Journal of Organometallic Chemistry, 445 (1993) 111–114

JOM 23101

Stabilization of a catalytically syndiotactic-specific metallocene cation by trimethylphosphine. The crystal structure of $[(\eta^5\text{-}C_5H_4)CMe_2\text{-}\eta^5\text{-}(C_{13}H_8)ZrMePME_3]^+$ $[B(C_6F_5)_4]^-$

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(Received June 12, 1992)

Abstract

The reaction of $(\eta^5\text{-}C_5H_4)CMe_2\text{-}\eta^5\text{-}(C_{13}H_8)ZrMe_2$ with $(C_6H_5)_3CB(C_6F_5)_4$ in toluene at ambient temperature leads to the formation of the $[(\eta^5\text{-}C_5H_4)CMe_2\text{-}\eta^5\text{-}(C_{13}H_8)ZrMe]^+$ cation in solution. The chemically highly-reactive cation can be stabilized and isolated by addition of a stoichiometric amount of the Lewis base PMe_3 to the reaction mixture. The stabilized cation has been characterized by NMR spectroscopy and an X-ray diffraction study.

1. Introduction

Cationic Group 4 monoalkyl complexes have long been suspected to be the actual active species in the homogeneous catalysis of olefin polymerization [1–7]. They are formed when the catalyst precursor, the metallocene dichloride, is treated with the cocatalyst methylaluminoxane (MAO) or when a metallocene dimethyl is treated with an appropriate ionizing agent. The resulting cation is a 14-electron species, coordinatively and electronically unsaturated, and therefore able to coordinate olefins for successive insertion reactions into the metal–alkyl bond. This cationic model has been deduced from a variety of studies, such as electrodialysis [1], chemical trapping [3], X-ray photoelectron spectroscopy [8], and recently from the well defined aluminium-free stable ionic complexes [7,9–11] in combination with the stereochemical behaviour of the catalysts during propylene polymerization [12].

We report below the synthesis, characterization, and molecular structure of the ansa-metallocene methyl cation $[(C_5H_4CMe_2C_{13}H_8)ZrPMe_3Me]^+$. It is the first catalytically syndiotactic-specific ansametallocene methyl cation to be isolated and structurally characterized [13]. We regard the cation as the PMe_3^- stabilized form of the catalytically-active species.

2. Results and discussion

The dimethyl complex **1** reacts with $(C_6H_5)_3CB(C_6F_5)_4$ in toluene at room temperature to give a catalyst very active for polymerization of propylene to syndiotactic polypropylene. At a lower polymerization temperature (20°C), the microstructure and molecular weight of the polymer are similar to those of material prepared by the conventional MAO-activated system [14]. This indicates that in both cationic and the "neutral" systems the same active species and the same polymerization mechanisms are involved [15]. Attempts to isolate the organometallic product have so far failed. However, the addition of a stoichiometric amount of PMe_3 to the catalytically-active reaction mixture leads to the formation of the complex **2** in high yield.

Complex **2** shows no catalytic effect on olefin polymerization at 60°C. Obviously the PMe_3 ligand occu-

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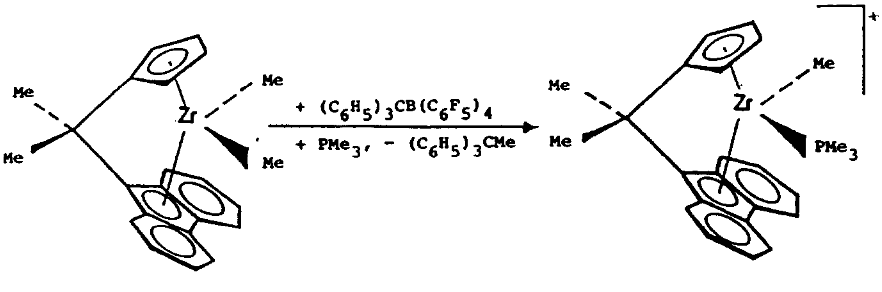
0022-328X/93/$6.00



1

$[B(C_6F_5)_4]^-$

2

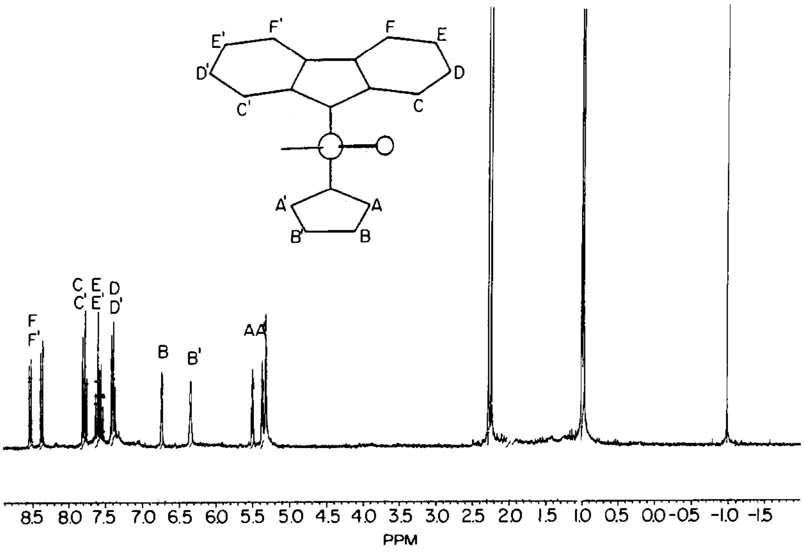


Fig. 1. ^1H NMR spectrum of **2** (300 MHz, in CD_2Cl_2, R.T.).

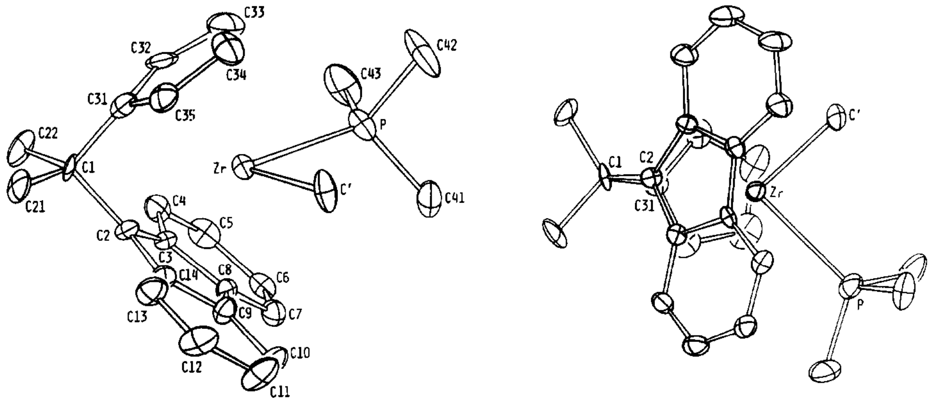


Fig. 2. Two views of the cation of **2** in the crystalline state. Selected distances (Å) and angles (°): Zr–C1 2.228(17), Zr–P 2.779(4), Zr–Z(Flu) 2.22, Zr–Z(Cp) 2.16; P–Zr–C′ 88.4(4), Z(Flu)–Zr–Z(Cp) 119.1(5), C_2–C_1–C_{31} 98.4(9). Z(Flu) and Z(Cp) are the centres of the rings containing C2 and C31.

pies the vacant coordination site at the metal centre and prevents the complexation and subsequent insertion of the olefin. Complex **2** was identified from ^{1}H NMR spectrum and by an X-ray structure determination.

2.1. *^{1}H NMR spectrum*

The ^{1}H NMR spectrum of **2** with the corresponding atom-numbering scheme is presented in Fig. 1. The characteristic double doublet, triple-triplet signal pattern for the fluorenyl protons and the familiar picture of two virtual triplets from the cyclopentadienyl protons of the parent metallocene complexes [13] have disappeared, and instead a more complex signal pattern is observed.

In the fluorenyl aromatic region two doublets at $\delta = 8.53$ and 8.37 ppm for FF′ protons and a virtual triplet at $\delta = 7.78$ ppm for CC′ protons are followed by two sets of two overlapping triplets at $\delta = 7.61$ and 7.40 ppm for EE′ and DD′ protons, respectively. The coupling constants for the doublet and the triplets are *ca.* 8.4 Hz. In the vinyl region there are four distinct multiplets, two at $\delta = 6.73$ and 6.34 ppm for the distal BB′ protons and two at $\delta = 5.50$ and 5.36 ppm for the proximal AA′ protons. The distal proton B′ shows a broad signal with a less resolved fine structure, probably due to dynamic exchange between complexed and free PMe_3. The two singlets at $\delta = 2.28$ and 2.24 ppm come from the protons of the methyl substituents in the bridge. The doublet at $\delta = 0.99$ ppm (J(PH) 2 Hz) and a singlet at $\delta = -0.98$ ppm comes from the methyl group of the PMe_3 and the terminal methyl ligand.

2.2. *X-ray structure of 2*

Two prespective views of the molecular structure of **2** are shown in Fig. 2, with the atom numbering scheme. The important bond distances and bond angles are given in Table 1.

As in similar metallocenes having a $C_5H_4CR_2C_{13}H_8$ chelating ligand system [12,13], the least squares planes defined by the two C_5 fragments in **2** are inclined towards the zirconium atom with respect to the C(1)–C(2) and C(1)–C(31) vectors (*cf.* Table 1). The effect is more pronounced for the cyclopentadienyl ring than the fluorenyl group, the inclination angles being 15.5° and 11.8° respectively. The distances between the zirconium atom and the two centroids differ only slightly in the structures of **1** [15] and **2**. This is due to the fact that the removed electron originates from a non-bonding metal orbital [16]. A noteworthy feature of this structure is the unusually small Me–Zr–PMe_3 angle of 88.4°, which is more typical for d^1 complexes [17,18]. An α-agostic Zr–H–C interaction could be responsible for this phenomenon by forcing the Zr–C bond to move closer to the Zr–P bond, but we have no experimental evidence for this.

TABLE 1. Selected distances (Å) and angles (°) for the cation of **2** [a]

Zr–C′	2.23(2)	Zr–C(9)	2.62(1)
Zr–P	2.779(4)	Zr–C(14)	2.52(1)
Zr–flu	2.22	Zr–C(31)	2.43(1)
Zr–Cp	2.16	Zr–C(32)	2.47(1)
Zr–C(2)	2.38(1)	Zr–C(33)	2.55(2)
Zr–C(3)	2.48(1)	Zr–C(34)	2.51(2)
Zr–C(8)	2.64(1)	Zr–C(35)	2.45(2)
C′–Zr–P	88.4(4)	flu plane/cp plane	108.9
Z(flu)–Zr–Z(Cp)	119.1	flu plane/C(1)–C(2) vector	11.8
C(2)–C(1)–C(31)	98.4(9)	Cp plane/C(1)–C(31) vector	15.5
C(21)–C(1)–C(22)	107.8(11)		

[a] Z(flu) and Z(Cp) denote the centres of the five membered rings of the fluorenyl and the cyclopentadienyl groups; flu plane and Cp plane are the corresponding best planes.

3. Experimental details

All experiments were conducted under purified nitrogen by standard glove box and Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation under nitrogen over sodium benzophenone and pentane was distilled under nitrogen from calcium chloride.

TABLE 2. Atomic coordinates for $[(\eta^5\text{-}C_5H_4)CMe_2\text{-}\eta^5\text{-}(C_{13}H_8)\text{-}ZrMePMe_3]^+$ (**2**)

Atom	x	y	z	U_{eq}
Zr	0.19928(10)	0.38429(9)	0.24869(8)	0.044(1)
C′	0.1508(14)	0.5097(13)	0.1786(10)	0.086(7)
C(1)	0.1269(10)	0.3140(8)	0.3949(8)	0.049(5)
C(2)	0.2363(8)	0.4024(7)	0.4020(7)	0.040(5)
C(3)	0.3475(9)	0.3825(7)	0.3950(7)	0.040(5)
C(4)	0.3994(11)	0.2893(9)	0.3924(8)	0.056(5)
C(5)	0.5127(11)	0.2995(10)	0.3874(9)	0.064(6)
C(6)	0.5796(10)	0.3958(10)	0.3799(8)	0.054(5)
C(7)	0.5272(10)	0.4817(9)	0.3760(8)	0.054(5)
C(8)	0.4128(9)	0.4754(8)	0.3827(7)	0.039(5)
C(9)	0.3404(10)	0.5540(8)	0.3827(8)	0.050(5)
C(10)	0.3676(12)	0.6627(9)	0.3753(10)	0.069(6)
C(11)	0.2878(13)	0.7237(9)	0.3798(12)	0.086(6)
C(12)	0.1841(12)	0.6824(10)	0.3947(11)	0.084(6)
C(13)	0.1550(12)	0.5781(9)	0.4017(9)	0.068(6)
C(14)	0.2391(10)	0.5120(8)	0.3984(8)	0.046(5)
C(21)	0.0450(12)	0.3621(11)	0.4389(10)	0.074(6)
C(22)	0.1687(12)	0.2236(10)	0.4379(10)	0.081(6)
C(31)	0.0645(10)	0.2734(9)	0.2944(9)	0.055(5)
C(32)	0.0989(11)	0.1978(9)	0.2381(10)	0.070(6)
C(33)	0.0482(14)	0.2044(13)	0.1480(11)	0.100(7)
C(34)	−0.0174(12)	0.2857(15)	0.1472(10)	0.094(7)
C(35)	−0.0091(10)	0.3279(11)	0.2380(10)	0.069(6)
P	0.3149(3)	0.3196(3)	0.1359(2)	0.067(2)
C(41)	0.4488(14)	0.4196(14)	0.1461(11)	0.099(7)
C(42)	0.2108(15)	0.2894(19)	0.0163(10)	0.138(7)
C(43)	0.3765(16)	0.1995(13)	0.1413(11)	0.107(7)

The ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument.

3.1. Preparation of $(C_5H_4)CMe_2(C_{13}H_8)ZrMe_2$ (1)

To a suspension of 2.00 g (4.6 mmol) of $(C_5H_5)CMe_2(C_{13}H_8)ZrCl_2$ in 100 ml of diethyl ether at −78°C was added 9.2 mmol of MeMgCl as a THF solution. The temperature was raised gradually to 20°C, the red colour of the solution changing to yellow. The solvents were subsequently evaporated and the yellow residue was extracted with pentane. Cooling of the pentane solution to −78°C gave small yellow crystals. Yield: 1.34 g (75%).

3.2. Preparation of $[(C_5H_4)CMe_2(C_{13}H_8)ZrPMe_3Me]^+[(C_6F_5)_4]^-$ (2)

To a solution of 0.4 g (1 mmol) of **1** in 150 ml of toluene containing 0.076 g (1 mmol) of PMe_3 at room temperature was added 1.03 g (1 mmol) of $(C_6H_5)_3CB(C_6F_5)_4$. The mixture was stirred for 0.5 h at this temperature. After removal of the toluene the remaining red solid was dissolved in dichloromethane and from the solution red crystals were obtained at −78°C. Yield: 0.7 g (64%).

3.3. Crystal structure determination

A crystal (approx. 0.05 × 0.15 × 0.30 mm) was sealed in a Lindemann glass capillary. All data were collected at room temperature using a Philips PW1100 diffractometer and graphite monochromated Mo Kα radiation (λ 0.71069 Å). Crystal data for $C_{49}H_{30}BF_{20}PZr$: triclinic, $P\bar{1}$, a 12.110(4), b 12.971a(4), c 16.628(6) Å, α 102.05(3), β 110.37(3), γ 99.09(3)°, D_c 1.622 for $Z = 2$, μ 3.2 cm^{-1}. A total of 6241 unique reflections was measured; $\theta/2\theta$ operation; $\theta_{(max)}$ 23°; Lp correction; no absorption correction. The set of 4855 reflections with $F_o > 3\sigma(F_o)$ was used for the subsequent calculations. The structure was solved by the Patterson method. The non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were omitted. Final values for R and $R_w(F)$: 0.114 and 0.123; maximum residual electron density in a final F synthesis: 0.8 e Å^{-3}. Partial decomposition of the crystal during the X-ray measurements is responsible for the relatively large R indices. The SHELX-76 program system [19] was used for the calculations. Atomic coordinates for the complex cation are listed in Table 2.

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