Ruthenium Alkylidene Initiated Living Ring-Opening Metathesis Polymerization (ROMP) of 3-Substituted Cyclobutenes

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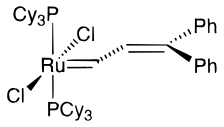
ABSTRACT: The synthesis and living ring-opening metathesis polymerization (ROMP) of substituted cyclobutenes were investigated with the functional group tolerant initiators $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**1**) and $(PCy_3)_2Cl_2Ru{=}CHPh$ (**2**). Synthetic methodology was developed for the synthesis of a wide variety of 3-functionalized cyclobutenes containing ether, ester, alcohol, amine, amide, and carboxylic acid substituents. Coordination of these functional groups to the propagating carbene was observed, resulting in the formation of a chelated propagating species with concomitant loss of one phosphine ligand from the metal center. Studies aimed at understanding this chelation and its effect on the polymerization were undertaken. On the basis of these results, the synthesis of a series of functionalized cyclobutenes was accomplished which minimized this chelation and allowed for living polymerizations. A new class of functionalized poly(butadiene)s were synthesized and their thermal properties analyzed by thermogravimetric analysis and differential scanning calorimetry.

Introduction

Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins has allowed for the synthesis of a wide range of functionalized polymers with control over polymer molecular weight and structure.[1−3] In particular, the ROMP of cyclobutenes to form poly(cyclobutene)s (equivalent to poly(butadiene)s) has been well documented, and this polymerization is driven by the high strain energy of the cyclobutene ring (29.8 kcal/mol).[4] Dall'Asta first observed the ROMP of cyclobutene in 1962 using $TiCl_4/Et_3Al$, resulting in high *cis*-poly(butadiene).[5] Two-component initiator systems such as $TiCl_4/(\pi\text{-}C_4H_7)_4Mo$,[6] $V(acac)_3/Et_3Al$,[7] $VCl_4/BuLi$,[8] $Cr(acac)_3/Et_3Al$,[7] $MoCl_3/Et_3Al$,[7] $MoCl_5/(\pi\text{-}C_4H_7)_4W$,[9] $MoCl_5/(\pi\text{-}C_4H_7)_2Mo$,[9] and $WCl_6/(\pi\text{-}C_4H_7)_4W$[9] were among the many later initiator systems used for the polymerization of cyclobutene and its derivatives. In addition, one component catalysts such as $Ph(MeO)C{=}W(CO)_5$,[10] $Ph_2C{=}W(CO)_5$,[11] and $RuCl_3$[12] were successful as well. Titanocene methylidenes were active for the polymerization of 3,4-diisopropylidenecyclobutene leading to a cross-conjugated polymer that was a precursor to conducting polymers.[13]

In none of these cases was a living polymerization of the cyclobutenes observed.[14,15] In the past few years, though, a few examples of the living polymerization of cyclobutenes were published. The attenuation of the rates of initiation and propagation using PMe_3 for $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ [Ar = 2,6-diisopropylphenyl] in the polymerization of cyclobutene led to the first living polymerization and the synthesis of block copolymers.[16,17] In a similar fashion, 3-methylcyclobutene and 3,3-dimethylcyclobutene were polymerized in a living manner using $Mo(CHC(CH_3)_2Ph)(NAr)(OC(CH_3)_2CF_3)_2$ [Ar = 2,6-diisopropylphenyl] and $PPhMe_2$.[18,19] The living polymerization of bicyclo[3.2.0]heptene using $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ was also observed.[20] Recently, the synthesis of poly(butadiene)s bearing acid and alcohol functionalities was accomplished through the living ROMP of 3,4-disubstituted cyclobutenes bearing benzyl ether and benzyl ester protecting groups.[21,22] Unfortunately, the introduction of the alcohol and carboxylic acid groups was accomplished only after a post-polymerization deprotection step due to the intolerance of the initiator toward these functionalities.

The ultimate goal would be the development of a methodology to allow for the living ROMP of highly functionalized cyclobutenes without the need for protection of functional groups, providing for the one-step synthesis of a wide range of functionalized poly(butadiene)s. This would allow for a more complete study of the properties of functionalized poly(butadiene)s that would be difficult to synthesize through other methods, and the synthesis of block copolymers with a number of functional groups would be possible, resulting in the formation of a wide range of new materials and a detailed study of the properties of block copolymers.[23] With the development of the highly functional group tolerant metathesis initiators $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (**1**)[24,25] and $(PCy_3)_2Cl_2Ru{=}CHPh$ (**2**),[26,27] such a



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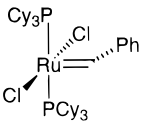

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goal seemed attainable. These and related complexes have been applied to the polymerization of cyclooctenes bearing a a variety of polar functional groups.[28,29] However, these polymerizations were not living due to the facile backbiting and chain transfer reactions that occurred during the polymerization. A system which could produce high initiation with no backbiting, chain transfer, or chain termination side reactions would result in a living polymerization producing polymers with low polydispersity.[14,15] This report presents the synthesis and polymerization of a series of 3-functionalized cyclobutenes. The development of a living polymerization of these cyclobutenes was achieved only after a complete understanding was obtained of the effect of the functional groups on the polymerization

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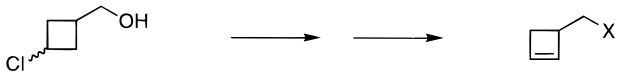
Table 1. Activation Energies for the Conrotatory Electrocyclic Ring-Opening of Selected Cyclobutenes

compound	E_a (kcal/mol)
cyclobutene	32.5
3-methylcyclobutene	31.6
3-chlorocyclobutene	29.4
3-acetoxycyclobutene	27.8
3-formylcyclobutene	27.0
3-ethoxycyclobutene	23.5

Scheme 1



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mechanism. Thermal analysis of the resulting functionalized poly(butadiene)s was accomplished by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Results and Discussion

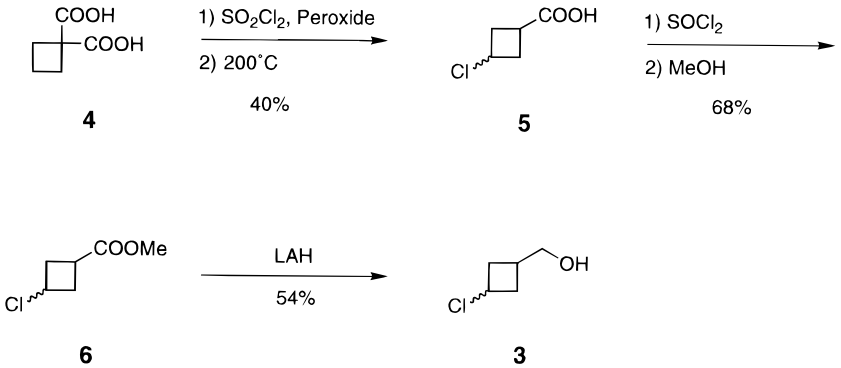
Initial Investigations. Before an intensive investigation of the synthesis and ROMP of 3-substituted cyclobutenes was undertaken, the factors affecting the stability of these compounds needed to be addressed. The conrotatory electrocyclic ring-opening of cyclobutenes to butadienes posed a complication for their use in polymerizations.[30] The presence of butadiene impurities in the monomer would lead to chain transfer through a side reaction of the propagating carbene with the butadiene olefins, thus broadening the polymer polydispersity (PDI) and preventing a living polymerization. The activation barriers for this ring-opening were determined for a series of 3-substituted cyclobutenes as presented in Table 1.[31−35] The presence of polar functionality in the 3-position lowered this activation barrier significantly.[33−35] In fact, 3-formylcyclobutene undergoes this ring-opening at 25 °C with a half-life of 50 h.[35] Due to these observations, placement of the functional group at least one carbon removed from the ring at the 3-position was proposed in order to provide more stable monomers in which this electrocyclic ring-opening reaction was minimized.

Utilization of a common intermediate which could be readily transformed into a series of functionalized cyclobutenes would simplify the synthetic approach. *cis, trans*-1-(3-Chlorocyclobutyl)methanol (**3**) appeared to be an attractive intermediate for this strategy. This compound provided not only a route for the incorporation of various functionalities through the elaboration of the alcohol substituent but also a route to the cyclobutene olefin by chloride elimination (Scheme 1). Compound **3** had been previously synthesized as illustrated in Scheme 2.[36,37] However, the low overall yield (15%) prompted an investigation into a more efficient synthesis of this compound. By simple reduction of carboxylic acid **5** with BH_3−THF,[38] compound **3** was formed in quantitative yield as illustrated in Scheme 3. After optimization of the first step coupled with the high yielding reduction step, a higher overall yield (50%) than the literature value was achieved with the elimination of one step in the procedure.

With an efficient synthesis of **3**, cyclobutenes bearing benzyl ether, trityl ether, and alcohol functionalities were synthesized as shown in Scheme 4. Alkylation of **3** with either benzyl bromide or trityl chloride and subsequent elimination of the resulting ethers **7** and **9** with K^+t-BuO^- in DMSO resulted in good yields of benzyl [1-(2-cyclobutenyl)methyl] ether (**8**) and [1-(2-cyclobutenyl)methyl] trityl ether (**10**), respectively. Attempted elimination with other bases including $NaNH_2$ (THF), LDA (THF), K^+t-BuO^- (THF), DBU (benzene), and KH (THF) resulted in no reaction, which was consistent with results observed in similar systems.[36,37] Elimination of **3** resulted in (2-cyclobutenyl)methanol (**11**) in 25% yield using a literature procedure.[36,37] Esterification of **11** with benzoyl chloride resulted in 1-(2-cyclobutenyl)methyl benzoate (**12**) in 74% yield as in Scheme 5. As expected, all the cyclobutenes were thermally stable, resulting in the lack of butadiene formation even after heating to >90 °C.

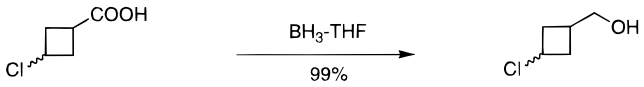
Initial polymerization of monomers **8**, **10**, **11**, and **12** was accomplished with initiator **1** as in Scheme 6. The polymerization of these monomers allowed for the investigation of the influence of functional groups of differing electronic and steric environments on the polymerization. Unfortunately, polymerization of (2-cyclobutenyl)methanol (**11**) resulted in a polymer that was insoluble in all the solvents compatible with initiator **1** including CH_2Cl_2, $CHCl_3$, toluene, benzene, and THF. The fact that polymer formation was observed was promising in that **1** appeared to be active for the polymerization of these cyclobutenes, in contrast to the results observed by Perrott and Novak for 3,4-disubstituted cyclobutenes with **1**.[21,22] Polymerization of **8**, **10**, and **12** presented no such complication. Optimal polymerization conditions employed for these monomers were at 45 °C in toluene with a monomer concentration ([M]) of 0.57 M (Table 2). Polymerization of these compounds at varying [monomer]:[initiator] ([M]:[I]) ratios was accomplished, allowing for the control over the polymer molecular weight for all three monomers. A linear correlation between the $\bar{M}_n$ and the [M]:[I] ratio was observed, providing initial support for a living polymerization (Figure 1). However, comparison of the PDIs of the polymers obtained showed that despite the fact that these monomers differed only in steric or electronic features reasonably far removed from the

Scheme 2



4 **5** **6** **3**

Scheme 3



5 **3**

Table 2. Initial Polymerization Results for Compounds 8, 10, and 12[a]

entry	monomer	[M]/[I]	rxn time (h)	$\bar{M}_n$[b]	PDI[b]
1	**8**	25.7	1.0−1.5	4900	1.18
2	**8**	53.1	1.0−1.5	8000	1.17
3	**8**	71.1	1.0−1.5	10700	1.17
4	**8**	96.7	1.0−1.5	15900	1.15
5	**8**	152	1.0−1.5	21300	1.16
6	**10**	8.70	<0.5	6500	1.60
7	**10**	51.6	<0.5	12600	1.44
8	**10**	94.6	<0.5	25900	1.31
9	**10**	189	<0.5	34900	1.30
10	**12**	26.0	<0.5	4200	1.70
11	**12**	47.1	<0.5	5600	1.65
12	**12**	70.6	<0.5	9000	1.60
13	**12**	131	<0.5	11100	1.57
14	**12**	218	<0.5	15300	1.71

[a] Polymerizations were run in toluene at 45 °C with [M] = 0.57 M. [b] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

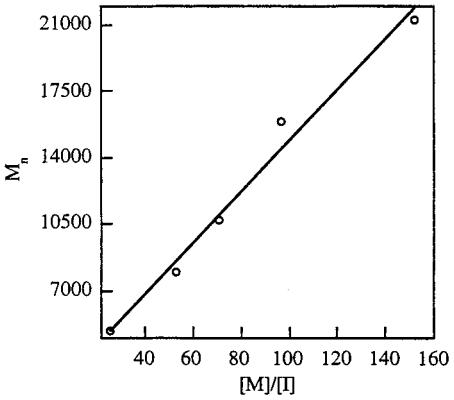


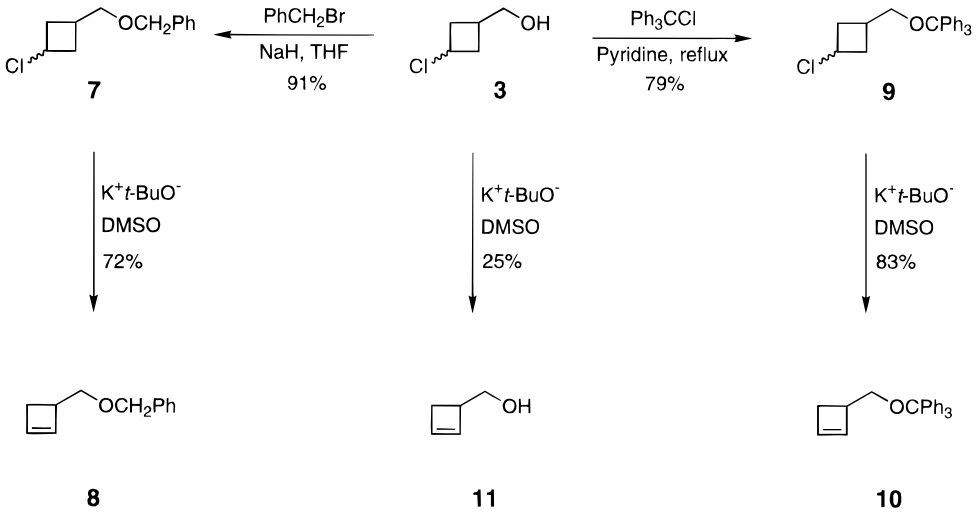
Figure 1. Molecular weight dependence of the polymerization of **8** on [M]/[I].

olefinic moiety, dramatic changes in the PDIs were observed. For benzyl [1-(2-cyclobutenyl)methyl] ether (**8**), the polymerization reached completion after 1−1.5 h and low PDIs between 1.15 and 1.18 were obtained (entries 1−5), while for [1-(2-cyclobutenyl)methyl] trityl ether (**10**), which differed from **8** predominantly in its steric environment surrounding the ether oxygen, the polymerization reached completion after <0.5 h and PDIs between 1.30−1.60 were obtained. 1-(2-Cyclobutenyl)methyl benzoate (**12**), which differed from **8** in the electronic character of the oxygen atom but was sterically similar, polymerized to completion in <0.5 h and resulted in even broader PDIs of 1.57−1.71 (entries 10−14).

In order to gain more insight into the causes for these PDI differences, the propagating carbenes were investigated by ^{1}H and ^{31}P NMR. The monomers were polymerized under the standard conditions at 45 °C in toluene-d_8 ([M] = 0.57 M) for 1 h, and then they were analyzed by ^{1}H and ^{31}P NMR. For the benzyl ether (**8**), two distinct regions were observed at 19.84 and 17.73 ppm for the α-H of the carbene in the ^{1}H NMR in a ratio of 1.00:8.91 (Table 3). By ^{31}P NMR, a major species at 57.76 ppm and a minor species at 37.35 ppm were observed in addition to free PCy_3 at 10.82 ppm which integrated to 1.02 relative to the species at 57.76 ppm. For the trityl ether (**10**), again two distinct regions were observed in the ^{1}H NMR at 19.86 and 18.41 ppm in a 1.00:1.43 ratio (Table 3). ^{31}P NMR showed a multiplet at 38.90 ppm and a multiplet at 36.60−35.21 ppm with free PCy_3 at 10.80 ppm integrating to 1.05 relative to the peak at 38.90 ppm. Finally, the benzoate ester (**12**) had multiplets at 19.83 and 17.79 ppm in a 1.80:1.00 ratio in the ^{1}H NMR (Table 3), and the ^{31}P NMR showed peaks at 40.28 ppm and a broad multiplet from 37.01 to 35.00 ppm with free PCy_3 integrating to 1.01 relative to the peak at 40.28 ppm. These results were compared with the species observed for the polymerization of cyclooctadiene (COD), which resulted in a broad triplet at 19.67 ppm in the ^{1}H NMR and 36.42 ppm in the ^{31}P NMR with no observed free PCy_3.

On the basis of these combined results, it was proposed that the upfield resonance in the ^{1}H NMR corresponded to a mono(phosphine) propagating species (**B**) and the downfield resonance corresponded to the normal bis(phosphine) species (**A**). The results were based primarily on the fact that the polymerization of COD, which showed the absence of free PCy_3, resulted in a ^{1}H NMR carbene resonance at 19.67 ppm, similar to the values at 19.84, 19.86, and 19.83 ppm for compounds **8**, **10**, and **12**. In addition, the more upfield resonances in the ^{1}H NMR between 17.73−18.41 ppm appeared to correspond with the more downfield shifts in the ^{31}P NMR based on integration measurements, and these downfield resonances in the ^{31}P NMR inte-

Scheme 4



7 **3** **9**

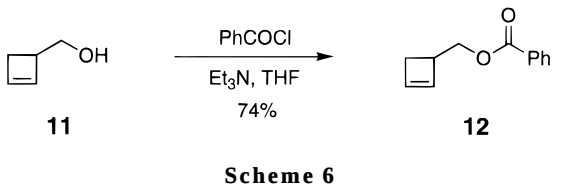
8 **11** **10**

Table 3. ^{1}H NMR Analysis of the Polymerization Propagating Species

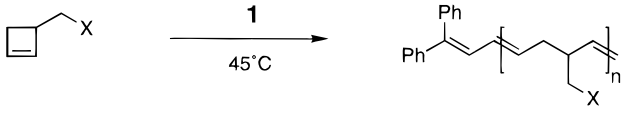
polymer	X	% initiation with 5 equiv of [M][a]	^{1}H NMR carbene resonance **A**[b]	**B**[b]	ratio **B**/**A**[b]	10^3K_{eq}[b]
poly(**8**)	OCH_2Ph	>99	19.84	17.73	8.91	81
poly(**10**)	$OC(Ph)_3$	25	19.86	18.41	1.43	8.5
poly(**12**)	OC(O)Ph	15	19.83	17.79	0.567	2.0
poly(**11**)	OH	>99		17.70	>99.0	>990
poly(**15**)	$N(i\text{-}Pr)_2$	>99		17.97	>99.0	>990
poly(**17**)	OCH_2COOH	>99		17.74	>99.0	>990
poly(**18**)	OCH_2COOMe	>99	19.80	17.91	12.5	120
poly(**19a**)	OCH_2CONMe_2	>99		17.84	>99.0	>990
poly(**19b**)	$OCH_2CON(i\text{-}Pr)_2$	>99		17.76	>99.0	>990

[a] Polymerizations were run in toluene-d_8 at 45 °C for 1 h at [M] = 0.11 M and [I] = 0.022 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer. [b] Polymerizations were run in toluene-d_8 at 45 °C for 1 h at [M] = 0.57 M and [I] = 0.010 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer.

Scheme 5



Scheme 6



grated with equal intensity to those of the free PCy_3. Considering that the propagating species for the polymerization of COD is identical to that for cyclobutene, the observation of free PCy_3 in the polymerization of these substituted cyclobutenes must be the result, in part, of the functional groups on the cyclobutene ring. The most probable explanation for the role of the functional group was coordination of this group to the metal center resulting in stabilization of the mono(phosphine) species. This was consistent with the observed ratios of mono- and bis(phosphine) species observed. The more Lewis basic benzyl ether (**8**) resulted in the highest preference of monophosphine species followed by the more bulky trityl ether (**10**), and lastly the more electron poor benzoate ester (**12**).

The mono(phosphine) (**B**) and bis(phosphine) species (**A**) were proposed to be in equilibrium as presented in Scheme 7. In order to help support this hypothesis, free PCy_3 (10.6 equiv) was added to the benzyl ether polymerization described above. If there were an equilibrium between monophosphine (**B**) and bis(phosphine) species (A) as presented in Scheme 7, then the ratio of the two species in the ^{1}H NMR should shift upon the addition of PCy_3. As discussed above, the ratio of the resonances at 19.84 and 17.73 ppm was 1.00:8.91 initially; however, after the addition of phosphine, this ratio shifted to 1.46:1.00. The calculated equilibrium constant[39] should have been identical in both cases, and it was calculated for both, resulting in $K_{eq} = 8.1 \times 10^{-2}$ before the addition of phosphine and $K_{eq} = 7.3 \times 10^{-2}$ after the addition. These values were within the experimental error expected based on the use of NMR integration for these measurements. Another experiment used to support

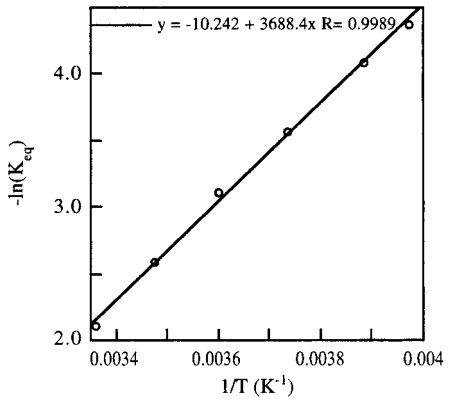
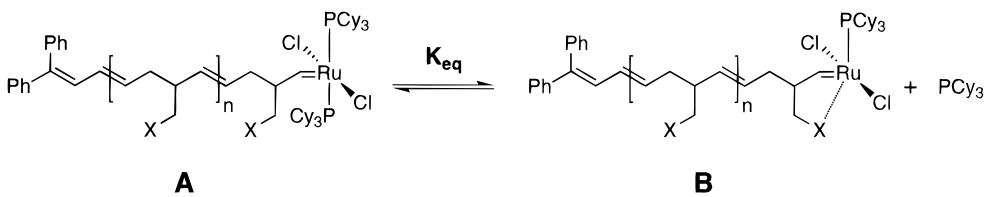


Figure 2. Van't Hoff plot of the benzyl [1-(2-cyclobutenyl)-methyl] ether (**8**) polymerization propagating species.

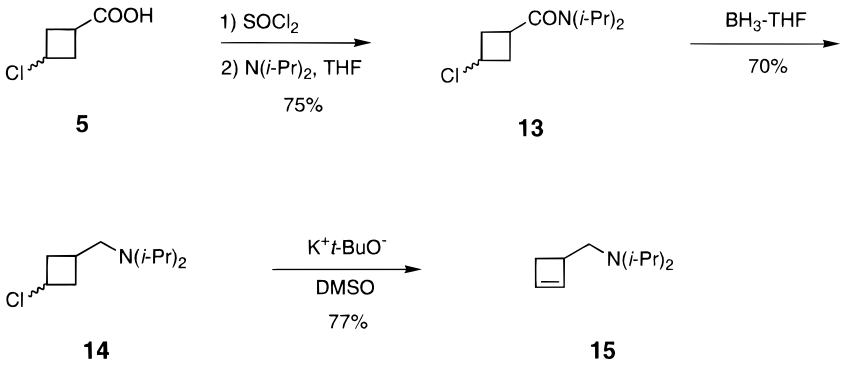
the equilibrium proposed in Scheme 7 was to study the ratio of the two propagating species at variable temperatures. Polymerization of the benzyl ether (**8**) was accomplished as above, and the equilibrium constants were determined through NMR integration of the ^{1}H NMR resonances of the propagating species **A** and **B**. If the reaction mixture is cooled, entropically-driven processes should be more disfavored relative to enthalpically-driven ones, thus resulting presumably in the increase of species **A** at lower temperatures. This was the observed trend which is represented in a van't Hoff plot (Figure 2). From the van't Hoff plot, the standard enthalpy and entropy of the equilibrium were determined as 7.3 ± 0.7 kcal/mol and 20 ± 2 cal/mol·K, respectively. These values were consistent with the expected large and positive entropy term due to the loss of free PCy_3 and chelation of the ether functionality and the positive enthalpy term resulting from loss of the ruthenium−phosphine bond in exchange for the weaker ruthenium−ether bond.

In addition to the nearest neighbor chelation illustrated in Scheme 7, several alternate hypotheses for the nature of this coordination were envisioned. First, the mono(phosphine) complex could have been the result of simple coordination of the monomer to the propagating species, resulting in loss of phosphine. However, this hypothesis was ruled out by two experiments. One, polymerization of COD as described above in THF-d_8 instead of toluene-d_8, resulted in no free phosphine or

Scheme 7



Scheme 8



significant shift in either the ^{1}H carbene resonance (19.43 ppm) or the ^{31}P NMR resonance (36.14 ppm). If coordination of the ether functionality of the monomer to the metal center was occurring, resulting in loss of phosphine, free phosphine should have been observed when the polymerization of COD was run in THF. Second, the percentage of mono- and bis(phosphine) species were found to be invariant during the polymerization, even after all the monomer had been consumed. Another mechanistic consideration was intermolecular coordination of a functional group from another polymer chain instead of the proposed intramolecular coordination. This proposal was excluded for the same reasons as the monomer coordination proposal. The fact that THF resulted in no free phosphine even when used in large excess as solvent contradicted an intermolecular coordination proposal. The large, positive entropy term determined above also tended to exclude this intermolecular coordination. One final possibility was that the coordination was intramolecular as proposed, but that the coordination was not limited to the nearest neighbor functional group and could have occurred through other side chains on the polymer further removed from the propagating species. Intuitively chelation through the 5- or 6-membered ring that results from nearest neighbor coordination seemed more reasonable than chelation resulting in larger, more kinetically and thermodynamically disfavored ring sizes, but this proposal cannot be completely excluded.

The question still remained as to what effect, if any, the relative amounts of mono- and bis(phosphine) propagating species had on the observed PDIs for the polymerization of **8**, **10**, and **12**. In an effort to understand the differing PDIs displayed in Table 2, the relative k_p/k_i values were examined for these polymerizations. First, 5 equiv of monomers **8**, **10**, **12** ([M] = 0.11 M) were treated with initiator **1**, and the percent initiation was measured by ^{1}H NMR integration of the propagating carbene α-protons (Table 3). The percent initiation observed was used as a measure of the relative k_p/k_i values for the different polymerizations. For monomer **8** complete initiation was observed, while for the trityl ether (**10**) 25% initiation was observed and for the benzoate ester (**12**) 15% initiation was observed. Complete initiation of **1** with the trityl ether (**10**) was accomplished only after the addition of another 20 equiv of **10**, and the initiation of **1** with the benzoate ester (**12**) resulted only after the addition of ~30 equiv of **12**. Therefore, as the degree of chelation increased, a reduction in the relative k_p/k_i was observed. A reduction in the k_p/k_i should have resulted in more narrowly dispersed polymers, and this was the observed trend.[23]

The attenuation of k_p/k_i in metathesis polymerizations through the addition of Lewis basic compounds has precedent in the literature. As described in the introduction, the addition of phophines to certain W and Mo alkylidenes slowed k_p relative to k_i through preferential binding of the base to the propagating carbene.[16−19] The addition of quinuclidine to the polymerization of acetylene with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ [Ar = 2,6-diisopropylphenyl] led to lower values of k_p/k_i, which was again explained by preferable binding of the quinuclidine to the propagating species over the starting complex.[40] THF was also observed to slow propagation when used as a solvent in the polymerization of cyclooctatetraene with W(CHC(CH$_3$)$_3$)(NAr)(OC(CF$_3$)$_2$CH$_3$)$_2$ [Ar = 2,6-diisopropylphenyl].[41] Evidence for binding of functionality on the polymer backone itself in affecting rates of propagation has been observed as well. In the polymerization of 5-(alkylthio)cyclooctenes with a metallacyclic aryloxo(chloro)neopentylidenetungsten complex, the rate of polymerization was determined to be dependent on the steric parameters of alkyl group present on the sulfur. With bulkier alkyl groups, more rapid polymerization was achieved, presumably due to blocking of sulfur coordination to the metal center.[42] In the living polymerization of bicyclo[3.2.0]heptene with (PPh$_3$)$_2$Cl$_2$Ru=CHCH=CPh$_2$, weak coordination of olefins in the backbone to the propagating species was proposed as well resulting in an attenuation of k_p/k_i.[20]

Polymerization of monomers bearing even more Lewis basic functional groups than the benzyl ether should have resulted in an even higher ratio of mono- to bis(phosphine) propagating species (**B**/**A**). Despite the fact that the polymerization of (2-cyclobutenyl)methanol (**11**) resulted in an insoluble material, polymerization of 5 equiv of **11** ([**11**] = 0.11 M) was possible without polymer precipitation. Complete initiation was observed with only one propagating species at 17.70 ppm in the ^{1}H NMR (Table 3) and 56.79 ppm in the ^{31}P NMR with 1.05 equiv of free PCy$_3$; no bis(phosphine) species was present. The insolubility of poly(**11**) prevented a more intensive study of this polymerization, so the polymerization of a cyclobutene bearing an amine side chain was studied. This too was expected to result in complete chelation with no bis(phosphine) species due to the Lewis basicity of the amine, yet initiator **1** was known to have a decreased activity and/or to decompose in the presence of amines.[43] Therefore, the sterically hindered diisopropyl(1-(2-cyclobutenyl)methyl)amine (**15**) was chosen as a target.

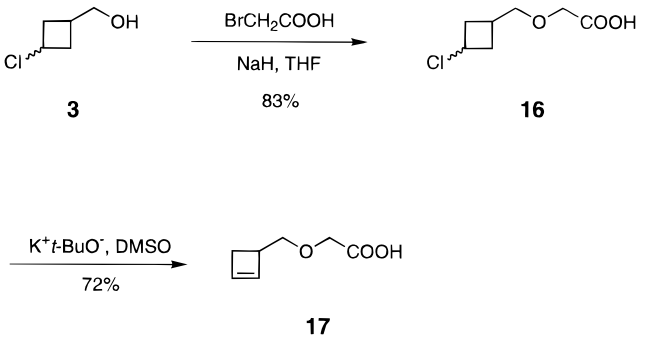
The synthesis of **15** was achieved through several relatively straightforward, high-yielding steps as shown in Scheme 8. Formation of the acid chloride of **5** with thionyl chloride followed by treatment with diisopropylamine resulted in amide (**13**) in 75% yield. BH$_3$−THF reduction of the amide[38,44] followed by elimination using the standard conditions resulted in diisopropyl(1-(2-cyclobutenyl)methyl)amine (**15**) in good yield. Treatment of **1** with 5 equiv of **15** ([**15**] = 0.11 M) resulted in

complete initiation of **1**. Polymerization under the standard conditions of [**15**] = 0.57 M, at 45 °C, in toluene-d_8 resulted in complete formation of a new propagating carbene at 17.97 ppm in the ^{1}H NMR. In the ^{31}P NMR, a multiplet at 43.68 ppm was observed in a 1.00:1.11 ratio with free phosphine at 10.79 ppm. So, as expected, a higher degree of coordination was observed for the more Lewis basic amine resulting in a $K_{eq} \geq 9.9 \times 10^{-1}$ compared to the value of 8.1×10^{-2} for the benzyl ether (**8**) (Table 3). Complete conversion of **15** to polymer required 4.5 h at 45 °C with no polymer precipitation compared to **11**, and a linear correlation between the $\bar{M}_n$ and the [M]:[I] ratio was observed. Low PDIs between 1.13 and 1.25 were obtained as expected due to the complete formation of the chelated mono(phosphine) propagating species. This chelation was consistent with the longer reaction time necessary for complete polymerization due to a significant reduction in k_p. However, decomposition of the propagating carbene was evident in both the ^{31}P NMR and in the GPC. As the polymerization neared completion, the formation of a new species at 23.47 ppm in the ^{31}P NMR was observed, presumably as the result of some decomposition pathway. In addition, at higher [M]:[I] ratios, broadening in the PDI was observed in the GPC due to a low molecular weight tail which was also consistent with decomposition of the propagating species.

Attempted Manipulation of the Chelation Effect. From the initial investigations, the importance of the presence of a Lewis basic functionality in the monomer was evident. With more Lewis basic functional groups, mono(phosphine) chelated propagating species were favored over the bis(phosphine) species, resulting in a reduction in the relative k_p/k_i and therefore producing more narrowly dispersed polymers. One problem, though, was that all of these monomers resulted in differing amounts of the two propagating species and different reaction rates. If a major goal is the application of these polymerizations in the synthesis of block copolymers, difficulties may arise due to this variance in the properties of the propagating species. Ideally, monomers used in block copolymer synthesis should appear similar in their reaction with the propagating species, therefore producing more narrowly dispersed blocks.

As a result, a new series of monomers were synthesized, bearing both an ether linkage and a secondary functional group. The ether linkage was incorporated in order to aid in the synthesis of more narrowly dispersed polymers based on the earlier research in the attenuation of k_p/k_i. In addition, the hope was that the monomers would have similar polymerization rates since they all contain the Lewis basic ether group, and therefore they would be applicable for the synthesis of narrowly dispersed block copolymers. Alkylation of **3** with bromoacetic acid followed by elimination using the standard conditions resulted in [3-oxa-4-(2-cyclobutenyl)]butyric acid (**17**) as in Scheme 9. Compound **17** contained both the ether linkage as well as the carboxylic acid group which allowed for the installation of a series of other functional groups (Scheme 10). Synthesis of methyl [3-oxa-4-(2-cyclobutenyl)]butyric acid (**18**) with K_2CO_3 and MeI was accomplished in 73% yield. Treatment of **17** with thionyl chloride followed by the addition of the resulting acid chloride to either dimethyl amine in H_2O or diisopropyl amine in THF resulted in *N*,*N*-dimethyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (**19a**) and *N*,*N*-diisopropyl-[3-oxa-4-(2-cyclobutenyl)]butyramide (**19b**) in yields of 71 and 87%, respectively.

Scheme 9



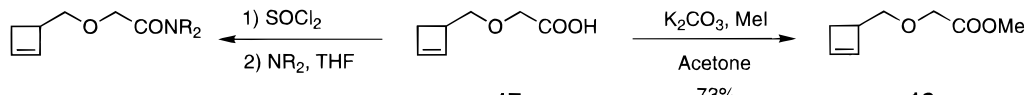
3 **16** **17**

Polymerizations were attempted at 45 °C in toluene with [M] = 0.57 M for monomer **18** and **19a**,**b**, while THF was required for compound **17** for solubility reasons. As predicted due to the presence of the ether functionality, complete initiation was observed with 5 equiv of **17**, **18**, and **19a**,**b** under the standard conditions (Table 3). Polymerization of **18** resulted in the formation of two propagating species in the ^{1}H NMR at 19.80 and 17.91 ppm in a ratio of 1.00:12.54 (Table 3) which was slightly higher than the ratio observed for the benzyl ether (**8**). In the ^{31}P NMR, multiplets at 57.94 and 36.91 ppm were present with free PCy_3 integrating to 1.01 relative to the species at 57.94 ppm. The polymerization was complete after 2 h, and the dependence of the $\bar{M}_n$ on the [M]:[I] was linear. As for the amine **15**, significant broadening of the PDI was observed at higher [M]:[I] ratios, which was the result of a low molecular weight tail in the GPC consistent with catalyst decomposition. In addition, during the polymerization, the appearance of a new peak at 48.01 ppm was observed in the ^{31}P NMR, also favoring some decomposition reaction of the propagating species.

Polymerization of **17** resulted in the formation of one propagating species in the ^{1}H NMR at 17.74 ppm representative of the chelated mono(phosphine) species. However, in the ^{31}P NMR, in addition to the multiplet at 56.84, a multitude of other species were present and only a minor amount of free PCy_3 was observed. Monitoring of the polymerization by ^{1}H NMR revealed that conversion reached a maximum at ~70% even though the propagating carbene was still evident at 17.74 ppm. In order to understand why only minimal free PCy_3 was observed even though the propagating carbene was a mono(phosphine) species, PCy_3 was reacted with compound **17** under identical conditions used in the polymerization. After 1 h, a new peak at 53.57 ppm was observed in a 1:2.13 ratio with free PCy_3, presumably through protonation of the phosphine. It was unclear why the multitude of decomposition products were observed during the polymerization, but a pathway resulting in the removal of free PCy_3 from the solution was evident. Such a side reaction would have locked the propagating carbene in the chelated form and therefore could have slowed if not prevented further polymerization.

Polymerization of **19a** and **19b** resulted in interesting results as well. Both of these compounds fully initiated **1** with the addition of 5 equiv of monomer as described above. However, once **1** was initiated, no further polymerization was observed, and in fact ~80% monomer remained after the initiation in the above experiment. ^{1}H NMR of the attempted polymerizations of these compounds revealed one carbene resonance at 17.84 and 17.86 ppm respectively. ^{31}P NMR revealed multiplets at 56.94 and 56.70 ppm respectively with 1.00 equiv of free PCy_3. Presumably, coordination of the

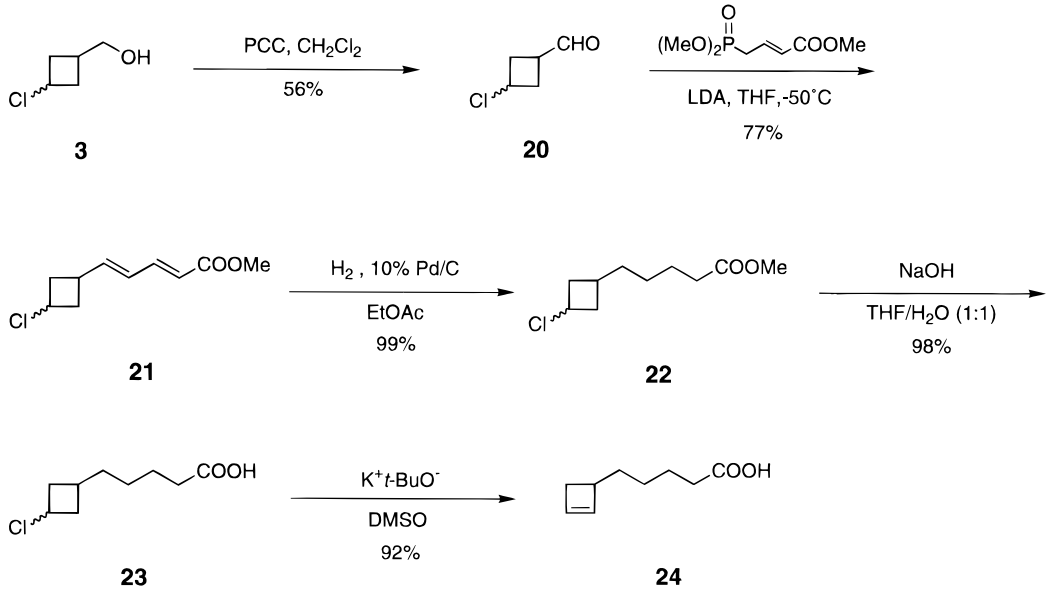
Scheme 10



19a: R=Me 71%

19b: R=*i*-Pr 87%

Scheme 11



amide to the metal center in addition to the ether group resulted in stronger chelation, thus preventing further propagation. Due to the similar results obtained for the dimethylamide **19a** and the more bulky diisopropylamide **19b**, it was unlikely that this coordination was occurring through the nitrogen. Instead, this secondary coordination appeared to be occurring through the amide carbonyl, which would have been less sensitive to the steric environment around the nitrogen, thus explaining the similar results obtained for **19a** and **19b**.

The incorporation of the ether functionality was successful in lowering the k_p/k_i as observed with the complete initiation of **1** with only 5 equiv of **17**, **18**, and **19a**,**b**. However, the chelation was detrimental in that propagation rates were reduced significantly, even resulting in the absence of propagation for compounds **19a** and **19b**. In addition, with slower propagation rates, decomposition pathways which might have otherwise been suppressed became important. While these monomers have found application in the synthesis of side-chain liquid crystalline polymers,[45] the goal of achieving a living polymerization was never reached.

Living Polymerization Results. The development of initiator **2** provided a solution to the above difficulties. Although both complexes **1** and **2** resulted in the same propagating species, compound **2** had been shown to have much higher rates of initiation than compound **1**.[26,27] To test the initiation for this system, **2** was used to polymerize the benzoate ester (**12**) with a [**12**]:[**2**] ratio of 220:1. The resulting polymer had an $\bar{M}_n$ = 29 500 and a PDI = 1.22 compared with the results using **1** which gave an $\bar{M}_n$ = 15 300 and a PDI = 1.71. The PDI was significantly reduced due to higher initiation of this complex compared to **1**. Treatment of **2** with 5.0 equiv of **12** using the standard procedure resulted in complete initiation compared to the 15% initiation observed with **1**.

Using complex **2**, polymerization appeared possible to produce low polydisperse polymers without the need for the chelated mono(phosphine)s propagating species. Therefore, a series of compounds was synthesized which did not contain the ether linkage in the side chain (Scheme 11). The removal of the ether group should have reduced the amount of chelated mono(phosphine) propagating species present during the polymerization, thus increasing the propagation rates and hopefully minimizing any decomposition side reactions. Oxidation of **3** with PCC[46] resulted in moderate yield of *cis*,*trans*-3-chlorocyclobutanecarboxaldehyde (**20**). This was subjected to a Horner−Emmons reaction[47,48] with trimethyl 4-phosphonocrotonate using the method of Roush[49] to generate **21**. Hydrogenation of the diene with Pd/C and subsequent saponification of the ester produced nearly quantitative yield of **23**. Elimination using the standard conditions resulted in 5-(2-cyclobutenyl)pentanoic acid (**24**) in 92% yield. Conversion of **24** into a series of functionalized cyclobutenes was then attempted (Scheme 12). Reduction of **24** with LAH produced 5-(2-cyclobutenyl)pentanol (**25**) in quantitative yield. Treatment of **24** with thionyl chloride followed by reaction with butylamine resulted in *N*-butyl-[5-(2-cyclobutenyl)]pentanamide (**26**) in 85% yield. Finally, alkylation of the carboxylic acid **24** with K_2CO_3 and MeI gave a quantitative yield of the methyl [5-(2-cyclobutenyl)]pentanoate (**27**). These four monomers **24**−**27** contained a variety of functional groups; however, with the functional group well removed from the ring system, it was predicted that the amount of chelation would be similar and the monomers would react at similar rates.

Optimal polymerization conditions were at room temperature for 2 h with a [M] = 0.17 M using initiator **2**. A slight reduction in the PDIs was observed at lower [M], resulting in the optimum concentration at 0.17 M. THF was chosen as a solvent because the polymers of the acid and alcohol monomers **24** and **25** were insoluble

Scheme 12

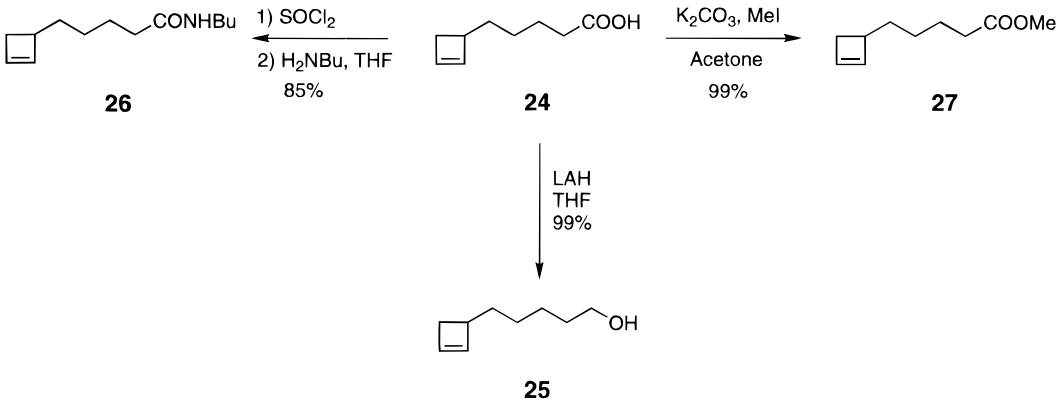


Table 4. ^{1}H NMR Analysis of Polymerization Propagating Species

polymer	X	% initiation with 5 equiv of [M][a]	^{1}H NMR carbene resonance **A**[b]	^{1}H NMR carbene resonance **B**[b]	ratio **B**/**A**[b]	10^3K_{eq}[b]
poly(**24**)	$(CH_2)_3COOH$	>99	19.49	17.90	0.41	1.2
poly(**25**)	$(CH_2)_4OH$	>99	19.49	17.79	0.57	2.1
poly(**26**)	$(CH_2)_3C(O)NHBu$	>99	19.47	17.89	0.35	0.89
poly(**27**)	$(CH_2)_3COOMe$	>99	19.49	17.89	0.51	1.7

[a] Polymerizations were run in THF-d_8 at room temperature for 1 h at [M] = 0.11 M and [I] = 0.022 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer. [b] Polymerizations were run in THF-d_8 at room temperature for 1 h at [M] = 0.17 M and [I] = 0.0099 M and analyzed by ^{1}H NMR using a JEOL GX-400 spectrometer.

in all other solvents compatible with **2**. As seen in Table 4, complete initiation was observed by employing 5 equiv of monomers **24**−**27** with **2**. Analysis of the carbene propagating species by ^{1}H and ^{31}P NMR was then undertaken. The ^{1}H NMR for the polymerization of **24**−**27** were similar in the four cases, so only the results for **24** will be discussed in detail (Table 4). Two species at 19.49 and 17.90 ppm were observed in a ratio of 1.00:0.41. ^{31}P NMR displayed nearly identical spectra for the four cases and the results for **24** were representative with a multiplet at 38.58 ppm for the chelated species and a series of peaks from 37.11 to 34.19 ppm for the bis(phosphine) species. Free PCy_3 was found at 10.80 ppm, integrating 1.00:1.02 with the multiplet at 38.58 ppm. So, as expected, the bis(phosphine) species was favored over the chelated mono(phosphine) species, and the observed ratios were similar for all four compounds (Table 4). In contrast to the polymerization of **17**, free phosphine was present in the polymerization of **24**, and no decomposition products were observed. To further examine this, PCy_3 was reacted for 1 h with **24** under the conditions used in the polymerization at room temperature in THF with [**24**] = 0.17 M and [PCy_3] = 0.01 M. Unlike for **17**, no reaction was observed. To better compare the two cases, the reaction was repeated using the same conditions as for **17** at 45 °C with [**24**] = 0.57 M and [PCy_3] = 0.01 M. In this case, only a minor species was observed at 52.82, integrating to 8.9% compared with free PCy_3. The marked difference in reactivity of **17** and **24** with free PCy_3 was proposed to be the result simply of the difference in acidity expected for these carboxylic acids. Using pentanoic acid and methoxyacetic acid as models for **24** and **17**, the pK_a values are 4.80 and 3.57,[50] providing a plausible reason for reduced protonation of PCy_3 by **24**. The lack of reactivity of **24** with PCy_3 was one explanation for the successful polymerization of **24** compared to the decomposition found in the polymerization of **17**. Further study of these polymerizations is necessary to conclusively determine the cause of these contrasting polymerization results.

In order to fully investigate these polymerizations, the dependence of the $\bar{M}_n$ on the [M]:[I] ratio was studied.

Table 5. Polymerization Results for Monomers 24−27[a]

entry	monomer	[M]/[I]	$\bar{M}_n$[b]	PDI[b]
1	**24**	25.0	5000	1.15
2	**24**	50.0	9200	1.16
3	**24**	75.0	12400	1.16
4	**24**	104	15700	1.16
5	**24**	150	20300	1.19
6	**25**	25.0	4200	1.15
7	**25**	50.4	7400	1.15
8	**25**	75.6	10100	1.17
9	**25**	101	13800	1.15
10	**25**	161	23300	1.20
11	**26**	25.2	4800	1.11
12	**26**	50.4	8800	1.11
13	**26**	73.3	11400	1.11
14	**26**	105	16400	1.12
15	**26**	151	20800	1.12
16	**27**	25.3	4600	1.14
17	**27**	50.5	8000	1.14
18	**27**	73.5	11800	1.13
19	**27**	106	16100	1.15
20	**27**	143	23100	1.16

[a] Polymerizations were run in THF at room temperature with [M] = 0.17 M. [b] Determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards.

The dependence was linear for all four monomers providing for control over the polymer molecular weight, and the polymers produced were of low polydispersity between 1.11 and 1.20 in all cases (Table 5). Figure 3 illustrates the dependence for the polymerization of carboxylic acid **24**. The linear dependence observed was supportive of a living polymerization,[14,15] but further proof was necessary. In addition to the molecular weight study, evidence for the lack of chain transfer and chain termination reactions must be demonstrated to prove that a polymerization is living. A sequential monomer addition experiment was proposed to address the living nature of these polymerizations.[14] This experiment was run for all four monomers, but the results for the polymerization of carboxylic acid **24** were representative. Using initiator **2**, 25 equiv of **24** were polymerized for 2 h under the standard conditions. The solution was then divided into three portions. Portion

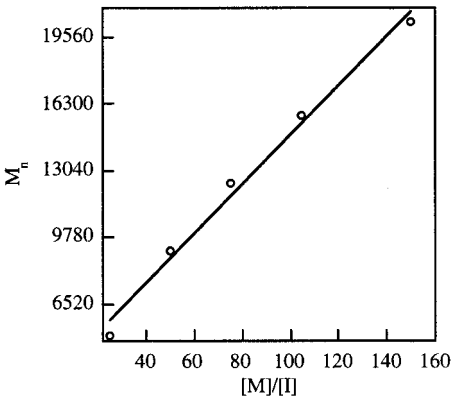


Figure 3. Molecular weight dependence of the polymerization of **24** on [M]/[I].

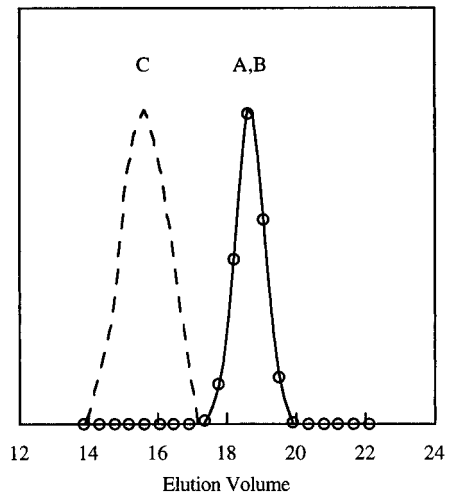


Figure 4. Sequential monomer addition experiment (A) with 25 equiv of **24** after 2 h, (B) with 25 equiv of **24** after 6 h and (C) after an additional 350 equiv of **24** was added.

A was removed and analyzed by GPC. Portion B was left stirring for an additional 4 h. To portion C was added, an additional 350 equiv of monomer, and this was left to react for 4 h. Portions B and C were then analyzed by GPC. As seen in Figure 4, no significant change was observed from the 2 h reaction (A) and the 6 h reaction (B). After 2 h, the $\bar{M}_n = 4400$ and PDI = 1.14, and after 6 h, $\bar{M}_n = 4400$ and PDI = 1.14. If any significant chain transfer processes had been operative during this time, broadening of the PDI would have been observed. Portion C in which an additional 350 equiv of **24** had been polymerized resulted in a $\bar{M}_n = 53\,400$ and PDI = 1.34. Despite the fact that the PDI broadened, a clean shift in the GPC peaks was accomplished, proving that no chain termination processes were occurring. Chain termination would have resulted in inactive chain ends after the polymerization of the first 25 equiv of monomer which would have produce a bimodal GPC trace after additional polymerization. The absence of both chain transfer and chain termination reactions was indicative of a living polymerization of the monomers **24**−**27**.

Polymer Characterization. Through polymerization of these substituted cyclobutenes, a new group of poly(butadiene)s bearing a wide range of functional groups was prepared (Table 6). Even though the polymerization yields were quantitative by ^{1}H NMR, isolated yields were lower due to loss in the purification step. No significant bias in the olefin configuration was evident for these polymerizations with between 40 to 50% *cis*-olefin present in the polymer backbone. These

Table 6. Polymerization Results

polymer	X	% yield[a]	% *cis*-olefin[b]
poly(**8**)	OCH_2Ph	87	40
poly(**10**)	$OC(Ph)_3$	91	nd[c]
poly(**12**)	OC(O)Ph	95	50
poly(**15**)	$N(i\text{-}Pr)_2$	79	nd[c]
poly(**18**)	OCH_2COOMe	84	40
poly(**24**)	$(CH_2)_3COOH$	93	50
poly(**25**)	$(CH_2)_4OH$	95	50
poly(**26**)	$(CH_2)_3CONHBu$	92	50
poly(**27**)	$(CH_2)_3COOMe$	96	50

[a] Isolated yields after purification. [b] Determined by ^{1}H NMR integration of the olefinic resonances. [c] Not determined; the olefinic resonances were not resolved well enough to determine this value accurately.

Table 7. Polymer Thermal Behavior

polymer	X	T_g (°C)[a]	T_d(argon) (°C)[b]	T_d(air) (°C)[b]
poly(**8**)	OCH_2Ph	−22.6	306	254
poly(**10**)	$OC(Ph)_3$	69.4	308	240
poly(**12**)	OC(O)Ph	24.0	349	341
poly(**15**)	$N(i\text{-}Pr)_2$	−15.8	294	249
poly(**18**)	OCH_2COOMe	−42.9	334	311
poly(**24**)	$(CH_2)_3COOH$	1.3	352	359
poly(**25**)	$(CH_2)_4OH$	−37.1	220	265
poly(**26**)	$(CH_2)_3CONHBu$	0.1	283	259
poly(**27**)	$(CH_2)_3COOMe$	−46.6	345	286

[a] Analysis by differential scanning calorimetry with a scan rate of 10 °C/min. [b] Analysis by thermal gravimetric analysis with a scan rate of 10 °C/min.

results were consistent with that seen previously for initiators **1** and **2**.[28] An accurate determination was impossible for poly(**10**) and poly(**15**) due to the lack of resolution of the olefinic resonances in the ^{1}H NMR spectrum. On the basis of analysis of the olefin region of the ^{13}C NMR spectrum of the polymers, a lack of regioselectivity for monomer insertion in the polymerizations was determined,[51] again consistent with previous observations with these initiators in similar systems.[28] If chelation occurs during the initial monomer coordination step, one might expect some regioselectivity due to energetic differences in the two possible chelate ring sizes. The lack of regioselectivity observed in these polymerizations is thus supportive of the proposal that chelation occurs after the ring-opening metathesis step and therefore plays no role in affecting the regioselectivity of monomer insertion.

Analysis of the thermal properties of these polymers was undertaken as well using both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 7). The T_g values for these polymers ranged from −46.6 to +69.4 °C, demonstrating the striking influence of the side chains on the phase transitions of these poly(butadiene)s; however, no melting transitions were observed for any of the materials. TGA results were compared using the T_d, the temperature at 10% decomposition. T_d values between 220 and 349 °C were observed in an inert atmosphere, but no consistent trend was evident.

Conclusions

The synthesis of 3-substituted cyclobutenes bearing a wide range of functionalities was demonstrated. The polymerization of these compounds with initiators **1** and **2** was accomplished, resulting in a series of new functionalized poly(butadiene)s. In probing the polymerization mechanism, coordination of Lewis basic functional groups on the polymer side chains to the metal center was observed. This coordination produced a new,

chelated mono(phosphine) propagating species in addition to the expected bis(phosphine) species, which resulted in the attenuation of the k_p/k_i for these polymerizations. While this coordination led to lowered PDIs using initiator **1**, propagation rates were significantly reduced in these polymerizations and often decomposition of the propagating species was evident. The combination of higher initiation employing complex **2** and the removal of the functional group further from the ring system resulted in the living polymerization of functionalized cyclobutenes bearing carboxylic acid, alcohol, amide, and ester functionalities. Future investigations will focus on the application of these monomers for the preparation of multifunctionalized block copolymers.

Experimental Section

General Data. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on both a GE QE-300 Plus (300.1 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer and a JEOL GX-400 (399.65 MHz ^{1}H; 100 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. Unless otherwise noted, the majority of the spectra were recorded on the GE QE-300 Plus. ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 standard. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. CH_2Cl_2 gel permeation chromatographs were obtained on a HPLC system using an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed-bed columns, and a Knauer differential-refractometer using a 1.0 mL/min flow rate. THF gel permeation chromatographs were obtained on a HPLC system using an Altex Model 426 pump, a Rheodyne Model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed-bed columns, and a Viscotek Model 200 differential refractometer/viscometer using a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported vs monodispersed polystyrene standards. Differential scanning calorimetry was measured on a Perkin-Elmer DSC-7, and thermogravimetric analysis was carried out on a Perkin-Elmer TGA-2.

Materials. When dry solvents were used, they were distilled from CaH_2 as well. All other solvents were reagent grade and used without purification. 1,1-Cyclobutanedicarboxylic acid, sulfuryl chloride, BH_3−THF, benzyl bromide, trityl chloride, NaH, potassium *tert*-butoxide, benzoyl chloride, thionyl chloride, dimethylamine, diisopropylamine, bromoacetic acid, dimethylamine, MeI, pyridinium chlorochromate, lithium diisopropylamide, palladium on activated carbon, and ethyl vinyl ether were purchased from the Aldrich Chemical Co. and used without further purification. 2,2′-Azobis(2-methylpropionitrile) was purchased from Eastman Laboratory Chemicals and used without further purification. Technical grade trimethyl 4-phosphonocrotonate was purchased from Lancaster Synthesis.

Determination of the Percent Initiation of Complexes 1 and 2 with the Cyclobutenes. In a drybox, an aliquot (0.60 mL) of a stock solution of initiator **1** or **2** dissolved in toluene-d_8 or THF-d_8 (0.022 M) was removed. In a separate vial, the desired cyclobutene (5.0 equiv relative to **1** or **2**) was weighed out. The initiator solution was then transferred to the cyclobutene vial and agitated until a solution resulted. This was then transferred to an NMR tube and capped with a septum. The NMR tube was then removed from the drybox and placed in an oil bath at either room temperature or 45 °C for 1 h. At this time, a ^{1}H NMR was taken and the percent initiation was determined by integration of the H_α carbene resonances present.

Temperature Dependence of the Coordination Equilibrium Constant in the Polymerization of Benzyl [1-(2-Cyclobutenyl)methyl] Ether (8). In a drybox, a stock solution of initiator **1** in toluene-d_8 (28.0 mg, 3.00 mL) was prepared and a 0.60 mL aliquot was removed. Benzyl [1-(2-cyclobutenyl)methyl] ether (**8**) (60.0 mg, 57.0 equiv) was weighed out and combined with the initiator solution in an NMR tube. The tube was capped with a septum and removed from the box. The tube was heated to 45 °C for 1 h, and then it was allowed to cool to room temperature. The ratio of chelated and nonchelated propagating species was determined by integration of the respective carbene resonances at 17.73 and 19.84 ppm at temperatures from −21.5 to +24.6 °C. NMR spectra were recorded using a JEOL GX-400 spectrometer. At each temperature, multiple spectra were recorded until a constant value was acheived to ensure that the equilibrium had been reestablished.

Large Scale Preparation of Poly(8, 10, 12, 15, and 18). In a drybox, the desired amount of initiator **1** was weighed into a large vial. The cyclobutene was added to a separate vial and dissolved in toluene or THF (0.57 M). This solution was then transferred to the initiator vial, and a stir bar was added. The vial was capped and removed from the box. This vial was then heated to 45 °C until the reaction was complete. Removal of the solvent was accomplished *in vacuo*, and the resulting tacky solid was stirred with acidic methanol (5 mL of 1 M HCl/200 mL MeOH) for 1 h. This was then followed by washing with methanol (2 × 50 mL) and finally diethyl ether (2 × 50 mL). Simple removal of the residual solvent *in vacuo* yielded pure polymer.

Large Scale Preparation of Poly(24−27). In a drybox, the desired amount of initiator **2** was weighed into a large vial. The cyclobutene was added to a separate vial and dissolved in THF (0.17 M). This solution was then transferred to the initiator vial, and a stir bar was added. The vial was then capped, removed from the box, and then left to sir at room temperature for 2 h. Ethyl vinyl ether (600 equiv) was then added, and this was left for 30 min to quench the reaction. Removal of the solvent was accomplished *in vacuo*, and the resulting tacky solid was washed with diethyl ether (4 × 20 mL). Simple removal of the residual solvent under vacuum yielded pure polymer.

Poly(8), X = OCH_2Ph. The yield of polymer was 87%. ^{1}H NMR (CD_2Cl_2): δ 7.38−7.17 (bm, 5H), 5.42−5.18 (bm, 2H), 4.43−4.36 (bm, 2H), 3.38−3.20 (bm, 2H), 2.76−2.59 (bm, 1H), 2.40−1.83 (bm, 2H). ^{13}C NMR ($CDCl_3$): δ 138.82, 133.11−127.55 (m, backbone C−olefin), 128.25, 127.42, 127.34, 73.61, 73.53, 72.94, 42.99−29.68 (m, backbone C−alkyl). IR (thin film on a NaCl plate): 3062, 3028, 3005, 2851, 2786, 1496, 1453, 1361, 1205, 1102, 1028, 968, 735, 697 cm^{-1}.

Poly(10), X = $OC(Ph)_3$. The yield of polymer was 91%. ^{1}H NMR (CD_2Cl_2): δ 7.60−6.95 (bm, 15H), 5.20−4.93 (bm, 2H), 3.02−2.88 (bm, 2H), 2.62−1.77 (bm, 3H). ^{13}C NMR (CD_2Cl_2): δ 144.37, 133.25−128.47 (m, backbone C−olefin), 128.74, 127.64, 126.79, 86.35, 86.23, 66.84, 66.81, 66.78, 43.74−29.62 (m, backbone C−alkyl). IR (thin film on a NaCl plate): 3057, 3021, 2916, 2862, 1596, 1490, 1448, 1219, 1153, 1068, 1032, 898, 763, 745, 705, 632 cm^{-1}.

Poly(12), X = OC(O)Ph. The yield of polymer was 95%. ^{1}H NMR ($CDCl_3$): δ 8.21−7.83 (bm, 2H), 7.58−7.18 (bm, 3H), 5.56−4.98 (bm, 2H), 4.37−3.96 (bm, 2H), 2.88−2.65 (bm, 1H), 2.51−1.83 (bm, 2H). ^{13}C NMR ($CDCl_3$): δ 166.25, 132.82, 132.31−128.92 (m, backbone C−olefin), 130.27, 129.48, 128.30, 67.19, 66.98, 42.17−29.36 (m, backbone C−alkyl). IR (thin film on a NaCl plate): 3063, 3009, 2947, 2850, 1716, 1602, 1584, 1451, 1378, 1314, 1272, 1176, 1113, 1070, 1026, 970, 911, 709, 687 cm^{-1}.

Poly(15), X = N(*i*-Pr)$_2$. The yield of polymer was 79%. ^{1}H NMR ($CDCl_3$): δ 5.41−4.99 (bm, 2H), 3.02−2.88 (bm, 2H), 2.56−1.61 (bm, 5H), 0.84 (bs, 12H). ^{13}C NMR ($CDCl_3$): δ 134.74−128.51 (m, backbone C−olefin), 50.23, 50.05, 49.98, 49.73, 49.43, 49.29, 47.63, 47.55, 42.92−30.60 (m, backbone C−alkyl), 21.68, 19.81. IR (thin film on a NaCl plate): 2963, 2933, 2870, 1654, 1468, 1382, 1361, 1207, 1170, 1115, 1065, 965, 883, 758, 718 cm^{-1}.

Poly(18), X = $OCH_2OCOOMe$. The yield of polymer was 84%. ^{1}H NMR ($CDCl_3$): δ 5.50−5.07 (bm, 2H), 3.95 (bs, 2H), 3.61 (bs, 3H), 3.45−3.19 (bm, 2H), 2.80−1.79 (bm, 3H). ^{13}C NMR ($CDCl_3$): δ 170.61, 132.47−128.09 (m, backbone C−olefin), 74.50, 68.08, 51.41, 42.54−29.06 (m, backbone C−alkyl). IR (thin film on a NaCl plate): 3005, 2952, 2908, 2858, 1757, 1740, 1437, 1352, 1282, 1209, 1140, 974, 884, 765, 706 cm^{-1}.

Poly(24), X = $(CH_2)_3COOH$. The yield of polymer was 95%. ^{1}H NMR (acetone-d_6): δ 11.24−9.62 (bs, 1H), 5.56−5.00

(bm, 2H), 2.55−1.06 (bm, 11H). ^{13}C NMR (acetone-d_6) δ: 175.81, 136.88−128.96 (m, backbone C−olefin), 44.20−25.75 (m, C−alkyl). IR (thin film on a NaCl plate): 3570−2257 (b), 1709, 1458, 1412, 1286, 1232, 1093, 968, 939, 810, 766, 668 cm^{-1}.

Poly(25), X = $(CH_2)_4OH$. The yield of polymer was 96%. ^{1}H NMR (THF-d_8): δ 5.54−5.04 (bm, 2H), 3.74−3.37 (bm, 3H), 2.78−1.00 (bm, 11H). ^{13}C NMR (THF-d_8): δ 137.34−125.86 (m, backbone C−olefin), 62.70, 44.59−30.80 (m, backbone C−alkyl), 34.08, 28.32, 27.21, 27.08. IR (thin film on a NaCl plate): 3656−3072 (b), 2999, 2927, 2851, 1473, 1432, 1406, 1356, 1330, 1271, 1151, 1071, 1055, 968, 882, 752, 729 cm^{-1}.

Poly(26), X = $(CH_2)_3C(O)NHBu$. The yield of polymer was 92%. ^{1}H NMR ($CDCl_3$): δ 7.37−6.68 (bs, 1H), 5.43−4.91 (bm, 2H), 3.31−3.05 (bm, 2H), 2.42−1.01 (bm, 15H), 0.86 (bt, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 173.46, 135.89−125.41 (m, backbone C−olefin), 43.19−24.97 (m, C−alkyl), 39.15, 31.64, 20.08, 13.77. IR (thin film on a NaCl plate): 3294, 3083, 2956, 2860, 1655, 1560, 1459, 1438, 1376, 1331, 1261, 1228, 1153, 1116, 1075, 1023, 969, 921, 891, 734, 644 cm^{-1}.

Poly(27), X = $(CH_2)_3COOMe$. The yield of polymer was 96%. ^{1}H NMR ($CDCl_3$): δ 5.41−4.98 (bm, 2H), 3.63 (s, 3H), 2.28−1.03 (bm, 11H). ^{13}C NMR ($CDCl_3$): δ 173.83, 136.23−127.72 (m, backbone C−olefin), 51.16, 43.14−33.62 (m, backbone C−alkyl), 34.17, 29.70, 27.18, 27.10, 27.01, 26.86, 25.45, 25.33, 25.02. IR (thin film on a NaCl plate): 3009, 2999, 2918, 2850, 1740, 1456, 1436, 1362, 1318, 1250, 1197, 1172, 1107, 1017, 970, 883, 847, 766 cm^{-1}.

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Supporting Information Available: Text giving experimental procedures for the synthesis of compounds **3**, **5**, and **7**−**27** and tables of polymerization results for monomers **15** and **18** (13 pages). Ordering information is given on any current masthead page.

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