

# Pentamethylcyclopentadienyl–aminoborole derivatives of zirconium and hafnium with alkyl and allyl ligands<sup>1</sup>

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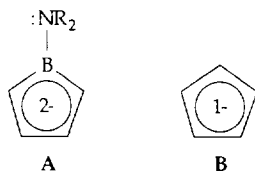
## Abstract

The preparations of new alkyl, iodo, and allyl derivatives of zirconium and hafnium with pentamethylcyclopentadienyl and aminoborole ancillary ligands are described. The dialkyl complexes  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{ZrR}_2\text{Li}$  ( $\text{R} = \text{Me}$ ,  $\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{CH}_3$ ,  $\text{C}\equiv\text{CMe}_3$ ,  $\text{CH}_2\text{Ph}$ ) are prepared from  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{ZrCl}\cdot\text{LiCl}$  and two equivalents of  $\text{RLi}$ .  $\text{Cp}^*\text{ZrI}_3$  is prepared from  $\text{Cp}^*\text{ZrCl}_3$  and  $\text{BI}_3$ . Treatment of  $\text{Cp}^*\text{ZrI}_3$  with  $\text{Li}_2(\text{THF})\{\text{C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}$  yields  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{ZrI}\cdot\text{LiI}(\text{THF})$ . Treatment of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MCl}\cdot\text{LiCl}$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ) with allyl magnesium bromide yields  $\text{Cp}^*\{\eta^5\text{-C}_4\text{Me}_4\text{BN}(\text{CHMe}_2)_2\}\text{M}(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ). Addition of donor ligands to  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$  yields  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{L})$  ( $\text{L} = \text{PMe}_3$ ,  $\text{CO}$ ) and  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^1\text{-C}_3\text{H}_5)(\text{py})$ . The results of X-ray structure determinations for  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$  and  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$  are reported.

**Keywords:** Allyl; Cyclopentadienyl; Zirconium; Aminoborole; Hafnium

## 1. Introduction

The aminoborollide ligand (**A**), first synthesized by Herberich and coworkers [1–3], is a  $6\pi$  dianionic heterocycle that is a divalent analog of the cyclopentadienide anion (**B**).



As such, substitution of one  $(\eta^5\text{-C}_5\text{H}_5)^-$  by one  $(\eta^5\text{-C}_4\text{H}_4\text{BNR}_2)^{2-}$  provides a means of preparing metallocene analogs that have an additional negative charge

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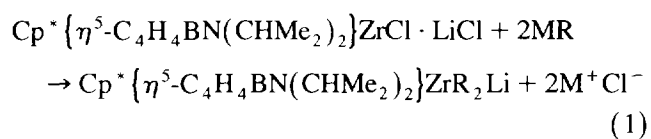
<sup>1</sup> Dedicated with great admiration and affection to Malcolm L.H. Green on the occasion of his 60th birthday.

relative to the corresponding metallocenes. For example, we have previously reported the preparation and structural characterization of lithium dichloro-pentamethylcyclopentadienyl–aminoborole zirconate and hafnate [4],  $(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MCl}_2\text{-Li}(\text{THF})_2$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ;  $\text{THF} = \text{tetrahydrofuran}$ ), complexes that are isoelectronic to the familiar Group 4 neutral ‘bent metallocene’ dichlorides,  $\text{Cp}_2\text{MCl}_2$  ( $\text{Cp} = \text{cyclopentadienyl}$  and substituted cyclopentadienyl).

There is currently a great deal of interest in Group 4 metallocene dihalides as precursors to  $\alpha$ -olefin polymerization catalysts [5]. The catalytically active cations generated in these systems,  $[\text{Cp}_2\text{MR}]^+$ , are extremely Lewis acidic, and commonly either form unreactive tight ion pairs or react irreversibly with the counter-anions [6]. Indeed, the catalytic activity is often related to the extent of ion separation, even when polyfluorinated tri- or tetra-aryl borate anions are employed. Thus, our original interest was in preparing neutral alkyl derivatives of the type  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MR}$  ( $\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$ ;  $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ) that are isoelectronic to metallocenium cation  $[\text{Cp}_2\text{MR}]^+$  catalysts. Such neutral analogs should, in principle, be more stable, and the

complications arising from ion pairing would be obviated. Further, availability of the neutral Group 4 analogs would allow comparisons among the isoelectronic series shown below. Thus, the effects of changing the overall charge and metal may be examined independently of one another.

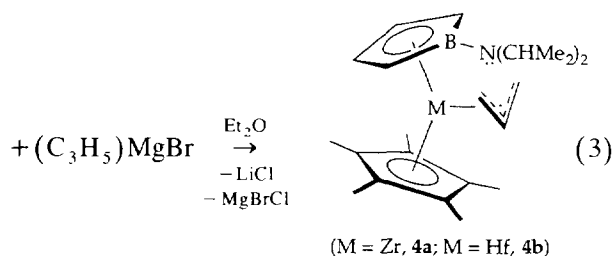
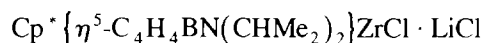
alents of the appropriate alkyl lithium or potassium reagent (Eq. (1)).



(R = Me, **1a**; R = C≡C-*p*-C<sub>6</sub>H<sub>4</sub>Me, **1b**;

ligand has a well precedented ability to chelate to  $d^0$  early transition metals [8], and has even been shown to form stable complexes of the type  $[\text{Cp}^*_2\text{M}(\eta^3\text{-C}_3\text{H}_5)]^+$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) [9], isoelectronic to the desired complexes  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{M}(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{M} = \text{Zr}, \text{Hf}$ ).

Treatment of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MCl} \cdot \text{LiCl}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) with allyl magnesium bromide in diethyl ether does indeed yield the desired allyl complexes,  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{M}(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{M} = \text{Zr}$  (**4a**),  $\text{Hf}$  (**4b**)), free of coordinated solvent and halide (Eq. (3)).



The zirconium allyl, **4a**, is isolated in 75% yield from petroleum ether as a deep green microcrystalline solid. The deep blue hafnium analog, **4b**, is best purified by recrystallization from hot heptane. Both derivatives display a molecular plane of symmetry ( $^1\text{H}$  and  $^{13}\text{C}$  NMR);

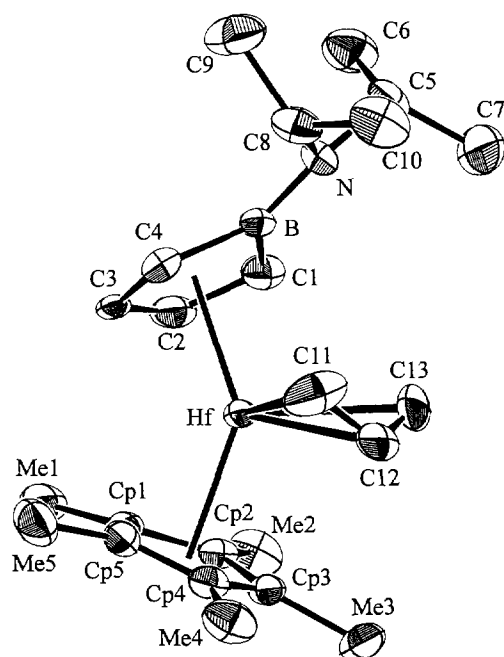


Fig. 1. ORTEP diagram of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$  (**4b**).

Table 1  
Selected distances ( $\text{\AA}$ )<sup>a</sup> and angles (deg)<sup>a</sup> for  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$  (**4b**)

Hf–Cp <sup>*</sup>	2.185	Hf–C1	2.428(8)
Hf–C11	2.460(10)	Hf–C2	2.365(8)
Hf–C12	2.423(10)	Hf–C3	2.374(8)
Hf–C13	2.451(10)	Hf–C4	2.421(8)
B–C1	1.559(12)	Hf–B	2.691(9)
B–C4	1.572(12)	C11–C12–C13	124.1
B–N	1.414(10)	Cp <sup>*</sup> –Hf–Centroid <sub>B<sub>0</sub></sub>	134.9
C1–C2	1.411(11)	C5–N–B	124.3
C2–C3	1.392(12)	C8–N–B	118.4
C3–C4	1.424(11)	C8–N–C5	114.9
C11–C12	1.364(14)		
C12–C13	1.369(14)		

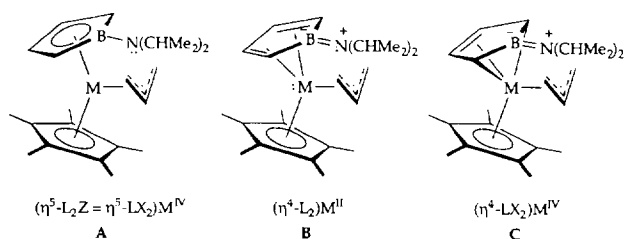
the allyl hydrogens appear as an  $\text{AM}_2\text{X}_2$  spin system at room temperature (300 MHz), consistent with 'locked'  $\eta^3$ -coordination. This  $\text{AM}_2\text{X}_2$  spin system is maintained even at 80°C (300 MHz for **4b**), indicating that the allyl is strongly  $\eta^3$  coordinated. Addition of donors dramatically lowers the barrier for  $\eta^3$ – $\eta^1$  interconversion. At room temperature, in the presence of one equivalent of a donor ligand (e.g. THF,  $\text{PMe}_3$ , pyridine), the allyl hydrogens appear as an  $\text{AX}_4$  spin system, consistent with rapid  $\eta^3$ – $\eta^1$  interconversion on the NMR time scale.

In order to confirm the  $\eta^3$ -coordination of the allyl, a single-crystal of **4b** was selected, and an X-ray structure obtained. An ORTEP drawing of the molecule is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. Overall, the bond distances and angles for the  $\text{Cp}^*$  and aminoborole ligands are very similar to those found in the structure of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{HfCl} \cdot \text{LiCl}(\text{Et}_2\text{O})_2$  [10]. The B–N bond distance of 1.414(10)  $\text{\AA}$  indicates considerable double bond character. As expected, the allyl ligand is bound symmetrically: the  $\text{C}_1$ – $\text{C}_3$  bonds are essentially identical and the hafnium–carbon distances are all very similar.

The beautiful colors for  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{M}(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{M} = \text{Zr}, \text{Hf}$ ), like  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MCl} \cdot \text{LiCl}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ), stand in contrast to most zirconocene and hafnocene derivatives, which are commonly pale yellow to colorless. In order to establish the nature of the low energy transitions responsible for their colors, the electronic spectra of **4a** and **4b** were examined. The deep green color of **4a** is due to a broad transition centered around  $\lambda = 749 \text{ nm}$  (pentane), with an extinction coefficient  $\epsilon$  of  $2000 \text{ M}^{-1} \text{ cm}^{-1}$ . The blue color of the hafnium analog arises from a broad transition with  $\lambda_{\text{max}} = 656 \text{ nm}$  (pentane) and  $\epsilon = 2500 \text{ M}^{-1} \text{ cm}^{-1}$ .

Undoubtedly, the electronic transition in the visible region is a direct or indirect consequence of a zirconium- or hafnium-aminoborole interaction. Several resonance structures contribute to the bonding of the

aminoborole complexes: structure **A**, the borollidyl form described as ( $\eta^5\text{-L}_2\text{Z} = \eta^5\text{-LX}_2$ ) in the Green classification [11], in which the ligand is a divalent cyclopentadienyl analog; structure **B**, the diene-like ( $\eta^4\text{-L}_2$ ) form, which Herberich et al. concluded is the best valence bond description for late metal aminoborole complexes [3]; and structure **C**, the divalent ( $\eta^4\text{-LX}_2$ ) form whose bonding resembles that of early transition metal diene complexes [12].



In resonance forms **A** and **C**, the metal is formally tetravalent,  $d^0$ , whereas in form **B**, the metal is divalent,  $d^2$ .

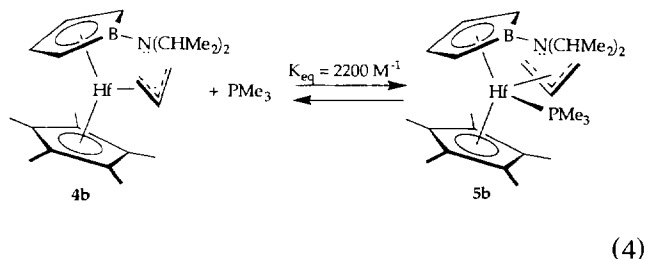
These limiting resonance pictures of the bonding suggest three possibilities for the electronic transitions in the visible region: (1) resonance structures **A** and **C** are the best descriptions of the ground state, implying a ligand-to-metal-charge-transition (LMCT), excited state  $\sim \{\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}^{(+)}\text{M}^{\text{III}(-)}(\eta^3\text{-C}_3\text{H}_5)\}^*$ ; (2) resonance structure **B** is the best ground state description, implying a metal-to-ligand-charge-transition (MLCT), excited state  $\sim \{\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}^{(-)}\text{M}^{\text{III}(+)}(\eta^3\text{-C}_3\text{H}_5)\}^*$ ; or (3) resonance structure **B**, whereby the formal  $d^2$  metal center undergoes a ligand field excitation.

The observed blue shift in the transition upon substitution of hafnium (**4b**) for zirconium (**4a**) is clearly inconsistent with option (2), an MLCT, since hafnium should be more easily oxidized resulting in a red shift. Therefore, the transition must be due to either an LMCT or a ligand field transition. The small solvatochromic shifts ( $\lambda_{\text{max}} = 646 \text{ nm}$  (toluene,  $\epsilon = 3200 \text{ M}^{-1} \text{ cm}^{-1}$ );  $\lambda_{\text{max}} = 644 \text{ nm}$  (methylene chloride,  $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ )) and molar extinction coefficients observed for **4b** would generally argue in favor of a ligand field transition [13]. However, as other  $d^0$  metallocenes with unambiguous LMCTs display similarly small solvatochromic shifts [14] and extinction coefficients [15], it is difficult to exclude LMCT on this basis alone. On balance, given the covalent nature of these organometallic complexes, the visible transitions of **4a** and **4b** are probably best described as having mixed LMCT/ $d-d$  character. (The magnitude of the blue shift (ca.  $2000 \text{ cm}^{-1}$ ) is also less than the energy difference

observed for 'pure' LMCT transitions upon descending the triad from **4d** to **5d** metal, for example with ionic halide complexes  $[\text{MX}_n]^{y-}$  (typically blue shifted  $6000$  to  $9000 \text{ cm}^{-1}$ ; see Ref. [13]). Since the aminoborollide-metal bonding for **4d** and **5d** is better viewed as more covalent, the orbitals involved in the transitions are necessarily of more mixed character.

We have also investigated the reactivity of the allyl complexes, **4a** and **4b**. Although we have not yet examined these catalytic reactions in detail, addition of ethylene (2 atm,  $25^\circ\text{C}$ ) to both allyl complexes results in rapid formation of polyethylene; addition of  $\text{SiPh}_2\text{H}_2$  to **4a** results in rapid dehydrogenative dimerization to  $\text{Ph}_2\text{HSi-SiHPh}_2$  ( $^1\text{H NMR}$ ).

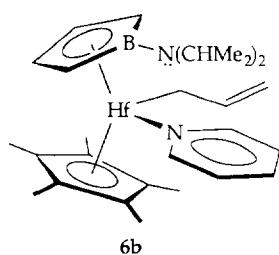
The addition of  $\text{PMe}_3$  results in a large blue shift in the visible transition of the allyl complexes, with the color changes from green to orange for **4a**, from blue to yellow for **4b**. This dramatic color change permitted study of this equilibrium by titrating **4b** with  $\text{PMe}_3$  and monitoring the disappearance of the band in the visible region with UV-vis spectroscopy. At  $23^\circ\text{C}$ ,  $K_{\text{eq}}$  for the addition of  $\text{PMe}_3$  to the hafnium allyl, **4b**, was found to be  $2200 \text{ M}^{-1}$  (Eq. (4)).



As discussed previously, in the presence of  $\text{PMe}_3$ , the allyl hydrogens appear as an  $\text{AX}_4$  spin system, which indicates only that there is rapid  $\eta^3-\eta^1$  interconversion of the allyl and does not distinguish between ( $\eta^1\text{-C}_3\text{H}_5$ ) and ( $\eta^3\text{-C}_3\text{H}_5$ ) structures for **5b**. IR spectroscopy has been found to be a useful method for distinguishing between  $\eta^3$ - and  $\eta^1$ -coordinated allyls [16]. The presence of a medium-to-weak intensity stretch at  $1523 \text{ cm}^{-1}$  in the IR spectrum of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{PMe}_3)$  is consistent with  $\eta^3$ -coordination. Moreover, the magnitude of blue shift in the visible transition on coordination of  $\text{PMe}_3$  (bleaching of the blue color to yellow) also argues in favor of  $\eta^3$ -coordination, since the 18-electron complex,  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{PMe}_3)$ , has no vacant orbital of low energy to participate in the LMCT.

Addition of pyridine to allyl **4b** results in a less dramatic color change, from blue to purple. The NMR spectrum of the pyridine adduct is similar to that of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{PMe}_3)$ ;

however, IR evidence suggests that the allyl ligand is  $\eta^1$ -bound in this case. (Complex **6b** shows a medium intensity peak in the IR spectrum at  $1602\text{ cm}^{-1}$ . It is not possible to definitively assign this as an  $\eta^1$ -allyl stretch, as pyridine also absorbs in this region; however, based on the intensity of the stretch, and the fact that it appears at slightly higher energies than those of free pyridine, we think that this assignment is the most reasonable one.) Since pyridine almost certainly coordinates to hafnium in the wedge of the pseudometallocene, ( $\eta^3$ - $\text{C}_3\text{H}_5$ ) coordination may well be precluded. A relatively low energy LMCT ( $\lambda_{\text{max}} \sim 540\text{ nm}$ ) is in accord with the 16-electron formulation for  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\text{py})(\eta^1\text{-C}_3\text{H}_5)$  (**6b**):



Unfortunately, the low stabilities of complexes **5b** and **6b** prevented their full characterization.

The reports by Stryker and coworkers [17] and others [18] on the formation of stable  $d^0$  Group 4 allyl-carbonyl complexes encouraged us to try the addition of CO to allyl complex **4b**. Addition of 1 atm of CO to **4b** resulted in a color change from blue to orange-red. The  $^1\text{H}$  NMR spectrum for this new compound (**7b**) is complex, with two resonances in the  $\text{Cp}^*$  region in ca.

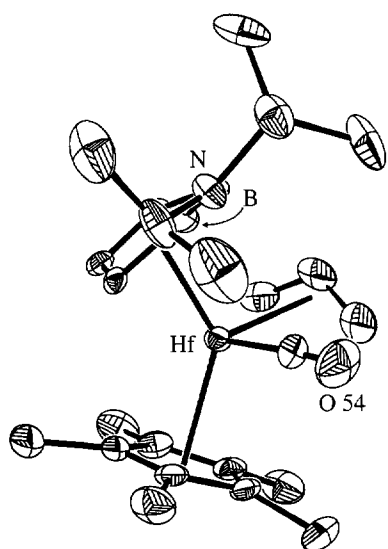
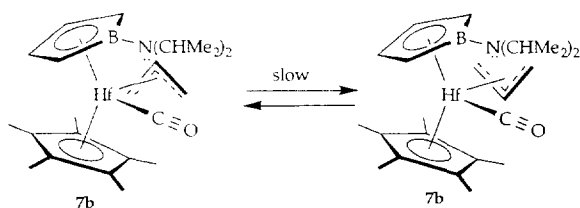


Fig. 2. ORTEP diagram of  $\text{Cp}^*\{\text{C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$  (**7b**).

Table 2  
Selected distances ( $\text{\AA}$ )<sup>a</sup> and angles (deg)<sup>a</sup> for  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$  (**7b**)

Hf–C54	2.143(12)	C54–O54	1.172(12)
Hf–C52	2.512(10)	Hf–C51	2.509(10)
Hf–C53	2.492(10)	B–N	1.435(13)
C51–C52	1.37(2)	C52–C53	1.379(14)
C51–C52 C53	125.2	C41–N–C31	117.5
B–N–C31	118.1	B–N–C41	123.2
Hf–C54–O54	176.4		

2:1 ratio. The IR spectrum shows an intense stretch at  $1997\text{ cm}^{-1}$ , consistent with the presence of a hafnium-bound carbonyl, and the  $^{13}\text{C}$  NMR shows two resonances ( $\delta$  236.3, 236.0) in the metal-bound CO region. In the absence of light and potential ligands (i.e.  $\text{PMe}_3$ , excess CO, etc.), samples of **7b** are stable in solution for up to several weeks, and it may be stored at  $-20^\circ\text{C}$  in a glove box refrigerator for months without noticeable decomposition. In the presence of excess CO or ligands such as  $\text{PMe}_3$ , decomposition to as yet uncharacterized products occurs. Given the difficulties in interpreting the very complex NMR spectra for **7b**, and the encouraging evidence from the IR and  $^{13}\text{C}$  NMR spectra that the new complex is quite stable, we sought to obtain structural evidence that the complex was a bona fide  $d^0$  carbonyl. Recrystallization of a toluene solution of **7b** by slow cooling from  $23^\circ\text{C}$  to  $-80^\circ\text{C}$  resulted in the isolation of 20% yield of small red-orange crystals. An X-ray diffraction study confirmed the structure as  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$ . A drawing with 30% thermal ellipsoids is shown in Fig. 2, and selected bond distances and angles are shown in Table 2. In contrast to its orientation in  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$ , the allyl ligand is rotated so that the central carbon is directed towards the aminoborollide ligand in the carbonyl adduct. This difference led us to wonder whether the two species observed by NMR are not merely due to the presence of two rotational isomers of the allyl ligand, i.e. slow rotation of the  $\eta^3$ -allyl on the NMR time scale (Eq. (5)).

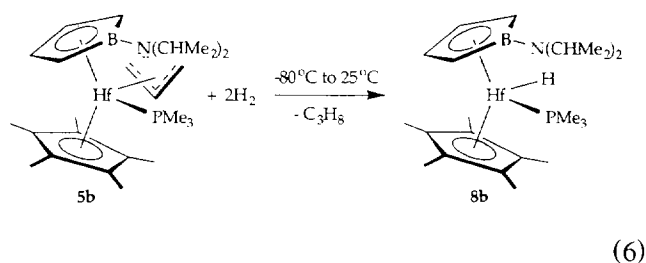


(5)

Additional evidence for this hypothesis comes from Stryker and coworkers, who reported that the allyl ligand of the CO complex,  $[\text{Cp}_2^*\text{Zr}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})]^+$ , isoelectronic to **7b**, is static on the NMR time scale,

with all five allyl protons inequivalent. Finally, we note that samples of recrystallized  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{-BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_5\text{H}_3)(\text{CO})$  have identical NMR spectra to samples generated in situ from **4b** and CO, supporting the notion that the two observed species are due to some interconversion slow on the NMR time scale. It is unclear why only one carbonyl stretch for the two rotamers is observed in its IR spectrum. It is possible that the stretches are simply too close in energy to be resolved by our instrument ( $4\text{cm}^{-1}$  resolution). The relatively low energy of this stretch, compared with other  $d^0$  Group 4 carbonyls [17,18], suggests that the aminoborollide ligand can provide additional electron density at hafnium (via resonance structure analogous to **B** above) to accommodate  $\pi$  acidic CO.

Addition of dihydrogen (1 atm,  $-80^\circ\text{C}$ ) to  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_5\text{H}_3)(\text{PMe}_3)$  results in formation of the  $\text{PMe}_3$  coordinated hydride,  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\text{H})(\text{PMe}_3)$  (**8b**), which is stable for about 12 h at room temperature under 1 atm of  $\text{H}_2$  (Eq. (6)).



The  $^1\text{H}$  NMR spectrum of the  $\text{PMe}_3$  hydride is consistent with the expected  $C_1$  symmetry. The Hf–H resonance appears at high field ( $\delta = 14.4\text{ppm}$ ), as has been observed for other hafnium hydrides [19], and the hydrogens of the aminoborole ring appear as four broad singlets between 5.4 and 4.0 ppm. Addition of dihydrogen to the allyl **4b** or to the zirconium analog (with or without added  $\text{PMe}_3$ ) results in propane and decomposition to a variety of unidentified products.

### 3. Experimental section

All manipulations were performed using glove box and high-vacuum line techniques [20]. Solvents were dried over Na–benzophenone and stored over Na–benzophenone (THF, ether) or titanocene [21] (toluene, petroleum ether, heptane). NMR solvents: benzene- $d_6$  was dried over  $\text{LiAlH}_4$  and then over sodium metal; THF- $d_8$  was purified by vacuum transfer from Na–benzophenone.

Argon was purified by passage over MnO on vermiculite and activated 4 Å molecular sieves. The com-

plexes  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{MCl} \cdot \text{LiCl}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) were prepared according to the previously published procedure [4].  $\text{Cp}^*\text{ZrCl}_3$  [22] and  $\text{Cp}^*\text{HfCl}_3$  [17] were prepared from  $\text{LiCp}^*$  and the metal tetrahalides (Aesar) following the literature procedures.  $\text{Li}_2(\text{THF})\{\text{C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}$  was prepared following the procedure of Herberich et al. [1].  $\text{AllylMgBr}$  (Aldrich), CO (Matheson),  $\text{BI}_3$  (Aldrich), and  $\text{PMe}_3$  (Aldrich) were all used as-received. Pyridine (Aldrich) was purified by vacuum transfer from  $\text{CaH}_2$ .  $\text{LiC}\equiv\text{CR}$  ( $\text{R} = p\text{-C}_6\text{H}_4\text{CH}_3, \text{CMe}_3$ ) was prepared by reaction of the corresponding  $\text{HC}\equiv\text{C-R}$  with  $\text{LiCMe}_3$  in THF at  $0^\circ\text{C}$ . The solid methyl lithium used was obtained by evaporating solvent from the commercially available (Aldrich) ether solution.

NMR spectra were carried out on a Bruker AM-500 spectrometer at 500 MHz for proton and 125.8 MHz for carbon and a GE QE300 spectrometer at 300 MHz for proton and 75.5 MHz for carbon. IR spectra were recorded on a Perkin–Elmer 1600 Series FTIR. UV–vis spectra were recorded on a Hewlett-Packard 8452A and a Cary 14 spectrophotometer modified by OLIN using a 1.0 mm path length, air-free cell. Elemental analyses were carried out by Mr. Fenton Harvey at Caltech. Generally, it has proven to be the case that satisfactory elemental analyses for these borollide derivatives are difficult to obtain, even for crystalline samples. For some compounds, but not all, addition of  $\text{V}_2\text{O}_5$  to the samples prior to combustion does improve the results.

#### 3.1. $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Zr}(\text{CH}_3)_2\text{Li}$ (**1a**)

A swivel frit assembly was charged with 0.16 g (0.35 mmol) of  $\text{Cp}^*\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{ZrCl} \cdot \text{LiCl}$  and 0.02 g (1 mmol) of MeLi.  $\text{Et}_2\text{O}$  (25 ml) was condensed onto the solids at  $-78^\circ\text{C}$ . The suspension was stirred under argon atmosphere at room temperature. The color of the solution changed first to green, and became yellow within 1 h. The solution was stirred 2 h more, filtered to eliminate LiCl, and the solvent was removed under reduced pressure. The bright yellow foam obtained was dissolved in 10 ml of petroleum ether, the solution was cooled to  $-78^\circ\text{C}$  and **1a** was collected by filtration as a yellow solid. (0.11 g, yield 70%).

$^1\text{H}$  NMR (benzene- $d_6$ –THF- $d_8$ , 300 MHz): 5.22 (m, 2H, H3, H4); 3.92 (m, 2H, H2, H5); 3.67 (sept.,  $^3J_{\text{H-H}} = 6.6\text{ Hz}$ , 2H,  $2\text{CH}(\text{CH}_3)_2$ ); 2.03 (s, 15H,  $\text{Cp}^*$ ); 1.32 (d,  $^3J_{\text{H-H}} = 6.6\text{ Hz}$ , 12H,  $2\text{CH}(\text{CH}_3)_2$ );  $-0.23$  (s, 6H,  $2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 75 MHz): 120.2 (s, 5C,  $(\text{C}_5(\text{CH}_3)_5)$ ); 106.5 (s, C3, C4); 89.0 (br, C2/5); 47.0 (s,  $2\text{CH}(\text{CH}_3)_2$ ); 23.5 (s,  $4\text{CH}_3$ ); 11.6 (s, 5C,  $\text{C}_5(\text{CH}_3)_5$ ). Elemental anal. Found: C, 60.16; H, 9.20; N, 3.26.  $\text{C}_{22}\text{H}_{39}\text{BLiZr}$ . Calc.: C, 61.95; H, 9.22; N, 3.28%.

### 3.2. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Zr(C\equiv C-p-C_6H_4Me)_2Li$ (**1b**)

A swivel frit assembly was charged with 0.23 g (0.49 mmol) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}ZrCl \cdot LiCl$  and 0.14 g (1.1 mmol) of  $LiC\equiv C-p-C_6H_4-Me$ .  $Et_2O$  (25 ml) was vacuum transferred onto the solids at  $-78^\circ C$ . The blue suspension was allowed to warm to room temperature slowly and was stirred overnight. No change in the color of the solution was observed. The suspension was filtered, the solvent was removed under reduced pressure. The resulting blue foam was dissolved in 25 ml of petroleum ether, filtered, and the volatiles removed. 0.19 g (yield 73%) of **1b** as a blue solid soluble in petroleum ether was obtained.

$^1H$  NMR (THF- $d_8$ , 300 MHz): 7.18 (d,  $^3J_{H-H} = 8.1$  Hz, 2H<sub>o</sub>); 7.02 (d,  $^3J_{H-H} = 8.1$  Hz, 2H<sub>p</sub>); 5.57 (m, H3, H4); 4.69 (m, H2, H5); 3.48 (sept.,  $^3J_{H-H} = 6.6$  Hz, 2CH(CH<sub>3</sub>)<sub>2</sub>); 2.23 (s, 3H, CH<sub>3</sub>); 2.08 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.06 (d,  $^3J_{H-H} = 6.6$  Hz, 12H, 2CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}C\{^1H\}$  NMR (THF- $d_8$ , 75 MHz): 143.5 (s, C≡C); 135.8 (s, 1C<sub>p</sub>); 130.5 (s, 2C<sub>o</sub>); 128.5 (s, 2C<sub>m</sub>); 126.7 (s, C≡C); 123.7 (s, 1C<sub>i</sub>); 116.3 (s, C3, C4); 114.3 (s, 5C, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 93.0 (br, C2, C5); 47.0 (s, 2CH(CH<sub>3</sub>)<sub>2</sub>); 23.5 (s, 2CH(CH<sub>3</sub>)<sub>2</sub>); 20.4 (s, 1CH<sub>3</sub>); 11.6 (s, 5CH<sub>3</sub>, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). Elemental anal. Found: C, 71.93; H, 8.8; N, 2.47. C<sub>38</sub>H<sub>47</sub>BLiNZr. Calc.: C, 72.82; H, 7.6; N, 2.2%.

### 3.3. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Zr(C\equiv C-CMe_3)_2Li$ (**1c**)

The above procedure was followed by using 0.20 g (0.43 mmol) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}ZrCl \cdot LiCl$  and 0.1 g (1.1 mmol) of  $LiC\equiv CMe_3$ . 0.15 g (yield 50%) of **1c** as a blue solid.

$^1H$  NMR (benzene- $d_6$ , 300 MHz): 5.57 (m, H3, H4); 4.69 (m, H2, H5); 3.83 (sept.,  $^3J_{H-H} = 6.6$  Hz, 2CH(CH<sub>3</sub>)<sub>2</sub>); 2.06 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.37 (br, 2CH(CH<sub>3</sub>)<sub>2</sub>); 1.16 (s, 18H, 2CMe<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ , 75 MHz): 116.6 (s, 5C, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 109.7 (s, C3, C4); 47.4 (s, 2CH(CH<sub>3</sub>)<sub>2</sub>); 31.4 (s, 6CH<sub>3</sub>, 2C(CH<sub>3</sub>)<sub>3</sub>); 12.4 (s, 5CH<sub>3</sub>, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

### 3.4. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Zr(CH_2Ph)_2Li$ (**1d**)

A swivel frit assembly was charged with 0.25 g (0.55 mmol) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}ZrCl \cdot LiCl$  and 0.15 g (1.1 mmol) of  $KCH_2Ph$ .  $Et_2O$  (30 ml) was condensed onto the solids at  $-78^\circ C$ , and the mixture was stirred overnight at room temperature. Volatiles were removed under reduced pressure from the resulting red solution. The orange solid obtained was taken up in 15 ml of  $Et_2O$ , and filtered. Volatiles were evaporated under reduced pressure. The solid product was washed

twice with 10 ml of petroleum ether to afford 0.21 g (yield 68%) of **1d** as an orange solid.

$^1H$  NMR (THF- $d_8$ , 300 MHz): 6.78 (pt,  $^3J_{H-H} = 7.5$  Hz, 4H<sub>m</sub>); 6.66 (d,  $^3J_{H-H} = 7.5$  Hz, 4H<sub>o</sub>); 6.37 (d,  $^3J_{H-H} = 7.5$  Hz, 4H<sub>p</sub>); 4.64 (m, H3, H4); 3.55 (sept.,  $^3J_{H-H} = 6.6$  Hz, 2CH(CH<sub>3</sub>)<sub>2</sub>); 3.24 (m, H2, H5); 1.93 (d,  $^2J_{H-H} = 9.3$  Hz, 2H, 2CHHPh); 1.78 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.08 (d,  $^3J_{H-H} = 6.6$  Hz, 12H, 2CH(CH<sub>3</sub>)<sub>2</sub>); 1.03 (d,  $^2J_{H-H} = 9.3$  Hz, 2H, 2CHHPh).  $^{13}C\{^1H\}$  NMR (THF- $d_8$ , 75 MHz): 158.7 (s, 2C<sub>i</sub>); 126.2 (s, 4C<sub>m</sub>); 125.3 (s, 4C<sub>o</sub>); 116.3 (s, 2C<sub>p</sub>); 113.8 (s, 5C, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 113.1 (s, C3, C4); 89.0 (br, C2, C5); 54.8 (s, 2CH<sub>2</sub>Ph); 46.8 (s, 2CH(CH<sub>3</sub>)<sub>2</sub>); 23.1 (s, 2CH(CH<sub>3</sub>)<sub>2</sub>); 11.3 (s, 5CH<sub>3</sub>, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). Elemental anal. Found: C, 68.14; H, 9.3; N, 2.2. C<sub>42</sub>H<sub>66</sub>BLiNO<sub>2</sub>Zr. Calc.: C, 69.53; H, 9.09; N, 1.93%.

### 3.5. $Cp^*ZrI_3$ (**2**)

A swivel frit assembly was charged with 1.98 g (5.9 mmol) of  $Cp^*ZrCl_3$  and 2.27 g (5.8 mmol) of  $BI_3$ . Toluene (50 ml) was condensed onto the solids at  $-78^\circ C$ . The resulting orange solution was stirred overnight. Volatiles were removed and 30 ml of petroleum ether was condensed onto the residue. The suspension was stirred 1 h, filtered, and the solid was washed once with 30 ml of petroleum ether. 3.08 g (86% yield) of **2** as a bright yellow solid was obtained.

$^1H$  NMR (benzene- $d_6$ , 300 MHz) 1.93 (s, 15H);  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ , 75 MHz): 131.2 (s, 5C, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 15.5 (s, 5C, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). Elemental anal. Found: C, 20.40; H, 2.68. C<sub>10</sub>H<sub>15</sub>I<sub>3</sub>Zr. Calc.: C, 19.78; H, 2.47%.

### 3.6. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}ZrI \cdot LiI(THF)_2$ (**3**)

A swivel frit assembly was charged with 1.98 g (3.26 mmol) of  $Cp^*ZrI_3$  and 0.81 g (3.25 mmol) of  $(THF)Li_2(C_4H_4BN(CHMe_2)_2)$ . Toluene (60 ml) was condensed onto the solids at  $-78^\circ C$ . The blue-green suspension was stirred overnight at room temperature under an argon atmosphere. The suspension was filtered and the solvent was removed under reduced pressure. The resulting solid was suspended in 30 ml of petroleum ether, filtered and washed once with petroleum ether to afford a green solid (1.45 g, yield 60%).

$^1H$  NMR (benzene- $d_6$ , 300 MHz): 5.67 (m, 2H, H3, H4); 5.15 (m, 2H, H2, H5); 3.96 (sept.,  $^3J_{H-H} = 6.6$  Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>); 3.57 (m, 4H, THF); 2.01 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 1.46 (br, 6H, 2CH(CH<sub>3</sub>)<sub>2</sub>); 1.26 (d br,  $^3J_{H-H} = 6.6$  Hz, 6H, 2CH(CH<sub>3</sub>)<sub>2</sub>); 1.16 (m, 4H, THF).  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ , 75 MHz): 120.2 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 114.6 (C3, C4); 111.7 (br, C2, C5); 69.2 (THF); 47.9 (CH(CH<sub>3</sub>)<sub>2</sub>); 24.9 (THF); 23.5 (br, CH(CH<sub>3</sub>)<sub>2</sub>); 22.7 (br, CH(CH<sub>3</sub>)<sub>2</sub>); 13.6 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

Elemental anal. Found: C, 37.43; H, 5.26; N, 1.67.  $C_{20}H_{33}BI_2LiNZr$ . Calc.: C, 36.90; H, 5.10; N, 2.10%.

### 3.7. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Zr(\eta^3-C_3H_5)$ (**4a**)

A swivel frit assembly was charged with 0.79 g (1.7 mmol) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}ZrCl \cdot LiCl$ .  $Et_2O$  (50 ml) was condensed onto the solid at  $-78^\circ C$ . At room temperature, 1.8 ml (solution 1.0 M in  $Et_2O$ ) of allyl magnesium bromide was syringed into the frit against an argon counterflow. The blue solution turned green immediately and was stirred for 3 h. Volatiles were removed and the product was extracted with two portions of 50 ml each of petroleum ether. The suspension was filtered and the solvent was removed under reduced pressure. 0.55 g (yield 75%) of **5** as a green microcrystalline solid was obtained.

$^1H$  NMR (benzene- $d_6$ , 300 MHz): 6.92 (tt, 1H,  $H_c$  allyl); 5.45 (br, 2H, H3, H4); 4.23 (br, 2H, H2, H5); 3.92 (d,  $^3J_{H-H} = 15.3$  Hz,  $H_{anti}$ , allyl); 3.58 (sept.,  $^3J_{H-H} = 6.6$  Hz,  $2CH(CH_3)_2$ ); 1.92 (d,  $^3J_{H-H} = 8.7$  Hz,  $H_{syn}$ , allyl); 1.48 (s, 15H,  $C_5(CH_3)_5$ ); 1.28 (d,  $^3J_{H-H} = 6.6$  Hz, 12H,  $2CH(CH_3)_2$ ).  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ , 75 MHz): 138.0 (s, 1CH, allyl); 114.0 (s, 5C,  $C_5(CH_3)_5$ ); 111.6 (br, C3, C4); 89.0 (br, C2, C5); 64.2 (br,  $2CH_2$ , allyl); 47.6 (s,  $2CH(CH_3)_2$ ); 23.8 (s,  $2CH(CH_3)_2$ ); 10.4 (s,  $5CH_3$ ,  $C_5(CH_3)_5$ ).  $^1H$  NMR (THF- $d_8$ , 300 MHz): 7.01 (q,  $^3J_{H-H} = 11.7$  Hz, 1CH, allyl); 5.33 (m, H3, H4); 3.81 (m, H2, H5); 3.43 (h,  $^3J_{H-H} = 6.6$  Hz,  $2CH(CH_3)_2$ ); 2.72 (d br,  $^3J_{H-H} = 11.7$  Hz,  $2CH_2$ , allyl); 1.80 (s,  $5CH_3$ ,  $C_5(CH_3)_5$ ); 1.08 (d,  $^3J_{H-H} = 6.6$  Hz,  $2CH(CH_3)_2$ ).  $^{13}C\{^1H\}$  NMR (THF- $d_8$ , 300 MHz): 137.7 (s, 1CH, allyl); 113.6 (s, 5C,  $C_5(CH_3)_5$ ); 111.1 (s, C3, C4); 87.7 (br, C2, C5); 63.4 (s,  $2CH_2$ , allyl); 47.2 (s,  $2CH(CH_3)_2$ ); 23.2 (s,  $2CH(CH_3)_2$ ); 9.9 (s,  $5CH_3$ ,  $C_5(CH_3)_5$ ). UV-vis (pentane): 749 (2000). Elemental anal. Found: C, 61.61; H, 8.81; N, 3.68.  $C_{23}H_{38}BNZr$ . Calc.: C, 64.3; H, 8.8; N, 3.2%.

### 3.8. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)$ (**4b**)

A swivel frit assembly was charged with 2.00 g (3.86 mmol) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}HfCl \cdot LiCl$ .  $Et_2O$  (75 ml) was condensed onto the solid at  $-78^\circ C$ . At  $0^\circ C$ , 4 ml (solution 1.0 M in  $Et_2O$ , 1.05 equivalents) of allyl magnesium bromide were syringed into the frit against an argon counterflow. After stirring for 3 h, the resulting green solution was filtered and the volatiles evaporated at reduced pressure. Using a new frit, the solid was taken up in 50 ml of toluene and filtered. The insoluble solids were washed repeatedly, until the filtrate was pale blue in color. Volatiles evaporated under reduced pressure. The residue was slurried in 30 ml of petroleum ether and a deep blue solid isolated by filtration at  $-78^\circ C$ . Crude yield 1.40 g (70%). Recrystallization from hot heptane afforded

700 mg (35%) of crystalline  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)$ . In order to obtain satisfactory elemental analysis, it was necessary to recrystallize the sample a second time and to grind the sample with  $V_2O_5$  to facilitate oxidation.

$^1H$  NMR (benzene- $d_6$ , 500 MHz): 6.99 (m, 1H,  $H_c$  allyl); 5.34 (m, 2H, H3, H4); 4.02 (m, 2H, H2, H5); 3.66 (d,  $^3J_{H-H} = 15.4$  Hz, 2H,  $H_{anti}$  allyl); 3.58 (sept.,  $^3J_{H-H} = 6.8$  Hz, 2H,  $2CH(CH_3)_2$ ); 1.70 (d,  $^3J_{H-H} = 9$  Hz,  $H_{syn}$  allyl); 1.35 (s, 15H,  $C_5(CH_3)_5$ ); 1.28 (d,  $^3J_{H-H} = 6.8$  Hz, 12H,  $2CH(CH_3)_2$ ).  $^{13}C$  NMR (benzene- $d_6$ , 125.8 MHz): 135.4 (d,  $^1J_{C-H} = 147$  Hz,  $C_m$  allyl); 112.3 (s,  $C_5(CH_3)_5$ ); 107.31 (d,  $^1J_{C-H} = 158$  Hz, C3, C4); 81.5 (br, C2, C5); 61.77 (t,  $^1J_{C-H} = 157$  Hz,  $C_t$  allyl); 48.51 (d,  $^1J_{C-H} = 133$  Hz,  $CH(CH_3)_2$ ); 24.58 (q,  $^1J_{C-H} = 125$  Hz,  $CH(CH_3)_2$ ); 10.81 (q,  $^1J_{C-H} = 126$  Hz,  $C_5(CH_3)_5$ ). IR (Nujol): 1504(w); 1437(m); 1426(s); 1322(s). UV-vis (pentane): 656 (2500); 330 (3800); 236 (10000). Elemental anal. Found: C 53.31; H, 7.71; N, 2.85.  $C_{23}H_{38}BHfN$ . Calc.: C, 53.37; H, 7.34; N, 2.70%.

### 3.9. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)(PMe_3)$ (**5b**)

A swivel frit assembly was charged with 150 mg  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)$ . Petroleum ether (10 ml) was condensed in. Using a gas bulb, 1.1 equivalents (0.32 mmol)  $PMe_3$  was condensed in at  $-78^\circ C$ . The solution was warmed to room temperature, then the resulting yellow-green solution was filtered at  $-78^\circ C$ , yielding 60 mg (50%) of  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)(PMe_3)$  as a pale green solid.

$^1H$  NMR (benzene- $d_6$ , 300 MHz): 5.58 (br, 1H,  $H_c$  allyl); 4.87 (br, 2H, H3, H4); 3.55 (sept.,  $^3J_{H-H} = 6.7$  Hz, 2H,  $2CH(CH_3)_2$ ); 2.7 (br, 2H, H2, H5); 2.51 (d-br, 4H,  $H_t$  allyl); 1.65 (s, 15H,  $C_5(CH_3)_5$ ); 1.4 (d-br, 12H,  $2CH(CH_3)_2$ ); 0.95 (d,  $^2J_{P-H} = 7$  Hz, 9H,  $P(CH_3)_3$ ). IR (Nujol): 1523(w); 1415(s); 1356(m); 1329(s).

### 3.10. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^1-C_3H_5)(py)$ (**6b**)

A J. Young-type NMR tube was charged with 35 mg (0.068 mmol)  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)$  and 0.75 ml benzene- $d_6$ . A gas bulb was used to add 1.0 equivalent of pyridine, resulting in a color change from blue to purple. The IR spectrum was obtained by evaporating the solvent and making a mull of the residue.

$^1H$  NMR (benzene- $d_6$ , 300 MHz): 8.2 (br, 2H,  $H_o$  py); 7.00 (quint.,  $^3J_{H-H} = 12$  Hz, 1H,  $H_c$  allyl); 6.70 (m, 1H,  $H_p$  py); 6.52 (m, 2H,  $H_m$  py); 5.56 (br, 2H, H3, H4); 4.24 (br, 2H, H2, H5); 3.41 (sept.,  $^3J_{H-H} =$



6.7 Hz, 2H,  $2CH(CH_3)_2$ ); 2.89 (d,  $^3J_{H-H} = 12$  Hz, 4H, H, allyl); 1.57 (s, 15H,  $C_5(CH_3)_5$ ); 1.1 (br, 12H,  $2CH(CH_3)_2$ ). IR (Nujol): 1602(m); 1440(s); 1407(m); 1325(s).

### 3.11. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)(CO)$ (**7b**)

A swivel frit assembly was charged with 0.50 g  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)$ . Toluene (15 ml) was condensed into the frit. CO (1 atm) was admitted to the frit with the solution at room temperature. The solution was stirred vigorously for 3 min, during which time the color changed from deep blue to red-orange. The solution was cooled to  $-78^\circ C$ , and the excess CO removed. The solution was warmed to room temperature, then slowly cooled to  $-78^\circ C$  and allowed to remain at that temperature overnight. Filtration at the same temperature yielded 100 mg (18%)  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)CO$  as an orange-red microcrystalline solid.

$^1H$  NMR (benzene- $d_6$ , 500 MHz): 5.90 (br, 1H); 5.46 (br, 2H); 4.78 (br, 2H); 4.59 (br, 1H); 4.48 (m, 2H); 4.02 (m, 1H); 3.62 (br-overlapping, 3H); 3.36 (br-overlapping, 5H); 3.08 (d,  $J_{H-H} = 8.8$  Hz, 1H); 2.98 (d,  $J_{H-H} = 8.9$  Hz, 2H); 2.81 (m, 2H); 2.68 (br, 1H); 2.43 (d,  $J_{H-H} = 15.6$  Hz, 1H); 2.27 (m, 2H); 2.21 (m, 2H); 1.83 (br, 1H); 1.62 (m, 2H); 1.57 (s, 30H); 1.47 (s, 16H); 1.40 (br-mult., 6H); 1.3 (br-mult., 19H); 1.17 (br, 10H).  $^{13}C\{^1H\}$  NMR (benzene- $d_6$ , 125.8 MHz): 236.5; 236.1; 123.5; 121; 109.59; 108.6; 107.7; 96.7; 80 (br); 75.3 (br); 71 (br); 63.3 (br); 62.3; 55.0; 54.5; 53.8; 49.2; 48.0; 46.2; 46.6; 23.9 (br); 23.5 (br); 23 (br); 11.4; 11.0. IR (Nujol): 1997(s); 1432(s); 1407(m); 1328(s); 1245(m); 1198(s). Elemental anal. Found: C, 50.34; H, 6.51; N, 2.39.  $C_{24}H_{38}BHfNO$ . Calc.: C, 52.84; H, 6.96; N, 2.57%.

### 3.12. $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(H)(PMe_3)$ (**8b**)

A J. Young-type NMR tube was charged with 25 mg  $Cp^*\{\eta^5-C_4H_4BN(CHMe_2)_2\}Hf(\eta^3-C_3H_5)(PMe_3)$  and 0.75 ml benzene- $d_6$ . On the vacuum line, the tube was filled with 1 atm of  $H_2$ . Upon mixing, the solution changed color briefly to red, then became deep blue.  $^1H$  NMR (benzene- $d_6$ , 300 MHz): 14.4 (s, 1H, Hf-H); 5.76 (m, 1H); 5.40 (m, 1H); 5.06 (m, 1H); 4.06 (m, 1H); 3.56 (sept.,  $^3J_{H-H} = 6$  Hz, 2H,  $CH(CH_3)_2$ ); 2.00 (s, 15H,  $C_5(CH_3)_5$ ); 1.39 (d,  $^3J_{H-H} = 6.7$  Hz, 12H,  $CH(CH_3)_2$ ); 0.74 (d,  $^2J_{P-H} = 4$  Hz, 9H,  $P(CH_3)_3$ ).

### 3.13. Polymerization of ethylene by **4a** and **4b**

A small glass bomb was charged with either **4a** (100 mg) or **4b** (12 mg) and 10–15 ml of toluene. 1–2 g ethylene was purified by condensing into a solution of

200 mg titanocene in 25 ml toluene. The ethylene was transferred into the glass bomb containing the catalyst solution at 77 K and the solution allowed to thaw behind a blast shield. Polymerization (evident by formation of a white precipitate) began while the solution was still cold, resulting in the solution warming to slightly above room temperature. The solution became too viscous to stir due to the precipitated polymer. Yield ca. 1 g polyethylene.

### 3.14. Dimerization of $Ph_2SiH_2$

**4a** (100 mg) was treated with excess  $Ph_2SiH_2$  in toluene at room temperature. A brown solution with some precipitate formed immediately. Recrystallization of the resulting solid from toluene resulted in a 1.3 g yield of white  $(Ph_2SiH)_2$ , equivalent to ca. 15 turnovers.  $^1H$  NMR (benzene- $d_6$ , 300 MHz): 7.54 (m,  $H_{phenyl}$ ); 7.04 (m,  $H_{phenyl}$ ); 5.04 (s, Si-H).

### 3.15. X-ray experimental [23]

A dark blue crystal of **4b** was mounted with grease in a capillary on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were based on the setting angles of 25 reflections with  $11 < \theta < 13^\circ$ . The data were corrected for absorption and a 4.3% linear decay; Lorentz and polarization factors were applied. The hafnium coordinates were obtained from a Patterson map and the other heavy atoms from successive structure-factor Fourier calculations. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the Cp methyl groups were positioned from difference maps and the remaining placed at calculated positions; all were given a  $B$  1.2 times that of the attached atom. CRYM programs were used for structure solution and refinement. Weights  $w$  were calculated as  $1/\sigma^2(F_o^2)$ ; variances ( $\sigma^2(F_o^2)$ ) were derived from counting statistics plus an additional term,  $(0.014I)^2$ ; variances of the merged data were obtained by propagation of error plus another additional term,  $(0.014\langle I \rangle)^2$ . Crystallographic data are given in Table 3.

A dark blue crystal of **7b** was mounted with grease in a capillary on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were determined from the setting angles of 25 reflections with  $10.5 < \theta < 12.6^\circ$ . The data were corrected for absorption and a 1.0% linear decay; Lorentz and polarization factors were applied to the data, decay, and absorption corrections made, and the data averaged in point group  $2/m$ . Systematic absences uniquely determined the space group. Direct methods with SHELXS-86 located most of the non-hydrogen atoms. The remaining non-hydrogen atoms were located in a difference Fourier map. SHELXL-93 was used for refinement. Weights were calculated as above. All non-hydrogen atoms were refined anisotropically. The hydrogenic

Table 3  
Summary of crystal data and structure determination information for (4b) and (7b)

Formula	C <sub>23</sub> H <sub>38</sub> BHfN	C <sub>24</sub> H <sub>38</sub> BHfNO
Formula weight (amu)	517.86	545.85
Crystal system	triclinic	monoclinic
Space group (No.)	<i>P</i> '1 (2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)
<i>a</i> (Å)	8.959(3)	13.838(5)
<i>b</i> (Å)	9.538(3)	8.377(1)
<i>c</i> (Å)	13.911(8)	21.185(7)
$\alpha$ (deg)	88.55(4)	90
$\beta$ (deg)	86.15(4)	99.36(3)
$\gamma$ (deg)	74.36(3)	90
<i>V</i> (Å <sup>3</sup> )	1142.1(8)	2423.1(12)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.506	1.496
Absorption coefficient (cm <sup>-1</sup> )	45.32	43.18
Absorption correction	$\Psi$ scan	$\Psi$ scan
Range of relative transmission	0.67–1.22	0.85–1.11
2 $\theta$ range (deg)	2–45	3–50
Scan mode	$\omega$ scan	$\omega$ scan
Temperature (K)	295	293
<i>F</i> <sub>000</sub>	520	1096
Reflections collected	6709	9165
No. independent reflections (GOF <sub>merge</sub> )	2978 (1.10)	4244 (1.16)
Least squares refinement method	Full-matrix on <i>F</i> <sup>2</sup>	Full-matrix on <i>F</i> <sup>2</sup>
Maximum shift/error	0.03	0.02
<i>R</i>	0.031	0.104
<i>R</i> <sub>w</sub>	0.057	0.080
GOF	1.36	1.18
Max., min. peaks in diff. Fourier (e Å <sup>-3</sup> )	1.50, -0.69	1.22, -0.65

atomic positions were calculated and included in the structure factor calculations as riding atoms with fixed *U* values. Crystallographic data are given in Table 3.

#### 4. Supplementary material available

Tables of final parameters for the structures of Cp\* $\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)$  and Cp\* $\{\eta^5\text{-C}_4\text{H}_4\text{BN}(\text{CHMe}_2)_2\}\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})$ , assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and tables of observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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