Heterometallic hafnocene(+4) aluminum hydride complex $[(\eta^5\text{-}C_5H_5)_2Hf(H)(\mu_2\text{-}H)Al(H)Br(\mu_2\text{-}OC_4H_9)]_2$

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The $[Cp_2HfH_2Al(H)Br(OBu)]_2$ complex (**1**) was prepared by the reaction of Cp_2HfBr_2 with AlH_3 in THF and characterized by X-ray crystallography. The formation of dinuclear complex **1** proceeds through the intermediate formation (as a result of cleavage of THF molecules) of the $>Al(\mu\text{-}OBu)_2Al<$ fragment. The latter is linked to two hafnocene dihydride molecules by the Hf—H—Al hydrogen bridges. The Hf atom in complex **1** has a 16-electron environment.

Key words: hafnocene, aluminum hydride, crystal structure.

Heterometallic hydride complexes with aluminum and titanium-family metals have attracted considerable attention, because they play an important role in many catalytic and stereochemical transformations involving unsaturated compounds.[1,2] About half hundred such complexes have been characterized by X-ray crystallography. Among them, titanium(+3) complexes have received the most study, zirconium(+4) complexes have less representatives, and zirconium(+3) complexes are even less well studied.[1—4] However, no hafnium complexes have been characterized by X-ray crystallography.

In the present study, we synthesized the first heterometallic hafnium(+4) aluminum hydride complex $[Cp_2HfH_2Al(H)Br(OC_4H_9)]_2$ (**1**) by the reaction of Cp_2HfBr_2 with AlH_3 in THF and characterized this complex by X-ray crystallography.

Results and Discussion

It is known[1—4] that metal atoms in aluminum hydride complexes of metallocenes, in particular, of titanocene(+3) and zirconocene(+4), are generally linked through the double hydride bridge $>Al—(\mu\text{-}H)_2—M<$. The single-atom bridge $>Al—(\mu\text{-}H)—Lu<$ was found only in lutetium aluminum hydride $Cp_2Lu(\mu\text{-}H)AlH_3 \cdot NEt_3$.[2] It should be noted that the latter is formed only in the crystalline state as a result of solid-state decomposition of the dimer under X-ray irradiation. It is also well known that zirconocene(+4) and hafnocene(+4) borohydrides have the same $Cp_2M[(\mu\text{-}H)_2BH_2)]_2$ structure ($M = Zr$[5,6] or Hf[7]), in which the metal atom M is coordinated by four bridging hydrides of two bidentate BH_4 groups and has a 20-electron environment. Since zirconium and hafnium have similar coordination properties, we can expect that the metal atoms in hafnocene(+4) aluminum hydride complexes would be linked in a usual fashion, *i.e.*, through the double hydride bridge $>Hf(\mu\text{-}H)_2Al<$.

Based on this assumption, taking into account that the terminal halogen atoms in Group 4 metallocenes migrate to the aluminum atom upon complex formation with alanes,[2] and supposing that aluminum hydride compounds are structurally similar to borohydride compounds, we decided to use the reaction of Cp_2HfBr_2 with two equivalents of aluminum hydride in THF for the preparation of the Hf(+4)—Al complex.

Our experiments demonstrated that the reaction of AlH_3 with Cp_2HfBr_2 afforded a solution, which was concentrated to give colorless platelet crystals of complex **1**. From the element ratio in **1** (Hf : Al : Br = 1), it follows that the second equivalent of AlH_3 is not involved in the complex but, apparently, participates in exchange reactions in solution by accepting one-half of bromide ions from the starting Cp_2HfBr_2 and serving as one of the sources of hydride hydrogen included in complex **1**. It remains unclear how an excess of an aluminum component is consumed. Presumably, it merely remains in the mother liquor. However, secondary processes involving all compounds present in the solution cannot be ruled out.

In the region of vibrations of metal—hydride bonds, the IR spectrum of crystalline complex **1** shows a broad

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2082—2085, October, 2004.

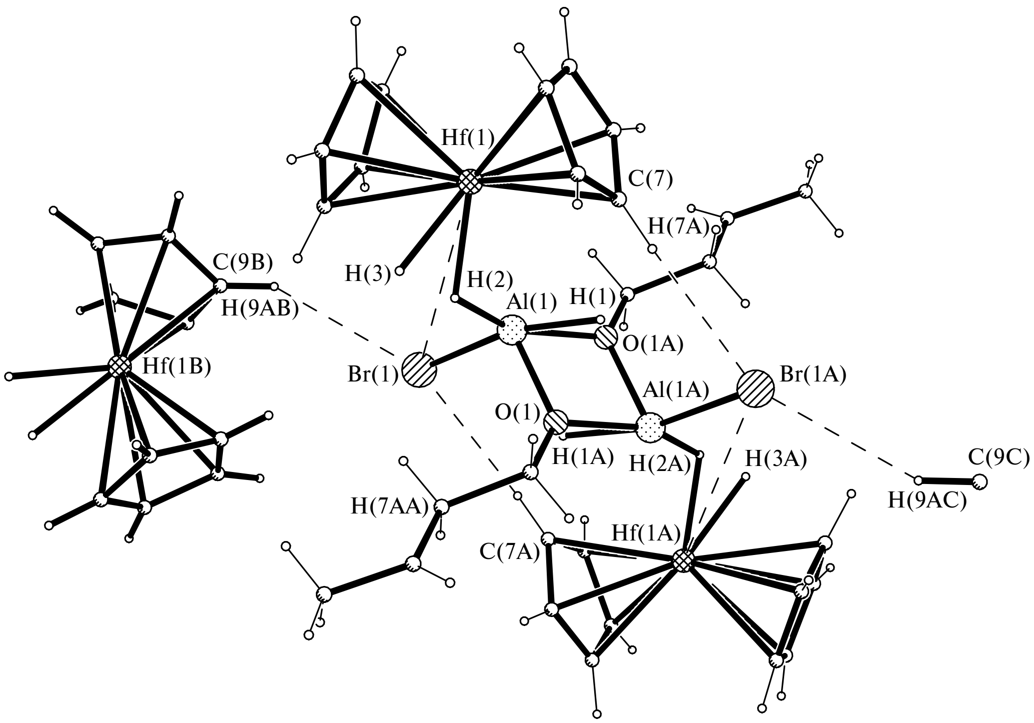


Fig. 1. Structure of complex **1**.

medium-intensity band with a maximum at 1629 cm^{-1} and a shoulder at 1600 cm^{-1}, which can be assigned both to ν(Al—H$_{\text{term}}$) (such bands can be observed[8] in a wavenumber region of 1650—1800 cm^{-1} depending on the coordination number of the aluminum atom) and ν(Hf—H$_{\text{term}}$) (such bands can be present[9] in the 1590—1650 cm^{-1} region). The group of bands at 1350—1450 cm^{-1} can apparently be assigned to vibrations of the Al—H—Hf bridge. It should be noted that stretching vibrations of the Hf—H—Hf bridge are observed[10] at ~1240 cm^{-1}. Therefore, the IR spectrum of complex **1** confirms the presence of M—H bonds, but the assignment of absorption bands to a particular type of metal—hydride bonds remains unclear.

Single-crystal X-ray diffraction study of complex **1** demonstrated (Fig. 1, Table 1) that this compound occurs as a centrosymmetric dimer, in which two dihydride fragments Cp$_2$HfH$_2$ are linked to the central [Al(H)Br(μ-OBu)]$_2$ fragment through the Hf—H—Al bridges.

The origin of the butoxy groups in complex **1** is quite evident (Scheme 1). These groups appear due to the cleavage of the ether bonds in the THF molecule under the action of AlH$_3$ [11] or, which is more likely, under the action of a stronger Lewis acid, *viz.*, monobromoalane, generated in the first step of the exchange reaction. These reactions yielding dinuclear complexes with the >Al(μ-OBu)$_2$Al< fragments have been observed earlier for aluminum hydride complexes with tantalum,[11] tungsten,[12] and rhenium[12] during their synthesis in a THF solution.

Table 1. Selected interatomic distances (*d*) and bond angles (ω) in molecule **1**

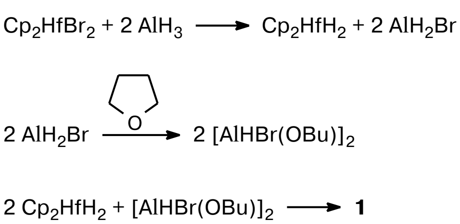
Bond*	*d*/Å	Angle	ω/deg
Hf(1)—Cp(1)	2.234(7)	Cp(1)—Hf(1)—Cp(2)	138.7
Hf(1)—Cp(2)	2.215(8)	H(3)—Hf(1)—H(2)	36.6
Hf(1)—Al(1)	2.893(4)	Al(1)—Hf(1)—H(2)	32.1
Hf(1)—H(3)	1.87	O(1a)—Al(1)—O(1)	78.0
Hf(1)—H(2)	1.89	Al(1)—Hf(1)—H(3)	68.1
Br(1)—Al(1)	2.285(5)	O(1)—Al(1)—Br(1)	106.5
Al(1)—O(1a)	1.83(1)	O(1)—Al(1)—H(1)	63.8
Al(1)—O(1)	1.828(9)	Br(1)—Al(1)—H(1)	160.6
Al(1)...Al(1a)	2.841(8)	Hf(1)—Al(1)—H(1)	83.7
Al(1)—H(1)	1.62	O(1)—Al(1)—H(2)	100.4
Al(1)—H(2)	1.63	Br(1)—Al(1)—H(2)	100.7
O(1)—Al(1a)	1.83(1)	H(1)—Al(1)—H(2)	97.7
O(1)—C(11)	1.42(2)	Hf(1)—Al(1)—H(2)	38.0
Br(1)...Hf(1)	4.374(3)	Cp(1)/Cp(2)	42.9(9)
Al(1)...H(3)	2.80		
Br(1)...H(9AB)**	2.95		
Hf(1)...H(1)	3.16		
Br(1)...H(1)	2.79		
Br(1)...H(7AA)	2.87		

* Cp are the centroids of the cyclopentadienyl rings.

** An intermolecular contact.

The structure of the [Al(H)Br(μ-OBu)]$_2$ fragment in complex **1** is in many respects typical of transition metal

Scheme 1



aluminum hydrides. The Al—O distances (1.827 Å) and the O(1)—Al(1)—O(1a) angle (78.0°) in the planar rhombic Al_2O_2 fragment of complex **1** are close or equal to the corresponding distances (1.843 and 1.839 Å) and angles (78.2 and 78.0°) in the $[(Me_3P)_3H_3W(AlH_3(\mu\text{-}OBu)]_2$ [12] and $[Cp_2TaAlH_3(\mu\text{-}OBu)]_2$ [11] complexes, respectively, and in the ethoxy-bridged titanium complex $[Cp_2Ti(AlH_3(\mu\text{-}OEt)]_2$ (1.85 Å, 77.5°).[2] The Al atom in complex **1** has a coordination number of 5, and its ligand environment is a distorted trigonal bipyramid, which is most typical of the structures of Ti(+3) and Zr(+4) aluminum hydrides.[2,3] The terminal H(1) atom and the Br(1) atom occupy the apices of the bipyramid, whereas the O(1) and O(1a) atoms and the bridging H(2) atom form the base of the bipyramid.

Considering that the hydrogen atoms in the vicinity of the heavy atom are located with a low accuracy (which is apparently the reason why it is often impossible to locate the hydrogen atoms in hafnium hydride complexes[4]), it can be stated that the Al—H(2) and Al—H(1) bond lengths (~1.6 Å) are approximately equal and are close to the Al—H bond lengths in the known dinuclear complexes.[2,3] The Hf—H(2) and Hf—H(3) bond lengths in the 16-electron Cp_2HfH_2 fragment of complex **1** are also approximately equal (~1.9 Å) and are nearly equal to the Hf—H bond lengths in the known polyhydride complexes $Hf_2H_3(BH_4)_3(NSiMe_2CHPMe_2)$[10] (1.91—1.95 Å), $Cp^*_3Hf_3H_2Cl_2(C_6H_8)$[13] (1.88—2.10 Å), and $Cp^*_4Hf_4H_6(C_6H_8)$[13] (1.79—1.98 Å) ($Cp^* = C_5Me_5$). In complex **1**, the Cp ligands are in an eclipsed conformation. The Cp—Hf—Cp angle (138.7°) is substantially larger than the angles typical of hafnocene chlorides (129—130°)[14] and approaches the angles observed in the monomeric 16-electron $Cp^*_2HfH_2$ complex (144.1 and 145.0°), in which, unfortunately, the hydride hydrogens were not located.[14]

The presence of an Hf—H—Al bridge in combination with a sizeable free space about the Hf atom are the most interesting distinguishing structural features of complex **1**. The Hf...Al (2.898 Å), Hf...H(1) (3.2 Å), and Hf...Br (4.374 Å) interatomic distances are substantially longer than the distances typical of the valent contacts (it should be emphasized once again that the inferences based on the analysis of the metal—hydride bond parameters should be regarded as tentative). However, under close examination of the structure of complex **1**, it can be seen that the distances between the Br atom and the nearest hydrogen atoms of the Cp rings, *viz*., Br(1)...H(7AA) (2.87 Å) and Br(1)...H(9AB) (2.95 Å), (see Fig. 1) are smaller than the sum of the corresponding van der Waals radii (3.02 Å)[15] and can be assigned to hydrogen bonds. Apparently, these bonds (both intra- and intermolecular) impart additional rigidity to the structure of complex **1**, the bulky bromine atom being located in the solid angle of the free space at the Hf atom thus shielding the latter. Hence, the steric effects caused by the combined influence of the bromine atom and the Al_2O_2 fragment are most probably responsible for the structural features of complex **1**, in particular, for the presence of the coordinatively unsaturated 16-electron Cp_2HfH_2 fragment and the unusual linkage between the latter and the Al atom through the Hf—H—Al bridge.

Interestingly, structures with different (mono-, bi, and tridentate) modes of coordination of borohydride groups to transition metals are known for metallocene borohydrides,[16,17] which are the closest analogs of aluminum hydrides. By contrast, as mentioned above, the bidentate coordination of the aluminum hydride groups is typical of the structures of metallocene aluminum hydrides, whereas complexes with tridentate coordination remain unknown.[1—4] The structure of complex **1** is actually the first example of a stable compound containing the monodentate aluminum hydride fragment.

Experimental

All operations associated with the preparation of the reagents and the synthesis were carried out under argon or *in vacuo*. Solvents were purified by refluxing and distillation over lithium aluminum hydride or sodium benzophenone ketyl; Cp_2HfBr_2 [18] and a solution of AlH_3 in diethyl ether[19] were prepared by standard procedures. The IR spectra were recorded on a UR-20 instrument.

Di[(μ-butoxo){μ-hydrido[bis(η⁵-cyclopentadienyl)hydridohafnium(IV)](bromo)(hydrido)aluminum{(III)}], $[Cp_2HfH_2\cdot\cdot Al(H)Br(OC_4H_9)]_2$ (1). Aluminum hydride (1.07 mmol, a solution in 13 mL of Et_2O) was added with stirring to a solution of Cp_2HfBr_2 (0.25 g, 0.53 mmol) in THF (16 mL) at 20 °C. The reaction mixture was stirred at 20 °C for one day, concentrated *in vacuo* to ~3 mL, and allowed to stand at ~20 °C for several days, after which colorless transparent crystals precipitated (0.13 g, 50%). The crystals were separated from the mother liquor, carefully washed with the solvent refrozen from the mother liquor, and dried *in vacuo*. Found (%): Al, 5.79; Br, 16.01; Hf, 35.90. $C_{28}H_{44}Al_2Br_2Hf_2O_2$. Calculated (%): Al, 5.49; Br, 16.25; Hf, 36.30. IR (KBr), ν/cm^{-1}: 611 (w), 665 (s), 777 (s), 824 (v.s), 892 (w), 916 (w), 961 (w), 985 (w), 1015 (v.s), 1068 (s), 1365 (w), 1441 (s), 1629 (s). One crystal was selected for X-ray crystallography.

X-ray crystallographic study of complex 1. Colorless prismatic crystals of $[Cp_2HfAlH_3BrOBu]_2$ (**1**) ($C_{28}H_{44}Al_2Br_2Hf_2O_2$, M = 983.40) are monoclinic, at 120 K a = 7.368(4) Å,

b = 11.792(6) Å, c = 18.551(9) Å, β = 100.306(9)°, V = 1586(1) Å^3, space group $P2_1/c$, Z = 2, d_{calc} = 2.059 g cm^{-3}. A total of 11276 reflections were measured on a Bruker SMART CCD diffractometer at 120 K (λMo-K$_\alpha$ radiation, $2\theta_{max}$ = 50.00°) from a single crystal of dimensions 0.3×0.4×0.5 mm, which was sealed in a capillary with argon. The intensities of reflections were processed using the SMART [20] and SAINT Plus programs.[21] Merging of equivalnt reflections gave 2633 independent reflections (R_{int} = 0.0704), which were used in the structure solution and refinement. The absorption correction (μ = 9.140 mm^{-1}) was applied using the SADABS program[22] (T_{max} and T_{min} are 0.746 and 0.263, 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 and refined using a riding model with fixed thermal parameters (U = 0.05). The H atoms of the Cp rings and Bu substituents were placed in geometrically calculated positions and refined using a riding model with U(H) = nU(C), where U(C) are the equivalent temperature parameters of their parent carbon atoms (n = 1.2 and 1.5, respectively). The final reliability factors were R_1 = 0.0625 (based on F_{hkl} for 1698 reflections with $I > 2\sigma(I)$), wR_2 = 0.1410 (based on F^2_{hkl} for a total of 2633 reflections), GOOF = 1.000, 163 parameters were refined.

All calculations were carried out using the SHELXTL PLUS 5 program package.[23]

The atomic coordinated and complete structural data for complex **1** were deposited with the Cambridge Structural Database (CCDC No. 227539).

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32561 and 03-03-32214).

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Received February 11, 2004;
in revised form May 25, 2004