Single Insertion of α-Olefins into the Cationic Complex $[Zr(CH_2Ph)_3]^+$ Affording Isolable $[Zr(CH_2Ph)_2(CH_2CHRCH_2Ph)]^+$ Adducts: A Model for the Insertion Mechanism in Ziegler–Natta Polymerization

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The zwitterionic complex $[Zr(CH_2Ph)_3\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}]$ (1) reacts smoothly at 25 °C with propene and higher α-olefins, such as 4-methyl-1-pentene, 1-vinylcyclohexane, and allylbenzene, affording the single-insertion adducts $[Zr(CH_2Ph)_2(CH_2CHRCH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (R = Me, **2**; R = CH_2CHMe_2, **4**; R = C_6H_{11}, **5**; R = CH_2Ph, **6**). Isolation and characterization of **2**, **4**, and **6** by NMR analysis reveal that the Zr cation is stabilized toward either further monomer insertion or β-hydrogen elimination by back-biting η^n-coordination of the δ-Ph ring and by η^2-coordination of the two benzyl ligands. An analogous, less stable adduct deriving from single insertion of ethene (R = H, **3**) has been detected at low temperatures by NMR. Thermolysis of **2** at 50 °C, as well as addition of Lewis bases such as tetrahydrofuran, results in decomposition via β-hydrogen elimination with formation of $CH_2{=}CMeCH_2Ph$. At 50 °C, **2** reacts with an excess of propene affording a mixture of atactic and isotactic polypropylene, probably after β-hydrogen elimination has occurred. In contrast, reaction of **2** with ethene proceeds already at 25 °C, affording polyethylene, possibly through further insertion in **2**. Compounds **2**–**6** are the first examples of adducts deriving from the insertion of olefins into the M—C bond of a group 4 metal complex which is an active Ziegler–Natta catalyst.

Introduction

The rapid development of homogeneous Ziegler–Natta catalysts based on group 4 metallocenes and methylalumoxane,[1] while opening new and interesting opportunities for industrial applications,[2] has allowed considerable advances in the understanding of the olefin polymerization mechanism. A major achievement in this respect has been the rationalization of the relationships between the local symmetry of the metallocene precatalyst and the stereochemistry of the resulting poly(α-olefins),[3] providing a powerful tool for "tailoring" the polymer structure almost at will. On the other hand, the synthesis of cationic group 4 alkylmetallocenes,[4] and, more recently, of analogous mono-Cp and Cp-free derivatives,[5] functioning as "single-component" olefin polymerization catalysts, has provided substantial evidence concerning the ionic nature of the true catalytic species.[6]

However, in spite of the availability of relatively simple, catalytically active molecular complexes, attempts to observe directly the individual polymerization steps, *e.g.*, by NMR monitoring of the reaction, were unsuccessful, owing to catalyst instability and/or high polymerization rates.[7] In particular, direct observation of primary reaction products deriving from the insertion of an olefin into a M–C bond has never been reported for group 4 metal complexes that function as Ziegler–Natta catalysts. To date, the models available for this reaction are the adducts derived from the single insertion of internal alkynes in complexes such as $[Cp_2MMe]^+$ (M = Ti or Zr).[6b,7a,8] However, single olefin insertions have been observed in catalytically inactive Cp_2Zr(benzyne) and $[Cp_2Zr(\eta^2\text{-}N,C\text{-pyridyl})]^+$ complexes,[9a,b] as well as in lanthanide $(C_5Me_5)_2MMe$ complexes (M = Lu, Y, Sc), which also promote ethylene polymerization.[9c,d] Although the classical *cis* ligand migratory insertion mechanism, originally proposed by Cossee and Arlman,[10] is currently widely accepted,

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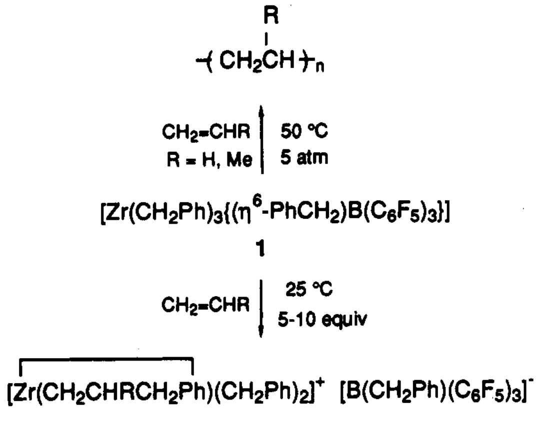
Scheme 1



2, R = Me; **3**, R = H; **4**, R = CH$_2$CHMe$_2$; **5**, R = C$_6$H$_{11}$; **6**, R = CH$_2$Ph

alternative chain growth mechanisms, involving metallacyclic or carbenoid intermediates, have been proposed.[11]

Following our recent synthesis and structural characterization[12] of the zwitterionic non-metallocene complex [Zr(CH$_2$Ph)$_3${(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$}] 1, which promotes the polymerization of ethylene and propene under rather mild conditions (50 °C, 5 atm of monomer pressure),[5b,12] we have found that compound 1 is particularly suited for mechanistic investigation of some of the key steps in olefin polymerization, *i.e.*, olefin insertion and β-hydrogen elimination. In this paper we report the results of an NMR study of the reaction of 1 with ethene, propene, and higher α-olefins, revealing the selective formation, under proper conditions, of single-insertion adducts, which, in many cases, have been isolated and characterized. The structure and the reactivity of these adducts provide a direct insight into the polymerization mechanism.

Part of this work has been the subject of a preliminary communication.[13]

Results and Discussion

Reaction of [Zr(CH$_2$Ph)$_3${(η^6-PhCH$_2$)B(C$_6$F$_5$)$_3$}] (1) with Propene: Isolation of [Zr(CH$_2$Ph)$_2$(CH$_2$CHMeCH$_2$Ph)]$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ (2). Monitoring by ^{1}H NMR the reaction of 1 with propene in 1,1,2,2-C$_2$D$_2$Cl$_4$ (25 °C, [C$_3$H$_6$]/[1] = 5–10) shows cleanly the formation of a single product, whose concentration approaches 100% of the Zr present after 30–40 min. The formation of secondary products and the precipitation of some polypropylene are observed only after a longer period of time. The product formed initially could be isolated as a red oil by precipitation with pentane. Redissolution in tetrachloroethane followed by the addition of toluene gave a red-orange solid, which was identified by ^{1}H, ^{13}C, and 2D COSY NMR analysis (see Table 1 and Figure 1) as the propene single-insertion adduct [Zr(CH$_2$Ph)$_2$(CH$_2$CHMeCH$_2$Ph)]$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ (2). The ^{1}H NMR spectrum of 2 is particularly informative, revealing several unusual structural features. The subspectrum of the ZrCH$_2$CHMeCH$_2$Ph moiety strongly suggests a backbiting coordination of the Ph ring to Zr:[14] two downfield doublets are observed for the *o*-Ph protons at δ 7.59 and 7.60; four different resonances are observed for the α-methylene protons (δ −0.72, H$_a$; 0.13, H$_b$) and the γ-methylene protons (δ 1.85, H$_d$; 2.89, H$_e$); moreover, a long distance coupling constant between H$_b$ and H$_e$ ($^4J_{H_bH_e}$ = 2.1 Hz) suggests a stereorigid W-conformation[15] of the four bonds between H$_b$ and H$_e$. Inspection of the models reveals that such a conformation is reasonably required when the Ph group is coordinated to Zr (see Figure 1). Actually, two W-conformations are conceivable, one in which the methyl group is in the equatorial position with respect to the ZrCH$_2$CHMeCH$_2$Ph ring, the other in which it is in the axial position. The observed coupling constants ($J_{H_aH_c}$ = 12.4 Hz; $J_{H_bH_c}$ = 2.1 Hz; $J_{H_cH_d}$ = 11.7 Hz; $J_{H_cH_e}$ = 6.3 Hz) are compatible with the former conformation. Analysis of the models reveals that the latter conformation leads to strong steric interactions between the methyl group and one of the benzyl ligands.

The two Zr-bound benzyl ligands are nonequivalent, as indicated by the four distinct ^{1}H resonances and the two distinct ^{13}C resonances observed for the methylene groups, as well as by distinct resonances for the two Ph groups; an η^2-coordination mode[16] is suggested by the two high-field resonances found at δ 5.98 and 6.02 for the *o*-Ph protons, and by the large J_{CH} coupling constants (140 Hz) observed for the methylenes in the ^{1}H coupled ^{13}C NMR spectrum. The anion is not coordinated to Zr, as suggested by the resonances of the BCH$_2$Ph aromatic protons, which are those expected for the "free" anion,[12] and supported by the observed poor solubility of 2 in toluene compared to the high solubility of the zwitterionic 1.

Variable temperature ^{1}H NMR analysis performed in CD$_2$Cl$_2$ between −90 and +20 °C shows few changes in the subspectrum of the ZrCH$_2$CHMeCH$_2$Ph moiety, while an upfield shift and a consistent broadening of the *o*-Ph proton resonances of the Zr-bound benzyl ligands are observed on decreasing temperature. The latter findings can be explained by a reduced fluxionality of the benzyl ligands at low temperature, possibly due to an increase in η^n-interaction (for instance, from η^2 to η^3), and by a fast suprafacial migration of Zr between the two now nonequivalent edges of the Ph rings. A similar temperature-dependent fluxional process was observed by Marks *et al.* for (C$_5$Me$_5$)Th(CH$_2$Ph)$_3$.[16a]

Reaction of 1 with *cis*-1-propene-d_1 under similar conditions affords [Zr(CH$_2$Ph)$_2$(CHDCHMeCH$_2$Ph)]$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ (2-d_1). The presence of a broad resonance at δ 0.11 for Zr–C*H*D··· and the absence of the resonance due to H$_a$, found at δ −0.72 in the spectrum of 2 (*i.e.*, deuterium occupies the position of H$_a$; see Figure

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

compd[b]	^{1}H NMR	assgnt[c]	^{13}C NMR	assgnt
				$ZrCH_2CHMeCH_2Ph$
$[Zr(CH_2Ph)_2(CH_2CHMeCH_2Ph)]^+$ (2)	-0.72 (t, $^2J = {}^3J = 12.4$, 1H)	H_a	79.7	α-CH_2
$[C_2D_2Cl_4]$, 298 K	0.13 (dt, $^2J = 12.4$, $^3J =$	H_b	50.7	CH
	$^4J(H_bH_e) = 2.1$, 1H)		42.3	γ-CH_2
	0.81 (d, $J = 6.2$, 3H)	$C\mathit{H}_3$	26.8	CH_3
	1.68, 1.80 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	130.3	*o-Ph*
	1.85 (t, $^2J = {}^3J = 11.7$, 1H)	H_d	129.2	*m-Ph*
	2.00 (m, 1H)	H_c	125.1	*p-Ph*
	2.25, 2.33 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	154.8	*ipso-Ph*
	2.89 (ddd, $^2J = 11.7$, $^3J =$	H_e	67.8, 69.0	Zr*C*H$_2$Ph
	6.3, $^4J(H_bH_e) = 2.1$, 1H)		($J_{CH} = 140$)	
	5.98, 6.02 (2d, $J = 7.3$, 4H)	$H_m,H_{m'}$	130.3, 130.6	*o*-ZrCH$_2$*Ph*
	7.17 (br t, 1H)	H_h	131.8, 132.7	*m*-ZrCH$_2$*Ph*
	7.20 (br m, 2H)	$H_g,H_{g'}$	129.3	*p*-ZrCH$_2$*Ph*
	7.32, 7.36 (2t, $J = 7.3$, 4H)	$H_n,H_{n'}$	127.7, 128.2	*ipso*-ZrCH$_2$*Ph*
	7.45, 7.50 (2t, $J = 7.3$, 2H)	$H_o,H_{o'}$		
	7.59, 7.60 (2d, $J = 5.5$, 2H)	$H_f,H_{f'}$		
$[Zr(CH_2Ph)_2(CH_2CH_2CH_2Ph)]^+$ (3)[d]	-0.42 (br t, $J = 6.1$, 2H)	ZrC*H*$_2$CH$_2$CH$_2$Ph		
$[CD_2Cl_2]$, 253 K	2.25 (br t, $J = 6.1$, 2H)	ZrCH$_2$C*H*$_2$CH$_2$Ph		
	2.48 (br t, $J = 6.1$, 2H)	ZrCH$_2$CH$_2$C*H*$_2$Ph		
	7.71, 7.75 (2d, $J = 7.3$, 2H)	*o*-ZrCH$_2$CH$_2$CH$_2$*Ph*		
	1.76, 2.32 (2d, $J = 11.0$, 4H)	ZrC*H*$_2$Ph		
	5.97 (d, $J = 7.3$, 4H)	*o*-ZrCH$_2$*Ph*		
				$ZrCH_2CHRCH_2Ph$
$[Zr(CH_2Ph)_2\{CH_2CH(CH_2CHMe_2)CH_2Ph\}]^+$ (4)	-0.74 (t, $^2J = {}^3J = 12.4$, 1H)	H_a	78.5	α-CH_2
$[C_2D_2Cl_4]$, 298 K	0.28 (dt, $^2J = 12.4$, $^3J =$	H_b	53.6	CH
	$^4J(H_bH_e) = 2.1$, 1H)		40.8	γ-CH_2
	0.82, 0.84 (2d, $J = 5.2$, 6H)	(C*H*$_3$)$_2$	130.5	*o-Ph*
	1.06 (m, 1H)	C*H*Me$_2$	129.5	*m-Ph*
	1.62, 1.85 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	125.1	*p-Ph*
	1.94 (m, 1H)	H_c	155.1	*ipso-Ph*
	2.02, 2.26 (2d, $J = 11.0$, 2H)	C*H*$_2$CHMe$_2$	68.3, 68.5	Zr*C*H$_2$Ph
			($J_{CH} = 140$)	
	2.28, 2.33 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	130.3, 130.8	*o*-ZrCH$_2$*Ph*
	6.02, 6.09 (2d, $J = 7.3$, 4H)	$H_m,H_{m'}$	131.8, 132.7	*m*-ZrCH$_2$*Ph*
	7.07 (br t, 1H)	H_h	129.6	*p*-ZrCH$_2$*Ph*
	7.17 (br m, 2H)	$H_g,H_{g'}$	51.1	*C*H$_2$CHMe$_2$
	7.48 (2t, $J = 7.3$, 4H)	$H_n,H_{n'}$	25.7	CH$_2$*C*HMe$_2$
	7.51 (2t, $J = 7.3$, 2H)	$H_o,H_{o'}$	22.8, 22.3	CH$_2$CH(*C*H$_3$)$_2$
	7.58, 7.60 (2d, $J = 7.7$, 2H)	$H_f,H_{f'}$		
$[Zr(CH_2Ph)_2\{CH_2CH(C_6H_{11})CH_2Ph\}]^+$ (5)[d]	-0.80 (t, $^2J = {}^3J = 12.4$, 1H)	H_a		
$[C_2D_2Cl_4]$, 298 K	0.28 (dt, $^2J = 12.4$, $^3J =$	H_b		
	$^4J(H_bH_e) = 2.1$, 1H)			
	6.01, 6.11 (2d, $J = 7.3$, 4H)	$H_m,H_{m'}$		
	7.62, 7.63 (2d, $J = 7.7$, 2H)	$H_f,H_{f'}$		
				$ZrCH_2CHRCH_2Ph$
$[Zr(CH_2Ph)_2\{CH_2CH(CH_2Ph)_2\}]^+$ (6)	-1.02 (t, $^2J = {}^3J = 12.4$, 1H)	H_a		
$[C_2D_2Cl_4]$, 298 K	0.20 (dt, $^2J = 12.4$, $^3J =$	H_b	72.9	α-CH_2
	$^4J(H_bH_e) = 2.1$, 1H)		56.9	CH
	1.68, 1.78 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	40.5	γ-CH_2
	2.00 (t, $^2J = {}^3J = 11.0$, 1H)	H_d	153.9	*ipso-Ph*
	2.04 (m, 1H)	H_c	46.8	CH(*C*H$_2$Ph)
	2.16, 2.67 (2 br d, $^2J = 11.0$, 2H)	CH(C*H*$_2$Ph)	139.4	*ipso*-CH(CH$_2$*Ph*)
	2.20, 2.46 (2d, $J = 10.2$, 2H)	$H_i,H_{i'}$ or $H_l,H_{l'}$	67.0, 70.8	Zr*C*H$_2$Ph
	2.90 (br d, $^2J = 11.0$, 1H)	H_e		
	5.98, 6.02 (2d, $J = 7.3$, 4H)	$H_m,H_{m'}$		
	7.17 (br t, 1H)	H_h		
	7.20 (br m, 2H)	$H_g,H_{g'}$		
	7.32, 7.36 (2t, $J = 7.3$, 4H)	$H_n,H_{n'}$		
	7.45, 7.50 (2t, $J = 7.3$, 2H)	$H_o,H_{o'}$		
	7.62, 7.64 (2d, $J = 5.5$, 2H)	$H_f,H_{f'}$		

[a] All chemical shifts are in ppm and J values in Hz. [b] For all the compounds, the anion is $[B(CH_2Ph)(C_6F_5)_3^-$. Selected NMR data ($C_2D_2Cl_4$, 298 K): ^{1}H δ 2.86 (br s, 2H, C*H*$_2$), 6.7–6.9 (m, 5H, C$_6$*H*$_5$); ^{13}C δ 32.0 (*C*H$_2$), 127.3 (*m-Ph*), 128.4 (*o-Ph*), 148.4 (*ipso-Ph*), 135.6, 136.5, 147.9 (J_{CF} = 186, *C*$_6$F$_5$). [c] See Figure 1 for indexing. [d] Not isolated.

1), indicates a *cis* addition to the double bond of propene and confirms the selective formation of only one of the two previously quoted conformations of the $\overline{\text{ZrCH}_2\text{CHMeCH}_2\text{Ph}}$ ring.

Variable temperature ^{1}H NMR experiments show no significant temperature-dependent isotopic perturbation[17] when the spectra of 2 and 2-d_1 are compared. The difference between the chemical shifts of ZrCH$_a$*H*$_b$CH··· and ZrCD*H*CH··· is 0.05 ppm at 20 °C and −0.04 ppm at −70 °C. This finding, as well as the normal values found for the J_{CH} coupling constants, and the absence of low frequency ν_{C-H} stretching in the IR spectrum of 2 exclude the presence of agostic interactions,[17] which have been observed in some cationic and zwitterionic zirconocene hydrocarbyl complexes.[4d,18]

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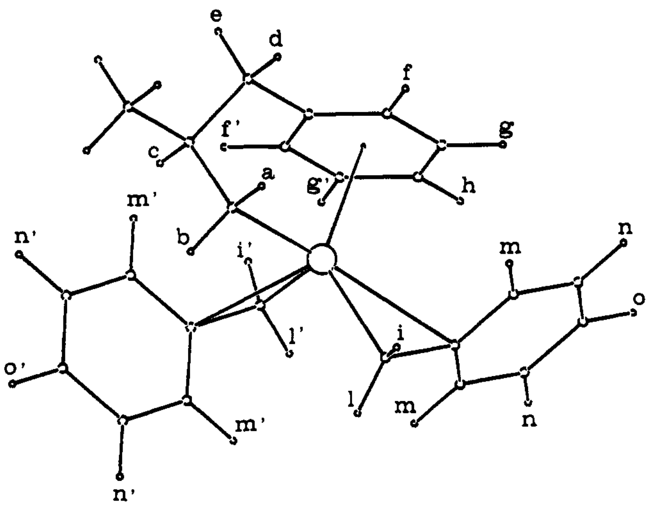

Figure 1. Ball-and-stick model for the cation $[Zr(CH_2Ph)_2(CH_2CHMeCH_2Ph)]^+$ (**2**). The structure, proposed on the basis of the NMR data, has been generated by using standard bond distances and angles for a tetrahedrally coordinated Zr, imposing a W-conformation of the four bonds between H_b and H_e and arbitrary torsion angles. Similar structures are proposed for the cations of **3**–**6** (substitute the Me group with –H for **3**, $-CH_2CHMe_2$ for **4**, $-C_6H_{11}$ for **5**, and $-CH_2Ph$ for **6**).

Reaction of 1 with Ethene: In Situ Formation of $[Zr(CH_2Ph)_2(CH_2CH_2CH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (3). Monitoring by ^1H NMR the reaction of **1** with ethene in $C_2D_2Cl_4$ at 25 °C shows the rapid consumption of the olefin (5–10 min) and the corresponding formation of polyethylene, while new intense resonances due to at least two different species appear immediately in addition to those of **1**. Attempts to isolate the primary reaction product operating similarly to the case of **2** resulted invariably in formation of a decomposition product.[19] However, monitoring by ^1H NMR the reaction in CD_2Cl_2 between –70 and –20 °C allowed us to observe the selective formation of the single insertion adduct $[Zr(CH_2Ph)_2(CH_2CH_2CH_2Ph)]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**3**). Two downfield doublets at δ 7.71 and 7.75, attributable to the *o*-Ph protons of the $ZrCH_2CH_2CH_2Ph$ moiety, are diagnostic of a back-biting Ph coordination, as found for **2**. Two triplets found at δ –0.42 and +2.48 for the α- and the γ-methylene protons, respectively, suggest that in this case no energy barrier exists for the interconversion between different ring conformations, due to the absence of the methyl substituent on the β-carbon. The two Zr-bound benzyl ligands are equivalent and coordinated in an η^2-fashion (only two doublets are observed for the diastereotopic CH_2Ph protons at δ 1.76 and 2.32 and one high-field resonance at δ 5.92 for the *o*-Ph protons). As in the case of **2**, a dynamic process possibly involving an increase of the amount of η^n-benzyl coordination is observed when the temperature is lowered.

At 0 °C, a second species, characterized by two aliphatic resonances at δ 0.11 and 1.57 (attributable to a $ZrCH_2CH_2\cdots$ moiety), develops during 15–20 min, reaching a concentration comparable to that of **3**. Correspondingly, two new doublets appear at δ 1.60 and 1.90 and one doublet at δ 6.28, attributable to the methylene and the *o*-Ph resonances, respectively, of two benzyl ligands. On this basis, we suggest that this second species is the propagating complex $[Zr(\eta^n\text{-}CH_2Ph)_2(CH_2CH_2)_n\cdots]^+$. After a longer time, resonances due to the above mentioned decomposition product[19] also appear in the spectrum.

Reaction of 1 with Higher α-Olefins. The reactivity of **1** with several higher α-olefins has been investigated by NMR under conditions analogous to those described above for propene. 4-Methyl-1-pentene reacts slowly at 25 °C (10–12 h), but rapidly at 50 °C (15–20 min), to give $[Zr(CH_2Ph)_2\{CH_2CH(CH_2CHMe_2)CH_2Ph\}]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**4**). Compound **4** was isolated similarly to **2** as a red-orange solid and characterized by NMR analysis (see Table 1), revealing a structure analogous to that of **2**. Particularly diagnostic are the resonances of the α-methylene protons of the $ZrCH_2CHRCH_2Ph$ moiety observed at δ –0.74 and +0.28 and those of the corresponding *o*-Ph protons at δ 7.58 and 7.60.

More hindered α-olefins also react with **1**. The bulky 1-vinylcyclohexane inserts slowly (20 h at 25 °C, ~60% yield), affording the corresponding adduct $[Zr(CH_2Ph)_2\{CH_2CH(C_6H_{11})CH_2Ph\}]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**5**). **5** was not isolated due to concurrent partial decomposition of **1**, but it was clearly identified *in situ* by ^1H NMR, showing the characteristic pattern of resonances diagnostic of a structure analogous to that of **2** (see Table 1).

In order to obtain further evidence on the structure of the single-transition adducts, **1** was allowed to react with allylbenzene, to yield $[Zr(CH_2Ph)_2\{CH_2CH(CH_2Ph)_2\}]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**6**), which was isolated as a red oil (see Table 1 for NMR data). In **6**, the methine carbon would not be chiral and so the adjacent methylene protons would be homotopic in the absence of the back-biting Ph coordination. The presence of two different resonances at δ –1.02 and +0.20 for the α-methylene protons confirms Ph coordination to Zr. Since in **6** two competitive back-biting Ph coordinations are conceivable, we allowed **1** to react with allylbenzene that was deuterated on the Ph ring, obtaining $[Zr(CH_2Ph)_2(CH_2CH\{(CH_2Ph)(CH_2C_6D_5)\})]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**6**-d_5). By comparing the ^1H NMR spectra of **6** and **6**-d_5, and in particular the intensities of the low-field resonances of the *o*-Ph protons of the Ph ring coordinated to Zr, it turns out that in **6**-d_5 there is roughly equal probability for C_6H_5 and C_6D_5 coordination. This finding is compatible, *e.g.*, with a fluxional process interconverting the two Ph coordinations.

Internal olefins do not react with **1**. Similar experiments performed with 2-butene did not result in any reaction at 25 °C and produced only decomposition products at higher temperatures.

Reactivity of 2: Implications for the Polymerization Mechanism. The unusual high stability of **2** toward either further monomer insertion or β-hydrogen elimination probably is due to the coordinative saturation of Zr. Assuming η^2-coordination for the two benzyl ligands and η^6-coordination for the back-biting Ph ring, the formal electron count for Zr is 16. Of course, different arene coordination modes (e.g., η^3)[14b] cannot be ruled out, although an η^6-coordination seems resonable on the basis of the analogous Ph coordination found in the crystal structure of **1**.[20]

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(19) The same decomposition product is formed slowly, together with toluene and bibenzyl, when solutions of **1** in $C_2D_2Cl_4$ are aged several hours, suggesting the formation of benzyl radicals and Cl abstraction from the solvent as a possible decomposition mechanism. Selected ^1H NMR resonances ($C_2D_2Cl_4$, 25 °C): δ 2.02, 2.26 (2d, AB system, ^2J = 10.0 Hz, 4H, CH_2Ph), 6.52 (d, 4H, *o-Ph*), 7.1–7.4 (m, 6H, *m,p-Ph*).

(20) A similar propene single-insertion adduct deriving from $[(C_5Me_5)Zr(CH_2Ph)_2]^+$ has been recently obtained and characterized by X-ray diffraction analysis, confirming η^6-coordination of the dangling Ph ring: unpublished results from our laboratory.

The lower activity in olefin polymerization of cationic Zr benzyl complexes with respect to the methyl analogues, at least at low temperatures, has been recently pointed out by Bochmann *et al.*,[21] who explained this finding in terms of the higher activation energy for the first insertion of the olefin into the Zr–η^2-benzyl bond. On the other hand, the results reported above, as well as similar results obtained for analogous mono-Cp benzyl complexes[20] (for which the first insertion of propene occurs quantitatively almost instantaneously), suggest that the formation of stable single-insertion intermediates could be an alternative explanation.

When warming a solution of **2** in $C_2D_2Cl_4$ to 50 °C, rapid decomposition occurs *via* β-hydrogen elimination, as indicated by the appearance of resonances for $CH_2{=}CMeCH_2Ph$ in the ^1H NMR spectrum.[22] Other major decomposition products are toluene, bibenzyl, an unidentified insoluble Zr compound, and Me_2CHCH_2Ph.[22] The last product could possibly originate from a reaction of **2** with an intermediate Zr hydride deriving from β-hydrogen elimination.

Decomposition *via* β-hydrogen elimination with formation of $CH_2{=}CMeCH_2Ph$ is observed also on adding tetrahydrofuran (THF) to a solution of **2** in $C_2D_2Cl_4$ at 25 °C. This behavior is quite peculiar, since other cationic group 4 hydrocarbyl complexes are stabilized by the coordination of Lewis bases.[4a–c,f] In this case, the formation of an unstable THF adduct of **2** containing η^1-bonded hydrocarbyls could account for the observed rapid β-hydrogen elimination due to the absence of π-bonding stabilization.

Warming **2** to 50 °C in the presence of an excess of propene leads to formation of some polypropylene, together with the same decomposition products observed in the thermolysis of **2**. ^{13}C NMR analysis indicates that the polymer obtained is a mixture of atactic and isotactic polypropylene, as reported previously,[5b] and does not show any detectable end group, due to the high molecular weight. These findings suggest that, at least in these conditions, polymerization of propene initiates mostly after β-hydrogen elimination has occurred. On the other hand, injection of ethene into a solution of **2** in $C_2D_2Cl_4$ at 25 °C results in rapid monomer consumption and formation of polyethylene. Further investigation is in progress in order to clarify if under more severe conditions propene polyinsertion can occur in **2**, as well as in order to explain the origin of both the atactic and the isotactic (with an "enantiomorphic sites" type microstructure[5b]) polymer fractions.[23]

Conclusions

The reaction of the cationic complex $[Zr(CH_2Ph)_3]^+$ with ethene, propene, and higher α-olefins affords cleanly the single-insertion adducts $[Zr(CH_2Ph)_2(CH_2CHRCH_2Ph)]^+$. The insertion of α-olefins is regiospecific and proceeds through *cis* addition to the double bond, providing a model for the insertion mechanism in Ziegler–Natta polymerization. The single-insertion adducts, which in many cases have been isolated and characterized, are stabilized toward either further monomer insertion or β-hydrogen elimination by the back-biting η^n-coordination of the Ph ring of the $ZrCH_2CHRCH_2Ph$ moiety and by η^2-coordination of the two benzyl ligands. However, β-hydrogen elimination occurs rapidly at higher temperatures. At 50 °C, polymerization of propene proceeds, possibly by a Zr hydride deriving from β-hydrogen elimination in the single-insertion adduct, yielding a mixture of isotactic and atactic polymer.

The selective occurrence of olefin insertion and β-hydrogen elimination at different temperatures suggests that this system could be particularly suited for kinetic studies aimed at addressing the steric and the electronic factors involved in both processes for different olefins.[9d] Other future developments include extension of this study to different unsaturated substrates, such as diolefins and alkynes, as well as to analogous mono-Cp and bis-Cp benzyl derivatives.

Experimental Section

General Procedures. All procedures were carried out under nitrogen by using standard Schlenk or glovebox techniques. Solvents were treated as follows: sulfur-free toluene,[5b] *n*-heptane, and THF were refluxed for 48 h over sodium–benzophenone and distilled before use; 1,1,2,2-tetrachloroethane was distilled from CaH_2. Deuterated solvents were filtered through activated basic alumina before use. Polymerization grade ethylene and propene (SON) were used without purification, while other olefins were filtered through activated basic alumina. $Zr(CH_2Ph)_4$, $B(C_6F_5)_3$, *cis*-$CHD{=}CHMe$, and $CH_2{=}CHCH_2C_6D_5$ were synthesized according to published procedures.[24–26] NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 250 MHz for ^1H and at 62.89 MHz for ^{13}C. The chemical shifts are reported vs tetramethylsilane and were determined by reference to residual ^1H and ^{13}C solvent peaks.

NMR Tube Reactions. To solutions of **1**[12] (20–50 μmol) prepared *in situ* in 1,1,2,2-$C_2D_2Cl_4$ (0.5–0.8 mL) were added 5–10 equiv of the olefin, and the reaction was monitored by ^1H NMR at the chosen temperature (see above). In many cases, the precipitation of polymer in the NMR tube was observed after a certain period of time.

Isolation and Characterization of the Single-Insertion Adducts. Single-insertion adduct **2** was prepared by allowing **1** (0.5 mmol) to react with 10 equiv of propene in tetrachloroethane (3 mL) at 25 °C for 1 h; addition of pentane resulted in the precipitation of a red oil, which was dissolved in 1 mL of tetrachloroethane, added to toluene, and kept overnight at −15 °C: the resulting waxy precipitate was washed with pentane and dried under vacuum, affording a red-orange solid (290 mg, 55% yield). **4** was obtained similarly as a red-orange solid from reaction of **1** and 4-methyl-1-pentene at 50 °C for 30 min (yield 70%). **6** and **6**-d_5 were obtained by allowing **1** to react with allylbenzene or allylbenzene-d_5 in tetrachloroethane at 25 °C for 18 h; precipitation with pentane gave red oils (40% yield). All the compounds were characterized by ^1H, ^{13}C, and homonuclear and heteronuclear COSY NMR analysis. The NMR data are reported in Table 1. Elemental analyses were not performed since all the compounds were obtained as oils or solids which tenaciously retain variable amounts of solvents.

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[22] Diagnostic ^1H NMR resonances ($C_2D_2Cl_4$, 298 K) for the mentioned decomposition products are: $CH_2{=}CMeCH_2Ph$ δ 1.75 (s, 3H, CH_3), 3.38 (s, 2H, CH_2Ph), 4.83 (d, 2H, $CH_2{=}C$); $PhCH_2CH_2Ph$ δ 2.93 (s, CH_2); Me_2CHCH_2Ph δ 0.97 (d, 6H, CH_3), 1.93 (m, 1H, CH), 2.53 (d, 2H, CH_2).

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