# Reaction of Vinyl Chloride with a Prototypical Metallocene Catalyst: Stoichiometric Insertion and *β*-Cl Elimination Reactions with *rac*-(EBI)ZrMe$^+$ and Catalytic Dechlorination/Oligomerization to Oligopropylene by *rac*-(EBI)ZrMe$_2$/MAO

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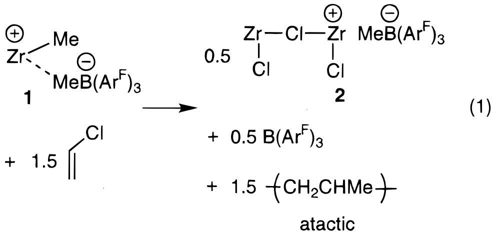
The development of catalysts for the coordination/insertion polymerization of vinyl chloride (VC) and other polar vinyl monomers is of interest because of the possibility that polymer composition, microstructure, and molecular weight can be controlled by manipulation of catalyst structure. Several recent patents and reports describe the polymerization of VC by group 4 metal single-site catalysts, including *rac*-(EBI)ZrMe$^+$ species (EBI = 1,2-bis(indenyl)ethylene), *rac*-(EBI)ZrMe$_2$/MAO (MAO = methylalumoxane), and other metallocene catalysts.[1] However, little information concerning the mechanisms of these reactions or the characterization of the resulting polymers is available.[2] To probe these issues, we have investigated the reactions of *rac*-(EBI)ZrMe$^+$ complexes with VC. Here we report that *rac*-(EBI)ZrR$^+$ species react with VC by insertion and rapid *β*-Cl elimination, and we describe several interesting ramifications of this chemistry.

Little is known about the reactions of early transition metal complexes with VC or other vinyl halides. The reaction of Cp*$_2$ScMe (Cp* = C$_5$Me$_5$) with vinyl fluoride yields Cp*$_2$ScF and propylene via insertion and subsequent *β*-F elimination.[3] Treatment of in-situ-generated Cp$_2$Zr(butene) with 2-haloalkenes (CH$_2$═CRX) yields Cp$_2$Zr(CR═CH$_2$)X oxidative-addition products (X = Cl, Br).[4] Additionally, the reaction of Cp$_2$TiCl$_2$/AlMe$_3$ (1/4) with CH$_2$═CRX substrates yields Cp$_2$Ti(CH$_2$CR═CH$_2$)X allyl species, most likely via AlMe$_3$-mediated *β*-X elimination of Cp$_2$Ti(CH$_2$CRXCH$_2$) titanacyclobutane intermediates.[5]

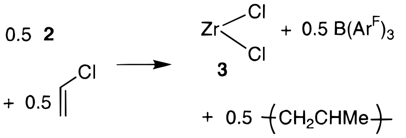
The reaction of VC with *rac*-(EBI)Zr(Me)(*μ*-Me)B(C$_6$F$_5$)$_3$ (**1**)[6,7] proceeds in two stages. In the first stage, which is complete within 5 min at 25 °C in CD$_2$Cl$_2$ solution, **1** reacts with a ca. 15-fold excess of VC to produce a dark red solution (eq 1). NMR studies reveal that 1.5 equiv of VC is consumed and a 1:1 mixture of B(C$_6$F$_5$)$_3$ and MeB(C$_6$F$_5$)$_3$$^-$ is formed. No poly(vinyl chloride) (PVC) is observed, but surprisingly, low-molecular-weight ($M_n$ = 500) atactic oligopropylene is formed (95% vs consumed VC).[8] No identifiable *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. However, low-temperature spectra reveal that [{*rac*-(EBI)ZrCl}$_2$(*μ*-Cl)][MeB(C$_6$F$_5$)$_3$] (**2**, 10/1 mixture of diastereomers) is the major Zr-containing species present (94% vs **1**).[9] The dinuclear cation of **2** is formally 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 a pure form. The $^1$H NMR signals for **2** are sharp below −50 °C but collapse upon warming of the sample and broaden into the baseline at ambient temperature. The variable-temperature (−73 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 the {*rac*-(EBI)ZrCl}$_2$(*μ*-Cl)$^+$ cation. Compound **2** decomposes above 40 °C (CD$_2$Cl$_2$) to **3** and other, unidentified products which precluded high-temperature NMR studies. Several related dinuclear metallocene cations have been characterized including [{*rac*-C$_2$H$_4$(C$_9$H$_{10}$)$_2$MCl}$_2$(*μ*-Cl)][AlCl$_4$] (M = Ti, Zr)[10] and red [{*rac*-(EBI)ZrMe}$_2$(*μ*-Me)][B(C$_6$F$_5$)$_4$].[11]



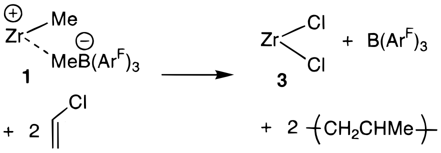
(1)

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

In the second stage of the reaction of **1** with VC, which is complete after 24 h at 25 °C, the initially formed red solution evolves to a yellow solution (eq 2). NMR studies establish that an additional 0.5 equiv of VC is converted to atactic oligopropylene and that the only organometallic species present in significant concentrations in the final reaction mixture are **3** (100% by $^1$H NMR, 81% isolated) and B(C$_6$F$_5$)$_3$ (only species observed by $^{19}$F NMR). The final yield of the oligopropylene determined by $^1$H NMR is >95% vs consumed VC. Thus, the overall reaction in stages 1 and 2 is that given in eq 3.



(2)



(3)

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[1] (a) Matsukawa, T.; Kiba, R.; Ikeda, T. Japan Patent 08208736 (Chisso Corp.); *Chem. Abstr.* **1996**, *125*, 276902. (b) Taeji, K.; Uozumi, T.; Soga, K. *Polym. Prepr. Jpn.* **1995**, *44*, 2. (c) Kiyoshi, E.; Saitoh, M. *Prepr. 7th SPSJ International Polymer Conference*, Yokohama, Japan, October 26, 1999; paper 27A06.

[2] The free radical polymerization of VC initiated by group 4 metallocenes under photochemical conditions has been reported: Nagy, S. M.; Krishnamurti, R.; Cocoman, M. K.; Opalinski, W. M.; Smolka, T. F. World Patent WO 9923124 A1 (Occidental Chemical); *Chem. Abstr.* **1999**, *130*, 338530.

[3] Burger, B. Ph.D. Thesis, California Institute of Technology, 1987.

[4] Takahashi, T.; Kotora, M.; Fischer, R.; Nishihara, Y.; Nadajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039.

[5] Hanzawa, Y.; Kowase, N.; Taguchi, T. *Tetrahedron Lett.* **1998**, *39*, 583.

[6] (a) Use of B(C$_6$F$_5$)$_3$ to generate cationic metal alkyl species: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (b) Generation of **1**: Dagorne, S.; Rodewald, S.; Jordan, R. F. *Organometallics* **1997**, *16*, 5541.

[7] Control experiments show that neither *rac*-(EBI)ZrMe$_2$ nor B(C$_6$F$_5$)$_3$, the precursors of **1**, reacts with VC under these conditions.

[8] (a) Cheng, H. N. *Macromol. Symp.* **1994**, *86*, 77. (b) $M_n$ values were determined by $^1$H NMR assuming one unsaturated end group per chain.

[9] (a) $^1$H NMR of **2** (CD$_2$Cl$_2$, −73 °C, indenyl H$^2$ and H$^3$ region, *J* in Hz) major isomer, $\delta$ 6.82 (d, *J* = 3, 1H), 6.48 (d, *J* = 3, 1H), 6.10 (d, *J* = 3, 1H), 5.91 (d, *J* = 3, 1H); minor isomer, 6.78 (d, *J* = 3, 1H), 6.38 (d, *J* = 3, 1H), 6.32 (d, *J* = 3, 1H), 5.96 (d, *J* = 3, 1H). (b) If stage 1 is terminated before completion (1 min at 25 °C followed by immediate cooling to −78 °C), the low-temperature $^1$H NMR spectrum contains additional resonances for an intermediate species that is assigned as *rac*-(EBI)Zr(Cl)(*μ*-Me)B(C$_6$F$_5$)$_3$ (**4**). $^1$H NMR (CD$_2$Cl$_2$, −73 °C, indenyl H$^2$ and H$^3$ and Me regions): $\delta$ 7.09 (d, *J* = 3, 1H), 6.42 (d, *J* = 3, 1H), 6.34 (d, *J* = 3, 1H), 6.05 (d, *J* = 3, 1H), −0.40 (s, 3H, MeB). Addition of [NBu$_3$Bn]Cl to a mixture of **4** and **2** results in complete conversion to **3**.

[10] Brintzinger, H. H. In *Ziegler Catalysts*; Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: New York, 1995; p 181.

[11] Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

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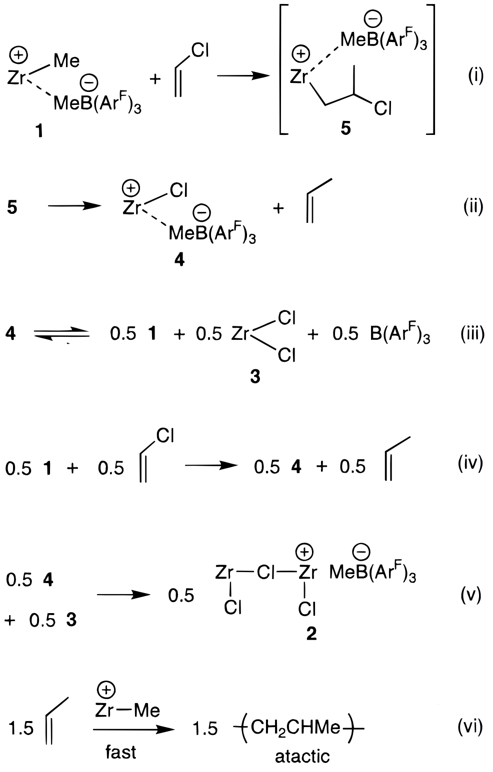
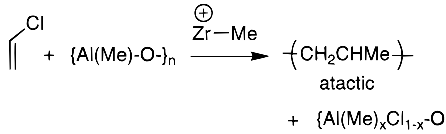
**Scheme 1**[a]



[a] Zr = *rac*-(EBI)Zr; Ar$^F$ = $C_6F_5$.

These observations can be rationalized by the mechanism in Scheme 1, 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 $\beta$-chloroalkyl complex [*rac*-(EBI)ZrCH$_2$CHClMe][MeB(C$_6$F$_5$)$_3$] (**5**, not observed), which undergoes rapid $\beta$-Cl elimination to yield *rac*-(EBI)Zr(Cl)($\mu$-Me)B(C$_6$F$_5$)$_3$ (**4**)[9b] and propylene (eqs i and ii). Complex **4** can undergo ligand redistribution reactions to regenerate up to an additional 0.5 equiv of **1** along with **3** and B(C$_6$F$_5$)$_3$ (eq iii). The regenerated **1** consumes an additional 0.5 equiv of VC (eq iv) to produce **4** and propylene. Intermediate **4** is ultimately trapped by **3** as the dinuclear species **2** (eq v). VC polymerization does not occur because VC insertion of **5** is not competitive with the $\beta$-Cl elimination in eq ii. However, the propylene that is produced in eqs ii and iv is rapidly oligomerized by *rac*-(EBI)ZrMe$^+$ (eq vi). Free propylene is not observed by $^1$H NMR monitoring, which implies that the propylene is oligomerized as fast as it is formed. It is well established that *rac*-(EBI)ZrR$^+$ produces low-molecular-weight atactic polypropylene under such monomer-starved conditions.[12,13] Equations i−vi in Scheme 1 sum to eq 1. In the slow second stage (eq 2) **2** undergoes slow cleavage/ligand redistribution processes to generate additional *rac*-(EBI)ZrMe$^+$, which reacts with VC as shown 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.

The VC insertion/$\beta$-Cl elimination reaction of *rac*-(EBI)ZrMe$^+$ can be adapted to a catalytic conversion of VC to atactic oligopropylene under conditions in which **4** is continuously realkylated. Thus, reaction of *rac*-(EBI)ZrMe$_2$/MAO (Al/Zr = 17 000) with VC in toluene yields atactic oligopropylene (eq 4).



(4)

This reaction proceeds by generation of *rac*-(EBI)ZrMe$^+$, VC insertion, and $\beta$-Cl elimination to yield propylene and a *rac*-(EBI)ZrCl$^+$ species that realkylated by MAO (or the AlMe$_3$ therein). The propylene is oligomerized by *rac*-(EBI)ZrR$^+$. In a typical reaction, an autoclave fitted with a glass insert was charged with *rac*-(EBI)ZrMe$_2$ (3 $\mu$mol) and MAO (10 g of a 30% toluene solution, 51 mmol of Al) and exposed to VC (1 atm constant pressure) for 20 h at 25 °C in the absence of light. Workup yielded 0.25 g (6 mmol on a monomer basis) of atactic oligopropylene ($M_n$ = 500) as a colorless oil; this yield corresponds to the conversion of $2 \times 10^3$ equiv of VC per equiv of *rac*-(EBI)ZrMe$_2$. Similar results were obtained when *rac*-(EBI)ZrCl$_2$/MAO and (C$_5$Me$_5$)$_2$ZrCl$_2$/MAO were used. The mixed Al-Me/Cl product was not characterized.

No chlorine incorporation in the oligopropylene produced by eq 4 can be detected by NMR or elemental analysis. Interestingly, 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%) are also detected. In contrast, in the absence of VC, *rac*-(EBI)ZrMe$_2$/MAO produces polypropylene with vinylidene end groups at low propylene pressures, as $\beta$-H elimination is the dominant chain-transfer process.[12] These results imply that chain transfer in the propylene oligomerization in eq 4 occurs primarily by VC insertion, $\beta$-Cl elimination, and realkylation; i.e., VC is a chain-transfer agent.[14]

In summary, *rac*-(EBI)ZrR$^+$ species insert VC to produce *rac*-(EBI)ZrCH$_2$CHClR$^+$ intermediates which undergo rapid $\beta$-Cl elimination. VC polymerization is not observed because VC insertion of *rac*-(EBI)ZrCH$_2$CHClR$^+$ species is not competitive with $\beta$-Cl elimination. While our results do not allow quantitative comparisons of reaction rates, it is clear that *rac*-(EBI)ZrR$^+$ species insert propylene much faster than they insert VC since only oligopropylene is observed even at high [VC]/[propylene] ratios. This difference may arise because *rac*-(EBI)ZrR$^+$ preferentially coordinates propylene rather than VC, or because VC coordinates through the chloride rather than the C=C bond. Additionally, VC insertion may be disfavored because the Cl substituent destabilizes the partial positive charge on the $\beta$-carbon in the insertion transition state.[15] It is likely that the PVC observed in previous studies was formed by free radical polymerization.[1] On the other hand, it may be possible to develop novel metallocene-catalyzed reactions of VC (or other polar monomers), such as the dechlorination/oligomerization reaction reported here, by incorporating suitable realkylation steps in the process.

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**Supporting Information Available:** Synthetic procedures and characterization data for new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (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.

(13) (a) It is conceivable that the chloride in **3** could have originated from the CH$_2$Cl$_2$ solvent. However, conducting the reaction in benzene-$d_6$ results in the generation of **3**, B(C$_6$F$_5$)$_3$, and oligopropylene; in this case the chloride in **3** must derive from VC. (b) Treatment of *rac*-(EBI)ZrMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [NHMe$_2$Ph][B(C$_6$F$_5$)$_4$] followed by reaction with VC also yields oligopropylene. The fate of Zr in these reactions has not been determined; however, the B(C$_6$F$_5$)$_4^-$ anion is unchanged.

(14) Consistent with this conclusion, the saturated chain ends are predominantly $^i$Bu groups; the $^i$Bu/$^n$Pr ratio is ca. 100/3 by $^{13}$C NMR.

(15) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.