Organometallics **1997,** *16,* 3751−3757

Borabenzene Derivatives. 26.[1] Syntheses of 1-Methylboratabenzene Complexes of Titanium, Zirconium, and Hafnium. Structures of $TiCl_3(C_5H_5BMe)$, $TiCl_2Cp(C_5H_5BMe)$, $ZrCl_2(C_5H_5BMe)_2$, and $ZrCl_2Cp^*(C_5H_5BMe)$[†]

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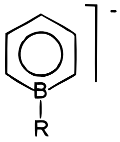
Received April 15, 1997[⊗]

The complexes $TiCl_3(C_5H_5BMe)$ (**6a**), $[MCl_3(C_5H_5BMe)]_x$ (**6b**, M = Zr; **6c**, M = Hf), and $MCl_2(C_5H_5BMe)_2$ (**7b**, M = Zr; **7c**, M = Hf) are obtained from the tetrachlorides MCl_4 (M = Ti, Zr, Hf) and $Li(C_5H_5BMe)$ (**3**), 2-$(Me_3Si)C_5H_5BMe$ (**4**), or 2-$(Me_3Sn)C_5H_5BMe$ (**5**) in excellent yields. The complexes $MCl_2Cp(C_5H_5BMe)$ (**8a**, M = Ti; **8b**, M = Zr) and $MCl_2Cp^*(C_5H_5BMe)$ (**9b**, M = Zr; **9c**, M = Hf) are made similarly from the corresponding cyclopentadienyl precursors MCl_3Cp (M = Ti, Zr) and MCl_3Cp^* (M = Zr, Hf). The redox potentials are shifted by 0.35−0.41 V to more anodic values than those for the corresponding Cp complexes. Molecule **6a** shows a piano-stool-type structure, while **7b**, **8a**, and **9b** possess typical bent sandwich structures.

Introduction

Boratabenzene ions[4−6] **1** are more akin to cyclopentadienide **2** than any other anion. They can form metal compounds with metallic elements from all parts of the periodic table.[7] Previous work has almost exclusively been devoted to complexes of the late transition metals.[8] However, papers on the first complexes of Zr,[9] Si and its homologs,[10] In[2] have now appeared, and data on compounds of Mg, Sc, Gd, Ti, and Sb have been presented.[7]



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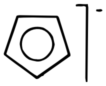

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The recent interest in borabenzene chemistry has been stimulated by the development of new syntheses of borabenzene[11] and boratabenzene derivatives[4,6] which, on a very practical level, now allow the study of rather synthetically demanding systems. In addition, replacement of cyclopentadienyl ligands with boratabenzene ligands promises to add a further facet to the use of titanium and zirconium metallocene derivatives as catalysts in Ziegler−Natta olefin polymerization[12] and as catalysts and reagents in organic synthesis.[13] In fact, Bazan, Ashe III et al. have already reported that their zirconium complexes in combination with MAO polymerize ethene with high activity.[9]

Results and Discussion

Syntheses. For the preparation of 1-methylboratabenzene complexes of Ti, Zr, and Hf we use the same general synthetic methods that are well-established in the cyclopentadienyl chemistry of these elements. However, it has to be kept in mind that boratabenzene ions **1** are less basic[14] and less nucleophilic[10] than cyclopentadienide **2**. It also turned out that basic solvents, e.g., THF, are often detrimental. As the source of the 1-methylboratabenzene ligand we use lithium 1-methylboratabenzene, $Li(C_5H_5BMe)$ (**3**),[6a] and the 1,2-dihy-

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[†] This paper is dedicated to Professor G. Huttner on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

(1) Part 25: see ref 2.

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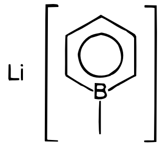
S0276-7333(97)00313-0 CCC: $14.00

Table 1. New Complexes and Selected Data on Syntheses

compound	educts	conditions	yield (%)
6a ($TiCl_3(C_5H_5BMe)$)	$TiCl_4$/**5**	hexane, 20 °C, 10 min	93
6b ($[ZrCl_3(C_5H_5BMe)]_x$)	$ZrCl_4$/**5**	hexane, 20 °C, 1 h	98
6c ($[HfCl_3(C_5H_5BMe)]_x$)	$HfCl_4$/**5**	hexane, 20 °C, 1 h	97
7b ($ZrCl_2(C_5H_5BMe)_2$)	$ZrCl_4$/**4**	hexane, 70 °C, 2 h	95
	$ZrCl_4$/**3**	toluene, 110 °C, 2 days	92
7c ($HfCl_2(C_5H_5BMe)_2$)	$HfCl_4$/**4**	hexane, 70 °C, 2 h	90
	$HfCl_4$/**3**	toluene, 110 °C, 2 days	60
8a ($TiCl_2Cp(C_5H_5BMe)$)	$TiCl_3Cp$/**5**	THF, −50 to 20 °C	63
8b ($ZrCl_2Cp(C_5H_5BMe)$)	$ZrCl_3Cp$/**4**	toluene, 60 °C, 2 h	70
9b ($ZrCl_2Cp^*(C_5H_5BMe)$)	$ZrCl_3Cp^*$/**3**	toluene/DME, 110 °C, 7 days	89
9c ($HfCl_2Cp^*(C_5H_5BMe)$)	$HfCl_3Cp^*$/**3**	toluene/DME, 110 °C, 7 days	85

droborinine derivatives 2-(Me_3Si)C_5H_5BMe (**4**)[10] and 2-(Me_3Sn)C_5H_5BMe (**5**).[10,15]



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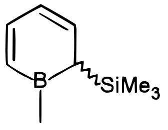

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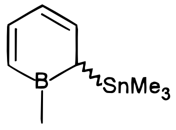

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Four types of complexes **6**−**9** with 1-methylboratabenzene ligands are described here. In Table 1 we give an overview of the syntheses used. Three entries are missing. In the case of **8c**, the synthesis was not attempted. Complex **9a** should be more stable than its nonmethylated analog **8a**, but several attempted syntheses failed. For **7a**, we find that this complex cannot be made by any of the conventional synthetic methods. It could be that **7a** will remain a nonexistent compound for reasons discussed below.

First we consider the complexes of type **6** with one aromatic ring ligand. The tin compound **5** reacts with $TiCl_4$ in hexane at temperatures above −60 °C. At ambient temperature, the reaction is completed within a few minutes to give the deep purple mononuclear complex $TiCl_3(C_5H_5BMe)$ (**6a**). It is necessary to use a slight excess of $TiCl_4$ because the product **6a** is slowly reduced by an excess of the tin compound **5**. If the silicon compound **4** is used as the ligand source, the reaction with $TiCl_4$ requires heating to 60 °C for 5 h.

Complex **6a** is the first boratabenzene complex of Ti to be described. It crystallizes as deep purple platelets and is remarkably volatile in that it sublimes in a vacuum above 20 °C/10^{-6} bar, while the analogous $TiCl_3Cp$[16] sublimes at 80 °C/10^{-6} bar. Solutions of **6a** in nonbasic solvents, such as benzene and even nitromethane and CF_3CO_2H, are unchanged after several days. On the other hand, solutions in basic solvents, such as THF and acetonitrile, decompose readily. For instance, when **6a** is dissolved in THF at −60 °C the purple solution color persists for several hours. When the temperature is then raised to 0 °C, the color slowly changes to green and light blue crystals of $TiCl_3(THF)_3$ deposit in 80% yield; other products could not be identified.[17]

The reaction of **4** in pentane with the tetrahalides $ZrCl_4$ and $HfCl_4$ affords the heavier homologs $[MCl_3(C_5H_5BMe)]_x$ (**6b**, M = Zr; **6c**, M = Hf; *x* unknown) as cream-colored powders.[18] The ^1H NMR spectra of **6b**,**c** show that these complexes readily undergo a dismutation to give the tetrahalides and dichlorobis(ligand) complexes $MCl_2(C_5H_5BMe)_2$ (**7b**, M = Zr; **7c**, M = Hf). The best samples of **6b**,**c** were >95% pure, but all attempts to obtain analytically pure, crystalline materials were unsuccessful.

Complexes with two aromatic ring ligands (**7**−**9**) were generally prepared in hydrocarbon solvents. We briefly discuss the problems encountered.

The reaction of $TiCl_3Cp$ with the tin compound **5** is very slow in hydrocarbon solvents, barely noticeable at ambient temperature. Since **8a** decomposes thermally at 60 °C, heating cannot remedy the situation. On the other hand, in THF the reaction sets in above −50 °C and small green crystals of **8a** are formed. This complex is saved from base-induced decomposition because of its low solubility in THF and its ready crystallization. When **8a** is dissolved in acetonitrile at ambient temperature, decomposition takes place within seconds. Note that both problems encountered here, the base-induced decomposition and the low reactivity of $TiCl_3Cp$, do not play a role in the preparation of the homologous zirconium compound **8b**.

The reaction of $ZrCl_3Cp^*$ with **3** in refluxing toluene is extremely slow. In the presence of 1 equiv of dimethoxyethane (DME), which solubilizes the lithium salt **3**, the reaction is accelerated. But even then, several days are required to form the product **9b** which is then obtained in near quantitative yield. Note that the known diisopropylamino derivative $ZrCl_2Cp^*(C_5H_5BNPr^i_2)$[9] (**10**) is also of type **9**. The hafnium system is completely analogous. However, with the titanium compound $TiCl_3Cp^*$, the reaction with **3** fails altogether and several alternatives ($TiCl_3Cp^*$/**5** in toluene or THF; **6a**/LiCp* or **6a**/Cp^*SnMe_3) were also unsuccessful.

Finally, we turn to the particularly interesting bis(boratabenzene) complexes **7**. The preparations of the Zr and Hf complexes **7b**,**c** are straightforward and give excellent yields of the intensely yellow **7b** and of the light yellow **7c**. Here again, the diisopropylamino compound $ZrCl_2(C_5H_5BNPr^i_2)_2$ (**11**) is already known.[9] All attempts to make an analogous Ti compound **7a** were met by failure.

Attempted Synthesis of 7a. In one series of experiments we used $TiCl_3(C_5H_5BMe)$ (**6a**) as the starting

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[15] In many instances, **5** may be replaced with the less costly butyl compound 2-(Bu_3Sn)C_5H_5BMe, see: Herberich, G. E.; Schmitz, A. Unpublished work.

[16] Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 4744.

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Table 2. ^1H NMR Data in CD_2Cl_2 (300 MHz)[a]

cmpd	2/6-H, δ	3/5-H δ	4-H δ	$^3J_{23}$	$^3J_{34}$	$^4J_{24}$	B−Me δ	other δ
3	6.48	7.30	6.48	9.8	7.0	1.3	0.57[b]	
6a	7.00	8.08	7.33	10.7	7.1	1.7	1.10	
6b	7.14	7.88	7.08	10.8	7.1	1.7	0.93	
6c	6.98	8.04	7.17	10.7	7.0	1.7	1.06	
7b	6.43	7.66	6.70	10.4	6.7	1.7	0.94	
7c	6.34	7.64	6.58	10.8	7.1	1.6	0.97	
8a[c]	5.97	7.76	6.86	10.7	7.0	1.5	1.10	6.66
8b	6.25	7.73	6.79	10.4	6.7	1.7	1.02	6.53
9b	6.38	7.47	6.19	10.7	6.7	1.8	0.93	1.70
9c	6.23	7.44	6.04	10.6	6.8	1.7	0.82	1.78

[a] δ reported in ppm and J in Hertz; multiplicities are dd for 2/6-H and 3/5-H, tt for 4-H, and s for other signals. *b*In CD_2Cl_2/DME, cf. ref 6a. [c] Measured at 500 MHz.

Table 3. ^{11}B and $^{13}C\{^1H\}$ NMR Data in CD_2Cl_2[a]

cmpd	B	C-2/6, δ^b	C-3/5, δ	C-4, δ	B−Me, δ^b	otherδ
3	36	126.7	132.8	107.9	4.0[c]	
6a	49	139.5	143.5	122.7	7	
6b	*d*	141	144.4	116.9	7	
6c	*d*	134	143.9	114.5	7	
7b	49	129.8	146.4	110.7	7	
7c	47	127.5	146.6	108.4	7	
8a[e]	46	126	150.4	114.1	7	123.2
8b	46	125.6	147.7	110.4	7	117.8
9b	44	128.7	143.2	106.2	6.4	125.8, 12.4
9c	47	127	144.3	104.4	7	123.5, 12.1

[a] $\delta(^{11}B)$ (ppm), measured at 28 MHz, and $\delta(^{13}C)$ (ppm), measured at 76 MHz. [b] Signal quadrupole broadened by neighboring ^{11}B nucleus. [c] In CD_2Cl_2/DME, cf. ref 6a. [d] Not measured. [e] $\delta(^{13}C)$ measured at 126 MHz.

material and tried to introduce a second 1-methylboratabenzene with the help of the lithium salt **3**, the silicon compound **4**, or the tin compound **5**. In all cases, paramagnetic products were obtained, which according to their mass spectra were the Ti(III) complexes $[TiCl(C_5H_5BMe)_2]_2$[19] or $[TiCl_2(C_5H_5BMe)]_2$.[20] When a pentane solution of **6a** was treated with the pentane-soluble magnesocene analog $Mg(C_5H_5BMe)_2$,[7] the reaction took place under very mild (−60 to 0 °C) and nonbasic conditions, but the products were the same Ti(III) species. In an alternative strategy we tried to oxidize $[TiCl(C_5H_5BMe)_2]_2$.[3] This compound is not oxidized by $PbCl_2$.[21] Oxidation with excess CuCl in toluene gives elemental copper and the trichloride **6a**. Oxidation with C_2Cl_6 (2 equiv) in toluene again produces **6a** and C_2Cl_4, eq 1; one boratabenzene ligand is destroyed. In summary, it seems that our failure to synthesize **7a** is mainly due to the easy reduction of **6a** and probably also of **7a**; the high sensitivity to base of Ti(IV) species is also a potential limiting factor.

$$[TiCl(C_5H_5BMe)_2]_2 + 2C_2Cl_6 \rightarrow \underset{\mathbf{6a}}{2TiCl_3(C_5H_5BMe)} + C_2Cl_4 + \{C_5H_5BMe\} \quad (1)$$

Characterization and General Properties. The new complexes were characterized by elemental analyses, mass spectra, and NMR spectroscopy (Tables 2 and 3). The ^{11}B chemical shifts of lithium boratabenzene salts are evidence of the delocalization of negative charge onto the boron center.[22] The interaction of the boratabenzene ligand with the d^0 metal(IV) centers considered here results in a transfer of electron density from the ligand to the metal and also reduces the electron density at the boron. As a consequence, most chemical shifts are downfield relative to those of **3**, and this effect is most pronounced at the 3,5-position of the boratabenzene ring. Qualitatively the observed deshieldings depend on the acceptor properties of the metal (Ti(IV) > Zr(IV), Hf(IV)) and the donor ability of the counter ligands (Cp* > Cp > C_5H_5BMe >> Cl).

Boron compounds with trigonal boron centers are Lewis acids if the boron center is not stabilized by π-interactions with neighboring groups. This Lewis acid property is fully suppressed in boratabenzene salts, and this remains true in most metal compounds with boratabenzene ligands.[8] It will reappear if the transfer of electron density from the ligand to the metal is rather strong. This has been observed first for cationic sandwich complexes with 1-phenylboratabenzene ligands, e.g., $[CoCp(C_5H_5BPh)]^+$,[23] where nucleophilic attack at boron is greatly facilitated.[8] It seems that the same situation is operating in the chemistry of boratabenzene complexes of titanium group metals since the titanium complexes **6a** and **8a** are rather sensitive to bases such as THF and acetonitrile.

Cyclopentadienyl and boratabenzene ligands have often been compared, and the 1-methyl- and 1-phenylboratabenzene ligands have been found to possess a more pronounced acceptor character.[8] As a consequence, redox potentials are shifted anodically in such a comparison, and this shift has been termed a borylene shift.[24] Typical borylene shifts for boratabenzene complexes range from 0.3 V for $[Cr(CO)_3(C_5H_5BMe)]^-$ to 0.8 V for $V(C_5H_5BMe)_2$ (per ring).[8] Cyclic voltammetry reveals a reversible 0/−1 process at 0.02 V vs SCE for **6a** in CH_2Cl_2; this is a remarkably anodic value for a reduction. Comparison with $TiCl_3(C_5H_4Me)$[25] gives a rough estimate of 0.37 V for the borylene shift for **6a**. For **8a**, the shift amounts to 0.35 V (cf. $TiCl_2Cp_2$[26]) and to 0.41 V for **7b** (cf. $ZrCl_2Cp_2$[27]).

The structure of **6a** is that of a piano-stool molecule (Table 4, Figures 1 and 2), while the structures of **7b**, **8a**, and **9b** are bent sandwich structures (Tables 5−7, Figures 3−6). For a boratabenzene ligand, the ligand plane could be defined as the best plane C_5B or alternatively as best plane C_5. In the structures to be considered here, the most pronounced ring folding is usually a bending of the boron away from the metal. Therefore, we find it preferable to describe the boratabenzene rings on the basis of the least-squares C_5 plane. Structural parameters related to the best planes are collected in Table 8 for comparison. Conformational

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[19] Brown crystals, green in hexane solution and brown in toluene; MS m/z (I_{rel}) 265 (100), mononuclear ion, dinuclear fragments with very low intensity (<1%); characterized as $[Ti(\mu\text{-}Cl)(C_5H_5BMe)_2]_2$ by X-ray structure analysis.[3]

[20] Purple solid; MS m/z (I_{rel}) 420 (25).[3]

[21] For the use of this mild and efficient oxidant, cf.: Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793.

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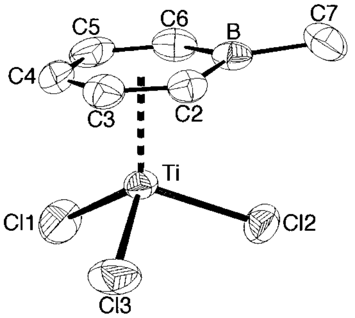

Figure 1. Displacement ellipsoid plot (PLATON)[28] of molecule **6a**. Ellipsoids are scaled to 50% probability.

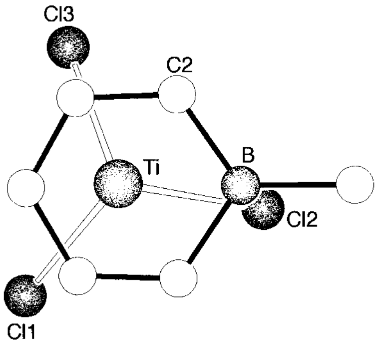

Figure 2. SCHAKAL[29] representation of molecule **6a** looking onto the C_5 plane of the boratabenzene ligand.

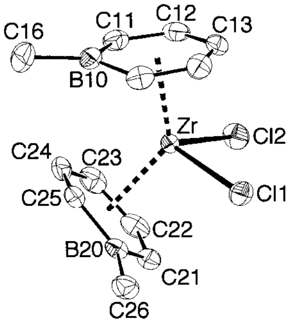

Figure 3. Displacement ellipsoid plot (PLATON)[28] of molecule **7b**. Ellipsoids are scaled to 30% probability.

Table 4. Selected Bond Distances (pm) and Bond Angles (deg) for 6a

(a) Bond Distances

Ti–Cl1	221.1(1)	Ti–Cl2	222.2(1)
Ti–Cl3	220.5(1)	C7–B	155.6(6)
Ti–C2	246.6(3)	C2–C3	138.1(5)
Ti–C3	240.3(3)	C3–C4	140.2(6)
Ti–C4	234.0(3)	C4–C5	138.8(5)
Ti–C5	240.5(3)	C5–C6	137.3(5)
Ti–C6	248.4(3)	C6–B	153.0(5)
Ti–B	265.3(4)	C2–B	151.7(5)

(b) Bond Angles

Cl1–Ti–Cl2	102.29(4)	C2–B–C6	111.0(3)
Cl1–Ti–Cl3	102.23(5)	C2–B–C7	124.7(3)
Cl2–Ti–Cl3	102.04(4)	C6–B–C7	124.2(3)
C3–C2–B	122.6(3)	C5–C6–B	122.2(3)
C2–C3–C4	121.0(3)	C4–C5–C6	122.0(4)
C3–C4–C5	120.6(4)		

information is given in the text or mentioned in the legends to the appropriate figures.

The piano-stool molecule **6a** consists of a boratabenzene ligand and a $TiCl_3$ fragment. The boratabenzene ligand is planar in its C_5 moiety (largest perpendicular displacement 1.6(3) pm for C4 toward the metal), while the boron atom is bent away from the metal with a folding angle of 6.3(7)° (displacement of 4.2(3) pm for the B atom). The $TiCl_3$ is a regular trigonal pyramid with Cl−Ti−Cl angles (ranging from 102.04(4)° to 102.29(4)°) that are intermediate between those of a

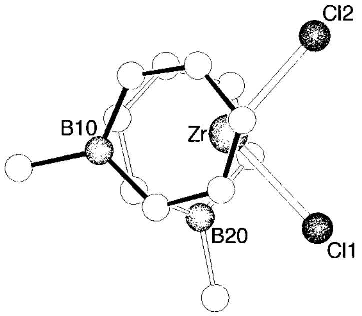

Figure 4. SCHAKAL[29] representation of molecule **7b** looking onto the $ZrCl_2$ plane.

Table 5. Selected Bond Distances (pm) and Bond Angles (deg) for 7b

(a) Bond Distances

Zr–Cl1	242.5(1)	Zr–Cl2	243.7(1)
Zr–C11	263.7(4)	Zr–C21	270.6(4)
Zr–C12	255.8(4)	Zr–C22	261.3(4)
Zr–C13	252.7(3)	Zr–C23	252.5(4)
Zr–C14	256.2(4)	Zr–C24	255.5(4)
Zr–C15	261.0(4)	Zr–C25	257.2(4)
Zr–B10	284.5(5)	Zr–B20	278.3(4)
C11–C12	138.4(6)	C21–C22	137.9(7)
C12–C13	136.3(8)	C22–C23	140.6(7)
C13–C14	136.9(7)	C23–C24	138.2(7)
C14–C15	138.1(7)	C24–C25	138.7(7)
C11–B10	152.3(7)	C21–B20	152.9(6)
C15–B10	152.8(7)	C25–B20	150.9(6)
C16–B10	158.0(7)	C26–B20	156.4(7)

(b) Bond Angles

Cl1–Zr–Cl2	95.33(4)		
C11–B10–C15	110.7(4)	C21–B20–C25	112.3(4)
C11–B10–C16	125.2(5)	C21–B20–C26	124.3(4)
C15–B10–C16	124.1(5)	C25–B20–C26	123.5(4)

Table 6. Selected Bond Distances (pm) and Bond Angles (deg) for 8a

(a) Bond Distances

Ti–Cl1	236.7(3)	Ti–Cl2	235.6(3)
Ti–C2	250(1)	Ti–C10	236.8(9)
Ti–C3	244(1)	Ti–C11	239(1)
Ti–C4	238(1)	Ti–C12	237(1)
Ti–C5	249.2(9)	Ti–C13	236(1)
Ti–C6	261(1)	Ti–C14	237.6(9)
Ti–B	270.8(9)		

(b) Bond Angles

Cl1–Ti–Cl2	93.7(1)	C2–B–C6	114(1)
C2–B–C7	123(1)	C6–B–C7	123(1)

Table 7. Selected Bond Distances (pm) and Bond Angles (deg) for 9b

(a) Bond Distances

Zr–Cl1	243.4(1)	Zr–Cl2	243.3(2)
Zr–C1	263.1(5)	Zr–C10	249.9(5)
Zr–C2	257.6(6)	Zr–C11	249.2(5)
Zr–C3	251.7(6)	Zr–C12	251.3(5)
Zr–C4	258.3(6)	Zr–C13	250.5(5)
Zr–C5	267.6(5)	Zr–C14	253.5(5)
Zr–B	282.7(7)		
C1–C2	138.2(8)	C4–C5	138.6(9)
C2–C3	140.6(9)	C3–C4	137.0(9)
C1–B	149.6(9)	C5–B	151.2(9)
C6–B	157(1)		

(b) Bond Angles

Cl1–Zr–Cl2	94.66(6)	C1–B–C5	111.4(6)
C1–B–C6	123.6(6)	C5–B–C6	125.1(6)

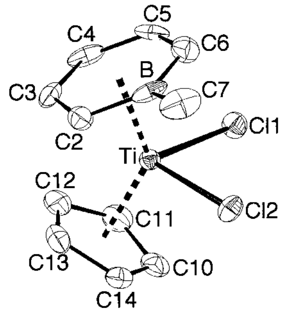

Figure 5. Displacement ellipsoid plot (PLATON)[28] of molecule **8a**. Ellipsoids are scaled to 30% probability. The Cl1−Ti−Cl2 bisector and the projection of the B−C4 direction on the $TiCl_2$ plane enclose an angle of 64°.

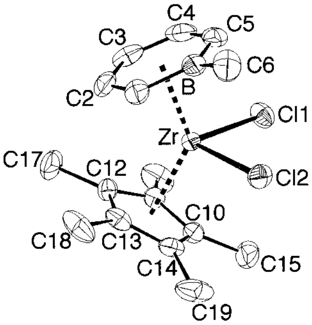

Figure 6. Displacement ellipsoid plot (PLATON)[28] of molecule **9b**. Ellipsoids are scaled to 30% probability. The Cl1−Zr−Cl2 bisector and the projection of the B−C3 direction on the $ZrCl_2$ plane enclose an angle of 56°.

tetrahedral and an octahedral fragment. The best ligand C_5 plane and the Cl_3 plane are coplanar (within the esd). The metal is closest to C4, and the slip distortion amounts to 14 pm.[30] The torsional position of the $TiCl_3$ group is described as the angle between the projections of the lines C4,B and Ti,Cl2 onto the boratabenzene C_5 plane; this angle is 10° (Figure 2). This observation suggests that the conformation with one Cl ligand eclipsed to the boron atom corresponds to the torsional ground state. There is some similarity to the complexes $Mn(CO)_3(C_5H_5BR)$ (R = Ph, Me), where the same conformational preference is observed experimentally[31a] and is also deduced from calculations.[31b] The distance Ti−B is longer than the neighboring bonds Ti−C2 and Ti−C6 by 17.8 pm, while differences of 10−15 pm are typical for 18 valence electron complexes of 3d metals.[32] This comparison shows that the boratabenzene ligand is η^6-bonded though the Ti−B overlap will be comparatively small.

Complex **7b** possesses two rather different boratabenzene ligands **A** and **B** with different torsional positions. For the bent sandwich structures the torsional position is described as the angle between the bisector of the two bonds Zr−Cl and the projection of the line C4,B onto the plane $ZrCl_2$. Ring **A** is similar to the ring in **6a**. This ring is planar in its C_5 moiety (largest perpendicular displacement 1.1(5) pm for C14 toward the metal) with the boron atom bent away from the metal (displacement of 16.6(6) pm for the B atom) and shows a torsional angle of 169° (Figure 4). Ring **B** is less regular (largest perpendicular displacement of 3.7(5) pm for C24 toward the metal; displacement of 7.1(5) pm for the boron away from the metal) and shows a transverse orientation with a torsional angle of 78°. By the same argument as that above for **6a**, the Zr−B distances should still be considered as bonding distances implying η^6-bonding for both rings. Both Zr−B bond lengths of 284.5(5) pm for ring **A** and 278.3(4) pm for ring **B** are shorter than in $ZrCl_2(C_5H_5BNPr^i_2)_2$ (**11**) (Zr−B 298 pm).[9] In **11**, the bonding π-interaction with the exocyclic dialkylamino donor substituent is antibonding with respect to the metal−boron interaction and causes the further lengthening of the Zr−B bond.[9] This situation is well-documented for complexes of boroles,[33] boratabenzenes,[5,34] and borepines.[35]

The structures of **8a** and **9b** allow a comparison of the M−C bonds for cyclopentadienyl and boratabenzene ligands. The bond lengths indicate stronger bonding for the Cp and Cp* ligands, in accord with the higher basicity of cyclopentadienide **2**. This effect is more pronounced for the Cp* ligand. The methyl groups increase the energy of the ligand HOMO. As a consequence the ligand-to-metal bonding is strengthened even more for the cyclopentadienyl ring and weakened for the competing boratabenzene ligand.

Conclusion

The first boratabenzene complexes of zirconium, **10** and **11**, that have been published[9] possess stabilizing *B*−dialkylamino groups. In this paper, we have described the first boratabenzene complexes of Ti and Hf as well as new Zr complexes without stabilizing substituents at boron. Our work indicates a limiting situation in boratabenzene chemistry: Increasing the transfer of electron density from the boratabenzene ligand to the central metal may cause sensitivity to reduction and base-induced decomposition. The Ti(IV) complexes **6a** and **8a** as well as the (as yet) nonexistent **7a** mark this limit.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH_2Cl_2 from CaH_2, toluene from sodium, and Et_2O and THF from sodium benzophenone ketyl. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected.

NMR spectra were recorded on a Varian VXR 300 spectrometer (^1H, 300 MHz; $^{13}C\{^1H\}$, 75.4 MHz), a Bruker WP 80 PFT (^1H, 80 MHz), and a PMR Firenze (^{11}B, 27.9 MHz) spectrometer. Chemical shifts were measured at ambient temperature and are relative to internal TMS for ^1H and ^{13}C and relative to $BF_3{\cdot}Et_2O$ as an external reference for ^{11}B. Mass

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(30) Defined as the distance between the projection of the metal onto the C_5 plane and the geometric mean of the projections of the atoms C_5B onto the C_5 plane.

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(32) See ref 8, p 204.

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(35) Ashe, A. J., III; Al-Taweel, S. M.; Drescher, C.; Kampf, J. W.; Klein, W. *Organometallics* **1997**, *16* 1884.

Table 8. Structural Information Related to Least-Squares Planes

	6a	**7b**	**8a**	**9b**
atoms in least squares plane **A**	C2−C6	C11−C15	C2−C6	C1−C5
max deviation from plane **A**, pm	1.6(3) for C4	1.1(5) for C14	4(1) for C5	2.2(6) for C2
distance metal−plane **A**, pm	198.2(1)	217.7(1)	206.5(2)	219.9(1)
distance boron−plane **A**, pm	9.1(3)	16.6(6)	8(1)	8.5(7)
slip distortion,[30] pm	13.8	10.1	20.1	15.9
atoms in least squares plane **B**	C11, C12, C13	C21−C25	C10−C14	C10−C14
max deviation from plane **B**, pm		3.7(5) for C24	0.0(1.0)	1.7(6) for C13
distance metal−plane **B**, pm	97.1(1)	218.6(1)	205.0(2)	220.7(1)
distance boron−plane **B**, pm		7.1(5)		
slip distortion,[30] pm	0.7	15.2	2.0	2.9
interplanar angle **A**,**B**, deg	0.9(1.4)	50.4(6)	49.9(3)	49.2(2)

Table 9. Crystal Data, Data Collection Parameters, and Convergence Results

	6a	**7b**	**8a**	**9b**
formula	$C_6H_8BCl_3Ti$	$C_{12}H_{16}B_2Cl_2Zr$	$C_{11}H_{13}BCl_2Ti$	$C_{16}H_{23}BCl_2Zr$
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	*Pbca* (No. 61)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
a, pm	1250.8(5)	759.8(2)	692.1(3)	1545(1)
b, pm	1183(1)	1275.2(4)	1188(2)	1317.9(6)
c, pm	1324.3(4)	1473.4(2)	1474.5(6)	1696.4(9)
β, deg			101.36(3)	
U, nm^3	1.960(2)	1.4276(6)	1.189(2)	3.454(4)
Z	8	4	4	8
d_{calcd}, g cm^{-3}	1.662	1.601	1.539	1.494
T, K	203	293	255	263
μ, cm^{-1}	16.25	11.10	11.30	9.27
θ_{max}, deg	27	30	26	25
cryst dimens, mm^3	0.50 × 0.36 × 0.28	0.50 × 0.30 × 0.30	0.45 × 0.45 × 0.12	0.55 × 0.55 × 0.20
abs cor	none	none	empirical	empirical
min rel trans			0.60	0.92
max rel trans			1.00	1.00
no. of reflns	4532	4636	2062	3080
no. of indep obsd reflns $I > 1.0\sigma(I)$	1451	3566	992	1823
no. of variables	133	155	136	181
R^a	0.036	0.045	0.080	0.048
$R_w{}^b$	0.036	0.052	0.064	0.055
residual electron density, e nm^{-6}	0.83	0.84	0.57	0.60

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

spectra were recorded on a Finnigan MAT-95 spectrometer at a nominal electron energy of 70 eV.

Cyclic voltammetry was carried out using a EG & G 175 voltage scan generator and a EG & G 173 potentiostat. For the measurements, a conventional three-electrode cell with a platinum-inlay working electrode, a platinum sheet counter electrode, and a saturated calomel (SCE) reference electrode was used. The solvent CH_2Cl_2 (Merck, p.a.) was filtered through highly active alumina and distilled under nitrogen. Solutions were ca. 10^{-3} M in electroactive species and 0.1 M in tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. TBAH was recrystallized from ethanol and dried in vacuo at 80 °C for 48 h. All potentials were measured relative to the $FeCp_2{}^{+/0}$ couple ($E_{1/2}$ 0.483 V in CH_2Cl_2),[36] which was added after the measurement.

Trichloro(1-methylboratabenzene)titanium (6a). Titanium tetrachloride (1.1 g, 5.82 mmol) was added dropwise to the tin compound **5** (1.36 g, 5.34 mmol) in hexane (10 mL) at −40 °C. A brown precipitate formed. When the reaction mixture was allowed to warm up to ambient temperature, the solid dissolved. The purple solution was filtered, concentrated until the first crystals appeared, and cooled to −30 °C to give purple crystals. Concentrating the mother liquor under vacuum and cooling to −30 °C gave a second crop of **6a** (a total of 1.22 g, 93%) as deep purple crystals, sensitive to air and water, mp 62 °C (no decomposition ≤250 °C), can be sublimed at 20−30 °C/10^{-6} bar; soluble in hexane; very soluble in toluene, CH_2Cl_2, nitromethane, and trifluoroacetic acid; decomposes in THF to give $TiCl_3(THF)_3$. Anal. Calcd for $C_6H_8BCl_3Ti$: C, 29.39; H, 3.29. Found: C, 29.15; H, 3.17. MS (EI): *m/z* (I_{rel}) 244 (20 M^+), 208 (100, $M^+ - HCl$). CV (CH_2Cl_2, TBAH, SCE, $v = 100$ mV/s): $E_{1/2}{}^{(1)} = 0.018$ V ($E_p{}^a = 0.067$, $E_p{}^c = -0.032$ V, $i_p{}^a/i_p{}^c = 0.9$, reversible); $E_{1/2}{}^{(2)} = -0.572$ V ($E_p{}^a = -0.525$, $E_p{}^c = -0.618$ V, $i_p{}^a/i_p{}^c = > 0.8$, quasireversible).

Trichloro(1-methylboratabenzene)zirconium (6b). A solution of **5** (1.42 g, 5.58 mmol) in hexane (10 mL) was added dropwise to a stirred suspension of freshly sublimed $ZrCl_4$ (1.3 g, 5.6 mmol) in hexane (10 mL) at 20 °C. The mixture continued to stir for 1 h. The creme-colored powder was washed with hexane (40 mL) and dried under a high vacuum to give **6b** (1.58 g, 98%), sensitive to air and water; donor solvents and aromatic solvents induce slow dismutation; therefore, **6b** is always somewhat contaminated (≤5%) by $ZrCl_4$ and $ZrCl_2(C_5H_5BMe)_2$ (**7b**).

Trichloro(1-methylboratabenzene)hafnium (6c). The tin compound **5** (1.04 g, 4.1 mmol) and freshly sublimed hafniumtetrachloride (1.31 g, 4.1 mmol) were treated and worked up as described for **6b** to give **6c** (1.50 g, 97%); general properties as for **6b**. **Dichlorobis(1-methylboratabenzene)zirconium (7b)**. Method 1: A mixture of sublimed $ZrCl_4$ (0.27 g, 1.16 mmol) and **4** (0.38 g, 2.32 mmol) in hexane was heated to 70 °C for 2 h. The reaction mixture was cooled to −30 °C to give a first crop of **7b**; the mother liquor was concentrated in a vacuum and then cooled again to afford a second crop of **7b** (a total of 0.38 g, 95%). Method 2: A mixture of sublimed $ZrCl_4$ (6.56 g, 28.15 mmol) and **3** (5.6 g, 57.26 mmol) in toluene (50 mL) was heated to 110 °C for 2 days. The orange suspension obtained was filtered through sand to remove the LiCl formed. Further workup of the filtrate as described above afforded **7b** (a total of 8.9 g, 92%). Yellow needles, somewhat sensitive to air and hydrolysis, mp 146 °C,

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sublimes at 40−50 °C/10^{-6} bar; in the cold barely soluble in hexane, soluble in hot hexane, and very soluble in toluene, CH_2Cl_2, THF, acetone, and CF_3CO_2H. Anal. Calcd for $C_{12}H_{16}B_2Cl_2Zr$: C, 41.90; H, 4.69, Found: C, 42.14; H, 4.69. MS (EI): m/z (I_{rel}) 342 (17, M^+), 251 (100, $M^+ - C_5H_5BMe$). CV (CH_2Cl_2, TBAH, SCE, $v = 100$ mV/s): $E_{1/2} = -0.978$ V ($E_p^a = -0.946$, $E_p^c = -1.010$ V, $i_p^a/i_p^c = 0.90$, reversible).

Dichlorobis(1-methylboratabenzene)hafnium (7c). Method 1: Reaction of $HfCl_4$ (0.32 g, 1.0 mmol) and **4** (0.33 g, 2.0 mmol) and workup as described for **7b** afforded **7c** (0.39 g, 90%). Method 2: Reaction of $HfCl_4$ (1.0 g, 3.12 mmol) and **3** (0.61 g, 6.24 mmol) and workup as decribed for **7b** produced **7c** (0.81 g, 60%). Light yellow needles, sensitive to air and hydrolysis, mp 133 °C, sublimes at 70−80 °C/10^{-6} bar; in the cold barely soluble in hexane, soluble in hot hexane, and very soluble in toluene, CH_2Cl_2, and THF. Anal. Calcd for $C_{12}H_{16}B_2Cl_2Hf$: C, 33.42; H, 3.74. Found: C, 33.25; H, 3.72. MS (EI): m/z (I_{rel}) 432 (20, M^+), 341 (100, $M^+ - C_5H_5BMe$).

Dichloro(cyclopentadienyl)(1-methylboratabenzene)titanium (8a). $TiCl_3Cp$ (0.57 g, 2.6 mmol) in THF (5 mL) and **5** (0.66 g, 2.6 mmol) in THF (2 mL) were combined at −60 °C. Above −50 °C the orange solution turned dark green and crystals began to deposit. After the mixture was warmed up to room temperature, the solid was collected and washed with pentane to afford **8a** (0.45 g, 63%) as small dark green crystals with a metallic luster, dec 60 °C; not sensitive to air, can be sublimed at 30−40 °C/10^{-6} bar; insoluble in pentane, soluble in toluene, and very soluble in CH_2Cl_2; decomposes slowly in THF and is destroyed in acetonitrile within seconds. Anal. Calcd for $C_{11}H_{13}BCl_2Ti$: C, 48.07; H, 4.77. Found: C, 48.07; H, 4.77. MS (EI): m/z (I_{rel}) 274 (5, M^+), 239 (97, $M^+ - Cl$), 183 (65, $CpTiCl_2^+$), 148 (100, $CpTiCl^+$), 91 (70, $C_5H_5BMe^+$). CV (CH_2Cl_2, TBAH, SCE, $v = 100$ mV/s): $E_{1/2}^{(1)} = 0.449$ V ($E_p^a = -0.399$, $E_p^c = -0.499$ V, $i_p^a/i_p^c = 0.91$, reversible); $E_{1/2}^{(2)} = -0.813$ V ($E_p^a = -0.758$, $E_p^c = -0.867$ V, $i_p^a/i_p^c = > 0.7$, quasireversible).

Dichloro(cyclopentadienyl)(1-methylboratabenzene)zirconium (8b). A solution of **4** (0.19 g, 1.16 mmol) in toluene (1 mL) was added to $ZrCl_3Cp$ (0.30 g, 1.16 mmol) in toluene (5 mL). The mixture was warmed to 60 °C for 2 h. Workup as described for **7b** (method 1) gave **8b** (a total of 0.26 g, 70%) as yellow crystals, not sensitive to air, mp 140−145 °C, can be sublimed at 100−110 °C/10^{-6} bar; barely soluble in hexane, soluble in toluene, and very soluble in CH_2Cl_2. Anal. Calcd for $C_{11}H_{13}BCl_2Zr$: C, 41.53; H, 4.12. Found: C, 41.42; H 4.17. MS (EI): m/z (I_{rel}) 316 (18, M^+), 225 (100, $CpZrCl_2^+$).

Dichloro(1-methylboratabenzene)(pentamethylcyclopentadienyl)zirconium (9b). A mixture of sublimed $ZrCl_3Cp^*$ (1.0 g, 3.0 mmol), **3** (0.30 g, 3.06 mmol), and DME (2 mL) in toluene (30 mL) was heated under reflux for 7 days. The yellow solution obtained was concentrated to half of its volume and filtered through sand to remove the LiCl formed. After removal of all volatiles, the residue was washed with hexane (2 × 3 mL), dissolved in toluene (20 mL), and cooled to −30 °C to give **9b** (1.04 g, 89%) as light yellow crystals, sensitive to hydrolysis, mp 177−178 °C, can be sublimed slowly at 120 °C/10^{-6} bar; slightly soluble in hexane, and soluble in toluene and in CH_2Cl_2. Anal. Calcd for $C_{16}H_{23}BCl_2Zr$: C, 49.49; H, 5.97. Found: C, 49.66; H, 6.13. MS (EI): m/z (I_{rel}) 388 (14, M^+), 295 (100, $Cp^*ZrCl_2^+$). CV (CH_2Cl_2, TBAH, SCE, $v = 100$ mV/s): $E_{1/2} = -1.429$ V ($E_p^a = -1.336$, $E_p^c = -1.522$ V, $i_p^a/i_p^c = 0.97$, reversible).

Dichloro(1-methylboratabenzene)(pentamethylcyclopentadienyl)hafnium (9c). Freshly prepared $HfCl_3Cp^*$ (1.1 g, 2.62 mmol), **3** (0.27 g, 2.76 mmol), toluene (20 mL), and DME (0.3 mL) were treated and worked up as described for **9b** to give **9c** (1.06 g, 85%) as light yellow crystals, somewhat sensitive to air and hydrolysis, mp 167−169 °C (dec), sublimes at 100−110 °C/10^{-6} bar; barely soluble in hexane, and soluble in toluene and in CH_2Cl_2. Anal. Calcd for $C_{16}H_{23}BCl_2Hf$: C, 40.41; H, 4.88. Found: C, 40.63; H, 4.99. MS (EI): m/z (I_{rel}) 476 (17, M^+), 385 (100, $Cp^*HfCl_2^+$).

Crystal Structure Determinations of 6a, 7b, 8a, and 9b. The data collection was performed on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator, $\lambda = 71.07$ pm). Crystal data, data collection parameters, and convergence results are given in Table 9.

For the rod-shaped crystals of **6a** and **7b**, no absorption correction was performed, whereas in the case of the platelets typical for **8a** and **9b**, empirical absorption corrections were applied before averaging over symmetry-related intensities. The structures were solved by direct methods[37] and refined on F with the local version of the SDP system.[38] In the final least-squares refinements, non-hydrogen atoms were assigned anisotropic displacement parameters; in the case of **6a**, H atoms were refined isotropically, whereas the hydrogen atoms were included in riding geometry with fixed displacement parameters (C−H = 98 pm, $U_{iso}(H) = 1.3\ U_{iso}(C)$) in the refinement of the structural model for the other compounds. We note that crystal quality and, hence, the precision of the structural results is significantly lower for **8a** than for the remaining structures. This is evidenced both in higher esd's and an unsatisfactory ratio between variables and observations.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **6a**, **7b**, **8a**, and **9b** (20 pages). Ordering information is given on any masthead page.

OM970313B

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(37) Sheldrick, G. M. *SHELXS-86, Program for Structure Solution*; Göttingen, Germany, 1986.

(38) Frenz, B. A. *ENRAF-Nonius*, SDP Version 5.0; Delft, The Netherlands, 1989.

(39) Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-407116 for **6a**, CSD-407115 for **7b**, CSD-407114 for **8a**, and CSD-407113 for **9b**, the names of the authors and this journal citation.