

## Isolation of a Single-insertion Intermediate in the Catalytic Polymerization of Propene by a Cationic Tris(hydrocarbyl) Zirconium Complex

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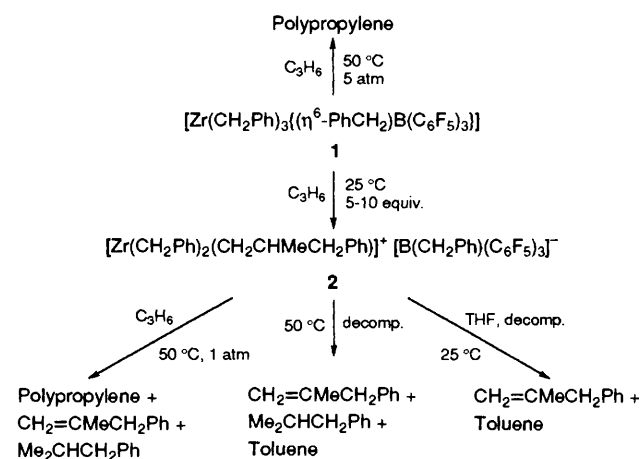
Propene reacts smoothly with the alkene polymerization catalyst  $[\text{Zr}(\text{CH}_2\text{Ph})_3\{(\eta^6\text{-PhCH}_2)\text{B}(\text{C}_6\text{F}_5)_3\}]$  **1** to give initially the single-insertion adduct  $[\text{Zr}(\eta^{\text{n-}}\text{CH}_2\text{Ph})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})]^+[\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]^-$  **2**, which has been isolated and characterized.

The development of two-component homogeneous Ziegler-Natta catalysts based on group 4 metallocenes and methylalumoxane,<sup>1</sup> and, more recently, of single-component catalysts such as cationic alkylmetallocenes,<sup>2</sup> offered new opportunities for elucidating the mechanism of alkene polymerization. Extensive information has been obtained from the relationships between the structure of the metallocene pre-catalyst and the stereochemical structure of the resulting polymers,<sup>3</sup> and substantial evidence has emerged concerning the structure of the active species.<sup>4</sup> However, direct observation of the individual polymerization steps has been precluded, owing to catalyst instability and/or high polymerization rates.<sup>5</sup> In particular, primary reaction products arising from insertion of alkenes into the M-C bond have never been directly observed for group 4 metal complexes.<sup>6†</sup> In view of this, several authors have suggested alternative chain-growth mechanisms, involving metallacyclic, carbenoid or agostic metal-alkyl intermediates,<sup>7</sup> in addition to the classical *cis* ligand migratory insertion mechanism proposed by Cossee and Arlman.<sup>8</sup>

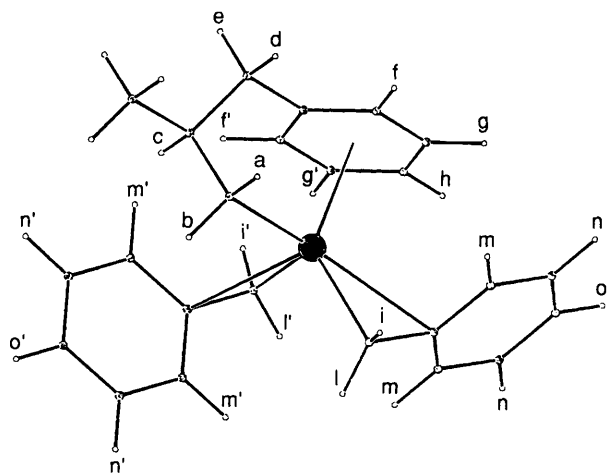
We have recently reported<sup>9a</sup> the synthesis and structural characterization of the zwitterionic non-metallocene complex

† However, insertion of propene into the M-C bond was cleanly observed for lanthanide  $[\text{M}(\text{C}_5\text{Me}_5)_2\text{Me}]$  complexes (M = Lu, Yb, Sc),<sup>6</sup> but these compounds do not promote propene polymerization.

$[\text{Zr}(\text{CH}_2\text{Ph})_3\{(\eta^6\text{-PhCH}_2)\text{B}(\text{C}_6\text{F}_5)_3\}]$  **1**, which promotes the polymerization of ethylene and propene under rather mild conditions (50 °C, 5 atm monomer pressure).<sup>9</sup> We have now investigated the reactivity of **1** with propene by NMR spectroscopy, providing a direct insight into the polymerization mechanism.



Scheme 1

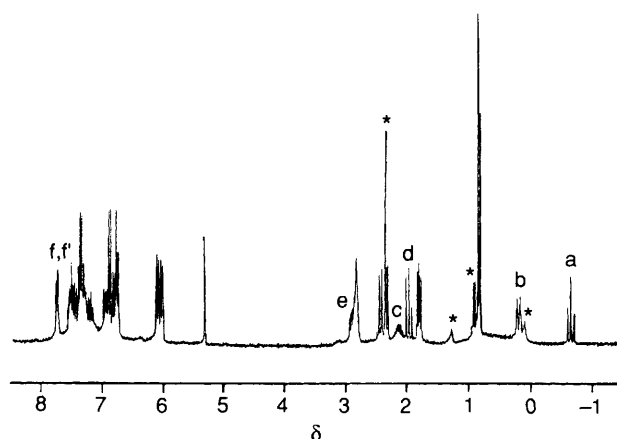


**Fig. 1** Ball-and-stick model for the cation  $[\text{Zr}(\text{CH}_2\text{Ph})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})]^+$ . The above structure, proposed on the basis of the NMR data, has been generated by using standard bond distances and angles for a tetrahedrally coordinated Zr, imposing a W-conformation of the four bonds between  $\text{H}_b$  and  $\text{H}_e$  and arbitrary torsion angles, tentatively assuming an  $\eta^2$ -coordination for the benzyl ligands. One of several conceivable isomers is depicted. A detailed analysis of the stereochemical features of **2** and related compounds is in progress: this issue, as well as the implications on the stereospecificity of the insertion, will be addressed in a future paper.

Monitoring by  $^1\text{H}$  NMR spectroscopy the reaction of **1** with propene in  $\text{C}_2\text{D}_2\text{Cl}_4$  ( $25^\circ\text{C}$ ,  $[\text{C}_3\text{H}_6]/[\text{1}] = 5\text{--}10$ ) shows the formation of the single-insertion adduct  $[\text{Zr}(\text{CH}_2\text{Ph})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})]^+[\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]^-$  **2**. The concentration of **2** approaches 100% of the Zr present after 20–30 min; only after a longer time are the precipitation of some polypropylene and the formation of secondary products observed. Complex **2** has been isolated by precipitation with pentane and recrystallization from  $\text{C}_2\text{H}_2\text{Cl}_4$ –toluene (yield 55%), and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D COSY NMR analysis,<sup>‡</sup> revealing several interesting structural features. The two Zr-bound benzyl ligands are non-equivalent, as indicated by the four distinct  $^1\text{H}$  resonances and the two distinct  $^{13}\text{C}$  resonances observed for the methylene groups; an  $\eta^2$ -coordination mode<sup>10</sup> is suggested by the large  $J_{\text{CH}}$  values (140 Hz) of the methylene groups, as well as by the two high-field resonances found at  $\delta$  6.04 and 6.10 for the *ortho*-aromatic protons.<sup>§</sup> The anion is not coordinated to Zr, as suggested by the absence of the high-field resonances for the  $\text{BCH}_2\text{Ph}$  aromatic protons observed in the spectrum of **1**<sup>9a</sup> and supported by the observed poor solubility of **2** in toluene compared to the high solubility of the zwitterionic **1**. The  $^1\text{H}$  NMR data (see Figs. 1 and 2) of the Zr– $\text{CH}_2\text{CHMeCH}_2\text{Ph}$

<sup>‡</sup> NMR data for **2**:  $^1\text{H}$  NMR (250 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ , see Figs. 1 and 2):  $\delta$  –0.66 (t,  $^2J = ^3J = 12.4$  Hz, 1H,  $\text{H}_a$ ), 0.19 [dt,  $^2J = 12.4$  Hz,  $^3J = ^4J(\text{H}_b\text{H}_e) = 2.4$  Hz,  $\text{H}_b$ ], 0.83 (d, 3H,  $\text{CH}_3$ ), 1.78, 1.80 (2 d, 2H,  $\text{H}_i$ ,  $\text{H}_i'$  or  $\text{H}_1$ ,  $\text{H}_1'$ ), 1.96 (t,  $^2J = ^3J = 11.7$  Hz, 1H,  $\text{H}_d$ ), 2.12 (m, 1H,  $\text{H}_c$ ), 2.33, 2.43 (2 d, 2H,  $\text{H}_j$ ,  $\text{H}_j'$  or  $\text{H}_2$ ,  $\text{H}_2'$ ), 2.85 (br s, 2H,  $\text{BCH}_2\text{Ph}$ ), 2.89 [ddd,  $^2J = 11.7$  Hz,  $^3J = 6.3$  Hz,  $^4J(\text{H}_b\text{H}_e) = 2.4$  Hz,  $\text{H}_e$ ], 6.04, 6.10 (2 d, 4H,  $\text{H}_m$ ,  $\text{H}_m'$ ), 6.7–6.9 (m, 5H,  $\text{BCH}_2\text{C}_6\text{H}_5$ ), 7.20 (br t, 1H,  $\text{H}_h$ ), 7.22 (br m, 2H,  $\text{H}_g$ ,  $\text{H}_g'$ ), 7.34 (m, 4H,  $\text{H}_n$ ,  $\text{H}_n'$ ), 7.45 (2 t, 2H,  $\text{H}_o$ ,  $\text{H}_o'$ ) and 7.73, 7.75 (2 d, 2H,  $\text{H}_f$ ,  $\text{H}_f'$ );  $^{13}\text{C}$  NMR (62.89 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $25^\circ\text{C}$ ), selected resonances: Zr( $\eta^2$ - $\text{CH}_2\text{Ph}$ )<sub>2</sub>:  $\delta$  67.8, 68.9 ( $J_{\text{CH}} = 140$  Hz,  $\text{CH}_2$ ,  $\text{C}'\text{H}_2$ ), 127.7, 127.2 ( $\text{C}_{\text{ipso}}$ ,  $\text{C}'_{\text{ipso}}$ ); Zr $\text{CH}_2\text{CHMeCH}_2\text{Ph}$ :  $\delta$  42.3 ( $J_{\text{CH}} = 129$  Hz,  $\text{C}_\gamma\text{H}_2$ ), 79.7 ( $J_{\text{CH}} = 120$  Hz,  $\text{C}_\alpha\text{H}_2$ ) and 148.4 ( $\text{C}_{\text{ipso}}$ ). The assignments have been confirmed by 2D COSY experiments.

<sup>§</sup> By analogy with the structures of **1**<sup>9a</sup> and of related benzyl derivatives of cationic metallocenes,<sup>5a,10c–e</sup> it is probable that the phenyl rings interact with Zr mainly through the *ipso* carbons. This type of  $\pi$ -interaction has been previously defined as  $\eta^2$ -coordination.<sup>9a,10c–e</sup>



**Fig. 2**  $^1\text{H}$  NMR spectrum of  $[\text{Zr}(\eta^2\text{-CH}_2\text{Ph})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})]^+[\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]^-$  **2** in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ . Starred peaks are due to traces of solvents (toluene and pentane) and silicon grease in the sample.

moiety are particularly informative: two doublets are observed for the *ortho*-Ph protons at  $\delta$  7.73 and 7.75, downfield from the *meta*- and *para*-protons ( $\delta$  7.22 and 7.20), suggesting the coordination of the Ph ring to Zr;<sup>9a,12</sup> noteworthy is also a long distance coupling between one of the  $\text{C}_\alpha\text{H}_2$  protons ( $\text{H}_b$ ) and one of the  $\text{C}_\gamma\text{H}_2$  protons ( $\text{H}_e$ ): the  $^4J(\text{H}_b\text{H}_e)$  value of 2.4 Hz suggests a stereorigid W-conformation<sup>11</sup> of the four bonds between  $\text{H}_b$  and  $\text{H}_e$ . Inspection of the models reveals that such a conformation is reasonably required when the Ph group is coordinated to Zr. The structure depicted in Fig. 1, in which Zr appears tetrahedrally coordinated and with a formal electron count of 16, could account for the observed stability of **2** towards either subsequent monomer insertion or  $\beta$ -hydrogen elimination, as well as for the lack of anion coordination as found in **1**.

Variable temperature  $^1\text{H}$  NMR analysis performed in  $\text{CD}_2\text{Cl}_2$  between  $-90$  and  $20^\circ\text{C}$  shows no substantial change in the subspectrum of the isobutylbenzene ligand, while an upfield shift and a consistent broadening of the *ortho*-Ph proton resonances of the Zr-bound benzyl ligands are observed with decreasing temperature. The latter findings can be explained by a reduced fluxionality of the benzyl ligands, possibly owing to an increased amount of  $\eta^2$ -interaction (for instance, from  $\eta^2$  to  $\eta^3$ ), and by a fast suprafacial migration of Zr between the two non-equivalent edges of the Ph rings. A similar behaviour was observed for  $[\text{Th}(\text{C}_5\text{Me}_5)(\text{CH}_2\text{Ph})_3]$ .<sup>10a</sup>

The presence of other sources of stabilization, such as agostic interactions,<sup>13</sup> which have been observed in some cationic and zwitterionic zirconocene hydrocarbyl complexes,<sup>14</sup> is not revealed in the case of **2** by NMR and IR analysis, showing normal values of  $J_{\text{CH}}$  coupling constants, no low frequency  $\nu_{\text{C-H}}$  stretching, and no substantial temperature-dependent isotopic perturbation<sup>13b,14b</sup> when comparing the  $^1\text{H}$  NMR spectra of **2** and appropriately deuterated  $[\text{Zr}(\text{CH}_2\text{Ph})_2(\text{CH}_2\text{CHMeCH}_2\text{Ph})] - \delta(\text{ZrCHDCHMeCH}_2\text{Ph}) = 0.05$  ppm at  $20^\circ\text{C}$ ;  $-0.04$  ppm at  $-70^\circ\text{C}$ . Of course, one cannot say if such stabilizing interactions are present or not in the propagating species obtained from **2** [e.g.  $\text{Zr}(\text{CH}_2\text{CHMe})_n\cdots$ ].

Addition of tetrahydrofuran (THF) to a solution of **2** in  $\text{C}_2\text{D}_2\text{Cl}_4$  results in decomposition with formation of  $\text{CH}_2=\text{CMeCH}_2\text{Ph}$ , possibly *via*  $\beta$ -hydrogen elimination in a transient THF adduct of **2** containing  $\sigma$ -bonded hydrocarbyl units. Thermolysis of **2** in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $50^\circ\text{C}$  yields  $\text{CH}_2=\text{CMeCH}_2\text{Ph}$  and  $\text{Me}_2\text{CHCH}_2\text{Ph}$  in equal amounts, besides toluene and an unidentified insoluble Zr compound; isobutylbenzene could possibly originate from a reaction of **2** with an intermediate Zr hydride derived from  $\beta$ -hydrogen elimination. Warming **2** to  $50^\circ\text{C}$  in the presence of an excess of propene leads to the formation of polypropylene, together

with  $\text{CH}_2=\text{CMeCH}_2\text{Ph}$  (which is eventually consumed) and  $\text{Me}_2\text{CHCH}_2\text{Ph}$ .  $^{13}\text{C}$  NMR analysis indicates that the polymer obtained is a mixture of atactic and isotactic polypropylene, as reported previously,<sup>9b</sup> and does not show any detectable end group, owing to the high molecular mass. These findings seem to suggest that polyinsertion initiates mostly on Zr-H bonds formed through  $\beta$ -hydrogen elimination. Work is in progress in order to establish if **2** undergoes further propene insertion under higher monomer pressure. This subject, as well as the reasons why insertion of propene in **1** is easier than in **2**, will be addressed in a future paper.

Similar experiments have been performed with other alkenes. Preliminary results indicate that reaction of **1** with ethylene proceeds faster, leading to the rapid formation of polyethylene; an analogous single-insertion intermediate has been detected, although not yet characterized owing to the concurrent appearance of secondary products. Higher alk-1-enes, such as the bulky 4-methylpent-1-ene, also react smoothly with **1**, affording adducts analogous to **2**, while internal alkenes, such as but-2-ene, are unreactive. A detailed study on the reactivity of **1** with several different alkenes and other unsaturated substrates is in progress and will be reported subsequently.

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