Pergamon

Polyhedron Vol. 14, No. 22, pp. 3177–3195, 1995
Elsevier Science Ltd
Printed in Great Britain

0277–5387(94)00464–1

THE ALKOXIDE LIGAND IN OLEFIN AND ACETYLENE METATHESIS REACTIONS

RICHARD R. SCHROCK

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

1. INTRODUCTION

Alkoxide or phenoxide ligands are ubiquitous in classical olefin and acetylene metathesis catalyst systems.[1–3] For example, one of the earliest and most successful tungsten systems for the metathesis of olefins was prepared from WCl_6, $EtAlCl_2$ (4 equiv.), and ethanol (1 equiv.),[3,4] while acetylene metathesis was observed to be successful only in the presence of phenols.[5,6] Therefore it is not surprising that alkoxide ligands have played a pivotal role in the development of relatively stable yet reactive alkylidene complexes[7] or alkylidyne complexes[8] in the past decade that are long-lived catalysts for the metathesis of olefins or acetylenes, respectively. These well-defined d^0 metathesis catalysts (counting the alkylidene ligand as a dianion and the alkylidyne ligand as a trianion) have also offered the opportunity of assessing the steric and electronic influence of a range of alkoxides in a given type of reaction in a semi-quantitative manner. In this article I will trace the development in my laboratories of alkoxide chemistry of alkylidene and alkylidyne complexes containing Ta, Mo, W, or Re that are catalysts or potential catalysts for the olefin or acetylene metathesis reaction. This article is not meant to be comprehensive. Contributions by other researchers to the chemistry of "d^0" alkylidene/alkoxide or alkylidyne/alkoxide complexes can be found in review articles[7–14] or in other articles in this issue.

GENERAL COMMENTS

There are several reasons why alkoxides are good candidates as "ancillary" ligands in the organometallic chemistry and catalysis of the early transition metals. First, early transition metal alkoxides are often relatively stable. It has been known for some time that early transition metal alkoxides such as $Ti(O^iPr)_4$ do not readily undergo the β-hydride elimination process that is so common for later (e.g. group 8) transition metals.[15,16] When early transition metal alkoxides do decompose, they often yield oxo complexes.[17–19] Phenoxide complexes are generally more stable than alkoxide complexes,[20–22] in part because they are more resistant to reactions that lead to oxo complexes. Second, the relatively high electrophilicity of an early transition metal makes dissociation of alkoxide ion, at least in a neutral species, unlikely. Third, since early transition metal chemistry is often carried out in the absence of water, protonolysis of the alkoxide is usually not an issue. Finally, formation of oligomeric or polymeric complexes that contain bridging alkoxides can be prevented if the alkoxide is sufficiently large. The last is a key point. Much of the advancement in the use of transition metal alkoxide complexes as catalysts in the last decade can be attributed to the use of "large" alkoxides that do not readily bridge and therefore stabilize reactive mononuclear species toward bimolecular decomposition reactions.

The nature of the M—OR bonding in an early transition metal complex and the influence of that bonding on chemistry at the metal is potentially more complex than it appears. Through X-ray structural studies there has been some attempt to correlate the M—O bond length and the M—O—R angle with the "degree of π bonding." However, a combination of σ effects and steric effects could produce some of the same results that one otherwise might attribute to π bonding alone.

Consequently, it has been increasingly recognized that there is little, if any, correlation between the M—O—R angle and the degree of π bonding.[23] The nature of the hybridization at oxygen alone could have significant steric and electronic consequences at the metal, but the possibility that one or both electron pairs on oxygen can be involved to varying degrees in π bonding between M and O further complicates the issue. Both σ and π bonding will be profoundly altered as the electron-withdrawing ability of the R group changes [e.g. from ^{t}Bu to Ph to $CMe(CF_3)_2$[24]] and as the sterics in a crowded situation force the M—O—R angle to increase. Finally, it should be noted that in a catalytic reaction, where the coordination number of the metal and its core geometry (and consequently the electronics and sterics at the metal) change dramatically during the course of the reaction, the nature of the interaction between the metal and an alkoxide ligand will change constantly.

One of the measurable properties of an alkoxide that provides some indication of the degree to which it could alter the reactivity of a metal is the pK_a of the corresponding alcohol. Some pK_a values in water for some relevant alcohols are listed in Table 1.[24,25] Note that perfluoro-t-butanol is almost as strong an acid in water as acetic acid ($pK_a = 4.75$[26]), and that the difference in pK_a between t-butanol and hexafluoro-t-butanol is approximately ten orders of magnitude. The proton affinity of $[(CF_3)_3CO]^-$ was shown to be intermediate between the proton affinities of Cl^- and Br^- via ion cyclotron resonance, while the electron affinity of the hexafluoro-t-butoxide radical was shown to be greater than the electron affinity of any halogen atom, and among the highest known for any organic radical.[27] It should also be noted that the pK_a of an ordinary phenol is approximately the same as hexafluoro-t-butanol (~ 10). Such data provide a rough idea of the magnitude of the differences one might anticipate between metal complexes containing different alkoxides, especially if two or three are bound to a given metal. More subtle, synergistic effects that alter the M—O—C angle are comparatively difficult to assess. Note that electronic differences between hexafluoroisopropoxide and hexafluoro-t-butoxide ligands, at least in terms of their similar pK_a values, would appear to be minimal. Therefore steric differences should dominate in reactions of analogous complexes that contain these two alkoxides.

Ta AND Nb

In the early days of tantalum alkylidene chemistry attention was focused on chloride derivatives that contained cyclopentadienyl or phosphine ligands.[10] For example, the reaction between $Ta(CH^tBu)(PMe_3)_2Cl_2$[28,29] and olefins yielded products that apparently resulted from rearrangement of metallacyclobutane intermediates [e.g. eq. (1)]; no metathesis products [e.g. eq. (2)] were observed. The conclusion that "replacing chloride ligands with alkoxide ligands tends to slow down the rate of rearrangement of a metallacyclobutane ring relative to metathesis"[29] [eqs (1) and (2), respectively], and the observation that t-butoxide complexes did not bind a phosphine as strongly as the analogous chloride complexes served as a guide for the development of alkoxide chemistry pertaining to metathetical reactions in the following decade. The feeling at the time was that rearrangement of an alkylidene to an olefin or bimolecular coupling of alkylidenes (especially

$$M{=}CHR + H_2C{=}CHR' \longrightarrow RCH{=}CHCH_2R' + RCH_2CH{=}CHR' + M \quad (1)$$

$$M{=}CHR + H_2C{=}CHR' \longrightarrow RCH{=}CH_2 + M{=}CHR' \quad (2)$$

Table 1. pK_a values of some relevant alcohols in water

Me_2CHOH	17.1	$(CF_3)PhCHOH$	11.9	$(CF_3)_2CHOH$	9.3		
Me_3COH	19.2	$(CF_3)(C_6F_5)_2COH$	9.2	$(CF_3)_2MeCOH$	9.6	$(CF_3)_3COH$	5.4
				$(CF_3)_2(C_6F_5)COH$	7.9		
C_6H_5OH	9.89	$2,4,6\text{-}Me_3C_6H_2OH$	10.89	C_6F_5OH	5.52	C_6Cl_5OH	5.23

methylenes) to give the olefin would be difficult to prevent for tantalum. This behavior could be part of the reason why tantalum shows negligible metathesis activity of the classical type.[1]

Several years later, after aryloxide complexes had left their mark on tungsten and molybdenum alkylidyne chemistry (see later), tantalum alkylidene chemistry was revisited in the form of Ta$(\mathrm{CH^tBu})(\mathrm{OAr})_3(\mathrm{THF})$ and $\mathrm{Ta(CH^tBu)(OAr')_3(THF)}$ complexes ($\mathrm{Ar} = 2,6\text{-}\mathrm{C_6H_3{}^iPr_2}$; $\mathrm{Ar'} = 2,6\text{-}\mathrm{C_6H_3Me_2}$).[30,31] A pseudo-five-coordinate tantallacyclobutane complex could be isolated upon addition of an olefin such as norbornene, the structure of which (Fig. 1) illustrates the space-filling role of a total of six isopropyl groups in the *ortho* positions of the aryl rings.[31] However, alkylidene complexes that contain β protons could still not be observed. Metatheses of acyclic olefins (terminal or internal) were also observed to be relatively short-lived, most likely because rearrangement of intermediate alkylidenes that contain β protons or bimolecular decomposition (especially of methylene complexes) continued to take place at a significant rate. An interesting finding was that the arylthiolate complex, $\mathrm{Ta(CH^tBu)(S\text{-}2,4,6\text{-}C_6H_2{}^iPr_3)_3(THF)}$, the structure of which showed THF to be bound *trans* to the neopentylidene ligand,[32] did not react with acyclic olefins, although it did react with norbornene. However, tantallacyclobutane complexes were not observed, and alkylidene complexes that were produced upon ring-opening of norbornene (which contain a β proton) were found to be relatively stable. In general, thiolate analogs of d^0 alkylidene or alkylidyne complexes that contain alkoxide or aryloxide ligands are relatively rare and their chemistry poorly explored.

ALKYNE METATHESIS BY Mo AND W ALKYLIDYNE COMPLEXES

The discovery of neopentylidyne complexes of the type $\mathrm{M(C^tBu)(CH_2{}^tBu)_3}$ and $\mathrm{M(C^tBu)Cl_3(dme)}$ (M = Mo or W[33,34]) created the possibility of preparing alkylidyne complexes that would be active for metathesis of alkynes (according to a proposal by Katz[35]). Interestingly, although a stable tungstacyclobutadiene complex forms readily upon addition of one equivalent of an internal alkyne to $\mathrm{W(C^tBu)Cl_3(dme)}$, that complex reacts further with alkyne to yield a mixture of reduced tungsten complexes that contain a peralkylated cyclopentadienyl ring [eq. (3)].[36] In contrast, alkoxide or phenoxide complexes of the type $\mathrm{W(C^tBu)(OR)_3S_x}$ (S = coordinating solvent, e.g. 1,2-dimeth-

$$\mathrm{W[C_3(^tBu)Et_2]Cl_3} \xrightarrow{1.5\ \mathrm{EtC{\equiv}CEt}} 0.5\ \mathrm{WCp'Cl_4} + 0.5\ \mathrm{WCp'Cl_2(EtC{\equiv}CEt)} \qquad (3)$$

$$\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5Et_4{}^tBu}$$

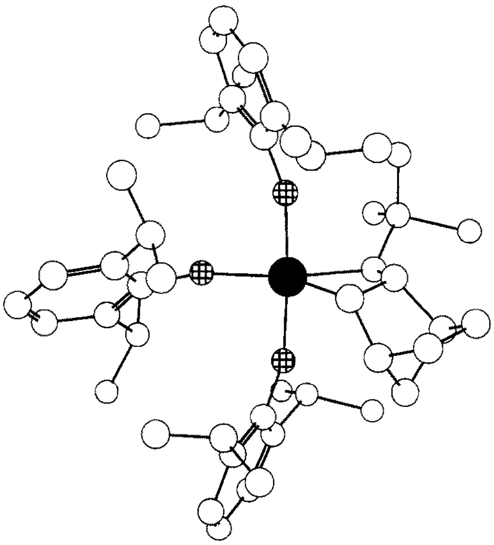


Fig. 1. A drawing depicting the molecular structure of the tantallacyclobutane complex formed in the reaction between $\mathrm{Ta(CH^tBu)(OAr)_3(THF)}$ and norbornene ($\mathrm{OAr} = \mathrm{O\text{-}2,6\text{-}C_6H_3{}^iPr_2}$) (reproduced from ref. 31 with permission).

oxyethane or THF) are successful to varying degrees as initiators of alkyne metathesis. W(C^{t}Bu)(O^{t}Bu)$_3$, a stable, highly "electron-deficient" species (a "12 electron species" not counting π electrons), is astoundingly active for the metathesis of ordinary internal alkynes.[37,38] Tungstacyclobutadiene intermediates are not observed. On the other hand, trigonal bipyramidal tungstacyclobutadiene complexes are observed when W(C^{t}Bu)(OAr)$_3$ is treated with an internal alkyne,[39] and they have been shown to metathesize acetylenes at rates that are independent of alkyne concentration, consistent with rate-limiting loss of alkyne from the tungstacyclobutadiene ring. Trigonal bipyramidal tungstacyclobutadiene complexes, W(C$_3$Et$_3$)(OR)$_3$, can also be prepared where OR = OCH(CF$_3$)$_2$ (Fig. 2) or OCMe(CF$_3$)$_2$.[40] (Note in Fig. 2 how the CF$_3$ groups of the hexafluoroisopropoxide ligands are virtually "eclipsed", presumably in order to minimize steric interactions.) They too are catalysts for the metathesis of internal acetylenes, but by two strikingly different mechanisms. W(C$_3$Et$_3$)[OCMe(CF$_3$)$_2$]$_3$ and related intermediates behave like OAr complexes; the rate-limiting step is loss of the alkyne from the metallacyclobutadiene ring. However, W(C$_3$Et$_3$)[OCH(CF$_3$)$_2$]$_3$ metathesizes alkynes slowly in an associative manner. Cyclopentadienyl complexes are not formed readily in any of the alkoxide systems, i.e. alkoxide ligands encourage reactions that lead to reformation of a d^0 complex that contains a multiple metal–carbon bond relative to "reductions" of the metal via formation of cyclopentadienyl rings. At this point it should be noted again that the pK_a values for phenols and hexafluoroalcohols are within one pK_a unit, and that to a first approximation the differences between the OCH(CF$_3$)$_2$ and OCMe(CF$_3$)$_2$ systems can be ascribed solely to steric factors. [The OCH(CF$_3$)$_2$ ligand in a complex such as that shown in Fig. 2 is simply too small to force an alkyne to be lost from the metallacyclobutadiene ring, small enough, in fact, to allow more alkyne to attack the metal, as in the analogous tungstenacyclobutadiene trichloride complex.] Interestingly, the attempted synthesis of W(C^{t}Bu)(O-2,6-C$_6$H$_3$^{t}Bu$_2$)$_3$ led to consumption of only two equivalents of phenoxide and formation of a neopentylidene complex via addition of a t-butyl C—H bond to the W≡C bond, a clear example of complications that can arise if unavoidable steric hindrance is found too near the metal.[39] Detrimental intramolecular reactions can be avoided, intermolecular decomposition reactions of pseudo-four-coordinate species can be prevented, and pseudo-five-coordinate metallacyclobutadiene complexes can be destabilized toward loss of alkyne, all at the same time, if the steric hindrance in alkoxide ligands is finely tuned and is not found in the immediate vicinity of the metal center.

A wide variety of molybdenum neopentylidyne complexes of the type Mo(C^{t}Bu)(OR)$_3$ [OR = O^{t}Bu, OCHMe$_2$, OCH$_2$^{t}Bu, OCMe(CF$_3$)$_2$, OCMe$_2$(CF$_3$), or OAr] or Mo(C^{t}Bu)(OR)$_3$(dme) [OR = OCH(CF$_3$)$_2$, OCMe(CF$_3$)$_2$, or OC(CF$_3$)$_3$] can also be prepared from Mo(C^{t}Bu)Cl$_3$(dme).[41] [When OR = OCMe(CF$_3$)$_2$ the metal is electrophilic enough to bind dme, but the coordination sphere is crowded enough so that dme is lost readily in solution; consequently both four-coordinate and six-coordinate species are known.] Internal acetylenes do not react with Mo(C^{t}Bu)(O^{t}Bu)$_3$, but they do react smoothly with all fluoroalkoxide or phenoxide complexes to give new, isolable

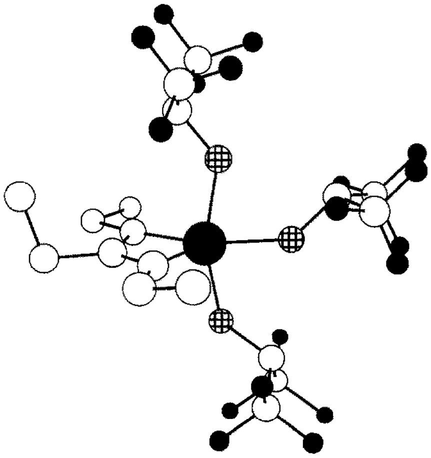
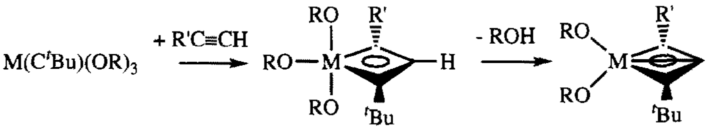


Fig. 2. A drawing depicting the molecular structure of W(C$_3$Et$_3$)[OCH(CF$_3$)$_2$]$_3$ (reproduced from ref. 40 with permission).

alkylidyne complexes. The $OCMe(CF_3)_2$, $OC(CF_3)_3$, and OAr complexes are excellent catalysts for the metathesis of internal alkynes, but molybdacyclobutadiene complexes are rarely observed. The main lessons learned from the Mo studies are that (i) molybdenum complexes in general are less reactive than their tungsten analogs, (ii) molybdacyclobutadiene complexes are much more prone to lose alkyne than tungstacyclobutadiene complexes, and (iii) molybdenum is more likely to polymerize alkynes, a reaction that often competes with metathesis.[42]

One of the unexpected findings in Mo and W alkylidyne chemistry was that reactions between terminal alkynes and neopentylidyne complexes yield "deprotiometallacyclobutadiene" complexes when OR is relatively electron-withdrawing [eq. (4)].[41,43] Several of these "deprotiocycles" have been isolated, often as adducts that contain two donor ligands, and characterized through X-ray studies. The β proton in a metallacyclobutadiene complex is probably lost intermolecularly, since the reaction is catalyzed by bases. So far deprotiometallacycles have been observed only when the relatively electron-withdrawing fluoroalkoxide or phenoxide ligands are present; apparently only then is the β proton acidic enough to be removed readily.



(4)

The fact that complexes such as $W(CEt)(O^tBu)_3$ do not decompose to EtC≡CEt and $(^tBuO)_3W{\equiv}W(O^tBu)_3$[9] led us to try to form alkylidyne complexes by adding an internal alkyne to $(^tBuO)_3W{\equiv}W(O^tBu)_3$ [eq. (5)].[44] This "cleavage reaction" works extremely well for a wide variety

$$(^tBuO)_3W{\equiv}W(O^tBu)_3 + R'C{\equiv}CR' \longrightarrow 2\,(^tBuO)_3W{\equiv}CR' \qquad (5)$$

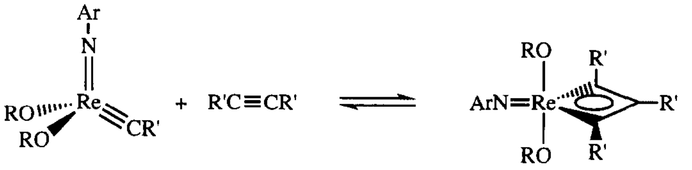
of alkynes,[45] even terminal alkynes, if the methylidyne complex is trapped as a five-coordinate base adduct. (Four-coordinate methylidyne complexes are unstable with respect to bimolecular decomposition to give W≡W complexes that contain bound acetylene.[46,47]) The cleavage reaction also works to some extent when the alkoxide in $(RO)_3W{\equiv}W(OR)_3$ is $OCH(CF_3)_2$,[48] $OCMe_2(CF_3)$,[48] or O-2,6-$C_6H_3Me_2$.[49] In the case of $(^tBuO)_3Mo{\equiv}Mo(O^tBu)_3$ the cleavage reaction works only for sterically less demanding and more reactive terminal alkynes, and to only a limited extent.[50] Competing alkyne polymerization is a common problem, especially for smaller alkynes. These results suggest that the reaction between an M≡M compound and an alkyne and that between an M≡C compound and an alkyne are related. Unfortunately, inaccessibility to a variety of $(RO)_3M{\equiv}M(OR)_3$ complexes has prevented a full exploration of the alkyne cleavage reaction.

There are several features of alkyne metathesis by pseudo-tetrahedral alkylidyne complexes that should be pointed out and compared with alkene metathesis by alkylidene complexes to be discussed later. The alkyne metathesis studies outlined above suggested that in general the more electrophilic the metal in a pseudo-four-coordinate complex, the faster it will react with an alkyne in a given set of steric circumstances to give a trigonal bipyramidal metallacyclobutadiene complex. Consequently we assume that the alkyne approaches the electrophilic metal on one of the three equivalent COO faces of the $M(CR')(OR)_3$ complex and binds weakly to it. When a two-electron donor base binds to an $M(CR')(OR)_3$ species, the observed species is that in which the base is bound *trans* to the alkylidyne (on the OOO face).[45,51] It is quite possible that the alkyne only rarely approaches the COO face to "bind" and form a metallacyclobutadiene complex compared to the number of times it (unproductively) interacts with the metal on the OOO face. Therefore the nature and energy of unoccupied orbitals other than the LUMO could play a significant role in determining the rate of a productive reaction. It should also be noted that a two-electron donor base can "block" a metathesis reaction by binding strongly to the metal to give a five-coordinate species, but the base need not necessarily bind to the same site as the metathesis substrate.

Several thiophenoxide analogs of alkylidyne phenoxide complexes have been prepared and shown to be relatively inactive for the metathesis of alkynes.[52]

RHENIUM ACETYLENE METATHESIS CATALYSTS

Concurrent with the development of W and Mo catalysts for alkyne metathesis was the search for "Re^{VII}" alkylidyne or alkylidene complexes. The first publications in this area reported the syntheses of species such as $Re(N^tBu)_2(CH^tBu)(CH_2{}^tBu)$ and $Re(C^tBu)(CH^tBu)(O^tBu)_2$.[53,54] However, neither compound reacted readily with several representative olefins or acetylenes. The development of new routes to Re^{VII} complexes[55,56] and the realization that alkoxide ligands were desirable for metathesis activity led to the discovery of complexes of the type $Re(C^tBu)(NAr)(OR)_2$ [OR = O^tBu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and OAr].[57] Only $Re(C^tBu)(NAr)[OCMe(CF_3)_2]_2$ was found to be active for the metathesis of internal alkynes. However, this "simple" reaction turned out to be relatively complex.[57] A rhenacyclobutadiene complex in theory can be formed in two ways, either by alkyne attack on one of two equivalent CNO faces, or by alkyne attack on the COO face of the pseudo-tetrahedral $Re(C^tBu)(NAr)(OR)_2$ species. The approximately TBP rhenacyclobutadiene complex ("type 1") that could be isolated and structurally characterized (Fig. 3; the Re=C bond is in an "axial" position) did not contain a symmetric (delocalized) ring and turned out to be inactive for alkyne metathesis. Furthermore, it was observed that certain alkynes with bulky substituents could be metathesized for a significant period of time. In these cases an unstable rhenacyclobutadiene complex ("type 2") could be observed at low temperatures by NMR that had the proposed symmetrical structure shown in eq. (6), one that is analogous to other TBP metallacyclobutadiene complexes (Fig. 2).



(6)

The first explanation that was offered was that a "small" alkyne attacks one of the CNO faces of the rhenium complex to form a type 1 metallacycle most rapidly. When the alkoxide is small and electron-withdrawing, and the acetylene does not contain bulky substituents, only the CNO face is attacked, and an inactive type 1 rhenacycle is formed. When attack at the CNO face becomes sterically untenable (a large alkoxide and a large substituent in the acetylene or alkylidyne ligand) then the acetylene adds to the COO face to give a type 2 rhenacycle. In the most extreme cases (involving diisopropylacetylene or di-sec-butylacetylene) the initial and all subsequent rhenacycles are of type 2. Under these conditions a type 1 rhenacycle does not form for steric reasons, as long as the alkoxide is large, and metathesis is therefore relatively long-lived. If the acetylene substituents are of intermediate size, metathesis is not long-lived because of "competitive face attack" by the acetylene on the CNO face and eventual formation of inactive type 1 rhenacycle. The second explanation offered was that alkyne attack on the COO face is always preferred, but "pseudo-

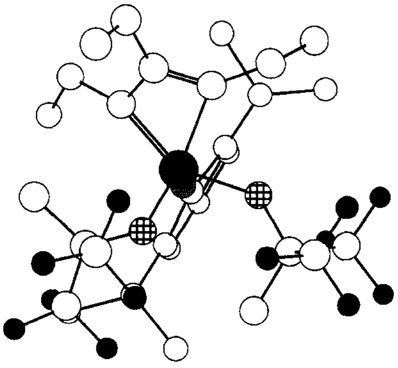
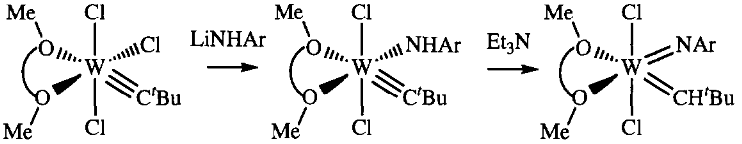


Fig. 3. A drawing depicting the molecular structure of $Re(C_3Et_3)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)[OCMe(CF_3)_2]_2$ (reproduced from ref. 57 with permission).

rotation" of the "initial" rhenacyclobutadiene complex leads to the inactive type 1 rhenacycle unless sterically prevented (in a non-obvious way) by large substituents on the rhenacycle. In either case the alkoxide again plays a crucial role: (i) it has to be electron-withdrawing in order to boost the reactivity of the metal; (ii) it has to be bulky enough to avoid immediate or eventual formation of a stable type 1 rhenacycle. These results awakened us to the fact that the "correct type" of intermediate could be present (here a rhenacyclobutadiene complex), but that in fact it could be too stable to be part of a catalytic cycle. The possibility of forming metallacycles via more than one mode of attack on a pseudo-tetrahedral molecule later also became an important consideration in W and Mo imido alkylidene chemistry.

IMIDO ALKYLIDENE COMPLEXES OF W AND Mo

The discovery of pseudo-octahedral oxo alkylidene complexes of tungsten of the type $W(O)(CH{}^tBu)(PR_3)_2Cl_2$[58] allowed "$W(O)(CH{}^tBu)(O{}^tBu)_2$" to be prepared by adding t-butoxide. However, $W(O)(CH{}^tBu)(O{}^tBu)_2$ proved too unstable to characterize. Since we felt that bimolecular decomposition reactions were responsible for its instability, we turned to synthesizing analogous imido alkylidene complexes in the belief that imido ligands would block bimolecular decomposition reactions more effectively than oxo ligands. Initial studies involving the readily available phenylimido ligand were promising,[59] but we felt that the parent phenylimido ligand might be too small to prevent bimolecular decomposition or disproportionation reactions of four-coordinate species. Therefore, we turned to the much more bulky 2,6-diisopropylphenylimido (NAr) ligand, a "dianionic equivalent" of the OAr ligand that had been employed successfully in acetylene metathesis systems. The imido alkylidene dichloride complex shown in eq. (7) was synthesized from a neopentylidyne complex.[60] From it (and later a bistriflate analog[61]) a variety of neutral, four-coordinate complexes of the type $W(CH{}^tBu)(NAr)(OR)_2$ could be prepared that contain relatively bulky alkoxides [$OR = O{}^tBu$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_2(CF_2CF_2CF_3)$, or OAr].[61-63] The activity of such species for the metathesis of ordinary internal olefins (e.g. *cis*-2-pentene) appeared to peak for the $OCMe(CF_3)_2$ species. New alkylidene complexes such as $W(NAr)(CHPh)[OCMe(CF_3)_2]_2$ (Fig. 4) could be isolated, and in some cases trigonal bipyramidal (TBP)



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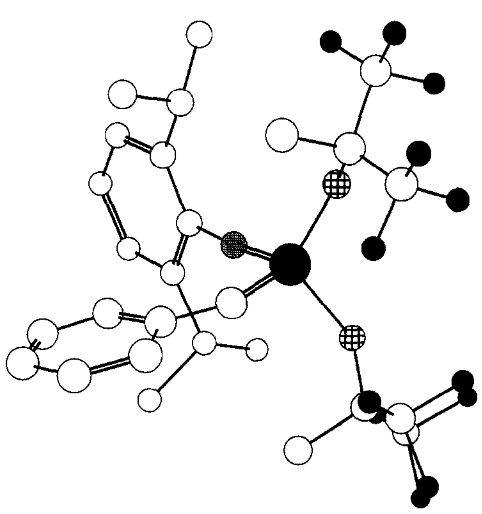
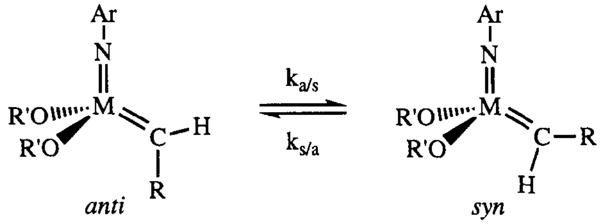


Fig. 4. A drawing depicting the molecular structure of $W(CHPh)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)[OCMe(CF_3)_2]_2$ (reproduced from ref. 62 with permission).

tungstacyclobutane complexes were stable enough to be observed or even isolated (Fig. 5). $W(CH^tBu)(NAr)[OCMe_2(CF_3)]_2$ reacted relatively slowly with 3-hexenes, while $W(CH^tBu)(NAr)(O^tBu)_2$ virtually did not react at all. Ethylene, a much more reactive olefin, reacted rapidly to give characterizable TBP tungstacyclobutane complexes such as $W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ or $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$. Ethylene also reacted with the less reactive $W(CH^tBu)(NAr)(OR)_2$ complexes [OR = O^tBu, $OCMe_2(CF_3)$, or OAr], but the course of those reactions could not be clarified. On the basis of this work it was proposed that the rate of reaction of alkylidene complexes with olefins correlated directly with the electron-withdrawing ability of the alkoxide, as found in acetylene metathesis systems described earlier. However, it was clear that steric factors limited the rate of reaction of alkylidene complexes in some cases [e.g. OR = $OC(CF_3)_2(CF_2CF_2CF_3)$] and that the stability of TBP metallacycles correlated inversely with the degree of substitution in the WC_3 ring (as one would expect).

Other studies provided more surprises.[61,64] The structure of $W(CH^tBu)(NAr)(O^tBu)_2$ was shown to be entirely analogous to that of $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$. Therefore the significant reactivity difference between the two could not be ascribed to gross structural differences. Secondly, both *syn* and *anti* rotamers of $W(CHSiMe_3)(NAr)(OAr)_2$ were observed [eq. (8)] and found to interconvert on the NMR time scale ($\Delta G\ddagger \approx 12$ kcal mol^{-1}). It was not clear at the time why rotamers could be observed in this case—only the *syn* rotamer had been observed before[62]—and why they interconverted readily. Perhaps the most revealing finding at the time was that ethylene would react with complexes of the type $W(CH^tBu)(NAr)(OR)_2$ [OR = O^tBu, $OCMe_2(CF_3)$, OAr] to give either trigonal bipyramidal or square pyramidal (SP) tungstacyclobutane complexes, or in some cases [OR = $OCMe_2(CF_3)$ or OAr] a mixture of interconverting SP and TBP species. In one case the lowest energy form depended upon the nature of the metallacycle, i.e. $W[CH_2CH(R)CH_2](NAr)(OAr)_2$ is a square pyramid when R = ^tBu, but a trigonal bipyramid when R = $SiMe_3$. It was proposed on the basis of kinetic studies that square pyramidal metallacycles are relatively stable toward loss of



(8)

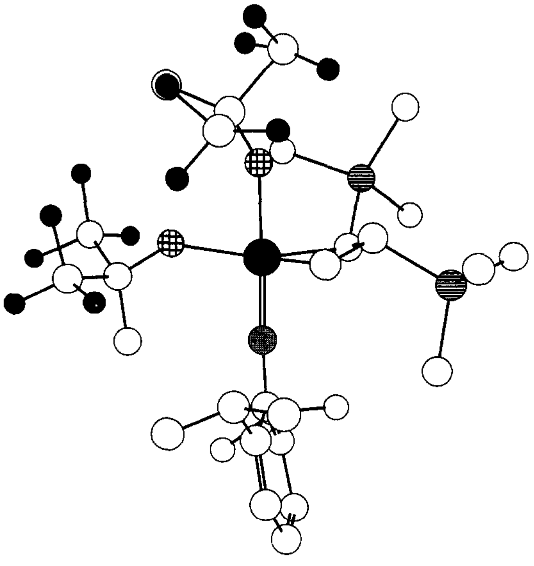


Fig. 5. A drawing depicting the molecular structure of $W[CH_2CH(SiMe_3)CH(SiMe_3)](NAr)[OCMe_2(CF_3)]_2$ (reproduced from ref. 62 with permission).

an olefin because the WC_3 ring is further from an "olefin/alkylidene" transition state than is the WC_3 ring in a trigonal bipyramidal metallacycle. For that reason complexes that contain relatively electron-withdrawing alkoxides (which are usually trigonal bipyramids) will lose an olefin more readily than those that contain relatively electron-donating alkoxides (which are usually square pyramids), in spite of the fact that the metal is "more electrophilic" when electron-withdrawing alkoxides are present, and that therefore (on a superficial level) metallacyclobutane complexes are less likely to lose an olefin. However, the fascination with tungstacycles began to wane when it was realized that observable metallacyclobutane complexes are likely simply to be "traps" with stabilities that depend on many factors. In order to maximize the rate of metathesis it would be best to try to avoid them completely. Since molybdacyclobutadiene complexes had been shown to be much less stable than tungstacyclobutadiene complexes in alkyne metathesis systems,[41] we turned to synthesizing molybdenum imido alkylidene complexes. The possibility that reactivity was also related to which pseudo-tetrahedral face of the catalyst was attacked in the imido alkylidene complex, or that *syn* or *anti* rotamers could have dramatically different activities, had not yet been considered.

The poor yields and tedious synthesis of $Mo(C^tBu)(CH_2{}^tBu)_3$[41] limited initial investigations into Mo imido alkylidene chemistry. However, small quantities of $Mo(NAr)(CH^tBu)(OR)_2$ [$OR = O^tBu$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$] complexes could be prepared by a route analogous to that shown in eq. (7), and the complex in which $OR = OCMe(CF_3)_2$ was shown to be especially active for the metathesis of internal olefins.[65] Other routes to $Mo(NAr)(CH^tBu)(OR)_2$ species were developed later,[66] the most general beginning with $[NH_4]_2[Mo_2O_7]$ and yielding $Mo(NAr)(CHCMe_2Ph)(triflate)_2(dme)$, a precursor to a wide variety of imido alkylidene complexes, in three steps.[67–69] Therefore a wide variety of Mo complexes of the type $Mo(NAr)(CHCMe_2Ph)(OR)_2$ became available for study.

At one point we became interested in preparing two-electron donor adducts of $M(CH^tBu)(NAr)(OR)_2$ (M = Mo or W) complexes in the belief that the structures of base adducts might be relevant to the structure of the "weak olefin adduct"[70] in an olefin metathesis reaction.[71] PMe_3 was found to attack the CNO face of *syn*-$M(CH^tBu)(NAr)(OR)_2$ rotamers to give (chiral) TBP species in which the phosphine is bound in an axial position [Fig. 6; eq. (9)]. Predictably, the base is bound strongly only when the alkoxide is electron-withdrawing, and less strongly in the Mo than in the analogous W complex. A relatively stable CNO adduct of the *syn* rotamer, the only observable rotamer in solution, forms first, but the CNO adduct of the *anti* rotamer is the thermodynamic product. The *anti* adduct is believed to form via loss of PMe_3 from the *syn* adduct, followed by rotation of the alkylidene to give (usually unobservable) *anti*-$M(CH^tBu)(NAr)(OR)_2$, and readdition of PMe_3 to it. Therefore the situation is that shown in eq. (9). The CNO adduct of the *syn* rotamer is believed to be formed less readily because of the developing steric interaction between the R substituent on the *syn* alkylidene and the isopropyl groups on the aryl ring of the NAr ligand (which lies in the trigonal plane of the TBP adduct; Fig. 6). In compounds that contain a but-

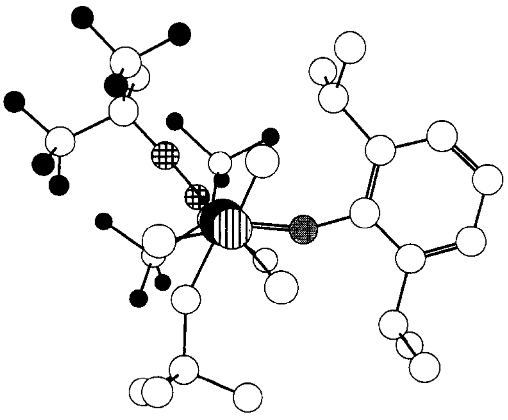
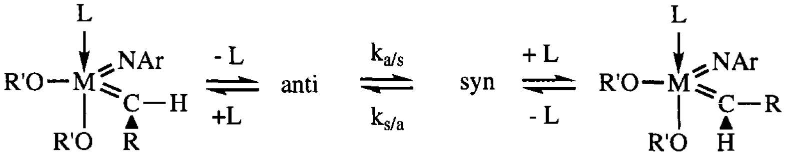


Fig. 6. A drawing depicting the molecular structure of *syn*-$Mo(CH^tBu)(NAr)[OCMe(CF_3)_2]_2(PMe_3)$ (reproduced from ref. 71 with permission).



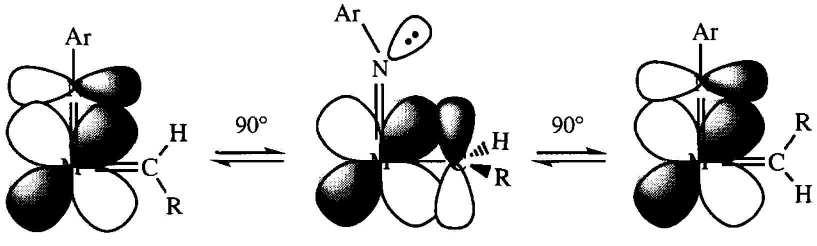
(9)

anti CNO adduct

syn CNO adduct

enylidene ligand, three isomers of five-coordinate quinuclidine adducts are observed to be in equilibrium, *syn* and *anti* CNO adducts analogous to those shown in eq. (9) and an adduct of a *syn* rotamer that has an achiral core as a result of addition of the base to either the COO or NOO face. As a consequence of these studies we recognized that (i) the structure of base adducts may or may not be analogous to the structure of the "initial weak olefin adduct" in a metathesis reaction, (ii) the observed base adduct could be either a thermodynamic or a kinetic product, (iii) in theory, the base could add to any of three different faces (CNO, COO, NOO) in a pseudo-tetrahedral complex, (iv) base adducts of the *anti* rotamers that were investigated were the most stable, and (v) in some cases rotamers could interconvert readily via a pseudo-tetrahedral species. Two conclusions would soon become especially relevant: (i) "rotamers should react with olefins at different rates;" (ii) "the rate at which rotamers interconvert could be an important factor in some circumstances."[71]

A detailed investigation of alkylidene rotation rates produced some results that dramatically illustrate the extent to which various alkoxides can change the nature of the metal at a fundamental level.[72,73] Low temperature ($-85°$C) photolysis of a wide variety of complexes of the type *syn*-Mo(NR′)(CHR″)(OR)$_2$ generated significant quantities of the *anti* rotamer. *Anti* to *syn* isomerization rate constants ($k_{a/s}$) were determined by NMR methods and correlated with the nature of R, R′, R″, and the solvent. Activation parameters were calculated in toluene-d_8 and THF-d_8 for the series Mo(NAr)(CHCMe$_2$Ph)(OR)$_2$ [where OR = OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_3$, or OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]. Values for $k_{a/s}$ were found to vary by up to seven orders of magnitude (at 298 K), the smallest values for $k_{a/s}$ being found in complexes that contain the most electron-withdrawing alkoxides in thf as a solvent. Equilibrium constants ($K_{eq} = k_{a/s}/k_{s/a}$) at 25°C were found to vary by up to approximately two orders of magnitude. Values for $k_{s/a}$ at 298 K were calculated and found to vary by up to six orders of magnitude in the same general direction as $k_{a/s}$. The main conclusion was that the rate of interconversion of *syn* and *anti* rotamers was "fast" for t-butoxide complexes ($k_{s/a} \approx 1$ s^{-1}) and "slow" for hexafluoro-t-butoxide complexes ($k_{s/a} \approx 10^{-5}$ s^{-1}). To a first (and qualitative) approximation, when the metal is relatively electron-rich the alkylidene that rotates by 90° can be stabilized by the orbital that lies in the N/Mo/C plane [eq. (10)]. When the metal is relatively electron-poor that orbital is energetically more closely matched with the energy



(10)

anti

syn

of a *p* orbital on the imido nitrogen atom and therefore is involved primarily in forming the pseudo triple bond to the imido ligand. The ease of rotation also varies to a significant degree with the nature of the imido and alkylidene ligands. For example, although there is little difference in the rate of alkylidene ligand rotation in hexafluoro-t-butoxide complexes that contain N-2,6-C$_6$H$_3$^{i}Pr$_2$ and N-2,6-C$_6$H$_3$Me$_2$ ligands, the alkylidene ligand in an analogous N-2-C$_6$H$_3$^{t}Bu complex rotates ~1500 times faster. The postulate is that the unsymmetrically substituted phenylimido ligand is more or less "permanently bent," thereby making the transition state shown in eq. (10) more accessible. Similar phenomena that lead to bending of alkoxide or phenoxide ligands could also significantly alter the accessibility of various transition states, although at present there is no way to measure the consequence of such phenomena.

SCF-Xα-SW calculations carried out on $\mathrm{Mo^{VI}}$ imido alkylidene complexes, $\mathrm{Mo(NH)(CH_2)(OH)_2}$ and $\mathrm{Mo(NH)(CH_2)(OCH_3)_2}$, confirm that the alkoxide oxygen $2p$ orbitals contribute to a significant extent to most molecular orbitals, and therefore that they should strongly affect the rate of *anti* ↔ *syn* interconversion and the reactivity of these complexes.[74] In the *syn* rotamer a low energy occupied orbital was found that had significant metal, alkylidene C_α, and alkylidene H_α character, and whose energy changed significantly as the $M—C_\alpha—H_\alpha$ angle was varied, i.e. an "agostic" $\mathrm{M(CH_\alpha)}$ interaction is present in the *syn* rotamer. An analogous interaction is not possible in the *anti* rotamer. Several high level calculations on imido alkylidene complexes that cover a variety of other issues have been reported.[75–77]

Relative to tantalum systems, W and Mo alkylidene complexes do not appear to be reduced as readily. One might expect the potential for the metal to be reduced via rearrangement of a metallacyclobutane ring or bimolecular coupling of alkylidene ligands to vary significantly from one alkoxide to another. Little is actually known at this stage about reductive processes. The one publication that addresses reduction of Mo complexes in the presence of olefins[78] suggests that both metallacycle rearrangement and alkylidene coupling can lead to reduction of the metal, but no obvious correlation of one or the other with the nature of the alkoxide ligand [e.g. $\mathrm{O^tBu}$ vs $\mathrm{OCMe(CF_3)_2}$] was found.

Re CATALYSTS FOR ALKENE METATHESIS

The list of four-coordinate $\mathrm{Re^{VII}}$ complexes that are potential olefin metathesis catalysts includes the neutral four-coordinate cousins of $\mathrm{M(NR')(CHR'')(OR)_2}$ (M = Mo or W) complexes, $\mathrm{Re(NR')_2(CHR'')(OR)}$ and $\mathrm{Re(CR')(CHR'')(OR)_2}$. An early complex of the latter type was $\mathrm{Re(CH^tBu)(C^tBu)(O^tBu)_2}$.[53,54] However, $\mathrm{Re(CH^tBu)(C^tBu)(O^tBu)_2}$ proved unreactive toward representative olefins.[79] [At that time (~ 1982) the importance of the alkoxide in determining metathesis activity was not recognized.] A few years later the role of alkoxide ligands had been recognized and more convenient routes were found to a variety of $\mathrm{Re(NR')_2(CHR'')(OR)}$ complexes, including $\mathrm{Re(CH^tBu)(NAr)_2[OCH(CF_3)_2]}$.[55,56] However, $\mathrm{Re(CH^tBu)(NAr)_2[OCH(CF_3)_2]}$ does not react readily with olefins, even norbornene (at 25°C). Finally, routes to $\mathrm{[Re(C^tBu)(CH^tBu)Cl_2]_x}$, a precursor to a family of complexes of the type $\mathrm{Re(C^tBu)(CH^tBu)(OR)_2}$, were developed, and a family of such complexes could therefore be prepared.[80,81] *Syn* and *anti* rotameric forms of $\mathrm{Re(C^tBu)(CH^tBu)(OR)_2}$ complexes could both be observed, but they were found to interconvert thermally or photochemically relatively slowly [$\Delta G^{\ddagger}_{298} \approx 25$ kcal mol^{-1} for OR = $\mathrm{O^tBu}$ and 30 kcal mol^{-1} for OR = $\mathrm{OCMe(CF_3)_2}$]. We rationalized that the reason for slow rotation is that the metal π orbital that lies in the C$=$Re$\equiv$C plane is involved in covalent bonding to the alkylidyne ligand and therefore is relatively inaccessible for stabilizing the rotated alkylidene ligand. An X-ray study of *syn*-$\mathrm{Re(C^tBu)(CH^tBu)[OCMe(CF_3)_2]_2(THF)}$[81] (Fig. 7) showed it to have a structure approximately halfway

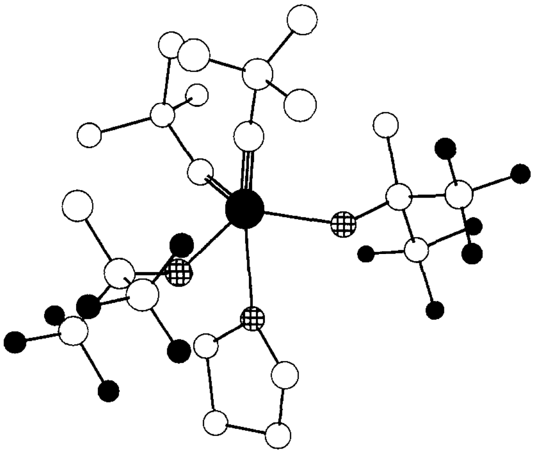


Fig. 7. A drawing depicting the molecular structure of *syn*-$\mathrm{Re(C^tBu)(CH^tBu)[OCMe(CF_3)_2]_2(THF)}$ (reproduced from ref. 81 with permission).

between a face-capped tetrahedron and a trigonal bipyramid (with THF approximately *trans* to the neopentylidyne ligand in each case). Only the $\mathrm{OCMe(CF_3)_2}$ derivative reacts readily with and metathesizes internal olefins,[82,83] but only in the absence of coordinating solvents such as THF or dme. In the presence of THF or dme, terminal olefins $\mathrm{R''CH{=}CH_2}$ ($\mathrm{R''}$ = Me, Et, Ph) react with $\mathrm{Re(C^tBu)(CH^tBu)[OCMe(CF_3)_2]_2}$ to give *syn*- or *anti*-$\mathrm{Re(C^tBu)(CHR'')[OCMe(CF_3)_2]_2S_2}$ (S = THF or 0.5 dme) in high yield. Relatively nucleophilic heteroatom-substituted (O, S, or N) terminal olefins react more rapidly than ordinary olefins with $\mathrm{Re(C^tBu)(CH^tBu)[OCMe(CF_3)_2]_2}$ in the presence of THF to yield complexes of the type *syn*- or *anti*-$\mathrm{Re(C^tBu)(CHX)[OCMe(CF_3)_2]_2(THF)_2}$ (X = OR, SR, $\mathrm{NR_2}$, or paradimethylaminophenyl). Evidently formation of a six-coordinate complex containing two equivalents of THF is favored when the alkylidene is relatively small. Terminal olefins can be metathesized, but a significant complication is subsequent reaction of the Re complex with ethylene. Separate studies showed that $\mathrm{Re(C^tBu)(CH^tBu)(OR)_2}$ complexes are reduced by ethylene in a reaction that is overall a 3+2 cycloaddition across the alkylidyne and alkylidene ligands to give $\mathrm{Re^V}$ metallacyclopentene complexes.[84] This is a new type of reaction that leads to "reduction" of the metal. Initial results suggest that this "reduction" is as facile for t-butoxide complexes as for hexafluoro-t-butoxide complexes.

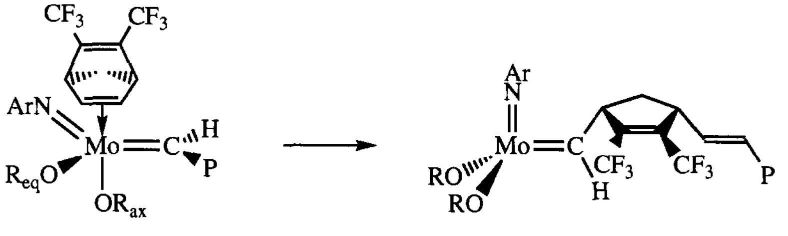
RING-OPENING METATHESIS BY W AND Mo IMIDO ALKYLIDENE COMPLEXES

Most of the studies concerning ring-opening metathesis by well-characterized metathesis catalysts have employed substituted norbornenes or norbornadienes.[11] Substituted norbornenes and norbornadienes are readily available in wide variety, and they usually react irreversibly with an alkylidene. Norbornene itself is the most reactive, and the resulting polynorbornene probably the most susceptible to secondary metathesis. The initial investigation, which was concerned with polymerization of norbornene itself by $\mathrm{W(NAr)(CH^tBu)(O^tBu)_2}$ as an initiator,[85] showed that low polydispersity polynorbornene was formed, presumably because the initial and propagating t-butoxide alkylidene complexes react only with the strained double bond in norbornene, not with the double bonds in the polymer formed as a consequence of ring-opening. Many subsequent studies, which involved an exploration of functionality tolerance, the synthesis of block copolymers, and ring-opening of other monomers, routinely employed Mo or W t-butoxide complexes.[11,86] Studies involving more reactive alkylidene initiators have been concerned primarily with substituted norbornenes and norbornadienes that for steric and/or electronic reasons are less reactive that norbornene itself. Polymers made from such monomers are therefore less susceptible to secondary metathesis reactions. However, since the reactivity of *syn* and *anti* rotamers is not likely to be the same, and since the rates of interconversion of *syn* and *anti* rotamers have been shown to vary dramatically, the polymerization process may not consist of a single propagating step.

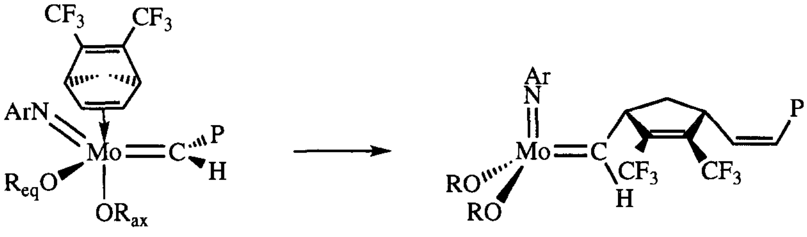
A detailed study of ROMP of disubstituted norbornadienes [e.g. 2,3-dicarbomethoxynorbornadiene or 2,3-bis(trifluoromethyl)norbornadiene] by Mo t-butoxide initiators[87] showed that they are polymerized in a well-behaved living manner to give essentially monodisperse homopolymers that are highly *trans* and highly tactic. Tacticity of the all-*trans* polymers must be controlled by the chirality of the alkylidene's β carbon atom in the growing chain ("chain-end control"). In contrast, polymerizations initiated by $\mathrm{Mo(CH^tBu)(NAr)[OCMe(CF_3)_2]_2}$ give low polydispersity all-*cis* poly(NBDF6) and poly(dicarbomethoxynorbornene) that are only ~75% tactic.[88] The living nature of the latter reaction can be ascribed to the relatively low reactivity of NBDF6 in general (powerful electron-withdrawing trifluoromethyl groups deactivate the olefinic bond), the low reactivity of the double bonds in the polymer (for both steric and similar electronic reasons), and the relatively low reactivity of the "deactivated" propagating alkylidene. The formation of all-*trans* polymers employing the t-butoxide initiator and all-*cis* polymers employing the hexafluoro-t-butoxide initiator is a dramatic illustration of how the nature of the alkoxide can determine polymer structure.

A theory as to how *cis*/*trans* selectivity arises resulted from a series of low temperature NMR studies. NBDF6 was shown to react rapidly and selectively with *anti*-$\mathrm{Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2}$ at −78°C in a mixture of *anti* and *syn* rotamers (generated photochemically at low temperature) to give a *syn* first-insertion product that contains a *trans* C=C bond [*anti* → *syn* + $\mathrm{I_t}$; eq. (11); P = polymer chain]. At higher temperatures (up to 25°C) the *syn* rotamer reacts very much more slowly to produce a *syn* first insertion product that contains a *cis*

C=C bond [*syn* → *syn*+1_c; eq. (12)]. Since little *anti* form is present under normal circumstances (no photolysis) and *syn* to *anti* conversion is slow ($\sim 10^{-5}$ s^{-1}), *cis* polymers are proposed to be formed from *syn* species via olefin attack (through the *exo* face) on the CNO face of the *syn* rotamer of the catalyst with C_7 of the monomer extending over the arylimido ring, as shown in eq. (12). If



anti **syn+1_t** (11)



syn **syn+1_c** (12)

the mode of attack is the same in the t-butoxide catalyst system, where *syn* and *anti* rotamers interconvert rapidly (~ 1 s^{-1}), then it is possible that the mechanism for forming *trans* polymers involves only the *anti* form of the propagating alkylidene species. In short, high-*cis* polymers can be formed via *syn* intermediates when rotamer isomerization rates are negligible on the time scale of polymerization, while high-*trans* polymers can be formed via *anti* intermediates when rotamer isomerization rates are fast on the time scale of polymerization. These studies reveal in a dramatic fashion that (i) in any catalyst system of this type *syn* and *anti* rotamers (essentially two types of catalysts) might be accessible, either via rotation of the alkylidene about the Mo=CHR bond, or via reaction of the Mo=CHR bond with a C=C double bond in the substrate (i.e. as part of chain growth itself), (ii) *syn* and *anti* rotamers may or may not interconvert readily on the time scale of polymerization, and (iii) reactivities of *syn* and *anti* rotamers might differ by many orders of magnitude. Unfortunately, the reactivity difference between *anti* and *syn* rotamers could be confirmed only for $OCMe(CF_3)_2$ catalysts, since *syn* and *anti* rotamers interconvert too readily in the t-butoxide system. If *trans* polymer always arises via CNO face attack on an *anti* rotamer, and *cis* polymer always arises via CNO face attack on a *syn* rotamer, regardless of the type of alkoxide present, then k_a must be greater than 10^5 k_s in order for all-*trans* polymer to result in the t-butoxide catalyst system (if we require $k_a[anti] > 10^2 k_s[syn]$ and $K_{eq} = 10^3 = [syn]/[anti]$). The low reactivity of *syn* rotamers relative to *anti* rotamers can be ascribed to the development of steric hindrance between the alkylidene substituent and the isopropyl groups on the NAr ligand as the monomer approached the CNO face (see, for example, Fig. 6). In the $OCMe(CF_3)_2$ system the *anti* rotamer is still much more reactive than the *syn* rotamer, but the *syn* rotamer itself is in this case also reactive.

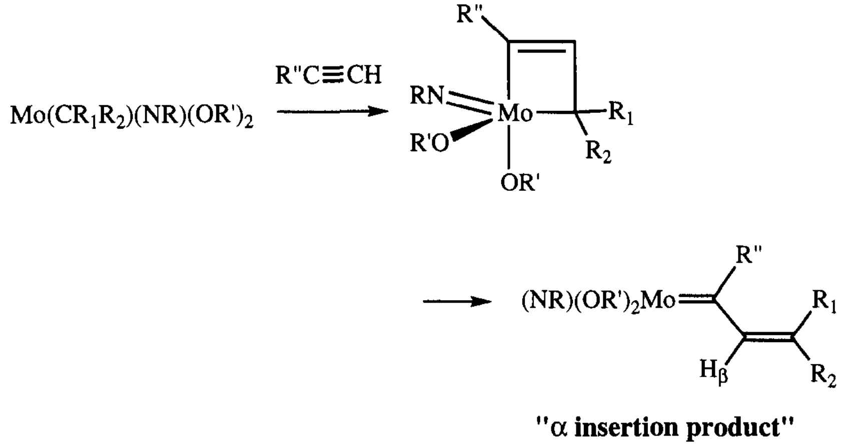
Consistent with the above proposals, it has been shown that especially unreactive monomers such as 1,7,7-trimethylnorbornene will react only with the *anti* rotamer of the $OCMe(CF_3)_2$ catalyst to give all-*trans* polymer, but at a (very slow) rate that is independent of monomer concentration. The calculated rate constant is essentially the same as the rate constant for conversion of a *syn* rotamer to an *anti* rotamer, consistent with *syn* to *anti* conversion being rate-limiting.[89]

A type of alkoxide that has been missing in studies of well-defined metathesis catalysts so far are those that are linked to one another, i.e. diolates. So far 3,3′-disubstituted binaphtholates or enantiomerically pure tartrate ligands have led to isolable species,[90] possibly in part since only diolates that form a seven-membered ring containing the metal can form the pseudo-four-coordinate species that appear to be the required intermediates in metathesis systems of this general type. The other reason for using binaphtholates and tartrates is that they are chiral and therefore could give rise to polymers whose tacticity is regulated by enantiomeric site control. Indeed, poly(NBDF6) prepared using (±)-Mo(N-2,6-$C_6H_3Me_2$)($CHCMe_2Ph$)[BINO($SiMe_2Ph)_2$] [BINO($SiMe_2Ph)_2$ is the binaphtholate that is substituted at the 3 and 3′ positions with an $SiMe_2Ph$ group] as the initiator was not only >99% *cis* but was >99% tactic. Analogous all-*cis*, highly tactic polymers prepared from enantiomerically pure dicarboalkoxynorbornadienes [2,3-($CO_2R^*)_2$ norbornadiene where R* is a chiral group such as 1*R*,2*S*,5*R*-(−)-menthyl] were shown to be isotactic by proton/proton correlation spectroscopy and decoupling experiments, while the all-*trans*, highly tactic polymers prepared using Mo($CHCMe_2Ph$)(NAr)($O^tBu)_2$ as the initiator were shown to be syndiotactic.[90] Related experiments employing enantiomerically pure disubstituted norbornenes (2,3-dicarbomethoxynorborn-5-ene, 2,3-dimethoxymethylnorborn-5-ene, and 5,6-dimethylnorborn-2-ene) gave high-*cis*, isotactic or high-*trans*, atactic polymers, respectively.

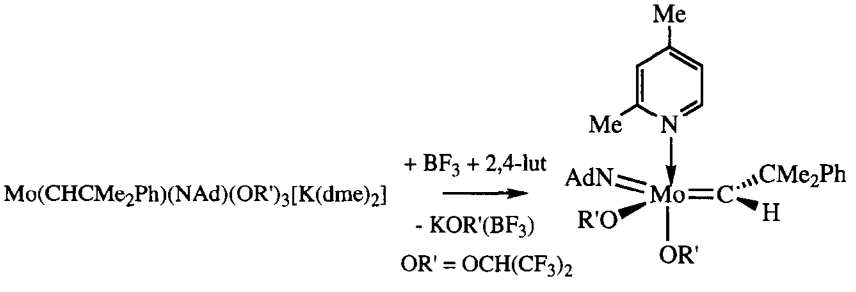
According to the model developed from reactivity studies of hexafluoro-t-butoxide complexes, *cis*, isotatic polymer should be the product of addition of monomer to the same CNO face of a *syn* alkylidene to give an insertion product that is a *syn* rotamer. However, at this stage it is not known whether this model holds for the binaphtholate complexes, in which interconversion of *syn* and *anti* rotamers appears to be relatively facile (as is true of phenoxide complexes in general[71]), or whether all-*cis* polymers can form via *anti* rotamers. In any case, the enormous importance of steric factors and relative rates of reactivities of rotamers is illustrated by the finding that the poly(NBDF6) prepared using (±)-Mo(N-2,6-$C_6H_3{}^iPr_2$)($CHCMe_2Ph$)[BINO($SiMe_2Ph)_2$] [instead of (±)-Mo(N-2,6-$C_6H_3Me_2$)($CHCMe_2Ph$)[BINO($SiMe_2Ph)_2$]] as the initiator was only ~70% *cis*! The tentative explanation is that the relative reactivity of *syn* vs *anti* rotamers is much greater in the N-2,6-$C_6H_3Me_2$ system since less steric hindrance develops when the substrate adds to the CNO face (*cf.* Fig. 6).

ALKYNE POLYMERIZATION BY Mo IMIDO ALKYLIDENE COMPLEXES

For some time it has been proposed that alkylidene complexes are responsible for polymerization of internal or terminal acetylenes by "classical" Mo and W catalysts.[91–93] One of the most soluble and highly conjugated polymers of this type is poly(*o*-TMSphenylacetylene), or poly(*o*-TMSPA).[93] However, *o*-TMSPA and other terminal acetylenes are not polymerized smoothly by any of the four-coordinate Mo alkylidene initiators of the type we have described here, all of which contain relatively bulky alkoxide ligands. For example, Mo(NAr)($CHCMe_2Ph$)($O^tBu)_2$ does not react readily with *o*-TMSPA at 25°C. Mo(NAr)($CHCMe_2Ph$)[OCMe($CF_3)_2]_2$ reacts very slowly with *o*-TMSPA, but the GPC of poly(*o*-TMSPA) prepared with this initiator is multimodal, consistent with multiple, possibly coupled pathways for chain growth. The GPC of poly(*o*-TMSPA) prepared with Mo(NAd)($CHCMe_2Ph$)[OCMe($CF_3)_2]_2$ (Ad = adamantyl) is unimodal, but polydispersities of polymers containing between 5 and 80 equivalents of *o*-TMSPA ranged between 1.2 and 1.4, in spite of the fact that Mo(NAd)($CHCMe_2Ph$)[OCMe($CF_3)_2]_2$ is converted virtually completely to the first "α-insertion product" upon addition of a slight excess of *o*-TMSPA [eq. (13)]. Acting on the assumption that "α-addition" is most feasible in the case of *o*-TMSPA in order to avoid steric interactions between α and β substituents in the intermediate metallacyclobutene complex, we decided that it would be most desirable to employ a complex that has a relatively small alkoxide. In this circumstance the bulky R″ group can be located in the α position of the intermediate metallacycle, more or less "over" the now sterically less demanding equatorial alkoxide [eq. (13)]. Unfortunately, however, Mo($CHCMe_2Ph$)(NR′)($OR)_2$ complexes in which OR is not a bulky alkoxide are unstable with respect to bimolecular decomposition, or more accurately, all attempts to prepare (e.g.) four-coordinate hexafluoroisopropoxide complexes have failed so far. However, base adducts can be prepared [eq. (14)]. All data for Mo($CHCMe_2Ph$)(NAd)[OCH($CF_3)_2]_2$(2,4-lutidine) are consistent with it being a *syn* rotamer having 2,4-lutidine bound to the CNO face.[94] This initiator is consumed completely upon addition of three equivalents of *o*-TMSPA to give a mixture of first-insertion and higher insertion products. Interestingly, all evidence available at this time suggests that the insertion products are essentially base-free, as judged by the appearance of resonances characteristic of free 2,4-lutidine as the initiator is consumed. Evidently, disubstituted alkylidenes of the type shown in eq. (13) are sufficiently crowded that 2,4-lutidine does not bind to



(13)



(14)

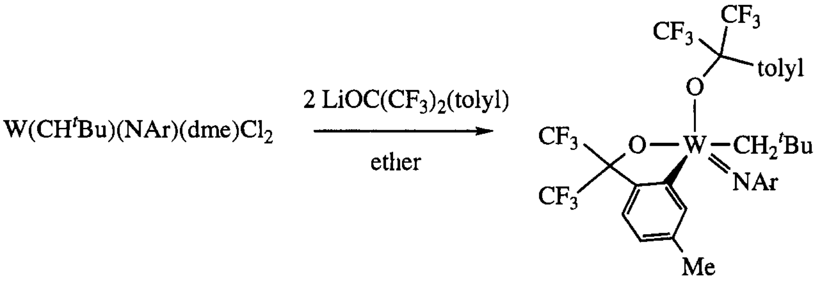
any significant degree, and they are relatively stable toward bimolecular decomposition or (*de facto*) any decomposition that might involve loss of an alkylidene α proton (e.g. to give an alkylidyne complex). Polymerizations of *o*-TMSPA proceed smoothly to give low polydispersity poly(*o*-TMSPA), where the relationship between M_n and the number of equivalents of *o*-TMSPA employed is linear, characteristic of a living polymerization that proceeds via a single type of chain growth and with a rate of initiation that approximately equals the rate of propagation. The surprising features of these "small alkoxide" initiators are that the "off rate" of the bases is high enough that they react readily with alkyne, and that propagation via base-free disubstituted alkylidenes is neither too fast (in which case only high polymer would be formed) nor too slow (in which case polymerization could be impractically slow). The fact that disubstituted alkylidene intermediates are still quite reactive was somewhat surprising and opens up the possibility that alkylidene complexes that contain a variety of "small" alkoxides might be stable if the alkylidene ligand is disubstituted.

Cyclopolymerizations of dipropargyl derivatives such as $(HC{\equiv}CCH_2)_2C(CO_2Et)_2$ by the Mo $(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$ initiator in dimethoxyethane have been shown to yield polyenes with a relatively low polydispersity.[95] The chain contains both five- and six-membered rings formed by tail-to-tail or head-to-tail cyclopolymerizations, respectively, that are a consequence of α or β addition of the first triple bond to an Mo=C bond. Dipropargyl diethylmalonate was polymerized slowly by catalysts such as $Mo(CH^tBu)(NAr)(O^tBu)_2$ to give polymers with a broad polydispersity. The issues here are complex, but related (*inter alia*) to the relative reactivity of rotamers and the rate at which they interconvert. The preparation of cyclopolymers with a relatively narrow distribution of chain lengths about a known average has allowed measurements to be made that show that the third-order hyperpolarizability (γ) in polyene oligomers saturates at approximately 100 double bonds.[96]

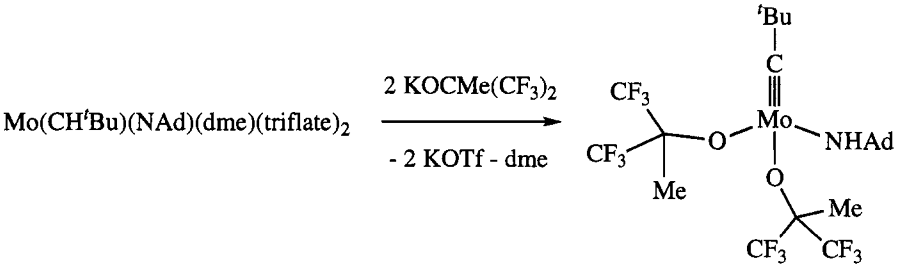
COMMENTS

One might get the impression on the basis of the work that has been described here that bulky alkoxides and phenoxides are not involved in any significant side reactions. Generally that is true.

However, slight variations can lead to significantly different behavior. I have mentioned already in the section dealing with alkylidyne complexes and acetylene metathesis that a CH bond in an *ortho* t-butyl group can be activated, a type of reaction that has been investigated extensively by Rothwell and co-workers.[97,98] A related example is the formation of a metallated neopentyl complex upon the attempted synthesis of an $OC(CF_3)_2$(tolyl) tungsten neopentylidene complex [eq. (15)].[61] A relatively recent finding[99] is that an ostensibly minor variation of a synthesis, in this case substituting $KOCMe(CF_3)_2$ for $LiOCMe(CF_3)_2$, leads to formation of the alkylidyne complex shown in eq. (16) instead of the known[69] $Mo(CH^tBu)(NAd)[OCMe(CF_3)_2]_2$ (Ad = adamantyl). When and exactly how the proton migration takes place is still unknown, although it is unlikely to take place in the bis-alkoxide complexes, since it has been known for some time that both $W(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$ and $W(C^tBu)(NHAr)[OCMe(CF_3)_2]_2$ are stable species that cannot be interconverted in the presence of triethylamine.[7] In such circumstances it is likely that the acidity of the alcohol formed upon deprotonation of the alkylidene will be a crucial determinant of whether the imido nitrogen atom is subsequently protonated.



(15)



(16)

CONCLUSIONS

It is clear that alkoxides, in a dramatic fashion, can "control the reactivity" of well-defined "d^0" alkylidene and alkylidyne complexes in olefin and acetylene metathesis reactions. The first requirement of course is to stabilize all intermediates in a metathesis reaction toward decomposition. Bulky alkoxides in particular are extremely useful in that they can prevent or significantly slow down bimolecular decomposition of alkylidene or alkylidyne intermediates in the catalytic reaction. However, bulky alkoxides also play many important roles within a given complex, only a few of which we have been able to document. One role is simply steric destabilization of metallacyclic intermediates. It is interesting to note that trigonal bipyramidal metallacyclic intermediates appear to be crucial types of intermediates in several metathesis reactions we have discussed, and interesting to speculate that such TBP intermediates are favored when the alkoxide is bulky and relatively electron-withdrawing. Unexpected findings include the overwhelming importance of *syn* and *anti* alkylidene rotamers in olefin metathesis reactions and the fact that the alkoxide can alter the rate of interconversion of alkylidene rotamers by many orders of magnitude. Since alkylidenes in classical metathesis systems are also likely to have an orientational preference in the vast majority of circumstances, many of the observations in classical systems that have been ascribed to steric effects within metallacycles (for example) might be traceable to *syn*/*anti* behavior of a type analogous to that found in the well-characterized complexes discussed here.

What is not obvious is why alkoxides in particular lead to stable but reactive alkylidene and alkylidyne complexes in metathesis systems, while complexes that contain other common bulky ligands (e.g. alkyls, thiolates, amides, etc.) in general are not found in successful long-lived metathesis catalysts. The common characteristic of the alternatives is that the element bound to the metal (C, N, S) is not as electronegative as oxygen. Chloride ligands, of course, are sufficiently electronegative, but they also readily bridge between metals and promote rapid disproportionation or other decomposition reactions. Fortunately, the number of readily available and varied alkoxide or phenoxide ligands is large, and therefore one can be chosen that will fit the requirements in a given catalytic metathesis reaction. We can assume that in the future many other examples of reactions catalyzed by early transition metal alkoxide complexes (e.g. Ziegler–Natta polymerizations, Lewis acid catalyzed Diels–Alder reactions, etc.) will be "controlled" by the alkoxide ligands.

Acknowledgements—R. R. S. thanks the National Science Foundation for supporting fundamental studies of complexes containing multiple metal–carbon bonds, the Navy for supporting studies in ring opening metathesis polymerization, the Department of Energy for supporting studies in the synthesis of polyenes, and the many graduate and postdoctoral students who have contributed their time, energy, and talent.

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