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Formation of Metallaboranes from the Group IV Transition Metals and Pentaborane(9): Crystal and Molecular Structure of $[(Cp_2Zr)_2B_5H_8][B_{11}H_{14}]$

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The reactions between $[(C_5H_5)_2MCl_2]$ (where M = Ti, Zr, Hf) and $Li[B_5H_8]$ in a variety of solvents have been investigated. In the case of Zr, a pale orange solid, μ-$(Cp_2ClZr)B_5H_8$ (**1**), is formed in 70% yield. Compound **1** exists as a B_5H_9 cage with a Cp_2ClZr moiety replacing a bridging H atom. The variable temperature NMR spectra of **1** reveal two fluxional processes, one ($\Delta G^\ddagger = 54$ kJ mol^{-1}) which renders a plane of symmetry in the molecule and a higher temperature one ($\Delta G^\ddagger = 48$ kJ mol^{-1}) which renders all the basal B atoms equivalent. Dynamic processes are suggested to account for these observations. Passage of a CH_2Cl_2 solution of **1** through silica gel affords **2**, $[(Cp_2Zr)_2B_5H_8][B_{11}H_{14}]$, a yellow, air-stable, crystalline solid, in 14% yield. The cation in **2**, $[(Cp_2Zr)_2B_5H_8]^+$, consists of a distorted spiro[2.2]pentane-like B_5 moiety comprising two B_3 triangles sharing a naked boron vertex. The two triangles are twisted 73° with respect to each other, and the two $[Cp_2Zr]$ groups bond in a trihapto arrangement to the two opposite B–B–B edges. Each exterior B–Zr edge is H-bridged, and the B atoms possess terminal hydrogens. Reactions of Cp_2HfCl_2 with $Li[B_5H_8]$ lead to the formation of the analogue of **2**, $[(Cp_2Hf)_2B_5H_8][B_{11}H_{14}]$ (**3**). The precursor to **3**, that is, the Hf analogue of **1**, is not observed. Reaction between $Li[B_5H_8]$ and Cp_2TiCl_2 afforded no identifiable products, but reaction with $CpTiCl_3$ resulted in cage coupling and the formation of $B_{10}H_{14}$.

Introduction

We have been interested, recently, in the preparation of bimetallapolyboranes based on smaller borane cages containing 3−7 boron atoms, especially those containing different metals.[1] A continuing goal of this work was to prepare species containing one "early" and one "late" transition metal. Much of the prior work in this area identified "late" transition metal metallapolyboranes,[2] but there are no examples of systems containing metals from both ends of the d block and many fewer examples containing "early" transition metals. Although the seminal work of the Fehlner group[3] and others[4] has identified many examples of small metallapolyboranes containing group 6 metals and several containing group 7 metals,[3m,o−s,5] there are very few examples of systems containing metals from groups 4 and 5. Except for tetrahydroborate complexes, only one titanaborane,[6] one niobaborane,[7] and two tantalaboranes[8] have been fully characterized, and of the latter, only one is a conventional cluster based on a standard borane framework.[8b] Thus, we set out first to prepare examples of metallapolyboranes from groups 4 and 5. This report describes our initial efforts to

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prepare group 4 and 5 metallapolyboranes using the reactions of LiB_5H_8 with various group 4 cyclopentadienyl metal halides. Herein, we describe the formation and characterization of novel zircona- and hafnapolyboranes and also attempts to prepare titanapolyboranes which result in cage fusion reactions. A preliminary report of the zirconium system has appeared.[9]

Experimental Section

General. Solvents used were reagent grade and were dried before use. Reactions were carried out on a standard vacuum line, and some reagents were introduced into vessels in a drybox.[10] Thin-layer chromatography (TLC) was performed using 20×20 cm^2 glass plates coated with 0.1 cm of silica gel (Aldrich standard grade with gypsum binder and fluorescent indicator) made from aqueous slurries followed by drying in air at 80 °C. Of the starting materials, B_5H_9 was obtained from laboratory stock and distilled on the vacuum line before use; [Cp_2ZrCl_2], [Cp_2TiCl_2], and [$CpTiCl_3$] were obtained from Alfa Aesar and used as received, as was [Cp_2HfCl_2], which was obtained from Strem. KH and LiMe were obtained from Aldrich, and the former was washed, before use, in pentane until it was a free flowing powder. The purity of KH was checked by measuring the H_2 evolved on reaction with CH_3OH at −78 °C. NMR spectral studies were carried out using a Varian Unity plus 300 spectrometer operating at 96.2 MHz for ^{11}B, 299.9 MHz for ^1H, and 121.4 MHz for ^{31}P. Chemical shifts (δ) are given in ppm to high frequency (low field) of 0.00 ppm ($SiMe_4$) for ^1H, 0.00 ppm for ^{31}P (85% H_3PO_4), and 0.0 ppm for ^{11}B (F_3BOEt_2 in $CDCl_3$). Selective decoupling experiments were performed on a Bruker ARX 500 spectrometer at 500.1 MHz for ^1H and 160.5 MHz for ^{11}B and at 202.5 MHz for ^{31}P. Low resolution mass spectra were measured on a VG ZAB-E in the FAB mode using 3-NBA, and the high-resolution data were obtained on a Kratos MS-50, in the FAB mode using Ar gas.

Synthesis of (Cp_2ZrCl)B_5H_8 (1). B_5H_9 (0.42 mL, 4.2 mmol) was condensed onto a solution of LiMe in diethyl ether (3.35 mL, 1.4 M, 4.7 mmol) at −78 °C in an extractor on the vacuum line. The mixture was stirred for 1 h and then frozen at −196 °C, and the methane generated was removed under vacuum. To the frozen mixture was added solid Cp_2ZrCl_2 (0.60 g, 2.05 mmol), and this was followed by the condensation of CH_2Cl_2 (1 mL) into the reaction vessel. The reaction mixture was warmed to −78 °C and stirred for 15 h. The solvents were removed from the resultant yellow solution under reduced pressure at this temperature. CH_2Cl_2 (5 mL) was condensed onto the solids at −78 °C and the resultant suspension filtered at this temperature. Removal of the solvent at −78 °C gave **1** as a pale orange solid (455 mg, 1.44 mmol, 70%). NMR spectral data (δ in ppm, $CDCl_3$ solution) (assignment [δ(^{11}B) (^1H in parentheses)]). 4 °C: B(2−5) [−9.5 (1.83, br s, 4H)], B(1) [−41.6, d, $J = 169$ Hz (0.85)]; δ(^1H) C_5H_5 [6.35], μH (−2.4, br s, 3H)]. −44 °C: B(2,3) [−6.2 (1.91, 0.86)], B(4,5) [−11.6 (2.40, 2.26)], B(1) [−41.6 (0.45)]; δ(^1H) C_5H_5 [6.35], $\mu H_{4,5}$ [−1.81], $\mu H_{3,4;2,5}$ [−2.73, 2.93]. −93 °C (CD_2Cl_2 solution): B(2,3) [ca. −6.2 (2.4, 2.26)], B(4,5) [splits into 2 br unresolved resonances (1.90, 0.88)], B(1) [−41.6 (0.78)]. LRMS in the FAB mode on a VG ZAB-E using 3-NBA gave the parent ion at $m/z = 318$ with the isotopic distribution for the envelope of $C_{10}H_{18}B_5ClZr$ matching quite well. Calcd for $C_{10}H_{18}B_5ClZr$: (m/q, *rel int*) 315, *8.59*; 316, *36.52*; 317, *83.37*; 318 *100.00*; 319, *71.93*; 320, *62.02*. Found: 315, *67.50*; 316, *77.36*; 317, *100.00*; 318 *99.75*; 319, *90.00*; 320, *73.33*.

Reaction of 1 with HCl. Diethyl ether (5 mL) was condensed at −78° onto pale orange solid **1** (120 mg, 0.37 mmol). The suspension was cooled to −196 °C, and HCl gas (0.39 mmol) was condensed onto the frozen mass. The mixture was warmed to −55 °C and stirred for 90 min, at which point the orange solid had become colorless. The volatiles from the reaction were removed in vacuo at −55 °C and collected at −196 °C over 18 h. The white solid was identified as Cp_2ZrCl_2 (102 mg, 95%), and the volatiles contained B_5H_9 as the only boron-containing product, by ^1H, ^{13}C, and ^{11}B NMR. This is characteristic of a metal atom in a bridging position of a pyramidal borane cluster.[11]

Synthesis of [(Cp_2Zr)$_2B_5H_8$][$B_{11}H_{14}$] (2). A solution of **1** (300 mg, 0.94 mmol) in CH_2Cl_2 (10 mL) was warmed to room temperature and filtered through a plug of silica in air. The solvent was removed from the resultant yellow solution in vacuo, giving a yellow solid, which was separated by TLC (75% CH_2Cl_2, 25% pentane eluant) giving two bands, decaborane(14) (colorless, $R_f = 0.9$) and **2** (yellow, $R_f = 0.2$) isolated as a yellow solid (43 mg, 14% based on Zr). NMR spectral data for **2**. ^{11}B (96.2 MHz) and

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Table 1. Crystal Data and Structure Refinement for **2**

identification code	lb5397s/lt/ccd
empirical formula	$C_{20}H_{42}B_{16}Zr_2$
fw	637.94
T	223(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	Cc
unit cell dimensions	$a = 16.21690(10)$ Å, $\alpha = 90°$ $b = 23.46760(2)$ Å, $\beta = 90.7450(10)°$ $c = 16.3222(2)$ Å, $\gamma = 90°$
V	6211.24(9) Å^3, $Z = 8$
density (calcd)	1.364 Mg/m^3
abs coeff	0.683 mm^{-1}
F(000)	2576
cryst size	$0.4 \times 0.2 \times 0.2$ mm^3
θ range for data collection	1.74−27.50°
index ranges	$-21 \le h \le 21$, $0 \le k \le 31$, $-21 \le l \le 21$
reflns collected	14 192
independent reflns	14 192 [R(int) = 0.0000]
abs correction	semiempirical, sadabs
max and min transmission	0.98 and 0.85
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	14 180/2/753
GOF on F^2	1.014
final R indices [$I > 2\sigma(I)$]	R1 = 0.0386, wR2 = 0.0867
R indices (all data)	R1 = 0.0514, wR2 = 0.0980
absolute structure parameter	0.02(3)
largest diffraction peak and hole	0.617 and −0.596 e Å^{-3}

^{1}H (299.9 MHz) (ppm, $CDCl_3$ solution, 25 °C) (relative intensity, assignment [δ(^{11}B) (^{1}H in parentheses)]): δ(^{11}B) B(2,3,4,5) [+2.7 (+3.05)], B(1A) [−13.4 (2.13)], B (2A−6A) [−15.1 (1.96)], B(7A−11A) [−16.1 (1.51)], B(1) [−28.2 (*no H*)]; δ(^{1}H) C_5H_5 [6.07] 20H, *endo-H*$_{\text{anion}}$ [−3.46] 3H, $\mu H_{B,Zr}$ [−5.15] 4H. A refers to the anion $[B_{11}H_{14}]^-$. HRMS (Kratos MS-50, FAB, Ar gas) gave *m/q* for cation **2** of $^{12}C_{20}{}^1H_{28}{}^{11}B_5{}^{90}Zr_2$ 503.0802 (obsd) and 503.0791 (calcd).

X-ray Diffraction Analysis. A colorless crystal of compound **2** was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed using a Siemens SMART charge coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source using graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.710 73 Å). Preliminary unit-cell constants were determined with a set of 45 narrow-frame scans (0.3° in ϖ). A total of 4026 frames of intensity data were collected with a frame width of 0.3° in ϖ at a crystal-to-detector distance of 4.91 cm. The double-pass method of scanning was used to reduce noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT[12a] was used for frame integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of the x,y,z centroids of 8192 reflections ($\theta < 26.0°$). Absorption corrections were applied to the data using equivalent reflections (SADABS).[12b] Crystal data and parameters for intensity data collection are listed in Table 1.

The SHELXTL-PLUS software package[12c] was used for structure solutions (by direct methods) and refinement. Full-matrix least-squares refinement was carried out by minimizing $\Sigma\omega(F_o{}^2 - F_c{}^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All the hydrogen atoms, except the cage hydrogens, were included in their calculated positions. Cage hydrogens which could be located from the difference Fourier map were included in the final refinement in fixed positions. One of the $[B_{11}H_{14}]^-$ anions is disordered. The disorder was resolved by including B(10) in two position (B10B and B10C) with 50% occupancy. The structure refinement parameters are given in Table 1, and selected bond angles and distances are given in Table 2. A complete list of positional and isotropic displacement coefficients for the hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms, and complete listings of bond distances and angles are available as Supporting Information.

Table 2. Bond Lengths (Å) and Angles (deg) for the Cation in $[(Cp_2Zr)_2B_5H_8][B_{11}H_{14}]$ **2**[a]

Bond Lengths			
Zr(1)−B(1)	2.498(4)	B(1)−B(5)	1.719(6)
Zr(1)−B(4)	2.525(4)	B(1)−B(4)	1.730(5)
Zr(2)−B(1)	2.473(4)	B(1)−B(3)	1.731(5)
Zr(2)−B(2)	2.512(4)	B(2)−B(3)	1.865(6)
B(1)−B(2)	1.712(6)	B(4)−B(5)	1.870(6)

Bond Angles			
B(2)−B(1)−B(5)	142.8(3)	B(1)−B(3)−B(2)	56.7(2)
B(2)−B(1)−B(4)	128.8(3)	B(1)−B(3)−Zr(1)	68.58(19)
B(5)−B(1)−B(4)	65.7(2)	B(2)−B(3)−Zr(1)	101.5(2)
B(2)−B(1)−B(3)	65.6(2)	B(1)−B(4)−B(5)	56.9(2)
B(5)−B(1)−B(3)	127.9(3)	B(1)−B(4)−Zr(1)	69.03(19)
B(4)−B(1)−B(3)	141.9(3)	B(5)−B(4)−Zr(1)	103.1(2)
B(2)−B(1)−Zr(2)	71.16(19)	B(1)−B(5)−B(4)	57.4(2)
B(5)−B(1)−Zr(2)	71.7(2)	B(1)−B(5)−Zr(2)	68.1(2)
B(4)−B(1)−Zr(2)	108.8(2)	B(4)−B(5)−Zr(2)	102.0(2)
B(3)−B(1)−Zr(2)	109.3(2)	B(1)−Zr(1)−Ca	114.2
B(2)−B(1)−Zr(1)	108.0(2)	B(1)−Zr(1)−Cb	114.1
B(5)−B(1)−Zr(1)	109.1(2)	B(4)−Zr(1)−Ca	114.1
B(4)−B(1)−Zr(1)	70.7(2)	B(3)−Zr(1)−Ca	102.0
B(3)−B(1)−Zr(1)	71.2(2)	B(1)−Zr(2)−Cc	114.9
Zr(2)−B(1)−Zr(1)	178.55(19)	B(1)−Zr(2)−Cd	113.7
B(1)−B(2)−B(3)	57.7(2)	B(5)−Zr(2)−Cc	102.8
B(1)−B(2)−Zr(2)	68.68(18)	B(2)−Zr(2)−Cd	100.8
B(3)−B(2)−Zr(2)	103.3(2)	Zr(1)−B(1)−Zr(2)	178.6

[a] Ca, Cb, Cc, and Cd are the centroids of the four C_5H_5 rings, starting with the one above Zr(1) in Figure 3 and moving clockwise.

Synthesis of $[(Cp_2Hf)_2B_5H_8][B_{11}H_{14}]$, (3). A solution of MeLi in $(C_2H_5)_2O$ (1.0 mL, 1.4 M, 1.4 mmol) was cooled to −78 °C, and B_5H_9 (0.12 mL, 1.2 mmol) was added. The mixture was stirred for 1 h at −50 °C and then frozen at −196 °C before Cp_2HfCl_2 (0.23 g, 0.6 mmol) was added, followed by the condensation of CH_2Cl_2 (5 mL). The reaction mixture was warmed to −35° and stirred for 18 h. The solvents were removed from the resultant yellow solution in vacuo at −35 °C. CH_2Cl_2 (25 mL) was condensed onto the residue at −78 °C and the resultant suspension filtered through SiO_2 at room temperature. Removal of the solvent gave a pale yellow solid, which was separated by preparative TLC to give a bright yellow solid **3**, $R_f = 0.2$. (44 mg, 0.054 mmol, 18%). ^{11}B (96.2 MHz) and ^{1}H (299.9 MHz) NMR spectral data in ppm ($CDCl_3$ solution, 25 °C) for **3** (assignment [δ(^{11}B) (^{1}H in parentheses)]): δ(^{11}B) B(2,3,4,5) [+2.8 (+3.20)], B(1A) [−13.4 (2.15)], B(2A−6A) [−15.2 (1.95)], B(7A−11A) [−16.1 (1.54)], B(1) [−33.2 (*no H*)]; δ(^{1}H) C_5H_5 [5.98], μH_{anion} [−3.46], $\mu H_{B,Hf}$ [−4.51]. Microanalysis [found(calculated)%]: C, 29.39 (29.57) %; H, 5.14 (5.21) %. Several attempts to isolate the intermediate species, analogous to **1**, were made but were unsuccessful. At temperatures high enough to effect reaction, species **3** is the major, and only isolable, product.

Reactions of Pentaborane(9) with Cyclopentadienyltitanium Halides. Stirring solutions of Cp_2TiCl_2 or Cp_2TiMe_2 with LiB_5H_8 at various temperatures and using different solvents did not afford identifiable products; however, reactions of LiB_5H_8 with $CpTiCl_3$

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[12] (a) Bruker Analytical X-ray Division, Madison, WI, 1997. (b) Blessing, R. H. *Acta Crystallogr*. **1995**, *A51*, 33. (c) Sheldrick, G. M. *SHELXTL-PLUS*; Bruker Analytical X-ray Division: Madison, WI, 1997.

afforded $B_{10}H_{14}$ in relatively high yields, so several different sets of conditions were used to explore this reaction.

Initial Reaction of $[B_5H_8]^-$ with $CpTiCl_3$. MeLi (2.0 mL ether solution, 2.8 mmol) was placed in a round-bottom flask under N_2 and placed on the vacuum line, and the flask was cooled to −196 °C and evacuated. B_5H_9 (2.7 mmol) was condensed into the flask. The flask was warmed to ambient for a few minutes with shaking and it was filled with N_2. A stirbar and addition tube containing $CpTiCl_3$ (0.6 g 2.7 mmol) were added. After freezing at −196 °C and evacuating, the $CpTiCl_3$ was added, and 10 mL of THF was condensed into the flask. Stirring for 3 h at −78 °C afforded a brown/black slurry. Filtration afforded a brown residue and a dark yellow filtrate. Attempts to isolate Ti-containing identifiable products from both fractions were unsuccessful. Several procedures failed, so the remaining material was evacuated, and sublimation afforded pure $B_{10}H_{14}$ (45 mg, 0.36 mmol, 26%), identified by its ^{11}B NMR spectra. The yield was based on the amount of B_5H_9 in the starting mixture. Measurement of the H_2 produced by destruction of the residual B_5H_9 gives an estimate of the amount of unreacted B_5H_9. This was ∼1.1 mmol, suggesting a 54% yield based on B_5H_9 consumed. During this process, it was clear that $B_{10}H_{14}$ had been lost during workup.

Reaction of B_5H_9 with $CpTiCl_3$. The previous procedure was used without deprotonation of the B_5H_9. A 0.73 mmol portion of $CpTiCl_3$ and 0.75 mmol of B_5H_9 were used in this experiment. After stirring for 3 days in THF, the solution color was unchanged, but some solid had been deposited. Removal of the solvent in vacuo led to the isolation of a mustard-colored solid, similar in appearance to the Ti starting material. Exposure to air during weighing resulted in the solid slowly turning black. The mass of the solid was the same as the starting material, and only very small traces of $B_{10}H_{14}$ and no other boron-containing species were observed in the NMR spectrum of the resultant black solution.

Use of a Nonstoichiometric Amount of $CpTiCl_3$. A nonstoichiometric amount of $CpTiCl_3$ was used in this case to see if the reaction can act catalytically. $CpTiCl_3$ (0.9 mmol) was allowed to react similarly with LiB_5H_8 prepared from 0.4 mmol B_5H_9, and the products were worked up so as to optimize isolation of $B_{10}H_{14}$. 0.16 mmol (20 mg) $B_{10}H_{14}$ resulted, representing 8% yield based on B_5H_9 in the starting mixture.

Small Scale "Stoichiometric" Reaction of $CpTiCl_3$ with LiB_5H_8. In this case, the same procedure as for the first reaction was used when 0.5 mmol of $CpTiCl_3$ was allowed to react with LiB_5H_8 prepared from 0.5 mmol of B_5H_9. $B_{10}H_{14}$ was isolated by CH_2Cl_2 extraction of the crude reaction mixture followed by sublimation to give 10 mg, 0.08 mmol, of $B_{10}H_{14}$ (32% based on $[B_5H_8]^-$ in the starting mixture). The amount of unreacted B_5H_9 was ∼0.36 mmol, suggesting a 65% yield of $B_{10}H_{14}$ based on B_5H_9 consumed.

Results and Discussion

The reaction of Cp_2ZrCl_2 with 2 equiv of LiB_5H_8 at temperatures below approximately −35 °C, in THF, methylene chloride, or diethyl ether, affords a major product that is insoluble in ether and only slightly soluble in chloroform and methylene chloride. Filtration of the initial reaction mixture and extraction using CH_2Cl_2 allows the product to be isolated and purified as a pale orange solid, **1**. Chemical and spectroscopic methods identify **1** as [2,3-μ-(Cp_2ClZr)-B_5H_8] in 70% yield. Although **1** was not stable enough for satisfactory elemental analysis, mass spectral analysis gives a parent ion and the correct isotope envelope around m/q = 318, consistent with the formula [$Cp_2ZrCl(B_5H_8)$].

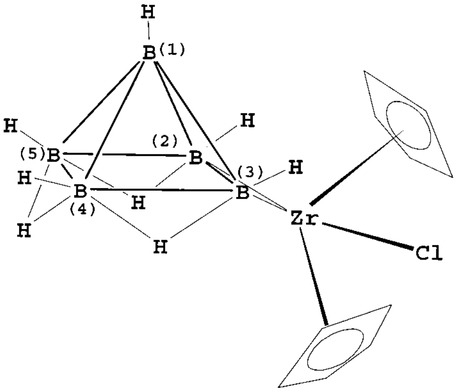

Figure 1. Proposed structure of [2,3-μ-(Cp_2ClZr)B_5H_8] (**1**).

NMR spectral data for **1**, which are given in the Experimental Section, also provide support for this formulation. The ambient temperature ^{11}B NMR spectrum exhibits a broad overlapping peak at −9.54 ppm of area 4 and a doublet, $J(^{11}B-^{1}H) = 169$ Hz, of area 1 at −41.6 ppm. This suggests a pyramidal B_5 cage, which the proton spectra confirm. The $^{1}H\{^{11}B\}$ spectra show overlapping broad resonances of area 4 at 1.88 ppm which couple to the ^{11}B peak of area 4 and a singlet at 0.85 ppm associated with the ^{11}B doublet of area 1. Also, the proton spectrum shows a broad single resonance at −2.45 ppm, area 3, suggesting the presence of three bridging H atoms. The C_5H_5 proton resonances were observed at 6.35 ppm. Treatment of **1** with HCl affords Cp_2ZrCl_2 and B_5H_9, essentially quantitatively, suggesting that the Cp_2ZrCl moiety occupies a bridging position in a B_5H_8 cage. This has been used previously to indicate the presence of bridging moieties in pyramidal borane cages.[11] Thus, we presume that the structure of **1** is that given in Figure 1.

At lower temperature, −44 °C, the ^{11}B NMR spectrum of **1** affords three resonances in area ratio 2:2:1 at −6.2, −11.6, and −46.1 ppm which couple, respectively, to three sets of ^{1}H resonances at 1.90 and 0.85, 2.40 and 2.25, and 0.75 ppm. In addition, the ^{1}H spectrum exhibits two resonances in the bridging region, one at −1.8 ppm, area 1, which couples to the ^{11}B resonance at −11.6, and one at −2.83 of area 2, which couples strongly to the ^{11}B resonance at −6.2 and weakly to the one at −11.6 ppm. This again tends to confirm a structure involving a B_5H_8 cage in which a bridging position is occupied by the Zr moiety, as indicated in Figure 1. At even lower temperatures, in the −93 °C region, the ^{11}B resonance at −11.6 has broadened substantially into two very broad resonances of approximately equal area centered at approximately −11.5 ppm. Although the ^{11}B resonance at −6.2 ppm broadens such that it is barely visible at −93 °C, it appears that all four basal boron atoms and their associated terminal H atoms occupy unique environments at very low temperatures, consistent with the structure depicted in Figure 1. Thus, our results suggest that **1** is fluxional and that there appear to be two processes occurring: one which renders the two sets of basal B atoms, B(2)-(3) and B(4)(5), equivalent and a higher energy process which renders all the basal boron atoms equivalent, on the NMR time scale.

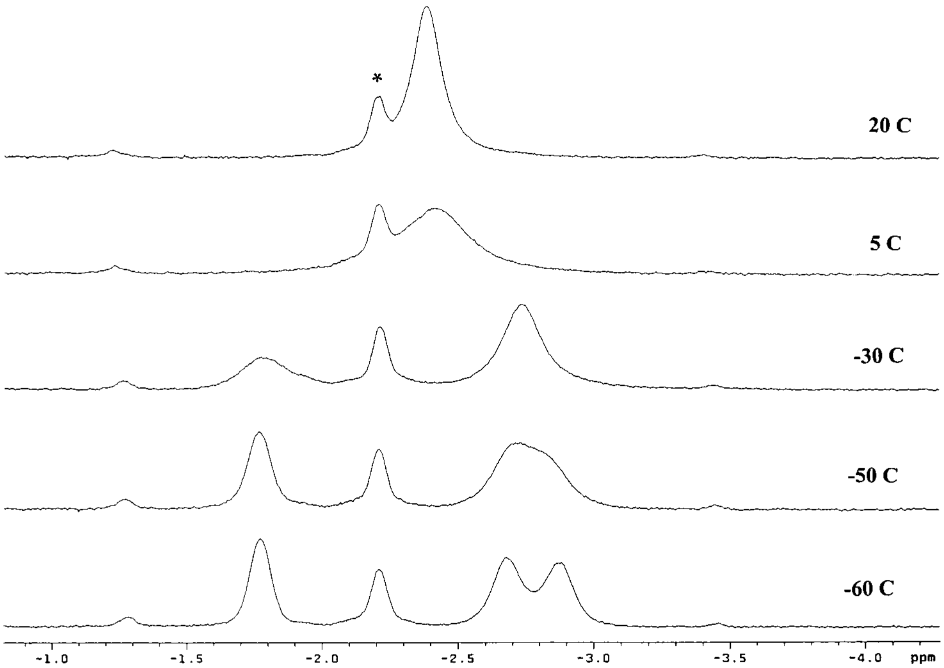

Figure 2. Variable temperature ^{1}H NMR spectrum of the B−H−B bridging region in **1**. ∗ indicates B_5H_9.

Our proposals about the fluxional processes are based on a detailed examination of the variable temperature proton NMR spectra of **1**. The behavior of the terminal basal proton resonances mirrors that of the basal boron atoms, with a single broad resonance at temperatures around ambient. Similarly, a single broad resonance is seen for the bridging H atoms. This suggests that the fluxional process, which renders the basal terminal B atoms equivalent, also renders the terminal H atoms equivalent and the bridging H atoms equivalent. This requires that the Cp_2Zr moiety be involved in the fluxional process. As the temperature is lowered, the first change observed is the collapse of the bridging H atom resonance at −2.4 ppm and the appearance of two new ones in 2:1 area ratio. As the two bridging resonances begin to sharpen, the basal terminal resonance also broadens and splits into two peaks at ∼2.3 and 0.86 ppm in 3:1 ratio. As the temperature is lowered further to −30 °C, the basal terminal H atoms further split into peaks of relative area 2:1:1, at 2.34, 1.93, and 0.84. At the lowest temperature recorded, −93 °C, four resonances (2.39, 2.26, 1.90, and 0.88 ppm) are observed for the basal terminal H atoms, and the three bridging H atoms are observed at −1.82, −2.74, and −2.29 ppm. At this temperature, the apical H atom is observed at 0.78 ppm, distinct from the closest basal terminal H atom, which is seen at 0.88 ppm. Measurement of the resonances at small temperature differences allowed estimation of the activation energy barriers for the two processes. The higher temperature process has a barrier of ∼48 kJ mol^{-1}, and the lower temperature one is 54 kJ mol^{-1}. The variable temperature ^{1}H NMR spectrum of the bridging region is given in Figure 2, and it highlights the two processes.

It is believed that pyramidal boranes are only fluxional when there is a basal B−B bond into which the bridging H atoms, or substituent replacing a bridging H atom, can migrate,[13] as it has been demonstrated that only the bridging H atoms move in such cases.[14] At the lowest temperatures, we can assume that **1** is static on the NMR time scale because all the atoms are observed as separate resonances, both in the ^{1}H and ^{11}B NMR spectra. This would result from an asymmetric arrangement of the two Cp and the Cl ligands on Zr. The first change observed in the spectra of **1** on warming, collapse of the basal boron resonances into two of equal area, concomitantly with collapse of the bridging H atom resonances and the emergence of two resonances in area ratio 2:1, suggests that B(2) and B(3) are equivalent, as are B(4) and B(5), with $\mu H_{3,4}$ and $\mu H_{2,5}$ being equivalent but different from $\mu H_{4,5}$. Thus, at this temperature, **1** has a plane of symmetry through the apical boron and bisecting the bonds B(2)−B(3) and B(4)−B(5). This can be explained by a rotation about the three-center two-electron bond between the Cp_2ZrCl moiety and the adjacent B(2)−B(3) atom pair as illustrated in Scheme 1. Such rotation would generate the required plane of symmetry in the time-averaged molecular structure. Thus, the experimental results are in accord with our hypothesis for the low-temperature fluxional process.

The process which renders all the basal boron atoms and their associated terminal H atoms equivalent, and also the bridging H atoms equivalent, must involve motion of the bridging H atoms around the basal region in some way, or motion of the Cp_2ZrCl moiety, or both. If the bridging H atoms are in motion at higher temperatures, then they must occupy sites on the Cp_2ZrCl moiety because there are no available B−B sites. Whether the H atom resides in a bridging B−Zr site, or on the Zr atoms as a terminal H atom at points during the process, cannot be determined; however, motion around the square base, such as the process shown

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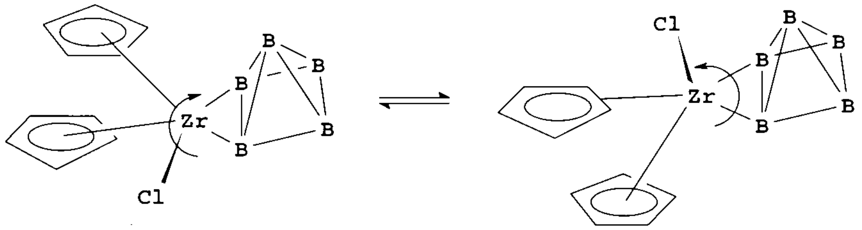
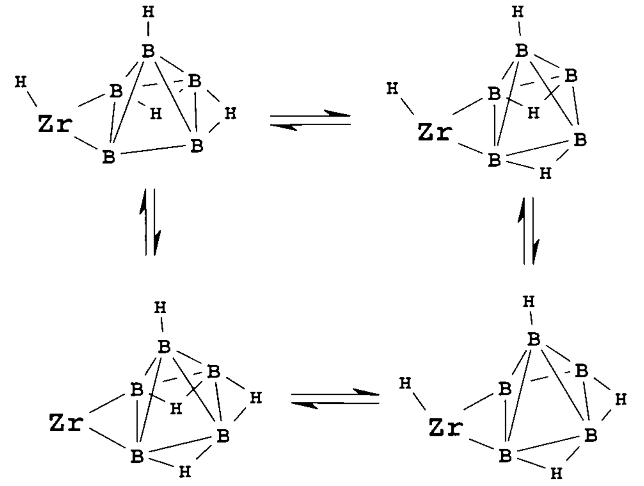
(13) Rush, P. K.; Barton, L. *Polyhedron* **1985**, *4*, 1741.

(14) Brice, V. T.; Johnson, H. D.; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 6629.

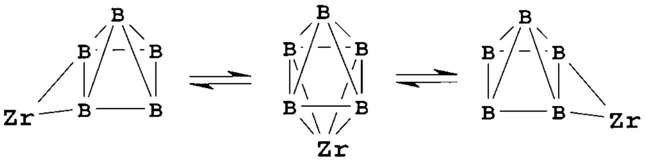
Scheme 1



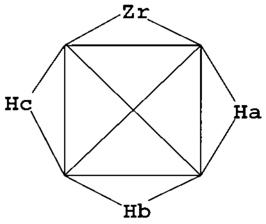
Scheme 2



Scheme 3



Scheme 4



in Scheme 2, is feasible. Scheme 2 indicates four possible tautomers, varying in the placement of the bridging hydrogens. In fact, there would be 20 possible tautomers, if one considered the two Zr−B bridging and the Zr terminal positions as sites for occupancy by the fluxional hydrogens. There is a growing number of examples of cyclopentadienyl zirconium hydride complexes for which there is hydrogen exchange between bridging and terminal H atoms on zirconium.[15] Indeed, some of the processes for which that type of fluxional motion is suggested involve borane species.[15e,f,h−j] Thus, the H atom can hop over the Zr moiety so that all the Hμ atoms become equivalent on the NMR time scale. An alternative or accompanying motion could be a rocking-type 1,3 shift in the Hμ positions as indicated in Scheme 3. Such processes have not previously been suggested for square pyramidal boranes, but there certainly are enough examples of octahedral clusters in borane chemistry to render this proposal feasible.[16] Indeed, we invoked a similar mechanism to account for the fluxional processes in the anion $[Fe(CO)_4B_6H_9]^-$.[17]

Support for the 1,2-shift mechanism illustrated in Scheme 2 arises from our observation of the lower energy fluxional process for this molecule. As temperature is raised, the bridging hydrogen region of the proton NMR spectrum changes from two peaks at −1.8 (integral (int) 1) and −2.8 (int 2) to a single peak at −2.4 (int 3). Before the coalescence, these peaks broaden, and it is seen that the integral 1 peak broadens significantly at a higher temperature than the integral 2 peak. The temperature difference between the broadening of these two peaks is ∼5 °. A comparison of the broadness of the peaks at half-height shows that the integral 2 peak is half as broad as the integral 1 peak as they approach coalescence (72 Hz vs 130 Hz). Further, below the coalescence point, both peaks are equally broad (∼60 Hz). This pattern suggests that, during the fluxional process, the environment of the protons causing the integral 2 peak changes more slowly than that causing the integral 1 peak. This is consistent with a 1,2 exchange of the Zr with an adjacent proton. If we assume that Zr and Ha in Scheme 4 are interchanged, then the environment of Hb is changed from trans to Zr to adjacent to Zr, and Hc changes from adjacent to Zr to trans to Zr. However, Ha is still adjacent to Zr, and so, its environment is unchanged. Therefore, the environment of the trans protons, which cause the integral 1 peak, changes more rapidly than that of the adjacent protons, only one of which is affected by the 1,2 shift. This will cause the broadening of the integral 1 peak to occur at a more rapid rate than that of the integral 2 peak. Overall, the repetition of this mechanism will render all bridging hydro-

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[15] (a) Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339. (b) Gozum, J. E.; Girolami, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 3829. (c) Gozum, J. E.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1992**, *114*, 9483. (d) Bakhmutov, V. I.; Visseaux, M.; Baudry, D.; Dormond, A.; Richard, P. *Inorg. Chem.* **1996**, *35*, 7316. (e) Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1230. (f) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. (g) Etkin, N.; Hoskin, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 11420. (h) Chow, A.; Liu, F.-C.; Fraenkel, G.; Shore, S. *Magn. Reson. Chem.* **1998**, *36*, S145. (i) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293. (j) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 2169.

[16] See for example: (a) Boone, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5036. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3255. (c) Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 383. (d) Jiang, F.; Fehlner, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 1860. (e) Bould, J.; Rath, N. P.; Barton, L. *Chem. Commun.* **1995**, 1285.

[17] Srivastava, D. K.; Rath, N. P.; Barton, L.; Ragaini, J. D.; Hollander, O.; Godfroid, R.; Shore, S. G. *Organometallics* **1993**, *12*, 2017.

gen atoms and all basal boron atoms equivalent, which is observed in the proton and boron NMR spectra. Because we expect that the H atom can "hop over" the Zr moiety, as seen in Scheme 2, this represents effective exchange of the Zr moiety and an adjacent H atom which is consistent with our NMR observations. Comparisons with recent work of Shore et al.[18a] and also Bercaw et al.[18b] suggest that such motion could involve exchange with the cyclopentadienyl hydrogen atoms as they observed in related systems, although we were not able to demonstrate such exchange. Our conclusions are that the 1,3 shift "tipping" motion is less favored.

Species **1** is not very stable at room temperature, and we were unable to obtain satisfactory elemental analysis, but if a methylene chloride solution is filtered through a plug of silica in air, a yellow solution is obtained from which an air-stable, yellow crystalline solid, **2**, is isolated. Compound **2** is identified unambiguously, from NMR spectra, elemental analysis, and high-resolution mass spectra, and also from an X-ray crystallographic study, as $[(Cp_2Zr)_2B_5H_8]^+[B_{11}H_{14}]^-$. Obtained in 14% yield, **2** is air stable both as a solid and in solution but decomposes slowly (over a period of days) in solution in air to give decaborane(10) as the only easily identifiable product.

NMR spectra of the crystalline product, **2**, indicate the presence of the $[B_{11}H_{14}]^-$ anion,[19] suggesting that the zirconium-containing species is cationic, which is consistent with the low solubility of the material. In addition to resonances due to $[B_{11}H_{14}]^-$, there are two resonances in the area ratio 4:1 in the $^{11}B\{^1H\}$ NMR spectrum suggesting a B_5 species. The coupled spectrum shows some broadening of the resonance of area 4 but no change in the area 1 resonance. Proton spectra are also consistent with the presence of the $[B_{11}H_{14}]^-$ anion.[19] The remaining resonances, not ascribed to solvent nor to anion, are observed in the ratio 5:1:1, that is, 20:4:4. The resonance of area 20 is assigned to the cyclopentadienyl moieties, and the other hydrogens are identified as boron-bonded H atoms from their broadening in the coupled ^1H spectrum. Selective decoupling confirms that all the cage H atoms are bonded only to the boron atoms producing the integral 4 peak above. These resonances, falling at 3.05 and −5.05 ppm, are assigned to terminal BH groups and bridging B−H−Zr groups, respectively. The high-resolution mass spectrum confirms that the cation consists of a species containing two Cp_2Zr moieties and a B_5H_8 group.

Crystals suitable for an X-ray diffraction study were grown by diffusion of pentane into a $CDCl_3$ solution of **2**. The structure of the cation is shown in Figure 3 and is consistent with the NMR data. Two crystallographically independent ion pairs are found in the unit cell. The cations are not significantly different from one another. All parameters listed are for cation A. The arrangement of the boron atoms resembles that of a distorted spiro[2.2]pentane molecule; the angle between the two planes is 73° rather than 90°. A stick drawing of the structure is given in Figure 4. Each boron atom bears a terminal hydrogen, and there are four Zr−H−B bridge bonds. A unique feature of the structure is that the central B atom does not bear a hydrogen atom. Such "naked" B atoms are normally only observed in macropolyhedral boranes at points of cage fusion and typically have high connectivity.[20] The latter is the case for B(1) which we consider to have connectivity of six. The B−B connections have normal B−B bonding distances: those between the naked boron and the others, ranging from 1.686(7) to 1.731(5) Å, and those on the periphery of the B_5 cluster, B(2)−B(3) and B(4)−B(5), which are not bridged by hydrogen atoms and are longer, ranging from 1.842(9) to 1.870(6) Å. The planes described by connecting the centroids of the Cp rings and the Zr are effectively orthogonal (99.7° and 100.9°) to the adjacent ZrB_3 planes which would be expected from orbital considerations.[21] The cation in compound **2** is thus similar to $[Cp_2Zr\{CH_2(BR_2)_2\}]^{22}$ in which the Zr coordinates similarly to a $\{CH_2(BR_2)_2\}$ moiety. The nonbridged Zr−B distances in **2**, ranging from 2.473(4) to 2.508(5) Å, are slightly longer than would be expected for a single Zr−B

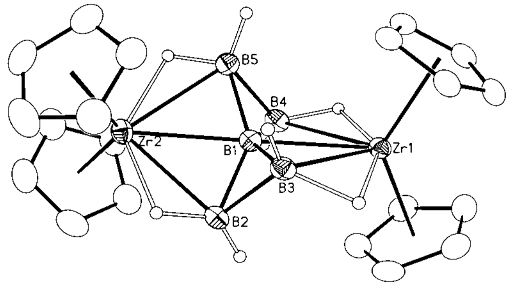

Figure 3. Structure of the cation in $[(Cp_2Zr)_2B_5H_8][B_{11}H_{14}]$ (**2**), with 50% probability thermal ellipsoids and the cyclopentadienyl groups abbreviated for clarity. The terminal H on B(4) is obscured.

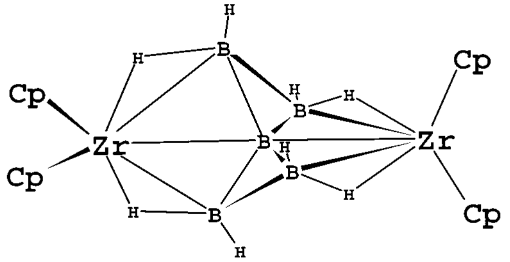

Figure 4. Alternative view of the cationic cluster of **2**, presented as a drawing.

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[18] (a) Shore, S. G.; Liu, F.-C. *Spec. Publ.*−*R. Soc. Chem.* **2000**, *253*, 28. (b) Chirik, P. J.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873.

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[20] (a) Barton, L. *Top. Curr. Chem.* **1982**, *100*, 169. (b) Bould, J.; Clegg, W.; Teat, S. J.; Barton, L.; Rath, N. P.; Thornton-Pett, M.; Kennedy, J. D. *Inorg. Chim. Acta* **1999**, *289*, 95. (c) Yao, H.-J.; Hu, C.-H.; Sun, J.; Jin, R.-S.; Zheng, P.-J.; Bould, J.; Greatrex, R.; Kennedy, J. D.; Ormsby, D. L.; Thornton-Pett, M. *Collect. Czech. Chem. Commun.* **1999**, *64*, 927. (d) Bould, J.; Ormsby, D. L.; Yao, H.-J.; Hu, C.-H.; Sun, J.; Jin, R.-S.; Shea, S. L.; Clegg, W.; Jelinek, T.; Rath, N. P.; Thornton-Pett, M.; Greatrex, R.; Zheng, P.-J.; Barton, L.; Stibr, B.; Kennedy, J. D. *Spec. Publ.*−*R. Soc. Chem.* **2000**, *253*, 171.

[21] (a) Lauher, J.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Bethon, R. A.; Rounsley, R. J.; Burns, R. C. *Polyhedron* **1993**, *12*, 2157.

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

bond (2.45 Å)[23] but are shorter than typical Zr−B bonds found in (η^5-C_2B_3)Zr moieties,[24] the only nonbridged Zr−B bonds available for comparison.[25] On the other hand, the Zr−B distances for the Zr−H−B bridge bonds, ranging from 2.512(4) to 2.526(4) Å, are shorter than those observed elsewhere,[26] suggesting a strong bonding interaction between the Cp_2Zr moiety and the borane cage. Thus, each Zr appears to be bonded in a *trihapto* mode to the boron cluster, the Zr−B central connection being shorter than the peripheral ones. The atoms Zr(1)−B(2)−B(1)−B(5) lie in a plane, as do Zr(2)−B(3)−B(1)−B(4), with an angle of 54.8° between the two planes. The central boron atom, B(1), lies almost exactly on a vector between the two Zr atoms. The angle Zr(1)−B(1)−Zr(2) is 178.6°.

An alternative description of the cationic cluster is that it is a metal-stabilized *hypho* cluster.[27] The *hypho*-pentaborane cluster[27] would be $[B_5H_8]$,$^{5-}$ and thus, the metal moieties would have to be formulated as $[Cp_2Zr^{3+}]$. Each would contribute three electrons to the borane cage. This appears to be an unreasonable assumption, because the formulation Cp_2Zr^{2+} has a d^0 configuration, so **2** must be added to the growing list of metallapolyboranes[3c−t,28] which contain fewer than the requisite number of electrons required by electron counting rules.[29] What is clear, however, for the structure of **2** and for the other known group 4 metallapolyborane, $[Cp_2Ti(B_6H_9)]_2$,[6] is that unusual structures derive from metallaboranes involving the early transition metals as has been observed by Fehlner et al.[3,8b,28]

The identification of the $[B_{11}H_{14}]^-$ anion in this reaction requires some comment. It was clearly identified by NMR spectroscopy, and this was confirmed by the X-ray diffraction study. The structure observed, an icosahedron of BH units with one removed, supports the recent results of Shore et al.[30] who identified this cluster with three non-*exo*-hydrogen atoms in the open face as a pair of B−H−B bridges and a normal *endo*-hydrogen atom. Because not all the cage hydrogen atoms were located in our study, we are unable to confirm this finding. We observed the three *endo*-hydrogens as a single resonance in the NMR spectra, as did Shore et al.,[19] but our structure determination was unable to satisfactorily distinguish the bridging from the *endo*-terminal H atoms in the open face of the anion. Our data suggest that our structure is a good one, and because of the nature of the two cations, it belongs to a different space group, *Cc* rather than group $P\bar{1}$, reported for the $[P(CH_3)_3H]^+$ salt.[30] The undecaborate anion is formed as solutions of $[B_5H_8]^-$ are allowed to warm to room temperature in the presence of B_5H_9.[31] In our case, passage through silica or the presence of the "Cp_2ZrCl" moiety may catalyze the formation of higher boranes. Such organometallic species are known to catalyze polymerization of unsaturated hydrocarbons[32a] and also the dehydrogenative coupling of silanes.[32b]

The reaction between cyclopentadienyltitanium halides and $[B_5H_8]^-$ proceeds differently from those of their Zr and Hf homologues. Stirring Cp_2TiCl_2 and $[B_5H_8]^-$ under a variety of conditions afforded no identifiable products, but reactions of $[B_5H_8]^-$ and $CpTiCl_3$ afforded relatively good yields of $B_{10}H_{14}$. Although attempts were not made to maximize the yields of the latter, there appears to be promise in this process for the conversion of B_5H_9 to $B_{10}H_{14}$. Varying the amount of $CpTiCl_3$ indicated that the reaction was stoichiometric rather than catalytic. A catalytic route may be possible if a cocatalyst is used to reoxidize the Ti(III) to Ti(IV), but it is important that the cocatalyst does not react further with the titanium complex. It is known that $PbCl_2$ will readily oxidize Ti(III) to Ti(IV), so we carried out some reactions of $CpTiCl_3/PbCl_2$ with $[B_5H_8]^-$. The results of this study show the pentaborane to be converted to unidentifiable boron-containing products, with only traces of $B_{10}H_{14}$ detected by NMR spectroscopy. The reaction of $PbCl_2$ with $B_5H_8^-$ gives small traces of $B_{10}H_{14}$. Given these findings, attempts to devise catalytic conversion of B_5H_9 to $B_{10}H_{14}$ were abandoned. Our results indicate that the yields of $B_{10}H_{14}$, based on $CpTiCl_3$, are the most consistent, suggesting that it is the limiting reagent in these reactions. In the $CpTiCl_3$-promoted conversion of B_5H_9 to $B_{10}H_{14}$, prior deprotonation of the B_5H_9 was necessary because only traces of $B_{10}H_{14}$ were obtained when B_5H_9 was used. If the reaction is carried out by first treating $CpTiCl_3$ with MeLi followed by addition of B_5H_9, most of the B_5H_9 remains unreacted in the reaction vessel. Apparently, the Ti−Me groups do not appear to be strong enough bases to deprotonate the pentaborane.

The experimental results suggested to us that a stoichiometry of 4 Ti(IV) for each mole of $B_{10}H_{14}$ produced was required. Assuming the reaction involved is described by the

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(24) For example see: (a) Thomas, C. J.; Jia, L.; Zhang, H.; Siriwardane, U.; Maguire, J. A.; Wang, Y.; Brooks, K. A.; Weiss, V. P.; Hosmane, N. S. *Organometallics* **1995**, *14*, 1365. (b) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630. (c) Mao, S. S. H.; Tilley, T. D.; Rheingold, A. L.; Hosmane, N. S. *J. Organomet. Chem.* **1997**, *533*, 257.

(25) There is a class of zirconium borides in which a B atom is located at the center of a Zr octahedron. The Zr−B distances are ~2.3 Å, but these are not really comparable to normal Zr−B bonds. Xie, X.; Reibenspies, J. H.; Hughbanks, T. *J. Am. Chem. Soc.* **1998**, *120*, 11391.

(26) A structure search identified 22 compounds containing Zr−B connections with one or two Zr−H−B bridges. The Zr−B distances range from 2.56 Å in $[\mu HCp_2Zr(\mu H)_2BC_4H_8\}_2]^+$ (Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 6106) to 3.23 Å in the cation $[Cp^*{}_2Zr(Me)(C_2B_9H_{12})]$ (Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc*. **1989**, *111*, 2728); the mean value is 2.62 Å.

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equation 4Ti(IV) + 4$[B_5H_8]^-$ → 4Ti(III) + $B_{10}H_{14}$ + 2B_5H_9, we obtained yields in the range 54−65% based on the equation and 26−32% based on the initial amount of B_5H_9 used. Pentaborane(9) is recovered in the reaction, so taking this into account, yields based on consumption of B_5H_9 or on the amount of Ti used are in the range 54−65%.

This latter chemistry is clearly similar to the metal-promoted fusion reactions of Grimes[33] and Sneddon.[34] The former work involves oxidative fusion which requires exposure of the intermediate to air, something which our system cannot tolerate, although our yields of $B_{10}H_{14}$ are about 1.5 times those reported for the $RuCl_3$-promoted conversion of $[B_5H_8]^-$ to $B_{10}H_{14}$.[33] The latter work by Sneddon et al. involves the catalytic conversion of B_5H_9 to 1:2′-$(B_5H_8)_2$, in the presence of $PtBr_2$, in 92% yield.[35] Treatment of 1:2′-$(B_5H_8)_2$ with Li(BEt_3H) affords $[B_9H_{14}]^-$ in 94% yield. Conversion of $[B_9H_{14}]^-$ salts to $B_{10}H_{14}$ proceeds in 40% yield,[31,36] and thus, extension of the Sneddon method to the preparation of $B_{10}H_{14}$ from B_5H_9 represents ∼34% yield. Although our method competes well with those just described, the "one pot" synthesis of $B_{10}H_{14}$ from B_5H_9 described by Shore et al.[36] represents the most convenient available route. These coupling or fusion methods have not led to better methods for $B_{10}H_{14}$ formation, but they all represent good general approaches to the formation of higher borane cages. Our contribution to this area continues, and we will report soon on this aspect of our work.

Conclusions

We have prepared and characterized some novel group IV metallaboranes. Compound **1**, μ-(Cp_2ClZr)B_5H_8, consists of a B_5H_8 cage with a $[Cp_2ZrCl]^+$ moiety substituting for a bridging proton. Compound **1** exhibits some novel dynamic behavior for which we propose explanations based on NMR data. Passage of **1** through silica affords $[(Cp_2Zr)_2B_5H_8]$-$[B_{11}H_{14}]$ (**2**), a rare cationic metallaborane with a novel structure. A hafnium analogue of **2**, $[(Cp_2Hf)_2B_5H_8][B_{11}H_{14}]$ (**3**), is also obtained, but the presumed precursor, the analogue of **1**, although probably formed, was not observed. The use of the analogous Ti starting materials reagents leads only to coupling of B_5H_9 to $B_{10}H_{14}$. These results portend well for study of other group 4 and 5 derivatives of the polyboranes.

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Supporting Information Available: Crystallographic data, positional parameters, anisotropic displacement parameters, and bond lengths and angles for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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