Russian Chemical Bulletin, International Edition, Vol. 54, No. 11, pp. 2496—2501, November, 2005

Heterometallic $(\mathrm{Zr^{III}})_2$—Al hydrides $[(\mathrm{Cp_2Zr})_2(\mu\text{-H})](\mu\text{-H})_2\mathrm{AlX_2}$ (X = Cl or Br): preparative synthesis and reactivity. Molecular structure of $[(\mathrm{Cp_2Zr})_2(\mu\text{-Cl})](\mu\text{-H})_2\mathrm{AlCl_2}$

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A procedure was developed for the synthesis of trinuclear cyclic $(\mathrm{Zr^{III}})_2$—Al hydrides $[(\mathrm{Cp_2Zr})_2(\mu\text{-H})](\mu\text{-H})_2\mathrm{AlX_2}$ (X = Cl (**1a**) or Br (**1b**)). These complexes were prepared in 60—65% yields by the reaction of $\mathrm{Cp_2ZrX_2}$ with $\mathrm{LiAlH_4}$ in the presence of $\mathrm{CoBr_2}$ and tolane. The structures of complexes **1a** and **1b** and iodide **1c** (X = I) were studied by NMR spectroscopy in solvents of different basicities (toluene, THF, and pyridine). Complex **1a** is unsolvated and monomeric in all solvents; complex **1b**, in toluene and THF; complex **1c**, in toluene only. At room temperature, complex **1a** does not catalyze hydrogenation of hex-1-ene and does not react with tolane, but reacts with the latter at high temperature to give bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene. The reaction of equivalent amounts of complex **1a** and HCl produces the $[(\mathrm{Cp_2Zr})_2(\mu\text{-Cl})](\mu\text{-H})_2\mathrm{AlCl_2}$ complex. The structure of the latter was established by X-ray diffraction.

Key words: zirconocene, zirconium(III), aluminum hydrides, synthesis, reactivity, structure.

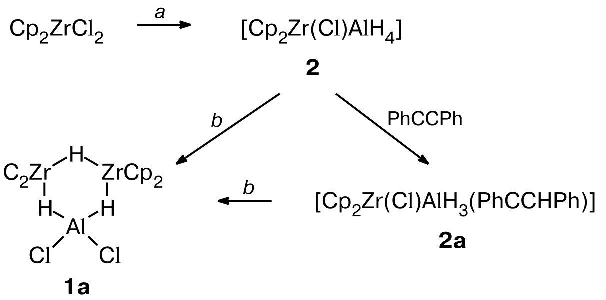
Trinuclear $(\mathrm{Zr^{III}})_2$—Al hydrides of the general formula $[(\mathrm{Cp_2Zr})_2(\mu\text{-H})](\mu\text{-H})_2\mathrm{AlX_2}$ (X = Cl (**1a**), Br (**1b**), or I (**1c**)), which have been synthesized recently, are characterized by an unusual combination of several reactive metal hydride centers and rather high stability. As a result, these compounds can be isolated in pure form, which is, on the whole, unusual for $\mathrm{Zr^{III}}$ hydrides.[1—3] However, known methods produce complexes **1** in low yields (~25%), which seriously complicates studies of their properties.[1—3]

In the present study, we developed a more efficient procedure for the synthesis of complexes **1a**,**b**, which allowed us to prepare these compounds in 60—65% yields. In addition, we examined the reactivity of complexes **1** toward basic and acidic reagents. We also devised a procedure for the synthesis of the $[(\mathrm{Cp_2Zr})_2(\mu\text{-Cl})](\mu\text{-H})_2\mathrm{AlCl_2}$ complex and established its crystal structure.

Results and Discussion

It is known[1—3] that complexes **1** can be prepared in ~25% yields by the reactions of equivalent amounts of $\mathrm{Cp_2ZrX_2}$ (X = Hal) and $\mathrm{LiAlH_4}$ in the presence of transition metal salts (for example, $\mathrm{CoBr_2}$). Although the formation of compounds **1** is a rather complicated process,[1,3] it can be formally represented as cobalt bromide-catalyzed decomposition of intermediate **2** generated in the first step of the reaction (Scheme 1).[3]

Scheme 1



Reagents and conditions: *a*. $\mathrm{LiAlH_4}$, $\mathrm{Et_2O—C_6H_6}$; *b*. $\mathrm{CoBr_2}$ (5 mol.%).

We studied features of reactions in the $\mathrm{Cp_2ZrX_2—LiAlH_4—CoBr_2}$ systems and found that the addition of a small amount of tolane to the reaction mixture substantially increases (up to 60—65%) the yields of

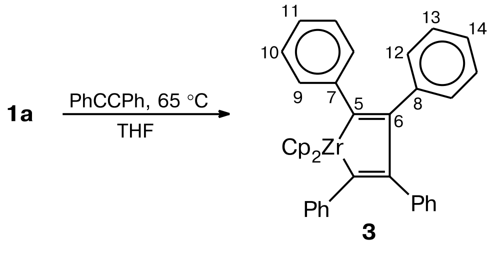
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2418—2423, November, 2005.

complexes **1a** and **1b**. The mechanism of this effect remains largely unclear. However, taking into account that tolane and other arylacetylenes readily undergo hydrometallation with zirconocene(IV) and aluminum hydrides to form the corresponding alkenyl derivatives,[4,5] it can be hypothesized that the formation of complex **1** in the presence of tolane occurs through hydride alkenyl complex **2a** rather than through hydride intermediate **2** (Scheme 1), which apparently decreases the energy barrier to the reaction. For example, cyclooctadiene substantially promotes thermolysis of Zr^{IV} hydrides $(Cp_2ZrHX)_n$ (X = Cl or CH_2PPh_2) giving rise to zirconocene(III) complexes.[6]

Complexes **1** were prepared in the highest yields with the use of the tolane to Cp_2ZrX_2 molar ratio of ~0.5. An increase in this ratio leads to a decrease in the yield because complexes **1** can react with tolane by themselves.

According to the NMR data, heating of a mixture of equivalent amounts of **1a** and tolane in THF-d_8 to the boiling point results in a decrease in the concentrations of these compounds. After completion of the reaction, the signal of tolane fully disappears. At the same time, new signals appear in the NMR spectra of the reaction mixture, δ: ^{1}H NMR, 6.97 (t, 4 H, C(10), *J* = 7.8 Hz); 6.65 (m, 16 H, C(9) and C(11)—C(14)); 6.33 (s, 10 H, Cp); ^{13}C{^{1}H} NMR, 195.43 (C(5)); 148.93 (C(7)), 142.83 (C(6)); 142.29 (C(8)); 131.53 (C(9)); 127.99 (C(10)), C(12)); 126.93 (C(13)); 124.75 (C(11)); 123.22 (C(14)); 112.9 (Cp). A comparison of these spectra with the published data[7—9] provides evidence for the formation of bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene (**3**) in the system under consideration (Scheme 2).

Scheme 2



At room temperature, complex **1a** does not react with tolane and does not exhibit catalytic activity in hydrogenation of hex-1-ene. Taking into account these facts as well as the fact that compounds **3** are formed upon generation of the Cp complex of low-valent zirconium in the presence of arylacetylenes,[9,10] it can be hypothesized that the reaction of **1a** with tolane at high temperature proceeds through thermolysis of **1a** yielding $[Cp_2Zr^{II}]$ as an intermediate. Therefore, the reactivity of **1a** in this process is similar to that of homonuclear hydride $[(C_5H_4Me)_2Zr^{IV}H_2)]_2$. Heating of the latter in tolane also affords compound **3**.[7,8]

Table 1. Signals in the ^{1}H NMR spectra of complexes **1a—c**

Complex	Solvent	^{1}H NMR (δ)		
		C_5H_5 (s, 20 H)	Al—H—Zr (br.s, 2 H)	Zr—H—Zr (s, 1 H)
1a	Toluene-d_8	5.57	−2.0 (−2.00)*	−8.34
	THF-d_8	6.04	−2.0 (−1.99)*	−7.96
	Pyridine-d_5	6.15	−1.7 (−1.71)*	−7.77
1b	Toluene-d_8	5.52	— (−1.40)*	−8.20
	THF-d_8	6.08	−1.6 (−1.58)*	−7.71
1c	Toluene-d_8	5.53	— (−0.94)*	−7.91

* The corresponding signal in the ^{1}H{^{27}Al} NMR spectrum.

Earlier,[1—3] we have noted that complex **1a**, in spite of the fact that the Al atom is coordinatively unsaturated, is not solvated by such bases as diethyl ether, 1,4-dioxane, and THF. In continuation of our studies, we investigated the structures of complexes **1a—c** by NMR spectroscopy in solvents that differ in solvating power (in toluene, THF, and pyridine).

As can be seen from Table 1, the positions of the signals of the Cp ligands in the spectra of complexes **1** measured in a given solvent are virtually independent of the nature of halide involved in the complex, and the signals of the Zr—H—Zr bridges depend only slightly on the halide. By contrast, the peaks of the bridging Al—H—Zr hydrides shift downfield in going from **1a** to **1b** and then to **1c**. In all spectra, these signals are partially or completely broadened due to dynamic processes in the $[H_2Al(Hal)_2]$ fragment and the influence of the ^{27}Al nucleus, as have been demonstrated using complex **1a** as an example.[3]

A comparison of the spectra of complex **1a** in various solvents shows that the signals of all groups of protons are gradually shifted downfield but remain to be of the same type in going from toluene-d_8 to THF-d_8 and then to pyridine-d_5, which indicates that the structure of complex **1a** remains virtually unchanged. This is consistent with the fact that the ^{27}Al NMR spectrum of **1a** has peaks at δ 199.08 (in THF-d_8)[3] and 192.44 (in pyridine-d_5) corresponding to the four-coordinate aluminum atom.[11] Therefore, complex **1a** remains unsolvated not only in THF but also in pyridine.

The ^{1}H NMR spectrum of bromide **1b** in THF-d_8 is also, on the whole, similar to that in toluene-d_8. In the latter solvent, the signal for the bridging Al—H—Zr hydrides is completely broadened and appears at δ −1.40 in the $^1H\{^{27}Al\}$ NMR spectrum measured with selective decoupling from the signal at δ 191.90. The signals in the ^{27}Al NMR spectra of **1b** at δ 192.19 (in THF-d_8) and 191.90 (in toluene-d_8) are also indicative of the presence of the Al atom with coordination number 4.**[11]** We failed to measure a suitable ^1H NMR spectrum of **1b** in pyridine due, apparently, to lower stability of this complex (compared to complex **1a**) to strong bases.

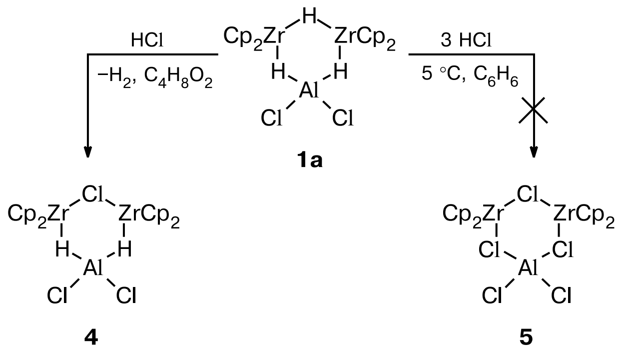
The ^1H NMR spectrum of iodide **1c** in toluene-d_8 is also, on the whole, similar to the spectra of the other complexes. In this spectrum, the signal of the Al—H—Zr bridge is also completely broadened and is observed at δ −0.94 only in the $^1H\{^{27}Al\}$ NMR spectrum decoupled from the ^{27}Al signal at δ 167.5. It is worthy of note that the latter signal is shifted upfield by ~30 ppm compared to the ^{27}Al NMR spectra of complexes **1a** and **1b**. However, this shift is typical**[12]** of the spectra of iodide derivatives of aluminum with coordination number 4. In addition to the main signal at δ 167.5, the ^{27}Al NMR spectrum of **1c** in toluene-d_8 shows several weak peaks at δ 221.2—181.1, which are apparently due to decomposition products. These impurities are manifested in the $^1H\{^{27}Al\}$ NMR spectrum as signals in the region from δ −3.28 to −3.75, which are unobserved in the ^1H NMR spectrum. Complex **1c** appeared to be unstable already in THF. In attempting to dissolve this compound, it rapidly decomposes with the formation of a precipitate.

Therefore, stability of complexes **1** to bases depends, as expected, on the nature of the halogen atom bound to the aluminum atom. Complex **1c** is rather stable only in aromatic and weakly solvating solvents, such as diethyl ether,**[3]** whereas complex **1a** remains unchanged in pyridine at 18 °C for ~1 day (NMR data). It should be noted that complex **1a** does not react with a fivefold excess of *N*-methylmorpholine in benzene and can be isolated from this solution as the crystal solvate **1a**$\cdot C_6H_6$.

The degradation process of complexes **1** in solution remains unclear. Prolonged storage or heating of **1a** is accompanied by a gradual increase in the intensities of broad peaks in the resonance region of Cp ligands at δ ≈ 5.2 and in the hydride region at δ ≈ −3.5 in the ^1H NMR spectra (in THF-d_8 or toluene-d_8). The ^{27}Al NMR spectrum also has signals of impurities at δ 223.8—227.2. Many of these impurities are characterized by peaks in the region from δ −3.28 to −3.75 in the $^1H\{^{27}Al\}$ NMR spectra, these signals being unobserved in the ^1H NMR spectra. Analogous phenomena were observed for **1b** and particularly for **1c**, whose samples, as mentioned above, usually contain such impurities. Relatively low stability of complex **1c** is, apparently, the main cause why the above-described procedure for the synthesis in the presence of tolane appeared to be inefficient for **1c**.

The reactivity of complexes **1** with respect to electrophilic agents, in particular, to HCl, is of considerable interest. Studies by NMR spectroscopy showed that a high electron density is localized on the hydride hydrogen atoms of the bridging Zr—H—Zr bonds in complexes **1** (δ ≈ −8). This is consistent with the fact that the reaction of equivalent amounts of **1a** and HCl is accompanied by elimination of H_2 and the replacement of hydride with the Cl atom to form complex **4** (Scheme 3).

Scheme 3



Like compounds **1a—c**,**[3]** complex **4** has the red color characteristic of zirconocene(III) derivatives and forms the well crystallizable crystal solvate **4**$\cdot 0.5C_4H_8O_2$ with 1,4-dioxane. X-ray diffraction study of a single crystal of **4**$\cdot 0.5C_4H_8O_2$ showed that the structural parameters of complex **4** (Fig. 1, Table 2) are similar to those of complexes **1**.

The structural similarity of compounds **1** and **4** is of considerable interest from the standpoint of binding in this type of complexes. It can be seen that the parameters of these structures depend only slightly on the nature of the X atom in the Zr—X—Zr bridge. This fact is in contradiction with the assumption that the X atom serves as a mediator for d^1—d^1 interactions between the zirconium centers (model **A**)**[3]** and is most likely indicative of the

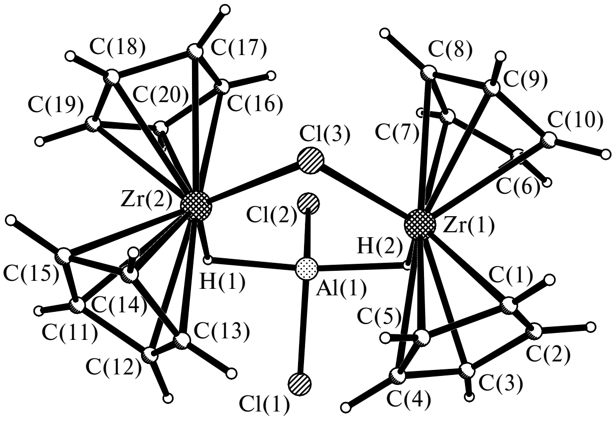
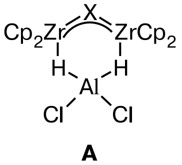


Fig. 1. Molecular structure of complex **4**.

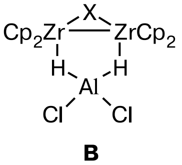
Table 2. Selected interatomic distances (*d*) and bond angles (ω) for complex **4**

Distance	*d*/Å	Angle	ω/deg
Zr(1)—Cl(3)	2.563(2)	Cl(3)—Zr(1)—H(2)	133(1)
Zr(1)—Al(1)	2.935(2)	Cl(3)—Zr(2)—Al(1)	96.21(5)
Zr(1)—H(2)	1.90(4)	Cl(3)—Zr(2)—H(1)	132(1)
Zr(2)—Cl(3)	2.562(2)	Al(1)—Zr(2)—H(1)	36(1)
Zr(2)—Al(1)	2.959(2)	Cl(1)—Al(1)—Cl(2)	106.50(9)
Zr(2)—H(1)	2.05(4)	Cl(1)—Al(1)—H(1)	93(1)
Al(1)—Cl(1)	2.156(2)	Cl(2)—Al(1)—H(1)	96(1)
Al(1)—Cl(2)	2.194(2)	Cl(1)—Al(1)—H(2)	100(1)
Al(1)—H(1)	1.78(4)	Cl(2)—Al(1)—H(2)	98(1)
Al(1)—H(2)	1.79(4)	H(1)—Al(1)—H(2)	158(2)
		Zr(2)—Cl(3)—Zr(1)	90.56(5)

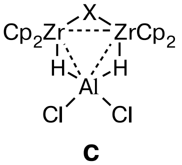
presence of the direct Zr—Zr bond in **1** (model **B**) or binding with delocalization of d electrons over the orbitals of three metals, Zr_2Al (model **C**).[3] Model **B** agrees well with the NMR data on the presence of Al atoms with coordination number 4 in molecule **1**. However, model **C** is, on the whole, more preferable because, as we have mentioned earlier,[3] it provides an explanation for high stability of complexes **1** (recall that zirconocene(III) hydrides in the solid phase have not been documented earlier due to their low stability[13,14]) and the absence of solvation of the coordinatively unsaturated Al atom in these complexes. In this connection, it should be noted that the distance between the Al atom and the O atom of the dioxane molecule in the crystal solvate $\mathbf{4} \cdot 0.5C_4H_8O_2$ is larger than 4 Å, *i.e.*, the H_2AlCl_2 fragment in molecule **4** is not bound to dioxane in the crystalline phase. The ^1H NMR spectra of complex **4** in benzene-d_6 (δ: 5.52 (s, 20 H, Cp)) and THF-d_8 (δ: 5.69 (s, 20 H, Cp)) (signals of the Zr—H—Al bridges are observed only in the $^1H\{^{27}Al\}$ NMR spectra at δ −3.24 (benzene-d_6) and −3.41 (THF-d_8) measured with decoupling from the ^{27}Al signals at δ 223.89 and 223.27, respectively) show that complex **4** is unsolvated in THF as well. Therefore, the conclusions drawn about binding in complexes **1** refer equally to complex **4**.



A



B



C

X = H, Cl

We failed to prepare a stable product in which all hydride hydrogen atoms are replaced with chlorine atoms and the cyclic $(Zr^{III})_2$—Al structure is retained. Interestingly, the reaction of complex **1a** with three equivalents of HCl (see Scheme 3) affords a red-orange solution, from which a red substance can be isolated. The elemental composition of the latter approximately corresponds to the formula $\mathbf{5} \cdot nC_6H_6$ (*n* = 1 or 2). However, this compound is thermally unstable. At room temperature, it rapidly loses the red color characteristic of Zr^{III} complexes. The ^1H NMR spectrum of the resulting colorless product (in benzene-d_6) has an intense peak at δ 5.93, which can be assigned to Cp_2ZrCl_2, and two weaker signals (δ 6.07 and 5.17), whose assignment remains unclear. Within the framework of model **C**, instability of complex **5** can be accounted for by an increase in the Zr...Al distance after the replacement of the bridging Zr—H—Al bond with the Zr—Cl—Al bond, which weakens the three-center $(Zr^{III})_2$—Al bond stabilizing the molecule. It should be noted that the $[Cp_2Zr^{III}(\mu\text{-}Cl)]_2$ dimer, whose formation could be expected in this case, is very unstable.[14,15] Another possible decomposition product, *viz.*, the $Cp_2Zr^{III}(\mu\text{-}Cl)_2AlCl_2$ complex, remains unknown and, judging from low stability of hydride analogs,[11,13,14] does not exist.

Therefore, the bridging hydride bonds Zr—H—Al (unlike the Zr—X—Zr bridge) are necessary for stability of cyclic $(Zr^{III})_2$—Al complexes. Presumably, it is these bonds combined with the strong electron-withdrawing properties of the $Al(Hal)_2$ fragment[3] that stabilize such trimetallic structures. This is, apparently, responsible for unusual stability of these complexes in solution and in the crystalline state, which is in marked contrast to zirconocene(III) hydride complexes of other types.[13,14]

Experimental

All operations were carried out under argon or *in vacuo* using the standard Schlenk technique. Solvents were purified by refluxing and distillation from sodium benzophenone ketyl or lithium aluminum hydride. The NMR spectra were recorded on Bruker DPX 300 (^1H and $^{13}C\{^1H\}$) and Bruker AMX 500 (^{27}Al and $^1H\{^{27}Al\}$) instruments relative to the residual signal of solvent as the standard: toluene-d_8 (^1H, δ 2.09; $^{13}C\{^1H\}$, δ 20.4), THF-d_8 (^1H, δ 1.73; $^{13}C\{^1H\}$, δ 25.3), and pyridine-d_5 (^1H, δ 8.71; $^{13}C\{^1H\}$, δ 149.90). The ^{27}Al NMR spectra were measured relative to a 0.1 *M* aqueous $Al_2(SO_4)_3$ solution as the external standard. For the $^1H\{^{27}Al\}$ NMR spectra, only ^{27}Al selectively decoupled peaks are given.

[(μ-Hydrido){di[bis(η^5-cyclopentadienyl)]zirconium(III)}]di(μ-hydrido)di(chloro)aluminum(III), $[(Cp_2Zr)_2(\mu\text{-}H)](\mu\text{-}H)_2AlCl_2$ (1a). A solution of $LiAlH_4$ (3.32 mmol) in Et_2O (19.2 mL) was added with stirring to a solution of Cp_2ZrCl_2 (0.97 g, 3.32 mmol), tolane (0.30 g, 1.66 mmol), and anhydrous $CoBr_2$ (15 mg) in a mixture of benzene (150 mL) and diethyl ether (35 mL) at 40 °C for 30 min. The mixture was carefully refluxed for 3 h and kept at room temperature for 16 h. The red solution was separated from the dark precipitate by decantation, concentrated *in vacuo* to one-half of the initial volume, and kept at room temperature for 16 h. The dark-red crystals that precipitated (0.52 g, 50%) were separated from the mother liquor, washed with the solvent recondensed from the mother liquor, and dried *in vacuo*. Found (%): Al, 4.61; Cl, 12.53; Zr, 29.90.

$C_{26}H_{29}AlCl_2Zr_2$ (**1a**·C_6H_6). Calculated (%): Al, 4.35; Cl, 11.41; Zr, 29.36. The ^{1}H NMR spectra of the product are identical to those published in the literature[3] (300 MHz, δ, 20 °C), toluene-d_8: 7.13 (s, 6 H, C_6H_6); 5.57 (s, 20 H, Cp); ≈−2 (br.s, 2 H, Al—H—Zr); −8.34 (s, 1 H, Zr—H—Zr); THF-d_8: 7.31 (s, 6 H, C_6H_6); 6.04 (s, 20 H, Cp); ≈−2 (br.s, 2 H, Al—H—Zr); −7.96 (s, 1H, Zr—H—Zr). ^{1}H NMR (500 MHz, pyridine-d_5, 20 °C), δ: 7.34 (s, 6 H, C_6H_6); 6.15 (s, 20 H, Cp); ≈ −1.7 (br.s, 2 H, Al—H—Zr); −7.77 (s, 1 H, Zr—H—Zr). ^{13}C{^{1}H} NMR (75.5 MHz, pyridine-d_5, 20 °C), δ: 128.75 (s, C_6H_6); 103.74 (s, Cp). ^{27}Al NMR (130.32 MHz, pyridine-d_5, 20 °C), δ: 192.44 (br.s).

After isolation of the first portion of crystals, the mother liquor was again concentrated to one-half of the initial volume and kept at ~20 °C for 16 h, after which an additional amount (0.14 g, 14%) of crystals of **1a**·C_6H_6 was obtained.

[(μ-Hydrido){di[bis](η^5-cyclopentadienyl)]zirconium(III)}]di(μ-hydrido)di(bromo)aluminum(III), [(Cp_2Zr)$_2$(μ-H)](μ-H)$_2$AlBr$_2$ (1b) was prepared analogously to **1a**. Dark-red crystals were obtained in a yield of 0.39 g (45%) from a solution of Cp_2ZrBr_2[16] (0.92 g, 2.41 mmol), tolane (0.22 g, 1.21 mmol), $CoBr_2$ (17 mg), and $LiAlH_4$ (2.41 mmol, a solution in 11 mL of Et_2O) in a mixture of diethyl ether (40 mL) and benzene (150 mL). Found (%): Al, 3.90; Br, 21.93; Zr, 25.99. $C_{26}H_{29}AlBr_2Zr_2$ (**1b**·C_6H_6). Calculated (%): Al, 3.80; Br, 22.50; Zr, 25.68. ^{1}H NMR (300 MHz, THF-d_8, 20 °C), δ: 7.31 (s, 6 H, C_6H_6); 6.08 (s, 20 H, Cp); −1.58 (br.s, 2 H, Al—H—Zr); −7.71 (s, 1 H, Zr—H—Zr). ^{27}Al NMR (130.32 MHz, THF-d_8, 20 °C), δ: 192.19 (br.s). ^{1}H NMR (300 MHz, toluene-d_8, 20 °C), δ: 7.08 (s, 6 H, C_6H_6); 5.52 (s, 20 H, Cp); −7.93 (s, 1 H, Zr—H—Zr).^{27}Al NMR (130.32 MHz, toluene-d_8, 60 °C), δ: 191.90 (br.s); 221.6 (s). ^{1}H{^{27}Al} NMR (500.13 MHz, toluene-d_8, 60 °C), δ: −1.40 ({191.90}, s, Al—H—Zr); −3.28 ({221.6}, s).

An additional amount of crystals of **1b**·C_6H_6 (0.13 g, 15%) was obtained by concentrating the mother liquor once again.

[(μ-Hydrido){di[bis(η^5-cyclopentadienyl)]zirconium(III)}]di(μ-hydrido)di(iodo)aluminum(III), [(Cp_2Zr)$_2$(μ-H)](μ-H)$_2$AlI$_2$ (1c) was prepared (as **1c**·C_6H_6) according to a known procedure.[3] ^{1}H NMR (300 MHz, toluene-d_8, 20 °C), δ: 7.08 (s, 6 H, C_6H_6); 5.53 (s, 20 H, Cp); −7.93 (s, 1 H, Zr—H—Zr). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8, 20 °C), δ: 103.74 (s, Cp); C_6H_6 overlaps with the signal of the solvent. ^{27}Al NMR (130.32 MHz, toluene-d_8, 60 °C), δ: 221.2 (s); 214.6 (s); 200.3 (s); 185.7 (s); 181.1 (s); 167.5 (br.s). ^{1}H{^{27}Al} NMR (500.13 MHz, toluene-d_8, 60 °C), δ: −3.57 ({221.2, 214.6}, s); −3.48({200.3}, s); −3.71 ({185.7, 181.1}, s); −0.94({167.5}, s, Al—H—Zr).

The reaction of complex 1a with tolane was studied in a sealed NMR tube. The spectra of a mixture of tolane (10.7 mg, 0.06 mmol) and complex **1a**·C_6H_6 (37.3 mg, 0.06 mmol) in THF-d_8 (0.6 mL) were recorded before and after heating to 65 °C. The ^{1}H NMR spectrum measured before heating (300 MHz, 20 °C) corresponded to a superposition of the spectra of **1a**·C_6H_6 (δ): 7.31 (s, 6 H, C_6H_6); 6.04 (s, 20 H, Cp); ~−2 (br.s, 2 H, Al—H—Zr); −7.96 (s, 1 H, Zr—H—Zr) and free tolane (δ): 7.50 (m, 4 H); 7.35 (m, 6 H). After heating, the ^{1}H NMR spectrum (300 MHz, 20 °C) contained, along with signals of C_6H_6 and residual **1a**, signals at δ 6.97 (t, 4 H, C(10), *J* = 7.8 Hz); 6.65 (m, 16 H, C(9) and C(11)—C(14)); 6.33 (s, 10 H, Cp). The ^{13}C{^{1}H} NMR spectrum (75.5 MHz, 20 °C) had, along with signals of C_6H_6 (δ 128.91, s) and residual **1a** (δ 103.85, s, Cp), signals at δ 195.43 (C(5)); 148.93 (C(7)); 142.83 (C(6)); 142.29 (C(8)); 131.53 (C(9)); 127.99 (C(10), C(12)); 126.93 (C(13)); 124.75 (C(11)); 123.22 (C(14)); 112.9 (Cp). The ^{27}Al NMR spectrum (130.32 MHz, 60 °C) contained, along with the signal of residual **1a** (δ 199.08, br.s), signals at δ 47.0 (s); 223.8 (br.s). ^{1}H{^{27}Al} NMR (500.13 MHz, 60 °C), δ: −3.55({223.8}, s). The assignment of the signals in the spectra was made based on comparison with the intensities of peaks published in the literature[7,8,10] and C—H correlations.

[(μ-Chloro){di[bis(η^5-cyclopentadienyl)]zirconium(III)}]di(μ-hydrido)di(chloro)aluminum(III), [(Cp_2Zr)$_2$(μ-Cl)](μ-H)$_2$AlCl$_2$ (4). Complex **1a**·C_6H_6 (0.30 g, 0.48 mmol), which was prepared as described above, was dissolved in warm 1,4-dioxane (40 mL). The solution was cooled to 20 °C, and gaseous HCl (0.48 mmol) was added with vigorous stirring to the gas phase over the solution through septum using a syringe for 30 min. The reaction mixture was stirred at room temperature for 20 min and at 50 °C for 1 h and then concentrated *in vacuo* to ~8 mL. Benzene (30 mL) was added to the resulting red oil and the mixture was allowed to stand for 16 h. The needle-like orange crystals that precipitated (0.09 g, 30%) were separated, washed with the cold solvent recondensed from the mother liquor, and dried *in vacuo*. Found (%): Al, 4.21; Cl, 17.22; Zr, 30.01. $C_{22}H_{26}AlCl_3OZr_2$ (**4**·0.5$C_4H_8O_2$). Calculated (%): Al, 4.34; Cl, 17.09; Zr, 29.32. ^{1}H NMR (300 MHz, 20 °C, benzene-d_6), δ: 5.25 (s, 20 H, Cp); 3.34 (s, 4 H, dioxane). ^{27}Al NMR (130.32 MHz, 20 °C, benzene-d_6), δ: 223.89 (br.s). ^{1}H{^{27}Al} NMR (500 MHz, 20 °C, benzene-d_6), δ: −3.24{223.89} (s). ^{1}H NMR (300 MHz, 20 °C, THF-d_8), δ: 5.69 (s, 20 H, Cp); 3.56 (s, 4 H, dioxane). ^{27}Al NMR (130.32 MHz, 20 °C, THF-d_8), δ: 223.27 (br.s). ^{1}H{^{27}Al} NMR (500 MHz, 20 °C, THF-d_8), δ: −3.41{223.27} (s). One crystal was chosen for X-ray diffraction study.

X-ray diffraction characterization of complex 4·0.5$C_4H_8O_2$. Orange needle-like crystals of complex **4**·0.5$C_4H_8O_2$ ($C_{22}H_{26}AlCl_3OZr_2$, M = 622.20, the dioxane molecule lies on an inversion center) are monoclinic, at 120 K *a* = 16.473(5) Å, *b* = 9.347(3) Å, *c* = 16.739(5) Å, β = 116.821(6)°, *V* = 2300(1) Å^3, space group $P2_1/c$, *Z* = 4, D_{calc} = 1.797 g cm^{-3}. X-ray diffraction data (17343 reflections) were collected on a Bruker SMART CCD diffractometer at 120 K (λMo-K$_\alpha$ radiation, $2\theta_{max}$ = 58.00°) from a single crystal of dimensions 0.2×0.2×0.5 mm sealed in a capillary. The X-ray data were processed using the SMART[17] and SAINTPlus[18] programs. After merging of equivalent reflections, the data set consisted of 5867 independent reflections (R_{int} = 0.1047). An absorption correction (μ = 1.305 mm^{-1}) was applied using the SADABS program[19] (T_{max} and T_{min} are 0.695 and 0.147, respectively). The structure was solved by direct methods. All nonhydrogen atoms were located from difference electron density maps and refined anisotropically by the least-squares method against F^2_{hkl}. The hydride hydrogen atoms were located from difference maps and refined isotropically. The H atoms in the Cp groups were placed in geometrically calculated positions and refined using a riding model with *U*(H) = 1.2*U*(C), where *U*(C) are the equivalent displacement parameters of their parent carbon atoms. The final reliability factors were R_1 = 0.0567 (based on F_{hkl} for 2983 reflections with $I > 2\sigma(I)$), wR_2 = 0.1258 (based on F^2_{hkl} for a total of 5867 reflections), GOOF = 0.839, 270 parameters were refined.

All calculations were carried out using the SHELXTL PLUS 5 program package.[20]

The atomic coordinates and complete structural data for complex $\mathbf{4} \cdot 0.5C_4H_8O_2$ were deposited with the Cambridge Structural Database (CCDC refcode 227538).

We thank Prof. M. F. Lappert and Dr. A. G. Avent (University of Sussex) for valuable advice and help in recording NMR spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-32561).

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Received November 24, 2004;
in revised form July 19, 2005