# BISCYCLOPENTADIENYLZIRCONIUM(IV) HYDRIDOALUMOHYDRIDE,

ITS REACTION WITH DIBORANE AND THE SYNTHESIS OF  $[(\eta^5-C_5H_5)_2Zr^{IV}(BH_4)\{H_2A1(BH_4)_2\}]$ 

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Only a few complexes with a covalent AlH<sub>4</sub> group have been isolated:  $Cp_2TiAlH_4$  [1] (Cp =  $n^5-C_5H_5$ ),  $CH_2(C_5H_4)_2TiAlH_4$  [2],  $Cp_2Zr(H)AlH_4$  [3], and  $Cp_2NbAlH_4$  [4]. Stabilization of aluminum hydride compounds is achieved by the donor properties of the cyclopentadienyl ligand. ESR [5] and PMR spectroscopy [4] has shown that the AlH<sub>4</sub> group in  $Cp_2TiAlH_4$  and  $Cp_2NbAlH_4$  is attached to the transition metal through two bridging hydrogen atoms. There is apparently bidentate bonding of the AlH<sub>4</sub> group with Zr in  $Cp_2Zr(H)AlH_4$ .

Upon reaction with diborane, aluminum hydrides may add up to four  $BH_3$  groups to form borohydridoaluminates  $[AlH_{4-n}(BH_4)_n]^-$  [6]. In this work, we studied the reaction of diborane with an aluminum hydride group covalently bound to Zr and showed that the  $BH_3$  group adds only at the terminal hydrogen atoms. A new method was developed for the preparation of starting  $Cp_2Zr(H)AlH_4$  based on the reaction of LiAlH<sub>4</sub> with  $Cp_2Zr(BH_4)_2$ . The thermal decomposition of  $Cp_2Zr(H)AlH_4$  was also studied.

# RESULTS AND DISCUSSION

Wailes and Weigold [3] obtained  $Cp_2Zr(H)AlH_4$  by the reaction of  $Cp_2ZrHC1$  with LiAlH<sub>4</sub> in THF. LiCl was initially precipitated from the reaction mixture by the addition of a small amount of benzene. The addition of large amounts of benzene gave the precipitation of  $Cp_2Zr(H)AlH_4$ . The product yield did not exceed 30%. Our synthetic method is based on the use of  $Cp_2Zr(BH_4)_2$  as the starting material. The reaction of  $Cp_2Zr(BH_4)_2$  with LiAlH<sub>4</sub> at 20°C in 1:1 benzene—THF is not accompanied by gas liberation and does not lead to the reduction of Zr(IV). The  $Cp_2Zr(H)AlH_4$  product slowly settles as a precipitate. The formation of zirconium aluminum hydride apparently proceeds through several steps. In the first step, the action of  $LiAlH_4$  on zirconium bisborohydride leads to the loss of one BH<sub>3</sub> group and the formation of  $Cp_2Zr(H)BH_4$ . The capacity of  $Cp_2Zr(BH_4)_2$  to lose a BH<sub>3</sub> group upon the action of Lewis bases such as Me<sub>3</sub>N was previously noted by James et al. [7].  $Cp_2Zr(BH_4)_2$  undergoes analogous decomposition upon the action of the weaker base, Bu<sub>4</sub>NBH<sub>4</sub>, which abstracts a BH<sub>3</sub> group to form Bu<sub>4</sub>NB<sub>2</sub>H<sub>7</sub>

$$Cp_{2}Zr(BH_{4})_{2} + Bu_{4}NBH_{4} \rightleftharpoons Cp_{2}Zr(H)BH_{4} + Bu_{4}NB_{2}H_{7}$$

All the components of this equilibrium are readily detected by IR spectroscopy: The spectrum of this system in benzene solution shows new bands at 1945 and 1620  $\text{cm}^{-1}$  characteristic for

 $\sum 2r(H)BH_4$  and bands at 2405, 2380 (sh), and 2050 cm<sup>-1</sup> related to the  $B_2H_7$  ion [8]. The action of  $Bu_4NAlH_4$  on  $Cp_2Zr(BH_4)_2$  also leads to the loss of a  $BH_3$  group and its addition to the  $AlH_4$  anion to form the  $[AlH_3BH_4]$  anion, which is stable as the tetrabutylammonium salt

$$Cp_2Zr(BH_4)_2 + Bu_4NAlH_4 \rightleftharpoons Cp_2Zr(H)BH_4 + Bu_4NAlH_3BH_4$$

The reaction of  $Cp_2Zr(BH_4)_2$  with LiAlH<sub>4</sub> with 1:1 mole ratio of the reagents, as in the case of Bu<sub>4</sub>NAlH<sub>4</sub>, apparently gives  $Cp_2Zr(H)BH_4$  and the complex LiAlH<sub>3</sub>BH<sub>4</sub> which is unstable in ethereal solution and readily dissociates into lithium borohydride and solvated aluminum hydride [9]. In the next step,  $Cp_2Zr(H)BH_4$  reacts with excess LiAlH<sub>4</sub> either by nucleophilic substitution of the BH<sub>4</sub> group by AlH<sub>4</sub><sup>-</sup> or by the abstraction of the second BH<sub>3</sub> group and subsequent addition of aluminum hydride to  $Cp_2ZrH_2$  to form  $Cp_2Zr(H)AH_4$ . Zirconium aluminum hydride in the nonsolvated state forms a precipitate, while LiBH<sub>4</sub> and solvated AlH<sub>3</sub> remain in solution.

Institute of New Chemical Problems, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1408-1412, June, 1984. Original article submitted August 8, 1983. Two BH<sub>3</sub> groups are added at the terminal Al—H<sub>t</sub> bonds of the AlH<sub>4</sub> group to form the Al(BH<sub>4</sub>)<sub>2</sub> fragment. The bands at 2500, 2445, 2240, 2150, 1115, and 485 cm<sup>-1</sup> in the IR spectrum of the adduct obtained (see Fig. 1) correspond to the formation of borohydride groups coordinated to the aluminum atom. Instead of two bands (1800 and 1720 cm<sup>-1</sup>) in the Al—H bond stretching region,  $Cp_2Zr(H)AlH_4$  shows a medium-intensity band at 1780 cm<sup>-1</sup>. This band is apparently related to vibrations of the Zr—H—Al bridging bonds. The band at 1780 cm<sup>-1</sup> noted by Wailes et al. [14] for { $Cp_2Zr(H-Al(CH_3)_3(\mu-H)$ }<sub>2</sub> in the same spectral region was also assigned to the Zr—H—Al bond. Substitution of H by D shifts this band to 1290 cm<sup>-1</sup>. The third BH<sub>3</sub> group in the adduct  $Cp_2Zr(H)AlH_4 \cdot 3BH_3$  adds at the Zr—H bond. The band at 1430 cm<sup>-1</sup> corresponding to vibrations of the Zr—H—Zr bond is lacking in the IR spectrum of the compound obtained and bands appear at 2445, 2405, 2240, 2150, and 1120 cm<sup>-1</sup> which are H

characteristic for a BH<sub>4</sub> group coordinated to zirconium Zr BH<sub>2</sub> [10]. The bands at 2445,

2240, 2150, and 1120  $\text{cm}^{-1}$  overlap with bands of the borohydride groups bound to aluminum. Thus, these IR spectra indicates the following structure for the compound obtained.



This complex is stable at 20°C, but it slowly decomposes at about 50°C. Rapid decomposition occurs at 70°C with the release of 0.2 mole  $Al(BH_4)_3$  and 0.3 mole  $H_2$  per mole of the starting material into the gas phase. The IR spectrum of the solid residue after the decomposition indicates that this process occurs at the Zr—H—Al bonds. The borohydride group bound directly to zirconium is retained.

The product,  $Cp_2Zr(BH_4)H_2Al(BH_4)_2$  is unstable in donor solvents and is sensitive to the action of even very weak bases. Thus, upon dissolution in benzene, this complex decomposes with the formation of zirconium bisborohydride,  $Cp_2Zr(BH_4)_2$ , which separates as a crystalline precipitate after distilling off the solvent under vacuum. The second decomposition product, a derivative of aluminum borohydride, condenses together with benzene in a liquid nitrogen trap. The loss of HA1(BH\_4)\_2 initially proceeds upon the action of benzene

$$Cp_2Zr(BH_4)H_2Al(BH_4)_2 \xrightarrow{Celle} Cp_2Zr(H)BH_4 + HAl(BH_4)_2$$

The product, Cp<sub>2</sub>Zr(H)BH<sub>4</sub> loses a BH<sub>3</sub> group from HA1(BH<sub>4</sub>)<sub>2</sub> to form Cp<sub>2</sub>Zr(BH<sub>4</sub>)<sub>2</sub>.

The amount of  $B_2H_6$  absorbed upon carrying out the reaction of  $Cp_2Zr(H)AlH_4$  with diborane in benzene is 2.5 moles per mole  $Cp_2Zr(H)AlH_4$ . This reaction gives  $Cp_2Zr(BH_4)_2$  and  $Al(BH_4)_3$ , which may be separated by vacuum distillation at about 20°C.

Thus, the nature of the reaction of zirconium aluminum hydride with diborane depends significantly on the reaction conditions. The capacity of the aluminum hydride ligand to add BH<sub>3</sub> groups only at the terminal Al—H<sub>t</sub> bonds in the reaction of solid Cp<sub>2</sub>Zr(H)AlH<sub>4</sub> with  $B_{2}H_{6}$  indicates the coordination of the covalent AlH<sub>4</sub> group to zirconium through two bridging hydrogen atoms.

### EXPERIMENTAL

Biscyclopentadienylzirconium bisborohydride,  $Cp_2Zr(BH_4)_3$  was obtained by the reaction of  $Cp_2ZrCl_2$  with LiBH<sub>4</sub> in benzene [15] and used without further purification. A sample of LiAlH<sub>4</sub> was recrystallized from ether—toluene. All the reactions were carried out in an atmosphere of dry nitrogen or argon. The solvents were dried and distilled over LiAlH<sub>4</sub>. The IR spectra of the samples in a mull or in a KBr pellet were taken on a UR-20 spectrophotometer.

<u>Preparation of  $Cp_2Zr(H)AlH_4$ .</u> A solution containing 7 mmoles LiAlH<sub>4</sub> in 20 ml THF was added in small portions at 20°C to a solution of 2.5 mmoles  $Cp_2Zr(BH_4)_2$  in 20 ml benzene. The mixture obtained was stirred with a magnetic stirrer and a precipitate began to form





Comparison of the IR spectra of  $Cp_2Zr(H)AlH_4$  and  $Cp_2Zr(BH_4)_2$  (Fig. 1) shows that the cyclopentadienyl groups remain unchanged upon the conversion of zirconium bisborohydride to zirconium hydridoalumohydride. The IR bands of  $Cp_2Zr(H)AlH_4$  not related to the  $Cp_2Zr$  fragment were assigned to metal—hydrogen bond vibrations. The bands at 1720 and 1800 cm<sup>-1</sup> should be assigned to the vAlH stretching vibrations of the AlH<sub>4</sub> group in accord with the spectra of neutral AlH<sub>3</sub>·L complexes [10]. The strong band at 1430 cm<sup>-1</sup> corresponds to the stretching vibration of the Zr—H—Zr bond. Known zirconium hydride compounds ( $Cp_2ZrH_2$ ,  $Cp_2ZrHCl$ , and  $Cp_2Zr(H)CH_3$ ) have polymer structure with bridging Zr—H—Zr bonds with broad IR bands at 1300-1520 cm<sup>-1</sup> [3]. The Zr—H<sub>t</sub> bond in the monomeric compounds,  $Cp_2Zr(H)BH_4$  gives rise to a band at 1620 cm<sup>-1</sup> and the band in the region for Zr—H—Zr vibrations is lacking [11]. The group of bands at 1320, 1240 (sh), and 1180 (sh) cm<sup>-1</sup> in the spectrum of  $Cp_2Zr(H)AlH_4$  is found in the region characteristic for stretching vibrations of M—H—Al bridging bonds [12]. The strong bands at 735 and 700 cm<sup>-1</sup> were assigned to  $\delta(AlH_2)$  deformation vibrations.

According to Wailes and Weigold [3],  $Cp_2Zr(H)AlH_4$  in THF solution begins to release hydrogen at 60°C. It has significant thermal stability in the solid state. We have found that  $Cp_2Zr(H)AlH_4$  does not undergo any noticeable conversion in vacuum up to 150°C though its color goes from white to pale lilac. Its IR spectrum is unaltered. Slow decomposition accompanied by gas liberation begins at about 160°C. Rapid gas evolution occurs at 200-220°C. The endothermic peak in the DTA corresponds to this process. The gas released is pure  $H_2$ ; three moles of hydrogen are liberated per mole of the starting compound. The amount of gas released corresponds to a 2.4% weight loss, which is greater than the amount of hydride hydrogen in  $Cp_2Zr(H)AlH_4$  ( $\sim 2.0\%$ ). The IR bands corresponding to metal—hydrogen bond vibrations dissappear in the spectrum of the solid residue after decomposition.

Under isothermal conditions at  $170^{\circ}$ C,  $Cp_2Zr(H)AlH_4$  releases two equivalents of  $H_2$  over 1 h and an additional equivalent of  $H_2$  over the next 2 h. Further maintenance of the sample at  $170^{\circ}$ C for 6-10 h does not lead to an increase in the liberated gas volume. Since  $Cp_2Zr-$ (H)AlH<sub>4</sub> liberated 0.5 equivalent  $H_2$  more than the hydride hydrogen content upon thermal decomposition, we may assume that cyclopentadienyl group is also involved in the decomposition process. The capacity of the  $C_5H_5$  group to lose  $H_2$  at relatively low temperatures has been noted by Razuvaev et al. [13]. The liberation of 1.5 moles  $H_2$  occurs upon heating  $Cp_2ZrH_2$  to 230°C. The  $C_5H_5$  group is the source of the third hydrogen atom.

We might expect that  $Cp_2Zr(H)AlH_4$  would add two  $BH_3$  groups upon reaction with diborane only at the terminal hydrogen atoms:  $AlH_2 \rightarrow Al(BH_4)_2$ , without affecting the hydrogen in the bridging position, or five  $BH_3$  groups at all the hydride hydrogen atoms. In the latter case, there is the possibility of the formation of a complex, in which two or one of the  $BH_4$  groups formed would occupy the bridging position between Zr and Al or the formation of two borohydrides,  $Cp_2Zr(BH_4)_2$  and  $Al(BH_4)_3$ .

The number of  $BH_3$  groups added to  $Cp_2Zr(H)AlH_4$  depends on the reaction conditions. In the solid state, zirconium aluminum hydride adds diborane. The maximum amount of absorbed diborane is 1.5 mole per mole hydride.

 $Cp_2Zr(H)AlH_4 + 1.5B_2H_6 \rightarrow Cp_2Zr(H)AlH_4 \cdot 3BH_3$ 

after 15-20 min. The amount of precipitate increased over time. The solid phase was separated from the solution after 2-3 h, washed with THF and dried in vacuum at 20°C to yield 0.30 g (1.3 mmole) Cp<sub>2</sub>Zr(H)AlH<sub>4</sub>. Found: Zr 33.9;  $H_{hydr}$  2.2; Al 11.1%. Calculated: Zr 35.9;  $H_{hydr}$  2.0; Al 10.6%. IR spectrum (v, cm<sup>-1</sup>): 3110 s, 1800 s, 1720 m, 1470 sh, 1430 s. br., 1380 sh, 1320 m, 1240 sh, 1180 sh, 1020 m, 840 m, 185 s, 735 s, 700 m, 583 m.

Reaction of  $Cp_2Zr(BH_4)_2$  with  $Bu_4NBH_4$ . A sample of 0.5 mole  $Bu_4NBH_4$  was added to a solution of 0.5 mmole  $Cp_2Zr(BH_4)_2$  in 20 ml benzene to give a clear solution. The IR spectrum of the solid product isolated from the solution after distilling off benzene in vacuum had bands at 2405, 2380 sh, 2050 ( $B_2H_7^{-1}$ ), 2290, 2220, 2145 ( $BH_4^{-1}$ ), 2445, 2145, 1945, 1620 cm<sup>-1</sup>

( ZrHBH<sub>4</sub>).

Reaction of  $Cp_2Zr(BH_4)_2$  with  $Bu_4NA1H_4$ . A sample of 0.4 mmole  $Bu_4NA1H_4$  was added to a solution of 0.4 mmole  $Cp_2Zr(BH_4)_2$  in 20 ml benzene and stirred. The solvent was evaporated under vacuum from the clear solution obtained. The IR spectrum of the solid product had bands at 2410 s, 2280 sh, 2210 s, 1745 m (A1H\_3BH\_4<sup>-</sup>), 2445 s, 2410 s, 2145 s, 2050 w, 1950 s, 1620 m cm<sup>-1</sup> (ZrHBH\_4).

Reaction of  $Cp_2Zr(H)AlH_4$  with  $B_2H_6$  without Solvent. In a typical experiment, the reaction vessel with 0.15 g (0.6 mmole)  $Cp_2Zr(H)AlH_4$  was connected to a vacuum system equipped with a mercury manometer and containing 5-6 mmoles  $B_2H_6$ . Diborane was condensed onto the solid sample at -196°C and warmed over 1 h to about 20°C. This operation was repeated several times. Then, the product was maintained for 8 h at about 20°C and 400 torr diborane pressure.

A total of 0.9 mmole  $B_2H_6$  was absorbed over this time. The amount of diborane absorbed was found by the difference in the pressure within the system. The weight of the solid sample after the reaction was 0.18 g, which corresponded to the addition of three  $BH_3$  groups to one mole  $Cp_2Zr(H)AlH_4$ . Found: B 10.2; Zr 31.0; Al 9.5%. Calculated for  $(C_5H_5)_2Zr(H)-AlH_4 \cdot 3BH_3$ : B 10.9; Zr 30.9; Al 9.2%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3110 s, 2500 s, 2445 s, 2405 s, 2240 m, 2150 s, 1780 m, 1480 m, 1320 m, 1115 s, 1020 m, 845 m, 815 s, 485 s.

Reaction of  $Cp_2Zr(H)A1H_4$  with  $B_2H_6$  in Benzene. The reaction of 0.1 g (0.4 mmole)  $Cp_2Zr(H)A1H_4$  with diborane in 20 ml benzene was carried out by analogy to the above procedure. About 1 mmole  $B_2H_6$  was absorbed. The solution obtained was evaporated to dryness in vacuum at 20°C to yield 0.1 g  $Cp_2Zr(BH_4)_2$ . Found: B 8.9; Zr 35.4%. Calculated: B 8.6; Zr 36.3%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3110 s, 2445 s, 2400 s, 2235 w, 2150 s, 1480 s, 1380 m, 1300 w, 1118 s, 1018 m, 850 m, 845 m, 815 s.

#### CONCLUSIONS

1. A new method was developed for the synthesis of biscyclopentadienylzirconium(IV) hydroalumohydride,  $Cp_2Zr(H)AlH_4$  by the reaction of  $Cp_2Zr(BH_4)_2$  with LiAlH<sub>4</sub>.

2. The addition of up to three  $BH_3$  groups at Al—H and Zr—H bonds is observed in the reaction of  $Cp_2Zr(H)AlH_4$  with diborane, depending on the reaction conditions.

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ORGANIC DERIVATIVES OF DIVALENT YTTERBIUM

RYbx IN METALLATION REACTIONS

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Organic derivatives of divalent lanthanides, RLnX, are attracting ever increasing attention in light of their use in organic synthesis [1]. The usual method for their preparation is the oxidative addition of RX ( $\mathring{R}$  = Ar, Me, Bz,  $CH_2 = CH - CH_2$ ) to a zero-valent metal [2] or the reaction of organolithium compounds with LnX2 salts.

The direct metallation of organic compounds using organic derivatives of divalent lanthanides has virtually not been studied. The only report available concerns the preparation of bis(phenylethynyl)ytterbium by the reaction of phenylacetylene with bis(pentafluorophenyl)or bis(tert-butylethynyl)ytterbium [4]. The metallation of CH-acids by the action of RYbX has not been reported.

We have shown that PhYbX and CH<sub>3</sub>YbI prepared in situ readily react with various CH-acids, RH, with pKa from 18 to 26 [5] (R = phenyl-o-carboranyl, phenylethynyl, indenyl, pentafluorophenyl, 9-fluorenyl) in THF solution to form the corresponding ytterbium derivatives, RYbI. The compounds obtained were introduced without separation into reaction with D20, Me3SiCl or Ph<sub>3</sub>SnCl. In this case, RD, RSiMe<sub>3</sub> or RSnPh<sub>3</sub> were obtained in high yields. Distannane,  $[Ph_3Sn]_2$  was obtained in 5-7% yield in the reaction with  $Ph_3SnCl$ . Tolan was obtained in 40% yield in the reaction of phenylethynylytterbium iodide with iodobenzene

> $Ph(Me)YbI + R'H \rightarrow [R'YbI] + PhH(MeH)$ [R'YbI] D<sub>2</sub>O Me<sub>2</sub>SiCl R'D D'C PhsSnCl PhI R'SiMea R'SnPh. R'Ph

R' = phenyl-o-carboranyl, phenylethynyl, indenyl, pentafluorophenyl, and fluorenyl.

This synthesis requires the following reaction conditions: use of THF as the solvent, temperature range from -20° to +20°C, and the addition of the CH-acids to ArYbI or RYbI. As a consequence of the sensitivity of the organoytterbium compounds toward oxygen and atmospheric moisture, all the operations were carried out in an argon atmosphere.

The metallation in the reaction of PhYbI with phenyl-o-carborane and phenylacetylene should be carried out at the lowest possible temperature in order to avoid side reactions. In the case of the less reactive indene, the reaction is carried out at room temperature. The metallation of pentafluorobenzene is best carried out by the action of MeYbI. In the case of fluorene, the metallation is only 20% complete at 64°C over 3 h even using MeYbI and the reaction does not proceed at all with PhYbI. The metallation of triphenylmethane ( $pK_a =$ 33.5) cannot be achieved by the action of RYbI even under vigorous conditions (prolonged heating at reflux in THF).

The IR spectrum of R'D (R' = phenylethynyl) shows a band at 2600 cm<sup>-1</sup> ( $\nu C \equiv D$ ). The vCH/vCD ratio = 1.28 is characteristic for the stretching vibrations of terminal C-H and

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