Carbocationic Alkene Polymerizations Initiated by Organotransition Metal Complexes: An Alternative, Unusual Role for Soluble Ziegler–Natta Catalysts

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Contents

Mike Baird was born in Hamilton, Ontario, Canada in 1940. He obtained his Hon. B.Sc. degree from McMaster University in 1962 and his Ph.D. degree from the University of Toronto in 1965 (with the late A. D. Allen). His interests in organometallic chemistry were irreversibly stimulated by 18 months of postdoctoral research with the late Geoffrey Wilkinson at Imperial College, London, where he carried out early work on Wilkinson's catalyst and had the good fortune to synthesize the first thiocarbonyl and carbon disulfide complexes. Baird joined the faculty of Queen's University in 1967, where he is currently Professor of Chemistry. He was a Humboldt Fellow at the Technical University of Munich in 1975 and won the Alcan Lecture Award of the Chemical Institute of Canada in 1986 and the Queen's University Prize for Excellence in Research in 1998. His current research interests include fullerene–metal complexes, alkene polymerization and organic synthesis induced by organotransition metal complexes, and tumor inhibition by transition metal complexes.
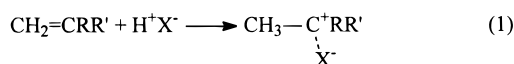
I. Introduction

Alkenes may be polymerized to their corresponding homopolymers via a variety of processes, of which the most important are free-radical polymerization, anionic polymerization, coordination/migration or Ziegler–Natta polymerization (the subject of most of the contributions to this topical issue), and carbocationic polymerization.[1] Although, as will be shown below, metal cations have long been known to behave as carbocationic initiators of alkene polymerization, such initiators have not contained the alkyl or hydrido ligands necessary for the compounds to serve as Ziegler–Natta catalysts. Furthermore, Ziegler–Natta catalysts and carbocationic initiators have generally been used to induce polymerization of rather different classes of alkenes—the key differences being the nature and number of the substituents on the carbon–carbon double bond—and thus the fields of carbocationic and Ziegler–Natta polymerization have developed almost completely independently.[1]

Nevertheless, it has recently been found that several well-characterized Ziegler–Natta catalysts can also induce carbocationic polymerization of one or more of styrene, isobutene, vinyl ethers, and N-vinylcarbazole, the latter three being quintes-

sential alkene monomers for carbocationic processes.[2] Furthermore, at least two monomers, styrene and isobutene, have been incorporated into polymers via both mechanisms; see below. Although the conclusions reached in these studies in most cases appear to be well founded, Ziegler–Natta and carbocationic polymerizations may in fact give materials with identical structures and end groups and mechanistic differentiation of the two processes can be nontrivial. Thus, it is possible that some carbocationic polymerizations have previously been incorrectly identified as Ziegler–Natta processes. Furthermore, although this has not yet been demonstrated, it seems likely that polymers formed via a Ziegler–Natta polymerization mechanism may subsequently undergo carbocationic addition steps which could effectively shut down Ziegler–Natta polymerization catalysis by the system. Thus the line between the two polymerization processes is becoming increasingly blurred. It is the purpose of this article to provide the reader first with useful background on the general field of carbocationic initiation of alkene polymerization and

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then to review the utilization of several classes of organotransition metal complexes, all Ziegler–Natta catalysts, as carbocationic initiators. In this way, it is hoped that the relationships between the two types of alkene polymerization processes will become apparent.

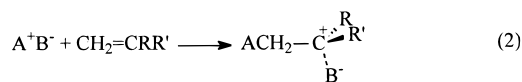## II. Carbocationic Initiation of Alkene Polymerization

Carbocationic processes for polymerization of alkenes $CH_2=CRR'$ (R, R′ = H, alkyl, aryl, alkoxy, amido) have been known for many years and, because of major commercial applications, have been the subject of intense scrutiny in both academic and industrial laboratories.[2] The active sites are carbocations which may be generated in a number of ways including protonation of the alkene (eq 1); in some

$$CH_2=CRR' + H^+X^- \longrightarrow CH_3-\overset{+}{C}RR' \qquad (1)$$
$$\overset{|}{X^-}$$

cases, such as the very effective initiation by siliconium ions R_3Si^+,[2k,l] protons are apparently introduced via reaction of these Lewis acids with adventitious water. Note that the product formed in the initiation stage involving protonation is the thermodynamically more stable secondary or tertiary carbocation CH_3- C^+RR', stabilized in part by interaction with the counteranion X^-. The counteranion must be a very poor nucleophile; otherwise ions will combine to give a neutral compound $CH_3CRR'X$. Indeed, a proper choice of anion is of crucial importance as many systems appear to involve equilibria between the active species and dormant species which arise from reversible termination and/or chain transfer.

Propagation involves repeated additions of alkene molecules to the carbocationic center, which migrates well away from the site of initial attack (Scheme 1). Thus, the C=C bond must be the most nucleophilic species in the system.

Carbocationic polymerization can also be initiated by a number of molecular Lewis acids such as BX_3, AlX_3, SbX_5, SnX_4, VCl_4, and TiX_4 (X = halide), the general process possibly proceeding as in eq 2 (AB = metal halide), although there is debate for some systems as to whether the active species are actually protons arising from hydrolysis of the metal halide by trace amounts of water (eq 3).

$$A^+B^- + CH_2=CRR' \longrightarrow ACH_2-\overset{+}{C}\overset{R}{\underset{B^-}{\overset{|}{\diagdown}}}R' \qquad (2)$$

$$MCl_n + 2H_2O \rightarrow H_3O^+ + [HOMCl_n]^- \qquad (3)$$

Here, as with activation by H^+, the cationic center A^+ is believed to interact with the alkene π system to form a σ bond at C-1 (essentially an η^1 mode of coordination; see below) and generate at C-2 a carbocationic center which is stabilized via interaction with the counteranion B^-. The carbocationic center formed may also be stabilized by weak Lewis bases. Propagation then proceeds as in Scheme 1.

It should be noted that the Lewis acids involved here are not recycled during propagation but rather are consumed irreversibly; they therefore do not behave as *catalysts* but rather as *initiators* of polymerization.[3] It is also obvious that only alkenes which form relatively stable carbocationic centers can polymerize in this way; these include isobutene and other 1,1-disubstituted alkenes, styrene, vinyl ethers, and vinylamines. In contrast, ethylene gives only low molecular weight oligomers while propylene and 1-alkenes give only low molecular weight polymers, typically with molecular weights substantially less than 10^5.[2] It is therefore clear just why Ziegler–Natta and carbocationic processes have been distinct areas of investigation even though similar complexes can initiate both (see below). Ethylene, propylene, and 1-alkenes are readily polymerized by good Ziegler–Natta catalysts but not by good carbocationic initiators. On the other hand, for steric reasons, 1,1-disubstituted alkenes do not readily form η^2 complexes and thus are not readily polymerized by good Ziegler–Natta catalysts, while vinyl ethers and amines contain conventional Lewis-base functionalities which often coordinate directly to transition metal Lewis-acid sites and thus poison Ziegler–Natta catalyst systems.

Chain-transfer processes generally involve deprotonation of the carbocationic end group by a monomer molecule (eq 4), aided by the anion B^-; the result is often a vinylidene end group. The resulting carboca-

$$P\sim CH_2\overset{+}{C}\overset{R}{\underset{B^-}{\overset{|}{\diagdown}}}R' + CH_2=CRR' \longrightarrow P\sim CH=CRR' + CH_3C^+RR'B^- \quad (4)$$
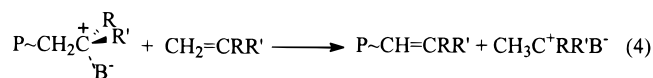
tion of eq 4 may then initiate new chain growth. If R and R′ contain hydrogen atoms on the carbons bonded to the carbocationic center, then other isomeric alkene end groups are also possible. Chain transfer is often the limiting factor on molecular

Scheme 1
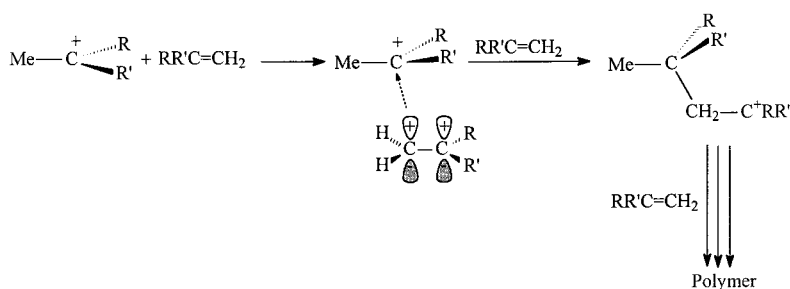
weights in industrial processes, and thus the nature of the stabilizing Lewis base is very important. The ratio of rate constants for chain propagation to chain transfer generally decreases on going to higher temperatures, and thus low temperatures are often required if high molecular weights are desired.

Chain termination occurs if trace amounts of good nucleophiles are present and can react irreversibly with the active carbocationic sites. In some cases, such species are added in order to cap the growing polymer chain with a desired end group.

III. Use of Cationic Transition Metal Complexes as Lewis-Acid Initiators

In addition to the above-mentioned neutral compounds of main group and transition elements in high positive oxidation states, a number of cationic transition metal complexes have also been investigated. These are generally more active than the neutral precursors, consistent with a carbocationic mechanism, and indeed, the correlations of molecular weights and conversions with temperature generally bear the signature of carbocationic processes. Although a number of monomers have been investigated, none have been examined intensively and few of the studies will be discussed further here. However, polymerizations of styrene and α-methylstyrene have been investigated in some detail, and these alkenes clearly are readily polymerized by cationic complexes.

In pioneering work, it was shown that chloride abstraction from $[Fe(NO)_2Cl]_2$ by silver or thallium-(I) salts gave the complex $[Fe(NO)_2(NCMe)_2](BF_4)_2$ which polymerizes styrene quantitatively in the temperature range from −20 to +40 °C in the poorly coordinating solvent methylene chloride over 22 h (M_w 88000−34000).[4a,b] α-Methylstyrene was polymerized faster but to lower molecular weight material, and isobutene was polymerized quantitatively to material of low molecular weight (M_w 10000) over 22 h. The analogous molybdenum and tungsten complexes $[M(NO)_2(NCMe)_4](BF_4)_2$ (M = Mo, W) behaved similarly, although the poorer coordinating solvent $MeNO_2$ was preferred for these systems.[4e] The complex $[Pd(NCMe)_4](BF_4)_2$ is also relatively reactive for the polymerization of styrene and α-methylstyrene, but $[Eu(NCMe)_4](BF_4)_2$ is less so.[4c,d,f,g]
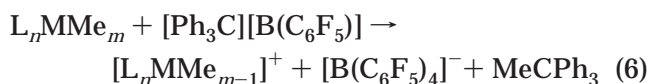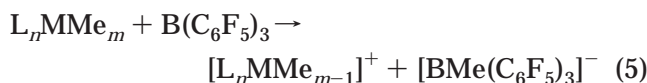
While these few results suggest that a wide variety of cationic complexes may behave as carbocationic initiators for alkene polymerizations, in fact none have been studied with anything like the rigor or attention to detail that polymerizations by conventional initiators have induced. Thus, little more may be said about them at present.

IV. Use of Cationic Organotransition Metal Complexes as Lewis-Acid Initiators

A relatively new development in the field of carbocationic polymerization reactions, and the primary focus of this contribution, follows the realization, only a few years ago, that a few cationic organometallic complexes which behave as excellent Ziegler−Natta catalysts for some monomers can also behave as

equally effective carbocationic initiators for others. Thus, the two distinctly different polymerization processes may be complementary or competitive in some situations, and it may arguably be important in designing polymerization processes to be aware of the implications of the possible duality. Research to date has focused on three main classes of complexes which behave in this way, monocyclopentadienyl complexes, metallocene complexes, and others.

The types of cationic organotransition metal complexes of interest here have in most cases been generated by reacting compounds of the general formula L_nMMe_m with the methyl carbanion abstracting reagents $B(C_6F_5)_3$ and Ph_3C^+, the latter principally as the $[B(C_6F_5)_4]^-$ salt (eqs 5 and 6).

$$L_nMMe_m + B(C_6F_5)_3 \rightarrow$$
$$[L_nMMe_{m-1}]^+ + [BMe(C_6F_5)_3]^- \quad (5)$$

$$L_nMMe_m + [Ph_3C][B(C_6F_5)] \rightarrow$$
$$[L_nMMe_{m-1}]^+ + [B(C_6F_5)_4]^- + MeCPh_3 \quad (6)$$

Dialkylmetallocene compounds, exemplified by Cp_2ZrMe_2, and half-sandwich compounds, exemplified by Cp^*TiMe_3, react in this way to form excellent Ziegler−Natta catalysts of the types $[Cp_2ZrMe]^+$ and $[Cp^*TiMe_2]^+$, respectively, and have been the subject of intense scrutiny.[5,6] However, these particular cationic complexes are also very strong Lewis acids and are among the first such species to be recognized as excellent carbocationic initiators and studied as such in detail.

Cationic metallocene-based Ziegler−Natta catalysts are well-described elsewhere.[5] Ten-electron, monocyclopentadienyl complexes of the type $[Cp'-MR_2]^+$ (Cp′ = cyclopentadienyl, substituted cyclopentadienyl; R = alkyl) are electronically less saturated and sterically less hindered than their metallocene counterparts and might be expected to exhibit even higher reactivities. Of importance here, early work showed that reaction of, e.g., Cp^*TiMe_3 with the highly electrophilic borane $B(C_6F_5)_3$ results in attack on the methyl ligand by the borane to give the methyl-bridged compound $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ (**A**). The nonclassically coordinated anionic borate

A
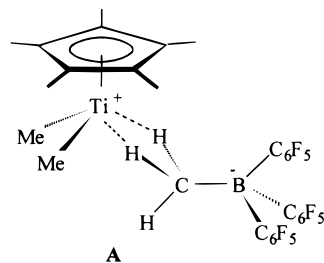
ligand in **A** is readily displaced by a variety of amines and phosphines L to form complexes of the type $[Cp^*TiMe_2L][BMe(C_6F_5)_3]$[6h] and by aromatic molecules to form arene complexes of the type $[Cp^*TiMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ (arene = benzene, toluene, etc.), isoelectronic with neutral metallocene compounds.[6b] Although no η^2-alkene complexes of the type $[Cp^*TiMe_2(\eta^2\text{-alkene})]^+$ have been reported,

$Cp*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and the arene complexes do provide apparent sources of the cationic species $[Cp*TiMe_2]^+$ and behave as very good initiators not only for the polymerization of ethylene,[6h,k] propylene,[6k] 1-hexene,[6l] and styrene,[6h] which are normally amenable to Ziegler−Natta processes, but also for isobutene,[6e] vinyl ethers,[6g] and styrene (below 0 °C),[6h] which are normally polymerized via carbocationic processes. Thus, species of the types $[Cp*TiMe_2(\eta^2\text{-}alkene)]^+$ and, by analogy with conventional carbocationic polymerization initiators, $[Cp*TiMe_2(\eta^1\text{-}alkene)]^+$ are presumed intermediates.

A. Homo- and Copolymerization of Isobutene

Isobutene is generally polymerized via carbocationic processes to form products with broad molecular weight distributions and exhibiting consistencies which vary from liquids for oligomers to solids for high molecular weight polymers.[2] The latter are tough elastomers which resemble unvulcanized natural rubber in tensile strength and elasticity and which also exhibit excellent barrier properties for gases. Cationic copolymerization of isobutene and isoprene also has a major commercial application in the production of butyl rubber, a copolymer containing up to 2.5% isoprene which is normally produced in halogenated solvents at cryogenic temperatures (−100 °C) using as initiator aluminum trichloride $(AlCl_3)$.[2,7a] To obtain polymers of high molecular weights, it is essential to carry out cationic polymerization processes at low temperatures (down to −100 °C) where the rates of chain-transfer reactions are reduced.
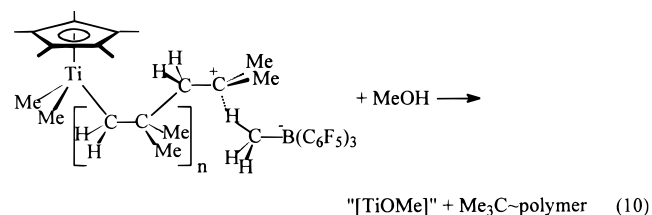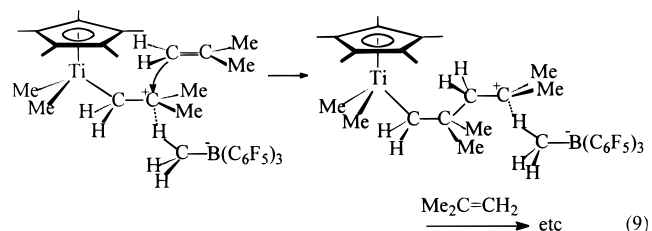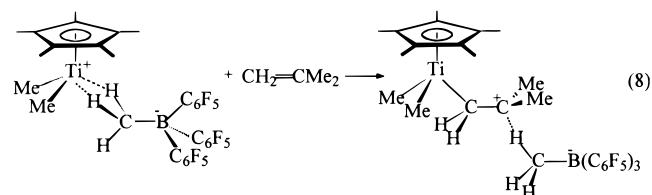
In research carried out in the temperature range from −40 to −75 °C, it was shown that isobutene polymerization is readily initiated by the successive additions of $Cp*TiMe_3$ and $B(C_6F_5)_3$ to solutions of isobutene in methylene chloride and toluene.[6e,m,8a] As anticipated for a carbocationic process,[2] it was found that lower temperatures generally resulted in higher molecular weights in both methylene chloride and toluene, with polydispersities usually ~2. The neutral compound $Cp*TiMe_3$ by itself did not initiate polymerization of isobutene, while control experiments with $B(C_6F_5)_3$ showed that the borane alone also does not behave as an initiator in toluene. Polymerization by $B(C_6F_5)_3$ does occur more readily in, e.g., methylene chloride because of proton formation from the reaction between $B(C_6F_5)_3$ and adventitious traces of water (eq 7).

$$2H_2O + B(C_6F_5)_3 \rightarrow H_3O^+ + [HOB(C_6F_5)_3]^- \quad (7)$$
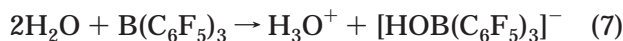
Better yields of polyisobutylene (PIB) are therefore formed in more polar solvents when the solvent is incompletely dried. However, a possible role for adventitious sources of proton initiators in the $Cp*TiMe_3/B(C_6F_5)_3$ system seems unlikely as $Cp*TiMe_3$ readily eliminates proton sources; the titanium−methyl bonds readily undergo protonolysis to methane.[6n] The possibility of proton initiators has also been ruled out because the polymerizations proceed in nonpolar solvents such as toluene, in

which $B(C_6F_5)_3/H_2O$ is ineffective, and also in the presence of conventional proton traps.[8a]

Polyisobutene (PIB), prepared utilizing conventional Lewis-acid initiators, is generally obtained as a head-to-tail polymer $(CH_2CMe_2)_n$,[2] and ^1H and ^{13}C-$\{^1H\}$ NMR spectra of polymers formed using **A** also exhibited the resonances expected for this structure.[6m,7b] Thus, initiation is believed to proceed as shown in eq 8 and propagation as in eq 9. In addition,

$$+ CH_2{=}CMe_2 \quad (8)$$

$$\xrightarrow{Me_2C{=}CH_2} etc \quad (9)$$

$$+ MeOH \longrightarrow$$

$$\text{"[TiOMe]"} + Me_3C{\sim}polymer \quad (10)$$

analyses of the end-group resonances indicated the presence of *tert*-butyl "head" groups, which arise from chain transfer as in eq 4 and solvolysis of the initiating species (eq 10).

Thus the polymerization results are consistent with a carbocationic polymerization mechanism, the isobutene presumably coordinating in an η^1 fashion to the $[Cp*TiMe_2]^+$ and the metal−alkene interaction being stabilized by a complementary interaction between the borate anion $[MeB(C_6F_5)_3]^-$ and the alkene. A carbocationic center is thus generated at C-2 of the isobutene molecule, and this is attacked by a second isobutene molecule acting as a nucleophile in a manner typical for conventional carbocationic polymerization processes (eqs 8 and 9). Propagation occurs as shown, and chain termination is effected by alcoholysis of the propagating species to yield a terminal *tert*-butyl group as indicated in eq 10.

NMR analyses of the "tail" end groups indicated the presence of vinylidene structures, as anticipated for the type of chain-transfer processes mentioned above, i.e.

$$P{\sim}CH_2{-}C^+Me_2 + CH_2{=}CMe_2 \longrightarrow P{\sim}CH_2{-}C{\overset{CH_2}{\underset{Me}{=}}} + Me_3C^+ \quad (11)$$
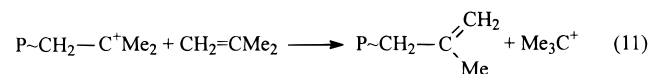
The conclusion that a cationic, highly electrophilic transition metal complex such as $[Cp*TiMe_2]^+$ can behave as a carbocationic polymerization initiator as well as a Ziegler−Natta catalyst is not surprising,

although there are few precedents for the hypothesized η^1 mode of coordination. Much more common, of course, is the η^2 mode of coordination which is normally involved in ethylene and 1-alkene polymerization catalyzed by metallocene compounds. However, as noted previously,[6e,m] η^1 structures of the type postulated here undoubtedly occur during nucleophilic attack on alkenes coordinated to electrophilic metals[9a] while near η^1 structures have been found in complexes of alkenes containing good π-donor substituents.[9b,c]

Nonetheless, the evidence for a carbocationic mechanism to this point is circumstantial and based largely on the presumption that isobutene polymerization must involve carbocationic initiation. However, it must be noted that, in principle, the polymeric products could also be formed via a Ziegler–Natta process, as in Scheme 2. This sequence of steps would

Scheme 2
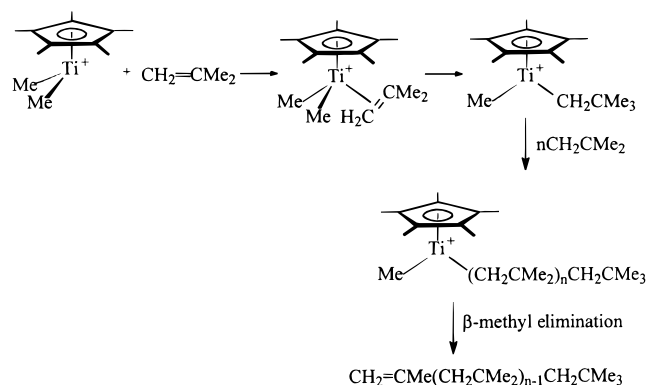
give the same *tert*-butyl headgroup and methylidene tail group as does the carbocationic process, giving rise to the possibility that the Ziegler–Natta process may in fact indeed pertain. Indeed, evidence for *copolymerization* of ethylene and isobutene via Ziegler catalysis has recently been reported,[8b] initiation being induced by the "single site" catalyst **B** (R = cyclododecyl) activated with, e.g., [Ph₃C][B(C₆F₅)].
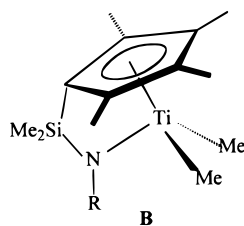

Strong evidence in support of the carbocationic mechanism in *homopolymerizations* of isobutene by **A**, however, is gained by analysis of the product formed on copolymerization of isobutene and isoprene.[6e,m] This commercially important copolymer[7a] is manufactured via a carbocationic process initiated by AlCl₃, and contains isoprene ($\sim$1%) incorporated only in a 1,4-manner, as in **C**.
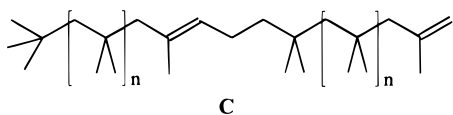

Copolymerization initiated by **A** proceeds readily at low temperatures and gives isobutene–isoprene copolymers structurally identical to those prepared commercially utilizing a conventional Lewis-acid initiator. That is to say, there is no incorporation of isoprene in a 1,2- or 3,4-fashion, as would be anticipated at least in part for a Ziegler–Natta process. As with polyisobutene, lower temperatures result in higher molecular weights (polydispersities $\approx$ 2) while materials with high M_w values and a low polydispersity index could be obtained only at very low contents of isoprene, consistent with observations that chain-transfer processes are extremely facile following isoprene incorporation.[2,7a]

Formation of a random copolymer via incorporation of small amounts of isoprene in the PIB would thus occur as in eq 12, via addition of isoprene to an isobutyl cationic center to form a stabilized allylic cation. Although attack by a molecule of isobutene
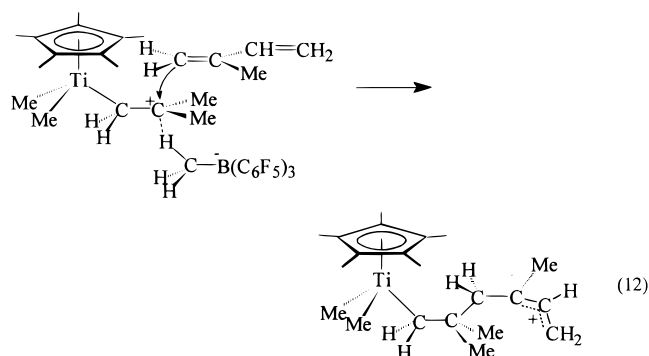

could, in principle, occur at C-2 or C-4 of the allylic cation to give the products of 1,2- or 1,4-addition, respectively, in general only 1,4-addition occurs. Chain-transfer processes resemble that of polyisobutene (eq 11) but now occur readily at isoprenyl termini as in eq 13.[6m] Observations that the copoly-

$$P\sim CH_2\overset{|}{\underset{Me}{C}}{}^+ - CH=CH_2 + CH_2=CMe_2 \longrightarrow P\sim CH=CMeCH=CH_2 + Me_3C^+ \quad (13)$$
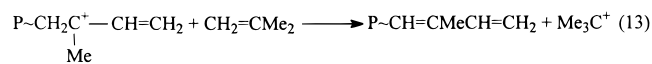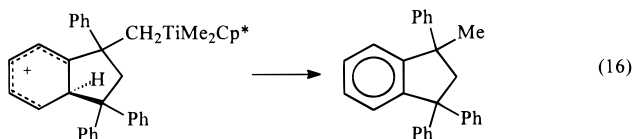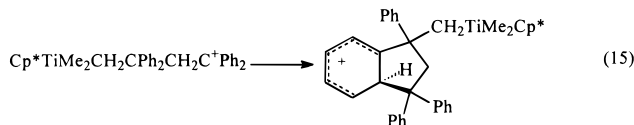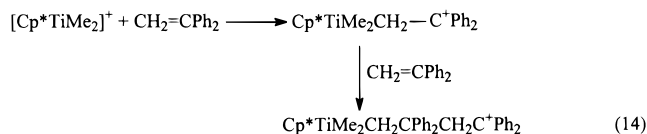
mer formed by **A** is apparently identical to that formed by conventional Lewis acids are extremely convincing evidence that carbocationic processes pertain in the former.

Further evidence that [Cp*TiMe₂]⁺ can behave as a carbocationic initiator was obtained from a study of its reaction with 1,1-diphenylethylene, an alkene which, for steric reasons, is not readily polymerized. Instead, it has been shown that interaction with strong Lewis acids results in dimerization to 1,3,3-triphenyl-3-methylindan (**D**).[6m] Isolation of this indan
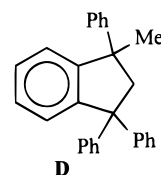

derivative is indeed evidence for carbocationic initiation, as it is probably formed by intramolecular cyclization of the cationic intermediate formed by

addition of two molecules of monomer, as in eq 14–16. The ultimate fate of the titanium was not deter-

$$[Cp^*TiMe_2]^+ + CH_2{=}CPh_2 \longrightarrow Cp^*TiMe_2CH_2{-}C^+Ph_2$$

$$\downarrow CH_2{=}CPh_2$$

$$Cp^*TiMe_2CH_2CPh_2CH_2C^+Ph_2 \qquad (14)$$

$$(15)$$

$$(16)$$

mined, but the same product was obtained by Sen et al.[10] from the reaction of 1,1-diphenylethylene at low temperature with electrophilic transition metal cations such as $[Pd(MeCN)_4][BF_4]_2$.

Further mechanistic debate concerning the mode-(s) of polymerization by the titanium system centers on the possibility that traces of water may react with the Cp^*TiMe_3 or **B** and, through hydrolytic processes of types shown in eqs 3 and 7, generate protons which may behave as the active polymerization initiator. While this may seem unlikely, given the fact that Cp^*TiMe_3 reacts quickly with water to give methane and inactive hydroxytitanium species,[6n] Shaffer and Ashbaugh have investigated the possibility by finding that isobutene polymerization was not prevented in the presence of the putative noncoordinating proton trap 2,6-di-*tert*-butylpyridine. If trace amounts of proton were responsible for initiating polymerization, it was expected that polymerization would not occur in the presence of the added amine. The subsequent observation that 2,6-di-*tert*-butylpyridine does in fact coordinate weakly to the cation $[Cp^*TiMe_2]^+$ as in either **E** or **F** does not detract from this conclusion.[6m]
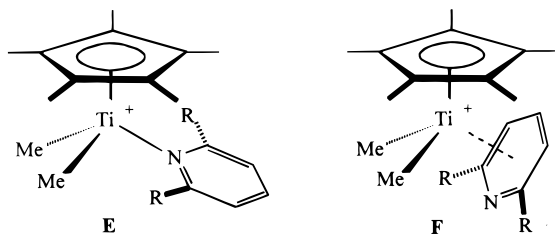
Two groups have shown that metallocene cations of the type $[Cp'_2MMe]^+$ (M = Zr, Hf; Cp' = cyclopentadienyl, substituted cyclopentadienyl) polymerize isobutene[8a,11a] and copolymerize isobutene and isoprene[11a] through what appear to be carbocationic processes. Good yields of high molecular weight polymers of low polydispersities were generally obtained, depending on the initiator and reaction conditions. Kinetic studies indicated that initiations by $[Cp_2MMe][B(C_6F_5)_4]$ (M = Zr, Hf) are slow relative to propagation and that chain transfer is active throughout the polymerization.[8a] Activation energies for homo- and copolymerization are comparable with

those of conventional Lewis-acid initiators,[11a] again suggesting similarities in mechanisms.

Isobutene polymerization initiators are also formed by treating hydrides of the type $[Cp'_2ZrH_2]_2$ with $B(C_6F_5)_3$,[11b] although the nature of the initiating species is not clear, and by treating the yttrium complexes $[Cp'_2YMe]_2$ with $B(C_6F_5)_3$, which gives $Cp'_2Y\{BMe(C_6F_5)_3\}$.[11c] Nonmetallocene complexes also exhibit interesting activities, and cationic $[Zr(N\{SiMe_3\}_2)_3]^+$, formed by reacting $ZrMe(N\{SiMe_3\}_2)_3$ with $B(C_6F_5)_3$,[11d] is a good initiator, exhibiting again a reaction profile consistent with a carbocationic process. Similarly, the species of unknown structure formed on treating $Ti(CH_2Ph)_4$ with $[Ph_3C][B(C_6F_5)]$ is also a good initiator; in this case, an absence of benzyl end groups in the products unambiguously rules out a Ziegler–Natta process.[12]
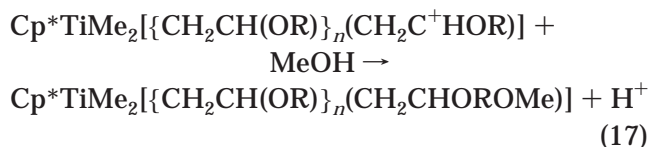
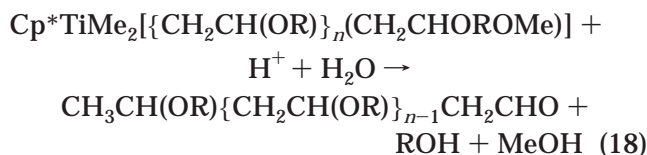## B. Polymerization of Vinyl Ethers, *N*-Vinylcarbazole

Vinyl ethers and *N*-vinylcarbazole (**G**) are amenable to carbocationic initiation of polymerization because the carbocationic center generated at C-2 is stabilized by π overlap with the lone pair electrons on the heteroatom. The polymers are readily pre-

G
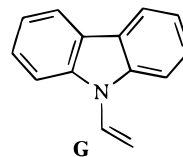
pared utilizing a number of Lewis-acid initiators and exhibit very useful properties.[2g] Initiation by **A** has been investigated in some detail,[6g] and it has been shown that the monomers $ROCH{=}CH_2$ (R = Me, Et, isobutyl), $EtOCH{=}CHMe$, 2,3-dihydrofuran, and *N*-vinylcarbazole are all readily polymerized to materials similar in terms of microstructures and molecular weights to those prepared utilizing conventional Lewis-acid initiators. Again, low temperatures were necessary for high molecular weights to be obtained, and further evidence for carbocationic initiation was found in the fact that 2,5-dihydrofuran was not polymerized. In this case, a carbocationic center cannot be stabilized by π overlap with the oxygen lone pair, nor is the monomer susceptible to polymerization by **A** via a Ziegler–Natta process.

The relevance of the carbocationic mechanism was also demonstrated for the polymerization of ethyl vinyl ether by end-group analysis following termination with aqueous methanol.[6g] An aldehydic resonance (δ 9.8) was observed in the ^{1}H NMR spectrum of the resulting polymer, the aldehyde functionality arising from hydrolysis of the acetal formed via nucleophilic attack by methanol on the active site of the growing polymer (eqs 17 and 18).

$$Cp^*TiMe_2[\{CH_2CH(OR)\}_n(CH_2C^+HOR)] +$$
$$MeOH \rightarrow$$
$$Cp^*TiMe_2[\{CH_2CH(OR)\}_n(CH_2CHOROMe)] + H^+$$
$$(17)$$

$$Cp^*TiMe_2[\{CH_2CH(OR)\}_n(CH_2CHOROMe)] +$$
$$H^+ + H_2O \rightarrow$$
$$CH_3CH(OR)\{CH_2CH(OR)\}_{n-1}CH_2CHO +$$
$$ROH + MeOH \quad (18)$$

The titanium-containing product was not determined, but certainly the three alkyl ligands would have been removed via protonolysis and the resulting titanium would be present as hydroxy and/or methoxy species. Possible initiation by the borane $B(C_6F_5)_3$ was also investigated. While initiation by this Lewis acid does occur, the polymers formed were of significantly lower molecular weights than was found with **A**.

Although vinyl ethers and *N*-vinylcarbazole are among the most reactive of alkenes in carbocationic polymerization processes, there are only two other reported examples of cationic organotransition metal complex initiator, one being the diazabutadiene platinum(II) complex **H** (L = MeCN), prepared via chloride abstraction from the neutral chloro precursor.[13]
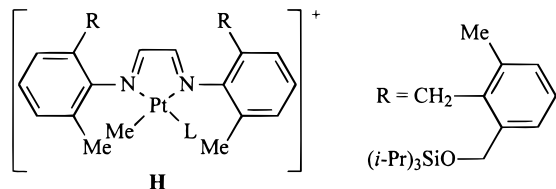
Again, the reaction patterns exhibited the signature of carbocationic processes and again the ^{1}H NMR spectrum of a poly(ethyl vinyl ether) sample exhibited an aldehyde resonance at δ 9.8.

The complex of unknown structure formed on treating $Ti(CH_2Ph)_4$ with $[Ph_3C][B(C_6F_5)]$ is also a good initiator for the polymerization of ethyl vinyl ether and *N*-vinylcarbazole but has not been studied in detail.[12]

C. Polymerization of Styrenes

Protonation of styrene yields a relatively stable benzylic cation and thus styrenes, especially when ring-substituted with electron-donating groups, are readily susceptible to carbocationic polymerization.[2] This was first noted in organometallic systems with **A**, although this initiator system is complicated. It behaves as a carbocationic initiator in aromatic solvents only below about −15 °C, giving atactic polystyrene.[6g,n,8a] On reacting with styrene either neat or in toluene at room temperature and above, however, **A** is converted to an extremely efficient Ziegler−Natta catalyst for syndiotactic polystyrene formation.[6g,14] Initiator **A** also initiates the copolymerization of *p*-methylstyrene and isobutene, but little else of relevance to this theme has seemingly been reported in the literature.

V. Comments on the Possible Effects Carbocationic Polymerizations May Have on Ziegler–Natta Processes

The fact that a variety of well-known Ziegler−Natta catalysts can also behave as carbocationic

initiators has interesting implications for Ziegler−Natta polymerizations of a variety of alkenes. Successful polymerizations of alkenes via both processes have the same requirements, specifically a vacant, highly Lewis-acidic site on a metal complex to which the monomer may coordinate, in combination with poorly coordinating solvents and counteranions which do not compete effectively for the metal inner coordination sphere. Thus research in both fields is driven by the same fundamental questions, and it may well become increasingly important to reflect on the capabilities and limitations of carbocationic processes while developing Ziegler−Natta catalysts. Indeed, as indicated above, some putative Ziegler−Natta processes may involve, at least in part, carbocationic initiation.

However, one should also be aware of possibilities that elements of carbocationic processes may directly influence Ziegler−Natta catalytic chemistry. For instance, polymers containing vinylidene end groups of the type $CH_2=CMe-polymer$ are often formed during Ziegler−Natta processes and might recoordinate to the metal cation in an η^1 fashion, as in **I** and **J** for monocyclopentadienyl and metallocene systems, respectively. If intermediates of these types were to
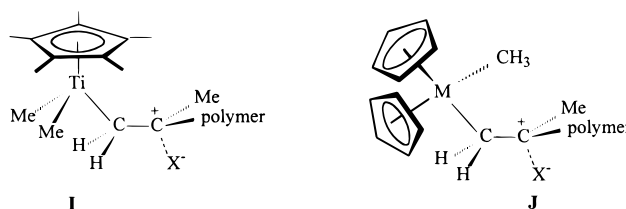
form, the catalyst sites would be converted to neutral metal species, cationic metal-centered sites would no longer be available, and the end results would be cessation of the Ziegler−Natta processes via de facto poisoning of the catalysts. To our knowledge, this type of chain-termination chemistry has not previously been observed or discussed. Alternatively, depending on the nature of the monomer(s), carbocationic polymerization could be initiated at the newly formed **I** and **J**, as in Scheme 1 or eqs 8 and 9, and possibly a block of a different kind of polymer would be added to any polymer already formed.

VI. Acknowledgments

VII. References

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