Reaction of Vinyl Chloride with Group 4 Metal Olefin Polymerization Catalysts

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Abstract: The reactions of three types of group 4 metal olefin polymerization catalysts, $(C_5R_5)_2ZrX_2$/activator, $(C_5Me_5)TiX_3$/MAO (MAO = methylalumoxane), and $(C_5Me_4SiMe_2N^tBu)MX_2$/activator (M = Ti, Zr), with vinyl chloride (VC) and VC/propylene mixtures have been investigated. Two general pathways are observed: (i) radical polymerization of VC initiated by radicals derived from the catalyst and (ii) net 1,2 VC insertion into L_nMR^+ species followed by β-Cl elimination. *rac*-(EBI)ZrMe$(\mu$-Me)B(C$_6$F$_5$)$_3$ (EBI = 1,2-ethylenebis-(indenyl)) reacts with 2 equiv of VC to yield oligopropylene, *rac*-(EBI)ZrCl$_2$, and B(C$_6$F$_5$)$_3$. This reaction proceeds by net 1,2 VC insertion into *rac*-(EBI)ZrMe$^+$ followed by fast β-Cl elimination to yield [*rac*-(EBI)-ZrCl][MeB(C$_6$F$_5$)$_3$] and propylene. Methylation of *rac*-(EBI)ZrCl$^+$ by MeB(C$_6$F$_5$)$_3^-$ enables a second VC insertion/β-Cl elimination to occur. The evolved propylene is oligomerized by *rac*-(EBI)ZrR$^+$ as it is formed. At high Al/Zr ratios, *rac*-(EBI)ZrMe$_2$/MAO catalytically converts VC to oligopropylene by 1,2 VC insertion into *rac*-(EBI)ZrMe$^+$, β-Cl elimination, and realkylation of *rac*-(EBI)ZrCl$^+$ by MAO; this process is stoichiometric in Al−Me groups. The evolved propylene is oligomerized by *rac*-(EBI)ZrR$^+$. Oligopropylene end group analysis shows that the predominant chain transfer mechanism is VC insertion/β-Cl elimination/realkylation. In the presence of trace levels of O$_2$, *rac*-(EBI)ZrMe$_2$/MAO polymerizes VC to poly(vinyl chloride) (PVC) by a radical mechanism initiated by radicals generated by autoxidation of Zr−R and/or Al−R species. Cp*TiX$_3$/MAO (Cp* = C$_5$Me$_5$; X = OMe, Cl) initiates radical polymerization of VC in CH$_2$Cl$_2$ solvent at low Al/Ti ratios under anaerobic conditions; in this case, the source of initiating radicals is unknown. Radical VC polymerization can be identified by the presence of terminal and internal allylic chloride units and other "radical defects" in the PVC which arise from the characteristic chemistry of PCH$_2$CHCl$\cdot$ macroradicals. However, this test must be used with caution, since the defect units can be consumed by postpolymerization reactions with MAO. (C$_5$Me$_4$SiMe$_2$N^{t}Bu)MMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalysts (M = Ti, Zr) react with VC by net 1,2 insertion/β-Cl elimination, yielding [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)MCl][B(C$_6$F$_5$)$_4$] species which can be trapped as (C$_5$Me$_4$SiMe$_2$N^{t}Bu)MCl$_2$ by addition of a chloride source. The reaction of *rac*-(EBI)ZrMe$_2$/MAO or [(C$_5$Me$_4$-SiMe$_2$N^{t}Bu)ZrMe][B(C$_6$F$_5$)$_4$] with propylene/VC mixtures yields polypropylene containing both allylic and vinylidene unsaturated chain ends rather than strictly vinylidene chain ends, as observed in propylene homopolymerization. These results show that the VC insertion of $L_nM(CH_2CHMe)_nR^+$ species is also followed by β-Cl elimination, which terminates chain growth and precludes propylene/VC copolymerization. Termination of chain growth by β-Cl elimination is the most significant obstacle to metal-catalyzed insertion polymerization/copolymerization of VC.

Introduction

The polymerization of olefins by insertion chemistry using Ziegler−Natta, Cr-based or, more recently, single-site metal catalysts provides a powerful approach to the synthesis of polyolefins with a high degree of control of polymer composition and structure.[1] A current challenge in this area is to develop catalysts capable of polymerizing or copolymerizing polar olefins, particularly CH$_2$=CHX monomers with functional groups directly bonded to the olefin unit, by insertion mechanisms.[2] While some success has been achieved in the copolymerization of acrylates and vinyl ketones with ethylene and propylene, a general solution to this problem remains elusive.[3] Here, we report studies directed to the long-term goal of developing metal catalysts for the insertion polymerization/copolymerization of vinyl chloride (VC).
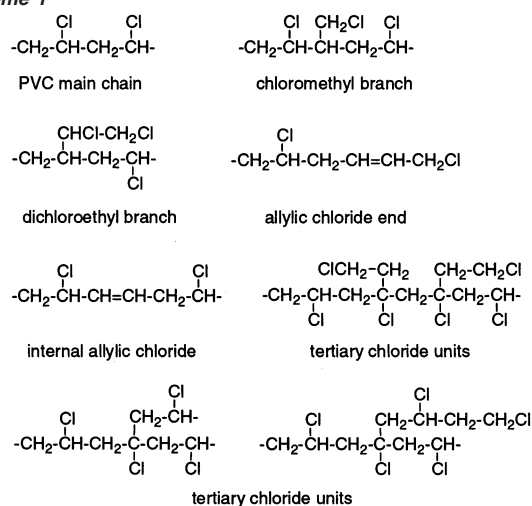
Poly(vinyl chloride) (PVC) and related copolymers are prepared commercially by radical polymerization of VC and can also be prepared using RLi or R$_2$Mg initiators.[4−6] PVC is an important commercial material because of its low cost, useful properties (e.g., good chemical resistance, good resistance to

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Scheme 1

$$-CH_2-CH-CH_2-CH-$$ (Cl, Cl)
PVC main chain

$$-CH_2-CH-CH-CH_2-CH-$$ (Cl, CH_2Cl, Cl)
chloromethyl branch

$$-CH_2-CH-CH_2-CH-$$ (CHCl-CH_2Cl, Cl)
dichloroethyl branch

$$-CH_2-CH-CH_2-CH=CH-CH_2Cl$$ (Cl)
allylic chloride end

$$-CH_2-CH-CH=CH-CH_2-CH-$$ (Cl, Cl)
internal allylic chloride

$$-CH_2-CH-CH_2-C-CH_2-C-CH_2-CH-$$ (ClCH_2-CH_2, CH_2-CH_2Cl, Cl, Cl, Cl, Cl)
tertiary chloride units

$$-CH_2-CH-CH_2-C-CH_2-CH-$$ (Cl, CH_2-CH-, Cl, Cl, Cl)
tertiary chloride units

$$-CH_2-CH-CH_2-C-CH_2-CH-$$ (Cl, CH_2-CH-CH_2-CH_2Cl, Cl, Cl)

burning), compatibility with a wide range of modifiers, and versatility in many applications. PVC homopolymer is an amorphous, rigid thermoplastic, and flexible PVCs can be prepared by plasticization, typically using phthalates. Important VC copolymers include VC−vinyl acetate, VC−acrylonitrile, and vinylidene chloride−VC copolymers, which are prepared commercially by radical copolymerization, and chlorinated polyethylene, which is prepared by the chlorination of polyethylene.

Interest in developing nonradical syntheses of PVC materials is driven by practical as well as fundamental reasons. A key practical issue is the control of PVC "defect sites".[7] Chain growth in radical VC polymerization occurs by the head-to-tail addition of active macroradicals to the monomer. However, several side reactions compete with chain growth and lead to the formation of the branch and "defect" structures illustrated in Scheme 1.[8] As summarized by Starnes et al.,[6,7] the head-to-head addition of VC to the growing chain leads to the formation of chloromethyl and 1,2-dichloroethyl branches. Allylic chloride end groups are formed by head-to-head addition followed by a 1,2-Cl shift and Cl transfer to the monomer. Internal allylic chloride units are generated by chain transfer to polymer, which
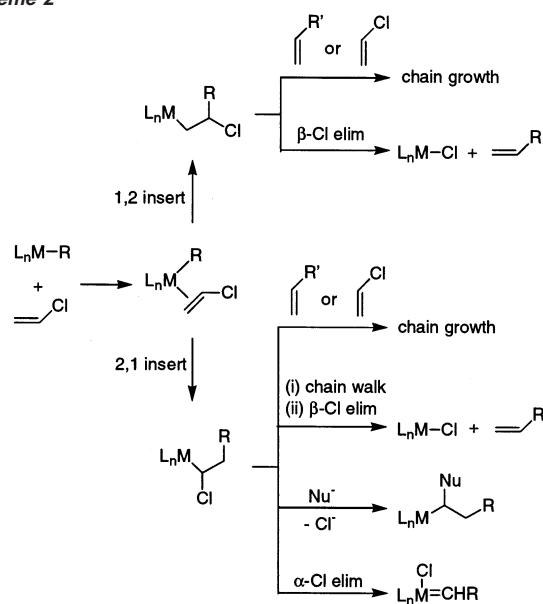
involves H atom abstraction from a backbone methylene group by the propagating radical and subsequent Cl transfer to the monomer. Tertiary chloride units are formed from backbone −CHCl− units by intramolecular (back-biting) or intermolecular H atom abstraction by propagating radicals, followed by monomer addition. PVC undergoes thermal degradation above $\sim$100 °C via autocatalytic dehydrochlorination and concomitant formation of polyene units, necessitating the use of stabilizers for processing and end use.[4,7] The internal allylic and tertiary chloride groups are the initiating sites for HCl loss. It has been shown that the chemical derivatization of the defect sites by alkylation with AlMe$_3$ or other reactions provides PVCs with enhanced thermal stability.[9,10] Metal-catalyzed insertion polymerization of VC may provide a direct approach to "low defect" PVC. It should also be noted that the defect sites, which can be identified by NMR,[6,8] are diagnostic for the free radical polymerization mechanism.

As for most free radical polymers, manipulation of PVC composition and microstructure is limited because it is difficult to modify the reactivity of the propagating macroradicals.[11] The development of insertion polymerization routes to PVC and VC copolymers may enable the control of tacticity, molecular weight, branching, end group structures, and other polymer properties through the tailoring of catalyst structure, as in conventional olefin polymerization. Target polymers of interest include stereoregular PVCs,[12] PVCs with tailored molecular weight distributions,[13] and linear copolymers of VC with ethylene or styrene prepared by direct synthesis.

Two modes of insertion polymerization or copolymerization of VC can be envisioned: 1,2 insertion or 2,1 insertion (Scheme 2). However, inspection of these reactions reveals several potential problems. A 1,2 insertion of VC into an L$_n$MR active species would generate an MCH$_2$CH$_2$ClR complex, which is anticipated to be prone to β-Cl elimination.[14] In fact, transition metal alkyls containing β-halogens are extremely rare, being limited to a few octahedral d^6 complexes, such as PtCl$_5$(CH$_2$CH$_2$Cl)$^{2-}$,[15] Pt(2,9-Me$_2$-phen)Cl$_3$(CH$_2$CH$_2$Cl),[16] and Ir(PMe$_2$Ph)$_2$(CO)-Br$_2$(CH$_2$CH$_2$Br),[17] several more highly halogenated complexes,[18]

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Scheme 2

R' or Cl

→ chain growth

L_nM–CHR(R)Cl

β-Cl elim → L_nM–Cl + =R

1,2 insert

L_nM–R + =Cl → L_nM–CH(R)=Cl

2,1 insert

R' or Cl

→ chain growth

(i) chain walk
(ii) β-Cl elim → L_nM–Cl + =R

L_nM–CH(R)CH$_2$Cl

Nu⁻ / –Cl⁻ → L_nM–CH(Nu)CH$_2$R

α-Cl elim → L_nM=CHR (Cl)

and perfluoroalkyl complexes.[19] Early metal MCH$_2$CHRX species are particularly susceptible to β-X elimination.[20] For example, Caulton recently reported that Cp$_2$ZrHCl reacts with vinyl fluoride by 1,2 insertion and β-F elimination yielding Cp$_2$ZrFCl and ethylene,[21] and Wolczanski showed that (^{t}Bu$_3$SiO)$_3$TaH$_2$ reacts with CH$_2$=CHX (X = F, Cl, Br) via 1,2 insertion and fast β-X elimination.[22,23] Additionally, Boone and co-workers recently reported that VC reacts with the active Fe–alkyl species in (pyridine–bisimine)FeCl$_2$/MAO-catalyzed ethylene polymerization by 1,2 insertion followed by β-Cl elimination.[24]

A 2,1 VC insertion would generate an MCHClCH$_2$R species which obviously cannot undergo β-Cl elimination without prior rearrangement (Scheme 2). Metal alkyls containing α-halogen substituents are, in fact, quite common.[25,26] However,

MCHClCH$_2$R species may be susceptible to nucleophilic displacement of the α-chloride[27] and, in non-d^0-metal cases, may undergo α-Cl elimination to generate carbene complexes.[28] Additionally, the electron-withdrawing α-Cl will decrease the nucleophilic character and migratory aptitude of the MCHClCH$_2$R group, inhibiting subsequent insertions.[29] However, CO insertion of Co(CO)$_3$LCH$_2$Cl (L = CO, PPh$_3$) has been observed.[30]

On the other hand, because VC is coordinated by the C=C bond rather than the chlorine in known metal VC complexes,[31] chlorocarbons are comparatively weak ligands,[32] and sp^2 C–X bonds generally are not prone to nucleophilic substitution;[33] side reactions between VC and L$_n$MR species leading to catalyst poisoning are expected to be less important than for more reactive monomers such as acrylates, vinyl esters, or acrylonitrile. Numerous literature reports and patents describe the polymerization of VC and the copolymerization of VC and olefins, by Ziegler–Natta or single-site olefin polymerization catalysts.[34–37] In some cases, these reactions were recognized as radical polymerizations, while, in other cases, nonradical

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(34) (a) Giannini, U.; Cesca, S. *Chim. Ind. (Milan)* **1962**, *44*, 371. (b) Yamazaki, N.; Sasaki, K.; Kambara, J. *J. Polym. Sci. B* **1964**, *2*, 487. (c) Misono, A.; Uchida, Y.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2366. (d) Higashi, H.; Watabe, K.; Namikawa, S. *J. Polym. Sci. B* **1967**, *5*, 1125. (e) Misono, A.; Uchida, Y.; Yamada, K.; Saeki, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2995. (f) Ulbricht, J.; Jurgen, G.; Manfred, G. *Angew. Makromol. Chem.* **1968**, 69. (g) Guyot, A.; Rocaniere, P. *J. Appl. Polym. Sci.* **1969**, *13*, 2019. (h) Pham, Q. T.; Rocaniere, P.; Guyot, A. *J. Appl. Polym. Sci.* **1970**, *14*, 1291. (i) Furukawa, J. *Pure Appl. Chem.* **1971**, *26*, 153. (j) Saito, M.; Suzuki, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 3639. (k) Haszeldine, R. N.; Hyde, T. G.; Tait, P. J. T. *Polymer* **1973**, *14*, 215. (l) Mejzlik, J.; Navratil, M.; Vilimova, L. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3457. (m) Haszeldine, R. N.; Hyde, T. G.; Tait, P. J. T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1703. (n) Florjanczyk, Z.; Kuran, W.; Sitkowska, J.; Ziolkowsko, A. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 343. (o) Belov, G. P.; Solovyova, T. I.; Smirnov, V. I. *Acta Polym.* **1990**, *41*, 178. (p) Yamazaki, N. *Prog. Polym. Sci. Jpn.* **1971**, *2*, 171.

Chart 1

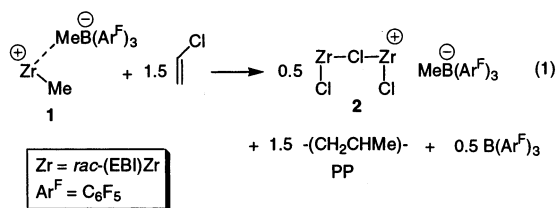Cp_2ZrX_2 *rac*-(EBI)ZrX$_2$ Cp*TiX$_3$ $(C_5Me_4SiMe_2N^tBu)MX_2$
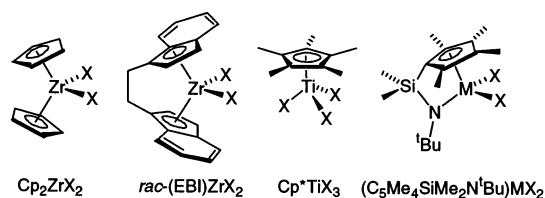
mechanisms were suggested. However, to date, in no case has an insertion mechanism been established.

This paper describes studies of the reaction of VC with three important types of group 4 metal olefin polymerization catalysts: zirconocene catalysts based on $(C_5R_5)_2ZrX_2$ complexes, half-sandwich Ti catalysts based on Cp*TiX$_3$ complexes (Cp* = C_5Me_5), and "constrained geometry" catalysts based on $(C_5Me_4SiMe_2N^tBu)MX_2$ (M = Ti, Zr) complexes (Chart 1). The objectives of this work were to determine how these catalysts react with VC and to identify the mechanism of VC polymerization previously reported with these systems.[38] In a subsequent paper, we will describe parallel studies with representative late-metal catalysts.[39] As will be seen, while VC insertion polymerization has not been achieved, the key issues which must be addressed in order to achieve this long-term goal have been identified.

Results and Discussion

Reaction of *rac*-(EBI)Zr(Me)(μ-Me)B(C_6F_5)$_3$ with VC. The reaction of *rac*-(EBI)ZrMe$_2$ with B(C_6F_5)$_3$ generates the ion pair *rac*-(EBI)Zr(Me)(μ-Me)B(C_6F_5)$_3$ (**1**, EBI = 1,2-ethylenebis-(indenyl)) which is an active olefin polymerization catalyst.[40] Compound **1** was chosen for initial studies because it is easy to generate and is soluble in hydrocarbon and chlorocarbon solvents, which facilitates NMR studies, and the C_2-symmetry may lead to stereoregular polymer if insertion polymerization were to occur. The reaction of **1** with VC proceeds in two stages. In the first stage (eq 1), which is complete within 5 min at 25 °C in CD$_2$Cl$_2$ solution, **1** reacts with VC (16-fold excess) to produce a dark red solution. NMR studies reveal that 1.5 equiv of VC is consumed and a 1:1 mixture of B(C_6F_5)$_3$ and MeB(C_6F_5)$_3^-$ is formed. No PVC is observed, but atactic

$$Zr = \textit{rac-}(EBI)Zr$$
$$Ar^F = C_6F_5$$

oligopropylene is formed (95% vs consumed VC). No identifi-

(35) (a) Matsukawa, T.; Kiba, R.; Ikeda, T. Japn. Patent 08208736 (Chisso Corp.). *Chem Abstr.* **1996**, *125*:276902. (b) For the use of (C$_5$R$_5$)$_2$ZrCl$_2$/MAO as a photoactivated initiator for free-radical VC polymerization, see: Nagy, S. M.; Krishnamurti, R.; Cocoman, M. K.; Opalinski, W. M.; Smolka, T. F. WO 9923124 A1 (Occidental Chemical). *Chem. Abstr.* **130**: 338530.
(36) (a) Endo, K.; Saitoh, M. *Polym. J.* **2000**, *32*, 300. (b) Endo, K.; Kaneda, N.; Waku, H.; Saitoh, M.; Emori, N. *J. Vinyl Addit. Technol.* **2001**, *7*, 177.
(37) Taeji, K.; Uozumi, T.; Soga, K. *Polymer Prepr. Jpn.* **1995**, *44*, 2.
(38) Preliminary reports of some aspects of this work have appeared. (a) Stockland, R. A., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 6315. (b) Jordan, R. F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 829. (c) Stockland, R. A., Jr.; Shen, H.; Foley, S.; Jordan, R. F. *Polym. Mater. Sci. Eng.* **2002**, *87*, 39.
(39) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F., manuscript in preparation.

able *rac*-(EBI)Zr indenyl H^2 or H^3 resonances are present in the ambient temperature 500 MHz ^{1}H NMR spectrum of the red solution after stage 1. However, low-temperature spectra reveal that [{*rac*-(EBI)ZrCl}$_2$(μ-Cl)][MeB(C_6F_5)$_3$] (**2**, ~10:1 mixture of diastereomers) is the major Zr-containing species present (94% vs **1**). The dinuclear cation of **2** is an adduct of *rac*-(EBI)ZrCl$^+$ and *rac*-(EBI)ZrCl$_2$ (**3**). The identity of **2** was confirmed by treatment with 0.5 equiv of [NBu$_3$Bn]Cl (CD$_2$Cl$_2$, 25 °C, 1 min) to quantitatively generate **3**; however, **2** could not be isolated in pure form. The ^{1}H NMR signals for **2** are sharp below −50 °C but broaden into the baseline at ambient temperature because of bridge/terminal Cl exchange.[41] Another intermediate, assigned as *rac*-(EBI)Zr(Cl)(μ-Me)-B(C_6F_5)$_3$ (**4**), was detected when the reaction of **1** and VC at 25 °C was quenched after 1 min by rapid cooling to −78 °C and then analyzed by low-temperature NMR.

In the second stage of the reaction of **1** with VC, which is complete after 24 h at 25 °C, the red solution of **2** evolves to a yellow solution (eq 2). NMR studies establish that an additional 0.5 equiv of VC is converted to oligopropylene and that the only significant organometallic products are **3** (100% by ^{1}H NMR, 81% isolated) and B(C_6F_5)$_3$ (only species observed by ^{19}F NMR). The final yield of the oligopropylene determined
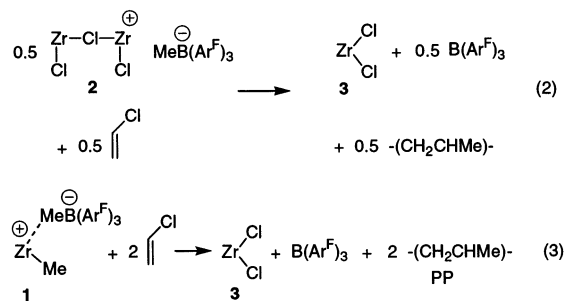
by ^{1}H NMR is >95% versus consumed VC. Thus, the overall reaction in stages 1 and 2 is that given in eq 3. Control experiments establish that neither *rac*-(EBI)ZrMe$_2$ nor B(C_6F_5)$_3$ react separately with VC under these conditions. The reaction of **1** and VC in benzene-d_6 proceeds in a similar fashion, although a higher temperature is required to convert **2** to **3** in this solvent. This result confirms that the Cl ligands in **2** and **3** are not derived from the CD$_2$Cl$_2$ solvent.

These observations are consistent with the mechanism in Scheme 3, although the precise series of steps is not known. In stage 1, VC inserts into the Zr−Me bond of **1** to generate a transient β-chloropropyl complex [*rac*-(EBI)ZrCH$_2$CHClMe]-[MeB(C_6F_5)$_3$] (**5**, not observed), which undergoes rapid β-Cl elimination to yield **4** and propylene (i, ii). Complex **4** undergoes ligand redistribution to regenerate **1** (0.5 equiv maximum) and form **3** and B(C_6F_5)$_3$ (iii). The regenerated **1** consumes an additional 0.5 equiv of VC (iv) to produce **4** and propylene. Ultimately **4** is trapped by **3** as the dinuclear species **2** (v). VC polymerization does not occur because **5** undergoes β-Cl

(40) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (b) Ewen, J. A.; Elder, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 179. (c) For generation of **1**, see: Dagorne, S.; Rodewald, S.; Jordan, R. F. *Organometallics* **1997**, *16*, 5541.
(41) The variable temperature (−73 °C to 25 °C) ^{1}H NMR spectra of **2** are unaffected by the addition of **3** (5 equiv), which implies that the fluxional process involves intramolecular bridge/terminal chloride exchange rather than reversible cleavage of {*rac*-(EBI)ZrCl}$_2$(μ-Cl)$^+$ to *rac*-(EBI)ZrCl$_2$ and *rac*-(EBI)ZrCl(CD$_2$Cl$_2$)$^+$. Compound **2** decomposes above 40 °C to **3** and other unidentified products which precluded high-temperature NMR studies.

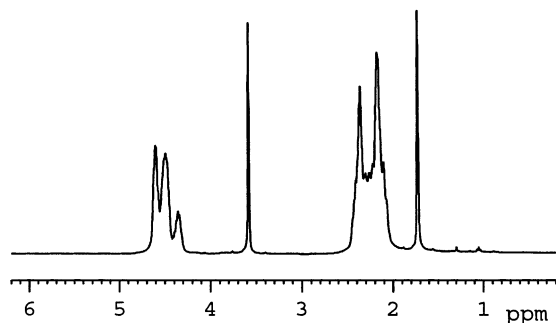**Scheme 3** [a]

[a] Zr = *rac*-(EBI)Zr; Ar^F = C$_6$F$_5$.

Scheme 4 [a]

[a] Zr = *rac*-(EBI)Zr.

elimination more rapidly than it inserts a second VC. Free propylene is not observed by ^{1}H NMR monitoring because it is oligomerized by *rac*-(EBI)ZrMe$^+$ as fast as it is formed (vi). It is well established that *rac*-(EBI)ZrR$^+$ produces low molecular weight, atactic polypropylene under such monomer-starved conditions.[42] In Scheme 3, i–v sum to eq 1. In the second stage (eq 2), **2** undergoes slow cleavage/ligand redistribution reactions to regenerate *rac*-(EBI)ZrMe$^+$, which in turn reacts with VC, as in Scheme 1, until all of the Zr/B–Me groups are consumed; this corresponds to the observed slow consumption of 0.5 equiv of VC.

Reaction of *rac*-(EBI)ZrMe$_2$/MAO with VC. The VC insertion/β-Cl elimination reaction of *rac*-(EBI)ZrMe$^+$, which converts VC to propylene, becomes catalytic under conditions where **4** is continually realkylated. This situation can be achieved using methylalumoxane (MAO) as the activator. For example, the reaction of *rac*-(EBI)ZrMe$_2$/MAO (Al/Zr = 17 000) with VC in toluene (25 °C, 20 h) yields atactic oligopropylene (eq 4) with ∼2 000 equiv of VC consumed per Zr.

As shown in Scheme 4, this reaction proceeds by generation of *rac*-(EBI)ZrMe$^+$, VC insertion and β-Cl elimination to yield

propylene and *rac*-(EBI)ZrCl$^+$, and realkylation of the latter species by MAO (or the AlMe$_3$ therein). The propylene is oligomerized by *rac*-(EBI)ZrR$^+$. The mixed Al–Me/Cl product was not characterized.

The oligopropylene produced in eq 4 and Scheme 4 is a low molecular weight (M_n = 500) atactic material which is isolated as a colorless oil. No chlorine was detected in this material by elemental analysis. ^{1}H NMR established that the unsaturated end groups of the oligopropylene are primarily allylic (CH$_2$=CHCH$_2$–, 95%), although a small fraction of vinylidene chain ends (CH$_2$=CMeCH$_2$–, 5%) was also detected. In contrast, in the absence of VC, *rac*-(EBI)ZrMe$_2$/MAO produces polypropylene with strictly vinylidene unsaturated end groups at low propylene pressures, as β-H elimination is the dominant chain transfer process.[42] These results indicate that chain transfer in the propylene oligomerization in Scheme 4 occurs primarily by VC insertion, β-Cl elimination, and realkylation; that is, VC/MAO acts as a chain transfer agent. To confirm this point, *rac*-(EBI)ZrMe$_2$/MAO-catalyzed batch propylene polymerizations were carried out under identical conditions in the presence and absence of VC. In the former case, the unsaturated end groups of the polymer were exclusively vinylidene, while, in the latter case, both allylic (76%) and vinylidene (24%) chain ends were observed.

As VC is present in large excess relative to propylene in eq 4 and Scheme 4, the formation of oligopropylene implies that *rac*-(EBI)ZrR$^+$ reacts more rapidly with propylene than with VC. This reactivity difference probably arises because propylene coordinates more effectively than VC to *rac*-(EBI)ZrR$^+$. In other work, we have shown that propylene binds more strongly than VC to the model system (C$_5$H$_4$Me)$_2$Zr(O^{t}Bu)$^+$.[43]

Reactions of Other Zirconocene Catalysts with VC. The reaction of VC with (C$_5$H$_5$)$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$, (indenyl)$_2$ZrMe$_2$/

(42) (a) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667. (b) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329.
(43) Stoebenau, E. J., III; Jordan, R. F. *Abstracts of Papers*, 224th National Meeting of the American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 2002; INOR-284.

Figure 1. ^{1}H NMR spectrum (400 MHz, THF-d_8, 50 °C) of PVC prepared with *rac*-(EBI)ZrMe$_2$/MAO/O$_2$ at 50 °C.

B(C$_6$F$_5$)$_3$, or *rac*-(EBI)ZrMe$_2$/[NHMe$_2$Ph][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ or C$_6$D$_5$Cl (25 °C, 24 h) generates oligopropylene. No PVC is formed in these reactions. Also, the reaction of VC with (C$_5$Me$_5$)$_2$ZrCl$_2$/MAO (Al/Zr = 1000; chlorobenzene), *rac*-(EBI)-ZrMe$_2$/dried MAO (Al/Zr = 1000; C$_6$D$_6$), or *rac*-Me$_2$Si(2-Me-4,5-benz-indenyl)$_2$ZrCl$_2$/MAO (Al/Zr = 2000; toluene) yields oligopropylene with no PVC formed. Thus, net 1,2 VC insertion and fast β-Cl elimination is a general feature of (C$_5$R$_5$)$_2$ZrR$^+$ species and precludes insertion polymerization of VC by zirconocene catalysts.

Influence of Oxygen on the Reaction of VC with Zirconocene Catalysts. Our observation that (C$_5$R$_5$)$_2$ZrR$^+$ species react with VC by net 1,2 insertion and fast β-Cl elimination under anaerobic conditions suggests that previously reported VC polymerizations mediated by metallocene catalysts are in fact radical polymerizations.[35a] One likely source of initiating radicals is autoxidation of Zr–R or Al–R species by adventitious oxygen. To probe this possibility, we investigated the influence of added O$_2$ on the reaction of *rac*-(EBI)ZrMe$_2$/MAO with VC.

The reaction of *rac*-(EBI)ZrMe$_2$/MAO (Al/Zr = 250) with liquid VC at 50 °C in the presence of a trace amount of O$_2$ results in the generation of PVC (~1% isolated yield, eq 5).
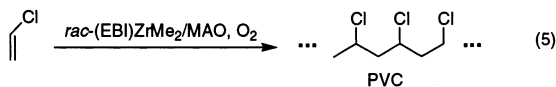
NMR data show that the PVC in eq 5 is formed by a radical mechanism. The tacticity of the PVC produced by *rac*-(EBI)-ZrMe$_2$/MAO/O$_2$ determined by ^{13}C{^{1}H} NMR (0.32 rr, 0.51 mr, 0.17 mm; α = mole fraction of r dyads = 0.58) is nearly identical to that of PVC prepared by radical polymerization at 58 °C (0.31 rr, 0.51 mr, 0.18 mm; α = 0.56).[44] The ^{1}H NMR spectrum of the PVC produced by *rac*-(EBI)ZrMe$_2$/MAO/O$_2$ is shown in Figure 1. An expansion of the "radical defect" region (δ 3.5–6.0) is compared to that of PVC prepared by radical polymerization at 58 °C in Figure 2. Resonances for the defect sites which are characteristic of a radical polymerization are clearly evident in both spectra in Figure 2. These results provide strong evidence that the VC polymerization in eq 5 occurs by a normal radical mechanism. The initiating radicals have not been identified, but it is well established that the autoxidation of (C$_5$R$_5$)$_2$ZrRX, (C$_5$R$_5$)$_2$ZrR$_2$, and AlR$_3$ compounds occurs by a radical chain mechanism involving R$^\bullet$ and RO$_2$$^\bullet$ radicals[45,46]

(44) PVC tacticity was determined by ^{13}C NMR. See: Nakayama, N.; Aoki, A.; Hayashi, T. *Macromolecules* **1994**, *27*, 63 and references therein.
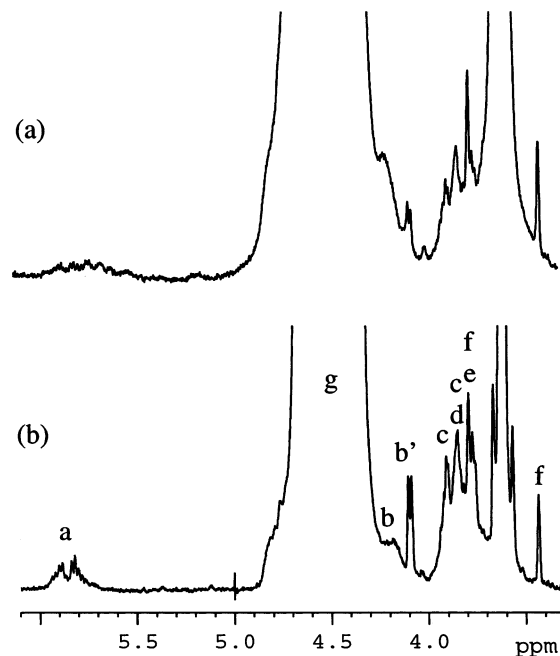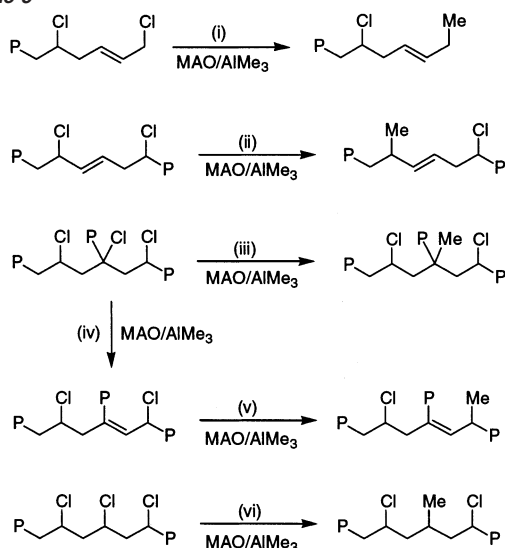

Figure 2. ^{1}H NMR spectra (400 MHz, THF-d_8, 50 °C, defect region) of PVC. (a) PVC prepared with *rac*-(EBI)ZrMe$_2$/MAO/O$_2$ at 50 °C. (b) Commercial PVC prepared at 58 °C. Assignments: response a, −CH=CHCH$_2$Cl and −CH$_2$CH=CHCHCl−; response b and b′, cis and trans −CH=CHCH$_2$Cl; response c, −CHClCH$_2$Cl; response d, −CH$_2$Cl branch; response e, −CH$_2$CH$_2$Cl; response f, ^{13}C satellites from solvent (THF-d_8); response g, −CHCl− main chain resonances.

and that AlR$_3$/O$_2$ combinations function as initiators of radical polymerizations.[47]

It should be noted the PVC from eq 5 differs from the conventional radical PVC in several respects: (i) the molecular weight distribution is unusually broad,[48] and (ii) the ^{1}H NMR spectrum contains broad peaks assignable to internal olefin units (δ 5.6, Figure 2) and triplet resonances (δ 0.96, 1.05, and 1.15) assignable to −CH$_2$CH$_3$ groups (Figure 3).[9] These features reflect postpolymerization reactions between the PVC defect sites and Al−R species, as discussed below.

Reaction of VC with (C$_5$Me$_5$)TiX$_3$/MAO Catalysts. One strategy for circumventing the β-Cl elimination reaction of MCH$_2$CHClR species that precludes VC insertion polymerization by zirconocene catalysts is to use a catalyst that inserts VC in a 2,1 fashion (Scheme 2). Monocyclopentadienyl titanium catalysts, that is, (C$_5$R$_5$)TiX$_3$/MAO, are of potential interest in this regard because these systems polymerize styrene to syndiotactic polystyrene by a 2,1 insertion mechanism.[49] In fact,

(45) (a) Brindley, P. B.; Hodgson, J. C. *J. Organomet. Chem.* **1974**, *65*, 57. (b) Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (c) Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041. (d) Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851. (e) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424.
(46) (a) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1968**, 1074. (b) Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387. (c) Davies, A. G.; Roberts, B. P. In *Free Radicals*; Kochi, J. K., Ed.: Wiley-Interscience: New York, 1973; Vol I, pp 547−590. (d) Alexandrov, Y. A.; Chikinova, N. V. *J. Organomet. Chem.* **1991**, *418*, 1.
(47) (a) Bhanu, V. A.; Kishore, K. *Chem. Rev.* **1991**, *91*, 99. (b) Milovskaya, E. B.; Zamoiskaya, L. V.; Kopp, E. L. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 420.
(48) PVC from eq 5: M_w = 180 000; M_n = 36 000; M_w/M_n = 5.0. Radical PVC prepared at 58 °C: M_w = 161 000; M_n = 74 700; M_w/M_n = 2.26.
(49) (a) Tomotsu, N.; Ishihara, N.; Newman, T. H.; Malanga, M. T. *J. Mol. Catal. A: Chem.* **1998**, *128*, 167. (b) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356. (c) Pellecchia, C.; Pappalardo, D.; Olivia, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593.

Figure 3. ^{1}H NMR spectra (400 MHz, THF-d_8, 50 °C, alkyl region) of PVC. (a) PVC prepared with *rac*-(EBI)ZrMe$_2$/MAO/O$_2$ at 50 °C. (b) PVC prepared with Cp*Ti(OMe)$_3$/MAO (**6**/MAO) at 25 °C. (c) PVC prepared with CpTiCl$_3$/MAO (**7**/MAO) at 25 °C. (d) Commercial PVC prepared at 30 °C. Resonances at 1.29 and 0.89 are due to process oil from the MAO and hexanes (a, b) and initiator residue (d).

Figure 4. ^{1}H NMR spectra (400 MHz, THF-d_8, 50 °C, defect region) of PVC. (a) PVC prepared with Cp*Ti(OMe)$_3$/MAO (**6**/MAO) at 25 °C. (b) PVC prepared with Cp*TiCl$_3$/MAO (**7**/MAO) at 25 °C. (c) Commercial PVC prepared at 30 °C.

Endo and Saitoh recently reported that Cp*TiX$_3$ catalysts (**6**, X = OMe; **7**, X = Cl) polymerize VC under MAO activation conditions.[36] The key requirements for polymerization were the use of CH$_2$Cl$_2$ solvent (very low conversions were reported in toluene) and low Al/Ti ratios (Al/Ti = 10). The PVC produced by **7**/MAO contained low levels of allylic chloride defects, and it was noted that some defect sites could have been consumed by alkylation by MAO. However, **6**/MAO produced PVC that did not contain defects (at the NMR detection limit), and in this case, "the polymerization was not inhibited although the polymer yields [were] somewhat decreased" in the presence of 4-*tert*-butyl-catechol or TEMPO (molar ratio inhibitor/Ti =1:1), suggesting the operation of a "nonradical" mechanism. We have also investigated the reaction of Cp*TiX$_3$/MAO catalysts with VC.

The reaction of **6**/MAO with VC in CH$_2$Cl$_2$ at 25 °C under anaerobic conditions ([Ti] = 0.0033 M, [Al] = 0.033 M, [VC] = 2.8 M; 24 h) yields PVC (eq 6, 36% conversion). **7**/MAO

also produces PVC under similar conditions but in lower yield (7% conversion). These results confirm that PVC is produced by **6**/MAO or **7**/MAO under the Endo and Saitoh conditions.

However, our results differ from the previous results in several respects. First, as illustrated in Figure 4, ^{1}H NMR analysis shows that the PVC produced by **6**/MAO contains normal radical defects, while that produced by **7**/MAO does not. In the latter case, broad resonances are observed at δ 5.4–5.7, which are assigned to internal olefin units. Second, as shown in Figure 3, for the PVC produced by **6**/MAO, a triplet at δ 1.05 is observed, which is assigned to −CH$_2$CH$_3$ groups,[9] whereas, for the PVC produced by **7**/MAO, broad resonances at δ 0.85 and 1.25 are present, which are assigned to −CH$_2$CHMe− units formed by methylation of main chain −CH$_2$CHCl− units. Third, the molecular weights are somewhat higher and the molecular weight distributions are broader (for **6**/MAO, M_n = 27 200 and M_w/M_n = 3.3; for **7**/MAO, M_n = 20 200 and M_w/M_n = 5.4) than the values reported by Endo and Saitoh (M_n = 11 000– 25 000; M_w/M_n = 1.7–2.0), and the polydispersity is higher for the PVC produced by **7**/MAO versus **6**/MAO. Fourth, **7**/MAO does not produce PVC under these conditions in the presence of excess benzoquinone or 4-*tert*-butyl-catechol (in-hibitor/Al = 3).[50] On the other hand, the tacticity of the PVC produced by **6**/MAO and **7**/MAO is in the range expected for radical polymerization.[51]

The best explanation for these observations is that both **6**/MAO and **7**/MAO initiate radical VC polymerization, but Al−Me species derived from the cocatalyst react with the PVC,

Scheme 5 [a]

[a] P = polymer chain.

as illustrated in Scheme 5. Al−Me species are expected to methylate the allylic chloride groups yielding internal olefin units (i, ii)[9,52] and to methylate or dehydrochlorinate tertiary chloride units (iii, iv); in the latter case, the allylic chloride units which are formed may be methylated in a subsequent step (v).[53] Al−Me species can also methylate main chain (secondary) −CH₂CHCl− groups at a slower rate (vi).[54] Carbocation intermediates in these reactions can add to olefin units, leading to chain coupling and resulting in the observed broad molecular weight distributions.[55]

The differences in the PVCs prepared by **6**/MAO versus **7**/MAO are ascribed to two factors. First, because of the higher PVC yield for **6**/MAO versus **7**/MAO, the molar ratio (Al−R groups in cocatalyst)/(defect units in PVC product) is lower in the former case, and therefore, consumption of the defect sites is expected to be less complete.[56] Second, and probably more important, while the details of the reactions of **6** or **7** with MAO and the AlMe₃ therein are not known (vide infra), it is expected that a substantial exchange of Ti−X and Al−R groups will

occur. For **6**/MAO, the resulting $[AlMe_y(OMe)_{1-y}(O)]_n$ and $AlMe_z(OMe)_{3-z}$ species will be less reactive, while, for **7**/MAO, the resulting $[AlMe_yCl_{1-y}(O)]_n$ and $AlMe_zCl_{3-z}$ species will be more reactive compared to $[AlMe(O)]_n$ and AlMe₃, because of the influence of −OMe versus −Cl substitution on the degree of association and Lewis acidity of the Al species.[57] Therefore, substantially less methylation of the defect sites and main chain units is expected for **6**/MAO versus **7**/MAO.

To test this explanation, the reaction of PVC with MAO was investigated. The reaction of PVC (prepared by radical polymerization) with MAO in CH₂Cl₂ under conditions similar to those of eq 6 ([Al] = 0.05 M; [PVC] = 0.44 M (monomer basis), 25 °C, 24 h) yields a dark red solution from which PVC was isolated in >90% yield. ¹³C NMR analysis established that the tacticity of the PVC is unchanged by the MAO treatment. However, as illustrated in Figure 5, ¹H NMR analysis of the treated PVC shows that allylic chloride units are completely removed and the −CHCl*CH₂*Cl, −*CH₂*Cl branch, and −CH₂*CH₂*Cl resonances are reduced in intensity. Also, the ¹H NMR spectrum of the MAO-treated PVC contains broad resonances at δ 0.85 and 1.25 which are assigned to −CH₂CHMe− units formed by the methylation of main chain −CH₂CHCl− units (cf. Figure 3c). GPC analysis established that the molecular weight distribution of the PVC is broadened significantly by the MAO treatment (before treatment, $M_w = 67\,300$, $M_w/M_n = 2.1$; after treatment, $M_w = 177\,000$, $M_w/M_n = 19.5$). To model the postpolymerization reaction in the **6**/MAO case, the above experiment was repeated except that 0.3 equiv of MeOH per Al was added to convert a fraction of the Al−Me groups to Al−OMe groups.[58] As shown in Figure 5, ¹H NMR analysis of the MAO/MeOH-treated PVC showed that the level of allylic chloride defects was reduced by only 33% and the −CHCl*CH₂*Cl, −*CH₂*Cl branch, and −CH₂*CH₂*Cl resonances were unaffected. These results confirm that the PVC radical defects react with MAO under the conditions of eq 6 and that this reaction is inhibited by the presence of Al−OMe groups.

The presence of radical defects in the PVC produced by **6**/MAO, the control experiments which show that radical defects in the PVC produced by **7**/MAO will be consumed by postpolymerization reactions with MAO, the absence of VC polymerization by **7**/MAO in the presence of radical inhibitors, and the similarity of the tacticity of the PVC produced by **6**/MAO and **7**/MAO to that of PVC produced by radical polymerization under similar conditions, leads us to conclude that Cp*TiX₃/MAO catalysts initiate radical polymerization of VC at low Al/Ti ratios in CH₂Cl₂. The differences between our results and those of previous investigators may reflect differences in the MAO used in the respective studies. As noted above, the PVC prepared by *rac*-(EBI)ZrMe₂/MAO/O₂ also exhibits features expected from postpolymerization reactions of PVC and MAO.

(50) An excess of inhibitor was used because the inhibitor may be consumed by a reaction with **7** or MAO. The lack of complete inhibition in the inhibitor experiments described in ref 36 (inhibitor/Ti/Al = 1:1:10) can be ascribed to the consumption of the inhibitor by such reactions. See: (a) Mahanthappa, M. K.; Huang, K.-W.; Cole, A. P.; Waymouth, R. M. *Chem. Commun.* **2002**, 502. (b) Ziemkowska, W. *Main Group Met. Chem.* **2000**, *23*, 337. (c) Boucher, D. L.; Brown, M. A.; McGarvey, B. R.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1999**, 3445. (d) Granel, C.; Jerome, R.; Teyssie, P.; Jasieczek, C. B.; Shooter, A. J.; Haddleton, D. M.; Hastings, J. J.; Gigmes, D.; Grimaldi, S.; Tordo, P.; Greszta, D.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 7133. (e) Carrera, M. A.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1986**, *315*, 329.

(51) The PVC produced by **6**/MAO (0.36 rr, 0.49 mr, 0.15 mm, α = 0.61) and **7**/MAO (0.40 rr, 0.48 mr, 0.12 mm, α = 0.63) is slightly more syndiotactic than PVC produced by suspension polymerization at this temperature (0.33 rr, 0.50 mr, 0.18 mm, α = 0.58; at 20 °C). Endo and Saitoh reported the tacticity of PVC prepared by **6**/MAO to be 0.34 rr, 0.50 mr, 0.16 mm, and α = 0.60. These small differences, which are near the limit of precision of the NMR measurement, are better ascribed to solvent effects than to a change in mechanism.

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(56) Assuming 5×10^{-4} allylic chloride groups per monomer unit in PVC prepared by radical polymerization at 25 °C, we estimate the ratio (mol Al in cocatalyst)/(mol allylic chloride units in PVC) to be 65 for the **6**/MAO reaction and 420 for the **7**/MAO reaction. The corresponding ratios (mol total Al−Me in cocatalyst)/(mol allylic chloride units in PVC) are estimated to be 84 and 580. ¹H NMR analysis of a commercial PVC sample prepared by radical polymerization at 20 °C established that the ratio (allylic chloride units)/(monomer unit) = 4.5×10^{-4}.

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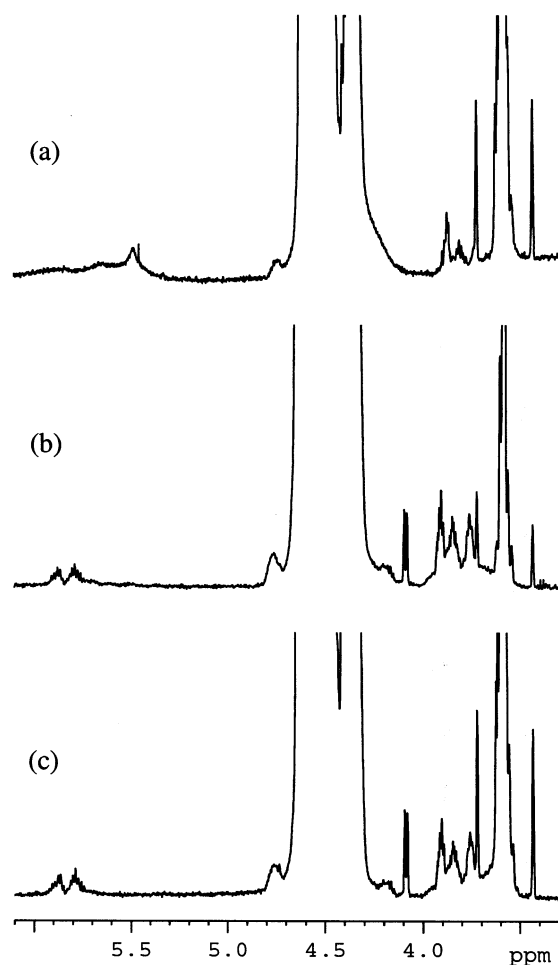
Figure 5. ^{1}H NMR spectra (500 MHz, THF-d_8, 50 °C, defect region) of commercial PVC before and after treatment with MAO. (a) PVC treated with MAO at 25 °C. (b) PVC treated with MAO/MeOH at 25°C. (c) Commercial PVC prepared at 80 °C prior to treatment.

Reaction of Cp*TiCl$_3$/MAO at High Al/Ti Ratios. The reaction of **7**/MAO with VC in C$_6$D$_6$ with MAO loadings more typical of those used for olefin polymerization ([Ti] = 7 mM, Al/Ti = 1000; [VC] = 0.92 M, 80 °C) yields atactic oligopropylene (eq 7). No PVC is formed under these conditions. NMR
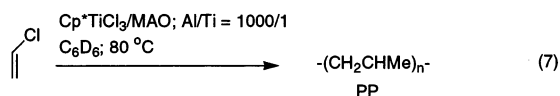
studies show that ~80 equiv of VC are consumed per Ti in this reaction. These results can be rationalized by a scheme analogous to Scheme 4. Thus, an active Ti–Me species undergoes 1,2 VC insertion to generate a TiCH$_2$CHClMe intermediate which undergoes rapid β-Cl elimination to yield propylene and a Ti–Cl species. The propylene is oligomerized by active Ti–R species, and the Ti–Cl product is realkylated by the MAO. Catalysts derived from Cp*TiX$_3$ precursors generally produce atactic polypropylene.[59]

Active Species in (C$_5$Me$_5$)TiCl$_3$/MAO Catalysts. The identity of the active species for α-olefin and styrene polym-

erization that are formed from (C$_5$R$_5$)TiX$_3$/activator catalysts is a subject of current investigation in several laboratories.[60] It is clear that (C$_5$R$_5$)TiX$_3$/activator systems are complicated and that a variety of Ti(IV), Ti(III), and possibly Ti(II) species can form, depending on the system and conditions. The current consensus is that the active species for α-olefin polymerization are Ti(IV) alkyls, and it is likely that a Ti(IV) species is responsible for the oligomerization of the propylene in eq 7. The identity and origin of the radicals that initiate VC polymerization in eq 6 are unknown. For example, it is possible that radicals are produced by autoxidation of Ti–R or Al–R species by trace O$_2$,[45–47] homolysis of Ti–R species,[61] reaction of Cp*Ti(III) species with the solvent, or transfer of a radical (R or Cl) from a Ti species to VC.

Constrained Geometry Catalysts. Another possible approach to favoring VC coordination and insertion over β-Cl elimination is to use a sterically open L$_n$M structure to minimize the steric inhibition of monomer coordination. "Constrained geometry" (C$_5$Me$_4$SiMe$_2$N^{t}Bu)MMe$^+$ catalysts (M = Zr, Ti), which exhibit high reactivity with α-olefins, styrene, and even isobutylene in copolymerization reactions with ethylene, are of interest in this regard.[62,63] Soga reported VC polymerization with constrained geometry catalysts, but no details were given.[37] We have also investigated the reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)MMe$^+$ species (M = Zr, Ti) with VC.

The cationic complex [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)]-[B(C$_6$F$_5$)$_4$] (**8**) was generated by the reaction of (C$_5$Me$_4$SiMe$_2$-N^{t}Bu)ZrMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$D$_6$ as described by Marks.[64] Compound **8** separates as liquid clathrate from C$_6$D$_6$ and decomposes in CD$_2$Cl$_2$ at room temperature. The reaction of **8** with VC (6 equiv) in C$_6$D$_6$ at 50 °C for 2 h results in the consumption of 1 equiv of VC and formation of an insoluble oil which is believed to be [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl]-[B(C$_6$F$_5$)$_4$] (**9**) or its C$_6$D$_6$ solvate. No PVC is formed. Oligopropylene could not be unambiguously identified by NMR because resonances from catalyst species interfere with anticipated oligopropylene resonances; however, a small amount of free propylene was detected in the volatiles. Complex **9** could not be characterized by NMR but was characterized by chemical derivatization. Thus, the volatiles were removed under vacuum, 1 equiv of [NBu$_3$Bn]Cl was added, and the mixture was taken

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Scheme 6 [a]

[a] (CGC)Zr = (C$_5$Me$_4$SiMe$_2$N^{t}Bu)Zr.

Scheme 7 [a]
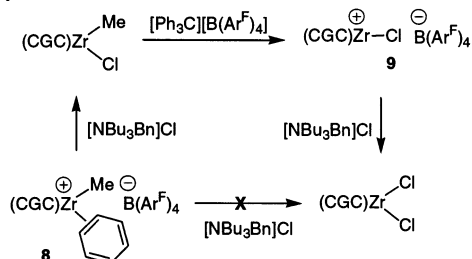
[a] (CGC)Zr = (C$_5$Me$_4$SiMe$_2$N^{t}Bu)Zr.

up in C$_6$D$_6$. NMR analysis established that the only significant organometallic species present in the final solution was (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$, which was produced in 50% yield versus that of **8**.

These results are consistent with 1,2 insertion of VC into **8** and fast β-chloride elimination to yield **9** and propylene, as illustrated in Scheme 6. Polymerization of propylene by (C$_5$Me$_4$SiMe$_2$N^{t}Bu)MR$^+$ catalysts affords atactic polypropylene, but as noted above, the fate of the propylene in Scheme 6 could not be unambiguously determined.[63a,64,65]

Control experiments confirm that [NBu$_3$Bn]Cl acts simply as a trap for **9** in Scheme 6. Complex **9** was generated as a liquid clathrate in C$_6$D$_6$ by the initial generation of (C$_5$Me$_4$-SiMe$_2$N^{t}Bu)Zr(Me)Cl by comproportionation of (C$_5$Me$_4$SiMe$_2$-N^{t}Bu)ZrCl$_2$ and (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe$_2$, followed by treatment with [Ph$_3$C][B(C$_6$F$_5$)$_4$] (Scheme 7). The reaction of **9** with 1 equiv of [NBu$_3$Bn]Cl yields (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$ in 63% yield. In contrast, exposure of **8** to the conditions of Scheme 6 in the absence of VC, followed by reaction with 1 equiv of [NBu$_3$Bn]Cl, yields (C$_5$Me$_4$SiMe$_2$N^{t}Bu)Zr(Me)Cl but not (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$.

To confirm that (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrR$^+$ species react with VC by 1,2 insertion and β-Cl elimination, as proposed in Scheme 6, NMR scale batch reactions of **8** and propylene in the absence and presence of VC were compared (23 °C, C$_6$D$_6$). In the absence of VC, the propylene was completely polymerized to low molecular weight atactic polypropylene containing only vinylidene unsaturated end groups, consistent with chain transfer by β-H elimination. In the presence of VC, however, the propylene was only partially polymerized (75%), and both allylic (13%) and vinylidene (87%) end groups were observed in the polymer, consistent with competitive chain transfer by β-H elimination and termination by 1,2 VC-insertion/β-Cl elimination.

The reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$/MAO (Al/Zr = 1000) with VC in toluene (80 °C, 2 h) yields a small amount

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of atactic polypropylene. No PVC is formed. Similar results were obtained over a range of reaction conditions (Al/Zr = 800−17 000; 25−80 °C, 2−24 h). These results can be accounted for by a 1,2 insertion/β-Cl elimination/realkylation process analogous to that observed for zirconocene/MAO and Cp*TiCl$_3$/MAO catalysts.

The titanium catalyst (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$/[Ph$_3$C]-[B(C$_6$F$_5$)$_4$] reacts with VC in a similar manner as the Zr analogue. The reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$ and [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] in C$_6$D$_6$ yields the dinuclear cation {(C$_5$Me$_4$SiMe$_2$-N^{t}Bu)TiMe}$_2$(μ-Me)$^+$.[64b] This species consumes 1 equiv of VC per Ti, yielding a (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiCl$^+$ species which is trapped by [NBu$_3$Bn]Cl to afford (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiCl$_2$. As for the Zr case, oligopropylene could not be definitively observed but free propylene was detected. More strikingly, (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] polymerizes propylene in the absence of VC to high molecular weight atactic polypropylene (M_n = 462 000, unsaturated end groups not detectable by ^{1}H NMR), whereas propylene polymerization in the presence of VC yields low molecular weight polypropylene (M_n = 1610) with allylic chain ends. These results show that (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiR$^+$ species react with VC by 1,2 insertion followed by β-Cl elimination.

Conclusions

The development of catalysts for insertion polymerization/copolymerization of VC and related CH$_2$=CHX monomers is a challenging goal. To probe the chemical issues underlying this problem, we have investigated the reactions of discrete olefin polymerization catalysts with VC and VC/propylene mixtures. In this study, three representative group 4 metal catalyst classes, that is, zirconocene, monocyclopentadienyl titanium, and constrained geometry Zr and Ti systems, were studied. Two general reaction pathways were observed: (i) radical polymerization of VC initiated by radicals derived from the catalyst and (ii) net 1,2 VC insertion followed by fast β-Cl elimination.

Radicals capable of initiating VC polymerization can be generated from group 4 metal catalysts in several ways. For *rac*-(EBI)ZrMe$_2$/MAO, trace O$_2$ is required for VC polymerization, implicating the autoxidation of Zr−R and/or Al−R species as the source of R$^\bullet$ and RO$_2$$^\bullet$ radicals which can initiate polymerization. For Cp*TiX$_3$/MAO catalysts in CH$_2$Cl$_2$ solvent at low Al/Ti ratios, radical VC polymerization occurs under anaerobic conditions. In this case, the source of initiating radicals is unknown. Radical polymerization of VC can be identified by the presence of terminal and internal allylic chloride units and other "radical defects" in the polymer, which arise from the characteristic chemistry of PCH$_2$CHCl$^\bullet$ macroradicals. However, the present study shows that this test must be used with caution, since the radical defect units can be consumed by postpolymerization reactions with the cocatalyst, as observed most strikingly for Cp*TiCl$_3$/MAO. Radical polymerization may complicate the reactions of metal catalysts with VC but can be avoided by using nonredox active metal catalysts, anaerobic reaction conditions, and radical inhibitors.

The second pathway observed in reactions of group 4 L$_n$MR$^+$ species and VC is the formation of L$_n$MCl$^+$ and CH$_2$=CHR products. While no intermediates have been observed, this reaction most likely proceeds by 1,2 insertion to

yield $L_nMCH_2CHClR^+$ species which undergo rapid β-Cl elimination. It is also possible that $L_nMCHClCH_2R^+$ species are formed by 2,1 VC insertion and rearrange to β-chloroalkyl species prior to elimination. VC insertion of group 4 L_nMR^+ species can be facile, occurring readily, for example, at -10 °C for *rac*-(EBI)ZrMe$^+$ and 50 °C for $(C_5Me_4SiMe_2N'Bu)$-ZrMe$^+$. However VC insertions are slower than analogous propylene insertions, probably because VC binds more weakly than propylene to d^0 L_nMR^+ cations. Multiple VC insertions leading to VC polymerization are not observed for group 4 metal catalysts because $L_nMCH_2CHClR^+$ species undergo β-Cl elimination faster than they coordinate and insert VC.

The reaction of *rac*-(EBI)ZrMe$_2$/MAO or $[(C_5Me_4SiMe_2$-N'Bu)ZrMe][B(C_6F_5)_4]$ with propylene/VC mixtures yields oligopropylene containing both allylic and vinylidene chain ends rather than strictly vinylidene (unsaturated) chain ends, as observed in propylene homopolymerization by these catalysts. These results show that VC insertion into $L_nM(CH_2CHMe)_nR^+$ active species is also followed by β-Cl elimination, which terminates chain growth and precludes propylene/VC copolymerization.

The ultimate products from VC insertion/β-Cl elimination of group 4 L_nMR^+ species reflect the downstream chemistry available to the system. For example, *rac*-(EBI)ZrMe$_2$/B(C_6F_5)_3 consumes 2 equiv of VC per Zr because the product of the first insertion/β-Cl elimination, $[rac\text{-(EBI)ZrCl}][MeB(C_6F_5)_3]$ (**4**), contains a reactive $MeB(C_6F_5)_3^-$ anion which realkylates the *rac*-(EBI)ZrCl$^+$ cation, enabling a second VC insertion/β-Cl elimination to occur. In this system, the evolved propylene is oligomerized by *rac*-(EBI)ZrR$^+$ as it is formed. For $(C_5R_5)_2$-ZrX$_2$/MAO and Cp*TiCl$_3$/MAO at high Al/Ti ratios, realkylation of the L_nMCl^+ species formed by β-Cl elimination by MAO is efficient, and catalytic conversion of VC to oligopropylene can be achieved; however, this process is stoichiometric in Al$-$Me groups. In contrast, for $[(C_5Me_4SiMe_2N'Bu)MMe]$-$[B(C_6F_5)_4]$ (M = Ti, Zr), VC insertion/β-Cl elimination yields $[(C_5Me_4SiMe_2N'Bu)MCl][B(C_6F_5)_4]$ species which do not react further and can be trapped as $(C_5Me_4SiMe_2N'Bu)MCl_2$ by addition of a chloride source.

The facility of β-Cl elimination of group 4 $L_nMCH_2CHClR^+$ species is not surprising, as this reaction is highly exothermic because of the higher bond dissociation energies of M$-$Cl versus M$-$C bonds for early metals.[66] Assuming a Zr(IV)$-$olefin bond strength of 15 kcal/mol,[67] we estimate the conversion of $(C_5R_5)_2ZrCH_2CHClR^+$ to $(C_5R_5)_2ZrCl(CH_2=CHR)^+$ to be exothermic by $\sim$42 kcal/mol.[68] Additionally, the barrier to β-Cl elimination is expected to be low because of the favorable geometry of the transition state for syn elimination. Termination of chain growth by β-Cl elimination is the most significant obstacle to insertion polymerization/copolymerization of VC. Possible approaches to avoiding this reaction include using late metal catalysts for which M$-$R and M$-$Cl bond strengths are more comparable[39] and designing catalysts for which 2,1 VC insertion is favored.

Experimental Section

General Procedures. All experiments were performed using standard Schlenk or vacuum line techniques or in a nitrogen-filled drybox. Pentane, hexane, and toluene were distilled from sodium/benzophenone or purified by passage through columns of activated alumina and a BASF R3-11 oxygen removal catalyst. Dichloromethane, chlorobenzene, dichloromethane-d_2, and chlorobenzene-d_5 were dried over CaH$_2$ and distilled. Nitrogen was purified by passage through columns containing activated 4-Å molecular sieves and a Q-5 oxygen scavenger. MAO (30 wt % solution in toluene; 13.4 wt % Al) was obtained from Albemarle; this material contained a small amount of a process oil that was characterized as described below. B(C_6F_5)_3, [Ph_3C][B(C_6F_5)_4]$, and $[NHMe_2Ph][B(C_6F_5)_4]$ were obtained from Boulder Scientific. Lecture bottles of vinyl chloride (VC) were purchased from Aldrich and used without further purification. VC containing 14 ppm H$_2$O was obtained from Geon and dried by passage through 4-Å molecular sieves. Benzoquinone, 4-*tert*-butylcatechol, (indenyl)$_2$ZrMe$_2$, Cp*$_2$ZrCl$_2$, and Cp*TiCl$_3$ were obtained from Aldrich. Cp*Ti(OMe)$_3$ was obtained from Strem. *rac*-(EBI)ZrMe$_2$, *rac*-(EBI)ZrCl$_2$, *rac*-Me$_2$Si(2-Me-4,5-benz-indenyl)$_2$ZrCl$_2$, Cp$_2$ZrMe$_2$, and $(C_5Me_4SiMe_2N'Bu)MMe_2$ (M = Ti, Zr) were prepared according to literature methods.[62,64,69–71]

Gel permeation chromatography (GPC) was performed on a Polymer Labs PL-220 instrument using PLGel mixed B columns with refractive index detection and calibration versus narrow polystyrene standards. Elemental analyses were performed by Midwest Analytics. NMR spectra were recorded at ambient temperature unless specified otherwise. ^1H and ^{13}C chemical shifts are reported relative to SiMe$_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. ^{11}B chemical shifts are reported relative to BF$_3$·Et$_2$O. ^{19}F chemical shifts are reported relative to CFCl$_3$. All coupling constants are given in hertz.

Control Experiments. NMR experiments using internal standards and product isolation experiments show that the following compounds do not react with VC under the specified conditions: (i) B(C_6F_5)_3 in CD$_2$Cl$_2$ (25 °C, 86 h): (ii) AlMe$_3$ in C$_6$D$_6$ (100 °C, sealed tube, overnight);[72] (iii) dried MAO in C$_6$D$_6$ (100 °C, sealed tube, 30 min); (iv) AlMe$_3$ and dried MAO in C$_6$D$_6$ (25 °C, overnight); (v) MAO in toluene (25 °C, 20 h); (vi) *rac*-(EBI)ZrMe$_2$ in C$_6$D$_6$ (100 °C, 3 h).

Process Oil in MAO. A Schlenk tube was charged with MAO (5.44 g of a 30 wt % solution in toluene; Al = 26.8 mmol) and toluene (20 mL). The clear solution was added via pipet to acidified methanol (100 mL of a 1 M HCl solution) to quench the MAO. The resulting solution was extracted with hexanes (3 × 30 mL). The extract was dried under vacuum, yielding a small amount of an opaque pale yellow oil. ^1H NMR (THF-d_8): δ 1.30 (br, 2H), 0.88 (m, 1H).

Generation of *rac*-(EBI)ZrMe(μ-Me)B(C_6F_5)_3 (1).[40c] An NMR tube was charged with *rac*-(EBI)ZrMe$_2$ (0.011 g, 0.029 mmol) and B(C_6F_5)_3 (0.015 g, 0.029 mmol), and toluene (0.01 g, 0.1 mmol; internal standard) and CD$_2$Cl$_2$ (0.5 mL) were condensed in at -196 °C. The tube was sealed, warmed to -78 °C, and placed in an NMR probe that was precooled to -73 °C. A ^1H NMR spectrum was obtained which confirmed that **1** had formed quantitatively. ^1H NMR of **1** (CD$_2$Cl$_2$, -63 °C): δ 7.53–7.38 (m, 5H, indenyl), 7.18 (t, $^3J_{HH} = 3$ Hz, 1H, indenyl), 7.12 (d, $^3J_{HH} = 3$ Hz, 1H, indenyl), 6.69 (t, $^3J_{HH} = 9$ Hz, 1H, indenyl), 6.31 (d, $^3J_{HH} = 3$ Hz, 1H, indenyl), 6.22 (t, $^3J_{HH} = 9$ Hz, 1H, indenyl), 6.11 (d, $^3J_{HH} = 3$ Hz, 1H, indenyl), 5.92 (d, $^3J_{HH} = 3$ Hz, 1H, indenyl), 3.82–3.68 (m, 1H, CH_2CH_2), 3.60–3.45 (m, 1H, CH_2CH_2), 3.45–3.31 (m, 2H, CH_2CH_2), -0.49 (s, 3H, Zr*Me*), -0.99 (s, 3H, *Me*B). **1** is stable in CD$_2$Cl$_2$ at -78 °C but decomposes significantly within 1 h at 25 °C in this solvent.

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Reaction of *rac*-(EBI)ZrMe(μ-Me)B(C₆F₅)₃ (1) and VC in CD₂Cl₂.
A CD₂Cl₂ solution of **1** (0.029 mmol) containing toluene (0.09 mmol) as an internal standard was prepared in an NMR tube as described above. VC (20.3 mL at 419 mm and 25 °C; 0.46 mmol) was condensed into the NMR tube at −196 °C. The tube was warmed to −78 °C and inserted into an NMR spectrometer probe which had been precooled to −88 °C. ¹H NMR spectra were recorded from −88 °C to 25 °C. No reaction between **1** and VC was detected below −10 °C. Above −10 °C, the VC resonances decreased in intensity and the resonances for **1** began to broaden into the baseline. At 25 °C, the resonances for **1** were absent and the solution was dark red. No PVC resonances were observed. However, resonances for atactic oligopropylene were observed. ¹H NMR (CD₂Cl₂, 25 °C): δ 1.60 (br, −C*H*), 1.2−0.7 (br, C*H₂* and −*Me*).[73] The tube was maintained at 25 °C for 24 h. The color of the solution changed from red to pale yellow. NMR analysis revealed that the only organometallic species present in the solution were *rac*-(EBI)ZrCl₂ (**3**, 100% by ¹H NMR) and B(C₆F₅)₃.[74] ¹H NMR integration established that 2 equiv of VC had been converted to oligopropylene. In a similar experiment using 0.053 mmol of **1**, benzene was added to the tube at this point to induce precipitation of **3**. The solid was collected by filtration, washed with benzene and hexane, and dried under vacuum to afford **3** as a pale yellow solid (0.018 g, 81%).

NMR Characterization of [{*rac*-(EBI)ZrCl}₂(μ-Cl)][MeB(C₆F₅)₃] (2). A CD₂Cl₂ solution of **1** (0.029 mmol) was generated in an NMR tube as described above. VC (20.3 mL at 419 mm and 25 °C, 0.46 mmol) was condensed in at −196 °C. The tube was warmed to 25 °C for 5 min. The volatiles were removed under vacuum, fresh CD₂Cl₂ was added by vacuum transfer, and NMR spectra were recorded at −73 °C. The ¹⁹F NMR spectrum established that a 1:1 mixture of B(C₆F₅)₃ and MeB(C₆F₅)₃⁻ was present. For B(C₆F₅)₃, ¹⁹F NMR (CD₂Cl₂, −73 °C): δ −127.5 (d, ³J_FF = 22 Hz, 6F, *o*-C₆F₅), −143.4 (t, ³J_FF = 21 Hz, 3F, *p*-C₆F₅), −160.4 (m, 6F, *m*-C₆F₅). For MeB-(C₆F₅)₃⁻: δ −132.5 (d, ³J_FF = 21 Hz, 6F, *o*-C₆F₅), −164.6 (t, ³J_FF = 20 Hz, 3F, *p*-C₆F₅), −167.2 (m, 6F, *m*-C₆F₅). The ¹H NMR spectrum established that [{*rac*-(EBI)ZrCl}₂(μ-Cl)][MeB(C₆F₅)₃] (**2**, 10:1 isomer ratio, >83% of the total *rac*-(EBI)Zr species) was the major *rac*-(EBI)-Zr species present and confirmed that MeB(C₆F₅)₃⁻ and atactic oligopropylene were present.[75] For major isomer of **2**, ¹H NMR (CD₂Cl₂, −73 °C): δ 7.70−7.10 (m, 8H, indenyl), 6.82 (d, ³J_HH = 3.0 Hz, 1H, indenyl), 6.48 (d, ³J_HH = 3.0 Hz, 1H, indenyl), 6.10 (d, ³J_HH = 3.0 Hz, 1H, indenyl), 5.91 (d, ³J_HH = 3.0 Hz, 1H, indenyl), 4.0−3.6 (m, 4H, C*H₂CH₂*). ¹³C NMR (CD₂Cl₂, −73 °C): δ 130.2 (s, ipso), 128.2 (dd, ¹J_CH = 163 Hz, ³J_CH = 8 Hz, CH), 127.6 (dd, ¹J_CH = 165 Hz, ³J_CH = 8 Hz, CH), 127.3 (dd, ¹J_CH = 162 Hz, ³J_CH = 8 Hz, CH), 126.9 (s, ipso), 126.8 (dd, ¹J_CH = 166 Hz, ³J_CH = 8 Hz, CH), 126.5 (s, ipso), 126.2 (dd, ¹J_CH = 166 Hz, ³J_CH = 8 Hz, CH), 125.4 (ipso), 123.9 (dd, ¹J_CH = 151 Hz, ³J_CH = 7 Hz, CH), 123.8 (s, ipso), 123.6 (s, ipso), 122.7 (dd, ¹J_CH = 149 Hz, ³J_CH = 7 Hz, CH), 120.8 (dd, ¹J_CH = 162 Hz, ³J_CH = 7 Hz, CH), 115.1 (d, ¹J_CH = 179 Hz, CH), 114.3 (d, ¹J_CH = 171 Hz, CH), 113.7 (d, ¹J_CH = 162 Hz, CH), 112.4 (d, ¹J_CH = 175 Hz, CH), 29.3 (t, ¹J_CH = 132 Hz, CH₂), 27.3 (t, ¹J_CH = 131 Hz, CH₂). For minor isomer of **2**, ¹H NMR (CD₂Cl₂, −73 °C): δ 7.70−7.10 (m, 8H, indenyl), 6.78 (d, ³J_HH = 3 Hz, 1H, indenyl), 6.38 (d, ³J_HH = 3 Hz, 1H, indenyl), 6.32 (d, ³J_HH = 3 Hz, 1H, indenyl), 5.96 (d, ³J_HH = 3 Hz, 1H, indenyl), 4.0−3.6 (m, 4H, CH₂CH₂). The ¹³C spectrum of the minor isomer was not discernible because of poor signal/noise and peak overlap with the major isomer.

In another experiment designed to quench the reaction before stage 1 was complete, the NMR tube containing the CD₂Cl₂ solution of **1** and VC was maintained at 25 °C for 1 min and then cooled to −78 °C and analyzed by low temperature ¹H NMR. Resonances for an intermediate assigned as *rac*-(EBI)ZrCl(μ-Me)B(C₆F₅)₃ (**4**) were ob-

served. ¹H NMR (CD₂Cl₂, −73 °C, C₅ region): δ 7.09 (d, ³J_HH = 3 Hz, 1H, indenyl C₅−H), 6.42 (d, ³J_HH = 3 Hz, 1H, indenyl C₅−H), 6.34 (d, ³J_HH = 3 Hz, 1H, indenyl C₅−H), 6.05 (d, ³J_HH = 3 Hz, 1H, indenyl C₅−H), −0.40 (br s, coordinated *Me*B(C₆F₅)₃⁻).

Conversion of 2 to *rac*-(EBI)ZrCl₂ (3). A CD₂Cl₂ solution of **1** (0.029 mmol) and toluene (0.01 g, 0.1 mmol; internal standard) was generated in an NMR tube as described above. The tube was maintained at −78 °C, and a ¹H NMR spectrum was obtained at −73 °C. The tube was removed from the spectrometer and cooled to −196 °C. VC (0.46 mmol) was condensed into the tube at −196 °C. The tube was warmed to 25 °C for 5 min, and the color changed from yellow to dark red because of the formation of **2**. The tube was then taken into the drybox where [NBu₃Bn]Cl (0.0045 g, 0.015 mmol) was added. The color of the solution immediately changed from dark red to pale yellow. The tube was removed from the drybox and placed in an NMR spectrometer probe that had been precooled to −73 °C, and a ¹H NMR spectrum was obtained. The only Zr-containing species detectable in the spectrum was **3**. Comparison of the integrated intensities for **1**, **3**, and the toluene internal standard established that **3** was formed quantitatively versus **1**.

Quantification of VC Consumption and Formation of 2 in Stage 1. A CD₂Cl₂ solution of **1** (0.29 mmol) containing toluene (0.01 g, 0.10 mmol; internal standard) and VC (0.46 mmol) was generated in an NMR tube as described above. The tube was warmed to −78 °C and inserted into an NMR spectrometer probe that had been precooled to −73 °C. A ¹H NMR spectrum was recorded. The tube was warmed to 25 °C for 5 min, and the color of the solution changed from pale yellow to dark red. A ¹H NMR spectrum was recorded at −73 °C. Comparison of the integrated intensities of the resonances for **1**, VC, and the toluene internal standard before and after the 25 °C reaction period revealed that 1.5 equiv of VC was consumed per Zr and that **2** had formed in >94% yield versus **1**.

Reaction of *rac*-(EBI)ZrMe₂/MAO and VC. A 250 mL stainless steel autoclave fitted with a glass insert was charged with *rac*-(EBI)-ZrMe₂ (0.001 g, 3 μmol) and MAO (10 g of a 30 wt % toluene solution; 51 mmol of Al; Al/Zr = 17 000). The autoclave was exposed to a constant feed of VC (1 atm) and was mechanically stirred for 20 h at 25 °C. The VC feed was terminated, the autoclave was vented, and the reaction mixture was poured into acidified methanol (50 mL of a 1 M HCl solution). The resulting mixture was extracted with hexane. The hexane extract was dried under vacuum, yielding 0.250 g of a colorless oil. The ¹H and ¹³C NMR spectra established that the colorless oil was atactic oligopropylene that contained a small amount of the process oil present in the MAO. ¹H NMR (1,1,2,2-C₂D₂Cl₄, 100 °C) δ 1.62 (m, −C*H*), 1.10 (m, C*H₂*-*anti*-meso and C*H₂*, racemic), and 0.96 (m, C*H₂*-*syn*-meso and −*Me*). The unsaturated end groups observable in the ¹H spectrum comprised 95% allylic (¹H NMR δ 5.83 (m, 1H, =C*H*R), 5.05 (m, 2H, =C*H₂*)) and 5% vinylidene (¹H NMR δ 4.79 (s, 1H, =C*H₂*), 4.72 (s, 1H, =C*H₂*)) chain ends. The number average molecular weight of the polymer (*M*ₙ) was determined from the ¹H NMR spectrum, assuming one unsaturated end group per chain. For the sample generated above, *M*ₙ = 563 (average degree of polymerization = 13). Elemental analysis of oligopropylene Anal. Calcd for (CH₂CHMe)ₙ: C, 85.63; H, 14.37. Found: C, 86.13; H, 13.56; Cl, not detectable.

Batch Polymerization of Propene by *rac*-(EBI)ZrMe₂/MAO in the Absence and Presence of VC. A 250 mL stainless steel autoclave vessel fitted with a glass insert was charged with *rac*-(EBI)ZrMe₂ (0.001 g, 3 μmol), MAO (10 g of a 30 wt % toluene solution; 51 mmol of Al; Al/Zr = 17 000), and propene (250 mL at 380 mm and 25 °C, 5.1 mmol). The mixture was stirred mechanically for 20 h at 25 °C. The autoclave was vented, and the reaction mixture was poured into acidified MeOH (50 mL of a 1 M HCl solution). A colorless precipitate formed and was separated by filtration, washed with MeOH, and dried under vacuum, yielding 0.135 g (63% based on propene) of a colorless solid. ¹H and ¹³C NMR analysis established that the solid was isotactic

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polypropylene ($M_n = 7500$). The unsaturated end groups were exclusively vinylidene. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$, 100 °C, olefin region): δ 4.79 (s, 1H, =CH_2); 4.72 (s, 1H, =CH_2).

The procedure described above was followed with the exception that VC (250 mL at 380 mm and 25 °C, 5.1 mmol) was added in addition to the propene. Workup yielded 0.085 g (40% based on propene) of isotactic polypropylene ($M_n = 7200$). The ^{1}H NMR spectrum established that unsaturated end groups consisted of 76% allylic (δ 5.83 (m, 1H, =CH_2), 5.05 (m, 2H, =CHR)) and 24% vinylidene (δ 4.79 (s, 1H, =CH_2) 4.72 (s, 1H, =CH_2)) chain ends. Since VC is acting as a chain transfer agent, the molecular weight of the polypropylene is expected to decrease when VC is present. The similarity of the M_n values of the polypropylene produced in the presence and absence of VC reflects the difference in % propene conversion. The lower % conversion in the presence of VC results in a higher average propene pressure which results in a higher M_n value of the resulting polymer.[42]

Reaction of *rac*-(EBI)ZrMe₂/MAO with VC in the Presence of Oxygen. A 250 mL stainless steel autoclave fitted with a glass insert was charged with *rac*-(EBI)ZrMe₂ (0.8 mg, 2 μmol), MAO (0.10 g of a 30 wt % toluene solution; 0.49 mmol of Al; Al/Zr = 250), VC (110 mL, 1.88 mol), and air (0.04 mL). The autoclave was stirred at 50 °C for 1 h and vented. The resulting mixture was poured into acidified methanol (50 mL of a 1M HCl solution). A solid precipitated and was separated by filtration, washed with methanol, and dried under vacuum to yield 1.1 g (1% conversion) of colorless PVC. ^{1}H NMR (THF-d_8, 50 °C): δ 4.59 (m, CHCl), 4.47 (m, CHCl), 4.34 (m, CHCl), 2.40–2.10 (m, CH₂). ^{13}C NMR (C_6D_5Cl, 100 °C): δ 57.1 (m, CHCl, rr triad), 56.1 (m, CHCl, mr triad), 55.2 (m, CHCl, mm triad), 47.5 (m, CH₂, rrr tetrad), 47.1 (m, CH₂, rmr tetrad), 46.7 (m, CH₂, mrr tetrad), 46.1 (m, CH₂, mmr tetrad), 46.0 (m, CH₂, mrm tetrad), 45.3 (m, CH₂, mmm tetrad); triad tacticity 0.32 rr, 0.51 mr, 0.17 mm (α = 0.58). GPC: $M_w = 180\,479$; $M_n = 36\,217$; $M_w/M_n = 5.0$. Use of higher amounts of oxygen did not result in the formation of PVC.

Reaction of Cp*Ti(OMe)₃/MAO and VC (Al/Ti = 10). A 100 mL Fisher–Porter bottle was charged with Cp*Ti(OMe)₃ (0.011 g, 0.040 mmol). VC (2.1 g, 34 mmol) was condensed in at −78 °C, and MAO (0.080 g of a 30 wt % toluene solution diluted with 10 mL of CH₂Cl₂; 0.40 mmol of Al) was injected by syringe. The bottle was warmed to room temperature and stirred for 24 h at 25 °C. The bottle was vented, and the reaction mixture was poured into acidified MeOH (50 mL of a 1M HCl solution). A solid precipitated and was separated by filtration, washed with MeOH, and dried under vacuum, yielding 0.76 g (36% conversion) of colorless PVC. GPC: $M_w = 91\,066$; $M_n = 27\,241$; $M_w/M_n = 3.3$. Tacticity by ^{13}C{^{1}H} NMR: 0.36 rr, 0.49 mr, 0.15 mm; α = 0.61.

Reaction of Cp*TiCl₃/MAO and VC (Al/Ti = 10). A 100 mL glass Fisher–Porter bottle was charged with Cp*TiCl₃ (0.014 g, 0.048 mmol). VC (2.1 g, 34 mmol) was condensed in at −40 °C, and MAO (0.100 g of a 30 wt % toluene solution diluted with 10 mL of CH₂Cl₂; 0.50 mmol of Al) was injected by syringe. The bottle was warmed to room temperature and stirred for 24 h at 25 °C. The bottle was vented, and the reaction mixture was poured into acidified MeOH (50 mL of a 1M HCl solution). A solid precipitated and was separated by filtration, washed with MeOH, and dried under vacuum, yielding 0.14 g (6.8% conversion) of colorless PVC. GPC: $M_w = 117\,928$; $M_n = 21\,950$; $M_w/M_n = 5.4$. Tacticity by ^{13}C{^{1}H} NMR: 0.40 rr, 0.48 mr, 0.12 mm; α = 0.64. This procedure was repeated at 10 times the scale, and 0.81 g (4% conversion) of PVC was obtained (α = 0.64). Similar results were obtained when the reaction was conducted in the absence of light.

Reaction of PVC with MAO. A Schlenk tube was charged with PVC (0.275 g, 4.4 mmol of monomer, commercial sample prepared at 80 °C), MAO (0.128 g of a 30 wt % solution in toluene; 0.63 mmol of Al), and CH₂Cl₂ (10 mL). The solution was stirred for 24 h at 23 °C. The solution turned dark red over 6 h. Acidified methanol (50 mL of a 1 M HCl solution) was added to quench the reaction and precipitate the PVC. The PVC was separated by filtration, washed with methanol

(3 × 50 mL), and dried under vacuum (0.256 g, 93%). GPC analysis: $M_w = 176\,770$, $M_n = 9039$, $M_w/M_n = 19.5$. GPC analysis of the untreated PVC: $M_w = 67\,314$, $M_n = 30\,658$, $M_w/M_n = 2.11$. In a similar experiment, PVC (prepared at 30 °C) was treated with MAO in the same fashion. ^{13}C NMR showed that the tacticity was essentially unchanged (before treatment 0.31 rr, 0.51 mr, 0.18 mm, α = 0.56; after treatment 0.34 rr, 0.49 mr, 0.17 mm, α = 0.58).

Reaction of PVC with MAO/MeOH. A Schlenk tube was charged with PVC (0.550 g, 8.8 mmol of monomer) and CH₂Cl₂ (20 mL), and MeOH (13 mg, 0.40 mmol, 0.3 equiv vs MAO, degassed and under N₂) was added by microsyringe. MAO (0.256 g of a 30 wt % solution in toluene; Al = 1.26 mmol) was added by syringe, and the solution was stirred for 24 h at 23 °C. The solution turned pale yellow and then colorless over the course of 1 h. The solution was added to acidified methanol (100 mL of a 1 M HCl solution). The PVC was separated by filtration, washed with methanol (3 × 30 mL), and dried under vacuum (0.502 g, 91%).

Reaction of Cp*TiCl₃/MAO and VC (Al/Ti = 1000). An NMR tube was charged with Cp*TiCl₃ (1.0 mg, 3.5 μmol) and dried MAO (3.5 mmol of Al; Al/Ti = 1000). C_6D_6 (0.5 mL) and toluene (0.06 mmol, internal standard) were added, and VC (0.46 mmol) was condensed in at −196 °C. The tube was warmed to room temperature, and a ^{1}H NMR spectrum was recorded. The tube was maintained at 80 °C for 24 h. The solution was dark red. The tube was cooled to room temperature, and a ^{1}H NMR spectrum was recorded which established the presence of atactic oligopropylene. No PVC was formed. Comparison of the integrated intensities of VC and toluene before and after the reaction established that 60% of the VC was consumed (79 equiv vs Ti).

Reaction of [(C₅Me₄SiMe₂N'Bu)ZrMe(C₆D₆)][B(C₆F₅)₄] and VC. An NMR tube was charged with (C₅Me₄SiMe₂N'Bu)ZrMe₂ (0.014 g, 0.038 mmol) and [Ph₃C][B(C₆F₅)₄] (0.035 g, 0.038 mmol), and C_6D_6 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to 23 °C, and [(C₅Me₄SiMe₂N'Bu)ZrMe(C₆D₆)][B(C₆F₅)₄] (**8**) was partially separated as an orange oil from the pale yellow solution. The ^{1}H NMR spectrum contained resonances for **8** and Ph₃CMe along with broad resonances assigned to the fraction of **8** present in the oil phase. VC (0.23 mmol) was added by vacuum transfer at −196 °C. The tube was maintained at room temperature for 2 h and then heated to 50 °C for 2 h. ^{1}H NMR analysis showed that 1 equiv of VC had been consumed versus Ph₃CMe, the Zr–Me resonances of **8** had disappeared, and new (C₅Me₄SiMe₂N'Bu)Zr resonances had appeared. The volatiles were removed under vacuum, leaving an orange oil presumed to be [(C₅Me₄SiMe₂N'Bu)ZrCl][B(C₆F₅)₄]. The NMR spectrum of the volatiles contained resonances for free propylene. Solid [NBu₃Bn]Cl (0.012 g, 0.038 mmol) was added to the orange oil, and C_6D_6 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature to afford a mixture of an orange oil ([NBu₃Bn][B(C₆F₅)₄]) suspended in a pale yellow solution. A ^{1}H NMR spectrum showed that (C₅Me₄SiMe₂N'Bu)ZrCl₂ had formed in 50% yield versus Ph₃CMe. Only resonances for free B(C₆F₅)₄⁻ were observed in the ^{19}F NMR spectrum.

Generation and Trapping of [(C₅Me₄SiMe₂N'Bu)ZrCl][B(C₆F₅)₄]. An NMR tube was charged with (C₅Me₄SiMe₂N'Bu)ZrMe₂ (0.011 g, 0.030 mmol) and (C₅Me₄SiMe₂N'Bu)ZrCl₂ (0.012 g, 0.030 mmol), and C_6D_6 (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to 23 °C. The ^{1}H NMR spectrum established that conversion to (C₅Me₄SiMe₂N'Bu)Zr(Me)Cl was complete. ^{1}H NMR (C_6D_6): δ 2.04 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.85 (s, 3H), 1.35 (s, 9H), 0.44 (s, 3H), 0.40 (s, 3H), 0.25 (s, 3H). Solid [Ph₃C][B(C₆F₅)₄] (0.055 g, 0.060 mmol) was added, and an orange oil (presumably [(C₅Me₄SiMe₂N'Bu)Zr(Cl)][B(C₆F₅)₄]) separated from the pale yellow solution. A ^{1}H NMR spectrum showed that Ph₃CMe was present. The tube was heated to 50 °C for 2 h. No change was observed by ^{1}H NMR. Solid [NBu₃Bn]Cl (0.019 g, 0.060 mmol) was added, yielding a mixture of an orange oil ([NBu₃Bn][B(C₆F₅)₄]) suspended in a pale yellow

solution. A ^{1}H NMR spectrum established that (C$_5$Me$_4$SiMe$_2$N^{t}Bu)-ZrCl$_2$ had formed in 63% yield versus Ph$_3$CMe. The ^{19}F NMR spectrum contained only resonances for free B(C$_6$F$_5$)$_4^-$.

Reaction of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)][B(C$_6$F$_5$)$_4$] with [NBu$_3$Bn]Cl. A suspension of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)]-[B(C$_6$F$_5$)$_4$] (0.033 mmol) in C$_6$D$_6$ was prepared in an NMR tube as described above. The tube was heated to 50 °C for 2 h. Solid [BnBu$_3$N]-Cl (0.033 mmol) was added, yielding a mixture of an orange oil in a pale yellow solution. A ^{1}H NMR spectrum of the solution phase established that (C$_5$Me$_4$SiMe$_2$N^{t}Bu)Zr(Me)Cl had formed in 60% yield versus Ph$_3$CMe; no (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$ was present.

Reaction of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)][B(C$_6$F$_5$)$_4$] with Propylene. A C$_6$D$_6$ solution of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)][B(C$_6$F$_5$)$_4$] (0.038 mmol) was prepared in an NMR tube as described above. Propylene (0.76 mmol) was condensed into the tube at −196 °C. The tube was warmed to 23 °C, at which point it became hot. A ^{1}H NMR spectrum obtained after 30 min at 23 °C established that the propylene was completely polymerized to low molecular weight atactic polypropylene. The unsaturated end groups were exclusively vinylidene. ^{1}H NMR (C$_6$D$_6$): δ 4.83 (s, 1H, =CH$_2$), 4.78 (s, 1H, =CH$_2$), 1.70 (br, −CH), 1.28 (br, CH$_2$-anti-meso), 1.13 (br, CH$_2$-racemic), 0.92 (CH$_2$-syn-meso and −Me). M_n (by ^{1}H NMR) = 1030 (average degree of polymerization = 24).

Reaction of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)][B(C$_6$F$_5$)$_4$] with Propylene in the Presence of VC. A C$_6$D$_6$ solution of [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrMe(C$_6$D$_6$)][B(C$_6$F$_5$)$_4$] (0.048 mmol) was prepared in an NMR tube as described above. VC (0.48 mmol) and propylene (0.48 mmol) were condensed into the NMR tube at −196 °C. The tube was warmed to 23 °C, at which point it became warm. A ^{1}H NMR spectrum obtained after 30 min at 23 °C established that 25% of the propene remained and atactic polypropylene had formed. No further change in the ^{1}H NMR spectrum was observed after 24 h. The unsaturated end groups observable in the ^{1}H NMR spectrum comprised 13% allylic (δ 5.78 (m, 1H, =CHR), 5.03 (m, 2H, =CH$_2$)) and 87% vinylidene (δ 4.83 (s, 1H, =CH$_2$), 4.78 (s, 1H, =CH$_2$)). Aliphatic ^{1}H NMR resonances (C$_6$D$_6$): δ 1.73 (br, −CH), 1.28 (br, CH$_2$-anti-meso), 1.13 (br, CH$_2$-racemic), 0.91 (CH$_2$-syn-meso and −Me). M_n (by ^{1}H NMR) = 942 (average degree of polymerization = 23).

Reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$/MAO and VC. A 100 mL Fisher−Porter bottle was charged with (C$_5$Me$_4$SiMe$_2$N^{t}Bu)ZrCl$_2$ (0.009 g, 0.02 mmol), MAO (4 g of a 30 wt % toluene solution; 20 mmol of Al; Al/Zr = 1000) and 20 mL of toluene. VC (2 mL, 1.8 g, 29 mmol) was condensed into the Fisher−Porter bottle tube at −196 °C. The bottle was heated to 80 °C for 2 h. The bottle was vented, and the reaction mixture was poured into acidified methanol (100 mL of a 1 M HCl solution). The resulting mixture was extracted with hexanes (3 × 50 mL). The extract was dried under vacuum, yielding 0.070 g of a pale yellow oil. The ^{1}H and ^{13}C NMR spectra established that the oil was atactic oligopropylene and contained a process oil from the MAO. The reaction was repeated with varying concentrations of MAO (800−17 000 Al/Zr), temperatures (25−80 °C), and times (2−24 h) with similar results.

Reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$/ [Ph$_3$C][B(C$_6$F$_5$)$_4$] and VC. An NMR tube was charged with (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$ (0.012 g, 0.037 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.034 g, 0.037 mmol), and C$_6$D$_6$ (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to 23 °C, and a dark orange oil separated from the pale yellow solution. The ^{1}H NMR spectrum contained resonances for the dinuclear complex [{(C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$],[64b] broad resonances at similar chemical shifts assigned to the fraction of the dinuclear complex that was present in the oil phase, and Ph$_3$CMe. VC (0.22 mmol) was added by vacuum transfer at −196 °C. The tube was heated to 50 °C for 1 h. ^{1}H NMR analysis revealed that 1 equiv of VC had been consumed versus Ph$_3$CMe. The volatiles were removed under vacuum leaving an orange solid presumed to be [(C$_5$Me$_4$SiMe$_2$N^{t}Bu)-TiCl][B(C$_6$F$_5$)$_4$]. The ^{1}H NMR spectrum of the volatiles contained weak resonances for free propylene. Solid [NBu$_3$Bn]Cl (0.011 g, 0.037 mmol) was added to the orange solid, and C$_6$D$_6$ (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to room temperature to afford a mixture of an orange oil suspended in a pale yellow solution. A ^{1}H NMR spectrum established that (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiCl$_2$ had formed in 40% yield versus Ph$_3$CMe. Only resonances for free B(C$_6$F$_5$)$_4^-$ were present in the ^{19}F NMR spectrum.

Reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] and Propylene. An NMR tube was charged with (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$ (0.046 mmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.046 mmol), and C$_6$D$_6$ (0.5 mL). Propylene (0.64 mmol) was condensed in at −196 °C. The tube was warmed to 23 °C, at which point partial gelling of the solution phase was observed. A ^{1}H NMR spectrum obtained after 30 min at 23 °C established that the propylene was completely consumed and atactic polypropylene had formed. No unsaturated end groups were discernible by ^{1}H NMR. The contents of the tube were added to acidified methanol (50 mL of a 1 M HCl solution) to precipitate the polypropylene. The polypropylene was separated by filtration, washed with methanol (3 × 20 mL), and dried under vacuum (25 mg). ^{1}H NMR (1,2-dichlorobenzene-d$_4$, 140 °C): δ 1.58 (br, −CH), 1.22 (br, CH$_2$-anti-meso), 1.07 (br, CH$_2$-racemic), 0.84 (CH$_2$-syn-meso and −Me). GPC: M_w = 1 672 000, M_n = 462 000, M_w/M_n = 3.6.

Reaction of (C$_5$Me$_4$SiMe$_2$N^{t}Bu)TiMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] with VC and Propylene. The above experiment was repeated except VC (0.46 mmol) and propylene (0.78 mmol) were condensed into the NMR tube at −196 °C. The tube was warmed to 23 °C, at which point it became warm to the touch. A ^{1}H NMR spectrum obtained after 30 min established that 6% of the propylene remained and atactic polypropylene had formed. The unsaturated end groups were exclusively allylic. The contents of the tube were added to acidified methanol (50 mL of a 1 M HCl solution); however, no polypropylene precipitate was observed. The resulting mixture was extracted with hexanes (3 × 20 mL), and the extract was dried under vacuum, leaving a small amount of an oil. ^{1}H NMR (1,2-dichlorobenzene-d$_4$, 140 °C): δ 5.73 (m, 1H, =CHR), 4.90 (m, 2H, =CH$_2$), 1.62 (br, −CH), 1.25 (br, CH$_2$-anti-meso), 1.11 (br, CH$_2$-racemic), 0.87 (CH$_2$-syn-meso and −Me). M_n determined by ^{1}H NMR = 1610 (average degree of polymerization = 38).