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Difluorenyl[2]borametallocenophanes of Group 4 Metals: Synthesis and Structure

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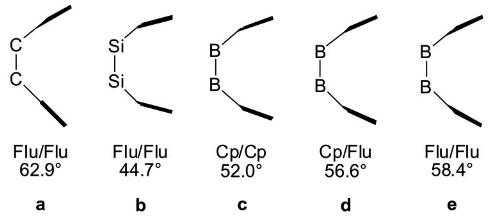
We report the synthesis of difluorenyl[2]borametallocenophanes of Zr and Hf. The ligand precursor has been synthesized starting from 1,2-dibromo-1,2-bis(dimethylamino)diborane(4) upon reaction with Li[$C_{13}H_9$]. All compounds have been fully characterized by multinuclear NMR spectroscopy and, in addition, selected examples by X-ray analysis.

Introduction

About twenty years ago, the scientific rationale for the design, synthesis and application of organometallic polymers was first conceptualized. Highly strained *ansa*-metallocenes, most commonly derived from transition metals of groups V to VIII, were proven to serve as facile precursors for these materials via ring-opening polymerization (ROP) protocols.[1] Of particular importance in this area are [1]silaferrocenophanes and the corresponding polyferrocenylsilanes subsequently obtained thereof.[2]

Besides, metallocenophanes and related constrained geometry complexes (CGC) of group IV metals have impressively demonstrated their vast potential as catalyst precursors for Ziegler–Natta type olefin polymerization. These complexes have shown both a very high catalytic activity and a tuneable, precise control of the stereoselective polymerization of propene. A great number of review articles affirms the importance for academia as well as industry.[3] In particular, difluorenylmetallocenophanes of zirconium and hafnium are known as highly active catalysts after activation with the common co-catalyst MAO. The resulting polymer generally has a very high molecular weight and a very low degree of branching.[4] Because of this, C_2H_4-,[4b] CH_2SiMe_2-[4a] and Si_2Me_4-bridged[4a] difluorenylzirconocenes have been synthesized and found to be good catalysts for olefin polymerization.

As in smaller aryl systems, e.g. cyclopentadienyl, also in the difluorenyl system, the introduction of an aminoboranediyl bridge is believed to be of some advantage with respect to the catalytic performance of such complexes. The small boron atom imposes high rigidity, and therefore, has the potential to improve the stereoselectivity of the catalyst. A larger tilt angle is meant to allow better access of the monomer to the metal center and thus enhance the catalytic activity (Scheme 1).



Scheme 1. Schematic representation of the influence of the bridging moiety on the tilt angle in cyclopentadienyl (Cp, C_5H_4)/fluorenyl (Flu, $C_{13}H_8$) zirconocenophanes (a, b;[5] c, d;[6] e [this work]).

In addition, a three-coordinate boron atom is generally to some extent Lewis acidic, a fact which is believed to enhance the catalytic activity of group IV [*n*]borametallocenophanes ($n = 1, 2$),[7] because it lowers electron density at the metal center.[5] We[8] and others[9] have studied the synthesis, structure and catalytic activity of group IV [1]borametallocenophanes and their related CGCs. These studies have shown those complexes to i) exhibit an enhanced activity for the polymerization of ethylene and ii) produce syndiotactic polypropylenes.

The 1,2-bis(dimethylamino)-1,2-di-η^1-fluorenyldiborane(4) has been described previously by Nöth, along with the corresponding metallocenophanes of Li, Na, K, Cs, Ca, Ba,[10] As, Sn and Pb.[11]

Consequently, we sought to extend the scope of such complexes by introducing group IV metal centers and in this paper we report the synthesis and characterization of a series of [2]borametallocenophanes of Zr and Hf with fluorenyl rings.

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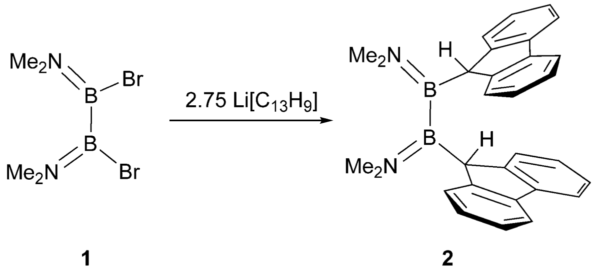
Results and Discussion

Ligand Precursors

In 1994 Nöth et al. described the synthesis of 1,2-bis(dimethylamino)-1,2-di-η^1-indenyldiborane(4)[12] and 1,2-bis(dimethylamino)-1,2-di-η^1-fluorenyldiborane(4) (**2**)[10] starting from 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) and Li[C_9H_7] or Li[$C_{13}H_9$]. According to this and our previously published method for the preparation of $(Me_2N)_2B_2(\eta^1\text{-}C_5H_5)_2$[13] and $(Me_2N)_2B_2(\eta^1\text{-}C_5H_5)(\eta^1\text{-}C_{13}H_9)$,[6] we prepared the ligand precursors from 1,2-dibromo-1,2-bis(dimethylamino)diborane(4) (**1**) in good yields (Scheme 2).



Scheme 2. Preparation of 1,2-bis(dimethylamino)-1,2-bis(η^1-fluorenyl)diborane(4) (**2**).

Constitution in the Solid State

Single crystals of the diprotonated pro-ligand were obtained from a concentrated toluene solution at –30 °C. The ligand crystallizes in the triclinic space group $P\bar{1}$. The molecule is twisted, with a dihedral C1-B–B–C14-angle of 66.8° (Figure 1).

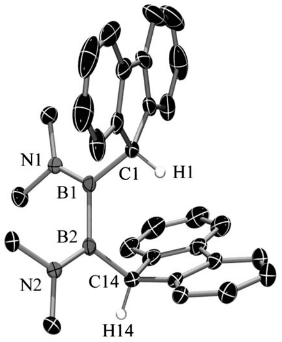
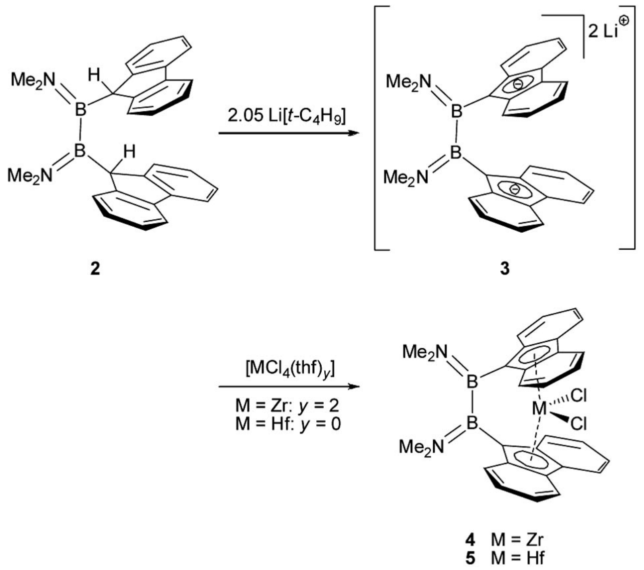


Figure 1. Crystal structure of $(Me_2N)_2B_2(\eta^1\text{-}C_{13}H_9)_2$ (**2**) (remaining hydrogen atoms omitted for clarity). Selected interatomic distances [Å] and angles [°]: B1–B2 1.709(3), B1–C1 1.625(3), B2–C14 1.613(3), B1–N1 1.392(3), B2–N2 1.399(3), torsion C1–B1–B2–C14 66.8, N1B1C1–N2B2C14 67.4, Flu/Flu 78.6.

Due to the protonated sp^3-hybridized *ipso*-carbon atoms, the planes of the fluorenyl rings adopt an almost orthogonal mutual disposition enclosing an angle of 78.6°. This constitution is comparable to the analogous monoborane $Me_2NB(\eta^1\text{-}C_{13}H_9)_2$ (78.2°)[14] and to that of 1,2-bis(dimethylamino)-1,2-bis(η^1-indenyl)diborane(4) (74.5°)[12] The boron bridge is a little shorter [1.709(3) Å] than in 1,2-diaryl-1,2-bis(dimethylamino)diboranes(4) [aryl = phenyl (C_6H_5) 1.714(4),[15] mesityl (C_9H_{11}) = 1.717(15),[15] indenyl (C_9H_7) = 1.726(4)[12]]. Only the dialkyldiboranes 1,2-bis(η^1-fluorenyl)-1,2-dipyrrolidinodiborane(4) [1.687(7) Å][16] and 1,2-bis(η^1-fluorenyl)-1,2-di-*tert*-butyldiborane(4) [1.697(4)][17] show shorter B–B distances. In comparison to the corresponding metallocenophanes, the boron–carbon bonds are slightly longer [1.625(3) and 1.613(3) Å] and additionally no bond length alternation like in $Me_2NB(\eta^1\text{-}C_{13}H_9)_2$ [1.693(13) and 1.559(13) Å][14] was observed.

Complexes of the Type $[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2MCl_2]$ [M = Zr (4), Hf (5)]

Metallocenophane complexes of **2** can be prepared via the dilithiated intermediate **3**[10] in a one-pot synthesis. 1,2-Bis(dimethylamino)-1,2-di-η^1-fluorenyldiborane(4) was treated with Li[*t*Bu] at –80 °C in toluene/diethyl ether, 10:1. After allowing the solution to slowly warm to room temperature, the reaction was stirred overnight, resulting in a bright yellow solution. This solution was taken without further purification and combined with the corresponding group IV metal halides providing the desired [2]borametallocenophanes, as depicted in Scheme 3. The raw products were washed several times with cold hexane, resulting in pure samples of **4** and **5**.



Scheme 3. Metal complexes of 1,2-bis(dimethylamino)-1,2-di-η^1-fluorenyldiborane(4) (**2**).

For a further investigation, mass spectra of the complexes were recorded, but all common techniques like EI, CI and ESI failed. In the case of MALDI-TOF(DCTP) (details see Experimental Section) we were able to obtain a mass spectrum of **4**, but not of **5**, which is most probably due to the lower stability of the hafnium complex.

Constitution in Solution

In the case of **4** and **5** we observed only a single set of three multiplets in the ^{1}H NMR spectra for the aromatic protons and two signals for the NMe_2 groups. In the ^{13}C NMR spectra two signals for the dimethylamino groups and surprisingly only two sharp and one very broad signal for the aromatic carbon atoms can be found, thus indicating dynamic behaviour at room temperature as observed before in the case of the related complexes $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2\text{-}ML_x]$ (ML_x = Fe,[18] $ZrCl_2$, $HfCl_2$, $TiCl_2$[6]).

In order to shed more light on this, NMR measurements at –50 °C were carried out. At low temperature, eight signals in the ^{1}H and twelve signals in the $^{13}C\{^1H\}$ NMR spectra were observed for the fluorenyl system, in agreement with NMR spectra previously recorded at room temperature for other bis(fluorenyl)[2]borametallocenophanes (M = Ca, Ba,[10] Sn, Pb[11]). However, the corresponding alkali metal derivatives (Li, Na, K, Cs) show only six signals in their $^{13}C\{^1H\}$ NMR spectra at room temperature, which was explained by a less effective coordination of the fluorenyl ring to the metal center, thus allowing rotation of the fluorenyl rings around the B–C bond.[10] The signal for the carbon atom attached to boron can not be observed due to the quadrupolar moment of the boron nucleus.

For the NMe_2 groups only two signals can be detected. This indicates a C_2-symmetric structure, with a twofold axis containing the metal atom and bisecting the B–B bond.

The values are summarized in Table 1. The assignment is based on ^{1}H–^{1}H and ^{1}H–^{13}C NMR correlation experiments and reinforced by simulation.

Constitution in the Solid State

The metallocenophanes **4** and **5** crystallize from concentrated benzene solutions at room temperature in the triclinic space group $P\bar{1}$ with two molecules of benzene in the asymmetric unit. Both molecules adopt the expected bent metallocene structure, with pseudo C_2-symmetry (Figure 2).

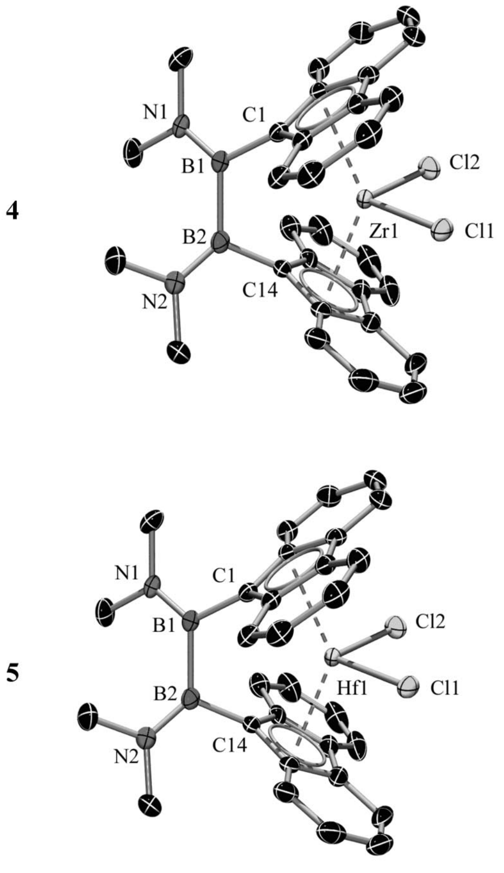
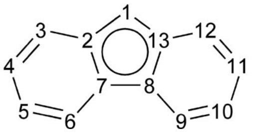


Figure 2. Crystal structures of compounds **4** and **5** (hydrogen atoms and solvent molecules omitted for clarity).

Due to the higher steric demand of the fluorenyl ligands, the tilt angle α is slightly larger [58.7° (**4**); 60.7°(**5**)] than in $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2ZrCl_2]$ (52.0°),[6] $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2HfCl_2]$ (52.0°),[13] $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)\text{-}ZrCl_2]$ (56.6°)[6] and $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)HfCl_2]$ (56.0°),[6] but still much smaller than in $[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2Li_2(thf)_5]$ (74.1°)[10] and $[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2\text{-}$

Table 1. NMR spectroscopic data (δ values, ppm) of compound **4** and **5** (CD_2Cl_2, br s = broad signal, assignment of the fluorenyl signals, see depicted numbering scheme).



Compound	^{1}H NMR	$^{13}C\{^1H\}$ NMR
4 (298 K)	3.05, 3.56 $[N(CH_3)_2]$, 7.08–7.17, 7.26–7.33, 7.76–7.80 (CH_{Ar})	42.7, 45.0 $[N(CH_3)_2]$, 124.7 (br s), 125.6, 128.1 (CH_{Ar}),
4 (223 K)	2.99, 3.51 $[N(CH_3)_2]$, 7.03 (H11), 7.16 (H12), 7.19 (H4), 7.24 (H10), 7.33 (H5), 7.65 (H3), 7.73 (H9), 7.80 (H6)	42.11, 45.2 $[N(CH_3)_2]$, 123.2 (C3), 123.6 (C9), 124.3 (C2,13), 124.7 (C6), 125.15 (C5), 125.18 (C10), 127.4 (C2,13), 127.49, 127.56, 127.62 (C4,11,12), 128.8, 129.4 (C7,8)
5 (298 K)	3.05, 3.56 $[N(CH_3)_2]$, 7.05–7.17, 7.26–7.34, 7.76–7.81 (CH_{Ar})	42.5, 45.0 $[N(CH_3)_2]$, 124.7 (br s), 125.6, 128.1 (CH_{Ar}),
5 (223 K)	2.99, 3.52 $[N(CH_3)_2]$, 7.00 (H11), 7.17 (H4), 7.18 (H12), 7.22 (H10), 7.30 (H5), 7.68 (H3), 7.73 (H9), 7.80 (H6)	42.15, 44.6 $[N(CH_3)_2]$, 123.1 (C3), 123.3 (C2,13), 123.4 (C9), 124.5 (C6), 124.8 (C10), 125.0 (C5), 126.9 (C2,13), 127.1 (C7,8) 127.2, 127.38, (C4,12), 127.43 (C11), 128.8 (C7,8)

Ca(thf)] (73.4°).[10] The angle δ (Flu^c–M–Flu^c, Flu^c is the centroid of the five-membered ring of $C_{13}H_8$) amount to 134.0° (**4**) and 134.8° (**5**), respectively. The distances between Flu^c and the metal center [2.279 and 2.264 Å (**4**), 2.251 and 2.270 Å (**5**)] are comparable to those of the [2]-carba-bridged zirconium analogue (2.284 and 2.253 Å).[4b] In both complexes, the metal center is not perfectly η^5-coordinated, but shows a marked distortion toward η^3-bonding, as indicated by carbon–metal bond lengths ranging between 2.46 to 2.69 (**4**) and 2.42 to 2.69 Å (**5**).

The B–N bond lengths are in each case around 1.39 Å, indicating the boron nitrogen double bond character. However, the B–C_{ipso} bond lengths of 1.58 Å give no hint of B–C π-interaction, as observed in η^1-fluorenylidene(2,2,6,6-tetramethylpiperidino)borane [B–C bond order 2: 1.422(7) Å][19] and discussed for $[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2Li_2\cdot 5thf]$ (B–C bond order 1.5: 1.526 Å).[10]

The B–B bond lengths are in the expected range. Selected bond lengths and angles are summarized in Table 2.

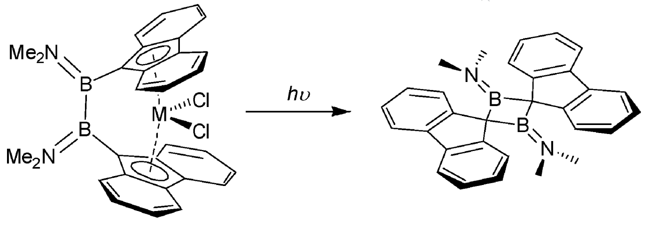
Table 2. Selected bond lengths [Å] and angles [°] of **4** and **5**.

	4	**5**
Tilt angle α	58.7	60.7
Torsion C1–B1–B2–C14	40.2	40.0
Flu^c–M–Flu^c (δ)	140.0	134.8
Cl1–M–Cl2	95.141(14)	94.86(3)
C1–B1–B2	109.9(12)	110.3(2)
C14–B2–B1	110.83(12)	110.2(2)
M–Cl1	2.4214(4)	2.3840(8)
M–Cl2	2.4116(16)	2.3938(7)
M– Flu^c1	2.279	2.251
M– Flu^c2	2.264	2.270
B1–C1	1.583(2)	1.576(4)
B2–C14	1.581(2)	1.577(4)
B1–B2	1.711(2)	1.716(5)
B1–N1	1.389(2)	1.396(4)
B2–N2	1.396(2)	1.397(4)

Rearrangement Reactions

All metallation reactions have to be carried out in browntinted glassware, as exposure of the reaction mixture to UV-light induces a almost quantitative rearrangement reaction (Scheme 4) as previously observed by Nöth and coworkers,[11] although isolated **3** as well as **4** and **5** seem to be stable against UV and visible light.

While a detailed mechanism of the rearrangement still remains unknown, it was suggested that the η^5-M bond is broken upon exposure to UV light and a bond between the *ipso*-carbon atoms is formed with ring contraction. The resulting 1,2 diboretane then rearranges to the thermodynamically favoured 1,3-diboretane.[11] While **6** has been previously characterized in solution by multinuclear NMR spectroscopy, its structure in the crystal is now reported for the first time. *N*,*N*,*N*′,*N*′-Tetramethyldispiro[fluorene-9,2′-[1,3]diboretane-4′,9′′-fluorene]-1′,3′-diamine (**6**) crystallizes in the orthorhombic space group *Fdd*2, with only one half of the molecule in the asymmetric unit (Figure 3).



4 M = Zr
5 M = Hf

6

Scheme 4. Rearrangement of **4** and **5** to *N*,*N*,*N*′,*N*′-tetramethyldispiro[fluorene-9,2′-[1,3]diboretane-4′,9′′-fluorene]-1′,3′-diamine (**6**).

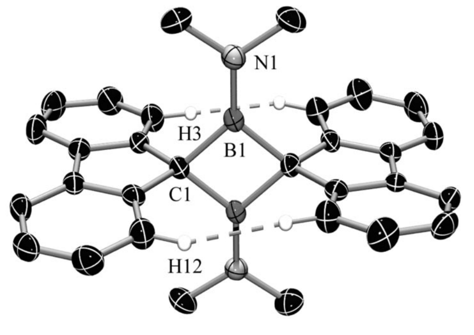


Figure 3. Crystal structure of **6** (remaining hydrogen atoms omitted for clarity).

Surprisingly, the rhombic B_2C_2 ring is planar and the puckering of the four-membered ring along the C1–C1′ axis amounts to only 0.27°. This finding is in contrast to the bis(trimethylsilylamino) derivative, in which the ring is folded about 23.1°, due to the higher steric demand of the $N(SiMe_3)_2$ groups.[19]

The $B(NMe_2)$ plane in **6** is nearly orthogonal to the plane of the fluorenyl ring (87.77°). The fluorenyl ring itself is not perfectly planar. The two C6-rings are bent to a "butterfly"-like structure, with an angle of 8.08° between the two aromatic ring systems. This deviation from planarity is probably due to a repulsion of the hydrogen atoms at C3 and C12. (H3···H3A 2.120 Å, H12···H12A 2.133 Å). The B–N bond length (1.360 Å) is significantly shortened by about 0.02 Å in comparison to those of the metallocenophanes **4** and **5**. The B–C distance [1.623(1) Å] is comparable to that of the pro-ligand **2**.

Selected bond lengths and angles of **6** are summarized in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] of **6**.

	6		**6**
B1–C1	1.623(1)	Flu/B1–$N(CH_3)_2$	87.77
B1–N1	1.360(3)	Flu/Flu′	3.72
B1–B1′	2.099	C2–C7/C8–13	8.08
C1–C1′	2.472		

Conclusions

The first difluorenyl[2]borametallocenophanes of Zr and Hf were obtained via multistep salt elimination reactions and analysed by various spectroscopic methods. In contrast to known [1]borametallocenophanes the title compounds are characterised by fluxional behaviour in solution, facilitated by the less rigid diboradiyl bridge. Variable-temperature ^{1}H NMR spectra indicated dynamic behaviour at ambient temperature, which was effectively frozen at –50 °C. Studies on the effect of the increased flexibility, which is believed to enhance the catalytic activity, are currently ongoing. Additionally, the synthesis of the title compounds was found to be accompanied by a light-induced rearrangement process, yielding a 1,3-diboretane. While corresponding rearrangements have been described for a few main-group metal derivatives of difluorenyldiboranes(4), the 1,3-diboretane obtained here was characterized by X-ray analysis for the first time.

Experimental Section

General: All manipulations were carried out under dry argon using common Schlenk techniques or a Labmaster Glovebox from M. Braun. Solvents were dried with a solvent purification system (SPS) from M. Braun and stored under argon over molecular sieves; reagents were dried and purified by standard procedures. All metallations have been performed in brown-tinted glassware.

$[ZrCl_4(thf)_2]$,[20] $Li[C_{13}H_9]$[14] and **1**[21] were obtained according to literature procedures. $HfCl_4$ and Li*t*Bu were obtained commercially and used without further purification. NMR: Bruker Avance 500 at 500.13 MHz (^{1}H, external standard TMS), 125.77 MHz ($^{13}C\{^{1}H\}$, external standard TMS) and 160.46 MHz (^{11}B, $BF_3{\cdot}OEt_2$ in C_6D_6 as external standard). Bruker Avance 200 at 200.13 MHz (^{1}H, internal standard TMS) and 64.22 MHz (^{11}B, $BF_3{\cdot}OEt_2$ in C_6D_6 as external standard). Elemental analyses (C, H, N) could not be obtained, because traces of lithium chloride could not be fully removed due to the limited solubility of the complexes. Mass spectra were recorded with a Thermo Finnigan Trio 1000-GCMS/LCMS (EI, CI) or a Bruker micrOTOF focus (ESI). The MALDI mass spectra were performed with a Bruker Daltonics autoflex II mass spectrometer, equipped with MidiNitrogen laser MNL (LTB Lasertechnik, Berlin) 337 nm. Calibration was performed externally with 1.00 µL of a mixture of 10 mg/mL PEG1000 (Lancaster) in methanol, a saturated solution 2,5-dihydroxybenzoic acid (Bruker Daltonics) in methanol and sodium iodide (1 mg/mL in methanol) 10:10:1. 1.00 µL of the sample solutions (2.00 mM in THF) and 2.00 µL of a 100 mg/mL matrix solution (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB; Fluka)) in THF were mixed and 0,50–1.00 µL were dropped onto the stainless steel target (MTP 384 massive target T; Bruker Daltonics #26755). Due to the isotopic distribution over a broad *m*/*z* region caused by chlorine, and/or zirconium the signal of monoisotopic signals was too small for some compounds in intensity for an accurate mass measurement. In this case, the most intense signal (X + *n*) of this isotopic distribution was taken as described and compared with the respective calculated value. For calculation of the respective mass values of the isotopic distribution, the software modul "Bruker Daltonics IsotopePattern" of the software Compass 1.1 from Bruker Daltonik GmbH, Bremen was used.

$(Me_2N)_2B_2(\eta^1\text{-}C_{13}H_9)_2$ (2): Compound **1** (3.75 g, 13.9 mmol) was added at 0 °C to a solution of $Li[C_{13}H_9]$ (6.57 g, 38.2 mmol) in toluene/diethyl ether (90 mL, 2:1) over approx. 20 min. While warming to room temperature the reaction mixture turns slightly yellow. After stirring for 48 h at ambient temperatures all volatiles were removed under reduced pressure. The product was extracted with toluene (20 mL) and washed three times with hexane (20 mL), resulting **2** (4.40 g, 74%) as a white solid. ^{1}H NMR (200 MHz, C_6D_6, 298 K): δ = 2.34, 2.86 [s, 12 H, $N(CH_3)_2$], 3.90 (s, 2 H, H1), 7.06–7.52 (m, 16 H, CH_{Flu}) ppm. ^{11}B NMR (64.22 MHz, C_6D_6, 298 K): δ = 48.11 ppm.

$[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2ZrCl_2]$ (4): Li*t*Bu (2.98 mL, 4.47 mmol, 1.5 mol/L in hexane) was added at –78 °C to a solution of **2** (0.96 g, 2.18 mmol) in toluene/diethyl ether (44 mL, 10:1) over approx. 10 min. The solution was slowly warmed to room temperature and stirred for 16 h. The solution of **3** was cooled to –78 °C and $[ZrCl_4(thf)_2]$ (0.86 g, 2.28 mmol) in diethyl ether (36 mL, –78 °C) was added in one portion. After stirring for 16 h at ambient temperatures all volatiles are removed under reduced pressure. The product was extracted with toluene (30 mL, 60 °C) and washed with hexane (4 × 20 mL, –60 °C) by centrifugation. The solid was dried in vacuo, resulting **4** (0.13 g, 10%) as a yellow powder. ^{1}H NMR (500 MHz, CD_2Cl_2, 223 K): δ = 2.99, 3.51 [s, 12 H, $N(CH_3)_2$], 7.03 (pt, $^{3}J_{H11,H12}$ = 8.5, $^{3}J_{H11,H10}$ = 7.5 Hz, 2 H, H11), 7.16 (d, $^{3}J_{H12,H11}$ = 8.5 Hz, 2 H, H12), 7.19 (pt, $^{3}J_{H4,H3}$ = 8.5, $^{3}J_{H4,H3}$ = 7.7 Hz, 2 H, H4), 7.24 (pt, $^{3}J_{H10,H9}$ = 8.4, $^{3}J_{H10,H9}$ = 7.5 Hz, 2 H, H10), 7.33 (pt, $^{3}J_{H5,H6}$ = 8.3, $^{3}J_{H5,H4}$ = 7.7 Hz, 2 H, H5), 7.65 (d, $^{3}J_{H3,H4}$ = 8.5 Hz, 2 H, H3), 7.73 (d, $^{3}J_{H9,H10}$ = 8.4 Hz, 2 H, H9), 7.80 (d, $^{3}J_{H6,H5}$ = 8.3 Hz, 2 H, H6) ppm. ^{11}B NMR (160.46 MHz, CD_2Cl_2, 298 K): δ = 44.0 ppm. $^{13}C\{^{1}H\}$ NMR (125.77 MHz, CD_2Cl_2, 223 K): δ = 42.1, 45.2 [$N(CH_3)_2$], 123.2 (C3), 123.6 (C9), 124.3 (C2,13), 124.7 (C6), 125.15 (C5), 125.18 (C10), 127.4 (C2,13), 127.49, 127.56, 127.62 (C4,11,12), 128.8, 129.4 (C7,8) ppm. MS (MALDI-TOF) *m*/*z* (X + 4 of $M^{\cdot+}$) = 600.093 (calcd. 600.086).

$[(Me_2N)_2B_2(\eta^5\text{-}C_{13}H_8)_2HfCl_2]$ (5): Li[*t*Bu] (3.28 mL, 4.91 mmol, 1.5 mol/L in hexane) was added at –78 °C to a solution of **2** (1.03 g, 2.34 mmol) in toluene/diethyl ether (44 mL, 10:1) over approximately 10 min. The solution was slowly warmed to room temperature and stirred for 16 h. The solution of **3** was cooled to –78 °C and $HfCl_4$ (0.79 g, 2.46 mmol) in diethyl ether (36 mL, –78 °C) was added in one portion. After stirring for 16 h at ambient temperature all volatiles are removed under reduced pressure. The product is extracted with toluene (30 mL, 60 °C) and washed with hexane (4 × 20 mL, –60 °C) by centrifugation. The solid is dried in vacuo, providing **5** (0.13 g, 10%) as an orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2, 223 K): δ = 2.99, 3.52 [s, 12 H, $N(CH_3)_2$], 7.00 (pt, $^{3}J_{H11,H12}$ = 8.5, $^{3}J_{H11,H10}$ = 7.7 Hz, 2 H, H11), 7.17 (pt, $^{3}J_{H4,H3}$ = 8.5, $^{3}J_{H4,H5}$ = 7.2 Hz, 2 H, H4), 7.18 (d, $^{3}J_{H12,H11}$ = 8.5 Hz, 2 H, H12), 7.22 (pt, $^{3}J_{H10,H9}$ = 8.4, $^{3}J_{H10,H11}$ = 7.4 Hz, 2 H, H10), 7.30 (pt, $^{3}J_{H5,H6}$ = 8.4, $^{3}J_{H5,H4}$ = 7.2 Hz, 2 H, H5), 7.68 (d, $^{3}J_{H3,H4}$ = 8.5 Hz, 2 H, H3), 7.73 (d, $^{3}J_{H9,H10}$ = 8.4 Hz, 2 H, H9), 7.80 (d, $^{3}J_{H6,H5}$ = 8.4 Hz, 2 H, H6) ppm. ^{11}B NMR (160.46 MHz, CD_2Cl_2, 298K): δ = 44.9 ppm. $^{13}C\{^{1}H\}$ NMR (125.77 MHz, CD_2Cl_2, 223 K): δ = 42.2, 44.6 [$N(CH_3)_2$], 123.1 (C3), 123.3 (C2,13), 123.4 (C9), 124.5 (C6), 124.8 (C10), 125.0 (C5), 126.9 (C2,13), 127.1 (C7,8) 127.2, 127.38 (C4,12), 127.43 (C11), 128.8 (C7,8) ppm.

The crystal data of **2** and **4** were collected using a Bruker X8Apex diffractometer with multi-layer mirror monochromated Mo-K_α radiation. The crystal data of **5** and **6** were collected using a Bruker Apex diffractometer with graphite-monochromated Mo-K_α radiation. Both diffractometers were equipped with CCD area detectors.

The structures were solved by direct methods, refined with SHELX software package (G. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112–122) 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 2: $C_{30}H_{30}B_2N_2$, M_r = 440.18, transparent block, $0.23 \times 0.11 \times 0.055$ mm^3, triclinic space group $P\bar{1}$, a = 9.8868(7) Å, b = 14.8990(10) Å, c = 18.4885(19) Å, α = 107.272(4)°, β = 93.201(4)°, γ = 106.556(3)°, V = 2463.3(3) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.187 g cm^{-3}, μ = 0.068 mm^{-1}, $F(000)$ = 936, T = 100(2) K, R_1 = 0.0850, wR^2 = 0.1607, 9593 independent reflections [$2\theta \leq 52.08°$] and 613 parameters.

Crystal Data for 4: $C_{39}H_{37}B_2Cl_2N_2Zr$, M_r = 717.45, orange block, $0.04 \times 0.09 \times 0.20$ mm^3, triclinic space group $P\bar{1}$, a = 10.6094(3) Å, b = 11.0459(3) Å, c = 15.7270(4) Å, α = 101.1170(10)°, β = 94.1700(10)°, γ = 111.0310(10)°, V = 1667.61(8) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.429 g cm^{-3}, μ = 0.522 cm^{-2}, $F(000)$ = 738, T = 100(2) K, R_1 = 0.0253, wR^2 = 0.0591, 6560 independent reflections [$2\theta \leq 52.14°$] and 415 parameters.

Crystal Data for 5: $C_{39}H_{37}B_2Cl_2HfN_2$, M_r = 804.72, yellow needle, $0.33 \times 0.08 \times 0.02$ mm^3, triclinic space group $P\bar{1}$, a = 10.6088(7) Å, b = 11.1434(8) Å, c = 15.7972(11) Å, α = 100.8700(10)°, β = 94.5160(10)°, γ = 110.9910(10)°, V = 1690.4(2) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.581 g cm^{-3}, μ = 3.275 mm^{-1}, $F(000)$ = 802, T = 166(2) K, R_1 = 0.0314, wR^2 = 0.0713, 8352 independent reflections [$2\theta \leq 56.72°$] and 470 parameters.

Crystal Data for 6: $C_{30}H_{28}B_2N_2$, M_r = 438.16, yellow block, $0.29 \times 0.15 \times 0.15$, orthorhombic space group $Fdd2$, a = 37.307(7) Å, b = 8.9253(16) Å, c = 14.342(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 4775.6(15) Å^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.219 g cm^{-3}, μ = 0.070 mm^{-1}, $F(000)$ = 1856, T = 173(2) K, R_1 = 0.0500, wR^2 = 0.1091, 2368 independent reflections [$2\theta \leq 52.18°$] and 154 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-721484 (for **4**), -721485 (for **5**) and -721486 (for **6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Additional information (^{1}H and ^{13}C NMR spectra of **4** and **5**. MALDI-TOF of **4**) can be found in the Supporting Information

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