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Isobutene Polymerization and Isobutene-Isoprene Copolymerization Catalyzed by Cationic Zirconocene Hydride Complexes

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ABSTRACT: The cationic zirconocene trihydrides $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+X^-$, generated from $[Cp'_2ZrH_2]_2$ with various trityl salts of weakly coordinating anions, are powerful initiators for the polymerization of isobutene (IB) and its copolymerization with isoprene (IP) ($Cp' = C_5H_4SiMe_3$). This study is concerned with the quantification of the effects of the counteranion and of trace moisture on IB/IP copolymers and the nature of the initiating species. Polymer molecular weights increase with decreasing anion nucleophilicity in the order $X = [B(C_6F_5)_4] \approx [H_2N\{B(C_6F_5)_3\}_2] > [CN\{B(C_6F_5)_3\}_2]$. Using $[Cp'_4Zr_2H_3]^+ [CN\{B(C_6F_5)_3\}_2]^-$, high copolymer molecular weights are found ($M_w \approx 5 \times 10^5$ g/mol at −35 °C). There is little reduction in either rate or molecular weight on addition of isoprene. Polymer molecular weights are substantially higher than with the $Et_2AlCl/{}^tBuCl$ initiator system under identical conditions. Water was shown to be an important chain-transfer agent; substoichiometric quantities of water reduced activity, and copolymer molecular weights decreased linearly with increasing $[H_2O]$. Mechanistic studies suggest that $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+$ does not itself act as a cationic initiator but is transformed into one or more other binuclear (polynuclear?) species, accompanied by alkene insertion into the Zr−H bond and a monomer hydrogenation step. Tentative structures for these reactive intermediates are suggested.

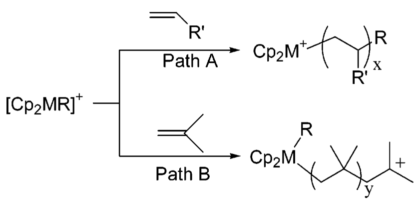
Introduction

The production of butyl rubber by the copolymerization of isobutene (IB) with isoprene (IP) is a large-scale industrial process. The commercial initiating system used is an $AlCl_3/H_2O$ slurry in chloromethane solvent, with protonation of monomer to give *tert*-butyl cations, which act as the propagating species.[1−3] Under these conditions, bases such as H_2O, Cl^-, and $AlCl_4^-$ will readily promote chain transfer, via deprotonation of the $-CMe_2^+$ terminus. To suppress chain transfer and hence to obtain sufficiently high molecular weight polymer ($M_n \sim 5 \times 10^5$ g/mol), polymerizations are carried out at temperatures of ∼−100 °C, a highly costly and energy-intensive process.

Kennedy has extensively investigated related aluminum-based initiating systems for cationic polymerization; these use CMe_3X initiators with R_3Al, R_2AlX, and $RAlCl_2$ co-initiators in MeCl solvent (R = alkyl, X = Cl, Br, or I).[2] This combination generates $CMe_3^+[R_nAlX_{(4-n)}]^-$ as the initiating species and results in rapid polymerization of isobutene. By working with low IB concentrations, higher molecular weight polyisobutene ($M_w > 3 \times 10^5$ g/mol) can be obtained at higher temperatures (e.g. −30 °C) than that formed in the $AlCl_3/H_2O$ process. BCl_3 can also be used in combination with alkyl halides.[1] A wide range of Lewis acidic metal halides are known to be effective initiators; while the details of the initiation mechanism can differ, they all act via halide abstraction to give carbocations stabilized by halometalate anions.[4−6]

The aim of our research has been to develop an initiating system that would deliver high molecular weight isobutene-isoprene copolymers at significantly higher temperatures (e.g. −35 °C), by minimizing the nucleophilicity of the components in the system, and by reducing nucleophilic impurities and trace moisture as far as is reasonably possible. Additionally, we have sought, from an environmental point of view, to use a nearly solvent-free system. Our approach has been to use highly reactive group 4 cations as initiating species, with essentially nonnucleophilic borates as anions.

Scheme 1



Cationic group 4 metallocenes with very weakly coordinating anions are well-known as catalysts in Ziegler-type polymerization of 1-alkenes.[7] Such species are typically formed by treatment of a metallocene methyl with an activator, such as $B(C_6F_5)_3$ or $CPh_3[B(C_6F_5)_4]$. The resulting ion pairs $[Cp_2MR]X$ ($X = RB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$) contain highly electrophilic organometallic metal alkyl cations that promote polymerization by an insertion mechanism (Scheme 1, path A). It is only fairly recently that species of this type have been investigated for activity in carbocationic polymerizations (Scheme 1, path B).

The very low nucleophilicity of perfluoroarylborates anions used in these systems is equally advantageous in cationic polymerizations since it disfavors deprotonation of the propagating carbocation and allows high polymer molecular weights to be reached at comparatively high temperatures. We and others have shown that metallocene alkyl cations paired with $MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$ are indeed very effective initiators for the polymerization of isobutene and its copolymerization with isoprene. Baird et al. have investigated $[Cp^*TiMe_3]/B(C_6F_5)_3$ and related titanium alkyl systems which polymerize isobutene and vinyl ethers,[8] while we

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have explored organometallic electrophiles such as $[AlCp_2]^+[MeB(C_6F_5)_3]^-$,[9] $(C_5H_4SiMe_3)_2Y(\mu\text{-}Me)B(C_6F_5)_3$,[10] and $[Zr\{N(SiMe_3)_2\}_3]^+$.[11] Kennedy has shown that $[SiMe_3]^+[B(C_6F_5)_4]^-$, formed in situ from $SiMe_3Cl$ and $Li[B(C_6F_5)_4]$, will produce copolymers with $M_w > 10^5$ at temperatures up to −8 °C, i.e., at the IB boiling point, and in near-neat monomer. It was suggested that the actual initiating species was $H^+[B(C_6F_5)_4]^-$, arising from trace quantities of H_2O in the system, since the addition of the proton trap 2,6-di-*tert*-butylpyridine resulted in significantly lower polymer yields.[12] Work in our group has involved $[Cp^R{}_2ZrMe_2]$ (Cp^R = Cp, Cp*, or $CpSiMe_3$) activated with either $B(C_6F_5)_3$ or $CPh_3[B(C_6F_5)_4]$, for isobutene homo- and copolymerizations in essentially neat monomer.[13] Shaffer et al. have used similar metallocenes in combination with “noncoordinating” anions, as well as main group alkyl initiators, such as SiR_3^+, SnR_3^+, and GeR_3^+ and polymerizations in chlorobenzene.[14] Most of these initiators give reasonably high molecular weight IB polymers ($M_w \sim 2 \times 10^5$ g/mol) at temperatures as high as −20 °C. The Exxon group concluded that the concentration of H_2O in the system was of great importance, and controlled amounts of water may be beneficial. There might be two initiation pathways, either by H^+ attack if the moisture content is of a similar level to that of the metallocene, or by the cationic metallocene in cases where the moisture concentration is significantly lower than that of the metallocene, particularly if a proton trap is added. Molecular weights of the resulting polymers from proton and metal-initiated reactions were very similar.[14]

We found earlier that, surprisingly, cationic zirconocene *hydride* complexes derived from the reaction of $[Cp'_2ZrH(\mu\text{-}H)]_2$ ($Cp' = C_5H_4SiMe_3$) with $CPh_3[B(C_6F_5)_4]$ are powerful initiators for the cationic polymerization of isobutene and its copolymerization with isoprene.[15] Activity was found to be considerably higher than the corresponding zirconocene dimethyl Cp'_2ZrMe_2, particularly at higher temperatures. This observation suggested that, contrary to expectations, the structure of the initiating species can have a significant effect in cationic polymerizations. For high activities, the optimal procedure was to premix cold (−78 °C) solutions of $[Cp'_2ZrH(\mu\text{-}H)]_2$ and $CPh_3[B(C_6F_5)_4]$ in a small amount of CH_2Cl_2 prior to injection into liquid isobutene. Reasonably high molecular weights ($M_w > 2 \times 10^5$ g/mol) were obtained at temperatures as high as −30 °C. However, on occasions there were problems with reproducibility, due possibly to variable trace moisture levels in the feed gas stream. Here we report an in-depths study of this system, including (i) NMR studies on the likely structure of the initiating species involved, (ii) the quantification of anion effects in cationic polymerizations, and (iii) the quantification of moisture effects. In particular, it is shown that by greater control over reaction temperature and moisture content and by introducing new counteranions significant increases in IB/IP copolymer molecular weights are possible, up to ca. $M_w \sim 5 \times 10^5$ at −35 °C. Data for the classical Et_2AlCl/Me_3CCl system[3] (under our near solvent-free conditions) have been included for comparison.

Results and Discussion

The complex $[Cp'_2ZrH(\mu\text{-}H)]_2$ reacts with 1 equiv of $CPh_3[B(C_6F_5)_4]$ to give the dinuclear species $[Cp'_4Zr_2H(\mu\text{-}H)_2][B(C_6F_5)_4]$ (**1**) (Scheme 2).[15] The low temperature ^1H NMR spectrum (<−60 °C, CD_2Cl_2) shows two bridging hydride ligands (δ −2.02 and −2.66), while the third is terminal (δ 4.55). At −30 °C, interchange of all three signals is fast on the NMR time scale, while above this temperature the compound decomposes in the chlorinated solvent, with Cp'_2ZrCl_2 as the eventual product. Essentially identical ^1H and ^{13}C NMR spectra are obtained when $[Cp'_2ZrH(\mu\text{-}H)]_2$ is reacted with trityl salts of different borate anions; e.g., $CPh_3[(C_6F_5)_3BCNB(C_6F_5)_3]$[16] results in $[Cp'_4Zr_2H_3][(C_6F_5)_3BCNB(C_6F_5)_3]$.

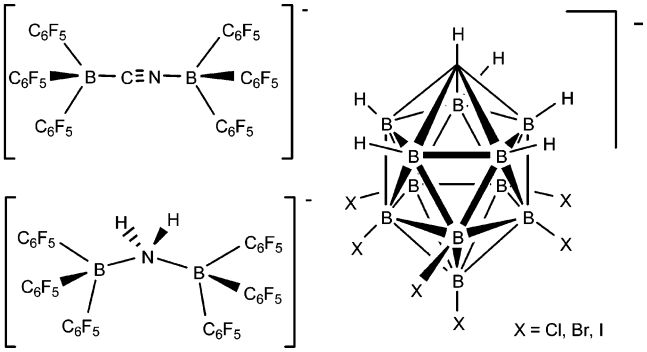
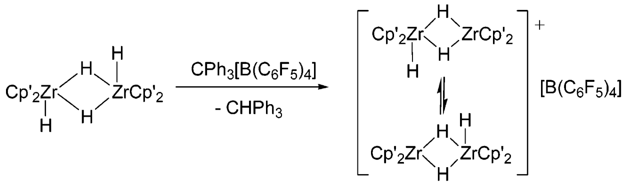


Figure 1. Structures of diborate and hexahalocarboranyl anions

Scheme 2



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Polymerization Studies. The system $[Cp'_2ZrH(\mu\text{-}H)]_2/CPh_3^+X^-$ (*X* = noncoordinating anion) has been used to conduct an extensive series of polymerizations, with the emphasis on control of reaction temperature and reduction of moisture to lowest feasible levels. The reaction temperature was maintained by the use of a vacuum-control system, such that the IB reflux rate under reduced pressure is adjusted to keep the internal reaction temperature at a predetermined constant value. This system was found to be very effective against the buildup of reaction exotherms, the normal temperature deviation being ±3 °C. As discussed above, control of trace moisture and drying of the IB feed gas was crucial; this was achieved by passing through an alumina column loaded with 10 wt % sodium. This system was found to be superior to previously used methods such as drying condensed isobutene over $Et_2AlOC_6H_{13}$.

Six different anions were used in this study. Most preliminary experiments involved the commonly used $[B(C_6F_5)_4]^-$. This work was extended to include the bulkier (and arguably less nucleophilic) diborate anions $[(C_6F_5)_3BCNB(C_6F_5)_3]^-$ and $[H_2N\{BC_6F_5)_3\}_2]^-$, both of which are known to give extremely active ethene and propene polymerization catalysts,[16,17] as well as the hexahalocarboranyl anions $[CB_{11}H_6X_6]^-$ (X = Cl, Br, or I, see Figure 1), kindly supplied by Prof C. A. Reed.[18] Table 1 shows a series of bulk homopolymerizations and copolymerizations using the initiating system $[Cp'_2ZrH_2]_2/CPh_3[(C_6F_5)_3BCNB(C_6F_5)_3]$ (1:1), which was chosen as the basis for comparison. In each case, dry IB was condensed directly into a rigorously dried vessel, fitted with a solid CO_2 condenser. The required quantity

Table 1. Isobutene (Co-) Polymerizations Initiated with $[Cp'_2ZrH_2]_2/CPh_3[CN\{B(C_6F_5)_3\}_2]$[a]

run no.	[init] × 10^5 (mol/L)	temp (°C)	IB (mL)	isoprene (mL)	time (min)	polymer yield (g)	$M_w \times 10^{-3}$ g/mol	$M_n \times 10^{-3}$ g/mol	M_w/M_n	isoprene incorp (mol %)
1.1	20	−78	100		0.33	2.8	1210	511	2.4	
1.2	15	−35	100		0.17	8.2	265	76.6	3.5	
1.3	10	−78	100		4	6.5	878	337	2.6	
1.4	10	−50	100		5	4.0	678	322	2.1	
1.5	10	−35	100		5	5.2	513	269	1.9	
1.6	7	−78	100	1.5	5	7.4	716	295	2.4	1.3
1.7[b]	5	−78	100	1.5	2	7.9	823	381	2.2	1.5
1.8	7	−50	100	1.5	3	5.5	573	284	2.0	1.5
1.9	7	−35	100	1.5	7	8.3	484	236	2.1	1.5
1.10	7	−35	97	3	8	6.8	454	220	2.1	2.9
1.11	7	−35	95	5	10	7.1	387	168	2.3	4.4
1.12	7	−25	100	1.5	3	7.8	275	148	1.9	1.5
1.13	6	−25	100	1.5	5	6.0	291	158	1.8	1.5

[a] Using isobutene as solvent. [b] 5 mL of CH_2Cl_2 added to improve solubility.

of isoprene was added by syringe and the system then equilibrated at the desired temperature. Meanwhile, the initiator mixture was prepared by adding $CPh_3[(C_6F_5)_3BCNB(C_6F_5)_3]$ in CH_2Cl_2 (5 mmol/L) to solid $[Cp'_2ZrH_2]_2$ at −78 °C. This solution was then injected into the rapidly stirred monomer, and the system was equilibrated at the required pressure. Polymerization was allowed to proceed until a significant increase in viscosity was observed (typically at 10−15% conversion), or terminated by methanol injection after 30 min if little reaction was found.

Isobutene homopolymerizations (Table 1, runs 1.1−1.5) were carried out with $1-2 \times 10^{-4}$ mol/L of $[Cp'_2ZrH_2]_2$ in the temperature range −78 to −35 °C. With an initiator concentration of 2×10^{-4} mol/L (20 μmol $[Cp'_2ZrH_2]_2$), polymerization proceeded so rapidly at all temperatures that reactions had to be stopped after 10−20 s, but at −50 °C or above, the resulting molecular weights were relatively low, $M_w < 3 \times 10^5$ g/mol, with $M_w/M_n > 3$. Reducing the amount of initiator to 10 μmol led to high molecular weight polymers with narrow polydispersities. As expected, polymer molecular weights decrease with increasing temperature, although the $[CN\{B(C_6F_5)_3\}_2]^-$ anion gave significantly higher M_w values over the whole temperature range, for example $M_w = 5.1 \times 10^5$ at −35 °C, in striking difference to the classical Al-based system.

High reactivity and molecular weights were also found in IB/IP copolymerizations (runs 1.6−1.13). As with the homopolymerizations, reactivity was broadly similar over the whole temperature range (typically 10−15% conversion after 5 min). At −35 °C with $[Zr_2^+] = 7 \times 10^{-5}$ mol/L and 1.5 mL of IP, ca. 14% conversion was reached after 7 min; i.e., there was no significant rate retardation in the presence of isoprene. Conversions remained high on increasing the temperature to −25 °C to give polymers with $M_w \approx 3 \times 10^{-5}$ g/mol.

At −78 °C, the solubility of the initiator in liquid isobutene was low, and the isolated polymer retained the faint orange color of some residual trityl salt. Addition of 5 mL of dichloromethane to the monomer before initiation increased initiator solubility, such that >20% conversion were obtained after just 2 min. The polymer molecular weight was found to increase slightly, from $M_w = 7.2 \times 10^5$ to 8.2×10^5 g/mol on addition of extra solvent at this temperature.

Most copolymers were prepared with a standard level of ca. 1.5 mol % isoprene incorporation. The molecular weights of these copolymers were somewhat lower than the corresponding homopolymers, but still comparatively high. The molecular weight difference between homo-and copolymers decreased with increasing temperature. At −35 °C, copolymer M_w values of up to 4.8×10^5 g/mol were found, unusually high for this temperature and almost identical to IB homopolymers.

Although molecular weights decreased slightly with increasing IP content, the zirconocene system is much less retarded by isoprene than Al-based comparisons. For example, over the range of 1.5−4.4 mol % IP incorporation, M_w decreased only from 4.8×10^5 to 3.9×10^5 g/mol. The polymer molecular weights at higher unsaturation levels were much higher than those reported for other initiating systems.[13−15]

For all copolymers, IP incorporation increased linearly with the feed concentration. In each case, isoprene was predominantly incorporated in the expected 1,4-trans configuration. In addition, a small quantity of a second unsaturated species was observed, giving rise to a doublet at δ 4.93 in the ^1H NMR spectrum. This has been assigned to a 1,4-trans double bond connected to a chain branching point in the 4-position.[19] Branching increased with reaction temperature, from less than 1 mol % at −78 °C to up to 10% at −15 °C. With some aluminum-based initiators, the branched polymer is the major product at higher temperatures.[19] To accurately calculate the degree of polymer unsaturation, therefore, the ^1H NMR signal at δ 4.93 must be taken into account.

Anion Effects. For evaluation of anion effects, IB and IB/IP polymerization results using $[Cp'_2ZrH_2]_2/CPh_3^+X^-$ as initiator, where X = $B(C_6F_5)_4$ or $H_2N\{B(C_6F_5)_3\}_2$, are given in Table 2, together with results for $[CN\{B(C_6F_5)_3\}_2]^-$ at higher temperatures for comparison. In IB homopolymerizations, low initiator solubility at lower temperatures was overcome by adding 5 mL of CH_2Cl_2/100 mL of IB prior to initiation. At −35 °C, high molecular weights ($M_w = 4.2 \times 10^5$ g/mol) and narrow polydispersities were found ($M_w/M_n \approx 2.0$), even with high activities. The highest molecular weight homopolymers over the whole temperature range were very similar to those obtained with $[CN\{B(C_6F_5)_3\}_2]^-$ as anion. With the amido diborate $[H_2N\{B(C_6F_5)_3\}_2]^-$ (runs 2.8−2.11), reactivity was found to be somewhat higher than with the cyano-bridged anion. Addition of 5 mL of CH_2Cl_2 to the reaction medium enhanced the polymerization rate at −78 °C (cf. runs 2.8 and 2.9); this is most probably due to improved solubilization, and hence improved initiation efficiency, of the $[Cp'_2ZrH_2]_2/CPh_3^+$-$[H_2N\{B(C_6F_5)_3\}_2]^-$ mixture at low temperatures. Reactions at −35 °C were rather faster than comparable runs with $[CN\{B(C_6F_5)_3\}_2]^-$. Thus, ca. 13% conversion was obtained after 1.5 min, with $[Zr_2^+] = 7 \times 10^{-5}$ mol/L.

Table 2. Counteranion Effect on IB (Co-) Polymerizations[a]

run no.	anion X^-	[init] × 10^5 M	temp (°C)	IB (mL)	IP (mL)	time (min)	polymer yield (g)	$M_w \times 10^{-3}$ g/mol	$M_n \times 10^{-3}$ g/mol	M_w/M_n	isoprene incorp (mol %)
2.1[b]	$B(C_6F_5)_4^-$	10	−78	100		2	1.9	1670	585	2.9	
2.2[b]	$B(C_6F_5)_4^-$	10	−50	100		1.5	3.2	901	467	1.9	
2.3[b]	$B(C_6F_5)_4^-$	10	−35	100		1	6.2	420	205	2.0	
2.4	$B(C_6F_5)_4^-$	10	−78	100	1.5	30	1.9	598	243	2.5	1.1
2.5	$B(C_6F_5)_4^-$	10	−35	100	1.5	6	3.1	342	179	1.9	1.3
2.6	$B(C_6F_5)_4^-$	7	−35	100	1.5	2	4.9	379	198	1.9	1.3
2.7	$B(C_6F_5)_4^-$	7	−25	100	1.5	10	3.2	238	120	2.0	1.3
2.8	$H_2N\{B(C_6F_5)_3\}_2^-$	7	−78	100	1.5	10	3.3	608	325	1.9	1.3
2.9[b]	$H_2N\{B(C_6F_5)_3\}_2^-$	7	−78	100	1.5	3	7.0	518	243	2.1	1.4
2.10	$H_2N\{B(C_6F_5)_3\}_2^-$	7	−50	100	1.5	4	4.6	462	234	2.0	1.4
2.11	$H_2N\{B(C_6F_5)_3\}_2^-$	6	−35	100	1.5	3	10.8	353	186	1.9	1.5
2.12	$CN\{B(C_6F_5)_3\}_2^-$	7	−50	100	1.5	3	5.5	573	284	2.0	1.5
2.13	$CN\{B(C_6F_5)_3\}_2^-$	7	−35	100	1.5	7	8.3	484	236	2.1	1.5

[a] Initiator system $[Cp'_2ZrH_2]_2/CPh_3[X]$ initiator, isobutene solvent. [b] +5 mL CH_2Cl_2.

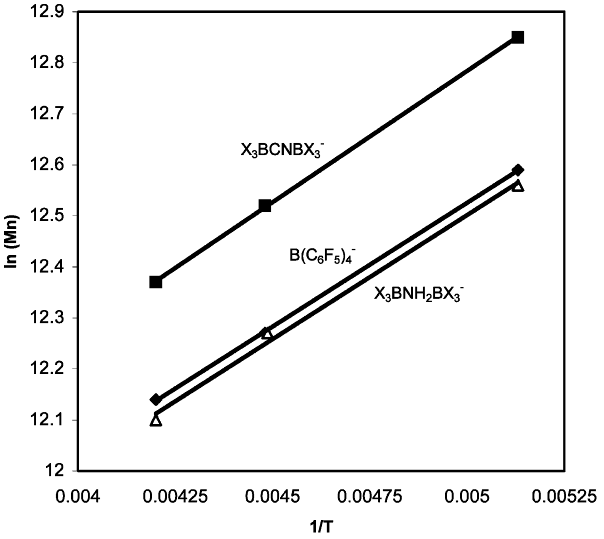

Figure 2. Temperature dependence of M_n for isobutene/isoprene copolymerizations with $[Cp'_2ZrH_2]_2/CPh_3$[borate] as a function of the counteranion ($X = C_6F_5$).

For IB/IP copolymerizations (runs 2.4−2.13), a distinct anion effect on molecular weights was observed. Broadly similar reactivities were seen, but molecular weights were consistently lower with $[B(C_6F_5)_4]^-$ compared to $[CN\{B(C_6F_5)_3\}_2]^-$. Thus, for $[B(C_6F_5)_4]^-$ and $[H_2N\{B(C_6F_5)_3\}_2]^-$ the highest copolymer M_w values at −35 °C were found to be 3.5−3.8 × 10^5 g/mol, compared to 4.8 × 10^5 g/mol for $[CN\{B(C_6F_5)_3\}_2]^-$. For $[B(C_6F_5)_4]^-$ there was a larger molecular weight difference between homo- and copolymers than with the cyano-bridged anion.

A comparison of copolymerization results with all three anions shows clearly that the cyano-bridged diborate leads to the highest molecular weights. This is illustrated by a plot of ln(M_n) vs 1/*T* (Figure 2). The results for the $[B(C_6F_5)_4]^-$ and $[H_2N\{B(C_6F_5)_3\}_2]^-$ systems are very similar, a situation that reflects the findings in Ziegler-type polymerizations.[17] We explain this by the lower polarity and coordinative tendency of the linear $[CN\{B(C_6F_5)_3\}_2]^-$ compared to the angular $[H_2N\{B(C_6F_5)_3\}_2]^-$, while the mononuclear $[B(C_6F_5)_4]^-$ has a higher charge per boron, and hence a higher nucleophilicity, than either of the diborates.

The carboranyl anions $[CB_{11}H_6X_6]^-$ (X = Cl, Br, or I) are known for their high chemical stability, extremely low nucleophilicity and their ability to stabilize strong electrophiles such as $C_6H_7^+$ or $AlEt_2^+$.[18] It was therefore expected that these anions would be highly suitable as counteranions in cationic polymerizations. However, mixtures of $[Cp'_2ZrH_2]_2$ and $CPh_3[CB_{11}H_6X_6]$ under conditions identical to those described above produced only traces of polymer, even when the initiator concentration was increased to 3 × 10^{-4} mol/L. Increasing the ratio trityl salt:$[Cp'_2ZrH_2]_2$ to 1.5−2 did not result in polymer formation. The products formed from the reaction of $[Cp'_2ZrH_2]_2$ with $CPh_3[CB_{11}H_6X_6]$ appeared to be totally soluble in neat isobutene over the temperature range from −78 to −35 °C, so that lack of initiator solubility was apparently not a contributing factor in the low polymerization activity.

The reaction of $[Cp'_2ZrH_2]_2$ with $CPh_3[CB_{11}H_6I_6]$ was monitored by ^1H NMR spectroscopy (CD_2Cl_2, −70 °C). The spectrum showed the presence of 1 equiv of $CHPh_3$, as expected. However, the zirconium species observed were quite different from $[Cp'_4Zr_2H_3]^+$ and could no be identified. This is in contrast to the perfluoroarylborate reactions where the spectra of the cationic species were almost identical in all cases. With $[Cp'_2ZrH_2]_2/CPh_3$-$[CB_{11}H_6I_6]$, bridging hydride signals were observed at δ −2.95 and −3.15, i.e., at chemical shifts more consistent with a neutral complex than with a cationic trihydride. Broad singlets at δ 5.13, 4.63, 3.52, and 3.09 were consistent with terminal hydrides. All of these signals had approximately the same integration, but were presumably not part of the same species as they integrated less than 1 with respect to the $SiMe_3$ groups (for which there were at least four signals). It is possible that iodide abstraction from the anion occurred, resulting in a neutral hydrido halide product. Although no identifiable zirconocene species could be isolated from these reactions, it is clear that the reaction takes a different course from the perfluoroarylborates, to give products that were unsuitable as cationic initiators.

Effect of Water Concentration. One of the most likely chain-transfer agents in this system is trace moisture. We wished to evaluate the effect of water concentration in our system, as the use of more efficient feed gas drying procedures had resulted in significantly higher activities and polymer molecular weights.[20] It was reasoned that water would act on one hand as a poison, destroying a certain percentage of the initiator, and on the other as a chain-transfer agent. However, if a proton was formed in the hydrolysis of the zirconocene species, this might then itself initiate polymerization, as described by Shaffer for zirconocene methyls.[13] We set out to show that with metallocene hydrides, the lower the water concentration, the lower the yield.

To obtain significantly low quantities of trace moisture per reaction, a H_2O/CH_2Cl_2 emulsion was prepared

Table 3. Effect of $[H_2O]$ on Isobutene Copolymerizations[a]

run no.	$[H_2O]$ (μmol)	time (min)	polymer yield (g)	$M_w \times 10^{-3}$ g/mol	$M_n \times 10^{-3}$ g/mol	M_w/M_n
3.1	0	6	7.7	4.34	2.36	1.8
3.2	0.5	2	3.8	4.07	2.59	1.6
3.3	0.5	3	5.1	3.75	2.39	1.6
3.4	1	4	6.5	3.54	1.57	2.3
3.5	1	2	4.0	3.39	1.69	2.0
3.6	1.5	8	7.4	3.08	1.23	2.5
3.7	1.5	8	7.3	2.87	1.49	1.9
3.8	2	10	3.7	2.62	1.57	1.7
3.9	2	10	5.7	2.78	1.56	1.7
3.10	2.5	15	1.1	2.27	0.91	2.5
3.11	2.5	15	5.4	2.30	1.42	1.6
3.12	3	20	4.8	1.90	1.13	1.7
3.13	3	20	6.2	1.99	1.27	1.6

[a] Reaction conditions: $[Cp'_2ZrH_2]_2/CPh_3[CN\{B(C_6F_5)_3\}_2]$ initiator system, $[CPh_3^+] = 7 \times 10^{-5}$ mol/L, 100 mL of isobutene, 1.5 mL of isoprene, −35 °C.

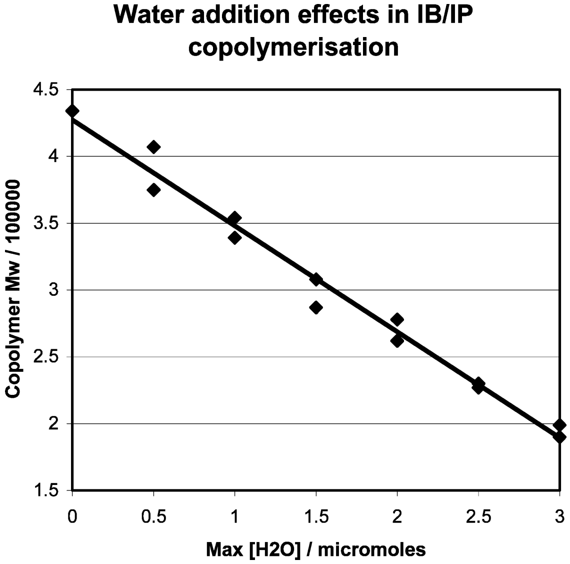

Figure 3. Dependence of IB/IP copolymer molecular weight on $[H_2O]$ at −35 °C. For conditions, see Table 3.

with a maximum $[H_2O] = 5 \times 10^{-3}$ mol/L. This emulsion was stirred vigorously under a nitrogen atmosphere for >6 h, before a small aliquot of this solution was added to the reaction vessel prior to initiation. The reaction chosen for study was the copolymerization with 100 mL of IB/1.5 mL of IP, $[Cp'_2ZrH_2]_2/CPh_3[B(C_6F_5)_4]$ initiator (7×10^{-5} mol/L), $T = -35$ °C. The residual moisture content of the IB gas after passing through the drying columns was found to be significantly less than 1 ppm (by weight). As ca. 1 mol of isobutene was used per experiment, less than 1 μmol of water was introduced by the feed gas stream, and therefore, the water added with the CH_2Cl_2 suspension should form the major part of the moisture in the system. The results are shown in Table 3 and Figure 3.

The rate of polymerization and the polymer molecular weight decreased approximately linearly with increasing water concentration. Thus, with $[H_2O] = 1 \times 10^{-5}$ mol/L, a yield of 6.5 g was obtained after 4 min ($M_w = 3.5 \times 10^5$ g/mol). Increasing $[H_2O]$ decreased both polymerization rate and polymer molecular weights: while $[H_2O] = 3 \times 10^{-5}$ mol/L gave ca. 10% conversion after 20 min and a lower M_w of 1.95×10^5, increasing $[H_2O]$ to 4×10^{-5} mol/L or higher resulted in a dramatic reduction in yield, with only traces of polymer obtained after 30 min. Unlike the previous reports for zirconocene and hafnocene methyl system,[13] addition of stoichiometric quantities of water led to complete deactivation of the zirconocene hydride system. These results indicate that, in our system at least, the presence of trace moisture does indeed lead to chain transfer in IB polymerizations. Molecular weights are a linear function of $[H_2O]$. It is clear that the benefits of low-nucleophilicity anions in IB/IP polymerizations can only be exploited if the moisture content is rigorously controlled.[21]

Comparison with Et_2AlCl/Bu^tCl System. For comparison with the zirconocene hydride system a similar set of experiments was conducted with a classical Lewis acid initiator, the Et_2AlCl/Bu^tCl system pioneered by Kennedy.[3] In the original work, polymerizations were performed in methyl chloride solvent, with a large excess of Et_2AlCl (>4 mmol). Under these conditions, polyisobutene formation was extremely quick, often explosively so. To counteract this, we reduced the aluminum concentration by a factor of 3 ([Al] = 0.016 mol/L) and Bu^tCl to a level similar to the initiator concentration in our hydride system ($[Bu^tCl] = 1.15 \times 10^{-4}$ mol/L). Stock solutions were made up in CH_2Cl_2. In the polymerizations, 100 mL of IB was condensed into the vessel, followed by 1.5 mL of IP (if required), the Et_2AlCl solution, and finally, after equilibration at the desired temperature, the Bu^tCl solution. An induction period was initially observed, the duration of which decreased with increasing temperature. Representative results are given in Table 4. Homopolymerizations proceeded rapidly, with good polymer yields. At higher $[Bu^tCl] = 2.3 \times 10^{-4}$ mol/L conversions rose to ca. 30%, while at $[Bu^tCl] = 1.15 \times 10^{-4}$ mol/L polymerizations proceeded more smoothly and gave higher molecular weights. As expected, molecular weights fell with increasing temperature, to $M_w \sim 2 \times 10^5$ g/mol at −35 °C.[22]

IB/IP copolymers produced with Et_2AlCl/Bu^tCl (1.5 vol % IP content) showed a general decrease in yields as well as molecular weights, compared to the homopolymerizations, particularly at low temperatures. The polydispersity indices were narrow, especially compared to those of the homopolymers. There was apparently little variation in copolymer molecular weights with temperature. Attempts to optimize the system showed no molecular weight improvements at −35 °C. The IP incorporation was predominantly 1,4-trans, at levels in

Table 4. Isobutene Polymerizations Initiated by $Et_2AlCl/^tBuCl$[a]

run no.	IB (mL)	IP (mL)	temp (°C)	time (min)	polymer yield (g)	convm (%)	$M_w \times 10^{-3}$ g/mol	$M_n \times 10^{-3}$ g/mol	M_w/M_n	IP incorp (mol %)
4.1	100		−78	8	12.0	20	752	196	3.8	
4.2	100		−50	8	5.6	9.5	417	41.1	10	
4.3	100		−35	0.5	8.6	14.5	180	72.9	2.5	
4.4	100	1.5	−78	10	4.4	7	231	101.4	2.3	1.2
4.5	100	1.5	−50	8	9.9	16.5	175	76.5	2.3	1.2
4.6	100	1.5	−35	13	5.5	9	188	91.0	2.1	1.1

[a] $[Et_2AlCl] = 0.016$ mol/L; $[^tBuCl] = 11.5 \times 10^{-5}$ mol/L.

Table 5. ^{1}H NMR Data for Zirconium Alkyl Complexes Formed from 1 and $CH_2{=}CRR'$ (CD_2Cl_2)

	δ(Cp-H)	δ($SiMe_3$)	$ZrCH_2Zr$ (ppm)	CH_CRR' (ppm)	Zr−H−Zr (ppm)
R, R′ = Me −30 °C	6.95, 6.86, 6.80, 6.70, 6.66, 6.55, 6.38, 6.27, 6.10	0.40−0.11	4.29 (t, *J* 9 Hz, H_B min), 3.45 (t, *J* 9 Hz, H_B maj), −2.45 (d, *J* 6 Hz, H_A maj), −2.74 (d, *J* 7.5 Hz, H_A min)	3.03 (m, H_C maj), 2.13 (m, H_C min), 0.89 (d, *J* 7 Hz, 6H, $CH_C\mathit{Me}_2$)	−1.96 (s, maj), −2.12, (s, min)
R = Me, R′ = ^{t}Bu −40 °C	7.04, 6.91, 6.79, 6.55, 6.42, 6.28, 6.02	0.31, 0.29, 0.27, 0.26	4.24 (dd, *J* 11, 7.5 Hz, H_B), −2.33 (t, *J* 7.5 Hz, H_A)	3.17 (dd, *J* 11, 7.5 Hz, H_C), 0.96 (d, *J* 7 Hz, 3H, $CH\mathit{Me}^t$Bu), 0.89 (s, 9H, $^t\mathit{Bu}$)	−1.57 (s)
R = Me, R′ = $CH_2{}^t$Bu −30 °C	6.98, 6.85, 6.72, 6.60, 6.56, 6.50, 6.39, 6.22, 6.07	0.38−0.09	4.12 (t, *J* 9 Hz, H_A maj), 3.89 (t, *J* 9 Hz, H_A min), −2.98 (d, *J* 9 Hz, H_B min), −3.02 (d, *J* 9 Hz, H_B maj)	3.06 (m, H_C maj), 2.81 (m, H_C min), 1.11 (d, *J* 7 Hz, 2H, $C\mathit{H}_2{}^t$Bu), 1.05 (d, 3H, *J* 7 Hz, $CH\mathit{Me}R'$), 0.88 (s, 9H, $CH_2{}^t\mathit{Bu}$)	−1.93 (s, maj), −2.05 (s, min)
R, R′ = Ph −40 °C	7.03, 6.94, 6.80, 6.61. 6.45, 6.31, 6.06	0.34−0.08	4.63 (t, *J* 10 Hz, H_B), −2.61 (dd, *J* 10, 4 Hz, H_A)	7.45−7.10 (10H, Ph), 5.37 (dd, *J* 10 4 Hz, H_C)	−1.79 (s)

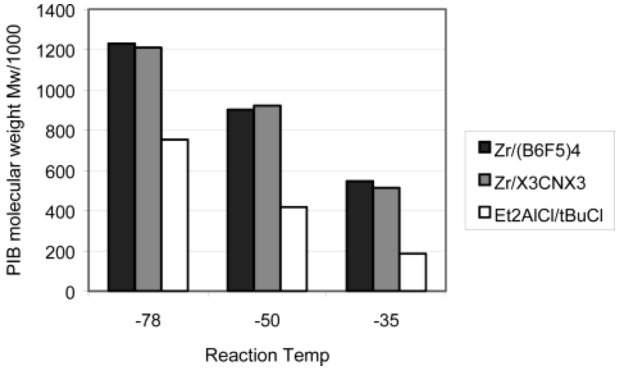

Figure 4. Comparison of polyisobutene molecular weights produced with $[Cp'_2ZrH_2]_2$ / CPh_3[borate] and $Et_2AlCl/{}^tBuCl$ systems.

the range 1.0−1.2 mol %, i.e., slightly lower than with the zirconocene system.

It is clear that polymer molecular weights obtained with the aluminum system were significantly lower than those obtained with $[Cp'_2ZrH_2]_2/CPh_3^+$, particularly at higher temperatures (Figure 4). Presumably, aluminate anions such as $[Et_2AlCl_2]^-$ are much more likely to promote chain transfer than the very weakly nucleophilic perfluoroaryl borates. Furthermore, the high concentrations of aluminum necessary for the classical system make control of reaction conditions more difficult, particularly in polymerizations in nearly neat IB.

Mechanistic Studies. The reaction of **1** with isobutene was followed by a series of NMR experiments. In all reactions, the dinuclear species **1** was preformed in CD_2Cl_2 at −78 °C. The monomer (typically 5 equiv per Zr) was then added and the sample introduced to the spectrometer at −70 °C. Initial experiments with isobutene gave a series of highly complex NMR spectra. Loss of the binuclear cation **1** was observed, together with the formation of 1 equiv of $CHMe_3$ per Zr, due to hydrogenation of one isobutene. Several organometallic products were observed which proved difficult to identify initially. The results suggested however that **1** was not itself the initiating species but merely a precursor. To investigate this process further, a series of model reactions were carried out using more bulky monomers, which were capable of undergoing cationic reactions without polymerization.

The course of the reaction is best illustrated using 1,1-diphenylethene instead of isobutene. Diphenylethene is known to dimerize cationically to 1-methyl-1,3,3-triphenylindane (**2**), a process studied extensively by Sigwalt using triflic acid as the initiator.[23] The mechanism of the proton-initiated dimerization is shown in Scheme 3. Sigwalt was able to observe the cationic intermediates by ^{1}H NMR (CD_2Cl_2, −70 °C), notably the monomeric cation $\mathbf{M}^+$ (δ 3.75 for $C\mathit{H}_3CPh_2^+$) and the dimer cation $\mathbf{D}^+$ (δ 4.8 for $CH_3CPh_2C\mathit{H}_2CPh_2^+$). In our NMR experiments, no signals due to $\mathbf{M}^+$ or $\mathbf{D}^+$ were observed at any stage, indicating that within detection limits protic impurities do not play a role in the dimerization process initiated by the zirconocene hydride system.

Scheme 3

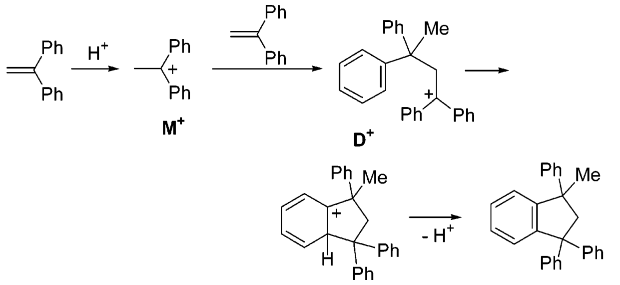

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Figure 5 shows a series of ^{1}H NMR spectra for the reaction of **1** with 10 equiv 1,1-diphenylethene (i.e., monomer:Zr ratio = 5:1) at various temperatures. Figure 6 gives a graph showing the relative concentrations of all observed species as the reaction progresses. At −70 °C there was no reaction between **1** and 1,1-diphenylethene (spectrum A). After warming to −40 °C, hydrogenation of 1 equiv of diphenylethene per **1** was observed over the space of 4 h, with the corresponding loss of signals due to the trihydride cation $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+$ (spectrum B). Meanwhile, a set of four new signals was observed, which increased in intensity at about the same rate as the signals due to **1** decreased. These new resonances were apparently all connected to one new zirconocene “species X” and consist of a doublet of doublets at δ 5.4 and δ −2.6 (J_{HH} = 10 and 4 Hz), a sharp triplet at δ 4.6 (J_{HH} = 10 Hz), and a singlet at δ −1.8 which was not coupled to the other signals (see Tables 5 and 6). The chemical shifts of all except the latter varied significantly with temperature, indicating some close relationship between the coupled protons.

On warming the sample to −10 °C, catalytic dimerization to give indane **2** was observed; this occurred more quickly at 0 °C. As stated above, none of the intermediates reported by Sigwalt were observed, from which we conclude that H^+ addition and buildup of the relatively stable $\mathbf{M}^+$ and $\mathbf{D}^+$ are unlikely to be involved. Also observed was a second hydrogenation step to CH_3CHPh_2, although this was much slower than the first and was only complete after 10 h, even after warming to 0 °C. Since **1** contains only three hydrides while the

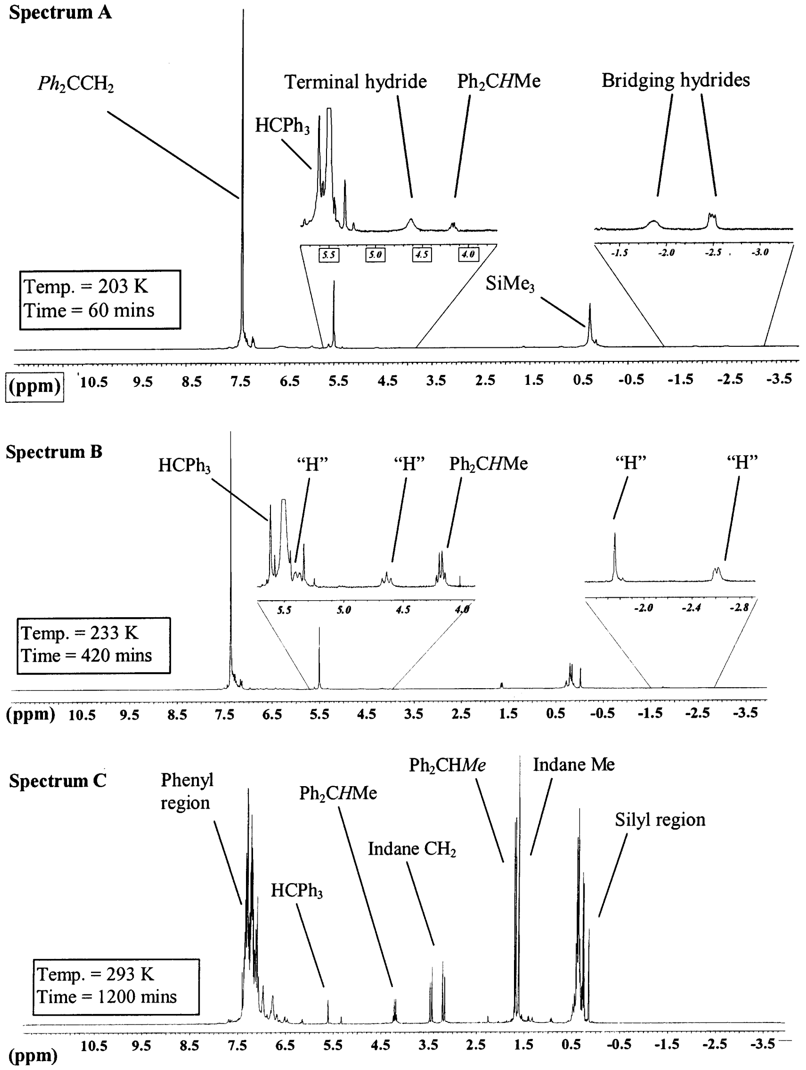


Figure 5. ^{1}H NMR spectra (CD_2Cl_2) of reaction of **1** with diphenylethene ($Ph_2C{=}CH_2$/Zr ratio = 5:1).

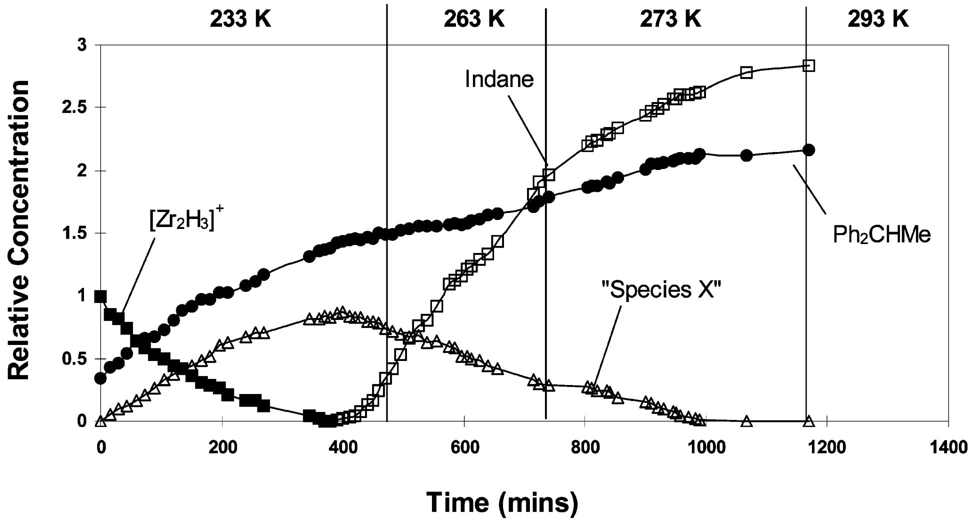


Figure 6. Relative concentrations of zirconocene species observed during the reaction of **1** with diphenylethene. Curves show relative intensities of $[Cp'_4Zr_2H_3]^+$ (■), triphenylmethylindane (□), diphenylethane (●), and "species X" (△).

hydrogenation of two molecules of diphenylethene requires four, we assume that an additional hydrogen atom is obtained by a relatively slow C−H activation reaction from the monomer or some other source (e.g. solvent or cyclopentadienyl rings). The formation of the indane and CH_3CHPh_2 was accompanied by the loss of signals for "species X". At the end of the reaction, i.e., on complete consumption of 1,1-diphenylethene, one equiv of CH_3CHPh_2 per Zr and 3 equiv of indane **2** were present, while signals due to "X" were no longer detectable (spectrum C). Only when the 1,1-diphenylethene had been consumed was there appreciable decomposi-

Table 6. ^{13}C NMR Data for Zirconium Alkyl Complexes Formed from 1 and $CH_2{=}CRR'$ (CD_2Cl_2)

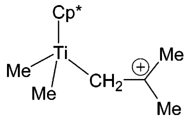
^{13}C NMR CD_2Cl_2	$C_5H_4SiMe_3$ (ppm)	$Si(CH_3)_3$ (ppm)	$ZrCH_2Zr$ (ppm)	CHRR′ (ppm)
R, R′ = Me	122.2, 120.4, 120.1, 119.6, 118.8, 116.7, 115.6	0.67, 0.51, 0.24, −0.13, −0.33	123.3	41.2 (C^2), 24.0 (C^2Me_2)
R = Me, R′ = ^{t}Bu	124.7, 124.1, 123.9, 123.6, 122.2, 120.5, 118.1	0.58, 0.24, −0.14, −0.30	115.3	53.6 (C^2), 30.0 (C^2Me^tBu), 29.5 (C^2Me^tBu)
R = Me, R′ = $CH_2{}^t$Bu	124.1, 122.9, 122.4, 120.8, 119.7, 119.4, 119.1, 117.7	0.76, 0.48, 0.38, 0.19, −0.10, −0.35	124.1	41.4 (C^2), 31.6 (CMe_3), 31.3 (C^2MeR'), 31.1 ($CH_2{}^t$Bu)
R, R′ = Ph	124.8, 123.9, 123.3, 122.4, 120.5, 119.7	0.60, 0.30, −0.12, −0.41	112.2	130.0−127.5 (C_6H_5), 59.2 (C^2)

tion of the zirconium species, e.g., due to halide abstraction from CD_2Cl_2, after warming to room temperature. The intermediates seem more stable, therefore, than typical cationic zirconocene alkyls such as $[Cp_2ZrMe]^+$ which decomposes rapidly in chlorinated solvents at temperatures >−40 °C.

If the trihydride **1** was quickly brought to −10 °C in the presence of diphenylethene, no indane formation was observed initially, since the hydrogenation process is faster. This indicated that **1** is not the initiating species. If the second zirconocene "species X" was left at −40 °C for a prolonged period, allowing the second hydrogenation to occur, again no indane was formed on warming to −10 °C. Thus, the identity of "species X" was important, as this appeared to be relevant for initiation, even if it was not an actual initiating species.

The identity of this species was investigated further by a series of $^1H-^{13}C$ and $^1H-^1H$ correlation experiments. These involved maintaining "species X" at −40 °C after the first hydrogenation step. $^1H-^{13}C$ HETCOR experiments showed that the ^1H NMR resonances at δ −2.6 and 4.6 both correlated with a ^{13}C resonance at δ 112, while the ^1H signal at δ 5.4 correlated with a ^{13}C signal at δ 59. In the $^1H-^1H$ COSY experiment, correlations were seen from the δ 4.6 signal to those at δ −2.6 and 5.4, confirming that these three protons were all in the same organic fragment. The ^1H resonance at δ −1.8 correlated to no other protons or carbons, indicative of a metal hydride.

For isobutene polymerizations initiated by $C_5Me_5TiMe_3/B(C_6F_5)_3$, Baird has postulated a monomer adduct **3** as initiating species.[8] For reactions initiated by a zirconocene hydride, a similar product **4** could be envisaged, produced by addition of monomer to the Zr−H bond. Alternatively, we showed some time ago[15] that zirconocene bis(isobutyl) complexes react with CPh_3^+ under C−H activation, to give cationic allyl complexes **5**.



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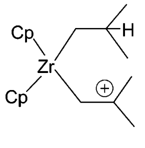

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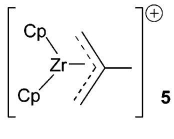

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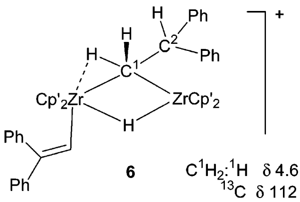
The data discussed above indicate, however, that the reaction is rather more complex. There was no evidence for either **4** or **5**. The NMR data suggest that the "X" formed from **1** and monomer contains a $[ZrCH_2CHPh_2]$ fragment. The large chemical shift difference between the two α-CH_2 signals is indicative of an agostic interaction of one of the C−H bonds with a zirconium center, and the chemical shift of the hydride singlet is typical for a bridging rather than terminal hydride. It is suggested therefore that "species X" is binuclear, like its precursor **1**. Structure **6** satisfies most of the NMR observations.



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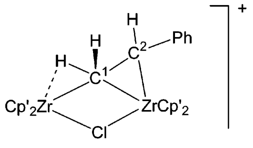
C^1H_2: ^1H δ 4.6, -2.6
^{13}C δ 112

C^2HPh_2: ^1H δ 5.4
^{13}C δ 59



7

C^1H_2: ^1H δ 4.63, -5.55
^{13}C δ 92.5

C^2HPh: ^1H δ 5.17
^{13}C δ 86.3

The proposal gains support by Erker's isolation and crystallographic identification of a related binuclear complex **7**, synthesized by protonation of a chloro/alkenyl-bridged precursor.[24] The bridging carbon atom C^1 has square pyramidal structure, and one hydrogen is agostically bound to Zr, while the other has two possible orientations perpendicular to the Zr^1,Zr^2,C^1,C^2 plane, leading to the possibility of two stereoisomers. The chemical shifts observed are remarkably similar to those of **6**.

Other structural details of **6** are less certain. To satisfy the tetravalent nature of each zirconium center, one of these has to carry an anionic ligand, here shown as a vinyl. Such a ligand could be introduced by C−H activation of a monomer. This reaction would generate the additional hydrogen needed for the second monomer hydrogenation step referred to above.

The ^{13}C NMR spectrum does indeed provide some evidence for the formation of a zirconium vinyl. In addition to the ^{13}C resonances described above, a low-field signal was observed at δ 196.0. The chemical shift is close to values found for α-C of authentic cationic zirconium vinyl complexes, for example $[Cp^*{}_2Zr(CMeCMe_2)(THF)]^+$ (δ ~208)[25] and $[Cp_2Zr(CMeCMe_2)]^+$ (δ ~189.9).[26] In cases (see below) where the unknown "species X" exists as two stereoisomers, two such low-field signals were observed, suggesting that these ^{13}C NMR resonances were not due to an organic carbocation (cf. CPh_3^+: δ 210). However, although structural fragments of **6** could be assigned with some certainty, overlapping monomer signals prevented the unequivocal identification of "species X".[27]

The assignments and structural proposals made in the case of 1,1-diphenylethene reactions were supported by NMR experiments with other nonpolymerizing monomers, such as 2,4,4-trimethylpent-1-ene and 2,3,3-trimethylbut-1-ene. Analogous processes and structures were found. Thus, hydrogenation was again observed as the first step in the reaction, and sets of resonances similar to those described for **6** were found (Tables 5 and 6).

On addition of 10 equiv of 2,3,3-trimethylbut-1-ene to **1** at −70 °C, no reaction was observed after 30 min.

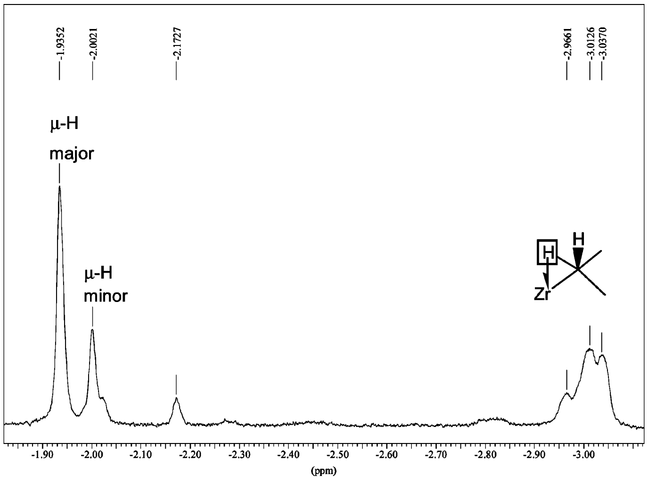


Figure 7. ^{1}H NMR spectrum of the reaction of **1** with 2,4,4-trimethyl-pent-1-ene; high-field region (CD_2Cl_2, −30 °C, 5 equiv per Zr). The signal for agostic C−H is composed of overlapping sets for two isomers.

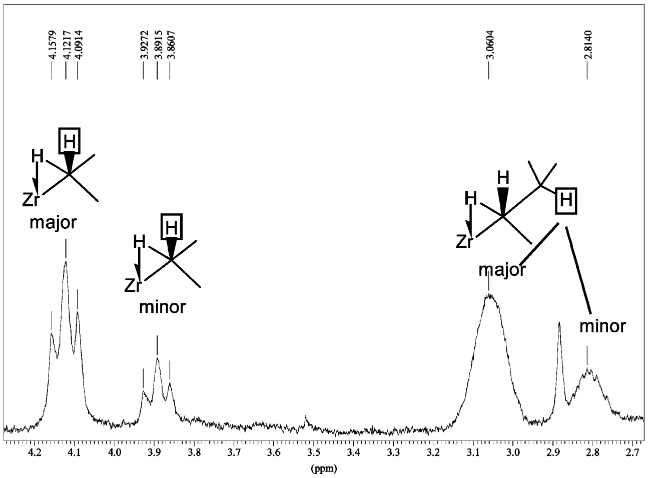


Figure 8. ^{1}H NMR spectrum of the reaction of **1** with 2,4,4-trimethyl-pent-1-ene in the Zr-alkyl region (CD_2Cl_2, −30 °C, 5 equiv per Zr).

Subsequent warming to −40 °C resulted in rapid loss of signals due to **1**, with formation of a [Zr_2CH_2CH-Me^tBu]-containing analogue of “species X” and 0.5 equiv of 2,2,3-trimethylbutane per Zr. Multiplets at δ −2.33 and 4.24 were assigned to the agostic and nonagostic hydrogens of Zr_2CH_2R, respectively, and the bridging hydride was found at δ −1.57. A low-field ^{13}C NMR resonance was again observed, δ 193. Oligomerization of the monomer was very slow at this temperature. On warming to −30 °C, loss of all signals due to 2,3,3-trimethylbut-1-ene and the zirconium alkyl species was observed within 30 min, with corresponding formation of oligomer.

When 10 equiv of 2,4,4-trimethylpent-1-ene were added to **1** at −70 °C, ca. 85% of the monomer rapidly inserted into a Zr−H bond. Two stereoisomers of the resulting [$Zr_2CH_2CHMeCH_2{}^tBu$] species were observed, in a 5:2 ratio. For the bridging hydride, two singlets were seen at δ −2.00 and −2.05. The signals assigned to agostic $ZrCH_2R$ (δ −3.33) appeared as two overlapping broad multiplets at this temperature. After warming the sample to −50 °C, complete formation of the Zr-alkyl species was observed, along with 0.5 equiv of 2,2,4-trimethylpentane per Zr. Signals assigned to agostic C−H (δ −3.16) and bridging hydrides (δ −1.96 and −2.02) had moved to higher frequency, with a relative intensity of 1:1. No significant oligomerization was observed at this temperature, even after 2 h. A ^{13}C NMR signal at δ 194 was seen, analogous to that found for diphenylethene addition; this was again assigned to a Zr−vinyl. After warming the sample to −30 °C, the signal due to agostic $ZrCH_2R$ was now split into two multiplets for the two stereoisomers (δ −2.98 and −3.02), but the spectrum was much the same as at the lower temperatures (see Figures 7 and 8). Oligomer formation now commenced, with corresponding loss of signals due to the zirconium alkyl complex.

By reference to these model experiments, it was now possible to interpret the original NMR spectra obtained in the reaction of trihydride **1** with isobutene. It was apparent that, in analogy to the 2,4,4-trimethylpent-1-ene addition, there were two isomers of “species X”, in a 2:1 ratio. There were two different [$Zr_2CH_2CHMe_2$] fragments, two low field ^{13}C NMR resonances (δ 193 and 194) and two ^{1}H NMR signals (δ −2.05 and −2.22, at −70 °C) in the region assigned to bridging hydride ligands. When 5 equiv of IB per Zr were added to **1** at −70 °C, partial hydrogenation (<0.5 equiv $CHMe_3$ per Zr) and some polymer were observed by ^{1}H NMR, and a small amount of insoluble polymer precipitate was seen. A 1:3 mixture of **1** and the Zr−isobutyl isomers was observed, with 1 equiv of free IB remaining. Conversion of **1** to the Zr−isobutyl species occurred slowly over 30 min at −70 °C, such that the ratio of **1** to isobutyl complexes was now 1:4. The concentration of free isobutene was correspondingly reduced. Addition of a further 10 equiv of IB resulted in complete formation of the two Zr−isobutyl isomers (ratio 2:1).

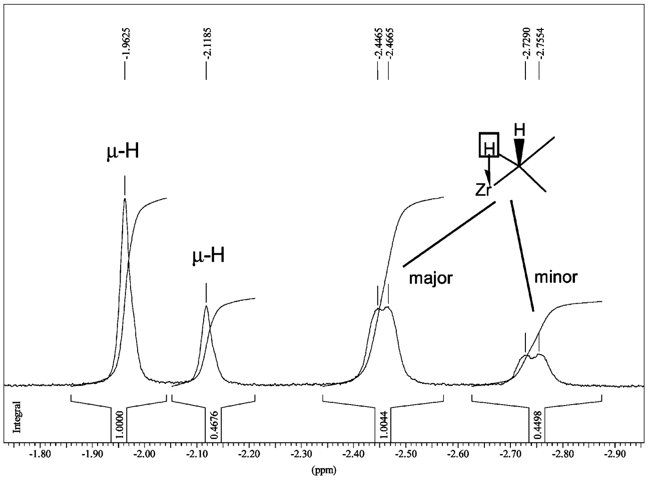


Figure 9. ^{1}H NMR spectrum (CD_2Cl_2, −30 °C) of the reaction of **1** with isobutene, high-field region.

On warming the sample to −50 °C and then to −30 °C, signals assigned to agostic $Zr_2CH_2CHMe_2$ were observed to move to significantly higher frequency, by up to 0.4 ppm. In contrast, for the minor isomer, the signal assigned to nonagostic $ZrCH_2CMe_2$ moved to *lower* frequency, from δ 4.7 to δ 4.3. Spectra obtained at −30 °C are shown in Figures 9 and 10. This temperature dependence was analogous to that observed in the model experiments. The signals assigned to bridging hydrides varied only slightly with temperature (by 0.1 ppm). The free IB in solution (ca. 5 equiv per Zr initially) was consumed slowly over time (∼ 15% reduction in signal intensity over 40 min). After consumption of the monomer, decomposition of the zirconium species to give

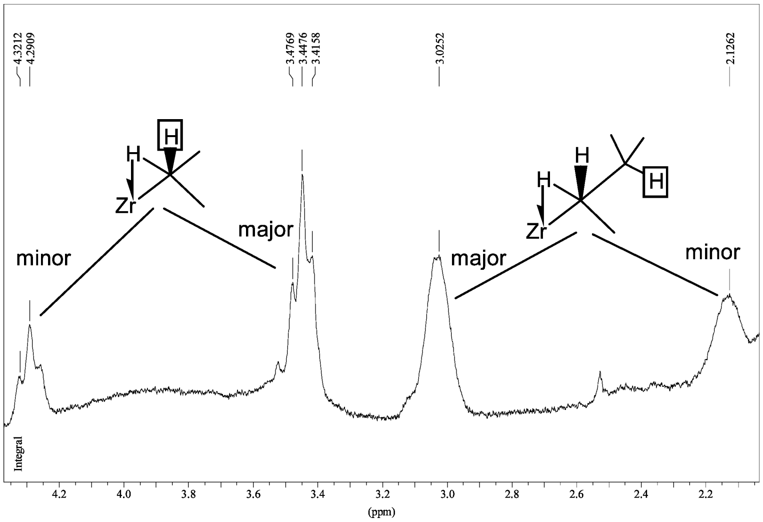
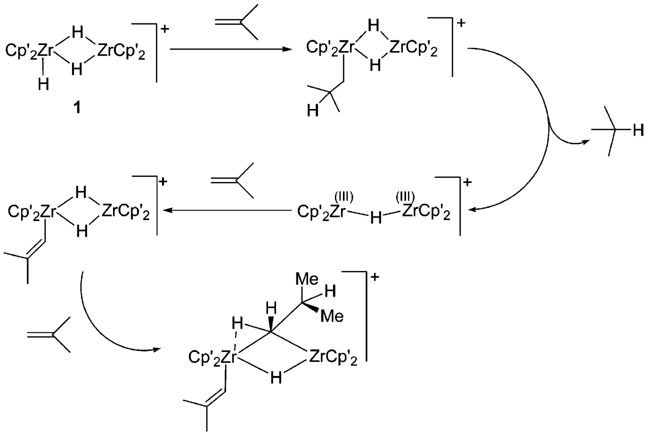


Figure 10. ^{1}H NMR spectrum (CD_2Cl_2, −30 °C) of the reaction of **1** with isobutene, Zr−CH_2 region.

Scheme 4. Possible Mechanism for the Reaction of 1 with Isobutene To Give μ-Alkyl Products of Type 6



mainly Cp'_2ZrCl_2 was observed; 1 equiv of $CHMe_3$ per Zr and some polyisobutene were also seen.

From the above NMR experiments, it seems clear that in all cases monomer inserts into a Zr−H bond. The square-pyramidal nature of the bridging carbon in **6** would account for the possibility of stereoisomers, as in **7**. In the case of 1,1-diphenylethene, the onset of cationic chemistry correlates with the buildup of **6** and the disappearance of **1**. We interpret this as an indication that **1** is not itself the cationic initiator. Instead, the hydride ligands are used in the hydrogenation of isobutene. The first step appears to be the insertion of monomer into a Zr−H bond. At least one species present during the polymerization appears to have a Zr−isobutyl fragment and a bridging hydride ligand. Two complete hydrogenations processes occur, with the second one being much slower than the first. It was postulated that a C−H activation step was involved, although evidence for this is circumstantial. A possible mechanism for formation of the bridging alkyl species is given in Scheme 4. On the other hand, as so often in catalysis, the possibility that “species X” is a side-product and not actually involved in the catalytic process cannot be ruled out.

Conclusions

The combination of $[Cp'_2ZrH_2]_2$ with various trityl salts of weakly coordinating anions gives binuclear cationic trihydrides $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+X^-$ which are powerful initiators for the polymerization of isobutene and its copolymerization with isoprene. The temperature dependence of M_n is indicative of a cationic mechanism. The polymer molecular weight is a function of the counteranion and increases in the order X = $[B(C_6F_5)_4] \approx [H_2N\{B(C_6F_5)_3\}_2] < [CN\{B(C_6F_5)_3\}_2]$. The hexahalocarborane anions $[CB_{11}H_6X_6]^-$ (X = Cl, Br, or I) were surprisingly not useful with our hydride system; halide abstraction from the carborane was suspected, based on NMR experiments. Using $[Cp'_4Zr_2H_3][CN\{B(C_6F_5)_3\}_2]$, high polymer molecular weights are obtained over a wide temperature range, with low initiator concentrations. Copolymer molecular weights at higher temperatures ($M_w \approx 5 \times 10^5$ g/mol at −35 °C) are among the highest reported for such conditions. Contrary to expectations, there is little reduction in either rate or molecular weight on addition of isoprene.

The highest molecular weights are obtained only under scrupulously dry conditions. Addition of substoichiometric quantities of water to the reaction medium resulted in a decrease in activity, while complete loss of activity was observed if $[H_2O] \approx [Zr]$. Copolymer molecular weights decreased linearly with increasing $[H_2O]$.

The zirconocene hydride system is found to give significantly higher molecular weight polyisobutene and poly(isobutene-*co*-isoprene) than the classical $Et_2AlCl/{}^tBuCl$ under neat-monomer conditions. The highest copolymer molecular weights obtained with the aluminum system at −35 °C were $M_w \approx 2 \times 10^5$, less than half that found with zirconocene hydrides. There are two main reasons for this difference: the aluminum system is inherently harder to control due to the high concentrations of co-initiator needed, and, most importantly, any chloroaluminate anions formed are much more likely to promote chain transfer than the weakly coordinating anions used in our system.

To gain some mechanistic understanding, the nature of the initiating species formed from reaction of $[Cp'_4Zr_2H_3][B(C_6F_5)_4]$ with isobutene or related monomers was probed in a series of NMR experiments. In each case, the major product of the reactions appears to be a binuclear alkyl- and possibly also hydride-bridged species, formed by insertion of monomer into a Zr−H bond. These binuclear species are stable for varying periods of time at low temperature (in the presence of excess monomer), depending on the bulkiness of the monomer. On warming to −30 °C or higher (up to −10 °C in the case of 1,1-diphenylethene), dimerization or oligomerization ensues, with accompanying loss of the NMR signals of the zirconocene species. It cannot be conclusively established whether these binuclear alkyl/hydride-bridged products are themselves the initiating species, but they clearly lead to initiation. In diphenylethene reactions, no NMR signals due to either $CH_3CPh_2^+$ or $CH_3CPh_2CH_2CPh_2^+$ were observed, suggesting that proton-initiation appears not to operate in the present case.

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of dried nitrogen, using standard Schlenk techniques. Dichloromethane was dried over calcium hydride and distilled under nitrogen, then stored in an ampule over 4A molecular sieves. NMR solvents were dried over activated 4A molecular sieves and degassed by several freeze−pump−thaw cycles, then stored in Young tap-sealed ampules under nitrogen. Isobutene was dried by passing through columns of 10 wt % sodium or potassium on activated alumina and of activated 4A molecular sieves. Isoprene was purified by filtration through a column of activated alumina, drying over sodium and vacuum distillation prior to use. Other monomers for NMR reactions were used as received. The compounds $[Cp'_2ZrH_2]_2$,[28] $[Cp'_4Zr_2H_3][B(C_6F_5)_4]$,[15a] $CPh_3[B(C_6F_5)_4]$,[29] $CPh_3[CN\{B(C_6F_5)_3\}_2]$,[16] and $CPh_3[H_2N\{B(C_6F_5)_3\}_2]$[18] were prepared using literature procedures. NMR spectra were recorded on a Bruker DPX300 instrument and referenced to residual solvent protons. Polymer molecular weights were determined by gel permeation chromatography in tetrahydrofuran using a PL GPC-220 instrument equipped with a refractive index and a PD2040 dual-angle light scattering detector and PL gel 2 × mixed bed-B, 30 cm, 10 μm columns. The concentration of water in the isobutene gas supply was measured using a Meeco Accupoint LP2 moisture transmitter, incorporating an electrolytic P_2O_5-containing cell, in which output current is proportional to $[H_2O]$ entering the cell.

NMR Reaction of $[Cp'_2ZrH_2]_2$ with $CPh_3[CN\{B(C_6F_5)_3\}_2]$. A solution of $CPh_3[CN\{B(C_6F_5)_3\}_2]$ (35 mg, 27.1 μmol) in CD_2Cl_2 (0.7 mL) at −78 °C was added via syringe to an NMR tube containing $[Cp'_2ZrH_2]_2$ (20 mg, 27.1 μmol), also at −78 °C. The mixture was shaken to dissolve the solids, and then quickly inserted into the precooled (−70 °C) NMR probe.

^1H NMR (CD_2Cl_2, −70 °C): 6.53 (br, s, 4H), 6.47 (m, 2H), 6.26 (bs, 2H), 5.89 (bs, 4H), 5.58 (bs, 4H); 4.55 (br, s, 1H, Zr−H_{term}), 0.24 (s, 36H, $SiMe_3$), −2.08 (d, J_{HH} = 15 Hz, 1H, μ-H), −2.68 (d, J_{HH} = 15 Hz, 1H, μ-H); $HCPh_3$ δ 7.31 (t, 6H, J_{HH} = 6.8 Hz, *m*-H), 7.23 (t, 3H, J_{HH} = 6.8 Hz, *p*-H), 7.11 (d, 6H, J_{HH} = 6.8 Hz, *o*-H), 5.60 (s, 1H, *H*CPh_3).

^{13}C NMR (CD_2Cl_2, −70 °C): δ 149.67 (*o*-C, C_6F_5), 144.2 (ipso-$HCPh_3$), 141.59 (*p*-C_6F_5), 138.56 (*m*-C_6F_5), 131.17 (*o*-$HCPh_3$), 129.82 (*m*-$HCPh_3$), 126.96 (*p*-$HCPh_3$), 116.97 (br, Cp′), 111.35 (br, Cp′), 56.55 (H*C*Ph_3), 0.47 ($SiMe_3$), 0.23 ($SiMe_3$).

^{19}F NMR (CD_2Cl_2, −70 °C): δ −134.01 (d, J_{FF} 21 Hz, *o*-F), −135.16 (d, J_{FF} 20 Hz, *o*-F), −158.17 (t, J_{FF} 21 Hz, *p*-F), −158.35 (t, J_{FF} 20 Hz, *p*-F), −164.89 (t, J_{FF} 21 Hz, *m*-F), −165.17 (t, J_{FF} 20 Hz, *m*-F).

NMR Reaction of $[Cp'_2ZrH_2]_2$ with $CPh_3[CB_{11}H_6I_6]$. A solution of $CPh_3[CB_{11}H_6I_6]$ (31 mg, 27 μmol) in CD_2Cl_2 (0.7 mL) at −78 °C was added via syringe to an NMR tube containing $[Cp'_2ZrH_2]_2$ (20 mg, 27 μmol), also at −78 °C. The red color of the trityl salt was observed to fade to a pale yellow. The mixture was shaken to dissolve the solids, and then quickly inserted into the precooled (−70 °C) NMR probe.

^1H NMR (CD_2Cl_2, −70 °C): Cp′ 7.00 (bs, 1H), 6.81 (br, s, 2H), 6.45 (br, s, 2H), 6.35 (br, s, 2H), 6.12 (br, s, 2H), 6.04 (br, s, 2H), 5.99 (m, br, 2H), 5.74 (s, 1H), 5.60 (br, s, 2H); hydrides 5.13 (s, 0.5H), 4.63 (bs, 0.5H), 3.52 (bs, 0.5H), 3.09 (bs, 0.5H), −2.95 (d, *J* 14.0 Hz), −3.15 (dd, *J* 14.0, 5.3 Hz); $SiMe_3$ 0.41, 0.28, 0.25, 0.19, 0.16, 0.11. Data for the $CHPh_3$ byproduct are not listed.

^{13}C NMR (CD_2Cl_2, −70 °C): δ 144.2 (*ipso*-$HCPh_3$), 129.83 (*m*-$HCPh_3$), 129.00 (*p*-$HCPh_3$), 126.98 (*p*-$HCPh_3$); Cp′ 120.30, 118.18, 114.66, 113.45, 112.13, 111.28; $SiMe_3$: 1.54, 1.00, 0.70, 0.58.

Polymerization Model Reactions. Chilled CD_2Cl_2 (0.4 mL, at −78 °C) was added to a cold NMR tube (−78 °C) containing solid $[Cp'_2ZrH_2]_2$ and $CPh_3[B(C_6F_5)_4]$ (ca. 20 μmol of each). After shaking to ensure complete reaction and formation of **1**, the required quantity of monomer (either isobutene, 1,1-diphenylethene, 2,4,4-trimethylpent-1-ene, or 2,3,3-trimethylbut-1-ene) was added via syringe. After thorough mixing, the tube was inserted into the precooled (−70 °C) spectrometer. The temperature was then varied as described in the text. NMR spectra are given in Tables 5 and 6.

Polymerization Reactions. Polymerizations were carried out in an all-glass 250 mL three-necked vessel, with a dry ice condenser attached. The top of the condenser was attached, via a three-way tap, to a nitrogen line and a vacuum-control system. The apparatus was flame-dried prior to use. After the vessel and condenser were cooled with dry ice/acetone, the appropriate quantity of dried isobutene was condensed in. Isoprene (if required) was then added via syringe and the system equilibrated at the desired temperature.

For reactions using $CPh_3[B(C_6F_5)_4]$ as activator, solid $[Cp'_2ZrH_2]_2$ and trityl salt were weighed into a Schlenk flask for each run. Prechilled (−78 °C) CH_2Cl_2 (2 mL) was then added to the precooled flask to form the initiator precursor. With the less soluble $CPh_3[CN\{B(C_6F_5)_3\}_2]$ and $CPh_3[NH_2\{B(C_6F_5)_3\}_2]$, a stock solution was prepared at room temperature and then cooled to −78 °C. The required quantity (typically 2 mL) of this solution was then added to solid $[Cp'_2ZrH_2]_2$ and the mixture equilibrated at −78 °C.

For the aluminum initiator system, stock solutions of Et_2AlCl (1 M) and Bu^tCl (0.0575 M) were prepared in CH_2Cl_2. Initially, 1.6 mL of the Et_2AlCl solution was added to the reactor by syringe and the mixture left to equilibrate at the given temperature before addition of the required quantity of precooled Bu^tCl solution.

The required pressure was set on the vacuum apparatus. To the rapidly stirred (800 rpm) monomer was then added the initiator solution by syringe. Rapid transfer is required to prevent decomposition of the zirconium species. The system was quickly brought to the required pressure so that the internal temperature was automatically controlled by the vacuum system, i.e., by the reflux rate of isobutene. Reactions were terminated by methanol addition (10 mL) when a significant increase in viscosity was observed (normally 10−15% conversion), or after 30 min. After venting excess monomer, the polymer was washed with methanol and dried at 60 °C to constant weight.

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(20) Molecular weights reported here are substantially higher than those reported by us previously for related systems,[9−11,13] largely due to differences in feed gas purity.

(21) After the completion of this work, Wu et al. published a study of $[H_2O]$ in IB polymerization using the $MeOH/BF_3$ initiating system. In line with our results, they found that increasing the $[H_2O]$ results in lower polymer molecular weights and broader molecular weight distributions: Wu, Y. X.; Gu, X. L.; Qiu, Y. X.; Fan, G. Q.; Wu, G. Y. *Acta Polym. Sin.* **2002**, *4*, 498.

(22) These polymer molecular weights were lower than some of those obtained by Kennedy (e.g., $M_w = 3.6 \times 10^5$ g/mol at -35 °C and 1×10^6 g/mol at -50 °C). However, Kennedy's polymerizations were performed in methyl chloride solvent and typically used small quantities of isobutene (2−3 mL). Under these conditions reaction exotherms are less likely than with our solvent-free system.

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(27) It is conceivable that the ^{13}C NMR signals around δ 200 are caused by an entirely different species and may indicate the existence of metal-bound monomer with cationic character, akin to **4**. However, conclusive data for this, as well as other possibilities including trinuclear and Cp-metalated structures for which there is some precedence,[15a] could no be obtained.

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