

Communications to the Editor

Preparation and Molecular Structure of [(Cp₂Zr)₂B₅H₈][B₁₁H₁₄]: A Dizirconaborane Containing a Cation Exhibiting a Novel Cluster Type

Rhodri Ll. Thomas, Nigam P Rath, and Lawrence Barton*

Department of Chemistry
University of Missouri—St. Louis
St. Louis, Missouri 63121

Received August 1, 1997

With the exception of tetrahydroborate complexes, few small metallocopolyboranes containing early transition metals have been reported.¹ Thus, only one titanaborane² and a small number of nioba-³ and tantalaboranes⁴ have been fully characterized. As part of our program to prepare group 4 and 5 metallocopolyboranes, the reactions of LiB₅H₈ with various cyclopentadienyl metal halides have been investigated. This report includes preliminary results of our studies of zirconium derivatives and describes the preparation and structural characterization of a novel zirconaborane cation.

Reaction of Cp₂ZrCl₂ with 2 equiv of LiB₅H₈ at temperatures below ca. -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 CH₂Cl₂ allows the product to be isolated and purified as a pale orange solid (**1**). Chemical and spectroscopic methods identify **1** as [2,3-μ-(Cp₂ZrCl)₂B₅H₈].⁵ Details of **1**, which is formed in 70% yield, will be published later. If a methylene chloride solution of **1** is filtered through a plug of silica gel 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,⁶ elemental analysis, and high-resolution mass spectra (HRMS),⁷ and also from an X-ray crystallographic study,⁸ as [(Cp₂Zr)₂B₅H₈]⁺[B₁₁H₁₄]⁻. 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 exposed to air to give decaborane(14) as the only easily identifiable product.

NMR spectra of the crystalline product (**2**) indicate the presence of the [B₁₁H₁₄]⁻ anion⁹ suggesting that the zirconium-containing species is cationic, which is consistent with the low solubility of the material. In addition to resonances due to [B₁₁H₁₄]⁻, there are two resonances in the area ratio 4:1 in the ¹¹B{¹H} NMR spectrum suggesting a B₅ species. The coupled spectrum shows some broadening of the area 4 resonance but no change in the area 1 resonance. Proton spectra are also consistent with the presence of the [B₁₁H₁₄]⁻ anion.⁹ The remaining resonances, not ascribed to solvent or anion, are observed in the ratio of 5:1:1, i.e., 20:4:4. The area 20 resonance is assigned to the cyclopentadienyl resonances, and the other hydrogens are identified as boron-bonded H atoms from their broadening in the coupled ¹H spectrum. Selective decoupling confirms that all of 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 HRMS confirms that the cation consists of a species containing two Cp₂Zr moieties and a B₅H₈ group.

Crystals suitable for an X-ray diffraction study were grown by diffusion of pentane into a CDCl₃ solution of **2**. The structure is shown in Figure 1 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 being 73° rather than 90°. 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.¹⁰ This latter is the case for B(1), which we consider to have a connectivity of 6. The B-B connections have normal B-B bonding distances: those between the naked boron and the others ranging from 1.704(6) to 1.730(5) Å and those on the periphery of the B₅ cluster, B(2)-B(3) and B(4)-B(5), which are not bridged by hydrogen atoms, are longer, at 1.860(6) and 1.865(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 ZrB₃ planes, which would be expected from orbital considerations.¹¹ Compound **2** is thus similar to [Cp₂Zr{CH₂(BR₂)₂}]¹² in which the Zr coordinates similarly to a {CH₂(BR₂)₂} moiety. The nonbridged Zr-B distances in **2**, ranging from 2.474(4) to

(1) (a) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, 32, 519. (b) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1982; Part 6, Chapter 41, pp 879–945. (c) Barton, L.; Srivastava, D. K. In *Comprehensive Organometallic Chemistry, II*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1995; Vol. 1, Chapter 8, pp 275–373.

(2) Denton, D. L.; Godfroid, R. A.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1996**, 35, 791.

(3) Grebenik, P. D.; Leach, J. B.; Pounds, J. M.; Green, M. L. H.; Mountford, P. J. *Organomet. Chem.* **1990**, 382, C1.

(4) Ting, C.; Messerle, L. J. *Am. Chem. Soc.* **1989**, 111, 3449.

(5) ¹¹B (160.5) and ¹H (500.1 MHz) NMR data for **1**: (ppm, CDCl₃ solution, 229 K) (assignment [δ(¹¹B) (¹H in parentheses)]): δ(¹¹B) 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) C₅H₅ [6.35], μH_{4,5} [-1.81], μH_{3,4,2,5} [-2.73, 2.93]. LRMS gave, for the highest mass peak in the highest mass envelope, as m/z = 318, (¹²C₁₀-¹H₁₈¹¹B₄¹⁰B⁹⁰Zr³Cl), with a correct overall isotope distribution for the envelope. These peaks are small, and peaks for the Cp₂ZrCl fragment dominate the spectrum. Treatment of **1** with HCl affords Cp₂ZrCl₂ and B₅H₉, essentially quantitatively, suggesting that the Cp₂ZrCl moiety occupies a bridging position.

(6) ¹¹B (96.2 MHz) and ¹H (299.9 MHz) NMR data for **2**: (ppm, CDCl₃ solution, 298 K) (relative intensity, assignment [δ(¹¹B) (¹H in parentheses)]): δ(¹¹B) 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(¹H) C₅H₅ [6.07] 20H, endoH_{anion} [-3.46] 3H, μH_{B,Zr} [-5.15] 4H. A refers to the anion [B₁₁H₁₄]⁻.

(7) Anal. Calcd for C₂₀H₄₂B₁₆Zr₂ (**2**): C, 37.65, H, 6.64. Found: C, 38.79; H, 6.74. HRMS (Kratos MS-50, FAB, Ar gas) gave m/q for cation **2** of ¹²C₂₀¹H₂₈¹¹B₅⁹⁰Zr₂ 503.0802 (obsd) and 503.0791 (calcd).

(8) Crystallographic data for **2**: C₂₀H₄₂B₁₆Zr₂, monoclinic, Cc, a = 16.21690(10) Å, b = 23.46760(10) Å, c = 16.3222(2) Å, β = 90.7450(10)°, V = 6211.24(9) Å³, Z = 8 (two crystallographically independent ion pairs), D_c = 1.364 Mg m⁻³. Of the 14 192 reflections collected (Siemens SMART CCD diffractometer, Mo Kα, 293 K), 14 192 were independent and 14 180 were observed [4σ(F_o)]. All of the metallaborane hydrogens were located from difference Fourier maps but only selected ones could be refined freely; the rest of the located H atoms were fixed. The hydrogen atoms of the anion were treated using an appropriate riding model. In one anion (B), the absent vertex is disordered over two positions, B(10B) and B(10C) with occupancies of 54 and 46%, respectively. S = 1.014, R₁ = 0.0386, wR₂ = 0.0867.

(9) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1987**, 26, 3638.

(10) Barton, L. *Top. Curr. Chem.* **1982**, 100, 169.

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

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

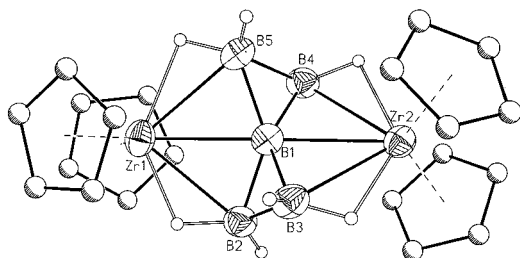


Figure 1. Molecular structure of the cation in $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_8][\text{B}_{11}\text{H}_{14}]$ (**2**) with 50% probability thermal ellipsoids and the cyclopentadienyl groups abbreviated for clarity. The terminal H on B(4) is obscured. Selected interatomic distances (in angstroms): from Zr(1) [B(1)] 2.474(4), [B(2)] 2.511(4), [B(5)] 2.534(4); from Zr(2) [B(3)] 2.539(4), [B(1)] 2.497(4), [B(4)] 2.528(4); from B(1) [B(2)] 1.704(6), [B(3)] 1.730(5), [B(4)] 1.728(5), [B(5)] 1.720(6); B(2)–B(3) 1.860(6); B(4)–B(5) 1.865(6). 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 angle between the two triangular BBB planes is 73° .

2.497(4), are essentially what would be expected for a single Zr–B bond (2.45 \AA)¹³ but are shorter than typical Zr–B bonds found in $(\eta^5\text{-C}_5\text{H}_5)_3\text{Zr}$ moieties,¹⁴ the only nonbridged Zr–B bonds available for comparison. On the other hand, the Zr–B distances for the Zr–H–B bridge bonds, ranging from 2.511(4) to 2.539(4) \AA , are shorter than those observed elsewhere,¹⁵ 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.

An alternative description of the cluster is that it is a metal-stabilized *hypho*-cluster.¹⁶ The *hypho*-pentaborane cluster¹⁶ would be $[\text{B}_5\text{H}_9]^{4-}$; thus, the metal moieties would have to be formulated as $[\text{Cp}_2\text{Zr}^{3+}]$ and each would contribute 3 electrons

(13) Männig, D.; Nöth, H.; Schwartz, M.; Weber, S.; Wietelmann, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 998.

(14) 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.

(15) A Cambridge Structural Database search identified 16 compounds containing Zr–B connections with one or two Zr–H–B bridges. The Zr–B distances range from 2.57 $[\text{Cp}_2\text{Zr}(\text{Cl})(\mu\text{H})_2(\text{BC}_4\text{H}_8)]$ (Jordan, G. T.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1087) to 3.23 $[\text{Cp}^*\text{-Zr}(\text{Me})(\text{C}_2\text{B}_9\text{H}_{12})]$ (Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728); the mean value is 2.70 \AA .

(16) (a) Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin: New York, 1963; p 221. (b) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *94*, 3013. (c) Alcock, N. W.; Colquhoun, H. G.; Sawyer, J. F.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton. Trans.* **1982**, 2243.

to the borane cage. This appears to be an unreasonable assumption since the formulation $\text{Cp}_2\text{Zr}^{2+}$ has a d^0 configuration, so **2** must be added to the growing list of species which do not obey electron counting rules. What is clear, however, for the structure of **2** and that for the other known group 4 metalla-polyborane, $[\text{Cp}_2\text{Ti}(\text{B}_6\text{H}_9)]_2$,² is that unusual structures derive from metallaboranes involving the early transition metals as has been observed for molybdena- and chromaboranes described recently by Leach et al.^{17a} and Fehlner et al.,^{17b} respectively.

The formation of the $[\text{B}_{11}\text{H}_{14}]^-$ anion in this reaction requires some comment. The undecaborate anion is formed when solutions of $[\text{B}_5\text{H}_8]^-$ are allowed to warm to room temperature in the presence of B_5H_9 .¹⁸ 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^{19a} and also the dehydrogenative coupling of silanes.^{19b} We have observed that when attempting to prepare Ti analogues of **1** and **2**, we have formed relatively large amounts of $\text{B}_{10}\text{H}_{14}$. These observations are the subject of current study.

Clearly the formation of **2** is a novel and exciting observation, especially since cationic metallaboranes are rare, and it portends well for study of other group 4 and 5 derivatives of the polyboranes. We are in the process of investigating this chemistry.

Acknowledgment. This work was supported by the Petroleum Research Fund of the American Chemical Society, (ACS-PRF no. 31001-AC3). We also acknowledge instrumentation grants from the NSF (no. CHE-9309690 and CHE-9318696), the DOE (grant no. DE-FG02-92CH10499), and the UM–St. Louis Center for Molecular Electronics. We thank Professor Michael Gross of the Washington University Mass Spectrometry NIH Research Resource (grant. no. P41RR094) for the mass spectra.

Supporting Information Available: Experimental details for the preparation of **1** and **2** and spectroscopic data for **1** and crystallographic data, positional parameters, anisotropic displacement parameters and bond lengths and angles for **2** (19 pages). See any current masthead page for ordering and Internet access instructions.

JA972638P

(17) (a) Bullick, J.; Grebenik, P. D.; Green, M. L. H.; Hughes, A. K.; Leach, J. B.; McGowan, P. C. *J. Chem. Soc., Dalton Trans.* **1995**, 67. (b) Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.

(18) Wermer, J. R.; Shore, S. G. *Mol. Struct. Energ.* **1986**, *5*, 13 and references therein.

(19) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 11. (b) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1, pp 327–387.