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A Hydrocarbon Structure Reactivity Study in ADMET Chemistry. 1. 1,1-Disubstituted and Trisubstituted Olefins

J. Konzelman and K. B. Wagener*

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611-7200

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ABSTRACT: The ADMET chemistry of 1,1-disubstituted, 1,2-disubstituted, and trisubstituted alkenes has been examined in the presence of the Lewis acid free metathesis catalysts M(CHR′)(NAr)(OR)$_2$ where M = W (**1**) or Mo (**2**), Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$, R′ = CMe$_2$Ph, and R = CMe(CF$_3$)$_2$, and the specific interaction of each olefin with the catalysts has been monitored by ^{1}H NMR. Successful metathesis depends on both the substitution pattern of the olefin and the catalyst employed. The molybdenum-based catalyst promotes the metathesis of 1,1-disubstituted alkenes but only through cross-metathesis with internal olefins which are no greater than disubstituted. The tungsten-based catalyst is unable to promote metathesis chemistry with these substituted olefins.

Introduction

The advent of highly active, well-defined Lewis acid free catalysts has led to a renaissance in metathesis polymerization chemistry.[1] One of the many recent advances in olefin metathesis has been acyclic diene metathesis (ADMET) polymerization, a new step condensation polymerization (Figure 1).[2−10] Unsubstituted hydrocarbon monomers as well as functionalized monomers containing ethers,[2] thioethers,[3] silanes,[4] siloxanes,[5,6] ketones,[7] esters,[8] carbonates,[9] and conjugated π systems[10] all have been polymerized to yield linear polyalkenylenes (unsaturated polyolefins). The electronic effects of some of these functionalities in ADMET chemistry have been elucidated, and a phenomenon identified as the negative neighboring group effect has been established. This paper describes the steric effects on the reactivity of substituted olefins, specifically 1,1-disubstituted, 1,2-disubstituted, and trisubstituted olefins.

Virtually all of the metathesis reactions of 1,1-disubstituted olefins cited in the literature use a classical Lewis acid catalyst system.[1] It is now known that classical catalysis systems interfere with ADMET chemistry via competing reactions, principally the vinyl addition reaction.[11] Therefore, classical catalysts were avoided in this study, and the work was confined to the use of the highly active Lewis acid free Schrock alkylidenes of the type M(CHR′)(NAr)(OR)$_2$ where M = W (**1**) or Mo (**2**), Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$, R′ = CMe$_2$Ph, and R = CMe(CF$_3$)$_2$.[12,13] We have found that the tungsten and molybdenum versions exhibit marked differences in reaction rate in the ADMET chemistry of unsubstituted and substituted hydrocarbon dienes. The reactivity of each catalyst has been investigated to further define these differences, as well as to utilize them in controlling the primary polymer structure.

Since the ADMET polymerization of linear hydrocarbon α,ω-dienes produces well-characterized linear polyalkenylenes of unequivocal structure, the incorporation of substituents in the monomer should provide a synthetic route to a variety of unique polymeric structures. The model studies described herein define the steric limitations for such monomers; we now know what is required to synthesize well-defined, branched, unsaturated hydrocarbon polymers.

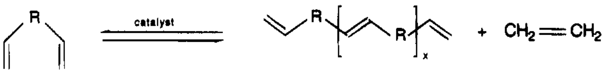

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

Results and Discussion

I. Thermodynamic Considerations and Steric Crowding. Thermodynamic data reveal that the metathetic disproportionation of 1,1-disubstituted olefins is energetically unfavorable. For example, isobutene at 25 °C has a theoretical equilibrium distribution of 1.4 mol % for each of the products, while the equilibrium values for the higher analogs are even lower.[14] Despite such small equilibrium values, the disproportionation of 2-methylbutene has been driven to 95% completion by the removal of ethylene,[15] and this same approach has been successful in ADMET polymerizations of unsubstituted dienes. These successes can be attributed to the fact that, under the proper reaction conditions (bulk polymerization, or nearly so, in the case of ADMET chemistry), a change in the state of matter is observed. Ethylene emerges from the reaction mixture as a gas, and its evolution drives the unfavorable equilibrium toward completion.

In addition to ADMET bimolecular coupling of model compounds and ADMET polymerization chemistry, this condensation process can be used to synthesize trisubstituted and tetrasubstituted cyclic alkenes.[16−18] For example, Grubbs and Fu have employed the molybdenum-based catalyst utilized in ADMET chemistry to prove this point. While these cyclization reactions are examples of olefin metathesis, they differ significantly from ADMET or ROMP chemistry. ROMP is enthalpically driven by the release of ring strain, and polymer is produced via chain propagation, addition-type chemistry. The cyclizations reported by Grubbs and Fu are entropically favored intramolecular reactions, where in this case the substituents actually provide for a favorable change in entropy. In contrast to both of these situations, ADMET polymerization is an equilibrium step propagation, condensation-type reaction that requires the removal of an equilibrium product to drive the reaction to completion.

Since the ADMET mechanism involves the bimolecular condensation of two olefins without the benefit of

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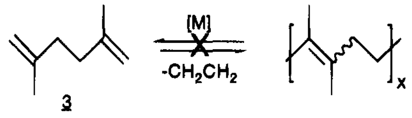

Figure 2. Attempted metathesis of 2,5-dimethyl-1,5-hexadiene (**3**) with catalysts **1** and **2**.

release of monomer ring strain, subtle changes in monomer structure, such as introducing substituents, have a marked effect on reactivity. Certainly there is no substituent-induced entropic boost here, for the relative position of the substituent with respect to the alkene, as well as the catalyst metal center, determines the activity of a specific polymerization mixture.

The issue, of course, is steric crowding. Here we describe the investigation of the metathetic activity of a series of 1,1-disubstituted and trisubstituted olefins with steric crowding in mind. Differences in catalytic ability of the molybdenum- and tungsten-based catalysts also have become clear, where the most striking difference is that the molybdenum catalyst **2** produces polymer structures containing trisubstituted alkenes, while the tungsten version is incapable of producing such a polymer.

II. ADMET Behavior of 1,1-Disubstituted Dienes.

A. Symmetrical 1,1-Disubstituted Aliphatic α,ω-Dienes. The potential monomer, 2,5-dimethyl-1,5-hexadiene (**3**), was used to investigate the influence of alkyl substituents on the metathesis activity in ADMET polymerizations. This compound was of particular interest since successful metathesis would produce a polymer best described as a methyl-substituted polyisoprene (Figure 2). However, both tungsten and molybdenum catalysts, **1** and **2**, failed to produce the tetrasubstituted olefin, as pure **3** was isolated from each attempted metathesis reaction.

No reaction between the diene and the initial alkylidene was observed for either catalyst—nothing happens at all. The NMR spectrum of the solution of **3** and the tungsten catalyst **1** showed that the signal corresponding to the alkylidene proton (9.0 ppm) remained unchanged from that of the pure catalyst.[16] Further, the methylene proton signal of the olefin of **3** (4.8 ppm) remained unchanged (Figure 3a), and the proton signal accompanying the production of ethylene (5.3 ppm)[11] was not observed. Analogously, the solution of 2,5-dimethyl-1,5-hexadiene (**3**) and the molybdenum catalyst **2** exhibited the original alkylidene proton signal at 12.2 ppm[13] and the unreacted diene resonances without the detection of an ethylene signal (Figure 3b). Any reaction of the initial alkylidene would have resulted in the release of the 3-methyl-3-phenylbutene (**4**) accompanied by the relative decrease in the original alkylidene proton signal. These spectra did not change, even upon incubating the solutions at 50 °C for up to 72 h. Steric interaction obviously is playing a role in these reactions.

The metathesis "catalyst" added to these reactions is actually a precatalyst, since, as mentioned above, the actual catalytic species is generated *in situ* by the metathesis reaction of the initial alkylidene with the alkene reactant. This chemistry is illustrated below in Figure 4. The data obtained for compound **3** suggest that steric interaction of the precatalyst with a 1,1-disubstituted (methyl-substituted) carbon–carbon double bond prevents the formation of the true catalytic alkylidene.

B. 2-Substituted Aliphatic Dienes in the Presence of the Tungsten Catalyst. To further probe the matter, an unsymmetrical diene, 2-methyl-1,5-hexadiene (**5**; Figure 5a), was exposed to Schrock's tungsten-based catalyst. In this case, one of the double bonds is monosubstituted, while the other is disubstituted.

In fact, a reaction is observed for this compound—it "dimerizes" via the expulsion of ethylene. The ^{13}C NMR spectrum of the product solution (Figure 5b) shows that the dimer, 2,9-dimethyl-1,5,9-decatriene (**6**), is produced as a result of the exclusive metathesis of the monosubstituted double bond. The alkene region (110–150 ppm) of the ^{13}C NMR spectrum of the reactant shows that **5** has four carbon signals, one for each sp^2 carbon of the two different olefins: CH_2 (110.0 ppm), disubstituted sp^2 carbon (145.4 ppm), CH_2 (114.2 ppm), and CH monosubstituted sp^2 (138.4 ppm). While the $-CH{=}CH_2$ carbons are absent in the spectrum of the reaction product **6**, the 1,1-disubstituted carbon signal remains. Only the monosubstituted double bond metathesizes to form an internal olefin unit represented by the cis/trans carbon signals (129.8 and 130.0 ppm), and the terminal methylene carbons are ejected as ethylene. There is no doubt that the true catalytic species, illustrated in Figure 4, is being generated during the course of this dimerization reaction, and yet the 1,1-disubstituted double bond did not undergo metathesis.

The total lack of participation of the 1,1-disubstituted alkene unit of **5** in the metathesis reaction with catalyst **1** indicates that the monosubstituted double bond possesses a substantially greater reactivity than the 1,1-disubstituted unit.

Generation of the actual catalytic species (Figure 4), the methylidene of catalyst **1**, is another test of metathetic activity. Ethylene was introduced to react with the "precatalyst" **1** to produce the methylidene,[12] the true catalytic entity, in the presence of **3**. The mixture was allowed to stand for 2 h before the ethylene was subsequently removed. No further reaction was observed, leading to the conclusion that the 1,1-disubstituted double bond of **3** is inert to the tungsten catalyst (**1**), in both the precatalytic and catalytic forms (Figure 6a). Steric hindrance obviously dictates the products attainable with the tungsten-based catalyst, at least for aliphatic dienes.

C. Unsymmetrical Substituted Aliphatic Dienes in the Presence of the Molybdenum Catalyst. The metathesis of 2-methyl-1,5-hexadiene (**5**) with the molybdenum catalyst (**2**) proved to be much more dramatic than with the tungsten version. In fact, the incipient reaction was quite violent, with the rapid generation of ethylene causing the solution to foam. Analysis revealed that the monomer initially dimerized to 2,9-dimethyl-1,5,9-decatriene (**6**) solely by the metathesis of the unsubstituted vinyl group, as had been the case for the tungsten. However, the reaction continued to proceed slowly, as the substituted vinyl groups underwent *cross-metathesis* with the internal olefins to produce a polymer, **7**, the structure of which is essentially identical to 1,4-polyisoprene (Figure 6b). This is the first known example of 1,1-disubstituted double bonds being condensed by ADMET chemistry to generate a polymer structure. Apparently, the molybdenum catalyst is far more active toward this chemistry than is tungsten, and the reasons for this enhanced activity remain unknown.

D. NMR Characterization of 1,4-Polyisoprene Synthesized by the ADMET Polymerization of 2-Methyl-1,5-hexadiene (5). The proton spectral analysis of the ADMET polymer **7** is consistent with the spectra of anionically synthesized 1,4-polyisoprene.[17] The ^{1}H NMR of polymer **7** exhibits the internal olefin signal (5.1 ppm), while a small amount of unreacted

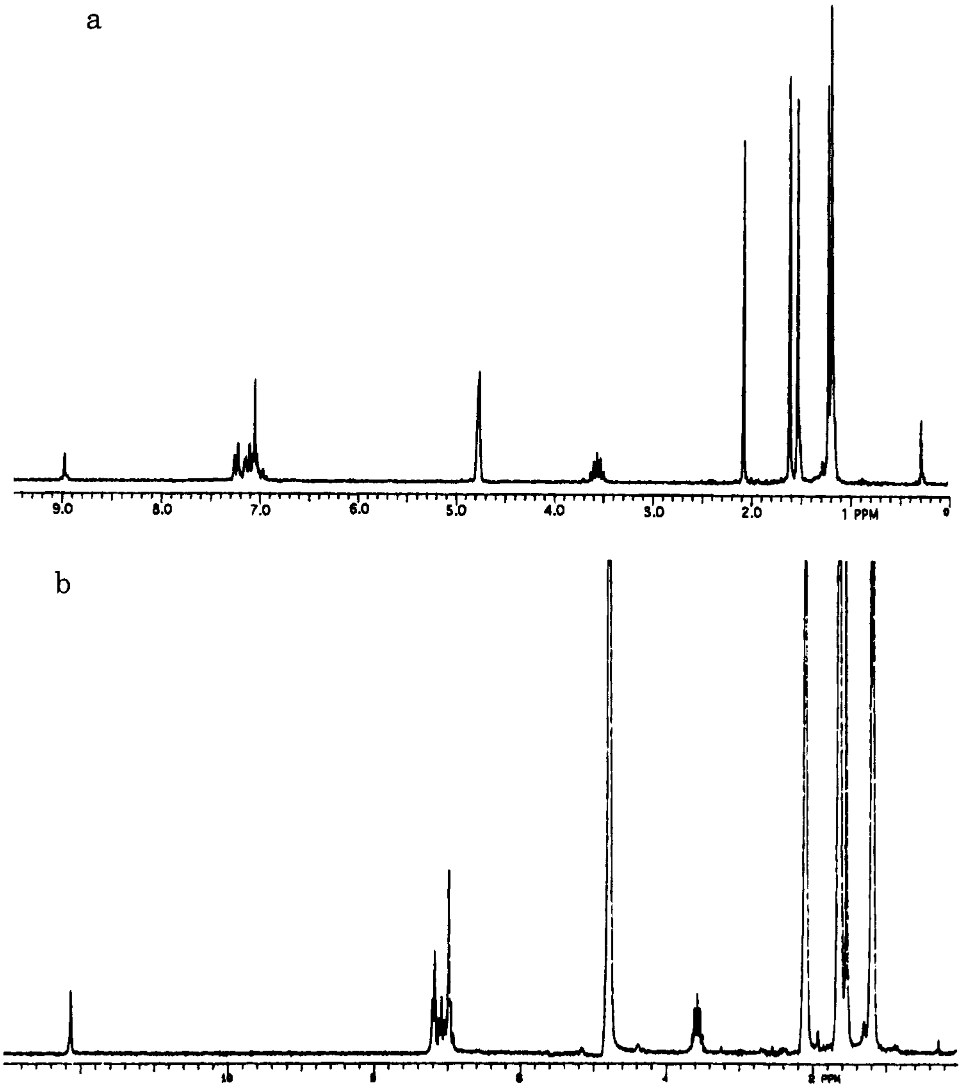

Figure 3. Attempted metathesis of 2,5-dimethyl-1,5-hexadiene (**3**): (a) **3** in the presence of the tungsten catalyst **1**. (b) **3** in the presence of the molybdenum catalyst **2**.

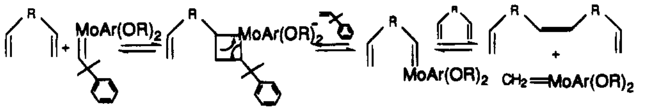

Figure 4. *In situ* generation of the actual catalytic species.

vinyl protons are also detected at 4.7 and 5.4 ppm. The two different methylene proton signals overlap at 2.0 ppm, producing a broad signal with a shoulder. The relative contributions of the *E* and *Z* isomers are revealed by the two separate proton signals at 1.7 (*E*) and 1.6 ppm (*Z*), while the *Z*/*E* ratio for polymer **7** calculated from the integration of these resonances is 0.54.

Figure 7 displays the quantitative ^{13}C NMR of ADMET polymer **7**, which also essentially matches the carbon spectrum for anionically synthesized 1,4-polyisoprene (from isoprene).[18] The ADMET polymer's *E*/*Z* ratio, calculated from the resonances at 125.1 (*Z*) and 124.3 ppm (*E*), is 0.53 and is in agreement with the ^{1}H NMR integration.

Additional carbon signals appear for polymer **7**. Specifically, the resonance at 130.0 ppm is due to a small amount of unsubstituted internal olefin that remains from the dimer, 2,9-dimethyl-1,3,5-decatriene (**6**). Further, since ADMET chemistry preserves the identity of end groups, the ^{13}C NMR spectrum shows signals at 110.0 and 145.4 ppm which correspond to the methyl-substituted double bonds of the end groups. The number-average molecular weight calculated from the integration of these end-group resonances relative to the internal olefinic carbons is 6800 (4900 VPO). The relatively low molecular weight is most likely a result of the low rate of the cross-metathesis reaction involving the methyl-substituted olefin units, and this molecular weight will increase with prolonged reaction times.

1,4-Polyisoprene also has been synthesized by the ring-opening metathesis polymerization (ROMP) of 1-methylcyclobutene using $Ph_2C{=}W(CO)_5$, as the catalyst. The polymer microstructure is significantly different, however, for the ROMP polymer consists of 80% isoprene units and 20% disubstituted and tetrasubstituted double bonds.[19] No disubstituted or tetrasubstituted double bonds are present in the ADMET polymer. Only pure 1,4-polyisoprene is formed.

One possible explanation for this ADMET reaction preference is a bias toward the formation of monosubstituted alkylidenes, since the presence of a methyl substituent directly on the vinyl group may prevent alkylidene formation. It is conceivable that the 1,1-disubsituted alkene participates in productive metathesis solely as the second olefin, and not as the alkylidene. In this way, the methyl substituent is located only on the *β* carbon of the metallacycle (Figure 8). Although there is no direct evidence supporting this explanation, the failure of 2,5-dimethyl-1,5-hexadiene

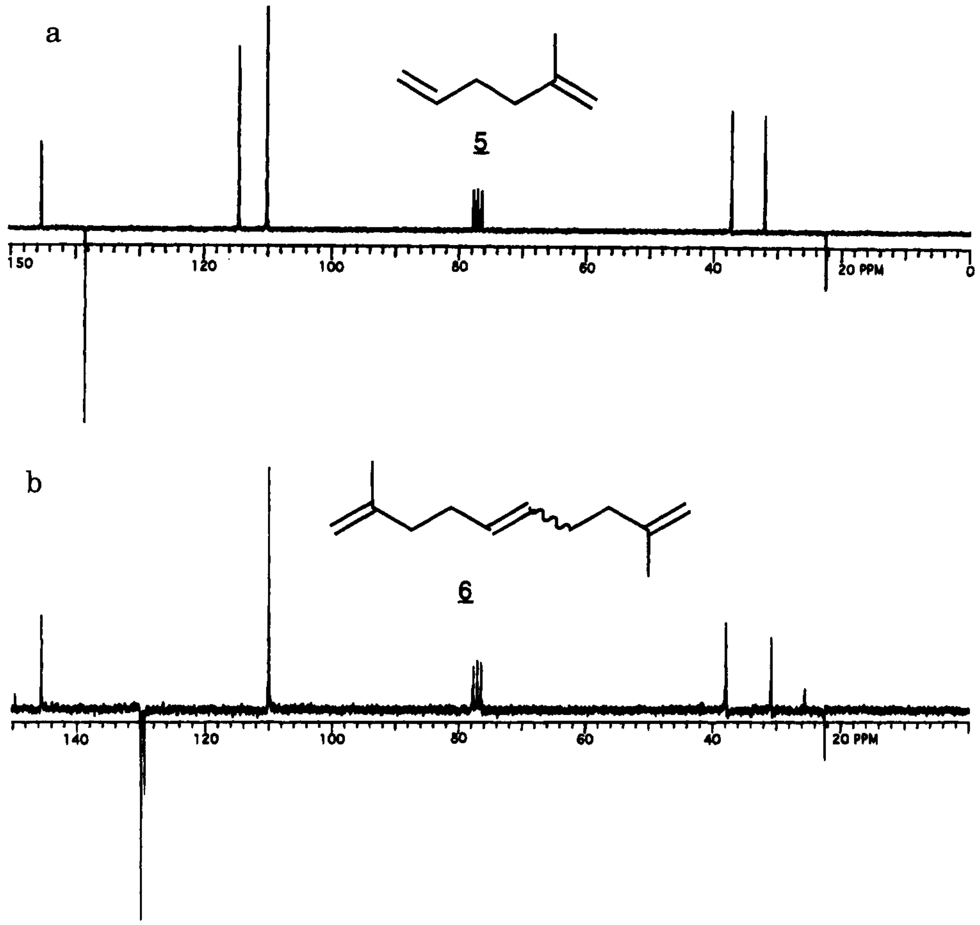

Figure 5. ^{13}C NMR analysis of the dimerization of 2-methyl-1,5-hexadiene (**5**) with the tungsten catalyst (**1**). (a) APT ^{13}C NMR spectrum of 2-methyl-1,5-hexadiene (**5**). (b) APT ^{13}C NMR spectrum of 2,9-dimethyl-1,5,9-decatriene (**6**).

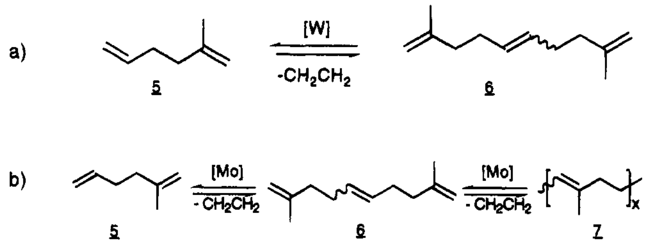

Figure 6. Reaction of 2-methyl-1,5-hexadiene (**5**) with catalyst **1** and **2**. (a) Metathesis of **5** with catalyst **1**. (b) Metathesis of **5** with catalyst **2**.

(**3**) to interact with the molybdenum catalyst **2** lends support to this theory.

E. 1,1-Disubstituted Aromatic Dienes. While the energetics of the formation of a tetrasubstituted olefin are unfavorable for nonconjugated aliphatic 1,1-disubstituted dienes, the delocalization energy associated with aromatic conjugation in the metathesis product might favor the forward reaction. Further, the planar phenyl ring might relieve some of the steric constraints associated with the formation of a tetrasubstituted alkene. Thus, the 1,1-disubstituted aromatic monomer, 1,4-diisopropenylbenzene (**8**), was probed regarding its metathesis behavior (Figure 9).

Only starting materials were isolated after repeated attempts to metathesize **8** with each catalyst **1** and **2**. ^{1}H NMR spectra of a solution containing both **8** and the tungsten catalyst (**1**) demonstrated that **8** was inert to the precatalyst. Ethylene was added to these reaction mixtures in an effort to test the metathesis activity of **8** with the methylidenes derived from catalysts **1** and **2** but failed to result in any productive metathesis.

III. ADMET Behavior of Trisubstituted Olefins.

A. ADMET Cross-Metathesis of a Trisubstituted Olefin. Theoretical thermodynamic equilibrium data show that the disproportionation of 2-methyl-2-butene (**9**) is more favorable than the disproportionation of isobutene.[20] Accordingly, the metathesis activity of 2-methyl-2-butene (**9**) was studied in a closed system to test the feasibility of the formation of a tetrasubstituted alkene with the ADMET catalysts **1** and **2**. Previous attempts at producing such an olefin with these catalysts failed, but the metathesis of **9** represents our first attempt at employing a trisubstituted alkene, as well as the most favorably substituted alkene, since the methyl groups present the smallest steric influence on the metathesis reaction.

After allowing the reaction with each catalyst to stand undisturbed for 1 week, the solutions were analyzed via high-resolution gas chromatography coupled mass spectroscopy. Integration of the gas chromatogram of each of these solutions revealed mixtures of *cis*- and *trans*-2-butene (**10**), 2-methyl-2-butene (**9**), and 2,3-dimethyl-2-butene (**11**) in relative concentrations that closely matched the predicted values for a thermodynamic equilibrium (Table 1). Although it is presented in Table 1 that trisubstituted olefins undergo metathesis with catalyst **1** and **2** to yield tetrasubstituted products, tetrasubstituted products cannot be formed with substituents larger than methyl groups as shown by the investigation presented below.

B. Symmetrical Trisubstituted Dienes. 3,6-Dimethyl-2,6-octadiene (**12**) was chosen to examine this substitution pattern, as its ADMET polymerization would produce the polymer structure anticipated for the failed polymerization of 2,5-dimethyl-1,5-hexadiene (**3**).

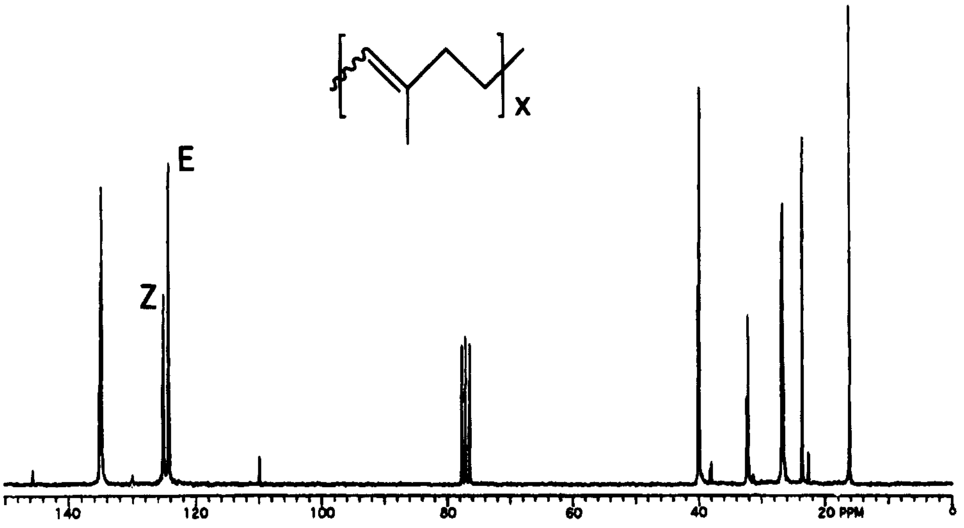

Figure 7. ^{13}C NMR spectrum of polyisoprene produced by the ADMET polymerization of **5** with catalyst **2**.

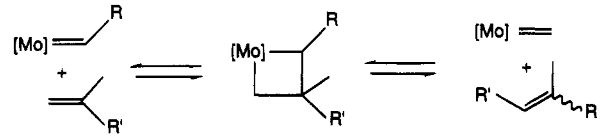

Figure 8. Proposed metallacycle produced in the ADMET synthesis of polyisoprene from 2-methyl-1,5-hexadiene (**5**); [Mo] represents catalyst **2**.

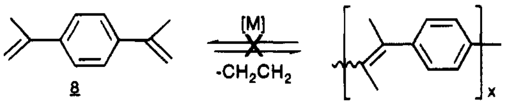

Figure 9. Attempted metathesis of 1,4-diisopropenylbenzene.

Table 1. Equilibrium Disproportionation of 2-Methyl-2-butene[a]

catalyst	2-methyl-2-butene (**9**)	2,3-dimethyl-2-butene (**11**)	2-butene (**10**) (cis & trans)
theoretical	85.1	7.45	7.45
1	83	8.7	8.3
2	84	7.9	7.7

[a] Values are reported in mole percents.

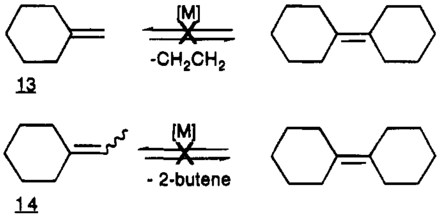

Figure 10. Attempted metathesis of exocyclic model compounds.

In this case, the reaction would produce 2-butene rather than ethylene as the small molecule. Any success in the polymerization of **12** would represent an extension of the metathesis reaction of 2-methyl-2-butene (**9**). One of the methyl groups of **9** is replaced with a larger alkyl chain in **12**. Further, the trisubstituted olefin will exploit the more favorable equilibrium as compared with 1,1-disubstituted olefins.

However, the potential monomer **12** showed no productive metathesis with either catalyst **1** or **2**. The addition of ethylene to these reaction mixtures also failed to bring about the metathesis of the trisubstituted alkenes, a test referred to earlier in this paper. The fact that there is no reaction between **12** and catalyst **1** or **2** suggests that the size of the substituents can restrict productive metathesis. Further, it can be stated that any ADMET polymerization which requires the formation of a tetrasubstituted olefin appear to be unattainable.

IV. ADMET Behavior of Exocyclic Olefins. A. 1,1-Disubstituted Exocyclic Olefins. Methylenecyclohexane (**13**) was employed as a model compound in an effort to reduce the steric constraints in the metathesis reaction of 1,1-disubstituted olefins; tying back the alkyl substituents to a six-membered ring might enhance the access to the olefin by the catalyst metal center (Figure 10). While methylenecyclohexane (**13**) did not dimerize in the presence of either catalyst **1** or **2**, the ^{1}H NMR monitored interactions illustrate that these catalysts exhibit marked differences in activity toward **13**.

The molybdenum catalyst **2** appeared not to interact with methylenecyclohexane (**13**) at all. The persistence of the initial alkylidene (12.2 ppm), in addition to the absence of the proton signals corresponding to the release of 3-methyl-3-phenylbutene (**4**) (6.0 ppm) and ethylene (5.3 ppm), illustrates that the precatalyst remains intact. However, the tungsten catalyst (**1**) does undergo the exchange reaction with the precatalyst, releasing 3-methyl-3-phenylbutene (**4**). Nonetheless, this is as far as the reaction proceeds, for ethylene is not released.

The ^{1}H NMR spectrum of the reaction mixture after 72 h of reaction shows that some of the initial alkylidene remains unreacted, even though an excess of **13** was present. Steric "pinning" helps but does not drive the chemistry to completion.

B. Trisubstituted Exocyclic Olefins. The participation of methylenecyclohexane (**13**) in the precatalyst exchange reaction was encouraging, so the chemistry was extended to 2-ethylidenecyclohexane (**14**). Compound **14** possesses an internal olefin, which is reported to be more reactive with the tungsten catalyst (**1**) than terminal olefins.[12] Thus, 2-ethylidenecyclohexane tests the combined effects of the increased reactivity of an internal olefin, combined with a lowered steric interaction as two of the substituents are part of a 6-membered ring.

Again, trisubstitution proves to be an insurmountable barrier for substituents other than methyl. Neither catalyst **1** nor **2** produces any productive metathesis with **14**. The ^{1}H NMR spectra of these solutions after 72 h illustrate no interaction of the original alkylidene of either catalyst with **14**. Further, metathesis of **14** with the addition of ethylene to the solution also failed to bring about productive metathesis. Obviously, steric bulk caused by the substituents on the olefin is the controlling factor in ADMET chemistry. Figure 10 illustrates the observations made for the exocyclic model study.

Conclusions

This model compound study of the olefin metathesis reactivity of 1,1-disubstituted and trisubstituted alkenes with catalysts **1** and **2** demonstrates the steric influence exerted by the alkyl substituent of the olefin functional group. These steric constraints have a significant amount of control over the ADMET reaction. The disproportionation of the trimethyl-substituted alkene **9** results in an equilibrium distribution of reactants and products (Table 1), while all attempts at metathesizing trisubstituted olefins, containing even one alkyl group larger than a methyl, failed.

The reactivities of the two different catalysts **1** and **2** with respect to the metathesis of 1,1-disubstituted and trisubstituted olefins are similar, as neither catalyst affords the homomethathesis polymerization of 1,1-disubstituted α,ω-dienes. In contrast, the molybdenum catalyst **2** showed an enhanced reactivity over the tungsten catalyst **1** toward the cross-metathesis between an internal olefin (1,2-disubstituted) and a 1,1-disubstituted alkene in the polymerization of 2,9-dimethyl-1,5,9-decatriene. The molybdenum catalyst (**2**) produces trisubstituted olefins from this cross-metathesis reaction, while the tungsten catalyst (**1**) is completely ineffective. What appears to be inherent with both catalyst systems is the inability to produce polymers with tetrasubstituted double bonds as well as products which must go through a tetrasubstituted metallacycle intermediate. The difference in reactivity, demonstrated by the two catalysts, is significant and its application to polymer synthesis is the subject of a future report.

Experimental Section

General Procedures. Nuclear magnetic resonance (NMR) (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained on a Varian XL-200 Series NMR superconducting spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Spectra were obtained in $CDCl_3$ with 1% TMS unless otherwise noted. Ultraviolet spectra were collected on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrometer with pentane as solvent. Infrared spectroscopy was performed on a Perkin-Elmer F9 FTIR spectrophotometer; samples were run neat when possible; otherwise, a Nujol mull of the sample was prepared. Low-resolution gas chromatography was performed on a HP 5880A gas chromatograph. Mass spectroscopy was performed on a Finnigan 4500 gas chromatograph/mass spectrometer. Elemental analyses of compounds were performed by Atlantic Microlab Inc. in Norcross, GA.

Catalysts. Two Lewis acid free metathesis catalysts, $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = tungsten or molybdenum, were prepared according to literature methods.[12,13] Catalysts were stored dry under an inert atmosphere.

Purification of Reagents and Solvents. The sensitivity of these catalysts to water and oxygen, as well as the requirments of purity, dictated by the step condensation nature of the polymerization reaction, required that all reagents be of the utmost purity.[22] All volatile reagents were dried by stirring over calcium hydride in a round-bottomed flask stoppered with a drying tube filled with Drierite for 48 h or until evolution of hydrogen gas was no longer evident. The predried reagent was then attached to a high-vacuum line and degassed a minimum of four times via freeze–pump–thaw cycles. The compound was then stirred for 24 h with intermitten degassing, with the frequency depending on hydrogen evolution. When the reagent appeared dry, it was transferred under vacuum to a potassium-mirrored flask and stirred for 24 h; additional mirrored flasks were utilized when necessary. When dry, the reagent was transferred into a storage flask that could be sealed and removed from the vacuum line.

Solid reagents were sublimed under reduced pressure and stored under argon in a drybox, while nonvolatile oils were heated under high vacuum (10^{-6}) for 48 h.

Toluene was purified by shaking with a dilute basic solution of $KMnO_4$ in water, followed by water and then concentrated sulfuric acid until the acid layer remained clear. The toluene was then washed with water, dried over magnesium sulfate, and distilled from calcium hydride. Finally, this predried toluene was distilled from a sodium–potassium alloy. Deuterated benzene was purchased from Aldrich Chemical Co., gold label, opened under an inert atmosphere, and stored over 4-Å sieves.

General ADMET Reaction Conditions. The reaction conditions employed for all polymerizations and model studies were similar to those previously described.[22–27] All reactions were carried out on a high-vacuum (10^{-6} mmHg) line to ensure dryness. All glassware was flame dried under vacuum. The application of an intermittent vacuum was employed to remove any condensate. The reaction temperature was kept below 50 °C to avoid catalyst decomposition. Reaction flasks were equipped with a gas trap and a dry ice/isopropyl alcohol condenser so that ethylene could be removed from the reaction without the loss of reactant.

NMR Solution Reactions. Solution reactions were performed in benzene-d_6 and monitored via ^1H NMR. Typically, 25 mg of the catalyst, $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, where M was either tungsten or molybdenum, was dissolved in 500 μL of benzene-d_6 in an inert atmosphere. This solution was added to an NMR tube equipped with a Young valve. Ten microliters of the alkene was then directly syringed into the tube and the valve closed. The reaction was then monitored by ^1H NMR immediately and followed for the course of the reaction.

Attempted Metathesis of 2,5-Dimethyl-1,5-hexadiene (3). This compound was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. Twenty milligrams of $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was used for this reaction. At the end of the 72-h reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Synthesis of 2,9-Dimethyl-1,5,9-decatriene (6) with the Tungsten Catalyst (1). The diene **5** was purchased from Aldrich Chemical Co. as 99% pure and dried as described above. Twenty milligrams of $W(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$ was used for this reaction. At the end of the 72-h reaction period, all volatiles were vacuum transferred into a clean flask for analysis. The clear liquid consisted entirely of the dimer, 2,9-dimethyl-1,5,9-decatriene (**6**). Yield: 94%. ^1H NMR: δ 1.72 (s, 6H), 2.11 (br, m, 8H), 4.73 (br, d, 4H), 5.42 (br, m, 2H). ^{13}C NMR: δ 22.2, 25.8, 30.8, 37.9, 110.0, 129.9, 130.1, 145.9. IR (neat, cm^{-1}): 2930.4, 1779.4, 1649.4, 1447.0, 966.4. Elem Anal. Calcd for $C_{12}H_{20}$: C, 87.80; H, 12.20. Found: C, 87.43; H, 12.31.

Synthesis of Polyisoprene (7) with the Molybdenum Catalyst (2). The monomer, **5** (1.0 g), was purchased from Aldrich Chemical Co. as 99% pure and dried as already described. Twenty milligrams of $Mo(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$ was used for this reaction. The reaction was allowed to continue until stirring via magnetic agitation became impossible (2–5 days). The resulting polymer was dissolved in toluene and passed through a column of alumina, followed by freeze drying from chloroform. Yield: 92%. ^1H NMR: δ 1.65 (d, 3H), 2.05 (br, 4H), 5.15 (br, m, 2H). ^{13}C NMR: δ 16.1, 22.4, 23.6, 26.4, 32.2, 32.3, 38.0, 38.1, 39.8, 40.1, 110.2, 124.2, 125.3, 134.8 (multiple signals), 145.8. SEC: $M_w = 9400$, PDI = 1.97. VPO: $M_n = 4920$. M_n (NMR): 6800. Elem Anal. Calcd for C_5H_8: C, 88.34; H, 11.76. Found: C, 88.01; H, 11.85. IR (neat, cm^{-1}): 2992.3, 1665.3, 1447.4, 1376.6. TGA (onset): 364.23 °C. DSC: $T_g = -71.87$ °C.

Synthesis of 1,4-Diisopropenylbenzene (8). This compound was synthesized according to a literature method.[23] Yield: 65%. ^{1}H NMR: δ 2.14 (s, 6H), 5.06 (m, 2H), 5.38 (m, 2H), 7.41 (s, 4H). ^{13}C NMR: δ 21.9, 112.2, 125.8, 140.0, 143.2. Elem Anal. Calcd for $C_{12}H_{14}$: C, 91.14; H, 8.86. Found: C, 91.10; H, 8.83.

Attempted Metathesis of 1,4-Diisopropenylbenzene (8). This reaction was performed in a 50-mL round-bottomed flask with a Rotoflow valve attached. In an argon-filled drybox, 1.0 g of 1,4-diisopropenylbenzene was dissolved in a minimal amount of dry toluene in the reaction flask. Once dissolved, 20 mg of catalyst $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was added directly. The reaction flask was sealed and removed from the drybox and attached to the high-vacuum line. The reaction was stirred for 24 h at room temperature, with intermittent vacuum applied on an hourly basis for 10 h. The reaction was heated to 50 °C for the next 48 h, again, intermittent vacuum was applied on an hourly basis for 10 h/day. After the allotted 72-h reaction time, the remaining toluene was stripped off and the contents of the flask analyzed.

Disproportionation of 2-Methyl-2-butene (9). Compound **9** was purchased from Aldrich Chemical Co. as 99% pure and was dried as previously described. In an argon-filled drybox, 2.0 mL of this reactant was syringed into a 50-mL round-bottomed flask equipped with a Rotoflow valve. The catalyst, 20 mg of $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was then dissolved in the liquid reactant and the Rotoflow closed. The reaction flask remained sealed for the entire reaction period of 1 week; at that time, the side arm of the flask was stoppered with a suba seal septum. The Rotoflow was then opened and a sample removed for analysis via high-resolution GC/MS. GC/MS: 1st peak (2-butene), M^+, 56.0664; M(100) 41.0452; 2nd peak (2-methyl-2-butene), M^+, 70.0688; M(100) 55.0582; 3rd peak (2,3-dimethyl-2-butene): M^+, 84.0946; M(100) 69.0644.

Synthesis of 3,6-Dimethyl-2,6-octadiene (12). Compound **12** was synthesized via Wittig reaction.[26] Acetonylacetone, 11.7 mL (100 mmol), in 25 mL of THF was added dropwise to a stirring, cold (−78 °C) solution of the ylide derived from ethylttriphenylphosphonium bromide (200 mmol) in THF, allowed to warm, and then refluxed overnight. THF was distilled off, and the remaining solids were extracted with pentane. The pentane was removed via rotary evaporation, and 13.6 g of the expected product was isolated by vacuum transferring the remaining liquid from the salts. Yield: 99%. ^{1}H NMR: δ 1.58 (m, 3H), 1.65 (m, 3H), 2.08 (m, 2H), 5.18 (m, 1H). ^{13}C NMR: δ 13.1, 13.2, 23.8, 29.8, 30.2, 37.9, 38.3, 118.1, 118.9, 136.0, 136.2. GC/MS: M^+, 138.1405; M(100), 123.1441. Elem Anal. Calcd for $C_{10}H_{18}$: C, 86.96; H, 13.04. Found: C, 86.85; H, 13.10.

Attempted Metathesis of 3,6-Dimethyl-2,6-octadiene (12). Compound **12** was synthesized and dried as described previously. Twenty milligrams of $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was used for this reaction. At the end of the 72-h reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted Metathesis of Methylenecyclohexane (13). Compound **13** was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. Twenty milligrams of $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was used for this reaction. At the end of the 72-h reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

Attempted Metathesis of 2-Ethylidenecyclohexane (14). Compound **14** was purchased from Aldrich Chemical Co. as 99% pure and was dried as described previously. The reaction flask was prepared in an analogous fashion to the reaction of 3-methyl-1,3-pentadiene. Twenty milligrams of $M(CHCMe_2C_6H_5)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3CF_3)_2]_2$, with M = W or Mo, was used for this reaction. At the end of the 72-h reaction period, all volatiles were vacuum transferred into a clean flask for analysis.

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