

Communications

Synthesis and Molecular Structure of Novel Organohydroborate Zirconocene Complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})(\mu\text{-O})(\text{BC}_8\text{H}_{14})]_2$

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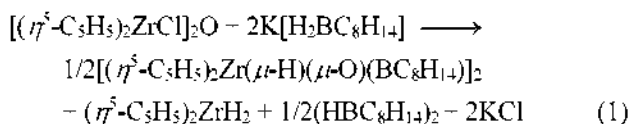
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Organohydroborate derivatives of Group 4 and Group 5 metallocene have received less attention^{1,2} while the metallohydroborate compounds have been intensively investigated.³ The M-H-B three-center, two electron bond is present in covalent hydroborate metal complexes in which B-H or M-H bond may serve as the electron pair donor to an unsaturated metal center or a trivalent boron to form the hydrogen-bridged bond.⁴ Described here is the synthesis and molecular structure of a novel organohydroborate zirconocene complex with M-H-B bond, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})(\mu\text{-O})(\text{BC}_8\text{H}_{14})]_2$. The zirconium compound is prepared in the reaction of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2\text{O}^5$ with $\text{K}[\text{H}_2\text{BC}_8\text{H}_{14}]$ (eq. 1).⁶ The solid is stable under a nitrogen atmosphere at room temperature for several weeks while decomposition occurs when it is exposed to air.



The molecular structure of the complex was determined from a single crystal X-ray diffraction analysis.⁷ The molecular structure and the selected bond distances and angles are shown in Figure 1. The complex has a crystallographically imposed center of symmetry. Two $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2$ fragments are linked by two organohydroborate ligands $(\mu\text{-H})(\mu\text{-O})\text{BC}_8\text{H}_{14}$, through oxygen atoms. The zirconium atoms are associated with 18 valence electrons. The zirconium-oxygen distances of the bridging organohydroborate group are 2.1182(10) Å and 2.1352(10) for Zr-O and Zr-O#1, respectively. These are consistent with the zirconium-oxygen distances of the bridging ethoxyl group Zr-O in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OEt})(\text{OEt}_2)(\mu\text{-OEt})_2\text{O}][\text{HB}(\text{C}_6\text{F}_5)_3]_2$ which is intermediate between the Zr-O distance of the Zr-OEt₂ linkage and the Zr-O distance of Zr-OEt linkage.⁸ The Zr-O-Zr#1 angle is 106.96(4)° and this smaller angle is attributed to the steric bulk of the organohydroborate ligand.

The bridge hydrogen (H1b1) was located and the position and isotropic thermal parameters were refined. Zr-H and Zr-B distances are 1.959(1) and 2.654(2) Å, respectively and

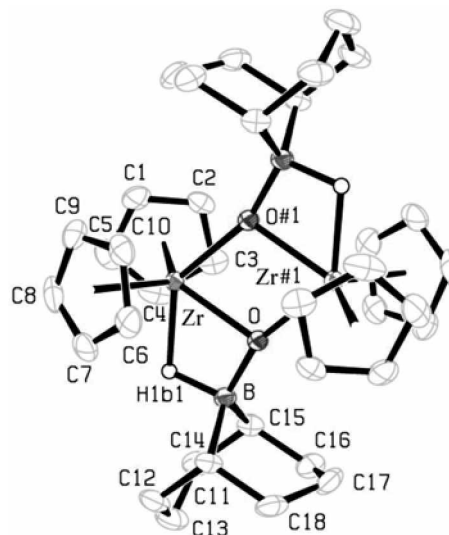


Figure 1. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})(\mu\text{-O})(\text{BC}_8\text{H}_{14})]_2$ with 50% probability thermal ellipsoids. Selected bond distances (Å): Zr-B = 2.654(2), Zr-H = 1.959(16), Zr-O = 2.1182(10), Zr-O#1 = 2.1352(10), Zr-Cp_{centroid(C1-C5)} = 2.250, Zr-Cp_{centroid(C6-C10)} = 2.261, B-H = 1.309(16), B-O = 1.485(2), Selected bond angle (deg): Cp_{centroid(C1-C5)}-Zr-Cp_{centroid(C6-C10)} = 126.1, Cp_{centroid(C1-C5)}-Zr-B = 96, Zr-B-H = 44.9(7), Zr-O-B = 93.19(8).

Zr-B-H angle is 44.9(7)°. These distances and angle are consistent with other systems with Zr-H-B bridges.^{9,10} The broad signal at -3.33 ppm in ¹H NMR spectrum assignable to the bridge hydrogen bound to boron and zirconium atoms was observed and the broad ¹¹B NMR signal has a chemical shift consistent with the presence of Zr-H-B bridge.⁶ Compared to other $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}$ complexes, the longer Zr-Cp_{centroid} distances (2.250 Å for Zr-Cp_{centroid(C1-C5)} and 2.261 Å for Zr-Cp_{centroid(C6-C10)}) and the smaller Cp_{centroid}-Zr-Cp_{centroid} angle (126.2°) result from the larger steric bulk of the organohydroborate $(\mu\text{-H})(\mu\text{-O})\text{BC}_8\text{H}_{14}$ ligands.¹⁰

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Supplementary material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 259797).

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- Preparation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})(\mu\text{-O})(\text{BC}_8\text{H}_{14})_2]$. In the drybox 529.7 mg (1.0 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2\text{O}]$ and 320.2 mg (2.0 mmol) of $\text{K}[\text{H}_2\text{BC}_8\text{H}_{14}]$ were put into a flask. After degassing, 30 mL of THF was transferred into the flask at -78°C . The solution was warmed to room temperature and stirred for 24 hours. During this process the solution turned cloudy due to the formation of KCl which was removed by filtration. Volatile components were removed by means of dynamic high vacuum leaving a white solid. The solid was redissolved in ether and the solution was filtered to remove impurities. A white solid $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\mu\text{-H})(\mu\text{-O})(\text{BC}_8\text{H}_{14})_2]$ was obtained in 46% yield upon removal of the solvent under vacuum. Crystal, suitable for X-ray diffraction, was obtained by crystallization from toluene. $^1\text{H NMR}$ (THF_{d_6} , 30°C) 6.2 (s), 1.84-1.53 (br m), 1.30 (br s), -3.33 (br s) ppm; $^{11}\text{B NMR}$ (THF_{d_6} , 30°C) 56.16 (br s) ppm; IR (KBr) 2916 (s), 2888 (s), 2834 (s), 1657 (w), 1444 (s), 1384 (m), 1325 (m), 1283 (s), 1260 (vs), 1199 (s), 1163 (m), 1197 (s), 1020 (vs), 953 (m), 886 (m), 870 (m), 799 (vs), 744 (s) cm^{-1} .
- Crystal data (-73°C): monoclinic, space group $P2_1$, $a = 10.3610(10)$ Å, $b = 10.2080(10)$ Å, $c = 15.087(2)$ Å, $\beta = 96.419(5)^\circ$, $V = 1585.7(3)$ Å³, ρ (calcd) = 1.506 g/cm³, $f_w = 712.82$, $Z = 2$, $\mu = 0.689$ mm⁻¹, R_1 (3631 independent reflections with $I > 2\sigma(I)$ and 244 parameters) = 0.0222 and $wR_2 = 0.0520$. Diffraction data (Enraf-Nonius Kappa CCD, Mo $K\alpha$) were corrected for Lorentz and polarization effects by use of the Denzo-SMN package. Absorption correction was applied with the SORTAV program provided by MaXus software.
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