[1]Borahafnocenophanes: Synthesis, Structure and Catalytic Activity

Holger Braunschweig,*[a] Mario Kraft,[a] Krzysztof Radacki,[a] and Sascha Stellwag[a]

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Various [1]borahafnocenophanes of the general formula$[R_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2]$ [R = CH_3, **13**; R = C_2H_5, **14**; R_2 = $(CH_2)_5$, **15**] were synthesised in high yields by a convenient two-step, one-pot synthesis, and their constitution in solution elucidated from multinuclear NMR spectroscopic data. Suitable single crystals of complexes **13** and **15** were subjected to X-ray diffraction studies, thus providing the first structural data of [1]borahafnocenophanes. The catalytic activity of the new complexes in the Ziegler–Natta polymerisation of ethylene was studied and compared to that of corresponding [1]borazirconocenophanes.

Introduction

Over the past few decades Group 4 metallocenophanes have been studied intensively due to their potential as Ziegler–Natta-type catalysts for the polymerisation of olefins.[1] By tailoring the ligand framework and the *ansa*-bridge in particular, highly active and, with respect to the polymerisation of propene, highly stereoselective catalysts were designed.[2–4] R_2C, R_4C_2 and R_2Si bridges have been commonly incorporated.[5–7] The introduction of a boranediyl bridge, i.e. a $B{=}NR_2$ moiety, is believed to be of some advantage with respect to the catalytic performance of such *ansa* complexes, since the small boron atom imposes high rigidity, and therefore has a potential to improve the stereoselectivity of the catalyst, especially at higher temperature, where the polymerization is usually performed. In addition, a three coordinate boron atom is to some extent Lewis-acidic, a fact that is believed to enhance the activity of the Group 4 metal centre. Thus, [1]borametallocenophanes and related constrained-geometry complexes (CGC)[8] of Ti and Zr were put into focus very recently.[9,10] Shapiro and Reetz reported the first [1]borazirconocenophanes **1** and **2**,[11] which displayed a phenylboranediyl-moiety linking the two η^5-coordinated ligands. These complexes, however, could only be obtained as adducts with Et_2O, THF, SMe_2 or PMe_3 (Figure 1), therefore cancelling the Lewis acidity of the boron atom. Rufanov et al. reports the isolation of a metallocenophane incorporating a base-free three-coordinate boron bridge,[12] although these results are not reproducible and the complex is poorly characterized. Hence, the validity of this assignment is still in question.[10] Attempts to synthesise analogous zirconocene complexes in the absence of Lewis-bases have so far failed.[11] The reaction of **1** with $Li[C_6F_5]$ was reported by Lancaster to yield the corresponding anionic *ansa*-zirconocene **3**.[13]

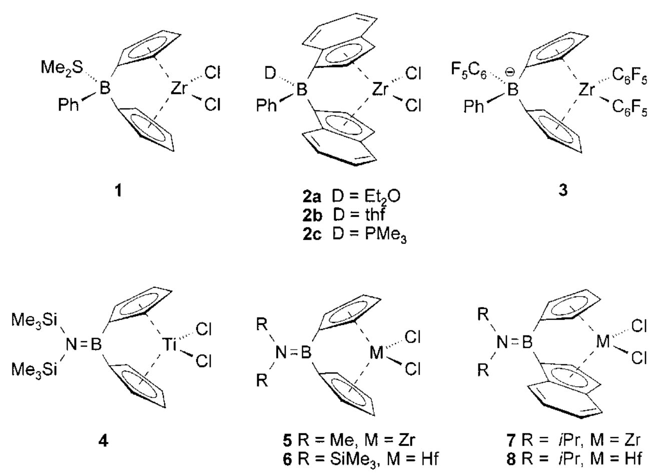


Figure 1. Boron-bridged metallocenes of Ti, Zr, and Hf.

In 1999 we reported on the titanium complex **4** as the first base-free [1]borametallocenophane of Group 4,[14] and in the same year we and Ashe extended the use of the aminoboranediyl-bridge to the synthesis of the corresponding zirconium complexes.[15,16] Subsequently, the chemistry of base-free [1]borazircono- and titanocenophanes was developed to some extent, providing evidence for their enhanced properties as Ziegler–Natta-type catalysts.[8,14–19] In sharp contrast to those Ti- and Zr-based *ansa* complexes, knowledge of corresponding [1]borahafnocenophanes is restricted to the brief spectroscopic characterisation of only two examples, $[(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2]$ (**6**) and $[iPr_2NB(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)HfCl_2]$ (**8**).[15] Structural studies, as well as information on their performance as catalysts, however, remained elusive.

[a] Department of Chemistry, Julius Maximilians Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany
Fax: +49-931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de

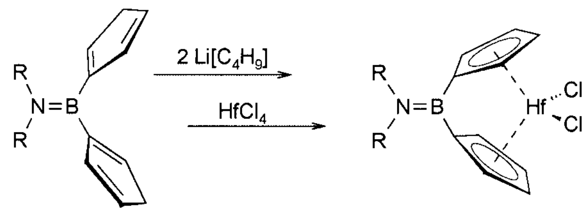
In this paper we address this deficiency and report on a series of new [1]borahafnocenophanes, their characterisation in the crystalline state and their use as catalysts for the polymerisation of ethylene.

Results and Discussion

As described earlier the reaction of amino(dihalo)borane R_2NBX_2 (R = Me, *i*Pr, $SiMe_3$; X = Cl, Br) with two equiv. of $Na[C_5H_5]$ leads straightforwardly to the respective amino(biscyclopentadienyl)borane in excellent yields.[17] The reaction of Et_2NBBr_2 (**9**) and $(CH_2)_5NBBr_2$ (**10**) with 2 equiv. $Na[C_5H_5]$ gave, at reaction times of 16 h, $Et_2NB(\eta^1\text{-}C_5H_5)_2$ (**11**) and $(CH_2)_5NB(\eta^1\text{-}C_5H_5)_2$ (**12**), respectively, in almost quantitative yields [Equation (1)]. The constitution in solution of the biscyclopentadienyl ligand precursors has been studied and reported elsewhere.[17] As shown in Equation (1), in the initial product the boron is bound to a sp^3-hybridised carbon, yielding the kinetically favoured product; below room temperature a sigmatropic proton rearrangement takes place to give the thermodynamically favoured product.

The rearrangement process leads to two new isomers per Cp-ring in which boron is bound to sp^2-hybridised carbon atoms. The rearrangement is not reversible, presumably due to interactions between the vinylic π-electrons of the adjacent carbon atoms with the empty p_z-orbital of boron. A nomenclature to distinguish between the three isomers was introduced, describing the positions of the double bonds in the Cp ring with respect to the boron atom: **a**llylic/**a**llylic (aa), **v**inylic/**a**llylic (va) and **v**inylic/**h**omoallylic (vh).[17] In biscyclopentadienylborane systems 6 isomers are theoretically possible (aa/aa, aa/va, aa/vh, va/va, va/vh and vh/vh), however only the three isomers in which boron is bound to a sp^2-hybridised carbon (va/va, va/vh and vh/vh) are expected at ambient temperatures. Due to these isomeric mixtures the resulting ^{1}H and the ^{13}C NMR spectra of both ligand precursors (**11** and **12**) are complex. A low field shift of around 10 ppm in the ^{11}B NMR was reported for $R_2NB(\eta^1\text{-}C_5H_5)_2$ (R = Me, *i*Pr, $SiMe_3$) compared to the corresponding amino(dihalo)boranes;[15,17] for **11** and **12** similar shifts to lower field compared to the parent boranes were observed.

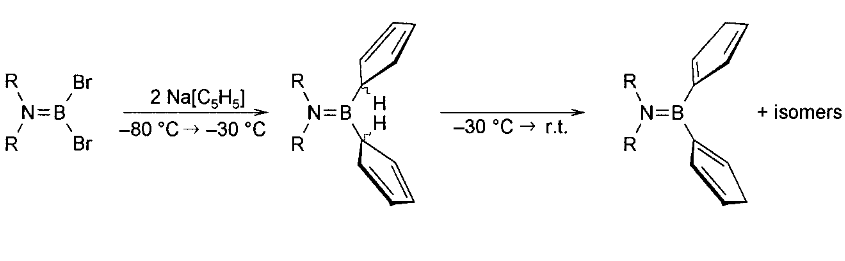
The hafnium complexes $[Me_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2]$ (**13**), $[Et_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2]$ (**14**) and $[(CH_2)_5NB(\eta^5\text{-}C_5H_4)_2HfCl_2]$ (**15**) are obtained according to Equation (2) in a convenient two-step, one-pot reaction, starting from the ligand precursors $R_2NB(\eta^1\text{-}C_5H_5)_2$ and 2 equiv. BuLi and subsequent treatment with $HfCl_4$. The dimetallation of the ligand precursor is carried out at –80 °C with subsequent warming to ambient temperatures, yielding quantitatively the dilithiated Cp derivative that is treated in situ with $HfCl_4$ at low temperature. Complexes **13**, **14** and **15** are sparingly soluble in toluene but soluble in CH_2Cl_2 and proved to be stable in the solid state towards decomposition over weeks when stored at room temperature.



13 R = CH_3
14 R = C_2H_5
15 R,R = $-(CH_2)_5-$ (2)

The structure of **13**–**15** in solution was derived from multinuclear NMR spectra, showing the expected two pseudo triplets in the ^{1}H NMR spectra for the AA′BB′ spin system of the cyclopentadienyl protons at δ = 5.66, 6.73 (**13**), 5.65, 6.73 (**14**) and 5.31, 6.33 ppm (**15**). The carbon signals for the Cp-rings in the ^{13}C NMR spectra are all in the same range at 110 and 125 ppm, respectively. The signals for the C_{ipso} of the Cp ring could not be detected in the room temperature ^{13}C NMR spectra of **13**–**15** due to quadrupolar ^{13}C-^{11}B coupling.[20] Virtually unaffected by the complexation of the ligand is the ^{11}B NMR signal of **13**–**15**, as reported before.[8]

Pale yellow crystals of **13** and **15** suitable for X-ray diffraction were obtained from toluene at –35 °C (Figure 2). Their crystal structures are compared with those of the complexes $[(\eta^5\text{-}C_5H_5)_2HfCl_2]$[21] (**16**), $[Me_2C(\eta^5\text{-}C_5H_4)_2HfCl_2]$[22] (**17**) and $[Me_2Si(\eta^5\text{-}C_5H_4)_2HfCl_2]$[23] (**18**). All bond lengths and angles discussed here are summarised



11 R = C_2H_5
12 R,R = $-(CH_2)_5-$ (1)

in Table 1, and Figure 3, part a, defines the angles α, δ and θ used in the discussion.

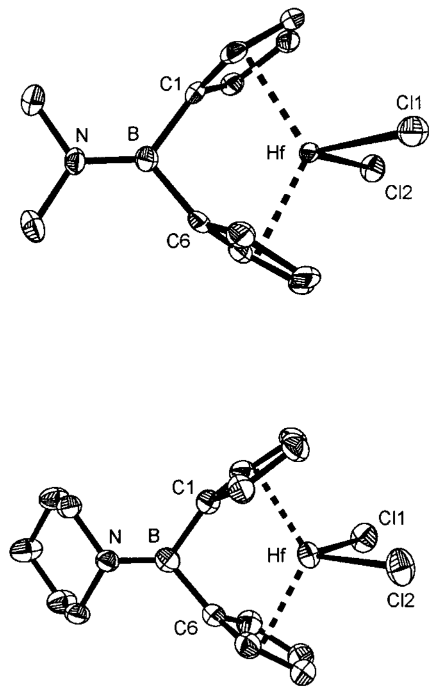


Figure 2. Structure of **13** (left) and **15** (right) in the solid state (ellipsoids at 50% probability); selected distances and angles see Table 1.

Table 1. Selected angles [°] and bond length [Å] of $(CH_3)_2NB(\eta^5\text{-}C_5H_4)_2ZrCl_2$ (**5**), $(CH_3)_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2$ (**13**), $(CH_2)_5NB(\eta^5\text{-}C_5H_4)_2HfCl_2$ (**15**), $(\eta^5\text{-}C_5H_5)_2HfCl_2$ (**16**), $(CH_3)_2C(\eta^5\text{-}C_5H_4)_2HfCl_2$ (**17**) and $(CH_3)_2Si(\eta^5\text{-}C_5H_4)_2HfCl_2$ (**18**).

Complex	5	13	15	16	17	18
tilt angle α	65.5	64.7	64.9	53.5	70.1	57.7
Cl–M–Cl	100.9	99.6(1)	99.2(1)	96.2	98.9	97.6
δ	120.8	121.4	121.7	129.2	117.1	127.6
θ	105.9	105.2(3)	105.5(2)	/	99.4	93.7
M–Cl	2.443	2.404(1)	2.413(1)	2.423	2.409	2.421
M–Cp^c	2.198	2.178	2.178	2.179	2.173	2.182
N–B	1.384	1.369(5)	1.371(4)	/	/	/
B–C_{ipso}	1.573	1.578(5)	1.581(4)	/	/	/
d	/	1.066	1.061	0.935	1.134	0.964
Reference	[16]	this work		[21]	[22]	[23]

Introducing the bridging unit causes changes in the geometry of the molecule with respect to the parent compound **16**. The *tilt angle α* increases with the incorporation of smaller bridging atoms, according to the trend C > B > Si; an α value of 53.5° is found for **16**, 57.7° for **18**, 64.7° for **13**, 64.9 for **15** and 70.1° for **17**. Virtually the same trend is found for the angle δ, being of 129.2° for **16**, 127.6° for **18**, 121.7° for **15**, 121.4° for **13** and 117.1° for **17**, respectively, highlighting the close relationship between α and δ. Furthermore, it is interesting to consider the values of θ for the four structures. These indicate a smaller deviation from the ideal tetrahedral angular value (109°) in **17** than in **18**, according to the smaller covalent radius of C with respect to Si. This results in a shorter C_{ipso}–E (E = C, **17**; E = Si, **18**) bond and a larger θ value for **17** (99.4°) than **18** (93.7°). The corresponding angles for **13** and **15** are 105.2(3)° and 105.5(2)°, respectively, reflecting the distortion of these complexes (a value of θ = 120° would be expected given the sp^2-hybridization of B). However, a direct comparison of the angle θ for the 4 structures is not possible, due to the different hybridisation of the bridging atoms.

An important factor for the polymerisation activity is the position of the metal centre relative to the Cp-centroids, which is described by the angle δ (Figure 3, part b). The polymerisation activities might increase when the metal protrudes from the wedge created by the Cp-ligands, due to a better accessibility of the metal centre to the incoming olefin. As expected, there is a relationship between the *tilt angle α* and the distance (d) of the metal from the vector connecting the Cp-centroids. The differences in the values d for the new compounds with respect to the parent complex, expressed in per cent, demonstrate the effect of the bridging moiety.[22] In **16** the distance d is 0.935 Å; a similar value is found for **18** (0.964 Å), with a change of 3.1%, while in the carbon bridged complex **17** the metal protrudes 1.134 Å (21.3%) away from the Cp-Cp vector. In both boron bridged complexes **13** and **15** the hafnium centre displays similar deviations with respect to its position in **16**, 1.066 Å (14.0%) and 1.061 Å (13.5%).

The B–N distance is typical for a corresponding double bond [1.369(5) Å for **13** and 1.371(4) Å for **15**] and similar to that found in the Zr complex $[Me_2NB(\eta^5\text{-}C_5H_4)_2ZrCl_2]$ (**5**) (B–N distance 1.384 Å). The angle θ in the compounds **13** and **15** [105.2(3)° and 105.5(2)°] is virtually the same as

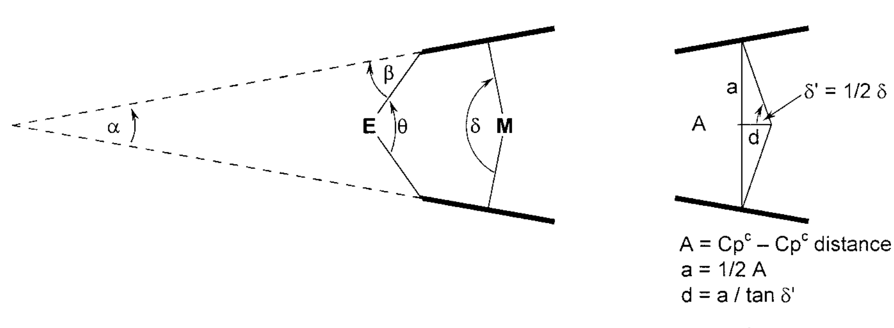


Figure 3. Structural parameter of *ansa*-metallocenes.

that observed in **5** (105.9°), as is the *tilt angle α* (**13**, 64.7°, **15**, 64.9° and **5**, 65.5°). The remaining structural parameters of **13** and **15**, especially those related to bond length and angles at the metal centre, are similar to those of **5**, reflecting the similar size of Zr and Hf.

The structural changes in the so-called *unstrained* complexes **13** and **15** compared to the parent complex **16**, are less pronounced then those observed in related *strained ansa*-metallocenes.[24] The small boron bridge in [1]boraferrocenophanes causes a more pronounced change in the geometric parameters compared to the parent ferrocene, e.g. *tilt angles* of about 32° are usually observed in [1]boraferrocenophanes.[25]

Polymerisation of Ethylene

The [1]borahafnocenophanes **13** and **14** were studied as catalysts for the polymerisation of ethylene. After activation with a 4500 fold excess of MAO the complexes polymerise ethylene at slightly elevated temperature with an activity of about 260 $kg_{PE}\cdot mol_{Hf}^{-1}\cdot h^{-1}$. As to be expected from studies on various Zr- and Hf-based catalyst systems,[2,26,27] the activity displayed here is lower than that of corresponding [1]-borazirconocenophanes by a factor of 7.[28] However, the molecular masses (M_w) of the obtained PE-samples as determined by GPC-methods were found to be 19200 $g\cdot mol^{-1}$ for **13** and 34500 $g\cdot mol^{-1}$ for **14**, thus being significantly higher than in the case of Zr.

Conclusions

The synthetic method described in this paper and previously reported for titanium and zirconium complexes provides a general route to Group 4 [1]borametallocenophanes. Determination of the first crystal structures of [1]borahafnocenophanes **13** and **15** allows for a direct comparison of important structural parameters to those of corresponding complexes of Ti and Zr. It is now demonstrated that [1]-borametallocenophane complexes of all three Group 4 metals can act as active catalysts in olefin polymerisation when sufficiently activated. The activity of [1]borahafnocenophanes was found to be lower than that of comparable zirconium complexes, but the resulting polymers are characterised by a higher molecular weight. Studies on the catalytic behaviour of Group 4 [1]borametallocenophanes as a function of the steric and electronic properties of the ligand framework are ongoing.

Experimental Section

All manipulations were carried out under dry argon 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. Dibromo(diethylamino)borane,[29] dibromo(piperidino)borane,[30] Me_2NB-(η^1-$C_5H_5)_2$[17] and $Na[C_5H_5]$[31] were obtained according to literature procedures. $Li[C_4H_9]$ and $HfCl_4$ were obtained commercially and used without further purification. 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 (^1H, internal standard TMS), 100.61 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS).

Mass spectra were recorded with a Thermo Finnigan Trio 1000 and with a Finnigan MAT 8200. Elemental analyses (C, H, N) were obtained from a Carlo–Erba elemental analyzer, model 1160. The polymerisation experiments were carried out in a 500-mL glass autoclave from Büchi.

$Et_2NB(\eta^1$-$C_5H_5)_2$ (11): $(C_2H_5)_2NBBr_2$ (1.75 g, 7.20 mmol) is added to a suspension of $Na[C_5H_5]$ (1.21 g, 14.40 mmol) in hexane (40 mL) at –80 °C. The mixture is allowed to come to ambient temperature and is subsequently stirred for 16 h. Insoluble materials are removed by centrifugation and the solvent is removed in vacuo yielding 1.45 g (94%) **11** as a yellow oil. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C, isomeric mixture of **va/va**, **va/vh** and **vh/vh**): δ = 1.11, 1.16, 1.20 [t, $^3J(H,H)$ = 7.02 Hz, 18 H, CH_3], 3.05, 3.09, 3.12 (m, 12 H, CH_{2Cp}), 3.21, 3.26, 3.36 (q, $^3J_{H,H}$ = 7.02 Hz, 12 H, CH_2), 6.3–6.7 (m, 18 H, CH_{Cp}) ppm. ^{11}B NMR (64 MHz, CD_2Cl_2, 25 °C): δ = 37.9 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, isomeric mixture of **va/va**, **va/vh** and **vh/vh**): δ = 16.23, 16.40, 16.41 (CH_3), 43.23, 43.67, 43.77, 44.17, 46.85, 46.94 (CH_2, CH_{2Cp}); 131.97, 133.21, 133.26, 135.89, 137.13, 137.26, 137.35, 138.95, 141.74 (CH_{Cp}) ppm. MS: *m/z* (%) = 213 (75) [M^+], 198 (100) [M^+ – CH_3], 148 (60) [M^+ – C_5H_5], 141 (35) [M^+ – $(C_2H_5)_2$], 77 (92) [$C_5H_6B^+$]. $C_{14}H_{20}BN$ (213.13): calcd. C 78.90, H 9.46, N 6.57; found C 79.32, H 9.57, N 6.37.

$(CH_2)_5NB(\eta^1$-$C_5H_5)_2$ (12): As described for **11**, $Na[C_5H_5]$ (1.44 g, 16.20 mmol) is suspended in hexane (40 mL) and reacted with $(CH_2)_5NBBr_2$ (2.07 g, 8.10 mmol) at –80 °C. Insolubles are removed by centrifugation and all volatiles are removed in vacuo, yielding 1.68 g (92%) **12** as a yellow oil. ^1H NMR (400 MHz, C_6D_6, 25 °C, isomeric mixture of **va/va**, **va/vh** and **vh/vh**): δ = 1.3–1.5 (m, 18 H, CH_{2pip}), 2.90, 3.00, 3.08 (m, 12 H, CH_{2Cp}), 3.2–3.4 (m, 12 H, CH_{2pip}), 5.5–7.2 (m, 18 H, CH_{Cp}) ppm. ^{11}B NMR (64 MHz, C_6D_6, 25 °C): δ = 36.8 ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C, isomeric mixture of **va/va**, **va/vh** and **vh/vh**): δ = 26.14, 26.18, 29.27, 29.32, 29.37, 43.75, 47.17, 47.46, 50.66, 50.99, 51.34 (CH_{2pip}, CH_{2Cp}), 132.36, 132.45, 133.80, 133.84, 136.31, 137.36, 138.02, 138.15, 139.07, 139.63, 141.37, 141.95 (CH) ppm. MS: *m/z* (%) = 225 (75) [M^+], 166 (88) [M^+ – C_5H_5], 77 (100) [C_5H_6B], 65 (35) [C_5H_5]. $C_{15}H_{20}BN$ (225.14): calcd. C 80.02, H 8.95, N 6.22; found C 80.38, H 8.73, N 6.48.

[$Me_2NB(\eta^5$-$C_5H_4)_2HfCl_2$] (13): A solution of $Me_2NB(\eta^1$-$C_5H_5)_2$ (0.98 g, 5.30 mmol) in hexane (40 mL) is treated at –80 °C with $Li[C_4H_9]$ (4.24 mL, 10.60 mmol). After warming up to ambient temperature the mixture was stirred for further 16 h. The resulting suspension is centrifuged and the solid washed with 40 mL hexane, suspended in toluene, and then treated with $HfCl_4$ (1.70 g, 5.30 mmol) at –80 °C. The pale yellow reaction mixture is allowed to come to room temperature and stirred for 16 h, insolubles are removed by centrifugation and the solution is concentrated and stored at –35 °C. 1.93 g (84%) **13** was isolated as pale yellow crystals. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 3.11 (s, 6 H, CH_3), 5.66 (pt, 4 H, CH_{Cp}), 6.73 (pt, 4 H, CH_{Cp}) ppm. ^{11}B NMR (64 MHz, CD_2Cl_2, 25 °C): δ = 37.7 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 40.33 (CH_3), 110.13, 124.67 (CH_{Cp}) ppm. MS: *m/z* (%) = 433 (100) [M^+], 418 (16) [M^+ – CH_3], 397 (11) [M^+ – HCl], 389 (27) [M^+ – $(CH_3)_2N$], 368 (49) [M^+ – C_5H_5], 353 (28) [M^+ – C_5H_5 – CH_3]. $C_{12}H_{14}BCl_2HfN$ (432.46): calcd. C 33.33, H 3.26, N 3.24; found C 33.71, H 3.74, N 3.03.

[$Et_2NB(\eta^5\text{-}C_5H_4)_2HfCl_2$] (14): As described for **13**, $Et_2NB(\eta^1\text{-}C_5H_5)_2$ (1.08 g, 4.80 mmol) was treated at –80 °C with Li[C_4H_9] (3.84 mL, 9.60 mmol) and subsequently with $HfCl_4$ (1.54 g, 4.80 mmol). Compound **14** was obtained as a pale yellow microcrystalline material (1.53 g, 69%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.27 (t, $^3J_{H,H}$ = 7.20 Hz, 6 H, CH_3), 3.45 (q, $^3J_{H,H}$ = 7.20 Hz, 4 H, CH_2), 5.65 (pt, 4 H, CH_{Cp}), 6.73 (pt, 4 H, CH_{Cp}) ppm. ^{11}B NMR (64 MHz, CD_2Cl_2, 25 °C): δ = 38.1 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 16.20 (CH_3), 43.72 (CH_2), 109.89, 124.58 (CH) ppm. MS: *m/z* (%) = 461 (100) [M^+], 389 (56) [M^+ – $(C_2H_5)_2N$], 353 (44) [M^+ – $(C_2H_5)_2N$ – HCl]. $C_{14}H_{18}BCl_2HfN$ (460.51): calcd. C 36.51, H 3.94, N 3.04; found C 36.84, H 4.29, N 2.78.

[$(CH_2)_5NB(\eta^5\text{-}C_5H_4)_2HfCl_2$] (15): As described for **13**, $(CH_2)_5NB(\eta^1\text{-}C_5H_5)_2$ (0.86 g, 3.80 mmol) was treated at –80 °C with 2.5 M Li[C_4H_9] (2.96 mL, 7.60 mmol) and subsequently with $HfCl_4$ (1.22 g, 3.80 mmol). Compound **15** was obtained as a pale yellow microcrystalline material (1.35 g, 78%). Recrystallisation from toluene yielded single crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.1–1.3 (m, 6 H, CH_{2pip}), 3.00 (m, 4 H, CH_{2pip}), 5.31 (pt, 4 H, CH_{Cp}), 6.66 (pt, 4 H, CH_{Cp}). ^{11}B NMR (64 MHz, C_6D_6, 25 °C): δ = 36.8. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 24.76, 28.19, 49.50 (CH_{2pip}), 109.64, 124.48 (CH_{Cp}). MS: *m/z* (%) = 474 (38) [M^+], 438 (100) [M^+ – HCl], 351 (55) [M^+ – HCl – $(CH_2)_5N$]. $C_{15}H_{18}BCl_2HfN$ (472.52): calcd. C 38.13, H 3.84, N 2.96; found C 38.51, H 4.19, N 2.63.

Polymerization: A 500-mL glass autoclave equipped with a 15 mL dropping funnel was charged with toluene (200 mL) and methylaluminoxan solution (30 mL, 10 wt.-% in toluene). A solution of the complex (5 mL) 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 and adding acidic methanol (30 mL) to quench the excess of MAO. The resulting mixture was stirred in methanol (800 mL) for 1 h and then filtered and dried at 90 °C, giving the polyethylene as a white powder, which was analyzed by high temperature gel permeation chromatography.

Crystal Structure Determination: The crystal data of **13** and **15** were collected at Bruker APEX diffractometer with CCD area detector and graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods, refined with the 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 positions and were included in structure factor calculations. **Crystal Data for 13:** $C_{12}H_{14}BCl_2HfN$ M_r = 432.44, pale yellow block, 0.28 × 0.18 × 0.17, monoclinic, space group $P21/n$, a = 11.4561(9) Å, b = 10.0071(8) Å, c = 12.0774(9) Å, β = 105.013(1)°, V = 1337.32(18) Å^3, Z = 4, $\rho_{calcd.}$ = 2.148 g·cm^{-3}, μ = 8.174 cm^{-2}, F(000) = 816, T = 193 K; R_1 = 0.0188, w_R = 0.0491, 2649 independent reflections [$2\theta \leq 52.16°$] and 154 parameters. **Crystal Data for 15:** $C_{22}H_{26}BCl_2HfN$ M_r = 564.64, pale yellow plates, 0.23 × 0.23 × 0.10, triclinic, space group P–1, a = 9.752(2) Å, b = 11.627(3) Å, c = 11.884(3) Å, α = 118.441(3)°, β = 101.620(3)°, γ = 101.310(3)°, V = 1091.8(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.717 g·cm^{-3}, μ = 5.028 cm^{-2}, F(000) = 552, T = 173 K; R_1 = 0.0191, w_R = 0.0483, 4298 independent reflections [$2\theta \leq 52.1°$] and 244 parameters.

CCDC-260992 and -260993 contain the supplementary crystallographic data for this paper. 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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