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# Active Sites in a Heterogeneous Organometallic Catalyst for the Polymerization of Ethylene

Damien B. Culver, Rick W. Dorn, Amrit Venkatesh, Jittima Meeprasert, Aaron J. Rossini, Evgeny A. Pidko, Andrew S. Lipton, Graham R. Lief,\* and Matthew P. Conley\*



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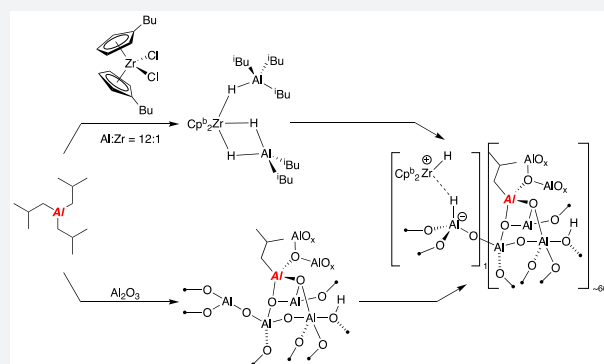


Article Recommendations



Supporting Information

**ABSTRACT:** Heterogeneous derivatives of catalysts discovered by Ziegler and Natta are important for the industrial production of polyolefin plastics. However, the interaction between precatalysts, alkylaluminum activators, and oxide supports to form catalytically active materials is poorly understood. This is in contrast to homogeneous or model heterogeneous catalysts that contain resolved molecular structures that relate to activity and selectivity in polymerization reactions. This study describes the reactivity of triisobutylaluminum with high surface area aluminum oxide and a zirconocene precatalyst. Triisobutylaluminum reacts with the zirconocene precatalyst to form hydrides and passivates  $\text{—OH}$  sites on the alumina surface. The combination of passivated alumina and zirconium hydrides formed in this mixture generates ion pairs that polymerize ethylene.



## INTRODUCTION

Ziegler and co-workers discovered that mixtures of triethylaluminum and zirconium acetylacetonate polymerize ethylene to high-density polyethylene under mild conditions in 1953, and two years later Natta reported that  $\text{TiCl}_4$  and  $\text{Et}_2\text{AlCl}$  mixtures polymerize propylene to stereoregular products (Figure 1a).<sup>1,2</sup> Derivatives from these initial discoveries evolved to heterogeneous catalysts used industrially that account for a majority of the polypropylene (PP, ~50 millions tons) and polyethylene (PE, ~100 million tons) produced per year. A key question related to the initial Ziegler–Natta solution catalysts was how the metal and the activator interact to form active organometallic species for polymerization reactions. This question becomes more difficult to address considering that most Ziegler–Natta catalysts are significantly more active when supported on  $\text{MgCl}_2$ .<sup>3</sup> Reactions of  $\text{Cp}_2\text{TiCl}_2$  ( $\text{Cp}$  = cyclopentadienyl) with  $\text{Et}_2\text{AlCl}$  provided preliminary evidence for the formation of ionized organometallic active species in polymerization reactions.<sup>4</sup>  $\text{Cp}_2\text{TiCl}_2/\text{Et}_2\text{AlCl}$  mixtures are not particularly active in polymerization, but the serendipitous discovery of methaluminoxane (MAO) activators resulted in soluble metallocene catalysts that have activities approaching those of heterogeneous Ziegler–Natta catalysts.<sup>5</sup> The isolation of reactive  $\text{Cp}_2\text{ZrMe}(\text{THF})^+$  established that cationic organometallic zirconium species are active in polymerization reactions,<sup>6</sup> and the design of efficient activators to form cationic organometallics led to general strategies that allowed for explicit molecular design of the

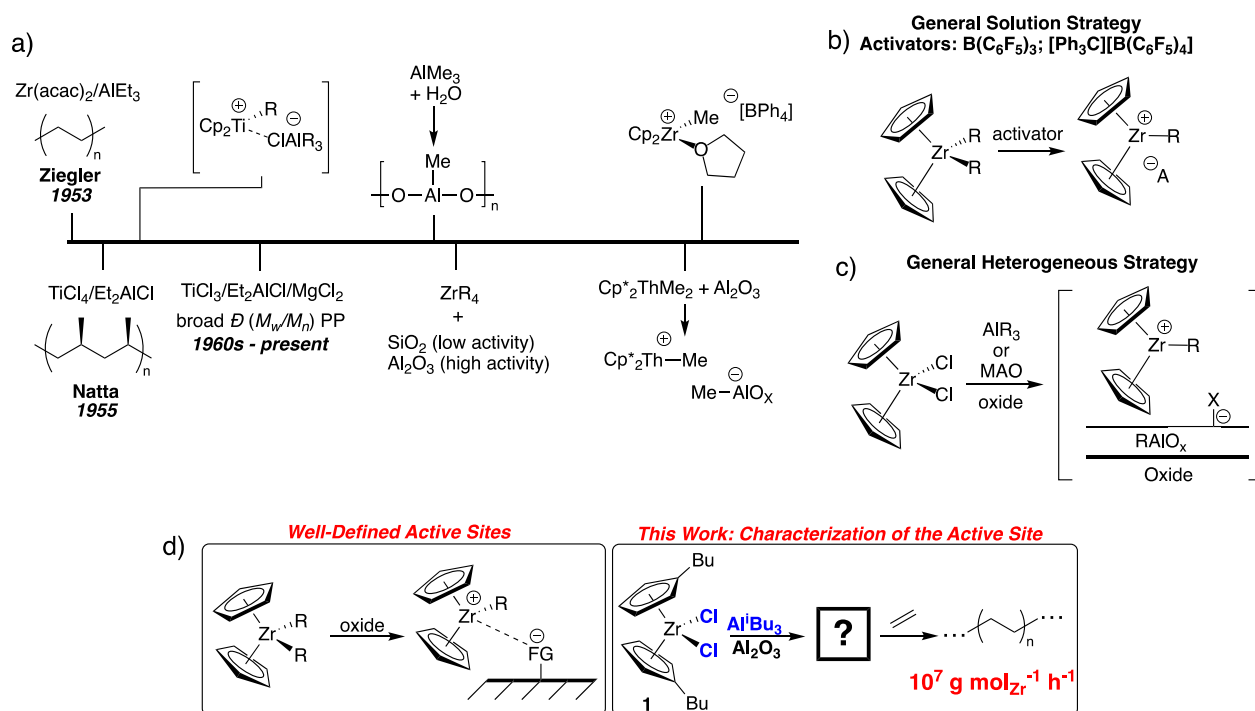
active site in polymerization reactions (Figure 1b).<sup>7,8</sup> These activators play important roles in generating catalysts that regulate molecular weight properties of the polymer and in copolymerization reactions in solution.<sup>9–11</sup>

Strategies to form cationic organometallic species on heterogeneous supports, the more important industrial class of catalysts for polymerization reactions, usually involve formulations containing a high surface area oxide, an excess of alkylaluminum (or MAO), and a metallocene precatalyst (Figure 1c).<sup>12,13</sup> Complications arising from the low quantity of active sites present in these catalysts prevent a detailed structural understanding of the active site. However, complementary studies of organometallics supported on oxides, which are likely important in these heterogeneous catalysts, arrived at similar conclusions as studies in solution. Tetraalkyl zirconium complexes supported on silica have low activity in polymerization reactions, but alumina supports provide much higher activities.<sup>14,15</sup> The origin of this support effect was not clear until solid-state NMR studies showed that  $\text{Cp}^*\text{ZrMe}_2$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) reacts with  $\text{Al}_2\text{O}_3$  to form  $[\text{Cp}^*\text{ZrMe}][\text{Me-AlO}_x]$  ion pairs,<sup>16,17</sup> which

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**Figure 1.** Evolution in the understanding of the Ziegler–Natta catalyst for olefin polymerization, showing key discoveries for homogeneous (top) and heterogeneous (bottom) catalysts (a). Current strategy to activate metallocenes in solution (b). Current strategy used industrially to form activated metallocenes on surfaces (c). Formation of well-defined sites on oxides with preformed organometallics, and the objective of this study to determine the active site structure in a model industrial catalyst for polymerization of ethylene (d).

also occurs in reactions of organozirconium complexes supported on  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2/\text{Al}_2\text{O}_3$ .<sup>18</sup> This model suggests that preformed organometallics interact with an appropriate oxide to form electrophilic ion pairs that are active in polymerization reactions, a strategy employed by several groups to understand these catalysts (Figure 1d).<sup>19–23</sup> Though compelling, these model systems differ significantly from heterogeneous catalysts used for most industrial applications because they are derived from precatalysts containing preformed M–R groups and do not contain a large excess of alkylaluminum required in commercial polymerization reactions with metallocene chloride precatalysts.

This study describes the generation and characterization of the catalytically active sites in a ternary 1,1'-dibutylzirconocene dichloride ( $\text{Cp}^b_2\text{ZrCl}_2$ , **1**)/triisobutylaluminum ( $\text{Al}^i\text{Bu}_3$ )/ $\text{Al}_2\text{O}_3$  catalyst for the polymerization of ethylene (Figure 1d).<sup>24,25</sup> This mixture is complex and results in a network of reactions in solution and on the surface of  $\text{Al}_2\text{O}_3$  to ultimately form catalytically active  $[\text{Cp}^b_2\text{Zr-H}][\text{H-AlO}_x]$  ion pairs on the  $\text{Al}^i\text{Bu}_3$ -passivated  $\text{Al}_2\text{O}_3$  surface. The formation of ion pairs relates this catalytic mixture to the solution organometallic catalysts and well-defined heterogeneous catalysts shown in Figure 1.

## RESULTS AND DISCUSSION

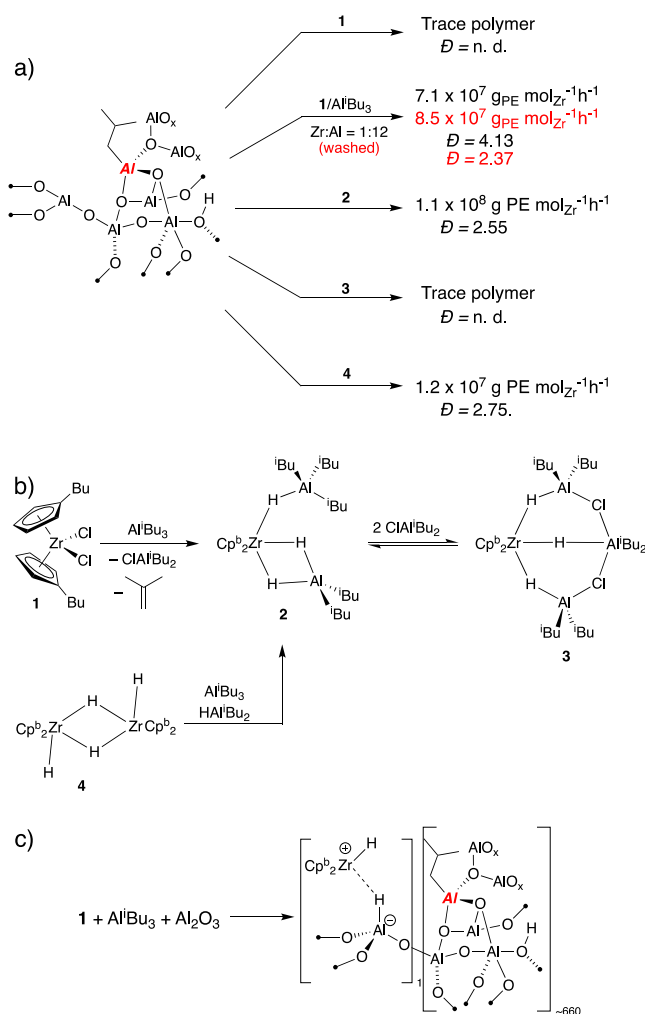
A mixture of **1**,  $\text{Al}^i\text{Bu}_3$ , and  $\text{Al}_2\text{O}_3$  at a Zr/Al molar ratio of 1:12 ( $[\text{Zr}] = 150 \mu\text{mol g}_{\text{Al}_2\text{O}_3}^{-1}$ ) is very active in ethylene polymerization ( $8.4 \times 10^7 \text{ g}_{\text{PE}} \text{ mol}_{\text{Zr}}^{-1} \text{ h}^{-1}$ ) and produces a modestly narrow distribution of high molecular weight PE ( $M_n = 90.8 \text{ kg mol}^{-1}$ ;  $D = M_w/M_n = 4.25$ ). ICP-OES analysis of the isolated solid catalyst after washing shows that only  $0.65 \mu\text{mol}$  of Zr  $\text{g}_{\text{cat}}^{-1}$  is present, indicating that most of the metallocene does not adsorb to the alumina surface. Omitting **1**,  $\text{Al}^i\text{Bu}_3$ , or

$\text{Al}_2\text{O}_3$  from the reaction mixture results in negligible polymerization activity (see the Supporting Information).

$\text{Al}^i\text{Bu}_3$  and  $\text{Al}_2\text{O}_3$  are expected to form a complex mixture of hydrolyzed alkylaluminum species bound to the  $\text{Al}_2\text{O}_3$  surface,<sup>26</sup> some of which may activate **1** similar to MAO in solution. The reaction of  $\text{Al}_2\text{O}_3$  calcined at  $600^\circ\text{C}$  ( $\sim 3 \text{ -OH nm}^{-2}$ ,  $0.93 \text{ mmol -OH g}_{\text{Al}_2\text{O}_3}^{-1}$ ) with excess  $\text{Al}^i\text{Bu}_3$  in pentane forms  $0.86 \text{ mmol}$  of isobutane  $\text{g}_{\text{Al}_2\text{O}_3}^{-1}$  indicating that most of the  $\text{-OH}$  groups on alumina react with  $\text{Al}^i\text{Bu}_3$ . Isobutene ( $0.19 \text{ mmol g}_{\text{Al}_2\text{O}_3}^{-1}$ ) and  $\text{HAl}^i\text{Bu}_2$  also form in this reaction.

The  $^{13}\text{C}$  cross-polarization magic angle spinning NMR (CPMAS) spectrum of  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  contains signals at 26 and 18 ppm for the Al– $^i\text{Bu}$  fragment (Figure S7).  $^1\text{H}$ – $^{27}\text{Al}$  dipolar recoupled insensitive nuclei enhancement polarization transfer (D-RINEPT) experiments recorded under fast MAS ( $\nu_r = 50 \text{ kHz}$ ) show that  $^1\text{H}$  NMR signals from the Al– $^i\text{Bu}$  fragment are near Al(IV) and Al(VI) sites on the  $\text{Al}_2\text{O}_3$  surface (see the Supporting Information for details). This result is consistent with a high coverage of Al– $^i\text{Bu}$  groups on the  $\text{Al}_2\text{O}_3$  surface. DFT studies of a hydrated (110)  $\text{Al}_2\text{O}_3$  surface containing  $3 \text{ -OH nm}^{-2}$  show exergonic adsorption and grafting of  $\text{Al}^i\text{Bu}_3$  onto the surface to form tetrahedral  $(\equiv\text{AlO})_2\text{Al}^i\text{Bu}(\text{O}(\text{AlO}_x)_2)$  shown in Figure 2a (see Supporting Information for details). Though a distribution of tetrahedral  $(\equiv\text{AlO})_2\text{Al}^i\text{Bu}(\text{O}(\text{AlO}_x)_2)$  is likely present on the alumina surface, the structure of these sites has little influence on catalysis because **1** reacts with  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  to form inactive polymerization catalysts, showing that MAO-type sites are not present on  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ .

$\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  is clearly not involved in the activation of **1** but is undoubtedly relevant to formation of active sites in this catalyst. Polymerization activity is recovered when  $\text{Al}^i\text{Bu}_3/$



**Figure 2.** Polymerization activity of  $(\equiv\text{AlO})_2\text{Al}^i\text{Bu}(\text{O}(\text{AlO}_x)_2)$ , formed from the reaction of  $\text{Al}^i\text{Bu}_3$  with  $\text{Al}_2\text{O}_3$ , with 1 or products of the reaction of 1 and excess  $\text{Al}^i\text{Bu}_3$  (a). The aluminum originating from the  $\text{Al}^i\text{Bu}_3$  is shown in red. Products formed in the reaction of 1 with excess  $\text{Al}^i\text{Bu}_3$  and the independent synthesis of 2, the major product in this reaction mixture (b). Generation of  $[\text{Cp}^b\text{Zr-H}][\text{H-AlO}_x/\text{Al}^i\text{Bu}_3]$  that is consistent with polymerization activity data (c).

$\text{Al}_2\text{O}_3$  is contacted with a mixture of 1 and  $\text{Al}^i\text{Bu}_3$  ( $\text{Zr}/\text{Al} = 1:12$ ). Removal of excess  $\text{Al}^i\text{Bu}_3$  from the solid catalyst prior to polymerization results in a catalyst that produces narrow molecular weight distributions of polymer ( $\bar{D} = 2.37$ ; Figure 2a) close to the expected value characteristic of single-site behavior ( $\bar{D} = 2$ ).

Under typical polymerization conditions,  $\text{Al}^i\text{Bu}_3$  is present at sufficient excess to fully saturate the  $\text{Al}_2\text{O}_3$  surface and react with 1. Indeed, the reaction of 1 with 12 equiv of  $\text{Al}^i\text{Bu}_3$  in deuterated methylcyclohexane ( $\text{C}_7\text{D}_{14}$ ) at typical concentrations for polymerization reactions forms a mixture of isobutene,  $\text{ClAl}^i\text{Bu}_2$ ,  $\text{HAl}^i\text{Bu}_2$ ,  $\text{Cp}^b\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)(\text{Al}^i\text{Bu}_3)$  (2), and  $\text{Cp}^b\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)_3(\mu\text{-Cl})_2$  (3, Figure 2b). The  $^1\text{H}$  NMR spectrum of this mixture at  $-40^\circ\text{C}$  ( $2:3 \approx 4:1$ ) contains Zr–H signals at  $-0.98$ ,  $-1.32$ , and  $-1.72$  ppm for 2 as well as the Zr–H signals for 3, which was previously reported.<sup>27</sup> 2 can be independently generated by mixing  $[\text{Cp}^b\text{ZrH}_2]_2$  (4) with equimolar  $\text{Al}^i\text{Bu}_3$  and  $\text{HAl}^i\text{Bu}_2$ .

The formation of 2 involves Zr–Cl for Al– $^i\text{Bu}$  exchange to form  $\text{ClAl}^i\text{Bu}_2$  and Zr– $^i\text{Bu}$  intermediates that undergo  $\beta$ -H

elimination to form Zr–H species and isobutene. Reactions of Zr–H with Al–Cl regenerate Zr–Cl and form  $\text{HAl}^i\text{Bu}_2$  that is needed to form 2 and 3. The large excess of  $\text{Al}^i\text{Bu}_3$  facilitates exhaustive exchange with the metallocene to ultimately form  $\text{Cp}^b_2\text{ZrH}_2$ , which is trapped by  $\text{HAl}^i\text{Bu}_3$  and  $\text{Al}^i\text{Bu}_3$  to form 2.

Figure 2a summarizes the polymerization activity of 2, 3, or 4 in the presence of  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ . 2 reacts with  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  to form active polymerization catalysts with similar activities and polymer properties as *in situ* catalysts, but 3 does not form active polymerization catalysts when contacted with  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ , showing that the alkylaluminum activator can dramatically affect polymerization productivities. 4 also reacts with  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  to form an active polymerization catalyst ( $1.2 \times 10^7 \text{ g PE mol}_{\text{Zr}}^{-1} \text{ h}^{-1}$ ;  $\bar{D} = 2.75$ ). The slightly lower activity of 4/ $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  is probably related to the higher Zr loading in this material ( $7.6 \mu\text{mol Zr g}_{\text{cat}}^{-1}$ ), which is beneficial for mechanistic studies. This collection of data indicates that  $\text{Al}^i\text{Bu}_3$  reacts with 1 to form 2, which is activated by  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  to form the ionized  $[\text{Cp}^b_2\text{Zr-H}][\text{H-AlO}_x/\text{Al}^i\text{Bu}_3]$  shown in Figure 2c.

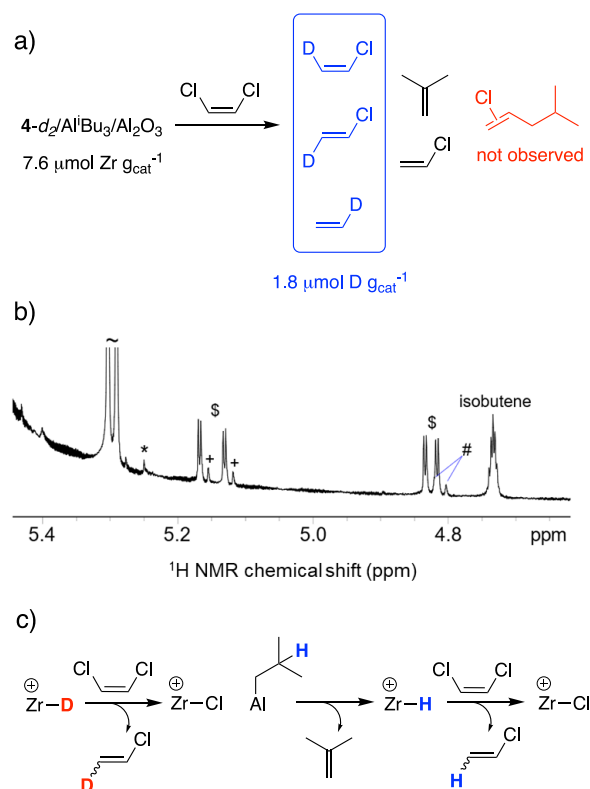
$[\text{Cp}^b_2\text{Zr-H}]^+$  sites in 4/ $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are expected to insert vinyl halides and undergo fast  $\beta$ -halide elimination to form unreactive  $[\text{Cp}^b_2\text{Zr-X}]^+$ .<sup>28,29</sup> Quantification of the products in this reaction correlates with the amount of zirconium sites capable of olefin insertion. The reaction of 4- $d_2$ / $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  (62% Zr–D) with excess *cis*-dichloroethylene forms *cis*/*trans*-vinyl chloride- $d_1$ , vinyl chloride, isobutene, and a small amount of ethylene (Figure 3a). An excerpt of the  $^1\text{H}$  NMR spectrum of this reaction mixture is shown in Figure 3b. On the basis of the  $^1\text{H}$  NMR peak integrals,  $1.8 \mu\text{mol g}^{-1}$  of vinyl chloride- $d_1$  form in this reaction, indicating that 23% of Zr–D $^+$  present in 4- $d_2$ / $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are active in olefin insertion reactions; this value is higher than suspected for heterogeneous polymerization catalysts formed in the presence of alkylaluminum activators but significantly lower than the active site counts for cationic metallocenes in solution.<sup>30</sup>

The unlabeled products probably form by the successive reactions of Zr–D $^+$  with *cis*-dichloroethylene shown in Figure 3c. Following  $\beta$ -chloride elimination, the surface-bound Zr–Cl $^+$  ( $\sim 0.02 \text{ nm}^{-2}$ ) is alkylated by a nearby Al– $^i\text{Bu}$  ( $\sim 3 \text{ nm}^{-2}$ ) that regenerates a Zr–H $^+$  and forms isobutene. Subsequent reaction of Zr–H $^+$  and *cis*-dichloroethylene results in the formation of vinyl chloride and Zr–Cl $^+$ . This scenario is consistent with the 1:1 ratio of isobutene: vinyl chloride- $d_0$  obtained from the  $^1\text{H}$  NMR spectrum in Figure 3b.

Deuterium is an NMR-active quadrupolar isotope (spin  $I = 1$ ). Solid-state  $^2\text{H}$  NMR spectra show characteristic broad powder patterns that are a result of interactions between the nuclear electric quadrupole moment,  $eQ$ , and the electric field gradient (EFG) tensor  $V$ , eq 1. The line shape of a  $^2\text{H}$  MAS NMR spectrum at the slow exchange limit is described by the quadrupolar coupling constant ( $C_Q$ , eq 2) and the asymmetry parameter ( $\eta$ , eq 3). Terminal M–D are expected to have  $\eta = 0$ , bridging M–D–M that deviate from linearity is expected to have  $\eta \neq 0$ , and  $C_Q$  is expected to increase as the effective nuclear charge increases.<sup>31</sup> Thus,  $^2\text{H}$  MAS NMR is capable of distinguishing between a variety of possible Zr–D structures in 4- $d_2$ / $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ .

$$V = \begin{bmatrix} V_{11} & 0 & 0 \\ 0 & V_{22} & 0 \\ 0 & 0 & V_{33} \end{bmatrix} \quad (1)$$





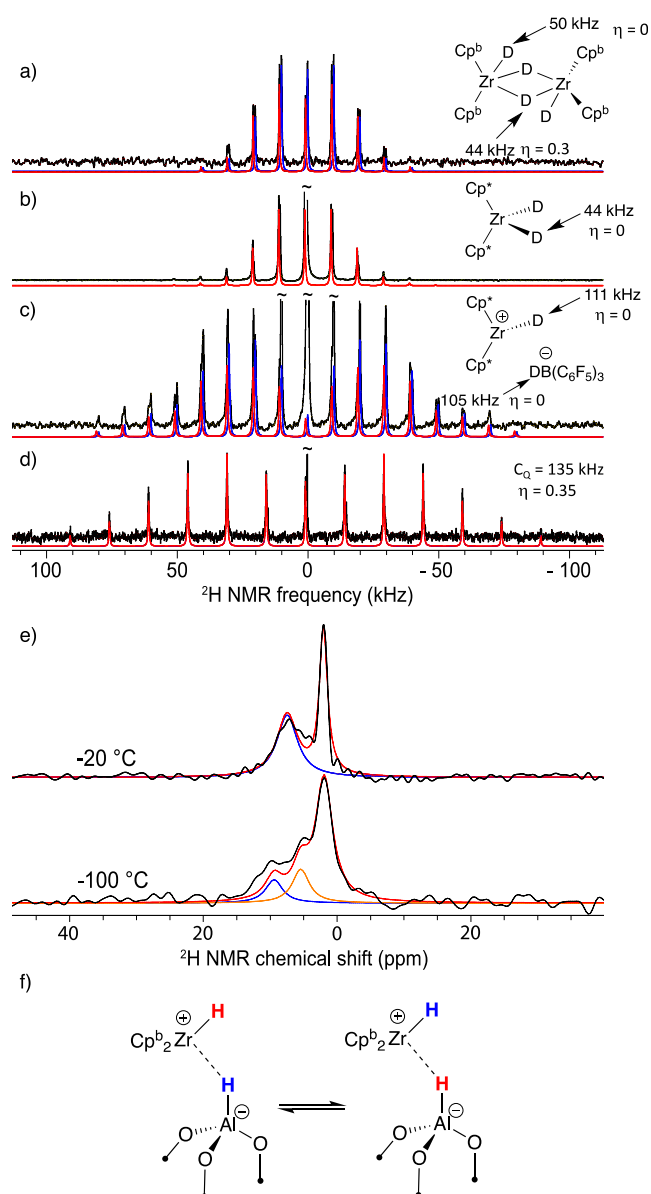
**Figure 3.** Reaction of  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  with *cis*-dichloroethylene to form reaction products (a). Excerpt of the  $^1\text{H}$  NMR spectrum from 4.6–5.4 ppm (b). The symbols above each signal in (b) correspond to  $\sim = {}^{13}\text{C}$  satellite from *cis*-dichloroethylene;  $*$  = ethylene;  $\$$  = vinyl chloride;  $+$  = *trans*-vinyl chloride- $d_1$ ;  $\#$  = *cis*-vinyl chloride- $d_1$ . Proposed mechanism that accounts for formation of vinyl chloride- $d_1$  and vinyl chloride- $d_0$  (c).

$$C_Q = \frac{e^2 Q V_{33}}{h} \quad (2)$$

$$\eta = \frac{V_{11} - V_{22}}{V_{33}} \quad (3)$$

**Figure 4** shows  $^2\text{H}$  MAS NMR spectra for  $4\text{-}d_2$ , monomeric  $(\text{C}_5\text{Me}_5)_2\text{ZrD}_2$ ,<sup>32–34</sup>  $[(\text{C}_5\text{Me}_5)_2\text{ZrD}][\text{DB}(\text{C}_6\text{F}_5)_3]$ ,<sup>35</sup> and  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ . The  $C_Q$  and  $\eta$  values extracted from this data are consistent with the expectations mentioned above. The  $^2\text{H}$  MAS NMR spectrum of  $4\text{-}d_2$  is shown in **Figure 4a** and contains two sets of peaks assigned to the terminal  $\text{Zr}-\text{D}$  at 5.3 ppm with a  $C_Q$  of 50 kHz and  $\eta = 0$ , and the bridging  $\text{Zr}-\text{D}-\text{Zr}$  at  $-3.3$  ppm with a  $C_Q$  of 44 kHz and  $\eta = 0.3$ , close to values reported for  $[\text{Cp}_2\text{ZrD}_2]_2$ .<sup>36</sup> The magnitude of  $C_Q$  for the  $\text{Zr}-\text{D}$  in  $(\text{C}_5\text{Me}_5)_2\text{ZrD}_2$  ( $C_Q = 44$ ;  $\eta = 0$ , **Figure 4b**) is similar to  $4\text{-}d_2$ , indicating that neutral  $\text{Zr}-\text{D}$  are characterized by small  $C_Q$  values. The  $^2\text{H}$  MAS NMR spectrum of  $[(\text{C}_5\text{Me}_5)_2\text{ZrD}][\text{DB}(\text{C}_6\text{F}_5)_3]$ , shown in **Figure 4c**, contains a signal for the  $\text{Zr}-\text{D}^+$  at 9.3 ppm with a  $C_Q$  of 111 kHz ( $\eta = 0$ ) and a signal at 0.7 ppm ( $C_Q = 105$ ;  $\eta = 0$ ) for the  $\text{D}-\text{B}(\text{C}_6\text{F}_5)_3$ . Both  $(\text{C}_5\text{Me}_5)_2\text{ZrD}_2$  and  $[(\text{C}_5\text{Me}_5)_2\text{ZrD}][\text{DB}(\text{C}_6\text{F}_5)_3]$  also contain a sharp signal with a narrow  $C_Q \approx 20$  kHz for  $\text{sp}^3$  C–D bonds that are under fast rotational exchange on the  $^2\text{H}$  NMR time scale, indicating that some deuterium is incorporated into the  $\text{C}_5\text{Me}_5$  ligand.<sup>37</sup>

The  $^2\text{H}$  MAS NMR spectrum of  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  obtained at 18.8 T at 15 kHz spinning and  $-20^\circ\text{C}$  is shown in **Figure**



**Figure 4.**  $^2\text{H}$  MAS NMR spectrum of dimeric  $[\text{Cp}_2\text{ZrD}_2]_2$  (a), monomeric  $\text{Cp}^*_2\text{ZrD}_2$  (b),  $[\text{Cp}^*\text{ZrD}][\text{DB}(\text{C}_6\text{F}_5)_3]$  (c), and  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  recorded at  $-20^\circ\text{C}$  (d). Expansion of the  $^2\text{H}$  MAS NMR spectrum from 45 to  $-40$  ppm of  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  recorded at  $-20^\circ\text{C}$  (top) and  $-100^\circ\text{C}$  (e). Experimental spectra are shown in black, and simulations are shown in red, blue, or orange. Zr–H/H–Al exchange consistent with the  $^2\text{H}$  MAS NMR data (f).

**4d.** This spectrum contains signals at 2.0 and 7.5 ppm. The signal at 2.0 ppm ( $C_Q = 32$  kHz,  $\eta = 0.2$ ) is also present in  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  and is assigned to the natural abundance  $^2\text{H}$  signal from  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ , but could also be a result of H/D exchange between **4** and  $\text{Al}-^i\text{Bu}$  groups that occurs in the synthesis of  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ . The signal at 7.5 ppm has  $C_Q$  of 129 kHz and  $\eta$  of 0.35 is suggestive of a bridging  $\text{Zr}-\text{D}^+$  site and supports the formation of  $[\text{Cp}_2\text{Zr}-\text{D}][\text{D}-\text{AlO}_x]$  as the active species in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ . However, the signal for the  $[\text{D}-\text{AlO}_x]$  site is not present in the spectrum in **Figure 4d**. An expansion of the  $^2\text{H}$  MAS spectrum recorded at  $-20^\circ\text{C}$  and  $-100^\circ\text{C}$  is shown in **Figure 4e**. The spectrum at  $-100^\circ\text{C}$  contains a signal at 1.9 ppm for the surface  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  ( $C_Q = 30$  kHz,  $\eta = 0.3$ ), which is slightly broader than the signal

recorded at  $-20\text{ }^{\circ}\text{C}$ . This spectrum also contains signals at 9.3 ppm ( $C_Q = 150\text{ kHz}$ ,  $\eta = 0$ ), similar to the chemical shift of the  $\text{Zr}-\text{D}^+$  in  $[(\text{C}_5\text{Me}_5)_2\text{Zr}-\text{D}]^+$  and assigned to the terminal  $\text{Zr}-\text{D}^+$  of the cationic  $[\text{Cp}^b_2\text{Zr}-\text{D}]^+$  fragment in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ , and 5.3 ppm ( $C_Q = 100\text{ kHz}$ ,  $\eta = 0.5$ ) assigned to the anionic  $[\text{D}-\text{AlO}_x]^-$  fragment in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ .

These results are consistent with the exchange process shown in Figure 4f. At  $-20\text{ }^{\circ}\text{C}$ , the  $^2\text{H}$  NMR signals for  $[\text{Cp}^b_2\text{Zr}-\text{D}][\text{D}-\text{AlO}_x]^-$  undergo site exchange that results in average chemical shifts, reduced  $C_Q$ , and perturbed  $\eta$  values that depend on the motion these two sites, which accounts for the observation of only one  $^2\text{H}$  NMR signal in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  at  $-20\text{ }^{\circ}\text{C}$ . Similar behavior was encountered in metallocenium  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^+$  ion pairs,<sup>38</sup> suggesting that the  $[\text{D}-\text{AlO}_x]^-$  anions are weakly coordinated to the zirconium deuteride cation in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ . At  $-100\text{ }^{\circ}\text{C}$ , this exchange process is slow on the  $^2\text{H}$  NMR time scale, and individual signals for  $[\text{Cp}^b_2\text{Zr}-\text{D}][\text{D}-\text{AlO}_x]^-$  in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are obtained.  $-100\text{ }^{\circ}\text{C}$  is cold enough to slow the exchange between the active sites in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  but not cold enough to slow rotation in the  $\text{sp}^3\text{ C}-\text{D}$  bonds in  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  ( $C_Q \approx 170\text{ kHz}$ ). The  $C_Q$  and  $\eta$  values for the  $[\text{Cp}^b_2\text{Zr}-\text{D}]^+$  fragment in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are in agreement with the trends observed in the representative molecular zirconium deuterides shown in Figure 4.

The bridging  $\text{Zr}-\text{D}-\text{Al}$  in  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  is similar to other cationic zirconium hydrides containing bridging  $\text{Zr}-\text{H}-\text{E}$  ( $\text{E} = \text{B}(\text{C}_6\text{F}_5)_3, \text{HAIR}_2$ ) in solution.<sup>39–41</sup> In many cases, displacement of the bridging hydride by ethylene is slow relative to chain growth in olefin polymerization reactions in solution.<sup>42–45</sup> DFT studies of  $[\text{Cp}_2\text{ZrMe}][\text{MeAlO}_x]^-$ , formed from the reaction of  $\text{Cp}_2\text{ZrMe}_2$  with fully dehydroxylated alumina, showed that the metallocenium fragment is more weakly coordinated to certain sites on the alumina surface than a typical  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^+$  weakly coordinating anion.<sup>46</sup> This study, and the dynamics of  $4\text{-}d_2/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  from the  $^2\text{H}$  MAS NMR data reported here, suggests that  $[\text{D}-\text{AlO}_x]^-$  is also bound more weakly to the  $[\text{Cp}^b_2\text{Zr}-\text{D}]^+$  fragment than typical bridging hydrides in solution and is consistent with the high polymerization activity of  $4/\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$ .

## CONCLUSION

The combination of **1**,  $\text{Al}^i\text{Bu}_3$ , and  $\text{Al}_2\text{O}_3$  results in active catalysts for the polymerization of ethylene that approach single-site behavior under appropriate conditions. Excess  $\text{Al}^i\text{Bu}_3$  is essential in this mixture to rapidly react with the  $-\text{OH}$  sites on  $\text{Al}_2\text{O}_3$  and to activate **1** to form **2**.<sup>47</sup> Both of these reactions result in unexpected reaction products that play critical interconnected roles that lead to the formation of active sites in this catalyst. The distribution of  $(\equiv\text{AlO})_2\text{Al}^i\text{Bu}(\text{O}(\text{AlO}_x)_2)$  present in  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are not capable of reacting with **1** to form active sites. This result is surprising given the well-known ability of partially hydrolyzed alkylaluminums to activate metallocene precatalysts in solution.<sup>9</sup> However, the  $\text{Al}-^i\text{Bu}$  groups in  $\text{Al}^i\text{Bu}_3/\text{Al}_2\text{O}_3$  are critical because they prevent the reaction of  $-\text{OH}$  on  $\text{Al}_2\text{O}_3$  with the zirconium hydrides formed by the reaction of  $\text{Al}^i\text{Bu}_3$  and **1**. Passivation of  $-\text{OH}$  groups on  $\text{Al}_2\text{O}_3$  with  $\text{Al}^i\text{Bu}_3$  allows **2** to react with Lewis sites still present on the passivated  $\text{Al}_2\text{O}_3$  surface<sup>48,49</sup> and is similar to the reactions of  $\text{Cp}^*_2\text{ThMe}_2$  with fully dehydroxylated alumina reported over 35 years ago.<sup>17</sup> The data presented here connects a typical ternary heterogeneous catalyst formulation relevant to industry to well-defined organo-

metallics supported on oxides and homogeneous metallocene catalysts. This understanding gives a simple model to guide catalyst formulations that may result in heterogeneous catalysts for the synthesis of advanced polyolefin materials using a more rational structure–property optimization strategy.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscentsci.1c00466>.

Experimental details, computational details solid-state NMR spectra, FTIR data (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Matthew P. Conley – Department of Chemistry, University of California, Riverside, California 92507, United States;

orcid.org/0000-0001-8593-5814;

Email: [matthew.conley@ucr.edu](mailto:matthew.conley@ucr.edu)

Graham R. Lief – Bartlesville Research and Technology Center, Chevron Phillips Chemical, Bartlesville, Oklahoma 74003, United States; Email: [liefgr@cpchem.com](mailto:liefgr@cpchem.com)

### Authors

Damien B. Culver – Department of Chemistry, University of California, Riverside, California 92507, United States;

orcid.org/0000-0001-8294-6059

Rick W. Dorn – Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

Amrit Venkatesh – Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States; orcid.org/0000-0001-5319-9269

Jittima Meeprasert – Inorganic Systems Engineering Group, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Delft 2629 HZ, The Netherlands

Aaron J. Rossini – Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States; orcid.org/0000-0002-1679-9203

Evgeny A. Pidko – Inorganic Systems Engineering Group, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Delft 2629 HZ, The Netherlands; orcid.org/0000-0001-9242-9901

Andrew S. Lipton – Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States; orcid.org/0000-0003-4937-4145

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acscentsci.1c00466>

### Notes

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