

Note

# Synthesis and molecular structure of boron-bridged constrained geometry complexes of zirconium and hafnium

Holger Braunschweig<sup>a,\*</sup>, Frank M. Breitling<sup>a,b</sup>, Krzysztof Radacki<sup>a</sup>, Fabian Seeler<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

<sup>b</sup> Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

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## Abstract

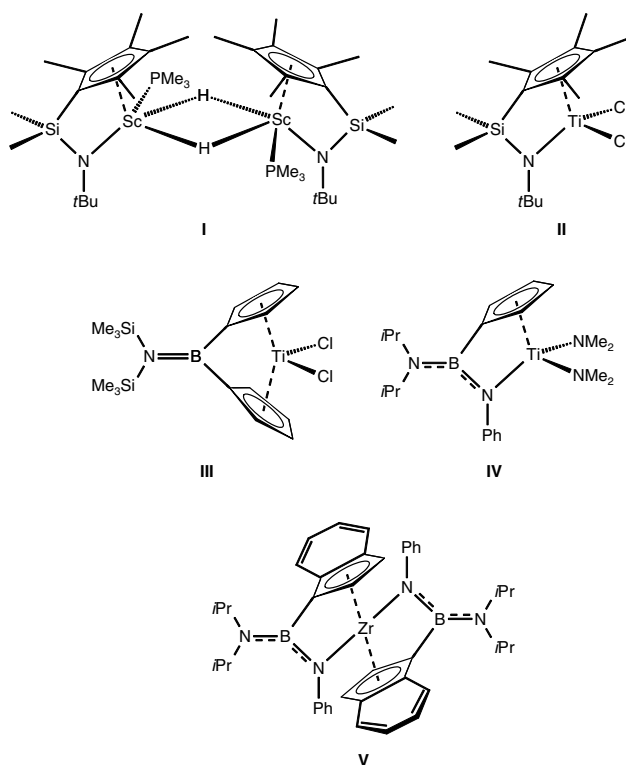
The boron-bridged constrained geometry complexes  $[M\{\eta^5\text{-}\eta^1\text{-}(\text{C}_5\text{H}_4\text{B}(\text{NiPr}_2)\text{NPh}\})(\text{NMe}_2)_2]$  ( $M = \text{Zr}$  (**1**),  $\text{Hf}$  (**2**)) and  $[\text{Zr}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_9\text{H}_6\text{B}(\text{NiPr}_2)\text{NPh}\})(\text{NMe}_2)_2]$  (**3**) have been prepared by reaction of the respective neutral ligand precursors ( $\eta^1\text{-C}_5\text{H}_5\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$  and  $(1\text{-C}_9\text{H}_7)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$ ) with  $[M(\text{NMe}_2)_4]$  ( $M = \text{Zr}, \text{Hf}$ ) with elimination of two equivalents of  $\text{HNMe}_2$ . All new compounds have been characterised by means of multinuclear NMR spectroscopy and X-ray diffraction experiments.

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## 1. Introduction

Linked cyclopentadienyl-amido ligands were first introduced by Bercaw et al. [1] for the synthesis of scandium(III) complexes, e.g. **I**. Shortly thereafter, research groups both in academia [2] and industry [3] reported the utilization of such ligands for the synthesis of corresponding Group 4 complexes, e.g. **II**. Frequently, complexes incorporating ligands of the aforementioned type are referred to as constrained geometry complexes (CGCs), owing to the chelate bite angle imposed by the cyclopentadienyl and amido donors. When activated with suitable co-catalysts such as MAO these CGCs serve as highly active olefin polymerisation catalysts [4] and produce polymers with exceptional characteristics, e.g. long chain branching, resulting in low density and advantageous mechanical properties [5]. Besides the well-studied application of Group 4 CGCs in olefin polymerisation, a number of reports on their catalytic characteristics with regard to various organic transformations have appeared in the literature [6–9].



\* Corresponding author. Tel.: +49 931 888 5260; fax: +49 931 888 4623.

E-mail address: [h.braunschweig@mail.uni-wuerzburg.de](mailto:h.braunschweig@mail.uni-wuerzburg.de) (H. Braunschweig).

The presence of a bridging moiety between the cyclopentadienyl and amido fragments in CGCs appears to be crucial for the observed reactivity of these compounds [10]. The identity of the bridging element affects the Cp(centroid)–M–N angle and may be utilised to fine tune the activity. Introduction of a boranediyl bridge appeared to be particularly interesting for several reasons [11]: (i) the small size of the boron atom should result in a more acute Cp(centroid)–M–N angle, a feature that was previously associated with a higher polymerisation activity, and (ii) in a more rigid ligand framework that may be advantageous in the catalysis of asymmetric organic transformations, and (iii) the potentially Lewis acidic moiety in proximity to the catalytically active centre may positively affect its reactivity. Consequently, we extended the synthetic method for the preparation of boron-bridged ligand precursors [12] and corresponding metallocenes [13,14] that are stabilized by an amino substituent, e.g., **III**, to the synthesis of related boron-bridged CGC ligand precursors [15] and corresponding titanium CGCs [16], e.g., **IV**. The latter could be obtained by reaction of the respective ligand precursors with  $[\text{Ti}(\text{NMe}_2)_4]$  via amine elimination. Previously, we have not been able to isolate the zirconium or hafnium congeners following this approach. Similarly, two-fold deprotonation of a boron-bridged CGC ligand precursor and reaction with  $\text{ZrCl}_4$  did not result in the formation of the desired CGC, but yielded the bis-ligand metallocene **V** [15a].

In the present paper, we report the synthesis of the first boron-bridged CGCs of zirconium and hafnium via amine elimination and their structural characterisation by means of X-ray diffraction.

## 2. Results and discussion

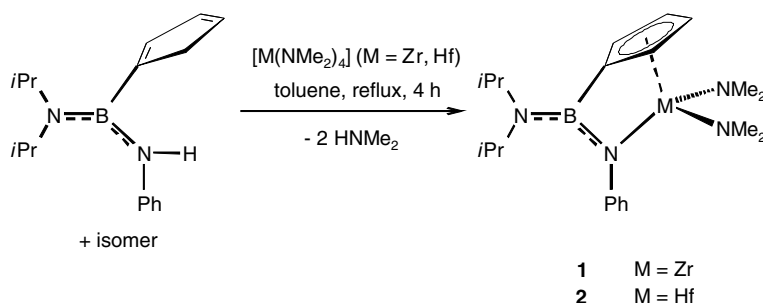
### 2.1. Synthesis and spectroscopic characterisation

We previously reported the synthesis of boron-bridged titanium CGCs via amine elimination. Thus,  $(\eta^1\text{-C}_5\text{H}_5)\text{-B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{Ph}$  reacts with  $[\text{Ti}(\text{NMe}_2)_4]$  at slightly elevated temperature (40 °C) to give corresponding  $[\text{Ti}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{NPh}\}(\text{NMe}_2)_2]$  in high yield [16a]. Likewise, various related boron-bridged CGC ligand precursors

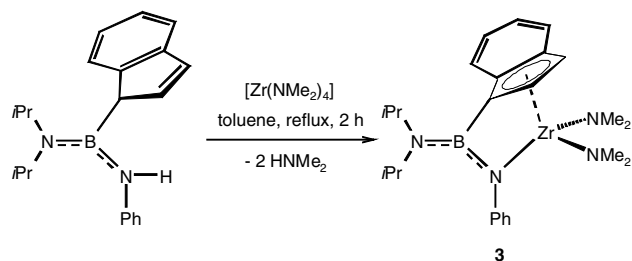
react with  $[\text{Ti}(\text{NMe}_2)_4]$  in toluene under reflux conditions to give the corresponding titanium CGCs [16b]. In the light of these positive results we re-examined our earlier findings that isolation of boron-bridged CGCs of the higher homologues zirconium and hafnium by a corresponding route is not viable.

Indeed, reaction of  $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{Ph}$  with  $[\text{M}(\text{NMe}_2)_4]$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) at reflux in toluene for several hours and subsequent purification by means of recrystallisation gave the corresponding CGCs  $[\text{M}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{NPh}\}(\text{NMe}_2)_2]$  ( $\text{M} = \text{Zr}$  (**1**),  $\text{Hf}$  (**2**)) in reasonable yields in the form of colourless crystals (Scheme 1). Under very similar conditions,  $(1\text{-C}_9\text{H}_7)\text{B}(\text{N}i\text{Pr}_2)\text{N}(\text{H})\text{Ph}$  reacted with  $[\text{Zr}(\text{NMe}_2)_4]$  to yield the corresponding complex  $[\text{Zr}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_9\text{H}_6)\text{B}(\text{N}i\text{Pr}_2)\text{NPh}\}(\text{NMe}_2)_2]$  (**3**) as colourless crystals (Scheme 2). It seems to be rather essential to perform these reactions under reflux conditions to oust the amine formed and consequently drive the reactions to the product side. NMR analyses of the crude products suggest unbridged complexes to be the major side products. On the other hand, decomposition of the formed CGCs due to the high temperatures applied appears to be negligible.

Complexes **1–3** were characterised by multinuclear 1D and 2D NMR spectroscopy.  $^{11}\text{B}$  NMR chemical shifts for **1–3** very much resemble those of the respective ligand precursors.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1–3** are unremarkable. The resonances of the respective boron substituted carbon atoms give rise to broad signals in the  $^{13}\text{C}$  NMR spectrum of **1** and **2**, while the corresponding signal in the  $^{13}\text{C}$  NMR spectrum of **3** could not be detected at  $-20$  °C, due to quadrupolar  $^{13}\text{C}\text{--}^{11}\text{B}$  coupling [17]. Apart from that, all expected  $^1\text{H}$  and  $^{13}\text{C}$  resonances were observed. The spectra closely resemble the spectra of the respective titanium congeners  $[\text{Ti}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_5\text{H}_4)\text{B}(\text{N}i\text{Pr}_2)\text{NPh}\}(\text{NMe}_2)_2]$  and  $[\text{Ti}\{\eta^5\text{-}\eta^1\text{-}(\text{C}_9\text{H}_6)\text{B}(\text{N}i\text{Pr}_2)\text{NPh}\}(\text{NMe}_2)_2]$  with only slight differences in chemical shifts [16]. As observed for these diamino titanium complexes [18], the resonances corresponding to the  $i\text{Pr}_2\text{N}$  moieties of **1–3** in the ambient temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are significantly broadened. Such line broadening may be ascribed to rotation about the  $i\text{Pr}_2\text{N}\text{--B}$  linkage on the NMR time scale. However, in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1–3** recorded at  $-20$  °C the signals corresponding to the  $i\text{Pr}_2\text{N}$



Scheme 1.



Scheme 2.

groups are sharp and the hyperfine structures of the signals in the  $^1\text{H}$  NMR spectra (two doublets corresponding to  $\text{Me}_{i\text{Pr}}$  and two heptets corresponding to  $\text{CH}_{i\text{Pr}}$  in the spectra of the  $C_5$  symmetric Cp derivatives **1** and **2**, four doublets corresponding to  $\text{Me}_{i\text{Pr}}$  and two heptets corresponding to  $\text{CH}_{i\text{Pr}}$  in the spectrum of the  $C_1$  symmetric indenyl derivative **3**) are clearly resolved. These observations are consistent with inhibition of the rotation about the  $i\text{Pr}_2\text{N}-\text{B}$  bonds in **1–3** on the NMR time scale at low temperatures.

## 2.2. X-ray structure determination of complexes **1–3**

The structures of CGCs **1–3** in the solid state could be determined by X-ray diffraction experiments. All three compounds crystallise in the triclinic space group  $P\bar{1}$ . Table 1 compares selected structural parameters of **1–3**. Fig. 1 depicts the molecular structure of **3** as a representative example.

The gross structures of the new complexes **1–3** are very similar with the structures of their respective titanium analogues  $[\text{Ti}\{\eta^5\text{:}\eta^1\text{-(C}_5\text{H}_4\text{)B(NiPr}_2\text{)NPh}\}(\text{NMe}_2)_2]$  and  $[\text{Ti}\{\eta^5\text{:}\eta^1\text{-(C}_9\text{H}_6\text{)B(NiPr}_2\text{)NPh}\}(\text{NMe}_2)_2]$  [16]. If one considers the  $C_5$  aromatic rings in all these complexes as  $\eta^1$ -moieties, the geometry at the transition metal can be viewed as a distorted tetrahedron. The main structural differences between the complexes arise from the different radii of the coordinated transition metals. The larger zirconium and hafnium centres (when compared to the titanium centres) result in a lengthening of all bonds involving the metal centre. Concurrently, the  $\text{N}(1)-\text{M}-\text{C}_5$  angles become more acute by ca.  $5^\circ$ , while the  $\text{N}(1)-\text{B}-\text{C}(1)$  angles

Table 1  
Comparative selected geometric parameters for complexes **1–3**

	<b>1</b> [M = Zr, R1 = C(12), R2 = C(15)]	<b>2</b> [M = Hf, R1 = C(12), R2 = C(15)]	<b>3</b> [M = Zr, R1 = C(19), R2 = C(16)]
M–C <sub>5</sub> (Å) <sup>a</sup>	2.182	2.162	2.196
$\phi$ (°) <sup>b</sup>	4.2	3.8	4.3
$\delta$ (Å) <sup>c</sup>	0.16	0.14	0.16
M–N(1) (Å)	2.1530(17)	2.1233(18)	2.1363(14)
M–N(3) (Å)	2.0571(19)	2.0225(19)	2.0466(15)
M–N(4) (Å)	2.0314(19)	2.0415(19)	2.0354(15)
B–N(1) (Å)	1.438(3)	1.444(3)	1.446(2)
B–N(2) (Å)	1.408(3)	1.414(3)	1.406(2)
B–C(1) (Å)	1.614(3)	1.608(3)	1.607(2)
N(1)–M–C <sub>5</sub> (°) <sup>a</sup>	94.1	94.9	94.9
N(1)–B–N(2) (°)	130.8(2)	130.7(2)	129.50(15)
N(1)–B–C(1) (°)	105.08(18)	105.18(18)	105.45(13)
N(2)–B–C(1) (°)	124.14(19)	124.2(2)	125.04(15)
$\sum[\text{X–B–Y}]$ (°) <sup>d</sup>	360.0	360.0	360.0
$\Delta\text{B}$ (Å) <sup>e</sup>	0.007	0.006	0.006
B–N(2)–R1 (°)	122.89(18)	123.14(18)	122.52(14)
B–N(2)–R2 (°)	122.72(18)	122.37(19)	123.14(14)
R1–N(2)–R2 (°)	114.38(17)	114.45(17)	114.30(13)
$\sum[\text{X–N(2)–Y}]$ (°) <sup>d</sup>	360.0	360.0	360.0
$\Delta\text{N}(2)$ (Å) <sup>e</sup>	0.009	0.016	0.017
$\tau[\text{B–N(2)}]$ (°) <sup>f</sup>	2.2	2.1	1.1
M–N(1)–B (°)	103.37(13)	103.14(14)	103.06(10)
M–N(1)–Ph (°)	123.15(13)	123.88(14)	124.70(10)
B–N(1)–Ph (°)	131.99(18)	131.59(19)	131.53(13)
$\sum[\text{X–N(1)–Y}]$ (°) <sup>d</sup>	358.5	358.6	359.3
$\Delta\text{N}(1)$ (Å) <sup>e</sup>	0.110	0.106	0.076
B–C(1)–C <sub>5</sub> (°) <sup>g</sup>	29.4	30.4	30.5
$\Delta\text{B}[\text{C}_5]$ (Å) <sup>h</sup>	0.792	0.814	0.816

<sup>a</sup> “C<sub>5</sub>” refers to the centroid of the five-membered aromatic ring.

<sup>b</sup>  $\phi$  is the angle between the normal to the [C<sub>5</sub>] ring plane and the M–C<sub>5</sub> ring centroid vector.

<sup>c</sup>  $\delta$  is the offset of the M centre away from a position perpendicularly beneath the C<sub>5</sub> ring centroid.

<sup>d</sup> Sum of the angles around the central atom.

<sup>e</sup>  $\Delta X$  is the deviation of atom X from the plane of its substituents.

<sup>f</sup> Torsion angle about linkage.

<sup>g</sup> Angle of B–C(1) bond to [C<sub>5</sub>] ring plane.

<sup>h</sup> Deviation of B from [C<sub>5</sub>] plane.

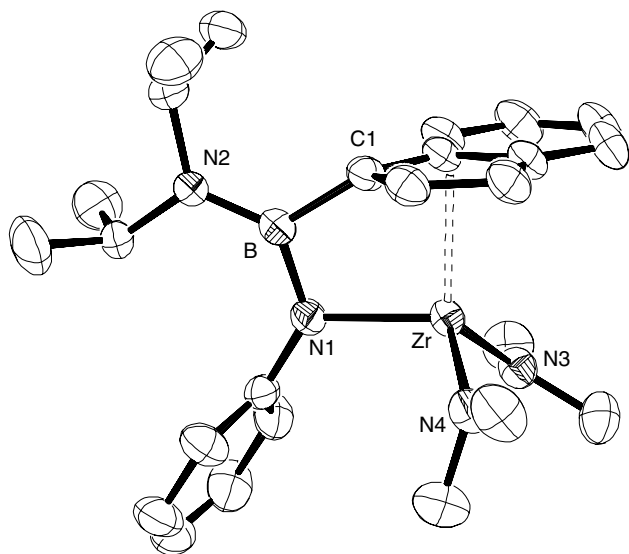


Fig. 1. ORTEP representation of the molecular structure of **3**. Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity.

become more obtuse by ca.  $1.5^\circ$ . In all these structures, both the B and N(2) centres have trigonal planar geometries and these trigonal planes are almost coplanar in the respective molecules. There are no noteworthy intermolecular interactions in the crystals of **1–3**.

Comparison of the structures of CGC **3** and the related bis-ligand metallocene  $[\text{Zr}\{\eta^5\text{-}\eta^1\text{-(C}_9\text{H}_6\text{)B(NiPr}_2\text{)NPh}\}_2]$  [**15a**] discloses only minor differences in the coordination of the respective linked indenyl-amido ligands to the zirconium centres. Most prominently, the Zr–C<sub>5</sub> distance in **3** is significantly shorter (2.196 vs. 2.228 Å) and presumably results from lower electron density at this zirconium centre. Likewise, the slight shortening of the Zr–N(1) distance in **3** may be rationalised (2.1363(14) vs. 2.1570 Å). These differences in bond lengths are accompanied by smaller changes in the other structural parameters of the chelating ligand, the most significant being the larger twist of the trigonal planes surrounding B and N(2) in the bis-ligand metallocene ( $5.1^\circ$ ) when compared with **3** ( $1.1^\circ$ ).

### 3. Conclusions

The synthesis of the first boron-bridged CGCs of zirconium and hafnium by reaction of the neutral ligand precursors with  $[\text{M}(\text{NMe}_2)_4]$  (M = Zr, Hf) via amine elimination is straightforward. X-ray diffraction experiments demonstrated a close structural resemblance of the obtained complexes with their titanium analogues.

### 4. Experimental

#### 4.1. General methods

All manipulations were performed under a dry atmosphere of argon using standard Schlenk line and dry box

techniques. Solvents were dried utilising an M. Braun Solvent Purification System and stored under argon over molecular sieves. Deuterated solvents were degassed, dried and stored over molecular sieves.  $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$  [**15c**],  $(1\text{-C}_9\text{H}_7)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$  [**15a**],  $[\text{Zr}(\text{NMe}_2)_4]$  [**19**] and  $[\text{Hf}(\text{NMe}_2)_4]$  [**19**] were prepared by previously published methods.

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker DRX 300 spectrometer.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker 200 Avance spectrometer. All chemical shifts are reported in ppm. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to internal solvent resonances and are reported relative to  $\text{SiMe}_4$ . Assignments were made from the analysis of  $^1\text{H}$ ,  $^{13}\text{C}\text{-HMQC-COSY}$  NMR experiments. Chemical shifts for  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra were referenced to  $\text{BF}_3\cdot\text{OEt}_2$  as an external standard.

#### 4.2. Synthesis of $[\text{Zr}\{\eta^5\text{-}\eta^1\text{-(C}_5\text{H}_4\text{)B(NiPr}_2\text{)NPh}\}_2(\text{NMe}_2)_2]$ (**1**)

Solutions of the ligand precursor  $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$  (0.64 g, 2.39 mmol) and  $[\text{Zr}(\text{NMe}_2)_4]$  (0.64 g, 2.39 mmol), both in toluene (20 mL), were combined at ambient temperature. During reflux for 4 h, the initially almost colourless solution became bright yellow in colour. All volatiles were removed in vacuo, the dark yellow residue was re-dissolved in hexane, concentrated and stored for recrystallisation at ambient temperature. Large colourless crystals of **1** (0.74 g, 1.67 mmol, 70%) were obtained after several hours.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ ):  $\delta = 0.86$  (d,  $^3J_{\text{H-H}} = 6.7$  Hz, 6H,  $\text{Me}_{\text{IPr}}$ ), 1.40 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 6H,  $\text{Me}_{\text{IPr}}$ ), 2.75 (s, 12H,  $\text{NMe}_2$ ), 3.19 (m,  $^3J_{\text{H-H}} = 6.9$  Hz, 1H,  $\text{CH}_{\text{IPr}}$ ), 3.38 (m,  $^3J_{\text{H-H}} = 6.7$  Hz, 1H,  $\text{CH}_{\text{IPr}}$ ), 6.04 (pt, 2H,  $\text{CH}_{\text{CP}}$ ), 6.50 (pt, 2H,  $\text{CH}_{\text{CP}}$ ), 6.64–6.71 (m, 2H, *o*- $\text{CH}_{\text{Ph}}$ ), 6.77–6.85 (m, 1H, *p*- $\text{CH}_{\text{Ph}}$ ), 7.07–7.16 (m, 2H, *m*- $\text{CH}_{\text{Ph}}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ ):  $\delta = 21.2$  ( $\text{Me}_{\text{IPr}}$ ), 26.8 ( $\text{Me}_{\text{IPr}}$ ), 43.1 ( $\text{NMe}_2$ ), 43.9 ( $\text{CH}_{\text{IPr}}$ ), 46.0 ( $\text{CH}_{\text{IPr}}$ ), 98.6 (BC), 113.6 ( $\text{CH}_{\text{CP}}$ ), 118.5 ( $\text{CH}_{\text{CP}}$ ), 120.3 (*p*- $\text{CH}_{\text{Ph}}$ ), 123.9 (*o*- $\text{CH}_{\text{Ph}}$ ), 128.2 (*m*- $\text{CH}_{\text{Ph}}$ ), 153.5 (*ipso*- $\text{C}_{\text{Ph}}$ ).  $^{11}\text{B}$  NMR (64 MHz, benzene- $d_6$ ):  $\delta = 27.8$ .

#### 4.3. Synthesis of $[\text{Hf}\{\eta^5\text{-}\eta^1\text{-(C}_5\text{H}_4\text{)B(NiPr}_2\text{)NPh}\}_2(\text{NMe}_2)_2]$ (**2**)

Following the same procedure as for the preparation of **1**,  $(\eta^1\text{-C}_5\text{H}_5)\text{B}(\text{NiPr}_2)\text{N}(\text{H})\text{Ph}$  (0.86 g, 3.21 mmol) was treated  $[\text{Hf}(\text{NMe}_2)_4]$  (1.14 g, 3.21 mmol) in toluene (40 mL). Recrystallisation from toluene at  $-30^\circ\text{C}$  yielded pure **2** (1.06 g, 1.99 mmol, 62%) in the form of colourless crystals suitable for X-ray diffraction experiments.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ ):  $\delta = 0.85$  (d,  $^3J_{\text{H-H}} = 6.7$  Hz, 6H,  $\text{Me}_{\text{IPr}}$ ), 1.40 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 6H,  $\text{Me}_{\text{IPr}}$ ), 2.77 (s, 12H,  $\text{NMe}_2$ ), 3.20 (m,  $^3J_{\text{H-H}} = 6.9$  Hz, 1H,  $\text{CH}_{\text{IPr}}$ ), 3.36 (m,  $^3J_{\text{H-H}} = 6.7$  Hz, 1H,  $\text{CH}_{\text{IPr}}$ ), 6.02 (pt, 2H,  $\text{CH}_{\text{CP}}$ ), 6.49 (pt, 2H,  $\text{CH}_{\text{CP}}$ ), 6.65–6.72 (m, 2H, *o*- $\text{CH}_{\text{Ph}}$ ),

6.78–6.85 (m, 1H, *p*-CH<sub>Ph</sub>), 7.08–7.16 (m, 2H, *m*-CH<sub>Ph</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, –20 °C): δ = 21.1 (Me<sub>*i*Pr</sub>), 26.7 (Me<sub>*i*Pr</sub>), 43.0 (NMe<sub>2</sub>), 43.9 (CH<sub>*i*Pr</sub>), 46.1 (CH<sub>*i*Pr</sub>), 98.6 (BC), 113.2 (CH<sub>Cp</sub>), 118.0 (CH<sub>Cp</sub>), 120.6 (*p*-CH<sub>Ph</sub>), 124.2 (*o*-CH<sub>Ph</sub>), 128.1 (*m*-CH<sub>Ph</sub>), 153.2 (*ipso*-C<sub>Ph</sub>). <sup>11</sup>B NMR (64 MHz, benzene-*d*<sub>6</sub>): δ = 27.2.

#### 4.4. Synthesis of [Zr {η<sup>5</sup>:η<sup>1</sup>-(C<sub>9</sub>H<sub>6</sub>)B(NiPr<sub>2</sub>)NPh}-(NMe<sub>2</sub>)<sub>2</sub>] (3)

Following the same procedure as for the preparation of **1**, (1-C<sub>9</sub>H<sub>7</sub>)B(NiPr<sub>2</sub>)N(H)Ph (0.61 g, 1.92 mmol) was treated with [Zr(NMe<sub>2</sub>)<sub>4</sub>] (0.51 g, 1.92 mmol) in toluene (30 mL). Recrystallisation from hexane at –80 °C yielded pure **3** (0.53 g, 1.08 mmol, 56%) in the form of a colourless microcrystalline material. Recrystallisation from hexane at 4 °C yielded crystals of **3** suitable for X-ray diffraction experiments. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, –20 °C): δ = 0.94 (d, <sup>3</sup>J<sub>H–H</sub> = 6.7 Hz, 3H, Me<sub>*i*Pr</sub>), 0.99 (d, <sup>3</sup>J<sub>H–H</sub> = 6.7 Hz, 3H, Me<sub>*i*Pr</sub>), 1.47 (d, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, 3H, Me<sub>*i*Pr</sub>), 1.48 (d, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, 3H, Me<sub>*i*Pr</sub>), 1.96 (s, 6H, NMe<sub>2</sub>), 2.89 (s, 6H, NMe<sub>2</sub>), 3.32 (m, <sup>3</sup>J<sub>H–H</sub> = 6.8 Hz, 1H, CH<sub>*i*Pr</sub>), 3.51 (m, <sup>3</sup>J<sub>H–H</sub> = 6.7 Hz, 1H, CH<sub>*i*Pr</sub>), 6.35–7.78 (m, 11H, CH<sub>Ind/Ph</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, –20 °C): δ = 21.2 (Me<sub>*i*Pr</sub>), 21.5 (Me<sub>*i*Pr</sub>), 26.5 (Me<sub>*i*Pr</sub>), 27.0 (Me<sub>*i*Pr</sub>), 40.7 (NMe<sub>2</sub>), 43.9 (CH<sub>*i*Pr</sub>), 44.3 (NMe<sub>2</sub>), 46.5 (CH<sub>*i*Pr</sub>), 102.2 (CH<sub>Ind-5-ring</sub>), 120.2 (*p*-CH<sub>Ph</sub>), 122.8 (CH<sub>Ind-6-ring</sub>), 123.1 (*o*-CH<sub>Ph</sub>), 123.3 (CH<sub>Ind-5-ring</sub>), 123.8 (CH<sub>Ind-6-ring</sub>), 124.1 (CH<sub>Ind-6-ring</sub>), 124.8 (CH<sub>Ind-6-ring</sub>), 127.7 (*quaternary*

C<sub>Ind</sub>), 128.2 (*m*-CH<sub>Ph</sub>), 131.0 (*quaternary* C<sub>Ind</sub>), 153.2 (*ipso*-C<sub>Ph</sub>), BC resonance not observed. <sup>11</sup>B NMR (64 MHz, benzene-*d*<sub>6</sub>): δ = 28.5.

#### 4.5. X-ray structure determination of compounds 1–3

A crystal of appropriate size was mounted on a glass fiber with silicone grease. The crystal was transferred to a Bruker SMART APEX diffractometer with CCD area detector, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus to an appropriate temperature. Preliminary orientation matrix and cell constants were determined by collection of 100 frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected [20]. The raw data were integrated with SAINT [21]. Cell dimensions were calculated from all reflections. Data analysis was performed with XPREP [22]. The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on comparison of redundant and equivalent reflections was applied with SADABS [23]. The structures were solved via direct methods and refined with the SHELX software package and expanded using Fourier techniques [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. The crystallographic data, parameters of the X-ray experiments and refinements for compounds 1–3 are listed in Table 2.

Table 2  
Summary of the crystal data and details of data collection and refinement for compounds 1–3

Data	1	2	3
Empirical formula	C <sub>21</sub> H <sub>35</sub> BN <sub>4</sub> Zr	C <sub>21</sub> H <sub>35</sub> BHfN <sub>4</sub>	C <sub>25</sub> H <sub>37</sub> BN <sub>4</sub> Zr
Formula weight (g mol <sup>-1</sup> )	445.56	532.83	495.62
Temperature (K)	173(2)	173(2)	193(2)
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.4986(8)	9.4684(11)	9.735(2)
<i>b</i> (Å)	9.7515(8)	9.8068(13)	9.947(2)
<i>c</i> (Å)	13.8010(11)	13.8449(19)	13.809(3)
α (°)	101.5630(10)	101.509(2)	88.482(4)
β (°)	103.7000(10)	103.455(2)	80.798(5)
γ (°)	102.6290(10)	102.932(3)	75.240(4)
<i>V</i> (Å <sup>3</sup> )	1168.23(17)	1174.9(3)	1276.3(5)
<i>Z</i>	2	2	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.267	1.506	1.290
Absorption coefficient (mm <sup>-1</sup> )	0.482	4.451	0.449
<i>F</i> (000)	468	532	520
θ Range for data collection (°)	1.58–26.18	1.57–26.06	2.12–27.53
Reflections collected	24671	13292	12377
Independent reflections [ <i>R</i> <sub>int</sub> ]	4659 [0.0271]	4628 [0.0200]	5821 [0.0182]
Maximum/minimum transmission	0.93/0.81231	0.39/0.2651	0.94/0.758
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4659/0/244	4628/0/252	5821/0/288
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.086	1.065	1.051
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0315, <i>wR</i> <sub>2</sub> = 0.0916	<i>R</i> <sub>1</sub> = 0.0153, <i>wR</i> <sub>2</sub> = 0.0390	<i>R</i> <sub>1</sub> = 0.0283, <i>wR</i> <sub>2</sub> = 0.0737
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0328, <i>wR</i> <sub>2</sub> = 0.0927	<i>R</i> <sub>1</sub> = 0.0159, <i>wR</i> <sub>2</sub> = 0.0393	<i>R</i> <sub>1</sub> = 0.0303, <i>wR</i> <sub>2</sub> = 0.0750
Minimum/maximum residual electron density (e Å <sup>-3</sup> )	0.655/–0.513	0.653/–0.361	0.498/–0.263



## 5. Supplementary data

Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278300 (1), 278304 (2) and 278301 (3). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax(int) +44(1223)336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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