Reactions of Bis(pentafluorophenyl)borane with Phosphine Olefin Complexes of Zirconocene

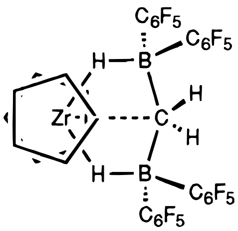
Yimin Sun,[†] Warren E. Piers,*[,†] and Steven J. Rettig[‡]

Departments of Chemistry, University of Calgary, 2500 University Drive NW,
Calgary, Alberta T2N 1N4, Canada, and University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia V6T 1Y6, Canada

Received May 29, 1996[⊗]

*Summary: Zirconocene olefin complexes $Cp_2Zr(PPh_2Me)(\eta^2\text{-}RCH{=}CH_2)$ (R = H, Et, Ph) react rapidly with 2 equiv of $[HB(C_6F_5)_2]_n$ to give the zwitterionic products $Cp_2Zr\{\eta^3\text{-}[CH(R)CH_2BH(C_6F_5)_2]\}$ (R = H (**2a**), Et (**2b**), Ph (**2c**)) and the borane−phosphine adduct $Ph_2MeP{\cdot}HB(C_6F_5)_2$. Spectroscopic and structural evidence confirms an interaction between zirconium and the β-carbon attached to boron, resulting in pentacoordinated carbon.*

We recently reported[1] the unusual complex **1**, which we isolated from the reaction of Cp_2ZrMe_2 and the highly electrophilic borane $[HB(C_6F_5)_2]_n$.[2] A recent computational treatment of a model of **1**[3] supported our original intuitive picture of the molecule as consisting of Cp_2Zr^{2+} and the ligand $[CH_2\{HB(C_6F_5)_2\}_2]^{2-}$. Like related BH_4^- ligands, where electron density is concentrated on the more electronegative hydrogen atoms, the chelating $[CH_2\{HB(C_6F_5)_2\}_2]^{2-}$ donor has substantial negative charge localization on the methylene carbon which is stabilized by donation to the σ-acceptor $2a_1$ orbital[4] of the metallocene fragment, resulting in a close contact between the zirconium center and a pentacoordinate carbon atom. Our serendipitous discovery of **1** prompted us to search more rationally for other examples of this class of hypercarbon with a view toward obtaining a better understanding of cation-anion interactions in catalytically active zwitterionic compounds.[5] The reaction of the borane $[HB(C_6F_5)_2]_n$ with zirconocene olefin complexes proved a successful strategy for this purpose.[6]



1

The zirconocene ethylene, 1-butene and styrene complexes $Cp_2Zr(\eta^2\text{-}RCH{=}CH_2)$ were prepared as described in the literature[7] and trapped with diphenylmethylphosphine; *exo* isomers for R = Et, Ph were obtained exclusively. In each case, when these complexes were treated with 2 equiv of $[HB(C_6F_5)_2]_n$, a rapid reaction ensued, as indicated by red-orange to yellow color changes. In addition to the zwitterionic zirconium-containing products $Cp_2Zr\{\eta^3\text{-}[CH(R)CH_2BH(C_6F_5)_2]\}$ (R = H (**2a**), Et (**2b**), Ph (**2c**)), 1 equiv of the borane−phosphine adduct $Ph_2MeP{\cdot}HB(C_6F_5)_2$ (identified by its separate synthesis) was produced (Scheme 1). The choice of this phosphine imparted optimal solubility properties on the adduct byproduct for separation from **2a**−**c**; even so, in the case of **2a** and **2c**, this adduct could not be completely removed via fractional crystallization (see Supporting Information). Thus, 1 equiv of $[HB(C_6F_5)_2]_n$ is required to remove the stabilizing phosphine, allowing the second equivalent of borane to react with the base-free zirconacyclopropane.[8] This second step must be rapid relative to the first, since reactions of $Cp_2Zr(\eta^2\text{-}C_2H_4)(PPh_2Me)$ with just 1 equiv of borane gave a 1:1:1 mixture of starting material, **2a**, and $Ph_2MeP{\cdot}HB(C_6F_5)_2$.[9]

Compounds **2a**−**c** were fully characterized via multinuclear NMR techniques.[10] ^{11}B and ^{19}F NMR spectra confirmed the incorporation of a $B(C_6F_5)_2$ unit, and the chemical shifts of the resonances in the ^{11}B NMR spectra (2.0, −1.5, and 0.4 ppm) appeared between the spectral ranges associated with neutral (*ca.* 0−20 ppm) and anionic (*ca.* −20 to 0 ppm) tetracoordinate boron.[11] Although somewhat broadened by the quadrupolar boron nuclei, proton NMR spectra indicated the olefinic fragment was intact but did not imply the presence or

---

* To whom correspondence may be addressed. FAX: 403-289-9488. Email: wpiers@chem.ucalgary.ca.

[†] University of Calgary.

[‡] University of British Columbia.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

[1] (a) 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. (b) Piers, W. E.; Spence, R. E. v. H. U.S. Patent 5,496,960, March 5, 1996 (University of Guelph).

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

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

[4] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[5] (a) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (b) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (c) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

[6] (a) Erker and Binger[6b] have shown that reactions of boranes (and other Lewis acids[6c]) with coordinated alkynes lead to complexes with unusual planar, tetracoordinate carbon centers. The electronic factors which stabilize these carbon centers[6d] are similar to those which lead to pentacoordinate carbon centers of the type presented here. (b) Binger, P.; Sandmeyer, F.; Krüger, C.; Erker, G. *Tetrahedron* **1995**, *51*, 4277. (c) Erker, G. *Comments Inorg. Chem.* **1992**, *13*, 111. (d) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *105*, 753.

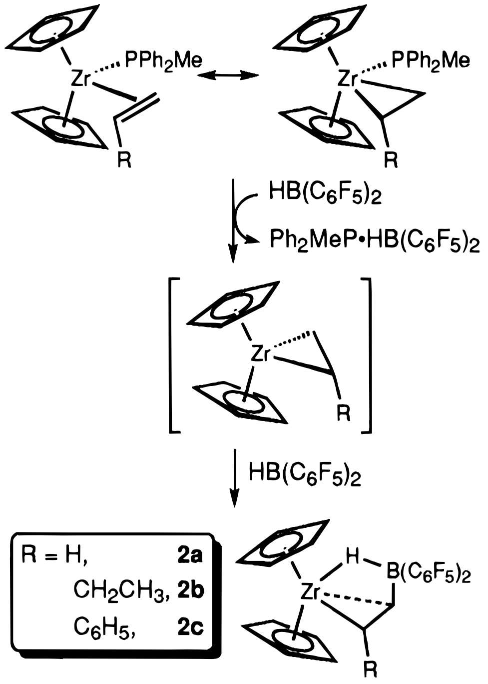
[7] Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761.

[8] (a) Similar chemistry is proposed to occur when the less electrophilic catecholborane (HBcat) is reacted with olefin complexes of Cp_2Ti,[8b] but quite different chemistry occurs in analogous reactions of $Cp^*{}_2Ti(\eta^2\text{-}C_2H_4)$[8c] with the same borane. (b) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696. (c) Motry, D. H.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 6615.

[9] Complex **2a** reacts reversibly with a further equivalent of $[HB(C_6F_5)_2]_n$ to produce, intially, the seven-membered heterocycle-containing species $Cp_2Zr[HB(C_6F_5)_2CH_2CH_2B(C_6F_5)_2H]$. This material decomposes thermally to yield a variety of products, including **2a**, the previously identified bis(borate) complex $Cp_2Zr[H_2B(C_6F_5)_2]_2$,[1] and $CH_3CH_2B(C_6F_5)_2$. We do not yet fully understand this decomposition process, particularly the origin of $CH_3CH_2B(C_6F_5)_2$.

S0276-7333(96)00422-0 CCC: $12.00

Scheme 1



absence of an interaction between C_β and zirconium. The best spectral evidence in support of a Zr−C_β contact was furnished by HMQC experiments,[12] which showed high-field ^{13}C chemical shifts of −6.0, 1.6, and 0.4 ppm for the β-carbons of **2a**−**c**, respectively. These data are similar to the value of δ 0.5 ppm found for the pentacoordinate methylene carbon of **1** and are markedly different from the shifts of between 25 and 35 ppm typically observed for the carbons bonded to boron in $RCH_2B(C_6F_5)_2$.[7]

The spectroscopic evidence in favor of close contact between Zr and C_β was augmented by an X-ray structural analysis of **2a**.[13] An ORTEP diagram, along with selected metrical data, is given in Figure 1. The Zr−C(12) distance of 2.455(7) Å, while slightly longer than the Zr−C length of 2.419(4) Å found for **1**, is clearly within bonding range for these two nuclei.[14] As in **1**, the pentacoordinated carbon atom occupies the central position of the metallocene wedge, allowing for direct interaction with the $2a_1$ σ-acceptor orbital on zirconium; however, in **2a** the bond is weaker because the carbon is bonded to only one σ-donating borate group. The closely related complex $[Cp_2ZrCH_2CH(AlEt_2)_2]^+[Cp]^-$ reported in the 1970s by Kaminsky and co-workers also contained a short Zr−C_β contact of 2.39 Å.[15,16]

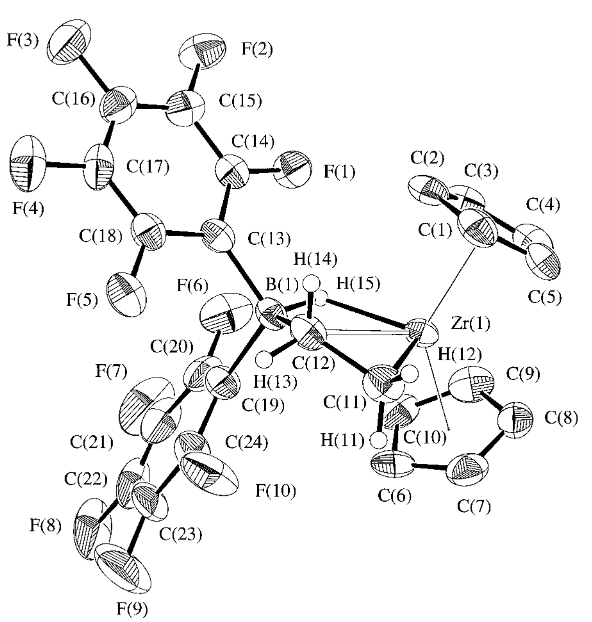


Figure 1. ORTEP diagram of **2a** (50% probability). Selected bond distances (Å): Zr−C(11), 2.193(7); Zr−C(12), 2.455(7); B−C(12), 1.689(9); B−H(15), 1.20(5); Zr−H(15), 2.01(4); Zr−Cp_{cent}, 2.20, 2.19. Selected bond angles (deg): Zr−C(11)−C(12), 80.4(4); C(11)−C(12)−B, 129.1(5); C(12)−B−H(15), 113(2); B−H(15)−Zr, 104(2); H(15)−Zr−C(11), 101(1); Zr−C(12)−H(14), 107(3); Zr−C(12)−H(13), 148(3); Zr−C(12)−C(11), 61.7(3); Zr−C(12)−B, 74.6(3); Cp_{cent}−Zr−Cp_{cent}, 130.8.

The geometry about C(12) is highly distorted from an ideal trigonal bipyramid, as demonstrated by the nonlinear B−C(12)−C(11) angle of 129.1(5)°. The closing of this angle (from a B−C−B angle of 149.3(4)° in **1**) is a consequence of having the smaller C(11) methylene unit spanning the Zr−C(12) linkage as opposed to a B−H moiety, as in **1**. C(12), the hydrogens attached to it (refined isotropically), and the zirconium atom are coplanar (sum of the angles 359.7°), but these atoms do not form an ideal trigonal plane about C(12) (see caption to Figure 1). Whereas the Zr, C(12), B, and H(15) atoms are close to being coplanar (the RMS deviation from the plane is 0.078 Å), C(11) dips out of the equatorial plane bisecting the Cp rings.

This structure, if static, would result in four separate signals in the ^1H NMR spectrum for the protons of the ethylene fragment; however, the methylene hydrogens on C_α and C_β in **2a** were equivalent in the room-temperature ^1H NMR spectrum (as were the protons of the Cp ligands). When the temperature was lowered

---

(10) All NMR spectra were recorded in C_6D_6 at 23 °C. **2a**: ^1H NMR δ 5.13 (s, 10H, C_5H_5), 2.63 (t, 2H, $ZrCH_2CH_2B$), 0.67 (t, 2H, $ZrCH_2CH_2B$), −2.72 (q, 1H, HB); $^{13}C\{^1H\}$ NMR δ 109.3 (C_5H_5), 64.9 ($ZrCH_2CH_2B$), −6.0 (br, $ZrCH_2CH_2B$); ^{19}F NMR δ −132.8 (br, 4F, *o*-F), −157.1 (t, 2F, *p*-F), −162.8 (m, 4F, *m*-F); ^{11}B NMR δ 2.0. **2b**: ^1H NMR δ 5.28, 5.09 (s, 10H, C_5H_5), 3.05 (m, 1H, $ZrCH(CH_2CH_3)CH_2B$), 2.27, 1.75 (m, 2, CH_2CH_3), 1.00 (t, 3H, CH_2CH_3), 2.55, −1.27 (br, m 2H, CH_2B), −2.62 (q, 1H, HB); $^{13}C\{^1H\}$ NMR δ 109.0, 108.6 (C_5H_5), 94.7 ($ZrCH(CH_2CH_3)CH_2B$), 37.63 (CH_2CH_3), 18.39 (CH_2CH_3), 1.6 (br,CH_2B); ^{19}F NMR δ −131.2, −134 (br d, 4F, *o*-F), −156.6, −157.7 (tr, 2F *p*-F), −162.7 (m, 4F, *m*-F); ^{11}B NMR δ −1.5. **2c**: ^1H NMR δ 6.8−7.4 (m, 5H, C_6H_5), 5.18, 5.13 (s, 10H, C_5H_5), 4.34 (q, 1H, $ZrCH(Ph)CH_2B$), 2.80, −0.40 (br m, 2H CH_2B), −2.62 (q, 1H, HB); $^{13}C\{^1H\}$ NMR δ 110.6, 109.8 (C_5H_5), 86.0 ($ZrCH(C_6H_5)CH_2B$), −2.47 (br,CH_2B); ^{19}F NMR δ −131.4, −134 (br d, 4F, *o*-F), −156.1, −157.0 (t, 2F, *p*-F), −162.5 (m, 4F, *m*-F); ^{11}B NMR δ 0.4.

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

(12) Heteronuclear multiple quantum coherence (HMQC) is a 2-D inverse detection NMR experiment which we have found useful for detecting resonances of carbon nuclei bonded to quadrupolar nuclei such as boron: Bax; A.; Subramanian S. *J. Mag. Reson.* **1986**, *67*, 565.

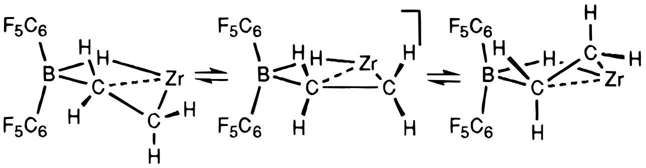
(13) Crystals were obtained from samples of **2a** containing ∼10% $Ph_2MeP\cdot HB(C_6F_5)_2$ recrystallized in toluene−hexanes (1:1). The yellow crystals of **2a** were readily distinguishable from colorless crystals of the adduct. Crystal data for **2a**: $C_{24}H_{15}F_{10}BZr$, fw 595.40, monoclinic, $P2_1/n$, $a = 15.005(2)$ Å, $b = 7.505(1)$ Å, $c = 20.9320(8)$ Å, $\beta = 108.459(5)°$, $V = 2236.0(4)$ Å^3, $Z = 4$, $F_{000} = 1176$, $D_{calcd} = 1.769$ g cm^{-3}, $2\theta_{max} = 155.4°$, Cu Kα radiation, $\lambda = 1.541\ 78$ Å, $T = 294$ K, 5083 measured reflections, 4898 unique, 2397 reflections with $I > 3.0\sigma I$, $R = 0.037$, $R_w = 0.035$, GOF = 1.87, no. of parameters = 346.

(14) (a) Cf. the Zr−C_{inside} length in $Cp_2Zr(PMe_3)(\eta^2\text{-}C_2H_4)$ of 2.373 Å[14b] and the Zr−C_{methyl} bonds in $Cp_2Zr(CH_3)_2$ of 2.27 Å.[14c] (b) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83. (c) Hunter, W. E.; Hrncir, D. C.; Vann Bynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

(15) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(16) The complex $[Cp'_2Zr(THF)CH_2CH_2SiMe_3]^+[BPh_4]^-$ also has a close Zr−Cβ contact of 2.58 Å: Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

Scheme 2



to −80 °C, the spectrum remained unchanged, save for normal viscosity broadening effects. The puckered five-membered ring therefore must be undergoing facile inversion through a planar intermediate as depicted in Scheme 2, to average the diastereotopic methylene hydrogen and Cp environments of the solid-state structure.

In conclusion, the cationic zirconiun center is stabilized by both the bridging hydrogen and the *β*-carbon atoms attached to the anionic borate counterion at the end of the alkyl group in complexes **2a**−**c**. Our studies on this chemically intriguing class of compounds, including their olefin chemistry, are continuing.

Acknowledgment. This work was generously supported by the NOVA Research & Technology Corp. of Calgary, Alberta, Canada and the NSERC of Canada's Research Partnerships office (CRD program). W.E.P. thanks the Alfred P. Sloan Foundation for a fellowship (1996−1998), Professors R. Hoffmann and R. Gleiter for a preprint of ref 3, and a reviewer for bringing Kaminsky's compounds to our attention as well as several other helpful comments.

Supporting Information Available: Text giving experimental details and tables giving crystal data, atomic coordinates, anisotropic displacement parameters, and all bond lengths, bond angles, and torsion angles for **2a** (17 pages). Ordering information is given on any current masthead page.

OM960422A