ORGANOMETALLICS

ARTICLE

pubs.acs.org/Organometallics

Investigation of the Reactivity of Hydroxyborate Salts with Group IV Metal Complexes: Synthesis and Structural Characterization of the Zirconium and Hafnium Ionic Complexes $[PPN]^+[Cp_2MMe(OB(C_6F_5)_3)]^-$

Vinciane Kelsen,[†] Christophe Vallée,*[,†] Erwann Jeanneau,[‡] Christine Bibal,[§] Catherine C. Santini,*[,§] Yves Chauvin,[§] and Hélène Olivier-Bourbigou[†]

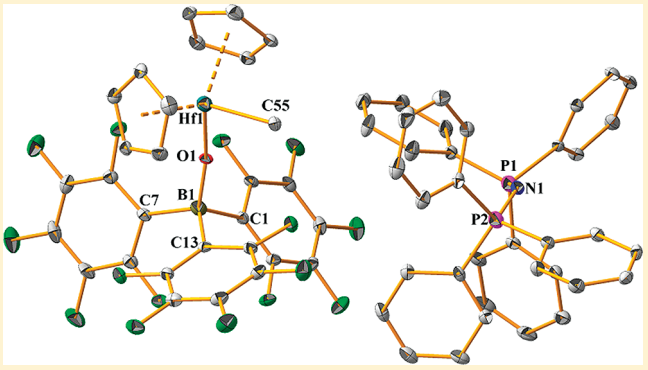
[†]IFP Energies Nouvelles, Rond-point de L'Échangeur de Solaize, BP 3, 69360, Solaize, France

[‡]Centre de Diffractométrie Henri Longchambon, Université de Lyon, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

[§]Université de Lyon, ICL, C2P2, UMR 5265 CNRS-ESCPE Lyon-Université Lyon1, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Supporting Information

ABSTRACT: The syntheses of some novel fluorinated and nonfluorinated hydroxyborate salts, $[Q]^+[HOB(C_6F_5)_3]^-$ and $[Q]^+[HOBPh_3]^-$ ($[Q]^+$ = aprotic cation), are reported. The reactivities of both salts with group IV metal complexes were compared. The reaction of $[PPN]^+[HOB(C_6F_5)_3]^-$ ($[PPN]^+$ = bis(triphenylphosphoranylidene)ammonium) with Cp_2ZrMe_2 and Cp_2HfMe_2 resulted in the formation of the ionic complexes $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ and $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ in high yields. These complexes were fully characterized, and the covalent characteristics of the M−O and B−O bonds were established by X-ray crystallographic structural determination.



INTRODUCTION

The catalytic properties of organometallic complexes are controlled by two factors: the identity of the metal center and the nature of the coordinated ligands. Modifying the identity or structure of the ligands coordinated to the metal center strongly influences the rate of the catalyzed reaction and the selectivity toward certain products.[1] Thus, the search for new ligand frameworks with unique electronic and steric properties remains important. Boroxide ligands $[OB(Mes)_2]^-$ (where Mes = mesityl) have been described by several groups, and their reactivity has been demonstrated with a number of different metals.[2−8] The π-accepting properties of these ligands, which are facilitated by the presence of an empty p-orbital on the central boron atom, are of interest for the development of catalyst complexes. Such ligands are able to accept electron density from the lone pair electrons of oxygen atoms, modifying the electronic environment of the metal center. The reaction of the borinic acid $(Mes)_2BOH$ with group IV metal complexes was recently described, and these reactions were shown to produce boroxide complexes, such as $MCp_2\{OB(Mes)_2\}Cl$ (where M = Ti, Zr), which displayed an M−O−B core.[9,10]

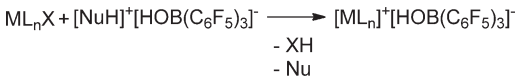
Very few examples of boron-containing ligands have been reported to date. In organometallic chemistry, hydroxyborate anions predominantly exist as the counterions of organometallic complexes, such as $[L_nM]^+[HOB(C_6F_5)_3]^-$ (where M = Cr, Fe, Co,[11] Ru,[12] Mo,[13] Ni,[14] Pt,[15,16] Pd,[17] Ti,[18] V,[19] Zn[20]). These complexes generally are the result of a protonolysis reaction by the protic functional group of the associated cation (Scheme 1).

Direct reactions of the borate hydroxyl group that yield an M−O−B core are seldom observed. Moreover, the nature of the M−O and O−B bonds generally remains ill-defined. For example, the aluminum derivative $LAlOB(C_6F_5)_3$, in which L represents an anionic β-diketiminato ligand, is formed by reaction of the borinic acid adduct $H_2O{\cdot}B(C_6F_5)_3$ (which is similar to $[H]^+[HOB(C_6F_5)_3]^-$) with $LAlMe_2$. The electronic characteristics of the Al−O bond of $LAlOB(C_6F_5)_3$ remain the subject of debate.[21] X-ray diffraction data of this complex suggest that there are four possible resonance structures that exhibit delocalization of a negative charge on the aluminum, oxygen, and boron atoms (Scheme 2).

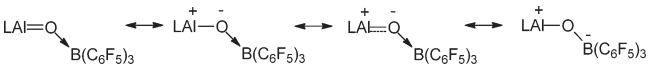
Furthermore, the reaction of $H_2O{\cdot}B(C_6F_5)_3$ with $TaCp^*R_4$ complexes was found to yield the oxo complex $Cp^*R_2Ta{=}O{\cdots}B(C_6F_5)_3$, in which the tantalum−oxygen double bond is datively coordinated to the boron atom.[22] Finally,

Received: March 29, 2011
Published: July 28, 2011

Scheme 1. Protonolysis of an M−X Bond by the Protic Functional Group of the $[NuH]^+$ Cation



Scheme 2. Four Proposed Resonance Structures of the Al−O−B Complex Framework[a]



[a] L = β-diketiminato ligand.

it has been shown that $Cp^*_2ZrOB(C_6F_5)_3$ results from a stepwise reaction between $[HNEt_3]^+[HOB(C_6F_5)_3]^-$ and $Cp^*_2ZrMe_2$. The nature of the Zr−O−B bonds of this complex has never been discussed.[23]

The chemistry of hydroxyborate ligands deserves further attention because this class of ligands possesses a variety of potential electronic and steric properties. Hydroxyborate ligands experience greater steric hindrance than boroxide ligands because of the tetracoordinate nature of the boron. The induced anionic charge on the boron atom could be offset by the presence of electron-withdrawing fluorine atoms that could act as "electron pumps". Substitution of pentafluorophenyl rings by other alkyl or aryl groups could yield an effective method for modifying the electronic and steric properties of hydroxyborate ligands.

A limiting factor impeding the development of their chemistry is related to their synthesis, i.e., the reaction of an amine with the water adduct $H_2O\cdot B(C_6F_5)_3$ to produce $[HNEt_3]^+[HOB(C_6F_5)_3]^-$. In this salt, both N−H and O−H protons could induce the cleavage of the M−C bond of alkyl complexes, as is observed with the organometallic compound $Cp^*_2ZrMe_2$.[23]

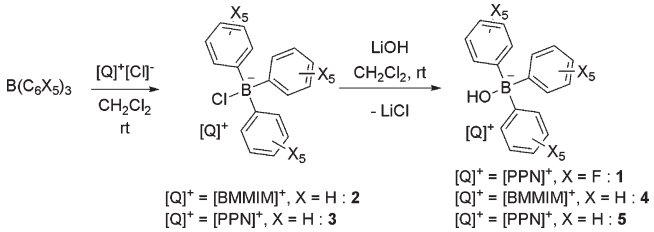
Initially, our aim was to develop a versatile, one-pot synthetic method for preparing $[Q]^+[HOB(C_6F_5)_3]^-$ salts, in which $[Q]^+$ represents an aprotic cation.[24,25] Indeed, preliminary studies of their reactivity with Cp_2ZrMe_2 demonstrated that protonolysis of the Zr−Me bond and formation of the ionic complex $[Q]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ were taking place.[24] However, in the absence of X-ray crystallographic structural data for the complex, the order of the Zr−O bond remained unclear.

In this paper, the syntheses of the fluorinated salt $[PPN]^+[HOB(C_6F_5)_3]^-$ ($[PPN]^+$ = bis(triphenylphosphoranylidene)ammonium) and its nonfluorinated analogues, $[BMMIM]^+[HOBPh_3]^-$ ($[BMMIM]^+$ = 1-butyl-2,3-dimethylimidazolium) and $[PPN]^+[HOBPh_3]^-$, are described. Spectroscopic features of these complexes and their reactivity with Cp_2ZrMe_2 are reported, and the properties of these hydroxyborate ligands are compared. In addition, the synthesis of the ionic complex $[Q]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ was significantly improved, and this technique was applied to the synthesis of its hafnium analogue, $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$. These complexes were fully characterized, and crystal structures of the complexes are also reported and discussed.

RESULTS AND DISCUSSION

The synthesis of the hydroxyborate salt $[Q]^+[HOB(C_6F_5)_3]^-$, in which $[Q]^+$ = 1-butyl-3-methylimidazolium

Scheme 3. Synthesis of Hydroxyborate Salts



$[BMIM]^+$, 1-butyl-2,3-dimethylimidazolium $[BMMIM]^+$, 1-ethyl-3-methylimidazolium $[EMIM]^+$, 1,3-dibutylimidazolium $[BBIM]^+$, *N,N*-butylmethylpyrrolidinium $[BMPy]^+$, tetrabutylphosphonium $[Bu_4P]^+$, and tetraphenylphosphonium $[Ph_4P]^+$, has been described previously.[24] Following a similar methodology, $[PPN]^+[Cl]^-$ was added to a solution of tris(pentafluorophenyl)borane in methylene chloride to yield the chloroborate salt $[PPN]^+[ClB(C_6F_5)_3]^-$. The product of this reaction was allowed to react with anhydrous LiOH without further purification, affording the desired hydroxyborate species $[PPN]^+[HOB(C_6F_5)_3]^-$ (**1**), in excellent overall yield (95%). Colorless crystals suitable for X-ray diffraction analysis were grown by the slow diffusion of *n*-pentane into a concentrated solution of **1** in methylene chloride.

This methodology was extended to the synthesis of the nonfluorinated salts $[Q]^+[HOBPh_3]^-$, in which $[Q]^+ = [BMMIM]^+$ (**4**) and $[PPN]^+$ (**5**), from triphenylborane. Chloroborate salts $[BMMIM]^+[ClBPh_3]^-$ (**2**) and $[PPN]^+[ClBPh_3]^-$ (**3**) were obtained by the addition of their corresponding salts $[Q]^+[Cl]^-$ to BPh_3 in methylene chloride. Precipitation of these salts in toluene produced white solids. ^{11}B NMR spectra of the compounds in CD_2Cl_2 exhibited broad peaks at 26.2 ppm for **2** and 19.4 ppm for **3**. These boron resonances were surprisingly shifted downfield when compared with their fluorinated analogues $[Q]^+[ClB(C_6F_5)_3]^-$ (around −7 ppm), but these resonances were not shifted as far downfield as that observed in the tricoordinated boron compound Ph_2BCl (62.8 ppm).[26]

In the second step of the synthesis, the chloroborate salts **2** and **3** were allowed to react with anhydrous LiOH. The products of this reaction were the hydroxyborate salts $[BMMIM]^+[HOBPh_3]^-$ (**4**) and $[PPN]^+[HOBPh_3]^-$ (**5**), which were recovered as a colorless viscous oil and a white powder, respectively. ^{11}B NMR spectra of these products revealed broadened resonances around −0.80 ppm, similar to the chemical shift observed in NMR spectra of the $[HOBPh_3]^-$ anion, which was associated with the cationic complex $[(\eta^6\text{-Ar})(PCy_3)Ru{=}PHMes^*]^+$ (Ar = *p*-cymene, Mes* = 2,4,6-tri-*tert*-butylphenyl, 1.43 ppm).[27] The −OH group appeared as a broad singlet at 0.70 ppm and at 0.49 ppm in the ^1H NMR spectra of **4** and **5**, respectively. This hydroxyl functionality was shifted upfield between 1 and 2 ppm as compared with the hydroxyl functionalities in the fluorinated analogues $[Q]^+[HOB(C_6F_5)_3]^-$. The −OH group in the nonfluorinated anion was observed to be less acidic than those in the fluorinated analogues. This difference in acidity may be explained by the strong electron-withdrawing characteristics of the C_6F_5 aromatic rings. A second possible explanation may involve the presence of intramolecular H···F interactions in the fluorinated anion $[HOB(C_6F_5)_3]^-$ (*vide infra*), in which the F atoms donate electron density to the proton. These electronic effects, notably because of the presence

dx.doi.org/10.1021/om2002798 |*Organometallics* 2011, 30, 4284–4291

of intramolecular H···F interactions in the fluorinated anions, were also observable using IR spectroscopy. The IR spectra of the $[Q]^+[HOB(C_6F_5)_3]^-$ and $[Q]^+[HOBPh_3]^-$ compounds exhibited a difference of about 60 cm^{-1} between the two different $\nu_{(OH)}$ bands; the $\nu_{(OH)}$ absorption bands were located at 3620 and 3617 cm^{-1} for **4** and **5**, respectively. The corresponding $\nu_{(OH)}$ absorptions of the $[Q]^+[HOB(C_6F_5)_3]^-$ salts were observed in the range 3680−3700 cm^{-1}.

$[PPN]^+$ cations are known to favor the formation of crystalline solids. It has been proposed that this property may arise from interactions between cations in the solid state.[28] This property was observed when the molecular structure of compound **1**, shown in Figure 1, was resolved.[29] Compound **1** crystallizes in the triclinic space group $P\bar{1}$ and is monomeric, in contrast to bis(pentafluorophenyl)borinic acid, which has been shown to be a cyclic trimer in the solid state.[30] The B−O and O−H bond lengths were determined to be 1.475 and 0.799 Å, respectively. The length of the B−O bond is in the range of B−O bonds in tris(pentafluorophenyl)hydroxyborate that have been cited in the literature (1.500 Å in $[7\text{-azaindolium}]^+[HOB(C_6F_5)_3]^-$,[31] 1.470 Å in $[N\text{-isoquinolinium}]^+[HOB(C_6F_5)_3]^-$,[32] 1.466 Å in $[btmgbH]^+[HOB(C_6F_5)_3]^-$[33] (btmgb = 1,2-bis(*N,N,N′,N′*-tetramethylguanidino)benzene)). This B−O bond is longer than that observed in the borinic acid $(Mes)_2BOH$, which exhibits an average B−O bond length of 1.368 Å.[34] This difference is likely due to the empty p-orbital of the tricoordinated boron atom of borinic acid, which can accept lone pair electrons from the oxygen atom. In the case of hydroxyborate anions, the boron atom is not a π-electron acceptor.[35] In compound **1**, the hydroxyl proton forms hydrogen bonds with two fluorine atoms located on different C_6F_5 rings (H31−F5: 2.279 Å, H31−F6: 2.122 Å). A similar phenomenon has previously been described in the compound $[7\text{-azaindolium}]^+[HOB(C_6F_5)_3]^-$.[31] These H···F interactions may be the cause of the monomeric character of the anion $[HOB(C_6F_5)_3]^-$. Bond lengths between boron B(1) and C_{ipso} (C(1), C(7), and C(13)) in compound **1** are an average of 1.668 Å. The lengths of these bonds are longer than the B−C_{ipso} bonds observed in bis(pentafluorophenyl)borinic acid (average B−C_{ipso} bond length of 1.612 Å) because of an increase in steric hindrance around the boron atom in the hydroxyborate anion of **1**.

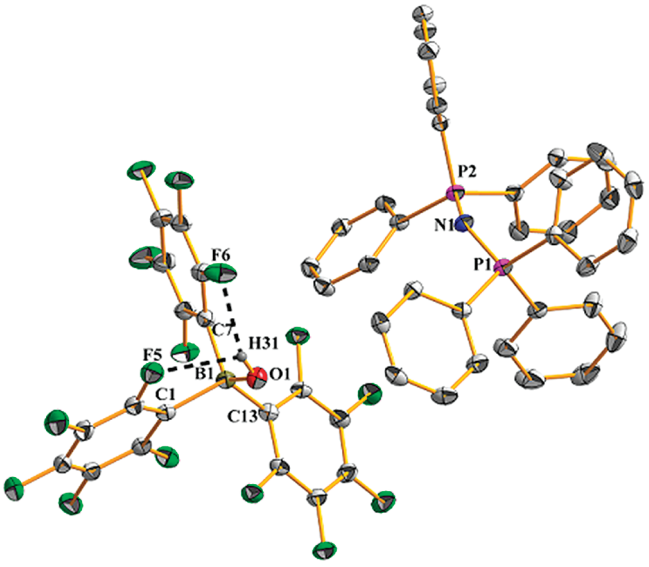


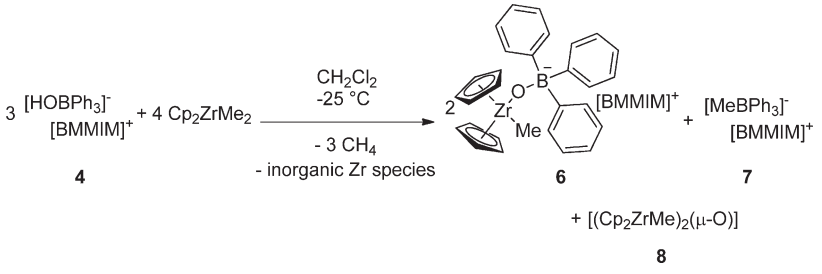
Figure 1. Molecular structure of $[PPN]^+[HOB(C_6F_5)_3]^-$ (**1**) with thermal displacement ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): B(1)−O(1) 1.476 (3), B(1)−C(1) 1.677 (3), B(1)−C(7) 1.672 (3), B(1)−C(13) 1.656 (3), O(1)−H(31) 0.799 (2), H(31)−F(5) 2.286 (2), H(31)−F(6) 2.125 (2), N(1)−P(1) 1.579 (2), N(1)−P(2) 1.581 (1), B(1)−O(1)−H(31) 106.2 (1) and P(1)−N(1)−P(2) 139.1 (1).

The reactivity of hydroxyborate anionic ligands with the metallocene complex Cp_2ZrMe_2 was also investigated. We first focused on the uncommon anion $[HOBPh_3]^-$, whose reactivity has never been reported to the best of our knowledge.

The addition of one equivalent of **4** to a solution containing Cp_2ZrMe_2 resulted in the formation of a small amount of white precipitate (Scheme 4). This solid was separated by filtration and was identified as an inorganic zirconium species on the basis of its elevated melting point, which was greater than 430 °C. ^{1}H NMR analysis of the filtrate suggested that formation of the expected complex, $[BMMIM]^+[Cp_2ZrMe(OBPh_3)]^-$ (**6**, 50% according to ^{1}H integration), of the borate salt $[BMMIM]^+[MeBPh_3]^-$ (**7**, 28% according to ^{1}H integration), and also of the bimetallic complex $(Cp_2ZrMe)_2(\mu\text{-O})$ (**8**, 22% according to ^{1}H integration) had occurred. Toluene was used to extract **8** from the mixture of products. Attempts to separate compound **6** from compound **7** failed, likely because of the similar physical properties of these two compounds.

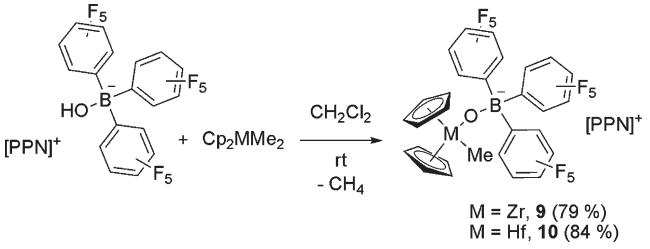
Complex **6** was identified by NMR resonances observed at −0.04 ppm in the ^{1}H NMR and at 13.2 ppm in the ^{13}C NMR, assigned to $\delta_{Zr\text{-}Me}$. This carbon chemical shift is located further upfield than that of the fluorinated analogue complex $[BMMIM]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (17.5 ppm).[24] A similar difference in chemical shifts is observed between complexes $Cp_2ZrMe(OPh)$[36] ($\delta(^{13}C)$ CH_3 = 22.4 ppm) and $Cp_2ZrMe(OC_6F_5)$[37] ($\delta(^{13}C)$ CH_3 = 27.2 ppm). The downfield shift of the methyl carbon resonance of the fluorinated complexes is consistent with the presence of fluorine atoms, which withdraw electron density from the phenyl rings and make the metal more electropositive through an inductive effect. Similar to the fluorinated analogue complex $[BMMIM]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$,

Scheme 4. Reaction of a Non-fluorinated Hydroxyborate Salt with Cp_2ZrMe_2



dx.doi.org/10.1021/om2002798 |*Organometallics* 2011, 30, 4284–4291

Scheme 5. Reaction of a Fluorinated Hydroxyborate Salt with Cp_2ZrMe_2 and Cp_2HfMe_2



the protons of the cyclopentadienyl rings are detected at 5.75 ppm in the ^{1}H spectrum, and the carbon atoms are detected at 109.4 ppm in the ^{13}C NMR spectrum of the compound. The boron resonance of the $-OBPh_3$ moiety in **6** is observed at 1.83 ppm in the ^{11}B NMR spectrum, which is similar to the ^{11}B NMR chemical shift of the starting anion in **4** (-0.80 ppm).

The unexpected anion $[MeBPh_3]^-$ was identified by the characteristic quadruplet peak located at 0.22 ppm in the ^{1}H NMR spectrum, which corresponds to its methyl group, and by the resonance of its boron atom at -11.74 ppm in the ^{11}B NMR spectrum.[38] Formation of this species may be the result of an exchange reaction between a methyl ligand in the zirconium complex and the hydroxyl group of the boron atom, resulting in the formation of a $[MeBPh_3]^-$ anion and $Cp_2Zr(Me)(OH)$. The resulting complex, $Cp_2Zr(Me)(OH)$, could react further with the starting complex, Cp_2ZrMe_2, to produce the dimeric complex $(Cp_2ZrMe)_2(\mu\text{-}O)$ (**8**) and the inorganic zirconium species during consecutive exchange reactions. In contrast, no traces of $[MeB(C_6F_5)_3]^-$ were detected in the reaction of fluorinated $[HOB(C_6F_5)_3]^-$ with Cp_2ZrMe_2.[24] Two possible explanations for the formation of $[MeBPh_3]^-$ from the nonfluorinated ligand are the lower acidity of the hydroxyl functional group of $[HOBPh_3]^-$ and the weakness of its B−O bond. According to a previous report,[39] the molecular structure of this anion possessed a B−O bond length of 1.60 Å, remarkably longer than that observed in $[HOB(C_6F_5)_3]^-$ (1.475 Å).

Reaction of $[Q]^+[HOB(C_6F_5)_3]^-$ with Cp_2ZrMe_2 allowed isolation of the $[Q]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ class of ionic complexes. No side reaction leading to the formation of $[MeB(C_6F_5)_3]^-$ was observed.[24] When $[Q]^+$ was $[BMIM]^+$, $[BMMIM]^+$, $[EMIM]^+$, $[BBIM]^+$, $[BMPy]^+$, $[Bu_4P]^+$, or $[Ph_4P]^+$, the ionic complexes were obtained as liquids, preventing X-ray characterization and confirmation of the exact nature of their B−O and Zr−O bonds. In addition, the syntheses were performed in toluene, producing a low yield (30−40%) of the $[Q]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ complexes.

To promote the crystallization of these ionic complexes, $[PPN]^+$ was used as the counterion, as it is known to promote the crystallization of anions. In addition to this synthetic variation, the reaction was also carried out in methylene chloride instead of toluene (Scheme 5). These modifications and the use of a slight excess of Cp_2ZrMe_2 resulted in the isolation of $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (**9**) with a considerable increase in the reaction yield (79%). The method developed here was also extended to the synthesis of the hafnocene complex $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ (**10**). In the case of the zirconocene Cp_2ZrMe_2, the reaction occurred at −25 °C within 2 h, whereas the reaction between **1** and Cp_2HfMe_2 was slower and required 8 days of stirring at room temperature for

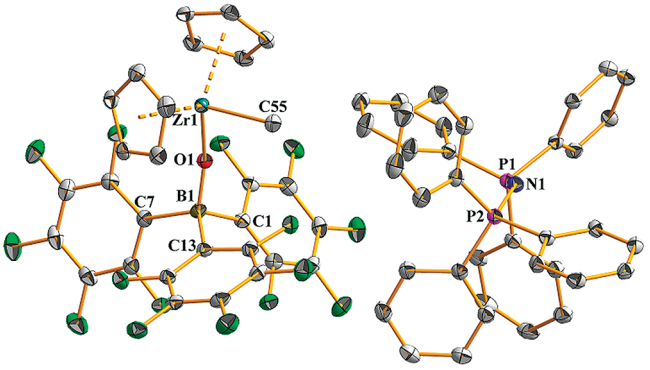


Figure 2. Molecular structure of $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (**9**) with displacement ellipsoids drawn at the 30% probability level.

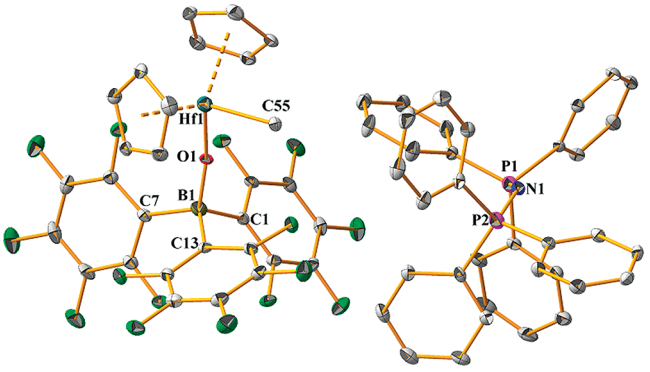


Figure 3. Molecular structure of $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ (**10**) with displacement ellipsoids drawn at the 30% probability level.

completion. Slow diffusion of *n*-pentane into concentrated solutions of **9** and **10** in methylene chloride produced colorless and yellow crystals of the Zr and Hf species, respectively. Compounds **9** and **10** were analyzed by ^{1}H, ^{11}B, ^{19}F, and ^{13}C NMR spectroscopy, and their spectroscopic and structural features were all found to be very similar.

Replacement of one of the methyl groups of the metallocene compound Cp_2MMe_2 by the hydroxyborate ligand produced a small downfield shift of the remaining methyl group by approximately 0.2 ppm in the ^{1}H NMR spectra (-0.22 ppm for **9** and -0.34 ppm for **10**) when compared with the parent complexes of the general formula Cp_2MMe_2. In addition, the ^{1}H NMR resonance of the Cp ligand is observed at approximately 5.70 ppm. In the ^{11}B NMR spectra, the observed singlet is slightly broadened as compared with the resonance of the hydroxyborate anion. Only a small shift of the ^{11}B NMR resonance peaks is observed for both ionic metallocene complexes (-3.62 ppm for **9** and -3.06 ppm for **10**). This negative ^{11}B NMR chemical shift is characteristic of the $OB(C_6F_5)_3^-$ group with tetracoordination of boron.[40,41] The ^{19}F NMR spectra exhibit the three predicted sets of multiplets attributed to the ortho, meta, and para positions of the aryl ring. The ortho-fluorine resonance was shifted slightly upfield from -136 ppm to -133 ppm in the ionic metallocene complexes. In the ^{13}C NMR spectra of the complexes, the Cp resonance remains largely unaffected (average shifts of 110 and 109 ppm for Cp_2MMe_2 and the grafted ionic complexes, respectively), and the chemical shift of the Me resonance undergoes a small downfield shift from 29.5 ppm to 17.5 ppm for the Zr

dx.doi.org/10.1021/om2002798 |*Organometallics* 2011, 30, 4284–4291

Table 1. Crystal Structure and Refinement Data for $[PPN]^+[HOB(C_6F_5)_3]^-$ (1), $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (9), and $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ (10)

	1	9	10
formula	$C_{36}H_{30}NP_2\cdot C_{18}HBF_{15}O$	$C_{36}H_{30}NP_2\cdot C_{29}H_{13}BF_{15}ZrO$	$C_{36}H_{30}NP_2\cdot C_{29}H_{13}BF_{15}HfO$
fw	1067.56	1303.01	1390.28
temperature (K)	150	150	150
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.7244 (3)	12.4937 (3)	12.4775 (4)
b (Å)	14.0170 (4)	13.2762 (3)	13.2598 (5)
c (Å)	16.7119 (4)	18.9678 (4)	18.9597 (8)
α (deg)	67.3774 (9)	106.3210 (10)	106.314 (3)
β (deg)	88.0710 (10)	100.3220 (10)	100.432 (3)
γ (deg)	64.5140 (10)	105.6740 (10)	105.730 (3)
V (Å^3)	2452.33 (11)	2794.12 (11)	2783.2 (2)
Z	2	2	2
D_{calc} (Mg m^{-3})	1.446	1.549	1.659
abs coeff (mm^{-1})	0.19	0.35	2.03
θ range for data collection	0.4 to 27.9	0.4 to 27.9	3.39 to 29.55
no. of reflns collected	11 718	25 025	70 499
no. of indep reflns	11 718	13 340	14 119
reflns with $I > 2\sigma(I)$	7993	9638	12 171
no. of data/restrains/params	11 718/0/668	13 340/0/775	14 119/0/776
goodness of fit on $F^{(x)}$	$1.08^{(1)}$	$1.12^{(1)}$	$0.96^{(2)}$
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.047$, $wR_2 = 0.050$	$R_1 = 0.040$, $wR_2 = 0.040$	$R_1 = 0.050$, $wR_2 = 0.120$
R indices (all data)	$R_1 = 0.072$, $wR_2 = 0.089$	$R_1 = 0.064$, $wR_2 = 0.068$	$R_1 = 0.062$, $wR_2 = 0.12$
largest diff peak and hole (e Å^{-3})	0.37 and −0.28	0.45 and −0.50	2.31 and −2.52

species and from 35.8 ppm to 20.3 ppm for the Hf species. These values are within the range expected for neutral zirconium species, such as $Cp_2Zr(Me)(OCMe_2CH_2CH_2CH{=}CH_2)$ (17.4 ppm for Me and 110.4 ppm for Cp)[42] and $Cp_2Zr(Me)\{O(C_6H_3)(CH_3)\text{-}CH_2PPh_2\}$ (20.5 ppm for Me and 111.6 ppm for Cp).[43]

X-ray diffraction studies were performed on **9** and **10**. Their molecular structures are shown in Figures 2 and 3, respectively. Crystallographic data for both compounds are summarized in Table 1, and selected bond lengths and angles are shown in Table 2. In the solid state, **9** and **10** are monomeric and crystallize in the triclinic space group $P\bar{1}$.

For complex **9**, the Zr−O bond length of 1.912 Å is equal to that observed in $Cp^*_2ZrOB(C_6F_5)_3$.[23] This bond length is also similar to the Zr−O single bond described in the bimetallic complex $[(Cp_2ZrMe)_2(\mu\text{-}O)]$[44] (1.948 Å) and greater than the Zr=O bond length in the complex $Cp^{Et^*}{}_2Zr(O)(NC_5H_5)$ ($Cp^{Et^*} = \eta\text{-}C_5Me_4Et$) (1.804 Å),[45] suggesting that a Zr−O bond order of 1 is present in compound **9**. Furthermore, this Zr−O bond is in the same range as that of Zr−O−B bonds described in the neutral complex $[Zr\{OB(Mes)_2\}_3(\mu\text{-}OH)]_2$ (average Zr−O bond length of 1.955 Å).[9] The B−O bond length of 1.452 Å is in the same range as that of the hydroxyborate anion (B−O bond length of 1.475 Å) and is longer than that of $[Zr\{OB(Mes)_2\}_3\text{-}(\mu\text{-}OH)]_2$ (average B−O bond length of 1.370 Å). All of these structural data confirmed that zirconium is linked to the hydroxyborate anion via a simple covalent bond.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (9) and $[PPN]^+[Cp_2HfMe\text{-}(OB(C_6F_5)_3)]^-$ (10)

	9	10
M(1)-O(1)	1.912 (2)	1.922 (3)
O(1)−B(1)	1.452 (3)	1.445 (6)
M(1)-C(55)	2.330 (2)	2.308 (5)
M(1)−Cp1	2.2579 (3)	2.2350 (2)
M(1)−Cp2	2.2557 (2)	2.2358 (2)
P(1)−N(1)	1.589 (2)	1.582 (4)
P(2)−N(1)	1.578 (2)	1.584 (4)
M(1)−O(1)−B(1)	161.0 (2)	160.2 (3)
Cp1−M(1)−Cp2	128.12 (1)	128.21 (1)
Cp1−M(1)−O	109.86 (5)	109.4 (1)
Cp2−M(1)−O	110.15 (5)	110.1 (1)
P(1)−N(1)−P(2)	137.4 (1)	137.4 (3)
C(55)−M(1)−O(1)	99.07 (8)	99.2 (2)

The Zr−Me and average Zr−Cp bond lengths are 2.331 and 2.26 Å, respectively, which are slightly longer than those observed in Cp_2ZrMe_2 (Zr−Me bond lengths of 2.280 and 2.273 Å; average Zr−Cp bond lengths of 2.23 Å). This increase in the bond length is likely due to steric hindrance present in the complex that is induced by the bulky hydroxyborate group. In **9**,

dx.doi.org/10.1021/om2002798 |*Organometallics* 2011, 30, 4284–4291

no interactions are observed between the zirconium center and the fluorine atoms in C_6F_5, in contrast to the results reported by Siedle.[23]

The structure of $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ (**10**) is very similar to that of the analogous zirconium complex **9**. The Hf−O bond length of 1.927 Å is similar to that observed in the homobimetallic complex $(Cp_2HfMe)_2(\mu\text{-}O)$ (average Hf−O bond length of 1.943 Å)[46] and is in the same range as those observed in $LAl(Me)(\mu\text{-}O)Hf(Me)Cp_2$ (L = CH(N(Ar)-(CMe))$_2$, Ar = 2,6-$iPr_2C_6H_3$)[45] (1.919 Å) and $Hf(OB(Mes)_2)_4$[10] (1.902 and 1.916 Å). In **10**, the B−O bond length (1.437 Å) is slightly shorter than that observed in **1** (1.475 Å) but is longer than that observed in the boroxide complex $Hf(OB(Mes)_2)_4$[10] (average B−O bond length of 1.388 Å). In addition, the Hf−Me bond length (2.312 Å) is similar to those observed in the homobimetallic complex $(Cp_2HfMe)_2(\mu\text{-}O)$[46] (average Hf−Me bond length of 2.350 Å) and in $LAl(Me)(\mu\text{-}O)Hf(Me)Cp_2$[47] (2.281 Å).

The covalent character of the M−O and O−B bonds in ionic complexes **9** and **10** was demonstrated via analysis of their molecular structures. These data support the relevance of considering hydroxyborate anions to be a novel class of ligands for organometallic complexes. In addition to the uniqueness of their electronic and steric properties, the presence of an anionic charge on the boron atom may present new opportunities for the immobilization of complexes in ionic liquids.

CONCLUSIONS

In this paper, the reactivities of the fluorinated and nonfluorinated hydroxyborate anions $[Q]^+[HOB(C_6F_5)_3]^-$ and $[Q]^+[HOBPh_3]^-$ with Cp_2ZrMe_2 were compared. The decreased acidity and the weaker B−O bond of $[HOBPh_3]^-$ compared with its fluorinated analogue led to the formation of multiple products as the result of an exchange reaction involving the methyl group of the zirconium complex and the hydroxyl group of the borate ligand. In contrast, selective protonolysis of the M−Me bond (where M = Zr and Hf) is observed between $[PPN]^+[HOB(C_6F_5)_3]^-$ (**1**) and Cp_2ZrMe_2 or Cp_2HfMe_2, producing the ionic complexes $[PPN]^+[Cp_2ZrMe(OB(C_6F_5)_3)]^-$ (**9**) and $[PPN]^+[Cp_2HfMe(OB(C_6F_5)_3)]^-$ (**10**) in high yields. The covalent character of the M−O and O−B bonds in both complexes is confirmed by analysis of their molecular structures. Investigation of the reactivity of the fluorinated hydroxyborate anions with other metals is underway.

EXPERIMENTAL SECTION

All manipulations were performed using either a glovebox or high vacuum line techniques. Starting materials were purchased from Aldrich and Strem Chemicals. $B(C_6F_5)_3$ was treated with Me_3SiCl and sublimed prior to use. Solvents were purchased from SDS and dried using a solvent purification system (SPS-M-Braun). The water content of these solvents was periodically determined by Karl Fischer titration.

^1H NMR (300 MHz), ^{11}B NMR (96.3 MHz), $^{19}F\{^1H\}$ NMR (282 MHz), and $^{13}C\{^1H\}$ NMR (75 MHz) spectra were recorded on a Bruker AC 300 MHz instrument at room temperature. Deuterated solvent (CD_2Cl_2) was purchased from Eurisotop. Chemical shifts are reported in ppm vs $SiMe_4$ in ^1H and ^{13}C NMR spectra, vs BF_3 in diethyl ether for ^{11}B NMR spectra, and vs CCl_3F in ^{19}F NMR spectra. All coupling constants are reported in hertz.

Mass spectra were collected on an Agilent 6890 N apparatus with an Agilent 5975B inert XL EI/CI MSD mass spectrometer.

C, H, N elemental analysis of samples was performed by the Service Central d'Analyses of CNRS (Vernaison, France) and by the Mikroanalytisches Labor Pascher (Remagen, Germany).

X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data were collected using ψ scans. The structures were solved by direct methods using SIR97 software,[48] and refinement was performed by a full-matrix least-squares analysis on F or F^2. No absorption correction was used.

Synthesis of $[PPN]^+[HOB(C_6F_5)_3]^-$ (1). A solution of $[PPN]^+[Cl]^-$ (8.75 mmol, 5.025 g) in methylene chloride (25 mL) was added to a solution of $B(C_6F_5)_3$ (8.75 mmol, 4.480 g) in methylene chloride (25 mL) at room temperature. After stirring overnight, the reaction mixture was concentrated to one-half of the original volume and then added via a cannula to a suspension of anhydrous LiOH (10.5 mmol, 251 mg) in 20 mL of methylene chloride. Five days of stirring at room temperature were necessary to allow the reaction to proceed to completion. The white LiCl precipitate was then filtered, and the solvent was removed under vacuum to leave **1** as a white powder (8.31 mmol, 8.871 g).

Yield: 95%. ^1H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 1.67 (s, 1H, OH); 7.40−7.55 (m, 24H, CH *o*-, *m*-Ph); 7.60−7.70 (m, 6H, CH *p*-Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −4.10. ^{19}F NMR (282 MHz, CD_2Cl_2) (δ, ppm): −135.8 (d, 6F, $^3J_{FF}$ = 21.6 Hz, *o*-F); −163.0 (t, 3F, $^3J_{FF}$ = 19.6 Hz, *p*-F); −166.5 (m, 6F, *m*-F). ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 127.4 (dd, $^1J_{PC}$ = 107.9 Hz, P-C); 129.8 (m, *m*-CH); 132.5 (m, *o*-CH); 134.1 (t, $^4J_{PC}$ = 1.3 Hz, *p*-CH); 136.7 (dm, $^1J_{CF}$ = 247 Hz, C-F); 138.4 (dm, $^1J_{CF}$ = 242 Hz, C-F); 148.3 (dm, $^1J_{CF}$ = 240 Hz, C-F). IR: ν(OH) = 3698 cm^{-1}. Anal. Calcd for $C_{54}H_{31}BF_{15}NOP_2$: C, 60.75; H, 2.93; N, 1.31. Found: C, 60.91; H, 2.95; N, 1.27. HRMS (ESI), positive mode: $[PPN]^+$ 538.1849, calculated for $[C_{36}H_{30}NP_2]^+$ 538.1853; negative mode: $[HOB(C_6F_5)_3]^-$ 528.9887, calculated for $[C_{18}HBF_{15}O]^-$ 528.9881.

Synthesis of $[BMMIM]^+[ClBPh_3]^-$ (2). A solution of $[BMMIM]^+[Cl]^-$ (3.5 mmol, 660 mg) in methylene chloride (10 mL) was added to a solution of BPh_3 (5.95 mmol, 1.441 g) in methylene chloride (10 mL) at room temperature. After 8 h of stirring, the reaction mixture was concentrated to one-half the original volume and then slowly added via a cannula to 30 mL of toluene at room temperature to precipitate the chloride compound $[BMMIM]^+[ClBPh_3]^-$. The white precipitate was filtered, washed with 2 × 20 mL of toluene, and then dried under vacuum to leave **2** as a white solid (3.40 mmol, 1.463 g).

Yield: 97%. ^1H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 0.95 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3); 1.33 (sextet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 1.70 (quintet, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2); 2.41 (s, 3H, CH_3); 3.63 (s, 3H, CH_3); 3.91 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2); 7.11 (d, 1H, $^3J_{HH}$ = 2.0 Hz, CH); 7.13−7.23 (m, 9H, CH BPh); 7.24 (d, 1H, $^3J_{HH}$ = 2.3 Hz, CH); 7.40−7.49 (m, 6H, CH BPh). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): 26.2 (broad). ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 10.2 (CH_3); 13.6 (CH_3); 19.9 (CH_2); 31.9 (CH_2); 35.8 (CH_3); 48.9 (CH_2); 121.2 (CH); 123.1 (CH); 126.4 (CH BPh); 126.8 (CH BPh); 135.6 (CH BPh); 143.7 ($C(CH_3)$). Anal. Calcd for $C_{27}H_{32}BClN_2$: C, 75.27; H, 7.49; N, 6.50. Found: C, 74.80; H, 7.74; N, 6.56. MS (ESI), positive mode: $[BMMIM]^+$ 153.1385, calculated for $[C_9H_{17}N_2]^+$ 153.1392; negative mode: $[ClBPh_3]^-$ 277.0962, calculated for $[C_{18}H_{15}BCl]^-$ 277.0955.

Synthesis of $[PPN]^+[ClBPh_3]^-$ (3). Compound **3** was obtained as a white solid using the same procedure as described for compound **2**, substituting $[PPN]^+[Cl]^-$ for $[BMMIM]^+[Cl]^-$.

Yield: 96%. ^1H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 7.09 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH *p*-BPh); 7.16 (t, 6H, $^3J_{HH}$ = 7.3 Hz, CH *m*-BPh); 7.40−7.55 (m, 30H, 24 CH *o*, *m* Ph PPN^+ + 6 CH *o*-BPh); 7.60−7.70 (m, 6H, CH *p* Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): 19.4 (broad). Anal. Calcd for $C_{54}H_{45}BClNP_2$: C, 79.47; H, 5.56; N, 1.72. Found: C, 78.45; H, 5.48; N, 1.68.

Synthesis of $[BMMIM]^+[HOBPh_3]^-$ (4). A solution of $[BMMIM]^+[ClBPh_3]^-$ (1.16 mmol, 500 mg) in methylene chloride (10 mL) was added to a suspension of anhydrous LiOH (1.392 mmol, 33 mg) in methylene chloride (10 mL) at room temperature. After stirring overnight, the white LiCl precipitate was filtered, and the solvent was removed under vacuum to leave $[BMMIM]^+[HOBPh_3]^-$ as a colorless, viscous oil (1.16 mmol, 478 mg).

Yield: >99%. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 0.70 (s, 1H, OH); 0.92 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3); 1.21 (sextuplet, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 1.51 (q, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2); 1.96 (s, 3H, CH_3); 3.11 (s, 3H, CH_3); 3.5 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2); 6.59 (d, 1H, $^3J_{HH}$ = 2.2 Hz, CH); 6.63 (d, 1H, $^3J_{HH}$ = 2.2 Hz, CH); 6.88 (m, 3H, CH *p*-BPh); 7.00 (m, 6H, CH *m*-BPh); 7.31 (m, 6H, CH *o*-BPh). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −0.81. ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 9.6 (CH_3); 13.6 (CH_3); 19.9 (CH_2); 31.9 (CH_2); 35.3 (CH_3); 48.5 (CH_2); 120.9 (CH); 122.9 (CH); 123.3 (CH *p*-BPh); 126.5 (CH *m*-BPh); 133.5 (CH *o*-BPh); 143.1 (C(CH_3)). IR: ν(OH) = 3620 cm^{-1}. Anal. Calcd for $C_{27}H_{33}BN_2O$: C, 78.64; H, 8.07; N, 6.79. Found: C, 74.19; H, 8.08; N, 6.76.

Synthesis of $[PPN]^+[HOBPh_3]^-$ (5). Compound **5** was obtained as a white solid using the same procedure as described for compound **4**, substituting $[PPN]^+[ClBPh_3]^-$ for $[BMMIM]^+[ClBPh_3]^-$.

Yield: >99%. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 0.49 (s, 1H, OH); 6.90 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH *p*-BPh); 7.04 (t, 6H, $^3J_{HH}$ = 7.3 Hz, CH *m*-BPh); 7.29 (d, 6H, $^3J_{HH}$ = 7.9 Hz, CH *o*-BPh); 7.40−7.55 (m, 24H, CH *o*, *m* Ph); 7.60−7.70 (m, 6H, CH *p* Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −0.82. ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 123.3 (CH *p*-BPh_3); 126.5 (CH *m*-BPh_3); 127.4 (dd, $^1J_{PC}$ = 108.1 Hz, P-C); 129.8 (m, *m*-CH); 132.5 (m, *o*-CH); 133.4 (CH *o*-BPh_3); 134.1 (t, $^4J_{PC}$ = 1.3 Hz, *p*-CH). Anal. Calcd for $C_{54}H_{46}BNOP_2$: C, 81.31; H, 5.81; N, 1.72. Found: C, 79.98; H, 5.90; N, 1.64.

Synthesis of $[BMMIM]^+[Cp_2MeZrOBPh_3]^-$ (6). A solution of $[BMMIM]^+[HOBPh_3]^-$ (**4**) (0.63 mmol, 258 mg) in methylene chloride (8 mL) was added dropwise to a solution of Cp_2ZrMe_2 (0.63 mmol, 163 mg) in methylene chloride (8 mL) at −25 °C. After stirring for 2 h at room temperature, the reaction mixture was filtered to remove the small amount of white precipitate that formed during the reaction. Two different liquid phases were observed upon addition of 20 mL of toluene. The colorless top phase contained $(Cp_2ZrMe)_2(\mu$-O), and the light yellow bottom phase contained a mixture of $[BMMIM]^+$-$[Cp_2MeZrOBPh_3]^-$ (**6**) and $[BMMIM]^+[MeBPh_3]^-$ (**7**). Attempts to separate **6** from **7** failed.

Spectral Characterization of ***6***. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): −0.04 (s, 3H, CH_3); 0.96 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3); 1.26 (sextuplet, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2); 1.58 (quintuplet, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2); 1.97 (s, 3H, CH_3); 3.17 (s, 3H, CH_3); 3.59 (t, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2); 5.75 (s, 10H, CH Cp); 6.49 (d, 1H, $^3J_{HH}$ = 2.1 Hz, CH); 6.58 (d, 1H, $^3J_{HH}$ = 2.2 Hz, CH); 6.82 (m, 3H, CH p-Ph); 6.89 (m, 6H, CH Ph); 7.04 (m, 6H, CH Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): 1.83. ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 9.6 (CH_3); 13.2 (CH_3, Zr-Me); 13.7 (CH_3); 19.9 (CH_2); 31.8 (CH_2); 35.4 (CH_3); 48.9 (CH_2); 109.4 (CH, Cp); 121.0 (CH; 122.6 (CH); 122.7 (CH Ph); 126.1 (CH Ph); 134.0 (CH Ph); 143.2 (C(CH_3)).

Spectral Characterization of ***7***. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): 0.22 (q, 3H, $^2J_{BH}$ = 3.9 Hz, CH_3); 0.95 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3); 1.28 (sextuplet, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2); 1.60 (quintuplet, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 2.04 (s, 3H, CH_3); 3.24 (s, 3H, CH_3); 3.64 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2); 6.55 (d, 1H, $^3J_{HH}$ = 2.2 Hz, CH); 6.63 (d, 1H, $^3J_{HH}$ = 2.2 Hz, CH); 6.82 (m, 3H, CH *o*-Ph); 6.97 (m, 6H, CH Ph); 7.29 (m, 6H, CH Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −11.74. ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 9.4 (CH_3); 13.30 (q, CH_3, B-Me); 13.6 (CH_3); 19.9 (CH_2); 31.9 (CH_2); 35.3 (CH_3); 48.7 (CH_2); 121.0 (CH); 122.0 (CH Ph); 122.6 (CH); 126.0 (q, CH Ph); 134.7 (d, CH Ph); 143.3 (C(CH_3)); 167.6 (q, C Ph).

Synthesis of $[PPN]^+[Cp_2MeZrOB(C_6F_5)_3]^-$ (9). A solution of $[PPN]^+[HOB(C_6F_5)_3]^-$ (0.64 mmol, 679 mg) in methylene chloride (3 mL) was added dropwise to a solution of Cp_2ZrMe_2 (0.79 mmol, 198 mg, 1.2 equiv) in methylene chloride (3 mL) at −25 °C. After stirring for 2 h at room temperature, the yellow solution was concentrated and then washed with 25 mL of toluene. The pale brown oil obtained after decanting the supernatant was washed a second time with toluene. The solvent was removed under vacuum to leave **9** as a pale brown oil (0.51 mmol, 665 mg). Slow diffusion of *n*-pentane into a concentrated solution of **9** in methylene chloride yielded colorless crystals.

Yield: 79%. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): −0.22 (s, 3H, CH_3); 5.73 (s, 10H, CH Cp); 7.40−7.55 (m, 24H, CH *o*, *m* Ph); 7.59−7.69 (m, 6H, CH *p* Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −3.62. ^{19}F NMR (282 MHz, CD_2Cl_2) (δ, ppm): −133.0 (m, 6F, *o*-F); −163.78 (t, 3F, $^3J_{FF}$ = 19.8 Hz, *p*-F); −167.0 (m, 6F, *m*-F). ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 17.5 (CH_3, Zr-Me); 109.6 (CH Cp); 127.4 (dd, $^1J_{PC}$ = 108.2 Hz, P-C); 129.8 (m, *m*-CH); 132.5 (m, *o*-CH); 134.1 (t, $^4J_{PC}$ = 1.7 Hz, *p*-CH); 136.7 (dm, $^1J_{CF}$ = 247 Hz, C-F); 138.3 (dm, $^1J_{CF}$ = 242 Hz, C-F); 148.1 (dm, $^1J_{CF}$ = 240 Hz, C−-F). Anal. Calcd for $C_{65}H_{41}BF_{15}NOP_2Zr$: C, 59.92; H, 3.33; N, 1.07. Found: C, 59.84; H, 3.18; N, 1.12.

Synthesis of $[PPN]^+[Cp_2MeHfOB(C_6F_5)_3]^-$ (10). A solution of $[PPN]^+[HOB(C_6F_5)_3]^-$ (0.197 mmol, 210 mg) in methylene chloride (1 mL) was added dropwise to a solution of Cp_2HfMe_2 (0.295 mmol, 100 mg, 1.5 equiv) in methylene chloride (1 mL) at room temperature. After stirring for 8 days, the solvent was removed under vacuum to yield a yellow powder. This powder was washed with 10 mL of toluene. The pale brown oil obtained after decanting the supernatant was washed a second time with toluene. The solvent was removed under vacuum to leave **10** as a pale brown powder (0.165 mmol, 230 mg). Slow diffusion of *n*-pentane into a concentrated solution of **10** in methylene chloride yielded yellow crystals.

Yield: 84%. ^{1}H NMR (300 MHz, CD_2Cl_2) (δ, ppm): −0.34 (s, 3H, CH_3); 5.70 (s, 10H, CH Cp); 7.40−7.55 (m, 24H, CH *o*, *m* Ph); 7.60−7.69 (m, 6H, CH *p* Ph). ^{11}B NMR (96.3 MHz, CD_2Cl_2) (δ, ppm): −3.62. ^{19}F NMR (282 MHz, CD_2Cl_2) (δ, ppm): −132.94 (m, 6F, *o*-F); −163.90 (t, 3F, $^3J_{FF}$ = 19.9 Hz, *p*-F); −167.03 (m, 6F, *m*-F). ^{13}C NMR (75 MHz, CD_2Cl_2) (δ, ppm): 20.3 (CH_3, Zr-Me); 109.1 (CH Cp); 127.4 (dd, $^1J_{PC}$ = 108.2 Hz, P-C); 129.8 (m, *m*-CH); 133 (m, *o*-CH); 134.1 (t, $^4J_{PC}$ = 1.4 Hz, *p*-CH); 136.8 (dm, $^1J_{CF}$ = 247 Hz, C-F); 138.3 (dm, $^1J_{CF}$ = 243 Hz, C-F); 148.2 (dm, $^1J_{CF}$ = 238 Hz, C-F). Anal. Calcd for $C_{65}H_{41}BF_{15}NOP_2Hf$: C, 56.15; H, 3.12; N, 1.01. Found: C, 56.21; H, 3.11; N, 1.02.

■ ASSOCIATED CONTENT

Supporting Information. CIF files providing X-ray crystallographic data for **1**, **9**, and **10** are available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: santini@cpe.fr (Tel: (+33)472431810); christophe.vallee@ifpen.fr (Tel: (+33)437702153).

■ ACKNOWLEDGMENT

The authors wish to thank IFP Energies Nouvelles (Lyon, France) and the ANRT for financial support.

■ REFERENCES

(1) van Leeuwen, P. W. N. M. *Homogeneous Catalysis, Understanding the Art*; Kluwer Academic Publishers: Dordrecht, 2004.

(2) Zhao, P. J.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 1876.
(3) Birch, S. J.; Boss, S. R.; Cole, S. C.; Coles, M. P.; Haigh, R.; Hitchcock, P. B.; Wheatley, A. E. H. *Dalton Trans.* **2004**, 3568.
(4) Nulewicz-Ostrowska, R.; Lulinski, S.; Pindelska, E.; Serwatowski, J. *Inorg. Chem.* **2002**, *41*, 2525.
(5) Gibson, V. C.; Mastroianni, S.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2001**, *40*, 826.
(6) Chen, H.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2884.
(7) Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Organometallics* **2004**, *23*, 5159.
(8) Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **2002**, 4168.
(9) Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Organometallics* **2005**, *24*, 3279.
(10) Cole, S. C.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2004**, 3428.
(11) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325.
(12) Bellachioma, G.; Cardaci, G.; Foresti, E.; Macchioni, A.; Sabatino, P.; Zuccaccia, C. *Inorg. Chim. Acta* **2003**, *353*, 245.
(13) Beddows, C. J.; Burrows, A. D.; Connelly, N. G.; Green, M.; Lynam, J. M.; Paget, T. J. *Organometallics* **2001**, *20*, 231.
(14) Kalamarides, H. A.; Iyer, S.; Lipian, J.; Rhodes, L. F.; Day, C. *Organometallics* **2000**, *19*, 3983.
(15) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525.
(16) Baar, C. R.; Jennings, M. C.; Puddephatt, R. J.; Muir, K. W. *Organometallics* **1999**, *18*, 4373.
(17) Barlow, G. K.; Boyle, J. D.; Cooley, N. A.; Ghaffar, T.; Wass, D. F. *Organometallics* **2000**, *19*, 1470.
(18) Choukroun, R.; Lorber, C.; Vendier, L. *Eur. J. Inorg. Chem.* **2004**, 317.
(19) Choukroun, R.; Lorber, C.; Vendier, L.; Lepetit, C. *Organometallics* **2006**, *25*, 1551.
(20) Kotzen, N.; Goldberg, I.; Vigalok, A. *Organometallics* **2009**, *28*, 929.
(21) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Walfort, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4294.
(22) Sanchez-Nieves, J.; Frutos, L. M.; Royo, P.; Castano, O.; Herdtweck, E. *Organometallics* **2005**, *24*, 2004.
(23) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.
(24) Bibal, C.; Santini, C. C.; Chauvin, Y.; Vallee, C.; Olivier-Bourbigou, H. *Dalton Trans.* **2008**, 2866.
(25) Bibal, C.; Santini, C. C.; Chauvin, Y.; Olivier Bourbigou, H.; Vallée, C. (IFP) WO 09024675, 2008.
(26) Thomas, J. C.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5055.
(27) Menye-Biyogo, R.; Delpech, F.; Castel, A.; Pimienta, V.; Gornitzka, H.; Riviere, P. *Organometallics* **2007**, *26*, 5091.
(28) Lewis, G. R.; Dance, I. *J. Chem. Soc., Dalton Trans.* **2000**, 299.
(29) The hydrogen atoms were all located in successive Fourier difference map analyses. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H = 0.93(2) and O---H = 0.82(2) Å) and U_{iso}(H) (range from 1.2 to 1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.
(30) Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Organometallics* **2003**, *22*, 1588.
(31) Focante, F.; Camurati, I.; Resconi, L.; Guidotti, S.; Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2006**, *45*, 1683.
(32) Hewavitharanage, P.; Danilov, E. O.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 10653.
(33) Peters, A.; Wild, U.; Hubner, O.; Kaifer, E.; Himmel, H. J. *Chem.—Eur. J.* **2008**, *14*, 7813.
(34) Weese, K. J.; Bartlett, R. A.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2409.
(35) The comparison between the anion $[HOB(C_6F_5)_3]^-$ and $(C_6F_5)_2BOH$ was not relevant because its trimeric structure revealed an interaction between oxygen and a boron atom of a second molecule, which undoubtedly increased the B—O bond length. Conversely, borinic acid $(Mes)_2BOH$ crystallizes as a tetramer because of hydrogen bonding involving the OH groups.
(36) Firth, A. V.; Stewart, J. C.; Hoskin, A. J.; Douglas, D. W. *J. Organomet. Chem.* **1999**, *591*, 185.
(37) Perrotin, P.; El-Zoghbi, I.; Oguadinma, P. O.; Schaper, F. *Organometallics* **2009**, *28*, 4912.
(38) Zhu, D. M.; Kochi, J. K. *Organometallics* **1999**, *18*, 161.
(39) Otkidach, D. S.; Pletnev, I. V. *J. Mol. Struct. (THEOCHEM)* **2001**, *536*, 65.
(40) Millot, N.; Cox, A.; Santini, C. C.; Molard, Y.; Basset, J. M. *Chem.—Eur. J.* **2002**, *8*, 1438.
(41) Di Saverio, A.; Focante, F.; Camurati, I.; Resconi, L.; Beringhelli, T.; D'Alfonso, G; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2005**, *44*, 5030.
(42) Carpentier, J. F.; Wu, Z.; Lee, C. W.; Stromberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750.
(43) Miquel, L.; Bassobert, M.; Choukroun, R.; Madhouni, R.; Eichhorn, B.; Sanchez, M.; Mazieres, M. R.; Jaud, J. *J. Organomet. Chem.* **1995**, *490*, 21.
(44) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.
(45) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.
(46) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284.
(47) Gurubasavaraj, P. M.; Mandal, S. K.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Noltemeyer, M. *Inorg. Chem.* **2007**, *46*, 1056.
(48) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.