

## A Zwitterionic Zirconocene Alkyl Complex as a Single-Component $\alpha$ -Olefin Dimerization Catalyst

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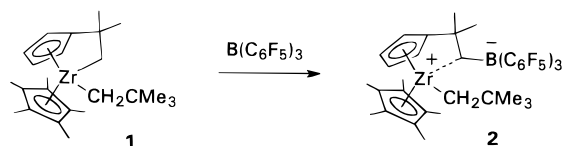
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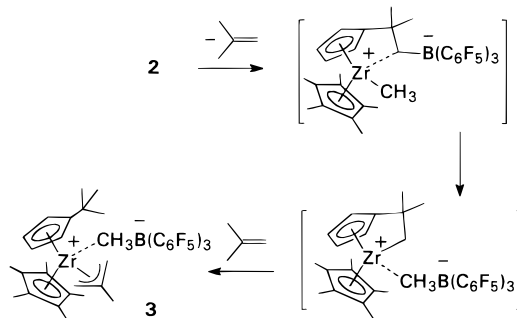
Group 4 metal metallocene-type systems have attracted intense interest due to their ability to act as highly active olefin polymerization catalysts in conjunction with various cocatalysts.<sup>1</sup> Substantial evidence is now present for the role of cationic 14-electron metallocene alkyls as active catalyst species.<sup>2</sup> There is a significant influence of the complementary anion on activity and selectivity of these catalysts.<sup>3</sup> A potential means of directing cation–anion interactions is the covalent tethering of the anionic moiety to the metallocene ligand system, where the positioning of the anion relative to the catalytically active cationic metal center should affect catalyst performance in a specific way. Recently, several examples of such zwitterionic metallocene complexes with a  $-\text{B}(\text{C}_6\text{F}_5)_3$  group attached to one of the Cp ligands (either directly<sup>4</sup> or via a  $\text{CH}_2$  spacer<sup>5</sup>) have been reported. However, in ethene polymerization experiments with these systems, no direct effect of the tethering of the anion on catalyst performance was evident. Here we describe the preparation of a novel zwitterionic zirconocene alkyl complex in which the anionic moiety is attached to one of the cyclopentadienyl ligands via a two-carbon backbone. This zwitterionic system is a highly selective single-component  $\alpha$ -olefin dimerization catalyst, in contrast with analogous non-zwitterionic systems that, under the same conditions, produce higher oligomers. The catalyst deactivates rather rapidly, probably through allylic C–H activation of the olefin. A crystal structure of a zwitterionic zirconocene  $\eta^3$ -allyl complex is presented.

Reaction of the cyclometalated complex  $\text{Cp}^*(\eta^5\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2)\text{ZrNp}$  (**1**,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Np} = \text{CH}_2\text{CMe}_3$ ) with  $\text{B}(\text{C}_6\text{F}_5)_3$  results in selective electrophilic attack of the borane on the methylene group of the cyclometalated ligand to give the zwitterionic zirconocene neopentyl complex  $\text{Cp}^*[\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]\text{ZrNp}$  (**2**, Scheme 1).<sup>7</sup> Its <sup>19</sup>F NMR spectrum at  $-40$

### Scheme 1



### Scheme 2



$^{\circ}\text{C}$  shows a fully frozen-out rotation of the  $\text{B}(\text{C}_6\text{F}_5)_3$  group, but no indication for direct  $\text{C}-\text{F}\cdots\text{Zr}$  interaction.<sup>8</sup> Instead, a moderate upfield shift of the  $\text{B}-\text{CH}_2$  protons suggests some residual interaction of this methylene group with the metal center. The diastereotopic neopentyl methylene protons exhibit vastly different chemical shifts ( $\delta$   $-1.13$  and  $4.29$  ppm) and a relatively small  $^2J_{\text{HH}}$  of  $7.0$  Hz, while the <sup>13</sup>C NMR resonance of the methylene carbon is shifted strongly downfield ( $\delta$   $129.80$  ppm). The latter may be suggestive of the presence of an  $\alpha$ -agostic interaction.<sup>9</sup>

Complex **2** is thermolabile and decomposes in bromobenzene solution at ambient temperature with a half-life of about 1 h to give the  $\eta^3$ -2-methylallyl complex  $\text{Cp}^*(t\text{-BuC}_5\text{H}_4)\text{Zr}(\eta^3\text{-}2\text{-C}_4\text{H}_7)\text{[MeB}(\text{C}_6\text{F}_5)_3]$  (**3**). Although no intermediates could be observed in the reaction, it probably proceeds through initial  $\beta$ -Me elimination<sup>10</sup> to give a zwitterionic methyl species and isobutene, followed by transfer of the borane to the methyl group and subsequent allylic C–H activation<sup>10</sup> of the isobutene (Scheme 2). In this case, the zwitterionic character of the complex is lost through transfer of the borane moiety to a metal-bound methyl group. The kinetic lability of the boron–alkyl bond in alkyl–perfluorotriarylborate metallocene complexes has recently been established conclusively.<sup>11</sup> In this case there appears to be a thermodynamic bias for formation of the  $\text{MeB}(\text{C}_6\text{F}_5)_3$  anion.

The zwitterionic zirconocene **2** acts as a single-component catalyst in its reactions with olefins. It is a highly selective (though only moderately active) catalyst for the head-to-tail dimerization of  $\alpha$ -olefins. In bromobenzene solution (ambient temperature), 1-pentene is converted to 2-propyl-1-heptene with  $>99\%$  selectivity and no concomitant isomerization of the excess 1-pentene. Initial activity corresponds to  $850$  turnovers  $\text{h}^{-1}$ , but

$34.11$  (q,  $J = 125$  Hz,  $\text{CMe}_3$ ),  $28.13$  (q,  $J = 128$  Hz, Me),  $25.21$  (q,  $J = 126$  Hz, Me),  $13.0$  (very br,  $\text{BCH}_2$ ),  $12.69$  (q,  $J = 126$  Hz,  $\text{Cp}^*\text{Me}$ ); <sup>19</sup>F NMR ( $\text{C}_6\text{D}_5\text{Br}$ ,  $282$  MHz,  $-40$   $^{\circ}\text{C}$ ):  $\delta$   $-126.9$  ( $2\times$ ),  $-129.5$  ( $2\times$ ),  $-131.2$ ,  $-132.2$  ( $o\text{-F}$ ),  $-158.3$ ,  $-158.5$ ,  $-158.9$  ( $p\text{-F}$ ),  $-161.0$ ,  $-162.1$ ,  $-163.1$ ,  $-163.4$ ,  $-163.7$ ,  $-165.0$  ( $m\text{-F}$ ).

(8) Coordination of one of the F-substituents on a  $\text{C}_6\text{F}_5$  fragment to an electrophilic metal center generally leads to a substantial ( $>50$  ppm) upfield shift of its <sup>19</sup>F NMR resonance. See: (a) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491. (b) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem.* **1995**, *107*, 1867.

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(6) Compound **1** is prepared by thermolysis of  $\text{Cp}^*(t\text{-BuC}_5\text{H}_4)\text{ZrNp}_2$  in benzene at  $80$   $^{\circ}\text{C}$  over 16 h.

(7) **2**: <sup>1</sup>H NMR ( $\text{C}_6\text{D}_5\text{Br}$ ,  $300$  MHz,  $25$   $^{\circ}\text{C}$ )  $\delta$   $6.85$ ,  $6.75$ ,  $5.69$ ,  $4.89$  (m, Cp CH),  $4.29$  (d,  $J = 7.0$  Hz, ZrCHH),  $1.65$  (s, Cp\*),  $1.32$  (s, Me),  $1.16$  (s,  $\text{CMe}_3$ ),  $0.75$  (br, BCHH),  $0.44$  (s, Me),  $-0.15$  (br, BCHH),  $-1.13$  (d,  $J = 7.0$  Hz, ZrCHH); <sup>13</sup>C NMR ( $\text{C}_6\text{D}_5\text{Cl}_4$ ,  $100.6$  MHz,  $-20$   $^{\circ}\text{C}$ )  $\delta$   $148.8$  (br d,  $o\text{-CF}$ ),  $141.21$  (s, Cp C),  $138.5$  (br d,  $p\text{-CF}$ ),  $137.2$  (br d,  $m\text{-CF}$ ),  $129.80$  (dd,  $J = 101$ ,  $111$  Hz, ZrCH<sub>2</sub>),  $125.02$  (s, Cp\* C),  $123.8$  (br s,  $\text{C}_6\text{F}_5$  C),  $114.78$  (d,  $J = 178$  Hz, Cp CH),  $111.35$  (d,  $J = 179$  Hz, Cp CH),  $110.43$  (d,  $J = 143$  Hz, Cp CH),  $107.41$  (d,  $J = 178$  Hz, Cp CH),  $43.25$  (s,  $\text{CMe}_3$ ),  $36.51$  (s,  $\text{CMe}_2$ ),

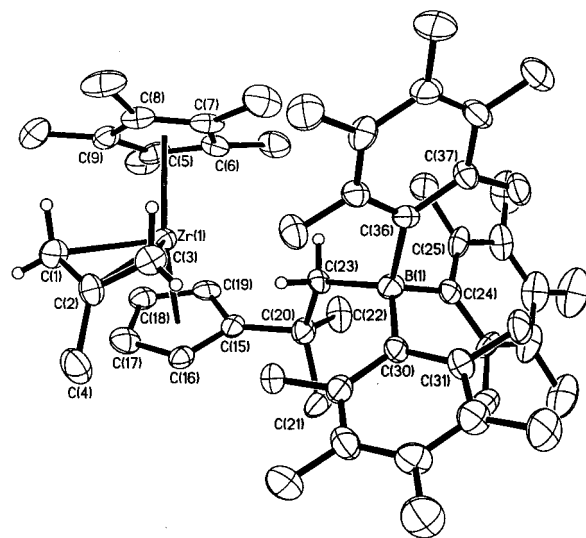
**Table 1.** Relative Amounts of Di-, Tri-, and Tetramer Formed in the Oligomerization of 1-Pentene with Various Zirconocene Catalysts ( $C_6D_5Br$  Solvent, 20 °C, Dimer Content Normalized to 100)

catalyst	cocatalyst	C <sub>10</sub>	C <sub>15</sub>	C <sub>20</sub>
<b>2</b>	none	100	0.5	0
<b>1</b>	Ph <sub>3</sub> C[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	100	72	33
Cp* <sub>2</sub> ( <i>t</i> BuCp)ZrMe <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	100	46	20
Cp* <sub>2</sub> ( <i>t</i> BuCp)ZrMe <sub>2</sub>	Ph <sub>3</sub> C[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	100	79	46

the catalyst deactivates quite rapidly, limiting total conversion to 410 turnovers of 1-pentene. With propene similar reactivity is observed, forming 2-methyl-1-pentene. This high selectivity for dimerization is characteristic of the zwitterionic system, as conversion of 1-pentene with related nonzwitterionic catalysts results in formation of significant amounts of higher oligomers (Table 1).<sup>12</sup> The selectivity of **2** for dimerization resembles that observed for Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO at low Al:Zr ratios, where the coordinating power of Al–Cl moieties is held responsible for the observed selectivity.<sup>13</sup>

We attempted to obtain information on the catalyst deactivation process. By <sup>19</sup>F NMR no evidence was found for perfluoroaryl or fluoride transfer. Electrospray MS did not show evidence for borane-to-alkyl transfer; instead the C<sub>5</sub>H<sub>5</sub>CM<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> anion (resulting from hydrolysis under sampling conditions) was observed. This shows that the zwitterionic nature of the complex is retained even after deactivation. 1-Pentene dimerization activity could be partly restored by addition of small amounts of ethene to the reaction mixture, and by CG, additional products could be observed with C<sub>10+2n</sub> (*n* = 1, 2, 3...) carbon backbones. This suggests that catalyst deactivation occurs through allylic C–H activation of  $\alpha$ -olefins to give zwitterionic  $\eta^3$ -allyl species. This type of deactivation is known for Group 3 metal and lanthanide metallocenes and some cationic zirconocene systems.<sup>14</sup> The observed reactivity also corresponds to our finding that the (nonzwitterionic) allyl complex **3** is unreactive toward  $\alpha$ -olefins but reactive toward ethene.<sup>15</sup>

A well-defined zwitterionic  $\eta^3$ -allyl complex was obtained from the reaction of **2** with isobutene. Allylic C–H activation of the isobutene leads to the zwitterionic 2-methylallyl complex Cp\*<sub>2</sub>[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CM<sub>2</sub>CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]Zr( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>) (**4**), which was characterized by single-crystal X-ray diffraction.<sup>16</sup> The structure, shown in Figure 1, unequivocally establishes the presence of a covalent link between the borane and the  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CM<sub>2</sub>CH<sub>2</sub> moiety and the absence of direct C–F...Zr interactions. The B–CH<sub>2</sub>



**Figure 1.** Structure of **4**. Selected bond distances (Å) and angles (deg): Zr(1)–C(1) = 2.412(10), Zr(1)–C(2) = 2.593(8), Zr(1)–C(3) = 2.513(9), C(1)–C(2) = 1.408(12), C(2)–C(3) = 1.382(13), C(2)–C(4) = 1.514(12), B(1)–C(23) = 1.607(12), Zr(1)···C(23) = 3.307(10), C(15)–C(20)–C(23) = 107.4(7), (20)–C(23)–B(1) = 120.9(7). The second independent molecule of **4** in the crystal does not differ significantly.

methylene group is directed toward the metal center and, although the Zr···CH<sub>2</sub>B distance of 3.307 Å is much longer than in cationic zirconocene complexes with the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> anion (2.640(7) Å in Cp\*<sub>2</sub>ZrMe[MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>17</sup>), the anion does seem to occupy one coordination site around the metal center. The  $\eta^3$ -2-methylallyl group is shifted to one side of the “cleft” of the bent metallocene fragment, with the C(3) methylene carbon lying nearly in the plane defined by the metal center and the two cyclopentadienyl centroids. Although direct interaction between the anion and the metal center appears to be relatively small compared to complexes with the MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> anion, in the zwitterion, the anion is less likely to move out of the coordination sphere of the metal to form a solvent-separated ion pair due to the covalent tethering to the ligand system.

In conclusion, we have prepared a new well-defined zwitterionic zirconocene alkyl complex **2** and established that the covalent tethering of the anionic moiety to the ligand system drastically affects the catalyst performance relative to corresponding non-zwitterionic systems, making **2** a highly selective  $\alpha$ -olefin dimerization catalyst.

**Supporting Information Available:** Experimental procedures, preparation, and characterization data for compounds **1–4** and crystal data, atomic coordinates, thermal parameters, and listings of interatomic distances and angles for **4** (27 pages). See any current masthead page for ordering and Web access instructions.

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(12) Reaction mixtures of 1-pentene in  $C_6D_5Br$  with, instead of **2**, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and 1 equiv of H<sub>2</sub>O, and in  $C_6D_6$  with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone or (H<sub>2</sub>O)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as catalyst, showed no noticeable conversion of the  $\alpha$ -olefin under otherwise similar conditions. This suggests that acid catalysis as the source of the observed dimerization activity is unlikely. The above Lewis acidic reagents in combination with H<sub>2</sub>O are known to be able to initiate cationic polymerisation of styrene. See, for example: Shaffer, T. D.; Ashbaugh, J. R. *Polym. Prepr.* **1996**, *37*, 339.

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(15) In experiments on NMR-tube scale, in the absence of an excess of  $\alpha$ -olefin, both zwitterionic complexes **2** and **4** convert ethene (1 bar) to polyethene.

(16) Suitable crystals of **4**·1.5CH<sub>2</sub>Cl<sub>2</sub> were grown by cooling a dichloromethane solution of **4** to –40 °C. Crystal data (173 K): triclinic *P*1, *a* = 12.344(2) Å, *b* = 18.086(3) Å, *c* = 20.101(3) Å,  $\alpha$  = 107.50(2)°,  $\beta$  = 92.770(12)°,  $\gamma$  = 94.766(10)°; *V* = 4252.6(12) Å<sup>3</sup>; *D*<sub>calcd</sub> = 1.626 g/cm<sup>3</sup> (*Z* = 4). A total of 16 760 reflections were collected (SMART CCD diffractometer, Mo K $\alpha$  radiation). Refinement against all 11 634 independent data (8727 observed, 1166 parameters) converged to *R*<sub>1</sub> = 0.081. The unit cell contains two independent molecules of **4** that do not differ significantly in geometry and disordered solvent molecules.

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