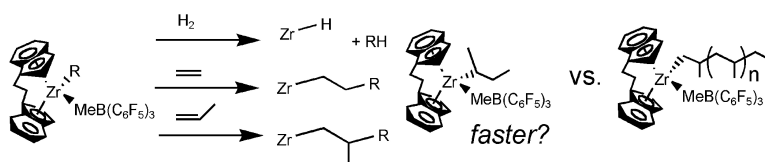Communication

Reactivity of Secondary Metallocene Alkyls and the Question of Dormant Sites in Catalytic Alkene Polymerization

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Reactivity of Secondary Metallocene Alkyls and the Question of Dormant Sites in Catalytic Alkene Polymerization

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Pooling of catalyst as inactive or dormant species decreases catalytic efficiency. Concordantly, for metallocene-catalyzed propene polymerizations[1] it is commonly accepted that catalyst efficiency is lessened by accumulation of catalyst in the form of dormant 2° metal polymeryls[2] at the expense of more reactive 1° metal polymeryls. Empirical support for such buildup of 2° polymeryls comes from (1) propene hydrooligomerization reactions that reveal high fractions of butyl end groups resulting from hydrogenolysis of 2° alkyls[3] and (2) microstructure analysis of propene/ethene [1-13C] copolymers.[4] These results led to estimates of 40−95% of the catalyst in the form of dormant 2° sites.[4] Secondary alkyls result from 2,1-insertion of propene, a relatively infrequent event for common metallocene catalysts (ca. 1 per hundreds of insertions).[5] Thus, significant accumulation of 2° polymeryls requires that they react hundreds-fold more slowly with propene than 1° polymeryl active sites. Herein we demonstrate the converse: for [*rac*-(C₂H₄(1-indenyl)₂)ZrMe][MeB(C₆F₅)₃]-catalyzed polymerizations, 2° zirconium alkyls are *remarkably reactive* and cannot constitute a dormant species.

Previous kinetic and quench/label studies in our laboratory provided no evidence for the accumulation of 2° zirconium polymeryls.[6] For example, quenching catalytic polymerization solutions in the initial rate regime (catalyst = [*rac*-(C₂H₄(1-indenyl)₂)ZrMe][X], where [X] = [MeB(C₆F₅)₃]⁻, [B(C₆F₅)₄]⁻, or [MeAl(C₆F₅)₃]⁻; monomer = 1-hexene or propene) with MeOD results in D-labels at the primary position that account for >90% of the total catalyst present. No D-labels were found in secondary positions of the quenched polymer. Direct observation of propagating species by low-temperature (<−40 °C) NMR shows only 1° zirconium polymeryls, and the rates of propene and 1-hexene polymerization match well with those extrapolated from higher temperatures. One can reasonably argue that the steady-state distribution of catalyst species found under normal catalytic conditions has not been reached during low temperature or rapid-quench conditions. For such scenarios, the positions of D-labels in the polymer need not reflect the catalyst speciation during working catalytic conditions. Therefore, we took a less ambiguous approach: direct measurement of the reactivity of 1° and 2° zirconium alkyls.

Light yellow zirconocene complexes, *rac*-(C₂H₄(1-indenyl)₂)Zr-(Me)(*n*-butyl) (**2**) and *rac*-(C₂H₄(1-indenyl)₂)Zr(Me)(*sec*-butyl) (**3**), are generated in situ from *rac*-(C₂H₄(1-indenyl)₂)Zr(Me)(Cl) (**1**) and 1 equiv of the corresponding alkyllithium reagent in toluene-*d*₈ at −30 °C for 3 h.[7] The reaction of **1** with *sec*-butyllithium is not stereoselective; two diastereomers of **3** are formed in approximately equal amounts (Figure 1). Warming either **2** or **3** to room temperature results in methane evolution and uncharacterized green compounds. Reaction of **2** or **3** at −80 °C with B(C₆F₅)₃ produces the bright orange ion pairs **4** and **5**, respectively. The ion pair **5** comprises equal amounts of two diastereomers. Small amounts of unreacted **1** and *rac*-(C₂H₄(1-indenyl)₂)ZrMe₂ remain
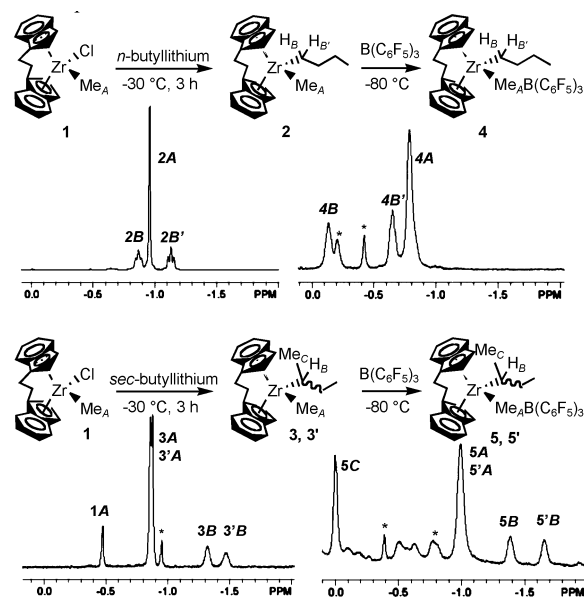

Figure 1. ¹H NMR spectra taken in toluene-*d*₈ at −80 °C that demonstrate the formation of dialkyls **2** and **3** (two diastereomers) and their transformation to contact ion pairs **4** and **5** (two diastereomers). Asterisks denote impurities due to **6** and **7**.

after consumption of the alkyllithium reagent. However, the ion pairs produced upon addition of B(C₆F₅)₃, [*rac*-(C₂H₄(1-indenyl)₂)-Zr(Cl)][MeB(C₆F₅)₃] (**6**), and *rac*-(C₂H₄(1-indenyl)₂)Zr(Me)[MeB-(C₆F₅)₃] (**7**) are inert in subsequent reactions.

Thermal instability limits the conditions for which the reactions of the ion pair diastereomers of **5** can be observed. At −80 °C, the two diastereomers of **5** isomerize to **4** quantitatively with similar half-lives of about 5 h; at −40 °C, the isomerization half-life is ca. 20 min.

Addition of 5−10 equiv of propene to **5** at −80 °C in toluene-*d*₈ enables direct comparison of the rates of propene insertion into 1° and 2° zirconium alkyls without significant isomerization. The first insertion of propene into the Zr−*sec*-butyl bond is first-order in [**5**] and [propene] with a rate constant of 0.09(2) M⁻¹ s⁻¹ at −80 °C; no significant distinction between the diastereomers of **5** could be made. For [propene] = 0.01 M this corresponds to a ∼13 min half-life for disappearance of **5**. Subsequent insertions of propene into the resulting 1° zirconium polypropenyl proceed with the second-order rate constant 0.13(1) M⁻¹ s⁻¹ at −80 °C, a value that is consistent with prior measurements at higher temperatures.[7] Thus, at −80 °C, propene 1,2-insertion into a model 2° zirconium alkyl is nearly as fast as insertion into the subsequent 1° zirconium alkyl. Because formation of 2° Zr−polymeryls is such an infrequent event, *the observed ratio of propene insertion rates (k²°/k¹° ≈ 1/1.4) precludes significant accumulation of catalyst as dormant secondary sites.*

If secondary alkyls are not dormant sites, why do hydrooligomerization studies exhibit such high concentrations of butyl end groups? Direct measurement of hydrogenolysis rates provides the critical data. Reaction of H_2 with the zirconium alkyl ion pairs yields $[rac\text{-}(C_2H_4(1\text{-indenyl})_2)Zr(Me)][HB(C_6F_5)_3]$ and the corresponding alkane. Hydrogenolysis rates are first-order in [Zr–alkyl] and [H_2]; at -40 °C, the reaction rate constants are $3.1(8) \times 10^{-2}$ and $2.1(7) \times 10^{-2}$ M^{-1} s^{-1} for reactions of 0.002 M H_2 and 0.008 M concentrations of the 1° zirconium alkyls $[rac\text{-}(C_2H_4(1\text{-indenyl})_2)\text{-}Zr(\text{polypropenyl})(MeB(C_6F_5)_3)]$ and $[rac\text{-}(C_2H_4(1\text{-indenyl})_2)Zr\text{-}(\text{polyhexenyl})(MeB(C_6F_5)_3)]$, respectively. In marked contrast, reaction of 0.003 M H_2 with 0.008 M **5** at -80 °C completes in less than 90 s, giving a conservative lower limit for the rate constant of 3 M^{-1} s^{-1}. Even ignoring the 40° temperature difference, *H_2 reacts at least 100-hundred times faster with a model 2° zirconium alkyl than with authentic 1° Zr–polymeryls of propene and hexene*. Thus, it appears that propene hydrooligomerization results in high fractions of butyl end groups by virtue of the much higher reactivity of 2,1-insertion products with H_2, not because the catalyst accumulates as 2° Zr polymeryls.[3] This result has important implications for understanding polymer molecular weight control as effected by chain transfer to H_2: catalyst responsivity to H_2 in the feed should correlate, at least partially, with the frequency of 2,1-insertions.
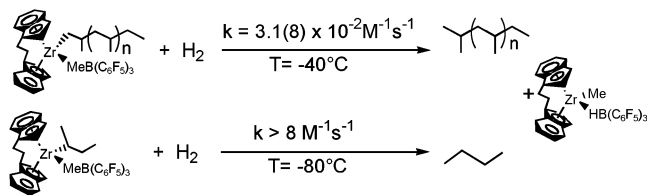
Do ethene insertion rates follow the reactivity trends exhibited by hydrogenolysis reactions? Ethene insertion rates are too fast to measure directly by NMR, even at -80 °C. Therefore, a competition experiment between **4** and **5** was devised. Complex **5** was generated, then allowed to isomerize to **4** until a 1:1 mixture of the two species was obtained. Approximately 0.5 to 1 equiv (based on the combined concentrations of **4** and **5**) of ethene [1-^{13}C] were added at -80 °C. The ^{13}C NMR spectra of the Zr–CH_2–R region for the competition and control experiments are shown in Figure 2.
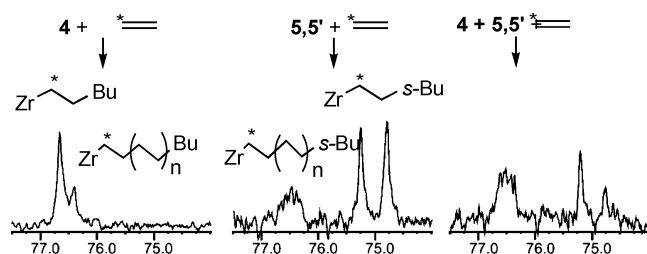

Figure 2. ^{13}C NMR spectra in the Zr–CH_2–R region showing species formed upon the addition of ca. 0.5 to 1 equiv of ethene [1-^{13}C] at -80 °C to **4** (far left), **5** (middle), and a 1:1 mixture of **4** and **5** (ca. 3:1 mixture of diastereomers) in a competition experiment.

Resonances for single insertion of ethene [1-^{13}C] appear at 76.7 ppm for **4** and 75.3 and 74.8 ppm for the diasteromers of **5**; multiple insertions yield resonances in the range of 76.3–76.6 ppm. Clearly,

ethene insertion into **5** is at least as fast as insertion into **4**. Note that the 1° alkyl model, **4**, used here is not substituted in the β-position and, hence, is expected to be 5–100 times more reactive toward ethene insertion than β-substituted polymeryl intermediates.[9] We conclude that 2° Zr–polymeryls, as represented by **5**, react faster with ethene by 1 or 2 orders of magnitude relative to 1° Zr–polypropenyl intermediates.

Knowledge of the fundamental reactivities of metal alkyl isomers is essential to understanding selectivity and activity patterns in metal-catalyzed transformations. This work demonstrates that (1) secondary alkyls are not dormant in 1-alkene polymerization catalyzed by $[rac\text{-}(C_2H_4(1\text{-indenyl})_2)Zr(Me)(MeB(C_6F_5)_3)]$ and (2) prior hydrogenolysis and ethene incorporation data may reflect the higher reactivity of secondary alkyls rather than their dormancy. Modification of catalytic components such as counterions, solvent, and scavengers can dramatically influence polymerization rates. Whether our conclusions generalize to such modifications is unclear.

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(5) Analysis of polypropene microstructure data obtained from ^{13}C NMR data of propene polymerizations (1.0×10^{-4} M $rac\text{-}(C_2H_4(1\text{-indenyl})_2)ZrMe_2$, 1.5×10^{-4} M $B(C_6F_5)_3$, 0.20−6.2 M propene in toluene, 20−30 °C) show that 2,1-regioerrors occur about once every 200 insertions.

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(7) (a) Representative NMR data (8.5×10^{-3} M, toluene-d_8, -80 °C): **1** ^{1}H Zr–CH_3 −0.46. **2** ^{1}H Zr–$CHH'R$ −0.85, Zr–$CHH'R$ −1.16, Zr–CH_3 −0.95. **4** ^{1}H Zr–$CHH'R$ −0.11, Zr–$CHH'R$ −0.64, Zr–CH_3–B −0.78; ^{11}B −14.2. **3** ^{1}H Zr–$CHCH_3R$ −1.33, −1.49, Zr–$CHCH_3R$ 0.92, 0.73, Zr–CH_3 −0.85, −0.88. **5** ^{1}H Zr–$CHCH_3R$ −1.67, −1.40, Zr–$CHCH_3R$ −0.01, 0.96 Zr–CH_3–B −1.00; ^{11}B −14.4, −14.5. **6** ^{1}H Zr–CH_3–B −0.19; ^{11}B −13.5. (b) See Supporting Information for full experimental details.

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