## Preliminary Communication

# Single insertion of propene into a cationic zirconium(IV) complex: isolation and X-ray crystal structure of $[(C_5Me_5)Zr(CH_2CHMeCH_2Ph)(CH_2Ph)][B(CH_2Ph)(C_6F_5)_3]$

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### Abstract

The reaction of propene with the half-sandwich salt complex $[Cp'Zr(CH_2Ph)_2][B(CH_2Ph)(C_6F_5)_3]$ (1) ($Cp' = C_5Me_5$) affords cleanly the single-insertion adduct $[Cp'Zr(CH_2CHMeCH_2Ph)(CH_2Ph)][B(CH_2Ph)(C_6F_5)_3]$ (2). The crystal structure of 2 reveals an unusual 'back-biting' $\eta^6$-arene coordination to the $d^0$ metal, accounting for the unexpected stability of this compound either towards further propene insertion or towards $\beta$-hydrogen elimination.

*Key words:* Zirconium; Insertion; X-ray structure; Arene; $\pi$-Bonding

### 1. Introduction

The chemistry of cationic Group 4 alkylmetallocenes has been developed extensively in the last few years [1], mainly because complexes of this type have been shown to be catalytically active in olefin polymerization, and have been implicated as the active species in the methylalumoxane-based homogeneous Ziegler–Natta catalysts [2]. In the course of our studies on the synthesis and the catalytic activity of 'non-metallocene' cationic Group 4 metal complexes [3], we have recently reported the quite peculiar reactivity with olefins of the zwitterionic complex $[Zr(CH_2Ph)_3\{(\eta^6\text{-}PhCH_2)B(C_6F_5)_3\}]$ (3), which affords either single-insertion adducts or high-molecular-weight polymers, depending on the reaction conditions [4]. The unexpected stability of single-insertion adducts such as $[Zr(CH_2CHMeCH_2Ph)(CH_2Ph)_2]^+$ was explained by an unusual 'back-biting' $\pi$-coordination to Zr of the Ph group of the 3-phenyl-2-methylpropyl ligand [4,5]. Here, we report the synthesis and the crystal structure of the analogous complex $[Cp'Zr(CH_2CHMeCH_2Ph)(CH_2Ph)][B(CH_2Ph)(C_6F_5)_3]$ (2) confirming the chelating nature of the isobutylbenzene ligand via the intramolecular $\eta^6$-arene coordination to Zr.

### 2. Results and discussion

The recently reported benzyltris(pentafluorophenyl)borate salt of the half-sandwich cationic complex $[Cp'Zr(CH_2Ph)_2]^+$ (1) reacts rapidly with ethene (25°C and 1 atm), affording linear polyethylene [6]. In contrast, polymerization of propene proceeds only under more severe conditions (50°C; 5 atm) [3c, 6]. Monitoring the reaction of 1 with propene (2–5 equiv.) at 25°C in $C_6D_5Cl$ by $^1H$ NMR spectroscopy shows the rapid (seconds) and clean (≈ 100%) formation of the single-insertion adduct 2.

Compound 2 has been isolated (see the Experimental section), and characterized by X-ray diffraction and NMR analysis. The crystal structure of 2 [7] consists of discrete cations and $[B(CH_2Ph)(C_6F_5)_3]^-$ anions. The structure of the cation (Fig. 1) reveals that the otherwise highly electron-deficient Zr is saturated by intramolecular $\eta^6$-coordination with the 3-Ph ring. Consequently, no significant cation–anion bonding interaction is present, unlike in $[CpZr(CH_2Ph)_2][B(CH_2Ph)(C_6F_5)_3]$ (4) for which the coordination to Zr of the Ph ring of the anion was observed [6]. The coordination geometry around Zr, as defined by C11, C18, and the centroids of the Cp′ and the Ph rings, is pseudotetrahedral. The Cp′ centroid–Zr–Ph centroid angle is 135°, which is similar to the values observed for Cp′–Zr–Cp′ angles in cationic metallocenes [8]. The average Zr–C(Ph) distance is 2.72 Å, very close to those observed in the zwitterionic $Zr^{IV}$ arene complexes 3 and 4 mentioned above [3d, 6], but considerably longer than the average Zr–C(Ph) distance (2.42 Å) found for the $Zr^{II}$ complex $[Zr(\eta^6\text{-}PhMe)(PMe_3)_2Cl_2]$ [9]. This finding, expected in view of the lack of back-bonding in $d^0$ metal $\pi$-complexes, suggests that reference to $Zr^{II}$ complexes when proposing models for the putative $d^0$ metal–olefin complexes invoked as Ziegler–Natta catalytic intermediates is inappropriate [10]. The other metrical parameters are unexceptional, with the benzyl group behaving as a normal, undistorted $\eta^1$-ligand.

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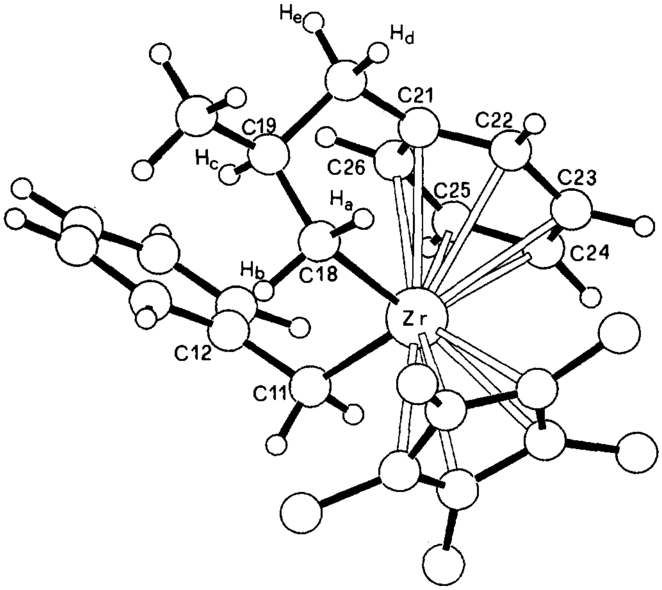

Fig. 1. Crystal structure of $[Cp'Zr(CH_2CHMeCH_2Ph)(CH_2Ph)]^+$. Relevant distances (Å) and angles (°): Zr–Cp′ (centroid) 2.22(2), Zr–C11 2.29(2), Zr–C18 2.26(2), Zr–C21 2.72(2), Zr–C22 2.71(2), Zr–C23 2.69(2), Zr–C24 2.70(3), Zr–C25 2.74(2), Zr–C26 2.74(2); C11–Zr–C18 102.2(8), C11–Zr–Cp′ 104.8(7), C11–Zr–Ph (centroid) 106.4(8), C18–Zr–Cp′ 106.0(7), C18–Zr–Ph 98.1(8), Cp′–Zr–Ph 135.0(7), Zr–C11–C12 125(1). Hydrogen atoms, except those of Cp′, are included at idealized positions.

NMR analysis (see the Experimental section) indicates that the solid state structure of **2** is maintained in solution. Noteworthy is the $^1H$ subspectrum of the $ZrCH_2CHMeCH_2Ph$ moiety. These are five distinct resonances observed for the aromatic protons, which confirm Ph coordination to Zr. Moreover, the chemical shifts of the $CH_2$ protons on C18 and C20 (see Fig. 1) ($\delta = -0.01$, $H_a$; 0.45, $H_b$; 2.11, $H_d$; 2.99, $H_e$), the $^3J$(H, H) coupling constants ($^3J(H_aH_c) = 13.9$ Hz; $^3J(H_bH_c) = 1.5$ Hz), and a long range coupling constant ($^4J(H_bH_e) = 1.5$ Hz) indicate a rigid conformation of the $\overline{ZrCH_2CHMeCH_2Ph}$ ring, with the Me substituent locked in a pseudo-equatorial position, as observed in the solid state. A set of lower intensity ($\approx$ 1:4) resonances with a pattern similar to the main ones is observed in the $^1H$ and the $^{13}C$ NMR spectra, suggesting the presence of a second diastereomer of **2**. Actually, two diastereomeric pairs of enantiomers are conceivable for **2**, due to the presence of two chiral centres at Zr and C19. Attempts at fractional crystallization were unsuccessful. Interconversion of the two isomers is not observed by NMR monitoring up to 60°C.

Further propene insertion in **2** does not occur at 25°C and 1 atm at an appreciable rate. However, under the same conditions, **2** does promote polymerization of ethene, although with an activity ($\approx$ 6 kg polyethylene (mol Zr)$^{-1}$ h$^{-1}$) lower than that of **1** [6]. Work is in progress to establish unambiguously whether ethene polyinsertion occurs in **2** and not in some secondary product [4], although under these conditions NMR monitoring showed no evidence of decomposition.

## 3. Experimental section

All operations were carried out under rigorously anhydrous conditions under argon in a glove-box.

### *3.1. Synthesis of 2*

$[Cp'Zr(CH_2Ph)_2][B(CH_2Ph)(C_6F_5)_3]$ was prepared in situ by allowing $[Cp'Zr(CH_2Ph)_3]$ (200 mg, 0.4 mmol) and $B(C_6F_5)_3$ (205 mg, 0.4 mmol) to react in 5 ml of 1,2,4-$C_6H_3Cl_3$ [6]. Propene (20 ml) was injected into the solution at 25°C. The solution changed almost instantaneously from yellow-orange to red. Heptane was added, resulting in the precipitation of a red solid, which was collected, washed with toluene and pentane, and dried under vacuum. Yield 330 mg (80%). Anal. Found: Zr 8.9%. $C_{52}H_{42}BF_{15}Zr$ calcd.: Zr 8.69%. $^1H$ NMR (250 MHz, 25°C, $C_2D_2Cl_4$, assignments confirmed by 2D-COSY): $\delta = -0.01$ (t, $^2J = {}^3J = 13.9$ Hz, 1H; $H_a$), 0.45 (dt, $^2J = 13.9$ Hz, $^3J = {}^4J(H_bH_e) = 1.5$ Hz, 1H; $H_b$), 0.92 (d, 3H; $CH_3$), 1.51, 1.78 (2d, AB system, $^2J = 12.4$ Hz, 2H, $ZrCH_2Ph$), 1.97 (s, 15H; Cp′), 2.08 (m, partially obscured, 1H; $H_c$), 2.11 (m, 1H; $H_d$), 2.81 (br. s, 2H, $BCH_2$), 2.99 (m, $^4J(H_bH_e) = 1.5$ Hz, 1H; $H_e$), 6.49 (t, 1H, *m*-$\eta^6$-Ph), 6.55 (d, 2H; *o*-$ZrCH_2Ph$), 6.7–6.9 (m, 5H; $BCH_2$*Ph*), 6.77 (d, 1H, *o*-$\eta^6$-Ph), 6.90 (t, 1H, *p*-$\eta^6$-Ph), 7.06 (d, 1H; *o*′-$\eta^6$-Ph), 7.28 (t, 2H; *m*-$ZrCH_2$*Ph*), 7.68 (t, 1H; *m*′-$\eta^6$-Ph); lower intensity resonances due to a diastereomer of **2** ($\approx$ 20%) are detected: $\delta = -0.24$ (t, $J = 12.1$ Hz, 1H; $H'_a$), 1.05 (d, 3H; $CH'_3$), 3.10 (m, 1H; $H'_e$), 7.50 (t, 1H; *m*-$\eta^6$-Ph′). $^{13}C$ NMR (62.89 MHz, 25°C, $C_2D_2Cl_4$, assignments confirmed by DEPT, selected resonances, in square brackets those due to the minor isomer): $\delta =$ 11.9 [11.8] ($C_5$*Me*$_5$), 26.5 [27.4] (Me), 43.0 [45.2] (CHMe*C*$H_2$Ph), 51.4 [51.8] (CH), 67.2 [70.4] (Zr*C*$H_2$Ph), 82.7 [84.5] (Zr*C*$H_2$CHMe), 123.4 (*C*$_5$Me$_5$), 144.3 [147.9] (*ipso*-$ZrCH_2Ph$), 160.7 [159.3] (*ipso*-$\eta^6$-Ph).

### *3.2. Polymerization of ethene*

A solution of **2** (20 mg) in 1,2,4-$C_6H_3Cl_3$/PhMe (10 ml, 1:2) was saturated with ethene at 25°C/1 atm and stirred for 15 min. The reaction was quenched with MeOH. Yield 30 mg of polyethylene.

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7 Single crystals of **2** were obtained by slow diffusion of heptane into a solution of **2** in trichlorobenzene/toluene (1:1) at room temperature. Crystallographic data: space group $P2_1/n$ monoclinic; $a = 9.369(2)$, $b = 15.296(4)$, $c = 32.727(8)$ Å, $\beta = 96.14(2)°$, $V = 4663(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.495$ g cm$^{-3}$. Data collected on a Siemens D4 diffractometer (Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å); angular range: $2° < \theta < 22°$; scan range ($\omega$-scan) $\omega_{calcd} \pm 0.6°$; scan speed variable from 3.0 to 29.3° min$^{-1}$ depending on intensity; 4971 independent reflection measured, 2153 ($F > 2\sigma_F$) used in refinement; structure solved by Patterson and Fourier transform methods and refined by using isotropic thermal parameters for all non-H atoms except Zr, treated anisotropically; H atoms, except those of Cp′, included at idealized positions in the final cycles of refinement. Maximum residual density 0.6 e Å$^{-3}$; $R = 0.086$. Supplementary material including full crystallographic data has been deposited at the Cambridge Crystallographic Data Centre.

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