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# Heterometallic zirconocene(III) aluminum hydride complex $(\mathrm{Cp_2ZrH})_2\mathrm{HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6}$

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The heterometallic zirconocene(III) aluminum hydride complex $(\mathrm{Cp_2ZrH})_2\mathrm{HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6}$ was synthesized by reduction of $\mathrm{Cp_2ZrCl_2}$ with lithium aluminum hydride in the presence of $\mathrm{Cp_2TiBH_4}$ and 1,4-dioxane, and its structure was established by X-ray diffraction analysis.

**Key words:** zirconium, titanium, metallocenes, reduction, aluminum, hydrides, chlorides, crystal solvates, 1,4-dioxane.

Hydride complexes of zirconium and aluminum play an important role in many catalytic and stereochemical reactions. Unlike titanocene(IV) halides, which are readily reduced, zirconocene(IV) halides react with $\mathrm{LiAlH_4}$ or $\mathrm{AlH_3 \cdot L}$ to form hydride and aluminum hydride derivatives of zirconocene(IV),[2—7] *i.e.*, tetrahydroaluminates and alanes do not reduce the $\mathrm{Zr^{IV}}$ atom under normal conditions. However, we have demonstrated[8] that this reduction can be performed in the presence of $\mathrm{Ti^{III}}$ hydride complexes. This procedure was used for the synthesis of the first heterometallic aluminum zirconocene(III) complex $(\mathrm{Cp_2ZrH})_2\mathrm{HAlCl_2}$ (**1**).

As part of our investigation on the scope of this procedure and its possible use in the synthesis of zirconocene(III) derivatives, we prepared crystal solvate of complex **1** with 1,4-dioxane and benzene whose structure differs substantially from that of complex **1**. In the present study, we report the procedure for the synthesis and the results of X-ray diffraction study of this compound.

## Results and Discussion

Organometallic hydride complexes of $\mathrm{Zr^{III}}$ are few in number and are difficultly accessible.[4,6] Recently, using complex **1** as an example, we have demonstrated[8] that these compounds can be synthesized by reduction of $\mathrm{Zr^{IV}}$ derivatives according to the reaction

$$\mathrm{Cp_2ZrCl_2 + Cp_2TiBH_4 + LiAlH_4} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{2}}{\{\mathrm{Cp_2ZrX(\mu\text{-}H)_2AlX'(\mu\text{-}H)_2TiCp_2}\}} \longrightarrow \mathbf{1} + [\mathrm{Ti}], \quad (1)$$

X, X′ = Cl, $\mathrm{BH_4}$

Although the mechanism of this reaction is not entirely known, some characteristic features of reaction (1) provide evidence that $\mathrm{Zr^{IV}}$ reduces in trinuclear complex **2**, which then decomposes into complex **1** and a titanium ([Ti]) compound of unknown composition.

It is remarkable that the bonds in the metal hydride fragment of structure **1** are noticeably nonequivalent and this fragment "is ready" to undergo cleavage along the *aa′* line (Fig. 1, *a*). In the expectation that this dissociation in the corresponding solvent would afford new compounds, we reproduced the synthesis of complex **1** in the presence of 1,4-dioxane.

It appeared that the use of dioxane did not hinder the formation of complex **1**. However, in the presence of dioxane, this complex was isolated from the solution as a crystal solvate $(\mathrm{Cp_2ZrH})_2\mathrm{HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6}$ (**3**) (Fig. 1, *b*) rather than as an individual compound.

Complex **3** precipitated from the solution as pink crystals (complex **1** was obtained as red crystals), which were readily soluble in benzene. In the crystalline state and, particularly, in a solution, complex **3** rapidly reacted with traces of atmospheric oxygen and moisture to give colorless zirconium(IV) derivatives.

In the crystal structure of compound **3** (Fig. 1), $(\mathrm{Cp_2ZrH})_2\mathrm{HAlCl_2}$ (**1**), benzene, and dioxane together form a molecular packing. In complex **3,** the shortest distance between the aluminum atoms and the oxygen atoms of the dioxane molecule is larger than 3.5 Å, which is indicative of the absence of the valence interaction between these fragments. This fact is quite unexpected. In the chemistry of alanes[9] and aluminum hydride complexes of transition metals,[10] the presence of Lewis bases in the system always leads to either solvation of the molecule at the aluminum atom or decomposition of the molecule to solvated components.

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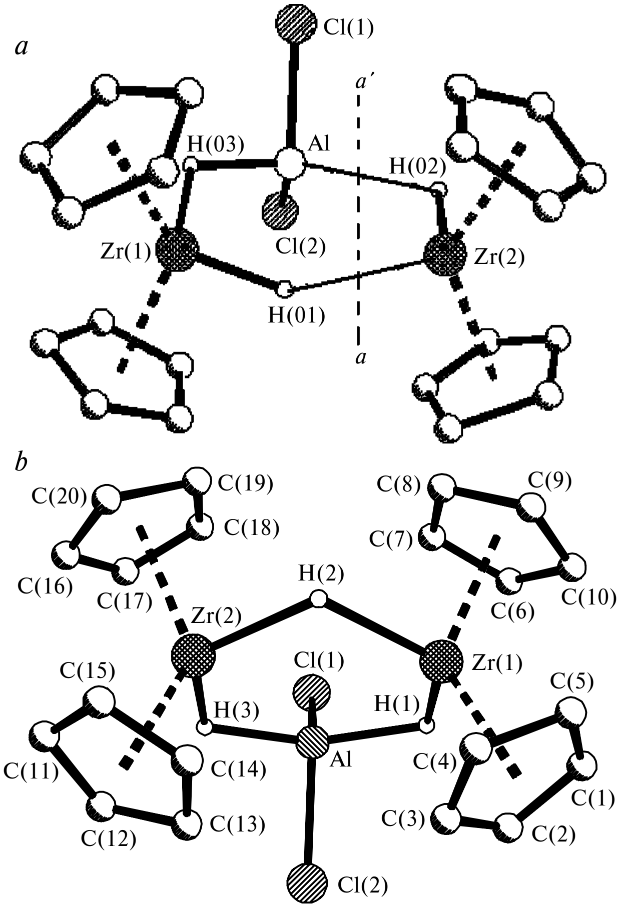

**Fig. 1.** Molecular structure of the complexes $(Cp_2ZrH)_2HAlCl_2$ (**1**) (data published in the literature[8]) (*a*) and $(Cp_2ZrH)_2HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6$ (**3**) (*b*).

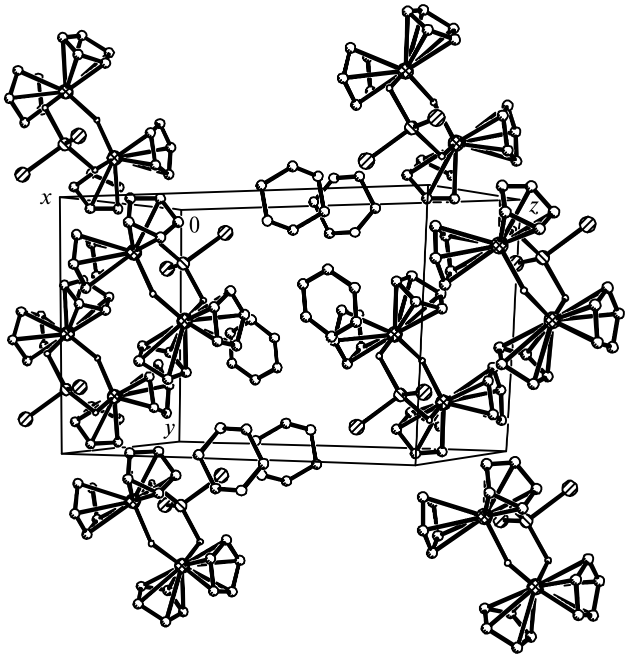

**Fig. 2.** Crystal packing of the solvate $(Cp_2ZrH)_2HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6$ (**3**).

The molecular structure of **3**, like that of **1**, is based on the six-membered metal hydride ring $Zr_2AlH_3$ in which the metal atoms are linked to each other through hydride bridges (Fig. 1, *b*, Table 1). In compound **3**, the interatomic Zr(1)...Al and Zr(2)...Al distances (2.912 and 2.911 Å, respectively), the Zr(1)—Cp and Zr(2)—Cp distances (2.21 and 2.19 Å, respectively), and the corresponding angles have virtually equal values. The following pairs of the metal—hydride bonds in this ring also have close values: Zr(1)—H(2) and Zr(2)—H(2) (2.07 and 2.03 Å); Zr(1)—H(1) and Zr(2)—H(3) (1.84 and 1.81 Å); and Al—H(1) and Al—H(3) (1.77 and 1.70 Å). Hence, the structure of **3** is similar to those possessing the mirror symmetry plane.

In its own crystalline phase, *i.e.*, in the absence of the solvent in the crystal lattice, the molecular structure of $(Cp_2ZrH)_2HAlCl_2$ (**1**) differs substantially from that in **3** (Fig. 1, *a*). The metal hydride ring in **1** is substantially asymmetrical. Thus, although the Zr(1)—H(1) and Zr(2)—H(3) distances have close values (1.84 and 1.84 Å) the distances in the Zr(1)—H(2) and H(2)—Zr(2) pair (2.02 and 1.69(1) Å, respectively) and in the Al—H(1) and Al—H(3) pair (1.90 and 1.67(1) Å, respectively) are noticeably nonequivalent.[8]

When complex **1** is compared with **3**, it is apparent that the symmetrical structure of **3** is, on the whole, less strained and more "reasonable" than the structure of **1**. Apparently, the symmetry of **3** is achieved due to the fact that crystal solvate **3** is more loose than **1** (the densities of **3** and **1** are 1.536 and 1.682 g cm$^{-3}$, respectively)[8] and, probably, due to nonvalent contacts between the $(Cp_2ZrH)_2HAlCl_2$, dioxane, and benzene molecules. In this connection, it should be noted that the $(C_{10}H_8)[CpTiH)]_2 \cdot HAlEt_2$ complex, which is the

**Table 1.** Principal bonds lengths (*d*) and bond angles (ω) in molecule **1b**

| Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|
| Zr(1)—H(1) | 1.84 | H(1)—Zr(1)—H(2) | 118.6 |
| Zr(1)—H(2) | 2.07 | H(2)—Zr(2)—H(3) | 117.5 |
| Zr(2)—H(2) | 2.03 | H(1)—Al—H(3) | 145.9 |
| Zr(2)—H(3) | 1.81 | H(1)—Al—Cl(1) | 98.0 |
| Al—H(1) | 1.77 | H(1)—Al—Cl(2) | 101.5 |
| Al—H(3) | 1.70 | H(3)—Al—Cl(1) | 103.6 |
| Al—Cl(1) | 2.171 | Cl(1)—Al—Cl(2) | 97.5 |
| Al—Cl(2) | 2.181 | H(3)—Al—Cl(2) | 97.5 |
| Zr(1)—Al | 2.912 | Al—Zr(2)—Zr(1) | 53.24(8) |
| Zr(2)—Al | 2.911 | Cl(1)—Al—Cl(2) | 105.8(2) |
| Zr(1)—Zr(2) | 3.485 | Cl(1)—Al—Zr(1) | 118.97(17) |
| | | Cl(2)—Al—Zr(1) | 118.99(17) |
| | | Cl(1)—Al—Zr(2) | 119.61(17) |
| | | Cl(2)—Al—Zr(2) | 117.97(17) |
| | | Zr(1)—Al—Zr(2) | 73.52(9) |

**Table 2.** Details of X-ray diffraction study and crystallographic characteristics of crystal solvate **3**

| Molecular formula | $C_{30}H_{37}AlCl_2O_2Zr_2$ |
|---|---|
| $M$ | 709.92 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$/Å | 9.510(2) |
| $b$/Å | 10.745(2) |
| $c$/Å | 15.631(3) |
| $\alpha$/deg | 98.14(3) |
| $\beta$/deg | 91.50(3) |
| $\varphi$/deg | 103.48(3) |
| $V$/Å$^3$ | 1534.7(5) |
| $Z$ | 2 |
| $D$/g cm$^{-3}$ | 1.536 |
| Diffractometer | Syntex $P\bar{1}$ |
| Radiation | Cu-K$\alpha$ ($\beta$ filter) |
| $\theta$ Scan range/deg | 2.86—55.07 |
| Absorption coefficient/mm$^{-1}$ | 0.00024(5) |
| Crystal dimensions/mm | 0.20×0.10×0.10 |
| Number of reflections | |
| $R$ ($I > 2\sigma(I)$) | 2665 |
| $R_1$ | 0.0544 |
| $wR_2$ | 0.0951 |

only compound containing the six-membered metal hydride ring $Ti_2AlH_3$ whose structure was unambiguously established,[11] also possesses the symmetry plane.

Hence, the asymmetry of molecule **1** should be considered as a consequence of the packing effects rather than as a reflection of the tendency of compound **1** to dissociation or disproportionation.[8]

## Experimental

All operations associated with the preparation of the reagents and the synthesis were carried out either under an atmosphere of argon or *in vacuo*. The solvents were purified by refluxing and distillating over lithium aluminum hydride or sodium under argon.

**Complex $(Cp_2ZrH)_2HAlCl_2 \cdot C_4H_8O_2 \cdot C_6H_6$ (3).** A solution of $LiAlH_4$ (1.7 mmol) in $Et_2O$ (12 mL) was added with stirring to a mixture of $Cp_2ZrCl_2$ (0.50 g, 1.7 mmol) and $Cp_2TiBH_4$ [12] (0.33 g, 1.7 mmol) in benzene (60 mL) at 5 °C. Then the reaction mixture was stirred at 5 °C for 20 min and the precipitate of LiCl was filtered off. The filtrate was kept at 40 °C for 3 h and concentrated to 1/3 of the initial volume. Then 1,4-dioxane (1 mL) was added and the mixture was kept at ~20 °C for 12 h. The pink crystals that precipitated (0.12 g, 20%) were separated from the mother liquor, washed, and dried *in vacuo*. Found (%): Al, 3.87; Zr, 25.71; Cl, 9.96. $C_{30}H_{37}AlCl_2O_2Zr_2$. Calculated (%): Al, 3.81; Zr, 25.67; Cl, 10.01.

**X-ray diffraction study of complex 3.** The details of X-ray diffraction study of a single crystal of complex **3**, which was sealed in a glass capillary, and the principal crystallographic characteristics are given in Table 2. The structure was solved by the heavy-atom method and refined anisotropically by the full-matrix least-squares method using the SHELXTL-PLUS and SHELXL-93 program packages. The positional parameters of the hydride atoms were revealed from the difference electron density synthesis. Their coordinates and isotropic thermal parameters were refined. The coordinates of the other hydrogen atoms were calculated from geometric considerations and refined with fixed thermal and positional parameters. Absorption was ignored. The crystallographic data were deposited with the Cambridge Structural Database (CCDC No. 159473).

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