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Novel μ_3-oxo complexes prepared from $Cp^*Zr(BH_3R)_3$ (R = H, CH_3) and $B(C_6F_5)_3$ in diethyl ether†

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From the reactions of Cp^*ZrCl_3 with 3 equiv. of $LiBH_3R$ (R = CH_3, Ph), the organotrihydroborate complexes, $Cp^*Zr(BH_3CH_3)_3$, **1**, and $Cp^*Zr(BH_3Ph)_3$, **2**, were isolated. One of the Zr–H–B bonding interactions in **2** could be described as an intermediate case between the bidentate and tridentate modes. Reactions of **1** and $Cp^*Zr(BH_4)_3$, **3**, with Lewis acid $B(C_6F_5)_3$ in diethyl ether produced the novel 14-electron ionic compounds $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BCH_3)\}][HB(C_6F_5)_3]$, **4**, and $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BOC_2H_5)\}][HB(C_6F_5)_3]$, **5**, respectively. These two unique compounds resulted from a sequential cleavage of Zr–H–B bonds of **1** and **3** and C–O bonds of ether followed by the formation of O–B bonds. The solid state single crystal X-ray analyses revealed that both compounds have similar structures. A μ_3-oxygen bridges two zirconiums and a boron atom. The latter three atoms are further connected by three μ_2-bridging ethoxy groups giving rise to three four-membered metallacycles within the structure of each cation.

Introduction

Group 4 transition metal hydroborate complexes are of interest due to their fluxional behavior, the nature of the bonding interaction between the BH_4^- ligand and a metal,[1,2] their ability to function as reducing agents[3] and precursors in the preparation of hydride complexes[4] as well as their applications in the chemical vapour deposition (CVD) of ZrB_2 and HfB_2 films[5] and in hydroboration as catalysts.[6] The terahydroborate zirconocene complexes have been studied since the 1960's.[1] Recently the related Group 4 organohydroborate complexes have also been reported.[7–13] Many zirconocene-based organohydroborate compounds have been prepared and studied by Shore and co-workers[7–10] as well as by our group.[12,13] These organohydroborate compounds display interesting dynamic properties[8] and bonding interactions between the organohydroborate ligand and the metal.[9] Compared with the zirconocene compounds, the half-sandwich zirconocene compounds possess a face that is more open to attack and has more coordination sites available, which may result in interesting bonding interactions and different chemical behavior. However, the related organohydroborate complexes are not well studied. To our knowledge, only a handful of examples of the half-sandwich zirconocene hydroborate and organohydroborate complexes have been reported.[10,14,15] Thus, we are interested in exploration of the half-zirconocene organohydroborate chemistry. Here we would like to report the results of our recent study on the preparation of the half-sandwich zirconocene organotrihydroborate compounds and their reaction with a Lewis acid $B(C_6F_5)_3$.

Results and discussion

Formation and spectroscopic study of $Cp^*Zr(BH_3CH_3)_3$, 1, $Cp^*Zr(BH_3Ph)_3$, 2, $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BCH_3)\}][HB(C_6F_5)_3]$, 4, and $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BOC_2H_5)\}][HB(C_6F_5)_3]$, 5

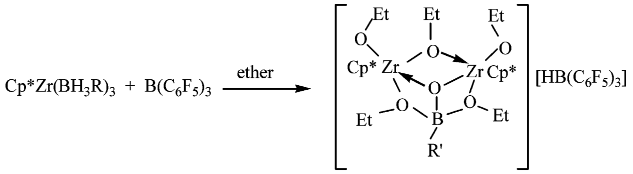
Compounds $Cp^*Zr(BH_3CH_3)_3$, **1**, and $Cp^*Zr(BH_3Ph)_3$, **2** were prepared from the reaction of Cp^*ZrCl_3 with 3 equiv. of $LiBH_3R$ (R = CH_3, Ph) in diethyl ether, as shown in eqn (1).

$$Cp^*ZrCl_3 + 3LiBH_3R \xrightarrow{\text{ether}} Cp^*Zr(BH_3R)_3 \qquad (1)$$

(R = CH_3, Ph)

Both compounds were crystallized from ether solution at −35 °C. While compound **1** is very soluble in ether, compound **2** has a low solubility in this solvent. Their ^{11}B NMR spectra display a broad signal at −5.50 ppm for **1** and a broad quartet ($J_{B-H} = 69$ Hz) at −4.32 ppm for **2**. These resonances are downfield with respect to those of the free anions ($LiBH_3Ph$: −26.5 ppm; $LiBH_3CH_3$: −30.9 ppm).[12,16] In the proton NMR spectra, the BH hydrogens of **1** and **2** appear as broad quartets at 1.37 and 2.28 ppm, respectively.

Compounds $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BCH_3)\}][HB(C_6F_5)_3]$, **4**, and $[(\mu_3\text{-O})(\mu_2\text{-OC}_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BOC_2H_5)\}][HB(C_6F_5)_3]$, **5**, were prepared from the reaction of **1** and $Cp^*Zr(BH_4)_3$,[15] **3**, respectively, with $B(C_6F_5)_3$ in ether according to eqn (2),



(R = CH_3, R' = CH_3 (**4**); R = H, R' = OC_2H_5 (**5**)) (2)

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and isolated from a ether–hexane two-layered system. Crystals of **4** and **5** are only slightly soluble in ether while they decompose in other commonly used solvents. In fact, decomposition of **4** is so fast that its resonances could not be identified in the proton NMR spectrum. Decomposition of **5** in d_8-toluene is slower, and by comparing the intensity of the signals of the time-elapsed spectra it was possible to identify its original ^{1}H NMR signals. Although four different bonding environments for an ethoxy group can be found in **5**, they cannot be distinguished in its proton NMR spectrum, which displays only one set of signals for all of them. The CH_2 protons appear at 3.19 ppm (q, J_{H-H} = 7.0 Hz) and the CH_3 protons appear at 0.98 ppm (t, J_{H-H} = 7.0 Hz). In the ^{13}C NMR the ethoxy methylene and methyl signals appear at 65.55 and 14.61 ppm, respectively. The hydride signal of the anion $[HB(C_6F_5)_3]^-$ is not observed in the proton NMR spectrum, possibly due to its broadness. The instance of terminal and bridging alkoxide group proton chemical shifts being the same has been observed previously.[10,17] Two boron signals are observed for each compound in a freshly prepared solution. A doublet signal at −26 ppm (d, J_{B-H} = 93 Hz) in each spectrum is assigned to the anion $[HB(C_6F_5)_3]^-$. The cation boron signals appear as singlets at 30.5 ppm for **4** and 17.6 ppm for **5**. Unlike the proton NMR spectra, the boron NMR spectra do not provide any information with regard to the decomposition of these compounds in solution. It is possible that decomposition occurs at the electron deficient metal center, and the boron atom of the anion and the four-coordinated boron atom of the cation are not affected at the beginning of decomposition.

The reaction of $Cp^*Zr(BH_3Ph)_3$ with $B(C_6F_5)_3$ in diethyl ether was also studied. The boron NMR spectrum of the product mixture displayed three boron signals, with two major ones appearing at 27.38 (s) and −26.19 ppm (d, J_{B-H} = 91 Hz). This result suggested the formation of a product similar to compound **4**. However, we have not met with success in isolation of this product.

Shore and co-workers[10] have prepared compound $[(\mu_2\text{-}OC_2H_5)\{CpZr(OC_2H_5)(OC_4H_{10})\}]_2[HB(C_6F_5)_3]_2$ from the reaction of $CpZr\{BH_2(C_5H_{10})\}_3$ with $B(C_6F_5)_3$ in diethyl ether. Formation of **4** and **5** may follow a similar pathway producing an intermediate $[(\mu_2\text{-}OC_2H_5)\{Cp^*Zr(OC_2H_5)(OC_4H_{10})\}]_2[HB(C_6F_5)_3]_2$, which is an analog of Shore's compound. It is possible that this intermediate reacts further by coordination of a bridging oxygen to BH_3 formed in previous steps followed by a hydride transfer from $[HB(C_6F_5)_3]^-$ to the ethyl group giving rise to an intermediate $[(\mu_2\text{-}OC_2H_5)(\mu_2\text{-}OBH_3)\{Cp^*Zr(OC_2H_5)(OC_4H_{10})\}_2][HB(C_6F_5)_3]$. Repeated attacks by the coordinated BH_3 moiety on the ethyl groups of coordinated ether molecules resulting in bond formation between the oxygen and boron atoms will produce $[(\mu_3\text{-}O)(\mu_2\text{-}OC_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BH)\}][HB(C_6F_5)_3]$. Reaction of the last BH hydrogen of this intermediate with ether will furnish final product **5**. When the boron source is $(BH_2CH_3)_2$, which has only two BH hydrogens available, further reaction of the intermediate $[(\mu_2\text{-}OC_2H_5)\{Cp^*Zr(OC_2H_5)(OC_4H_{10})\}]_2[HB(C_6F_5)_3]_2$ will produce compound **4**. The fact that these reactions do not stop at the formation of $[(\mu_2\text{-}OC_2H_5)\{Cp^*Zr(OC_2H_5)(OC_4H_{10})\}]_2[HB(C_6F_5)_3]_2$ may be attributed to a better electron donor ability of the Cp* ligand, and/or the nature of the hydroboranes. Studies of the factors affecting the formation of **4** and **5** are in progress.

Molecular structures of 1, 2, 3, 4, and 5

The structure of $Cp^*Zr(BH_4)_3$ (compound **3** first synthesized by Wolczanski and Bercaw[15]) is included for comparison. The molecular structures of **1–5** were determined by single-crystal X-ray diffraction analysis. Crystallographic data and selected bond distances and bond angles are given in Tables 1–4. The molecular structures of **2**, **4**, and **5** are shown in Fig. 1–3. The molecular structures of **1** and **3** are similar to that of **2** and they are included in the ESI.†

The coordination geometry of zirconium atoms in the molecular structures of **1–3** can be described best as a distorted tetrahedron. At the corners of each tetrahedron are the center of a Cp* ring and three boron atoms connected to a zirconium atom through bridging hydrogens. The metal–boron distance has been used as a criterion for determining the bonding mode between the metal and the hydroborate ligand.[1,18] Hedberg *et al.* estimated the expected Zr–B distances for a bidentate mode to be in the range 2.39–2.59 Å and for a tridentate mode to be in the range 2.28–2.40 Å.[14] The average Zr–B distances for **1–3** increase in the order **3** < **1** < **2**, which is consistent with the bulkiness of the fourth substituent

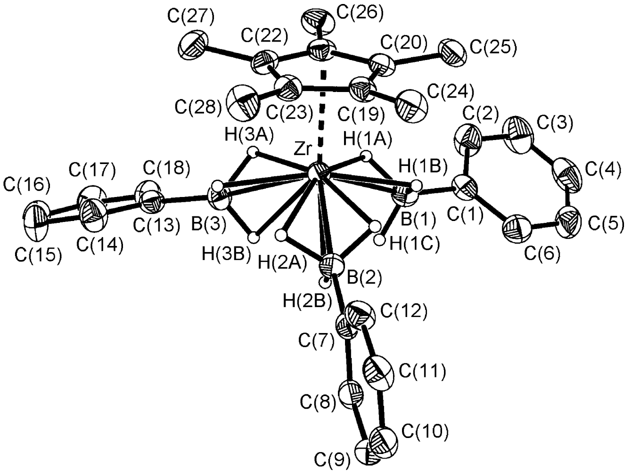

Fig. 1 Molecular structure of $Cp^*Zr(BH_3Ph)_3$, **2**, showing 50% probability thermal ellipsoids.

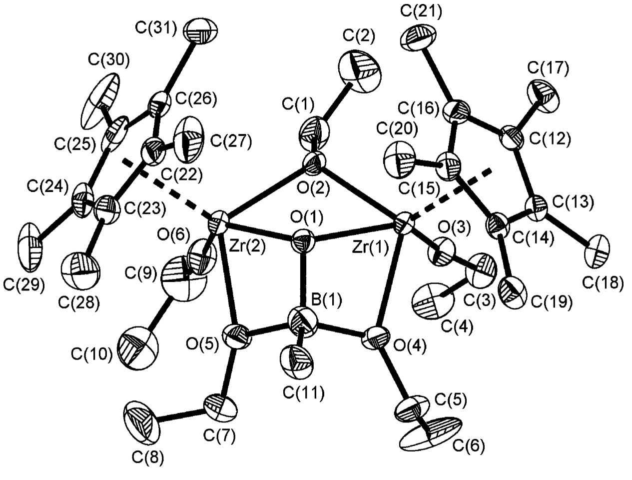

Fig. 2 Molecular structure of the cation in $[(\mu_3\text{-}O)(\mu_2\text{-}OC_2H_5)_3\{(Cp^*Zr(OC_2H_5))_2(BCH_3)\}][HB(C_6F_5)_3]$, **4**, showing 30% probability thermal ellipsoids.

Table 1 Crystal data and structure refinement for Cp*Zr(BH_3CH_3)$_3$, **1**, Cp*Zr(BH_3Ph)$_3$, **2**, and Cp*Zr(BH_4)$_3$, **3**

Empirical formula	$C_{13}H_{33}B_3Zr$	$C_{28}H_{39}B_3Zr$	$C_{10}H_{27}B_3Zr$
M	313.04	499.24	270.97
T/K	150(2)	150(2)	150(1)
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	$P4(3)$	$P2(1)/n$	$P\bar{1}$
a/Å	7.8250(3)	8.8868(1)	7.0619(8)
b/Å	7.8250(3)	14.7203(2)	8.4186(9)
c/Å	28.7350(11)	20.4718(3)	13.4982(15)
α/°			84.077(2)
β/°		91.1669(5)	88.589(2)
γ/°			66.427(2)
V/Å^3	1759.46(12)	2677.49(6)	731.47(14)
Z	4	4	2
ρ_{calcd}/g cm^{-3}	1.182	1.238	1.230
Crystal size/mm	0.30 × 0.30 × 0.30	0.25 × 0.25 × 0.20	0.20 × 0.20 × 0.10
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
θ limits/°	2.60–27.50	1.70–27.50	1.52–27.50
Index ranges	$-10 \le h \le 10$ $-10 \le k \le 10$ $-37 \le l \le 37$	$-11 \le h \le 11$ $-19 \le k \le 18$ $-26 \le l \le 26$	$-9 \le h \le 9$ $-10 \le k \le 10$ $-17 \le l \le 17$
Reflns collected	17156	20179	9665
Unique reflns	4028	6152	3345
F(000)	664	1048	284
Completeness to θ (%)	100.0	100.0	99.7
μ/mm^{-1}	0.605	0.424	0.717
Max., min. transm.	0.8394, 0.8394	0.940, 0.867	0.9318, 0.8699
Data/restraints/params	4028/1/181	6152/0/326	3345/0/175
$R_1{}^a[I > 2.0\sigma(I)]$	0.0257	0.0410	0.0364
$wR_2{}^b$(all data)	0.0643	0.1152	0.0873
R_{int}	0.0366	0.0712	0.0351
GOF on F^2	1.052	1.077	1.155

^{a} $R_1 = \sum\|F_o\| - |F_c\|/\sum\|F_o|$. ^{b} $wR_2 = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2\}^{1/2}$.

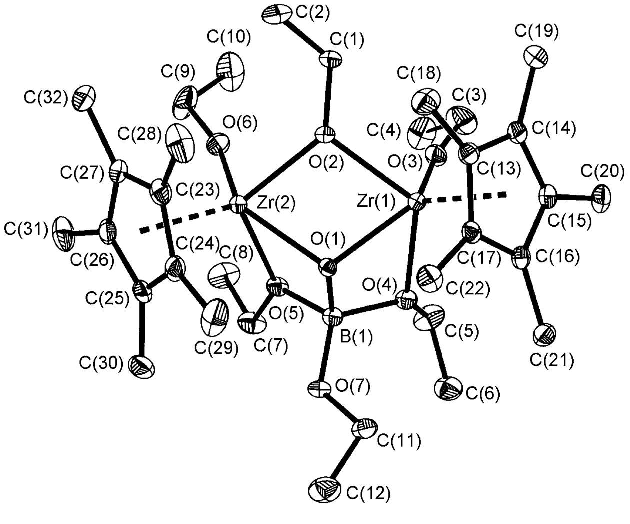

Fig. 3 Molecular structure of the cation in [(μ_3-O)(μ_2-OC_2H_5)$_3${(Cp*Zr(OC_2H_5))$_2$(BOC_2H_5)}][HB(C_6F_5)$_3$], **5**, showing 30% probability thermal ellipsoids.

on the boron atom. The Zr–B distances and the hydrogen bridge Zr–H_b bond distances of compounds **1** and **3** are in the range 2.366(3)–2.387(3) Å and 2.02(3)–2.34(4) Å, respectively. These distances are consistent with those generally observed for the tridentate bonding mode, namely, the Zr–B distances in the range of 2.276(11)–2.403(29) Å and the Zr–H_b bond distances in the range of 2.04(5)–2.36(7) Å.[14,19]

Table 2 Crystal data and structure refinement for [(μ_3-O)(μ_2-OC_2H_5)$_3${(Cp*Zr(OC_2H_5))$_2$(BCH_3)}][HB(C_6F_5)$_3$], **4**, and [(μ_3-O)(μ_2-OC_2H_5)$_3${(Cp*Zr(OC_2H_5))$_2$(BOC_2H_5)}][HB(C_6F_5)$_3$], **5**

Empirical formula	$C_{49}H_{59}B_2F_{15}O_6Zr_2$	$C_{50}H_{60}B_2F_{15}O_7Zr_2$
M	1233.02	1262.04
T/K	150(2)	295(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2(1)/c$	$P2(1)2(1)2(1)$
a/Å	10.5767(5)	14.6566(5)
b/Å	16.4862(8)	18.0175(6)
c/Å	32.1655(17)	20.3699(7)
β/°	93.389(1)	
V/Å^3	5598.9(5)	5379.2(3)
Z	4	4
ρ_{calcd}/g cm^{-3}	1.463	1.558
Crystal size/mm	0.50 × 0.32 × 0.20	0.36 × 0.30 × 0.25
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
θ limits/°	1.27–27.50	1.51–27.49
Index ranges	$-13 \le h \le 12$ $-21 \le k \le 17$ $-41 \le l \le 41$	$-18 \le h \le 19$ $-23 \le k \le 23$ $-26 \le l \le 26$
Reflns collected	49575	54149
Unique reflns	12748	12348
F(000)	2504	2564
Completeness to θ (%)	99.2	100.0
μ/mm^{-1}	0.466	0.488
Max., min. transm.	0.9126, 0.8005	0.8877, 0.8438
Data/restraints/params	12748/4/689	12348/2/704
$R_1{}^a[I > 2.0\sigma(I)]$	0.0695	0.0412
$wR_2{}^b$(all data)	0.2137	0.0899
R_{int}	0.0591	0.0591
GOF on F^2	1.089	1.029

^{a} $R_1 = \sum\|F_o\| - |F_c\|/\sum\|F_o|$. ^{b} $wR_2 = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2\}^{1/2}$.

Table 3 Selected bond lengths (Å) and angles (°) for Cp*Zr(BH_3CH_3)$_3$, **1**, Cp*Zr(BH_3Ph)$_3$, **2**, and Cp*Zr(BH_4)$_3$, **3**

	1	**2**	**3**
Zr–B	2.367(3)	2.375(3)	2.366(3)
	2.374(3)	2.389(3)	2.369(4)
	2.387(3)	2.413(4)	2.378(4)
Zr–H_b	2.02(4)	2.04(3)	2.02(3)
	2.03(5)	2.04(3)	2.03(3)
	2.04(4)	2.05(3)	2.08(3)
	2.06(4)	2.14(3)	2.09(4)
	2.10(4)	2.15(3)	2.11(4)
	2.18(4)	2.22(3)	2.13(3)
	2.29(4)	2.26(3)	2.29(4)
	2.31(4)	2.30(3)	2.33(3)
	2.33(3)		2.34(4)
Zr···H		2.475	
B–H_b	1.06(4)	1.08(3)	1.02(3)
	1.09(3)	1.09(3)	1.02(4)
	1.14(4)	1.09(3)	1.05(4)
	1.14(4)	1.09(3)	1.07(4)
	1.17(4)	1.12(3)	1.08(4)
	1.17(4)	1.14(3)	1.11(4)
	1.21(4)	1.15(3)	1.12(4)
	1.22(4)	1.18(2)	1.16(3)
	1.29(3)	1.22(3)	1.20(4)
B–H_t			1.06(4)
			1.09(4)
			1.11(4)
Zr–B–R_t[a]	168.2(2)	163.4(2)	168(2)
	172.3(2)	171.8(2)	170(2)
	174.2(3)	174.9(2)	171(2)

[a] R_t = C for **1** and **2**, R_t = H_t for **3**.

The Zr–B distances in **2** are 2.375(3), 2.389(3), and 2.413(4) Å. The two short Zr–B distances and their corresponding Zr–H_b distances are consistent with the tridentate bonding mode. The Zr–B distance of 2.413(4) Å is longer than expected for a bond distance characteristic of the tridentate mode. The corresponding Zr–H distance of 2.475 Å is significantly longer than the sum of the covalent radii of Zr and H atoms (1.91 Å) and generally observed Zr–H_b distances. However, it is shorter than a sum of the covalent radius of Zr (1.50 Å)[20] and the van der Waals radius of H (1.20 Å).[21] An additional piece of judgment in favor of the tridentate bonding mode is the linearity of the Zr–B–C angles. The corresponding Zr–B–C angle is 163.4(2)°, which is 5° smaller than the smallest of Zr–B–C (H_t) angles in **1** and **3**. Thus, the longest Zr–H distance of 2.475 Å would suggest an agostic interaction between Zr and H, and the coordination between the Zr and this phenyltrihydroborate ligand could be described as an intermediate between the bidentate and tridentate modes. This deviation from the tridentate bonding mode can be accounted for by steric reasons. It is worth noting that the average B–H_b and B–H_t distances in **3** are about the same (1.09 Å). This is in contrast with an observation that for most tetrahydroborate compounds the B–H_b distances are slightly longer than the B–H_t distances.[1,22]

Compounds **4** and **5** are ionic, with cation charges being balanced by that of the [$HB(C_6F_5)_3$]$^-$ anion. The molecular structures of these cations are similar. A μ_3-oxygen bridges two zirconiums and a boron atom, and these three atoms are further connected through three μ_2-bridging ethoxy groups. Overall, there are three four-membered metallacycles within the structure of each cation. The bond angles in each of the four-membered rings in both cations are also comparable. Except for those of Zr1–O4–B1

Table 4 Selected bond lengths (Å) and angles (°) for [(μ_3-O)(μ_2-OC_2H_5)$_3${(Cp*Zr(OC_2H_5))$_2$(BCH_3)}][$HB(C_6F_5)_3$], **4**, and [(μ_3-O)(μ_2-OC_2H_5)$_3${(Cp*Zr(OC_2H_5))$_2$(BOC_2H_5)}][$HB(C_6F_5)_3$], **5**

	4	**5**		**4**	**5**
Zr(1)–O(1)	2.147(3)	2.120(2)	O(3)–C(3)	1.428(7)	1.407(5)
Zr(1)–O(2)	2.177(3)	2.149(2)	O(4)–C(5)	1.433(7)	1.433(4)
Zr(1)–O(3)	1.908(4)	1.906(2)	O(5)–C(7)	1.427(7)	1.450(4)
Zr(1)–O(4)	2.178(4)	2.194(2)	O(6)–C(9)	1.419(8)	1.417(4)
Zr(2)–O(1)	2.121(3)	2.156(2)	O(7)–C(11)		1.431(4)
Zr(2)–O(2)	2.144(3)	2.161(2)	O(1)–B(1)	1.460(7)	1.454(4)
Zr(2)–O(5)	2.174(4)	2.200(2)	O(4)–B(1)	1.532(8)	1.521(4)
Zr(2)–O(6)	1.914(4)	1.908(2)	O(5)–B(1)	1.523(8)	1.510(5)
Zr(1)–Zr(2)	3.3680(7)	3.3608(4)	O(7)–B(1)		1.407(4)
O(2)–C(1)	1.474(7)	1.449(4)	B(1)–C(11)	1.578(9)	
O(3)–Zr(1)–O(2)	90.82(15)	91.40(10)	C(3)–O(3)–Zr(1)	170.5(4)	169.3(3)
O(3)–Zr(1)–O(4)	90.78(16)	89.10(10)	C(5)–O(4)–Zr(1)	138.9(4)	132.5(2)
O(1)–Zr(1)–O(2)	70.91(13)	71.16(8)	C(7)–O(5)–Zr(2)	136.9(4)	136.9(2)
O(1)–Zr(1)–O(4)	63.35(13)	63.38(8)	C(9)–O(6)–Zr(2)	175.1(6)	164.1(3)
O(2)–Zr(1)–O(4)	113.20(13)	120.85(9)	Zr(2)–O(2)–Zr(1)	102.44(14)	102.47(9)
O(1)–Zr(2)–O(2)	72.05(13)	70.25(8)	C(5)–O(4)–B(1)	121.5(5)	122.5(3)
O(1)–Zr(2)–O(5)	63.23(14)	62.71(8)	C(7)–O(5)–B(1)	122.6(5)	122.7(3)
O(2)–Zr(2)–O(5)	116.06(14)	110.01(9)	O(1)–B(1)–O(5)	98.0(4)	99.8(3)
O(6)–Zr(2)–O(2)	91.83(17)	89.32(10)	O(1)–B(1)–O(4)	98.8(4)	99.3(3)
O(6)–Zr(2)–O(5)	89.00(19)	93.06(10)	O(5)–B(1)–O(4)	110.3(5)	112.5(3)
B(1)–O(1)–Zr(1)	100.8(3)	100.14(18)	O(1)–B(1)–C(11)	120.2(6)	
B(1)–O(1)–Zr(2)	101.4(3)	100.5(2)	O(5)–B(1)–C(11)	113.4(5)	
B(1)–O(4)–Zr(1)	97.1(3)	94.82(17)	O(4)–B(1)–C(11)	114.2(5)	
B(1)–O(5)–Zr(2)	97.1(3)	96.76(18)	B(1)–O(7)–C(11)		117.3(3)
Zr(2)–O(1)–Zr(1)	104.18(15)	103.62(9)	O(7)–B(1)–O(1)		120.7(3)
C(1)–O(2)–Zr(1)	126.7(3)	119.0(2)	O(7)–B(1)–O(5)		108.8(3)
C(1)–O(2)–Zr(2)	117.4(3)	126.7(2)	O(7)–B(1)–O(4)		114.7(3)

(97.1(3) in **4**, 94.82(17) in **5**), O4–B1–O1 (98.8(4) in **4**, 99.3(3) in **5**), and O1–B1–O5 (98.0(4) in **4**, 99.8(3) in **5**), the difference for each pair of angles is less than 1°. Each zirconium atom in **4** and **5** is further coordinated to a Cp* ring and a terminal ethoxy group. Thus, the coordination of each zirconium can be described best as a distorted square pyramid with a Cp* ring occupying the apical position and four oxygens occupying four distorted basal sites. The boron atom is tetra-coordinated, in addition to three oxygens it is either bonded to a methyl group in **4** or an additional ethoxy group in **5**.

The terminal Zr–O bond distances are about 1.908 Å in both compounds. This distance falls in the range 1.89–1.94 Å observed previously for the terminal Zr–O distances in zirconium alkoxides.[23,24] The corresponding Zr–O–C angles of 170.5(4), 175.1(6)° in **4** and 169.3(3), 164.1(3)° in **5** are consistent with a strong O → Zr π-donation[17] or an increased ionic character of the Zr–O bond.[20,25] The bridging Zr–O bond distances vary in both cations. However, they increase in the order Zr–O1 < Zr–O2 < Zr–O4, Zr–O5, and are longer than those of the terminal Zr–O bonds. These bridging Zr–O bond distances fall in the range 2.121(3)–2.178(4) Å in **4** and 2.120(2)–2.200(2) Å in **5**. They are comparable with the bridging Zr–O distances in other zirconium alkoxides and zirconium oxides (2.098(8)–2.2215(2) Å).[17,24,26] The bonding environments of O4 and O5 in **4** and O5 in **5** are nearly planar. The sums of angles around these oxygens are 357.5, 356.6, and 356.4°, respectively. Other bridging oxygens are nonplanar, with the sums of the angles around O1 and O2 being 306.38 and 346.54° in **4**, and 304.26 and 348.17° in **5**.

Conclusions

Novel μ_3-oxo compounds, **4** and **5**, were isolated from the reactions of half-sandwich zirconocene hydroborate compounds with $B(C_6F_5)_3$. Although C–O bond cleavage mediated by Group 4 metal complexes is not uncommon, it is the structure of these compounds possessing three four-membered metallacycles that is unique. It is possible that these μ_3-oxo compounds form as a result of the sequential cleavage of Zr–H–B bonds and C–O bonds of ether, and the formation of B–O bonds, albeit at this point it could not be corroborated by observation of the corresponding intermediates.

Experimental section

All manipulations were carried out on a standard high vacuum line or in a drybox under an atmosphere of nitrogen. Diethyl ether and hexane were dried over Na/benzophenone and were freshly distilled prior to use. Cp*ZrCl$_3$, LiBH$_4$, and $B(C_6F_5)_3$ were purchased from Strem Chemicals and used as received. LiBH$_3$CH$_3$,[16] LiBH$_3$Ph,[16] and Cp*Zr(BH$_4$)$_3$[15] were prepared according to literature methods. Elemental analyses were obtained on a Hitachi 270–30 spectrometer. Proton spectra (δ(TMS) = 0.00 ppm) were recorded either on a Bruker Avance DPX300 spectrometer operating at 300.132 MHz or Bruker Avance II spectrometer operating at 400.130 MHz. ^{11}B spectra (externally referenced to $BF_3\cdot OEt_2$ ($\delta = 0.00$ ppm)) were recorded on a Bruker Avance DPX300 spectrometer operating at 96.294 MHz. Infrared spectra were recorded on a Jasco FT/IR-460 Plus spectrometer with 2 cm^{-1} resolution.

X-Ray crystal structure determination

Suitable single crystals were mounted and sealed inside glass fibers under nitrogen. Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K and 295(2) K. Cell parameters were retrieved and refined using DENZO-SMN[27] software on all reflections. Data reduction was performed with the DENZO-SMN[27] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using the SORTAV[28] program. Structure analysis was made using the SHELXTL program on a personal computer. The structure was solved using the SHELXS-97[29] program and refined using the SHELXL-97[30] program by full-matrix least-squares on F^2 values. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the borons were found from the difference Fourier map and refined isotropically. Hydrogen atoms attached to the carbons were fixed at calculated positions and refined using a riding mode. Detailed crystal data are listed in Tables 1 and 2.

Preparation of Cp*Zr(BH$_3$CH$_3$)$_3$ 1

In the drybox Cp*ZrCl$_3$ (333.0 mg, 1.0 mmol) and LiBH$_3$CH$_3$ (111.0 mg, 3.1 mmol) were placed into a flask. The flask was evacuated, and 20 mL of diethyl ether was condensed into it at −78 °C. The system was warmed to room temperature and stirred overnight. The LiCl thus formed was separated from the solution by filtration. A white solid was obtained after removal of the solvent from the filtrate. Colorless crystals of **1** (240.0 mg, 77% yield) were obtained after crystallization from Et$_2$O at −35 °C. IR(KBr, cm^{-1}): 2980 m, 2939 s, 2904 m, 2854w, 2831w, 2238vw, 2169vw, 2065br, s, 1652vw, 1632vw, 1487w, 1461w, 1430 m, 1376w, 1308 s, 1227vs, 1104w, 1073w, 1020w, 962w, 805vw, 679vw and 667vw. ^{11}B NMR (diethyl ether, δ): −5.60 ppm (q, J_{B-H} 69). ^{11}B NMR (C_6D_6, δ): −5.50 ppm (q, J_{B-H} 69). ^{1}H NMR (C_6D_6, δ): 1.84 (15H, s, Cp*), 1.37 (9H, br q, BH$_3$) and 0.49 ppm (9H, br q, J_{H-H} 4.2, CH$_3$,). Anal. Found: C, 49.81; H, 10.63. Calc. for $C_{13}H_{33}B_3Zr$: C, 49.88; H, 10.63%.

Preparation of of Cp*Zr(BH$_3$Ph)$_3$ 2

A 50 mL flask was charged with 332.8 mg (1.0 mmol) of Cp*ZrCl$_3$ and 294.0 mg (3.0 mmol) of LiBH$_3$Ph. The flask was evacuated, and about 15 mL of Et$_2$O was condensed into it at −78 °C. The system was warmed to room temperature and stirred for 12 h. The LiCl was removed by filtration followed by solvent removal under vacuum. The white solid left in the flask was dissolved in Et$_2$O and kept at −35 °C for crystallization furnishing **2** as colorless crystals (290 mg, 58% yield). IR(KBr, cm^{-1}): 3067vw, 3056vw, 3010vw, 2977vw, 2962vw, 2916vw, 2860vw, 2215br, vw, 2076br, m, 1944vw, 1490vw, 1483vw, 1432w, 1426vw, 1382w, 1364vw, 1341w, 1283s, 1265vs, 1160m, 1151m, 1125s, 1088w, 1054w, 1028m, 1000w, 983vw, 908vw, 804w, 793w, 739s, 733s, 698s, 670vw, 663vw, 574w and 471vw. ^{11}B NMR (C_6D_6, δ): −4.32 ppm (br). ^{1}H NMR (C_6D_6, δ): 7.56–7.09 (15H, m, Ph), 2.28 ppm (9H, br q, BH$_3$) and 1.84 (15H, s, Cp*). Anal. Found: C, 66.82; H, 7.83. Calc. for $C_{28}H_{39}B_3Zr$: C, 67.36; H, 7.87%.

Preparation of $[(\mu_3\text{-O})(\mu_2\text{-OC}_2\text{H}_5)_3\{(\text{Cp*Zr(OC}_2\text{H}_5))_2(\text{BCH}_3)\}][\text{HB(C}_6\text{F}_5)_3]$ 4

In the drybox 156.0 mg (0.5 mmol) of $\text{Cp*Zr(BH}_3\text{CH}_3)_3$ and 256.0 mg (0.5 mmol) of $\text{B(C}_6\text{F}_5)_3$ were placed into a 50 mL flask. The flask was degassed, and about 10 mL of diethyl ether was transferred into it at −78 °C. The system was warmed to room temperature and stirred overnight. After reducing the volume of the clear solution to about 3 mL, it was transferred into a tube and layered with hexane for crystallization. The title compound was obtained as colorless crystals (140.0 mg, 45% yield). IR(KBr, cm^{-1}): 2980w, 2927w, 2870vw, 2403vw, 1636w, 1506m, 1465vs, 1380w, 1319vw, 1273m, 1250vw, 1119m, 1069m, 1036w, 970s, 931w, 878vw, 805vw, 764vw, 710vw, 667vw, 656vw, 599vw, 583vw, 564vw, 549vw and 461vw. ^{11}B NMR (diethyl ether, δ): 30.64 (s) and −25.85 ppm (d, $J_{\text{B–H}}$ 93). ^{11}B NMR (d_8-THF, δ): 30.46 (s) and −26.09 ppm (d, $J_{\text{B–H}}$ 93). Anal. Found: C, 47.32; H, 4.60. Calc. for $\text{C}_{49}\text{H}_{59}\text{B}_2\text{F}_{15}\text{O}_6\text{Zr}_2$: C, 47.73; H, 4.82%.

Preparation of $[(\mu_3\text{-O})(\mu_2\text{-OC}_2\text{H}_5)_3\{(\text{Cp*Zr(OC}_2\text{H}_5))_2(\text{BOC}_2\text{H}_5)\}][\text{HB(C}_6\text{F}_5)_3]$ 5

In the drybox 135.0 mg (0.5 mmol) of $\text{Cp*Zr(BH}_4)_3$ and 256.0 mg (0.5 mmol) of $\text{B(C}_6\text{F}_5)_3$ were placed into a 50 mL flask. The flask was degassed, and about 10 mL of diethyl ether was transferred into it at −78 °C. The system was warmed to room temperature and stirred overnight. After reducing the volume of the clear solution to about 3 mL, it was transferred into a tube and layered with hexane for crystallization. The title compound was obtained as colorless crystals (190.0 mg, 60% yield). IR(KBr, cm^{-1}): 2985w, 2923w, 2879vw, 2404vw, 1648m, 1602vw, 1520m, 1508m, 1466vs, 1381m, 1349vw, 1322vw, 1274w, 1197w, 1160vw, 1106m, 1078m, 1025w, 972s, 879vw, 834vw, 787w, 762w, 743vw, 727vw, 688w, 674w, 663w, 622vw, 600vw, 567vw, 554vw and 471vw. ^{11}B NMR (diethyl ether, δ): 17.62 (s) and −25.87 ppm (d, $J_{\text{B–H}}$ 93). ^{11}B NMR (d_8-toluene, δ): 17.63 (s) and −25.92 ppm (d, $J_{\text{B–H}}$ 94). ^{1}H NMR (d_8-toluene, δ): 3.19 (q, $J_{\text{H–H}}$ 7.0, CH_2), 1.81 (s, Cp*) and 0.98 (t, $J_{\text{H–H}}$ 7.0, CH_3). ^{13}C NMR (d_8-toluene, δ): 122.0 ($C\text{CH}_3$), 65.55 (CH_2), 14.61 (CH_3) and 10.69 ppm ($\text{C}C\text{H}_3$). Anal. Found: C, 47.09; H, 4.75. Calc. for $\text{C}_{50}\text{H}_{61}\text{B}_2\text{F}_{15}\text{O}_7\text{Zr}_2$: C, 47.55; H, 4.87%.

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