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[2]Borametallocenophanes of Group 4 Metals: Synthesis and Structure

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Abstract: We report a series of [2]borametallocenophanes of Ti, Zr, and Hf with various ligand systems. The ligands have been synthesized in high yields starting from 1,2-dibromo-1,2-bis(dimethylamino)diborane(4) upon reaction with Na[C_5H_5] and Li[$C_{13}H_9$], respectively. All compounds were fully characterized by multinuclear NMR spectroscopy and, for selected examples, by X-ray analysis.

Keywords: metallocenes · boron · hafnium · metallocenophanes · titanium · zirconium

Introduction

Metallocenophanes have been the focus of intense research for more than a decade due to their interesting chemistry and their highly useful application in areas such as material sciences and catalysis. For example, *ansa*-metallocenes derived from transition metals of Groups V to VIII[1] have been successfully employed for the generation of organometallic polymers by ring-opening polymerization (ROP); polyferrocenylsilane is the most prominent example.[2]

Likewise, metallocenophanes of early transition metals, in particular constrained geometry complexes (CGC) of Group 4 metals, have attracted much interest due to their vast potential as catalyst precursors for Ziegler–Natta type olefin polymerization. Besides a very high catalytic activity of the metallocenophanes, the facile ligand design of such complexes allows precise control of the stereoselective polymerization of propene. A wealth of review articles concerning this topic underscores the importance for academia and industry.[3]

By tailoring the ligand framework and the *ansa*-bridge in particular, highly active catalysts were designed and experimentally realized. Commonly R_2C, R_4C_2, and R_2Si bridges were incorporated and studied intensively with regard to their activity in ethylene and propylene polymerization.[3e,4]

The introduction of an aminoboranediyl bridge into the [1]borametallocenophanes is believed to be of some advantage with respect to the catalytic performance of such complexes, since the small boron atom imposes high rigidity, and therefore, has the potential to improve the stereoselectivity of the catalyst. In addition, a three-coordinate boron atom is to some extent Lewis acidic, a fact which is believed to enhance the catalytic activity of Group 4 [*n*]borametallocenophanes ($n=1, 2$).[5]

We[6] and others[7] have studied the synthesis, structure, and catalytic activity of Group 4 [1]borametallocenophanes and their related constrained geometry complexes. These studies have shown those complexes i) to exhibit an enhanced activity for the polymerization of ethylene and ii) to produce syndiotactic polypropylenes.

Reports on [*n*]carba-bridged metallocenophanes showed that the chain length of the resulting polymer is distinctly longer when a [2]carba-bridged catalyst is utilized as opposed to a [1]carba-bridged catalyst.[3e] Hence, we became interested in the question whether [2]borametallocenophanes are similarly advantageous and recently we communicated the first diaminodiborane(4)diyl-bridged complexes of the type $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2MCl_2]$ ($M=Zr$, Hf).[8] Preliminary polymerization results for these complexes already suggested a significantly improved polymerization performance over the unbridged zirconocene. Consequently, we sought to extend the scope of such complexes by varying both the metal center and the ligand framework, and herein we report the synthesis and characterization of a series of [2]borametallocenophanes of Ti, Zr, and Hf with ligand systems containing cyclopentadienyl and fluorenyl rings.

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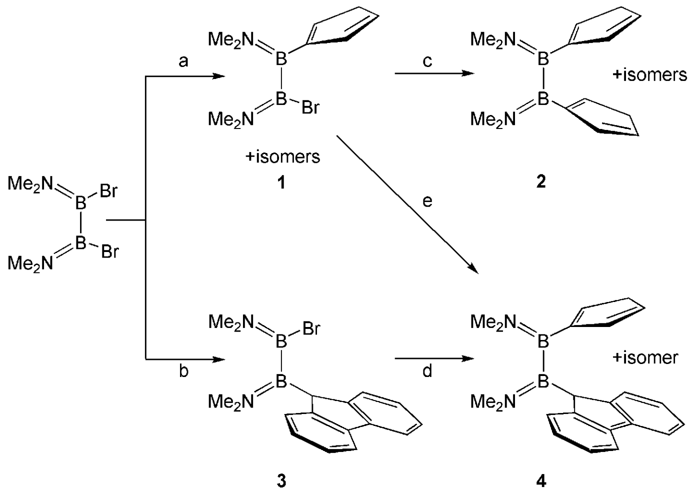
Results and Discussion

Ligand precursors: In 1994 Nöth et al. described the syntheses of 1,2-bis(dimethylamino)-1,2-bis(η^1-indenyl)diborane(4) and 1,2-bis(dimethylamino)-1,2-bis(η^1-fluorenyl)diborane(4) starting from 1,2-bis(dimethylamino)-1,2-dichlorodiborane(4) and Li[C_9H_7] or Li[$C_{13}H_9$]. The corresponding 1,2-bis(dimethylamino)-1,2-bis(η^1-cyclopentadienyl)diborane(4) (**2**), however, is not accessible by this route.[9] Based on our successful synthesis of **2** via the monosubstituted intermediate **1**, by employing the more reactive 1,2-bis(dimethylamino)-1,2-dibromodiborane(4),[8] we obtained **4** as the first diborane(4) species bearing one cyclopentadienyl (Cp) and one fluorenyl (Flu) group as a potentially useful ligand precursor for the generation of stereoregular syndiotactic polypropylene (Scheme 1).[8]



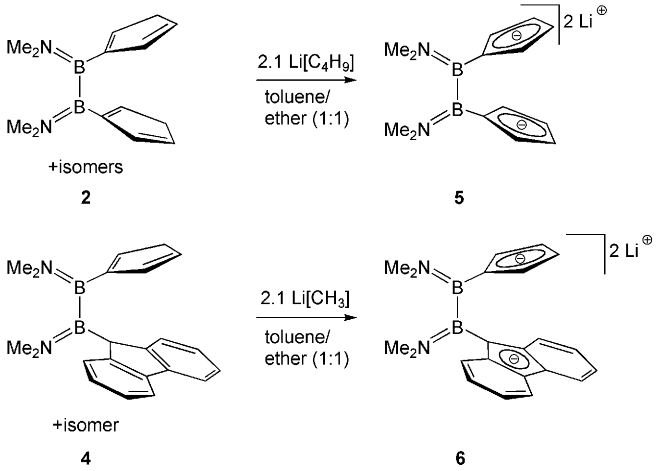
Scheme 1. a) 1 equiv Na[C_5H_5], toluene, RT; b) 1 equiv Li[$C_{13}H_9$], toluene, RT; c) 1.2 equiv Na[C_5H_5], toluene/diethyl ether (1:1), RT; d) 1.2 equiv Na[C_5H_5] toluene/diethyl ether (1:1); e) 1 equiv Li[$C_{13}H_9$], toluene/diethyl ether (1:1), RT.

Compound **2** can be obtained by reacting 1,2-bis(dimethylamino)-1,2-dibromodiborane(4) with two equivalents of Na[C_5H_5] in the presence of diethyl ether (Scheme 1). After workup, **2** is isolated as a yellow oil in almost quantitative yields. The NMR spectroscopic data reveal the presence of isomers, as already observed and thoroughly studied for amino[bis(cyclopentadienyl)]boranes.[10] Owing to the presence of up to three isomers, the ^{1}H and ^{13}C NMR spectra are rather complex. The ^{11}B NMR spectrum displays a signal at $\delta = 46.0$ ppm, which is deshielded with respect to that of the starting diborane(4).

Compound **4** can be obtained by two different routes (Scheme 1); higher yields, though, are obtained by reacting the 1,2-bis(dimethylamino)-1,2-dibromodiborane(4) with Li[$C_{13}H_9$] in toluene to yield **3**, which subsequently is treated with a slight excess of Na[C_5H_5] in a 1:1 mixture of toluene and diethyl ether. The multinuclear NMR spectra reveal two sets of signals in a 2:1 ratio, due to the presence of the thermodynamically favored *va* and *vh* isomers.[10] By employing proton–proton and proton–carbon correlation NMR experiments, all signals could be assigned, and in the following discussion the corresponding ^{13}C NMR signals are given in parentheses. For the main isomer the methyl groups give rise to signals at $\delta = 2.36$, 2.40, 2.71, and 2.74 ppm ($\delta = 40.10$, 40.45, 45.39 and 45.62 ppm), the signal for the CH_2 fragment of the Cp ring is observed as multiplet at $\delta = 2.60$ ppm (45.83 ppm) and the proton attached to the *ipso*-carbon of the fluorenyl ring can be detected at $\delta = 4.15$ ppm. The corresponding ^{13}C NMR signal was detected at $\delta = 46.7$ ppm as a broad resonance, due to the quadrupolar coupling to boron. Three multiplets at $\delta = 6.23$, 6.45, and 6.55 ppm ($\delta =$ 133.69, 135.95, and 138.65 ppm) were assigned in the proton NMR spectrum to the Cp ring, and the eight protons of the fluorenyl ring give rise to two multiplets at $\delta = 7.80$, 7.42 ppm and a complex area between $\delta = 7.2$ and 7.3 ppm. Here, the corresponding ^{13}C NMR signals were observed at $\delta = 120.35$, 125.53, 126.60, and 126.63 ppm; the remaining two resonances for the quaternary carbons were found at $\delta = 142.33$ and 149.85 ppm. Similarly, for the minor isomer four signals in the ^{1}H NMR spectrum were detected for the methyl groups at $\delta = 2.37$, 2.42, 2.70, and 2.78 ppm ($\delta =$ 40.04, 40.39, 40.95, and 45.07 ppm). The aliphatic protons on the Cp and fluorenyl fragment were found at $\delta = 2.70$ and 4.16 ppm ($\delta = 43.42$ and 46.7 ppm). The latter ^{13}C NMR signal was broadened due to the quadrupolar coupling to boron. The olefinic protons on the Cp give rise to three multiplets at $\delta = 5.87$, 6.22, and 6.28 ppm ($\delta = 131.44$, 137.24, and 137.36 ppm) and the aromatic protons of the fluorenyl ring can be detected as a complex area ranging from $\delta = 7.2$ to 7.6 ppm. In the ^{13}C NMR spectrum four signals correlate to the complex area at $\delta = 120.50$, 124.83, 125.35, and 125.75 ppm. Two additional signals were found and assigned to the quaternary carbons of the fluorenyl ring at $\delta = 142.65$ and 149.25 ppm. As observed before, for both isomers only one ^{11}B NMR signal at $\delta = 47.40$ ppm was detected.[10]

Deprotonation of the ligand precursors: Compounds **2** and **4** can be reacted in a toluene/diethyl ether mixture (1:1) at low temperatures with various lithium organyls to yield the deprotonated ligand species **5** and **6** (Scheme 2).

A solution of **2** in a 1:1 mixture of toluene and diethyl ether was treated with 2.1 equivalents of Li[C_4H_9] at −80 °C and slowly allowed to warm to room temperature, resulting in a colorless suspension. Compound **5** can be isolated in high yields as an amorphous and pyrophoric off-white powder, which is soluble in THF. The NMR spectroscopic data of **5** provide evidence for the coordination of two molecules of ether per ligand. In the ^{1}H NMR spectrum two pseudo-triplets were observed at $\delta = 5.76$ and 6.01 ppm, respectively, corresponding to the protons of the cyclopentadienyl rings, which exhibited an AA′BB′ spin system, and hence, C_2 symmetry in solution. The corresponding carbon signals in the ^{13}C NMR spectrum at $\delta = 106.11$ and 113.78 ppm are in line with this description. The signal for the carbon atom attached to boron cannot be observed due



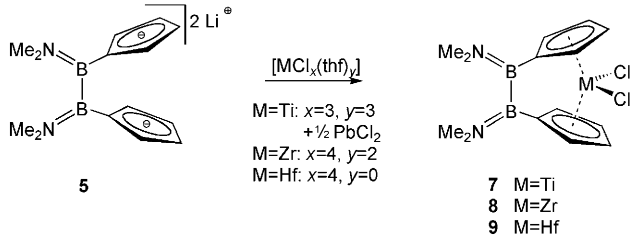
Scheme 2. Deprotonation of the ligands **2** and **4**.

to the quadrupolar moment of the boron nucleus. The methyl groups attached to nitrogen give rise to two signals at $\delta = 3.01$ and 3.18 ppm ($\delta = 41.15$, 46.71 ppm), thus indicating hindered rotation with respect to the B–N bonds. The ^{7}Li NMR spectrum shows a signal at $\delta = -5.75$ ppm and the ^{11}B NMR spectrum reveals a signal at $\delta = 45.77$ ppm, the latter of which is comparable to that of **2**.

In a similar reaction, a solution of **4** is treated with Li[CH$_3$] in a 1:1 mixture of toluene and diethyl ether at low temperatures. The dilithiated species **6** can be obtained in high yields as a pale orange pyrophoric powder. As for **5**, the NMR spectroscopic data of **6** reveal the presence of coordinated diethyl ether. Owing to the different substitution pattern of the boron atoms, four signals in the ^{1}H NMR spectrum for the methyl groups at $\delta = 3.01$, 3.22, 3.33, and 3.34 ppm are observed, which correlate with the signals at $\delta = 41.25$, 43.62, 45.27, and 46.00 ppm in the ^{13}C NMR spectrum. The four protons of the cyclopentadienyl ring give rise to two signals at $\delta = 5.68$ and 6.04 ppm, which together with signals in the carbon NMR spectrum at $\delta = 107.56$ and 110.20 ppm indicate C_s symmetry in solution. Correspondingly, the fluorenyl ring exhibits four signals for the eight protons at $\delta = 6.47$, 6.86, 7.55, and 7.81 ppm, respectively. Here, the respective signals for the carbon atoms are found at $\delta = 113.20$, 118.46, 119.61, and 120.12 ppm. Further signals in the ^{13}C NMR spectrum at $\delta = 127.26$ and 142.30 ppm are assigned to the quaternary carbons of the fluorenyl fragment. In the ^{7}Li NMR spectrum a signal is observed at $\delta = -5.36$ ppm, and the ^{11}B NMR spectrum shows a signal at $\delta = 47.80$ ppm, hence being almost identical to the signal observed for **4** ($\delta = 47.40$ ppm).

Complexes of the type [(Me$_2$N)$_2$B$_2$(η^5-C$_5$H$_4$)$_2$MCl$_2$] (M = Ti, Zr, Hf): The lithiated ligand **5** was allowed to react with the corresponding Group 4 metal halides, that is, [TiCl$_3$(thf)$_3$], [ZrCl$_4$(thf)$_2$],[8] and HfCl$_4$,[8] at low temperatures (Scheme 3).

The titanium complex **7** must be synthesized via a Ti^{III} precursor followed by oxidation to the final Ti^{IV} species due to the redox behavior of Ti under these conditions.[11] The NMR spectra of **7**–**9** are very similar, as expected, and the corresponding data are shown in Table 1. Two signals for the methyl groups as well as two pseudo-triplets for the cyclopentadienyl rings indicate C_{2v} symmetry in solution. Accordingly, four signals are observed in the ^{13}C NMR spectrum, two assigned to the methyl groups and two to the aromatic five-membered ring systems. A signal for the carbon atom attached to boron in the ^{13}C NMR spectrum could not be observed due to the quadrupolar coupling with boron. The boron signals in the ^{11}B NMR spectrum are marginally highfield shifted with respect to those of the ligand precursor **2**.

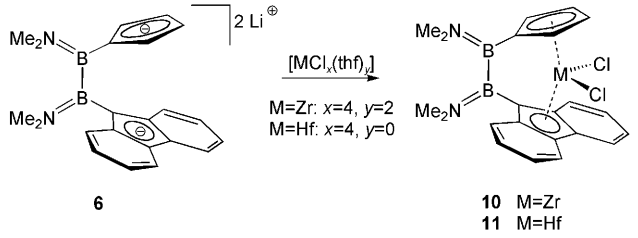


Scheme 3. Metal complexes of ligand **5**.

Table 1. NMR spectroscopic data and yields of compounds **7**–**9**.

Compound	^{1}H NMR [ppm]	^{11}B NMR [ppm]	^{13}C NMR [ppm]	Yield [%]
7	2.97, 3.13 (Me) 6.17, 6.85 (CH$_{Cp}$)	43.5	40.71, 45.28 (Me) 120.78, 129.83 (CH$_{Cp}$)	64
8	2.99, 3.13 (Me) 6.17, 6.85 (CH$_{Cp}$)	42.9	40.55, 45.19 (Me) 116.69, 125.31 (CH$_{Cp}$)	68
9	2.98, 3.13 (Me) 5.96, 6.64 (CH$_{Cp}$)	42.9	40.65, 45.22 (Me) 114.95, 123.84 (CH$_{Cp}$)	72

Complexes of the type [(Me$_2$N)$_2$B$_2$(η^5-C$_5$H$_4$)(η^5-C$_{13}$H$_8$)MCl$_2$] (M = Zr, Hf): Similar to the procedure described before, **10** and **11** are obtained by treating a suspension of **6** in a toluene/diethyl ether mixture (1:1) at −80 °C with the metal halides (Scheme 4).



Scheme 4. Metal complexes of ligand **6**.

As to be expected, the NMR-spectroscopic data of the complexes are very similar, and in the ^{1}H NMR spectrum of, for example, **10**, four signals for the methyl groups at $\delta = 2.91$, 3.09, 3.35, and 3.36 ppm ($\delta = 40.71$, 42.05, 45.16, 45.19) can be found at room temperature. The CH groups of the

Cp ring arise at $\delta=5.98$ (pt) and 6.32 (pt) ppm, and the eight hydrogen atoms of the fluorenyl ring can be detected as multiplets at $\delta=7.28$, 7.38, 7.56, and 8.05 ppm. Even though the corresponding carbon atoms in the fluorenyl ring could be assigned in the ^{13}C NMR spectrum (CH_{flu}: $\delta=$ 124.75, 124.88, 125.90, 128.44; $C_{q/flu}$: $\delta=127.63$ ppm), the signals for the carbon atoms of the cyclopentadienyl ring are not visible at ambient temperature, and the ^{11}B NMR resonance ($\delta=43.49$ ppm) is somewhat shielded with respect to that of the free ligand.

At −50 °C, however, the signals associated with the Cp ring could be detected as four multiplets at $\delta=5.90$, 6.02, 6.21, and 6.37 ppm in the ^{1}H NMR spectrum and corresponding resonances in the ^{13}C NMR spectrum at $\delta=112.45$, 115.41, 119.98, and 127.10 ppm.

Dynamic behavior of bis(cyclopentadienyl) complexes in solution: In 1997, Wrackmeyer, Herberhold et al. described the diboranediyl-bridged *ansa*-ferrocene $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2Fe]$. This [2]boraferrocenophane exhibits a dynamic process in solution due to a motion of the cyclopentadienyl rings, that is switching between a staggered and eclipsed conformation (Figure 1), which becomes only apparent at low temperatures.[12] This dynamic process was ascribed to the common property of amino-substituted diboranes(4) to avoid conformations in which the axes passing through the boron p_z orbitals adopt a parallel orientation.[9,12,13]

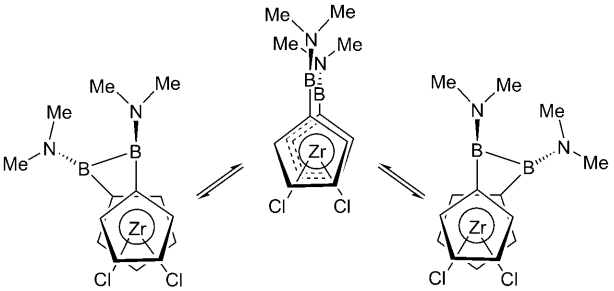


Figure 1. Dynamic process of [2]borametallocenophanes.

The Zr complex **8** was chosen as an representative example to study the dynamic behavior of the bis(cyclopentadienyl)complexes described here. As in the case of the aforementioned *ansa*-ferrocene,[12] **8** exhibits, at ambient temperature, signal patterns in the ^{1}H and ^{13}C NMR spectra corresponding to C_{2v} symmetry, giving evidence for a dynamic process that is fast compared to the NMR time scale. At lower temperatures, however, a gradual line broadening in the ^{1}H NMR spectrum is observed, and at −60 °C the signals for the favored staggered conformer become detectable in the ^{1}H and ^{13}C NMR spectra. At room temperature, two pseudo-triplets at $\delta=6.17$ and 6.85 ppm for the AA′BB′ spin system were observed, which at −60 °C split into four multiplets at $\delta=5.91$, 6.17, 6.70, and 6.75 ppm for the eight Cp protons, thus indicating a decrease of the symmetry from C_{2v} to C_s. Figure 2 shows the aromatic area of the proton NMR spectrum for **8** at different temperatures. The free enthalpy for the dynamic process in **8** was calculated to be $\Delta G^{++}_{251K}=52\pm1$ kJ mol^{-1} thus being only slightly higher by 8 kJ mol^{-1} than the value reported for the *ansa*-ferrocene.

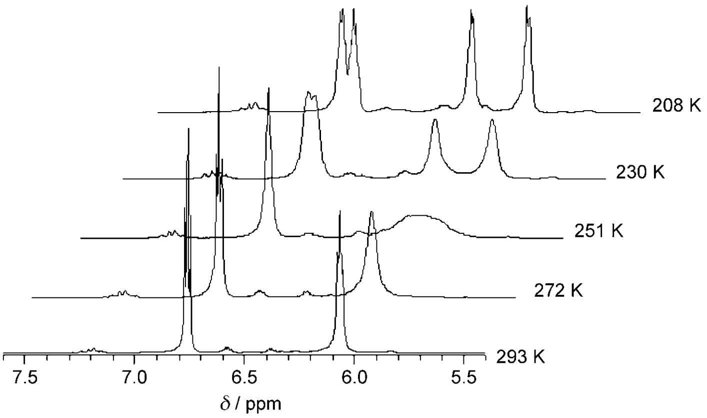


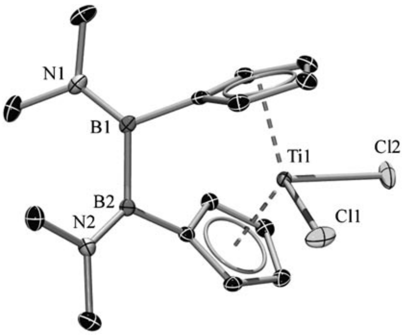
Figure 2. ^{1}H NMR variable-temperature experiment of **8**, recorded in CD_2Cl_2.

Constitution of the complexes in the solid state: Single crystals for **7**, **8**, and **9**[8] suitable for X-ray analyses were obtained by storing concentrated toluene solutions at −30 °C. Compound **7** crystallizes in the orthorhombic space group *Pbca*, compounds **8** and **9** in the monoclinic space group $P2_1/n$, and the respective molecules adopt C_2 symmetry (Figure 3).

The differences in the structural parameters of **7**–**9** are rather small and can be attributed to the different size of the central metals. The most notable impact imposed by the varying covalent radii of Ti, Zr, and Hf on the overall geometry is reflected by i) the tilt angle α, ranging from 48.8° (**7**) to 52.0° (**8**) and 51.8° (**9**), ii) by the angle δ, representing the angle between the centroids of the aromatic rings and the metal center, ranging from 132.4° (**7**), to 130.4° (**8**) and 130.7° (**9**), and iii) by the distance between the metal center and the centroid of the aromatic rings, which is distinctly shorter for **7** (2.070, 2.073 Å) than for **8** (2.205, 2.207 Å) and **9** (2.188, 2.191 Å). For all three complexes the geometry of the -B(NMe$_2$)-B(NMe$_2$)- bridge is unobtrusive and comparable to that in other [2]borametalloarenophanes.[1d,g,i,j,14] Selected bond lengths and angles are summarized in Table 2.

It is noteworthy that all three complexes adopt the aforementioned favored staggered conformation in the crystal, thus avoiding a linear arrangement of the C_{ipso}-B-B-C_{ipso} moieties as indicated by corresponding dihedral angles of about 50°.

Single crystals of **10** and **11** were obtained by storing concentrated toluene solutions at ambient temperature. Both compounds crystallize in the monoclinic space group $P2_1$ and the molecules adopt C_1 symmetry (Figure 4). The structural data confirm the predicted bent *ansa* geometry. The distances between the centroids of the cyclopentadienyl rings and the metal centers are similar to those observed for



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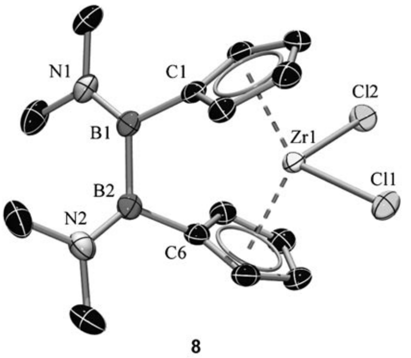

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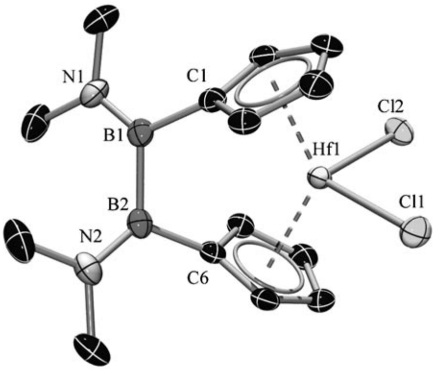

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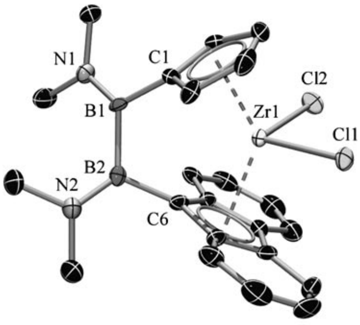
Figure 3. Crystal structures of compounds **7**–**9**.

7, **8**, and **9** (**10**: 2.195 Å, **11**: 2.173 Å). However, the distances between the metals and the center of the aromatic five-membered ring of the fluorenyl ligand are significantly increased by about 0.1 Å (**10**: 2.294 Å, **11**: 2.278 Å). This observation can be attributed to the fact that the fluorenyl ligand does not exhibit a regular η^5-coordination mode. The metal–carbon distances to the carbon atoms opposite to C_{ipso} (**10**: 2.712, 2.716 Å, **11**: 2.693, 2.699 Å) are about 0.25 Å longer than those to the *ipso*-carbons themselves (**10**: 2.453 Å, **11**: 2.438 Å). A similar geometry was already described by Lee et al. for the analogous [2]carbametallocenophanes.[15]

Table 2. Bond lengths [Å] and angles [°] of the crystal structures of **7**–**9**.

	7	**8**	**9**
tilt angle α	48.8	52.0	51.8
torsion C_{ipso}-B-B-C_{ipso}	49.3	51.4	51.1
Cp^c1 M-Cp^c2 (δ)	132.4	130.4	130.7
Cl1 M-Cl2	94.9(4)	96.9(2)	95.8(3)
C1-B1-B2	106.4(3)	108.6(2)	108.2(2)
C6-B2-B1	107.4(3)	109.6(2)	109.3(2)
M−Cl1	2.335(1)	2.461(1)	2.437(1)
M−Cl2	2.374(1)	2.452(1)	2.427(1)
M−Cp^c1	2.070	2.205	2.188
M−Cp^c2	2.073	2.207	2.191
B1−C1	1.589(6)	1.587(3)	1.589(4)
B2−C6	1.588(6)	1.585(3)	1.584(4)
B1−B2	1.698(6)	1.708(3)	1.707(5)
B1−N1	1.383(5)	1.385(3)	1.382(4)
B2−N2	1.383(5)	1.387(3)	1.388(4)



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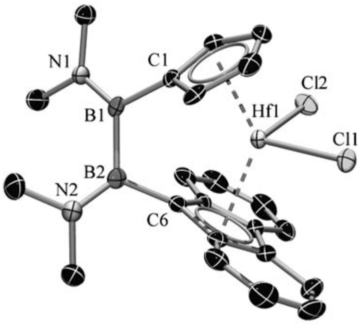

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Figure 4. Crystal structures of compounds **10** and **11**.

The tilt angles α (56.5° for **10** and 56.0° for **11**) as well as the deformation angles δ (132.5° for **10** and 132.9° for **11**) are only marginally greater than those of the aforementioned bis(cyclopentadienyl) species **7**–**9**. Likewise, the overall geometry of the bridging diborane(4)diyl unit is comparable and all pertinent structural parameters are unobtrusive. Selected bond lengths and angles are summarized in Table 3.

Conclusion

[2]Borametallocenophanes of Ti, Zr, and Hf are accessible by a convenient multistep high-yield synthesis, similar to the synthesis of [1]borametallocenophanes. Due to the diboranediyl bridge the ligand system is not as rigid as that in boranediyl-bridged metallocenes, as was demonstrated by their

Table 3. Bond lengths [Å] and angles [°] of the crystal structures of **10** and **11**.

	10	**11**
tilt angle α	56.6	56.0
torsion C_{ipso}-B-B-C_{ipso}	47.0	46.9
Cp^c-M-Flu^c (δ)	132.5	132.9
Cl1 M-Cl2	96.83(6)	96.28
C1-B1-B2	108.5(4)	108.7(4)
C6-B2-B1	112.0(4)	110.9(4)
M−Cl1	2.4336(16)	2.4046(11)
M−Cl2	2.24219(18)	2.4048(12)
M−Cp^c1	2.195	2.173
M−Cp^c2	2.294	2.278
B1−C1	1.588(8)	1.579(7)
B2−C6	1.582(7)	1.573(6)
B1−B2	1.698(8)	1.696(7)
B1−N1	1.396(7)	1.393(6)
B2−N2	1.392(7)	1.381(6)

constitution in solution. Studies on the effect of the lack of rigidity, which is believed to enhance the catalytic activity, are ongoing. Furthermore, the polymerization performance of the presented complexes will be investigated in the near future.

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 and stored under argon over molecular sieves; reagents were dried and purified by standard procedures. $[TiCl_3(thf)_3]$,[16] $[ZrCl_4(thf)_2]$,[16] 1,2-bis(dimethylamino)-1,2-dibromodiborane(4)[17] were obtained according to literature procedures. $Li[C_4H_9]$ and $Li[CH_3]$ were obtained commercially and used without further purification. NMR: Bruker Avance 500 at 500.13 MHz (^{1}H, internal standard TMS), 125.77 MHz (^{13}C{^{1}H}, APT, internal standard TMS) and 160.46 MHz (^{11}B, $BF_3{\cdot}OEt_2$ in C_6D_6 as external standard), Bruker DRX 300 at 116.64 MHz (^{7}Li, external standard LiCl). Elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyzer, model 1160. Mass spectra were recorded with a Thermo Finnigan Trio 1000. Experimental and spectroscopic details for $(Me_2N)_2B_2(\eta^1\text{-}C_5H_5)_2$ (**2**) and $[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2MCl_2]$ (M = Zr (**8**), Hf (**9**)) are published elsewhere.[8]

$(Me_2N)_2B_2(\eta^1\text{-}C_5H_5)Br$ (1): 1,2-Bis(dimethylamino)-1,2-dibromodiborane(4) (1.35 g, 5.00 mmol) was added at room temperature to a suspension of $Na[C_5H_5]$ (0.44 g, 5.00 mmol) in toluene (20 mL). After 12 h all volatiles were removed under reduced pressure and the product was extracted with hexane (40 mL). Removing all volatiles gave **1** as yellow oil in quantitative yields (1.27 g). NMR data reveal the presence of the two expected isomers. Main isomer: ^{1}H NMR (500.13 MHz, C_6D_6, 297 K): δ = 2.15, 2.64, 2.70, 2.78 (s, 18 H, CH_3), 3.11 (m, 2 H, $CH_{2\ Cp}$), 6.56, 6.64, 6.89 ppm (m, 3 H, $CH_{\ Cp}$); ^{11}B NMR (160.46 MHz, C_6D_6, 297 K): δ = 40.98 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 297 K): δ = 40.10, 40.40, 42.67, 44.85 (CH_3); 43.38 ($CH_{2\ Cp}$); 132.48, 136.90, 139.78 ppm ($CH_{\ Cp}$).

$(Me_2N)_2B_2(\eta^1\text{-}C_{13}H_9)Br$ (3): 1,2-Bis(dimethylamino)-1,2-dibromodiborane(4) (0.74 g, 2.74 mmol) was added slowly over a few minutes at room temperature to a suspension of $Li[C_{13}H_9]$ (0.47 g, 2.74 mmol) in toluene (20 mL). The reaction mixture was stirred for 24 h, filtered, and all volatiles removed under high vacuum to give **3** as a pale yellow oil (0.78 g, 79 %). ^{1}H NMR (500.13 MHz, C_6D_6, 297 K): δ = 2.03, 2.36, 2.53, 2.56 (s, 12 H, CH_3), 4.19 (bs, 1 H, BCH), 7.21, 7.49, 7.70, 7.77 (m, CH_{Flu}) 7.25–7.35 ppm (kB, CH_{Flu}); ^{11}B NMR (160.46 MHz, C_6D_6, 297 K): δ = 43.04 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 297 K): 42.88, 40.42, 40.06, 45.21 (CH_3); 42.49 (BCH); 120.48, 120.74, 125.52, 126.45, 126.53, 126.85 126.89, 127.25 (CH_{Flu}); 141.97, 142.90, 148.03, 148.92 ppm (C_q).

$(Me_2N)_2B_2(\eta^1\text{-}C_5H_5)(\eta^1\text{-}C_{13}H_9)$ (4): 1,2-Bis(dimethylamino)-1,2-dibromodiborane(4) (0.74 g, 2.74 mmol) was added slowly over a few minutes to a suspension of $Li[C_{13}H_9]$ (0.47 g, 2.74 mmol) in toluene (20 mL). After stirring for 20 min the insoluble material was removed by centrifugation. The filtrate was then added to a suspension of $Na[C_5H_5]$ (0.25 g, 2.75 mmol) in diethyl ether (20 mL). The reaction mixture was stirred for 24 h, filtered, and all volatiles were removed under high vacuum to give **4** as a pale yellow oil (0.73 g, 79 %). The NMR data reveal the presence of two isomers in a 2:1 ratio. Major isomer: ^{1}H NMR (500.13 MHz, C_6D_6, 297 K): δ = 2.36, 2.40, 2.71, 2.74 (s, 12 H, CH_3), 2.60 (m, 2 H, $CH_{2\ Cp}$), 4.15 (s, 1 H, BCH), 6.23, 6.45, 6.55 (m, 3 H, $CH_{\ Cp}$), 7.2–7.6 ppm (m, 8 H, CH_{Flu}); ^{11}B NMR (160.46 MHz, C_6D_6, 297 K): δ = 47.40 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 297 K): δ = 40.10, 40.45, 45.39, 45.62 (CH_3), 45.83 ($CH_{2\ Cp}$), 46.7 (b, BCH), 120.35, 125.53, 126.60, 126.63 ($CH_{\ Flu}$), 133.69, 135.95, 138.65 ($CH_{\ Cp}$), 142.33, 149.85 ppm ($C_{q\ Flu}$). Minor isomer: ^{1}H NMR (500.13 MHz, C_6D_6, 297 K): δ = 2.37, 2.42, 2.70, 2.78 (s, 12 H, CH_3), 2.7 (m, 2 H, $CH_{2\ Cp}$), 4.16 (s, 1 H, BCH), 5.87, 6.22, 6.28 (m, 3 H, $CH_{\ Cp}$), 7.2–7.6 ppm (m, 8 H, $CH_{\ Flu}$); ^{11}B NMR (160.46 MHz, C_6D_6, 297 K): δ = 47.40 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 297 K): δ = 40.04, 40.39, 40.95, 45.07 (CH_3), 43.42 ($CH_{2\ Cp}$), 46.7 (b, BCH), 120.50, 124.83, 125.35, 125.75 ($CH_{\ Flu}$), 131.44, 137.24, 137.36 ($CH_{\ Cp}$); 142.65, 149.25 ppm ($C_{q\ Flu}$).

$Li_2[(Me_2N)_2B_2(\eta^1\text{-}C_5H_4)_2]$ (5): The ligand precursor **2** (1.09 g, 4.56 mmol) was dissolved in a 1:1 mixture of toluene and diethyl ether (30 mL) and cooled to −80 °C. After addition of $Li[C_4H_9]$ (5.7 mL, 1.6 M) the reaction mixture was allowed to come to ambient temperature and was stirred for a further 16 h. The suspension was filtered and the colorless solid washed two times with pentane (10 mL) followed by drying under high vacuum to give **5** as an off-white powder (1.06 g, 92 %). ^{1}H NMR (500.13 MHz, [D$_8$]THF, 297 K): δ = 3.01, 3.18 (s, 12 H, CH_3), 5.76, 6.01 ppm (pt, 8 H, $CH_{\ Cp}$); ^{7}Li NMR (116.64 MHz, [D$_8$]THF, 297 K): δ = −5.75 ppm; ^{11}B NMR (160.46 MHz, [D$_8$]THF, 297 K): δ = 45.77 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, [D$_8$]THF, 297 K): δ = 41.15, 46.71 (CH_3); 106.11, 113.78 ppm ($CH_{\ Cp}$).

$Li_2[(Me_2N)_2B_2(\eta^1\text{-}C_5H_4)(\eta^1\text{-}C_{13}H_8)]$ (6): The ligand precursor **4** (0.80 g, 2.35 mmol) was dissolved in a 1:1 mixture of toluene and diethyl ether (30 mL) and cooled to −80 °C. After addition of $Li[CH_3]$ (1.1 mL, 1.6 M) the reaction mixture was allowed to come to ambient temperatures and was stirred for a further 16 h. The suspension was filtered and the solid washed two times with pentane (10 mL) followed by drying under high vacuum to give **6** as a pale orange pyrophoric powder (0.72 g, 87 %). ^{1}H NMR (500.13 MHz, [D$_8$]THF, 297 K): δ = 3.01, 3.22, 3.33, 3.34 (s, 12 H, CH_3), 5.68, 6.04 (pt, 4 H, $CH_{\ Cp}$), 6.47, 6.86, 7.55, 7.81 ppm (m, 8 H, $CH_{\ Flu}$); ^{7}Li NMR (116.64 MHz, [D$_8$]THF, 297 K): δ = −5.36 ppm; ^{11}B NMR (160.46 MHz, [D$_8$]THF, 297 K): δ = 47.80 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, [D$_8$]THF, 297 K): δ = 41.25, 43.62, 45.27, 46.00 (CH_3), 107.56, 110.20 ($CH_{\ Cp}$), 113.20, 118.46, 119.61, 120.12 ($CH_{\ Flu}$), 127.26, 142.30 ppm ($C_{q\ Flu}$).

$[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)_2TiCl_2]$ (7): $[TiCl_3(thf)_3]$ (1.57 g, 4.25 mmol) was added at −100 °C to a suspension of **5** (1.70 g, 4.25 mmol) in toluene (40 mL). While warming to room temperature, the reaction mixture darkened. After stirring for 2 h at room temperature $PbCl_2$ (0.59 g, 2.13 mmol) was added. After 16 h the insoluble material was removed by centrifugation, and the mother liquor was concentrated and stored at −30 °C, which gave **7** as a dark red crystalline material (0.97 g, 64 %). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 297 K): δ = 2.97, 3.13 (s, 12 H, CH_3), 6.17 (pt, 4 H, CH_{Cp}), 6.85 ppm (pt, 4 H, CH_{Cp}); ^{11}B NMR (160.46 MHz, CD_2Cl_2, 297 K): δ = 43.5 ppm; ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 297 K): δ = 40.71, 45.28 (CH_3), 120.78, 129.83 ppm (CH_{Cp}); MS (CI): *m/z* (%): 356 (100) [M^+], 320 (70) [$M^+ - HCl$], 284 (70) [$M^+ - 2HCl$]; elemental analysis (%): calcd: C 47.14, H 5.65, N 7.85; found: C 47.38, H 5.91, N 7.36.

$[(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)ZrCl_2]$ (10): $[ZrCl_4(thf)_2]$ (0.74 g, 2.00 mmol) was added at −80 °C to a suspension of **6** (0.74 g, 2.00 mmol) in toluene/diethyl ether (1:1; 30 mL). While warming to room temperature the reaction mixture turned orange. After stirring for 16 h at ambient temperature, all volatiles were removed under reduced pressure. The product was extracted with toluene (20 mL). The mother liquor was concentrated and stored at room temperature, which gave **10** as a yellow crystalline material (0.78 g, 76 %). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 223 K): $\delta = 2.85$, 3.03, 3.30, 3.31 (s, 12H, CH_3), 5.90, 6.02, 6.21, 6.37 (m, 4H, CH_{Cp}), 7.24, 7.31, 7.38, 7.52, 7.58, 8.04 ppm (m, 8H, CH_{Flu}); ^{11}B NMR (160.46 MHz, CD_2Cl_2, 223 K): $\delta = 43.6$ ppm; ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 223 K): $\delta = 39.66$, 40.93, 44.17, 44.24 (CH_3), 112.45, 115.41, 119.98, 127.10 (CH_{Cp}), 123.82, 124.30, 124.58, 124.69, 125.39, 125.58, 127.81, 128.09 (CH_{Flu}), 125.98, 126.80, 126.90, 128.75 ppm ($\text{C}_{\text{q Flu}}$); elemental analysis (%): calcd: C 52.83, H 4.84, N 5.60; found: C 52.64, H 4.97, N 5.34.

[$(Me_2N)_2B_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)HfCl_2$] (11): $HfCl_4$ (0.70 g, 2.20 mmol) was added at −80 °C to a suspension of **7** (0.74 g, 2.00 mmol) in toluene/diethyl ether (1:1; 30 mL). While warming to room temperature the reaction mixture turned orange. After stirring for 16 h at ambient temperature, all volatiles were removed under reduced pressure. The product was extracted with toluene (20 mL). The mother liquor was concentrated and stored at room temperature, to give **11** as a yellow crystalline material (1.05 g, 87 %). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 223 K): $\delta = 2.83$, 3.03, 3.30 (s, 12H, CH_3), 5.78, 5.95, 6.12, 6.28 (m, 4H, CH_{Cp}), 7.12–7.24, 7.38, 7.49, 7.53, 8.10 ppm (m, 8H, CH_{Flu}); ^{11}B NMR (160.46 MHz, CD_2Cl_2, 223 K): $\delta = 42.4$ ppm; ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, 223 K): $\delta = 40.39$, 41.66, 44.79, 44.86 (CH_3), 110.56, 114.13, 117.99, 125.70 (CH_{Cp}), 118.83, 124.10, 124.19, 124.40, 125,03, 127.77, 127.86 (CH_{Flu}), 125.48, 125.77, 125.89, 127.98 ppm ($\text{C}_{\text{q Flu}}$); elemental analysis (%): calcd: C 44.98, H 4.12, N 4.77; found: C 43.83, H 4.20, N 4.53.

The crystal data of **7** was collected by using a Bruker X8 Apex diffractometer with multilayer mirror monochromated $\text{Mo}_{\text{K}\alpha}$ radiation. The crystal data of **8–11** were collected by using a Bruker Apex diffractometer with CCD area detector and graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation. Both diffractometers were equipped with CCD area detectors. The structures were solved by using direct methods, refined with Shelx software package (G. Sheldrick, *Acta Crystallogr. Sect. 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 **7**: $C_{14}H_{20}B_2Cl_2N_2Ti$, $M_r = 356.74$, orange block, $0.20 \times 0.19 \times 0.10$ mm^3, orthorhombic space group *Pbca*, $a = 12.9671(4)$, $b = 12.4285(4)$, $c = 20.3215(5)$ Å, $V = 3275.05(17$ Å^3, $Z=8$, $\rho_{\text{calcd}} = 1.447$ g cm^{-3}, $\mu = 0.841$ mm^{-1}, $F(000) = 1472$, $T = 100(2)$ K, $R_1 = 0.0334$, $wR^2 = 0.0751$, 5060 independent reflections [$2\theta \leq 64.12°$] and 190 parameters.

Crystal data for **8**: $C_{14}H_{20}B_2Cl_2N_2Zr$, $M_r = 400.06$, white plates, $0.38 \times 0.32 \times 0.17$ mm^3, monoclinic space group $P2(1)/n$, $a = 9.7689(15)$, $b = 12.1977(18)$, $c = 14.909(2)$ Å, $\beta = 104.442(3)°$, $V = 1720.4(4)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.545$ g cm^{-3}, $\mu = 0.942$ mm^{-1}, $F(000) = 808$, $T = 173(2)$ K, $R_1 = 0.0250$, $wR^2 = 0.0660$, 3403 independent reflections [$2\theta \leq 52.1°$] and 190 parameters.

Crystal data for **10**: $C_{22}H_{24}B_2Cl_2N_2Zr$, $M_r = 500.17$, yellow needle, $0.35 \times 0.09 \times 0.06$ mm^3, monoclinic space group $P2(1)$, $a = 12.205(7)$, $b = 9.705(5)$, $c = 19.294(11)$ Å, $\beta = 102.838(10)°$, $V = 2228(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.491$ g cm^{-3}, $\mu = 0.744$ mm^{-1}, $F(000) = 1016$, $T = 173(2)$ K, $R_1 = 0.0514$, $wR^2 = 0.0991$, 8754 independent reflections [$2\theta \leq 52.26°$] and 524 parameters.

Crystal data for **11**: $C_{22}H_{24}B_2Cl_2HfN_2$, $M_r = 587.44$, yellow block, $0.26 \times 0.12 \times 0.08$ mm^3, monoclinic space group $P2(1)$, $a = 12.1775(9)$, $b = 9.6626(7)$, $c = 19.3330(14)$ Å, $\beta = 102.7990(10)°$, $V = 2218.3(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.759$ g cm^{-3}, $\mu = 4.954$ mm^{-1}, $F(000) = 1144$, $T = 173(2)$ K, $R_1 = 0.0291$, $wR^2 = 0.0555$, 10228 independent reflections [$2\theta \leq 56.68°$] and 524 parameters.

CCDC-688097 (**7**), CCDC-688158 (**10**), CCDC-688159 (**8**), and CCDC-688160 (**11**) 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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