Volume 35
Number 5
February 28, 1996

Inorganic Chemistry

Communications

Organodiborate Ring Transformations Promoted by Zirconocene and Hafnocene Dichlorides. Preparation and Structure of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$

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Received October 16, 1995

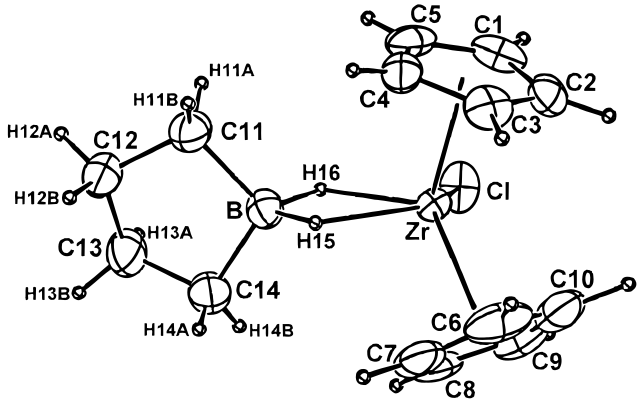

Figure 1. Molecular structure of $(C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ (ORTEP plot with 50% probability ellipsoids). Selected bond distances (Å): Zr−B = 2.572(3), Zr−Cl = 2.4974(7), Zr−C_{av} for Cp ring containing C(1)−C(5) = 2.491, Zr−Cl_{avg} for Cp ring containing C(6)−C(10) = 2.501, Zr−H(15) = 2.00(3), Zr−H(16) = 1.97(3), B−H(15) = 1.24(2), B−H(16) = 1.22(3), B−C(11) = 1.611(4), B−C(14) = 1.606(4). Selected bond angles (deg): C(11)−B−C(14) = 105.0(3), H(15)−B−H(16) = 97(2), H(15)−Zr−H(16) = 55(1), Zr−H(15)−B = 102(2), Zr−H(16)−B = 105(2).

The organodiborate anion $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ is a 10-membered ring structure with a transannular B−H−B bridge. It is prepared through the reaction of $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ with KH.[1] This anion normally functions as a hydride transfer reagent,[2] similar to trialkoxyborohydrides in the reduction of metal carbonyls.[3] The reactions are driven by the regeneration of $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$, a very stable and relatively inert organodiborane.[4] In principle, this anion could also act as a ligand for the formation of hydrogen bridged complexes with d- and f-block metals. However, in attempts to form such complexes, the anion underwent unanticipated ring transformations. Its reactions with zirconocene dichloride and with hafnocene dichloride produce $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, **1** (Figure 1), and $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$, **2** (eq 1),[5] the first examples

$$(\eta^5\text{-}C_5H_5)_2MCl_2 + K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2] \rightarrow \underset{\mathbf{1},\,\mathbf{2}}{(\eta^5\text{-}C_5H_5)_2MCl\{(\mu\text{-}H)_2BC_4H_8\}} + {}^1/_2B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2 + KCl \quad (1)$$

$$M = Zr, \mathbf{1};\ Hf, \mathbf{2}$$

in which $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ disproportionates to form a 5-membered borocyclopentane ring. Rearrangement is facilitated by the presence of the electron-deficient 16 electron metal center. **1** and **2** are white solids, stable at room temperature under vacuum. NMR and IR spectra are consistent with the bridged structure (Figure 1). The ^{11}B NMR spectra of **1** and **2** consist of a triplet at +16.7 ppm ($J(^{11}B,^1H) = 56$ Hz) and +12.5 ppm ($J(^{11}B,^1H) = 53$ Hz), respectively. These resonances are downfield relative to those of their bis(tetrahydroborate) analogues.[6b−c] Two strong bands at 2065 and 2004 cm^{-1}, characteristic of B−H−M stretching modes, are present in the IR spectrum of **1**.[6] Time-elapsed boron-11 NMR spectra provide insight into the intermediates produced in the formation of **1**. Scheme 1 depicts a proposed reaction pathway based upon these spectra. Six minutes after initiating the reaction, all of

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(5) Preparation of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2B(C_4H_8)\}$, **1**. (The preparation of **2** is similar.) A 1.23 g amount (4.21 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (Aldrich) was added to a rapidly stirred solution of $[KB_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2H_2]$ (4.49 mmol) in 40 mL of THF which was then stirred overnight at room temperature and then filtered. THF and $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ were removed under dynamic vacuum. The resulting pale yellow solid was dissolved in 5 mL of THF and layered with 35 mL of hexanes at 0 °C. A crop of off-white crystals formed. They were filtered, washed with hexanes, and dried under vacuum to yield 0.977 g (3.00 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2B(C_4H_8)\}$, **1**, 71%. ^{11}B NMR (THF-d_8): δ 16.7 (t, J = 56 Hz). ^1H NMR (THF-d_8): δ6.34 (s), 1.44 (br mult), 0.92 (br mult), 0.19 (br s), −2.17 (br, s). Anal. Calcd for $C_{14}H_{20}BClZr$: C, 51.61; H, 6.19; B, 3.32; Cl, 10.88; Zr, 28.00. Found: C, 51.43; H, 6.15; B, 3.21; Cl, 10.99; Zr, 27.34.

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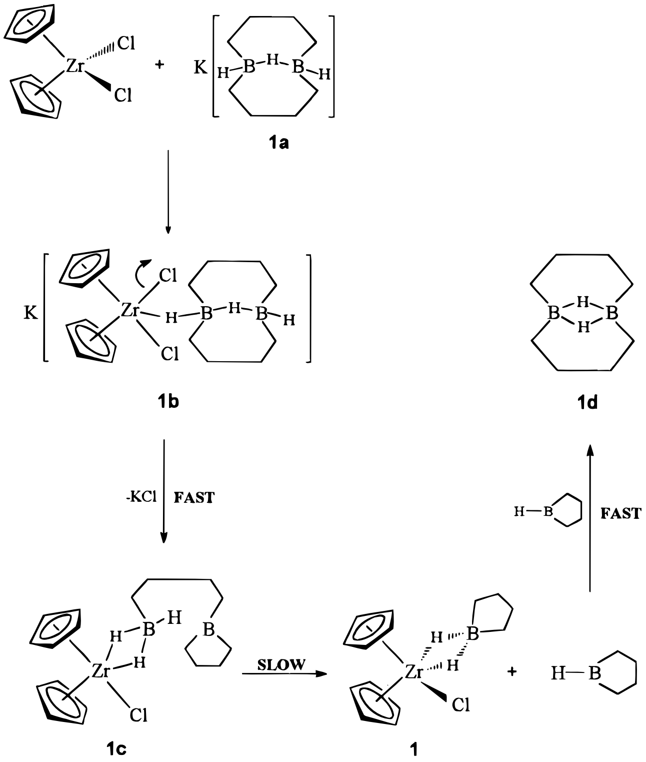
Scheme 1. Plausible Pathway for the Formation of $(C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$



the $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, **1a**, is consumed. A reasonable initial step would involve coordination of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ to the electron deficient Zr through a hydrogen bridge bond to form **1b**, an 18 electron complex. Departure of Cl^- from **1b** and rapid molecular rearrangement result in the formation of the intermediate **1c**. ^{11}B NMR signals at +88.1 (s) and +5.8 ppm (q, $J(^{11}B,^1H) = 71$ Hz) in a 1:1 ratio support the presence of **1c**. The broad downfield resonance is indicative of a trialkylborane.[1b,7] The coupling constant for the upfield quartet is intermediate for terminal and bridge B−H coupling which is consistent with the bridge hydrogens rapidly exchanging with the terminal hydrogen. (Rapid exchange of bridging and terminal hydrogens of metallo tetrahydroborates at room temperature is well known.[6b,12]) Over the next 2 h, signals for **1c** disappear while those for $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$, **1d**, (+28.2 ppm)[8] and **1** appear in a 1:1 ratio that is constant as they increase in intensity with time. Formation of **1** results in elimination of the cyclic borane $HB(C_4H_8)$ which rapidly dimerizes to the transannular hydrogen bridged organoborane **1d**.

The structure of **1** was determined from a single-crystal X-ray analysis[9] (Figure 1). It is an analogue of the tetrahydroborate complexes $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BH_2\}$ and $(\eta^5\text{-}C_5H_5)_2Zr\{(\mu\text{-}H)_2BH_2\}_2$.[10] Bridging hydrogens of **1** were located and their positions and isotropic thermal parameters were refined. Distances that involve bridging hydrogen and the Zr−B distance of 2.572(3) Å are consistent with distances observed in other bidentate borohydride systems.[11] The bridging hydrogens of **1** are inequivalent on the ^1H NMR time scale at room temperature in THF-d_8. Two resonances at −2.17 and +0.19 ppm are observed. These collapse into a single signal at −0.97 ppm at 50 °C.

In ammonia, the bridge system undergoes heterolytic cleavage at −40 °C to yield $[H_2BC_4H_8]^-$ and the solvent separated cation $[(\eta^5\text{-}C_5H_5)_2ZrCl(NH_3)_x]^+$ (eq 2). Evidence for the ionic product

$$(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\} + xNH_3 \rightarrow [(\eta^5\text{-}C_5H_5)_2ZrCl(NH_3)_x][H_2BC_4H_8] \quad (2)$$

$$(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\} + NH(CH_3)_2 \rightarrow (\eta^5\text{-}C_5H_5)_2ZrClH_2 + NH(CH_3)_2HBC_4H_8 \quad (3)$$

is given by a clean ^{11}B NMR spectrum which is a sharp triplet at −20.8 ppm (J = 76 Hz) at −40 °C that is assigned to $[H_2BC_4H_8]^-$. This reaction parallels the unsymmetrical cleavage of B_2H_6 by NH_3 to give $[BH_2(NH_3)_2][BH_4]$.[13] The hydrogen bridge system of **1** is cleaved homolytically by methylamines (eq 3). The ^{11}B NMR spectrum for the reaction with $NH(CH_3)_2$ consists of a doublet at −2.4 ppm (J = 89 Hz) at −40 °C which is assigned to $NH(CH_3)_2HBC_4H_8$.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 94-09123. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center. G.T.J. is grateful for an industrial fellowship funded by Procter & Gamble.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1** (11 pages). Ordering information is given on any current masthead page.

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(9) Crystal data (−60 °C): space group $P2_1/n$ (No. 14), $a = 8.594(1)$ Å, $b = 14.807(3)$ Å, $c = 11.170(3)$ Å, $\beta = 96.42(2)°$, $V = 1412.6$ Å^3, ρ(calcd) = 1.532 g cm^{-1}, MW = 325.799, $Z = 4$, $\mu = 9.3$ cm^{-1}. Diffraction data (Enraf-Nonius CAD4, Mo Kα) were corrected for Lorentz and polarization, and absorption (empirical) effects. Structure solution involved a combination of MULTAN 11/82 and difference Fourier syntheses. $R_F = 0.018$ and $R_w = 0.027$ (219 variable parameters refined) for 1540 reflections [$I \geq 3\sigma(I)$] of 1816 independent reflections ($4° \leq 2\theta \leq 45°$).

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