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Triorganyl- and Diorganyloxozirconium Hydridoborates – Synthesis and Structures[‡]

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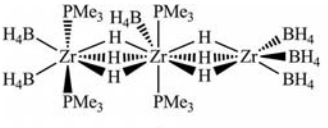
The reactions of $Zr(OBu)_4$ and $Zr(OEt)_4$ with $H_3B{\cdot}THF$ in THF led to $HB(OR)_2$ and $B(OR)_3$, but no zirconium tetrahydroborate $[(RO)_{4-n}Zr(BH_4)_n]$ could be isolated. On the contrary, the reactions of $[tBu_3CO]_{4-n}ZrCl_n$ and $[tBu_3SiO]_{4-n}ZrCl_n$ with $LiBH_4$ generated the tetrahydroborates $[(RO)_3Zr(BH_4)]$ and $[(RO)_2Zr(BH_4)_2]$. These can be used to produce by hydroborate exchange dihydridodiorganyl borates $[(RO)_{4-n}Zr(H_2BC_8H_{14})_n]$ and byproducts. The structures of the new zirconium hydridoborates have been determined by X-ray crystallography. Compound $[(tBu_3CO)_3Zr(H_2BC_8H_{14})]$ shows site-disordered dihydroborate units with agostic Zr–H–C interactions, while $[(tBu_3SiO)_2Zr(H_2BC_8H_{14})_2]$ is quite symmetric (C_2/c). The corresponding tetrahydridoborates possess in most cases $\mu^3{}_1$-bonded ZrH_3BH groups.

Introduction

In contrast to the unknown titanium(IV) tetrahydroborate, the element homologous zirconium and hafnium compounds $M(BH_4)_4$ show a marked increase in thermal stability and resist reduction even at moderately increased temperatures.[1] On the other hand, $[Ti(BH_4)_3]_2$ is sufficiently stable and its structure is well known.[2] However, neither $Zr(BH_4)_3$ nor $Hf(BH_4)_3$ have yet been characterized.[3] The higher stability of the Zr and Hf compounds against reduction is due to the fact that they have a filled 3d shell in the case of Zr and completely filled 4d and 4f shells in the case of Hf. Therefore, the chemistry of Zr and Hf hydridoborates and their derivatives are much better developed[1,4] than that of the corresponding Ti^{III} hydridoborates.[5]

Typical examples are compounds **1** and **2**, as shown by G. S. Girolami et al.[6] The high stability of zirconium tetrahydridoborates should allow their synthesis from $Zr(OR)_4$ compounds and $H_3B{\cdot}THF$. The most stable zirconium hydridoborates contain zirconocene units.[7] They can be obtained from Cp_2ZrCl_2 and $LiBH_4$ or $LiH_{4-n}BR_n$ compounds.



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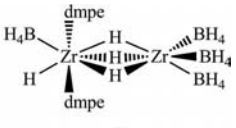

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Results and Discussion

We first studied the temperature-dependent reactions of $Zr(OBu)_4{\cdot}HOBu$ with $H_3B{\cdot}THF$ by ^{11}B NMR spectroscopy, because this zirconium alkoxide is monomeric. An excess of $H_3B{\cdot}THF$ was used, and ^{11}B NMR spectroscopic data were recorded starting at –50 °C in steps of 10 °C up to 40 °C. Figure 1 shows the changes of the proton-coupled ^{11}B NMR spectra (Table 1). The reactions lead already at low temperatures to $HB(OBu)_2$ and $B(OBu)_3$ as well as $H_3B{\cdot}THF$ ($\delta^{11}B$ = –28.9, 19, and 0.6 ppm). At about –30 °C, two new species appeared at $\delta^{11}B$ = –18.2 and –23.9 ppm. The broad signal at δ = –23.9 ppm can be assigned to $[(BuO)_3Zr(BH_4)]$ (**4**) (see Table 2). This species is converted to $[(BuO)_2Zr(BH_4)_2]$ (**5**), δ = –18.2 ppm, $^1J(^{11}B^1H)$ = 76 Hz, which is the dominating species up to 0 °C. In spite of the excess of $H_3B{\cdot}THF$, the final products are neither $Zr(BH_4)_4$ nor $[(BuO)_nZr(BH_4)_{4-n}]{\cdot}THF$. Equations (1) to (4) describe the formation of compounds **4** to **6**. In spite of the enrichment of the $[BuOZr(BH_4)_3]$ species, no single crystals could be isolated. This may be due to the fact that compounds $Zr(BH_4)_4$ or $Zr(BH_4)_4{\cdot}(THF)_n$ are not formed because their precursor **6** is most likely not monomeric.

$$2\,Zr(OBu)_4{\cdot}HOBu + H_3B{\cdot}THF \rightarrow 2\,\underset{3}{Zr(OBu)_4} + (BuO)_2BH + 2\,H_2 + THF \qquad (1)$$

$$2\,Zr(OBu)_4 + 3\,H_3B{\cdot}THF \rightarrow 2\,\underset{4}{(BuO)_3ZrBH_4} + (BuO)_2BH + 3\,THF \qquad (2)$$

$$2\,\underset{4}{(BuO)_3ZrBH_4} + 3\,H_3B{\cdot}THF \rightarrow 2\,\underset{5}{(BuO)_2Zr(BH_4)_2} + (BuO)_2BH + 3\,THF \qquad (3)$$

$$2\,(BuO)_2Zr(BH_4)_2 + 3\,H_3B{\cdot}THF \rightarrow 2\,\underset{6}{(BuO)Zr(BH_4)_3} + (BuO)_2BH + 3\,THF \qquad (4)$$

For this reason, we hoped that the corresponding EtO compounds might crystallize more readily [Equation (5)].

[‡] Metal Hydridoborates and Hydridoborato Metallates, 34. Part 33: Ref.[17]

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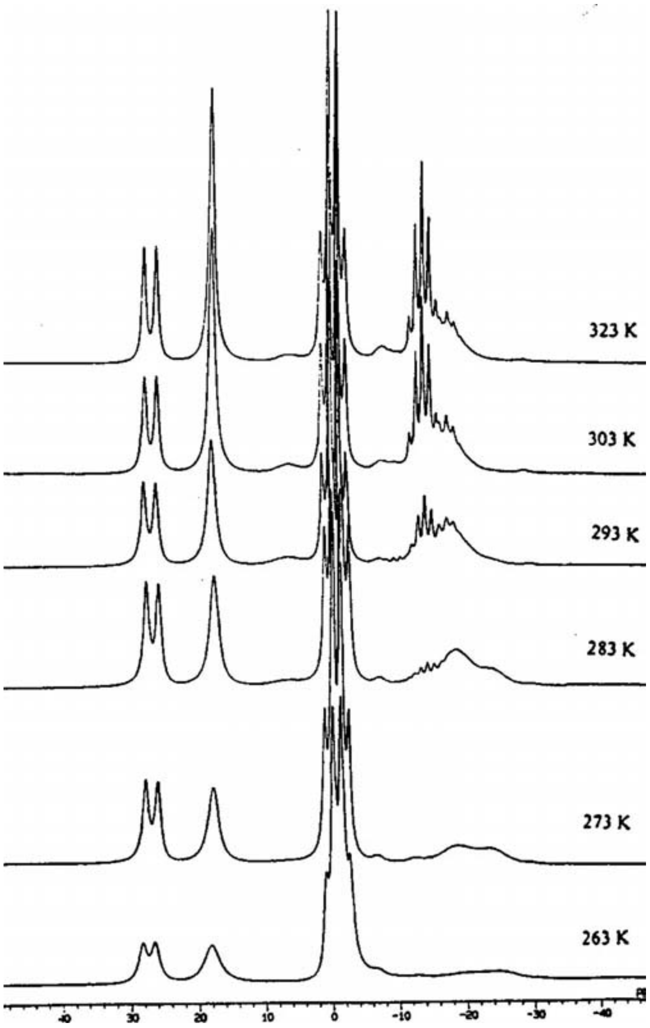


Figure 1. Proton-coupled NMR spectra for the reaction of $(BuO)_4Zr{\cdot}HOBu$ with an excess of $H_3B{\cdot}THF$ in the temperature range –10 °C to 40 °C.

We therefore reacted $Zr(OEt)_4$ (**7**) with $H_3B{\cdot}THF$ in THF solution (see Table 3). After addition of $Zr(OEt)_4$ to $H_3B{\cdot}THF$, dissolved in THF, and heating the mixture to 60 °C for 7 h, the dominant ^{11}B NMR signal showed the formation of $[(EtO)Zr(BH_4)_3]$ (**8**) [$\delta^{11}B$ = –12.5 ppm, $^{1}J(^{11}B^{1}H)$ = 86 Hz]. However, this was only a weak signal.

Table 2. ^{11}B NMR chemical shifts [ppm] and $^{1}J(^{11}B^{1}H)$ coupling constants [Hz] of *n*-butanolatozirconium- and *tert*-butanolatotitanium(IV) tetrahydridoborates.

$[(BuO)_3Zr(BH_4)]$	–24.0/–	$(tBuO)_3Ti(BH_4)$	–23.0/87
$[(BuO)_2Zr(BH_4)_2]$	–17.5/79	$(tBuO)_2Ti(BH_4)_2$	–12.4/85
$[(BuO)Zr(BH_4)_3]$	–13.9/86	$(tBuO)Ti(BH_4)_3$	Unstable
$[(tBu_3CO)_2Zr(BH_4)_2]$	–17.1/86		

On further heating, a stronger signal appeared at $\delta^{11}B$ = 15 ppm in the brown solution. Obviously the polymeric character of $Zr(OEt)_4$[8] prohibits well-defined $EtO/(BH_4)$ exchanges. Therefore, reactions of $Zr(OEt)_4$ with $H_3B{\cdot}THF$ are not suitable for preparing proper $[(EtO)_nZr(BH_4)_{4-n}]$ compounds. A better route seemed, therefore, a reaction of $(RO)_{4-n}ZrCl_n$ with $LiBH_4$ or $NaBH_4$. The synthesis of $(tBu_3CO)_2ZrCl_2$ (**9**) was first described by T. V. Lubben et al.[9] from $(tBu_3CO)_4Zr$ and $ZrCl_4$. Chloride **9** reacted with $LiBH_4$ to produce $[(tBu_3CO)_2Zr(BH_4)_2]$ (**10**) [Equation (6)], and the IR spectrum shows clearly that both BH_4 groups are bonded to the Zr atom by two different tridentate μ^3-groups, because two sets of BH_n frequencies are observed.

$$\underset{\mathbf{7}}{Zr(OEt)_4} + 5\,H_3B{\cdot}THF \rightarrow \underset{\mathbf{8}}{EtOZr(BH_4)_3} + EtOBH_2 + (EtO)_2BH + 5\,THF \quad (5)$$

$$\underset{\mathbf{9}}{(tBu_3CO)_2ZrCl_2} + 2\,LiBH_4 \rightarrow \underset{\mathbf{10}}{(tBu_3CO)_2Zr(BH_4)_2} + 2\,LiCl \quad (6)$$

An X-ray diffraction study of the structure of a single crystal of **10** reveals (see Figure S1) that the symmetry of this molecule is close to *C*2. Compound **10** reacts with NEt_3 or PMe_3 in small amounts of toluene [Equations (7), (8), and (9)]. The ^{11}B NMR spectra show that these bases remove BH_3 groups from **10**, and in the case of PMe_3 there are equilibria between the donor-substituted compound **12** and the solvate-free compound **10**. It may well be that PMe_3 also removes two BH_3 groups as shown in Equations (8) and (9), but zirconium hydride **13A** could neither be isolated nor characterized by IR spectroscopy.

$$(tBu_3CO)_2Zr(BH_4)_2 + Et_3N \rightarrow \underset{\mathbf{11}}{(tBu_3CO)_2ZrH(BH_4)} + H_3B{\cdot}NEt_3 \quad (7)$$

$$\underset{\mathbf{12}}{(tBu_3CO)_2Zr(BH_4)_2} + 2\,PMe_3 \leftrightarrow \underset{\mathbf{13}}{(tBu_3CO)_2ZrH(BH_4)PMe_3} + H_3B{\cdot}PMe_3 \quad (8)$$

$$(tBu_3CO)_2ZrH(BH_4)PMe_3 \leftrightarrow \underset{\mathbf{13A}}{(tBu_3CO)_2ZrH_2} + H_3B{\cdot}PMe_3 \quad (9)$$

Table 1. Temperature dependence of the interaction of $H_3B{\cdot}THF$ (excess) with $Zr(OBu)_4{\cdot}HOBu$ at various temperatures. ^{11}B NMR chemical shifts [ppm], coupling constants [Hz] (in parentheses), and relative intensities in square brackets.

	$HB(OBu)_2$	$B(OBu)_3$	$H_3B{\cdot}THF$	$[(BuO)Zr(BH_4)_3]$	$[(BuO)_2Zr(BH_4)_2]$	$[(BuO)_3ZrBH_4]$
–10 °C	27.5 (159)	18.2	–0.6 (106)	–24.0.	–19.0.	
Rel. int.	[2.4]		[10.5]	[0.4]	[0.6]	
0 °C	27.5 (159)	18.2	–0.6 (106)	–24.0	–18.5.	–14.3 (84)
Rel. int.	[1.0]	[0.6]	[3.7]	[0.2]	[0.6]	[0.2]
10 °C	27.5(159)	18.2	–0.5 (106)	–24.0,	–17.5 (76)	–14.2 (88)
Rel. int.	[0.6]	[0.5]	[1.4]	[0.2]	[0.5]	[0.6]
20 °C	27.5 (157)	18.2	–0.4(106)		–17.5 (88)	–14.0 (85)
Rel. int.	[0.5]	[0.57]	[1.4]		[0.3]	[0.2]
30 °C	27.4 (167)	18.2	–0.2 (106)		–17.5 (79)	–13.9 (88)
Rel. int.	[0.45]	[0.7]	[1.6]		[0.2]	[0.8]
40 °C	27.4 (159)	18.2	–0.1(106)		–17.5 (88)	–13.8 (88)
Rel. int.	[0.5]	[0.7]	[1.5]		[0.0]	[0.9]

Table 3. ^{11}B NMR chemical shifts [ppm] for the reaction of $Zr(OEt)_4$ with $H_3B·THF$ in toluene solution.

Product	$HB(OEt)_2$	$B(OEt)_3$	$H_3B·THF$	$(EtO)_xZr(BH_4)_{3-x}$	
1 h/r.t.	28.5	19.2	0.93	–18, broad	
7 h/60 °C	28.5	19.3	1.1	$EtOZr(BH_4)_3$ [–12.5, (^1J = 86 Hz)]	
15 h/60 °C	28.4	19.1	1.0	$EtOZr(BH_4)_3$ [–12.4,(^1J = 86 Hz)]	–16, broad
30 h/60 °C	28.4	19.2	0.81		–16, broad

Slightly yellow brown crystals separated from the solution within four months, which were shown by X-ray crystallography to be [$(t\mathrm{Bu}_3CO)_3Zr(BH_4)$] (**14**), and not [$(t\mathrm{Bu}_3CO)_2Zr(BH_4)_2$] (**10**). This result shows that not only an OR/BH_4 ligand exchange but also a (BH_4)/($t\mathrm{Bu}_3CO$) exchange according to Equation (10) is possible at –30 °C. A related exchange was observed upon treating [$(t\mathrm{Bu}_3CO)_3ZrMe$] with Me_3COH at 70 °C for 15 days. Whether these reactions need a Zr^{III} species as catalyst could not be reliably determined.

$$2\ \underset{\mathbf{10}}{(t\mathrm{Bu_3CO})_2\mathrm{Zr(BH_4)_2}} \leftrightarrow \underset{\mathbf{14}}{(t\mathrm{Bu_3CO})_3\mathrm{Zr(BH_4)}} + \underset{\mathbf{15}}{(t\mathrm{Bu_3CO})\mathrm{Zr(BH_4)_3}} \qquad (10)$$

$$\underset{\mathbf{14}}{(t\mathrm{Bu_3CO})_3\mathrm{Zr(BH_4)}} + \mathrm{Li(H_2BC_8H_{14})} \rightarrow \underset{\mathbf{16}}{(t\mathrm{Bu_3CO})_3\mathrm{Zr(H_2BC_8H_{14})}} + \mathrm{LiBH_4} \qquad (11)$$

$$\underset{\mathbf{10}}{(t\mathrm{Bu_3CO})_2\mathrm{Zr(BH_4)_2}} + \mathrm{Li(H_2BC_8H_{14})} \rightarrow \underset{\mathbf{17}}{(t\mathrm{Bu_3CO})_2\mathrm{Zr(BH_4)(H_2BC_8H_{14})}} + \mathrm{LiBH_4} \qquad (12)$$

$$(t\mathrm{Bu_3CO})_2\mathrm{Zr(BH_4)_2} + 2\ \mathrm{Li(H_2BC_8H_{14})} \rightarrow \underset{\mathbf{18}}{(t\mathrm{Bu_3CO})_2\mathrm{Zr(H_2BC_8H_{14})_2}} + 2\ \mathrm{LiBH_4} \qquad (13)$$

Compound **14** is the most stable amongst the (*tert*-butyloxo)zirconium tetrahydridoborates. Therefore, we expected that it might be ready for a BH_4/H_2BR_2 exchange, according to Equation (11). Indeed, its reaction with lithium 9,9-dihydrido-9-borabicyclononane showed that compound **14** disappeared within an hour. After this time, the ^{11}B NMR signal for **14** at –17.4 ppm [$^1J(^{11}B^1H)$ = 71 Hz, 10% intensity] and for $LiH_2BC_8H_{14}$ [δ = –13.4 ppm (t, 42%)] diminished, and new signals appeared at $\delta^{11}B$ = 9, 16.6, and 3.5 ppm in addition to a signal at δ = –39.2 ppm [quint., $^1J(^{11}B^1H)$ = 81 Hz, 20%] for $LiBH_4$. The signal at δ = 16.6 ppm is due to [$(t\mathrm{Bu}_3CO)_3Zr(H_2BC_8H_{14})$] (**16**), while the resonance at 3.5 ppm results from [$(t\mathrm{Bu}_3CO)_2Zr(H_2BC_8H_{14})_2$] (**18**).[10] Compound **17** could not be detected.

After 16 h, additional ^{11}B NMR signals at δ = –21.8, (3.5%) and 29.2 ppm (8%, broad, no multiplets observable) with relative intensities 4:5 and a signal at δ = 57.0 ppm (s) were observed. The signal at –21.8 ppm is due to [$(t\mathrm{Bu}_3CO)Zr(BH_4)_3$] (**15**),[11] and he signals at $\delta^{11}B$ = 29.2 and 57.0 ppm represent $(HBC_8H_{14})_2$ and $Me_3CO–BC_8H_{14}$, respectively. Within this time about 85% of compound **10** reacted astonishingly not only by $BH_4/H_2BC_8CH_{14}$ exchanges but also by the change of a $(t\mathrm{Bu}_3O)_2Zr$ unit into a $(t\mathrm{Bu}_3CO)_3Zr$ group [Equations (12) and (13)]. The crystal structure of [$(t\mathrm{Bu}_3CO)_2Zr(H_2BC_8H_{14})_2$] (**18**) could be determined.

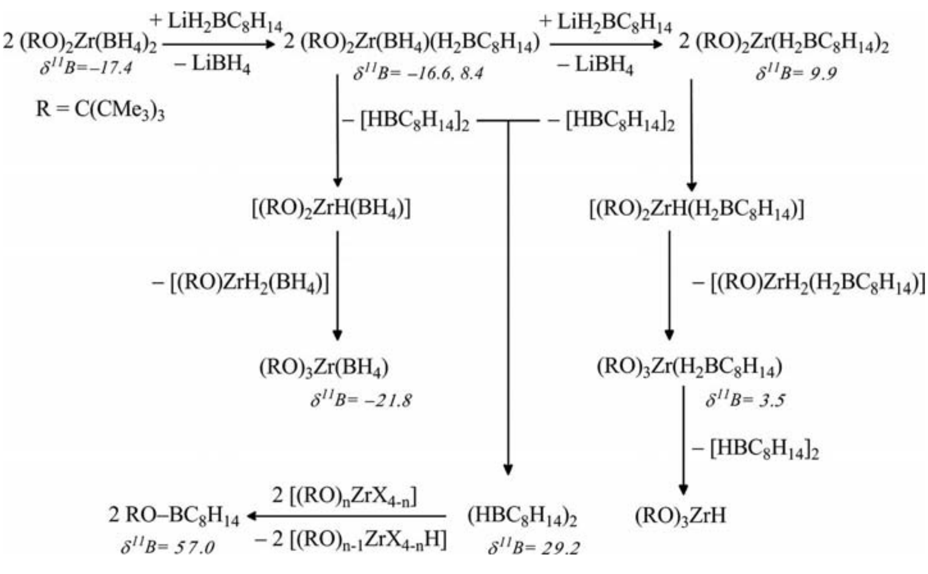
Because the reactions of zirconium tetraalkoxides with $H_3B·THF$ in THF solution are difficult to control, we switched to reactions of alkoxozirconium halides with $LiBH_4$ in diethyl ether or THF. A typical example is the reaction of lithium(2,6-diisopropylphenolate) with zirconium(IV) tetrachloride bis(tetrahydrofuran) according to Equation (14) at –78 °C, which afforded **19** in 21% yield. H. Yasuda et al. had previously shown that bis(2,6-methylphenolato)silicon dichloride bis(tetrahydrofuran) can be prepared from $ZrCl_4(THF)_2$ and 2,6-(methylphenoxy)trimethylsilyl ether.[12] In our case, **19** separated within three weeks as colorless crystals suitable for an X-ray structure determination.

$$2\ 2{,}6\text{-}i\mathrm{Pr_2C_6H_3OLi} + \mathrm{ZrCl_4(THF)_2} \rightarrow \underset{\mathbf{19}}{(2{,}6\text{-}i\mathrm{Pr_2C_6H_3O})_2\mathrm{ZrCl_2(THF)_2}} + 2\ \mathrm{LiCl} \qquad (14)$$

$$(2{,}6\text{-}i\mathrm{Pr_2C_6H_3O})_2\mathrm{ZrCl_2} + 2\ \mathrm{LiBH_4} \rightarrow \underset{\mathbf{20}}{(2{,}6\text{-}i\mathrm{Pr_2C_6H_3O})_2\mathrm{Zr(BH_4)_2}} + 2\ \mathrm{LiCl} \qquad (15)$$

Reactions of $(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_2ZrCl_2·(THF)_2$ (**19**) with two equivalents of $LiBH_4$ in Et_2O produced excellent yields of [$(2,6\text{-}i\mathrm{Pr}_2C_6H_3O)_2Zr(BH_4)_2$] (**20**) [Equation (15)]. However, the ^{11}B NMR signals depended strongly on the ratio of the reagents and their concentration. Separate signals for $LiBH_4$ and zirconium tetrahydridoborate were not observed. A 1:1 reaction of $LiBH_4$ with **19** in Et_2O led to a ^{11}B NMR signal at δ = –23.4 ppm [$^1J(^{11}B^1H)$ = 87 Hz]. Addition of one more equivalent of $LiBH_4$ shifts the ^{11}B NMR signal to –25.5 ppm [$^1J(^{11}B^1H)$ = 83 Hz], and a molar ratio of 1:4 leads to $\delta^{11}B$ = –28.4 ppm [$^1J(^{11}B^1H)$ = 79 Hz]. Scheme 1 shows possible equilibrium processes, which also include ionic species. This can be concluded from the observation that, after removal of the solvents, an oily residue was obtained, which – after treatment with hexane – shows a $\delta^{11}B$ NMR quintet at δ = –16.5 ppm [$^1J(^{11}B^1H)$ = 74 Hz], corresponding to [$(RO)_2Zr(BH_4)_2$]. The residue, when treated with benzene, led to a ^{11}B NMR signal at δ = –38.9 ppm ($LiBH_4$). This change of the resonances indicates that $LiBH_4$ is present in the solution (Scheme 1).

N. Wiberg et al.[13] have shown that the tris(*tert*-butyl)silyl group (supersilyl) leads to compounds that mostly yield excellent crystals and allow the preparation of a large number of rather unusual main group supersilyl derivatives. The starting material, sodium supersiloxide **21** can be readily prepared from supersilylsodium and N_2O in THF solution as shown in Equation (16). Compound **21** was first prepared in 1975[14] by base-catalyzed hydrolysis of tris(*tert*-butyl)silane, followed by metalation. However, this route takes more time than the reaction according to Equation (16). The reaction of $ZrCl_4$ with **21** in diethyl ether led, irrespective of the ratio $ZrCl_4/t\mathrm{Bu}_3Si\text{-}Na(THF)_2$, only to compound **22** [Equation (17)]. Obviously, this metathesis prefers the sterically most possible oxosubstitution. The reaction of **22** with $LiBH_4$ according to Equation (18) generates tris[tri(*tert*-butyl)siloxo]zirconium tetrahydridoborate (**23**) in excellent yield. This compound is quite stable but is



Scheme 1.

surpassed in stability by [(tBu$_3$SiO)$_2$Zr(BH$_4$)$_2$], which is stable for several weeks. Because of the good stability of **23**, we expected that PMe$_3$ might remove a BH$_3$ group to generate zirconium hydride [(tBu$_3$SiO)$_3$ZrH] (**24**) [Equation (19)].

$$(t\mathrm{Bu})_3\mathrm{SiNa} + \mathrm{N_2O} + 2\,\mathrm{THF} \rightarrow \underset{\textbf{21}}{(t\mathrm{Bu}_3)_3\mathrm{SiONa(THF)_2}} + \mathrm{N_2} \qquad (16)$$

$$3\,(t\mathrm{Bu}_3)\mathrm{SiONa(THF)_2} + \mathrm{ZrCl_4} \rightarrow \underset{\textbf{22}}{[t\mathrm{Bu_3SiO}]_3\mathrm{ZrCl}} + 3\,\mathrm{NaCl} + 6\,\mathrm{THF} \qquad (17)$$

$$[t\mathrm{Bu_3SiO}]_3\mathrm{ZrCl} + \mathrm{LiBH_4} \rightarrow \underset{\textbf{23}}{[t\mathrm{Bu_3SiO}]_3\mathrm{Zr(BH_4)}} + \mathrm{LiCl} \qquad (18)$$

$$[t\mathrm{Bu_3SiO}]_3\mathrm{Zr(BH_4)} + \mathrm{PMe_3} \rightarrow \underset{\textbf{24}}{[t\mathrm{Bu_3SiO}]_3\mathrm{ZrH}} + \mathrm{H_3B{\cdot}PMe_3} \qquad (19)$$

When excess PMe$_3$ was used in THF solution, a ^{11}B NMR signal at δ = –36 ppm [$^1J(^{11}\mathrm{B}^1\mathrm{H})$ = 96 Hz, $^1J(^{31}\mathrm{P}^{11}\mathrm{B})$ = 60 Hz] was observed as a doublet of a quartet, which is typical for the formation of H$_3$B·PMe$_3$. The signal at δ^{11}B = –21.2 ppm for **23** had vanished. However, it was impossible to reliably assign a proton signal to the expected ZrH fragment of **24** for the following reason: this fragment should lead to a signal in the range 4 to 9 ppm,[15] which would overlap with signals due to the PMe$_3$ unit. An even greater problem is the fact that the expected ZrH/CH intensity ratio should be 1:81, which makes it hard to reliably determine the ZrH species by ^{1}H NMR spectroscopy. Furthermore, the IR spectrum was not helpful, because the Zr–H vibrations fall into the range of those of the *tert*-butyl groups.[16] So our hope rested on single-crystal X-ray structures. The crystals of **24** are trigonal, space group $P\bar{3}$ with $a = b$ = 27.607(9) Å and c = 24.601(7) Å, However, we could not solve the structure although a trigonal fragment with a Zr(OSi)$_3$ core was detected as in ref.[11a] The NMR spectroscopic data of **25** are in agreement with a double-bridging BH$_2$ group [$^1J(^{11}\mathrm{B}^1\mathrm{H})$ = 57 Hz], which is typical for such a compound, although the ^{11}B NMR signal at 3.2 ppm is at the lower end of the expected region. There was only one set of ^{1}H-, ^{13}C-, and ^{29}Si NMR resonances, which indicates high symmetry in solution and also free rotation of the *tert*-butyl groups as well as opening and closing of the Zr–H–B bonds [Equations (20), (21), (22), and (23)].

$$[t\mathrm{Bu_3SiO}]_3\mathrm{ZrBH_4} + \mathrm{Li[H_2BR_2]} \rightarrow \underset{\textbf{25}}{[t\mathrm{Bu_3SiO}]_3\mathrm{Zr(H_2BR_2)}} + \mathrm{LiBH_4} \qquad (20)$$

$$[t\mathrm{Bu_3SiO(BH_4)_2} + \mathrm{Li[H_2BR_2]} \leftrightarrow [t\mathrm{Bu_3Si\,O}]_2\mathrm{Zr(BH_4)(H_2BR_2)}\}\mathrm{Li} \leftrightarrow \underset{\textbf{26}}{[t\mathrm{Bu_3SiO}]_2\mathrm{Zr(H_2BR_2)_2}} + \mathrm{LiBH_4} \qquad (21)$$

$$[t\mathrm{Bu_3Si\,O}]_3\mathrm{Zr(H_2BC_8H_{14})} \rightarrow 2\ \underset{\textbf{27}}{[t\mathrm{Bu_3SiO}]_3\mathrm{ZrH}} + \mathrm{(HBC_8H_{14})_2} \qquad (22)$$

$$2\,[t\mathrm{Bu_3Si\,O}]_3\mathrm{Zr(H_2BR_2)} + \mathrm{HBR_2} \rightarrow \underset{\textbf{28}}{[t\mathrm{Bu_3Si\,O})_2\mathrm{ZrH(H_2BR_2)}} + t\mathrm{Bu_3Si}\,_3\mathrm{Si{-}O{-}BR_2} \qquad (23)$$

$(\mathrm{R_2 = C_8H_{14}})$

Molecular Structures

Tris[tri(*tert*-butyl)methanolato]zirconium(IV) tetrahydroborate (**14**) crystallizes in a monoclinic system, space group $P2_1/c$ with Z = 4 (see Figure 2). The structure was solved by the Patterson method, and the heavy atom positions were refined anisotropically. The CH hydrogen atoms were placed in calculated positions and were treated in the refinement by the riding model. The positions of the HB hydrogen atoms were taken from the Fourier map and included in the final refinement with isotropic thermal parameters. Figure 2 shows a view of molecule **14**. Neglecting H atoms, the symmetry around the Zr atom is close to C_{3v} with almost equal Zr–O distances of 1.98(2) Å and O–Zr–O bond angles ranging from 112.56(9) to 114.82(9)°. The longer Zr–O bonds and the opening of the 6 O–Zr–O bond angles offer the BH$_4$ group a closer contact with the Zr atom, and the B–Zr–O angles span a close range from 104.6(1) to 105.3(1)°. The Zr–O–C bond angles are close to being linear, with values around 170.3(2)°. The observed Zr–B distance of 2.34(2) Å corresponds with a tridentate BH$_4$

group; Zr–B distances of 2.33 to 2.40 Å were observed for other tricoordinate BH_4 groups of comparable zirconium tetrahydridoborates.[10]

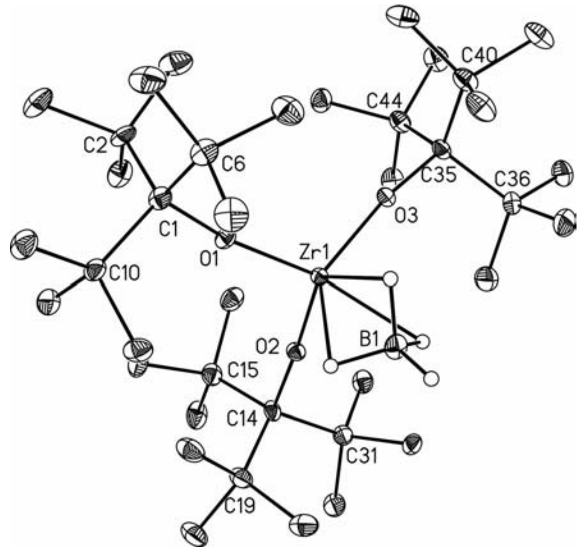


Figure 2. The molecular structure of $(tBu_3CO)_3Zr(BH_4)$ (**14**). Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–O1 1.946(2), Zr1–O2 1.949(2), Zr1–O3 1.946(2), O1–C1 1.475(4), O2–C4 1.462(4), O3–C35 1.461(4), Zr1–B1 2.380(4), B1–H1 1.02(4); Zr1–O1–C1 170.02(2), Zr1–O2–C14 170.1(2), Zr1–O3–C35 170.8(2), O2–Zr1–O3 113.11(9), O1–Zr1–B1 104.6(1), O2–Zr1–B1 105.3(1), O3–Zr1–B1 105.3(1).

The colorless bis[tri(*tert*-butyl)methanolato]zirconium(IV) bis(tetrahydridoborate) (**10**) also crystallizes in the monoclinic space group *C*2/*c* with *Z* = 4. Its Zr atom is situated on a crystallographically symmetric C_2 axis (see Figure 3). Therefore, the two BH_4 groups as well as the two $[tBu_3CO]_2$ groups are equivalent. The BH_4 ligands attach as μ^3-groups onto the Zr center. The Zr–B distances are somewhat shorter than those in compound **14** [2.362(3) vs. 2.380(4) Å]. The Zr–O bonds are also shorter [1.904(2) vs. 2.46(2) Å], and so are the C–O bonds [1.448(3) vs. 1.463(3) Å]. While the O–Zr–O bond angle is 115.2(1)°, the B–Zr–B bond angle is perfectly tetrahedral [109.4(2)°]. The presence of only two tBu_3CO groups allows the BH_4 groups to get closer to the Zr center as shown by a Zr···B distance of 2.362(3) Å. For the same reason, the Zr–O–C bond angles open to 173.9°, which may also be the consequence of the longer C–O bonds, although these effects are not drastic at all. The structure of this compound is similar to bis(phenoxo)zirconium bis(tetrahydridoborate)–tetrahydrofuran.[19]

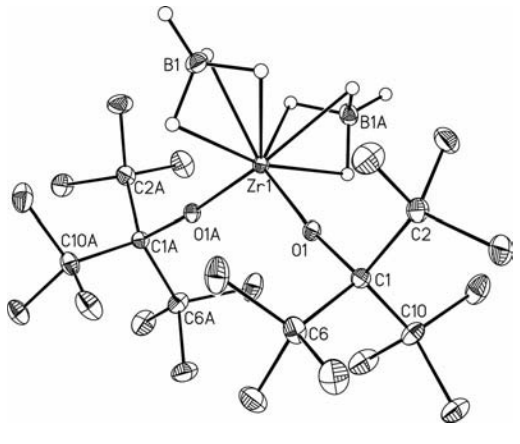


Figure 3. The molecular structure of $(tBu_3CO)_2Zr(BH_4)_2$ (**10**). Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–O1 1.904(2), C1–O1 1.448(3), Zr1–B1 2.362(3), Zr1–H2 2.16(3), Zr1–H3 2.15(3), Zr1–H4 2.07(3), B1–H1 1.09(3), C1–C2 1.628(4), C1–C6 1.618(4), C1–C10 1.629(4), C2–C3 1.540(5); Zr1–O1–C1 173.9(2), O1–Zr1–O1A 115.2(1), O1–Zr1–B1 107.3(9), B1–Zr1–B1A 109.4(2), C1–O1–Zr1 183.9(2), H1–B1–H2 117(2), H1–B1–H3 114(2), H1–B1–H4 118(2), H2–B1–H3 100(2), H2–B1–H4 105(2), H3–B1–H4 102(2).

Compound **19** also crystallizes in a monoclinic system. The structure was first solved in space group *C*2, but the refinement did not merge properly. It turned out that there were two independent molecules in the unit cell. After several attempts, we could finally solve the structure in space group *C*2/*c* (see Figure 4). The Zr atoms lie on a twofold axis. The two molecules differ only in the orientations of the substituents and show only small differences in bond lengths and bond angles. The Zr atoms of compound **19** are octahedrally surrounded by four oxygen atoms and two Cl atoms. The phenoxy groups and THF molecules are *cis*-oriented in an equatorial plane of the octahedron. The planarity of the equatorial plane is perfect with 259.9°.

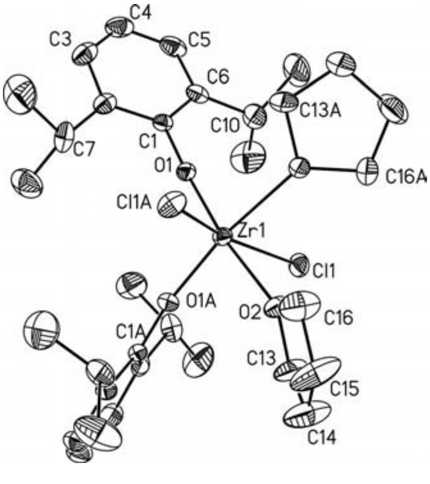


Figure 4. The molecular structure of $(2,6\text{-di-}iPr_2C_6H_3O)_2ZrCl_2(OC_4H_8)_2$ (**19**). Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–O1 1.931(2), Zr1–O2 2.292(3), C1–O1 1.373(4), Zr1–Cl1 2.478(1); O1–Zr1–O1A 100.0(2), Zr1–O2–C13 120.5(3), O1–Zr1–O2 171.4(1), Cl1–Zr1–O1A 94.41(8), Cl1–Zr1–O2A 81.95(8), O1–Zr1–Cl1A i4.41(8), Cl1–Zr1–O2a 82.97(8), Cl1–Zr1–Cl1A 19.7(6), C1–O1–Zr1 171.8(2), O2–Zr1–O1A 88.3(1), O2–Zr1–O2A 83.5(1), O1–Zr1–Cl1 98.58(8), O2–Zr1–Cl1 82.97(8), Zr1–O2–C16 131(3), C13–O2–C16 107.2(3).

As expected, the bond angles between the phenolato groups are rather open with 100.0(2) and 97.8(2)°. The Cl–Zr1–Cla bond angles are 159.75(6)°, and the Cl2–Zr2–Cl2a angle is 158.59(6)°. The THF molecules stand *trans* to the phenolato groups [171.4(1)°], and the phenolato groups include O–Zr–O angles of 94.41(8)° while the Cl–Zr–O atoms make angles of 94.41(8)° (O1–Zr1–Cl1a) and 82.97(8)° (O2–Zr–Cl1a) with adjacent THF molecules. Once again, the Zr1–O1–C1 angles are almost 180° [171.8(2) (for C21–O3–Zr2 171.1(2)°)]. For additional data, see Figure 4. Thus, the structure of this molecule fits well into the structures of other (RO)$_2$ZrCl$_2$ (THF)$_n$ compounds.[9,18]

Figure 5 shows the structure of compound [(*t*Bu$_3$CO)$_2$-Zr(H$_2$BC$_8$H$_{14}$)$_2$] (**18**). The colorless monoclinic compound has space group *C*2/*c*. Its Zr atom sits on a C_2 axis. Therefore, one (*t*Bu$_3$C)$_3$SiO group and one H$_2$BC$_8$H$_{14}$ are symmetry-generated., Whereas the B–Zr–B angle is only 103.6(2)°, the O–Zr–O bond angle is 114.5(1)° as a result of the steric request of the siloxy groups. The Zr–B distance is quite long [2.576(5) Å], which is typical for a dicoordinated H$_2$B group. It is 0.21 Å longer than the distance between Zr and a tricoordinate H$_3$B group.[9] From the Zr–C distances one can deduce that there is no agostic interaction. The Zr–O–C bond angles are 171.5(2)°, and the Zr–O bond length is rather short with 1.900(2) Å.

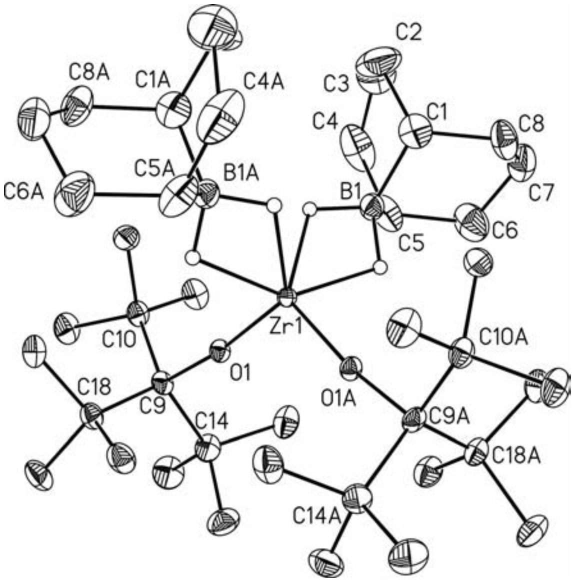


Figure 5. The molecular structure of (*t*Bu$_3$CO)$_2$Zr(H$_2$BC$_8$H$_{14}$)$_2$ (**18**). Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–B1 2.576(5), Zr1– O1 1.900(2), Zr – H1 1.93(5), Zr1–H2 1.90(4), Zr1–H1 1.93(5), B1–H1 1.11(5), B1–H2 1.17(5), B1–C1 1.563(7), B1–C5 1.610(7); B1–Zr1–B1A 103.6(2), B1–Zr1–O1 106.2(1), O1–Zr1–O1A 114.5(1), B1–Zr1–O1A 113.0(3), Zr1–O1 C9 171.5(2).

Compound **23** crystallizes in the monoclinic space group *P*2$_1$/*c*. Although practically all hydrogen atoms were revealed in the Fourier map, those bonded to C atoms were placed in calculated positions and refined as riding on the C atoms. The boron-bonded hydrogen atoms were refined isotropically in contrast to all heavy atoms, which were refined anisotropically. Selected bond lengths and bond angles are listed in Figure 6. The zirconium atom can be described with a local C_{3v} symmetry by neglecting the Zr···H–B interactions. The O–Zr–O bond angle is 114.5(1)°, and the B–Zr–O angles are 106.2(1)°. The Zr···B distance is 2.576(5) Å, which fits into the range of distances in other zirconium tetrahydridoborates.[1,3,5] The Zr–O bonds are 1.937(2) Å, that is, they are shorter than those in [(*t*Bu$_3$CO)$_3$-ZrBH$_4$].[6]

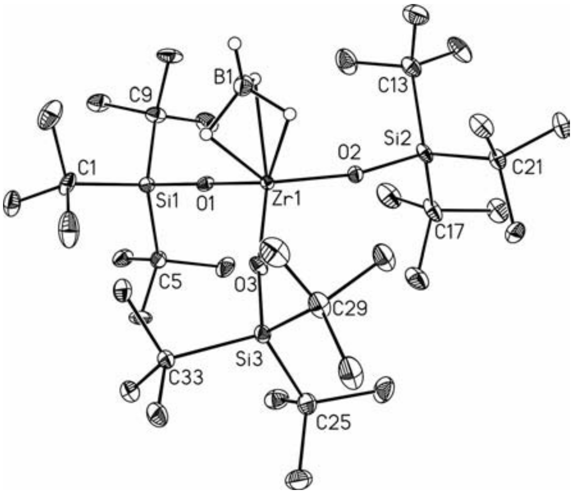


Figure 6. The molecular structure of (*t*Bu$_3$SiO)$_3$Zr(BH$_4$) (**23**) without (left) and with (right) the disorder of the BC$_8$H$_{14}$ group. Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–O1 1.936(3), Zr1–O2 1.931(3), Zr1–O3 1.938(3), Zr1–B1 2.371(7), Zr1–H2 2.00(6), Zr1–H3 2.14(4). Zr1–H4 2.09(6), B1–H1 1.06(6), O1–Si1 1.668(4), O2–Si2 1.672(3), O3–Si3 1.660(4), Si1–C1 1.923(5), Si1–C5.924(5), Si1–C9 1.920(6), Si2–C13 1–934(6), Si2–C17 1.921(5), Si2–C21 1.921(6), Si3–C25 1.931(6), Si3–C29 1.924(6), Si3–C33 1.916(5), B1–H2 1.18(6), B1–H3 1.08(5), B1–H4 1.13(6); O1–Zr1–O2 111.5(1), O1–Zr1–O3 110.2(1), O2–Zr1–O3 110.2(2), O2–Zr1–H2 88(2), O2–Zr1–H4 94(2), O3–Zr1–H2 88(2), O3–Zr1–H4 136(2), O1–Zr1–H4 92(2), O1–Zr1–H3 135(1), O2–Zr1–H4 94(2), O1–Zr1–B1 108.4(2), O2–Zr1–B1 108.2(2), O3–Zr1–B1 108.2(2), Zr1–O1–Si1 170.8(2), Zr1–O2–Si2 169.1(2), Zr1–O3–Si3 169.0(2), C1–Si1–C5 112.6(2), C13–Si2–C17 112.9(3), C29–Si3–C25 113.2(3).

The zirconium atom of [(*t*Bu$_3$SiO)$_3$Zr(BH$_4$)] (**23**) can be described by a local C_{3v} symmetry neglecting the Zr···H–B interactions. The O–Zr–O bond angles are 110.6° on average and the B–Zr–O angles 108.2°. The Zr···B distance is 2.371(7) Å, which lies in the range of other zirconium tetrahydridoborates.[3,5,7] The Zr–O bonds are 1.935(3) Å on average, i.e. shorter than in [(*t*Bu$_3$CO)$_3$Zr(BH$_4$)],[8] and the Zr–O–Si bonds angles are quite wide with 170.8°.

[(*t*Bu$_3$SiO)$_3$Zr(H$_2$BC$_8$H$_{14}$)] (**25**) crystallizes in colorless prisms in the monoclinic system from benzene solution at –10 °C, space group *P*2$_1$/*c*. Although many of the positions of the CH atoms could be determined from the Fourier map, they were refined as riding models. The positions of the BH hydrogen atoms were isotropically refined. It should be noted that, due to the site occupation factors (1 for H1 but 0.6 and 0.4 for H2 and H3), there is a disorder for the BC$_8$H$_{14}$ fragments. Figure 7 shows two different molecular structures of compound **25**, on the left-hand side with an occupation factor of one and on the right-hand side with one disordered BC$_8$H$_{14}$ group; C41 is almost positioned at a pseudo-C_3 axis. The two disordered parts (only one is shown) can be transferred into one another by means of a pseudo-C_3 axis. The atoms Zr1, H1, H2 and B2 do not lie

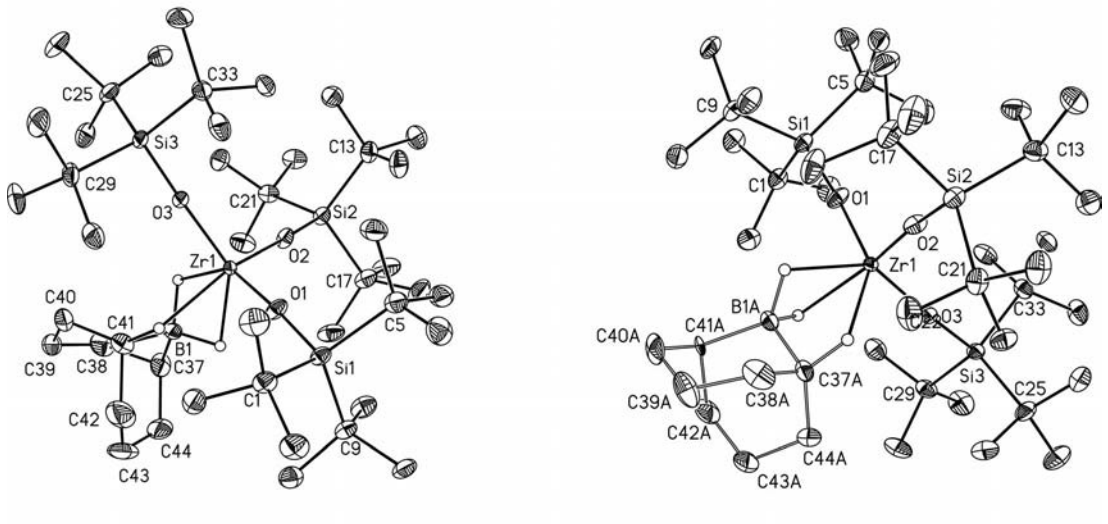


Figure 7. Two molecules of the molecular structure of (tBu$_3$SiO)$_3$Zr(H$_2$BC$_8$H$_{14}$) (**25**). Thermal ellipsoids are presented at the 25% probability level. Bond lengths [Å] and bond angles [°]: Zr1–O1 1.936(2), Zr1–O2 1.933(2), Zr1–O3 1.949(2), Zr1–H1 1.95(3), Zr1–H2 2.14(4), Zr1–H3 2.11(9), Zr1···B1 2.455(5), Zr1–B1A 2.406(7), O1–Si1 1.671(2), O2–Si2 1.668(2), O3–Si3 1.668(2), Si1–C1 1.923(3), Si1–C5 1.929(3), Si1–C9 1.931(3), Si2–C13 1.924(3), Si1–C17 1.926(3), Si1–C21 1.920(3), Si3–C25 1.919(3), Si1–C29 1.928(3), Si1–C33 1.923(3), B1–H1 1.30(4), B1–H2 1.19(5), B1A–H1 1.30(4), B1–C37 1.60(2), B1–C41 1.587(8); O1–Zr1–O2 109.03(7), O1–Zr1–O3 109.79(7), O2–Zr1–O3 110.63(7), O1–Zr1–H1 88.2(10), O2–Zr1–H1 95.1(10), O3–Zr1–H1 140.4(10), O2–Zr1–H3 154(3), O1–Zr1–H3 82(3), O1–Zr1–H2 146(1), H1–Zr1–H2 58(2), H2–Zr1–H3 77(3), O1–Zr1–B1A 122.7(2), O1–Zr1–B1A 94.6(2), O3–Zr1–B1A 108.6(2).

in a plane. The interplanar angle H1–Zr1–H2/H1–B1–H2 is 36°. Even more striking are the Zr1–B1–C41 angle of 85.7(4)° and the Zr1–B1–C37 angle of 162.6(9)°. This corresponds with agostic Z···H–C interactions. It is not clear whether the 9-H$_2$BBN part B is due to a weaker β-agostic interaction or crystallographic factors due to difficulties in locating electron maxima of the disordered atoms in close positions are responsible for the different bonding parameters (see Table 4). The disorder of the H$_2$BC$_8$H$_{14}$ is shown in Figure 7.

Table 4. Comparison of selected bonding parameters (bond lengths in Å; angles in °) of the differently positioned 9-borabicyclononane groups of **25**. Figure 7 shows two orientations of the two disordered BC$_8$H$_{14}$ groups.

Zr–B1	2.406(7)	Zr1–C41	2.782(7)	Zr1–B1–C41	85.7(4)
Zr1–B1A	2.454(7)	Zr1–C41A	2.937(7)	Zr1–B1A–C41A	90.6(3)

Conclusion

Among the two routes to alkoxozirconocene tetrahydridoborates, the reactions of the tetraalkoxozirconium compounds with H$_3$B·THF were not successful as a preparative method for synthesizing alkoxozirconium tetrahydridoborates. Although a RO/HB exchange was noted, these reactions did not proceed sufficiently selectively. One of the main questions was whether the 2,6-isopropylphenolate titanium compounds[17,18] would react with H$_3$B·THF, LiBH$_4$, or LiBH$_2$R$_2$ more specifically than the zirconium compounds Zr(OBu)$_4$, Zr(OEt)$_4$, Zr(OBu)$_3$Cl, or [tBu$_3$SiO]$_3$-ZrCl. Unexpectedly, none of the reactions proceeded specifically. The best results were obtained by treating (RO)$_3$ZrCl with LiBH$_4$.[19] Moreover, the reaction of [(RO)$_3$ZrBH$_4$] or [(RO)$_2$Zr(BH$_4$)$_2$] with Li[H$_2$BC$_8$H$_{14}$] led to [(RO)$_2$Zr(H$_2$BC$_8$H$_{14}$)$_2$] or [(RO)$_3$Zr(H$_2$BC$_8$H$_{14}$)] with agostic Zr–H–C bonding in compound **25**.

In summary, the preparative results were more or less disappointing due to the formation of many byproducts. On the other hand, the X-ray structure elucidations of the hydridoborates add interesting aspects to the structures of substituted metal tetrahydrido- and metal dihydridodiorganyl borates.

Experimental Section

Reaction of Zr(OBu)$_4$·HOBu with BH$_3$·THF: Zr(OBu)$_4$·BuOH (8.55 mL) dissolved in THF (5 mL) was added with stirring stepwise to a BH$_3$·THF solution in THF (0.98 M, 11 mL) until no more gas evolved. An NMR tube was filled up to 1 cm height with this solution, which was then cooled to –78 °C. Then more BH$_3$·THF solution was added until the NMR tube was filled up to 6 cm. The resulting solution was put into the NMR spectrometer precooled to –50 °C, and undecoupled ^{11}B NMR spectra were recorded by warming the NMR tube in 10 °C steps after every recording. NMR spectroscopic data could be assigned only reliably for temperatures greater than –10 °C. Spectra are presented in Figure 1, and data are listed in Table 1.

Attempts to Synthesize [(BuO)$_3$ZrBH$_4$] (4): Zr(OBu)$_4$·BuOH (1.87 mL, 5.2 mmol) was placed in a nitrogen-filled 25 mL bulb. While stirring, a solution of H$_3$B·THF (4.2 mL, 2.5 M, 10.5 mMol) was added dropwise. At the beginning, H$_2$ evolution was observed. After this had stopped, the solvent was removed in vacuo. Attempts to crystallize the residue from various solvents failed. For the solution, the following ^{11}B NMR signals were observed at $\delta = 28.9$ $[HB(OBu)_2]$, 19 $[B(OBu)_3]$, –18.2 $[(BuO)_2Zr(BH_4)_2$ (**5**)] and –23.9 ppm $[(BuO)_3ZrBH_4$ (**4**)] with relative intensities of 1:13:3:8.

Attempts to Synthesize $[(BuO)_3ZrBH_4]$ (4): In analogy to the previous experiment, $(BuO)_4Zr\cdot BuOH$ (1.87 mL, 5.2 mmol) was treated with $H_3B\cdot THF$ (2.5 M, 8.32 mL, 20.8 mmol) while stirring. The following ^{11}B NMR spectra were recorded and assigned: $\delta^{11}B = 29.0$, $HB(OBu)_2$, 19.7, $B(OBu)_3$, –12.6 $[(BuO)_3ZrBH_4$ (**4**)], –16 ppm $[(BuO)_2Zr(BH_4)_2$ (**5**)]. The last two peaks had a ratio of 8:3. After evaporating the solvents in vacuo, only $HB(OBu)_2$ and $B(OBu)_3$ could be removed as liquids. Attempts to obtain single crystals of **4** or **5** were not successful.

$Zr(OEt)_4$ (7): To stirred ethanol (60 mL) was added $ZrCl_4$ (15 g, 64.4 mmol) in portions within 1.5 h. Then Et_3N (35.7 mL, 0.257 mol) was added, and the suspension was kept at reflux for 1 h followed by the addition of benzene (100 mL) at ambient temperature. The suspension was heated to reflux for 5 h followed by filtration to remove insoluble material at 20 °C. To the filtrate was added some pentane to complete the precipitation. After filtration, the solvent was removed from the filtrate in vacuo, leaving behind $Zr(OEt)_4$ (8 g, 46%) as a slightly yellow powder. M.p. not defined. NMR ($CDCl_3$): $\delta^1H = 1.23$ ($OCH_2\mathit{C}H_3$), 4.14 ppm ($O\mathit{C}H_2CH_3$); $\delta^{13}C = 19.5$ ($CH_2\mathit{C}H_3$), 75.0 ppm ($O\mathit{C}H_2$).

Attempts to Synthesize $[(EtO)_2Zr(BH_4)_2]$ (8): $Zr(OEt)_4$ (100 mg) was dissolved in toluene (30 mL). To this solution was added an excess of $H_3B\cdot THF$ (7 mmol in 5 mL of THF). The following ^{11}B NMR spectroscopic data were recorded: After 1 h at 20 °C: $\delta = 28.5$ $(EtO)_2BH$, 19.2 $(EtO)_3B$, 0.9 ($H_3B\cdot THF$), –18 ppm [broad, $(EtO)_xZr(BH_4)_{3-x}$]. ^{11}B NMR signals after 7 h at 60 °C: $\delta = 28.5$, 19.3, 1.1, –12.5 ppm [$^1J(^{11}B^1H) = 86$ Hz, $(EtO)Zr(BH_4)_3$]. Signals after 15 h at 60 °C: 28.4, 19.1, 1.0, –12.4 [$^1J(^{11}B^1H) = 86$ Hz, $(EtO)Zr(BH_4)_3$], –16 ppm [broad, $(EtO)_xZr(BH_4)_{3-x}$]. No single crystals could be isolated.

Bis(tri-*tert*-butylmethanolato)zirconium Bis(tetrahydridoborate) (10): Into a nitrogen-filled 100 mL bulb were added $ZrCl_4$ (2.71 g, 11.6 mmol) and $LiOC\mathit{t}Bu_3$ (4.88 g, 23.2 mmol) followed by cold diethyl ether (100 mL) at –78 °C while stirring. After the addition, the suspension was allowed to attain room temperature. Stirring was continued for 7 h. Then the ether was removed by distillation, and the residue was treated with hexane (50 mL). After filtration, the residue was treated with Et_2O (50 mL). To the resulting solution was added $LiBH_4$ (500 mg, 23 mmol). After 30 min of stirring, the solvent was evaporated. The residue was treated with hexane (80 mL), and the suspension was cleared by filtration. The filtrate was then reduced to ca. 40 mL in volume and then cooled to –78 °C for crystallization. After 24 h 1.7 g of crystals were isolated (25%); m.p. 143–145 °C (gas evolution). $\delta^1H = 1.95$ ppm [quint., $^1J(^{11}B^1H) = 86$ Hz]. $\delta^{13}C = 33.54$ ($\mathit{C}H_3$), 46.05 ($C\mathit{Me}_3$), 103.17 ppm ($O\mathit{C}$). $\delta^{11}B = -17.13$ ppm [quint., $^1J(^{11}B^1H) = 86.7$ Hz]. $C_{26}H_{62}B_2O_2Zr$ (581.56): calcd. C 60.1, H 12.03, found C 59.6, H 11.57.

Reaction of 10 with Pyridine: To a solution of **10** (0.5 mmol) in C_6D_6 was added an excess of pyridine (2 mmol). The resulting solution was checked by NMR spectroscopy. $\delta^1H = 1.40$, 1.50, 1.58 (br., s, Me_3C), 3.7 [quart., $^1J(^{11}B^1H) = 98$ Hz, $H_3B\cdot Py$], 6.83, 8.67 ppm [o, m, ($C\mathit{H}$)]. $\delta^{11}B = -17.52$ [quint, $^1J(^{11}B^1H) = 86.5$ Hz, $(\mathit{t}Bu_3CO)_2ZrH(BH_4)$], –9.8 ppm [quart., $^1J(^{11}B^1H) = 98.4$ Hz, $H_3B\cdot Py$].

Reaction of 10 with Triethylamine: A fourfold excess of Et_3N was added to a C_6D_6 solution of **10** (0.5 mmol). NMR spectroscopic data were recorded 72 h after mixing the components: $\delta^{11}B = -17.61$ [quint., $^1J(^{11}B^1H) = 87.2$ Hz, **10**], –1.55 ppm [quart., $^1J(^{11}B^1H) = 97.5$ Hz, $H_3B\cdot NEt_3$]. After heating the solution for 96 h, the following NMR spectroscopic data were recorded: $\delta^{11}B = -20.4$ [quint., $^1J(^{11}B^1H) = 92.8$ Hz, $(\mathit{t}Bu_3CO)_3Zr(BH_4)$ (**14**)], –17.5 [quint., $^1J(^{11}B^1H) = 86.4$ Hz, $(\mathit{t}Bu_3CO)_2Zr(BH_4)_2$, 10], –11.5 ppm [quart., $^1J(^{11}B^1H) = 97.5$ Hz, $H_3B\cdot NEt_3$]. On storing the solution for 10 d at room temperature single crystals of $(\mathit{t}Bu_3CO)_3Zr(BH_4)$ (**14**) separated. Only a few of these crystals had the quality for X-ray crystallography. IR: $\tilde{\nu} = 2527$ (BH_t), 2226 (BH_b) cm^{-1}. NMR spectroscopic data of the solution (C_6D_6): $\delta^1H = 1.40$, 1.42 ppm [s, $(\mathit{Me}_3C)_3CO$]; $\delta^{11}B = -21.8$ [quint., $^1J(^{11}B^1H) = 93$ Hz, $(\mathit{t}Bu_3O)_3Zr(BH_4)$ (**14**)], –12.9 ppm [quart., $^1J(^{11}B^1H) = 96.9$ Hz, $H_3B\cdot NEt_3$].

Reaction of 10 with Trimethylphosphane: To a C_6D_6 solution of **10** was added an 18-fold excess of PMe_3. ^{11}B NMR spectra were recorded at room temperature, at –60 °C, and at –30 °C. NMR spectroscopic data at –60 °C: $\delta^1H = 8.68$ ppm [d, $^2J(^{31}P^1H) = 43.5$ Hz, $(\mathit{t}Bu_3CO)_2ZrH(BH_4)PMe_3$]; $\delta^{31}P = -60.7$ (PMe_3), –31.1 ppm [d, $^2J(^{31}P^1H) = 44.6$ Hz, H_3PMe_3]. NMR spectroscopic data at –30 °C: $\delta^1H = 8.68$ ppm [d, $^2J(^{31}P^1H) = 40.3$ Hz, $(\mathit{t}Bu_3CO)_2ZrH(BH_4)PMe_3$]; $\delta^{31}P = -60.7$ (PMe_3), –31.1 [d, $^2J(^{31}P^1H) = 44.5$ Hz, $(\mathit{t}Bu_3CO)_2ZrH(BH_4)PMe_3$ (**13**)], –1.8 ppm (quart., $H_3B\cdot PMe_3$, not well resolved). At room temperature: $\delta^1H = 1.22$ (s), 1.46 (s, Me_3C), 8.95 ppm [quint. $^2J(^1H^1H) = 2.93$ Hz, $(\mathit{t}Bu_3CO)_2ZrH(BH_4)$]. $\delta^{13}C = 32.55$, 34.36 (br. Me_3C), 44.99, 45.78 ($Me_3\mathit{C}$), 102.99 ppm ($\mathit{C}O$). $\delta^{11}B = -20.4$ [quint., badly resolved, $^1J(^{11}B^1H) = 93$ Hz, $(\mathit{t}Bu_3CO)_3$ $Zr(BH_4)$ (**14**)], –35.9 ppm [dq, $^1J(^{31}P^{11}B) = 95.7$ Hz, $H_3B\cdot PMe_3$].

Bis(2,6-diisopropylphenolato)zirconium Dichloride Bis(tetrahydrofuran) (19): To $ZrCl_4$ (2.46 g, 10.6 mmol) was added tetrahydrofuran (2 mL). After stirring for 1 h, the solvent was evaporated in vacuo and Et_2O (60 mL) was added to the residue. Then the lilac-colored suspension was added dropwise at –78 °C to a solution of 2,6-$\mathit{i}Pr_2C_6H_3OLi$ in Et_2O (80 mL). After stirring the mixture for 20 h, the suspension was filtered. About 50% of the filtrate was evaporated in vacuo. From the greenish brown solution, colorless crystals (suitable for an X-ray structure analysis) of **19** separated within two weeks at –30 °C. Yield: 800 mg of **19** (11%), m.p. 165 °C. NMR (C_6D_6): δ^1H: = 1.26 ($C\mathit{H}_2$-CH_2O), 1.36 [$^3J(^1H^1H) = 6.84$ Hz, $CH(CH_3)_2$], 4.00 (CH_2–CH_2), 4.16 [sept., $^1J(^1H^1H) = 6.84$ Hz, $CHCMe_3$], 6.95 [t, $^3J(^1H^1H) = 7.84$ Hz, *p*-$C\mathit{H}$], 7.12 ppm [d, $^3J(^1H^1H) = 7.84$ Hz, *m*-$C\mathit{H}$]; $\delta^{13}C = 24.56$ ($CH\mathit{C}H_3$), 25.32, 26.50 ($\mathit{C}HMe$, $CH_2\mathit{C}H_2$), 73.51 ($\mathit{C}H_2O$), 122.05, 123.54 138.88, 157.17 ppm ($\mathit{C}6$). $C_{32}H_{50}O_4Cl_2Zr$ (660.87): calcd. C 58.16, H 7.63; found C 58.14, H 7.63.

Bis(tri-*tert*-butylmethanolato)zirconium Bis(9,9-dihydrocyclononyl-9-borate) (18): To $[(\mathit{t}Bu_3CO)_2Zr(BH_4)_2]$ (**10**) (720 mg, 1.19 mmol) and $LiH_2BC_8H_{14}\cdot THF$ (1220 mg, 4.45 mmol) was added Et_2O (40 mL). After stirring for 1 h, the following ^{11}B NMR signals were recorded: $\delta^{11}B = -39.2$ [quint. $^1J(^{11}B^1H) = 81$ Hz, 20%], –17.4 [coupl. not observed, $C_8H_{14}BH_2ZrBH_4$, 9%], –13.4 [t, $^1J(^{11}B^1H) = 71$ Hz, BH_2Li, 42%], 8.4 [coupl. not obs., $\mathit{B}H_2ZrBH_4$, 9%], 9.9 ppm [coupl. not obs., $(C_8H_{14}\mathit{B}H_2)_2Zr$, 10%]. After 16 h the following signals were found: $\delta^{11}B = -39.2$ [quint. $^1J(^{11}B^1H) = 81$ Hz, $LiBH_4$, 24%], –21.8 [coupl. not obs., $O_3Zr(\mathit{B}H_4)$, 4%], –17.4 4 [coupl. not observed, $Zr(\mathit{B}H_4)_2$, 5%], –16.6 [coupl. not observed, $C_8H_{14}BH_2Zr$, 9%], –13.4 [t, $C_8H_{14}BH_2Li$, $^1J(^{11}B^1H) = 71$ Hz, 19%], 3.5 [coupl. not observed, $O_3ZrH_2\mathit{B}$, 4%], 8.4 [coupl. not observed, $(\mathit{B}H_2)Zr$, 5%], 9.9 [coupl. not observed, $(R_2\mathit{B}H_2)Zr$, 24%], 29.2 [coupl. not observed, $(C_8H_{14}\mathit{B}H)_2$,5%], 57.0 ppm [s, $C_8H_{14}BOCMe_3$, 5%]. After removing the solvent in vacuo, hexane (70 mL) was added to the residue, and the colorless solution was concentrated to 5 mL. After storing the solution at –30 °C for two weeks, colorless crystals of $(\mathit{t}Bu_3CO)_2Zr(H_2BC_8H_{14})_2$ (**18**) sepa-

Table 5. Crystallographic data obtained for [tri(*tert*-butyl)methanolato]- and [tri(*tert*-butyl)siloxo]zirconium hydridoborates.

Compound	**10**	**14**	**18**	**19**	**23**	**25**
Chem. formula	$C_{26}H_{62}B_2O_2Zr$	$C_{39}H_{85}BO_3Zr$	$C_{42}H_{86}B_2O_2Zr$	$C_{32}H_{50}Cl_2O_4Zr$	$C_{36}H_{85}BO_3Si_3Zr$	$C_{45}H_{98}BO_3Si_3Zr$
Form. weight	519.60	704.10	735.99	660.84	752.34	873.53
Cryst. dimensions [mm]	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.4	0.3 × 0.4 × 0.6	0.4 × 0.3 × 0.2	0.25 × 0.25 × 0.3	0.2 × 0.3 × 0.3
Color	colorless	colorless		slightly green		
Cryst. system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$	$C2$	$P2_1/c$	$P2_1/c$
a [Å]	14.900(3)	20.994(4)	12.9750(1)	25.319(4)	21.87(1)	19.053(4)
b [Å]	8.235(1)	12.265(2)	20.6357(1)	9.643(2)	12.763(9)	13.065(2)
c [Å]	25.025(4)	16.736(3)	19.038(1)	18.011(3)	17.34(1)	22.434(4)
α [°]	90	90	90	90	90	90
β [°]	104.20(1)	109.57(1)	90.728(1)	128.58(3)	109.58(2)	102.591(6)
γ [°]	90	90	90	90	90	90
V [Å^3]	2976.8(8)	4060(1)	5096.9(5)	3451(1)	4558(5)	5450(2)
Z	4	4	4	4	4	4
ρ (calcd.) [Mg/m^3]	1.159	1.152	0.996	1.272	1.096	1.065
μ [mm^{-1}]	0.388	0.303	0.244	0.505	0.348	0.300
$F(000)$	1136	1552	1683	1392	1648	1916
Index range	$-17 \leq h \leq 0$	$-24 \leq h \leq 23$	$-17 \leq h \leq 14$	$-28 \leq h \leq 28$	$-18 \leq h \leq 29$	$-24 \leq h \leq 24$
	$-9 \leq k \leq 0$	$-14 \leq k \leq 0$	$-26 \leq k \leq 26$	$-10 \leq k \leq 5$	$-15 \leq k \leq 15$	$-11 \leq k \leq 18$
	$-28 \leq l \leq 29$	$-1 \leq l \leq 18$	$-24 \leq l \leq 24$	$-20 \leq l \leq 20$	$-21 \leq l \leq 21$	$-27 \leq l \leq 27$
2θ [°]	54.0	48.00	58.42	47.00	58.40	58.82
Temp. [K]	183(2)	163(2)	173(2)	193	153(2)	163(2)
Refl. collected	2718	6767	14527	7303	24381	30977
Refl. unique	2612	6012	4698	4076	7698	10243
Refl. observed (4σ)	2455	5986	2835	4027	5338	8175
R (int.)	0.0537	0.0666	0.0575	0.0443	0.0537	0.0276
No. variables	440	436	256	361	440	603
Weight scheme[a] x/y	0.0356/5.0593	0.0088/7.4739	0.0527/18.8406	0.0232/1.0978	0.0077/21.8932	0.0333/4.9229
GOOF	1.082	1.080	1.091	1.050	1.176	1.132
Final R (4σ)	0.0331	0.0366	0.0480	0.0265	0.0521	0.0347
Final $wR2$	0.0767	0.0733	0.1197	0.0307	0.1247	0.0858
Larg. res. peak [e/Å^3]	0.385	0.431	0.574	0.204	0.692	0.665

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

rated, which were characterized by X-ray crystallography. Yield: 120 mg (12 %). NMR (in C_6D_6): δ^1H = 1.11–1.18 [m, 2 H, $(C_8H_{14}BH_2)_2Zr$], 1.35 [s, 81 *H*. $(H_3C)_3C$], 1.32–2.07 ppm [m, 12 *H*, (C_8H_{14})]. δ^{13}C = 24.78 [C_8H_{14}], 33.28 [C_8H_{14}], 33.62 [$(CH_3)C$], 46.11 [$(CH_3)_3CCO$], 103.89 ppm [$(CH_3)_3CCO$], δ^{11}B = 9.9 ppm [(t, badly resolved), $C_8H_{14}BH_2Zr$]. IR: $\tilde{\nu}$ = 1955 (w), 2017 (m), 2083 (st), 2109 (st), 2137 (st), 2172 (m), 2223 (st), 2253 (m) cm^{-1}.

Tris[tri(*tert*-butyl)siloxo]zirconium 9,9-Dihydridocyclononyl-9-borate (25): To a solution of [$(t\text{Bu}_3\text{SiO})_3\text{ZrBH}_4$] (620 mg, 0.82 mmol) was added a solution of Li[$H_2BC_8H_{14}$] (0.88, 3.22 mmol) in Et_2O (30 mL). The resulting solution showed, after 2 h, NMR signals at δ^{11}B (Et_2O) = –39.8 [quint, $^1J(^{11}B^1H)$ = 80 Hz, $LiBH_4$], –14.4 [t, $^1J(^{11}B^1H)$ = 71 Hz, H_2BZr], 2.7 [t, $^1J(^{11}B^1H)$ = 57, BH_2Zr], 56.9 ppm (*t*, $C_8H_{14}BH)_2$. After stirring at ambient temperature for 16 h, the solvent was removed. The remaining solid was treated with hexane (70 mL), and the resulting solution was reduced in volume to about 4 mL. Colorless crystals of [$t\text{Bu}_3\text{SiO}]_3\text{Zr}$-[$H_2BC_8H_{14}$] (**25**) separated at –30 °C. Yield: 40 mg. NMR (C_6D_6): δ^1H = 1.09–1.17 (m, $C_8H_{14}BH_2Zr$), 1.26 (s, 81 H, *Me*$_3$C), 1.33, –2.13 ppm (12 *H*, C_8H_{14}); δ^{13}C = 23.11 [(Me$_3$*C*)Si], 24.78 (C_8H_{14}), 30.60 (CH_3), 33.46 ppm (C_8H_{14}); δ^{11}B = 3.2 ppm [*t*, $^1J(^{11}B^1H)$ = 57 Hz]; δ^{29}Si = 10.9 ppm; IR (Nujol): $\tilde{\nu}$ = 2017 cm^{-1} [broad, B–H bridge bond]. Product **25** could not be prepared from [$t\text{Bu}_3\text{SiO}]_3\text{ZrCl}$ and $LiH_2BC_8H_{14}$.

X-ray Crystallography: X-ray crystallographic data were collected with a Siemens P4 diffractometer equipped with a low-temperature device and an area counter. Single crystals were selected from a suspension of the crystals in perfluoroether oil at –40 to –30 °C under a cover of N_2 gas. The selected crystal was mounted with the oil on a glass fiber and fixed on the goniometer, which was cooled to –60 or –70 °C. Reflection data were collected on five different sets of ω and θ orientations by changing ω in steps of 1.2°. For the determination of the unit cell, absorption correction, data reductions, and determinations of other structural parameters, the programs SADABS, SMART and SAINT[20] were used. Positions of non-hydrogen atoms were calculated in anisotropic modes and those of hydrogen atoms usually in the riding mode for the respective CH atom. The positions of the hydrogen atoms of the Zr(BH_4) part were all isotropically refined. The structures were solved with the program SHELXL97.[21] The data are presented in Table 5.

CCDC-818234, -818235, -818236, -818237, -818594, and -836002 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.

Supporting Information (see footnote on the first page of this article): ^{11}B NMR spectrum of the reaction of **10** with PMe_3 in toluene after two days and parts of the molecular structure of compound **25**.

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[1] J. A. Jensen, J. E. Gozum, D. M. Pollina, G. S. Girolami, *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644; J. C. Whitmore, F. J. Cyrin, *J. Mol. Struct.* **1978**, *50*, 21–28; B. E. Smith, H. F. Shurcell, D. D. James, *J. Chem. Soc., Dalton Trans.* **1978**, 710–722; I. S. Chuang, T. J. Marks, W. J. Kenelly, J. R. Kolb, *J. Am. Chem. Soc.* **1977**, *99*, 7539–7545; A. Haaland, D. J. Shorokhov, A. V. Tutukin, H. V. Volden, O. Swang, G. S. McGrady, N. Kaltsoyannis, A. J. Downs, C. Y. Tang, J. F. C. Turner, *Inorg. Chem.* **2002**, *41*, 6646–6655; J. E. Gozum, G. S. Girolami, *J. Am. Chem. Soc.* **1991**, *113*, 3829–3837; J. A. Jensen, G. S. Girolami, *J. Chem. Soc., Dalton Trans.* **1986**, 1160–1162.

[2] V. V. Volkov, K. G. Myakishev, H. N. Seitsev, *USSR* **1975**, CAN 85463; C. J. Dain, A. J. Downs, D. W. H. Rankin, *Angew. Chem.* **1982**, *94*, 557–558; R. G. Egdell, J. C. Green, *Inorg. Chim. Acta* **2008**, *361*, 462–466; D. M. Goeddem, G. S. Girolami, *Inorg. Chem.* **2006**, *45*, 1380–1388; A. L. Johnson, M. G. Davidson, M. F. Mahon, *Dalton Trans.* **2007**, 5405–5411.

[3] B. V. Zhuk, G. A. Somrechev, A. M. Obe′dkov, *Izv. Akad. Nauk SSSR* **1977**, *5*, 1201–1205; F. C. Gennari, L. Fernandez-Albanesi, I. J. Rios, *Inorg. Chim. Acta* **2009**, *362*, 3731–3737; I.-S. Chuang, T. Marks, J. Kennelly, J. R. Kolb, *J. Am. Chem. Soc.* **1977**, *99*, 7359–7364.

[4] F. Lacroix, C. E. Plecnik, S. Liu, F.-C. Liu, E. A. Meyers, S. G. Shore, *J. Organomet. Chem.* **2003**, *687*, 69–77; S. G. Shore, E. Ding, X. Cheng, S. Liu, B. Du, F. Lacroix *ACS National Meeting, New Orleans, Abstr. Papers*, **2003**, *Inorg.* p. 440; X. Chen, F.-C. Liu, C. E. S. Liu, B. Du, E. A. Meyers, S. G. Shore, *Organometallics* **2004**, *23*, 2100–2106; F. C. Liu, S. C. Chen, G.-H. Lee, S. M. Peng, *J. Organomet. Chem.* **2007**, *692*, 2375–2384; T. J. Marks, J. Williams, J. R. Kolb, L. A. Shimp, *Inorg. Chem.* **1972**, *11*, 2540–2546.

[5] K. Franz, H. Nöth, *Z. Anorg. Allg. Chem.* **1973**, *397*, 153–157; K. Franz, H. Fußstetter, H. Nöth, *Z. Anorg. Allg. Chem.* **1976**, *47*, 99–113; M. F. Lappert, W. P. Leung, R. A. Bartlett, P. P. Power, *Polyhedron* **1989**, *8*, 1883–1890.

[6] J. E. Gozum, S. R. Wilson, G. S. Girolami, *J. Am. Chem. Soc.* **1992**, *114*, 9483–9492; B. E. Smith, B. D. James, J. A. Dilts, *J. Inorg. Nucl. Chem.* **1968**, *38*, 1973–1978.

[7] D. C. Bradley, F. M. Abd-El Halim, E. A. Sadek, W. Wardlaw, *J. Chem. Soc., Dalton Trans.* **1952**, 2032–2035; B. Sotaray, E. Rosta, S. Brsky, S. Teper, *J. Organomet. Chem.* **1999**, *582*, 267–272.

[8] S. K. Anand, J. J. Singh, R. K. Multani, B. D. Jain, *Bull. Chem. Soc. Jpn.* **1969**, *42*, 554–568; D. C. Bradley, W. Wardlaw, *J. Chem. Soc.* **1951**, 280–285.

[9] T. V. Lubben, P. T. Wolczanski, G. D. Van Duyne, *Organometallics* **1984**, *3*, 977–983.

[10] F.-C. Liu, S.-C. Chen, G. H. Lee, S. M. Peng, S. G. Shore, *J. Organomet. Chem.* **2007**, *692*, 2375–2384; X. Chen, F. C. Liu, E. Christine, S. Liu, B. Du, E. A. Meyers, S. G. Shore, *Organometallics* **2004**, *23*, 2100–2106.

[11] a) Part of the Ph.D. Thesis of J. Knizek, University of Munich, **1999**; b) Part of the Ph.D. Thesis of M. Schmidt-Amelunxen, University of Munich, **1995**.

[12] H. Yasuda, Y. Nakayama, K. Takei, A. Nakamura, Y. Kai, N. Kanehisha, *J. Organomet. Chem.* **1994**, *473*, 105–116.

[13] N. Wiberg, *Frontiers of Organosilicon Chemistry*, Royal Society of Chemistry, London, **1991**, 2632–2670.

[14] E. M. Dexheimer, L. Spitaler, *J. Organomet. Chem.* **1975**, *102*, 21–27.

[15] B. D. James, R. K. Nanda, M. G. H. Wallbridge, *Inorg. Chem.* **1967**, *6*, 1979–1983; J. Mariquez, D. R. McAlister, R. D. Scanner, J. E. Bercaw, *J. Am. Chem. Soc.* **1978**, *100*, 2716–**2725**.

[16] M. Hesse, H. Meier, B Zech, *Spektroscopische Methoden in der organischen Chemie*, 4th Edition, Georg Thieme Publ., Stuttgart, **1991**.

[17] Metal Hydridoborates and Hydridoborato Metallates, 33: J. Knizek, H. Nöth, *Eur. J. Inorg. Chem.* **2011**, 1888–1900.

[18] M. Schwenk, Diploma Thesis, University of Munich, **1993**.

[19] F. C. Liu, J. Liu, E. A. Mayers, S. G. Shore, *Inorg. Chem.* **1998**, *37*, 3293–2200; A. Forazza, A. Floriani, A. Chiesi-Villa, C. Guastino, *Inorg. Chem.* **1991**, *30*, 145–148.

[20] *SADABS*, *SMART*, *SAINT*, Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, **1996**.

[21] G. M. Sheldrick, *SHELXL 97*, *Program for Crystal Structure Solution and Refinement*, University of Göttingen, **1997**.

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