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Cationic Zirconocene Hydrides: A New Type of Highly Effective Initiators for Carbocationic Polymerizations

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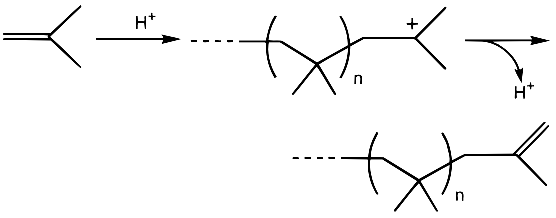
Summary: The reaction of [CPh_3][$B(C_6F_4R)_4$] with [Cp'_2ZrH_2]$_2$ ($Cp' = C_5H_4SiMe_3$) gives the new binuclear hydrido complexes [$Cp'_4Zr_2H_3$][$B(C_6F_4R)_4$] ($R = F$, $SiPr^i_3$), which are highly active initiators for the polymerization of isobutene and isobutene−isoprene copolymerizations at near-zero concentrations of ionizing solvents. The structure of the trinuclear hydride [$Cp'_5(\eta^1{:}\eta^5$-$C_5H_3SiMe_3)Zr_3H_4$]$^+$[$B(C_6F_4SiPr^i_3)_4$]$^-$ is reported.

The copolymerization of isobutene and isoprene to butyl rubber is a large-scale industrial process based on a $AlCl_3/H_2O$ solution as “catalyst” in an ionizing solvent (chloromethane).[1] The polymerization is initiated by protons and follows a carbocationic mechanism, with tertiary carbocations as the propagating species (eq 1). Since under such conditions, especially in the presence of nucleophiles such as H_2O, Cl^- and $AlCl_4^-$, chain transfer via deprotonation of the $-CMe_2^+$ cations is facile, polymers of adequately high molecular weight are only obtained at very low (−100 °C) temperatures, a costly and energy-intensive procedure.



(1)

Cationic group 4 metallocenes stabilized by very weakly coordinating anions are well-known as Ziegler−Natta catalysts for the polymerization of 1-alkenes.[2] The feature common to all these compounds is the highly electrophilic metal center and the essentially nonnucleophilic character of the anion. Such systems should therefore (a) be capable of acting as cationic initiators and (b) minimize nucleophile-assisted chain transfer and, hence, allow cationic polymerizations to be conducted at significantly higher temperatures. Indeed, as we and others have shown, several types of cationic or zwitterionic early-transition-metal, lanthanide, and main-group organometallic complexes are active in this way, including $Cp^*TiMe_2(\mu$-$Me)B(C_6F_5)_3$,[3] [$AlCp_2$]$^+$,[4] $(C_5H_4SiMe_3)_2Y(\mu$-$Me)B(C_6F_5)_3$,[5] [$Zr\{N(SiMe_3)_2\}_3$]$^+$,[6] Cp_2ZrMe_2/[CPh_3][$B(C_6F_5)_4$]/H_2O,[7] $Cp_2ZrMe_2/B(C_6F_5)_3$,[8] and [$SiMe_3$][$B(C_6F_5)_4$],[9] which give high-molecular-weight isobutene polymers at temperatures as high as −20 °C.

Although after a few monomer additions to the first initiation product the course of the polymerization should be independent from the organometallic species and at best be influenced by the nature of the counteranion, we observed that for a given anion different organometallic species exhibit very different initiator efficiencies, with some leading to high polymer yields, while others give comparably low conversions before becoming inactive. We now find that cationic zirconocene hydrides constitute a new family of unusually effective initiators, in particular for the polymerization and copolymerization of isobutene at near-zero concentrations of chlorocarbon solvents.

Cationic zirconocene hydrides [Cp_2ZrH]$^+$ and [$Cp_2ZrH(L)$]$^+$ have previously been made by hydrogenolysis of the corresponding methyl complexes; all are mononuclear.[10,11] In contrast, the reaction of [CPh_3][$B(C_6F_4R)_4$][10d,12] with [Cp'_2ZrH_2]$_2$ ($Cp' = C_5H_4SiMe_3$)[13] gives the binuclear complexes [$Cp'_4Zr_2H_3$][$B(C_6F_4R)_4$] (**1**: **a**, $R = F$; **b**, $R = SiPr^i_3$) (Scheme 1).[14] The reaction

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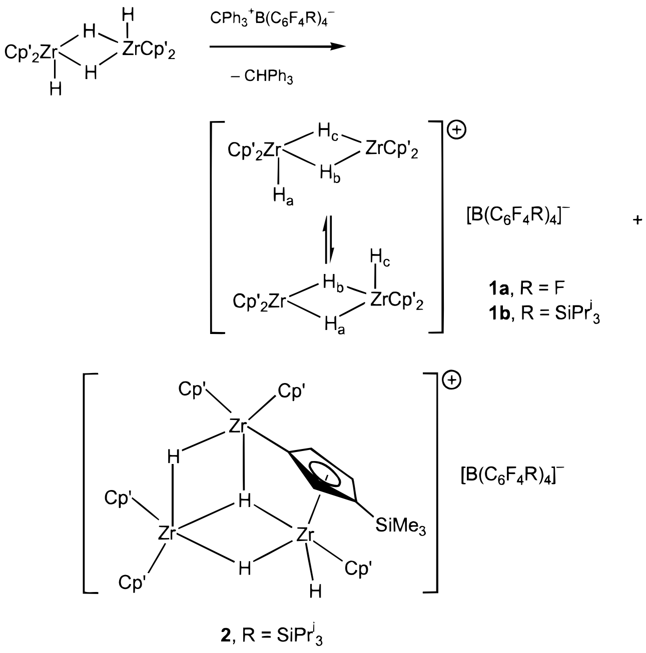
Scheme 1



is quantitative. If an excess of CPh_3^+ over $[Cp'_2ZrH_2]_2$ is employed, **1** is again formed together with unreacted CPh_3^+; there is no further reaction to mononuclear $[Cp'_2ZrH]^+$.

The compounds are obtained as colorless crystals from toluene. Two of the hydride ligands are bridging (**1a**: δ −2.02 and −2.66), the third is terminal (δ 4.55).[15] The compounds are fluxional. Below −60 °C all three hydride resonances are resolved; at −50 °C the signal for H_a and H_c (−2.02 and 4.55) coalesce, while H_b (−2.66) begins to broaden. At −30 °C interchange of all three hydrides is fast on the NMR time scale. The compounds are stable in dichloromethane solution up to −30 °C for a period of hours but decompose at higher temperatures.

The reaction of $[Cp'_2ZrH_2]_2$ with either 1 or 2 equiv of $B(C_6F_5)_3$ proceeds in an analogous manner to give $[Cp'_4Zr_2H_3][HB(C_6F_5)_3]$ (**1c**); again, there is no evidence for a mononuclear cationic hydride. In addition to the signals for $[Cp'_4Zr_2H_3]^+$ seen for **1a** and **1b**, the H−B signal of **1c** is found at δ 3.49 (−90 °C). Compound **1c** is less stable in CD_2Cl_2 and begins to decompose at −30 °C.

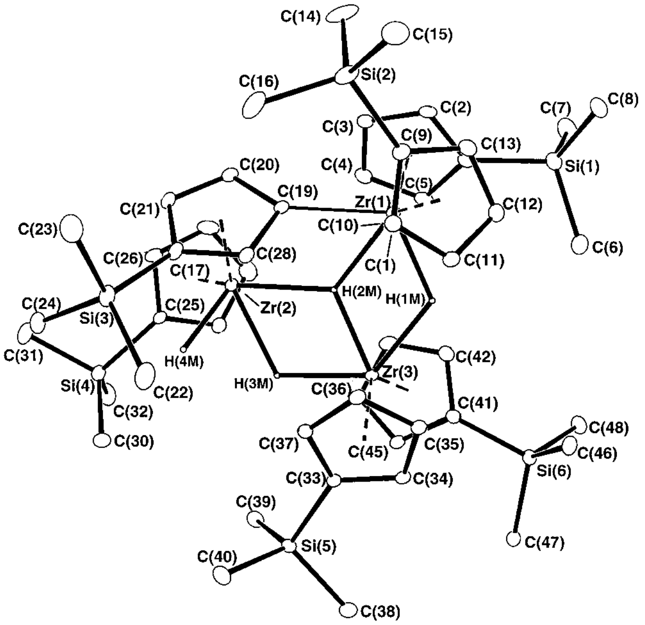


Figure 1. Structure of the cation in **2**. Selected bond lengths (Å) and angles (deg): Zr(1)−C(19) = 2.304(6), Zr(1)−H(1) = 2.04(5), Zr(1)−H(2) = 2.24(6), Zr(3)−H(1) = 2.11(5), Zr(3)−H(2) = 2.00(6), Zr(3)−H(3) = 2.02(6), Zr(2)−H(2) = 2.18(6), Zr(2)−H(3) = 2.17(6), Zr(2)−H(4) = 1.73(5); C(19)−Zr(1)−H(1) = 118(2), C(19)−Zr(1)−Zr(3) = 88.40(14), H(1)−Zr(1)−H(2) = 59(2), H(2)−Zr(2)−H(3) = 62(2), H(2)−Zr(2)−H(4) = 117(3), H(3)−Zr(2)−H(4) = 66(3), H(1)−Zr(3)−H(2) = 62(2), H(2)−Zr(3)−H(3) = 67(2), H(1)−Zr(3)−H(3) = 129(2).

The synthesis of **1** may be accompanied by the formation of cationic zirconocene hydrides of higher nuclearity, as shown by the isolation of a second hydrido complex during the recrystallization of **1b**, $[Cp'_5(\eta^1{:}\eta^5\text{-}C_5H_3SiMe_3)Zr_3H_4]^+[B(C_6F_4SiPr^i{}_3)_4]^-\cdot 3.5(\text{toluene})$ (**2**), as pale yellow-green crystals, evidently the product of metalation of one of the Cp′ ligands. The compound was identified by X-ray diffraction. The cation (Figure 1) is trinuclear, with one Zr−C σ-bond to a neighboring Cp′ ligand and three roughly coplanar bridging hydrides and one terminal hydride. This large cation is stabilized by the bulky anion $[B(C_6F_4SiPr^i{}_3)_4]^-$ [10d] and contains 3.5 (disordered) toluene molecules of crystallization.[16]

For isobutene polymerizations equimolar amounts of $[Cp'_2ZrH_2]_2$ and $[CPh_3][B(C_6F_5)_4]$ were mixed in cold (−78 °C) CH_2Cl_2. Aliquots of this solution were injected into liquid isobutene equilibrated at the given temperatures (Table 1).[17] Rapid polymerization ensues. Whereas under these conditions polymerizations initiated with $Cp_2ZrMe_2/B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$[7,8] are typically isothermal or lead only to small temperature increases, initiation with the hydride system produced a significant polymerization exotherm. The conversion rates and polymer yields are dramatically higher than in the case of Cp_2ZrMe_2 under otherwise identical conditions, while the polymer molecular weights are comparable. Although isoprene is known as a powerful retardant of both polymer yields and polymer molecular weights,[1]

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(14) Preparation of **1a**: A toluene solution (20 mL) of $[CPh_3][B(C_6F_5)_4]$ (0.5 g, 0.54 mmol) was added to a stirred toluene solution (5 mL) of $[ZrCp'_2H_2]_2$ (0.4 g, 0.55 mmol) cooled to 0 °C. The reaction mixture was stirred at this temperature for 30 min before it was warmed to room temperature and all volatiles were removed in vacuo. The white solid residue was washed with light petroleum to remove $HCPh_3$. The compound proved insufficiently soluble in toluene for recrystallization. Anal. Calcd for $C_{56}H_{55}BF_{20}Si_4Zr_2$: C, 47.6; H, 3.92. Found: C, 48.0; H, 4.3. Preparation of **1b**: A toluene solution (20 mL) of $[CPh_3][B(C_6F_4SiPr^i{}_3)_4]$ (0.8 g, 0.54 mmol) was added to a stirred toluene solution (20 mL) of $[ZrCp'_2H_2]_2$ (0.4 g, 0.54 mmol) cooled to 0 °C. The reaction mixture was stirred at this temperature for 30 min. The solution was filtered and placed in a refrigerator (5 °C) to give a small yield of **1b** as colorless crystals. Crystalline **1b** is only sparingly soluble in toluene. Anal. Calcd for $C_{92}H_{139}BF_{16}Si_8Zr_2$: C, 56.18; H, 7.12. Found: C, 56.2; H, 7.2. Preparation of **2**: When the toluene filtrate from the preparation of **1b** was stored at 5 °C for several days, small pale yellow-green crystals of **2** separated (ca. 0.4 g). The crystals readily lose solvent on evacuation but proved suitable for X-ray diffraction. The hydride signals could not be located by NMR.

(15) In contrast, a related binuclear tungsten hydride has a symmetrical structure, $[(Cp_2WH)_2(\mu\text{-}H)]^+$: Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208.

(16) Crystal data: $C_{108}H_{165}BF_{16}Si_{10}Zr_3\cdot 3.5C_7H_8$; space group $P2_1/n$; monoclinic; a = 20.3249(11) Å; b = 29.797(2) Å; c = 24.0124(11) Å; β = 97.026(2)° at 160 K; V = 14433.3(13) Å^3; Z = 4; final R indices ($I > 2\sigma(I)$) R1 = 0.0761, wR2 = 0.1890 for 24 803 absorption-corrected reflections (R(int) = 0.1100).

Table 1. Isobutene Homo- and Copolymerizations with Cationic Zirconocene Methyl and Zirconocene Hydride Precursors[a]

run no.	Zr complex	amt of Zr (μmol)	temp (°C)	amt of isobutene (mL)	initiator solvent (amt, mL)	amt of isoprene (mL)	time (min)	polymer yield (g)	IB conversn (%)	$M_w \times 10^{-3}$	M_w/M_n	isoprene incorp (mol %)
1	Cp_2ZrMe_2	50	−78	100	CH_2Cl_2 (1.5)		20	7.3	13	2,260	1.7	
2	Cp_2ZrMe_2	50	−30	100	CH_2Cl_2 (1.5)		20	0.3	0.5	554	3.5	
3	Cp_2ZrMe_2	50	−78	100	CH_2Cl_2 (1.5)	2.0	20	1.5	2.6	458	2.1	1.6
4	Cp'_2ZrMe_2	50	−70	100	CH_2Cl_2 (1.5)	1.5	30	3.3	5.7	396	2.7	1.6
5	Cp'_2ZrMe_2	50	−30	100	CH_2Cl_2 (1.5)	1.5	30	4.1	7.1	85	4.1	1.3
6	$[Cp'_2ZrH_2]_2$	33	−78	100	CH_2Cl_2 (1.0)		15	40.0[b]	70	465	8.9	
7	$[Cp'_2ZrH_2]_2$	50	−35	100	CH_2Cl_2 (3.0)		30	32.0[b]	56	214	2.7	
8	$[Cp'_2ZrH_2]_2$	33	−30	100	CH_2Cl_2 (1.0)	1.5	20	23.8	42	142	2.7	1.3
9	$[Cp'_2ZrH_2]_2$	15	−30	60	$C_6H_4F_2$/tol (0.5)[c]		3	7.5	22	225	3.2	
10	$Cp_2Zr(allyl)_2$	15	−30	60	CH_2Cl_2 (0.5)		30	8.9	26	136	7.2	

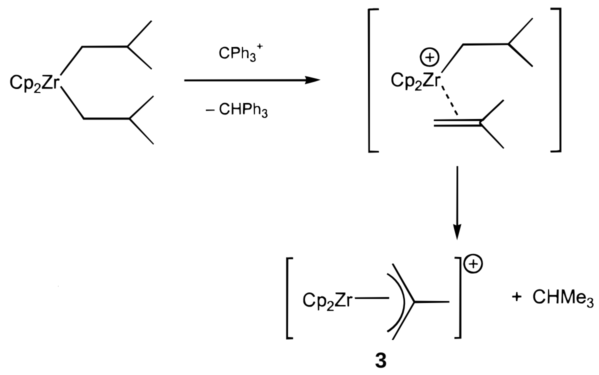
[a] Conditions: 60 or 100 mL of isobutene; initiation by appropriate amounts of premixed solutions of 0.05 M zirconocene complex in CH_2Cl_2 and 0.1 M $[CPh_3][B(C_6F_5)_4]$ in CH_2Cl_2 (except for entry 9); stirring rate 1000 rpm. The reactions were terminated by injection of 2 mL of methanol. [b] Exothermic reaction. [c] 1,2-Difluorobenzene/toluene 60:40 (v/v).

the conversion rates and molecular weights of the isobutene−isoprene copolymers obtained with the zirconocene hydride initiators are remarkably similar to the values for isobutene homopolymers made under comparable conditions, especially at reaction temperatures of −50 °C and above. Of particular significance is the high conversion in the isobutene−isoprene copolymerization at −30 °C (Table 1, entry 8), i.e., under conditions where the $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ system produces only trace amounts of copolymer.

Whereas in conventional polymerizations chloromethane is present in high concentration to ensure adequate ionization of the initiator system, the reactions reported here proceed rapidly with very low concentrations of chlorocarbons. As entry 9 shows, chlorinated solvents are not in fact required; very similar results are obtained using a 60:40 mixture of 1,2-difluorobenzene and toluene as the solvent for the initiator mixture. Remarkably, the high initiating efficiency is specific to zirconocene hydrides, whereas analogous hafnocene hydrides $[Cp'_2HfH_2]_2$ give significantly lower polymer yields.

There is evidence that complexes **1** do not act as initiators themselves but are converted to give as as yet unidentified species, possibly via C−H activation processes;[18] notably, the polymerization of isobutene is accompanied by the hydrogenation of one molecule of isobutene per zirconium. The initiation mechanism with cationic hydrides differs therefore fundamentally from that of zirconocene methyls. Since insertion of isobutene into the Zr−H bonds was suspected, attempts were made to generate the resulting isobutyl cation, $[Cp_2Zr(CH_2CHMe_2)]^+$, by reacting $Cp_2Zr(CH_2CHMe_2)_2$ with $[CPh_3][B(C_6F_5)_4]$. However, the reaction proceeds according to Scheme 2 to give the allyl complex $[Cp_2Zr(\eta^3\text{-methallyl})]^+$ (**3**). The reaction is fast even at −78 °C; there was no evidence for a cationic isobutyl intermediate. Complex **3** is also a powerful polymerization initiator (Table 1, entry 10).

Scheme 2



Cationic allyl complexes of type **3** have been discussed as deactivation products of 1-alkene polymerization catalysts.[19] Recent theoretical studies have shown that the reaction $[Cp_2Zr(alkyl)]^+ \rightarrow [Cp_2Zr(allyl)]^+ + H_2$ is indeed favorable and explains the occurrence of internal unsaturation in polyethylene.[20] Scheme 2 suggests that the related reaction $[Cp_2Zr(alkyl)]^+ + \text{olefin} \rightarrow [Cp_2Zr(allyl)]^+ + \text{alkane}$ is similarly facile and likely to be another contributory factor in the formation of allylic complexes during Ziegler−Natta polymerizations.

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Supporting Information Available: Text and tables giving spectroscopic data, X-ray structure determination, and crystal data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The initiator stock solution was prepared by adding a cold (−78 °C) dichloromethane solution of $[CPh_3][B(C_6F_5)_4]$ to an equimolar amount of $[Cp'_2ZrH_2]_2$ kept at −78 °C. Isobutene polymerizations were carried out in a rigorously dried double-jacketed all-glass reactor fitted with an internal thermocouple. Isobutene was dried by passing through $CaCl_2$, P_2O_5, and 4A molecular sieves and stored over $Et_2AlOHex$; isoprene was distilled from sodium and stored over 4A molecular sieves. During the polymerization runs the reactor was open to a paraffin bubbler to prevent pressure buildup. The required quantity of isobutene was condensed into the reactor at 1 bar and equilibrated at the required temperature for 30 min at a stirring rate of 800 rpm. An aliquot of the initiator solution was added via syringe. The polymerizations were terminated by injecting 2 mL of methanol. Reaction times for less active initiators was 30 min; in other cases the polymerization was terminated when a significant increase in viscosity was apparent, which corresponded to about 50−60% conversion. The polymer was precipitated with methanol, washed, and dried at 60 °C for 48 h.

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