M(CH-t-Bu)(NAr)(O-t-Bu)$_2$ 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.[12]

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,[4] although tungstacycles made from norbornene *have* been observed in related tungsten catalyst systems,[11b] and both tungstacyclobutane and molybdacyclobutane complexes have been observed in reactions between substituted norbornenes and norbornadienes and catalysts of this general type.[13]) 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)$_2$ and unreacted aldehyde. If pivaldehyde is used in the Wittig-like reaction, the result is a series of "odd" polyenes containing 2x+1 double bonds. If 4,4-dimethyl-*trans*-2-pentenal is used then a series of "even" polyenes containing 2x+2

(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(13) G. Bazan, unpublished results.