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Evaluation of Cyclopentene-Based Chain-Transfer Agents for Living Ring-Opening Metathesis Polymerization

R. R. Schrock,* K. B. Yap, D. C. Yang, H. Sitzmann, L. R. Sita, and G. C. Bazan

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 18, 1988; Revised Manuscript Received January 18, 1989*

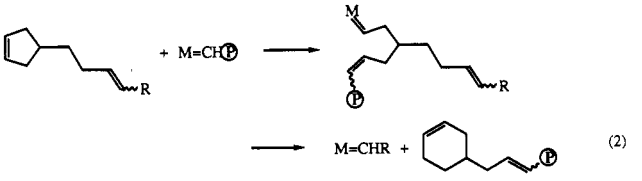
ABSTRACT: Potential chain-transfer (CT) reagents for removing a growing polymer from living ROMP catalysts of the type M(CH(P))(NAr)(O-*t*-Bu)$_2$ (M = Mo, W; (P) = polymer; Ar = 2,6-diisopropylphenyl) and regenerating an alkylidene complex initiator are evaluated. They are based on the principle that a cyclopentene ring will be opened upon reaction with the W=CH(P) double bond, and a cyclohexene ring will be reformed employing the double bond in an appropriate alkenyl side chain. While 1-(2-cyclopentenylmethyl)-2-phenylethene will react with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to give W(CHPh)(NAr)(O-*t*-Bu)$_2$ in 60% yield, other potential chain-transfer reagents for W catalysts fail to varying degrees for a variety of reasons. Analogous reactions involving molybdenum catalysts were somewhat more successful. The most significant problem is that the double bond in the alkenyl side chain of the alkenylcyclohexene (the rearrangement product of the CT reagent) ultimately reacts with a relatively small alkylidene ligand (e.g., a propylidene ligand) in the just-formed initiator. We conclude that although the principle is valid, the double bond in an ideal CT reagent would have to be considerably more reactive than that in a cyclopentene and/or the catalyst would have to discriminate more efficiently between the double bond in the cyclic olefin and that in the side chain.

Introduction

Well-characterized alkylidene complexes of the type M(CH-*t*-Bu)(NAr)(OR)$_2$ (M = Mo or W; Ar = 2,6-diisopropylphenyl; R = O-*t*-Bu, OCMe$_2$(CF$_3$), or OCMe(CF$_3$)$_2$)[1] have been found to react readily with norbornenes, but not with ordinary acyclic olefins, when R = O-*t*-Bu.[2] This property has allowed essentially monodisperse living homopolymers and block copolymers to be prepared by ring-opening metathesis polymerization (ROMP).[2-4] Since these catalysts have been "deactivated" toward reaction with ordinary olefins, the polymers currently are cleaved from the metal in a Wittig-like reaction with an aldehyde (eq 1; (P) = polymer). One positive aspect of this technique

$$M{=}CH(P) + PhCHO \rightarrow M{=}O + PhCH{=}CH(P) \quad (1)$$

is that one should be able to specifically cap the polymers with a variety of potentially interesting functionalities. However, if relatively low molecular weight polymers or oligomers are being prepared (e.g., polyenes[3b]), then it would be desirable to regenerate the catalyst by using a chain transfer agent. But the very nature of such catalysts will not allow one to employ ordinary olefins for this purpose,[5] a technique that can be employed with some success in systems containing very reactive and therefore not perfectly living "classical" ROMP catalysts.[6] A potential solution to this problem is based on the fact that ring-opening polymerization is disfavored at 25 °C for cyclohexene, and cyclohexene is known to be evolved from polymeric systems if it can form in a metathetical cyclization reaction.[6b,c] Consequently, by attaching an alkenyl side chain to a relatively reactive cyclic olefin such that a cyclohexene can reform after the cyclic olefin is opened, it should be possible to regenerate the alkylidene complex. An example employing a derivatized cyclopentene is shown in eq 2. The free energy decrease for the reaction can be



(2)

ascribed largely to the exothermicity of expanding a five-membered ring to a six-membered ring. Other derivatized reactive cyclic olefins might be employed (e.g., norbornenes), but we felt that cyclopentenes should be relatively available and should be sufficiently reactive relative to an ordinary olefin to accomplish the task. What we present here is an evaluation of this approach for several cyclopentene reagents using the M(CHR)(NAr)(O-*t*-Bu)$_2$ catalyst systems (M = Mo or W).

Results and Discussion

Reactions of Cyclopentene with W(CH-*t*-Bu)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(O-*t*-Bu)$_2$ (1a). When 50–200 equiv of

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Table I
Polydispersity of Polypentenamers Prepared Employing 1a[a]

time, h	T, °C	M_w	M_n	PDI
1	25	27586	18590	1.48
2	25	30543	19980	1.53
4	25	11613	6586	1.76
1	−40	16718	15486	1.08
2	−40	21330	19150	1.11
4	−40	2527	19955	1.23

[a] 234 equiv of cyclopentene were added to **1a** in toluene-d_8 and aliquots quenched with benzaldehyde. M_w and M_n were measured by GPC in dichloromethane versus polystyrene standards.

cyclopentene are added to **1a** in C_6D_6, the singlet resonance at 8.05 ppm characteristic of the α proton in the neopentylidene ligand in **1a** decreases in intensity and a triplet resonance at ~8.45 ppm ($J_{HH} \approx 7$ Hz) appears that we ascribe to the alkylidene α proton in W[(CHCH$_2$CH$_2$CH$_2$CH)$_n$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$). Often the triplet resonance is broad (because n is a distribution) and/or weak relative to resonances in the rest of the spectrum (when n is large). At room temperature the equilibrium concentration ([M]$_e$) of cyclopentene is approximately 0.8 M; at −40 °C ~95% of the original monomer concentration has been converted into polypentenamer. A plot of ln [M]$_e$ versus $1/T$ gives $\Delta H° = -4.0$ kcal/mol and $\Delta S° = -0.069$ (kcal/mol)/K. This reversible ring-opening polymerization of cyclopentene is entirely analogous to that observed in systems employing classical olefin metathesis catalysts.[6]

We could show that the polypentenamer that is being observed in these experiments is largely living by removing cyclopentene in vacuo and determining by ^{1}H NMR integration versus an internal standard how much W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is reformed (eq 3). We found that

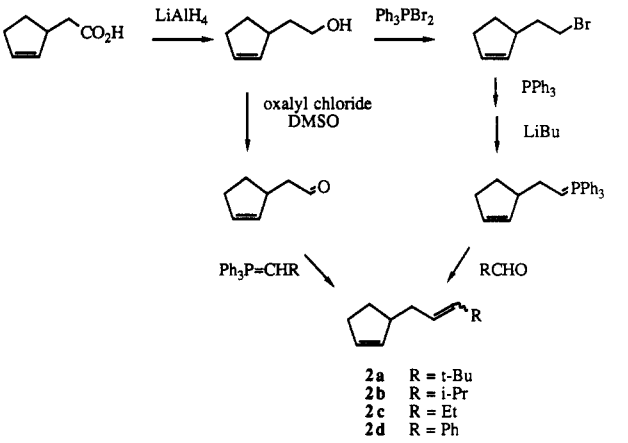
$$\text{W[(CHCH}_2\text{CH}_2\text{CH}_2\text{CH)}_n\text{CH-}t\text{-Bu](NAr)(O-}t\text{-Bu)}_2 \xrightarrow{-n\text{C}_5\text{H}_8} \text{W(CH-}t\text{-Bu)(NAr)(O-}t\text{-Bu)}_2 \quad (3)$$

82–86% of **1a** could be recovered after solutions of W[(CHCH$_2$CH$_2$CH$_2$CH)$_n$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ were stood for as long as 2 h at 25 °C or −40 °C at a concentration of ~0.015 M. Since there is little difference between the results at 25 °C and those at −40 °C, we suspect that a significant fraction of the ~15% **1a** that is not recovered can be ascribed to manipulative losses (in particular hydrolysis or reaction with oxygen) and that the living polymer is relatively stable toward any decomposition that destroys the W=C bond at this concentration over a period of 2 h. Note that these experiments do not tell us whether cyclic oligomers are being formed since those cyclic oligomers also would be degraded to cyclopentene.

Cyclopentene (234 equiv) was added to **1a** in toluene and aliquots were removed at times between 1 and 4 h and quenched with 3 equiv of benzaldehyde. GPC analysis of the resulting polymer showed that the polydispersity increases slightly with time (Table I). The fact that M_n decreases dramatically between 2 and 4 h at 25 °C suggests either that catalyst decomposition after 2 h becomes significant or that cyclic oligomers are being formed. An analogous set of experiments at −40 °C produced polypentenamers with a significantly lower initial polydispersity that increases more slowly with time (Table I) and for which M_n does not decrease significantly between 2 and 4 h.

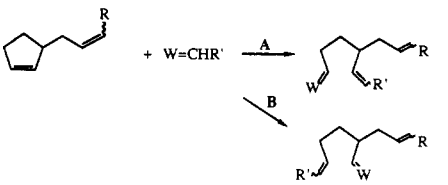
These studies demonstrate that cyclopentene is ring-opened readily in a relatively well-controlled reaction and that the polymer is largely living and relatively stable over a period of 2 h at 25 °C at concentrations of ~0.01 M. Therefore we can be confident that a chain-transfer (CT) reaction of the general type shown in eq 2 at least will be possible in catalyst systems of this type.

Scheme I
Preparation of 3-Substituted Cyclopentenes



Relative Stabilities of Several Alkylidene Complexes. Preliminary studies have suggested that W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**1a**) is much more stable than W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$ (**1b**),[7] W(CHEt)(NAr)(O-*t*-Bu)$_2$ (**1c**),[1a] or W(CHPh)(NAr)(O-*t*-Bu)$_2$ (**1d**).[5b] **1c** can be prepared in situ by adding 2.1 equiv of lithium *tert*-butoxide to a mixture of W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (~20%) and the tungstacyclobutane complex W(CHEt-CHEtCHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (~80%).[1a] The yields are 70% or better according to ^{1}H NMR integration of the propylidene α-proton resonance versus an internal standard (see Experimental Section for details). In toluene-d_8, ~10% of **1c** prepared in this manner (at a concentration of ~10 mM) is lost over a period of 1–2 h, although after 24 h only ~30% of **1c** remains; at −40 °C, ~70% of **1c** survives over a period of 24 h. **1d** is approximately as unstable as **1c**, while **1b** is relatively robust, even in relatively concentrated solutions (~0.1 M). For these reasons it is believed that W(CHR)(NAr)(O-*t*-Bu)$_2$ complexes decompose in a bimolecular process that does not involve β protons, although that remains to be proved. These qualitative observations establish that although alkylidene complexes such as W(CHEt)(NAr)(O-*t*-Bu)$_2$ cannot be isolated, they can be prepared in situ and are stable toward decomposition over a relatively short period of time and under relatively dilute conditions (~10 mM or less). These results are consistent with the finding above that W[(CHCH$_2$CH$_2$CH$_2$CH)$_n$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ species are stable in dilute solution at 25 °C over a period of 2 h.

Synthesis of 3-Alkenyl-Substituted Cyclopentenes. We chose to evaluate 3-alkenyl-substituted cyclopentenes as CT reagents first since they can be prepared readily from commercially available 2-cyclopentene-1-acetic acid as shown in Scheme I in high overall yield and for a variety of R groups. A potential disadvantage of 3-alkenylcyclopentenes versus 4-alkenylcyclopentenes is the necessary regiospecificity in the ring-opening step (eq 4); if the ring

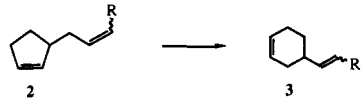


(4)

opens the "wrong way" (path B), then the only possibility would appear to be reformation of the five-membered ring

or further reaction of the W=C bond with another cyclopentene double bond. (Formation of a cyclobutene ring would be disfavored.) The syntheses shown in Scheme I give a mixture of cis and trans isomers; we did not expect that to be a problem as far as chain transfer is concerned, and this was confirmed in subsequent investigations.

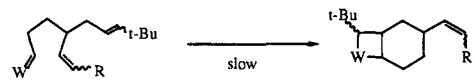
Reactions of 3-Alkenylcyclopentenes with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Virtually no change was observed in 24 h by ^{1}H NMR in a sample consisting of a mixture of **1a** (~10 mM) and 5 equiv of **2a** in C_6D_6. In this case the possible observable reactions are conversion of **2a** into the cyclohexene product **3a** (eq 5). or polymerization of



2 3 (5)

[R = t-Bu (3a), i-Pr (3b), Et (3c), Ph (3d)]

2a. In the analogous reaction between **1c** and **2a**, a successful alkylidene transfer would be indicated by formation of **1a**. However, after 1 h only a trace of the alkylidene proton resonance due to **1a** could be observed along with those due to **1c** and **2a**. In light of the results of studies that follow, we conclude that **2a** is a poor prospect as a chain-transfer reagent, either because it is simply too bulky overall to react with W(CHR)(NAr)(O-*t*-Bu)$_2$ complexes or because the cyclohexene ring cannot form readily if a *tert*-butyl group must be present in the trisubstituted tungstacyclobutane intermediate (eq 6).

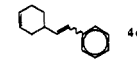


(6)

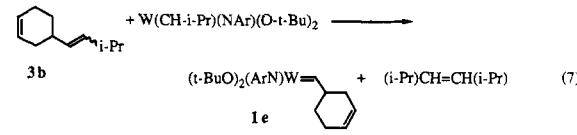
In contrast, the reaction between **1a** and 4 equiv of **2d** under similar conditions gave W(CHPh)(NAr)(O-*t*-Bu)$_2$ (**1d**) (~90%) within 1 h at 25 °C. When 4 equiv of **2d** were added to a living oligomer generated by reacting **1a** with 10 equiv of norbornene, the doublet resonance for the alkylidene H_α of the living oligomer at 8.37 ppm in the ^{1}H NMR spectrum disappeared and that for **1d** appeared in ~60% yield (by integration). However, formation of **1d** confirms that the chain-transfer reaction can be successful at concentration levels that are at the upper end of the range of concentrations that one would expect to find in a typical ring-opening polymerization reaction. Formation of **1d** is likely to be especially favorable for thermodynamic reasons, owing to the stabilizing effect of an adjacent negative charge on the alkylidene α-carbon atom by the phenyl group. For the same reason, **1d** is a poor initiator for ring-opening polymerization of norbornene;[5b] **2d** therefore could not be employed to regenerate ROMP catalysts. It was employed here only to illustrate that chain transfer can proceed readily in an especially favorable case. At this stage it is unclear whether the moderate (60%) yield of **1d** is a consequence of problems with the chain-transfer reaction itself or simply is the result of **1d** slowly decomposing after it is formed in high yield.

The reaction between **1a** and 4 equiv of **2b** to give W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$ (**1b**) (H_α doublet at 8.23 ppm in C_6D_6) also was successful. The alkylidene resonance for **1b** could be observed growing in after 10 min, but after 5 h the ratio of **1b** to **1a** was still only about 9:1. The reaction does not go to completion under these conditions because **1b** reacts with **2b** to give **3b** more rapidly than **1a** reacts with **2b** to give **1b**, so that **2b** ends up being consumed before all **1a** is consumed. The puzzling aspect of these experiments is that with time (1–4 days at −40 °C) a second doublet resonance appears at 8.28 ppm, one that is characteristic of another alkylidene complex having a single proton on its β-carbon atom. There are three possible explanations. The first is that the second doublet can be assigned to an isomer of W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$, in particular a rotomer in which the isobutylidene ligand is turned "away" from the imido ligand. (The isopropyl group in W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$ is almost certainly turned toward the imido ligand on the basis of a crystal structure of the analogous neopentylidene complex.[8]) The second possibility is that the C_5 ring has opened the "wrong" way and does not close for some reason (path B, eq 4). The third possibility is that the cyclohexene product (**3b**) slowly reacts with **1b** to give the cyclohexenyl-substituted alkylidene complex **1e** shown in eq 7.

Table II
Distribution of Products of the Reaction between 1c with 3c after Quenching with Benzaldehyde

product	yield, equiv W^{-1}
 3c	8.14[a]
 4c	0.09
 4e	0.10

[a] The theoretical amount of product is 12 equiv.



(7)

In an analogous reaction between **1a** and **2c**, a triplet resonance characteristic of **1c** at 8.4 ppm appears within 10 min. After ~20 min the ratio of **1a** to **1c** was approximately 1:1 (Figure 1A). However, even at this time, what appears to be the same doublet resonance as was observed in the system just described becomes visible and continues to grow so that after ~80 min the ratio of triplet:doublet:singlet is ~1:1:1 (Figure 1B). In an analogous reaction between **1a** and **2c**-d_1 (containing the CH_2CH=CDEt alkenyl side chain) W(CDEt)(NAr)(O-*t*-Bu)$_2$ was observed to form (by ^{2}H NMR), but the doublet at ~8.3 ppm still appeared in the ^{1}H NMR spectrum after approximately the same period of time as in the experiment employing **2c**. In an analogous reaction between **1c** (generated in situ as described above) and **2c** the doublet at 8.3 ppm appears rapidly (within 10 min) at the expense of the triplet resonance for **1c**, while resonances for **2c** are replaced by those for **3c**. The results of these experiments eliminate the possibility that the doublet at 8.3 ppm can be ascribed to a rotomer of W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$.

The third possible explanation can be tested by treating **1c** with the cyclohexene product **3c** (12 equiv) and quenching the mixture with benzaldehyde. The products **4c** and **4e** (Table II) arise from the Wittig-like reaction of **1c** and **1e**, respectively, with benzaldehyde and were identified by GLC comparison with authentic samples. Their ratio is ~1:1, but the total yield is only 19% (versus W). The yield of **4c** generated by quenching **1c** (generated in situ) in the same manner is similarly low, but the yield of PhCH=CH(*t*-Bu) (**4a**) formed upon quenching **1a** is high (89%). Therefore we propose that the LiOCMe(CF$_3$)$_2$ that is present in the systems in which **1c** is generated in situ interferes in a quenching reaction involving benzaldehyde. The main point, however, is that treating **1c** with **3c** generates **1e**, a product of an *ordinary* metathesis reaction of the double bond in the alkenyl side chain of **3c**. We conclude that the third proposal is correct; the mystery H_α doublet resonance in all systems can be as-

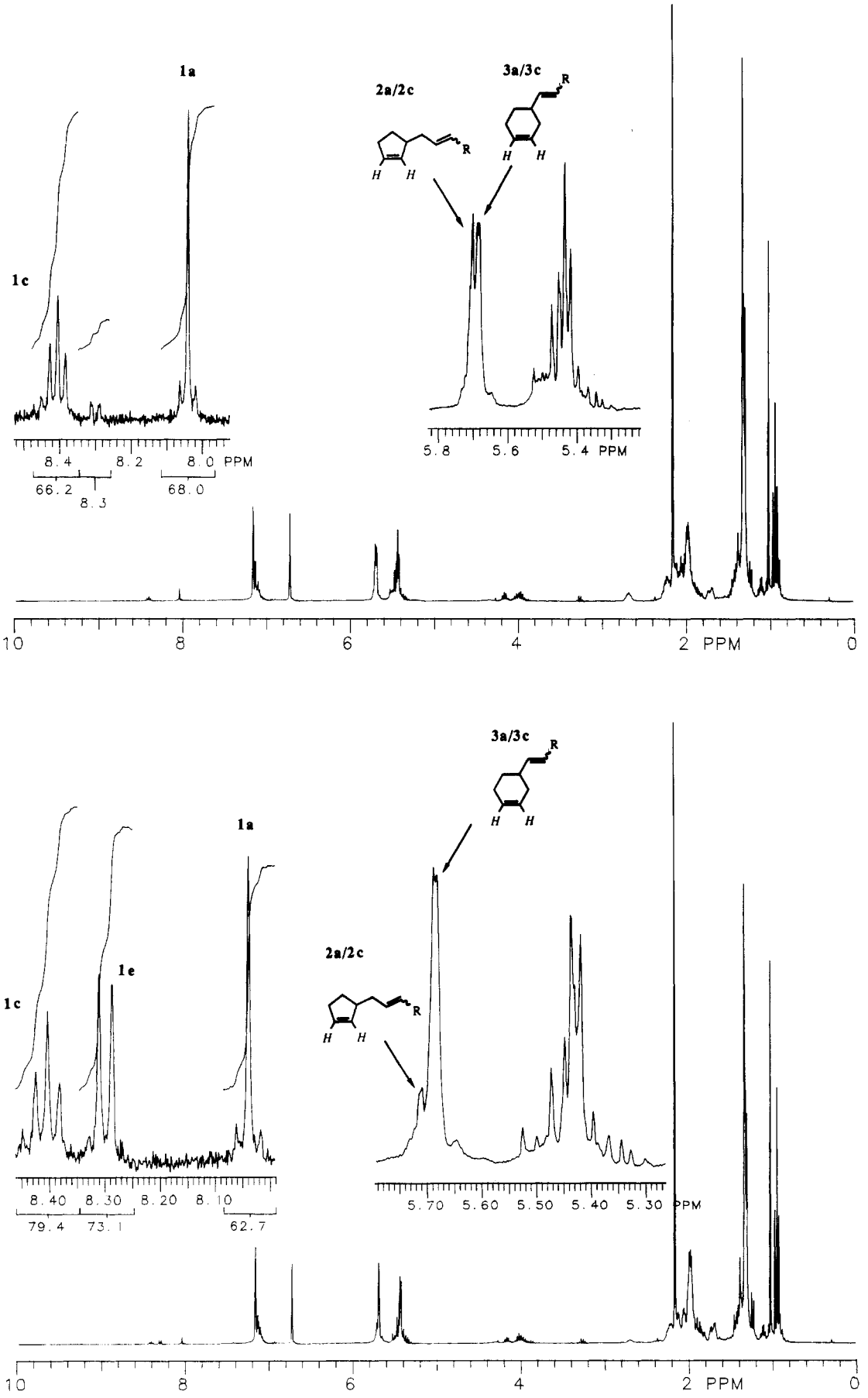
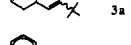
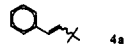


Figure 1. NMR studies of the reaction between **1a** (0.02 M) and **2c** (0.13 M) in C_6D_6 at 25 °C after (A, top) 20 min and (B, bottom) 80 min.

Table III
Major Products from the Reaction between 1a and 2c after Quenching

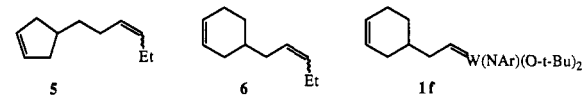
product	10-min rxn, equiv W^{-1}	120-min rxn, equiv W^{-1}
 2c	4.0	0.34
 3c	0.99	3.4
 4c	0.34	0.13
 3a	0.46	0.67
 4a	0.30	0.054
 4e		0.19

cribed to **1e**. **1e** builds up with time because the alkylidene ligand in it is sterically the most bulky of those possible in the system, and therefore **1e** is the least reactive compared to other possible alkylidene complexes. In situations where an alkylidene complex is especially stable for electronic reasons (e.g., **2d**), **1e** probably would not be observable.

The above conclusion (that **1e** forms via an ordinary metathesis reaction) implies that other ordinary olefins should be metathesized at an observable, if slow, rate. In the reaction between **1c** (~10 mM) and 5 equiv of *cis*-4-methyl-2-pentene, **1c** was completely converted into W(CH-*i*-Pr)(NAr)(O-*t*-Bu)$_2$ (**1b**) in 2 h. Therefore metathesis of ordinary double bonds certainly is possible, although it is relatively slow in most cases. It should be pointed out that the rate of metathesis of an ordinary double bond by W(CHR)(NAr)(O-*t*-Bu)$_2$ complexes will be highly dependent upon the size of R. Although **1c** is converted into **1b** by *cis*-4-methyl-2-pentene, **1a** *does not react* to any significant extent with *cis*-4-methyl-2-pentene in the same period of time, consistent with the much lower reactivity of neopentylidene complexes in general.[5b]

The products of the reaction between **1a** and **2c** were examined more closely in order to confirm our proposal. As shown in Table III, **3a** and **3c**, and the products of quenching **1a**, **1c**, and **1e** (**4a**, **4c**, and **4e**), are all observed. Between 10- and 120-min reaction time the relative amounts of each change as one would predict on the basis of the proposed reaction course. In particular, **4e** becomes the predominant product of quenching alkylidene complexes, consistent with **1e** being the major alkylidene complex present after 120 min. We also observe many minor high boiling products that elute where high boiling metathesis products are expected to elute, as shown by preparing several independently. Unfortunately the complexity of the metathesis product mixture and the fact that they cannot be resolved under our GLC conditions precluded positive identification. Nevertheless, we feel that these results support the proposal and that the reaction pathway has been established beyond reasonable doubt.

Reactions of 4-Alkenylcyclopentenes. 4-Alkenylcyclopentenes were initially more attractive candidates as chain-transfer agents, since no regiochemical problem can arise (eq 2). One disadvantage is that they cannot be prepared as readily as 3-alkenylcyclopentenes, especially if one wants to prepare a family containing different CHR groups at the end of the side chain. Nevertheless, we felt it important to prepare **5** and test it as a chain-transfer reagent. The results overall are similar to those we have already described, except the "new H_α resonance" is a *triplet* at ~8.4 ppm (overlapping with the expected propylidene triplet resonance), since it is the alkylidene H_α resonance for **1f**, which is formed when the rearrangement product **6** reacts with alkylidenes in the system (primarily W(CHEt)(NAr)(O-*t*-Bu)$_2$) at the double bond in the alkenyl side chain. Although 4-alkenylcyclopentenes are in principle more attractive than 3-alkenylcyclopentenes as chain-transfer agents, the point is moot since both fail for the same reason.



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Reaction of Chain-Transfer Agents with Living Polynorbornene. A final test of the prospect of employing 3-alkenylcyclopentenes as chain-transfer agents consisted of following the reaction between M[(CHC$_5$H$_8$CH)$_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ and **2c** by ^{1}H NMR.

The course of the reaction employing Mo[(CHC$_5$H$_8$CH)$_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ (average x = 20)[1b] at a concentration of 0.02 M and **2c** (0.12 M; 6 equiv) in C$_6$D$_6$ can be followed in the region of the alkylidene proton resonances as shown in Figure 3. (An internal mesitylene standard was present.) The highest field resonance is the neopentylidene α-hydrogen resonance in the Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ that is left over after addition of 2 equiv of norbornene to it. The doublet ascribable to Mo[(CHC$_5$H$_8$CH)$_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ disappears smoothly as that for Mo(CHEt)(NAr)(O-*t*-Bu)$_2$ appears at 11.56 ppm. The conversion is nearly complete before the doublet ascribable to the molybdenum analogue of **1e** begins to become significant. Only a small amount of the remaining Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ reacts with **2c** during the course of this experiment.

An analogous reaction employing W[(CHC$_5$H$_8$CH)$_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ and **2c** under the same conditions is shown in Figure 2. The reaction is qualitatively faster (virtually over in 15 min) but also less selective toward formation of W(CHEt)(NAr)(O-*t*-Bu)$_2$ (**1c**) versus **1e**. This result is consistent with qualitative observations that suggest that molybdenum catalysts are in general significantly less reactive than their tungsten analogues.[1b] Therefore the more reactive tungsten species are likely to be less discriminating, i.e., W(CHEt)(NAr)(O-*t*-Bu)$_2$ will react more readily with the double bond of the alkenyl side chain in **3c** than will Mo(CHEt)(NAr)(O-*t*-Bu)$_2$. If specificity is desired in the capping reaction, then the molybdenum catalyst would seem more likely to provide it.

In Figures 2 and 3, we have also noted a second triplet downfield from the main propylidene resonance (marked * in Figures 2 and 3). We believe this resonance is due to either the ring-opened form of the chain-transfer reagent (path a, eq 4) or possibly the methylcyclopentenylidene resulting from a metathetical reaction between a metal alkylidene **1c** (or its molybdenum analogue) and the starting chain-transfer reagent **2c** at the double bond in the alkenyl side chain. Identification of this minor species is not crucial at this stage, but it may be yet another complicating factor if ROMP of another monomer (in order to prepare blocks) were attempted using such mixtures of initiators.

Conclusion

Although these studies suggest that it may be possible under the right circumstances to cleave off a given polynorbornene chain and regenerate the catalyst initiator (with the molybdenum catalyst system at least), preliminary studies suggest that carrying out this transformation

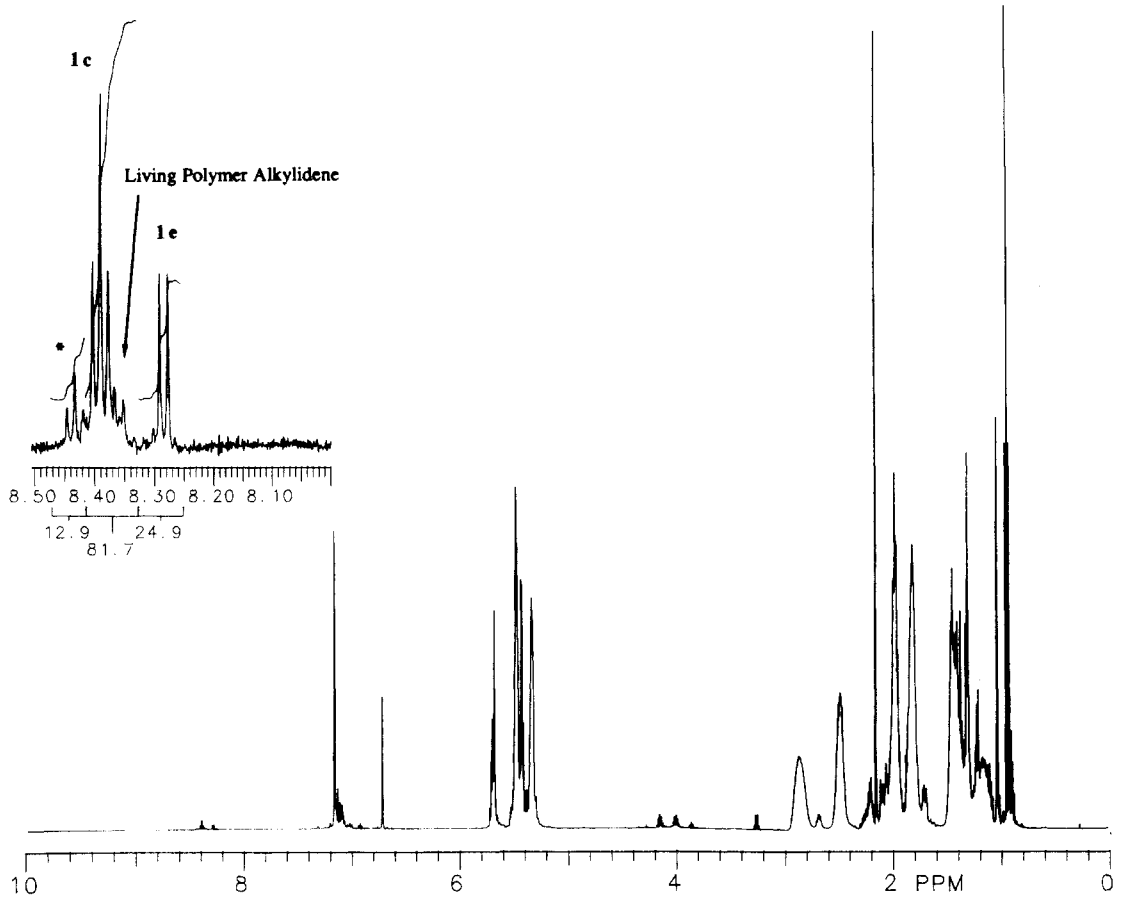

Figure 2. NMR studies of the reaction between W[$(CHC_5H_8CH)_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ (0.02 M) and **2c** (0.12 M) in C_6D_6 at 25 °C after 15 min.

in a realistic time period and in a quantitative manner may be difficult. In retrospect, cyclopentenes probably are not going to be the best chain-transfer reagents. Although activity of catalysts of the type described here can vary significantly and the advantage of the less active molybdenum catalyst system over that of tungsten has been demonstrated, the cyclopentene double bond probably is simply not reactive enough relative to an ordinary double bond to make chain-transfer fast and quantitative. Therefore, reagents that have a much more reactive double bond in the ring (e.g., norbornenes or cyclobutenes) would be much more desirable, although it is not known whether ring closure to give cyclohexenes will be successful in general. Finally, if chain transfer is to be truly useful, the initiating alkylidene complex must be regenerated in high yield and it must be stable over the time required to carry out the chain-transfer reaction. Although these are severe requirements, the studies reported here are only the first studies of this approach, and we would not be justified in stating that a successful combination of catalyst and chain-transfer agent could not be developed.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina. NMR data are listed in parts per million downfield from TMS. Coupling constants are quoted in hertz. Obvious multiplicities and routine constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[1a] was prepared as described in the literature. All other reagents were purchased from commercial sources and purified by standard techniques. GLC studies were done on a Shimadzu GC-9A gas chromatograph equipped with FID.

Preparation of Compounds. 2-(2-Cyclopentenyl)-1-ethanol. 2-(2-Cyclopentenyl)-1-ethanol was prepared by standard reduction of 2-cyclopentene-1-acetic acid with 1 equiv of $LiAlH_4$. The product was distilled at 58–61 °C and ~5 mm to yield 15.71 g (140 mmol, ~88% yield) of the alcohol. ^{1}H NMR δ 5.66 (m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 3.55 (br, 2, CH_2OH), 2.98 (br, 1, CH_2OH), 2.75 (m, 1, $\overline{CH{=}CHCH_2CH_2CH}$), 2.20–1.35 (complex m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2CH_2}$Br).

2-(2-Cyclopentenyl)-1-bromoethane. A mixture of 2-(2-cyclopentenyl)-1-ethanol (20 g, 178 mmol) and 47.5 g of triphenylphosphine (181 mmol, 1.02 equiv) dissolved in ~250 mL of dry dichloromethane was chilled in an ice bath. *N*-Bromosuccinimide (31.3 g, 79 mmol, 1.0 equiv) was added carefully in small portions while the reaction was stirred at 0 °C. After the addition was complete, this solution was allowed to warm to room temperature over a period of ~4 h. This magenta-colored mixture was then poured into ~800 mL of pentane. The mixture was chilled to 0 °C and filtered. The solvents were removed on a rotary evaporator and the oily liquid transferred in vacuo at 0.001 μm with the aid of a warm water bath into a liquid nitrogen cooled receiver. GC analysis of this product shows it to be ~92% pure, the major contaminant being unreacted alcohol. The yield is 18.7 g (107 mmol, ~60%). This material is sufficiently pure to be used without further purification. ^{1}H NMR ($CDCl_3$) δ 5.74–5.64 (dm, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 3.40 (m, 2, CH_2Br), 2.81 (m, 1, $\overline{CH{=}CHCH_2CH_2CH}$), 2.29–1.42 (complex m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$). This method of bromination in our hands produces a higher yield than those employing PBr_3, $SOBr_2/SOCl_2$, or triphenylphosphine dibromide.

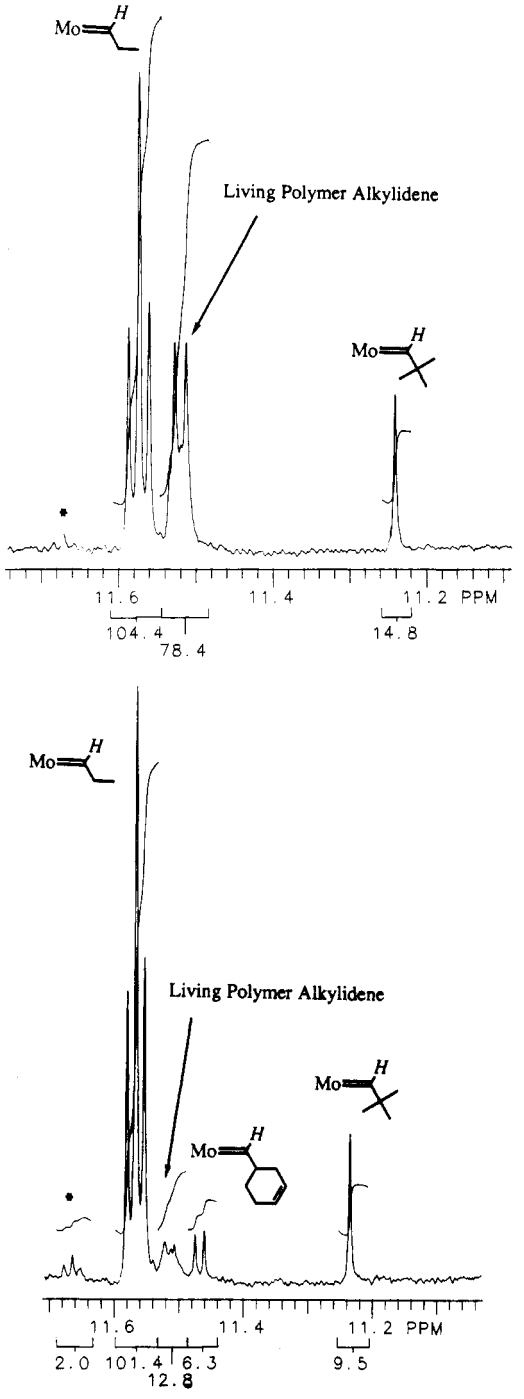

Figure 3. NMR studies of the reaction between Mo-[$(CHC_5H_8CH)_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$ (0.02 M) and **2c** (0.12 M) in C_6D_6 at 25 °C after (a, left) 17 min and (b, right) 90 min.

Chain-Transfer Reagents 2a and 2d (General Procedure). The triphenylphosphonium salt of 2-(2-cyclopentenyl)-1-bromoethane was first prepared from 6.0 g of the bromide (34 mmol) and 9.0 g of triphenylphosphine (34 mmol, 1 equiv) by warming the mixture to ~60 °C until the triphenylphosphine dissolved. The temperature was then raised to ~100 °C and the mixture stirred for ~4 h. After ~1 h the mixture appeared cloudy. Toward the end of the reaction period, efficient stirring became difficult since the mixture thickened to a fairly transparent yellowish orange solid. The solid was cooled to room temperature and dissolved in warm chloroform. Ether was added slowly to the chloroform solution until the phosphonium salt began to precipitate, and the mixture was subsequently cooled to −78 °C. Ether was slowly added periodically until precipitation appeared to be largely complete. The mixture was kept overnight at −78 °C and more ether was then added to complete precipitation. The mother liquor was then decanted away from the remaining solids which were then placed under vacuum. The flask was allowed to warm to room temperature and the gently warmed further to ~50 °C. After ~2 h, a fluffy white solid remained (12.0 g, 27.4 mmol, ~80% crude yield). If manipulated, the solid tends to turn into a gum.

1-(2-Cyclopentenylmethyl)-2-*tert*-butylethene (2a). The solid from the previous reaction was suspended in ~250 mL of diethyl ether and the suspension was chilled to −78 °C. *n*-Butyllithium was added slowly (~10.4 mL, 2.65 M in hexane, 27.6 mmol, 1 equiv) to the stirred suspension. The reaction was warmed to room temperature and stirred for about 6 h. The reaction mixture slowly turned a deep red–orange, gas was evolved, and powdery tan-colored solids precipitated out as the original solids dissolved. The reaction mixture was then chilled to −78 °C, treated with 3.4 mL of pivaldehyde (31 mmol, 1.1 equiv), and warmed to room temperature. After 24 h the reaction was treated with ~500 mL of pentane, chilled to ~0 °C, dried over magnesium sulfate, and filtered. The solvents were removed in vacuo to give ~5 mL of crude **2a** as a brown oil. Crude **2a** was stored over magnesium sulfate and later transferred in vacuo to a liquid nitrogen cooled receiver at 0.05 μm with the aid of a heat gun. Approximately 1.32 g of **2a** is obtained by this method (~29%). It was purified by preparative GLC: ^{1}H NMR δ 5.70 (m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 5.46–5.20 (m, 2, $CH_2CH{=}CH$-*t*-Bu), 2.64 (m, 1, $\overline{CH{=}CHCH_2CH_2CH}$), 2.20 (m, 4, $\overline{CH{=}CHCH_2CH_2CH}$), 1.94 (m, 1) and 1.46 (m, 1, $CH_2CH{=}CH$-*t*-Bu), 1.11 (s, 9, CMe_3).

1-(2-Cyclopentenylmethyl)-2-phenylethene (2d). Procedures analogous to those above were followed employing benzaldehyde. A higher temperature must be used in the preliminary distillation step. Crude **2d** was purified by preparative GLC: ^{1}H NMR δ 7.36–7.12 (m, 5, H_{aryl}), 6.56–6.40 (m, 1) and 6.28–6.21 (m, 1, $CH{=}CH$Ph), 5.77 (m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 2.78–2.80 (br m, 1, $\overline{CH{=}CHCH_2CH_2CH}$), 2.40 (br m, 4, $\overline{CH{=}CHCH_2CH_2CH}$), 1.99–1.49 (m, 2, $CH_2CH{=}CHPh$).

2-Cyclopentene-1-acetaldehyde. The Swern oxidation procedure[9] using oxalyl chloride, dimethyl sulfoxide, and 11.48 g of 2-cyclopentene-1-ethanol (102 mmol) was employed. The crude product was distilled (bp 92 °C at ~30–40 mm) to give 8.12 g (72%) of the aldehyde. ^{1}H NMR ($CDCl_3$) δ 9.76 (s, 1, CHO), 5.76 (m, 1) and 5.64 (m, 1, $CH{=}CH$), 3.12 (m, 1, $CHCH_2$), 2.45–1.43 (complex m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$).

Triphenylpropylidenephosphorane. Triphenylpropylphosphonium bromide (60 g, 156 mmol) was suspended in 500 mL of ether in a Schlenk flask under dinitrogen. The mixture was chilled to −78 °C and *n*-butyllithium (2.5 M, 62.29 mL, 156 mmol, 1 equiv) was added to the cooled suspension via a syringe over a period of 20 min. After the addition was complete, the mixture was allowed to warm to 0 °C and stir for 3 h. In a drybox, the LiBr was filtered off and the orange–red supernatant concentrated to give a reddish solid which was recrystallized from ether to give 36.2 g (76%) of the ylide as an orange–red solid: ^{1}H NMR δ 7.71 (m, 6) and 7.05 (m, 9, H_{aryl}), 2.45 (m, 2, $CHCH_2CH_3$), 1.41 (dt, J_{HP} = 2.5, J_{HH} = 7.4 Hz, 3, CH_2CH_3), 1.22 (m, 1, P=$CHCH_2$).

1-(2-Cyclopentenylmethyl)-2-ethylethene (2c). 2-Cyclopentene-1-acetaldehyde (13 g, 105 mmol) was dissolved in 250 mL of ether and the solution was cooled to −78 °C. Triphenylpropylidenephosphorane (40.95 g, 134 mmol) was added as powder over a period of 15 min. The mixture was then warmed to room temperature and stirred for 3 h. The reaction was quenched with 50 mL of water. The aqueous layer was discarded and the mixture filtered to remove triphenylphosphine oxide. The mixture was extracted with pentane and solids were again filtered off. Concentration of the pentane extract left an oil which was distilled (bp 95 °C at 60 mm) to give 10.3 g of the product (72%): ^{1}H NMR δ 5.70 (m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 5.44 (m, 2, $CHCH_2CH{=}CHCH_2CH_3$), 2.67 (m, 1, $\overline{CH{=}CHCH_2CH_2CH}$), 2.25–1.39 (complex m, 8, $\overline{CH{=}CHCH_2CH_2CHCH_2CH{=}CHCH_2CH_3}$), 0.91 (t, J_{HH} = 7.3 Hz, 3, CH_3).

1-(2-Cyclopentenylmethyl)-2-ethylethene-*2-d* (2c-d_1). $\overline{CH{=}CHCH_2CH_2CHCH_2CH{=}CDCH_2CH_3}$ was prepared in a manner analogous to the preparation of **2c**. 1-Dideuterio-1-

propanol was prepared by reduction of propionic acid with $LiAlD_4$, and 1-dideuterio-1-bromopropane by treating the alcohol with HBr/H_2SO_4:[10] ^1H NMR δ 5.70 (br m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 5.42 (br m, 1, $CH_2CH{=}CDEt$), 3.7 (br m, 1, $\overline{CH{=}CHCH_2CH_2CH}$) 2.4-1.9 (m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 1.5–1.3 (m, 2, $CDCH_2CH_3$), 0.91 (t, 3, $CDCH_2CH_3$). This material was further purified by preparative GLC.

1-(2-Cyclopentenylmethyl)-2-isopropylethene (2b). Triphenylisobutylphosphonium bromide (12.25 g, 30.68 mmol) was suspended in 200 mL of ether and the mixture was cooled to −78 °C. *n*-Butyllithium (2.5 M, 12.27 mL) was added to the suspension over a period of 20 min. The mixture was warmed to 0 °C and stirred for 2 h and then warmed to room temperature and stirred for 30 min. The orange solution was cooled back to −78 °C and 2-cyclopentene-1-acetaldehyde (3.38 g, 30.68 mmol) was added. The mixture was warmed to room temperature, stirred for 2 h, and quenched with 50 mL of water. The organic layer was separated and filtered to remove triphenylphosphine oxide. The filtrate was concentrated, pentane was added, and more triphenylphosphine oxide was filtered off. Concentration of the filtrate gave an oil which was distilled at 92 °C and 30 mm to give 3.5 g (76%) of the product: ^1H NMR ($CDCl_3$) δ 5.70–5.65 (m, 2, $\overline{CH{=}CHCH_2CH_2CH}$), 5.4–5.1 (m, 2, $CH{=}CHCH(CH_3)_2$), 2.8–1.1 (complex m, 8, $\overline{CH{=}CHCH_2CH_2CHCH_2}CH{=}CHCH(CH_3)_2$), 0.92 (d, 6, $CH(CH_3)_2$).

(3-Cyclohexenyl)methanal.[10] This material also was prepared by the Swern oxidation procedure[9] utilizing oxalyl chloride and dimethyl sulfoxide and 10 g of (3-cyclohexenyl)methanol (89.15 mmol). Distillation of the crude product at ~7–15 mm yields the pure product (bp 57.5–60 °C; yield 7.7 g, 70 mmol, ~78%): ^1H NMR ($CDCl_3$) δ 9.64 (s, 1, CHO), 5.65 (m, 2, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 2.45 (m, 1, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 2.19–1.6 (complex m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$).

1-(3-Cyclohexenyl)-2-ethylethene (3c). Triphenylpropylphosphonium bromide (3.50 g, 9.08 mmol) was suspended in ~60 mL of dry diethyl ether and the suspension was chilled to −78 °C. *n*-Butyllithium (4.5 mL, 2.01 M, 9.0 mmol, 0.99 equiv) was then added via syringe and the reaction warmed to room temperature and stirred for 2 h. The reaction was again chilled to −78 °C and quenched with an ethereal solution containing 1.01 g of (3-cyclohexenyl)methanal. The reaction was warmed to room temperature, stirred overnight, and filtered. The solids were washed with pentane and the solvents removed from the filtrate in vacuo (1.01 g crude yield, 7.4 mmol, ~82%). The crude product was distilled at ~1 mm to yield pure **3c** (bp 25–28 °C), 0.56 g (4.1 mmol, ~45%). Capillary GLC shows this material to be ~96% pure: ^1H NMR ($CDCl_3$) δ 5.66 (m, 2, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 5.45–5.15 (m, 2, $CHCH{=}CHCH_2CH_3$), 2.5 (m, 1, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 2.05–1.3 (complex m, 8, $CH_2CH{=}CHCH_2CH_2CHCH{=}CHCH_2CH_3$), 0.95 (t, 3, CH_2CH_3).

(3-Cyclohexenyl)bromomethane. This compound was prepared in a manner analogous to that for 2-(2-cyclopentenyl)-1-bromoethane, using 25.0 g (3-cyclohexenyl)methanol (0.22 mol). The crude product was distilled at ~1 mm (bp 42–46 °C; yield 26.13 g, 0.15 mmol, ~68%). GLC analysis showed the product to be ~96% pure: ^1H NMR ($CDCl_3$) δ 5.63 (br, m, 2, $CH{=}CH$), 3.34 (d, 2, $CHCH_2Br$), 2.2–1.3 (complex m, 7, $\overline{CH{=}CHCH_2CH_2CHCH_2}$).

1-(3-Cyclohexenyl)-2-*tert*-butylethene (3a). The Grignard was prepared in the normal fashion from 2.04 g of (3-cyclohexenyl)bromomethane (11.7 mmol) and was treated with pivaldehyde to yield (after the usual workup) crude 1-(3-cyclohexenyl)-2-*tert*-butyl-2-ethanol (yield 1.00 g, 5.5 mmol, ~47%): ^1H NMR (C_6D_6) δ 5.53 (br m, 2, $CH{=}CH$), 3.4–3.3 (m, 1, CHOH-*t*-Bu), 3.15 (s, 1, OH), 2.2–1.9 (m, 3, $CHCH_2CHOH$-*t*-Bu), 1.8–0.9 (m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 0.78 and 0.76 (s, 9, CMe_3, diastereomeric compound).

Crude 1-(3-cyclohexenyl)-2-*tert*-butyl-2-ethanol (1 g, 5.5 mmol) was dehydrated with $POCl_3$ in pyridine.[11] The crude alkene was obtained as a yellow oil (0.62 g, 3.8 mmol, ~69%) that was purified by preparative GLC: ^1H NMR δ 5.68 (dm, 2, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 5.52, 5.46, 5.41, 5.38, 5.35, 5.33 (m, $CH{=}CH$-*t*-Bu), 2.3–1.1 (complex m, 7, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 1.01 (s, 9, CMe_3).

1-(3-Cyclohexenyl)-2-phenylethene (3d). This compound was prepared in a manner analogous to that used to prepare **3c**, using 7.90 g of benzyltriphenylphosphonium bromide (18.2 mmol) and 2.1 g of (3-cyclohexenyl)methanal (19.1 mmol, 1.05 equiv). The crude product, 3.1 g of cloudy yellowish oil, was distilled at ~1 mm (bp 76–89 °C) by using an oil bath (~130–140 °C) to yield 2.68 g of the colorless product (14.5 mmol, ~80%). The cis and trans isomers of the product can be separated by preparative GLC. ^1H NMR δ 7.3–7.0 (m, 5, H_{aryl}), 6.4–6.09 and 5.5–5.4 (m, 2, $CH{=}CHPh$), 5.68 and 5.61 (m, 2, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 2.3 (m, 1, $\overline{CH{=}CHCH_2CH_2CHCH_2}$), 2.2–0.9 (m, 6, $\overline{CH{=}CHCH_2CH_2CHCH_2}$).

4-(3-Hexenyl)cyclopentene. 3,4-Epoxycyclopentene[12] was prepared from freshly cracked cyclopentadiene, sodium carbonate, and 40% peracetic acid in 1.2 L of dichloromethane. It was rearranged to 3-cyclopentenone[13] by using a catalytic amount of tetrakis(triphenylphosphine)palladium in dichloromethane at 0 °C. 3-Cyclopentenone was reduced with $LiAlH_4$ virtually quantitatively to 3-cyclopenten-1-ol by standard methods. The crude material is pure enough to be used in subsequent steps. On a larger scale it can be purified by distillation at 71–73 °C (46 mm). Isomeric purity was determined by converting the alcohol to its acetate derivative with acetic anhydride and pyridine and analysis by GLC.[14]

4-Bromocyclopentene was prepared by adding 5.1 g (29 mmol) of *N*-bromosuccinimide slowly in portions to a solution of 2 g (24 mmol) of 3-cyclopenten-1-ol and 7.5 g (29 mmol) of triphenylphosphine in 25 mL of dichloromethane at 0 °C. The mixture was allowed to warm to room temperature, stirred for 2 h, diluted to four times its volume with pentane, and cooled in an ice bath. The solids were filtered off and washed with pentane, and the filtrate was concentrated in vacuo. Pentane was added to the residue and the solids were filtered off. The process was repeated twice more. The final step produced 2.8 g (80% yield) of 4-bromocyclopentene. It could be used directly or purified by distillation.

A Grignard reagent was prepared from 4.86 g (33 mmol) of 4-bromocyclopentene and 1.21 g (50 mmol) of magnesium in 30 mL of tetrahydrofuran. The reaction was initiated with a crystal of iodine. The Grignard reagent was transferred into a new flask via a cannula. This solution was cooled to 0 °C and 5.43 g (33.3 mmol) of 1-bromo-*cis*-3-hexene in 10 mL of tetrahydrofuran was added followed by 5 mL of a 0.1 M solution of Li_2CuCl_4 in tetrahydrofuran (0.015 equiv). The mixture was allowed to warm to room temperature and stir overnight. The reaction was quenched by pouring it into 50 mL of ice-cold saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the solvents removed in vacuo to give 4 g of crude 4-(3-hexenyl)cyclopentene. Pure product was obtained by preparative GLC.

Typical Reaction of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (1a) with Chain-Transfer Reagents. Approximately 30 mg (0.036 mmol) of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was dissolved in C_6D_6 and 5 mg of mesitylene added as an integration standard. Approximately one-third of this solution was withdrawn and used as a reference. To the remaining solution ~4 equiv (based on 0.024 mmol of catalyst in the remaining solution) of the appropriate chain-transfer reagent was added. This solution was split into two equivalent portions and one was treated with 17 mg of norbornene (0.180 mmol, 15 equiv based on 0.012 mmol of remaining catalyst). Integration of the mesitylene aromatic protons versus the alkylidene signal(s) can be used as a check to determine if the alkylidene is decomposing. Because the alkylidene α-proton

resonance in the living oligomer is a well-defined doublet, this signal can be integrated relative to the same mesitylene protons in the third sample to show that alkylidene is still present, even if the alkylidene signal generated by the reaction of the catalyst with the chain-transfer reagent is indistinguishable from the base line or otherwise obscured.

Typical Reaction of Chain-Transfer Reagents with W(CHEt)(NAr)(O-*t*-Bu)$_2$. A solution of W(CHEt)(NAr)-[(OCMe(CF$_3$)$_2$]$_2$(3-hexene)$_{0.9}$[1a] (10 mg, 0.01 mmol per sample required) in toluene-d_8 was chilled to −40 °C. A suspension of 1.9 mg of LiO-*t*-Bu (0.02 mmol, 2 equiv per sample in toluene-d_8) also was chilled to −40 °C. The solvent volume was adjusted so that after combination with the solutions of the appropriate chain-transfer reagents and fractionation of the reaction mixture(s) into the desired number of NMR samples, the volume of each final NMR sample would be appropriate. It is desirable to add a slight excess (~5%) of LiO-*t*-Bu. Mesitylene was added to the solution of the alkylidene complex as an NMR integration standard; one drop (approximately 6 mg) is a desirable quantity in a 30- or 40-mg scale reaction. The two chilled solutions are combined and allowed to stir while being warmed to room temperature for approximately 15 min. One sample is then reserved as a reference, while the others are treated with toluene-d_8 solutions of the appropriate chain-transfer (or other) reagents. Approximately 70% of the hexafluoro-*tert*-butoxide alkylidene complex (δ $^1H_\alpha$ 9.2 ppm (t)) is converted to the *tert*-butoxide complex (δ $^1H_\alpha$ 8.43 ppm (t)) according to NMR spectra. Approximately 70% of the *tert*-butoxide propylidene complex thus prepared remains after a period of ~24 h if stored at −40 °C; about 30% remains if the sample is stored at room temperature for ~24 h.

Analysis of the Products from the Reaction of W(CHEt)(NAr)(O-*t*-Bu)$_2$ with 3c. W(CHEt)(NAr)(O-*t*-Bu)$_2$ was prepared in situ as described above (0.021 mmol). Mesitylene, 10 mg, was used as an NMR internal standard. One-third of this solution is reserved for the NMR integration standard, one-third for a different experiment, and the final portion was treated with a solution of 4 mg of **3c** (0.029 mmol, 4 equiv). The reaction was allowed to proceed for ~120 min. The ^1H NMR spectrum after ~40 min showed the expected doublet in place of the original propylidene triplet. The samples were then quenched with ~20 μL of benzaldehyde (21 mg, 0.20 mmol, 28 equiv) and filtered through alumina. GLC analysis showed starting material, β-3-cyclohexenylstyrene, and β-ethylstyrene. The actual ratio of cyclohexene to catalyst may be back-calculated from the double internal standards (vide infra); for this run it was 6:1. Peaks consistent with traces of 1-(2-cyclopentenylmethyl)-1-ethylethene also were observed in the mixture, although the amount was too small to enable confirmation.

Analysis of Products from the Reaction of 1a with 2c. W(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (30 mg, 0.052 mmol) was dissolved in a small amount of C_6D_6 containing 10 mg of mesitylene. 2-(2-Cyclopentenylmethyl)-1-ethylethene (31 mg, 0.23 mmol, 4 equiv) was added to C_6D_6 containing 8 mg of toluene-d_8 as a GLC internal standard. Approximately one-third of each of these solutions was reserved as standards. The remaining portions were combined and allowed to react for ~10 min. One-half was quenched with 20 μL of benzaldehyde (21 mg, 0.20 mmol, 9 equiv based on one-third of the original amount of catalyst) and the other half was monitored by ^1H NMR for ~70 min. This sample and the NMR internal standard sample were then quenched with another 20 μL of benzaldehyde. Both quenched samples were then filtered through alumina and analyzed by GLC. The peaks were correlated with proposed products by co-injection with samples of the proposed products synthesized by classical methods and identified by ^1H NMR. The double internal standards used in this experiment allowed the actual ratio of chain-transfer reagent to catalyst to be calculated from the ratio of standards: in this case 8:1 for the 10-min reaction and 9:1 for the 120-min reaction. The catalyst concentration was determined from the ratio of the styrenes to mesitylene in the GLC trace (the expected molar ratio is 0.63:1 styrene/mesitylene for this experiment). The organic products could be quantitated relative to toluene-d_8, the expected ratio being 2.8:1 organics/toluene-d_8. The ratio measured from the reserved GLC sample was 2.6:1.

Analysis of Products from the Reaction of W(CHEt)(NAr)(O-*t*-Bu)$_2$ with 2a. A sample of the propylidene complex (0.021 mmol) containing 10 mg of mesitylene as an internal standard was prepared. One-third of this sample was reserved as a standard and another third used for another experiment. **2a** (5 mg, 0.03 mmol, 4 eq) combined with 12 mg of C_6D_6 (as a GLC internal standard) in toluene-d_8 was added to the remaining third. A ^1H NMR spectrum after ~65-min reaction time showed a trace of the neopentylidene complex, but primarily a triplet in the alkylidene region. The solution was quenched with 20 μL of benzaldehyde (0.21 mg, 28 equiv) after ~120-min total reaction time, filtered through alumina, and analyzed by GLC. The actual ratio of chain-transfer reagent to catalyst can be back-calculated (vide supra) to be 2.3:1. Only starting material was seen, plus some β-ethylstyrene (from quenching of the propylidene complex with benzaldehyde).

Cyclopentene Polymerization. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (28 mg, 0.05 mmol) was dissolved in 3 mL of toluene and the solution was treated with 1 mL (774 mg, 11.4 mmol, 234 equiv) of cyclopentene. Aliquots were removed after 1, 2.2, and 4 h and quenched with 4 μL of benzaldehyde (0.04 mmol, 3 equiv based on one-quarter of the starting matertial). The solvents were removed from the quenched solutions in vacuo, and the polymer samples were dissolved in dichloromethane, filtered through alumina, and analyzed by GPC. A similar experiment was performed at −40 °C. The results are shown in Table I.

Reversibility of Cyclopentene Polymerization. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (66 mg, 9.11 mmol) was dissolved in 6 mL of toluene. This solution, 66 μL, was withdrawn as an NMR integration standard (contains one-ninth of the total amount of catalyst, or 7.3 mg, 0.01 mmol)). The solvents were removed from this sample and it was redissolved in C_6D_6 containing a mesitylene standard. Toluene, 66 μL, was added to bring the volume of the original solution back to 6 mL. This solution was then split into two 3-mL portions. (Each portion contains 29 mg, 0.05 mmol, of catalyst.) One portion was chilled to −40 °C for ~1 h, 1 mL of cyclopentene (774 mg, 11.4 mmol, 223 equiv) was added, and the sample was kept at −40 °C where it became gelatinous. The other half of the catalyst solution was treated with 1 mL of cyclopentene at 25 °C. Aliquots of 1 mL each were taken from each reaction at intervals of 0.25, 1, 2, and 4 h. Each aliquot contains 7.3 mg of catalyst. The volatile components were removed from the aliquots in vacuo, and the residue was dissolved in 800 μL of a solution composed of 10 mL of C_6D_6 and 49 mg of mesitylene as an integration standard. Comparison of the neopentylidene resonance and the mesitylene aromatic resonances in each of the samples yielded the amount of alkylidene recovered.

Chain Transfer Using 1-(2-Cyclopentenylmethyl)-1-ethylethene with a W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ Catalyst System. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (12 mg, 0.021 mmol) was dissolved in 300 μL of C_6D_6 and 100 μL of a standard solution consisting of 27 mg of mesitylene and 1 mL of C_6D_6 was added. To this catalyst solution was added in one portion a second solution composed of 40 mg of norbornene (0.42 mmol, 20 equiv) dissolved in 300 μL of C_6D_6. This was allowed to stir at room temperature for ~5 min and was then treated with a solution of 17 mg of 1-(2-cyclopentenylmethyl)-1-ethylethene (0.12 mmol, 6 equiv) in 300 μL of C_6D_6. The solution was filtered into an NMR tube and frozen until spectra could be run. ^1H NMR spectra were run at reaction times (after thawing) of 10, 17, 25, 40, 55, 70, 100, and 130 min.

Chain Transfer Using 1-(2-Cyclopentenylmethyl)-1-ethylethene with a Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ Catalyst System. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.021 mmol) was dissolved in 300 μL of C_6D_6 to which was added a 100 μL standard solution composed of 25 mg of mesitylene dissolved in 1 mL of C_6D_6. A second solution consisting of 40 mg of norbornene (0.42 mmol, 20 equiv) dissolved in 300 μL of C_6D_6 was added to this solution in one portion. This was allowed to stir at room temperature for ~5 min and was subsequently treated with a solution consisting of 17 mg of 1-(2-cyclopentenylmethyl)-1-ethylethene (0.12 mmol, 6 equiv). The reaction was filtered into an NMR tube and frozen until the spectra could be run. ^1H NMR spectra were run at reaction times of 7, 15, 30, 45, 60, and 90 min, following thawing of the sample. During this time period, the total alkylidene concentration decreased by ~30% as judged by inte-

gration against the mesitylene standard.

Chain Transfer Using W(CHPh)(NAr)(O-*t*-Bu)$_2$. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (20 mg, 0.035 mmol) was dissolved in ~1 mL of C_6D_6 containing 9 mg of mesitylene as an NMR standard. This solution was treated with 34 mg of norbornene (0.361 mmol, 10 equiv) in ~1 mL of C_6D_6. The solution was then split into two and one portion was treated with 12 mg of 1-(2-cyclopentenylmethyl)-2-phenylethene (0.065 mmol, 3.7 equiv) in C_6D_6. The alkylidene H_α resonance for the living polymer disappeared and that characteristic of the benzylidene proton in W(CHPh)(NAr)(O-*t*-Bu)$_2$ appeared in ~60% yield over a period of ~1 h.

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Registry No. **1a**, 107440-84-6; **1b**, 120173-01-5; **1c**, 112481-72-8; **1d**, 120204-18-4; **1e**, 120173-02-6; **2a**, 120172-98-7; **2b**, 120172-95-4; **2c**, 120172-96-5; **2d**, 120173-00-4; **3a**, 120172-99-8; **3c**, 20837-03-0; **4a**, 13705-23-2; **4c**, 824-90-8; **4e**, 116269-95-5; **5**, 120172-97-6; cyclopentene (homopolymer), 25103-85-9; polypentenamer, 28702-43-4; norbornene (homopolymer), 25038-76-0.

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Poly(anhydrides). 3. Poly(anhydrides) Based on Aliphatic–Aromatic Diacids

Abraham J. Domb,† Carlos F. Gallardo, and Robert Langer*

Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, Massachusetts 02139. *Received October 13, 1988; Revised Manuscript Received January 25, 1989*

ABSTRACT: Poly(anhydrides) containing aliphatic and aromatic moieties, poly(ω-(*p*-carboxyphenoxy)alkanoic anhydride), of the structure $-(COC_6H_4O(CH_2)_xCOO)_n-$ (x = 1, 4, and 7) were synthesized by either melt or solution polymerization with molecular weights of up to 44 600. These polymers displayed a zero-order hydrolytic degradation profile for 2–10 weeks. The longer the length of the alkanoic chain, the longer the degradation rate. Stability studies under anhydrous conditions showed that these polymers were stable in solid state for over 6 months at 25 °C but underwent reversible self-depolymerization in chloroform solution.

Introduction

The surface-eroding properties of poly(anhydrides) (PA) in aqueous medium makes them desirable for controlled release of therapeutic substances.[1-3] These PA degrade by hydrolysis into nontoxic acid derivatives and show favorable biocompatibility in tissue response and toxicological studies.[3] The hydrolytic degradation rates can be altered several thousand-fold by simple changes in the polymer backbone.[1] Aliphatic poly(anhydrides) degrade in a few days while some aromatic poly(anhydrides) degrade over a period of few years.[2] Aromatic polyanhydrides display a zero-order degradation profile.[2] These aromatic polymers have low solubility in common organic solvents and have high melting points; therefore they cannot be easily fabricated into either microspheres or films. The degradation rates of copolymers made of aliphatic and aromatic moieties vary between these extremes, depending on the aromatic content.[1-4] However, in such copolymers the aliphatic regions degrade faster, and thus the aromatic component content of the device increases for a long period of time,[5] leading to a lack of linearity in the degradation process. We now report on new poly(anhydrides) that display zero-order degradation profiles over variable periods of time (i.e., days to months). These polymers are soluble in common organic solvents and have low melting points.

In contrast to copolymers based on aliphatic and aromatic diacids, these new homopoly(anhydrides) have the aliphatic and aromatic moieties combined into one identity. These monomers can be viewed as containing an aromatic head and an aliphatic tail. The addition of a monomer to the growing polymeric chain could result in a head-to-head (i.e., aromatic–aromatic), head-to-tail, or tail-to-tail sequence. Consequently, these polymers are

† Current address: Nova Pharmaceutical Corporation, Baltimore, MD 21224.
* To whom correspondence should be sent.

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