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Syntheses and reactions of the bis-boryloxide $O(Bpin)_2$ (pin = $O_2C_2Me_4$)

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The reaction of the phosphine oxides, $OPEt_3$ **1** and $OPn\text{-}Bu_3$ **2** with pinacolborane (HBpin) results in phosphine oxide reduction and the formation of $O(Bpin)_2$ **3**. In contrast, the phosphine oxide $OPn\text{-}Bu_3$ reacts with $HB(C_6F_5)_2$ or $B(C_6F_5)_3$ to give only the donor–acceptor adducts. Compound **3** reacts with $HNPt\text{-}Bu_3$ to give the phosphinimonium borate salt, $[t\text{-}Bu_3PNH_2][(Bpin(OBpin)_2]$ **6**, while reaction with Cp_2ZrMe_2 affords the species $Cp_2Zr(OBpin)_2$ **7**.

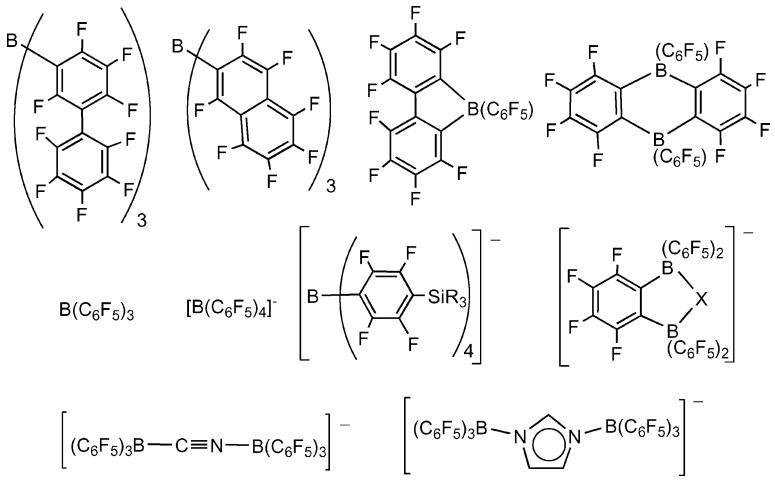
Introduction

The utility of methylalumoxane (MAO) as an activator for zirconocene olefin polymerization catalysts was discovered 25 years ago.[1] In this role MAO functions to alkylate early metal catalyst precursors and subsequently abstract an alkyl group to generate a coordinatively unsaturated metal cation and a weak or non-coordinating anion. The need to use typically 1000 equivalents of MAO to effect precatalyst activation as well as intellectual properties issues prompted researchers to seek alternative activators. Perhaps the most successful alternatives were developed by Exxon researchers in the 1980's and are based on Lewis acidic fluorinated-aryl-borane and the corresponding non-coordinating borates. More recently the research groups of Marks,[2–9] Piers,[10–14] and Bochmann[15] have developed a variety of more complex fluorinated B- and Al-based[16–18] Lewis acid activators and non-coordinating anions (Scheme 1). Nonetheless, the commercial use of many of creative developments are limited by the broad range of compounds defined in Exxon patents.[19–24] In our efforts, we have focused on the study of the fundamental reactivity of Group 13 compounds with the view that new reactivity will offer alternative avenues to activators or non-coordinating anions. To this end, we continue to explore the chemistry of boranes. In recent work, we have described the steric effects on the reaction pathways of phosphinimines and dialkoxyboranes.[25] Phosphinimines with sterically small substituents on P underwent reduction to the corresponding phosphine upon reaction with borane. In this manuscript, we probe the application of this finding to the reduction of phosphine oxides. The reaction of pinacolborane with phosphine oxides provides a facile and clean route to a bis-boryloxide which is readily converted to an unusual phosphinimonium bis-boryloxide-borate salt. Reactivity of the bis-boryloxide with dimethylzirconocene is also described and the implications regarding the potential utility of these compounds is considered.

Experimental

General data

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres glovebox. Solvents were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. HBpin (pinacolborane), $Pn\text{-}Bu_3$, PEt_3, and N_3SiMe_3 were used as received from Sigma-Aldrich. Modified literature procedures were used to synthesize the phosphinimines.[26] ^1H, $^{11}B\{^1H\}$, ^{19}F, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance spectrometers. These spectrometers operate at either 300 or 500 MHz for ^1H NMR spectroscopy. Deuterated benzene and toluene were purchased from Cambridge Isotopes Laboratories, vacuum distilled from the appropriate drying agents and freeze–pump–thaw-degassed (3×). C_6D_6 was used to record the NMR spectra unless otherwise indicated. For ^1H and $^{13}C\{^1H\}$ NMR spectra, trace amounts of protonated solvents were used as reference and NMR chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra are referenced to 85% H_3PO_4, and $^{11}B\{^1H\}$ NMR spectra are referenced to $BF_3{\cdot}OEt_2$



Scheme 1 Some B-based activators and non-coordinating anions.

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and ^{19}F NMR spectra are referenced to CCl_3F. Combustion analyses were performed at the University of Windsor Chemical Laboratories.

Syntheses

Synthesis of OPR_3 (R = Et 1, *n*-Bu 2). These compounds were prepared in a similar fashion and thus one preparation is detailed. To neat $Et_3PNSiMe_3$ (4.0 g, 18.8 mmol) was added excess dry methanol (30 mL) *via* cannula at 25 °C. The resulting solution was refluxed for 16 h. The excess methanol, $MeOSiMe_3$ and $MeNH_2$ were removed *in vacuo* over a 6 h period. The product was crystallized from a pentane solution, dried *in vacuo* and recovered in 82% yield. **1**: ^1H NMR (ppm): 1.16 (m, 6H, CH_2Me), 0.86 (m, 9H, Me); $^{31}P\{^1H\}$ NMR (ppm): 46.2; $^{13}C\{^1H\}$ NMR (ppm): 20.6 (d, PCH_2, $^1J_{P\text{-}C}$ = 65.8 Hz); 6.2 (s, Me). Calcd: H: 11.27%, C: 53.72%; Found: H: 11.16%, C: 53.58%. **2**: 85% yield. ^1H NMR (ppm): 1.42 (m, 6H, PCH_2), 1.35 (m, 6H, $CH_2CH_2CH_2$), 1.23 (sextet, 6H, CH_2Me), $^3J_{H\text{-}H}$ = 4 Hz), 0.79 (t, 9H, Me, $^3J_{H\text{-}H}$ = 8 Hz); $^{31}P\{^1H\}$ NMR (ppm): 42.0; $^{13}C\{^1H\}$ NMR (ppm): 28.9 (d, PCH_2), $^1J_{P\text{-}C}$ = 32 Hz), 24.9 (d, $CH_2CH_2CH_2$, $^2J_{P\text{-}C}$ = 6 Hz), 24.7 (d, CH_2Me, $^3J_{P\text{-}C}$ = 2 Hz), 14.2 (s, Me). Calcd: H: 12.47%, C: 66.02%; Found: H: 12.49%, C: 65.98%.

Synthesis of $O(Bpin)_2$ 3.

Method (i). This method involves reaction of HBpin and one of **1, 2** or $OPPh_3$, thus one such preparation is detailed. HBpin (0.344 mL, 2.73 mmol) was added *via* syringe to a solution of **1** (0.150 g, 1.13 mmol) in 25 mL of toluene. The solution was heated at reflux for 72 h. Toluene and Et_3P were removed *in vacuo* and the product was dissolved in minimal amounts of pentanes. A crystalline product precipitated at −33 °C and the supernatant was removed. The crystals of **3** were washed with cold pentanes, dried *in vacuo* and isolated in 92% yield. X-Ray quality crystals were obtained by recrystallization from pentanes at −33 °C.

Method (ii). $ONMe_3$ (0.129 g, 1.72 mmol) was added to a 100 mL Schlenk flask to which 40 mL of toluene was added. HBpin (0.5 mL, 3.45 mmol) was slowly added to the toluene slurry. The flask was put under static vacuum and stirred for 1 h. The solvent and NMe_3 were removed *in vacuo* and the resulting white solid was dried *in vacuo* for 16 h. The white solid was isolated in 96% yield. ^1H NMR (ppm): 1.00 (s, Me); $^{13}C\{^1H\}$ NMR (ppm): 83.3 (s, BOC), 25.0 (s, Me); $^{11}B\{^1H\}$ NMR (ppm): 21.6 ($\upsilon_{\frac{1}{2}}$ = 750 Hz). Calcd: H: 8.96%; C: 53.39%; Found: H: 8.85% C: 53.16%.

Synthesis of (*n*-Bu_3PO)$HB(C_6F_5)_2$ 4 and (*n*-Bu_3PO)$B(C_6F_5)_3$ 5. These compounds were prepared in a similar fashion and thus one preparation is detailed. To a solution of **2** (0.041 g, 0.188 mmol) in 3 mL of toluene, was added a solution of $HB(C_6F_5)_2$ (0.065 g, 0.188 mmol) in 3 mL of toluene. The solution was stirred for 72 h. The solvent was removed *in vacuo* and the product was obtained in 88% yield. **4**: ^1H NMR (ppm): 1.30 (m, 6H, PCH_2), 1.00 (m, 12H, $CH_2CH_2CH_2Me$), 0.67 (t, 9H, Me, $^3J_{H\text{-}H}$ = 7 Hz), $^{31}P\{^1H\}$ NMR (ppm): 76.7; $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, ppm): 25.1 (d, $^1J_{P\text{-}C}$ = 64 Hz), 24.0 (d, $^2J_{P\text{-}C}$ = 15 Hz), 23.2, 13.3; ^{11}B NMR (ppm): −12.7; ^{19}F NMR (ppm): −136.5, −159.7, −165.3. Calcd: H: 5.00%, C: 51.09%; Found: H: 4.88%, C: 51.01%. **5**: 87% yield. ^1H NMR (ppm): 1.28 (m, 6H, PCH_2), 0.91 (m, 12H, $CH_2CH_2CH_2$), 0.62 (t, 9H, Me, $^3J_{H\text{-}H}$ = 7 Hz); $^{31}P\{^1H\}$ NMR (ppm): 71.8; $^{13}C\{^1H\}$ NMR (ppm): 148.8 (d(m), $^1J_{C\text{-}F}$ = 242 Hz, C_6F_5 (*o*-C)), 140.7 (d(m), $^1J_{C\text{-}F}$ = 249 Hz, C_6F_5 (*p*-C)), 138.0 (d(m), $^1J_{C\text{-}F}$ = 249 Hz, C_6F_5 (*m*-C)), 25.3 (d, PCH_2CH_2, $^1J_{P\text{-}C}$ = 66 Hz), 24.2 (d, $CH_2CH_2CH_2$), $^2J_{P\text{-}C}$ = 16 Hz), 23.3 (s, CH_2CH_2Me), 13.5 (s, CH_2Me); $^{11}B\{^1H\}$ NMR (ppm): −2.7 (br); ^{19}F NMR (ppm): −134.0, −157.7, −164.1. Calcd: H: 3.73%, C: 49.34%; Found: H: 3.72%, C: 48.82%.

Synthesis of [*t*-Bu_3PNH_2][$(Bpin(OBpin)_2$] 6. Solid **3** (0.03 g, 0.11 mmol) was added to a solution of *t*Bu_3PNH (0.024 g, 0.11 mmol) in 2 mL of pentane. A white solid precipitated from the pentane solution immediately. The mixture was stirred for 2 h and set aside to allow the solid to settle in the vial. The pentane soluble product (*t*$Bu_3PNBpin$) was decanted off and the solid was washed twice with 2 mL of pentane. The product was dried *in vacuo*, resulting in a fine white powder in 80% yield. X-Ray quality crystals grew from a toluene solution. ^1H NMR (partial, ppm): 1.11 (d, 27H, *t*-Bu, $^3J_{P\text{-}H}$ = 12 Hz), 1.11 (br s, 36H, BOCMe); $^{31}P\{^1H\}$ NMR (ppm): 61.9; $^{13}C\{^1H\}$ NMR (partial, ppm): 39.5 (d, *t*-Bu, $^1J_{P\text{-}C}$ = 45 Hz), 29.6 (s, *t*-Bu), 26.5 (s, OCMe), 25.3 (s, OCMe), $^{11}B\{^1H\}$ NMR (ppm): 21.9, 9.3. Calcd: C: 57.08%, H: 10.39%, N: 2.21%; Found: C: 57.23%, H: 10.40%, N: 2.23%.

Synthesis of $Cp_2Zr(OBpin)_2$ 7. To a solution of **3** (0.106 g, 0.398 mmol) in 25 mL of toluene was added solid Cp_2ZrMe_2 (0.050 g, 0.199 mmol). The solution was refluxed for 16 h, followed by removal of toluene and MeBpin *in vacuo*. The solid was washed three times with pentane, dissolved in a minimal amount of toluene and stored at −33 °C. Crystalline material precipitated from the pentane solution, the supernatant was decanted off, and the product was dried *in vacuo*. A white crystalline solid was collected in 82% yield. X-Ray quality crystals were obtained by recrystallization from pentane at −33 °C. ^1H NMR (ppm): 6.15 (s, 10H, Cp), 1.14 (s, 24H, Me); $^{13}C\{^1H\}$ NMR (ppm): 114.3 (s, Cp), 81.3 (s, BOC), 25.4 (s, Me); $^{11}B\{^1H\}$ NMR (ppm): 19.2. Calcd: H: 6.75%, C: 52.08%; Found: H: 6.79%, C: 51.85%.

X-Ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 second exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45–50.0°$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package. See Table 1 for crystallographic data.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[27] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on *F*. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the case of **3** the oxygen and chelate carbon atoms are disordered and were modelled with two orientations. For **7** disorder of the pinacolate chelates were modelled with two orientations of the O and C atoms in the chelate ring. In these cases the fractional atoms were refined isotropically and the hydrogen atoms for the pinacolate methyl groups were not included. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined with the exception of the phosphinammonium protons in **6** which were located and refined. The locations of the largest peaks in the final difference

Table 1 Crystallographic data

Crystal	**3**	**6**	**7**
Molecular formula	$C_{12}H_{24}B_2O$	$C_{30}H_{65}B_3NO_8P$	$C_{22}H_{34}B_2O_6Zr$
Formula weight	269.93	631.23	507.33
a/Å	6.544(4)	10.752(3)	20.276(11)
b/Å	21.289(13)	13.737(4)	13.162(8)
c/Å	11.767(7)	14.181(4)	19.540(11)
α/°	90	94.422(6)	90
β/°	95.599(12)	104.550(6)	100.694(13)
γ/°	90	106.244(6)	90
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
V/Å^3	1631.5(17)	1921.9(9)	5124(5)
D_{calc}/g cm^{-3}	1.099	1.091	1.315
Z	4	2	8
μ/mm^{-1}	0.081	0.114	0.461
θ range/°	1.91–23.27	1.50–23.32	1.85–23.29
Reflections	6727	8994	10468
Data $F_o^2 > 3\sigma(F_o^2)$	2340	5469	3687
Parameters	253	394	260
R^a	0.0974	0.0854	0.0942
$R_w{}^b$	0.2677	0.1554	0.2410
Goodness of fit	0.884	0.843	1.031

Data collected at 20 °C with Mo-Kα radiation ($\lambda = 0.71069$ Å).[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]\}^{\frac{1}{2}}$.

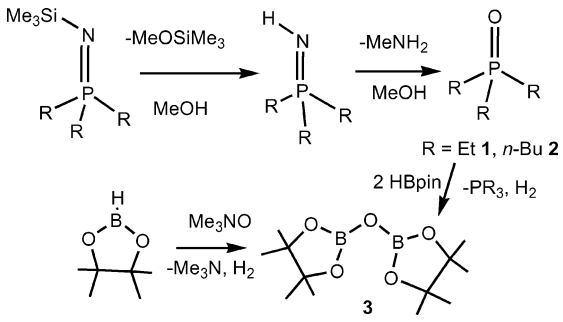
Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

CCDC reference numbers 266791–266793.

See http://www.rsc.org/suppdata/dt/b5/b504246a/ for crystallographic data in CIF or other electronic format.

Results and discussion

The alcoholysis of *N*-trimethylsilylphosphinimines is a firmly established route to *N*-H-phosphinimines.[26,28–32] While this reaction has been exploited extensively for the preparation of sterically bulky phosphinimines, the alcoholysis of less bulky phosphinimines to *N*-H-phosphinimines has been shown to be more sensitive, requiring the use of lower temperatures (−30 °C).[33] Herein, the analogous reactions of sterically unencumbered *N*-trimethylsilylphosphinimines at 25 °C are shown to result in the further transformation of *N*-H-phosphinimines to the corresponding phosphine oxides. In this fashion, the phosphine oxides, $OPEt_3$ **1** and $OPn\text{-}Bu_3$ **2** were obtained from the precursors $R_3PNSiMe_3$. The spectral data and elemental analyses confirmed the formulations of the products, **1** and **2**. The impact of steric effects on the reaction pathways in the protonolyses is reminiscent of those recently described for the reactions of phosphinimines and pinacolboranes where small substituents prompted P–N bond cleavage. By analogy, the close approach of the sterically unencumbered electropositive P atom and an alcohol O atom presumably prompts the transformation to phosphine oxide (Scheme 2).



Scheme 2 Synthesis of **3**.

The reactions of pinacolborane with the tertiary phosphine oxides **1, 2** or $OPPh_3$ were conducted in refluxing toluene for 72 h. $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy on the crude reaction mixture suggested the complete conversion to the corresponding tertiary phosphine and the formation of a single boron-containing compound **3**. The boron-containing product was the same in each of these three reactions. In the case of the reaction of **1**, the volatility of PEt_3 resulted in its facile removal by vacuum affording **3** cleanly in 92% yield. For the corresponding reaction of **2**, removal of $Pn\text{-}Bu_3$ was effected *via* precipitation of **3** from pentane at −33 °C giving **3** in 65% yield. Finally in the case of the reaction of $OPPh_3$ filtration through Celite and removal of pentane yielded **3** in 75% yield. X-Ray crystallography (Fig. 1) and ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy were consistent with the formulation of **3** as $O(Bpin)_2$.

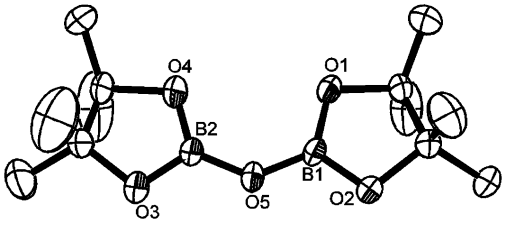


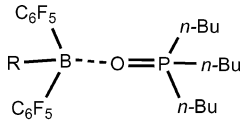
Fig. 1 ORTEP drawing of **3**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered oxygens and chelate carbons are shown.

X-Ray crystallographic data for **3** confirmed the formulation and revealed that although there was significant disorder of the oxygen positions, the average B–O bond distances for the bridging oxygen atom was 1.36(2) Å while the B–O–B′ angle in **3** was found to average 136(2)°. These bond distances are similar to those observed in the related boryloxides $O(B(terphenyl)_2)_2$ (1.340(2) Å and 1.347(2) Å),[34] $O(B(Cl(N\text{-}iPr_2)_2)_2$ (1.367(3) Å and 1.367(3) Å),[35] $O(B(N_3(Ph)_2C))_2$ (1.365(4) Å and 1.370(4) Å)[36] and $O(B(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_2)_2$ (1.370(2) Å and 1.359(2) Å).[37] The disorder of the pinacolate chelate rings precludes direct comparison with the related species $(Bpin)_2$[38] and $(Bpin)_2(OCMe_2CMe_2O)$.[39] The overall geometry of **3** is reminiscent of that recently reported for the species $HN(Bpin)_2$ where the B–N–B angle was found to be 132.9(3)°. However the B–O distances in **3** are significantly shorter than the B–N distance in $HN(Bpin)_2$ (1.419(6) Å).[25]

Several alternative syntheses of **3** were also uncovered. Prolonged reflux of pinacolborane in toluene (144 h), afforded numerous products including **3** which was isolated in 13% yield. An efficient route to **3** was shown to involve the reaction of Me_3NO with pinacolborane at 25 °C (Scheme 2), which affords **3** in 96% isolated yield. Similar reactions of trialkyl- or triarylboranes with amine oxides reported by Köster and Morita were shown to give trialkoxy- or triphenoxyboranes.[40] Similarly, reactions of species containing B–H bonds with amine-oxides afforded boryl-hydroxides. Thus, the reaction of pinacolborane and phosphine oxide or amine oxide is consistent with the proposed mechanism that results in reduction of the phosphine oxide or amine oxide and generation of the transient boryl-hydroxide species HOBpin which reacts immediately with excess borane to give **3**. A similar mechanism involving transient boryl-hydroxides has been previously suggested for the oxidation of organoboranes with amine oxides.[40]

Other researchers have probed reductions of Group 15 and Group 16 elements with boranes. Some years ago, Köster and Morita showed that $OPPh_3$ is reduced by B_2Pr_4, BPr_3, BEt_2H and $B(NR_2)_3$,[41] although these reactions result in multiple boron-containing products. More recently, reduction of OPR_3 has been shown to occur in the presence of excess $BH_3{\cdot}SMe_2$, producing phosphine-borane adducts.[42,43] In addition, the deoxygenation of sulfoxides (R_2SO) to sulfides effected by reaction with

HBcat (cat = $O_2C_6H_4$) has been recently reported by Westcott, Baker and co-workers.[44] In these reactions the diboryloxide complex O(Bcat)$_2$ analogous to **3** is formed. On the other hand, the direct syntheses of structurally related boryloxides from the hydrolysis of boryl-halides have been known for over 50 years.[35,36,45–47] In contrast to the above reductions of phosphine oxides, reaction of the borane HB(C$_6$F$_5$)$_2$[48] with **2** in toluene at 25 °C results in the formation of a new species **4**. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{19}F, and ^{11}B{^{1}H} NMR spectroscopy were consistent with the formulation of **4** as the borane–phosphine oxide adduct HB(C$_6$F$_5$)$_2$·OP*n*-Bu$_3$. Attempts to drive reduction of the coordinated phosphine oxide by treatment with excess borane HB(C$_6$F$_5$)$_2$ under reflux afforded only what appeared to be a complex and unresolvable mixture of products. The difference in reactivity between HB(C$_6$F$_5$)$_2$ and HBpin has been previously reported.[49] In an analogous manner the donor–acceptor compound B(C$_6$F$_5$)$_3$·OP*n*-Bu$_3$ **5** (Scheme 3) was isolated from the reaction of **2** and B(C$_6$F$_5$)$_3$. Related donor–acceptor adducts of B(C$_6$F$_5$)$_3$ have been previously reported in the literature[50,51]



R = H **4**, C$_6$F$_5$ **5**

Scheme 3

Reactions of O(Bpin)$_2$

Compound **3** reacts with HNP*t*-Bu$_3$ in pentane to form a white precipitate **6** in 80% yield. Compound **6** displayed a ^{31}P{^{1}H} NMR resonance at 61.9 ppm, consistent with the presence of a phosphinimonium cation, while the observations of ^{11}B{^{1}H} NMR resonances at 21.9 and 9.1 ppm are consistent with the presence of two unique B environments. While ^{13}C{^{1}H} and ^{1}H NMR data confirm the presence of pinacolate and phosphinimine units, the structure of **6** could not be unambiguously determined. Recrystallization of **6** from toluene afforded X-ray quality crystals. Crystallographic data revealed the formulation of **6** as the phosphinimonium borate salt, [*t*-Bu$_3$PNH$_2$][(Bpin(OBpin)$_2$] (Scheme 4, Fig. 2). The structural parameters of the phosphinimonium cation are unexceptional,[30,32] although the N-bound protons approach the anion with H···O(3) distances of 2.112 and 2.545 Å. The anion shown in Fig. 2, contains two three-coordinate B centres that are bridged by oxygen to the central four-coordinate B centre. The coordination spheres of each of the B centres are completed by the chelating pinacolate ligands. The B–oxide distances involving the three-coordinate centres, B(3)–O(6) and B(2)–O(3), are 1.289(10) Å and 1.308(8) Å, respectively, while the corresponding distances involving the four-coordinate centres B(1)–O(6) and B(1)–O(3) are 1.454(9) Å and 1.466(9) Å, respectively. The former distances are somewhat shorter than those seen in **3**, while the latter are longer. These differences

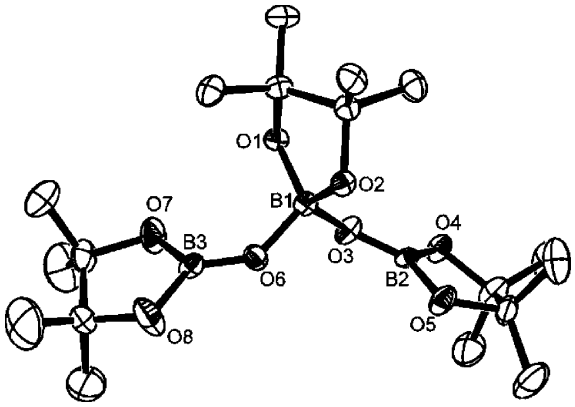
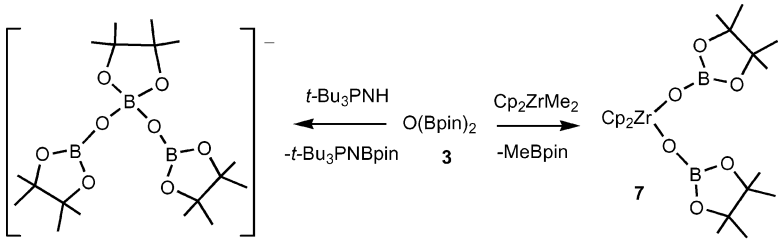


Fig. 2 ORTEP drawing of the anion of **6**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): B(1)–O(6) 1.454(9), B(1)–O(2) 1.455(8), B(1)–O(3) 1.466(9), B(1)–O(1) 1.492(8), B(2)–O(3) 1.308(8), B(2)–O(4) 1.368(8), B(2)–O(5) 1.372(8), B(3)–O(6) 1.289(10), B(3)–O(7) 1.342(9), B(3)–O(8) 1.401(10); O(2)–B(1)–O(1) 105.0(6), O(4)–B(2)–O(5) 111.0(7), O(7)–B(3)–O(8) 107.1(8), B(2)–O(3)–B(1) 138.7(6), B(3)–O(6)–B(1) 134.3(6).

are consistent with the presence of the anionic charge centred on the central B atom (B(1)). Similarly, the B–O bond lengths to the pinacolate ligands differ for the two B environments. In the case of the four-coordinate B centre these B–O bond lengths average 1.47(1) Å, while those incorporating the three-coordinate B centres range from 1.342(9) Å to 1.401(10) Å. The bite angles for the pinacolate ligands range from 105.0(6)° to 111.0(7)°, while the B–O–B′ angles 138.7(6)° and 134.3(6)° are similar to that seen in **3** (133.9(6)°). This geometry at B stands in contrast to the pseudo-tetrahedral geometry observed for the related bis-catecholatoborate salts.[39,52–54]

The mechanism of formation of **6** provokes some speculation. As the reaction is rapid, kinetic studies are not possible. Nonetheless, it is reasonable to propose that the reaction is initiated by a donor–acceptor interaction of the phosphinimine and one of the B centres of **3**, prompting B–O bond cleavage with concurrent formation of the borylphosphinimide by-product (*t*-Bu$_3$PNBpin) and formation of the transient boronic acid HOBpin. The latter species is trapped by reaction with **3** affording formation of the anion of **6** with concurrent proton transfer to phosphinimine providing the phosphinimonium cation. It is noteworthy that ^{1}H and ^{31}P{^{1}H} spectroscopy of the pentane soluble species are consistent with the presence of the by-product (*t*-Bu$_3$PNBpin). These data were identical to those recently reported for an independent synthesis of (*t*-Bu$_3$PNBpin).[25]

Compound **3** was also observed to react with Cp$_2$ZrMe$_2$ in refluxing toluene for 16 h to give a white solid in 82% yield. The product **7** exhibits NMR resonances consistent with the 1 : 1 ratio of Cp : pinacolate ligands. The ^{11}B{^{1}H} NMR spectrum shows a single resonance at 19.2 ppm. These data suggest a formulation of **7** as Cp$_2$Zr(OBpin)$_2$, which was confirmed *via* a single crystal X-ray diffraction study (Scheme 4, Fig. 3). The geometry about Zr is a typical pseudo-tetrahedron, with



[*t*-Bu$_3$PNH$_2$]$^+$

6

Scheme 4 Reactivity of **3**.

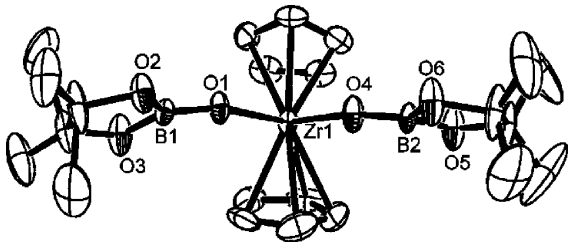
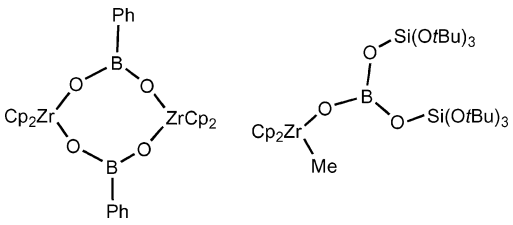


Fig. 3 ORTEP drawing of **7**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity, one orientation of the disordered chelate carbons are shown. Selected distances (Å) and angles (°): Zr(1)–O(4) 2.011(9), Zr(1)–O(1) 2.025(8), O(1)–B(1) 1.291(16), O(2)–B(1) 1.311(17), O(3)–B(1) 1.400(17), O(4)–B(2) 1.280(15), O(5)–B(2) 1.360(16), O(6)–B(2) 1.357(16); O(4)–Zr(1)–O(1) 97.6(3), B(1)–O(1)–Zr(1) 156.0(9), B(2)–O(4)–Zr(1) 154.2(9), O(2)–B(1)–O(3) 108.6(13), O(5)–B(2)–O(6) 108.3(12).

Zr–O bond distances of 2.011(9) Å and 2.025(8) Å with a O–Zr–O′ angle of 97.6(3)°. In comparison, the Zr–O bond distances and O–Zr–O′ bond angles in the zirconocene–alkoxide species, $Cp_2Zr(\mu\text{-}OCH_2CMe_2CH_2O)_2ZrCp_2$ and $Cp_2Zr(\mu\text{-}OCH_2C_6H_4CH_2O)_2ZrCp_2$ are 1.945(6) Å, 1.946(6) Å, 101.4(3)° and 99.4(1)°, respectively.[55] The longer Zr–O bond length in **7** is consistent with the presence of the Lewis acidic boron center. The larger angles at Zr in the zirconocene–alkoxides may be an artifact of the macrocyclic nature of these complexes. The B–O bond distances were determined to be 1.291(16) Å and 1.280(15) Å with Zr–O–B bond angles of 156.0(9)° and 154.2(9)°. In addition, the Bpin units are canted with respect to the ZrO_2 plane by only 18.0° and 5.7° respectively. This geometry places the acceptor B p-orbital approximately orthogonal to a vacant a_1 molecular orbital on Zr, thus providing for strong Zr–O and B–O π-bonding and accounting for the increase in the angle at O.

Previous reports regarding the chemistry of boryloxides have been sparse over the last 15 years. The groups of Power, Chisholm, Gibson and Serwatowski have utilized boryloxide ligands to form metal complexes of Li, Co, Mn, Fe, Al, Zn and Cd.[56–62] In addition only two examples of Zr complexes containing boryloxide ligands have been reported. Balkwill *et al.* have described the bimetallic complexes $(Cp_2Zr(\mu^2\text{-}O_2BAr))_2$ (Ar = Ph, C_6H_2-2,4,6-Me_3, C_6F_5) (Scheme 5).[63] synthesized *via* reaction of Cp_2ZrMe_2 with $ArB(OH)_2$ generated *via* hydrolysis of $(OBAr)_3$. These macrocyclic species exhibit shorter average Zr–O (1.985(2) Å) bonds and longer average B–O (1.350(6) Å) bonds. At the same time, the Zr–O–B angles range from 141.8(2)° to 156.7(2)° for the derivatives with Ar = Ph, C_6H_2-2,4,6-Me_3. The upper limit of this range is similar to the Zr–O–B angles seen in **7**, but presumably the macrocyclic nature of these complexes accounts for the lower end of this range. More recently, Tilley's group has also reported the structure of the related boryloxide derivative $Cp_2ZrMe(OB(OSi(O\textit{t}\text{-}Bu)_3)_2)$ (Scheme 5).[64] The Zr–O distance of 1.974(4) Å is slightly shorter than those in **7** while the bridging B–O bond distance and Zr–O–B angle are slightly larger at 1.329(3) Å and 160(2)°, respectively. These metric perturbations are consistent with the steric demands of the boryloxide substituents in $Cp_2ZrMe(OB(OSi(O\textit{t}\text{-}Bu)_3)_2)$.



Scheme 5 Known Zr–boryloxide species.

The facile formation of **7** from the reaction of Cp_2ZrMe_2 and **3** is thought to be initiated by interaction of the Lewis acidic B center with the Zr-bound methyl group. This prompts simultaneous formation of MeBpin and transfer of the boryloxide ligand to Zr. Presumably this process repeats to give **7**. All attempts to intercept the intermediate in this process were unsuccessful. This chemistry reflects both the acidity of the B centers and the reactivity of the B–O bonds in **3**. Thus, while the reactivity shown herein affords a new synthetic route to a B-based anion, the lability of the B–O bonds makes these boryloxides unsuitable for use as activators or non-coordinating anions. Efforts are underway to utilize this unique synthetic route to prepare related boryloxide salts in which the B–O bond strengths are enhanced by the introduction of electronically favorable and sterically demanding substituents. The results of these efforts will be reported in due course.

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References

1 H. Sinn, W. Kaminsky, H. J. Vollmer and R. Woldt, *Angew. Chem.*, 1980, **92**, 396.
2 M.-C. Chen and T. J. Marks, *J. Am. Chem. Soc.*, 2001, **123**, 11803.
3 Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 6287.
4 L. Li and T. J. Marks, *Organometallics*, 1998, **17**, 3996.
5 L. Li, C. L. Stern and T. J. Marks, *Organometallics*, 2000, **19**, 3332.
6 T. J. Marks and Y.-X. Chen, in Organoborane complexes with metallocenes for polymerization catalysts, *US Pat.*, 629165, 2001.
7 T. J. Marks, L. Li, Y.-X. Chen, M. H. McAdon and P. N. Nickias, in Perfluoro group-substituted boron-containing activator for transition metal complex catalysts for polymerization of olefins, *WO Pat.*, 9906412, 1999.
8 M. H. McAdon, P. N. Nickias, T. J. Marks and D. J. Swartz, in Activators for transition metal complex catalysts for polymerization of olefins, *WO Pat.*, 9906413, 1999.
9 M. V. Metz, D. J. Schwartz, C. L. Stern, T. J. Marks and P. N. Nickias, *Organometallics*, 2002, **21**, 4159.
10 L. D. Henderson, W. E. Piers, G. J. Irvine and R. McDonald, *Organometallics*, 2002, **21**, 340.
11 K. Koehler, W. E. Piers, A. P. Jarvis, S. Xin, Y. Feng, A. M. Bravakis, S. Collins, W. Clegg, G. P. A. Yap and T. B. Marder, *Organometallics*, 1998, **17**, 3557.
12 R. Roesler, B. J. N. Har and W. E. Piers, *Organometallics*, 2002, **21**, 4300.
13 V. C. Williams, G. J. Irvine, W. E. Piers, Z. Li, S. Collins, W. Clegg, M. R. J. Elsegood and T. B. Marder, *Organometallics*, 2000, **19**, 1619.
14 V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3244.
15 J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223.
16 T. J. Marks and Y.-X. Chen, in Synthesis and use of (polyfluoroaryl)fluoroanions of aluminum, gallium and indium as polymerization cocatalysts, *US Pat.*, 6130302, 2000.
17 T. J. Marks and Y.-X. Chen, in (Polyfluoroaryl)fluoroanions of aluminum, gallium, and indium of enhanced utility, uses thereof, and products based thereon, *US Pat.*, 6262200, 2001.
18 Y. Sun, M. V. Metz, C. L. Stern and T. J. Marks, *Organometallics*, 2000, **19**, 1625.
19 S. M. Chranowski, M. J. Krause and F. Y.-K. Lo, in Catalyst for use in olefin polymerization or copolymerization, *WO Pat.*, 9722635, 1995.
20 D. J. Crowther, R. A. Fisher, J. A. M. Canich, G. G. Hlatky and H. W. Turner, in Transition metal complexes and their manufacture for olefin polymerization catalysts, *WO Pat.*, 19930701, 1994.
21 H. W. Turner, C. S. Speed, B. J. Folie, D. J. Crowther, J. F. Walzer, Jr., R. A. Fisher, and G. A. Vaughan, in *High temperature olefin polymerization process using metallocene catalyst*, WO, 9722635, 1997.
22 H. W. Turner, G. A. Vaughan, R. A. Fisher, J. F. Walzer, Jr., C. S. Speed, B. J. Folie, and D. J. Crowther, in High-temperature olefin polymerization process, *US Pat.*, 5767208, 1998.

23 D. J. Upton, J. A. M. Canich, G. G. Hlatky and H. W. Turner, in Supported ionic transition metal catalysts and their manufacture for olefin polymerization, *WO Pat.*, 9403506, 1994.
24 J. F. Walzer, Jr., A. J. Dias, J. M. J. Frechet and S. B. Roscoe, in Polymeric supported catalysts for olefin polymerization, *WO Pat.*, 9855518, 1998.
25 S. B. Hawkeswood, P. Wei, J. Gauld and D. W. Stephan, *Inorg. Chem.*, 2005, **44**, in press.
26 D. W. Stephan, J. C. Stewart, F. Guerin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R. E. v. H. Spence, W. Xu, L. Koch, X. Gao and D. G. Harrison, *Organometallics*, 2003, **22**, 1937.
27 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
28 S. Courtenay, C. M. Ong and D. W. Stephan, *Organometallics*, 2003, **22**, 818.
29 C. M. Ong, P. McKarns and D. W. Stephan, *Organometallics*, 1999, **18**, 4197.
30 K. Dehnicke and J. Straehle, *Polyhedron*, 1989, **8**, 707.
31 K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19.
32 K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103.
33 L. Birkofer and S. M. Kim, *Chem. Ber.*, 1964, **97**, 2100.
34 I. Cynkier and N. Furmanova, *Cryst. Struct. Commun.*, 1980, **9**, 307.
35 W. Maringgele, M. Noltemeyer and A. Meller, *Organometallics*, 1997, **16**, 2276.
36 L. Weber, M. Schnieder, H.-G. Stammler, B. Neumann and W. W. Schoeller, *Eur. J. Inorg. Chem.*, 1999, 1193.
37 C. J. Cardin, H. E. Parge and J. W. Wilson, *J. Chem. Res. (S)*, 1983, 93.
38 H. Noth, *Z. Naturforsch., Teil B*, 1984, **39**, 1463.
39 S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker and J. C. Calabrese, *Inorg. Chem.*, 1993, **32**, 2175.
40 R. Koester and Y. Morita, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 580.
41 R. Koester and Y. Morita, *Angew. Chem.*, 1965, **77**, 589.
42 G. Keglevich, T. Chuluunbaatar, K. Ludanyi and L. Toke, *Tetrahedron*, 2000, **56**, 1.
43 G. Keglevich, M. Fekete, T. Chuluunbaatar, A. Dobo, V. Harmat and L. Tke, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4451.
44 D. J. Harrison, N. C. Tam, C. M. Vogels, R. F. Langler, R. T. Baker, A. Decken and S. A. Westcott, *Tetrahedron Lett.*, 2004, **45**, 8493.
45 J. Goubeau and H. Keller, *Z. Anorg. Allg. Chem.*, 1951, **267**, 1.
46 H. Noth and P. Schweizer, *Chem. Ber.*, 1964, **94**, 1464.
47 M. Komorowska, K. Niedenzu and W. Weber, *Inorg. Chem.*, 1990, **29**, 289.
48 D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809.
49 D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.
50 M. A. Beckett, D. S. Brassington, S. J. Coles and M. B. Hursthouse, *Inorg. Chem. Commun.*, 2000, **3**, 530.
51 M. A. Beckett, D. S. Brassington, M. E. Light and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 2001, 1768.
52 W. Clegg, A. J. Scott, F. J. Lawlor, N. C. Norman, T. B. Marder, C. Dai and P. Nguyen, *Acta Crystallogr., Sect. C.*, 1998, **54**, 1875.
53 W. Clegg, A. J. Scott, C. Dai, G. Lesley, T. B. Marder, N. C. Norman and L. Farrugia, *Acta Crystallogr., Sect. C*, 1996, **52**, 2545.
54 W. Clegg, A. J. Scott, M. R. J. Elsegood, T. B. Marder, C. Dai, N. C. Norman, E. G. Robins and N. L. Pickett, *Acta Crystallogr., Sect. C*, 1999, **55**, 733.
55 D. W. Stephan, *Organometallics*, 1990, **9**, 2718.
56 K. J. Weese, R. A. Bartlett, B. D. Murray, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1987, **26**, 2409.
57 H. Chen, R. A. Bartlett, M. M. Olmstead, P. P. Power and S. C. Shoner, *J. Am. Chem. Soc.*, 1990, **112**, 1048.
58 M. H. Chisholm, K. Folting, S. T. Haubrich and J. D. Martin, *Inorg. Chim. Acta*, 1993, **213**, 17.
59 V. C. Gibson, S. Mastroianni, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 826.
60 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1997, **16**, 2637.
61 R. Anulewicz-Ostrowska, S. Lulinski, J. Serwatowski and K. Suwinska, *Inorg. Chem.*, 2000, **39**, 5763.
62 S. Lulinski, S. Madura, J. Serwatowski and J. Zachara, *Inorg. Chem.*, 1999, **38**, 4937.
63 J. E. Balkwill, S. C. Cole, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2002, **41**, 3548.
64 K. L. Fujdala, A. G. Oliver, F. J. Hollander and T. D. Tilley, *Inorg. Chem.*, 2003, **42**, 1140.