

Cationic Alkylaluminum-Complexed Zirconocene Hydrides as Participants in Olefin Polymerization Catalysis

Steven M. Baldwin,[†] John E. Bercaw,^{*,†} and Hans H. Brintzinger^{*,‡}

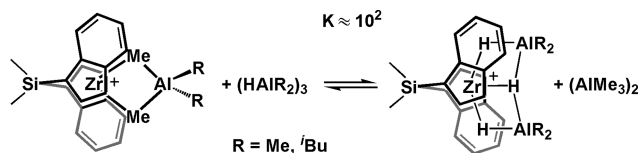
Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States, and Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

Received June 9, 2010; E-mail: Bercaw@caltech.edu; Hans.Brintzinger@uni-konstanz.de

Abstract: The alkylaluminum-complexed zirconocene trihydride cation $[(SBI)Zr(\mu-H)_3(Al^iBu_2)_2]^+$, which is obtained by reaction of $(SBI)ZrCl_2$ with $[Ph_3C][B(C_6F_5)_4]$ and excess HA^iBu_2 in toluene solution, catalyzes the formation of isotactic polypropene when exposed to propene at $-30\text{ }^\circ\text{C}$. This cation remains the sole observable species in catalyst systems free of $AlMe$ compounds. In the presence of $AlMe_3$, however, exposure to propene causes the trihydride cation to be completely converted, under concurrent consumption of all hydride species by propene hydroalumination, to the doubly Me-bridged cation $[(SBI)Zr(\mu-Me)_2AlMe_2]^+$. The latter then becomes the resting state for further propene polymerization, which produces, by chain transfer to Al, mainly $AlMe_2$ -capped isotactic polypropene.

Polymerization of α -olefins by zirconocene-based catalysts—while being applied on industrial scales—is still not sufficiently understood with regard to its mechanism, as exemplified by recent reports that about half the zirconocene content of such catalyst systems is present in the form of unidentified species.^{1,2} We have recently observed that the Me-bridged heterodinuclear cation $[(SBI)Zr(\mu-Me)_2AlMe_2]^+$, a known constituent of catalyst systems activated by methylalumoxane (MAO),³ reacts reversibly with alkylaluminum hydrides to form the previously unreported alkylaluminum-complexed zirconocene trihydride cation $[(SBI)Zr(\mu-H)_3(AlR_2)_2]^+$ (Scheme 1).⁴

Scheme 1



An equilibrium constant of ca. 10^2 , determined for the reaction shown in Scheme 1,⁴ indicates that substantial portions of any MAO-activated zirconocene catalyst will be converted to the trihydride cation whenever such a catalyst system acquires hydride equivalents. Since many recipes seek to increase the activity and/or stability of zirconocene-based catalysts by addition of diisobutylaluminum hydride⁵ or of triisobutylaluminum⁶ (from which hydride equivalents can be derived by elimination of isobutene), alkylaluminum-complexed zirconocene trihydride cations are likely to be abundant in such catalyst systems. We have thus set out to investigate which roles cationic trihydride complexes of this type

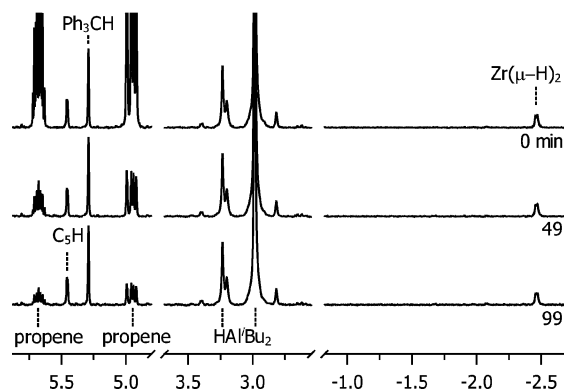


Figure 1. ^1H NMR spectra of a toluene- d_8 solution of the $\{Al^iBu_2\}$ -complexed trihydride cation $[(SBI)Zr(\mu-H)_3(Al^iBu_2)_2]^+$ immediately (top trace) and 49 and 99 min after warming to $-30\text{ }^\circ\text{C}$ in the presence of 20 equiv of propene (for experimental details, see Supporting Information).

might play in zirconocene-based catalyst systems for the polymerization of α -olefins.

When a solution of $[(SBI)Zr(\mu-H)_3(Al^iBu_2)_2]^+$, generated by reacting $(SBI)ZrCl_2$ in toluene- d_8 with 20 equiv of HA^iBu_2 and 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, is treated with 20 equiv of propene at $-30\text{ }^\circ\text{C}$, ^1H NMR spectra taken at regular intervals give results as shown in Figure 1: Diminishing signals of propene indicate its steady consumption, while signals due to HA^iBu_2 and the C_5H and $Zr(\mu-H)_2$ signals of $[(SBI)Zr(\mu-H)_3(Al^iBu_2)_2]^+$ at 5.45 and -2.47 ppm , respectively, remain constant in size throughout the reaction. Signals assignable to any new zirconocene or alkylaluminum species are not detectable in such catalyst systems after reaction with either 20 or 40 equiv of propene.

^{13}C NMR spectra of the polymer product, isolated from such a reaction mixture after quenching with acidified methanol,⁷ document the formation of isotactic polypropene (97% [mmmm]). Its ^1H NMR shows the customary vinylidene end groups,⁸ while GPC analysis yields a normal polydispersity index (PDI) of 1.90, together with an unexpectedly high mean degree of polymerization, $P_n \approx 1880$ (see Supporting Information).

That the mean chain lengths of the polymer products exceeds the initial $[\text{propene}]/[\text{Zr}]$ ratio by almost 2 orders of magnitude indicates that the available monomer is incorporated into Zr-bound polymer chains only at a small fraction of the Zr centers present. Such a situation will typically arise if chain growth is faster than chain initiation, which in this case probably occurs by insertion of propene into one of the Zr–H bonds of the hydride cation $[(SBI)Zr(\mu-H)_3(Al^iBu_2)_2]^+$, e.g., under formation of reactive contaction pairs of the type $[(SBI)ZrCH_2R^+ \cdots (F_5C_6)_4B^-]$.⁹

The NMR data of the polymer product show that chain growth is terminated mainly by β -hydride transfer from Zr-bound polymer

[†] California Institute of Technology.

[‡] Universität Konstanz.

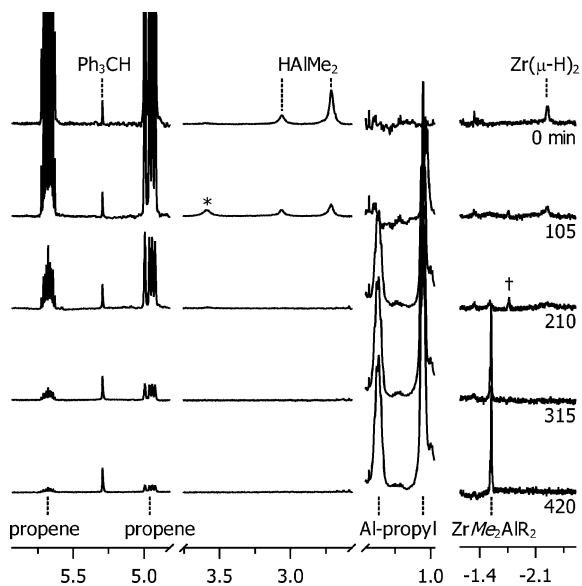


Figure 2. ^1H NMR spectra of a toluene- d_8 solution of the cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlMe}_2)_2]^+$ taken immediately (top trace) and 105, 210, 315, and 420 min after warming to -30°C in the presence of 40 equiv of propene. †, signal due to intermediate species;¹⁴ *, signal due to AlR_3 adduct of HAlMe_2 . For experimental details, see Supporting Information.

chains either to Zr or propene. Any zirconocene hydride thus generated, e.g., of the type $[(\text{SBI})\text{ZrH}^+\cdots(\text{F}_5\text{C}_6)_4\text{B}^-]$, would be expected to rapidly react either with propene to start a new chain or with HAl^iBu_2 under regeneration of the trihydride cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)_2]^+$, such that this cation remains the dominant catalyst resting state.

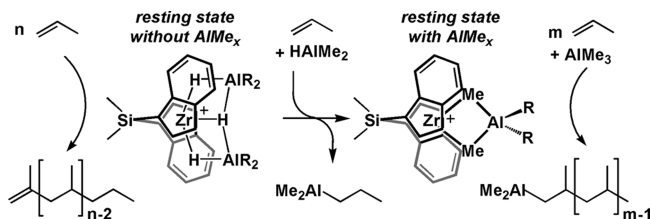
Closely related reaction systems containing the $\{\text{AlMe}_2\}$ -complexed trihydride cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlMe}_2)_2]^+$ ⁴ yield unexpected results. When a solution containing this cation—generated by adding 20 equiv of HAlMe_2 and 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to a solution of $(\text{SBI})\text{ZrCl}_2$ in toluene- d_8 —is exposed to propene at -30°C , we obtain the results represented in Figure 2: Over an initial period of ca. 2 h, the HAlMe_2 signal at 2.72 ppm¹⁰ diminishes together with the signals of propene, while $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Al}$ signals at 1.36 (sxt) and 1.05 ppm (t, J 7 Hz)¹¹ are growing in. These observations indicate that propene is reacting with HAlMe_2 via hydroalumination.¹²

Virtually the same results are obtained with reaction systems containing both the trihydride cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlR}_2)_2]^+$ and the dimethyl-bridged cation $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlR}_2]^+$, with R = Me or ^iBu —generated by adding first 10 equiv of HAl^iBu_2 and then 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and finally 50 equiv of AlMe_3 to a solution of $(\text{SBI})\text{ZrCl}_2$ in toluene- d_8 —upon exposure to propene at -30°C .

Olefin hydroaluminations are well known to be catalyzed by zirconocene hydrides;¹³ they are generally accepted to occur by olefin insertion into Zr-H bonds and subsequent alkyl-hydride exchange between Zr and Al centers. It is surprising that this reaction is catalyzed only if HAlMe_2 and/or AlMe_3 is present in the reaction medium and not at all with HAl^iBu_2 alone. From our present results we cannot determine which thermodynamic and/or kinetic factors are responsible for this difference in reactivity.¹⁴

During the course of this hydroalumination reaction, the signals of the trihydride cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlR}_2)_2]^+$ diminish in size together with the decreasing concentration of Al hydrides. Simultaneously, signals assignable to $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlR}_2]^+$ are growing

Scheme 2



in together with those of n -propyl- AlMe_2 . When Al hydride species are no longer detectable, the signals of $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlR}_2)_2]^+$ have likewise vanished, due to its conversion to $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlR}_2]^+$ according to Scheme 1.¹⁵

The ensuing catalyst system continues to consume propene, giving rise now to polypropene, which ^{13}C NMR data show to be as isotactic as that obtained with $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)_2]^+$. Most frequent in this polymer, however, are isopropyl end groups,¹⁶ which are to be expected if chain growth is mainly terminated by rather frequent polymer transfer to Al. Accordingly, GPC analysis yields a substantially diminished mean degree of polymerization, $P_n \approx 45$. After consumption of all Al hydride, the dimethyl-bridged complex $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlR}_2]^+$ becomes the sole detectable catalyst species in these reaction systems (Scheme 2).

The results presented above show that the $\{\text{Al}^i\text{Bu}_2\}$ -complexed cation $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{Al}^i\text{Bu}_2)_2]^+$, formed in the presence of HAl^iBu_2 , is a catalyst for propene polymerization, while its $\{\text{AlMe}_2\}$ -complexed analogue $[(\text{SBI})\text{Zr}(\mu\text{-H})_3(\text{AlMe}_2)_2]^+$, formed in the presence of HAlMe_2 , is primarily a catalyst for the hydroalumination of propene, being converted, in the course of this reaction, to the cation $[(\text{SBI})\text{Zr}(\mu\text{-Me})_2\text{AlR}_2]^+$, another catalyst for propene polymerization. Mechanistic features that might be responsible for this unexpected divergence in reactivity and the role of zirconocene hydride cations in MAO-activated polymerization catalysis will be subjects of further studies.

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Supporting Information Available: Details of experimental procedures and product characterizations for all reactions mentioned. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) For product analysis, polymerization reactions were conducted, under closely similar conditions, on a somewhat larger scale (see Supporting Information).
- (8) Other end groups were not detectable in NMR spectra of this polymer.
- (9) Evidence for such species in related catalyst systems and their role in slow initiation and fast propagation kinetics: Landis, C. R.; Christianson,

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- (10) In these reaction systems, which produce ClAlR_2 and n -propyl- AlR_2 ($\text{R} = \text{Me}$ or $t\text{Bu}$), additional H -Al signals are observed at lower fields, which are presumably due to adducts of HAlR_2 with these alkylaluminum species. Cf.: Eisch, J. J.; Rhee, S. G. *J. Organomet. Chem.* **1972**, *38*, C25. Eisch, J. J.; Rhee, S. G. *J. Organomet. Chem.* **1972**, *42*, C73.
- (11) For details of this assignment, see Supporting Information.
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- (14) Some intermediate required for alkyl-hydride exchange between Zr and Al centers might be accessible only when HAlMe_2 is present in the reaction medium.
- (15) During this stage of the reaction, a signal due to a fleeting species appears at -1.77 ppm and then disappears again.
- (16) For other end groups, see Supporting Information.

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