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Communication

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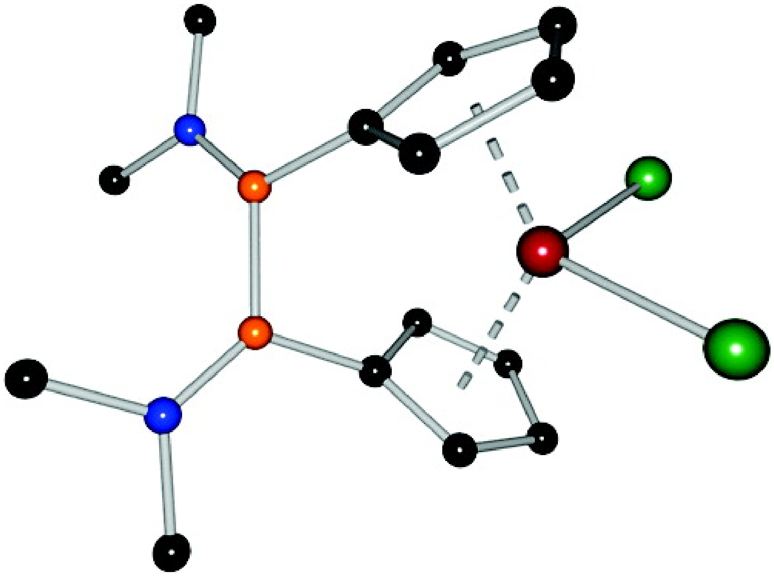

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[2]Borametallocenophanes of Zr and Hf: Synthesis, Structure, and Polymerization Activity

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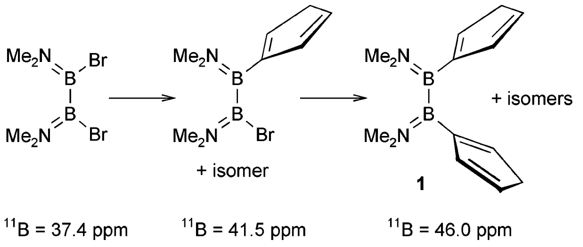
In the past two decades metallocenes, and *ansa* metallocenes in particular, have become one of the most important catalyst systems for the homogeneous Ziegler−Natta polymerization of olefins. The potential to alter the steric and electronic properties of these systems by different substitution at the cyclopentadienyl (Cp) ring or by incorporation of different bridging atoms has been experimentally realized in a host of examples, often giving rise to different polymer properties.[1] The wealth of review articles in this area underlines the importance of metallocenes and metallocenophanes.[2]

Comparative studies on the catalytic performance of group 4 compounds generally agree with the activity of Zr complexes being substantially higher than that of the corresponding Hf compounds under similar conditions. However, polymers obtained with Hf catalysts show in general a higher molecular weight.[3] In the past five years, we[4] and Ashe[5] have assayed the synthesis of the first donor-free group 4 [1]bora-bridged metallocenophanes.[6] We demonstrated that such complexes are active catalysts for ethylene polymerization,[7,8] however, leading to an average molecular weight of $M_w < 20\,000$, while Ashe demonstrated the capability of these complexes to polymerize propylene.[5] Likewise, we found Zr complexes to be higher in activity as compared to the corresponding Hf compounds.[7,8] 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.[9] Hence, we attempted the synthesis of a [2]borametallocenophane to obtain highly active Ziegler−Natta catalysts for ethylene polymerization, leading to PE of high molecular mass.

Nöth described in 1994 the synthesis of 1,2-bis(dimethylamino)-1,2-bis(η^1-indenyl)diborane(4) starting from 1,2-bis(dimethylamino)-1,2-dichloroborane(4) and Li(C_9H_7). It was reported that the corresponding 1,2-bis(dimethylamino)-1,2-bis(η^1-cyclopentadienyl)-diborane(4) (**1**) is not accessible via this route.[10]

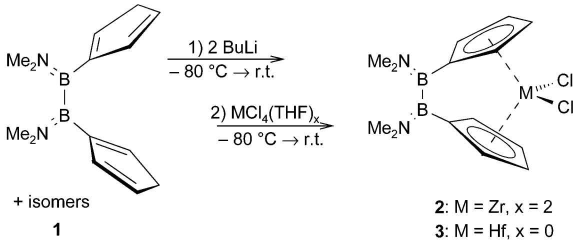
We attempted the synthesis of **1** starting from the 1,2-bis-(dimethylamino)-1,2-dibromodiborane(4), whose B−Br bonds could be expected to be more reactive than B−Cl bonds.[11] The reaction of 2.2 equiv of NaCp with 1 equiv of 1,2-bis(dimethylamino)-1,2-dibromodiborane(4) in a toluene/diethyl ether mixture (1:1) at ambient temperatures gave isomeric **1** in quantitative yields (eq 1). A reaction control showed that after 4 h half conversion had taken place, and ether was necessary to force the reaction to completion.

The ^{1}H and ^{13}C NMR spectra of **1** are complex due to the expected presence of various isomers.[11] The ^{11}B NMR spectrum shows a low-field shift of ca. 4 ppm per Cp ligand, from 37.4 to 41.5 to finally 46.0 ppm in **1**. In the intermediate product, only one signal in the ^{11}B NMR was seen at 41.5 ppm. **1** was used in the following reactions without further purification.



(1)

Treating **1** with 2 equiv of Li[C_4H_9] at −80 °C in toluene and subsequently with $ZrCl_4(THF)_2$ and $HfCl_4$, respectively, gave **2** as a yellow microcrystalline solid and **3** as a pale yellow crystalline material in good yields (eq 2).



(2)

The ^{1}H NMR spectrum of **2** shows two singlets for the methyl groups at 2.99 and 3.13 ppm, due to hindered rotation around the B−N bond, and two pseudo triplets at 6.07 and 6.76 ppm for the protons on the Cp ring. The resonance in the ^{11}B NMR spectrum is displayed at 42.9 ppm, similarly to the shift of the ligand precursor **1**, as already observed for strained[12] and nonstrained [1]borametallocenophanes.[4,6c] For **3**, the methyl groups give rise to signals at 2.98 and 3.14 ppm, and the pseudo triplets of the Cp protons are detected at 5.96 and 6.64 ppm, respectively; the bridging boron atom displays a signal at 42.9 ppm in the ^{11}B NMR spectrum, as does that of **2**.

Suitable crystals of **3** for X-ray diffraction were obtained from toluene at −35 °C, and the molecular structure is shown in Figure 1. The introduction of the bridging moiety causes significant changes in the geometrical parameters, and it is useful to discuss

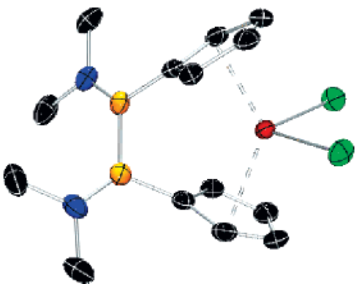


Figure 1. X-ray structure of **3** at 50% ellipsoid probability.

[†] Basell Polyolefine GmbH, Industriepark Höchst, 65926 Frankfurt.

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Table 1. Selected Angles [deg] and Bond Length [pm] of **3**, **4**, and **5**

	3	4	5
α	51.8	53.5	64.7
δ	130.7	129.2	121.4
Cl−Hf−Cl	96.87(2)	97.1	99.58(3)
$Hf-Cl_1$	243.7(1)	242.7	240.9(1)
$Hf-Cl_2$	242.7(1)	241.9	240.0(1)
$Hf-Cp^{c}_{1}$	217.5	217.9	217.3
$Hf-Cp^{c}_{2}$	218.1	217.9	218.3
B_1-*ipso*C_1	158.9(4)	−	157.3(5)
B_2-*ipso*C_2	158.4(4)	−	158.2(5)
B_1-N_1	138.2(4)	−	136.9(5)
B_2-N_2	138.8(4)	−	−
$Cp^{c}_{1}-Cp^{c}_{2}$ (A)	398.0	393.7	378.8
d	91.3	93.5	106.6

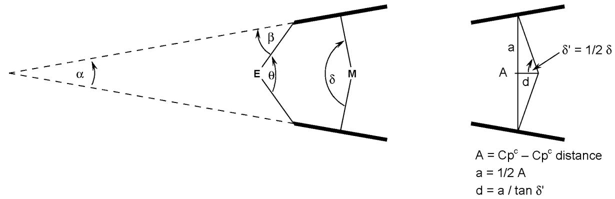

Figure 2. Structural parameters of metallocenophanes.

these in reference to the structures of the unbridged parent $[(\eta^5\text{-}C_5H_5)_2HfCl_2]$ (**4**)[13] and the [1]bora-bridged $[Me_2NB(\eta^5\text{-}C_5H_4)_2\text{-}HfCl_2]$ (**5**).[8] Selected bond lengths and angles appear in Table 1; Figure 2 defines the angles and the distances used in the discussion. The B−B separation in **3** [170.7(5) pm] is unremarkable compared to that of the related $[(Me_2N)_2B_2(\eta^6\text{-}C_6H_5)_2Cr]$ (**6**) [171.8(12) pm];[14] the average B−N separation is identical in both **3** and **6** (138.5(4) pm), as is the separation between the *ipso*-C of the Cp ring and the bridging boron (158.7(4) for **3**, versus 159.0(10) pm for **6**).

In nonbridged **4**, the planes of the Cp rings are tilted toward each other with an angle α of 53.5°, the corresponding $Cp^c-Zr-Cp^c$ angle (Cp^c = Cp centroid) is $\delta = 129.2°$. On the other hand, the presence of a single, small boron atom in the bridge, as in **5**, results in a higher tilt angle ($\alpha = 64.7°$) and, consequently, a smaller angle for $Cp^c-Zr-Cp^c$ ($\delta = 121.4°$). The single-atom bridge causes high rigidity and constrains the Cp rings to an eclipsed orientation. The [2]bora bridge in **3**, however, gives rise to very small differences in the geometry compared to the parent **4**, (for **3**, $\alpha = 51.8°$, $\delta = 130.4°$). The distance (A) between the Cp centroids follows the trend, **3** > **4** > **5**, with a distance of 398.0 pm in **3**, 393.7 pm in **4**, and 379.8 pm in **5**. Another parameter changed by incorporation of a bridging moiety is the position of the metal center, relative to the center of the Cp^c-Cp^c vector, which is related to the tilt angle α. The larger α becomes, the further the metal protrudes from the wedge created by the Cp ligand, as quantified by the distance *d*. A better accessibility of the metal center, that is, for an olefin, is assumed with increasing *d*.[15] The change in the position of the metal center in **3** relative to parent **4** is only marginal, but in the [1]bora-bridged **5** *d* changes considerably.

Preliminary polymerization experiments with ethylene showed that **2** and **3** are highly active catalysts after activation with MAO. Interestingly, both complexes show similar high activities of 28 538 (**2**) and 26 706 g(PE) $mmol^{-1}$ h^{-1} (**3**). The resultant polymer has a very high molecular mass: $M_v = 896\,000$ $gmol^{-1}$ for **2** and 1 600 000 $gmol^{-1}$ for the polymer obtained with **3**.

The detailed comparison of structural data shows that the corresponding parameters of **3** and **4** are remarkably similar, though there is a hindered rotation of the Cp ligands in the bridged complex. Hence, it may be assumed that the improved catalytic performance of **2** and **3** in particular is due to the electronic influence of the B_2 bridge rather than any geometrical changes imposed. Moreover, since the Hf atom in **3** is less accessible than that in **5**, the electronic advantage of **3** is brought into focus.

In conclusion, we have presented the synthesis of the first [2]-borametallocenophanes of zirconium and hafnium from a hitherto unknown diborane(4)-based ligand.

Furthermore, we have been able to show that these complexes are highly active Ziegler−Natta-type catalyst precursors that polymerize ethylene to give high molecular weight PE. These results further support the thesis that complexes with smaller tilt angles have a decreased chain termination rate in the polymerization process.[9] Very interestingly, the introduction of a B_2 bridge allowed the isolation of a hafnocene complex, whose activity was for the first time comparable to that of its Zr congener.

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Supporting Information Available: Experimental procedures and characterization data for new compounds (PDF) and X-ray crystallographic data for **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 791. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (c) Kaminski, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.
(2) Grimmer, N. E.; Coville, N. J. *S. Afr. J. Chem.* **2001**, *54*, 118; see Table 4 for a list of recent review articles concerning single site catalyst.
(3) (a) Kim, M. W.; Hong, E.; Han, K.; Woo, S. L.; Do, Y. *J. Organomet. Chem.* **1998**, *564*, 109. (b) Weiss, K.; Neugebauer, U.; Blau, S.; Lang, H. *J. Organomet. Chem.* **1996**, *520*, 171. (c) Jany, G.; Gustafsson, M.; Repo, T.; Aitola, E.; Dobado, J. A.; Klinga, M.; Leskelä, M. *J. Organomet. Chem.* **1998**, *553*, 173.
(4) (a) Braunschweig, H.; von Koblinski, C.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 69. (b) Braunschweig, H.; von Koblinski, C.; Mamuti, M.; Englert, U.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 1899.
(5) (a) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288. (b) Ashe, A. J., III; Fang, X.; Hokky, A.; Kampf, J. W. *Organometallics* **2004**, *23*, 2197.
(6) For recent reviews on boron-bridged *ansa* metallocenophanes, see: (a) Shapiro, P. J. *Eur. J. Inorg. Chem.* **2001**, 321. (b) Aldridge, S.; Bresner, C. *Coord. Chem. Rev.* **2003**, *244*, 71. (c) Braunschweig, H.; Breitling, F. M.; Gullo, E.; Kraft, M. *J. Organomet. Chem.* **2003**, *630*, 31.
(7) Kristen, M. O.; Braunschweig, H.; von Koblinski, C. Metallocene complexes suitable as olefin polymerization catalysts. EP 1140955, 2001.
(8) Braunschweig, H.; Kraft, M.; Radacki, K.; Stellwag, S. *Eur. J. Inorg. Chem.*, submitted for publication.
(9) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.
(10) Littger, R.; Metzler, N.; Nöth, H.; Wagner, M. *Chem. Ber.* **1994**, *127*, 1901.
(11) Braunschweig, H.; von Koblinski, C.; Neugebauer, M.; Englert, U.; Zheng, Z. *J. Organomet. Chem.* **2001**, *619*, 305.
(12) (a) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338. (b) Berenbaum, A.; Braunschweig, H.; Dirk, R.; Englert, U.; Green, J. C.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765.
(13) Soloveichik, G. L.; Arkhireeva, T. M.; Belskii, V. K.; Bulychev, B. M. *Metalloorg. Khim.* **1988**, *1*, 226.
(14) Braunschweig, H.; Homberger, M.; Hu, C.; Zheng, X.; Gullo, E.; Clentsmith, G.; Lutz, M. *Organometallics* **2004**, *23*, 1968.
(15) (a) Shaltout, R. M.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1995**, *503*, 205. (b) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardin, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525 and references therein.

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