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Base-Free Cationic Zirconium Benzyl Complexes as Highly Active Polymerization Catalysts

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Zirconium dibenzyl complexes $Cp_2Zr(CH_2Ph)_2$ (**1a**), $(C_5H_4SiMe_3)_2Zr(CH_2Ph)_2$ (**2a**) *rac*-Et-$(Ind)_2Zr(CH_2Ph)_2$ (**3a**), and *i*-Pr(Cp)(Flu)$Zr(CH_2Ph)_2$ (**4a**) react with $[CPh_3]^+B(C_6F_5)_4^-$ (**5**) in toluene to give base-free cationic zirconium benzyl complexes of the type $[Cp'_2Zr(CH_2Ph)]^+$-$B(C_6F_5)_4^-$ (**1b**–**4b**). The cationic complexes contain η^2-bonded benzyl groups; they are thermally significantly more stable than related methyl complexes, e.g. $[Et(Ind)_2Zr(CH_3)]^+$, and catalyze the polymerization of ethene and propene at 1 bar of monomer pressure. The activities increase with temperature and are similar to or better than those of the corresponding Cp'_2ZrCl_2/methylaluminoxane catalysts under comparable conditions; at 60°C **3b** exhibits an activity of >21 000 kg of polypropene/[(mol of Zr)·$[C_3H_6]$·h]. The temperature dependence of the steroeregularity and the molecular weight distribution of polypropenes produced with **3b** and **4b** closely reflects that of polymers produced with methylaluminoxane-activated catalysts. More electron-deficient zirconium benzyl complexes are less active catalysts, with the polymerization activity for ethene decreasing for $[Cp_2Zr(CH_2Ph)]^+ > [CpZr(CH_2Ph)_2]^+ > [Zr(CH_2Ph)_3]^+ \gg Zr(Ch_2Ph)_4$; polyethene produced with $[Zr(CH_2Ph)_3]^+$ has a high molecular weight (M_w = ca. 500 000, M_w/M_n = 2.8).

The role of cationic d^0 complexes of the type $[Cp_2M(R)]^+$ (M = Ti, Zr, Hf, Th) as the catalytically active species in the polymerization of α-olefins by homogeneous Ziegler–Natta catalysts is now well established.[1–9] As would be expected of coordinatively unsaturated complexes of early transition metals, these 14-electron species are highly susceptible to the presence of nucleophiles, and their efficiency as catalysts has been shown to be influenced and limited by the nature of the solvent, the presence of base, and the nature of the counteranion.[3–6,10] The tendency of anions such as BPh_4^- and $B(C_6H_4F)_4^-$ to coordinate to cationic d^0 metal centers and compete sucessfully with the olefin substrate for the coordination sites required for the catalytic chain growth reaction has been pointed out.[4d,e,6d,12] In agreement with these observations extremely weakly basic and poorly coordinating anions such as $B(C_6F_5)_4^-$ give the most active catalysts.[5a,6d]

Cationic metal alkyl complexes are generally synthesized by the protolysis of metal dialkyls with weakly acidic ammonium salts (eq 1).[4a,d–f,5,6,10,12] More recently, methyl abstraction with triphenylcarbenium salts has been employed (eq 2).[13,14b] Both methods allow the generation of cationic complexes in the absence of coordinating solvents

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[14] (a) A reviewer pointed out that under conditions of high dilution, as used in catalysis, coordination of weakly basic amines such as dimethylaniline is negligible and has no negative effect on catalyst activity. We agree with this view and have presented supporting evidence.[14b] In concentrated solutions, however, amines are extensively coordinated and can impede the isolation of base-free complexes. (b) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1.

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$$\mathrm{Cp_2MR_2 + [HNR'_2Ph]^+X^- \rightarrow [Cp_2MR]^+X^- + R{-}H + NR'_2Ph} \quad (1)$$

$$\mathrm{R' = Me, Et}$$

$$\mathrm{Cp_2MMe_2 + [CPh_3]^+X^- \rightarrow [Cp_2MMe]^+X^- + Ph_3C{-}Me} \quad (2)$$

or stable ligands and proceed readily in solvents of low polarity, such as toluene. However, with method 1 coordination of the aniline byproduct cannot be excluded[14] and is frequently encountered during attempts to isolate cationic base-free metal alkyl complexes from the reaction mixtures.[4e,12,15] Method 2 avoids the generation of basic byproducts; there is no noticeable influence of triphenylalkane on the catalytic efficiency of the system.

Reactions 1 and 2 and catalytic studies have so far almost exclusively concentrated on cationic methyl complexes, $[Cp_2M{-}CH_3]^+$. However, there are indications that such species have limited thermal stability (see below)[4d,12a] which may restrict the use of such systems at technically useful temperatures. We were interested in thermally more stable cationic metal alkyl complexes and expected that base-free benzyl complexes might be useful in this respect. Cationic zirconium benzyl complexes were first prepared by Jordan et al. via the oxidative dealkylation of $Cp_2Zr(CH_2Ph)_2$ with $AgBPh_4$ or $[Cp'_2Fe]BPh_4$.[16] Due to the insolubility of the oxidizing agents in noncoordinating solvents such as toluene these reactions proceed only in solvents such as THF or acetonitrile to give isolable adducts, $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(MeCN)]^+$ and $[Cp_2Zr(\eta^1\text{-}CH_2Ph)(THF)]^+$. The latter partially dissociates in dichloromethane to give $[Cp_2Zr(\eta^2\text{-}CH_2Ph)]^+$ which catalyzes the polymerization of ethene with moderate activity. Propene is not polymerized under these conditions.[16b] We report here the synthesis of base-free benzyl complexes and their use as catalyst precursors for the polymerization of ethene and propene.

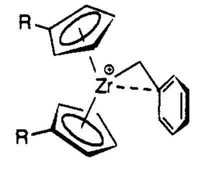
Results and Discussion

Synthesis of Neutral and Cationic Zirconium Benzyl Complexes. The zirconocene dibenzyl compounds **1a** and **2a** are prepared from Cp'_2ZrCl_2 and $PhCH_2MgCl$ by standard methods ($Cp' = C_5H_5, C_5H_4SiMe_3$). The use of a large excess of Grignard reagent, as recommended earlier,[17] or of KCH_2Ph[16b] was not found to be necessary to obtain halide-free products. The *ansa*-metallocene derivatives *rac*-$Et(Ind)_2Zr(CH_2Ph)_2$ (**3a**) and *i*-Pr(Cp)(Flu)$Zr(CH_2Ph)_2$ (**4a**) are prepared similarly as orange crystals. The hydrogens of the benzylic CH_2 groups in **3a** and **4a** are inequivalent and appear as a set of two doublets, similar to $(ETHI)Zr(CH_2Ph)_2$[16b] [ETHI = ethylenebis(tetrahydroindenyl)] but shifted to higher field due to the magnetic anisotropy of the indenyl and fluorenyl benzene rings (Table I).

The reaction of **1a**–**4a** in toluene with toluene solutions of $[CPh_3]^+B(C_6F_5)_4^-$ (**5**) proceeds smoothly at −78 to +20 °C to give cationic zirconium benzyl complexes in situ (eq 3). The reaction is accompanied by a color change from orange to brown-orange or red-brown. Following the reaction between **1a** and **5** in 1,1,2,2-$C_2D_2Cl_4$ by ^1H NMR at 0 °C confirms that the formation of **1b** is fast and gives 1 equiv of 1,1,1,2-tetraphenylethane as the byproduct. The $Zr{-}CH_2Ph$ signal of **1b** is observed at δ 3.21 ppm, 1.15 ppm downfield from the benzyl resonance of the neutral precursor **1a**. Small quantities of triphenylmethane were also identified, but no 1,2-diphenylethane (dibenzyl) was found which might have been expected if benzyl radicals had been formed in the course of the reaction. The corresponding $Zr{-}CH_2Ph$ resonance for **2b** occurs as a singlet at δ 3.49. The observation of a J(C–H) value of 132 Hz for $ZrCH_2Ph$ and of a high-field shifted ipso carbon of the benzylic phenyl group in the ^{13}C NMR spectrum of **1b** is in agreement with an η^2-coordination of the benzyl ligand.[16,18] The spectroscopic data for **1b** closely correspond to those reported by Jordan for $[Cp_2Zr(\eta^2\text{-}CH_2Ph)]^+$ in equilibrium with $[Cp_2Zr(CH_2Ph)THF)]^+$.[16] Solutions of **1b** in tetrachloroethane are fairly stable, and there is no noticeable decomposition (NMR) at 25 °C over a period of 1–2 h. The ^{19}F NMR spectrum is that of the undisturbed $B(C_6F_5)_4^-$ anion; there is no indication of fluorine coordination to zirconium.

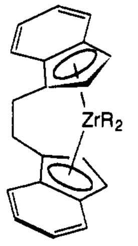
$$\mathrm{Cp'_2Zr(CH_2Ph)_2 + [CPh_3]B(C_6F_5)_4 \longrightarrow}$$

1a, $Cp' = C_5H_5$;
2a, $Cp' = C_5H_4SiMe_3$

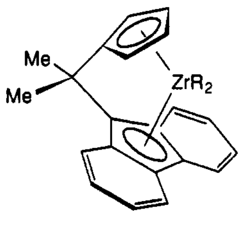


$$+\ \mathrm{Ph_3C{-}CH_2Ph} \quad (3)$$

1b, **2b**



3a, R = CH_2Ph
3b, $R_2 = (CH_2Ph)^+$
3c, R = Me



4a, R = CH_2Ph
4b, $R_2 = (CH_2Ph)^+$
4c, R = Me

The reaction of **3a** with $[CPh_3]B(C_6F_5)_4$ leads to **3b**. The presence of a stereorigid ligand framework in this complex implies that the hydrogens of the benzylic methylene group are inequivalent and appear as a set of two doublets. As may be expected, these are shifted to lower field on going from the neutral to the cationic complex, from δ −0.37 and +0.59 in **3a** to δ 0.12 and 3.31 ppm in **3b**. The increase in the chemical shift differences between the two benzylic hydrogens (**3a**, $\Delta\delta = 0.96$; **3b**, $\Delta\delta = 3.19$ ppm) is seen as further evidence for the adoption

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Table I. ^{1}H and ^{13}C NMR Data[a]

compd [solvent]	^{1}H NMR	assgnt	^{13}C NMR[b]	assgnt
$(C_5H_4SiMe_3)_2Zr(CH_2Ph)_2$ (**2a**) [C_6D_6]	0.21 (s, 18 H)[c]	$SiMe_3$	0.20	$SiMe_3$
	2.21 (s, 4 H)	$C\mathit{H}_2$Ph	62.5 (t, J_{CH} = 119.5)	$\mathit{C}H_2$Ph
	6.10–6.23 (m, 8 H)	Cp	117.2	Cp, C2
	7.07–7.40 (m, 10 H)	Ph	118.5	Cp, C1
			120.7	Cp, C3
			121.3	para C of Ph
			125.9	meta C of Ph
			128.5	ortho C of Ph
			153.3	Ph ipso
$Et(Ind)_2Zr(CH_2Ph)_2$ (**3a**)[d] [CD_2Cl_2]	–0.37 (d, 2 H, J = 11.2)[c]	$C\mathit{H}_2$Ph	27.9	$-CH_2CH_2-$
	0.59 (d, 2 H, J = 11.2)	$C\mathit{H}_2$Ph	68.4 (t, J_{CH} = 120.5)	$\mathit{C}H_2$Ph
	3.30 (m, 4 H)	$-CH_2CH_2-$	108.7	C2 of C_5
	5.69 (d, 2 H, J = 3.4)	Cp	114.1	C3 of C_5
	5.79 (d, 2 H, J = 3.4)	Cp	116.8	C1 of C_5
	6.53–7.63 (m)	Ph	120.8	C_6
			122.6	C_6
			123.5	C_6 ipso
			124.8	C_6
			125.3	C_6
			125.9	C_6 ipso
			124.7	Ph, para
			125.2	Ph, meta
			128.3	Ph, ortho
			152.7	Ph, ipso
3a [C_6D_6]	–0.34 (d, 2 H, J = 11.3)[c]	$C\mathit{H}_2$Ph		
	0.70 (d, 2 H, J = 11.3)	$C\mathit{H}_2$Ph		
	2.57 (m, 4 H)	$-CH_2CH_2-$		
	5.34 (d, 2 H, J = 3.4)	Cp		
	5.69 (d, 2 H, J = 3.4)	Cp		
	6.53–7.13 (m, 18 H)	Ph		
i-Pr(Cp)(Flu)$Zr(CH_2Ph)_2$ (**4a**)[d] [CD_2Cl_2]	–0.61 (d, 2 H, J = 10)[c]	$C\mathit{H}_2$Ph	29.0	$\mathit{C}Me_2$
	–0.23 (d, 2 H, J = 10)	$C\mathit{H}_2$Ph	40.4	$C\mathit{Me}_2$
	2.11 (s, 6 H)	CH_3	61.1 (t, J_{CH} = 122.6)	$\mathit{C}H_2$Ph
	5.24 ("s", br, 4 H)	Cp	102.2	Cp, C2
	6.59–8.28 (m, 18 H)	Flu, Ph	109.0	Cp, C1
			117.2	Cp, C3
			120.9	Flu
			123.4	Flu
			123.9	Flu
			124.5	Flu
			127.9	Flu
			129.4	Flu
			121.1	Ph, para C
			125.7	Ph, meta C
			128.4	Ph, ortho C
			150.6	Ph, ipso
4a [C_6D_6]	–0.52 (d, 2 H, J = 10.2)[c]	$C\mathit{H}_2$Ph		
	–0.22 (d, 2 H, J = 10.2)	$C\mathit{H}_2$Ph		
	1.50 (s, 6 H)	CH_3		
	4.88 (t, 2 H, J = 2.6)	C2 of Cp		
	5.22 (t, 2 H, J = 2.6)	C3 of Cp		
	6.26–7.67 (m, 18 H)	Flu, Ph		
$[Cp_2Zr(CH_2Ph)]B(C_6F_5)_4$ (**1b**) [$C_2D_2Cl_4$]	3.21 (s, 2 H)[e]	$C\mathit{H}_2$Ph	50.54 (t, J_{CH} = 132)[g]	$\mathit{C}H_2$Ph
	6.25 (s, 10 H)	Cp	111.5	Cp
	7.13 (d, 2 H, J = 6.5)	ortho H of Ph	123.3	Ph
	7.2–7.4 (m)[f]	Ph[f]	124.0	Ph ipso
			131.6	Ph
			132.0	Ph
			136.0 (d, J_{CF} = 245.6)	$B(C_6F_5)_4^-$, meta
			138.0 (d, J_{CF} = 259.4)	$B(C_6F_5)_4^-$, para
			142.4	$B(C_6F_5)_4^-$, ipso
			147.8 (d, J_{CF} = 241.1)	$B(C_6F_5)_4^-$, ortho
$[Et(Ind)_2Zr(CH_2Ph)]B(C_6F_5)_4$ (**3b**) [$C_2D_2Cl_4$]	0.12 (d, 1 H, J = 7.8)[e]	$C\mathit{H}_2$Ph	31.0[g–i]	$-\mathit{C}H_2\mathit{C}H_2-$
	3.31 (d, 1 H, J = 7.8)	$C\mathit{H}_2$Ph	56.7 (t, J_{CH} = 132)	$\mathit{C}H_2$Ph
	3.80 (m, 4 H)	$-CH_2CH_2-$	106.1	C_5
	5.43 (s, br, 1 H)	C_5	109.0	C_5
	6.17–6.26 (m, br, 3 H)	C_5	115.4	C_5
	7.07 (d, 2 H, J = 7.5)	ortho H of Ph	122.7	Ph
	7.2–7.4 (m)[f]	C_6, Ph[f]	124.6	Ph, ipso or para
			132.7	Ph, ipso or para
			132.9	Ph

[a] All shifts are in ppm and J values in Hz. [b] In $C_2D_2Cl_4$. [c] At 90 MHz. [d] Because of significant solvent shifts, the ^{1}H NMR data are given in CD_2Cl_2 and C_6D_6. [e] At 400 MHz, 0 °C. [f] Obscured by superimposed signals of Ph_3CCH_2Ph. [g] At 100.4 MHz, 0 °C. [h] ^{13}C NMR signals for the counteranion are identical to those given for **1b**. [i] Signals of the indenyl C_6 ring are partly obscured by Ph_3CCH_2Ph and could not be assigned with certainty.

of an η^2 bonding mode which, as models show, places only one of the two methylene hydrogens in close proximity to an indenyl ring, while the other shows a chemical shift close to that of **1b**. Although most of the phenyl and

Table II. Ethylene Polymerization with Bis(cyclopentadienyl)zirconium Benzyl Cations[a]

run	catalyst precursor [amt (μmol)]	amt of $[CPh_3]^+B(C_6F_5)_4^-$ (μmol)	temp (°C)	time (s)	yield PE (g)	activity[b] (10^6 g of PE/[(mol of Zr^+)·h])	insertion steps (s^{-1})	$10^{-3}M_w$	M_w/M_n
1	**1a** (9.66)	5.2	20	180	0	0	0		
2	**1a** (9.66)	5.2	60	60	0.093	1.1	8.3	81	4.7
3	**2a** (30.0)	5.1	25	90	0.094	0.74	5.7	41	2.6
4	**2a** (34.0)	5.1	60	30	0.237	5.6	43	57	2.1
5	**3a** (11.0)	4.87	25	60	0.339	4.2	32.3	124	4.0
6	**3a** (11.0)	1.95	60	30	0.272	17	129	144	4.0
7	**4a** (20.0)	9.75	0	180	0.201	0.41	3.2	110	3.0
8	**4a** (13.0)	4.87	25	60	0.153	1.9	14.6	75	3.6
9	**4a** (13.0)	4.87	60	60	1.287	16	122	430	8.6

[a] At 1 bar of C_2H_4 pressure. For polymerization conditions see Experimental Section. [b] Maximum $[Zr^+]$ concentration taken to be equal to initial $[CPh_3^+]$.

indenyl signals are obscured by tetraphenylethane the ^{13}C NMR spectrum of **3b** shows again a high-field shift of the benzylic ipso C, in agreement with an η^2-coordination.[18]

The reaction of **4a** with **5** in $C_2D_2Cl_4$ under analogous conditions leads to a color change from orange to red-brown and the formation of tetraphenylethane (NMR). In contrast to the cases discussed above the organometallic species, thought to be **4b**, could not be unequivocally identified and seems to be less stable in $C_2D_2Cl_4$ than **1b** or **3b**. Solutions of **4b** darkened significantly within a short space of time, with the precipitation of some dark brown material. Mixtures of **4a** and **5** in toluene gave products which were insufficiently soluble for spectroscopic characterization. The observation of the organic reaction products and the catalytic behavior of **4a**/**5** mixtures (see below) support the assumption that the reaction follows eq 3 and that **4b** should be tentatively formulated as an η^2-benzyl complex.

It has so far not proved possible to isolate pure complexes from reaction 3. Precipitation of the ionic products generated in toluene or tetrachloroethane solution by the addition of hexane or cyclopentane gave oily or amorphous compounds which contained decomposition products; they could not be induced to crystallize or freed from adhering solvent and tenaciously retained toluene and hexane or cyclopentane impurities, even after drying in vacuo at 10^{-3} mmHg/20 °C for several hours. For catalytic studies cationic zirconium complexes were therefore generated in situ.

Ethene Polymerizations. The polymerization of ethene with cationic zirconium benzyl complexes was studied in order to address three aspects: (1) the ligand influence in zirconocene systems, (2) the temperature dependence, and (3) the influence of coordinative unsaturation by comparing bis(Cp), mono(Cp), and Cp-free alkyl cations.

The activity and stereoselectivity of metallocene-based catalysts are strongly ligand dependent. Since the discovery by Brintzinger and Kaminsky[19] that *ansa*-metallocenes such as $Et(Ind)_2ZrCl_2$ activated by methylaluminoxane (MAO) produce highly isotactic polypropene with excellent activity, numerous related iso- and syndiospecific systems have been developed.[9,20] Apart from any stereocontrol that these complexes exert with α-olefins (a function of course not relevant with ethene), *ansa*-metallocenes are intrinsically more active than nonbridged bis(cyclopentadienyl) complexes. Table II shows that the polymerization activity of $[Cp'_2Zr(CH_2Ph)]^+$ cations increases in the order **1b** < **2b** < **3b** ≈ **4b**. The reactions were carried out in 20–30 mL of toluene in magnetically stirred 50-mL reactors. Polymerization is fast, and stirring usually became difficult after 60 s at 1 bar of ethene pressure. The reactions were terminated by injection of methanol after 30–60 s to avoid agitation problems. The turnover frequencies and activities (Table II) are significantly higher than those obtained with ligand-stabilized complexes $[Cp'_2MMe(L)]^+$ [3a,10a] and are comparable to those of Cp'_2ZrX_2/methylaluminoxane catalysts.[9d,21] **4b** gives the highest molecular weight polyethene in the series (M_w = 430 000).

There is a sharp increase in polymerization activity on raising the reaction temperature from 0 to 60 °C. This behavior contrasts with that of related cationic methyl complexes where polymerization is observed already at low temperatures[4d,e,12a] but decreases due to catalyst deactivation as the temperature is increased. Interestingly, there is no appreciable decrease in polyethene molecular weight with increasing polymerization temperature.

By contrast to the bis(cyclopentadienyl) cations $[Cp_2ZrR]^+$ which may be regarded as 14-electron species (neglecting the Zr–Ph interaction in the case of R = benzyl) cationic complexes such as $[CpZrR_2]^+$ (10 VE) and $[ZrR_3]^+$ (6 VE) are coordinatively and electronically less saturated and may possibly be expected to exhibit increased reactivity as a result. We have shown earlier that $Zr(CH_2Ph)_4$ reacts with $[NHMe_2Ph]BPh_4$ in dichloromethane or toluene to give isolable $(PhCH_2)_3Zr(\eta^6\text{-}C_6H_5BPh_3)$.[11] In this case one phenyl ring of the tetraphenylborate anion is coordinated to the metal, and no polymerization activity could be detected. Ligand-stabilized complexes of the type $[CpMMe_2(L)_2]^+$ (M = Ti, Zr) have also been reported.[11,22] Although the activity of tetrabenzylzirconium (**7a**) on its own is low, it is known to be an active polymerization

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Table III. Ethylene Polymerization with $[CpZr(CH_2Ph)_2]^+$ and $[Zr(CH_2Ph)_3]^+$ Cations[a]

run	catalyst precursor [amt (μmol)]	activator [atm (μmol)]	temp (°C)	time (s)	yield of PE (g)	activity[b] (10^6 g of PE/[(mol of Zr^+)·h])	insertion steps (s^{-1})	$10^{-3}M_w$	M_w/M_n
10	$CpZrR_3$ (19.0)	**5** (5.1)	20	180	0.060	0.23	1.8	71	3.6
11	ZrR_4 (161)		60	3600	0.016	9.9×10^{-5}	0.0001		
12	ZrR_4 (50)	$B(C_6F_5)_3$ (37.2)	25	300	trace				
13	ZrR_4 (50)	$B(C_6F_5)_3$ (37.2)	60	300	trace				
14	ZrR_4 (22.0)	**5** (21)	25	480	trace				
15	ZrR_4 (22.0)	**5** (21)	60	480	0.078	0.028	0.2	514	2.8

[a] At 1 bar of C_2H_4 pressure. For polymerization conditions see Experimental Section. [b] Maximum $[Zr^+]$ concentration taken to be equal to initial $[CPh_3^+]$.

Table IV. Propene Polymerization with $[Et(Ind)_2ZrMe]^+$[a]

run	temp (°C)	time (s)	yield of PP (g)	activity[b] (10^6 g of PP/[(mol of Zr^+)·$[C_3H_6]$·h])	insertion steps (s^{-1})	mp (°C)	$10^{-3}M_w$	M_w/M_n
16	24	360	0.036	0.24	0.47	137	65	3.0
17	0	360	0.133	0.59	1.7	145	52.5	2.7
18	−10	360	0.162	0.64	2.1	150	75.8	2.4
19	−20	360	0.230	0.82	3.1	151	91.3	2.3
20	−40	360	0.173	0.49	2.3	156	134	2.5

[a] At 1 bar of C_3H_6 pressure. $Et(Ind)_2ZrMe_2$ (**3c**) 12.5 μmol, $[CPh_3]B(C_6F_5)_4$ (**5**) 5.03 μmol. [b] Maximum $[Zr^+]$ concentration taken to be equal to initial $[CPh_3^+]$. For polymerization conditions see Experimental Section.

catalyst if attached to solid supports or in the presence of activators such as MAO.[23] In analogy to the cationic polymerization mechanism demonstrated for metallocene catalysts it seemed likely that in mono(Cp) and Cp-free systems, too, cationic metal alkyls would prove to be catalytically active provided they could be generated in the absence of donor ligands or coordinating anions. The complexes were generated in situ (eq 4). They are only sparingly soluble in toluene and proved to be too unstable for isolation and decomposed in tetrachloroethane-d_2 during attempted spectroscopic characterization.

$$Y\text{-}Zr(CH_2Ph)_3 + \mathbf{5} \rightarrow$$

6a, Y = Cp

7a, Y = CH_2Ph

$$[Y\text{-}Zr(CH_2Ph)_2]B(C_6F_4)_4 + Ph_3CCH_2Ph \quad (4)$$

6b, 7b

The ethene polymerization results (Table III) show that the catalytic activity decreases sharply in the series $[Cp_2ZrR]^+ > [CpZrR_2]^+ > [ZrR_3]^+$. Again, little polymerization is observed at room temperature. Tetrabenzylzirconium on its own has a very low activity, and the possibility that this is associated with a decomposition product rather than the tetraalkyl cannot be excluded. Mixtures of $Zr(CH_2Ph)_4$ and $B(C_6F_5)_3$, which give an orange-yellow product thought to be $[PhCH_2)_3Zr]$-$[PhCH_2B(C_6F_5)_3]$, also show very low catalytic activity. By contrast, the addition of $[CPh_3]^+$ raises the activity by 2 orders of magnitude.[24] The results support the assumption that the intermediacy of cationic metal alkyls as active species is not restricted to conventional metallocene catalysts. Although the activity of **7b** does not rival that of **1b**–**4b**, the molecular weight of the polyethene produced was unexpectedly high (M_w = ca. 500 000), suggesting that chain termination occurs less frequently than with related systems.

Propene Polymerization. The influence of the alkyl ligand on the efficiency of the catalysts is demonstrated by comparing the behavior of zirconium methyl complexes with that of the corresponding benzyl compounds for the polymerization of propene. Our results using *rac*-$Et(Ind)_2ZrMe_2$ (**3c**) as a catalyst precursor with 1 bar of propene are collected in Table IV. In order to reduce the influence of catalyst poisoning during the course of the reaction due to feedstock impurities and to maintain comparability with the results obtained for ethene, the propene polymerizations were usually terminated after 6–10 min. Runaway exotherms, as reported for cationic catalysts in the presence of a large excess of propene and high pressures,[9c] were not found in our system with polymerizations carried out at 1 bar. While this work was in progress, Chien et al. reported unexpectedly high propene polymerization activities for the system **3c**/**5** (1.5 bar of propene), particularly at low temperatures.[13] We do not find such an increase in activity with decreasing temperature in our system. There is a shallow activity maximum at −20 °C and a decrease as the temperature is raised, indicative of slow thermal decomposition of the catalyst, not unlike the pattern observed during ethene polymerizations with $[Ind_2TiMe]^+$.[4d]

By contrast, the benzyl derivatives **1b**, **3b**, and **4b**, generated in situ (eq 3), display the highest polymerization activities at 60 °C, with **3b** reaching activity values corresponding to over 21 000 kg of PP/[(mol of Zr)·$[C_3H_6]$·h] (Table V). This value is comparable to the ethene polymerization activity with this system (cf. entries 7 and 22). The activity of the syndiospecific catalyst **4b** is about 1 order of magnitude less than **3b** (cf. entries 22 and 26) but significantly higher than the previously reported catalyst system **4c**/$[NHMe_2Ph]B(C_6F_5)_4$ at 50 °C under pressure (20 g of PP/(g of cat·h), corresponding to ca. 50 kg of PP/[(mol of Zr)·$[C_3H_6]$·h].[9c] The nonstereorigid bis(cyclopentadienyl) complex **1b** gives atactic polypropene as a viscous oil. The melting points and the

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[24] The activities observed with **6a**/**5** and **7a**/**5** closely correspond to those recently reported for **6a** and **7a** activated with $[NHMe_2Ph]B(C_6F_5)_4$ under 5 bar of ethylene: Pellecchia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 663.

Table V. Propene Polymerization with Zirconium Benzyl Cations[a]

run	catayst precursor [amt (μmol)]	activator [amt (μmol)]	temp (°C)	time (s)	yield of PP, (g)	activity[b] (10^6 g of PP/ [(mol of Zr^+)·[C_3H_6]·h])	insertion steps (s^{-1})	mp (°C)	$10^{-3}M_w$	M_w/M_n	rel pentad intensity
21	**1a** (40.0)	**5** (10)	60	600	0.295	0.52	1.0	oil	*c*	*c*	
22	**3a** (15.0)	**5** (5.0)	60	360	0.926	21.53	12.2	95	22.9	2.2	mmmm 0.53
23	**3a** (15.0)	**5** (5.0)	23	360	0.774	4.69	9.9	139	51.7	2.1	mmmm 0.76
24	**3a** (15.0)	**5** (5.0)	0	600	0.133	0.35	1.1	143	54.1	2.2	*c*
25	**3a** (15.0)	**5** (5.0)	−20	600	0.015	0.032	0.12	153	72.8	2.5	*c*
26	**4a** (6.8)	**5** (4.5)	60	360	0.078	2.02	1.1	80	54.5	2.5	*c*
27	**4a** (17.0)	**5** (4.5)	23	600	0.073	0.29	0.64	131	42.5	2.0	rrrr 0.90
28	**4a** (34.0)	**5** (4.5)	0	600	0.018	0.053	0.16	145	43.9	2.1	*c*
29	**4a** (17.0)	**5** (4.5)	−20	600	0.026	0.062	0.23	153	77.4	2.0	*c*
30	$Et(Ind)_2ZrCl_2$ (4.0)	MAO (862)	60	360	0.430	12.5	7.1	106	11.9	1.9	mmmm 0.63
31	$Et(Ind)_2ZrCl_2$ (4.0)	MAO (862)	0	360	0.028	0.16	0.47	144	44.3	2.6	*c*
32	*i*-Pr(Cp)(Flu)$ZrCl_2$ (5.5)	MAO (862)	60	360	0.072	1.5	0.7	82	59.4	2.4	*c*
33	*i*-Pr(Cp)(Flu)$ZrCl_2$ (11.0)	MAO (1724)	0	600	0.053	0.064	0.12	139	58.4	1.8	*c*

[a] At 1 bar of propene pressure. [b] Maximum [Zr^+] concentration taken to be equal to initial [CPh_3^+]. [c] Not determined.

stereoregularity of the iso- and syndiotactic polymers (cf. relative pentad intensities, Table V) increase with decreasing polymerization temperature, a behavior previously noted with $Et(Ind)_2ZrCl_2$/MAO and related catalysts.[19,25]

Comparison of these activities with those of zirconocene dichloride/MAO catalysts reported in the literature is not without problems since the activities in these systems are strongly dependent on the pressure and the Al:Zr ratio. The results of propene polymerizations with MAO as the activator under 1 bar of monomer pressure have been included in Table V for comparison. The activity at 0 °C (entry 31) agrees closely with that observed by Chien et al. at that temperature under 1.5 bar of propene at a higher Al:Zr ratio.[25b] The data illustrate that the activity of cationic zirconium benzyl catalysts is broadly comparable or somewhat higher than that of conventional MAO-activated systems under identical conditions and far higher, in our hands, than that of cationic zirconium methyl complexes such as [$Et(Ind)_2ZrMe$]$^+$.

We explain the increased thermal stability of cationic zirconium benzyl catalysts compared to the analogous methyl complexes as the result of the η^2-coordination of the benzyl ligand which satisfies to some extent the electron requirement of the electron-deficient metal center by donating electron density from the benzylic phenyl ring into vacant zirconium orbitals; η^2-coordination may also stabilize the compounds against interaction with the anion and deactivation, e.g. via aryl transfer. The mean M–C bond energies of homoleptic alkyls MR_4 (M = Ti, Zr, Hf) are significantly greater for R = benzyl, where η^2-coordination is important, than, e.g., for R = CH_2CMe_3 (263 and 249 kJ mol^{-1}, respectively).[26] Even in the absence of η^2-bonding the bond enthalpy of M–benzyl tends to be higher than for M–methyl, for example in Cp_2TiR_2 [R = Me, *E*(M–C) = 274 kJ mol^{-1}; R = CH_2Ph, *E*(M–C) = 280 kJ mol^{-1}].[26c]

The same stabilizing influence is likely to be responsible for the relatively low catalytic activity at lower temperatures and is expected to increase the activation barrier for the first olefin insertion step into the metal–alkyl bond, on the assumption that an $\eta^2 \rightarrow \eta^1$ rearrangement of the benzyl ligand is required before substrate coordination can take place, followed by alkyl group migration from the metal to the coordinated substrate. A [Cp_2ZrR]$^+$ fragment has two LUMO's oriented in the plane bisecting the Cp–Zr–Cp angle;[27] one of these is involved in binding to the phenyl ring of the benzyl ligand. The second LUMO is potentially available for substrate bonding. However, although it is known that η^2-benzyl complexes form adducts with small ligands, such as nitriles, viz. [$Cp_2Zr(\eta^2\text{-}CH_2Ph)(NCMe)$]$^+$,[16] it seems unlikely that sterically more hindered (and weaker) ligands such as olefins, which have to coordinate side-on, can do so unless the benzyl ligand adopts an η^1 conformation, possibly stabilized by an α-CH interaction.[8a,28] Such a rearrangement would increase the activation barrier for olefin insertion; on the other hand, the increased stability of metal benzyl cations would allow a larger number of potentially active centers to survive at higher temperatures than in the case of methyl cations, to be available for a fast chain growth sequence once the initial activation barrier can be overcome.[29] A possible scenario is depicted in Scheme I. Naturally, after a number of insertions the nature of the active species derived from zirconium benzyl precursors is essentially indistinguishable from those produced from zirconium methyl cations, and similar chain-transfer rates and stereochemical control mechanisms will operate.

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(26) (a) Davidson, P. L.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (b) Martinho, Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Dias, A. R.; Martinho Simões, J. A. *Polyhedron* **1988**, *7*, 1531. The rates of CO insertion into Th–R bonds in Cp_3ThR also reflect the trend in bond enthalpies, R = Bu > Me > benzyl.[26d] (d) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

(27) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(28) A pentacoordinate bis(olefin) complex $MR(ol)_2$, which would be analogous to an $M(\eta^2\text{-benzyl})(ol)$ complex, has been postulated to explain the origin of low concentrations of stereoirregularities in syndiotactic polypropene; such a complex would at best be an energetically unfavorable minor component.[9b]

(29) It has been observed that in $Cp_2TiMeCl/MeAlCl_2$[30] and [Ind_2TiMe]$^+$ systems[4d] only part of the initially available Ti–Me bonds participate in chain growth reactions at relatively low monomer concentrations, consistent with a slower rate for the first olefin insertion step than for subsequent insertions, *k*(Ti–*n*-Pr)/*k*(Ti–Me) ≅ 94.[30] Similar results were obtained for the insertion of C_2H_4 into scandium–alkyl bonds in $Cp^*_2Sc\text{–}R$; the rates decrease in the order R = *n*-Pr > Me, reflecting the difference in bond dissociation energies.[31]

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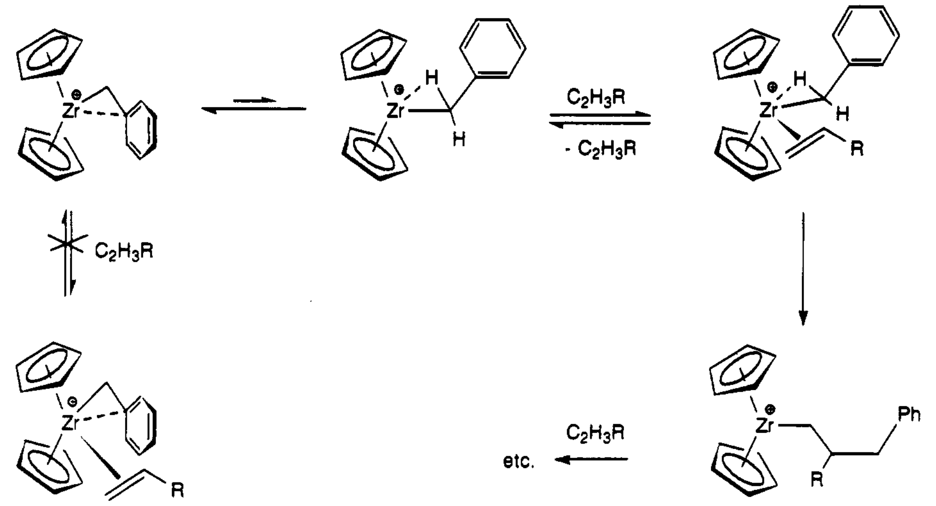
Scheme I



Conclusions

The reaction of zirconocene dibenzyl complexes with $[CPh_3]B(C_6F_5)_4$ in toluene gives base-free cationic zirconium benzyl complexes which contain η^2-coordinated CH_2Ph ligands. The Zr–phenyl interaction serves to reduce the electron deficiency of the metal center and is thought to be responsible for the observed increase in thermal stability compared to analogous cationic methyl complexes. Catalysts thus prepared are highly active for the polymerization of ethylene and propene at 1 bar of pressure, particularly in the temperature range >50 °C commonly employed for polymerizations. Under such conditions the activities are very similar to or in excess of those of metallocene dihalide/MAO systems. Comparable studies with $[CpZr(CH_2Ph)_2]^+$ and $[Zr(CH_2Ph)_3]^+$ demonstrate that a polymerization mechanism involving metal alkyl cations is not restricted to metallocene systems.

Experimental Section

General Procedures. All manipulations are performed under dried argon using standard vacuum line techniques. $Cp_2Zr(CH_2Ph)_2$,[32] $(C_5H_4SiMe_3)_2ZrCl_2$,[33] *rac*-Et(Ind)$_2$ZrCl$_2$,[34] *i*-Pr(Cp(Flu)ZrCl$_2$,[9a] methylaluminoxane,[35] and $[CPh_3]B(C_6F_5)_4$[13,14] were prepared according to literature procedures. Solvents were distilled under nitrogen from sodium (toluene), sodium–benzophenone (diethyl ether, THF), or CaH_2 (CH_2Cl_2). Deuterated solvents were stored over activated 4-Å molecular sieves and degassed by several freeze–thaw cycles. Ethene (BOC) was purified by passing through $CaCl_2$, P_2O_5, silicone oil/AlEt$_3$, and molecular sieve columns; propene (BOC) was dried by passing through $CaCl_2$, P_2O_5, and molecular sieves and distilled from $Et_2AlOC_6H_{13}$. NMR spectra were recorded on JEOL EX90Q and GX400 instruments and referenced to the residual solvent protons. ^{13}C NMR spectra of polypropene samples were recorded at 22.4 MHz in $C_2D_2Cl_4$ [$\delta(^{13}C)$ 73.8 pm] at 120 °C. A 70° pulse width was used with 6.5-s repetition time and 0.5-s delay time.

$(C_5H_4SiMe_3)_2Zr(CH_2Ph)_2$ (2a). To 2.4 g of $(C_5H_4SiMe_3)_2ZrCl_2$ (5.5 mmol) in 30 mL of diethyl ether was added dropwise at −78 °C 70 mL of a 0.16 M solution of $PhCH_2MgCl$ in diethyl ether (11.2 mmol). Light was excluded, and the mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed, the yellow-orange residue extracted with a toluene/petroleum ether mixture (9:1), and the product crystallized at −15 °C to give orange crystals of **2a**; dec temp 160 °C (1.9 g, 3.5 mmol, 64%). Anal. Calcd for $C_{30}H_{40}Si_2Zr$: C, 65.74; H, 7.42. Found: C, 65.57; H, 7.42.

***rac*-Et(Ind)$_2$Zr(CH$_2$Ph)$_2$ (3a).** Following the method described for **2a**, $Et(Ind)_2Zr(CH_2Ph)_2$ was prepared from $Et(Ind)_2ZrCl_2$ (1.2 g, 2.9 mmol) and $PhCH_2MgCl$. Orange crystals, dec temp >200 °C (0.6 g, 1.1 mmol, 38%). Anal. Calcd for $C_{34}H_{30}Zr$: C, 77.07; H, 5.72. Found: C, 76.90; H, 5.68.

***i*-Pr(Cp(Flu)Zr(CH$_2$Ph)$_2$ (4a)** was prepared by following the method given for **2a**; orange crystals, dec temp >95 °C (38%). Anal. Calcd for $C_{35}H_{32}Zr$: C, 77.29; H, 5.94. Found: C, 78.27; H, 6.05.

Et(Ind)$_2$ZrMe$_2$ (3c). To a suspension of 1.05 g of $Et(Ind)_2ZrCl_2$ (2.5 mmol) in diethyl ether at −78 °C was added MeLi in diethyl ether (1.5 M, 3.4 mL, 5.1 mmol). The mixture was allowed to warm to room temperature and stirred for 2 h. After removal of the solvent the residue was extracted with 40 mL of toluene. Repeated filtration was required to remove impurities. The filtrate was concentrated and left to crystallize at −15 °C to give the product as off-white chunky crystals (0.2 g, 0.53 mmol, 21%). ^1H NMR (C_6D_6): −0.95 (s, 6 H, Me), 2.6 – 2.8 (m, 4 H, CH_2CH_2), 5.65 (d, 2 H, Cp), 6.42 (d, 2 H, Cp), 6.9–7.4 (m, 8 H, aryl).

Generation of $[Cp_2Zr(CH_2Ph)]^+$ (1b). A 95-mg (0.1-mmol) sample of $Cp_2Zr(CH_2Ph)_2$ and 40 mg (0.1 mmol) of $[CPh_3]B(C_6F_5)_4$ (**5**) were cooled to −20 °C, and 0.8 mL of precooled $C_2D_2Cl_4$ was added. The mixture was warmed to −5 °C, at which point all the material had dissolved to give an orange-brown solution, and transferred to an NMR tube for spectroscopic characterization (Table I). Besides **1b**, 1 equiv of 1,1,1,2-tetraphenylethane is formed; traces of triphenylmethane were also identified. 1,2-Diphenylethane (dibenzyl) is absent. NMR data for Ph_3CCH_2Ph: ^1H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C) δ 4.06 (s, 2 H, CH_2), 6.75 (d, 2 H, J = 7.5 Hz, ortho H of CH_2Ph), 7.10 (t, 2 H, J = 7.3 Hz, meta H of CH_2Ph), 7.18 (t, 1 H, J = 7.3 Hz, para H of CH_2Ph), 7.30–7.36 (m, 18 H, CPh_3); ^{13}C NMR (100.4 MHz, $C_2D_2Cl_4$, 25 °C) δ 46.01 (CH_2Ph), 58.49 (CPh_3), 125.80 (CPh_3, para C), 125.88 (CH_2Ph, para C), 127.25 (CH_2Ph, meta C), 127.52 (CPh_3, ortho C), 129.67 (CPh_3, meta C), 131.05 (CH_2Ph, ortho C), 138.29 (CH_2Ph, ipso C), 146.49 (CPh_3, ipso C).

Generation of $[Et(Ind)_2Zr(CH_2Ph)]^+$ (3b). A 43-mg (0.08-mmol) sample of $Et(Ind)_2Zr(CH_2Ph)_2$ (**3a**) and 74 mg (0.08 mmol) of $[CPh_3]B(C_6F_5)_4$ (**5**) were cooled to −20 °C, and 0.8 mL of precooled $C_2D_2Cl_4$ was added. The mixture was warmed with agitation to −5 °C to give a red-brown solution. The product was characterized spectroscopically (Table I).

Reaction of $CpZr(CH_2Ph)_3$ with $[CPh_3]B(C_6F_5)_4$. The procedure for preparing samples of **1b** described above was

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followed. A 47-mg (0.11-mmol) sample of $CpZr(CH_2Ph)_3$ and 101 mg (0.1 mmol) of $[CPh_3]B(C_6F_5)_4$ (**5**) were reacted between −20 and −5 °C in 0.8 mL of $C_2D_2Cl_4$. The mixture gave a brown solution. Although the ^1H and ^{13}C NMR signals for Ph_3CCH_2Ph were readily identified, extensive decomposition took place, and no organometallic species could be identified.

General Procedure for Polymerization Reactions. A magnetically stirred 50-mL reactor was used which was flame-dried in vacuo prior to being charged with 20 mL of dry, sulfur-free toluene. The solvent was heated to the desired polymerization temperature and allowed to equilibrate with the olefin substrate at 1 bar of pressure. Aliquots of toluene solutions of zirconium alkyls were injected, followed by a solution of $[CPh_3]B(C_6F_5)_4$ in toluene. An excess of the metal dibenzyl complex was used to ensure complete reaction with the triphenylcarbenium salt; within the limits employed in this study this excess does not influence the activity of the catalysts. There was an immediate color change, accompanied by monomer consumption. The pressure was maintained at 1 bar throughout. The reaction was terminated by injecting 2 mL of methanol. The contents of the reactor were poured into methanol; the collected polymer was washed with acidified methanol, water, and methanol and dried at 60–80 °C for 16 h. Molecular weight determinations and NMR analysis were carried out on "as-prepared" polymer samples without fractionation. Propene polymerization activities were calculated by taking into account the temperature dependence of propene solubility in toluene.[25b]

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