# Zwitterionic alkene polymerization catalyst derived from $Cp_2Zr(\eta^2\text{-}C_2H_4)PPh_2Me$ and $B(C_6F_5)_3$

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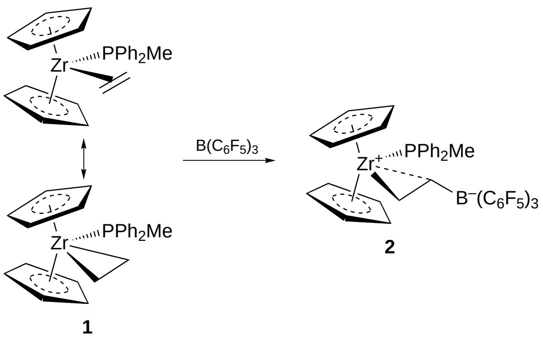
**The phosphine stabilized ethylene complex of zirconocene, $Cp_2Zr$, reacts with 1 equiv. of $B(C_6F_5)_3$ to form the girdle-type zwitterion $Cp_2Zr^+(PPh_3Me)CH_2CH_2B^-(C_6F_5)_3$ 2, which serves as an ethene polymerization catalyst either with or without added $B(C_6F_5)_3$.**

Bent metallocenes[1] are highly active for the polymerization of alkenic monomers to important commodity plastics.[2] Two principal factors contribute to this molecular fragment's ability to circumvent the barrier associated with the exothermic alkene enchainment process: the high electrophilicity of the formally 14 electron $[Cp_2M\text{–}R]^{n+}$ species and the ideally configured frontier orbital structure of the bent metallocene unit.[3] Since the former attribute is enhanced when $n = 1$, most commercially viable catalysts are based on group 4 metal cations; use of sufficiently weakly ccordinating counter-anions is necessary in order to attain high activities.

Zwitterionic analogs of cationic metallocenes, in which the counter-anion and the active cation are covalently linked in some fashion, have been touted as a way to modulate ion pairing in these catalysts, thus increasing activity.[4] Two classes of zwitterionic metallocenes have been reported: ring-type zwitterions in which the anion is affixed to one of the Cp donors,[5] and girdle-type betaines, where the counter-anion is located on the alkyl group occupying the reactive wedge of the metallocene.[6] In the latter type, the zwitterionic nature of the catalysts lasts only until the first termination step, while in the former, the charge separated structure is maintained throughout the polymerization process.

Girdle-type zwitterionic compounds have been accessed mainly through electrophilic attack by $B(C_6F_5)_3$[7] on suitable hydrocarbyl ligands of neutral group 4 bent metallocenes. Herein we report the reaction of the phosphine stabilized zirconocene ethylene complex, $Cp_2Zr(\eta^2\text{-}C_2H_4)PPh_2Me$[8] **1**, with this borane; the product may be considered to be the 'parent' girdle-type zwitterionic zirconocene.

When **1** is treated with one equivalent of $B(C_6F_5)_3$ in toluene, the zwitterionic product **2** is isolated as an orange solid in 92% yield (Scheme 1).† Although the phosphine ligand in the starting material is labile,‡ the electrophile preferentially attacks the coordinated alkene; no formation of $Ph_2MeP{\cdot}B(C_6F_5)_3$ was observed. The $^{11}B$ chemical shift of $\delta$ −10.8 for **2** is diagnostic for anionic, four-coordinate boron,[9] supporting the formulation of **2** as a zwitterionic species with a high degree of charge separation. For comparison, a $^{11}B$ NMR chemical shift of $\delta$ 2.0, more closely associated with neutral four-coordinate boron, was found for the product formed from reaction of **1** with $HB(C_6F_5)_2$,[10] which features a strong borate–zirconium cation interaction.[11]



**1**

**2**

**Scheme 1**

Although the $^{11}B$ NMR chemical shift of **2** is suggestive of significant charge separation, several spectral criteria are met which are suggestive of a strong β-CH agostic interaction[12] which electronically compensates the cationic zirconium center. Signals for the β-$CH_2$ protons and carbon atom appear upfield of the resonances for the α-methylene atoms in the $^1H$ and $^{13}C$ NMR spectra. At room temp., the averaged $J_{CH_\beta}$ coupling constant is 105 Hz, indicative of weakened C–H bonds at this position.[13] The coupling constant of 145 Hz for the α-C–H bonds is characteristic of an acute $Zr\text{–}C_\alpha\text{–}C_\beta$ bond angle, expected in the event of a β-agostic interaction.[12,14] Furthermore, when the $^1H$ NMR spectrum is monitored as the temperature is lowered, the signals for the $ZrCH_2CH_2B$ unit undergo decoalescence behavior until at −90 °C four signals reappear at $\delta$ 2.24 and 0.75 for the $Zr\text{–}CH_2$ pair and $\delta$ −0.05 and −1.55 for the two $CH_2B$ hydrogens. From the NMR data, the rate of exchange at coalescence (−67 °C) was determined[15] to be $1.46 \times 10^3\ s^{-1}$ and a $\Delta G^\ddagger$ of 9.0(5) kcal $mol^{-1}$ (1 cal = 4.184 J) was calculated for this exchange using the Eyring equation. This is a relatively high barrier for interchange of β-agostic protons in zirconocene cations, which is typically faster than the NMR timescale.[12,16]

The solid state structure of **2** also features this agostic motif. Suitable crystals of the compound were obtained from toluene; protons associated with the $ZrCH_2CH_2B$ moiety were located and refined isotropically.§ An ORTEP diagram of the compound is shown in Fig. 1 and pertinent metrical parameters are summarized in Table 1, along with analogous data for two related, non-zwitterionic compounds reported previously by Jordan and coworkers. Compound **2** is a zwitterionic analog of Jordan's ethyl cation[12] but is structurally more similar to the trimethylsilyl substituted derivative[16] in that the β-agostic alkyl group adopts an *endo* coordination geometry rather than the *exo* structure seen in the ethyl complex. Since the $Me_3Si$ group was essentially coplanar with Zr, $C_\alpha$ and $C_\beta$, Jordan proposed an organometallic γ silicon effect, in which the back lobe of the Si–$C_\beta$ bond donates to the zirconium center, as the basis for this observation. In **2**, the borate boron is tilted *ca.* 17° out of the Zr–C(12)–C(11) plane and the $C_\beta$–H bond is clearly involved in an agostic interaction with the deficient zirconium center. It is, however, feasible that the back lobe of the B–$C_\beta$ carbon may also be involved in the Zr–$C_\beta$ contact. At any rate, the observed strength of the β-agostic interaction in **2** suggests that the negative charge of the borate group is substantially localized on $C_\beta$, rendering it a more effective donor than the $C_\beta\text{–}SiMe_3$ group in Jordan's compound.

Although it could be argued that attack by $B(C_6F_5)_3$ at the *exo* carbon of the coordinated ethylene in **1** should be preferred on steric and electronic grounds,¶ the *endo* isomer of **2** appears to

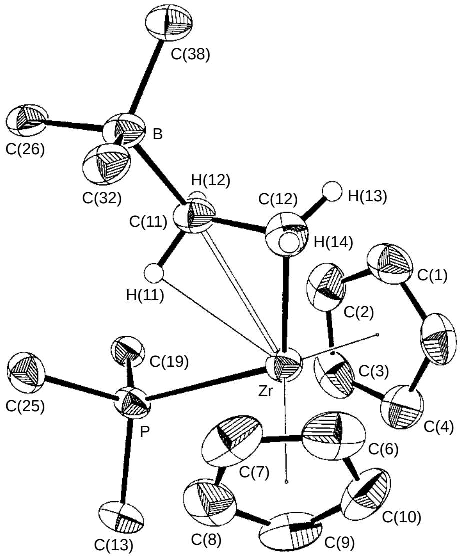
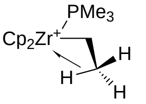
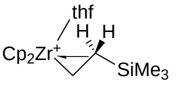


**Fig. 1** ORTEP diagram of girdle zwitterion **2**. Phenyl and pentafluorophenyl groups have been omitted for clarity. Key metrical parameters are given in Table 1.

**Table 1** Metrical parameters for **2** and related compounds

| | **2** |  |  |
|---|---|---|---|
| $Zr–C_{\alpha}$/Å | 2.260(4) | 2.290(9) | 2.26(2) |
| $Zr–C_{\beta}$/Å | 2.607(4) | 2.629(2) | 2.57(2) |
| $Zr–H_{\beta}$/Å | 2.39(3) | 2.16 | — |
| Zr–P,O/Å | 2.828(1) | 2.691(3) | 2.320(11) |
| $Zr–C_{\alpha}–C_{\beta}$/° | 85.3(2) | 84.7(5) | 84(1) |
| $P,O–Zr–C_{\alpha}$/° | 119.0(1) | 73.6(3) | 115.9(5) |
| $Zr–C_{\beta}$–B,Si/° | 164.9 | — | 174.1 |

be the kinetic as well as the thermodynamic product. Thus, when the reaction was monitored at −90 °C by $^{1}H$ or $^{31}P$ NMR spectroscopy, no intermediates were observed and only *endo*-**2** was formed. If attack at the *exo* carbon is preferred, rearrangement to *endo*-**2** must be very fast.

The zwitterion **2** polymerizes ethylene under ambient conditions,[17] although for optimal activity, an additional equivalent of $B(C_6F_5)_3$ is required. Activities of $3.2(4) \times 10^4$ g polymer (mol Zr atm h)$^{-1}$ ($M_w$ = 26 100, $M_w/M_n$ = 2.2) were observed in the absence of added $B(C_6F_5)_3$, while productivities more in line with expected values [$9.4(4) \times 10^5$; $M_w$ = 133 700; $M_w/M_n$ = 2.0] were found when **2** was treated with borane in the presence of ethene. Presumably, the added $B(C_6F_5)_3$ serves to sequester the phosphine ligand blocking the coordination site necessary for optimal polymerization rates. In the absence of ethene, a complex mixture of products results when **2** is treated with $B(C_6F_5)_3$, indicating that the 'naked' zwitterion is not stable in solution under these conditions.

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## Footnotes and References

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† *Synthesis* of **2**. Toluene (20 ml) was condensed into an evacuated flask cooled to −196 °C containing **1** (609 mg, 1.35 mmol) and $B(C_6F_5)_3$ (693 mg, 1.35 mmol). The mixture was warmed to −78 °C, stirred for 30 min and then warmed to room temp. The yellow slurry was concentrated and filtered. The solid was washed with hexane (15 ml) and **2** (1.2 g, 92%) was obtained as yellow powder. Partial $^{1}H$ NMR ($C_6D_6$, 23 °C): $\delta$ 1.50 (t, $J_{HH}$ 6.5 Hz, 2 H, $ZrCH_2CH_2B$), −0.74 (br, 2 H, $ZrCH_2CH_2B$). Partial $^{13}C\{^{1}H\}$ NMR ($C_6D_6$, 23 °C): $\delta$ 41.6 (s, $J_{CH}$ 145 Hz, $ZrCH_2CH_2B$), −14.0 (br m, $J_{CH}$ 105 Hz, $ZrCH_2CH_2B$).

‡ For example, the reaction of $PPh_2Me$ stabilized **1** with the more basic phosphine $PMe_3$ gave the trimethyl phosphine adduct $Cp_2Zr(\eta^2\text{-}C_2H_4)PMe_3$ essentially upon mixing.

§ *Crystal data* for **2**: $C_{43}H_{27}BF_{15}PZr$, $M$ = 961.67, orthorhombic, *Pbca, a* = 18.782(1), $b$ = 22.5024(9), $c$ = 18.740(2) Å, $U$ = 7920.3(9) Å$^3$, $D_c$ = 1.613 Mg m$^{-3}$ for $Z$ = 8. $F(000)$ = 3840.00, $\mu$(Cu-K$\alpha$) = 36.71 cm$^{-1}$, $\lambda$ = 1.541 78 Å, $T$ = 294 K. A total of 8944 reflections were collected using the $\omega$–2$\theta$ scan technique to a maximum 2$\theta$ value of 155°. The data were corrected for Lorentz and polarisation effects and the structure solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms associated with the β-ethyl moiety were refined isotropically, the rest were fixed in idealized positions with C–H = 0.98 Å. The final cycle of full-matrix least-squares refinement was based on 4690 observed reflections [$I > 3\sigma(I)$] and 567 variable parameters and converged (largest parameter shift was 0.003 times its esd) with $R$ = 0.034, $R_w$ = 0.034, GOF = 1.88. CCDC 182/687.

¶ A MacSpartan Plus *ab initio* calculation on $Cp_2Zr(PH_3)(\eta^2\text{-}C_2H_4)$ at the 3-21G* level showed that the HOMO is roughly equally distributed on the *exo* and *endo* carbons; a slightly higher charge density exists on the *exo* carbon, which is also sterically much more accessible.

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17 See ref. 5(*b*) for experimental conditions used in our laboratory.

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