Piperidino Substituted [1]Borametallocenophanes. Synthesis, Reactivity, and Structure

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ansa-Metallocenes and related complexes have considerable potential as catalyst precursors in the Ziegler-Natta type olefin polymerization. In the present paper we report about the synthesis of piperidinyl-substituted [1]borametallocenophanes of titanium and zirconium. Furthermore, the first example of a base stabilized alkyl-substituted [1]borazirconocenophane was fully characterized and tested for its properties in the polymerization of ethene.

Key words: ansa-Metallocene, Boron, Olefin Polymerization, Zirconium

Introduction

In the past 25 years the interest in group 4 metallocenes, and especially *ansa*-metallocenes and related contrained geometry complexes, arose due to their potential as Ziegler-Natta type catalysts for the olefin polymerization. Besides a very high catalytic activity of the metallocenophanes, the facile ligand design of such complexes allows a precise control of the stereoselective polymerization of propene. A wealth of review articles concerning this topic is reflecting the huge interest in such compounds [1].

The incorporation of a boron bridge has been associated with a number of beneficial characteristics, *e. g.* improved catalytic activity [2]. Furthermore, the potential of the Lewis acidic boron centre for an intramolecular activation is envisaged [3]. It is known that Lewis acidic boron compounds can be used as cocatalysts [4], and hence, the concept of intramolecular activation arose. However, the Lewis acidity of the boron atom in currently known [n]borametallocenophanes (Fig. 1, types I to III) and related complexes (Fig. 1, type IV) is mediated either by π-donation from an amino group or by the formation of base adducts (Fig. 1) [3, 5].

Shapiro *et al.* [6] and Reetz *et al.* [7] described the synthesis of aryl-substituted [1]borametallocenophanes, which were expected to exhibit a high Lewis acidity at the boron centre, but it was not possible to obtain such complexes free of Lewis bases. In the presence of ether, tetrahydrofuran or dimethylsulfide the isolated compounds proved to be the base adducts of
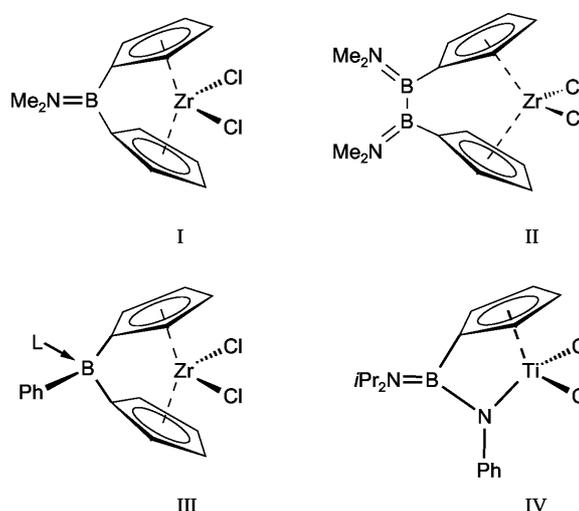

Fig. 1. Known types of [n]borametallocenophanes ($n = 1, 2$) and constrained geometry complexes.

the desired complexes and, hence, the Lewis acidity of the boron centre was cancelled (Fig. 1, type III). Rufanov *et al.* described the only example of a base free three-coordinated boron-bridged complex [8]. However, the complex was poorly characterized and the validity of this assignment was challenged by other authors [3].

We very recently followed therefore a new approach in order to realize a base free aryl-substituted boron bridged *ansa*-metallocene. Ferrocenylboranes seemed to be an ideal starting point due to the bulkiness of the substituent at boron and an albeit weak interaction of

$$\text{(1)}$$

1 a/a Isomer   **1 v/v Isomer**
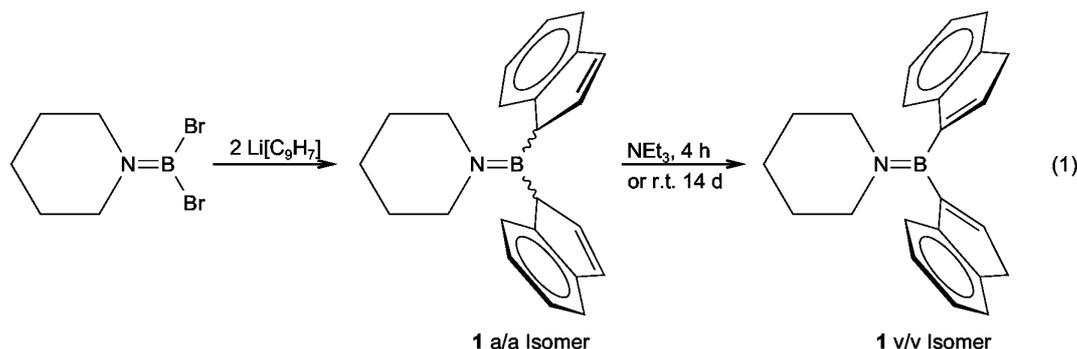
the HOMO orbital of iron with the boron centre that provides a modest stabilization of the latter, but still preserves its Lewis acidic character [9]. The syntheses of corresponding ligand precursors have been established, but attempts to obtain the ferrocenyl-substituted [1]borametallocenophanes have failed so far [10].

In the past years we [2, 11] and others [12] investigated the impact of aminoborylene-bridged [*n*]borametallocenophanes ($n = 1, 2$) and related constrained geometry complexes [13] towards their catalytic activity (Fig. 1, type I and II). Our group intensively studied the influence of the ligand framework, in particular the effect of the substituents at the amino fragment, on the catalytic performance. In the same context we studied as well differences between zirconium and hafnium complexes of the type [RR'NB(η^5-C$_x$H$_y$)(η^5-C$_{x'}$H$_{y'}$)MCl$_2$] (R, R' = alkyl, SiMe$_3$; C$_x$H$_y$, C$_{x'}$H$_{y'}$ = cyclopentadienyl, indenyl; M = Zr, Hf) [2e, f]. Preliminary results on the [2]borametallocenophanes have indicated a tremendous increase in the catalytic activity combined with the isolation of a polymeric material of very high molecular weight [2c]. Here we report the synthesis and structure of piperidino-substituted [1]borametallocenophanes of zirconium and titanium. Furthermore, we were able to isolate and fully characterize the first base-stabilized alkylborylene-bridged [1]zirconocenophane.

Results and Discussion

The ligand precursor **1** is obtained by salt elimination, reacting 2 equiv. of Li[C$_9$H$_7$] with (CH$_2$)$_5$NBBr$_2$ at r. t. As described above, in the isolated product the indenyl fragments are bound to the boron centre *via* the saturated carbon atom, thus adopting an allylic position (a/a isomer) and representing the kinetically favoured product (eq. (1)). The carbon atoms bound to boron are chiral, so that a diastereomeric mixture of isomers is
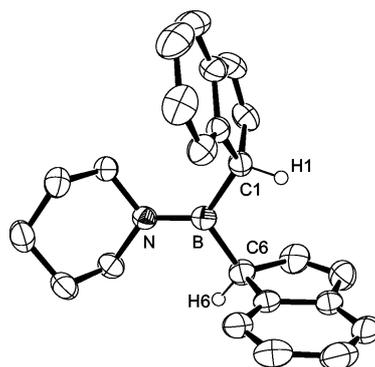

Fig. 2. Structure of **1 a/a** in the crystal (50% ellipsoid probability).

observed by multinuclear NMR spectroscopy. In contrast to previously reported diindenylboranes, the isomerisation to the thermodynamically more stable v/v isomer, in which the indenyl fragment is bound by an sp^2-hybridised carbon atom, is already proceeding at room temperature [2b, f, 14]. Full conversion is reached over a time of 14 days, but treating with a catalytic amount of NEt$_3$ speeds the process up to completion in only a few hours (eq. (1)).

This result was unexpected, since the corresponding dimethyl- and diethyl-substituted diindenylboranes do not isomerize at r. t., although the steric and electronic properties of these amino groups should be very alike. The NMR spectra of **1 v/v** clearly indicate the presence of only one isomer. In the proton NMR spectrum all observed signals have been assigned and show the typical signal patterns for vinylic bound indenyl rings, *i. e.* a pseudo-triplet for the olefinic proton and a doublet-like signal for the CH$_2$ group at the five-membered ring.

A single crystal of **1** was obtained by recrystallization from a concentrated hexane solution. **1 a/a** crystallizes in the monocline space group $P2_1/c$ adopting C_1-symmetry. The picture depicted in Fig. 2 shows the S,S conformer.
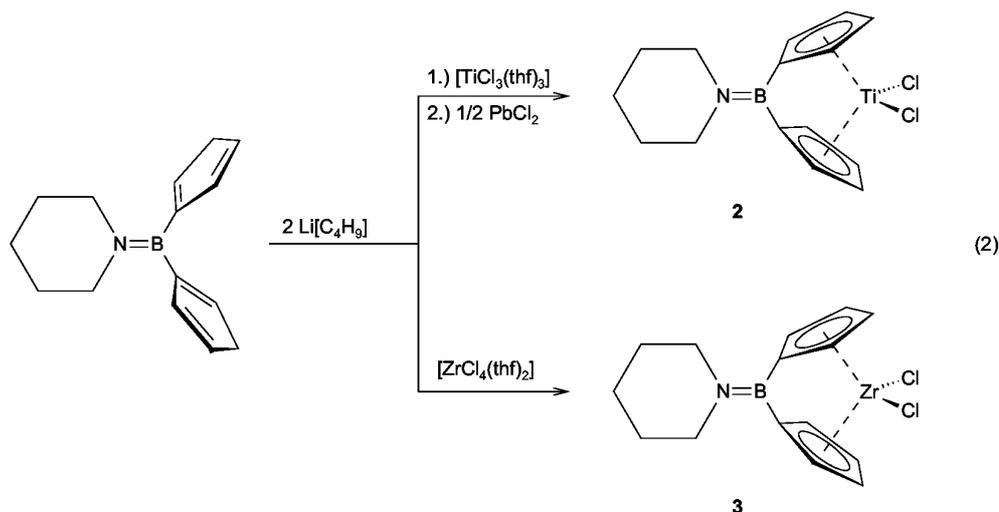
All bond lengths and angles reflect the expected values, *e. g.* 1.376(2) Å for the B–N distance is consistent with a B–N double bond. The planes around the boron and nitrogen centres are co-planar, allowing an optimal interaction of the free electron pair of the nitrogen with the empty p_z orbital of the boron atom. The B–C distances were found to be 1.605(3) and 1.600(3) Å, hence, almost identical with the previously reported values found for the allylically bound indenyl ring in iPr$_2$NB(η^1-C$_5$H$_5$)(η^1-C$_9$H$_7$) [1.6011(4) Å] [2b]. Compared to the crystal structure of (Me$_3$Si)$_2$NB (η^1-C$_9$H$_7$)$_2$, in which the indenyl rings are bound in the vinylic position, slight but distinct differences in the B–C bond lengths [1.575(5) and 1.563(7) Å] can be distinguished [14a]. The longer bond lengths in **1 a/a** can be explained by the lack of interactions of π electrons with the p_z orbital of boron, which are only present for sp^2-hybridized carbon atoms, and predominantly by the different hybridization states of the carbon atoms.

The complexes **2** and **3** have been synthesized by a well described procedure: deprotonation of the ligand precursor with Li[C$_4$H$_9$] followed by reaction with the metal halide, [ZrCl$_4$(thf)$_2$] or [TiCl$_3$(thf)$_3$], at low temperatures. In the case of the titanium complex, the Ti(III) species was then oxidized using PbCl$_2$ (eq (2)).

Both complexes were isolated in good yields, as a red microcrystalline product in the case of the titanium complex **2** and as a yellow solid for the corresponding zirconium compound **3**. Both complexes show the expected signals in the ^{1}H and ^{13}C NMR spectra, which are consistent with the data observed for the Hf complex [2e] (given in parentheses for the following discussion). In the ^{1}H NMR spectrum the signals for the three not nitrogen bound CH$_2$ groups of the piperidino fragment are overlapping; hence, they are only detected as a broad multiplet at 1.6 to 1.8 ppm (1.6–1.8 ppm). The two CH$_2$ groups bound to nitrogen are detected as a triplet at 3.55 ppm (3.53 ppm). The proton of the Cp-rings give rise to pseudo-triplets at 5.65 and 7.06 ppm (5.74 and 6.82 ppm) as to be expected for an AA'BB' spin system. Compared to the ligand precursor the ^{11}B NMR signal is only marginally high field shifted to 36.4 ppm (36.7 ppm). Five signals were observed in the carbon NMR spectrum, three for the piperidino fragment at 25.13, 28.53 and 53.30 ppm (25.07, 28.47, 49.99 ppm), and two for the Cp carbon atoms at 118.22 and 133.91 ppm (112.33 and 125.89 ppm). The NMR data indicate a C$_{2v}$ symmetry of both complexes in solution.

The unusual complex **4** has been isolated in the form of yellow crystals in reasonable yields, 0.55 g (28%, in respect of the used ligand precursor), as a side product of the synthesis of **3**. Compound **4** is obviously the product of a partial hydrolysis of **3**, due to traces of water being present during the preparation, and represents a base-stabilized alkyl-substituted [1]borametallocenophane (Fig. 3).

The constitution of **4** was derived from multinuclear NMR experiments including ^{1}H-^{1}H and ^{1}H-^{13}C COSY NMR spectroscopic data. The observation of three proton signals in the ^{1}H NMR spectrum for the Cp-protons (2 : 1 : 1) at 5.67, 6.69 and 6.77 ppm, which correlate with four signals in the ^{13}C NMR spectrum
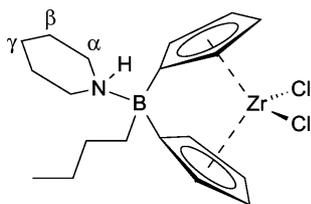
Fig. 3. Constitution of **4**.

at 109.52, 114.24, 124.72, and 127.42 ppm, indicates the diastereotopic nature of the protons and the non-equivalence of the carbon atoms at the Cp rings. The ipso-carbon atoms bound directly to the boron atom have not been detected, due to quadrupolar ^{13}C-^{11}B coupling [15]. Furthermore, all CH$_2$ groups of the piperidino fragment exhibit two signals in the proton NMR spectrum and only one in the carbon NMR spectrum, the protons hence being diasterotopic. The assignment of all signals for the piperidino and butyl protons was only possible by the use of correlation experiments (Fig. 4).

Due to the free rotation around the B–N single bond the α and β CH$_2$ groups (Fig. 3) show only one set of signals. The proton signals for the γ CH$_2$ group are observed at 1.60 and 2.02 ppm, respectively, and correlate with the carbon signal in the ^{13}C NMR spectrum at 23.75 ppm. The proton signals at 1.78 and 1.99 ppm have been assigned to the carbon signal at 26.16 ppm, and represent the β CH$_2$ group. For the α group the proton signals were found at 3.00 and 3.65 ppm corresponding with the signal in the ^{13}C NMR spectrum at 49.38 ppm. The proton bound to the nitrogen atom
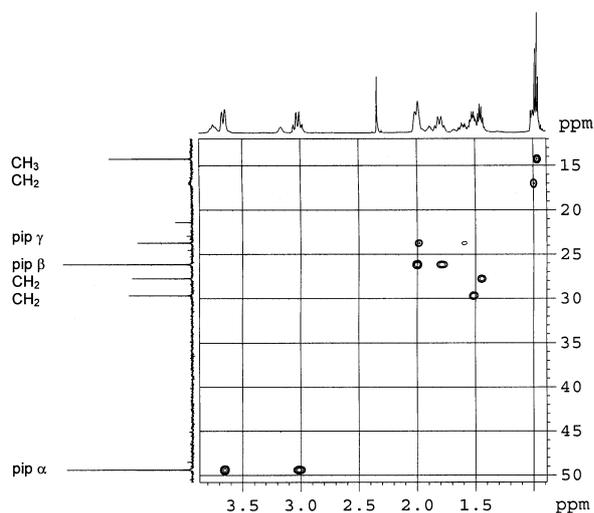
was not detected. Four signals in the proton and carbon NMR spectra were assigned to the butyl group; in the following discussion the proton-correlated ^{13}C NMR signals are given in parentheses. The boron-bound CH$_2$ group gives rise to a signal in the proton NMR at 1.10 ppm (broad at 17.0 ppm), the CH$_3$ group is observed at 0.97 ppm (14.25 ppm), and the central CH$_2$ groups were found as a broad multiplet between 1.4 and 1.6 ppm (27.76 and 29.69 ppm). The signal in the ^{13}C NMR spectrum for the carbon atom attached to the boron atom is very broad, due to the ^{11}B-^{13}C quadrupolar coupling [15], and was only detected in the correlation NMR experiment. As expected for a four-coordinated boron atom, the ^{11}B NMR spectrum shows a signal at $\delta = -3.5$, thus being 40.3 ppm high field shifted compared to the ligand precursor.

Single crystals suitable for an X-ray diffraction analysis were obtained by crystallizing **4** from a concentrated toluene solution at -35 °C. The constitution derived from the NMR spectroscopic data was confirmed by the structural analysis. **4** crystallizes in the monoclinic space group $P\bar{1}$ (Fig. 5).

The differences in the structural parameters, when compared to the known amino-substituted [1]borametallocenophanes, are limited to the bridging fragment. The geometry of the metal centres is almost identical; a tilt angle α of 65.5°, a deformation angle δ of 120.9°, an average distance between the metal centre and the Cp centroids of 2.173 Å and Zr–Cl distances of 2.469(1) and 2.470(1) Å are found in **4**, and hence, are very similar to the reported crystal structures of known [1]borametallocenophanes [2]. The differences found at the bridging moity can be explained by the higher coordination number of boron (four-versus three-coordinated). The observation of a B-N distance of 1.629(5) Å is reflecting the single bond charac-

Fig. 4. Aliphatic area of the ^{1}H-^{13}C COSY NMR spectrum of **4**.
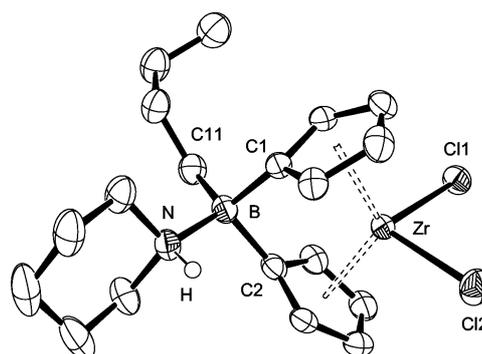
Fig. 5. Structure of **4** in the crystal (50% ellipsoid probability).
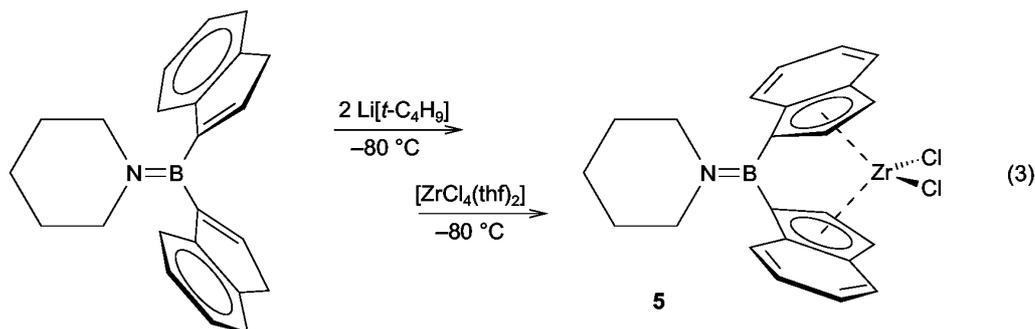
ter between the two atoms. Between the boron atom and the *ipso*-carbon atoms of the Cp rings B–C distances of 1.630(5) and 1.621(5) Å, respectively, were determined, which are about 0.05 Å longer than observed for the amino-substituted [1]borametallocenophanes. This lenghtening was attributed to the increased p character in the bonds of a four-coordinated boron atom [6]. Furthermore θ, that is the angle between the boron atom and the two *ipso*-carbon atoms, is decreased by 6°. Comparison of the crystallographic parameters of the bridging moiety with those of the compounds described by Shapiro, the SMe_2 and PMe_3 base adducts of the phenyl-substituted [1]borazirconocenophane, reveals only one significant difference. The angle between the alkyl fragment, the boron atom and the piperidino group is somewhat larger (4.2 and 9.9 °) than the corresponding angles found for the SMe_2 and PMe_3 adducts, respectively [6].

The diindenyl complex **5** was obtained from **1 v/v** in a convenient two step synthesis starting with the deprotonation employing 2 equivalents of $Li[t\text{-}C_4H_9]$, and followed by treatment with $[ZrCl_4(thf)_2]$ (eq. (3)).

5 is obtained as an orange microcrystalline material in reasonable yields of 2.08 g (75%) predominantely as the rac-isomer (rac-meso ratio 90 : 10), as the ^{1}H and ^{13}C NMR spectra reveal. Similar observations were made for the synthesis of the corresponding bis(trimethylsilyl)amino-substituted complexes of Ti and Zr, where exclusively the rac isomer was observed and isolated [2b]. In contrast, the dimethylamino and the diisopropylamino derivatives were formed under identical reaction conditions as 1 : 1 mixtures of both isomers [2e, 12a].

The protons of the piperidino fragment in the ^{1}H NMR spectrum give rise to two multiplets at 1.80 and 3.70 ppm, respectively, which correlate with the carbon signals at 24.58, 28.23, and 49.29 ppm. Two signals for the two protons attached to the five-membered ring of the indenyl ligand are observed at 5.80 and 6.75 ppm with the corresponding carbon signals at 112.89 and 114.22 ppm. For the CH groups in the annulated six-membered ring three multiplets in the ^{1}H NMR spectrum were found in a ratio of 1 : 2 : 1 at 7.05, 7.35, and 7.55 ppm; the carbon signals can be detected at 123.36, 124.85, 125.74, and 126.71 ppm. The quaternary carbon atoms of the indenyl rings gave signals at 122.34 and 131.53 ppm. Likewise, for **2** and **3** the *ipso*-carbon was not observed due to the quadupolar coupling between the boron and carbon atoms [15]. In conclusion, the signals of the multinuclear NMR experiments indicate a C_2 symmetry of **5** in solution.

We subjected compound **4** to polymerisation experiments, since very little is known about the catalytic performance of such base-stabilised [1]borametallocenophanes. The few data available, however, give evidence for only a moderate activity and very low molecular weights of the obtained polymers [6, 7]. Likewise, complex **4** performed poorly under the applied conditions (2 bar ethylene pressure, Al/Zr ratio 4500 : 1, 10 μmol catalyst). Independent of the polymerisation time, no polymeric material could be isolated.

The other complexes reported here were not subjected to polymerisation experiments, since we recently reported detailed studies on a series of amino-substituted [1]borazirconocenophanes and related hafnium complexes [2e, f], which proved for the Hf-analogue of **2** and **3** that the piperidino ligand does neither have a significant impact on the catalytic performance nor on the chain length of the obtained polymers [2f].

Experimental Section

All manipulations were carried out under a dry argon atmosphere with common Schlenk techniques. Solvents were dried with a solvent purification system (SPS) from M. Braun

columns and stored under argon over molecular sieves; reagents were dried and purified by standard procedures. Piperidino(dibromo)borane [16], $(CH_2)_5NB(\eta^1\text{-}C_5H_5)_2$ [2e], and $[ZrCl_4(thf)_2]$ [17] were obtained according to literature procedures. $Li[C_4H_9]$, $Li[t\text{-}C_4H_9]$, MAO and ethylene were obtained commercially and used without further purification. $Li[C_9H_7]$ was obtained *in situ* by treatment of indene with $Li[C_4H_9]$ at ambient temperatures.

NMR: Bruker Avance 200 at 64.21 MHz (^{11}B, $BF_3 \cdot OEt_2$ in C_6D_6 as external standard), Bruker Avance 400 at 400.13 MHz (^{1}H, internal standard TMS), 100.61 MHz (^{13}C{^{1}H}, APT, internal standard TMS), Bruker Avance 500 at 500.13 MHz (^{1}H, internal standard TMS), 125.61 MHz (^{13}C{^{1}H}, APT, internal standard TMS).

Mass spectra were recorded on a Thermo Finnigan Trio 1000 and on a Finnigan MAT 8200. Elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyzer, model 1106. The polymerisation experiments were carried out in a 500 ml glass autoclave from Büchi.

$(CH_2)_5NB(\eta^1\text{-}C_9H_7)_2$ (**1**)

1.89 g (15.46 mmol) $Li[C_9H_7]$ was suspended in 40 ml hexane and reacted with 1.97 g (7.73 mmol) $(CH_2)_5NBBr_2$ at ambient temperature. After stirring for 16 h the insolubles were removed by centrifugation. The resulting pale yellow solution was concentrated and stored at $-30\,^{\circ}$C. 2.24 g (89%) of **1 a/a** were isolated as a colorless crystalline solid.

^{1}H NMR (C_6D_6, 400 MHz): $\delta = 1.16-1.36$ (m, 6 H, $CH_{2\,Pip}$); 3.06 (br m, 2 H, BCH_{Ind}); 3.03 (m, 4 H, $CH_{2\,Pip}$); 6.45 (m, 2 H, CH_{Ind}); 6.85 (m, 2 H, CH_{Ind}); 7.1–7.4 (m, 8 H, CH_{Ind}). ^{11}B NMR (C_6D_6, 64 MHz): $\delta = 40.1$. ^{13}C NMR (C_6D_6, 100 MHz): $\delta = 25.20$, 28.29, 28.39 ($CH_{2\,Pip}$); 46.14 (br, BCH_{Ind}); 49.34 ($CH_{2\,Pip}$); 121.46, 123.70, 123.76, 124.43, 124.47, 125.63, 125.70, 130.86, 131.07, 138.31, 138.49 (CH_{Ind}); 145.72, 145.87, 148.43, 149.03 (C_{Ind}). MS *m/z* (%) (CI): 326 (7) [M$^+$]; 210 (42) [M$^+$ − Ind]; 117 (100) [Ind$^+$]; 86 (43) [Pip$^+$].

The isomerisation of the kinetically favoured a/a isomer into the thermodynamically more stable v/v isomer was achieved by treating a solution of 2.04 g (6.27 mmol) **1 a/a** in 40 ml toluene with a catalytic amont of NEt$_3$ at ambient temperature for 16 h. After removing all volatiles at high vacuum, **1 v/v** was obtained quantitatively as a colourless amorphous solid.

^{1}H NMR (C_6D_6, 400 MHz): $\delta = 1.35$ (m, 6 H, $CH_{2\,Pip}$); 3.18 (m, 4 H, $CH_{2\,Pip}$); 3.29 (m, 4 H, $CH_{2\,Ind}$); 6.52 (pt, 2 H, CH_{Ind}); 7.1–7.3 (m, 4 H, CH_{Ind}); 7.36 (m, 2 H, CH_{Ind}); 7.61 (m, 2 H, CH_{Ind}). ^{11}B NMR (C_6D_6, 64 MHz): $\delta = 38.6$. ^{13}C NMR (C_6D_6, 100 MHz): $\delta = 25.31$, 28.90 ($CH_{2\,Pip}$); 40.63 ($CH_{2\,Ind}$); 50.72 ($CH_{2\,Pip}$); 122.51, 124.00, 124.59, 126.56, 137.98 (CH_{Ind}); 144.71, 148.88 (C_{Ind}). MS *m/z* (%) (CI): 326 (38) [M$^+$]; 210 (100) [M$^+$ − Ind]; 117 (35) [Ind$^+$];

86 (26) [Pip$^+$]. $C_{23}H_{24}BN$ (325.26): calcd. C 84.93, H 7.44, N 4.31; found C 85.13, H 7.85, N 4.18.

$[(CH_2)_5NB(\eta^5\text{-}C_5H_4)_2ZrCl_2]$ (**3**)

1.48 g (5.92 mmol) of $(CH_2)_5NB(\eta^1\text{-}C_5H_5)_2$ was dissolved in 40 ml toluene, cooled to $-80\,^{\circ}$C and treated with 4.74 ml (11.84 mmol) of a 2.5 M $Li[C_4H_9]$ solution in hexane. The reaction mixture was allowed to warm up to ambient temperature. At around $-30\,^{\circ}$C the mixture turned cloudy, and after 16 h in to an almost colourless suspension. After centrifugation and washing with 30 ml of hexane the resulting solid was again suspended in toluene, cooled to $-80\,^{\circ}$C and treated with 2.23 g (5.92 mmol) $[ZrCl_4(thf)_2]$. During slow warming to room temperature the suspension turned orange. After 4 h all insoluble material was removed by centrifugation, the mother liquor concentrated and and stored at $-30\,^{\circ}$C. 1.52 g (67%) of **3** was isolated as a yellow microcrystalline material.

^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 1.6-1.8$ (m, 6 H, $CH_{2\,pip}$); 3.53 (pt, 4 H, $CH_{2\,pip}$); 5.74 (pt, 4 H, CH_{Cp}); 6.82 (pt, 4 H, CH_{Cp}). ^{11}B NMR (CD_2Cl_2, 64 MHz): $\delta = 36.7$. ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 25.07$, 28.47, 49.99 ($CH_{2\,pip}$); 112.33, 125.89 (CH_{Cp}). MS *m/z* (%): 384 (100) [M$^+$]; 348 (22) [M$^+$ − Cl]; 319 (47) [M$^+$ − Cp]; 300 (26) [M$^+$ − pip]; 84 (24) [pip$^+$]. $C_{15}H_{18}BCl_2NZr$ (385.25): calcd. C 46.77, H 4.71, N 3.64; found C 47.13, H 4.93, N 3.38.

Isolation of $\{[(CH_2)_5NH](C_4H_9)B(\eta^5\text{-}C_5H_4)_2ZrCl_2\}$ (**4**)

While performing the synthesis of **3**, **4** was isolated in yields of 28% (0.55 g) with respect to the ligand precursor as a yellow crystalline material. All spectroscopic data, X-ray diffraction and the polymerization experiment were performed with the isolated material.

^{1}H NMR (CD_2Cl_2, 500 MHz): $\delta = 0.97$ (t, 3 H, $^3J = 7.25$ Hz, $CH_{3\,Bu}$); 1.10 (m, 2 H, $CH_{2\,Bu}$); 1.4–1.6 (m, 4 H, $CH_{2\,Bu}$); 1.60, 1.78, 1.99, 3.00, 3.65 (m, 10 H, $CH_{2\,Pip}$); 5.67 (pt, 4 H, CH_{Cp}); 6.69, 6.77 (m, 4 H, CH_{Cp}); N–H not observed. ^{11}B NMR (CD_2Cl_2, 64 MHz): $\delta = -3.5$. ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 14.25$ ($CH_{3\,Bu}$); 17.0 (br), 27.76, 29.69 ($CH_{2\,Bu}$) 23.75, 26.16, 49.38 ($CH_{2\,pip}$); 109.52, 114.24, 124.72, 127.42 (CH_{Cp}). MS *m/z* (%): 384 (8) [M$^+$ − Bu]; 358 (8) [M$^+$ − pip]; 300 (40) [M$^+$ − pip − Bu]; 264 (24) [M$^+$ − pip − Bu − HCl]; 84 (100) [pip$^+$]; 56 (45) [Bu$^+$]. $C_{19}H_{28}BCl_2NZr$ (443.38): calcd. C 51.47, H 6.37, N 3.16; found C 51.13, H 6.22, N 3.18.

$[(CH_2)_5NB(\eta^5\text{-}C_5H_4)_2TiCl_2]$ (**2**)

The complex **2** was obtained in an analogous way to the synthesis described for **3**. 0.96 g (4.26 mmol) of the ligand precursor was dissolved in 40 ml toluene and reacted at low temperatures with 3.41 ml (8.52 mmol) of a 2.5 M $Li[C_4H_9]$

solution. After washing, the resulting colourless solid was again suspended in 40 ml of toluene and treated with 1.58 g (4.26 mmol) [TiCl$_3$(thf)$_3$] at $-100\,°C$. 3 h after the mixture reached room temperature, it turned dark, 0.59 g (2.13 mmol) PbCl$_2$ was added and stirred for further 16 h. The reaction mixture was centrifuged, concentrated and stored at $-30\,°C$ yielding 0.83 g (57%) of **2** as a dark red microcrystalline solid.

^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 1.6 - 1.8$ (m, 6 H, C*H*$_{2\,pip}$); 3.55 (m, 4 H, C*H*$_{2\,pip}$); 5.65 (pt, 4 H, C*H*$_{Cp}$); 7.06 (pt, 4 H, C*H*$_{Cp}$). ^{11}B NMR (CD$_2$Cl$_2$, 64 MHz): $\delta = 36.4$. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz): $\delta = 25.13$, 28.53, 53.30 (*C*H$_{2\,pip}$); 118.22, 133.91 (*C*H$_{Cp}$). C$_{15}$H$_{18}$BCl$_2$NTi (341.91): calcd. C 52.69, H 5.31, N 4.10; found C 52.23, H 5.22, N 4.38.

[(CH$_2$)$_5$NB(η^5-C$_9$H$_6$)$_2$ZrCl$_2$] (5)

A solution of 1.87 g (5.75 mmol) **1 v/v** was treated at $-80\,°C$ with 6.76 ml (11.50 mmol) of a 1.7 M Li[*t*-C$_4$H$_9$] solution. While warming to ambient temperature the reaction mixture turned cloudy and finally in to an almost colourless suspension. The solid was isolated by centrifugation and washed with 40 ml of hexane and again suspended in 40 ml of toluene. At $-80\,°C$ the suspension was reacted with 2.17 g (5.75 mmol) [ZrCl$_4$(thf)$_2$] and allowed to warm up to ambient temperature. After stirring for 4 h the insoluble material was removed by centrifugation, the mother liquor concentrated, and stored at $-30\,°C$. 75% (2.08 g) of **5** was isolated as an orange microcrystalline solid.

Spectroscopic data for the rac-isomer

^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 1.80$ (m, 6 H, C*H*$_{2\,pip}$); 3.70 (m, 4 H, C*H*$_{2\,pip}$); 5.80 (pd, 2 H, C*H*$_{Ind}$); 6.75 (pdd, 2 H, C*H*$_{Ind}$); 7.05 (m, 2 H, C*H*$_{Ind}$); 7.35 (m, 4 H, C*H*$_{Ind}$); 7.55 (pdt, 2 H, C*H*$_{Ind}$). ^{11}B NMR (CD$_2$Cl$_2$, 64 MHz): $\delta = 38.6$. ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz): $\delta = 24.58$, 28.23, 49.29 (*C*H$_{2\,pip}$); 112.89, 114.22, 123.36, 124.85, 125.74, 126.71 (*C*H$_{Ind}$); 122.34, 131.53 (*C*$_{Ind}$). MS *m/z* (%): 483 (100) [M$^+$]; 400 (69) [M$^+$ $-$ pip]; 363 (62) [M$^+$ $-$ Cl $-$ pip]; 115 (52) [Ind$^+$]. C$_{23}$H$_{22}$BCl$_2$NZr (485.37): calcd. C 56.92, H 4.57, N 2.89; found C 56.52, H 4.22, N 3.18.

Polymerization

A 500 ml glass autoclave equipped with a 15 ml dropping funnel was charged with toluene (200 ml) and methylalumi-noxan solution (30 ml, 10 weight % in toluene). 5 ml of a solution of **4** in toluene ($2 \cdot 10^{-3}$ M) was placed in the dropping funnel. The autoclave was pressurized with ethylene until a pressure of 2 bar was reached, simultaneously the temperature was raised to 60 °C. The polymerization was initiated by adding the complex to the toluene/MAO solution. At all times of the polymerization experiment the ethylene pressure was constantly maintained at 2 bar. The polymerization was stopped by ventilation of the autoclave after different times (5, 10, 15 and 60 min.) and adding acidic methanol (30 ml) to quench the excess of MAO. The resulting mixture was stirred in methanol (800 ml) for 1 h, whereby no polymeric material precipitated.

Crystal structure determination

The crystal data of **1** and **4** were collected on a Bruker APEX diffractometer with CCD area detector and graphite monochromated Mo-K$_\alpha$ radiation. The structure was solved using direct methods, refined with Shelx software package (G. Sheldrick, University of Göttingen 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and were included in structure factor calculations.

*Crystal data for **1**:* C$_{26}$H$_{31}$BN, $M_r = 368.33$, colourless block, $0.22 \times 0.22 \times 0.14$ mm, monoclinic, space group $P2_1/c$, $a = 12.47(2)$, $b = 10.820(17)$, $c = 16.18(3)$ Å, $\beta = 103.10(4)°$, $V = 2127(6)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.150$ g·cm^{-3}, $\mu = 0.065$ cm^{-2}, $F(000) = 796$, $T = 173(2)$ K, $R_1 = 0.0524$, $wR^2 = 0.1237$, 4253 independent reflections $[2\theta \leq 52.46°]$ and 281 parameters.

*Crystal data for **4**:* C$_{19}$H$_{28}$BCl$_2$NZr, $M_r = 443.35$, yellow plate, $0.26 \times 0.17 \times 0.04$ mm, triclinic, space group $P\bar{1}$, $a = 11.5435(10)$, $b = 14.0154(12)$, $c = 14.7745(13)$ Å, $\alpha = 115.8070(10)$, $\beta = 92.1140(10)$, $\gamma = 108.1580(10)°$, $V = 2002.7(3)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.470$ g·cm^{-3}, $\mu = 0.817$ cm^{-2}, $F(000) = 912$, $T = 193(2)$ K, $R_1 = 0.0535$, $wR^2 = 0.1032$, 7946 independent reflections $[2\theta \leq 52.3°]$ and 433 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-297271 and CCDC-297272. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request /cif.

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