Mexican and ancient Peruvian textiles dyed with indigoids; Drs. David S. Reese and Robert Robertson for valuable malacological pointers, references, and samples of shells and dyes; Drs. Jacques Soyer and Jean Michel Amouroux of the Banyuls-sur-Mer (France) marine station, for providing research facilities to collect Murex glandular secretions; Drs. Sidney M. Edelstein and David H. Abrahams for an initial reference sample of DBI; Dr. Ann F. Rhoads for obtaining the seeds of woad and madder and growing the plants; Dr. Harold F. Goldfine for information on fermentation processes; and Pamela Hearne, acting Registrar of the University Museum of the University of Pennsylvania, and other members of the curatorial staff, for permission to sample textiles from Egypt, Turkey, and Peru in the museum's collections.

Registry No. Royal purple, 19201-53-7.

Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition-Metal Alkylidene Complexes

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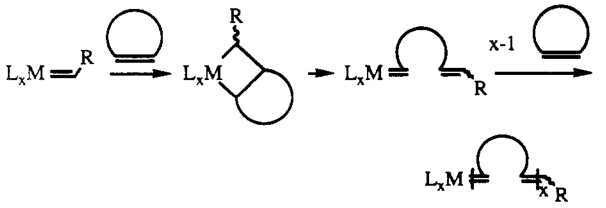
Organic polymers that have the narrowest possible distribution of molecular weights (a polydispersity approaching 1.00) can be prepared if the rate of initiation is approximately equal to or greater than the rate of propagation, each monomer unit adds irreversibly, and the rates of chain termination and chain transfer are slow on the time scale of the polymerization reaction itself.[1] Such "living" catalyst systems also allow one to add a second monomer after the first is consumed (or a third, etc.) to yield polymers that contain "blocks" of homopolymers connected to one another.[2] Although narrow molecular weight distributions and the ability to prepare block copolymers are not goals of all polymerization processes, only with such well-defined materials can one be as certain as possible about the polymer's molecular structure and size and, therefore, have the best opportunity to control bulk properties by variations at a molecular level. Surprisingly, living polymerization by transition-metal catalysts were virtually unknown until a few years ago when norbornene was polymerized in a living manner by ring-opening methathesis using a titanium catalyst.[3]

Ring-opening metathesis polymerization (ROMP) is the process shown in eq 1 (L_x denotes a generalized ligand coordination sphere). If the cyclic olefin is highly strained (e.g., norbornene), then the reaction is essentially irreversible. Ring-opening metathesis polymerization has been well-studied in systems that employ an empirically derived (here called "classical") Mo, W, or Re catalyst.[4] However, because of the high activity of most classical catalysts for the methathesis of ordinary olefins, the metal–carbon double bond at the end of the polymer chain reacts with carbon–carbon double bonds in the chain itself, either intramolecularly to give cyclic oligomers or intermolecularly to give linear oligomers. It is also generally true in classical systems that alkylidene complexes are generated in low yield and decompose over the course of a typical polymerization reaction.[4] All of these factors contribute to the formation of relatively broad molecular weight distributions if highly active metathesis catalysts are employed, and there is no possibility of preparing well-defined block copolymers.



(1)

Richard R. Schrock obtained his Ph.D. degree 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. du Pont de Nemours and Company, he moved to MIT, 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 of high oxidation state, early-metal complexes (especially those that contain an alkylidene or alkylidyne ligand), catalysis and mechanisms involving such species, the chemistry of high oxidation state dinitrogen and related complexes, and the controlled polymerization of olefins and acetylenes. He received the ACS Award in Organometallic Chemistry in 1985 and has been elected to the American Academy of Arts and Sciences.

The synthesis of relatively stable, well-defined alkylidene complexes for the metathesis of olefins has been perfected over the last decade.[5,6] I will focus on one type of catalyst here that contains molybdenum or tungsten, since the reactivity of such species toward olefins can be "tuned" accurately to the point where they become almost perfect ring-opening metathesis catalysts for highly strained monomers.

Catalyst Synthesis and Reactions Involving Ordinary Olefins

Although it has been known for several years that the metal should be in the highest possible oxidation state,[6] only relatively recently has it become possible to synthesize well-defined four-coordinate alkylidene complexes containing bulky ligands.[7] For molybdenum and

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(1) (a) Odian, G. *Principles of Polymerization*; Wiley: New York; 1981 (b) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. (c) Muller, A. H. E. In *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. 3, Chapter 26. (d) Swarc, M. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1983; Vol. 49.

(2) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic: New York, 1977.

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(4) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience, 1985.

(5) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249.

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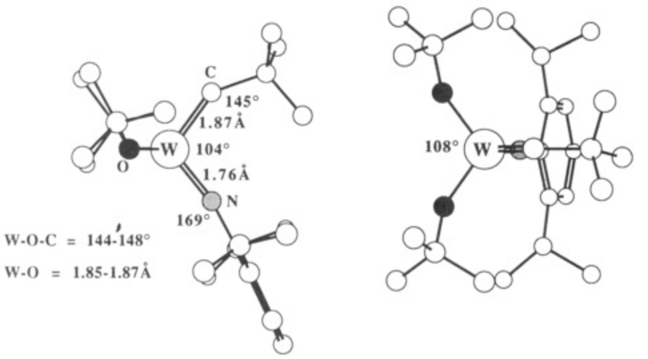
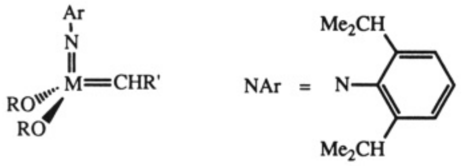
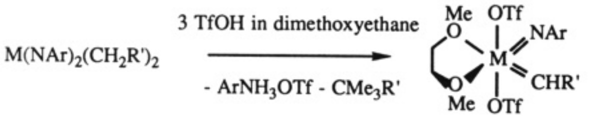


Figure 1. Two views of the structure of $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$.

tungsten, a suitable combination of ligands is two alkoxides and an imido ligand. Four-coordination allows relatively small substrate to attack the metal to give a five-coordinate intermediate metallacyclobutane complex, while bulky alkoxide and imido ligands prevent intermolecular reactions that would result in ligand scrambling to give inactive complexes or decomposition reactions that would destroy the alkylidene ligand.



Precursors to a wide variety of complexes now can be prepared readily as shown in eq 2 (M = Mo or W; R′ = *t*-Bu or CMe_2Ph; OTf = OSO_2CF_3).[8] One imido ligand is used as a "protecting group" in order to allow the required two alkyl ligands to be added to the metal selectively. It is then protonated and replaced by two triflate ligands. α-Hydrogen abstraction in the presumed intermediates, $M(NAr)(CH_2R')_2(triflate)_2$, must be fast. Their instability (in part) precludes their preparation by selective alkylation of monoimido species.



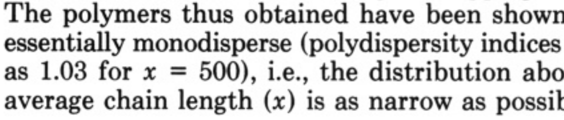
(2)

Addition of two bulky alkoxide or phenoxide ligands to $M(CHR')(NAr)(triflate)_2(dme)$ complexes results in loss of dimethoxyethane (for steric reasons) and formation of four-coordinate $M(CHR')(NAr)(OR)_2$ species. X-ray studies of $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$[7] and $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$[8a] (Figure 1) show them to be very similar pseudotetrahedral species in which the W=N—C angle is ~170° and the β-carbon atom of the alkylidene ligand lies in the same plane as N, W, and C_α and points toward the imido nitrogen atom (the syn rotamer). Complexes in which the alkylidene substituent points away from the imido nitrogen atom (the anti rotamer) have been observed in solution and have in several cases been shown to interconvert readily on the NMR time scale with the syn rotamer at 25 °C, presumably by simple rotation of the alkylidene ligand about the M=C bond.[8] The diisopropylphenyl imido ligand so far is the only one that has yielded relatively stable catalysts; it almost certainly plays a major role in slowing down bimolecular decomposition reactions and in directing steric interactions throughout these molecules and five-coordinate metallacyclobutane complexes formed from them.

The metathesis activity of $M(CHR')(NAr)(OR)_2$ complexes varies widely. For example, $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$[7] will metathesize *cis*-2-pentene at a rate of $\sim 10^3$ turnovers/min in toluene. In stark contrast, $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ will metathesize *cis*-2-pentene at a rate of only ~2 turnovers/h at 25 °C. This result is remarkable in view of the fact that these two species are virtually isostructural. The simplest explanation is that the metal–olefin interaction can be described as electrophilic attack by the metal on the olefin, and the metal is significantly more electrophilic in $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ than in $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. Quantitative studies of relative reactivities are complicated by the fact that complexes that contain relatively small alkylidene ligands (e.g., propylidene) not only are perhaps as much as 100 times more reactive than neopentylidene complexes but also are much less stable. The most prevalent mode of decompositon is not yet known, but evidence suggests that it is intermolecular. As expected on steric grounds, terminal olfins, and especially ethylene itself, react more rapidly than internal olefins. Metallacyclobutane intermediates have been observed in metathesis reactions, and several have been structurally characterized.[7,9]

Ring-Opening Metathesis Polymerization of Norbornenes and Norbornadienes

The key to controlled polymerization of norbornenes and 2,3–disubstituted norbornadienes is that while $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ complexes do not react readily with ordinary internal olefins, they do react rapidly with the strained double bond in norbornenes and norbornadienes. For example, $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ reacts with norbornene (presumably through the exo face of the olefin) even at −80 °C to give the living oligomers or polymers shown in eq 3 [**W**(CH-*t*-Bu) = $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$; *x* up to 500; the chain length in the oligomer is approximately a Poisson distribution about *x*]. These living polymers will react with aldehydes readily (e.g., benzaldehyde) to give the metal oxide in a Wittig-like capping reaction. The polymers thus obtained have been shown to be essentially monodisperse (polydispersity indices as low as 1.03 for *x* = 500), i.e., the distribution about the average chain length (*x*) is as narrow as possible, in-



(3)

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(7) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(8) (a) DePue, R. T.; Schrock, R. R.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics*, in press. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M.; Davis, W. M. *J. Am. Chem. Soc.*, in press.

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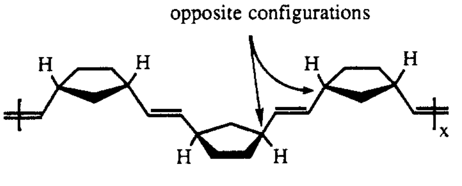
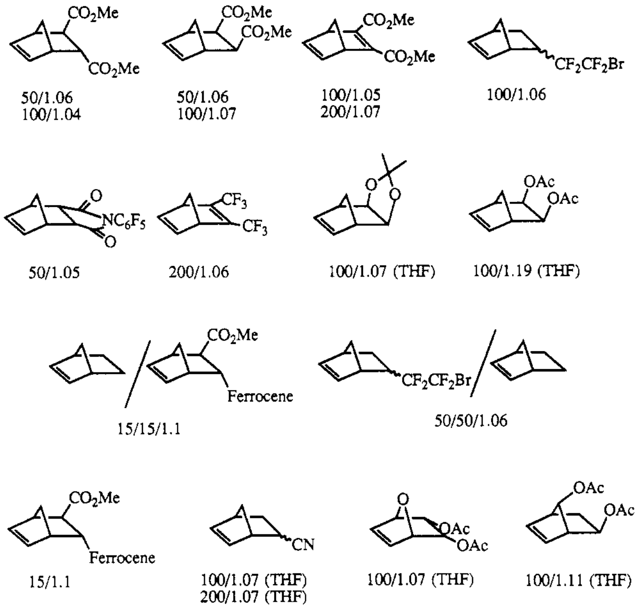
dicative of a well-behaved (irreversible) living polymerization.[10] The rate of initiation is slightly slower than the rate of propagation because of the bulky nature of the initial neopentylidene ligand, but the difference is not large and therefore does not broaden the molecular weight distribution detectably in the case of norbornene.[1b] The configuration about the first double bond in the polymer is solely trans, the polymer chain contains both cis (40%) and trans (60%) double bonds, and the Wittig reaction yields a double bond that is ~75% trans. Trans double bonds are generated in a metathesis step whenever norbornene adds to a M=C bond to yield a metallacycle in which the growing polymer chain and the norbornane skeleton are on opposite sides of the MC_3 ring. If both alkylidene rotamers are accessible, then the reaction is potentially more complicated, since their reactivities are not likely to be identical.

Additional stereochemistry in polynorbornene arises from the fact that two tertiary carbon atoms in norbornene [C(1) and C(4)] are chiral. Therefore norbornene can be opened to give a polymer in which the configurations of those two carbon atoms repeat along the chain [=(*R*,*S*)=(*R*,*S*)=(*R*,*S*)= is isotactic], alternate along the chain [=(*R*,*S*)=(*S*,*R*)=(*R*,*S*)= is syndiotactic], or do neither for any significant number of monomer units (atactic).[4a] Therefore any given olefinic carbon atom can be in a double bond that is either trans and racemic or meso, or cis and racemic or meso. Trans isotactic polynorbornene is one of four possible stereoregular polynorbornenes. In practice, tacticity in any polymer made from a norbornene employing any catalyst is rare.[4] Further substitution on the norbornene ring at a position unsymmetric with respect to the double bond creates the possibility of head-to-head (h,h), tail-to-tail (t,t), or head-to-tail (h,t) formation of the double bonds in the polymer, and a corresponding dramatic increase in stereochemical complexity.[4]

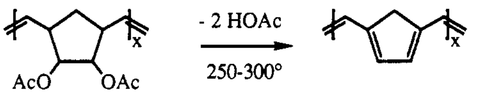


trans,isotactic

Chart I
Some Norbornenes and Norbornadienes That Can Be Polymerized by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Equivalents of Monomer/PDI)



Because of the ready availability of functionalized norbornenes by Diels–Alder reactions, it is highly desirable to be able to polymerize them to give a variety of low PDI homopolymers, or diblock or triblock copolymers. Tungsten does not appear to polymerize monomers than contain a variety of functionalities (Chart I) for reasons that are not yet clear, but molybdenum will.[11-14] (The 2,3 double bond in the 2,3-disubstituted norbornadiene derivatives is unreactive for steric reasons). PDIs are generally low for polymers containing up to several hundred monomer units. Some possible reasons why tungsten fails include the following: (i) the tungsten alkylidene reacts more readily with a given functionality or active protons in the polymer chain than molybdenum does; (ii) tungsten may be more sensitive to low levels of impurities than molybdenum; (iii) tungstacyclobutane rings may be relatively stable compared to molybdacyclobutane rings to the point where rearrangement of the tungstacycle becomes the rate-limiting step. One of the many potential uses for a functionalized polymer is as a percursor to an unsaturated system via elimination of one or more small molecules. The example shown in eq 4[11] is related to a method of synthesizing (for example) polyphenylene.[15]



(4)

Solvent is an important factor in ROMP of functionalized molecules. For example, it is not possible to polymerize 5-cyanonorbornene with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ *or* Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in a typical *noncoordinating* solvent such as toluene. In THF, however, Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ will polymerize 200 equiv of 5-cyanonorbornene rapidly to give a homopolymer with a polydispersity of 1.05, and 5-cyanonorbornene/norbornene diblocks with PDI = 1.05 (for a 100/100 diblock) have been prepared. THF may compete with the functionality for the metal and thereby inhibit a reaction between it and the alkylidene ligand. Another possibility is a bulk solvent effect that keeps the polar group pointed away from the metal into the solution. A third possibility is that THF is intimately involved in opening the intermediate metallacycles formed in these reactions.

An exciting recent finding is the high stereoregularity of a ring-opening reaction employing molybdenum.[12,13] 2,3-Bis(trifluoromethyl)norbornadiene is polymerized to give a polymer containing *only one of the four possible types* of olefinic carbon atoms (>98%) as deter-

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(10) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

(11) Bazan, G.; Cho, H.-N.; Schrock, R. R.; Gibson, V. C.; Feast, W. J.; Mitchell, J., unpublished results.

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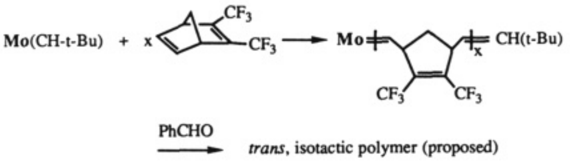
(13) Bazan, G.; Khosravi, E.; Schrock, R. R.; Gibson, V. C.; Feast, W. J.; O'Regan, M.; Thomas, J., submitted.

(14) Bazan, G.; Albagli, D., unpublished results.

(15) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1983**, 954.

mined by ^{13}C NMR. Observation of a melting point (200 °C) by differential scanning calorimetry confirms the crystalline nature of what is believed to be the first example of a stereoregular fluoropolymer. Upon following this reaction by ^{1}H NMR at low monomer levels, alkylidene proton resonances for each living oligomer [eq 5; **Mo**(CH-*t*-Bu) = Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$] where x = 1–4 or greater can be observed. Two nearly coincident alkylidene proton resonances are observed in a ratio of ~6:1 for the living oligomers in which x = 10 and 20, a result that suggests that both syn and anti alkylidene rotamers are present. However, whether rotamers are present or not does not preclude formation of a stereoregular polymer.[13] Tacticity results from addition of the norbornadiene double bond to the same face of the Mo═C bond, the one that is not blocked by trifluoromethyl groups, e.g., the front face in the syn rotamer shown below.



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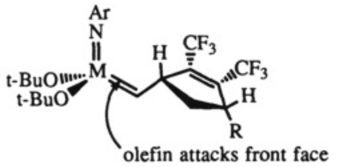
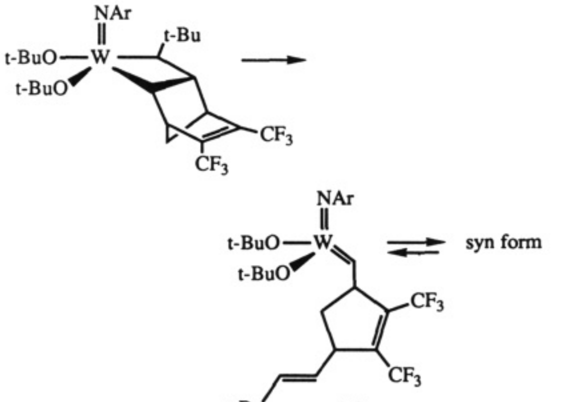


2,3-Bis(trifluoromethyl)norbornadiene is polymerized by W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to give a *low*-PDI polymer (PDI ≈ 1.2[12]). Addition of 1 equiv of this monomer to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ at −30 °C gives an unstable, but isolable, square-pyramidal metallacycle,[13] another demonstration of the greater stability of tungstacycles versus molybdacycles in general.[8] A low-temperature X-ray study of the unstable metallacycle showed it to be the one obtained by adding the exo face of the monomer to the syn rotamer of the neopentylidene complex, the only rotamer observable in that case (Figure 2, eq 6). Note that the imido ligand is oriented so that one isopropyl group partially blocks one face of the W═C bond and therefore forces the monomer to add to yield only the trans metallacycle (Figure 2, right view). The metallacycle is formed in a second-order reaction in which $\Delta H^\ddagger$ = 6.6 kcal mol^{-1} and $\Delta S^\ddagger$ = −40 eu. It rearranges in a first-order manner to give a mixture of the anti and syn forms of the "first insertion product" shown in eq 6 ($\Delta H^\ddagger$ = 22 kcal mol^{-1} and $\Delta S^\ddagger$ = −3 eu).[13] The anti rotamer most likely forms directly from the tungstacycle shown, while the syn rotamer is formed from the anti rotamer by rotation about the W═C bond.



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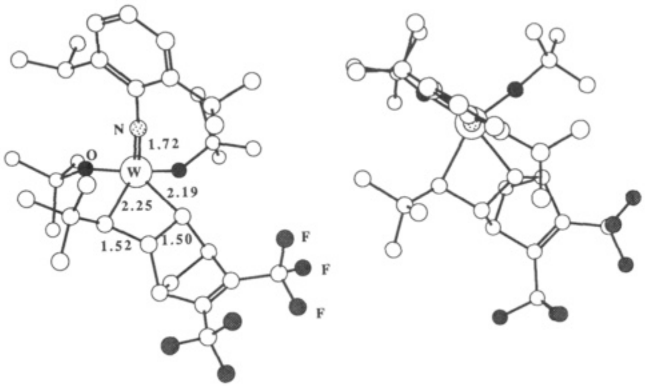


Figure 2. Two views of the tungstacycle made from W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 2,3-bis(trifluoromethyl)norbornadiene.

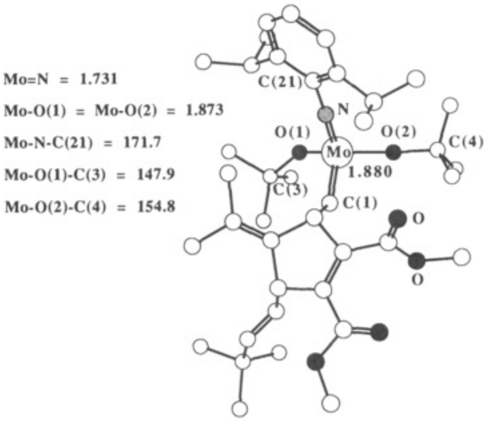
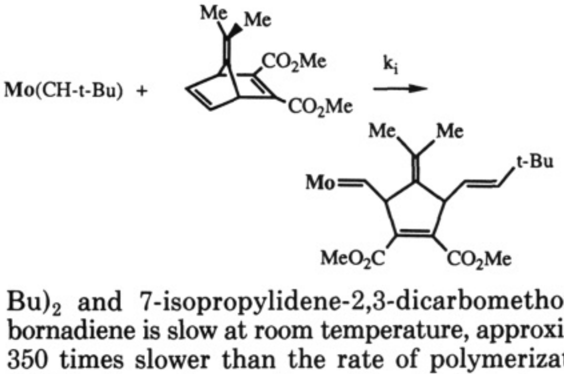


Figure 3. A view of the alkylidene complex made from Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 7-isopropylidene-2,3-dicarbomethoxynorbornadiene.

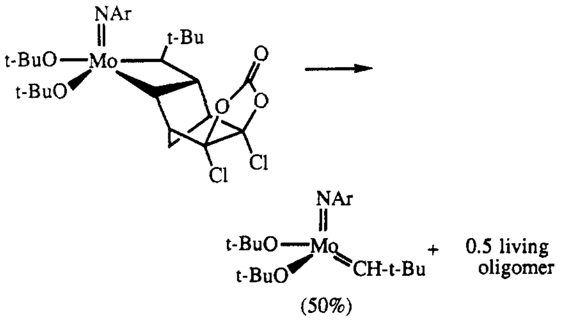
The rate of formation of a metallacycle should be greatly affected by substituents in the 7-position in a norbornadiene. An interesting example is shown in eq 7.[13] The reaction between Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 7-isopropylidene-2,3-dicarbomethoxynorbornadiene is slow at room temperature, approximately 350 times slower than the rate of polymerization of 2,3-dicarbomethoxynorbornadiene.[13] Only 1 equiv reacts readily, even at 40 °C, i.e., the rate of the "first insertion" step, although slow, is very much greater than the rate of the "second insertion" step ($k_p \approx 0$). The structure of this "first insertion" product was found to be syn (Figure 3). Note how the isopropylidene group protects one side of the Mo═C bond while a carbomethoxy group protects the other side. Therefore this alkyidene is much less reactive toward a second



(7)

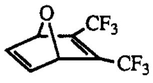
equivalent of the monomer than the initial neopentylidene complex is. Note that the terminal double bond is trans and that a carbonyl oxygen of a carbomethoxy group is *not* coordinated to the metal. Although functionalities have been observed to coordinate to the metal in metallacyclobutane complexes of this type,[9b] so far they have not been observed to coordinate in alkylidene complexes.

5,6-Dichloro-5,6-carbonatonorbornene reacts with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to give an observable metallacycle that we assume to have a structure analogous to that shown in eq 6 (eq 8).[16] When this metallacycle is heated, *the monomer is regenerated* to give ~50% of the starting neopentylidene complex. The liberated monomer then adds to the alkylidene that is formed when 50% of the metallacycle rearranges to give a living oligomer. This is the first observable circumstance where metallacycle formation is reversible for a norbornene. It is likely to be relatively rare, but encountered in related circumstances, i.e., whenever ring-opening is slow and the monomer is bulky.

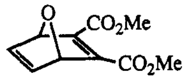


(8)

7-Oxanorbornadienes A, B, and C react with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to give isolable square-pyramidal *tert*-butyl-substituted metallacyclobutane complexes. That prepared from A is remarkably stable toward rearrangement to an alkylidene complex, that prepared from B is less so, and that prepared from C is the least stable. That prepared from C will rearrange slowly at 25 °C to give the expected "first insertion product". C can be polymerized (100 equiv) to a polymer with a PDI of 1.05, but only if the initial metallacycle prepared from 2–3 equiv of C is allowed to rearrange completely to the first insertion product before the remaining C is added. Evidently metallacycles that contain the growing polymer chain rearrange significantly more quickly than the initial one. (They have not yet been observed.) Therefore $k_i \ll k_p$ and the rate-limiting steps at 25 °C are different. Consequently a significantly higher polydispersity (~1.2) results if all the monomer is added to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ initially.



A



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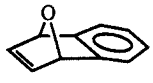


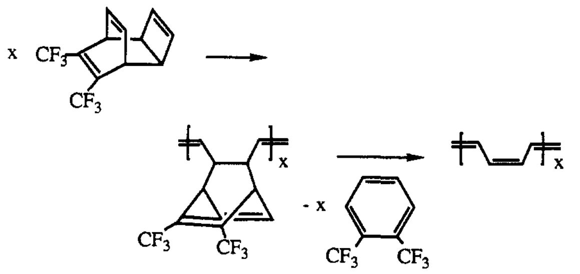
C

On the basis of available data, so far it appears that norbornenes that have substituents on carbons 5 or 6, or 2,3-disubstituted norbornadienes, are those that yield relatively stable metallacycles, and the initial (*tert*-butyl-substituted) metallacycle is *more* stable than subsequent metallacycles. Whether these findings can be ascribed to steric interactions in what might be called the "second shell" relatively far from the metal center, i.e., steric hindrance toward rearrangement to give the new alkylidene, or whether long-range electronic effects are also important, is not known at this time.

Two other areas of potential interest should be mentioned. The first is polymerization of norbornene-like monomers having transition or main-group metals, electroactive groups, etc., attached to them, especially if those groups are relatively bulky and unlikely to react with the sterically crowded catalyst. One example is the monomer than contains ferrocene shown in Chart I. Block copolymers containing it and 5-(trialkoxysilyl)norbornene have been prepared and attached to electrode surfaces.[14] It should now be possible to construct redox-active materials with specific morphologies and with prescribed dimensions. A second area of potential interest is chiral catalysts. Chiral catalysts might be prepared by using chiral diolates (tartrate derivatives, binaphtholates, etc.) or a chiral imido ligand. The ultimate achievement would be to polymerize one enantiomer in a racemic mixture to give a chiral polymer, leaving the other pure enantiomer behind. Although that particular circumstance would require a dramatic difference in the rate of polymerization of the two enantiomers (a difference in rate of at least 10^2), it now seems feasible and can be tested experimentally.

Preparation of Polyenes

An important application of ring-opening metathesis polymerization several years ago was the preparation of "polyacetylene" using the "precursor polymer" approach discovered by Feast.[17] 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT-F6) can be ring-opened by classical olefin metathesis catalysts to give a polymer from which hexafluoroorthoxylene is ejected upon heating to give polyacetylene (eq 9). This method has been employed to prepare oriented polyacetylene films by stretching the precursor polymer film before the retro-Diels–Alder reaction,[18] something that is not possible when classical "Ziegler–Natta" methods of preparing polyacetylene are employed.



(9)

It is possible, by using the *tert*-butoxide catalysts described here, to make a homologous series of polyenes that contain up to 15 double bonds by ring-opening TCDT-F6 in a controlled manner.[19] The method is

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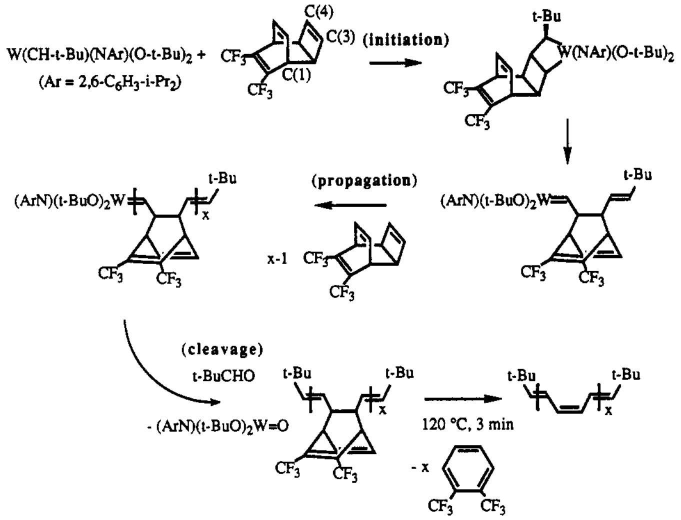
Scheme I
General Method of Preparing Polyenes



shown in Scheme I. The first double bond is trans, and trans propagation dominates (~75%). If pivaldehyde is used in the Wittig-like reaction, a series of "odd" polyenes containing $2x + 1$ double bonds results. If 4,4-dimethyl-*trans*-2-pentenal is used, then the resulting polyenes contain $2x + 2$ double bonds. Since evidence is accruing that relatively short conjugated sequences can sustain a soliton[20] and can have significant third-order nonlinear optical properties,[21] it is of fundamental interest to prepare well-defined unsubstituted polyenes. Interesting variations can be imagined, including capping with para-substituted benzaldehydes, or di- or trialdehydes.

Polyenes containing more than 17 double bonds could not be observed, only deep red to purple-black insoluble materials. The limit to polyene chain length could be the result of attack on the C(9)–C(10) double bond of TCDT-F6, a problem that would become more serious as more monomer is employed. However, one face to the C(9)–C(10) double bond should be protected by the bulk of the catalyst and the just-formed carbon–carbon double bond, while the other face should be protected to a large extent by the two trifluoromethyl groups. Analogous reactions involving the parent tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene *do* give relatively low yields of polyenes,[22] a result that we attribute to coupling that involves the now relatively unprotected double bonds in the bicyclic cyclohexadiene ring. (Coupling also was observed when TCDT was polymerized with classical catalysts.[17b]) Therefore it seems most likely that polyene chain length is not limited by coupling during preparation of polyTCDT-F6, or by some other quirk of the synthetic method, but by the inherent instability of long polyenes, which probably includes coupling of the relatively long members.

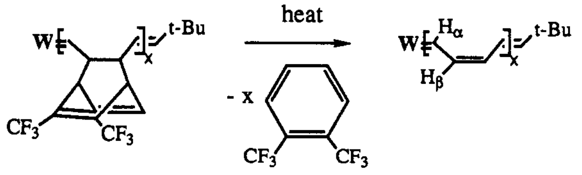
Polyenes have been prepared in diblock or triblock copolymers combined with polynorbornene.[23] For example, a triblock was prepared by adding x equiv of norbornene to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, followed by y equiv of TCDT-F6, and x equiv of norbornene again. Heating generated the polynorbornene/polyene/polynorbornene triblock. Between 10 and 30 of these macromolecules (depending on the polyene chain length) "aggregate" when the polyene block contains more than approximately 20 double bonds, a phenomenon that was ascribed to cross-linking of polyene chains. If enough TCDT-F6 is employed to generate a 50-ene in the triblock, then all of the macromolecules cross-link to yield dichloromethane-soluble red polymers with molecular weights approaching 500,000 (vs polystyrene). Ultimately, it may be possible to control the size of the cross-linked portion of such copolymers and to prepare polyenes in block copolymers that contain a wide variety of functionalities, redox centers (for self-doping), etc.

Another direction living TCDT-F6 technology could take is the generation of *isolated* polyenes diluted in a host polymer. Low concentrations of polyTCDT-F6 in homopolymer should be homogeneously dispersed, as should the polyene chains generated from polyTCDT-F6 if the retro-Diels–Alder reaction is carried out in the solid state. If such films can be oriented by stretching before the retro-Diels–Alder reaction, an anisotropic distribution of polyenes with a known distribution of chain length could be prepared. Such materials could be valuable in both fundamental and applied third-order nonlinear optical studies.

Other ring-opening polymerization reactions that give polyacetylene have been reported, one involving benzoTCDT (by a Ti catalyst[3]), one involving benzvalene[24] [by W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$], and other involving cyclooctatetraene[25] and substituted cyclooctatetraenes[26] [by the much more active W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ catalyst]. These reactions, especially the last, produce interesting and potentially useful materials, which may have interesting applications. However, at this stage these polymerization reactions do not appear to be as controllable as reactions involving TCDT-F6 and M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ catalysts.

Living Polyenes and the Polymerization of Acetylene

In the process of studying the formation of polyenes from polyTCDT-F6, it was discovered that the retro-Diels–Alder reaction could be carried out *before* the polyTCDT-F6 was cleaved off the metal in the Wittig-like reaction [eq 10; W = W(NAr)(O-*t*-Bu)$_2$] if x = 3. These " living polyenes" (in which the average number of double bonds in the chain is approximately seven) are stable at 50 °C for 45 min in solution at a



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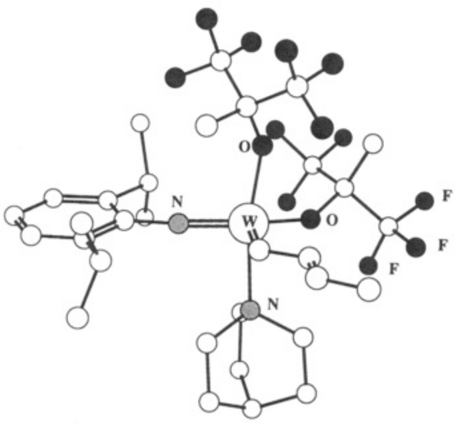
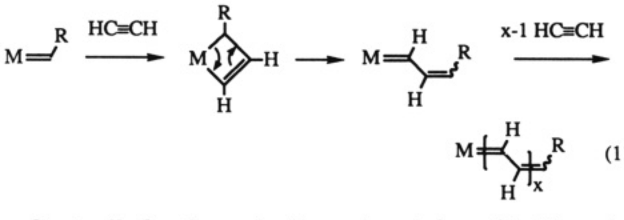


Figure 4. A view of the structure of W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$(quinuclidine).

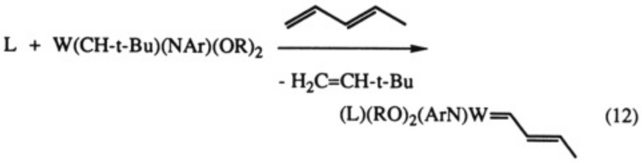
concentration of ~0.1 M or less. *No benzene is formed.* Therefore we felt that it might be possible to prepare them directly from acetylene in a reaction that is related to a ring-opening reaction (eq 11). There is good evidence in the literature that this type of polymerization reaction should be possible under the right circumstances.[27,28]



(11)

Controlled polymerization of acetylene (3–13 equiv) has now been accomplished employing W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in toluene in the presence of 5 equiv of quinuclidine.[29] After addition of excess pivaldehyde, HPLC analysis showed that the di-*tert*-butyl-capped polyenes (*t*-Bu)(CH=CH)$_x$(*t*-Bu) (x = 3–9) had been formed, the predominant polyenes being the all-trans forms containing three to nine double bonds. Again no other organic products, including benzene, could be detected by NMR or HPLC techniques. The most straightforward explanation is that quinuclidine binds to a significantly greater extent for steric reasons to the metal in a living polyene oligomer, W[(CHCH)$_x$(CH-*t*-Bu)](NAr)(O-*t*-Bu)$_2$, than to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and thereby slows the rate of propagation significantly more than initiation. Triblock copolymers (50 equiv of NBE at each end) can be obtained with molecular weights and polydispersities that are similar to those of the triblocks prepared by using TCDT-F6 noted above. Polymerization of more than 9 equiv of acetylene by tungsten does not appear to be well-behaved, perhaps because of destructive side reactions. However, preliminary results suggest that similar block copolymers prepared by employing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and up to 15 equiv of acetylene give bimodal distributions of macromolecules and "aggregates" that are similar to materials prepared by using the TCDT-F6 route.[30] Therefore it appears that side reactions between acetylene and molybdenum intermediates may be significantly slower than in the case of the tungsten catalyst. The controlled polymerization of acetylene and the prospect of controlling polymerization of terminal and internal acetylenes expand the possible combinations and permutations of monomers to be used in block copolymer synthesis employing well-defined ROMP catalysts.

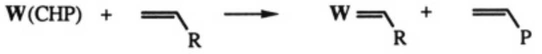
Vinyl alkylidene complexes can be prepared as shown in eq 12 [OR = OCMe$(CF_3)_2$ or OCMe$_2(CF_3)$; L = quinuclidine or PMe$_2$Ph].[31] Each product consists of two isomers in solution. One isomer that crystallized out when L = quinuclidine and OR = OCMe$(CF_3)_2$ was shown by an X-ray study to be an adduct of an anti vinyl alkylidene complex (Figure 4). Note that the base has added to the O/C/N face of tetrahedral anti W(*trans*-CHCH=CHMe)(NAr)[OCMe$(CF_3)_2$]$_2$ and that the phenyl ring of the imido ligand now lies in the equatorial plane. When the anti isomer is put back into solution, it is converted slowly into an equilibrium mixture containing ~35% of the anti isomer and 65% of what is believed to be an analogous TBP syn species. An analogous reaction involving *cis*-1,3-pentadiene produces a second set of syn and anti isomers. These complexes are similar (by NMR) to the quinuclidine adducts observed in the acetylene polymerization reaction discussed above and lend support to the proposal that living polyenes are formed under those circumstances.



(12)

Chain Transfer in ROMP Reactions

It is crucial for the long-term application of *tert*-butoxide catalysts for ring-opening polymerizations that some way be found to transfer the chain and re-form a reactive alkylidene complex (eq 13; P = polymer), instead of capping the chains and sacrificing the catalyst by treating the living polymer with an aldehyde.[32] The chain-transfer reaction must be rapid and go to completion, and the new alkylidene must be stable yet reactive. Preliminary experiments show that 1,3-pentadiene and (especially) styrene fulfill these criteria for polynorbornene employing the molybdenum catalyst.[33] In fact, it is possible to add excess styrene to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and then pulse the system 10 times with 80 equiv of norbornene, waiting for chain transfer to be complete after addition of each 80 equiv. The resulting polynorbornene has the correct molecular weight for a 100-mer and a polydispersity of 1.14. The



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success of many-step pulsed chain transfer will depend critically on the relative reactivity of the cyclic monomer and the chain-transfer agent and will be limited by impurities in the feed, by eventual slow decomposition of intermediates, and by incomplete chain transfer.

Concluding Remarks

Several features of these well-defined Mo and W alkylidene catalyst systems should be emphasized in closing. First, all five-coordinate metallacyclobutane intermediates are likely to be distorted significantly from ideal TBP or SP forms, both because of the bulky nature of the ligands and because of the strong electronic perturbations caused by the different ligands, especially by the imido ligand. A given distorted five-coordinate species should be able to rearrange relatively easily to another distorted species. Therefore a variety of readily interconvertible intermediate metallacyclobutane complexes should be accessible on the time scale of a polymerization reaction. Second, steric interactions in the coordination sphere well away from the metal center in four- or five-coordinate complexes probably can be as important as interactions near the metal in the primary coordination sphere. They apparently slow down ring-opening polymerization overall and, in the process, discriminate effectively between various reaction pathways. The fact that 5,6-disubstituted norbornenes and 2,3-disubstituted norbornadienes form relatively stable metallacyclobutane intermediates could be ascribed to a slowing down of the core rearrangement that is required prior to formation of the next alkylidene ligand. Third, all ligands except reactants and products are covalently bound to the metal. Therefore steric and electronic effects of the ligands that control reactivity and stereochemistry are maintained throughout the catalytic cycle, a circumstance that should be more successful relative to one in which catalysts contain labile donor ligands.

Living polymerizations that are as controlled as the ring-opening polymerizations discussed here are extremely rare. The fact that many functionalities can be tolerated by molybdenum catalysts, a wide variety of norbornenes and norbornadienes are readily available by Diels–Alder reactions, and acetylenes have some potential as comonomers in such systems creates the potential for applying this technology in a variety of interesting ways. Related catalysts based on rhenium[34] have been developed[35] that may be even more tolerant of functionalities and allow even more control over ring-opening reactions of highly strained monomers. Discovering the nature and controlling the reactivity of ROMP catalysts that contain later transition metals such as ruthenium[4a,36] remains a challenging goal, but one that now appears to be within reach.

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Localized Cyclic Triplet Diradicals. Lifetime Determination by Trapping with Oxygen

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Diradicals play a crucial role in photochemistry in that they constitute the link between covalent bonds, i.e., maximum electronic interaction, and "double radicals", i.e., no interaction of the odd electrons.[1] The lifetimes and chemical reactivity of triplet diradicals generally are governed by the relatively slow triplet–singlet intersystem crossing (ISC) to the singlet states, which in turn usually undergo rapid collapse to products. However, given sufficiently long lifetimes, both triplet and singlet diradicals will undergo chemical trapping. The quantitative study of the trapping of

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