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Bimetallic Zirconium Heterocycles Supported by Boron–Oxygen Ligands

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Reaction between bis(cyclopentadienyl)dimethylzirconium, $ZrCp_2(CH_3)_2$, and phenylboronic anhydride, $(PhBO)_3$, resulted in the formation of the heterocyclic dimer $[ZrCp_2\{\mu\text{-}O_2BPh\}]_2$ (**1**); no reaction was observed with the mesityl derivative, $(mesBO)_3$. Compound **1** was also synthesized from the protonolysis reaction between $ZrCp_2(CH_3)_2$ and in situ generated phenylboronic acid, $PhB(OH)_2$. This approach was extended to afford the analogous complexes $[ZrCp_2\{\mu\text{-}O_2BAr\}]_2$ (**2**, Ar = mes; **3**, Ar = C_6F_5) from the corresponding isolable arylboronic acids, $ArB(OH)_2$. The molecular structures of **1**–**3**, determined by X-ray diffraction techniques, revealed a common, dimeric motif consisting of a central "$Zr_2B_2O_4$" metallacycle. Variations in the bond parameters within the heterocycle are attributed to the differing steric and electronic properties of the aryl substituents at boron.

Introduction

The conversion of neutral, group 4 metallocene complexes to the cationic alkyl species purported to be active catalysts in the polymerization of α-olefins can occur using a number of different cocatalyst reagents. Partially hydrated aluminum alkyls (alumoxanes), in particular methylalumoxane (MAO), are extremely effective in this capacity, despite detailed structural information concerning the species responsible for activation of the transition metal center remaining elusive.[1] Investigation of the model system composed of $ZrCp_2(CH_3)_2$ and the *tert*-butylalumoxane cage, $[(^tBu)Al(\mu_3\text{-}O)]_6$, has shown that the reaction proceeds to afford an equilibrium mixture between the starting materials and the methyl transfer product, with concomitant formation of a zirconium−oxygen bond.[2] This observation suggests that simple alkyl group abstraction and formation of discrete ion pairs may not be the only process occurring within metallocene/alumoxane systems.

During the past decade, many structurally well-defined cocatalysts have been developed,[3] predominantly based on group 13 elements incorporating perfluoroaryl substituents.[4] As many of the important factors associated with a particular catalyst system are reliant on cation−anion interactions (e.g., activity, thermal stability), the development of new activating species is an ongoing area of research. Within this context, the perfluorophenoxide-containing salts $[Ph_3C][Al(OC_6F_5)_4]$ and $[Ph_3C][M(OC_6F_5)_6]$ (M = Nb, Ta) have recently been investigated and their reactions with zirconocene dimethyl complexes studied.[5] Reaction between $ZrCp_2(CH_3)_2$ and $[Ph_3C][Nb(OC_6F_5)_6]$ gave the phenoxide-transfer complex, $ZrCp_2(OC_6F_5)_2$, as the only product, highlighting the propensity for the formation of Zr−O linkages with systems that incorporate oxygen in the activating species.

The patent literature has reported that introduction of boron−oxygen compounds into metallocene/MAO polymerizations enhances the activity of the system.[6] It has also been demonstrated that ill-defined B/Al hybrid materials are active as cocatalysts,[7] although little work in determining the structure of the activator has been undertaken. The recently reported, *well-defined* boroalumoxane, $Al(^tBu_2Al)(^tBuAl)_2$-

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$(O_2BAr)_4$,[8] was postulated to possess latent Lewis acidity[2] and, hence, be suitable as a cocatalyst in olefin polymerization. Accordingly, it was demonstrated that combination with $ZrCp_2(CH_3)_2$ afforded a system that will polymerize ethylene, although details concerning the nature of the active species were not reported.

To determine how $ZrCp_2(CH_3)_2$ interacts with a range of boron−oxygen compounds typical of those utilized as additional components in cocatalyst systems, we report the investigation of the reactivity with arylboronic acids and anhydrides, $ArB(OH)_2$ and $(ArBO)_3$, respectively. In addition, with continued interest in the support of the metallocene and/or activator components on solid oxide phases (e.g., silica, alumina),[9] it is envisaged that the compounds resulting from this study may serve as models for possible interactions between metallocene/borate species supported on such materials.[10]

Experimental Section

General Experimental Procedures. All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. The compounds $ZrCp_2(CH_3)_2$[11] and $(mesBO)_3$[12] were synthesized according to literature procedures. $(PhBO)_3$ was synthesized by thermal dehydration of commercially available phenylboronic acid (Aldrich) and recrystallized from petroleum ether (40:60) under anhydrous conditions prior to storage under an inert (nitrogen) atmosphere. $mesB(OH)_2$ was synthesized using a modification of the procedure used by Morgan and Pinhey,[13] using trimethyl borate to replace triethyl borate. $C_6F_5B(OH)_2$ was made by literature methods[14] and recrystallized under anhydrous conditions from benzene. Elemental analyses were performed by S. Boyer at the University of North London. The NMR spectra were recorded using a Bruker WM-300 at 300.13 (^1H), 75.43 ($^{13}C\{^1H\}$), 282.23 (^{19}F) or AMX-500 spectrometer at 125.72 ($^{13}C\{^1H\}$), 160.42 (^{11}B) MHz.

Synthesis of $[ZrCp_2\{\mu\text{-}O_2BPh\}]_2$ (1). H_2O (36 μL, 1.03 mmol) was added via syringe to a solution of $(PhBO)_3$ (0.11 g, 0.34 mmol) in toluene (25 mL) and the mixture stirred at room temperature for 30 min. The resultant solution of $PhB(OH)_2$ was cooled to −78 °C, and a solution of $ZrCp_2(CH_3)_2$ (0.26 g, 1.03 mmol) in toluene (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 18 h, during which time a white precipitate formed. Removal of the volatile components afforded crude **1** as a white powder (0.21 g, 60%). Portions of the crude material were crystallized from a warm CH_2Cl_2 solution to give analytically pure **1** as colorless crystals. ^1H NMR (CD_2Cl_2, 298K): δ 7.71 (m, 2H, C_6H_5), 7.43 (m, 3H, C_6H_5), 6.35 (s, 10H, C_5H_5). ^{13}C NMR (CD_2Cl_2, 298 K): 135.5 (C_6H_5), 129.8 (C_6H_5), 128.0 (br, *ipso*-C_6H_5), 127.8 (C_6H_5), 113.5 (C_5H_5). MS (EI$^+$, *m/z*) 615 $[M_{(dimer)} - Cp]^+$. Anal. Calcd for $C_{16}H_{15}BO_2Zr$: C, 56.30; H, 4.43. Found: C, 56.19; H, 4.37.

Synthesis of $[ZrCp_2\{\mu\text{-}O_2Bmes\}]_2$ (2). $mesB(OH)_2$ (0.33 g, 2.00 mmol) was dissolved in toluene (30 mL) and added to a precooled (−78 °C) solution of $ZrCp_2(CH_3)_2$ (0.50 g, 2.00 mmol) in toluene (30 mL). The reaction was left to attain room temperature and stirred for 18 h, during which time a white precipitate formed. Removal of the volatile components in vacuo afforded **2** as a crude white powder that was crystallized from a warm CH_2Cl_2 solution to afford analytically pure, colorless crystals of **2** (0.35 g, 46%). ^1H NMR (C_6D_6, 298 K): δ 6.93 (s, 2H, C_6H_2), 6.04 (s, 10H, C_5H_5), 2.66 (s, 6H, 2,6-*Me*$_2$), 2.25 (s, 3H, 4-*Me*). ^{13}C NMR (C_6D_6, 298 K): δ 139.1 (C_6H_2), 136.3 (C_6H_2), 128.3 (C_6H_2), 127.7 (C_6H_2), 113.0 (C_5H_5), 23.1 (2,6-*Me*$_2$), 21.3 (4-*Me*). ^{11}B NMR (C_6D_6, 298 K): δ 48.0 (br, $\Delta\upsilon_{1/2} \sim 1000$ Hz). MS (EI$^+$, *m/z*) 763 $[M_{(dimer)}]^+$, 699 $[M_{(dimer)} - Cp]^+$, 645 $[M_{(dimer)} - mes]^+$. Anal. Calcd for $C_{19}H_{21}BO_2Zr$: C, 59.52; H, 5.52. Found: C, 59.72; H, 5.50.

Synthesis of $[ZrCp_2\{\mu\text{-}O_2B(C_6F_5)\}]_2$ (3). A solution of $ZrCp_2(CH_3)_2$ (0.21 g, 0.85 mmol) in toluene (20 mL) was added to a precooled (−78 °C) slurry of $C_6F_5B(OH)_2$ (0.18 g, 0.85 mmol) in toluene and subsequently allowed to warm to room temperature. The mixture was stirred at ambient temperature for 15 h, followed by removal of the volatile component in vacuo to afford an off-white solid. Crystallization from warm CH_2Cl_2 gave **3** as analytically pure colorless crystals (0.23 g, 62%). ^1H NMR (CD_2Cl_2, 298 K): δ 6.31 (s, 10H, C_5H_5). ^{13}C NMR (CD_2Cl_2, 298 K): δ 148.5 (d, $^1J_{CF} = 227.1$ Hz, C_6F_5), 141.3 (d, $^1J_{CF} = 256.4$ Hz, C_6F_5), 137.5 (d, $^1J_{CF} = 250.0$ Hz, C_6F_5), *ipso* carbon of C_6F_5 ring not observed, 114.0 (C_5H_5). ^{19}F NMR (CD_2Cl_2, 298 K): δ −133.3 (m, *o*-C_6F_5), −156.7 (t, $^3J_{FF} = 19.8$ Hz, *m*-C_6F_5), −164.2 (m, *p*-C_6F_5). ^{11}B NMR (CD_2Cl_2, 298 K): δ 42.2 (br, $\Delta\upsilon_{1/2} \sim 400$ Hz). MS (EI$^+$, *m/z*) 795 $[M_{(dimer)} - Cp]^+$. Anal. Calcd for $C_{16}H_{10}BF_5O_2Zr$: C, 44.56; H, 2.34. Found: C, 44.39; H, 2.20.

X-ray Crystal Structure Determination for Compounds 1, 2, and 3. Colorless crystals of **1** formed by allowing an NMR tube containing equimolar amounts of $ZrCp_2(CH_3)_2$ and $[PhBO]_3$ in C_6D_6 (ca. 400 μL) to stand for 2 days at ambient temperature. Colorless crystals of **2** and **3** were obtained by allowing a warm (ca. 35 °C), saturated dichloromethane solution of the compound to slowly attain ambient temperature. A sample of the crystals of **1**, **2**, and **3** was covered in oil, and a suitable single crystal was selected under a microscope and mounted on a Kappa CCD area detector. The structures were refined using SHELXL-97.[15]

Results and Discussion

To determine whether $ZrCp_2(CH_3)_2$ reacts with the arylboronic anhydrides $(RBO)_3$ (R = Ph, mes), the 1:1 reaction was monitored by ^1H NMR spectroscopy. The mesityl derivative did not react at ambient temperature, and gradual heating of the sample to 90 °C resulted in the formation of a mixture of products, indicated by the presence of multiple signals in the C_5H_5 region of the spectrum. In contrast, the

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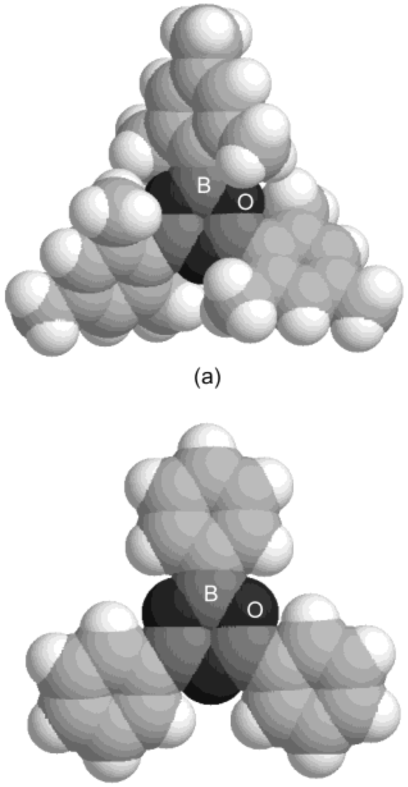


(a)

(b)

Figure 1. Space filling models of (mesBO)$_3$ (a) and (PhBO)$_3$ (b) (structural data taken from refs 16 and 17, respectively).

phenyl derivative reacted immediately upon mixing of the reagents, indicating that formation of a new species had occurred (ca. 50% conversion), that displayed two methyl resonances at δ 0.94 (3H) and 0.41 (3H), with a C_5H_5 peak at δ 5.67 (10H). Analysis of the sample after 15 h at room temperature, however, indicated that further reaction had occurred, again resulting in the formation of a mixture of products. Upon standing at room temperature for a further 2 days, colorless crystals formed in the NMR tube. These were subjected to X-ray analysis, which established that formation of the dimeric complex [ZrCp$_2$\{μ-O$_2$BPh\}]$_2$ (**1**) had occurred (see Figure 2).

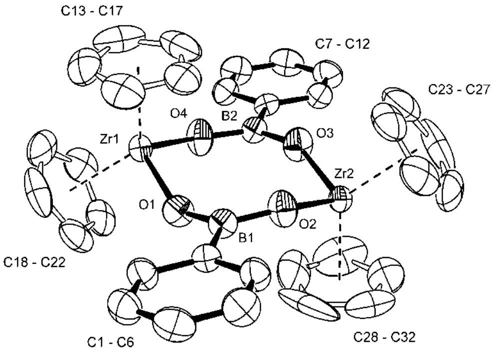
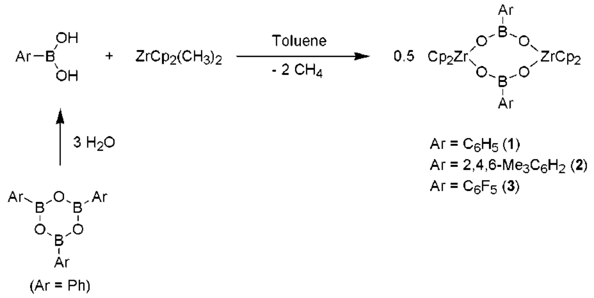


Figure 2. ORTEP diagram of [ZrCp$_2$\{μ-O$_2$BPh\}]$_2$ (**1**) with hydrogen atoms omitted for clarity.

Scheme 1



Investigation of the crystal structures of (mesBO)$_3$[16] and (PhBO)$_3$[17] offers a likely explanation for the different reactivity observed with ZrCp$_2$(CH$_3$)$_2$. The former compound (Figure 1a) adopts a propeller-like conformation of aryl groups about the planar "B$_3$O$_3$" ring (dihedral angles between mesityl ring and B$_3$O$_3$ plane = 35−41°), which results in shielding of the oxygen atoms by the 2,6-methyl substituents of the mesityl group. The phenyl substituents in (PhBO)$_3$ (Figure 1b) adopt a more coplanar configuration (C−C−B−O conformation angles 3−8°), rendering the oxygen atoms more accessible to the zirconium center. While the precise mechanism for the formation of **1** is currently unknown, the presence of adventitious water, or the reaction between (PhBO)$_3$ and hydroxyl functionalities on the glass surface, each resulting in the formation of small quantities of PhB(OH)$_2$ that subsequently protonate ZrCp$_2$(CH$_3$)$_2$ to form **1**, is a possible explanation. The important feature of the reaction, however, is the incorporation of a boron/oxygen containing fragment within the product via the formation of Zr−O linkages, illustrating a potential problem associated with the use of such species in cocatalyst mixtures. As no firm conclusions concerning the nature of the zirconocene/arylboronic anhydride interactions could be deduced from our study, we switched our attention to the reaction with arylboronic acids as a rational synthesis of complexes of type 1.

The literature preparation of phenylboronic acid, PhB(OH)$_2$, involves recrystallization of the anhydride from water with subsequent "drying" in a slow stream of air saturated with H$_2$O.[18] To prevent the possibility of hydrolysis of the zirconocene starting material, our approach consisted of the in situ hydration of a sample of the anhydride that had been prepared under anhydrous conditions. Subsequent reaction with 1 equiv of ZrCp$_2$(CH$_3$)$_2$ at −78 °C in toluene afforded a white precipitate upon warming to room temperature. Similar reactions between ZrCp$_2$(CH$_3$)$_2$ and the *isolable* phenylboronic acid derivatives ArB(OH)$_2$ [Ar = mes, C$_6$F$_5$] in toluene also resulted in formation of insoluble white powders (Scheme 1). In each case, removal of the volatile component and crystallization from dichloromethane afforded colorless crystals of [ZrCp$_2$\{μ-O$_2$BAr\}]$_2$ [Ar = Ph; (**1**); Ar = mes (**2**); Ar = C$_6$F$_5$ (**3**)] in moderate to good yields. Mass spectral analysis revealed signals for either the intact dimer (**2**) or the dimer with loss of a cyclopentadienyl ligand (**1**,

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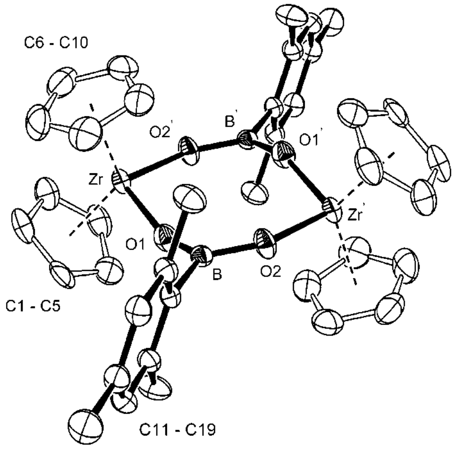

Figure 3. ORTEP diagram of $[ZrCp_2\{\mu\text{-}O_2Bmes\}]_2$ (**2**) with hydrogen atoms and dichloromethane solvate molecules omitted for clarity.

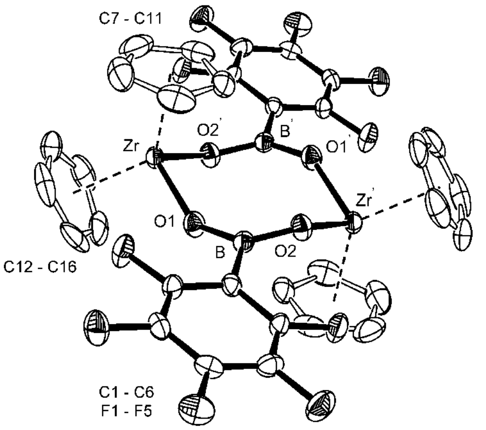

Figure 4. ORTEP diagram of $[ZrCp_2\{\mu\text{-}O_2B(C_6F_5)\}]_2$ (**3**) with hydrogen atoms omitted for clarity.

3), consistent with the metallacyclic structures illustrated in Scheme 1. To confirm the bonding in **2** and **3** and investigate the steric and electronic influences that the different aryl substituents confer to the heterocyclic core of the molecule in comparison with **1**, X-ray structural analyses were performed (Figures 2−4). Crystal data are summarized in Table 1, and selected bond lengths and angles are collected in Tables 2−4.

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
formula	$C_{32}H_{30}B_2O_4Zr_2$	$C_{38}H_{42}B_2O_4Zr_2\cdot 2CH_2Cl_2$	$C_{32}H_{20}B_2F_{10}O_4Zr_2$
fw	682.62	936.63	862.54
temp (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	8.2070(2)	9.0114(4)	7.6289(5)
b (Å)	17.2306(3)	10.0372(5)	10.7594(7)
c (Å)	20.8110(5)	12.5709(6)	10.7876(8)
α (deg)	90	69.285(2)	116.618(4)
β (deg)	90	87.880(3)	104.393(3)
γ (deg)	90	76.756(3)	92.155(4)
V (Å^3)	2942.9(1)	1034.02(8)	755.35(9)
Z	4	1	1
D_{calcd} (Mg/m^3)	1.54	1.50	1.90
abs coeff (mm^{-1})	0.74	0.80	0.79
final R indices[a,b] $[I > 2\sigma(I)]$	R1 = 0.033, wR2 = 0.085	R1 = 0.043, wR2 = 0.096	R1 = 0.037, wR2 = 0.086
R indices (all data)	R1 = 0.035, wR2 = 0.087	R1 = 0.056, wR2 = 0.102	R1 = 0.043, wR2 = 0.091

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[ZrCp_2\{\mu\text{-}O_2BPh\}]_2$ (**1**)

Zr(1)−O(1)	1.984(2)	Zr(2)−O(2)	1.980(2)
Zr(1)−O(4)	1.979(2)	Zr(2)−O(3)	1.968(2)
B(1)−O(1)	1.341(4)	B(2)−O(3)	1.351(4)
B(1)−O(2)	1.366(4)	B(2)−O(4)	1.349(4)
B(1)−C(1)	1.587(5)	B(2)−C(7)	1.573(4)
Zr(1)−C(13)	2.548(4)	Zr(2)−C(23)	2.538(4)
Zr(1)−C(14)	2.550(4)	Zr(2)−C(24)	2.527(4)
Zr(1)−C(15)	2.522(4)	Zr(2)−C(25)	2.521(5)
Zr(1)−C(16)	2.525(4)	Zr(2)−C(26)	2.514(4)
Zr(1)−C(17)	2.535(4)	Zr(2)−C(27)	2.542(5)
Zr(1)−C(18)	2.555(4)	Zr(2)−C(28)	2.520(6)
Zr(1)−C(19)	2.555(4)	Zr(2)−C(29)	2.535(5)
Zr(1)−C(20)	2.536(4)	Zr(2)−C(30)	2.504(4)
Zr(1)−C(21)	2.518(4)	Zr(2)−C(31)	2.507(4)
Zr(1)−C(22)	2.527(4)	Zr(2)−C(32)	2.493(5)
O(1)−Zr(1)−O(4)	100.90(11)	O(2)−Zr(2)−O(3)	100.98(11)
O(1)−B(1)−O(2)	122.4(3)	O(3)−B(2)−O(4)	121.2(3)
O(1)−B(1)−C(1)	119.6(3)	O(3)−B(2)−C(7)	119.7(3)
O(2)−B(1)−C(1)	118.0(3)	O(4)−B(2)−C(7)	119.1(3)
B(1)−O(1)−Zr(1)	144.7(2)	B(1)−O(2)−Zr(2)	144.4(2)
B(2) −O(4)−Zr(1)	148.3(2)	B(2)−O(3)−Zr(2)	153.0(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[ZrCp_2\{\mu\text{-}O_2Bmes\}]_2$ (**2**)

Zr−O(1)	1.971(2)	Zr−C(4)	2.523(7)
Zr−O(2′)	2.008(2)	Zr−C(5)	2.513(9)
B−O(1)	1.356(3)	Zr−C(6)	2.539(3)
B−O(2)	1.352(3)	Zr−C(7)	2.538(3)
B−C(11)	1.591(3)	Zr−C(8)	2.556(3)
Zr−C(1)	2.527(8)	Zr−C(9)	2.529(3)
Zr−C(2)	2.545(6)	Zr−C(10)	2.529(3)
Zr−C(3)	2.542(6)		
O(1)−Zr−O(2′)[a]	100.51(7)	O(1)−B−O(2)	121.1(2)
B−O(1)−Zr	156.7(2)	O(1)−B−C(11)	120.3(2)
B−O(2)−Zr′	141.8(2)	O(2)−B−C(11)	118.6(2)

[a] Symmetry transformations used to generate equivalent atoms (′): −*x*, −*y*, −*z*.

Compounds **1**−**3** form an analogous series of dimeric complexes, consisting of two “$ZrCp_2$” fragments linked by bridging $[\mu\text{-}O_2BAr]$ ligands, to afford a central eight-membered “$Zr_2B_2O_4$” metallacycle. The metal centers are positioned above and below the approximate plane defined by the boron and oxygen atoms, generating a “chair” like conformation within the heterocycle. In all cases, the zirconium atoms adopt distorted tetrahedral geometries, with Cp−Zr−Cp angles typical for the zirconocene fragment [**1** = 128.8° (av); **2** = 128.7(2)°; **3** = 129.6(1)°] and the Zr−C distances in the range expected for $[Zr^{VI}Cp_2]$ bonds.[19] The O−Zr−O angles [**1** = 100.95° (av); **2** = 100.51(7)°; **3** = 98.86(9)°] are similar to those observed in the related macrocyclic structures $[ZrCp_2\{\mu\text{-}OCH_2C(CH_3)_2CH_2O\}]_2$ and $[ZrCp_2\{\mu\text{-}OCH_2C_6H_4CH_2O\}]_2$ of 101.4(3)° and 99.4(1)°, respectively,[20] and the monomeric aryloxide derivatives $[ZrCp_2(OAr)_2]$ where Ar = 2,6-$Me_2C_6H_3$ [98.6(2)°] and Ar = 2,4,6-$Me_3C_6H_2$ [99.0° (av)].[21]

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{ZrCp_2}\{\mu\text{-}\mathrm{O_2B(C_6F_5)}\}]_2$ (**3**)

Zr−O(1)	1.996(2)	Zr−C(10)	2.522(4)
Zr−O(2′)	2.006(2)	Zr−C(11)	2.526(4)
B−O(1)	1.349(4)	Zr−C(12)	2.527(4)
B−O(2)	1.339(4)	Zr−C(13)	2.528(4)
B−C(1)	1.613(5)	Zr−C(14)	2.517(4)
Zr−C(7)	2.534(4)	Zr−C(15)	2.516(4)
Zr−C(8)	2.533(4)	Zr−C(16)	2.531(4)
Zr−C(9)	2.541(4)		
O(1)−Zr−O(2′)[a]	98.86(9)	O(1)−B−O(2)	123.6(3)
B−O(1)−Zr	146.3(2)	O(1)−B−C(1)	118.0(3)
B−O(2)−Zr′	140.8(2)	O(2)−B−C(1)	118.4(3)

[a] Symmetry transformations used to generate equivalent atoms (′): −*x*, −*y*, −*z*.

The average Zr−O distances [**1** = 1.98 Å; **2** = 1.99 Å; **3** = 2.00 Å] are shorter than the sum of the covalent radii for zirconium and oxygen (2.21 Å), previously attributed to either pπ−dπ donation from the oxygen lone pairs into the vacant orbitals on zirconium or an ionic contribution to the bonding.[22] The angles at oxygen vary considerably within the structures [**1** = 144.4(2)−153.0(3)°; **2** = 141.8(2)−156.7(2)°; **3** 140.8(2)−146.3(2)°], and although the general trend is that larger Zr−O−B angles result in shorter Zr−O bonds, caution must be exercised in interpreting this in terms of increased π-character in the Zr−O bond due to the additional presence of boron adjacent to the oxygen that may also be involved in π-interactions.[23] Indeed, the B−O bond distances in **1** [1.341(4)−1.366(4) Å] are generally shorter than in the parent phenylboronic acid [1.362−1.378 Å],[24] suggesting possible delocalization throughout the complete metallacycle for this particular compound. The inclusion of an electron-withdrawing, perfluorophenyl substituent in complex **3** has little overall effect on the B−O distances [B−O(1) = 1.349(4) Å; B−O(2) = 1.339(4) Å].

Viewing each compound through the axis defined by the two boron atoms, one can observe the different orientations of the C_6 ring with respect to the metallacycle (Figure 5). As may be expected, the mesityl groups in **2** are most perturbed from coplanar [angle between the planes defined by the C_6 ring and the BO_2C_{ipso} moiety = 68.56°] in order to accommodate the 2,6-methyl substituents. The corresponding angles are greatly reduced in **1** [C1−C6 = 1.61°; C7−C12 = 1.55°] and **3** [21.60°], reflecting the reduction in the steric demands of the aryl substituent. The near coplanar arrangement found in **1** generates the correct orbital alignment for overlap between the π-system of the aryl ring and the empty p-orbital of the boron atom. However, the B−C_{ipso} bond distances [1.587(5) Å; 1.573(4) Å] are found to be greater than in phenylboronic acid [1.563 Å; 1.562 Å],[24] illustrating that the disposition of the aryl groups about the metallacycle is likely a consequence of both steric and electronic interactions.

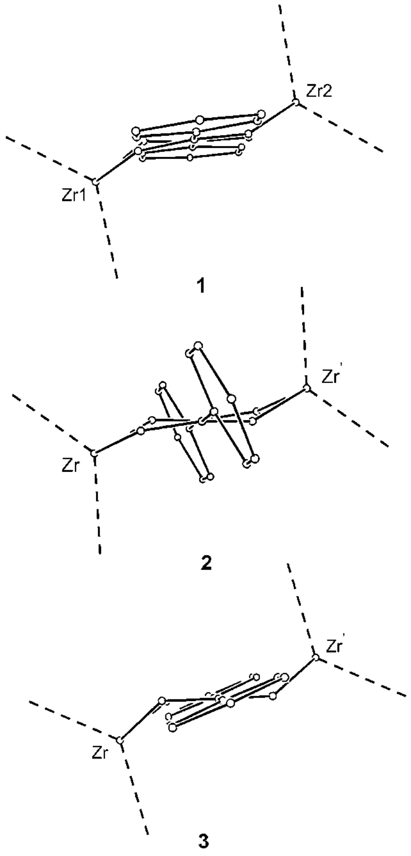

Figure 5. Compounds **1**, **2**, and **3** viewed along the B···B axis illustrating the different orientations of the C_6 ring of the aryl substituents with respect to the metallacycle. The cyclopentadienyl ligands and ring substituents have been omitted for clarity.

In summary, the prototypical group 4 metallocene dialkyl, $\mathrm{ZrCp_2(CH_3)_2}$, does not react with the bulky boronic anhydride $\mathrm{(mesBO)_3}$ but reacts rapidly with the phenyl derivative to ultimately afford the dimeric species $[\mathrm{ZrCp_2}\{\mu\text{-}\mathrm{O_2BPh}\}]_2$ (**1**) via an unknown reaction mechanism. The reactions between $\mathrm{ZrCp_2(CH_3)_2}$ and the phenylboronic acids $\mathrm{ArB(OH)_2}$ [Ar = Ph, mes, C_6F_5], however, proceed smoothly via protonolysis of the zirconium methyl groups to afford the dimeric complexes $[\mathrm{ZrCp_2}\{\mu\text{-}\mathrm{O_2BAr}\}]_2$ [Ar = Ph; (**1**); Ar = mes (**2**); Ar = C_6F_5 (**3**)] as white powders that are insoluble in toluene but may be crystallized from CH_2Cl_2. X-ray structural analyses of **1**−**3** reveal a common eight-membered metallacyclic core, with variations in the bond parameters arising from both steric and electronic properties of the aryl substituent.

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Supporting Information Available: X-ray crystallographic files for **1**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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