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Structure of a Zirconoxyborane Having a Zr–F–C Bridge

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Summary: Reaction of [Et_3NH][$(C_6F_5)_3BOH$] with $(Me_5C_5)_2ZrMe_2$ produces methane and $(Me_5C_5)_2ZrOB(C_6F_5)_3$. Crystal data (at −175 °C): $P2_1/n$, $a = 11.197(2)$ Å, $b = 16.076(4)$ Å, $c = 19.598(5)$ Å, $\beta = 93.90(0)°$, $Z = 4$. The structure reveals a $(C_6F_5)_3B$–O moiety coordinated to zirconium. One of the C_6F_5 groups is oriented so that its ortho fluorine forms a Zr–F–C bridge. The ^{19}F NMR spectrum at −88 °C reveals a static structure in which the shielded Zr–F–C fluorine resonates at −190.3 ppm. As the temperature is raised, all three C_6F_5 rings interconvert at the same rate in a process for which $\Delta G^{\ddagger} = 10 \pm 0.5$ kcal mol^{-1}.

We have been investigating strategies for synthesis of aluminum-free Ziegler–Natta type catalysts and have found that the reaction of [Et_3NH][$(C_6F_5)_3BOH$] with Cp_2ZrMe_2 (Cp ≡ η^5-C_5H_5) provides a catalyst capable of producing poly-1-hexene having M_w = 28 000 and M_n = 9100.[1] Efficient use of such catalysts requires knowledge of their self-decomposition reactions, for if such processes could be suppressed, higher yields of polymer might be obtained. A detailed study of the closely related Me_5Cp system has incisively identified an unusual decomposition product, $(Me_5Cp)_2ZrOB(C_6F_5)_3$ (**1**), which involves the formation of Zr–O and C–F–Zr bonds. This chemistry is arguably relevant to other materials containing coordinatively unsaturated cations and heavily fluorinated organic counterions.[2,3]

A solution of 0.039 g (0.1 mmol) of $(Me_5Cp)_2Zr(^{13}CH_3)_2$ in 0.25 mL of toluene-d_8 was added under nitrogen with stirring to a suspension of 0.063 g (0.1 mmol) of [Et_3NH][$(C_6F_5)_3B^{17}OH$] in 0.3 mL of the same solvent. Methane evolved, and the resulting clear orange solution was transferred to an NMR tube. ^{13}C NMR analysis of the very complex reaction mixture revealed $(C_2H_5)_3N$ and also a new peak at 41.7 ppm (J_{CH} = 117 Hz) that we surmise is due to $(Me_5Cp)_2Zr^{13}CH_3^+$, with which catalytic activity is associated.[4] The boron-containing anions present were $HOB(C_6F_5)_3^-$ and $MeB(C_6F_5)_3^-$ ($\delta(^{11}B)$ −2.7 and −14, respectively, in an 8:1 ratio). Two new ^{17}O peaks at 365 and 305 ppm were also observed; the chemical shifts are indicative of Zr–O bonds.[5] Then, after ca. 1 h, orange crystals of $(Me_5Cp)_2ZrOB(C_6F_5)_3$ (**1**) began to separate. After 48 h, this extremely air sensitive product (0.02 g) was isolated by filtration.[6]

An ORTEP view of the structure of **1**[7] is shown in Figure 1 along with selected metrical data. It reveals a $(Me_5Cp)_2Zr$ moiety bonded via an intervening oxygen atom to $(C_6F_5)_3B$. The B–O and Zr–O bond lengths are 1.460(6) and 1.912(3) Å, respectively.[8] The B–O bond is shorter than in [Et_3NH][$(C_6H_5)_3BOH$] itself (1.487(3) Å). An unusual feature of the structure is provided by one of the pentafluorophenyl groups, which is oriented in such a way that one of the ortho fluorines approaches the zirconium atom so that the Zr–F contact is 2.346(3) Å. This separation is ca. 0.1 Å longer than the longest Zr–F bonds found in "simple" zirconium fluoroanions,[9] but we believe that it represents a genuine C–F–Zr bridge bond, for the associated C–F bond is lengthened by 0.05 Å relative to d(C–F)$_{av}$. The F–Zr–O angle (75.6(1)°) indicates that fluorine occupies, possibly for steric reasons, a central rather than lateral coordination position. C–F–metal bridge bonds are uncommon in organometallic chemistry

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[1] A solution of 0.13 g of Cp_2ZrMe_2 in 1 mL of toluene was added with stirring to a suspension of 0.31 g of [Et_3NH][$(C_6F_5)_3BOH$] in 6 mL of toluene. After methane evolution had ceased, the orange oil that had separated was washed with more toluene and then hexane and vacuum-dried to provide 0.31 g of orange solid. A 0.01-g portion of this was stirred for 3 days at 25 °C with 0.76 g of 1-hexene. The reaction mixture was diluted with hexane, filtered, and evaporated under vacuum at 50 °C to afford 0.45 g of poly-1-hexene. GPC characterization employed polystyrene standards.

[2] Cationic group IV metallocene compounds have been reviewed by: Jordan, R. F. *Adv. Organomet. Chem.* **1991,** *32,* 325.

[3] (a) Brookhart, M.; Hauptman, M. *J. Am. Chem. Soc.* **1991,** *114,* 4437. (b) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991,** *113,* 8570. (c) Bochman, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992,** *424,* C5. (d) LaPointe, R. E. Eur. Pat. Appl. 91305955.6. (e) Turner, H. W.; Hlatky, G. G. Int. Pat. Appl. WO 91/12285. (f) Turner, H. W., Hlatky, G. G. Eur. Pat. Appl. 88300699.1. (g) Stevens, J. C.; Neithamer, D. R. Eur. Pat. Appl. 90309962.0 (h) Canich, J. M.; Hlatky, G. G.; Turner, H. W. Int. Pat. Appl. WO 92/00333. (i) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. 00870175.8. (j) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. 90870175.8. (k) Razavi, A.; Ewen, J. A.; Elder, M. J. Can. Pat. Appl. 2,027,144. (l) Hlatky, G. G.; Turner, H. W. Int. Pat. Appl. WO 91/14713. (m) Hlatky, G. G.; Upton, D. J.; Turner, H. W. Int. Pat. Appl. WO/90/09882. (n) Campbell, R. E., Jr. Eur. Pat. Appl. 90310495.8.

[4] Relative to internal Me_4Si and external BF_3·Et_2O. Cf. $\delta(^{13}C)$ and $\delta(^{11}B)$ 50.4 (J_{CH} = 122 Hz) and −14.0 (with added THF) in [$(Me_5C_5)_2ZrCH_3$][$MeB(C_6F_5)_3$]: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991,** *113,* 3623.

[5] McFarlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J.; Ed.; Plenum: New York, 1987; p 403. $\delta(^{17}O)$ and $\delta(^{11}B)$ for [Et_3NH][$(C_6F_5)_3BOH$] in $CDCl_3$ are 25 and −3.8 ppm relative to external H_2O and BF_3·Et_2O, respectively. This salt is obtained in quantitative yield from the reaction of Et_3N with $(C_6F_5)_3B$·$3H_2{}^{17}O$ (10% labeled) in toluene followed by recrystallization from hot toluene. A full description of our studies of $(C_6F_5)_3B$ complexes will be published separately.

[6] ^1H NMR: δ 1.68. ^{11}B NMR: δ 3.3. Anal. Calcd (found) for $C_{38}H_{30}BF_{15}OZr$: C, 51.3 (50.9); H, 3.4 (3.4); B, 1.2 (1.3); Zr, 10.2 (9.9).

[7] Crystal data (at −172 °C): $P2_1/n$, $a = 11.197(2)$ Å, $b = 16.076(4)$ Å, $c = 19.598(5)$ Å, $\beta = 93.90(0)°$, $Z = 4$, $D_c = 1.679$, $\mu = 4.148$ cm^{-1}, 5166 measured reflections, 4587 unique reflections, 3825 observed reflections with $|F_o| > 2.33\sigma(|F_o|)$, $2\theta(\max) = 45°$, $R = 0.046$, $R_w = 0.049$. Data were collected using monochromatized Mo Kα radiation. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles.

[8] The Zr–O bond is on the short end of the range found in dicyclopentadienylzirconium compounds; cf. 1.948(1) Å in $[Cp_2Zr(CH_3)]_2O$ (Hunter, W. E.; Hrcnir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983,** *2,* 750) and 2.236(2)–2.259(2) Å in $Cp_2Zr[HC(SO_2CF_3)_2]_2$ (Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Lamanna, W. M. *Organometallics* **1990,** *9,* 1290).

[9] Examples are as follows. (a) $Li_6BeF_4ZrF_8$ (CN 8), 2.05(1), 2.16(1) Å: Sears, D. R.; Burns, J. H. *J. Chem. Phys.* **1964,** *41,* 3478. (b) Na_2ZrF_6 (CN 7), 2.167(6)–2.012(7) Å: Brunton, G. *Acta Crystallogr.* **1969,** *B25,* 2164. (c) $CuZrF_6$·$4H_2O$ (CN 6), 1.982(6)–2.007(5) Å: Fischer, J.; Weiss, R. *Acta Crystallogr.* **1973,** *B29,* 1955. d(ZrF) in Cp_2ZrF_2 is 1.98(1) Å: Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971,** 2225.

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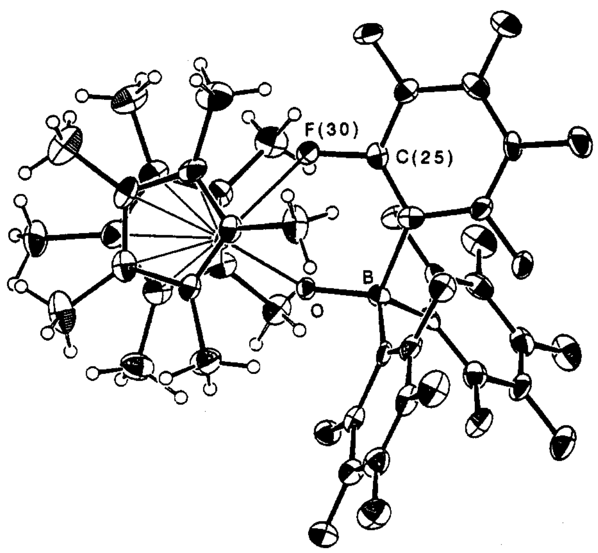

Figure 1. ORTEP drawing of $(Me_5Cp)_2ZrOB(C_6F_5)_3$ (33% probability ellipsoids. Selected bond distances (Å) and angles (deg): Zr–F, 2.346(3); B–O, 1.460(6); Zr–O, 1.574(3); C25–F30, 1.406(5); C–F(av), 1.350(6); B–O–Zr, 151.2(3); O–Zr–F, 75.6(1); cent–Zr–cent, 131.5.

Table I. ^{19}F NMR Chemical Shifts in 1 at −88 °C[a]

	F(2)[b]	F(3)	F(4)	F(5)	F(6)
ring A	−190.3	−164.4	−156.1	−158.7	−125.4
ring B	−132.8	−163.4	−158.4	−165.5	−125.4
rinc C	−134.2	−163.9	−159.6	−165.4	−130.3

[a] In toluene-d_8 at 376 MHz. Negative shifts are downfield of internal $CFCl_3$. [b] Fluorine positions are numbered clockwise, starting with the boron-substituted position relative to which F(2) (and F(6)) are ortho; F(3,5) are meta, and F(4) is para.

but have been observed in $Ru(SC_6F_4\text{-}\mu\text{-}F)(SC_6F_5)_2(PhPMe_2)_2$[10] and $[2,4,6\text{-}(CF_3)_3C_6H_2]Li$.[11] In $[(Me_5C_5)_2ThMe][B(C_6F_5)_4]$, active as a catalyst for ethylene polymerization, weak cation–anion interaction is presaged by long (2.675(5), 2.757(2) Å) Th–F contacts that exceed the sums of Th^{4+} and F^- ionic radii.[12]

A ^{19}F NMR study disclosed that the structure of 1 in toluene-d_8 solution is essentially that established above for the solid state and, therefore, the unique elongated C–F bond and the close Zr–F approach are not artifacts of crystal packing.[13] At −88 °C, the ^{19}F NMR spectrum of $(Me_5Cp)_2ZrOB(C_6F_5)_3$ displays 14 sharp ($w/2$ = ca. 100 Hz) resonances. One has twice the intensity of the rest and is due to two overlapping absorptions (cf. Table I). A ^{19}F COSY spectrum revealed three groups of mutually coupled absorptions that are assigned to three inequivalent C_6F_5 rings. Notable is one ^{19}F resonance of unit area that is shifted upfield by over 50 ppm from the region typical of F_{ortho} in C_6F_5 rings to −190.3 ppm. On this ground, it is assigned to the unique fluorine, F30, bridging Zr and C in a likewise unique C_6F_5 ring (ring A).[14] The ^{19}F shifts of the other four fluorine nuclei in this ring were determined by the COSY experiment and are given in Table I. The fluorine nucleus para to F30 is deshielded by 7 ppm relative to typical F_{meta} atoms in C_6 rings. The chemical shifts for the ^{19}F nuclei *within* the other two nonequivalent rings (rings B and C) also follow from the COSY data, but their location in the structure cannot be determined.

The ^{19}F resonances in 1 broaden rapidly above −75 °C. At −50 °C, the line widths of all six ortho fluorines are the same within experimental error. This indicates that three C_6F_5 rings are interconverting at approximately the same rate. Finally, at 25 °C, only three ^{19}F signals are apparent: F_{ortho} at −130.6 ($w/2$ = 1950 Hz), F_{meta} at −164.0 ($w/2$ = 1050 Hz), and F_{para} at −158.7 ($w/2$ = 60 Hz) ppm. Analysis of the ^{19}F DNMR data shows that the free energy of activation for *concomitant* interconversion of all three C_6F_5 rings in 1 is 10 ± 0.5 kcal mol^{-1}. We suggest that cleavage of the Zr–F bond is the primary contributor to this energy barrier. Subsequently, rotation about the C–B or B–O bonds, both expected to be comparable low-energy processes, would bring another F_{ortho}, in the same or different ring, respectively, into conjunction with zirconium.

No reaction between $(Me_5Cp)_2ZrMe_2$ and $[n\text{-}Pr_4N][(C_6F_5)_3BOH]$ is detectable by NMR. It therefore appears that 1 is formed by loss of methane from $(Me_5Cp)_2ZrMe^+$, produced by protonolysis of $(Me_5Cp)_2ZrMe_2$ by Et_3NH^+,[15] and $(C_6F_5)_3BOH^-$. We consider that a metal–fluorine bridge bond such as that demonstrated here may significantly affect the chemistry of highly electrophilic cations which are associated with putatively noncoordinating anions such as $(C_6F_5)_4B^-$ and $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$.[15,16]

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Supplementary Material Available: Details of the structure determination (Table S1), fractional atomic coordinates (Table S2), anisotropic thermal parameters (Table S3), bond distances and angles (Table S4), least-squares planes (Table S5), distances involving Cp ring centroids (Table S6), and a numbering scheme (Figure S1) (16 pages). Ordering information is given on any current masthead page.

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(14) The literature data base is too slender to allow prediction of the ^{19}F chemical shift for a metalloid–*F*–metal species, but the *difference* in shielding between bridging and nonbridging fluorines appears to be greater in tungsten than in zirconium compounds. For $[(Me_5Cp)_2ZrMe][(4\text{-}FPh)_4B]$, in which the cation and anion are considered to be linked by a Zr–F–C bond, $\delta(^{19}F)$ is −135.5 vs −121.1 for the nonparticipating C_6H_4F rings; see: Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. Even larger shieldings have been observed in *mer*-(*cis*-R_3P)$(CO)_3(NO)W(\mu\text{-}F)EF_n$ (EF_n = SbF_5, PF_5, BF_3): Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869; *J. Am. Chem. Soc.* **1989**, *111*, 6056. The ^{19}F chemical shifts in $WH(FBF_3)(CO)_3(PCy_3)_2$ are −147.0 and −257.8 ppm at 230 K: Van Der Sluys, L. S.; Kubat-Martin, K. A.; Kubas, G. J.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 306.

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