This approach has obvious potential for the *in situ* generation and/or evaluation of bisalkoxide or diolate catalysts. Precursors of this type also hold significant promise for the synthesis of surface-bound catalysts, e.g., to silica (*vide infra*).

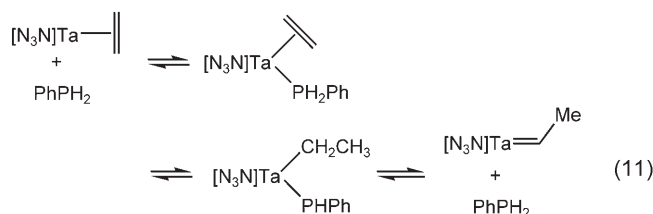
3 Generation of Alkylidenes from Olefins

In the beginning of high oxidation state alkylidene chemistry it was proposed that a significant mode of

decomposition of alkylidenes that contain one or more β hydrogens is rearrangement of that alkylidene to an olefin through a β hydride elimination process, e.g., as shown for an ethylidene complex in Eq. (10).

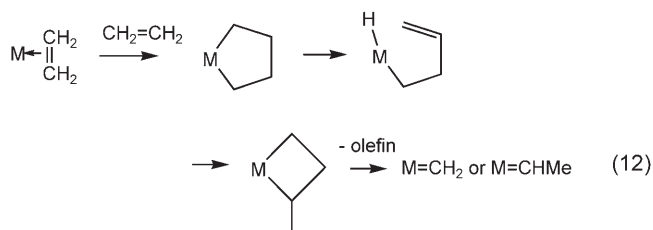


There was not, and still is not, any proof that rearrangement of alkylidenes to olefins is a general phenomenon relative to other modes of alkylidene decomposition (bimolecular coupling and metalacyclobutane rearrangement). In fact, evidence in the literature suggested that tungsten alkylidene complexes could be generated from olefins.^[34] In 1994 it was shown that a tantalum ethylene complex could be converted into an analogous ethylidene complex with a catalytic amount of phenylphosphine [Eq. (11)]



where $[\text{N}_3\text{N}]^{3-}=[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$.^[35] It was proposed that the strong α agostic interaction in the ethylidene product lowers the energy of the ethylidene relative to the ethylene complex and makes this transformation possible. Wolczanski now has shown that many $(\text{SiOx})_3\text{M}(\text{olefin})$ complexes [$\text{SiOx}=(t\text{-Bu})_3\text{SiO}$, $\text{M}=\text{Nb}$ or Ta] rearrange to $(\text{SiOx})_3\text{M}(\text{alkylidene})$ complexes upon heating, often at relatively high temperatures (150° or higher), and an equilibrium is established between the two.^[36] Evidence suggests that the mechanism involves formation of an alkyl intermediate through CH activation in a SiOx ligand followed by removal of an α proton, a process that is related to that shown in Eq. (11). However, the $[\text{SiOx}]^-$ and N_3N^{3-} tantalum and niobium complexes are not catalysts for facile metathesis of olefins. Therefore whether rearrangement of an olefin to an alkylidene is possible in an active metathesis system is still not known.

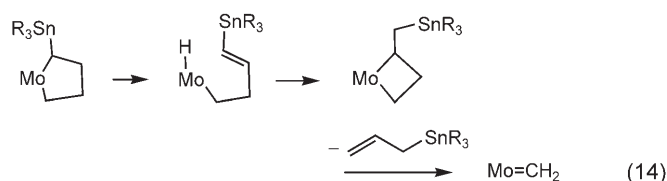
In 1979 it was discovered that tantalacyclopentanes of the type $\text{Cp}^*\text{Cl}_2\text{Ta}(\text{C}_4\text{R}_2\text{R}'_2)$ decompose *via* β hydride elimination followed by a contraction of the TaC_4 ring to a TaC_3 ring [Eq. (12)].^[37] Instead of a reductive elimination of the olefin at the alkenyl hydride stage, a tantalacyclobutane ring forms and rearranges *via* a second β hydride elimination. It was realized that in certain circumstances it might be possible



for metathesis of a metalacyclobutane ring to compete with its rearrangement *via* β hydride elimination, and that alkylidenes therefore could be formed from d^2 olefin complexes.^[37a] In 1985 another example of this counter intuitive “ring-contraction” mechanism, rearrangement of a rhenacyclopentane complex, $\text{Cp}^*(\text{CO})_2\text{Re}(\text{C}_4\text{H}_8)$, in the presence of a phosphine to yield methylcyclopropane, was published.^[38] In 2004 it was reported that vinyltributylstannane could be homologated to allyltributylstannane in the presence of Mo(IV) complexes and ethylene [Eq. (13)].^[39]



The crucial step was proposed to be a relatively rapid ring contraction of a “cross” metalacyclopentane (made from ethylene and vinylstannane), followed by metathesis of the resulting metalacyclobutane, as shown in Eq. (14).



In 2005 it was shown that certain olefin metathesis reactions could be initiated with Mo(IV) or W(IV) complexes.^[28] The M(IV) complexes that were employed included an ethylene complex, $\text{Mo}(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{rac-Biphen})(\text{CH}_2=\text{CH}_2)(\text{ether})$, as well as complexes that contain an unsupported $\text{M}=\text{M}$ double bond ($\text{M}=\text{Mo}$ or W). One of the $\text{M}=\text{M}$ species was prepared in a reaction that did not involve an alkylidene; therefore metathesis activity could not be ascribed to a small amount of residual alkylidene. The alkylidene species responsible for the (weak) metathesis activities could not be identified, nor could the mechanism of formation of an alkylidene.

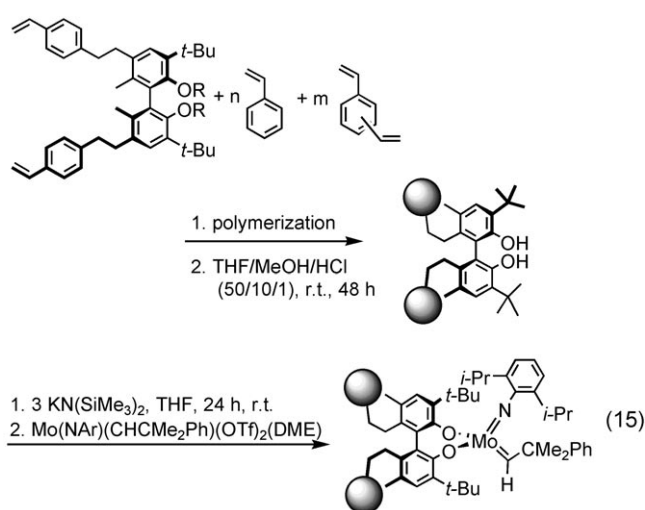
The main point is that there is gathering evidence that d^2 complexes can be transformed into (probably) d^0 alkylidene complexes that are active for metathesis. If formation of a relatively unreactive “final” decomposition product can be avoided, then “immortal”

metathesis catalysts (or at least very high turnovers) might be prepared.

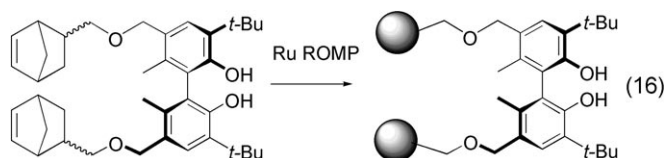
4 Well-Defined Catalysts Attached to Organic or Inorganic Supports through Covalent Bonds

4.1 Organic Supports

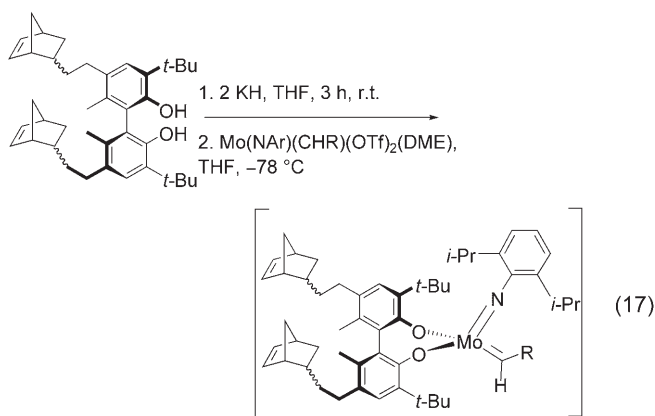
Several approaches have been employed in order to attach catalytically active Mo complexes to organic polymers. In the first approach^[40] polymerizable chiral diolates were incorporated into a polystyrene manifold first and an Mo imido alkylidene bistriflate was then attached [Eq. (15)]. Enantioselective ring-



opening and cross-metathesis reactions gave equivalent results when homogeneous and heterogeneous reaction conditions were compared and the amount of residual traces of molybdenum in the product of the heterogeneously catalyzed reaction is <1%. A variation of this approach^[41] involved polymerization of a norbornene-containing biphenol with Ru [Eq. (16)], followed by incorporation of Mo similarly.



An approach related to that shown in Eq. (16) employed the incipient Mo catalyst as the ROMP catalyst that creates a highly cross-linked polymer support *in situ* [Eq. (17)].^[42] $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OTf})_2$ (DME) itself does not react readily with norbornene.



However, when the ligand (as a dipotassium salt) is attached to Mo the resulting Mo complex is an active catalyst. The degree of polymer cross-linking directly effects the efficiency of the final catalyst system, i.e., a highly cross-linked material severely inhibits access of the substrate to the metal center. In some circumstances Mo alkylidene complexes bite back into the polymer backbone to produce short polymer fragments which are released into solution. It should be noted that bimolecular decomposition is not eliminated in a lightly cross-linked polymer, since the catalyst is actually relatively concentrated in the polymer and the polymer is still mobile.

Buchmeiser has successfully attached typical chiral and achiral bisalkoxide catalysts to an organic support through the *para* position of the arylimido ligand.^[43] Four anilines of the type 4-[6-X-(CH₂)₆]-2,6-R₂C₆H₂NH₂ (where X is Cl or Br and R = Me or *i*-Pr) were prepared and employed in the synthesis of bis-triflate imido alkylidene species in the traditional fashion. The triflates were displaced with alkoxides and the resulting catalysts were immobilized on Ag-perfluoroalkylsulfonate-modified polystyrene and polystyrene/divinylbenzene copolymers to yield the corresponding immobilized catalysts. The immobilized catalysts were employed in a series of ring-closing, ring-opening/cross, asymmetric ring-closing, and desymmetrization reactions. The enantiomerically pure catalysts produced *ees* that were virtually identical to those obtained with the corresponding homogeneous chiral catalysts (as high as 95 % *ee*). Attaching a catalyst through the imido group allows the attached species to behave in virtually the same manner as a homogeneous analogue. Bimolecular decomposition of intermediate alkylidenes is likely to still take place for reasons noted above.

4.2 Inorganic Supports

In the last decade significant progress has been made in surface organometallic chemistry.^[44] It is now possi-

ble to prepare d^0 organometallic species bound to silica that are largely or exclusively of one type, and precise details can be elucidated through modern solid state NMR studies. Hydrocarbon-based precursors that react readily with a surface SiOH group have proven extremely useful in generating these surface-attached species. Examples include Ta(CH-*t*-Bu)(CH₂-*t*-Bu)₃,^[45] M(C-*t*-Bu)(CH₂-*t*-Bu)₃ (M=Mo or W),^[2,46] and Re(C-*t*-Bu)(CH-*t*-Bu)(CH₂-*t*-Bu)₂.^[47] In the case of the Re species a silica-immobilized rhenium alkylidene alkylidyne complex (Si_sO)Re(C-*t*-Bu)(CH-*t*-Bu)(CH₂-*t*-Bu) (Si_s denotes a surface Si) is formed.^[48] Methyl oleate could be metathesized by this supported catalyst with turnover numbers (TON) of up to 900. DFT plane-wave calculations suggested that the silica surface has very similar properties to organic siloxy ligands incorporated in Re complexes for homogeneous processes.^[45e] Furthermore, EXAFS studies implied that an Re–O interaction with the surface leads to a significant change in the coordination around Re allowing for the formation of an additional coordination site.

Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)₂ has been shown to react with silica(700) (silica gel that has been calcined at 700°C), in which Si_sOH groups are relatively uniformly distributed on the surface at a distance that results in only one being able to react with the metal center.^[49] The surface species that are generated have the formula Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)(OSi_s), and are analogous to the molecular species described earlier.^[30] While the surface and molecular complexes are very similar electronically, the supported catalyst has greater lifetime under catalytic conditions. This provides direct evidence that site isolation is slowing or eliminating alkylidene dimerization. However, catalyst activity is eventually lost, which suggests that metalacyclobutane rearrangement is still operative. High catalyst turnover in a flow reactor also carries with it the possibility that impurities in the olefin feed eventually destroy catalyst centers. The analogous reaction between silica(700) and W(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)₂ generates analogous alkylidene complexes through loss of one alkyl ligand.^[50]

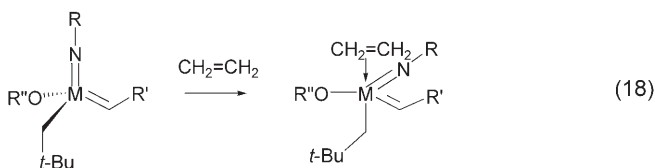
In the systems presented so far the metal complexes are bound to the solid surface in a monodentate fashion as a consequence of loss of only one alkyl ligand. Therefore the effect of surface irregularities in SiOH spacing is minimal and all metal centers are essentially identical. In contrast, the reaction of $W(C-t-Bu)(CH_2-t-Bu)_3$ with silica(200), in which SiOH groups are not separated as far from one another, two alkyl groups are lost to form a $W(C-t-Bu)(CH_2-t-Bu)(OSi)_2$ species, among others.^[51] Although the presence of W alkylidene rather than W alkylidyne species could not be established by spectroscopic methods, the grafted complex was active towards the metathesis of propene (initial TON 36 min) and methyl oleate

(initial TON 0.6 min). It was proposed that under the reaction conditions W alkylidene species are formed either by intramolecular H_a migration or formation of a W vinyl alkylidene upon reaction of the alkylidyne with a substrate molecule.

Alkoxide complexes also can be attached to an inorganic support.^[52] For example, in 2005 Balcar and co-workers reported the immobilization of Mo(NAr)-(CHCMe₂Ph)[OCMe(CF₃)₂] on mesoporous molecular sieves (MCM-41). Activity similar to the parent compound in the solvent-free metathesis of 1-heptene was found. The somewhat reduced activity of recycled catalyst was ascribed to inactivation of the carbene species by accumulation of impurities. The nature of the actual catalyst on the support in these circumstances was not elucidated.

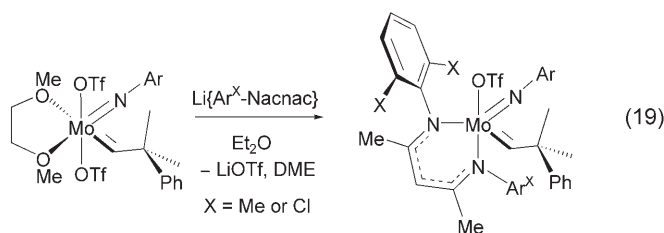
5 New Alkylidene Complexes as Metathesis Catalysts

Monoalkoxide complexes of the type M(NR)(CHR')(OR'')(CH₂-*t*-Bu) are interesting new catalysts, whether in homogeneous form or attached to silica. So far, the neopentyl group does not appear to give rise to any significant side reactions, and may in fact play an important electronic role (*vide infra*). An interesting feature is that the four-coordinate metal center is chiral, as are most metalacyclobutane intermediates, an exception being a trigonal bipyramidal form of an unsubstituted metalacycle in which the metalacycle α carbons occupy equatorial sites. They have potential as asymmetric catalysts if an enantiomerically pure auxiliary is present in one or more of the R, R', or R'' groups, and if one diastereomer is the only one present or the one that is significantly more reactive than all others. Unlike enantiomerically pure complexes that contain diolate ligands, where sterics alone determine to which face of the M=C bond the olefin adds (in either the *syn* or the *anti* isomer), the two faces of the M=C bond in M(NR)(CHR')(OR'')(CH₂-*t*-Bu) complexes are inequivalent for electronic reasons, i.e., the olefin can approach the metal *trans* to the neopentyl group or *trans* to the alkoxide. Calculations carried out on Re(CR)(CHR)(OR'')(CH₂R) complexes (in which the Re≡CR unit is equivalent to the M=NR unit) reveal that the complex is "predisposed" to binding the olefin *trans* to the CH₂R group rather than the alkoxide [Eq. (18)].^[20b] Other arguments sup-

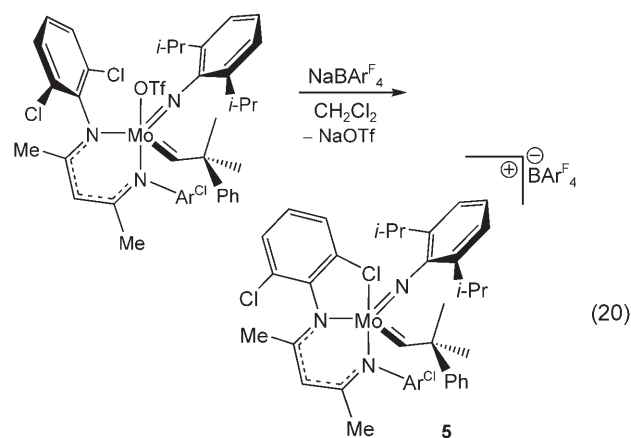


port the proposal that these species, especially silica-supported versions, are especially active metathesis catalysts. It should be noted that the asymmetric nature of all metalacycles that lead to productive metathesis are themselves chiral and possibly distorted from ideality and relatively unstable toward loss of olefin to give a metathesis product. It remains to be seen whether M(NR)(CHR')(OR'')(CH₂-*t*-Bu) complexes are also especially reactive (and therefore also especially unstable with respect to bimolecular decomposition) and whether asymmetric metathesis catalysts of this type can be prepared.

Virtually all high oxidation state olefin metathesis catalysts of tungsten and molybdenum are neutral. Cationic complexes are rare,^[53] and none had been reported that contain a non-coordinating anion until recently. Cationic alkylidene compounds that resemble Mo bis-alkoxide catalysts have been prepared that contain β -diketonates or β -diketiminates.^[54] For example, treatment of Mo(NAr)(CHCMe₂Ph)(OTf)₂ (DME) with Li{Ar^X-Nacnac} {Ar^X-Nacnac = [2,6-X₂C₆H₃NC(Me)]₂CH; X = Me, Cl} afforded the mono-triflate complexes shown in Eq. (19). Reaction of the



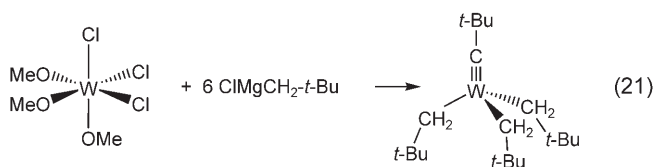
triflate complex (X = Cl) with NaBAR^F₄ (Ar^F = 3,5-(CF₃)₂C₆H₃) in CH₂Cl₂ afforded {Mo(NAr)-(CHCMe₂Ph)(Ar^{Cl}-Nacnac)}[BAR^F₄] cleanly in satisfactory yield [Eq. (20)]. Intramolecular weak coordination of a chlorine is an interesting way to create higher coordinate compounds that are more stable to



intermolecular reactions, yet react readily upon dissociation of the chlorine from the metal. The geometry of the cation in Eq. (20) is best described as a trigonal bipyramid with the bridging chlorine and one of the Nacnac nitrogen atoms occupying the axial positions. The structure is similar to the structures of various base adducts of four-coordinate alkylidene species with the alkylidene and imido groups residing in the equatorial plane. The cationic $\text{Ar}^{\text{Cl}}\text{-Nacnac}$ species was found to react with various olefins to yield metathesis products, although it is not yet known how long-lived are the alkylidenes in various reactions and what are the processes that lead to catalyst decomposition and loss of activity.

6 Developments in Alkylidyne Chemistry

High oxidation state alkylidyne chemistry developed concurrently with alkylidene chemistry.^[2,55] The key discoveries were tungsten and molybdenum compounds with the formula $(\text{Me}_3\text{CCH}_2)_3\text{M}\equiv\text{CCMe}_3$, prepared, for example, as shown in Eq. (21). Treatment



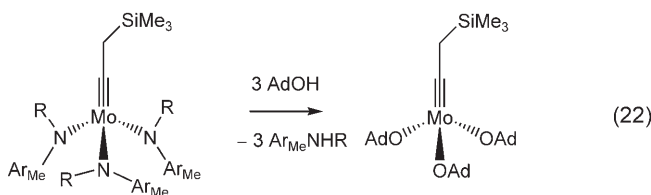
of $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$ with three equivalents of HCl in ether in the presence of dimethoxyethane gave blue $(\text{DME})\text{Cl}_3\text{W}\equiv\text{CCMe}_3$, which served as a starting point for synthesizing a wide variety of $\text{W}(\text{C-}t\text{-Bu})\text{X}_3$ species, especially those where X is a bulky alkoxide such as OCMe_3 , $\text{OCMe}(\text{CF}_3)_2$, $\text{OCMe}_2(\text{CF}_3)$, $\text{O-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3$, or $\text{O-2,6-Me}_2\text{C}_6\text{H}_3$. Tungsten alkylidyne tri-*tert*-butoxide complexes react rapidly with many ordinary internal alkynes to give new alkylidyne complexes. Trigonal bipyramidal metalacyclobutadiene intermediates have been isolated, crystallographically characterized, and studied.

The chemistry of high oxidation state molybdenum alkylidyne complexes has closely paralleled the chemistry of tungsten alkylidyne complexes. However, molybdenum chemistry has been limited by the poor yield of $(\text{Me}_3\text{CCH}_2)_3\text{Mo}\equiv\text{CCMe}_3$ (<35%) that is obtained upon adding MoO_2Cl_2 to $t\text{-BuCH}_2\text{MgCl}$ in THF. $\text{Mo}(\text{CR})(\text{DIPP})_3$ complexes are good catalysts for the metathesis of alkynes, and one molybdacyclobutadiene complex, $\text{Mo}(\text{C}_3\text{Et}_3)(\text{DIPP})_3$ has been observed in NMR spectra at low temperatures, although it is not stable enough with respect to loss of alkyne from the ring to be isolated. (An unstable, even not

observable, metalacycle is often advantageous for efficient alkyne metathesis.)

Recent theoretical studies have been carried out concerning the formation, reactions, and structures of alkylidyne complexes.^[56] Other recent notable studies concern the equilibrium between alkylidyne/alkyl and bisalkylidene isomers of tungsten,^[57] and the isolation of germyl- and stannyl-substituted alkylidynes.^[58]

Fürstner has pioneered the use of W alkyne metathesis in organic chemistry.^[6] A resurgence of interest in Mo alkyne metathesis catalysts might be ascribed to the apparent greater tolerance of certain functionalities by Mo versus W, and the more facile loss of an alkyne from a molybdacyclobutadiene intermediate. Cummins, who has published the synthesis of $\text{Mo}(\text{CH})(\text{NAr}_{\text{Me}}\text{R})_3$ ($\text{Ar}_{\text{Me}} = 3,5\text{-dimethylphenyl}$, $\text{R} = \text{tert-butyl}$),^[59] showed that other trisamido alkylidynes could be prepared through similar syntheses.^[60] Moreover, he also showed that addition of three equivalents of 1-adamantanol^[60a] or phenols^[60b] to trisamido complexes led to the analogous trisalkoxide or trisphenoxide complexes. For example, the triadaman-toxy (AdO) alkylidyne complex shown in Eq. (22)



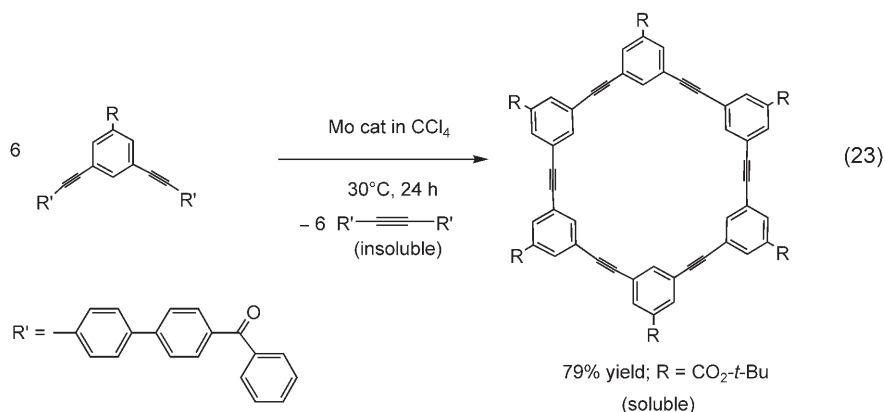
($\text{R} = \text{isopropyl}$) can be isolated as a crystalline solid. These trisalkoxide or trisphenoxide Mo alkylidyne complexes also were shown to be metathesis catalysts for internal alkynes, as expected.

Fürstner noticed that trisamido Mo species were “catalysts” for the metathesis of alkynes and diynes in the presence of dichloromethane.^[61,62] Among the products that could be identified from the reaction between dichloromethane and $\text{Mo}(\text{NAr}_{\text{Me}}\text{R})_3$ ($\text{R} = \text{tert-butyl}$) were $\text{MoCl}(\text{NAr}_{\text{Me}}\text{R})_3$ and $\text{Mo}(\text{CH})(\text{NAr}_{\text{Me}}\text{R})_3$. The latter was the most logical species to be responsible for metathesis, but it was found to be relatively unreactive towards alkynes. The actual catalyst responsible for the high reactivity in a wide variety of alkyne metatheses could not be identified. One possibility is some “mixed” (amido/chloro) species, i.e., $\text{Mo}(\text{CH})(\text{NAr}_{\text{Me}}\text{R})_{3-x}\text{Cl}_x$ where $x = 1$ or 2 .

Moore demonstrated that a “reductive recycle” strategy would produce complexes of the type $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R})_3$ in good yield.^[63] Reactions between $\text{Mo}(\text{NAr}_{\text{Me}}\text{R})_3$ and $\text{R}'\text{CHCl}_2$ ($\text{R}' = \text{H, Me, Et}$) in THF in the presence of excess Mg produced $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R})_3$ species in excellent yields. It was also shown that the $\text{Mo}(\text{CR}')(\text{NAr}_{\text{Me}}\text{R})_3$ species would react with trifluoro-*o*-cresol or perfluoro-*tert*-butyl al-

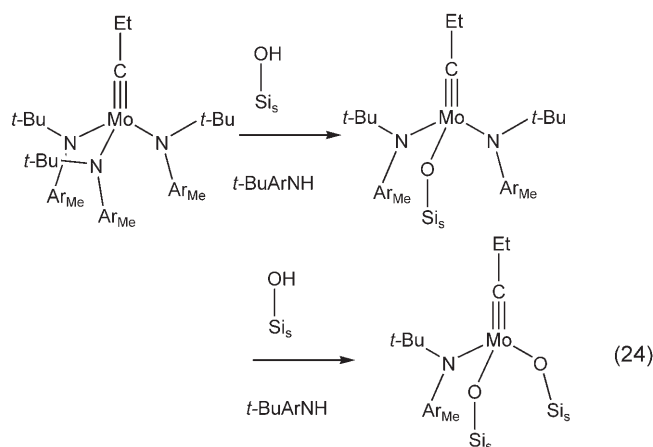
cohol to yield active metathesis catalysts, presumably the trisphenoxide or trisalkoxide species. These and other catalysts were prepared *in situ* and employed for a variety of internal alkyne metatheses where one of the products (e.g., 2-butyne or 3-hexyne) could be removed under vacuum.^[64]

An alternative “precipitate-driven” strategy, i.e., one where the unwanted symmetrical alkyne product is *insoluble* and the desired product *soluble*, has been shown to be a viable alternative to alkyne metathesis reactions that rely on formation of a volatile but often polymerizable by-product such as 2-butyne. For example, arylene-ethynylene macrocycles, such as the one shown in Eq. (23), can be synthesized in this manner.^[65] It was shown that formation of cyclic hexamers is thermodynamically controlled and driven through precipitation of the insoluble diarylacetylene by-product. Catalysts have also been prepared *in situ* and employed for the synthesis of poly(2,5-thienylene-neethynylene)s.^[66]



Recently, molybdenum trisamido alkylidyne catalysts have been grafted onto a silica surface [Eq. (24)].^[67] In this case 1.6–1.7 equivalents of (*t*-Bu)Ar_{Me}NH are liberated, a result that suggests that the metal is bound to the surface through both one and two Si–O bonds. The system shows high catalytic activity which is conserved for at least three recycling steps. No leaching of the metal catalyst from the surface was detected. Additionally, no alkyne polymerization (e.g., of 2-butyne) was found. Substrates like 2-propynylthiophene could be homodimerized under the reaction conditions.

A tungsten-based neopentylidyne species, W(C-*t*-Bu)(CH₂-*t*-Bu)(OAr)₂, can be prepared readily in ~50% yield through reaction of four equivalents of *t*-BuCH₂MgCl with W(OAr)₃Cl₃ in diethyl ether (Ar = 2,6-diisopropylphenyl).^[68] W(C-*t*-Bu)(CH₂-*t*-Bu)(OAr)₂ can be isolated from pentane as a highly crystalline yellow species. The diisopropylphenoxide ligands can be replaced with diphenylamido ligands to



give W(C-*t*-Bu)(CH₂-*t*-Bu)(NPh₂)₂ virtually quantitatively, and W(C-*t*-Bu)(CH₂-*t*-Bu)(NPh₂)₂ can then be treated with alcohols to yield other W(C-*t*-Bu)(CH₂-*t*-Bu)(OR)₂ species. W(C-*t*-Bu)(CH₂-*t*-Bu)(NPh₂)₂ also

holds promise for preparing a well-defined species on a silica surface. W(C-*t*-Bu)(CH₂-*t*-Bu)(OAr)₂ reacts readily with 2-butyne or 3-hexyne to produce trimethyl or triethyl tungstacyclobutadiene complexes, and internal alkynes are metathesized. The rates have not yet been determined.

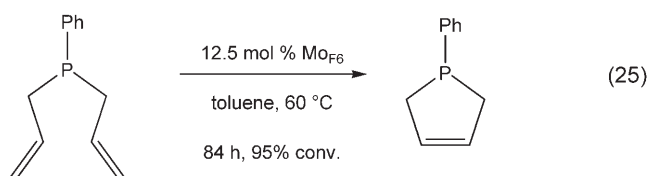
In general it has not been possible to metathesize terminal alkynes with well-defined alkyne metathesis catalysts.^[69] Coutelier and Mortreux^[70] have now found that W(C-*t*-Bu)(O-*t*-Bu)₃ (4 mol%) in the presence of quinuclidine in toluene will metathesize 1-heptyne to 6-dodecyne at 80°C in one minute; the yield of 6-dodecyne is 80–90%. The expected intermediate alkylidyne species can be observed, including known W(C-*t*-Bu)(O-*t*-Bu)₃(quinuclidine). It also was possible to ring close HC≡C(CH₂)₃O(CH₂)₂C≡CC₃H₇ to the expected ring-closed product in 25% yield. The authors stress that the reaction is far from being general. For example, attempts to extend the procedure to several other substrates failed.

7 Applications of Metathesis Catalysts in Organic Synthesis

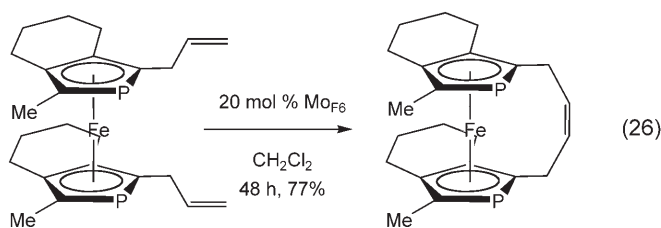
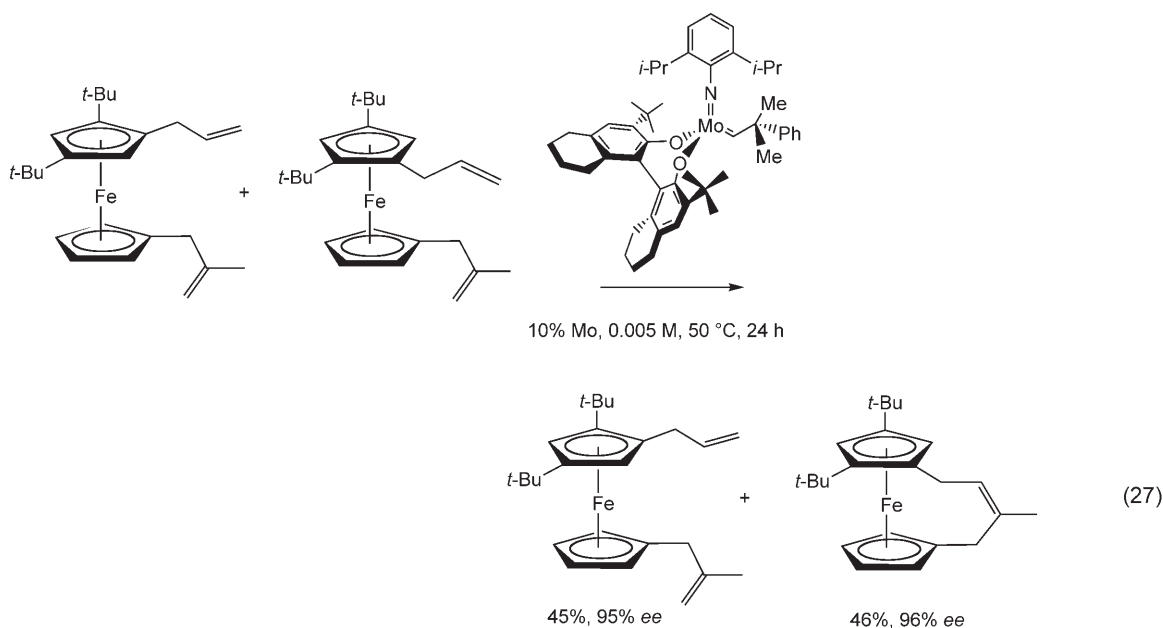
7.1 Alkene Metathesis

7.1.1 Metathesis of Phosphines, Aromatic Heterocycles, and Ferrocenes

Nolan and Gouverneur showed that borane-protected cyclic phosphines can be prepared by RCM using both Mo and Ru catalysts.^[71] In contrast, ring closure of unprotected diallyl(phenyl)phosphine could only be achieved using $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR}_{\text{F}_6})_2$ [Mo_{F_6} ; Eq. (25)]. It was assumed that binding of the phosphine to Ru is the cause of the observed low activity.^[72]

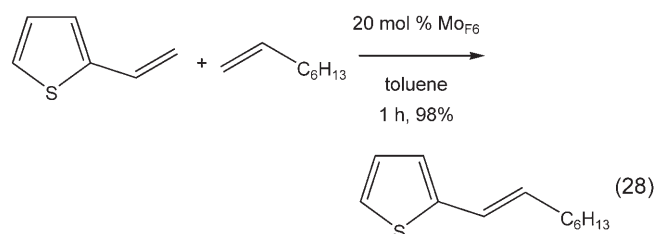


Analogously, the Mo_{F_6} catalyst has been employed in the preparation of 1,1'-diphospha[4]ferrocenophanes by intraannular RCM [Eq. (26)].^[73] Again, Ru catalysts proved to be inactive. The reaction had to be performed under dilute conditions in order to prevent formation of oligomers and polymers. Both *rac* and *meso* forms of the 1,1'-diphospha[4]ferrocenophanes were employed.



Recently it has been shown^[74] that the planar-chiral ferrocenes shown in Eq. (27) can be kinetically resolved ($k_{\text{rel}}=183$) through use of an enantiomerically pure molybdenum catalyst. Several other substitution patterns on the C=C bonds were less successful. An X-ray structure of the cyclized species confirmed the configuration shown.

In 2002 Kawai and co-workers compared Mo and Ru catalysts for the selective cross-coupling of aromatic vinylheterocycles with styrene and 1-octene [Eq. (28)].^[75] The homometathesis of such 2-vinylhe-

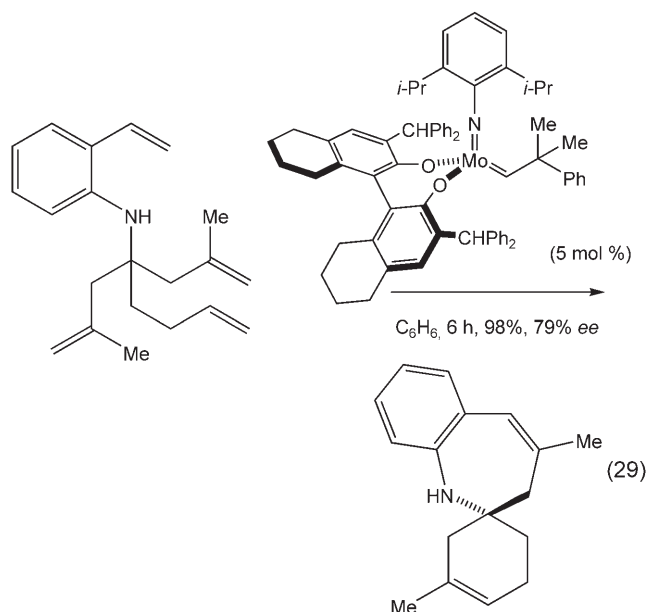


terocycles is not favored, most probably due to steric reasons because 2-(1,3)-butadienyl-substituted substrates effectively form the corresponding homodimers. Thiophene, furan, and pyrrole derivatives can be

transformed under such conditions. In contrast, 2-vinylpyridine gave no conversion, probably due to coordination of N to the metal center.

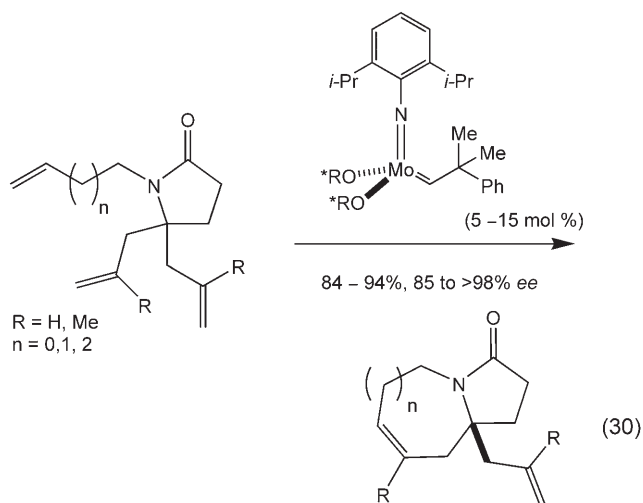
7.1.2 Enantioselective Metathesis of Amides and Amines

In recent years the scope of substrates for the synthesis of enantiomerically enriched building blocks has broadened substantially. Synthesis and application of Mo complexes incorporating new imido ligands and chiral diolates has led to the development of catalysts with increased reactivity and selectivity.^[5] Although metathesis of primary amines with Mo catalysts still remains a challenge, secondary cyclic amines can be prepared in good yields and enantioselectivities up to >98% *ee*.^[76] In Eq. (29) is shown an example of a de-

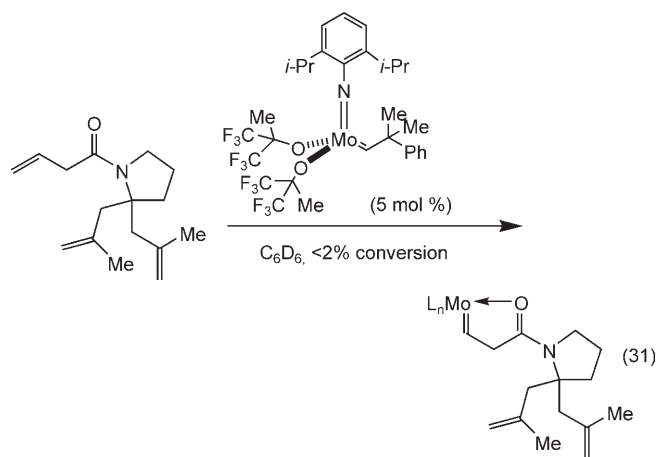


symmetrizing tandem ring closure of an amino-tetraene. It should be noted that for these reactions the Mo catalyst can be prepared *in situ* by mixing the commercially available Mo alkylidene bistriflate with the bispotassium salt of the chiral biphenolate. This method of *in situ* catalyst preparation is likely to be inferior in the long run to general methods that employ dipyrrolyl precursors (*vide supra*).

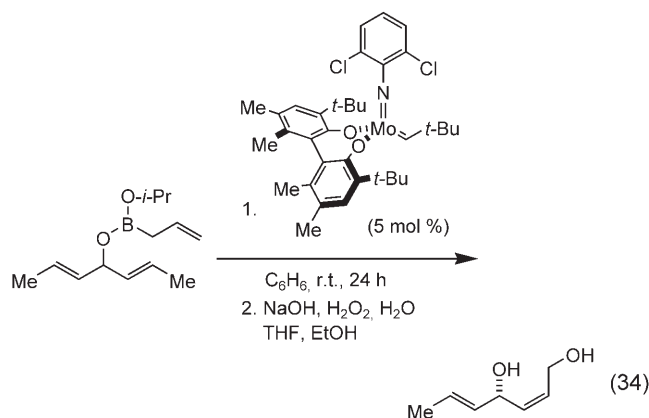
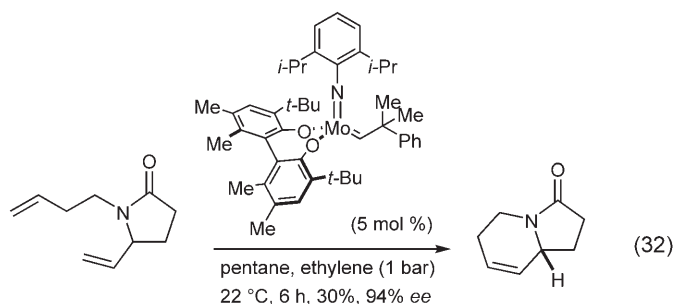
The methodology was further extended to the synthesis of aliphatic amines and amides. Bicyclic amides were prepared successfully by an asymmetric RCM of the corresponding trienes [Eq. (30)]. The method is substrate-sensitive and required ligand screening to obtain optimal yields and enantioselectivities; this is normal. It is noteworthy that a triene bearing only monosubstituted C=C double bonds ($R=H$) is trans-



formed to the bicyclic amide with good enantioselectivity. A mechanistic pathway was proposed where a spiro system is formed first followed by rearrangement to the 5-6 bicyclic compound. It is worth mentioning that the corresponding pyrrolidines can be fully converted under RCM conditions, but the enantioselectivities are significantly lower (30–40% *ee*). Furthermore, no reaction is observed when the carbonyl group is part of the olefinic side-chain [Eq. (31)], since (it is proposed) the carbonyl oxygen coordinates intramolecularly to the Lewis acidic metal center.



Bicyclic amides are not only accessible by desymmetrization but also by kinetic resolution. An example is provided in Eq. (32). In this case the enantioselectivity is significantly higher if the reaction is conducted under an atmosphere of ethylene (94% *ee* at 30% yield, $k_{rel}=8$). It is believed that both enantiomers of the triene react at similar rates, but the diastereomeric alkylidenes formed in the process ring-close at different rates. The diastereomer that closes

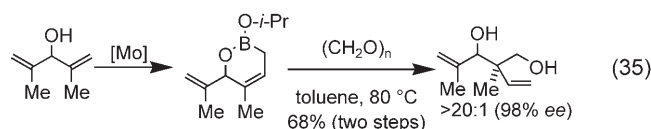


more slowly reacts predominantly with ethylene to regenerate the starting material. The substrate scope of this RCM methodology was broadened by suitably protected aliphatic amines. In this respect benzyl-, acetyl- and Cbz-protecting groups as well as intermediate protection as the catechol boronate were equally effective. When the secondary amine is directly adjacent to a quaternary carbon center no protection is required. It is assumed that internal chelation by the heteroatom is not favored in this case. The use of this new methodology was illustrated by the synthesis of enantiomerically enriched coniine [Eq. (33)].

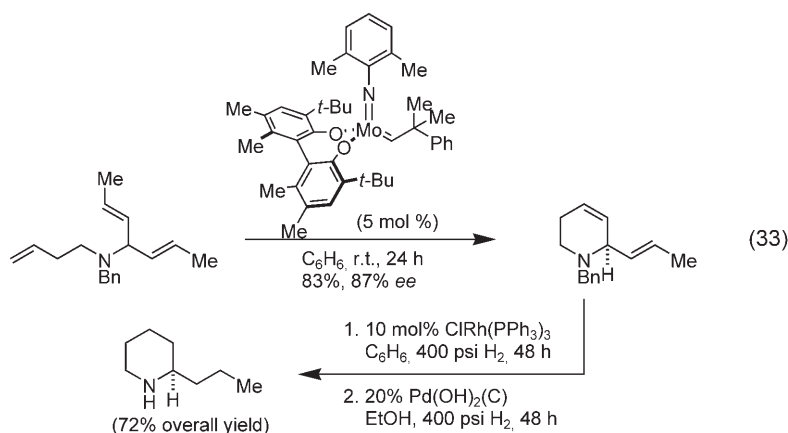
7.1.3 Enantioselective Metathesis of Allylboronates

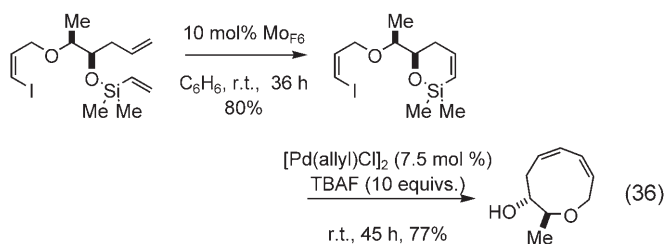
One of the challenging tasks that remains in metathesis chemistry is development of a highly enantioselective cross-metathesis methodology. Recently, progress has been made in this direction by connecting the cross-metathesis partners with an easily cleavable linker prior to an *intramolecular* metathesis reaction step.^[77] When the chiral catalyst is carefully selected, excellent enantioselectivities can be achieved [Eq. (34)]. The allylboronate starting materials are easily prepared by mixing the corresponding dienol with allyl diisopropyl borate and azeotropic removal of isopropyl alcohol. The cyclic borate products can be transformed in a number of ways. Oxidative cleavage

of the C–B bond provides the enantiomerically enriched dienediols. It was further demonstrated that subsequent reaction with *p*-formaldehyde allows the formation of an additional stereogenic quaternary carbon center with complete diastereoselectivity [Eq. (35)].



A related approach toward the synthesis of medium ring systems by ring-closing metathesis and subsequent palladium-catalyzed cross-coupling was reported by Denmark and Yang.^[78] Here, the problem of cross-metathesis is circumvented through use of a silyl ether bridge between the two alkene coupling partners. Specifically, various alkenols were reacted with dimethylvinylsilyl chloride and submitted to metathesis catalyzed by MoF_6 [Eq. (36)]. The Si–O linker is cleaved concomitant with formation of a medium ring system (8–12) by silicon-assisted cross-coupling employing $[(allyl)PdCl]_2$. The cross-coupling

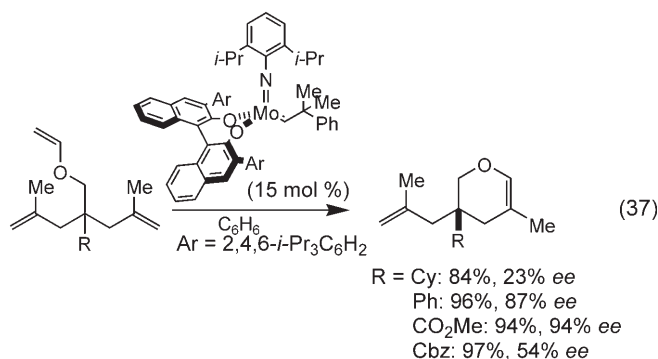




is highly stereospecific and yields synthetically valuable 1,3-dienes. Furthermore, the method allows flexible positioning of the hydroxy group without loss of reactivity.

7.1.4 Enantioselective Metathesis of Enol Ethers

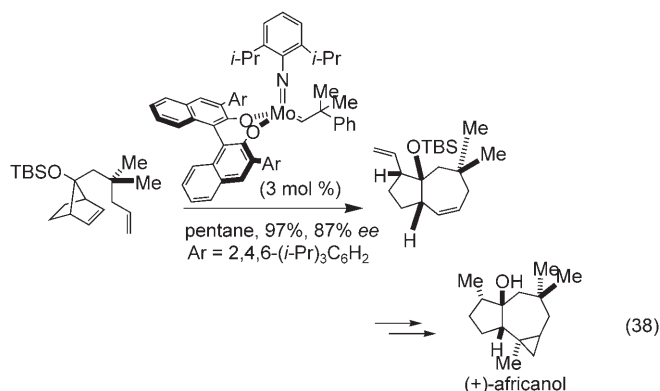
Enol ethers were successfully employed recently as substrates in enantioselective desymmetrizing RCM processes.^[79] In contrast to substrates discussed so far the C=C bond in these compounds is relatively electron rich. The corresponding metal complex intermediates in metathesis reactions are essentially Fischer-type carbenes and therefore have very different electronic properties compared to Mo alkylidenes. Ligand screening revealed that only sterically congested binaphthol-derived ligands provide sufficient reactivity and selectivity [Eq. (37)]. It should be men-



tioned that the enantioselectivities are considerably lower for 1,2-disubstituted alkenes than for 1,1-disubstituted olefins.

7.1.5 Enantioselective Synthesis of (+)-Africanol

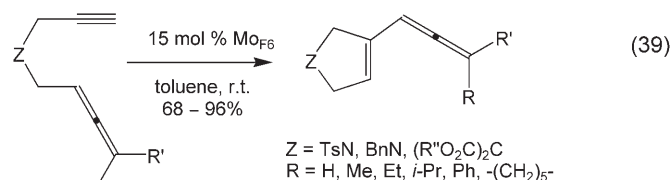
The use of enantioselective Mo-catalyzed RCM methodology was exemplified in 2004 in the synthesis of (+)-africanol [Eq. (38)].^[80,81] Catalyst screening revealed that a complex incorporating 3,3'-di-(2,4,6-triisopropyl-C₆H₂)-BINOL gave the best yield and enantioselectivity. It is interesting to note that the reaction



was carried out under almost solvent-free conditions (8M). Nevertheless, no homodimeric products were detected. In this respect it should be mentioned that a related substrate lacking the geminal methyl groups gave only homocoupling products, even under dilute conditions. The advanced intermediate was further transformed by a sequence of rhodium-catalyzed decarbonylation, carbonylation, and olefin isomerization as key steps.

7.1.6 Ring-Closing Metathesis of Allenynes

In 2005 Murakami and co-workers published a new synthesis of vinylallenes by ring-closing metathesis of allenynes [Eq. (39)].^[82] The substrate scope is limited

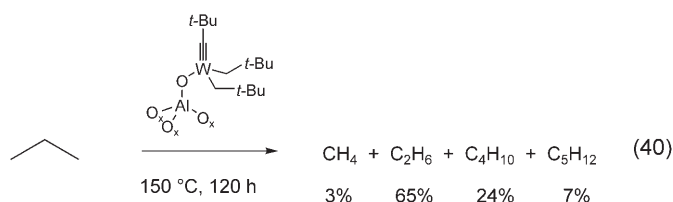


to *p*-Ts- and Bn-protected amines as well as malonic ester derivatives. Ether functionalities (Z=O), mono-substituted allenynes, or disubstituted alkynes are not reactive under these conditions. In addition, the product range is limited to substituted cyclopentenones. Mechanistic studies suggest that the reaction in fact proceeds through an Mo allenylidene species. No Mo allenylidene species have yet been isolated.

7.2 Alkane Metathesis

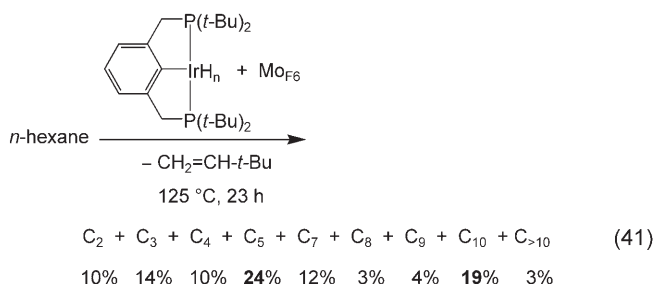
The controlled metathesis of alkanes has a high economic potential for the large-scale preparation of linear alkanes used for fuels. The first examples of alkane metathesis reactions employed heterogenous catalysts (Pt/W) and more recently tantalum alkylidenes.^[83] In 2005 it was reported that when W(C-*t*-

Bu)(CH₂-*t*-Bu)₃ was grafted onto alumina a heterogeneous catalyst, (Al₂O₃)W(C-*t*-Bu)(CH₂-*t*-Bu)₂ was formed, and it transformed propane into a mixture of alkanes [Eq. (40)].^[84] Good selectivity for unbranched

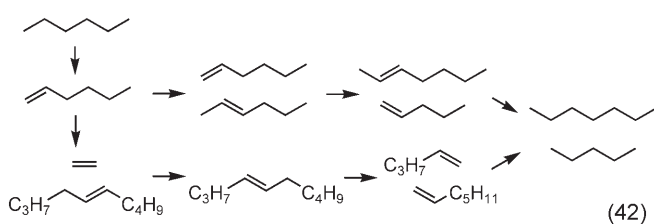


aliphatic products was observed. Moreover, it was demonstrated that the TON significantly increased (120 vs. 28 [C₃H₈]/[W]) upon hydrogenation of the catalysts. In this case it was proposed that a W(IV) dihydride species is formed, which is consistent with IR spectroscopic data. TEM studies suggested that, in contrast to silica-bound systems, isolated W centers are grafted to the surface through covalent Al₃-W bonds.

Recently, a homogeneous alkane metathesis system was published by Goldman and Brookhart.^[85] Two catalysts are present, a pincer-type Ir-dehydrogenation catalyst and MoF₆. When *n*-hexane was submitted to the reaction conditions (125 °C) an alkane mixture was obtained that showed preferential formation of pentane and decane [Eq. (41)]. No methane,



branched, or cyclic alkanes were detected. It was proposed that dehydrogenation to form 1-hexene is followed by Ir-catalyzed olefin isomerization and subsequent metathetic scrambling [Eq. (42)]. The alkenes are then reduced to the corresponding alkanes. At the elevated reaction temperatures slow decomposition of



the Mo catalyst was observed. A related heterogeneous catalyst system employing Re₂O₇/Al₂O₃ was developed which showed increased temperature stability. Ruthenium metathesis catalysts that have been employed so far are inactive for alkane metathesis. Although existing processes for alkane metathesis are still limited and of relatively low activity, improved systems could conceivably find extensive industrial use in the future.

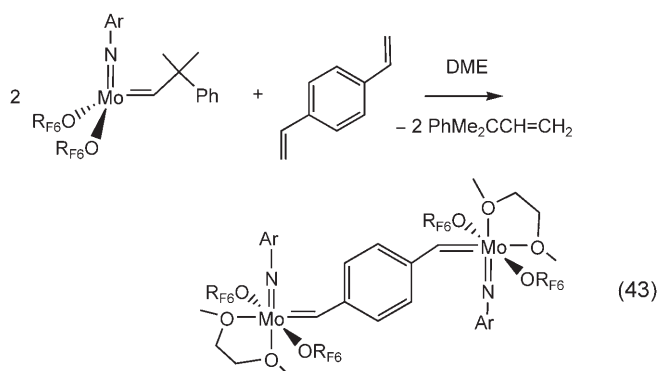
8 Advances in Controlled Polymer Synthesis

8.1 Synthesis of Triblock Copolymers Employing Bifunctional Initiators

Ring-opening metathesis polymerization (ROMP) of (especially strained) cyclic olefins is catalyzed by a variety of alkylidene complexes. In ROMP of a strained olefin the propagation step is essentially irreversible (e.g., with various norbornene derivatives) and secondary metathesis reactions of double bonds in the resulting polymer chain can be slow. Therefore the polymerization can be “living” under some specified set of conditions. If the rates of initiation and propagation are of approximately the same order of magnitude or greater, then it is possible to control the average polymer length simply by controlling the number of equivalents of monomer added. With several catalysts, it is possible to control polymer structure in a systematic manner, i.e., to prepare all *cis* or all *trans* polymers and polymers that are isotactic or syndiotactic.

Imido alkylidene complexes of Mo or W that initiate at a rate comparable to the propagation rate are amenable to the synthesis of block copolymers. Some of the most interesting copolymers in terms of their physical properties are triblocks, A_xB_yA_z, where x, y, and z are the average numbers of monomers of type A or B in each block. Triblock ROMP copolymers could be prepared if the B_y block were to be prepared with a bifunctional initiator. This method of making high purity triblock copolymers can be more reliable than the “linear” method (adding monomer A to an initiator, then B, then A).

Bifunctional bisalkylidene complexes have been prepared, among them the one shown in Eq. (43).^[86] This species was treated with two equivalents of Li-O-*t*-Bu to yield the analogous *tert*-butoxide species. Addition of divinylferrocene to Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ produced the bimetallic species {(R_{F6}O)₂(ArN)Mo[CH(C₅H₄)]₂Fe}, which likewise could be converted into an analogous *tert*-butoxide species.^[87] Triblock copolymers {poly[(MTD)_{x/2}-(DCMNBD)_y(MTD)_{x/2}] (MTD = methyltetraacyclodo-



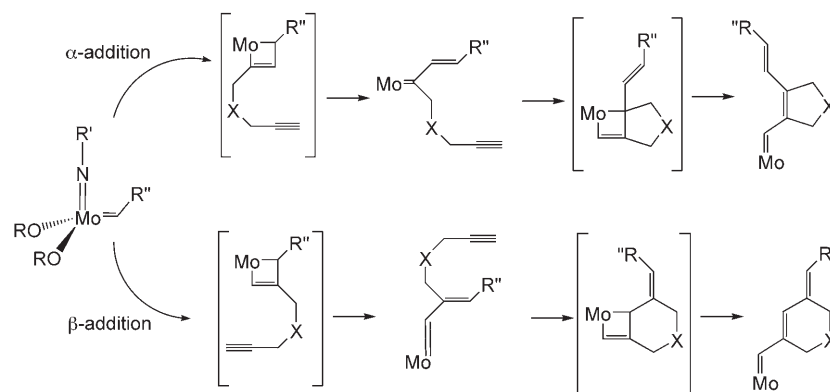
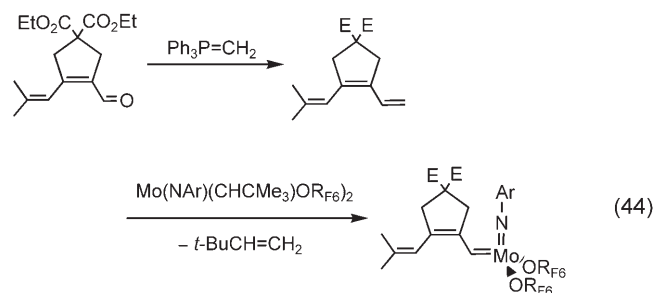
decene, DCMNBD = dicarbomethoxynorbornadiene) were prepared by adding y equivalents of DCMNBD to the bimetallic initiators followed (after consumption of DCMNBD) by x equivalents of MTD. These triblocks were shown to be of relatively high purity (free of homopolymer and diblock copolymer) and to have a relatively low PDI (≤ 1.2). MALDI-TOF mass spectra of ferrocene-containing species were obtained that were consistent with the polymerization process being living and having a molecular weight consistent with competitive initiation and propagation. Similar bifunctional initiators have been prepared recently by Buchmeiser.^[88]

8.2 Polyenes Prepared through Polymerization of Diethyl Dipropargylmalonate

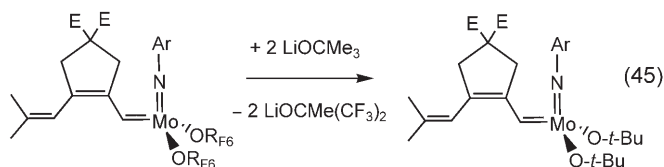
The polymerization of diethyl dipropargylmalonate (DEDPM) and related derivatives with well-defined Mo-based olefin metathesis catalysts, primarily Mo-(NAr)(CHCMe₂Ph)[OCMe(CF₃)₂]₂ (Ar = 2,6-*i*-Pr₂C₆H₃), in 1992 confirmed that high oxidation state Mo alkylidenes were catalysts for cyclopolymerization reactions of this general type.^[89] The resulting polymer formed using Mo(NAr)(CHCMe₂Ph)[OCMe(CF₃)₂]₂ as the initiator was shown to contain both five-membered and six-membered rings (Scheme 2).

Later it was shown that polyenes that contain all six-membered rings were formed when dicarboxylate catalysts of the type Mo(N-2-*t*-BuC₆H₄)(CHCMe₃)(O₂CCPh₃)₂ were employed.^[90] DEDPM polymers that contain only six-membered rings have λ_{max} values that are lower by 20–30 nm for a given apparent chain length than those for polymers that contain both five- and six-membered rings, consistent with a lower effective conjugation length, presumably as a consequence of twisting of the polymer chain. Buchmeiser and co-workers have shown that Mo(NAr)(CHCMe₂Ph)(OCMe₃)₂ catalysts in the presence of quinuclidine will polymerize DEDPM to yield polymers that contain >95% five-membered rings.^[91] Advantages of poly[1,6-heptadiynes] that contain only five-membered rings include the single alternating *cis,trans* structure and the potentially relatively rigid extended chain if conjugation is maintained. Polymer structure has important implications for the use of poly[1,6-heptadiynes] as “smart” materials for electronics and sensors.^[92]

Since *all* polymerizations that begin with neopentylidene or neophylidene initiators have a high rate of polymerization *versus* initiation in polymerizations of this type, initiators were required that would initiate rapidly relative to the rate of propagation. The most desirable initiator would be one that is analogous to that formed through polymerization of DEDPM. Species of this type were prepared as shown in Eqs. (44) and (45).^[93] Addition of DEDPM to the *tert*-butoxide



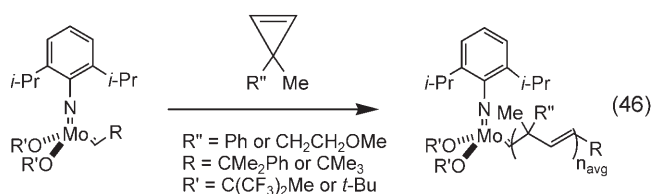
Scheme 2.



initiator led to polymers that contain largely five-membered rings and had a predictable molecular weight as a consequence of the slightly slower rate of propagation than initiation due to the steric influence of the growing polymer chain. The molecular weight of small polymers prepared with this initiator were shown through MALDI studies to be consistent with a rapid initiation and a living polymerization.

8.3 Cyclopropenes

ROMP of 3-methyl-3-phenylcyclopropene in tetrahydrofuran at room temperature as shown in Eq. (46) produced atactic all-*trans* ROMP polymers in 94–97% yield in minutes.^[94] The calculated number aver-

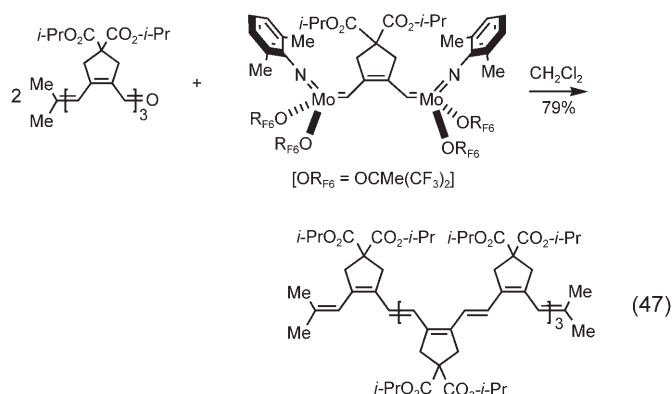


age molecular weights (M_n) (as determined by GPC versus polystyrene standards) for the samples were comparable to the theoretical molecular weights. The observed molecular weights of poly[3-methyl-3-phenylcyclopropene] showed a linear dependence versus the number of equivalents of monomer employed (up to 100 equivs.), as determined by GPC versus polystyrene standards. A Grubbs-type Ru initiator, $[(H_2IMes)(PCy_3)Cl_2RuCHC_6H_5]$ ($H_2IMes = 1,3$ -dimesitylimidazolidine), also was examined as an initiator, but the reactions (in CD_2Cl_2 and C_6D_6) were incomplete after 24 h. Several diblock and triblock copolymers were prepared successfully in high yields that had narrow polydispersities and glass transition temperatures that were ascribed to different tacticities and/or blockiness of the polymer backbone. This is the first report of ROMP polymerization of a cyclopropene.

9 Stoichiometric Reactions

The Wittig-like reactivity of high oxidation state alkylidenes has been employed for the synthesis of polyenes of significant length that are analogous to those

obtained through cyclopolymerization of dialkyl di-propargylmalonate to give polymers that contain five-membered rings (*vide supra*).^[95] The longest one (15 double bonds) was prepared as shown in Eq. (47).



The reactions are relatively fast and high yielding. Although this synthesis currently is limited by the relatively tedious syntheses of both the oligomeric aldehyde and the bimetallic alkylidene complex, the ability to prepare a single length soluble polyene with a single structure that contains 15 double bonds is potentially of significant value in terms of fundamental studies of such species. There seems to be no fundamental reason why even longer species cannot be prepared.

It has been known for some years that trialkoxytungsten alkylidyne complexes react readily with nitriles to give the analogous trialkoxytungsten nitrido species.^[96,97] Johnson and Gdula^[98] have now found that at least two *molybdenum* nitride complexes, $Mo(N)(OR)_3$ [$R = CMe(CF_3)_2$, $C(CF_3)_3$], will react with 3-hexyne slowly to give $EtC\equiv N$ and the alkylidyne complexes, $Mo(CEt)(OR)_3$ [Eq. (48)]. The reac-

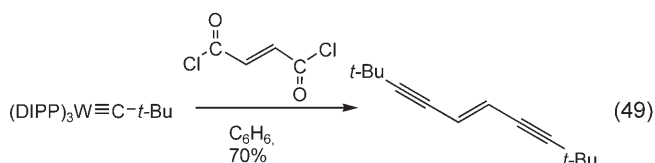


tion is apparently irreversible under the conditions employed (95°C in benzene over a period of days) and the $Mo(CEt)(OR)_3$ species can be isolated in good yields on a multigram scale. The reaction clearly is favored thermodynamically but is kinetically sluggish. Both $Mo(N)(OR)_3$ ^[99] and $W(N)(O-t-Bu)_3$ ^[100] are known to catalyze the degenerate exchange of N in nitriles.

It is interesting to note in the context of the above result that heterogeneous Re metathesis catalysts are formed when olefins are passed over supported rhenium oxides.^[101] It has been proposed that the alkylidene is formed through a metathesis-like reaction of a rhenium oxo with the olefin. Although no homogene-

ous version of a reaction between an oxo and an olefin to give an alkylidene has been demonstrated, recent gas-phase studies confirm that such a reaction does take place.^[102]

A brief description of a reaction between acetyl chloride and $W(C-t-Bu)(DIPP)_3$ ($DIPP=2,6$ -diisopropylphenoxide) to give $W(O)Cl(DIPP)_3$ (proposed) and $t-Bu-C\equiv C-Me$ was published in 1986.^[96] Grubbs and co-workers^[103] have now shown that when $W(C-t-Bu)(DIPP)_3$ is treated with stoichiometric amounts of aliphatic, conjugated aliphatic, or aromatic acid chlorides the corresponding $t-Bu$ -substituted alkynes are formed in good yields. The reaction is also successful for fumaroyl dichloride [Eq. (49)]. It was also shown



that the tungstacyclobutadiene complex, $W(C_3Et_3)(DIPP)_3$, would react with benzoyl chloride in ether to yield $Ph-C\equiv C-Et$, although the yield was only 25%. If more straightforward and general routes to the appropriate alkylidynes could be discovered stoichiometric reactions such as these could become valuable ways to make $C\equiv C$ bonds, especially in more complex molecules.

10 Concluding Comments

Studies of alkene and alkyne metathesis by high oxidation state catalysts continue to expand, both in terms of fundamentals and in terms of applications. It is now possible to control reactivity and selectivity to a high degree and to prepare essentially pure organic molecules and polymers with a single structure. Although existing routes to alkylidenes and alkylidynes are relatively general and useful, it would be desirable to develop even shorter routes to known catalysts or catalyst precursors, to develop new types of catalysts, and to utilize catalyst precursors extensively, perhaps in standard solutions. Important remaining challenges include increasing catalyst turnover, primarily by slowing or preventing catalyst decomposition. It also would be highly desirable to prepare silica-supported catalysts with a single structure, predictable and controllable reactivity, and long lifetime, and to learn how to regenerate catalysts.

It is often implied that Ru catalysts can or ultimately will accomplish all that Mo catalysts can accomplish, and that since Mo catalysts are sensitive to water and oxygen and to some (especially protic)

functionalities, Ru catalysts are the catalysts of choice. Such an assumption is scientifically unsound and shortsighted. Mo and Ru are different in several important ways, the most obvious being the reactivity of the $M=C$ bond. When Mo and Ru catalysts are compared side by side, which is (unfortunately) a rare event, it becomes clear that catalyst turnovers and selectivities can differ dramatically, somewhat, or little. Many examples have been presented in this review where Mo, in side by side comparisons, accomplishes what Ru does not. (Alkyne metathesis also is possible only with Mo and W catalysts.) Before proclaiming the superiority of Ru in olefin metathesis solely because it is relatively stable to air, it is wise to compare as many catalysts as possible side by side, and to draw conclusions on the basis of experimental data.

Acknowledgements

R.R.S. thanks the NIH (GM-59426 to Amir H. Hoveyda and R.R.S.), the NSF, and the DOE for supporting the research described in this article that originates in the labs of R.R.S., while C.C. thanks the German Academic Exchange Service (DAAD) for partial support through a postdoctoral fellowship.

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