Donor complexes of bis(1-indenyl)phenylborane dichlorozirconium as isospecific catalysts in propene polymerization

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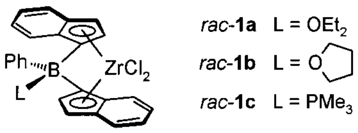
Chiral boron-bridged *ansa*-type zirconocenes can be prepared in a few simple steps; various donor molecules such as Et_2O, THF or PMe_3 undergo complexation at boron leading to catalysts having vastly different catalytic properties in Ziegler–Natta polymerization of propene; the PMe_3-containing catalyst is the most active and stereoselective (96% isotacticity).

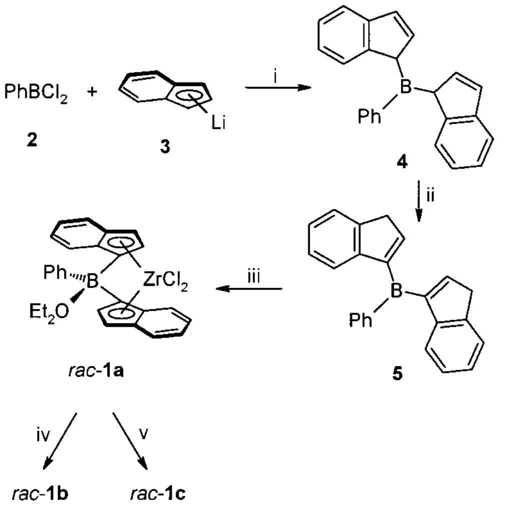
The nature of substituents and the substitution pattern of titanocenes and zirconocenes are known to exert a pronounced influence on their activity and selectivity as catalysts in Ziegler–Natta polymerization.[1] Recently, several zirconocenes borylated at the Cp-moiety have been prepared and tested as catalysts.[2,3] None of them showed activity in the polymerization of propene, and some even failed to polymerize ethene,[3] possibly due to decomposition caused by the co-catalyst methylalumoxane (MAO) which is generally required as an activator. Here, we describe the synthesis of donor-coordinated *ansa*-type zirconocenes **1** and their use as catalysts in the production of polypropene (PP). Significantly, it turns out that the nature of the donor ligand L determines the activity and stereoselectivity of the catalytic system, *i.e.* it can be used as a handle to control the polymerization.



The starting point for the synthesis of zirconocenes **1** was bis(1*H*-inden-1-yl)phenylborane **4**, readily accessible as a 1:1 mixture of *rac*- and *meso*-stereoisomers by the reaction of dichlorophenylborane **2** with indenyllithium **3** (Scheme 1). Although it was possible to convert **4** into the corresponding dianion by treatment with lithium bis(trimethylsilyl)amide (LiHMDS),[4] at least 20% of indenyllithium **3** was formed as an undesired side-product. This problem was solved by first isomerizing **4** into the thermodynamically more stable compound **5** in 95% yield by the action of catalytic amounts of PPr^i_3 and then effecting double deprotonation. Upon reacting $ZrCl_4$ with the intermediate dianion, a 1 : 1 mixture of *rac*-**1a** and *meso*-**1a** as well as non-identified side-products were formed.

Following removal of solid components, the solution was cooled to −20 °C, from which diastereomerically pure *rac*-**1a** crystallized as an orange–red solid in 12% yield. It was unambiguously characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy. Treatment of *rac*-**1a** with a solvent mixture of THF and CH_2Cl_2 led to the formation of *rac*-**1b** whereas the reaction with PMe_3 in toluene afforded adduct *rac*-**1c**. In both cases it was possible to obtain crystals suitable for an X-ray structural analysis (Fig. 1).† It should be mentioned that a different boron-bridged zirconocene has been described previously, but it was not possible to obtain crystals for an X-ray structural analysis, nor did it show activity towards ethene polymerization.[3] PMe_3 has been used to form adducts with other borylated metallocenes.[2c] The present C_1-symmetric compounds are structurally similar. In the case of *rac*-**1b** the angle between zirconium and the center of the two five-membered rings is 122.3(8)° (mean), which lies between that of the known Me_2C-bridged bis(indenyl)dichlorozirconium (118.2°)[5] and that of the Me_2Si-bridged analog (127.8°).[6] For *rac*-**1c** this angle was found to be 121.5(7)°, similar to that in *rac*-**1b**. Nevertheless, the Zr···B–O angle in*rac*-**1b** [120.4(6)°] is significantly smaller than the Zr···B–P angle in *rac*-**1c** [131.3(2)°].

In order to test the complexes in olefin polymerization, activation by treatment with MAO in toluene for 5 min was performed in all cases. Although compound *rac*-**1a** was found to be a fairly active catalyst (200–2600 kg PE mol[Zr]$^{-1}$ h^{-1})



Scheme 1 *Reagents and conditions*: i, Et_2O, −70 to 20 °C, 12 h (75–85%); ii, PPr^i_3 (2 mol%), Et_2O, 20 °C, 16 h (85%); iii, (*a*) LiHMDS (2.05 equiv.), Et_2O, −70 to 20 °C, 10 h; (*b*) $ZrCl_4$ (1 equiv.), toluene–Et_2O, −70 to 20 °C, 12 h; iv, THF–CH_2Cl_2 (1:1); v, PMe_3 (7 equiv.), toluene, −70 to 20 °C (21%).

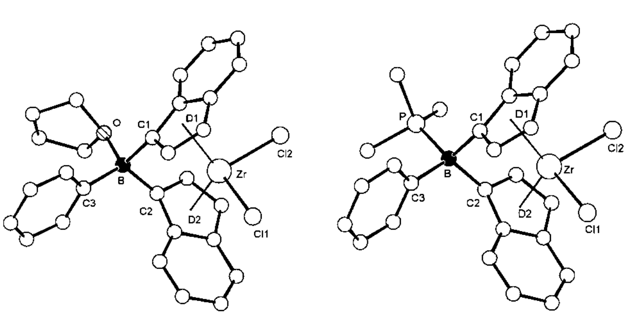


Fig. 1 Molecular structures of *rac*-**1b** (left) and *rac*-**1c** (right). Selected interatomic distances (Å) and angles (°): left (mean of two independent molecules): Zr···B 3.117(8), B–O 1.626(4), B–C3 1.603(5), Cl1–Zr–Cl2 99.5(3), D1–Zr–D2 122.3(8), Zr···B–O 120.4(6), Zr···B–C3 132.1(3), O–B–C3 107.5(2), C1–B–C2 101.5(2); right: Zr···B 3.173(3), B–P 2.006(3), B–C3 1.618(4), Cl1–Zr–Cl2 96.58(3), D1–Zr–D2 121.5(7), Zr···B–P 131.3(2), Zr···B–C3 126.7(4), P–B–C3 102.0(2), C1–B–C2 99.4(2).

Table 1 Polymerization of propene with *rac*-**1c** in toluene as solvent and MAO as activator[a]

T/°C	Al : Zr	Productivity/kg PP mol[Zr]$^{-1}$ h^{-1}	10^{-3} M_w/g mol^{-1}	Tacticity (% mmmm-pentades)
20	1000	326	315	96
40	220	783	161	93
40	1000	1052	129	90
40	5000	1232	97	93
60	1000	174	62	85

[a] *Polymerization conditions*: 2 bar propene, 1 h, *ca.* 30 μmol l^{-1} [Zr].

for ethene polymerization producing high molecular weight polymer ($M_w \approx 700000$ g mol^{-1} as determined by GPC), this complex turned out to be a rather poor catalyst for the polymerization of propene. For example, using a Al/Zr ratio of 1000, activities of only 10–75 kg PP mol[Zr]$^{-1}$ h^{-1} were observed at room temperature with the production of atactic oily PP ($M_w \approx 20000$ g mol^{-1}). In contrast, the phosphine adduct *rac*-**1c** displayed remarkably high activity and stereoselectivity (Table 1). ^{13}C NMR spectra of typical PP samples obtained at various polymerization temperatures demonstrate high degrees of isotacticity, *e.g.* 96% isotacticity at room temperature.

Thus, complex *rac*-**1c** is the first boron-bridged zirconocene which catalyzes the polymerization of propene. It competes well with other *ansa*-type zirconocenes, especially with respect to isotacticity and molecular weight.[5,6] Since the ether analog *rac*-**1a** is a poor catalyst, it is obvious that the nature of the donor ligand at boron is crucial. A possible explanation is that for *rac*-**1a** excess MAO induces decomplexation of the donor ligand, thereby initiating the decomposition of the *ansa*-metallocene, whereas for *rac*-**1c** the donor ligand PMe$_3$ remains bonded to boron throughout the polymerization. Whatever the exact explanation may be, it is clear that the use of PMe$_3$ provides a handle to control activity and tacticity. It remains to be seen whether other phosphines or different donor ligands induce similar effects.

Notes and references

† *Crystal data: rac*-**1b**: $C_{28}H_{25}BCl_2OZr$, M_r = 550.41, orange prism, crystal size 0.28 × 0.32 × 0.49 mm, a = 10.746(1), b = 15.510(3), c = 16.308(3) Å, α = 62.15(1), β = 82.92(1), γ = 83.25(1)°, U = 2379.2(7) Å^3, T = 293 K, triclinic, space group $P\bar{1}$ (no. 2), Z = 4, D_c = 1.54 g cm^{-3}, μ = 0.71 mm^{-1}. Enraf-Nonius CAD4 diffractometer, Mo-Kα X-radiation, λ = 0.71069 Å. 11215 measured reflections, no absorption correction, 10815 unique, 8006 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2 for all data with Chebyshev weights to R = 0.038 (obs.), wR = 0.105 (all data), 595 parameters, S = 1.02, H atoms riding, max. shift/error 0.001, residual ρ_{max} = 0.775 e Å^{-3}. CCDC 000/000.

rac-**1c**: $C_{27}H_{26}BCl_2PZr{\cdot}2.5CH_2Cl_2$, M_r = 766.69, orange prism, crystal size 0.18 × 0.32 × 0.32 mm, a = 33.5561(8), b = 10.9508(2), c = 20.6866(6) Å, β = 121.201(2)°, U = 6502.1(3) Å^3, T = 100 K, monoclinic, space group $C2/c$ (no. 15), Z = 8, D_c = 1.57 g cm^{-3}, μ = 0.98 mm^{-1}. Siemens SMART diffractometer, Mo-Kα X-radiation, λ = 0.71073 Å. 34678 measured reflections, no absorption correction, 11860 unique, 8996 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2 for all data with Chebyshev weights to R = 0.062 (obs.), wR = 0.137 (all data), 357 parameters, S = 1.13, H atoms riding, max. shift/error 0.001, residual ρ_{max} = 2.678 e Å^{-3} (0.789 Å from Cl6 in solute).

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