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# Transition metal-catalyzed reduction of $Zr^{IV}$ in $Cp_2ZrX_2-LiAlH_4$ and $Cp_2ZrX_2-AlH_3$ ( $X = Cl, Br, I$ ) systems: structural study of resulting zirconocene(III) aluminum hydride complexes

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## Abstract

The reactions of  $Cp_2ZrX_2$  ( $X = Cl, Br, \text{ or } I$ ) with  $LiAlH_4$  or  $AlH_3$  in the presence of catalytic amounts of transition metal compounds afford the  $Zr^{III}-Al$  hydride complexes  $[(Cp_2Zr)_2(\mu-H)](\mu-H)_2AlX_2$  (**1**). Complexes **1** were isolated as crystal solvates with either benzene or benzene and 1,4-dioxane of compositions  $[(Cp_2Zr)_2H](H)_2AlCl_2 \cdot C_6H_6$  (**2**),  $[(Cp_2Zr)_2H](H)_2AlBr_2 \cdot C_6H_6$  (**3**),  $[(Cp_2Zr)_2H](H)_2AlBr_2 \cdot C_4H_8O_2 \cdot C_6H_6$  (**4**), and  $[(Cp_2Zr)_2H](H)_2AlI_2 \cdot 2C_6H_6$  (**5**) and their structures were studied by X-ray diffraction analysis. Molecules **1** contain the six-membered  $Zr_2AlH_3$  ring as the central fragment, in which the metal atoms are linked by hydride bridges. The bonding models for **1** are considered and the reasons for stability of **1** are discussed.

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**Keywords:** Zirconocenes; Zirconium(III); Aluminum hydrides; Crystal structures

## 1. Introduction

Heterometal ( $Zr^{III}-M$ ) hydride complexes have been well characterized by ESR in solutions ( $M = Li, Na, K$  [1,2];  $Mg$  [3];  $Al$  [4]). However, the crystal structures of these complexes have long remained unknown because of their low stability [2]. Recently, we have demonstrated [5,6] that reduction of  $Zr^{IV}$  in the  $Cp_2ZrCl_2-LiAlH_4$  system was activated by stoichiometric amounts of Ti compounds. This method was used for the preparation of  $Zr^{III}-Al$  hydride  $[(Cp_2Zr)_2H](H)_2AlCl_2$  [5], and the crystal solvate  $[(Cp_2Zr)_2H](H)_2AlCl_2 \cdot 1,4\text{-dioxane} \cdot C_6H_6$  [6], which were isolated and investigated by X-ray diffraction analysis.

As part of our continuing studies, we developed a new procedure for the preparation of hydrides  $[(Cp_2Zr)_2H](H)_2AlX_2$  ( $X = Cl, Br, \text{ or } I$ ) (**1**) by reduction of  $Cp_2ZrX_2$  with  $LiAlH_4$  or  $AlH_3$  in the presence of

catalytic amounts of transition metal compounds, synthesized the crystal solvates  $[(Cp_2Zr)_2H](H)_2AlCl_2 \cdot C_6H_6$  (**2**)  $[(Cp_2Zr)_2H](H)_2AlBr_2 \cdot C_6H_6$  (**3**),  $[(Cp_2Zr)_2H](H)_2AlBr_2 \cdot C_4H_8O_2 \cdot C_6H_6$  (**4**), and  $[(Cp_2Zr)_2H](H)_2AlI_2 \cdot 2C_6H_6$  (**5**), and established their structures.

## 2. Results and discussion

**2.1. Formation of  $[(Cp_2Zr)_2H](H)_2AlX_2$  ( $X = Cl, Br, I$ ) complexes (**1**) by reactions of  $Cp_2ZrX_2$  with  $LiAlH_4$  or  $AlH_3$**

The formation of zirconocenes(III) as impurities, which can easily be detected from the appearance of a red color of the reaction solutions, has been observed earlier in the synthesis of  $Zr^{IV}$  hydrides and  $Zr^{IV}$  aluminum hydrides in the  $Cp_2ZrCl_2-LiAlH_4$  [7] and  $Cp_2ZrH_2-AlH_3 \cdot NR_3$  [8] systems. Because of poor solubility of  $Zr^{IV}$  hydrides containing the unsubstituted cyclopentadienyl ligands, the reactions in the above-mentioned systems are generally carried out in THF

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[7,8]. However, we found that an Et<sub>2</sub>O–benzene mixture (30–40% of Et<sub>2</sub>O) is the medium of choice for the preparation of complexes **1** by the reactions of Cp<sub>2</sub>ZrX<sub>2</sub> (X = Cl, Br, or I) with LiAlH<sub>4</sub> or AlH<sub>3</sub>. In this solvent, complexes **1** are moderately soluble and isolated from such solutions as readily crystallized solvates of composition **1** *n*C<sub>6</sub>H<sub>6</sub> (*n* = 1, 2).

The addition of one equivalent of LiAlH<sub>4</sub> in ether to a solution of Cp<sub>2</sub>ZrCl<sub>2</sub> in a benzene–ether mixture afforded a pale-reddish solution, which tended to yield a white amorphous precipitate containing LiCl and unidentified Zr<sup>IV</sup> hydride [9]. Upon heating at 40–45 °C for 5 h, the color of the solution became slightly more intense, and, on concentrating, red crystals of [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (**2**) could sometimes be isolated in trace amounts. Therefore, under this condition the process was accompanied by only insignificant reduction of Zr<sup>IV</sup> with the aluminum hydride group.

The additive of a catalytic amount of a compound containing another transition metal can substantially increase the yield of complex **2**. Thus, the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with LiAlH<sub>4</sub> performed in the presence of CoBr<sub>2</sub> under the same conditions produced a deep-red solution, from which complex **2** was isolated in 25% yield. In this case, like in the reaction in the absence of a catalyst, Zr<sup>IV</sup> hydride derivatives were partially isolated as a white precipitate.

In addition to CoBr<sub>2</sub>, we examined TiCl<sub>4</sub>, (Cp<sub>2</sub>TiCl)<sub>2</sub>, and (Cp<sub>2</sub>YCl)<sub>2</sub> as catalysts for the synthesis of **2**. A rough qualitative comparison revealed no substantial differences in the activities of all the catalysts under study. The exception is TiCl<sub>4</sub>. The use of the latter led to deep decomposition of the reaction mixture, giving rise to a dark-purple solution from which no crystalline compounds were isolated. Cobalt bromide was found to be the most convenient catalyst, because, being in the solid phase (CoBr<sub>2</sub> is rapidly reduced by the aluminum hydride group to cobalt metal [10a]), it can be readily separated from the reaction solution by filtration or decantation.

Under the same conditions, the reaction of Cp<sub>2</sub>ZrBr<sub>2</sub> with LiAlH<sub>4</sub>, unlike that of Cp<sub>2</sub>ZrCl<sub>2</sub>, did not produce a precipitate of Zr<sup>IV</sup> hydrides. In the presence of CoBr<sub>2</sub>, the homogeneous pale-reddish solution that formed turned dark-red. Upon concentration, this solution gave the red crystal solvate [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlBr<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (**3**). The addition of an excess of 1,4-dioxane afforded the complex as the crystal solvate [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlBr<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (**4**).

For Cp<sub>2</sub>ZrI<sub>2</sub>, the most unambiguous results were obtained in the reaction with an ethereal solution of AlH<sub>3</sub> rather than in the reaction with LiAlH<sub>4</sub>. The reaction in the Cp<sub>2</sub>ZrI<sub>2</sub>–AlH<sub>3</sub>–CoBr<sub>2</sub> system (molar ratio Zr/Al = 1) afforded a dark-red homogeneous solution, which yielded reddish-brown crystals of [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlI<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub> (**5**).

## 2.2. Structures of complexes 2–5

The crystal structures of **2–5** consist of molecules **1** packed together with benzene or with benzene and 1,4-dioxane. All molecules **1** (Table 1) are structurally similar. They contain the Zr<sub>2</sub>AlH<sub>3</sub> ring as the main fragment in which the metal atoms are linked by hydride bridges. Since the structures of these molecules have been discussed in detail earlier [5], let us note only selected common features.

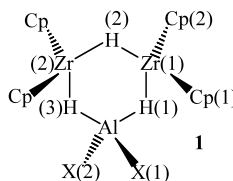
In the first synthesis [5], the [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub> complex was isolated from an ethereal–toluene mixture. The crystals of this compound contained no molecules of solvation because toluene, unlike benzene, was not included in the crystal lattice. In this complex, the metal-hydride bonds in the Zr<sub>2</sub>AlH<sub>3</sub> ring are substantially asymmetrical [5]. This fact suggests that the [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub> molecule is prone to decomposition and could either easily dissociate into Cp<sub>2</sub>Zr<sup>III</sup>(μ-H)<sub>2</sub>AlCl<sub>2</sub>·L and 1/2(Cp<sub>2</sub>Zr<sup>III</sup>(μ-H))<sub>2</sub> or undergo disproportionation to give Cp<sub>2</sub>Zr<sup>IV</sup>H(μ-H)<sub>2</sub>AlCl<sub>2</sub>·L and Cp<sub>2</sub>Zr<sup>II</sup>·L<sub>*n*</sub> under the action of the corresponding base L. To avoid a substantial change in the basicity of the medium, we used 1,4-dioxane as L. However, the more recent study [6] showed that the complex was isolated from an ether–benzene–1,4-dioxane mixture as the solvate [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, i.e., [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub> did not decompose under these conditions, whereas the Zr<sub>2</sub>AlH<sub>3</sub> ring in this solvate was already undistorted [6].

In solvates **2–5**, the Zr<sub>2</sub>AlH<sub>3</sub> rings are also undistorted, i.e., molecules **1** in **2–4** have an approximate or exact (in **5**) mirror symmetry with the symmetry plane passing through the Al atom and the bridging H atom of the Zr–H–Zr bond. Taking into account this fact, the asymmetry of [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub> in its own phase [5] should be considered as the effect of the molecular packing in the crystal rather than the manifestation of its tendency to dissociation or disproportionation.

The dioxane molecules in the compound [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlBr<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (**4**) (Table 1), like those in its analog [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, [6], are involved in the crystal lattice but are not coordinated to Al atoms. The NMR data (see below) demonstrated that THF was also not coordinated to [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlCl<sub>2</sub> in solution. Therefore, the coordinatively unsaturated Al atom [11] in molecules **1** does remain resistant to solvation by ether, 1,4-dioxane, or THF.

Crystalline samples **2**, **3**, and **5** give similar IR spectra. The spectrum of **2** differs from the spectra of **3** and **5** by the presence of strong absorption bands at 400–442 cm<sup>-1</sup>, which can be assigned to ν(Al–Cl<sub>*t*</sub>). All spectra have absorption bands at 800–850, 1007–1010, and 1024–1026 cm<sup>-1</sup> characteristic of the Cp ligands and broad–medium intensity bands at 1309–1315 cm<sup>-1</sup>,

Table 1  
Bond lengths (Å) and angles (°) for molecules **1** in the complexes **2–5**



Bond lengths	Complex (X)				Bond angles	Complex (X)			
	<b>2</b> (Cl)	<b>3</b> (Br)	<b>4</b> (Br)	<b>5</b> (I)		<b>2</b> (Cl)	<b>3</b> (Br)	<b>4</b> (Br)	<b>5</b> (I)
Zr(1)–Cp(1)	2.201	2.189	2.197	2.195	Cp(1)–Zr(1)–Cp(2)	131.1	131.3	130.1	130.0
Zr(1)–Cp(2)	2.202	2.184	2.192	2.190	H(1)–Zr(1)–Cp(1)	98.2	99.0	100.8	100.2
Zr(1)–H(1)	1.78	1.93	1.82	1.85	H(1)–Zr(1)–Cp(2)	97.5	100.5	97.4	98.7
Zr(1)–H(2)	2.08	1.95	2.11	2.03	H(2)–Zr(1)–Cp(1)	104.5	109.2	105.0	103.4
Zr(2)–H(2)	1.99	1.91	2.14	2.03	H(2)–Zr(1)–Cp(2)	107.7	104.5	103.6	108.1
Zr(2)–H(3)	1.78	1.81	1.87	1.85	H(2)–Zr(1)–H(1)	120.7	111.0	122.0	117.3
Al–H(1)	1.83	1.64	1.74	1.71	Zr(1)–H(1)–Al	108.9	107.4	104.3	108.4
Al–H(3)	1.73	1.83	1.76	1.71	Zr(2)–H(3)–Al	112.1	106.6	105.5	108.4
X(1)–Al	2.179	2.336	2.341	2.578	Zr(1)–H(2)–Zr(2)	117.8	129.7	110.9	119.1
X(2)–Al	2.168	2.348	2.345	2.595	X(1)–Al–X(2)	106.29	105.3	104.74	104.99
Zr(1)···Zr(2)	3.486	3.491	3.492	3.506	X(1)–Al–Zr(1)	119.09	119.0	119.57	120.49
Zr(1)···Al	2.901	2.875	2.898	2.893	X(2)–Al–Zr(1)	118.27	118.5	118.85	117.43
Zr(2)···Al	2.914	2.914	2.890	2.893	Zr(1)–Al–Zr(2)	73.66	74.2	74.21	74.58
Al···O <sub>dioxane</sub>			5.107		X(1)–Al–Zr(2)	118.54	117.3	120.35	120.49
					X(2)–Al–Zr(2)	118.87	121.1	117.78	117.43

which can be assigned to  $\nu(\mu\text{-H})$  by analogy with the spectra of  $\text{Zr}^{\text{IV}}$  hydrides and  $\text{Zr}^{\text{IV}}$  aluminum hydrides [4,7]. The absence of the characteristic bands  $\nu(\text{Al}-\text{H}_\text{t})$  ( $1700\text{--}1800\text{ cm}^{-1}$ ) and  $\nu(\text{Zr}-\text{H}_\text{t})$  ( $1520\text{--}1560\text{ cm}^{-1}$ ) in these spectra indicates that all these compounds are devoid of the terminal hydride atoms.

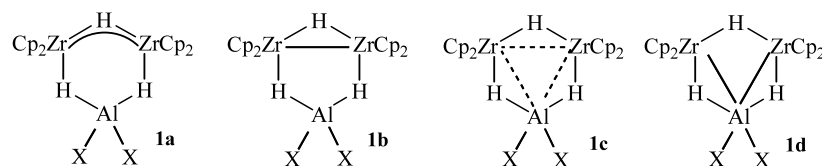
No paramagnetic species were detected in the red reaction solution formed after the reduction of  $\text{Zr}^{\text{IV}}$  in the  $\text{Cp}_2\text{ZrBr}_2\text{--LiAlH}_4\text{--CoBr}_2$  system. In the crystalline state at  $20^\circ\text{C}$ , bromide **3** is diamagnetic (Faraday method). Upon dissolution in THF- $d_8$  or toluene- $d_8$ , crystalline chloride **2** gives diamagnetic solutions.

The  $^1\text{H}$ -NMR spectrum of a solution of **2** in THF- $d_8$  (at  $20^\circ\text{C}$ ) has signals of benzene (s,  $\delta$  7.31 ppm, 6H) involved in the compound and Cp ligands (s,  $\delta$  6.04 ppm, 20H) along with a broad ( $w_{1/2} \approx 200$  Hz) singlet of the bridging hydrides Al–H–Zr at  $\delta \approx -2$  ppm (2H) and a narrow singlet at  $\delta -7.96$  ppm (1H) belonging to the Zr–H–Zr bridge. The signal at  $\delta -2$  ppm is broadened upon heating to  $60^\circ\text{C}$  and narrowed upon cooling (at  $-100^\circ\text{C}$ ,  $w_{1/2} \approx 30$  Hz). The  $^{27}\text{Al}$ -NMR spectrum of a solution of **2** in THF- $d_8$  shows an intense singlet at  $\delta$  199.08 ppm ( $w_{1/2} \approx 600$  Hz) and a weak (intensity  $\approx 1/100$  of the intensity of the peak at  $\delta$  199.08 ppm) singlet at  $\delta$  227.22 ppm. In the case of selective decoupling of  $^{27}\text{Al}$  at 199.08 ppm, the  $^1\text{H}\{^{27}\text{Al}\}$ -NMR spectrum shows a resonance of hydrides at  $\delta -2$  ppm as a narrow signal ( $w_{1/2} \approx 15$  Hz). In the case of selective decoupling of the signal at  $\delta$  227.22 ppm, the  $^1\text{H}\{^{27}\text{Al}\}$ -

NMR spectrum has a weak peak at  $\delta -3.5$  ppm, which is not observed in the  $^1\text{H}$ -NMR spectrum. Therefore, a broadening of the signal at  $\delta -2$  ppm in the  $^1\text{H}$ -NMR spectrum is, apparently, associated both with dynamic processes and the effect of the  $^{27}\text{Al}$  nucleus. The origin of the weak signal at  $\delta$  227.22 ppm in the  $^{27}\text{Al}$ -NMR spectrum and the related peak at  $\delta -3.5$  ppm in the  $^1\text{H}\{^{27}\text{Al}\}$ -NMR spectrum remains unclear. Presumably, these signals can be attributed to an impurity that formed upon partial decomposition of **2** in the course of the preparation of its solution in THF- $d_8$ .

Although the solubility of complex **2** in arenes is much lower than that in THF, the concentration of **2** in toluene- $d_8$  is high enough for the  $^1\text{H}$ -NMR spectrum to be recorded. A comparison of this spectrum [7.13 (s, 6H,  $\text{C}_6\text{H}_6$ ); 5.57 (s, 20H, Cp);  $\approx -2$  (s, br ( $w_{1/2} \approx 200$  Hz) 2H, Al–H–Zr);  $-8.36$  (s, 1H, Zr–H–Zr)] with the spectrum of **2** in THF- $d_8$  demonstrated that the  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlCl}_2$  molecules in these solutions have the same structure. This indicates that molecules of a strong base (THF) are not coordinated to the Al atom in solution, like the dioxane molecules in the crystal phase.

The diamagnetism of  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlCl}_2$  and  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlBr}_2$  (the structural similarity of all molecules **1** (Table 1) suggests that  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlI}_2$  is also diamagnetic) indicates that the  $d^1$  electrons of the  $\text{Zr}^{\text{III}}$  atoms in  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlX}_2$  are involved in strong interaction. By analogy with non-hydride  $\text{Zr}^{\text{III}}$

Fig. 1. The bonding models for molecules **1**

dimers [12–16], this interaction can be interpreted as either ( $\mu$ -H)-mediated coupling of the  $d^1$  zirconium centers (**1a**) or the direct Zr–Zr bond (**1b**). Three-center two-electron Zr–Al–Zr bond (**1d**) and the mode of binding with substantial delocalization of the  $d^1$  electrons (**1c**), which is intermediate between models **1b** and **1d**, can serve as alternative models.

The presence of the signal at  $\delta = 199.08$  ppm in the  $^{27}\text{Al}$ -NMR spectrum of complex **2**, which is in better agreement with the four-coordinate Al atom [4], and the strongly shielded ( $\delta \approx -8$  ppm) hydride in the Zr–H–Zr bridge in the  $^1\text{H}$ -NMR spectra are essential arguments in favor of models **1(a)** and **1(b)**. However, the observed resistance of the Al atom in the  $[(\mu\text{-H})_2\text{AlX}_2]$  fragment with respect to solvation by Lewis bases is more adequately explained within the framework of models **1(c)** and **1(d)**.

The results of the structural studies of molecules **1** do not allow us to unambiguously choose the binding model. All Zr $\cdots$ Zr distances (3.483–3.506 Å) in **1** (Table 2) are within the 3.233–3.677 Å range typical of the  $(\text{Cp}_2\text{Zr}^{\text{III}}\text{X})_2$  and  $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CpZr}^{\text{III}}\text{X})_2$  diamagnetic dimers with the non-hydride bridges X (X = P, Cl, I, or S) [12–16]. On the other hand, all distances Zr $\cdots$ Al in molecules **1** are 0.04–0.12 Å smaller than the corresponding distances in zirconocene(IV,  $d^0$ ) aluminum hydrides [4,8,17,18] in which the direct Zr–Al bond is absent. In molecules **1** (Table 2), the largest Zr $\cdots$ Al distances are observed for chlorides, whereas the largest Zr $\cdots$ Zr distance was found in iodide **5**. Within the framework of model **1(c)**, this fact can be attributed to a somewhat weakening of the direct Zr–Zr bond simultaneously with a strengthening of the three-center Zr–Al–Zr interaction as the electron-withdrawing properties of Al in molecules **1** increase upon the replacement of Cl with Br and then with I.

In this connection, it should be noted that attempts to synthesize halogen-free analogs of molecules **1** by the

reactions of  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlBr}_2$  with LiPh, LiBH<sub>4</sub>, or LiAlH<sub>4</sub> were unsuccessful.

Therefore, it is apparent these strong electron-withdrawing properties of the  $[\text{AlX}_2]$  fragment (X = Cl, Br, or I) are responsible for rather high stability of molecules **1**. Presumably, this also accounts for the easy formation of compounds **1** in the catalytic and stoichiometric [5,6] systems under consideration.

### 3. Conclusion

It is well known that catalytic amounts of transition metal compounds and finely dispersed metals, as such, substantially accelerate thermal decomposition of thermodynamically unstable aluminum hydride compounds [10b]. Thus, the rate of decomposition of LiAlH<sub>4</sub> or AlH<sub>3</sub> to give aluminum metal and hydrogen sharply increases in the presence of titanium compounds [10b]. At the same time, transition metals can exert an effect on the reducing properties of aluminum hydrides. For example, the LiAlH<sub>4</sub>+CoBr<sub>2</sub> (0.001 mol) system can reduce nitroarenes to the corresponding hydrazines, whereas the reactions involving LiAlH<sub>4</sub> afford only azo derivatives [10a].

On the other hand, it is also well known that homonuclear Zr<sup>IV</sup> hydride  $[(\text{C}_5\text{H}_4\text{CH}_3)_2\text{ZrH}(\mu\text{-H})]_2$  and Zr<sup>IV</sup> aluminum hydride  $[\text{Cp}_2\text{Zr}(\text{H})(\mu\text{-H})_2\text{AlH}_2]_n$  undergo thermal decomposition to give solid red products and H<sub>2</sub> at 75 °C [19] and 60 °C [7], respectively.

Considering all the above-mentioned facts and taking into account that traces of complex **2** are produced in the absence of a catalyst as well, it can be assumed that transition metal compounds, apparently, merely reduce the kinetic stability of zirconocene(IV) aluminum hydrides generated in the  $\text{Cp}_2\text{ZrX}_2\text{-LiAlH}_4$  (or AlH<sub>3</sub>) systems resulting in decomposition of these compounds to give molecules **1**.

### 4. Experimental

All operations were carried out in argon or vacuum using standard Schlenk techniques. Diethyl ether and 1,4-dioxane were refluxed over LiAlH<sub>4</sub> and then distilled immediately before use. Benzene was purified by distillation from sodium benzophenone ketyl. A solution of AlH<sub>3</sub> in OEt<sub>2</sub> was prepared according to Schlesinger's

Table 2  
The Zr $\cdots$ Zr and Zr $\cdots$ Al distances (Å) in  $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlX}_2$  (**1(X)**)

Complex	Zr $\cdots$ Zr	Zr $\cdots$ Al	Reference
<b>1(Cl)</b>	3.483	2.906, 2.904	[5]
<b>1(Cl)</b> ·C <sub>6</sub> H <sub>6</sub> ( <b>2</b> )	3.486	2.901, 2.914	This work
<b>1(Cl)</b> ·C <sub>6</sub> H <sub>6</sub> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	3.485	2.911, 2.912	[6]
<b>1(Br)</b> ·C <sub>6</sub> H <sub>6</sub> ( <b>3</b> )	3.491	2.875, 2.914	This work
<b>1(Br)</b> ·C <sub>6</sub> H <sub>6</sub> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> ( <b>4</b> )	3.492	2.890, 2.898	This work
<b>1(I)</b> ·2C <sub>6</sub> H <sub>6</sub> ( <b>5</b> )	3.506	2.893, 2.893	This work

method [20];  $\text{Cp}_2\text{ZrBr}_2$ ,  $\text{Cp}_2\text{ZrI}_2$  [21] and  $(\text{Cp}_2\text{YCl})_2$  [22] were prepared according to procedures published earlier. All other chemicals were commercial products. The IR spectra were recorded on an UR-20 spectrophotometer using Nujol mulls. The NMR spectra were recorded on Bruker DPX300 ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) and Bruker AMX500 ( $^{27}\text{Al}$  and  $^1\text{H}\{^{27}\text{Al}\}$ ) spectrometers.

#### 4.1. Reactions in $\text{Cp}_2\text{ZrCl}_2$ – $\text{LiAlH}_4$ –catalyst systems

The detailed procedure is described for the  $\text{CoBr}_2$  catalyst. The reactions in the presence of other catalysts were carried out analogously under the same conditions using the same amounts of  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{LiAlH}_4$ , and solvents.

##### 4.1.1. The procedure with the use of the $\text{CoBr}_2$ catalyst

A solution of  $\text{LiAlH}_4$  (1.06 mmol) in  $\text{Et}_2\text{O}$  (8 ml) was added dropwise to a stirred warm ( $40^\circ\text{C}$ ) solution of anhydrous  $\text{CoBr}_2$  (17.5 mg, 0.08 mmol) and  $\text{Cp}_2\text{ZrCl}_2$  (0.31 g, 1.06 mmol) in a mixture of benzene (60 ml) and  $\text{Et}_2\text{O}$  (30 ml) during 30 min. The grayish-brown reaction mixture was stirred at  $40$ – $45^\circ\text{C}$  for 5 h and then kept at room temperature overnight. The dark-red solution was separated from a dark precipitate by decantation, concentrated to one-half of the initial volume under vacuum, and kept overnight. The red crystals of complex **2** (0.08 g, 25%) that precipitated were separated from the mother liquor, carefully washed, and dried under vacuum. Anal. Found: Al, 4.60; Cl, 12.52; Zr, 29.88. Calc. for  $\text{C}_{26}\text{H}_{29}\text{AlCl}_2\text{Zr}_2$ : Al, 4.35; Cl, 11.41; Zr, 29.36%. One crystal was chosen for X-ray diffraction analysis. IR (Nujol,  $\text{cm}^{-1}$ ): 1462 (m, Nujol), 1377 (m, Nujol), 1309 (m, br), 1138 (m), 1125 (m), 1070 (w), 1063 (w), 1022 (m), 1009 (m), 824 (w), 800 (s), 767 (s), 730 (s), 675 (s), 685 (m), 605 (w), 442 (s), 424 (s).  $^1\text{H}$ -NMR, 300.1 MHz,  $20^\circ\text{C}$ , toluene- $d_8$ , calibration against the  $\text{CD}_2\text{H}$  signal of residual toluene (2.09 ppm):  $\delta = 7.13$  (s, 6H,  $\text{C}_6\text{H}_6$ ); 7.09, 7.02, 6.97 (toluene); 5.57 (s, 20H, Cp); 2.09 (toluene);  $\approx -2$  (br s,  $w_{1/2} \approx 200$  Hz, 2H, Al–H–Zr);  $-8.36$  (s, 1H, Zr–H–Zr).  $^1\text{H}$ -NMR,  $20^\circ\text{C}$ , THF- $d_8$ , calibration against the CDH signal of residual THF (1.73 ppm):  $\delta = 7.31$  (s, 6H,  $\text{C}_6\text{H}_6$ ); 6.04 (s, 20H, Cp); 3.59, 1.73 (THF);  $\approx -2$  (br s,  $w_{1/2} \approx 200$  Hz, 2H, Al–H–Zr);  $-7.96$  (s, 1H, Zr–H–Zr).  $^{13}\text{C}\{^1\text{H}\}$ -NMR, 75.5 MHz,  $20^\circ\text{C}$ , THF- $d_8$ , calibration against the CDH signal of residual THF (25.3 ppm):  $\delta = 128.91$  (s,  $\text{C}_6\text{H}_6$ ); 103.85 (s, Cp); 67.28 (quint, THF); 25.3 (quint, THF).  $^{27}\text{Al}$ -NMR, 130.32 MHz,  $20^\circ\text{C}$ , THF- $d_8$ , calibration against the external standard (1 M aqueous  $\text{Al}_2(\text{SO}_4)_3$ ):  $\delta = 199.08$  (br s,  $w_{1/2} \approx 600$  Hz); 227.22 (s).

##### 4.1.2. The procedure with the use of $\text{TiCl}_4$ (14.6 mg, 0.077 mmol, a solution in 1 ml of $\text{C}_6\text{H}_6$ ) as the catalyst

A black reaction mixture was cooled to  $20^\circ\text{C}$ , kept for some time, and decanted to obtain a dark-purple

solution. When concentrated, this solution yielded a non-crystalline purple precipitate of variable composition.

##### 4.1.3. The procedure with the use of $(\text{Cp}_2\text{TiCl})_2$ (17 mg, 0.04 mmol) as the catalyst

A dark-red reaction mixture was cooled to  $20^\circ\text{C}$ , filtered off from the white precipitate, concentrated to one-half of the initial volume under vacuum, and kept overnight. Red crystals of **2** (0.07 g, 25%) were isolated as described in Section 4.1.1. Anal. Found: Al, 4.62; Cl, 12.08; Zr, 30.08. Calc. for  $\text{C}_{26}\text{H}_{29}\text{AlCl}_2\text{Zr}_2$ : Al, 4.35; Cl, 11.41; Zr, 29.36%.

##### 4.1.4. The procedure with the use of $(\text{Cp}_2\text{YCl})_2$ (20 mg, 0.04 mmol) as the catalyst

The isolation was carried out as described in Section 4.1.3. Complex **2** was obtained in a yield of 0.08 g (25%). Anal. Found: Al, 4.60; Cl, 11.72; Zr, 30.17. Calc. for  $\text{C}_{26}\text{H}_{29}\text{AlCl}_2\text{Zr}_2$ : Al, 4.35; Cl, 11.41; Zr, 29.36%.

##### 4.1.5. The procedure without a catalyst

A pale-red reaction mixture was cooled to  $20^\circ\text{C}$ , filtered off from a white precipitate, concentrated to 1/5 of the initial volume under vacuum, filtered once again, concentrated to one-half of the volume, and kept overnight. A mixture of red crystals and a white solid (total weight: 0.05 g) was separated from the mother liquor, washed, and dried under vacuum. X-ray diffraction study demonstrated that the crystallographic parameters of the red crystal thus obtained were identical with those determined for **2** (Table 3).

#### 4.2. $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlBr}_2 \cdot \text{C}_6\text{H}_6$ (**3**) and $[(\text{Cp}_2\text{Zr})_2\text{H}](\text{H})_2\text{AlBr}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{C}_6\text{H}_6$ (**4**)

A solution of  $\text{LiAlH}_4$  (2.62 mmol) in  $\text{Et}_2\text{O}$  (12.2 ml) was added dropwise to a stirred warm ( $40^\circ\text{C}$ ) solution of anhydrous  $\text{CoBr}_2$  (35 mg, 0.16 mmol) and  $\text{Cp}_2\text{ZrBr}_2$  (1.00 g, 2.62 mmol) in a mixture of benzene (74 ml) and  $\text{Et}_2\text{O}$  (30 ml) during 1 h. The reaction mixture was stirred at  $40$ – $45^\circ\text{C}$  for 6 h and then kept at room temperature overnight. The resulting dark-red solution was decanted from a dark precipitate, 1 ml of the solution was placed in an ESR tube (no paramagnetic species were found), and the remaining solution was divided into two equal portions. One portion of the solution was concentrated to 0.5 of the initial volume under vacuum and then benzene (50 ml) was added. The precipitate of  $\text{LiBr}$  that formed was filtered off. The filtrate was concentrated to 50 ml and kept overnight. Red crystals of complex **3** (0.15 g, 32%) were separated from the mother liquor, carefully washed, and dried under vacuum. Anal. Found: Al, 3.89; Br, 21.90; Zr, 25.98. Calc. for  $\text{C}_{26}\text{H}_{29}\text{AlBr}_2\text{Zr}_2$ : Al, 3.80; Br, 22.50; Zr, 25.68%. One crystal was chosen for X-ray diffraction

Table 3  
Crystal data and structure refinement for 2–5<sup>a</sup>

Complex	2	3	4	5
Formula	C <sub>26</sub> H <sub>29</sub> AlCl <sub>2</sub> Zr <sub>2</sub>	C <sub>26</sub> H <sub>29</sub> AlBr <sub>2</sub> Zr <sub>2</sub>	C <sub>30</sub> H <sub>37</sub> AlBr <sub>2</sub> O <sub>2</sub> Zr <sub>2</sub>	C <sub>32</sub> H <sub>35</sub> AlI <sub>2</sub> Zr <sub>2</sub>
Formula weight	621.81	710.73	798.84	882.82
Crystal color	Red	Red	Red	Reddish-brown
Crystal size (mm <sup>3</sup> )	0.37 × 0.30 × 0.25	0.50 × 0.20 × 0.15	0.45 × 0.40 × 0.25	0.20 × 0.15 × 0.10
Crystal system	Triclinic	Triclinic	Triclinic	Tetragonal
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	14/ <i>m</i>
<i>a</i> (Å)	9.592(2)	9.701(2)	9.603(1)	20.152(3)
<i>b</i> (Å)	10.287(2)	10.205(2)	10.744(2)	20.152(3)
<i>c</i> (Å)	14.570(3)	14.770(3)	15.744(3)	12.964(3)
$\alpha$ (°)	71.03(2)	71.75(3)	98.21(1)	90
$\beta$ (°)	73.09(2)	72.27(3)	91.04(1)	90
$\gamma$ (°)	77.28(2)	77.91(3)	103.78(1)	90
<i>V</i> (Å <sup>3</sup> )	1288.2(5)	1312.1(5)	1559.2(4)	5265(2)
<i>Z</i>	2	2	2	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.603	1.799	1.702	2.228
$\theta$ Range (°)	1.52–24.90	1.50–25.13	2.19–24.92	1.87–26.98
Reflections collected	1597	2463	2680	1345
Unique reflections	1494	2324	2568	1269
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.653	1.048	1.057	0.839
Final <i>R</i> indices	0.0250	0.0383	0.0226	0.0183
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0667	0.1009	0.0589	0.0493

<sup>a</sup> Diffractometer: CAD4; temperature for data collection: 293 K; radiation type: Mo–K $\alpha$  ( $\beta$ -filter), wavelength: 0.71073 Å; collection method:  $\theta/\theta$ .

analysis. IR (Nujol, cm<sup>-1</sup>): 1510 (sh), 1462 (m, Nujol), 1456 (sh), 1445 (sh), 1377 (m, Nujol), 1315 (m, br), 1133 (m), 1080 (w), 1070 (w), 1024 (m), 1010 (m), 950 (w), 804 (s), 770 (s), 720 (sh), 687 (s), 610 (w).

1,4-Dioxane (30 ml) was added to another portion of the solution. The reaction solution was filtered, concentrated to one-half of the initial volume under vacuum, and kept overnight. Red crystals of complex **4** (0.15 g, 28%) were separated from the mother liquor, carefully washed, and dried under vacuum. Anal. Found: Al, 3.98; Br, 19.47; Zr, 22.91. Calc. for C<sub>30</sub>H<sub>37</sub>AlBr<sub>2</sub>O<sub>2</sub>Zr<sub>2</sub>: Al, 3.38; Br, 20.03; Zr, 22.86%. One crystal was chosen for X-ray diffraction analysis.

#### 4.3. [(Cp<sub>2</sub>Zr)<sub>2</sub>H](H)<sub>2</sub>AlI<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub> (**5**)

A solution of AlH<sub>3</sub> (2.04 mmol) in Et<sub>2</sub>O (20.1 ml) was added dropwise to a stirred warm (40 °C) solution of anhydrous CoBr<sub>2</sub> (35 mg, 0.16 mmol) and Cp<sub>2</sub>ZrI<sub>2</sub> (0.97 g, 2.04 mmol) in a mixture of benzene (60 ml) and Et<sub>2</sub>O (10 ml) for 1 h. The reaction mixture was stirred at 40–45 °C for 6 h and kept at room temperature overnight. The dark-red solution was decanted from a dark precipitate, concentrated to one-half of the initial volume under vacuum, and kept at room temperature overnight. Red-brown crystals of complex **5** (0.23 g, 25%) were separated from the mother liquor, carefully washed, and dried under vacuum. Anal. Found: Al, 3.27; I, 28.38; Zr, 21.79. Calc. for C<sub>32</sub>H<sub>35</sub>AlI<sub>2</sub>Zr<sub>2</sub>: Al, 3.06; I, 28.75; Zr, 20.66%. One crystal was chosen for X-ray diffraction analysis. IR (Nujol, cm<sup>-1</sup>): 1620 (w),

1462 (m, Nujol), 1377 (m, Nujol), 1305 (m, br), 1124 (m), 1075 (w), 1061 (w), 1025 (m), 1007 (m), 807 (s), 740 (m), 720 (m), 675 (s), 606 (w).

#### 4.4. X-ray diffraction study

The crystal structures of complexes **2–5** were established from X-ray diffraction data collected from single crystals sealed in glass capillaries. The conditions of data collection and selected crystallographic parameters of the complexes are presented in Table 3. The structures were solved by the heavy-atom method and refined anisotropically by the full-matrix least-squares with the use of the SHELXL-97 software package. The hydride hydrogen atoms were located from difference electron density syntheses, and their coordinates and isotropic thermal parameters were not refined. The positions of the remaining hydrogen atoms were calculated geometrically, and their coordinates were refined with fixed displacement and thermal parameters.

### 5. Supplementary material

Crystallographic data for the structural analysis were deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201018 for compound **2**, No. 201019 for **5**, No. 201020 for **4** and No. 201021 for **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033;

e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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