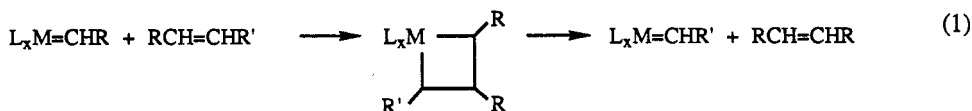


Recent advances in the chemistry and applications of high oxidation state alkylidene complexes

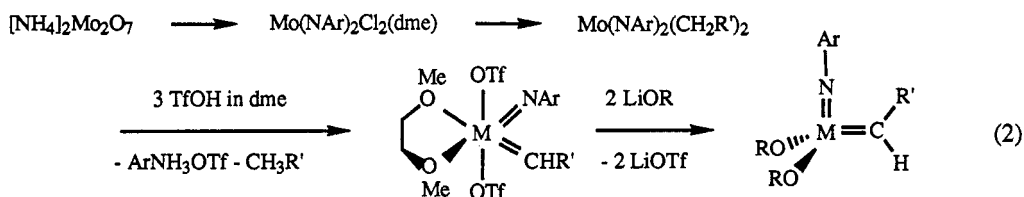
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Olefin metathesis (equation 1; L_x = some ligand coordination sphere) has been known for ~35 years (ref. 1), but until a few years ago the only catalysts available were "classical" catalysts (usually containing Mo, W, or Re), i.e., catalysts that were simple to make, but whose nature was not known in detail and whose activity therefore could not be controlled to a degree to which we have become accustomed in modern day catalysis chemistry. Such "black box" catalysts in general will not tolerate many donor functionalities, perhaps in part because little metal is actually active in such systems and absolute activity therefore has to be exceedingly high. Side reactions associated with "co-catalysts" such as aluminum halides are another significant complication.

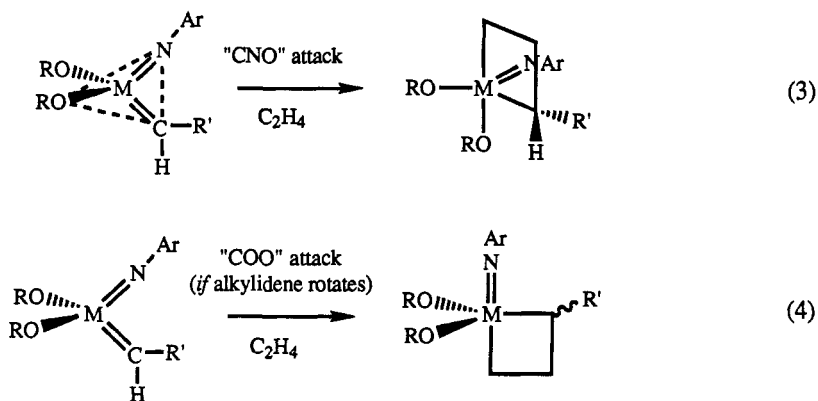


The discovery of high oxidation state alkylidene complexes of tantalum (ref. 2) in the mid 1970's seemed to promise that well-defined stable olefin metathesis catalysts were on the way, but nearly a decade of research was required before long-lived and stable catalysts with known structure and reactivity were prepared. Currently the most useful of these are four-coordinate neopentylidene or neophylidene ($CHR' = CHCMe_3$ or $CHCMe_2Ph$) complexes of molybdenum that contain two bulky alkoxides and a bulky diisopropylphenylimido (NAr) ligand, i.e., $Mo(CHR')(NAr)(OR)_2$ (ref. 3). Four-coordination allows a relatively small substrate to attack the metal to give a five-coordinate intermediate metallacyclobutane complex, while bulky alkoxide and imido ligands prevent decomposition reactions that destroy the alkylidene ligand or intermolecular reactions that would result in ligand scrambling to give inactive complexes. Synthetic routes have steadily improved to the point where a wide variety of Mo complexes now can be prepared readily, as shown in equation 2 ($R' = t-Bu$ or CMe_2Ph ; $OTf = OSO_2CF_3$; $dme = 1,2$ -dimethoxyethane) (ref. 4, 5), including those that contain imido ligands other than 2,6-diisopropylphenylimido (ref. 6). Addition of two bulky alkoxide ligands yields four-coordinate $Mo(CHR')(NAr)(OR)_2$ species.

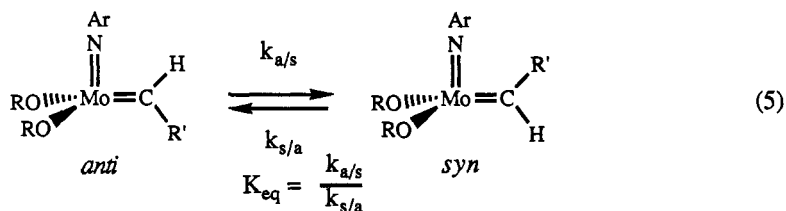


The metathesis activity of $Mo(CHR')(NAr)(OR)_2$ complexes varies widely. For example, $Mo(CH-t-Bu)(NAr)[OCMe(CF_3)_2]_2$ will initiate the metathesis of 500 equivalents of *cis*-2-pentene in less than one minute in toluene, while $Mo(CH-t-Bu)(NAr)(O-t-Bu)_2$ will initiate the metathesis of only a few equivalents of *cis*-2-pentene per hour (ref. 7). It is difficult to estimate very fast or very slow rates since the reactivity of the initial neopentylidene (or neophylidene) complex is much lower than that of a smaller alkylidene, and smaller alkylidene complexes are prone to intermolecular decomposition. The most reactive and therefore also the least stable of these is a methylene complex. Methylene complexes normally are observable only when stabilized by coordination of a base to give a five- or a six-coordinate species (ref. 4). Therefore the effect of a basic solvent can be profound, especially when the metal is relatively electrophilic (i.e., when the alkoxide is relatively electron-withdrawing, e.g., $OCMe(CF_3)_2$).

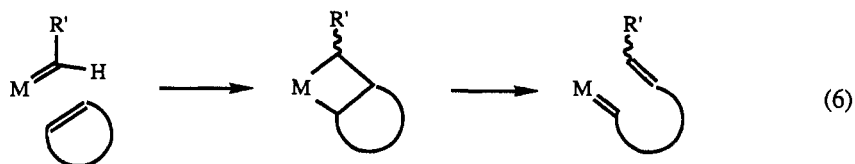
At present four-coordinate (base-free) catalysts are believed to be by far the most active. However, the details concerning how a metallacyclobutane intermediate is formed and decomposes are surprisingly complex. As shown in equation 3 an olefin can attack one of two "CNO" faces of the pseudo-tetrahedral



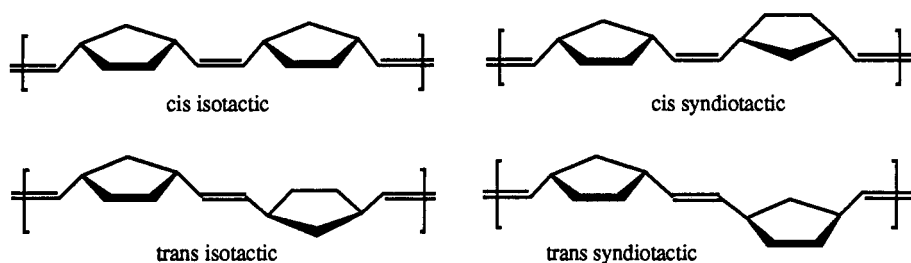
catalyst readily to give an initial "axial/equatorial" metallacycle. (The plane of the alkylidene ligand is coincident with the C/Mo/N plane.) However, it is possible to form a metallacyclobutane complex by attack on the "COO" face of the catalyst, if the alkylidene rotates by 90° before or during the process of addition of the olefin (equation 4). On the other hand, in recent theoretical studies (ref. 8) the authors concluded that a better description is a "direct" 2+2 cycloaddition of the C=C to the Mo=C bond to give a trigonal bipyramidal metallacycle that contains an axial alkoxide and an axial imido ligand. A potentially complicating feature of metallacycle formation is the presence of both *syn* and *anti* rotamers (equation 5) (ref. 9) whose reactivities are not likely to be the same and which may or may not interconvert readily.



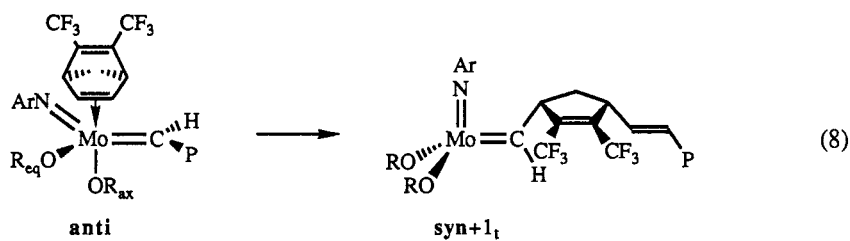
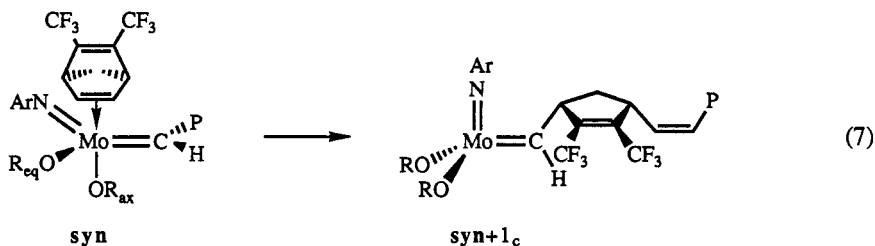
One of the first applications of classical metathesis catalysts was the synthesis of polymers from cyclic olefins (equation 6) (ref. 1, 10, 11). Well-defined metathesis catalysts found their application here first in what is now called ring-opening metathesis polymerization (ROMP) (ref. 12, 13, 14). The reason



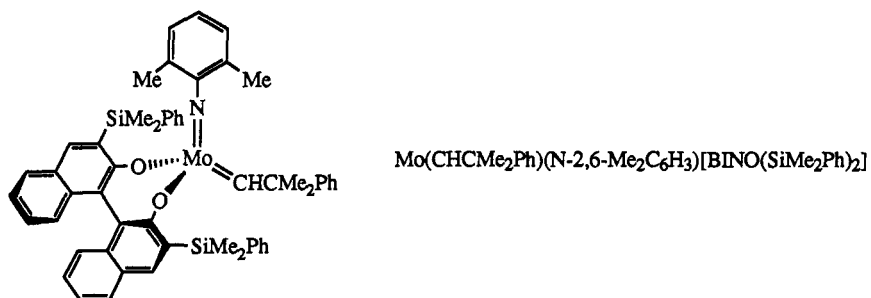
is that classical catalysts either are not "living," i.e., alkylidene intermediates decompose on the time scale of the polymerization reaction, or so little of a less active, but stable species is actually present that polymerization is intolerably slow. On the other hand, well-defined catalysts can be chosen so that the double bonds in monomers such as norbornenes are the only ones that react with the catalyst, intermediates are stable on the time scale of the polymerization reaction, and the reaction can be terminated in a well-defined Wittig-like reaction involving an aldehyde (usually a benzaldehyde). Therefore polymer chain length can be controlled within a narrow range and block copolymers can be prepared. The ability of well-defined catalysts to tolerate functionalities has allowed the synthesis of redox-active polymers (ref. 15), side-chain liquid crystal polymers (ref. 16), metal clusters (ref. 17), semiconductor clusters (ref. 18), and star block copolymers (ref. 19). However, a significant remaining challenge is to control the primary structure of a polymer prepared by ring-opening a norbornene or 2,3-disubstituted norbornadiene, since not only can the double bonds in the polymer be *cis* or *trans*, but tacticity arises from the fact that the tertiary carbon in a norbornene or norbornadiene is chiral. For example, four stereoregular chains of polynorbornene (as an example) can be formed (see below). The ability to control stereochemistry ultimately should allow one to control properties of the bulk ROMP polymer.



Recently we have found out just how important rotamers can be in reactions of alkylidene complexes of this general type (ref. 20, 21), at least in ROMP of certain types of monomers. Syn rotamers are favored in all *t*-butoxide complexes (*t*-butoxide itself, trifluoro-*t*-butoxide, and hexafluoro-*t*-butoxide) to the extent that K_{eq} (equation 5) can be as large as 5000. However, conversion of the syn to the anti rotamer can either be relatively facile (for a *t*-butoxide complex in toluene or thf $k_{s/a} \sim 0.5 \text{ s}^{-1}$) or extremely slow (for a hexafluoro-*t*-butoxide complex in toluene $k_{s/a} \sim 7 \times 10^{-5} \text{ s}^{-1}$, in thf $k_{s/a} \sim 2 \times 10^{-6} \text{ s}^{-1}$), and the reactivity of the anti rotamer of a hexafluoro-*t*-butoxide catalyst toward a monomer such as 2,3-bistrifluoromethylnorbornadiene (NBDF6) is at least two orders of magnitude greater than the syn rotamer. (Such a circumstance is roughly analogous to the "two path" mechanism of asymmetric hydrogenation (ref. 22) and doubtless other catalytic systems.) These kinetic results appear to correlate with the observed cis/trans content of poly(NBDF6). Poly(NBDF6) prepared from the hexafluoro-*t*-butoxide catalyst is all cis (ref. 23), since (it is postulated (ref. 21)) the monomer reacts only with the syn rotamer on a CNO face to give a syn insertion product (equation 7); the anti rotamer is inaccessible by alkylidene rotation or as a result of an insertion reaction. On the other hand, poly(NBDF6) prepared from the *t*-butoxide catalyst is all trans (ref. 24). The all trans polymer could arise if the monomer adds to the CNO face of the anti rotamer in roughly the same manner to give a trans double bond and a syn insertion product (equation 8) that can then be converted to the anti rotamer before it reacts with another equivalent of monomer. The all trans poly(NBDF6) is highly tactic, and the all cis poly(NBDF6) is $\sim 75\%$ tactic; tacticity must arise by chain end control under these circumstances.



Enantiomorphic site control is a potentially more certain method of controlling the stereochemistry of a polymerization reaction since the chiral center that determines how each monomer inserts is fixed and "mistakes" are not propagated. Poly(dicarbomethoxynorbornadiene) and poly(NBDF6) prepared employing racemic $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)[(\pm)\text{-BINO}(\text{SiMe}_2\text{Ph})_2]$ as the initiator were all cis and entirely tactic (ref. 25). The fact that the analogous catalyst that contains a *diisopropylphenylimido* ligand *fails* (the polymer contains only $\sim 75\%$ cis double bonds) is testament to the exceedingly fine steric balance in these sterically crowded species. The fact that syn and anti rotamers are readily interconverting in $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)[(\pm)\text{-BINO}(\text{SiMe}_2\text{Ph})_2]$ makes the hypothesis concerning the origin of all cis polymer proposed above potentially incorrect in this case, and the tacticity (syndio or iso) of the all cis polymers therefore still unknown.



The well-resolved and sharp proton NMR spectra of the all *cis*, tactic polymers suggested that it may be possible to determine the tacticity directly by proton NMR of polymers prepared from enantiomerically pure monomers, if the inequivalent olefinic protons can be resolved to an extent sufficient to determine whether they are coupled or not (ref. 26). In a *cis*,isotactic polymer the inequivalent olefinic protons would be coupled, while in a *cis*,syndiotactic polymer the inequivalent olefinic protons would not be coupled (see below). The homonuclear correlation spectrum of tactic *cis*-poly(2,3-dicarbomethoxynorbornadiene) shown in Fig. 1 proves that the olefinic protons are coupled and that this polymer therefore is isotactic. Similar arguments pertain to all *trans*,tactic polymer prepared with the $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{O}-t\text{-Bu})_2$ catalyst (ref. 24); in that case the olefinic protons are not coupled and the all *trans* polymer therefore is syndiotactic. It remains to be determined whether all *cis*,tactic poly(DCMNBD) (DCMNBD = 2,3-dicarbomethoxynorbornadiene) is isotactic. However, since we have seen no evidence that the principles that determine the *cis*/*trans* ratio and tacticity are *greatly* influenced by the chirality or lack thereof in the alkyl

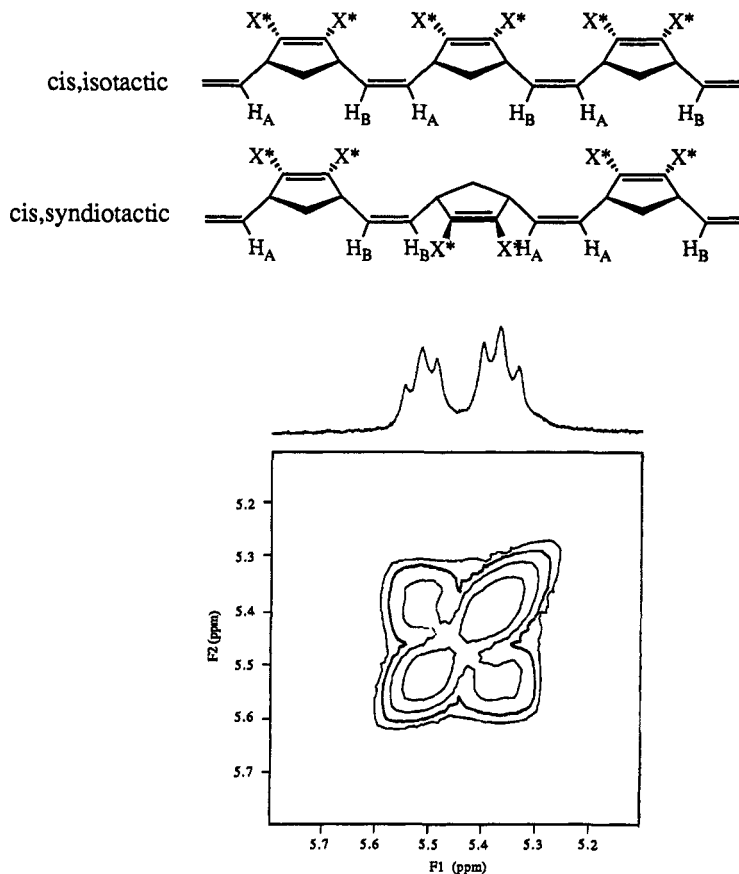
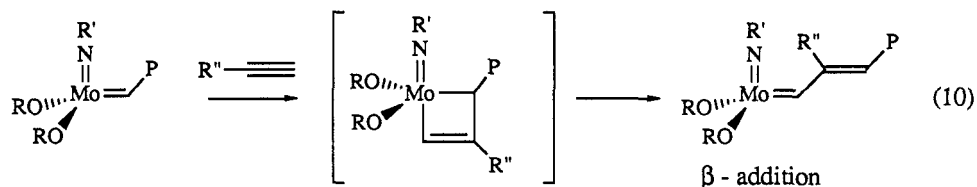
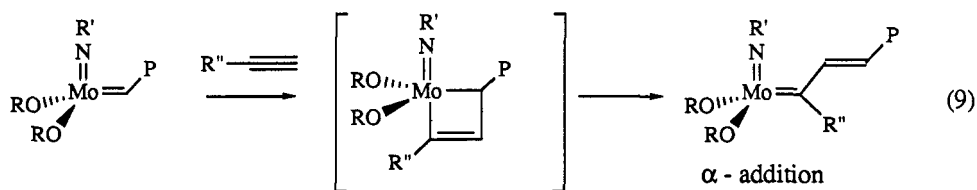


Fig. 1. The olefinic region of the 300 MHz homonuclear correlation spectrum of *cis*-poly(2,3-dicarbomethoxynorbornadiene) in CDCl_3 at 25 °C.

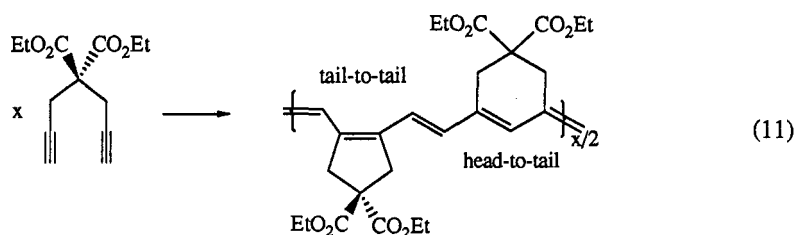
group of the ester, we believe that it is also most likely isotactic. It is not as secure to extend the results found here to *cis*-poly(NBDF6). However, since the nature of the substituent in a given type of monomer does not seem to result in a dramatic change in the structure of the resulting polymer, and since analogous poly(NBDF6) and poly(DCMNBD) samples are very similar to one another by ^{13}C NMR, we believe that the tactic *cis*-poly(NBDF6) prepared with the BINO catalyst is also most likely isotactic.

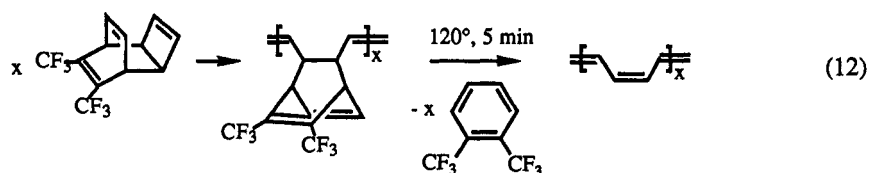
An important question is whether any other monomers can be polymerized by the BINO catalyst to give all *cis*, isotactic polymers. In fact, three enantiomerically pure 5,6-disubstituted norbornenes (dicarbomethoxy, dimethoxymethyl, and dimethyl) are polymerized smoothly to all *cis* polymers that by proton NMR have also been proven to be isotactic (ref. 26). However, the all *trans* polymers that are formed employing $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)(\text{O}-t\text{-Bu})_2$ as a catalyst are atactic (ref. 26, 27). It should be noted that isotacticity is consistent with addition of monomer to the same CNO face of one enantiomer of the catalyst, but it remains to be determined whether polymer is formed via *syn* or *anti* rotamer intermediates.

There is abundant evidence in the literature that alkynes are polymerized to give polyenes by "classical" olefin metathesis catalysts (ref. 28, 29). One version of this type of reaction is the cyclopolymerization of 1,6-heptadiyne derivatives (ref. 30, 31, 32, 33, 34, 35, 36). Polymerization of 1-alkynes or 1,6-heptadiyne derivatives by well-defined alkylidene catalysts that are also successful in living ROMP reactions has been a long-standing goal in my laboratory, since it would then become possible to design and prepare relatively complex block copolymers and phase-separated materials and to correlate non-linear optical properties of the polyenes with chain length, conformation, and substitution. In this circumstance an additional complication is that a terminal alkyne may add to a metal-alkylidene bond to give either the " α addition" or secondary vinyl alkylidene product (equation 9; P = polymer chain;) or the " β addition" or primary vinyl alkylidene product (equation 10). One would not expect primary and secondary vinyl alkylidene complexes to have the same reactivity. Perhaps this and other potential complexities pointed out earlier (e.g., rotamers) help explain why attempts to polymerize terminal acetylenes with well-defined alkylidene complexes to give low polydispersity polyenes has not been successful until recently.



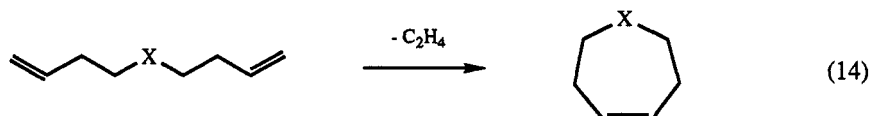
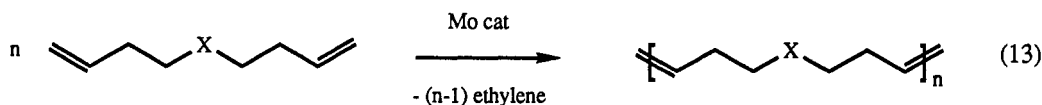
We have found that diethyldipropargylmalonate can be polymerized with $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ in 1,2-dimethoxyethane in a living manner to give a low polydispersity (~ 1.25) soluble polyene of a known type that has been shown to contain a mixture of five- and six-membered rings (equation 11). Interestingly, 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.0 2,5]deca-3,7,9-triene, which has been used to prepare polyenes indirectly in a living ROMP reaction (equation 12) (ref. 37, 38), competes with cyclopolymerization. Therefore soluble "hybrid" polyenes that contain a mixture of substituted and unsubstituted polyene chains (either random or block) can be prepared. Potential applications of this type of polyene are only beginning to be explored.



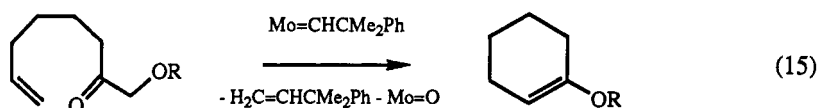


A recent, rare imido variation of an isolable well-defined molybdenum alkylidene complex in the general class of catalysts being discussed here is $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAdamantyl})[\text{OCMe}(\text{CF}_3)_2]_2$ (ref. 6). The characteristics of this species as a ROMP catalyst are dramatically different from those of all arylimido catalysts examined so far (ref. 21). In fact, ROMP of simple monomers such as 2,3-dicarbomethoxynorbornadiene so far has given surprisingly poor polymers in terms of polydispersities. On the other hand, $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAdamantyl})[\text{OCMe}(\text{CF}_3)_2]_2$ is an excellent catalyst for the polymerization of phenylacetylenes, especially those that are substituted with a bulky group in the ortho position, such as orthotrimethylsilylphenylacetylene (ref. 39). The reason why this catalyst produces low polydispersity polyphenylacetylenes and any details of the mechanism of polymerization are not yet known.

Other important recent results are variations of terminal olefin metathesis. Apparently molybdenum hexafluoro-*t*-butoxide complexes are the most effective, perhaps because molybdenacyclobutane complexes in general are much less stable than tungstacyclobutane complexes toward loss of olefin (ref. 40). The earliest example, "acyclic diene metathesis," or ADMET, is a step-growth condensation polymerization reaction in which ethylene is evolved (equation 13; $\text{X} = \text{O}$, for example) (ref. 41, 42, 43). Tolerance of functionalities is the most attractive feature of this reaction, although different *cis/trans* polymer structure is also important in some cases. In general, such reactions are not successful with classical catalysts because of side reactions. Under more dilute conditions, cyclization to give five-, six-, or seven-membered rings



becomes favorable (e.g., equation 14) (ref. 44, 45). Many variations have been found to be successful; in some cases even 1,2- or 1,1-disubstituted olefins can take part in the cyclization reaction, and again, many functionalities are tolerated. A stoichiometric "metathesis/carbonyl olefination" variation (e.g., equation 15) has been reported recently (ref. 46). The nature of the metal will be important in this type of reaction, since in general reactivity of an alkylidene toward the carbonyl functionality is higher for tungsten than for molybdenum; the reactivity of the carbonyl functionality would be expected to follow its usual trend (aldehyde > ketone > ester).



In as yet unpublished work, it has been shown that terminal olefins can be coupled efficiently to largely *trans* internal olefins by $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$ (ref. 7) and imido variations, especially in dimethoxyethane where $\text{Mo}(\text{CH}_2)(\text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2(\text{dme})$ is stable (ref. 4) and not readily reduced by ethylene, as is true in toluene (ref. 47). One might think that classical metathesis catalysts would serve this purpose, but functionality tolerance and longevity (leading to high turnover number) are the key arguments for the use of well-defined catalysts. Cross metathesis is possible if one olefin (the least expensive and/or most volatile) is employed in excess. Functionality tolerance has not been explored in any detail yet, but evidence so far suggests that directly functionalized olefins or (in one case) an olefin having a functionality in the allylic position cannot be coupled. Such findings would be analogous to those described in ADMET reactions (see above), where at least two methylene units must separate the functionality from the olefin.

CONCLUSIONS

Some of the most important of the points made here, along with some of what might be expected in the future, are the following:

1. It is now relatively simple to prepare precursors to a wide variety of catalysts containing Mo or W from metal oxides or oxyhalides on a relatively large scale in 3 or 4 high-yield steps.
2. Catalyst activity can be finely controlled.
3. Many functionalities are tolerated.
4. Polymerization systems can be living and we can look forward to a large degree of control over the primary structure of relatively complicated materials eventually.
5. Lewis acids, halides, and other potential "contaminants" are not present in systems involving these "well-defined" metathesis catalysts. Such characteristics would be especially important if polymers are prepared for electronic applications, for example.
6. Other monomers (e.g., acetylenes or other strained cyclic olefins) can be polymerized by well-defined ROMP initiators.
7. Catalysts are at present available that should allow new applications in organic chemistry to be explored.
8. Stoichiometric reactions may be economically feasible for certain highly prized molecules.

ACKNOWLEDGEMENTS

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