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## Chemistry of Bimetallic Linked Cyclopentadienyl Complexes

Progress report for the period 12/1/86 - 11/30/89

and

Publications appearing during grant period (page 18)

by

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## Progress Report

For the past several years this research project has been devoted to the chemistry of bimetallic cyclopentadienyl complexes, in particular homo- and heterobimetallic complexes containing peralkylated cyclopentadienyl rings linked via a relatively flexible CH<sub>2</sub>CH<sub>2</sub> bridge. The rationale was that two linked metals could behave cooperatively in catalytic reactions in ways that cannot be duplicated in systems containing monometallic catalysts. Most recently we have focused on *permethyl* linked cyclopentadienyl complexes containing two tungstens or one tungsten and a Group 8 or 9 metal (Co, Rh, or Ru). A variety of approaches toward this goal have been employed, all of them utilizing the tungstacyclobutadiene complex W(C<sub>3</sub>Me<sub>3</sub>)Cl<sub>3</sub>.<sup>1</sup> Several routes to bimetallic species are possible employing free MeC≡CCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>H or a complex containing the η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>C≡CMe ligand. A full paper describing these results is in press in *Inorganic Chemistry* (see separate package), so a description of the findings will not be repeated here. This paper will be the final publication of work on this subject from this laboratory, since although we have searched for several years for "linked cyclopentadienyl" chemistry that is unique, we have not found any. In fact, unpublished results of several experiments designed to test the efficacy of "linked cyclopentadienyl" chemistry analogous to known chemistry of "unlinked cyclopentadienyl" complexes indicate that employing a linked cyclopentadienyl ligand of the type we have chosen may be detrimental rather than helpful. The most important of these results is that attempted reduction of [W(triflate)Me<sub>3</sub>]<sub>2</sub>(η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>) with sodium amalgam in a manner analogous to that used to prepare [WCp\*Me<sub>3</sub>]<sub>2</sub>(μ-N<sub>2</sub>)<sup>2</sup> did not yield [WMe<sub>3</sub>]<sub>2</sub>(η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>)(μ-N<sub>2</sub>). In fact, we could not identify any product. We suspect that the energy required to orient the bimetallic system in a manner conducive to bimetallic reactions is too large (for steric reasons), and that intermolecular reactions (between two bimetallic complexes) related to what happens in analogous Cp\* systems therefore are favored. We cannot conclude that this approach is not valid in general, only that our choice of linking ligand was not ideal.

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(1) Latham, I. A.; Sita, L.R.; Schrock, R. R. *Organometallics* **1986**, *5*, 1508.

(2) (a) W. Finch, results to be published. (b) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557.

Nevertheless I have become relatively pessimistic as far as the future of the bimetallic approach is concerned, and therefore decided to turn to another area of increasing interest to me and my group that has no sponsor at this time, and that we already have demonstrated should produce more results of immediate interest.

Approximately three years ago we discovered how to prepare well-characterized alkylidene complexes of tungsten and molybdenum, and more importantly, how to control their activity for olefin metathesis and related metathesis reactions.<sup>3</sup> This led to their development as catalysts for the controlled (living) ring-opening of cyclic olefins.<sup>4</sup> This unique opportunity in polymer chemistry was sponsored in the beginning by the Division of Materials Research of the NSF as part of a collaboration in the Center for Material Science and Engineering at MIT. This program has evolved into studies of morphologies of block copolymers in collaboration primarily with Professor Robert Cohen in the Department of Chemical Engineering and Professor Mike Rubner of the Department of Material Science. Other projects took shape. One involving the ring-opening metathesis polymerization of functionalized norbornene-like derivatives is now being funded by the Office of Naval Research. Approximately halfway through the last DOE grant period Dr. Konrad Knoll, a NATO Postdoctoral Fellow, used some of these catalysts to develop a polymerization route to relatively long polyenes (up to 15 double bonds) having an unsubstituted backbone. This project was very successful and is continuing to develop into a full-fledged research area of significant promise. It is this area of research for which I am asking to be supported. Two publications already are in press that acknowledge DOE support for this work (see Attachment). The rest of this section describes and summarizes some of what has been accomplished.

Feast<sup>5</sup> discovered that tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-trienes (e.g., the 7,8-

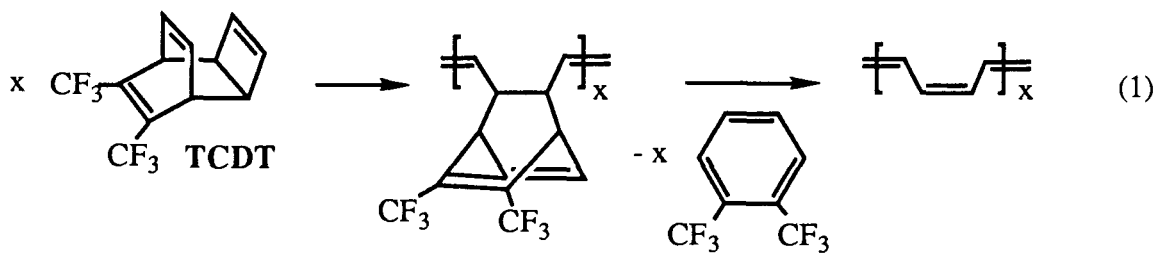
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(3) (a) Schrock, R. R. *J. Organometal. Chem.* **1986**, *300*, 249. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (c) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (d) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(4) (a) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169. (b) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243. (b) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(5) (a) Bott, D. C.; Brown, C. S.; Edwards, J. H.; Feast, W. J.; Parker D.; Winter, J. N. *Mol. Cryst. Liq. Cryst.*

bis(trifluoromethyl) derivative, TCDT) and related molecules can be ring-opened by classical olefin metathesis catalysts<sup>6</sup> to give a polymer from which an arene is ejected upon heating to give polyacetylene (equation 1). This method was an important breakthrough in polyacetylene research



since it could be employed to prepare oriented polyacetylene films by stretching the precursor polymer film before the retro-Diels-Alder reaction,<sup>7</sup> a significant advantage over classical "Ziegler-Natta" methods of preparing isotropic polyacetylene.<sup>8</sup> Since it had been shown that well-characterized catalysts of the type  $M(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$  ( $M = \text{Mo}$  or  $\text{W}$ ;  $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-i-Pr}_2$ ) would ring-open polymerize norbornenes in a controlled manner — three other well-characterized catalysts based on  $\text{Ti}$ ,<sup>9</sup>  $\text{Ta}$ ,<sup>10</sup> and  $\text{W}$ <sup>11</sup> will also ring-open polymerize norbornenes —

1985, 117, 9. (b) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* 1984, 25, 395. (c) Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* 1985, 202.

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(7) (a) Kahlert, H.; Leising, G. *Mol. Cryst. Liq. Cryst.* 1985, 117, 1. (b) Montaner, A.; Rolland, M.; Sauvajol, J. L.; Galtier, M.; Almairac, R.; Ribet, J. L. *Polymer* 1988, 29, 1101. (c) Perego, G.; Lugli, G.; Pedretti U. *Mol. Cryst. Liq. Cryst.* 1985, 117, 59.

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(9) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* 1986, 108, 733. (b) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* 1988, 21, 1961. (c) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* 1987, 20, 1488.

(10) (a) Wallace, K. C.; Schrock, R. R. *Macromolecules* 1987, 20, 448. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* 1988, 110, 4964.

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M(CH-t-Bu)(NAr)(O-t-Bu)<sub>2</sub> catalysts were thought to be good candidates for polymerizing (more accurately oligomerizing) TCDT in a controlled manner, thereby making it possible to prepare a distribution of polyenes whose lengths differ by four carbon atoms. This has been a highly successful approach.<sup>12</sup>

The general method for preparing polyenes is shown in Scheme I. The technique is based on the selective formation of a tungstacyclobutane ring employing the cyclobutene double bond in TCDT, presumably through the *exo* face of the C(3)-C(4) double bond. Intermediate tungstacyclobutane complexes are not observed. (Metallacycles also have not yet been observed in the case of norbornene polymerization with catalysts of this general type,<sup>4</sup> although tungstacycles made from norbornene *have* been observed in related tungsten catalyst systems,<sup>11b</sup> and both tungstacyclobutane and molybdacyclobutane complexes have been observed in reactions between substituted norbornenes and norbornadienes and catalysts of this general type.<sup>13</sup>) In this system the t-butyl group in the initial metallacycle must be exclusively *trans* to the norbornane ring system since this initial tungstacyclobutane complex rearranges to a new alkylidene complex (the "first insertion product") which has a *trans* terminal double bond. The new alkylidene complex can then react with another equivalent of TCDT to give a new tungstacyclobutane complex, etc., until a living polymer results (**1** in Scheme I) that contains on the average *x* equivalents of TCDT in ring-opened form. Each of the propagation steps can produce either a *cis* or a *trans* double bond, although *trans* propagation dominates (~75%). The organic oligomer is then cleaved from the metal in a quantitative Wittig-like reaction between the W=C bond and an aldehyde. The last step is a retro-Diels-Alder reaction that generates hexafluoroorthoxylene. The reaction mixture is then filtered through silica gel to remove W(O)(NAr)(O-t-Bu)<sub>2</sub> and unreacted aldehyde. If pivaldehyde is used in the Wittig-like reaction, the result is a series of "odd" polyenes containing 2*x*+1 double bonds. If 4,4-dimethyl-*trans*-2-pentenal is used then a series of "even" polyenes containing 2*x*+2

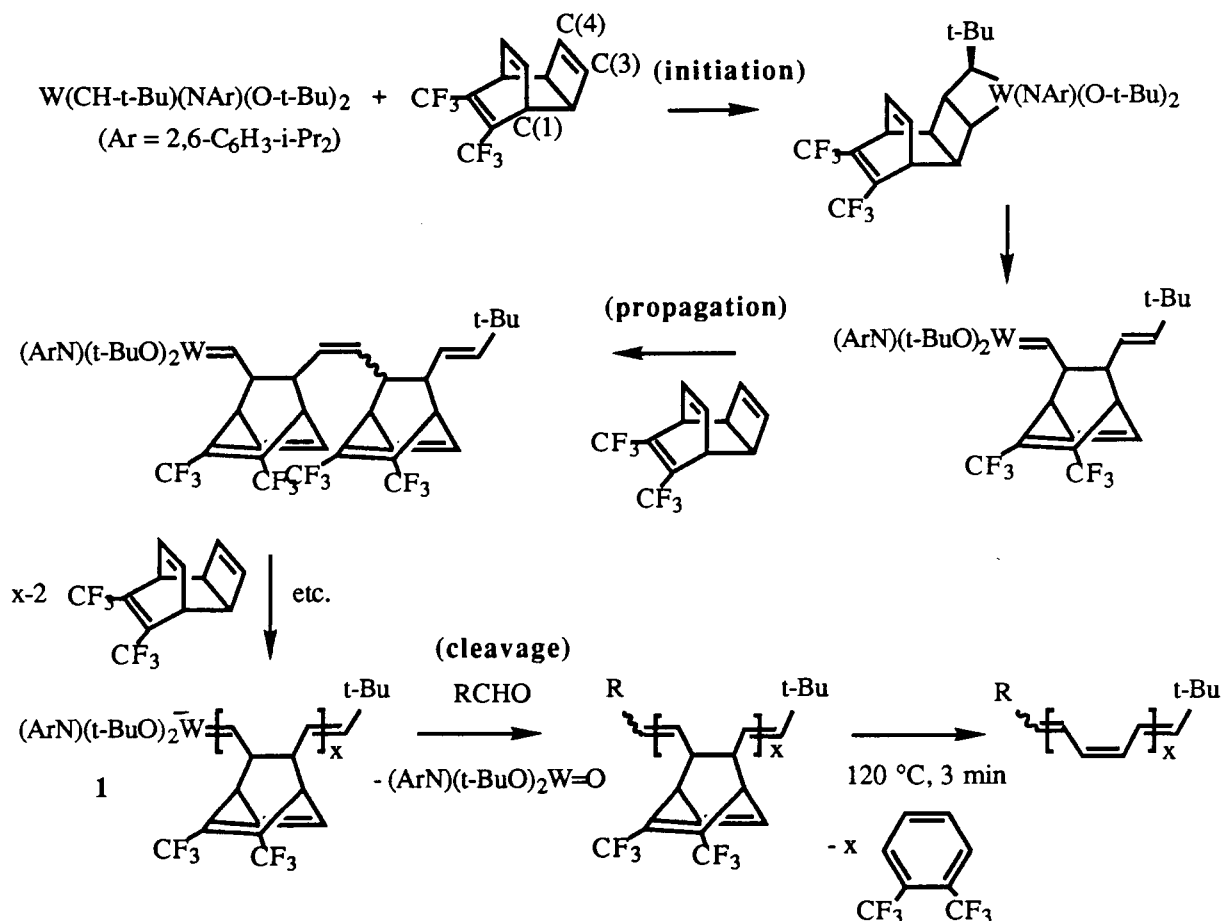
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(12) (a) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424. (b) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885. (c) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.*, in press (see Attachment).

(13) G. Bazan, unpublished results.

double bonds is formed. The total yield of the crude mixture of odd polyenes generated using 3-4 equiv of TCDT is high (>90% by weight) under "standard" conditions (3 min at 120 °C for the retro DA reaction).

Scheme I. General method for preparing polyenes.



An essential analytical tool for analyzing polyenes and polyene mixtures is reversed phase hplc in conjunction with a UV/Vis diode array detector operating in the range 240-600 nm using guaiazulene as an internal standard. The solvent is initially a 90:5:5 mixture of acetonitrile, dichloromethane, and water. After 30 min, water is removed over a period of 30 min and substituted with acetonitrile. Complete UV/Vis spectra are accumulated every 1.6 sec and correlated with the various peaks in the hplc trace. Although the extinction coefficients of the various length polyenes and the different isomeric forms differ significantly, relative yields of



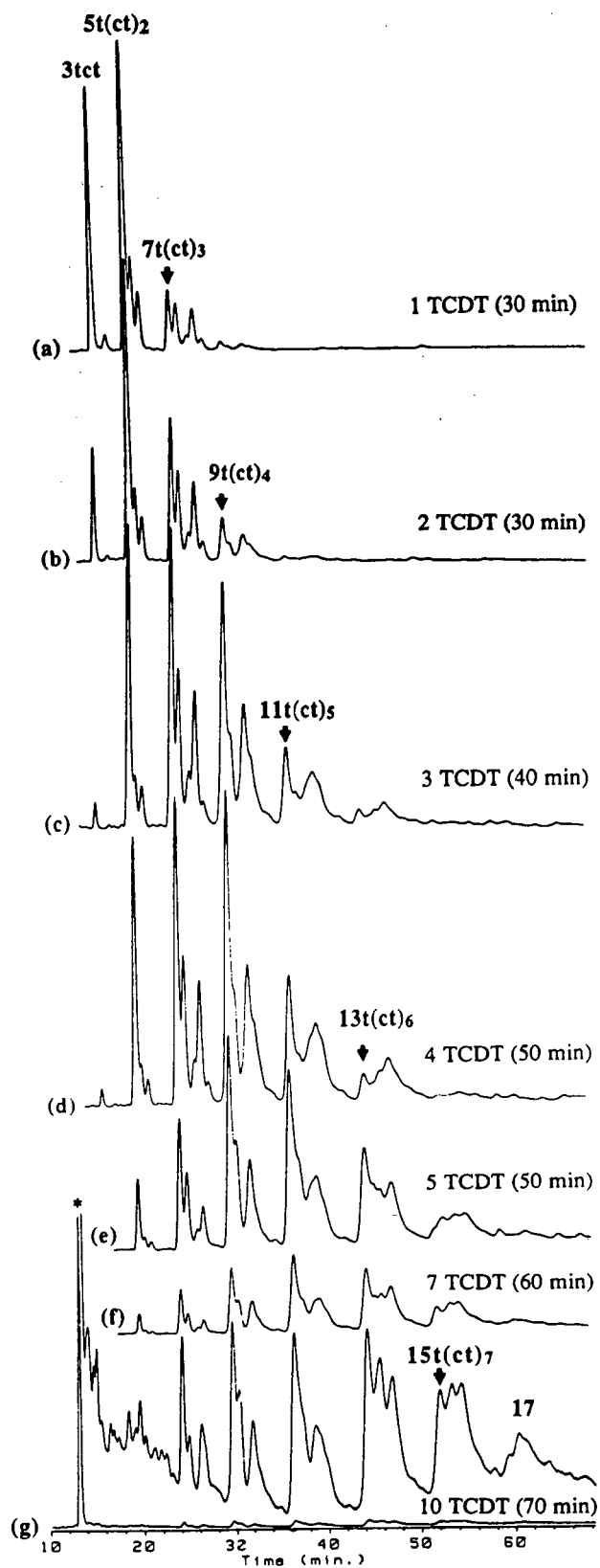
polyenes can be determined by integration, and many isomers can be identified by their absorption spectra. Many polyenes also have been isolated relatively pure by adsorption chromatography on silica gel at  $-40\text{ }^{\circ}\text{C}$  under dinitrogen and identified by exhaustive NMR and UV/Vis studies and correlation with hplc studies of complex mixtures.

Hplc results for odd polyenes prepared under standard conditions employing from 1 to 10 equiv of TCDT are shown in Figure 1. Under these conditions the odd polyenes of different lengths (but still mixtures of isomers) are separated cleanly from one another. Longer chains are produced when more TCDT is employed. However, note that (i) the maximum length polyene observable under these conditions appears to be the 17-ene, and (ii) the total yield employing 10 equiv of TCDT is very low (Figure 1g), even though the patterns of the distribution of observable polyenes is virtually the same as when fewer equivalents of TCDT are employed. The absolute yields of any given length polyene are plotted versus the number of equivalents of TCDT employed in Figure 2 (bottom) and the total yield in Figure 2 (top). For  $x$  equiv of TCDT the polyene with the maximum yield has a length slightly greater than  $2x+1$ , approximately  $2x + 3$ . For example, the yield of the 11-ene maximizes using only 4 equiv of TCDT. These results suggest that the rate of propagation is slightly faster than the rate of initiation, so that polyenes that are slightly longer than one would otherwise predict on the assumption that  $k_p \approx k_i$  and that the distribution can be predicted by the Poisson equation<sup>14</sup> are produced. Note that the total yield maximizes when 3 equiv of TCDT have been added. One possibility for the drop in polyene yield and the failure to observe any polyenes longer than the 17-ene is that the relatively long polyenes decompose (perhaps cross-link with each other) progressively more readily when they contain more than  $\sim 15$  double bonds.

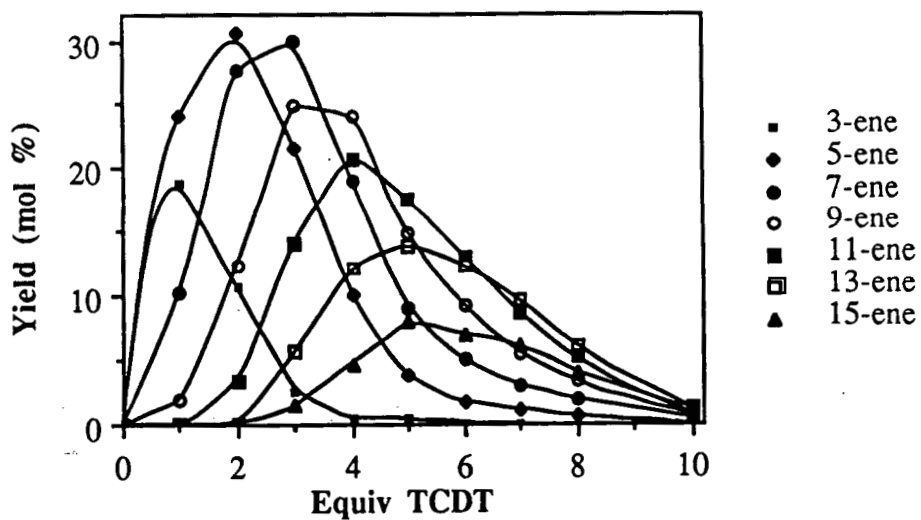
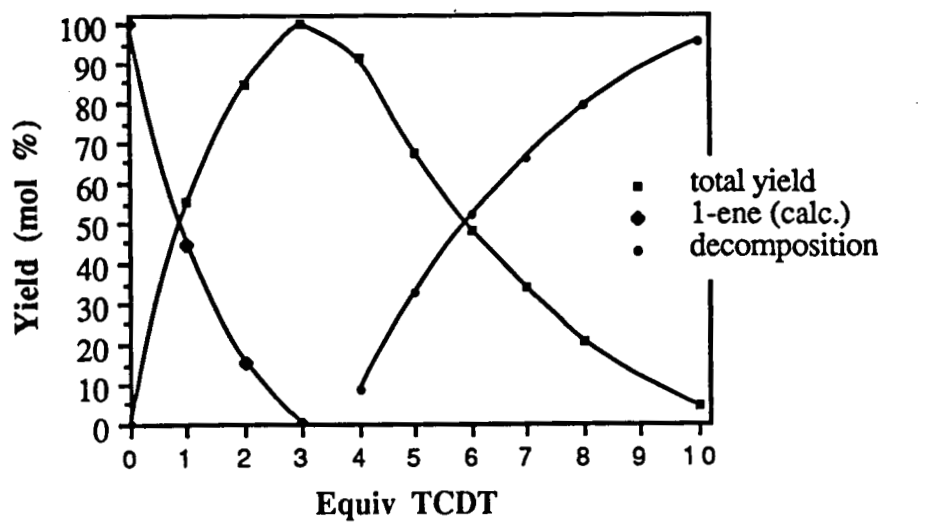
A major polyene isomer of a given length containing up to 11 double bonds can be separated from the other isomers with that chain length and from polyenes with other chain lengths in the crude mixture by adsorption chromatography on silica gel at  $-40\text{ }^{\circ}\text{C}$  under dinitrogen. The

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(14) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.

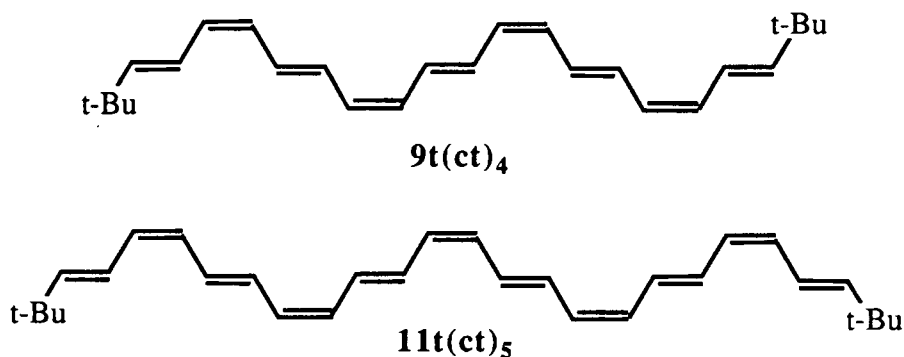


**Figure 1.** Hplc traces of odd polyenes prepared under standard conditions (120 °C / 3 min retro Diels-Alder reaction) employing from 1 to 10 equiv TCDT (\* = guaiazulene internal standard; times in parentheses are reaction times before quenching).



**Figure 2.** Absolute yields of odd polyenes (mixture of initial isomers; *trans*-di-*t*-butylethylene excepted) under standard conditions: individual polyenes (bottom); total polyenes (top).

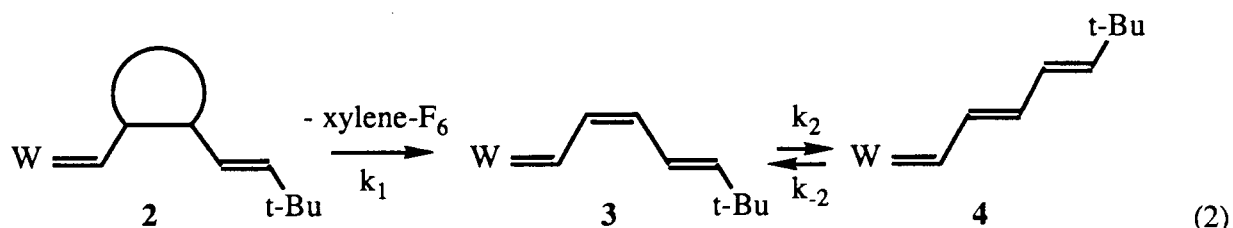
polyene mixtures must be generated under the standard conditions mentioned above and 3-4 equiv of TCDT must be employed for the best total yields. (Decreased yields are necessary in order to prepare the longer polyenes.) The isomer that is formed in largest amounts for the 3, 5, 7, 9, and 11-ene, and the one that elutes first by reversed phase hplc for all chain lengths (see Figure 1), also happens to be the one that elutes first in macro-scale column chromatography. It is the



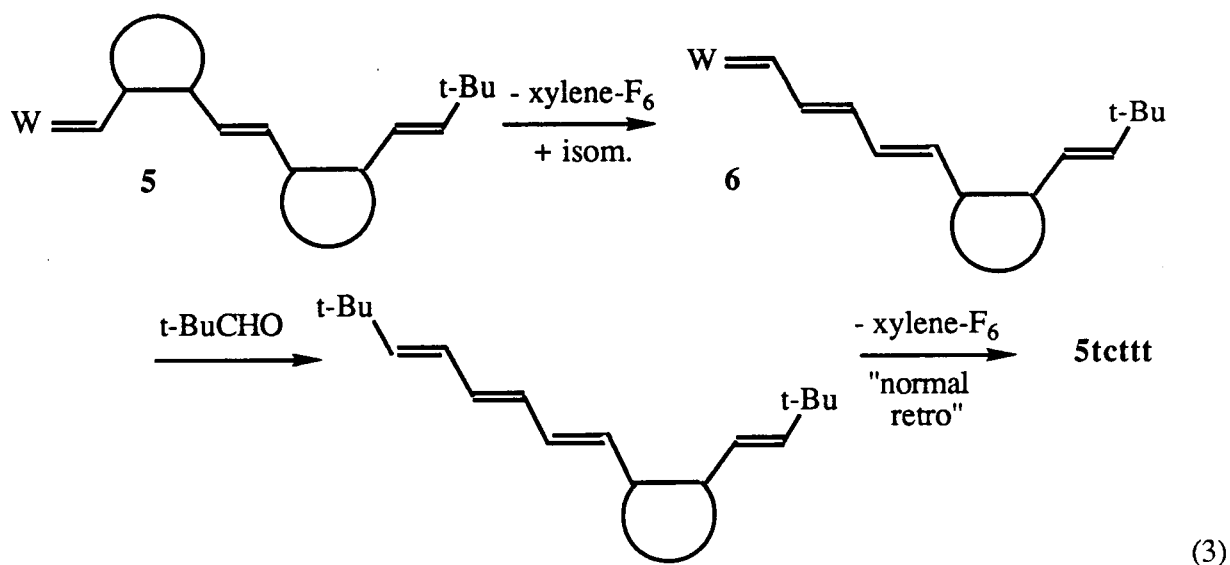
*trans(cis,trans)<sub>x</sub>*, or *t(ct)<sub>x</sub>*, or "alternating form" having either  $C_{2h}$  symmetry (e.g., **9t(ct)<sub>4</sub>** containing 9 double bonds) or  $C_{2v}$  symmetry (e.g., **11t(ct)<sub>5</sub>** containing 11 double bonds). Yields of the isolated alternating form can be as high as 60% (if the polyenes are relatively short). Another isomer or two of the 5-ene and the 7-ene could be identified by proton and carbon NMR as a small fraction in this leading cut. The number of isomers was too great for the 13-ene and the yields also too low for the 13 and the 15-ene to identify any but the alternating form by its UV/Vis spectrum in hplc studies. Mixtures of isomers of a given chain length each could be transformed into a mixture containing *trans*-rich isomers and ultimately into the pure all *trans* isomers (e.g., **7t<sub>7</sub>**, **9t<sub>9</sub>**, **11t<sub>11</sub>**, etc.) by various methods.

Polyenes containing an even number of double bonds can be prepared by adding 4,4-dimethyl-*trans*-2-pental (1.5 equiv) to the mixture of "living polyTCDT" alkylidene complexes, followed by heating to promote the retro DA reaction. The Wittig-like cleavage reaction is not *trans* selective in this case, presumably because 4,4-dimethyl-*trans*-2-pental is considerably less bulky than pivaldehyde near the carbonyl group, and so mixtures result that are roughly twice as complicated as mixtures of polyenes that contain an odd number of double bonds.

If solutions of living polyTCDT are allowed to stand or are heated before aldehyde is added, polyenes are formed that largely have three *trans* double bonds at the end of the chain. The reaction that accounts for these results is most clearly illustrated for **3t<sub>3</sub>** as shown in equation 2. An accelerated retro DA reaction takes place near the metal followed by a facile isomerization of the first C=C bond. Subsequent reaction of **4** with pivaldehyde would give **3t<sub>3</sub>**. If a solution of



living polyTCDT is stood for 270 min, and the oligomer is cleaved from the metal with pivaldehyde, but *not* heated to promote the retro DA reaction, then virtually only **3tct** and **3t<sub>3</sub>** are observed (no other polyene), since the only significant retro DA reaction occurs in the first unit away from the metal, but only the reaction shown in equation 2 produces an actual polyene. For example, the sequence shown in equation 3 (or related sequences) would not yield a polyene until the mixture is heated to 120°C where the "normal" retro DA reaction occurs.



If we assume that the sequence of reactions that give **3tct** and **3t<sub>3</sub>** is that shown in equation 2, and that **3** and **4** are in equilibrium, then it is possible to extract  $k_1$ ,  $k_2$ , and  $k_{-2}$  by modeling the reaction using data from time dependent hplc studies. The extracted values (at 24 °C) are  $k_1 = 6.5 \times 10^{-3} \text{ min}^{-1}$ ,  $k_2 = 1.7 \times 10^{-2} \text{ min}^{-1}$ , and  $k_{-2} = 5.1 \times 10^{-3} \text{ min}^{-1}$ . It is also possible to determine the rate of the retro DA reaction in the second TCDT unit away from the metal (e.g., in **6** in equation 3) by following the appearance of isomers of the 5-ene. The rate constant for this retro reaction is approximately  $6 \times 10^{-4} \text{ min}^{-1}$ . Therefore the retro Diels-Alder reaction in the first TCDT unit away from the metal is about 10 times faster than in the second TCDT unit. We assume for now that the rate of the retro DA reaction in the second monomer unit away from the metal does not differ significantly from that further out in the chain, or in a system free of metal, although additional studies will be required to prove this point.

500 MHz <sup>1</sup>H NMR studies of W(CH-t-Bu)(NAr)(O-t-Bu)<sub>2</sub> plus 1, 2, or 3 equiv of TCDT are shown in Figure 3. Addition of 1 equiv of TCDT to W(CH-t-Bu)(NAr)(O-t-Bu)<sub>2</sub> converts about half of it to an approximately 1:1 mixture of the "first insertion" product (**2**, equation 2) and the "second insertion" product (**5**, equation 3), plus a small amount of higher oligomers, on the basis of the intensities of the alkylidene proton resonances around 8 ppm (Figure 3a). The doublet at ~8.08 ppm can be ascribed to that for the alkylidene proton in the first insertion product on the basis of the fact that it is the first to appear, and that it decreases upon addition of a second equivalent of TCDT (Figure 3b). The doublet at ~7.93 ppm must be due to the alkylidene proton in the second insertion product. Resonances for alkylidene protons in higher living TCDT oligomers begin to fall on top of one another between 7.9 and 8.0 ppm (Figure 3c). Note that virtually all of the W(CH-t-Bu)(NAr)(O-t-Bu)<sub>2</sub> initiator is consumed upon addition of 3 equiv of TCDT (Figure 3c), consistent with the finding that the total yield of polyenes maximizes using 3 equiv of TCDT (Figure 2).

When the sample whose spectrum is shown in Figure 3a is heated to 50 °C for 45 min the spectrum shown in Figure 3e is obtained. We assign resonances at ~9.35 ppm to alkylidene α protons in "living polyenes" and resonances between 8 and 8.2 ppm to β protons in "living



polyenes," in part on the basis of preliminary studies in which specific vinyl alkylidene complexes have been prepared (see below). The major alkylidene  $\alpha$  proton doublet resonance can be ascribed to that for  $W=CH(CH=CH)_2(t-Bu)$ , the ultimate product of insertion of 1 equiv of TCDT, and the minor one to  $W=CH(CH=CH)_4(t-Bu)$  (cf. Figure 3a). The major alkylidene  $\beta$  proton resonance is a double doublet at  $\sim 8.15$  ppm. The total area of the resonance at 9.35 ppm represents the amount of conversion of initiator to a living oligomer, here of the type  $W=CH(CH=CH)_{2x+2}(t-Bu)$  (where  $x = 0$  (primarily), 1, and 2). If we assume that all propagation rates are strictly the same then it is possible to obtain an expression that relates  $\gamma$  ( $= k_p/k_i$ ) to the amount of initial initiator ( $I_0$ ), remaining initiator ( $I$  if  $I \neq 0$ ), and initial monomer ( $M_0$ ):<sup>15</sup>  $M_0/I_0 + \gamma \ln(I/I_0) + (1 - \gamma)(I/I_0 - 1) = 0$ . The group of resonances at  $\sim 9.3$  ppm are approximately as intense as that for the initiator so that  $I/I_0 = 0.5$ ,  $M_0/I_0 = 1$ , and therefore  $\gamma = k_p/k_i = 2.6$ . Since the resonance for the initiator overlaps that for the  $\beta$  protons, the accuracy of the value for  $k_p/k_i$  probably is not high, but it is of approximately the magnitude we expected. The fact that the rate of propagation is only 2-3 times the rate of initiation is consistent with the relatively bulky nature of the propagating alkylidene formed by opening TCDT.

If the sample whose spectrum is shown in Figure 3c is heated to 50° for 45 min a more complex set of resonances shown in Figure 3d are found, because a relatively large number of different chain lengths are present ( $x_{avg}$  in  $W=CH(CH=CH)_{2x+2}(t-Bu)$  is 3 with a range of 1 to 6). The initiator has now been virtually completely consumed. Resonances for olefinic protons further out the chain are found further upfield where protons in pure polyenes are found.

Several reports<sup>16,17,18</sup> suggest that it should be possible to polymerize mono- or

(15) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.

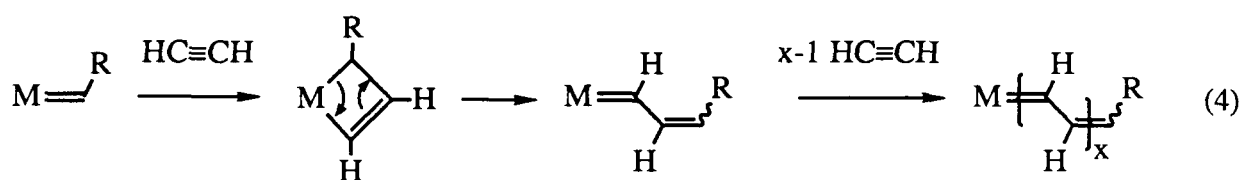
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disubstituted acetylenes employing alkylidene complexes via formation of metallacyclobutene intermediates. Therefore it should be possible under the right circumstances to polymerize acetylene itself in a controlled manner to give living polyenes using an alkylidene complex of the type used for ring-opening reactions (equation 4). There are several reasons why one might expect this to be most difficult for acetylene itself. One is the exothermicity of forming benzene by "back-biting" within a polyene chain. Another is the extraordinary reactivity of acetylene in general, e.g., toward insertion into a metal-carbon single bond in a relatively stable metallacyclobutene intermediate. However, we have now shown that polymerization of acetylene itself can be controlled by using an alkylidene catalyst.<sup>19</sup>

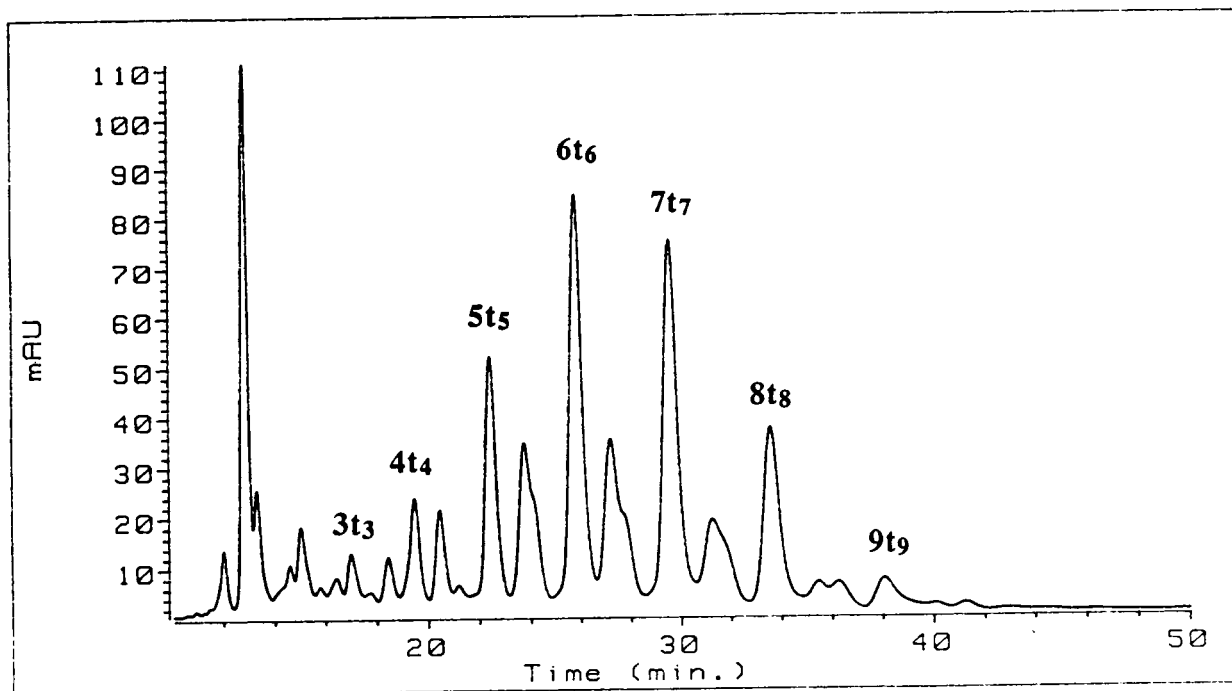


Addition of up to 60 equiv of acetylene to a solution of  $\text{W}(\text{CH}-t\text{-Bu})(\text{NAr})(\text{O}-t\text{-Bu})_2$  ( $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$ ) in pentane yields a black, intractable precipitate of what appears to be a form of polyacetylene on the basis of its solid state  $^{13}\text{C}$  NMR spectrum (broad singlet at 135 ppm).<sup>20</sup> However, if  $\text{W}(\text{CH}-t\text{-Bu})(\text{NAr})(\text{O}-t\text{-Bu})_2$  is treated with 3-13 equiv of acetylene in toluene in the presence of 5 equiv of quinuclidine, then yellow to red solutions are formed.<sup>21</sup> Addition of excess pivaldehyde to the red solution formed with 5 equiv of acetylene followed by hplc analysis showed that an estimated total of ~65% of the di-*t*-butyl-capped polyenes,  $(t\text{-Bu})(\text{CH}=\text{CH})_x(t\text{-Bu})$  ( $x = 3-9$ ) had been formed. The predominant polyenes are the all *trans* forms, **3t<sub>3</sub>**, **4t<sub>4</sub>**, **5t<sub>5</sub>**, **6t<sub>6</sub>**, **7t<sub>7</sub>**, **8t<sub>8</sub>**, and **9t<sub>9</sub>** (Figure 4). The percentage all *trans* form varies from ~70% for **4t<sub>4</sub>** to ~60% for **8t<sub>8</sub>**. *No other organic products, including benzene, could be detected by NMR (see below) or hplc*

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(21) Reaction conditions: 5 mg catalyst, 1 mL toluene, 45 min acetylene reaction time, 30 min quench reaction time (10 equiv pivaldehyde). Yields increase significantly if the reaction is quenched after 10 min instead of 30.

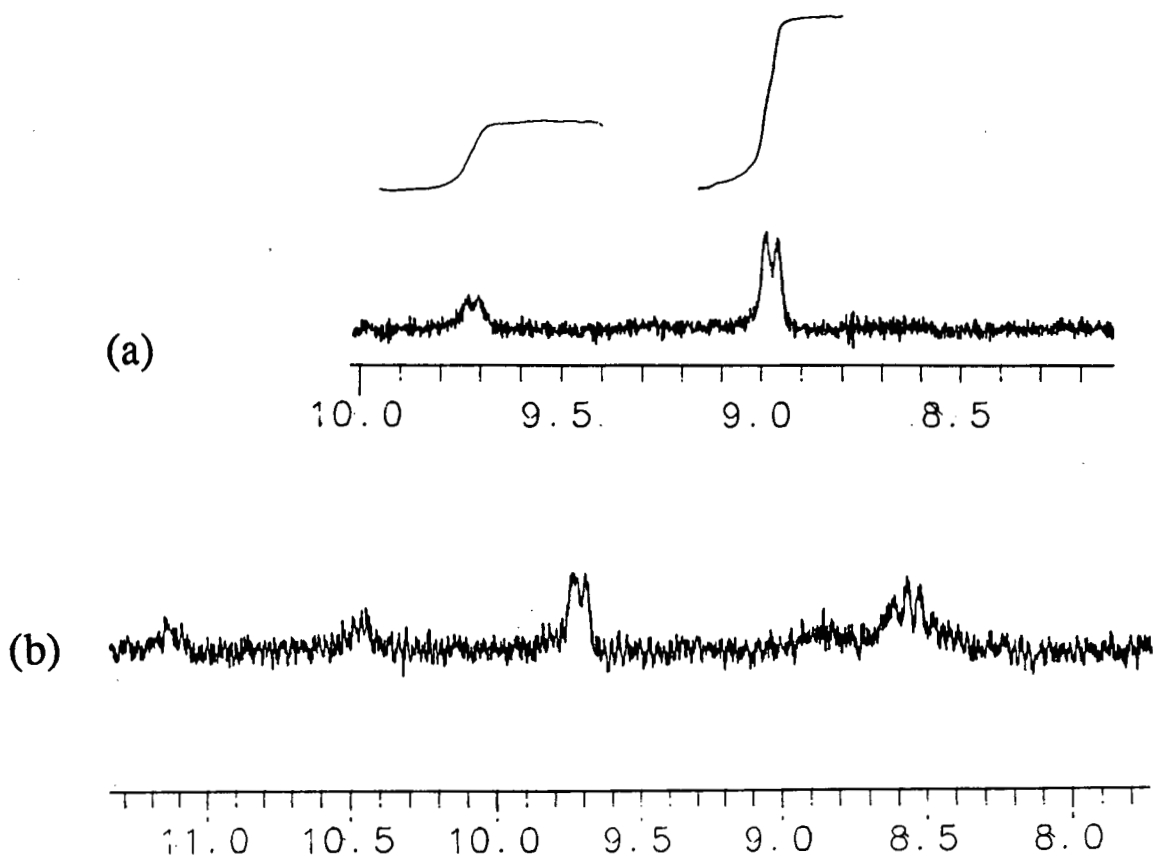


**Figure 4.** Reversed phase hplc study of polyenes  $(t\text{-Bu})(\text{CH}=\text{CH})_x(t\text{-Bu})$  prepared from  $\text{W}(\text{CH}(t\text{-Bu})(\text{NAr})(\text{O}-t\text{-Bu})_2$ , 5 equiv  $\text{HC}\equiv\text{CH}$  in the presence of 5 equiv quinuclidine, and pivaldehyde in toluene (\* guaiazulene internal standard).

*techniques*. The most straightforward explanation of the role of quinuclidine is that it binds to a significantly greater extent 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 *relative to* initiation. (Initiation may also slow down significantly.)

Low temperature  $^1H$  NMR spectra of  $W(CH-t-Bu)(NAr)(O-t-Bu)_2$  in the presence of quinuclidine (down to  $-60\text{ }^\circ C$ ) are consistent with this proposal, i.e., there is *no evidence* for a significant degree of adduct formation. However, the  $^1H$  NMR spectrum of living polynorbornene prepared from  $W(CH-t-Bu)(NAr)(O-t-Bu)_2$  and 50 equiv of norbornene in the presence of 5 equiv of quinuclidine shows a broad  $\alpha$  hydrogen resonance at 8.6 ppm instead of a well-defined doublet at 8.36 ppm. When this sample is cooled to  $-40\text{ }^\circ C$  two doublet alkylidene  $H_\alpha$  resonances are found at 9.72 and 8.97 ppm in a ratio of  $\sim 1:2$ , respectively (Figure 5a). These resonances can be ascribed to two isomers that contain coordinated quinuclidine. (The low temperature spectrum is unchanged if a total of 10 equiv of quinuclidine are added.) After adding 5 equiv of acetylene to this sample of living polynorbornene at  $25\text{ }^\circ C$  a spectrum recorded at  $-40\text{ }^\circ C$  revealed a complex set of broad resonances between  $\sim 11$  and  $\sim 8.5$  ppm (Figure 5b), but addition of another 50 equiv of norbornene at  $25\text{ }^\circ C$  yielded a sample whose NMR spectrum at  $-40\text{ }^\circ C$  was identical to that shown in Figure 5a, including the total intensity of the alkylidene resonances versus an internal standard. We conclude that quinuclidine partially binds to living polynorbornene at  $25\text{ }^\circ C$  and is exchanging rapidly on the NMR time scale, that the catalyst is still living after addition of 5 equiv of acetylene, and that living polynorbornene is regenerated upon addition of more norbornene. The complex set of resonances between  $\sim 11$  and  $\sim 8.5$  ppm can be ascribed to  $H_\alpha$  and  $H_\beta$  resonances, respectively, in the living polyenes that have two basic isomeric forms, *cis* or *trans*  $C_\beta-C_\gamma$  double bonds, and a distribution of chain lengths, on the basis of  $^1H$  NMR and  $^{13}C$  NMR studies of quinuclidine adducts of well-characterized vinyl alkylidene complexes (see below), and NMR studies of analogous living polyenes prepared indirectly employing TCDT (see above).

If  $W(CH-t-Bu)(NAr)(O-t-Bu)_2$  (0.025 M in toluene) is treated with 50 equiv of norbornene, then 3-9 equiv of acetylene, then 50 equiv of norbornene, and then capped by adding



**Figure 5.**  $^1\text{H}$  NMR spectra of  $\text{W}[(\text{NBE})_{50}(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2]$  in the presence of 5 equiv of quinuclidine at  $-40^\circ$  (a) before and (b) after addition of 5 equiv of acetylene.

10 equiv of benzaldehyde, triblock copolymers are obtained (Table I, Figure 6) with molecular weights and polydispersities that are similar to triblocks prepared using TCDDT.<sup>12b</sup> If acetylene is omitted in the sequence then essentially monodisperse polynorbornene is formed (last entry in Table I), virtually identical to what is observed in the absence of quinuclidine. The fact that the polydispersities and  $M_n$  values of the triblocks are virtually identical to those for polynorbornene itself suggests that the polymerization of up to 9 equiv of acetylene is largely well-behaved. That is not true if 11 or especially 25 equiv of acetylene are employed in analogous experiments. A *trimodal* distribution results (Figure 6), the central peak of which appears to be the expected macromolecule. One possibility is that aggregation (crystallization) or crosslinking of relatively long living polyenes leads to higher molecular weight material, a situation that also arises when long polyenes in blocks are prepared via the TCDDT route.<sup>12b</sup> The lower molecular weight material probably contains only the first poly NBE block; evidently acetylene polymerization was terminated in these species by some decomposition reaction. The fact that complexes of the type  $M(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$  are poor catalysts for the metathesis of ordinary internal olefins<sup>3</sup> probably is a significant factor in channeling the reaction in the direction shown in equation 1, and in eliminating "back-biting" to form benzene.

We have begun analogous studies of polyene synthesis employing  $\text{Mo}(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$ . So far we have found that TCDDT is ring-opened smoothly to ultimately give polyenes in an analogous fashion. Direct polymerization of acetylene is also successful, as is incorporation of polyenes into triblocks with norbornene. On the basis of preliminary gpc analyses of triblocks, molybdenum appears to be a better behaved acetylene polymerization catalyst, i.e., only peaks for the expected macromolecule and high molecular weight "aggregates" are found, not the low molecular weight material, *even employing 25 equiv of acetylene*. This result suggests that side reactions are minimized with the molybdenum catalyst. It may prove to be the most efficient and well-behaved of the two.

We have looked briefly at the parent Feast reagent, tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene, as a means of preparing polyenes under milder conditions than those that are required to promote the

Table I. Polydispersities of Polyene-Containing Triblock Copolymers

<u>NBE</u>	<u>HC≡CH</u>	<u>NBE</u>	<u>M<sub>w</sub></u>	<u>M<sub>n</sub></u>	<u>PDI</u>
50	3	50	19796	18174	1.09
50	5	50	18943	17745	1.07
50	7	50	19756	18134	1.09
50	9	50	19856	18249	1.09
50	11	50	27378	21297	1.29
50	25	50	223683	32659	6.85
100	—	—	19051	17916	1.06

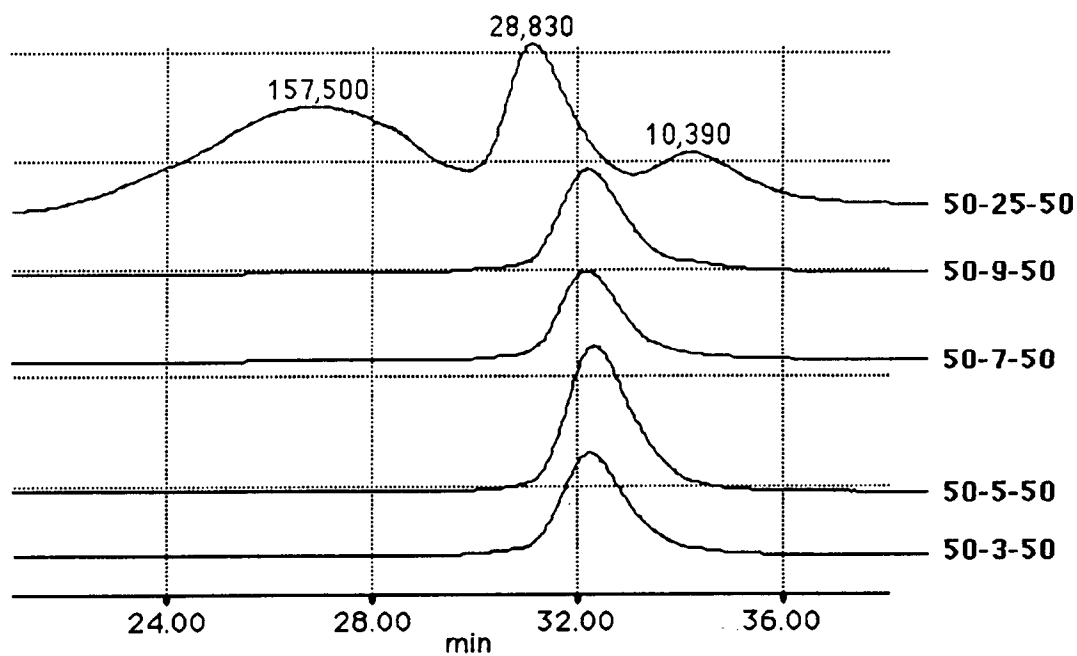
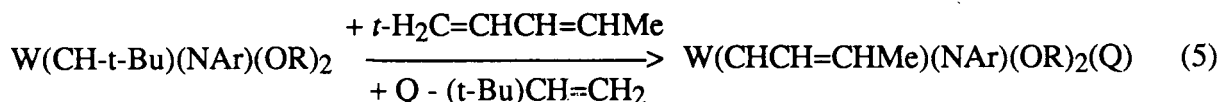


Figure 6. Gpc studies of NBE/polyene/NBE triblocks prepared employing acetylene (see Table I).

retro DA reaction in ring-opened TCDT. (The retro DA reaction in polytricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene takes place at lower temperatures than the bis CF<sub>3</sub> analog.<sup>5b</sup>) The results show that polyene yields employing tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene are, in fact, significantly lower than those employing TCDT, especially if the tungsten catalyst is used. We speculate that the double bonds that remain in the ring system in the ring-opened material are more readily attacked by M=C bonds, and the polymer thereby cross-linked. Any crosslinking of this nature sidetracks the reaction that leads to a polyene. However, crosslinking appears to be slowed down and possibly even virtually eliminated if phosphines are present, another example of the ever more important role added bases will play in catalytic reactions.

Because of the accumulating evidence that living polyenes are relatively stable, yet reactive, we looked for methods to prepare specific examples by non-catalytic methods. A suitable method turned out to be selective metathesis of a terminal diene with a neopentylidene complex. An example is shown in equation 5 (OR = OCM<sub>e</sub>(CF<sub>3</sub>)<sub>2</sub>, Q = quinuclidine). The initial product is a



1:5 mixture of two isomers, we propose the *syn* and *anti* alkylidene rotomeric forms, respectively. After several hours a 1.5:1 equilibrium mixture of *syn* and *anti* rotomers are found. An x-ray structure (Figure 7) showed that the isolated sample is an *anti* rotomer of basically a trigonal bipyramid formed by attack of the quinuclidine on the N/C/O face of the tetrahedron in the *anti* rotomer. It is interesting to note that this is the same basic core geometry found for the only other structurally characterized five-coordinate base adduct of this class, W(CH-*t*-Bu)(O)Cl<sub>2</sub>(PEt<sub>3</sub>).<sup>22</sup> The vinylalkylidene ligand is η<sup>1</sup>, as we had hoped. Bond distances and angles (Table II) are not unusual. Note how the diisopropylphenyl ring in the imido ligand, which is perpendicular to the N/W/C plane in the base-free benzylidene complex,<sup>3d</sup> has turned 90° in order to avoid steric

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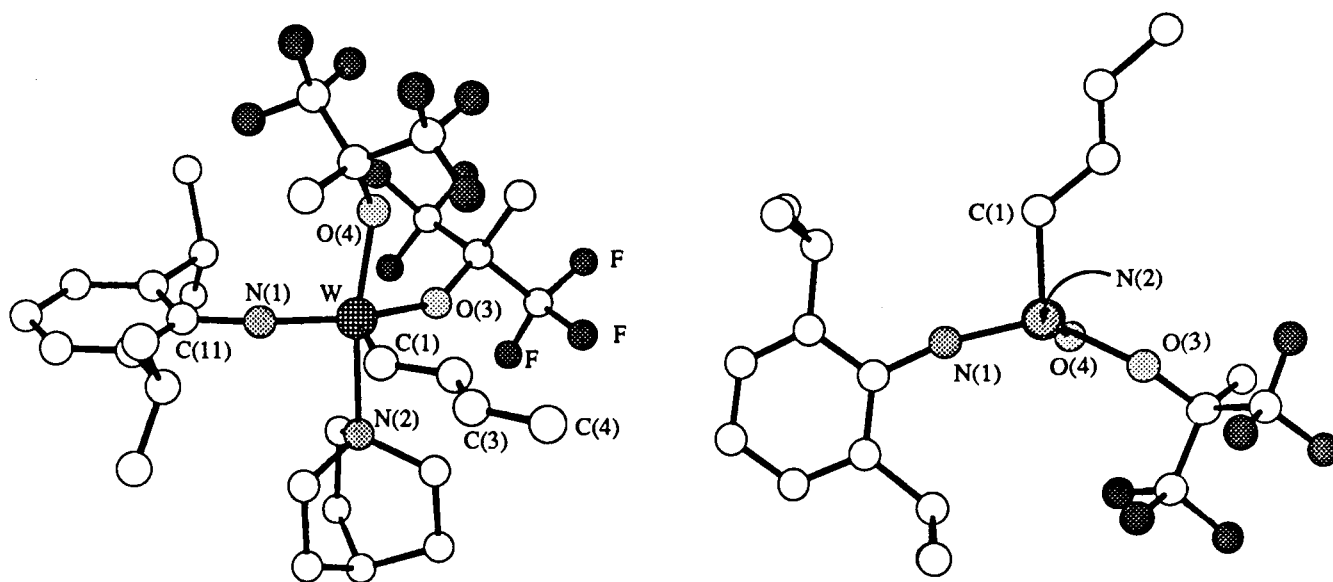


Figure 7. A view of trigonal bipyramidal  $W(\text{CHCH}=\text{CHMe})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2(\text{quinuclidine})$  (left) and a partial view from the position of the nitrogen of the quinuclidine ligand (right).

Table II. Selected Bond Distances (Å) and Angles (deg) for  $W(\text{CHCH}=\text{CHCHMe})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ .

W-N(1)	1.737 (5)	O(3)-W-N(2)	80.2 (2)
W-C(1)	1.942 (6)	O(4)-W-N(2)	163.9 (2)
W-O(3)	1.961 (4)	W-O(3)-C(31)	148.5 (4)
W-O(4)	1.985 (4)	W-O(4)-C(41)	135.7 (4)
W-N(2)	2.273 (5)	W-N(1)-C(11)	168.0 (4)
N(1)-W-C(1)	100.7 (2)	W-C(1)-C(2)	126.3 (5)
N(1)-W-O(3)	138.3 (2)	C(1)-C(2)-C(3)	126.7 (6)
N(1)-W-O(4)	100.7 (2)	C(2)-C(3)-C(4)	128.3 (7)
N(1)-W-N(2)	89.7 (2)	C(1)-W-N(2)	89.7 (2)
C(1)-W-O(3)	119.5 (2)	O(3)-W-O(4)	83.9 (2)
C(1)-W-O(4)	100.2 (2)		



interaction between an isopropyl group and the quinuclidine ligand. It is probably for this reason that the alkylidene is forced to be in the *anti* orientation. We speculate that the *syn* form has the same basic structure with an imido phenyl ring that is twisted out of the equatorial plane, although we cannot yet exclude the possibility that the core is different (e.g., a square pyramid). The *syn* form apparently crystallizes out selectively, since an NMR sample prepared from this crystalline sample at 25° again shows an initially low *syn/anti* ratio (1:5, assuming that the other isomer is a *syn* form) that favors the *syn* form (1.5:1) after about two hours.

Very recently we have found that although the reaction shown in equation 5 is not successful when R = t-Bu, it is successful if norbornene is first added to  $W(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$  to give a more reactive living polynorbornene complex. We hope to isolate a base adduct of that product soon. Further details can be found in the proposal proper.

**Publications appearing since last application**

1. *Preparation of Ditungsten Hexa(2,6-dimethylphenoxide) and its Reaction with Acetylenes to Give Tungstenacyclobutadiene Complexes*, Latham, I.A.; Sita, L.R.; Schrock, R. R. *Organometallics* **1986**, *5*, 1508-1510.
2. *Peralkylcyclopentadienyl Tungsten Polyhydride Complexes* Okuda, J.; Murray, R.C.; Dewan, J.C.; Schrock, R.R. *Organometallics* **1986**, *5*, 1681-1689.
3. *Heterobimetallic Complexes Connected by Peralkylated Cyclopentadienyl Rings*, Buzinkai, J.F.; Schrock, R.R. *Organometallics* **1987**, *5*, 1447-1452.
4. *High Oxidation State Monopentamethylcyclopentadienyl Tungsten Methyl Complexes Including the First  $d^0$  Complex Containing a Highly Distorted Methylene Ligand,  $W(\eta^5-C_5Me_5)(CH_3)_3(CH_2)$* , Liu, A.H.; Murray, R.C.; Dewan, J.C.; Santarsiero, B.D.; Schrock, R.R. *J. Am. Chem. Soc.* **1987**, *109*, 4282-4291.
5. *Bimetallic Complexes Containing the Bis(tetramethylcyclopentadienyl)ethane Ligand*, Buzinkai, J. F.; Schrock, R. R., *Inorg. Chem.*, in press (copy provided).
6. *Preparation of t-Butyl-Capped Polyenes Containing up to 15 Double Bonds*, Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.*, in press (copy provided).
7. *The Direct Polymerization of Acetylene to Give Living Polyenes*, Schlund, R., Schrock, R. R., Crowe, W. E., submitted to *J. Am. Chem. Soc.* in press (copy provided).

*Preprints removed.*