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Mechanistic Aspects of the Reactions of Bis(pentafluorophenyl)borane with the Dialkyl Zirconocenes Cp_2ZrR_2 ($R = CH_3$, CH_2SiMe_3, and $CH_2C_6H_5$)

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The reactions of bis(pentafluorophenyl)borane with simple dialkyl zirconocenes Cp_2ZrR_2 ($R = CH_3$, CH_2SiMe_3, CH_2Ph) proceed via initial alkyl/hydride exchange to yield "$Cp_2Zr(H)R$" and $RB(C_6F_5)_2$. Two reaction paths are then followed depending on whether further equivalents of $HB(C_6F_5)_2$ are present or not. If present, $HB(C_6F_5)_2$ reacts with the newly formed Zr−H moiety to form dihydridoborate compounds, ultimately yielding $Cp_2Zr[(\mu\text{-}H)_2B(C_6F_5)_2]_2$, **1**, and 2 equiv of $RB(C_6F_5)_2$. Compound **1** was characterized by X-ray crystallography. In the absence of more $HB(C_6F_5)_2$, the products of alkyl/hydride exchange react to eliminate RH and produce the borane-stabilized alkylidene compounds $Cp_2Zr(\mu\text{-}CH_2)[(\mu\text{-}H)B(C_6F_5)_2]$, **2**, and $Cp_2Zr\{\eta^3\text{-}CH(C_6H_5)[(\mu\text{-}H)B(C_6F_5)_2]\}$, **4**. The latter compound is formed cleanly in 92% yield and was characterized by X-ray crystallography. Mechanistic studies on these reactions involving partially deuterated compounds reveal that the alkyl/hyride exchange process is reversible and takes place via a stepwise alkide-abstraction−hydride-replacement sequence rather than a concerted, four-centered σ-bond metathesis type mechanism. This is most convincingly demonstrated by the observed inversion of stereochemistry observed when *erythro*-$Cp_2Zr[CH(D)CH(D)\text{-}t\text{-}C_4H_9](Cl)$ ($^3J_{HH} = 12.82 \pm 0.05$ Hz) is treated with excess $HB(C_6F_5)_2$, producing *threo*-$(C_6F_5)_2B{-}CH(D)CH(D)\text{-}t\text{-}C_4H_9$ ($^3J_{HH} = 5.00 \pm 0.05$ Hz). Further experiments reveal a H/D scrambling process involving the borane proton and the C_α−H positions of the zirconium alkyl groups ($R = CH_3$, CH_2Ph). For example, treatment of $Cp_2Zr(CD_2C_6D_5)_2$ with 1 equiv of $HB(C_6F_5)_2$ leads to a mixture of isotopomers of **4** and toluene, including $C_6D_5CH_3$ and $C_6D_5CH_2D$, suggesting a scrambling process in which the borane engages in multiple contacts with the metallocene reagent prior to alkane elimination. The H/D scrambling event is proposed to involve hydridoborate attack of the remaining alkyl group on the forming metallocene cation as $HB(C_6F_5)_2$ abstracts the other alkide ligand. The implications of these mechanistic studies within the realms of metallocene activation and metallocene-catalyzed hydroborations are discussed.

Introduction

The reactions of transition-metal complexes with secondary boranes $R_2B{-}H$ have received increased attention in recent years. This interest stems primarily from the fact that a wide range of organometallic compounds are effective mediators of the addition of B−H bonds across unsaturated organic functions, i.e., hydroboration.[1] While the earliest work in this relatively young area of research focused on the use of late-transition-metal-based catalysts,[2] it has recently been shown that early transition metals[3] and lanthanides[4] can also catalyze hydroboration reactions. In the absence of the oxidative addition reaction available to late-transition-metal catalysts,[5] these early-transition-metal systems utilize exclusively nonoxidative pathways that effect rapid alkyl/hydride exchange[6] between boron and the metal center for B−C bond formation (Scheme 1). This exchange process has been categorized as an example of σ-bond metathesis (σBM) and as such has been as-

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[1] Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.

[2] For selected examples, see: (a) Mannig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878. (b) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. (c) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 395. (d) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863.

[3] (a) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696. (b) Erker, G.; Noe, R.; Wingbermühle, D.; Petersen, J. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1213. (c) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909. (d) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127. (e) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1995**, *95*, 121.

[4] Harrison, K. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

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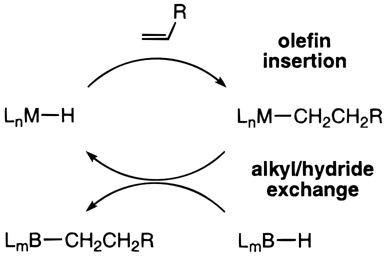
Scheme 1



sumed to occur via the four-centered transition state commonly invoked for σBM reactions. The most favored transition state for σBM involving B—H and early metal-transition-carbon—bonds leads to formation of B—C and M—H; generation of alkane and metal boryl products via an alternative σBM transition state has not, to our knowledge, been observed in these systems. Olefin insertion into the resultant M—H bond rapidly regenerates the metal alkyl species; in the absence of olefin, excess borane R_2B—H can complex M—H, forming a metal borate complex.[5a−b,7] Stoichiometric examples of alkyl/hydride exchange reactions were observed some time ago in the pioneering work of Marsella and Caulton in their study of the reactions of Cp_2ZrMe_2 with diborane[8] and have also been documented more recently in other systems.[7b,9] Despite these studies, however, a detailed picture of the mechanism for alkyl/hydride exchange between (ETM)—R and B—H has not been developed.

Many of the more recent studies examining these types of reactions have focused on relatively unreactive boronic esters such as catechol borane, not surprising in light of the reluctance of these boranes to add across C═C or C≡C bonds of their own volition. We, on the other hand, have been exploring the chemistry of the highly electrophilic borane bis(pentafluorophenyl)-borane, $HB(C_6F_5)_2$,[10] in this regard. While this borane is an extremely effective hydroboration reagent which requires no aid from a transition-metal catalyst to perform, it nonetheless is also highly reactive toward early-transition-metal organometallic compounds. This stoichiometric reactivity is germane to the realm of group 4 metal-catalyzed hydroborations. In addition to relevance to metal-catalyzed hydroboration chemistry, the interactions of highly Lewis acidic pentafluorophenyl-substituted boranes with group 4 metal metallocenes are of interest in the field of homogeneous olefin polymerization.[11] We have, therefore, examined the reactions of $HB(C_6F_5)_2$ with simple dialkyl zirconocenes in some detail. A preliminary account of the reactions of Cp_2ZrMe_2 with $HB(C_6F_5)_2$ has appearred.[12]

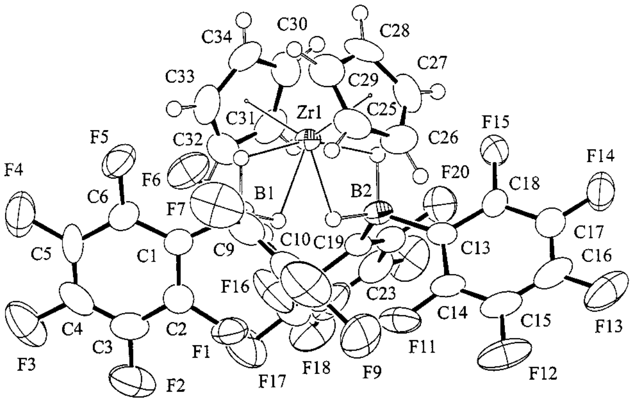
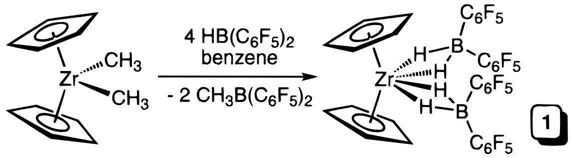


Figure 1. ORTEP drawing of the molecular structure of **1**.

Results and Discussion.

A. Synthetic Chemistry. In benzene or toluene, the reaction of 1 equiv of $HB(C_6F_5)_2$ with Cp_2ZrMe_2 gives an intractable mixture of products. In contrast, addition of 4 equiv of borane to the zirconocene results in one major zirconium-containing product as well as 2 equiv of $MeB(C_6F_5)_2$ (eq 1). The zirconocene product is the bis-dihydridoborate complex $Cp_2Zr[(\mu\text{-}H)_2B(C_6F_5)_2]_2$, **1**, a colorless white solid with poor solubility in aromatic hydrocarbons. Compound **1** is characterized by a relatively sharp triplet in the ^{11}B NMR spectrum ($^1J_{HB}$ = 64 Hz). In the ^1H NMR spectrum, a resonance centered around 0.38 ppm consisting of four broad humps separated by 64 ± 2 Hz (^{11}B, ~80% abundant, $I = ^3/_2$) corroborates the ^{11}B data. After our initial report,[12] we have obtained the solid-state structure of this molecule, confirming its formulation.



(1)

Figure 1 shows an ORTEP diagram of the molecule, while Table 1 gives selected metrical data. The hydrogen atoms bridging boron and zirconium were located on the Fourier difference map and refined in those positions. The molecule crystallizes with 1 equiv of benzene in the lattice. Parameters associated with the Cp ligands and C_6F_5 rings are unremarkable. The dihydridoborate ligands are bidentate, with Zr—H distances of ~2.0 Å and B—H lengths of ~1.25 Å. The Zr—B separations of 2.696(10) and 2.679(10) Å are somewhat longer than the 2.558(4) Å observed for the

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[5] Alkyl and dialkyl boranes can react with late-transition-metal compounds via nonoxidative pathways: (a) Baker, R. T.; Ovenall, E. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Organometallics* **1990**, *9*, 3028. (b) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Marder, T. B. *J. Am. Chem. Soc.* **1995**, *117*, 8777. (c) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175. (d) Hartwig, J. F.; Bhandari, S.; Rablen, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 1839.

[6] In this paper, "alkyl/hydride" exchange refers to an alkyl transfer from the metal to boron with concomitant transfer of hydride from boron to the metal. The term "hydride/alkyl" exchange, on the other hand, refers to the reverse process, i.e., alkyl from boron to metal and hydride from metal to boron.

[7] (a) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661. (b) Lantero, D. R.; Ward, D. L.; Smith, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 9699.

[8] Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2361.

[9] (a) Motry, D. H.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 6615. (b) Sun, Y.; Piers, W. E.; Rettig, S. J. *Organometallics* **1996**, *15*, 4110. (c) Hartwig, J. F.; Muhoro, C. N.; He, X. *J. Am. Chem. Soc.* **1996**, *118*, 10936. (d) Motry, D. H.; Brazil, A. G.; Smith, M. R., III *J. Am. Chem. Soc.* **1997**, *119*, 2743. (e) Sun, Y.; Spence R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132.

[10] Parks, D. J.; Spence, R. E. v. H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809.

[11] Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 345.

[12] Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1230.

Table 1. Selected Bond Distance and Angle Data for Complex 1

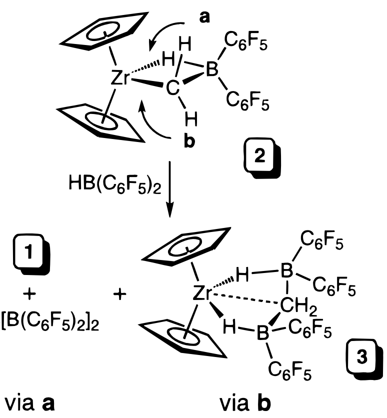
bond lengths (Å)		bond angles (deg)	
Zr(1)−C(25)	2.503(9)	H(1)−Zr(1)−H(2)	50.30
Zr(1)−C(26)	2.506(10)	H(1)−Zr(1)−H(3)	159.38
Zr(1)−C(27)	2.501(8)	H(1)−Zr(1)−H(4)	105.24
Zr(1)−C(28)	2.478(8)	H(2)−Zr(1)−H(3)	109.43
Zr(1)−C(29)	2.450(8)	H(2)−Zr(1)−H(4)	55.44
Zr(1)−C(30)	2.454(9)	H(3)−Zr(1)−H(4)	54.19
Zr(1)−C(31)	2.502(9)		
Zr(1)−C(32)	2.496(10)	H(1)−B(1)−H(2)	91.65
Zr(1)−C(33)	2.497(9)	H(3)−B(2)−H(4)	97.32
Zr(1)−C(34)	2.479(9)	C(1)−B(1)−C(7)	113.5(7)
		C(13)−B(2)−C(19)	113.2(7)
C(1)−B(1)	1.63(1)		
C(7)−B(1)	1.60(1)	C(2)−C(1)−C(6)	113.9(9)
C(13)−B(2)	1.61(1)	C(2)−C(1)−B(1)	119.6(8)
C(19)−B(2)	1.62(1)	C(6)−C(1)−B(1)	126.5(8)
		C(8)−C(7)−C(12)	113.7(9)
Zr(1)−H(1)	2.043	C(8)−C(7)−B(1)	121.9(9)
Zr(1)−H(2)	2.054	C(12)−C(7)−B(1)	124.4(9)
Zr(1)−H(3)	2.177	C(14)−C(13)−C(18)	113.9(9)
Zr(1)−H(4)	1.991	C(14)−C(13)−B(2)	121.0(8)
		C(18)−C(13)−B(2)	125.0(8)
B(1)−H(1)	1.234	C(20)−C(19)−C(24)	114.3(8)
B(1)−H(2)	1.193	C(20)−C(19)−B(2)	122.8(8)
B(2)−H(3)	1.295	C(24)−C(19)−B(2)	122.9(8)
B(2)−H(4)	1.243		
Zr(1)−B(1)	2.696(10)		
Zr(1)−B(2)	2.679(10)		

same parameter in the bidentate[13] borate complex $Cp_2Zr(H)(\eta^2\text{-}H_3BCH_3)$,[14] a reflection of the greater steric congestion in **1**. This crowding is apparent in the close nonbonded approaches between adjacent *ortho* fluorines (F(1)−F(16) = 2.64 Å; F(10)−F(11) = 2.73 Å) and partially accounts for the compound's moderate tolerance of air and moisture.

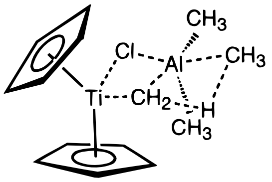
Production of **1** as in eq 1 involves initial alkyl/hydride exchange between B−H and $Zr-CH_3$ to produce a zirconium hydride complex. In the presence of excess borane, the Zr−H moiety is immediately complexed, forming a borate ligand, a process with precedence in transition-metal hydride chemistry.[5a−b,7] The facility of this latter process is demonstrated by the fact that **1** can also be prepared conveniently from the oligomeric dihydride $[Cp_2ZrH_2]_n$ and 2 equiv of $HB(C_6F_5)_2$.

A clean reaction between Cp_2ZrMe_2 and 1 equiv of $HB(C_6F_5)_2$ occurs under slightly different conditions. When carried out in *hexanes* as opposed to toluene, a nearly totally insoluble brick-red solid precipitates from the reaction medium while methane gas evolves (identified by ^1H NMR, 0.16 ppm). As described previously,[12] the product was identified as the $HB(C_6F_5)_2$-complexed zirconocene methylidene compound $Cp_2Zr(\mu\text{-}CH_2)[(\mu\text{-}H)B(C_6F_5)_2]$, **2** (an analogue of $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$, Tebbe's reagent[15]), by completely characterizing its PMe_3 adduct, **2**·PMe_3. Uncomplexed **2** is moderately stable as a solid but decomposes ($t_{1/2} \approx 20$ min) to a variety of products in benzene solution. In addition to reacting with Lewis bases, **2** reacts further with $HB(C_6F_5)_2$ to form mixtures of bis(borate) **1** (via attack from trajectory **a**, Scheme 2) and the intriguing complex $Cp_2Zr(\mu\text{-}H)_2(CH_2(B(C_6F_5)_2)_2)$, **3**, if the borane utilizes approach b. The bonding interactions in **3** have been described in detail elsewhere.[12,16]

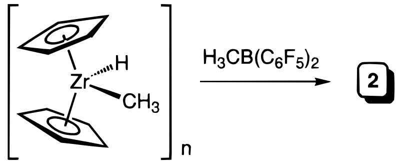
Scheme 2



Since formation of **2** is accompanied by loss of methane, it likely forms from the products of alkyl/hydride exchange in a way similar to that proposed for the formation of Tebbe's reagent.[17] According to this model, Cp_2TiCl_2 reacts with $AlMe_3$ to effect chloro/alkyl exchange and then methane elimination takes place from a six-membered transition state akin to that depicted in **I**. The observation that separately synthesized $[Cp_2Zr(H)Me]_n$ and $MeB(C_6F_5)_2$ react immediately in C_6D_6 to produce **2**[18] along with vigorous evolution of CH_4 (eq 2) supports the notion that alkane elimination takes place after alkyl/hydride exchange in these systems. This process must be extremely facile since the methyl hydrido zirconocene is an almost completely insoluble oligomer in benzene.



I



(2)

As the discussion above demonstrates, the effect of the solvent medium on the result of the reaction between Cp_2ZrMe_2 and $HB(C_6F_5)_2$ is dramatic. Although both outcomes likely involve alkyl/hydride exchange as a first step, subsequent reactivity is quite different, depending on the solvent environment. It is possible that in the aliphatic hydrocarbon medium the two products of exchange (i.e., "$Cp_2Zr(H)Me$" and $MeB(C_6F_5)_2$) are not effectively solvated and do not fully

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[13] Zr−B distances in tridentate borohydride ligands are substantially shorter, e.g. 2.341(3) Å in $Zr(\eta^3\text{-}BH_4)_4$: Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 403.

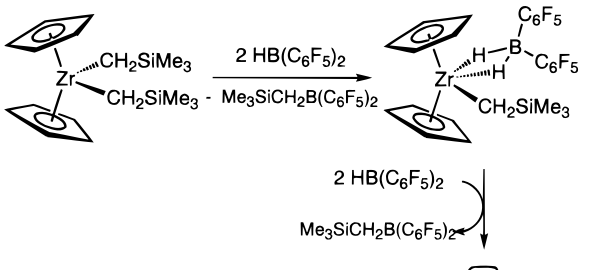
[14] Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339.

[15] (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37.

[16] Radius, U.; Silverio, S. J.; Hoffmann, R.; Gleiter, R. *Organometallics* **1996**, *15*, 3737.

[17] Ott, K. C.; de Boer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

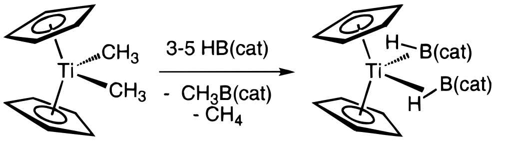
Scheme 3



1

escape from each other after alkyl/hydride exchange. Perhaps the borane reagent $HB(C_6F_5)_2$, which is very poorly hexane soluble, cannot effectively compete with $MeB(C_6F_5)_2$, which is hexane soluble, for the methyl hydrido zirconocene product. Furthermore, the extremely low solubility of product **2** in hexanes essentially precludes its further reactions with $HB(C_6F_5)_2$ (Scheme 3) in this solvent. Likely, each of these factors conspire to allow for the selective formation of **2** over **1** (and/or **3**) in hexane solvent as opposed to aromatic media.

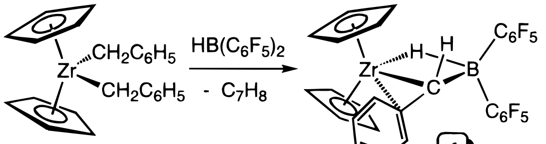
It is worthwhile comparing these results to the recently disclosed chemistry of Hartwig and co-workers who have examined the reactions of dimethyltitanocene with the less electrophilic boranes HB(cat) (cat = catecholate and substituted catecholates). While much of this work was done within the context of titanium-catalyzed alkene hydroboration chemistry,[3a] the boranes react with Cp_2TiMe_2 in the absence of olefins[9c] with loss of methane and MeB(cat), producing remarkable borane σ-complexes of titanocene (eq 3).[19] In the absence of detailed mechanistic studies, it thus appears that in the reactions of these very different boranes with Cp_2TiMe_2, alkyl/hydride exchange is again the initial reaction. However, formation of the σ-complex suggests that in the titanium chemistry, reductive elimination of CH_4 from in-situ-generated "$Cp_2Ti(H)Me$" (either spontaneous or borane-induced) competes effectively with the other possible reaction channels, i.e., borate formation or alkane loss involving MeB(cat). Clearly, subtle effects are at play in the reactions of HBR_2 with $Cp_2M(CH_3)_2$ derivatives.



(3)

The reactions of bulkier bis(trimethylsilylmethyl) zirconocene with $HB(C_6F_5)_2$ provide further support for an alkyl/hydride-exchange−borane-complexation sequence leading to **1** (Scheme 3). In this instance, the alkyl groups can be selectively removed one at a time by treatment of the zirconocene with 2 equiv of borane in sequence. The alkyl borate complex $Cp_2Zr(CH_2SiMe_3)[(\mu-H_2)B(C_6F_5)_2]$ could be isolated or treated with a further dual portion of borane to yield **1**. The alkyl borane byproduct of this reaction, $Me_3SiCH_2B(C_6F_5)_2$, characterized by a broad signal at 2.01 ppm for the methylene protons, was also generated by transmetalation[20] from $Cp_2Zr(CH_2SiMe_3)_2$ and $ClB(C_6F_5)_2$ to confirm its identity.

While the trimethylsilylmethyl group favors the pathway leading to formation of **1**, dibenzyl zirconocene reacts smoothly and cleanly with 1 equiv of $HB(C_6F_5)_2$ in the alkane elimination manifold, yielding the benzylidene analogue of **2** $Cp_2Zr\{\eta^3-CH(C_6H_5)[(\mu-H)B(C_6F_5)_2]\}$, **4**, and 1 equiv of toluene (eq 4). Sonication of the reaction mixture was employed to induce the reaction. Unlike **2**, complex **4** is stable in the absence of Lewis-base donors, due to the internal electronic stabilization provided by the phenyl group on C_α. Multihapto bonding in the benzyl moiety is suggested by the separate resonances observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra for each of the inequivalent phenyl hydrogen and carbon atoms of the C_6H_5 unit. One of the *ortho* C−H units is shifted upfield both in the ^1H (4.25 ppm) and $^{13}C\{^1H\}$ (98.0 ppm) NMR spectra, suggestive of interaction with the metal center.[21] Further, an increased $^1J_{CH}$ coupling constant of 133 ± 2 Hz[22] for the benzylic C−H bond in comparison to the value of 120 Hz measured for the methylene $^1J_{CH}$ coupling constant in $Cp_2Zr(CH_2C_6H_5)_2$ and those for normal sp^3-hybridized carbon centers[23] is indicative of a distorted geometry about this carbon atom. A broad resonance at −2.2 ppm in the ^1H NMR spectrum confirmed the presence of a B−(μ-H)−M group, while the chemical shift of the boron atom in the ^{11}B NMR spectrum (−16.6 ppm, whh = 190 Hz) is diagnostic of a four-coordinate boron center with anionic character.[24]



(4)

4

The solid-state structure of **4** was determined by X-ray analysis and confirmed many of the features deduced from the spectroscopic data; Figure 2 shows an ORTEP diagram of the compound, while Table 2 gives pertinent bond distance and angle data. In general terms, **4** may be formulated as a zwitterionic zirconocene[25] in which the borate counterion is attached covalently to the α-carbon of the alkyl ligand. The

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(18) As identified by its characteristic ^1H NMR spectrum.[12] (^1H NMR: 5.70 ppm, 10H; 5.30 ppm, 2H).

(19) See also: Muhoro, C. N.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1510.

(20) (a) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979. (b) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*, 4425. (c) Cole, T. E.; Quintanilla, R.; Rodewald, S. *Organometallics* **1991**, *10*, 3777. (d) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

(21) Addition of a small amount of THF to benzene solutions of **4** results in formation of an adduct in which the phenyl resonances for the benzylidene moiety return to a "normal" pattern. Although we have not fully characterized **4**·THF, it is apparent that the THF donor is able to displace the multihapto benzylidene ligand.

(22) (a) Because C1 is bonded to a boron atom, its resonance in the ^{13}C NMR spectrum was broad; measurement of the C1−H coupling constant was accomplished using the HMQC pulse sequence with gated decoupling. (b) Robinson V. J.; Bain, A. D. *Magn. Reson. Chem.* **1993**, *31*, 865. (c) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.

(23) This $^1J_{CH}$ value is similar to that found in cyclobutane: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972. Cf. also the $^1J_{CH}$ value of 120 Hz measured for the methylene C−H bonds in $Cp_2Zr(CH_2C_6H_5)_2$.

(24) Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2.

(25) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13.

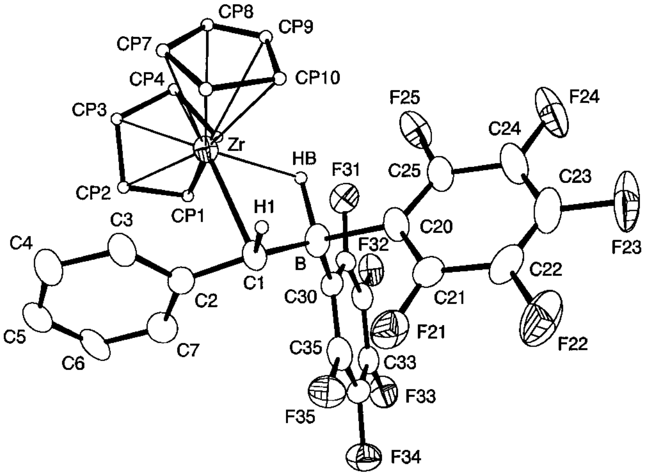


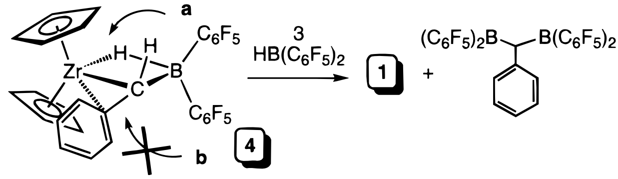
Figure 2. ORTEP drawing of the molecular structure of **4**.

Table 2. Selected Bond Distance and Angle Data for Complex 4

bond lengths (Å)		bond angles (deg)	
Zr−Cp1	2.509(8)	Zr−C1−C2	82.2(6)
Zr−Cp2	2.516(8)	Zr−C1−B	87.6(6)
Zr−Cp3	2.492(9)	C2−C1−B	133.5(8)
Zr−Cp4	2.526(10)	C1−C2−C3	117.3(9)
Zr−Cp5	2.506(9)	C1−C2−C7	126.3(9)
Zr−Cp6	2.518(12)	C3−C2−C7	116.2(8)
Zr−Cp7	2.477(13)	C2−C3−C4	122.1(9)
Zr−Cp8	2.413(17)	C3−C4−C5	119.0(10)
Zr−Cp9	2.492(22)	C4−C5−C6	118.5(10)
Zr−Cp10	2.532(15)	C5−C6−C7	122.9(10)
		C2−C7−C6	121.2(9)
Zr−C1	2.341(10)	C1−B−C20	113.8(8)
C1−C2	1.456(12)	C1−B−C30	124.0(9)
C1−B	1.545(15)	C20−B−C30	107.7(8)
C20−B	1.661(15)	Zr−HB−B	107(4)
C30−B	1.612(15)	Cp_{cent}-Zr-Cp_{cent}	127.10(5)
Zr−HB	2.02(7)		
B−HB	1.35(8)		
C2−C3	1.408(14)		
C2−C7	1.421(15)		
C3−C4	1.416(15)		
C4−C5	1.411(18)		
C5−C6	1.372(18)		
C6−C7	1.365(16)		

electron-deficient zirconium center gains electron density from a μ-hydride ligand shared with the boron center and the multihapto benzyl unit. The Zr−C1 distance of 2.341(10) Å is typical of a normal Zr−C_{alkyl} linkage,[26] and the Zr−C2 length of 2.583 Å, while longer, is within the range (2.627−2.648 Å) of M−C_{ipso} lengths observed in known η^2-benzyl complexes of zirconium.[27] Although the Zr−C3 distance is longer still at 2.737 Å, the perturbations in the chemical shifts of the C3−H unit discussed above argue for an η^3-bonding description. The geometery about C1 is indeed distorted, as evidenced by the acute Zr−C1−C2 and Zr−C1−B angles of 82.2(6)° and 87.6(6)°, respectively. The B−C1−C2 angle is 133.5(8)° because C2 dips below the plane of the metallocene which bisects the two Cp rings. Indeed, the centroid of C1−C2−C3 essentially lies in this plane, a further point in favor of an η^3-benzyl bonding description.

The multihapto benzylidene unit affects the reactivity of **4** with further equivalents of $HB(C_6F_5)_2$. By blocking the other face of the alkylidene unit, the coordinated phenyl group effectively precludes attack of the borane via approach b (eq 5) and formation of the benzylidene analogue of **3**. Consequently, the only zirconium product observed in this reaction is **1**. The diboryl toluene compound shown in eq 5 is presumed to be the other major product, on the basis of its NMR spectra (see Experimental Section), particularly the very broad[28] (whh ≈ 850 Hz) ^{11}B chemical shift of 74.0 ppm diagnostic for neutral borane centers.[24]



(5)

B. Mechanistic Studies. The poor solubility of $HB(C_6F_5)_2$ in solvents it does not react with tends to preclude detailed kinetic studies of these reactions. The stoichiometric synthetic studies described above, particularly those involving Cp_2ZrMe_2, point to an initial exchange reaction followed by competing processes leading either to borate **1** or Tebbe-type compounds such as **2** and **4**. While formation of borate ligands from metal hydrides and $HB(C_6F_5)_2$ seems a straightforward process, the nature of the alkyl/hydride exchange and the alkane elimination step leading to **2** and **4** are unclear. Experiments making use of deuterium labeling provide fundamental insights into these processes.

I. Alkyl/Hydride Exchange. 1,2-Dideuterated neohexyl groups have been used extensively as probes for determining the character of a reaction by observing the effect of the transformation on the stereochemistry of this group.[29] Through hydrozirconation,[30] organozirconium derivatives of such probes are readily prepared with >95% diastereospecificity.[31] We, thus, prepared *erythro*-$Cp_2Zr[CH(D)CH(D)\text{-}t\text{-}C_4H_9](Cl)$ as a model substrate for the alkyl/hydride exchange reaction with $HB(C_6F_5)_2$. This compound reacts rapidly with an excess (2.5−3 equiv) of $HB(C_6F_5)_2$ to give monoborate species $Cp_2Zr[(\mu\text{-}H)_2B(C_6F_5)_2]Cl$, **5**, as the zirconium-containing product. Compound **5**'s identity was confirmed via its independent synthesis from $[Cp_2Zr(Cl)H]_n$ (Schwartz's reagent) and $HB(C_6F_5)_2$ (see Experimental Section). As the $^1H\{^2H\}$ NMR spectra in Figure 3 demonstrate, the stereochemistry associated with the 1,2-d_2-neohexyl probe in the zirconium starting material (**A**) undergoes clean inversion (>95%) to yield *threo*-$(C_6F_5)_2B{-}CH(D)$-

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[26] (a) Hunter, W. E.; Hrncir, D. C.; Vann Bynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

[27] (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (c) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (d) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Abdul Malik, K. M. *Organometallics* **1994**, *13*, 2235.

[28] Due to the quadrupolar nature of the boron nucleus, extremely broad ^{11}B resonances are characteristic of 1,1-diboryl compounds.

[29] (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Igau, A.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2327. (c) Piers, W. E. *J. Chem. Soc. Chem. Commun.* **1994**, 309.

[30] Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 8, p 667.

[31] Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

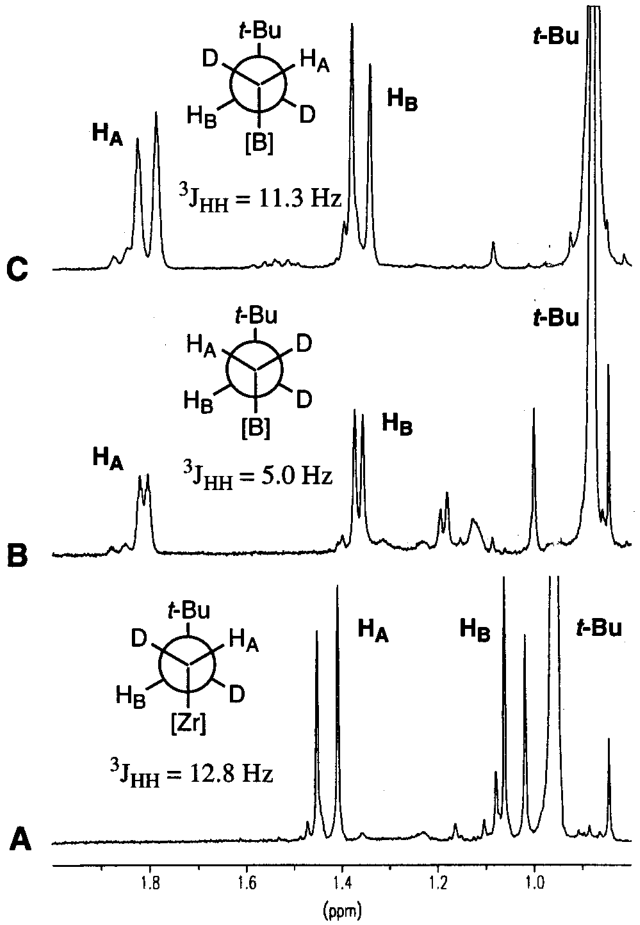
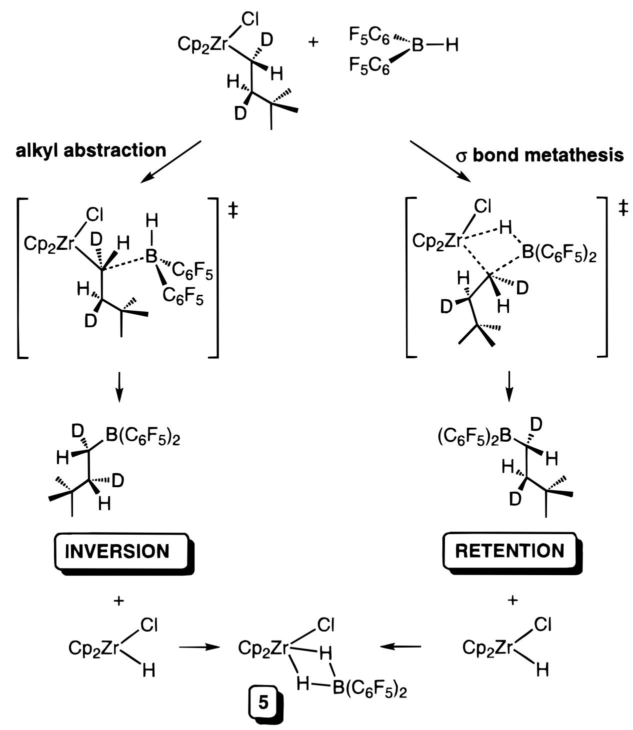


Figure 3. (A) Partial ^1H NMR spectrum of *erythro*-$Cp_2Zr[CH(D)CH(D)$-*t*-$C_4H_9](Cl)$. (B) Partial ^1H NMR spectrum of the product mixture obtained from reaction of *erythro*-$Cp_2Zr[CH(D)CH(D)$-*t*-$C_4H_9](Cl)$ and excess $HB(C_6F_5)_2$. (C) Partial ^1H NMR spectrum of *erythro*-$(C_6F_5)_2B-CH(D)CH(D)$-*t*-C_4H_9 formed from reaction of $HB(C_6F_5)_2$ and *E*-1-d_1-3,3-dimethyl-1-butene. All spectra were recorded at 300 MHz.

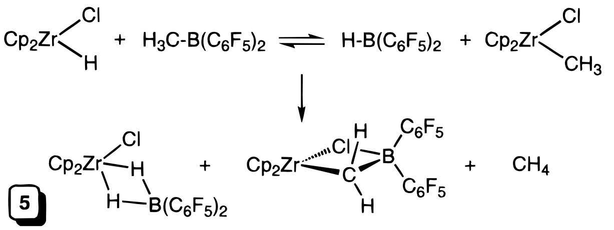
$CH(D)$-*t*-C_4H_9 ($^3J_{HH}$ = 5.00 ± 0.05 Hz) as the boron exchange product (**B**). For comparison, the top trace in Figure 3 (**C**) is that of *erythro*-$(C_6F_5)_2B-CH(D)CH(D)$-*t*-C_4H_9 ($^3J_{HH}$ = 11.30 ± 0.05 Hz), independently generated from *E*-1-d_1-3,3-dimethyl-1-butene and $DB(C_6F_5)_2$.

This result has significant mechanistic implications for the alkyl/hydride exchange step in these systems. A concerted, four-centered σBM-type mechanism would be expected to result in retention of configuration in the probe (Scheme 4). The observation of inversion is suggestive of a stepwise process in which the borane abstracts via backside attack of the alkyl group and replaces it with a hydride ligand from the resulting borate counterion, as depicted on the left-hand side of Scheme 4. Abstraction of alkide groups from alkyl zirconocenes by $B(C_6F_5)_3$ is a well-known method for generating metallocene cations.[27d,32] The fact that abstraction using $HB(C_6F_5)_2$ results in an inversion of stereochemistry at the abstracted carbon atom supports electrophilic attack on the back lobe of the Zr–C σ bonding orbital instead of in the internuclear region of this orbital, two possibilities which have been suggested for this process.[32] If this mechanism for alkyl/hydride exchange is general, there are also ramifications of this result vis-à-vis early-transition-metal catalyzed hydroborations, particularly asymmetric reductions where the stereochemistry at C_α is at issue. It should be noted that for less electrophilic boranes the alkide abstraction pathway may be disfavored and the concerted σBM pathway dominant; this is a question that remains to be addressed.

Scheme 4



Scheme 5



Alkide abstraction from Cp_2ZrMe_2 and derivatives using $B(C_6F_5)_3$ has been shown to be rapidly reversible;[33] not surprisingly, therefore, the alkyl/hydride exchange reactions involving $HB(C_6F_5)_2$ are also reversible. When $[Cp_2Zr(Cl)H]_n$ is treated with $H_3CB(C_6F_5)_2$, a product mixture is observed which can only form after hydride/alkyl exchange, which is the reverse of alkyl/hydride interchange[6] (Scheme 5). For example, the primary zirconium-containing product in this reaction is **5**, which forms from Schwartz's reagent and the $HB(C_6F_5)_2$ generated from hydride/alkyl exchange. A second product, whose appearance coincides with the elimination of CH_4, we assign as the chloride-bridged analogue of **2**, i.e., $[Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}Cl)B(C_6F_5)_2]$, on the basis of its ^1H (5.75 ppm, 10H; 2.97 ppm 2H) and ^{11}B (−4.0 ppm, cf. −1.1 ppm for **2**) NMR spectra. We have

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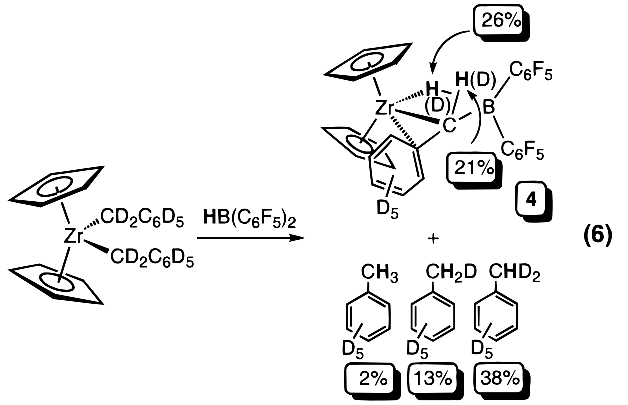
(32) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(33) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128.

not been able to synthesize this compound independently, and thus, this assignment is tentative. The presence of **5** and CH_4 in the product mixture of this reaction, however, is strong evidence for an antipodal hydride/alkyl exchange and shows that these processes are reversible under mild conditions. The rapid reversibility of this exchange is crucial for explaining the observed H/D scrambling phenomenon described in the next section.

II. H/D Scrambling. Crossover experiments aimed at probing the nature of the alkane elimination step were performed utilizing specifically deuterated reagents. The results of these experiments failed to address this point conclusively (vide infra) but revealed instead a H/D scrambling process which implies another level of complexity in the reactions of Cp_2ZrR_2 with $HB(C_6F_5)_2$. Reaction of $HB(C_6F_5)_2$ with $Cp_2Zr(CD_2C_6D_5)_2$ gives a complex mixture of isotopomers (eq 6), with the proton label distributed randomly among all possible locations except the phenyl group.[34] Significantly, all



three possible proton isotopomers of toluene are observed in the product mixture,[35] as demonstrated by the partial 400 MHz ^1H NMR spectrum shown in Figure 4 (toluene methyl region).[36] This observation leads to the conclusion that the borane engages in multiple contacts with the metallocene prior to alkane elimination and generation of products. Consistent with this is the observation that when $Cp_2Zr(CD_2C_6D_5)_2$ is treated with only 0.5 equiv of $HB(C_6F_5)_2$, a detectable amount of the proton label is incorporated into the benzylic positions (δ 1.82 ppm) of unreacted $Cp_2Zr(CD_2C_6D_5)_2$. In a separate experiment, it was determined that the benzylic protons of free toluene do not exchange (at room temperature or at 50 °C) with any of the protons of **4** by treating d_7-**4** with perproteo toluene. Thus, the protons are not scrambled in some process involving free toluene. Finally, the inverse experiment, i.e., the reaction of $Cp_2Zr(CH_2C_6H_5)_2$ with $DB(C_6F_5)_2$, yields similar results in that all benzylic positions plus the bridging hydride contain deuterium, as determined by $^2H\{^1H\}$ NMR spectroscopy.

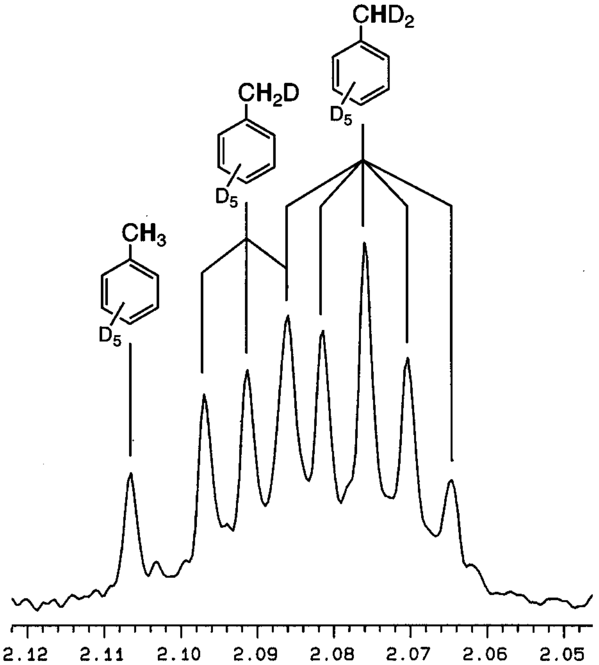


Figure 4. Partial 400 MHz ^1H NMR spectrum (toluene methyl region) of the product mixture formed in the reaction of $Cp_2Zr(CD_2C_6D_5)_2$ and $HB(C_6F_5)_2$.

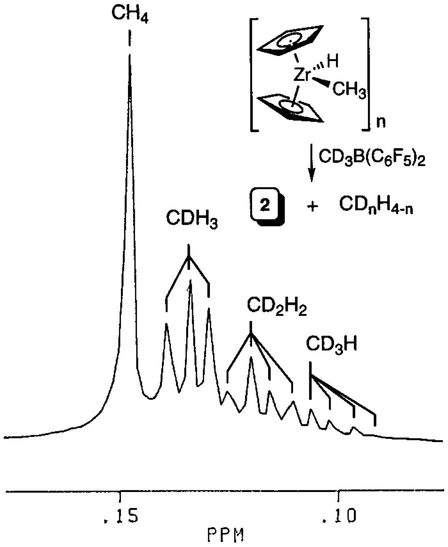


Figure 5. Partial 400 MHz ^1H NMR spectrum of the reaction between $[Cp_2Zr(H)Me]_n$ and $CD_3B(C_6F_5)_2$ showing the mixture of methane isotopomers produced. Portions of the mulitplets due to the CD_2H_2 (5 lines) and CD_3H (7 lines) isotopomers are obscured due to overlapping.

Scrambling of the deuterium label is also observed when one starts with the products of alkyl/hydride exchange; thus, in the reaction of $[Cp_2Zr(H)Me]_n$ with $CD_3B(C_6F_5)_2$, the full range of proton isotopomers of methane is produced (Figure 5). While the CDH_3 and CD_3H products may be accounted for by "simple" methane elimination, the presence of CH_4 and CD_2H_2 can only be explained by invoking H/D scrambling and multiple contacts between the two reagents. On the surface, this experiment suggests that the scrambling event occurs in the alkane elimination step *after* alkyl/hydride exchange; however, the facile reversibility of the alkyl/hydride and alkyl/alkyl exchanges must be considered before reaching this conclusion.

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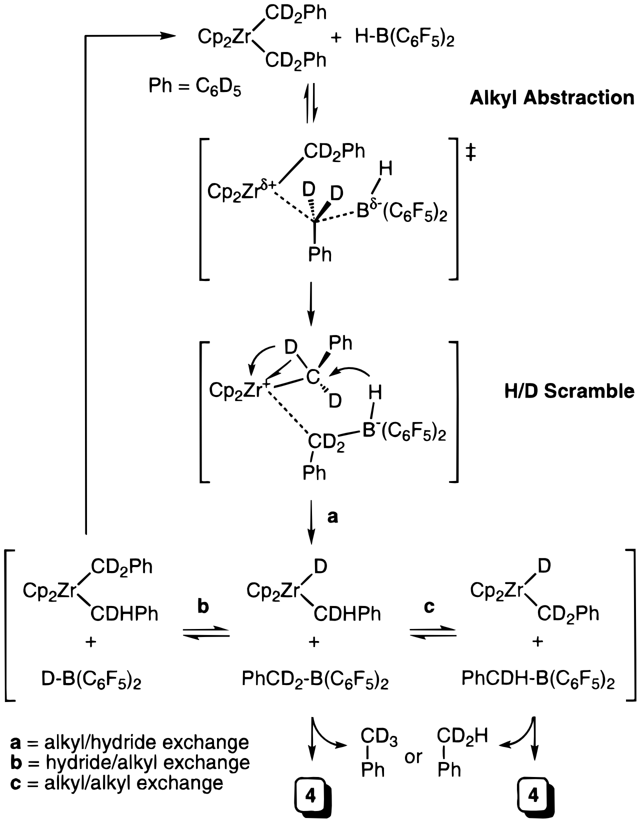
[34] (a) H/D exchange between the alkyl groups and the Cp ligands of Cp_2ZrR_2 compounds occurs at higher temperatures (≈165 °C).[34b] In none of the experiments described do we observe involvement of the Cp ligands. (b) Razuvaev, G. A.; Mar'in, V. P.; Andrianov, Y. A. *J. Organomet. Chem.* **1979**, *174*, 67.

[35] Toluene-d_8 may also have been present, but no attempt was made to detect and quantify this isotopomer.

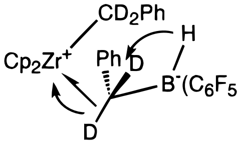
[36] The identity of $CHD_2C_6D_5$ was confirmed by its separate synthesis from $KCD_2C_6D_5$ and H_2O; quenching $KCH_2C_6H_5$ with D_2O gave an essentially identical pattern as that observed for $CH_2DC_6D_5$.

Scheme 6



A plausible explanation for these observations is depicted in Scheme 6, using the experiment of eq 6 as an example. As the benzyl group is abstracted from the zirconium center, the developing cationic center is stabilized by an α-agostic interaction. The hydridoborate counterion does not completely dissociate in this model but, instead, nucleophilically attacks the α-carbon atom; in so doing, the hydride displaces the agostic deuteron at C_α and alkyl/hydride exchange (a) is complete along with one H/D scrambling event. Although nucleophilic attack of an alkyl ligand at C_α is rare, halides have been shown to do this in some systems.[29a,37] In this case, the alkyl group is rendered susceptible to attack by the developing α-agostic interaction, and thus, another way to view this process is as nucleophilic attack on an incipient alkylidene ligand, which has ample precedent.[38] Of course, complete α elimination to yield a cationic alkylidene hydride is precluded in this system since the zirconium center is of d^0 electron configuration. As a fully concerted process, however, the H/D exchange event is not unlike the modified Green–Rooney mechanism for the insertion of olefins into d^0 metal–carbon bonds,[39] in which an α-agostic interaction stablizes the transition state of olefin insertion without undergoing complete elimination.

Consideration was also given to a H/D scrambling mechanism involving hydride transfer from the newly formed hydridoborate to the abstracted carbon with concomitant loss of a deuteron to the metal center, i.e. **II**. This process resembles internal hydride and alkyl[40] transfers observed in α-halo boronic esters. Two observations mitigate against such a mechanism for the H/D scrambling observed in the reactions described here. First, no deuterium incorporation into the $MeB(C_6F_5)_2$ product is observed when $Cp_2Zr(CH_3)Cl$ is treated with an excess of $DB(C_6F_5)_2$. Second, if a mechanism involving **II** was operative, the experiments described above involving *erythro*-$Cp_2Zr[CH(D)CH(D)$-t-$C_4H_9](Cl)$ would have led to at least some $(C_6F_5)_2B-CH_2CH(D)$-t-C_4H_9, which was not observed (see Figure 3). Thus, when the other metallocene girdle ligand is not an alkyl, as in these experiments where L = Cl, scrambling cannot occur and the alkyl/hydride exchange is completed by direct transfer of the borate hydride to the zirconium.[41]



II

Referring back to Scheme 6, after alkyl/hydride exchange and one H/D scrambling event, the initial product mixture of isotopomers can undergo irreversible elimination of toluene (in this case the $PhCD_3$ or $PhCD_2H$ isotopomers) or one of two exchanges: hydride/alkyl exchange (path b) or alkyl/alkyl exchange (path c). The latter event leads to the same mixture of toluene isotopomers upon elimination, but the former leads to dibenzyl zirconocene with a proton in the benzylic position which was formerly fully deuterated. This $Cp_2Zr(CDHPh)(CD_2Ph)$ isotopomer is now able to reenter the process (top of the Scheme 6) to interact with another equivalent of $HB(C_6F_5)_2$, accounting for the observation of $PhCDH_2$ and $PhCH_3$ in the mixture of toluenes produced. Note that entry into the process can also occur at the bottom of the Scheme 6, accommodat-

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(37) (a) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S.; Topich, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1606. (b) Magnuson, R. H.; Halpern, J.; Levitin, I. Y.; Vol'pin, M. E. *J. Chem. Soc. Chem. Commun.* **1978**, 44.

(38) Casey, C. P.; Miles, W. M. *J. Organomet. Chem.* **1983**, *254*, 333.

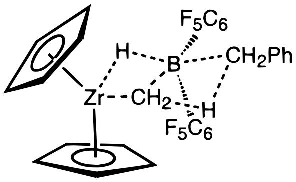
(39) (a) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (c) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (c) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (e) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

(40) (a) Matteson, D. S.; Kandil, A. A.; Soundararajan, R. *J. Am. Chem. Soc.* **1990**, *112*, 3964. (b) Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (c) Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsai, D. J. *Organometallics* **1983**, *2*, 1536.

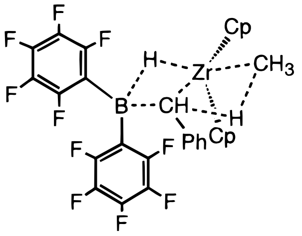
(41) A third possibility involving proton scrambling into the α position of the alkyl ligand in the alkyl hydride product of exchange (i.e., $Cp_2Zr(CD_2Ph)H$) via a σ-complex was proposed as the most likely mode of scrambling by a referee. We also considered this but rejected the possibility on the basis of the following considerations. While precedent for this mode of scrambling certainly exists, in the systems in which it has been observed,[40a,b] reductive elimination of RH is highly endothermic and scrambling occurs only at or near the high temperatures required for loss of RH. In the absence of Lewis bases,[40c] this scenario would also be the case for $Cp_2Zr(R)H$ and none of the experiments in which we observe facile scrambling were performed anywhere near the temperatures which would be required to induce reductive elimination of alkane from $Cp_2Zr(R)H$. Furthermore, in cases where selectively deuterated $Cp_2Zr(R)X$ (X = H or D) have been prepared,[40c,d,e] deuterium scrambling of the type that would require the intermediacy of a σ-complex would appear to be very slow at room temperature. (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172. (c) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687. (d) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246. (e) Gell, K. I.; Postin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

ing the scrambling observed in the reaction of $[Cp_2Zr(H)Me]_n$ with $CD_3B(C_6F_5)_2$. In this case, only one H/D scrambling event is necessary to allow for production of CH_4 and CH_2D_2 in the product mixture.

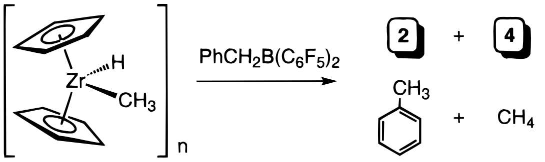
III. Alkane Elimination. The loss of alkane from $Cp_2Zr(H)R$ and $RB(C_6F_5)_2$ can occur via a six-membered transition state (**III**) similar to what has been proposed for the alkane elimination step in the formation of Tebbe's reagent (**I** above).[17] An alternative view of this elimination would invoke deprotonation of the boron methyl group as in **IV**, not unreasonable given the ability of boron to stabilize α-carbanions.[42] To distinguish between these two possibilities, the reaction of in-situ-generated $PhCH_2B(C_6F_5)_2$ with $[Cp_2Zr(H)Me]_n$ was carried out; elimination through **III** would be expected to produce toluene, while elimination via **IV** would result in the expulsion of methane. In fact, as shown in eq 7, this experiment does not provide a definitive result since both methane and toluene are observed as products, along with corresponding amounts of **2** and **4**. This could mean that both transition states are accessible, but in light of the facile alkyl/alkyl exchange in these systems (see Scheme 6), it seems likely that equilibration occurs before elimination from either **III** or **IV**. Thus, these experiments cannot distinguish between the two possibilities, although a significant preponderance of **4** over **2** in the product mixture (~3:1) points toward **IV** as the preferred transition state for elimination.



III



IV



(7)

Summary and Concluding Remarks

The reactions of the highly electrophilic borane $HB(C_6F_5)_2$ with even the simplest of the bent metallocenes, Cp_2ZrR_2, are striking for their complexity and variability with respect to changes in reaction conditions and the nature of R. We have shown that reversible alkyl/hydride exchange dominates in the initial stages of these reactions and that the intimate mechanism of this process involves alkide abstraction followed by replacement with a hydride from the resulting hydridoborate counterion. The latter can occur directly to the metal or via a H/D scrambling nucleophilic attack at the α-carbon of the second alkyl group on the metal, if present. When excess borane is present, Zr−H functions are trapped to form very stable hydridoborate complexes. In the absence of borane, the products of alkyl/hydride exchange, namely "$Cp_2Zr(H)R$)" and $RB(C_6F_5)_2$, react together to eliminate alkane and produce compounds that are essentially $HB(C_6F_5)_2$-complexed alkylidenes of zirconocene.

The alkide abstraction pathway represents a distinct nonoxidative mechanism for B−C bond formation in the reaction of metal carbon bonds with a secondary boranes. The other previously observed mechanism, namely σ-bond metathesis,[4,5d] is fundamentally different in terms of the effect on the stereochemistry of the α-carbon. It is, therefore, crucial to determine which mechanism is operative in this step for catalyzed hydroborations where the stereochemistry at C_α is at issue; this study helps to delineate the factors which cause one mechanism to dominate over the other. On the basis of this work, it appears that less electrophilic boranes engage in concerted, four-centered σ-bond metathesis and more electrophilic boranes, such as $HB(C_6F_5)_2$, utilize alkide abstraction as the primary mode of B−C bond formation. Caution must be taken in applying this generalization, since the Lewis acidity of the conjugate acid of $L_nM{-}R$ (i.e., L_nM^+) will likely also influence the favorability of each pathway. Further studies are necessary to address these questions in detail.

Experimental Section

General. General procedures have been described in detail elsewhere.[43] Routinely employed solvents (hexanes, toluene, and THF) were purified using the Grubbs purification system.[44] For the NMR data reported for new compounds, $^{19}F-^{19}F$ couplings are not given nor are the ^{13}C data for the pentafluorophenyl groups; the former were in all cases unremarkable, while the latter were not always detectable. The reagents Cp_2ZrCl_2, PMe_3, and $[Cp_2Zr(H,D)Cl]_n$ were purchased from Aldrich and used as received. Literature methods were used to prepare $[Cp_2ZrH_2]_n$,[45] $[Cp_2Zr(H)Me]_n$,[46] Cp_2ZrMe_2,[26a] $Cp_2Zr(CH_2SiMe_3)_2$,[47] $Cp_2Zr(CH_2C_6H_5)_2$,[48] $KCX_2C_6X_5$[49] (X = H, D), $XB(C_6F_5)_2$ (X = H/D,[10] Cl[50]), and *erythro*-$Cp_2Zr[CH(D)CH(D)\text{-}t\text{-}C_4H_9](Cl)$[31] and compounds **1**, **2**, **2**·PMe_3, and **3**.[12]

Preparation of $Cp_2Zr\{\eta^3\text{-}CH(C_6H_5)[(\mu\text{-}H)B(C_6F_5)_2]\}$, 4. To a flask containing $Cp_2Zr(CH_2C_6H_5)_2$ (403 mg, 1 mmol) and $HB(C_6F_5)_2$ (346 mg, 1 mmol) was added dry hexane (30 mL). The reaction suspension was sonicated for 20 min and then stirred for a further 1 h at room temperature. Over this time the yellow zirconocene starting material was replaced by an orange precipitate. This solid was isolated by filtration, washed with hexane, and pumped dry under vacuum. The

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yield of compound **4** was 602 mg, 0.92 mmol, 92%. ^{1}H NMR (C_6D_6): 7.14 (m, 1H, $C_6\mathit{H}_5$), 6.86 (m, 1H, $C_6\mathit{H}_5$), 6.68 (m, 2H, $C_6\mathit{H}_5$), 5.03 (s, 5H, $C_5\mathit{H}_5$), 4.43 (s, 5H, $C_5\mathit{H}_5$), 4.25 (m, 1H, $C_6\mathit{H}_5$), 2.43 (s, 1H, PhC*H*), −2.2 (br, 1H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6): 139.2 (*ipso*), 138.5, 133.3, 129.2, 123.8, 98.0 (*C*$_6$H$_5$), 109.4, 106.9 (*C*$_5$H$_5$), 69 (br, Ph*C*H). ^{11}B{^{1}H} NMR (C_6D_6): −16.6. ^{19}F{^{1}H} NMR (C_6D_6) −128.7 (1F), −130.8 (3F), −159.0 (1F), −159.9 (1F), −164.4 (1F), −164.6 (1F), −164.9 (2F). Anal. Calcd for $C_{29}H_{17}F_{10}ZrB$: C, 52.98; H, 2.61. Found: C, 53.33; H, 2.65. IR (KBr, Nujol, cm^{-1}): 1638 m, 1592 w, 1514 s, 1339 w, 1283 w, 1111 w, 1091 s, 1016 w, 972 s, 895 w, 824 s, 812 s, 766 m.

Reaction of 4 with $HB(C_6F_5)_2$. Compound **4** (10 mg, 0.015 mmol) was loaded into a 5 mm NMR tube along with $HB(C_6F_5)_2$ (16 mg, 0.045 mmol) and C_6D_6 (0.7 mL). The tube was capped, shaken, and briefly heated (~50 °C) until the contents of the tube were dissolved. The tube was gently heated for a further 10 min, until production of **1** was complete. The C_6D_6 was removed in vacuo, and the solid was extracted with 2 × 2 mL of hexanes. Removal of the hexanes and redissolution of the resulting solid in C_6D_6 gave a sample enriched in the borane coproduct, $C_6H_5CH[B(C_6F_5)_2]_2$. ^{1}H NMR (C_6D_6): 6.96 (m, 2H), 6.84 (m, 2H), 6.77 (m, 1H), 4.72 (br s, 1H). ^{13}C{^{1}H} NMR (partial, *C*$_6$F$_5$ resonances not reported): 137.5, 130.0, 129.3, 127.6 (*C*$_6$H$_5$), 59.8 (*C*HB$_2$, a DEPT experiment confirms the presence of one hydrogen atom bonded to this carbon). ^{11}B{^{1}H} NMR: 74.0 (whh ≈ 850 Hz). ^{19}F{^{1}H} NMR (C_6D_6): −131.2, −147.7, −162.3.

Reaction of $Cp_2Zr(CD_2C_6D_5)_2$ with *n* Equivalents of $HB(C_6F_5)_2$. $Cp_2Zr(CD_2C_6D_5)_2$ (12 mg, 0.03 mmol) and $HB(C_6F_5)_2$ (10 mg, 0.03 mmol or 5 mg, 0.015 mmol) were loaded into a 5 mm NMR tube. C_6D_6 was added, and the tube was immediately capped and shaken. A rapid color change ensued, and the sample was assayed by ^{1}H NMR spectroscopy. An analogous procedure using $Cp_2Zr(CH_2C_6H_5)_2$, $DB(C_6F_5)_2$, and C_6H_6 was also performed and analyzed via ^{2}H{^{1}H} NMR spectroscopy.

Preparation of $Cp_2Zr(CH_2SiMe_3)[(\mu\text{-}H_2)B(C_6F_5)_2]$. To an evacuated flask at −78 °C containing $Cp_2Zr(CH_2SiMe_3)_2$ (380 mg, 0.96 mmol) and $HB(C_6F_5)_2$ (666 mg, 1.92 mmol) was condensed hexane (20 mL). The reaction was warmed to room temperature and then sonicated for 1 h. During this time, a white precipitate formed, which was isolated by filtration, washed with a little hexane, and pumped dry under vacuum. The yield was 509 mg, 0.78 mmol, 81%. ^{1}H NMR (C_6D_6): 5.52 (s, 10H, $C_5\mathit{H}_5$), 0.93 (s, 2H, C*H*$_2$Si), 0.01 (s, 9H, SiC*H*$_3$), −0.9 (br, 2H, *μ-H*). ^{13}C{^{1}H} NMR (C_6D_6): 110.8 (Cp), 44.9 (*C*H$_2$), 3.3 (Si*C*H$_3$). ^{11}B NMR (C_6D_6): −8.7 (t, $^{1}J_{BH}$ = 67 Hz).^{19}F{^{1}H} NMR (C_6D_6): −133.7, −158.3, 164.0. Anal. Calcd for $C_{26}H_{23}F_{10}ZrBSi$: C, 47.64; H, 3.54. Found: C, 49.61; H, 3.54. IR (KBr, Nujol, cm^{-1}): 2190 w (br), 2115 w (br), 2038 w (br), 1644 m, 1515 s, 1334 w, 1286 w, 1112 m, 1098 m, 1015 w, 960 s, 852 m, 816 s.

Preparation of $MeB(C_6F_5)_2$. To a solution of Cp_2ZrMe_2 (252 mg, 1 mmol) in toluene (10 mL) was added a toluene solution of $ClB(C_6F_5)_2$ (760 mg, 2 mmol). The reaction was stirred for 1 h at room temperature and filtered to remove precipitated Cp_2ZrCl_2. The toluene was removed in vacuo, and the residue was transferred to a sublimator equipped with a water-cooled probe. Sublimation at ~30−40 °C under high vacuum yielded 552 mg (77%) of pure $MeB(C_6F_5)_2$. This material had NMR spectroscopic data identical to that reported by Marks et al.[14c]

Generation of $C_6H_5CH_2B(C_6F_5)_2$ and $Me_3SiCH_2B(C_6F_5)_2$. $Cp_2Zr(CH_2Ph)_2$ (9 mg, 0.02 mmol) was loaded into a 5 mm NMR tube along with $ClB(C_6F_5)_2$ (18 mg, 0.04 mmol). Benzene-*d*$_6$ was added, and the tube was capped and shaken. Undissolved material was centrifuged to the top of the tube, and the ^{1}H NMR spectrum was recorded. The presence of Cp_2ZrCl_2 was noted. $PhCH_2B(C_6F_5)_2$. ^{1}H NMR: 6.90−7.05 (m, $C_6\mathit{H}_5$, 5H), 3.27 (br m, BC*H*$_2$, 2H). ^{13}C{^{1}H} NMR: 137.4, 129.3, 129.0, 126.4 (*C*$_6$H$_5$), 39.1 (B*C*H$_2$). An identical procedure using $Cp_2Zr(CH_2SiMe_3)_2$ gave a solution of $Me_3SiCH_2B(C_6F_5)_2$. ^{1}H NMR: 2.01 (s, C*H*$_2$, 2H), −0.08 (s, SiC*H*$_3$, 9H).

Table 3. Summary of Data Collection and Structure Refinement Details for and 1 and 4

	1	**4**
formula	$C_{41}H_{22}B_2F_{20}Zr$	$C_{29}H_{17}BF_{10}Zr$
fw	1007.43	657.46
cryst syst	monoclinic	monoclinic
a, Å	14.042(5)	13.9296(15)
b, Å	18.776(5)	8.5508(9)
c, Å	15.567(4)	21.5196(18)
β, deg	105.46(2)	94.13(3)
V, Å^3	3995(1)	2556.5(4)
space group	$P2_1/n$	$P2_1/c$
Z	4	4
F(000)	1992.00	1304
d_{calc}, mg m^{-3}	1.691	1.71
μ, mm^{-1}	0.404	0.51
R1	0.046	0.051
R_w	0.045	0.047
gof	2.18	2.44

Reaction of $[Cp_2Zr(H)Me]_n$ with $MeB(C_6F_5)_2$. $[Cp_2Zr(H)Me]_n$ (15 mg, 0.06 mmol) was loaded into a 5 mm NMR tube and covered with ~0.3 mL of C_6D_6. A solution of $MeB(C_6F_5)_2$ (23 mg, 0.06 mmol) in C_6D_6 (0.3 mL) was layered onto this suspension; the tube was quickly capped and shaken. An immediate color change to that characteristic of **2** was observed along with gas evolution. Immediate ^{1}H NMR analysis (prior to decomposition of **2**) revealed the presence of methane along with **2** as the major metallocene product (~80%). Reaction using $CD_3B(C_6F_5)_2$ was carried out in an analogous fashion.

Reaction of Cp_2Zr(*erythro*-CH(D)CH(D)CMe$_3$)Cl with $HB(C_6F_5)_2$. Cp_2Zr(*erythro*-CH(D)CH(D)CMe$_3$)Cl (11 mg, 0.03 mmol) was loaded into a 5 mm NMR tube and dissolved in C_6D_6. Solid $HB(C_6F_5)_2$ (33 mg, 0.09 mmol) was added to the tube, which was then capped and shaken. After 5 min, undissolved material was centrifuged to the top of the tube and the ^{1}H{^{2}H} NMR spectrum was recorded.

Preparation of *erythro*-$(C_6F_5)_2BCH(D)CH(D)$-*t*-C_4H_9: To a suspension of $DB(C_6F_5)_2$ (18 mg, 0.05 mmol) in C_6D_6 (0.7 mL) was added *E*-1-*d*$_1$-3,3-dimethyl-1-butene (7 μL, 0.055 mmol) via syringe. The tube was capped and shaken, the suspension cleared. The sample was assayed by ^{1}H{^{2}H} NMR spectroscopy and found to be >95% pure. ^{1}H NMR (C_6D_6): 1.80 (C_α−*H*, d, 1H, $^{3}J_{HH}$ = 11.3 ± 0.3 Hz), 1.36 (C_β−*H*, d, 1H), 0.88 (C(C*H*$_3$)$_3$, s, 9H). ^{13}C{^{1}H} NMR (C_6D_6): 148.4, 146.0, 144.9, 142.3, 138.9, 136.4, (*C*$_6$F$_5$), 38.2 (t, C_β), 28.8 (C*C*H$_3$), 26.7(br, C_α). ^{19}F{^{1}H} NMR (C_6D_6) −132.4 (d, *J* = 18.4 Hz), −149.0 (t, *J* = 21.4 Hz), −162.8 (m). ^{11}B NMR (C_6D_6): 73.3.

Generation of $Cp_2Zr[\mu\text{-}H_2B(C_6F_5)_2](Cl)$. Schwartz's reagent (10 mg, 0.04 mmol) and $HB(C_6F_5)_2$ (15 mg, 0.042 mmol) were loaded into a 5 mm NMR tube, and C_6D_6 was added. The suspension was shaken and sonicated for 15 min and analyzed by multinuclear NMR spectroscopy. ^{1}H NMR (C_6D_6): 5.57 (s, 10H, $C_5\mathit{H}_5$), 0.42 (br q, 2H, *μ-H*, $^{1}J_{HB}$ = 68 ± 3 Hz). ^{11}B NMR (C_6D_6): −10.3 (t, $^{1}J_{BH}$ = 68 Hz).^{19}F{^{1}H} NMR (C_6D_6): −131.4, −155.7, 162.0.

Reaction of $[Cp_2Zr(H)Me]_n$ with $PhCH_2B(C_6F_5)_2$. A solution of $ClB(C_6F_5)_2$ (21 mg, 0.054 mmol) in C_6D_6 (0.4 mL) was rapidly added to a solution of $Cp_2Zr(CH_2Ph)_2$ (11 mg, 0.027 mmol) in C_6D_6 (0.3 mL) with vigorous stirring. The resulting solution was transferred to a 5 mm NMR tube and checked by ^{1}H NMR, revealing only signals for Cp_2ZrCl_2 and $PhCH_2B(C_6F_5)_2$. To this tube was added $[Cp_2Zr(H)Me]_n$ (13 mg, 0.055 mmol) without allowing it to contact the solution prior to capping. The tube was capped and shaken vigorously, and the sample was immediately analyzed by ^{1}H NMR spectroscopy.

X-ray Crystallography for 1. A summary of crystal data and refinement details for all structures is given in Table 3. Crystals of **1** were grown from a toluene solution at room temperature. Suitable crystals were placed in glass capillaries, taking precautions to prevent loss of solvent of crystallization, sealed, and mounted onto a Rigaku AFC6S diffractometer. Measurements were made using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at -73 °C with the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.1°. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The non-hydrogen atoms were refined anisotropically; hydrogen atoms bridging the B and Zr atoms were included in the refinement at postions located from a difference map, while the rest of the hydrogen atoms were included at geometrically idealized positions with C−H = 0.95 Å and were not refined. At convergence, R and R_w were 0.046 and 0.045. The maximum and minimum peaks on the final difference map were 0.72 and −0.79 $e^-/Å^3$, respectively. All calculations were performed using the TEXAN[51] crystallographic software package of Molecular Structure Corp.

X-ray Crystallography for 4. Single crystals suitable for X-ray crystallography were mounted in thin-walled glass capillaries and optically centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer. Measurements were made using graphite-monochromated Mo Kα radiation ($\lambda = 0.709\ 30$ Å). Unit cell dimensions were determined via least-squares refinement of the setting angles of 24 reflections, and intensity data were collected using the $\omega-2\theta$ scan mode in the range 29.00−34.00°. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved using direct methods. Aryl and Cp hydrogen atoms were placed in calculated positions ($D_{C-H} = 1.00$ Å), and H1 was located via inspection of a difference Fourier map and fixed; the temperature factors for these hydrogens were based upon the carbon atom to which they are bonded. HB was located via inspection of a difference Fourier map and refined. A weighting scheme based upon counting statistics was used with the weight modifier k in kF_o^2 (0.000 050) being determined via evaluation of the variation in the standard reflections that were collected during the course of data collection. Neutral atom scattering factors were taken from *International Tables for X-ray Crystallography*.[52] Values of R and R_w at convergence were 0.051 and 0.047, respectively. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[53] locally implemented on an IBM-compatible 80486 computer.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, H atom coordinates, and anisotropic thermal parameters for compounds **1** and **4** (25 pages). Ordering information is given on any current masthead page.

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