ANIONIC ZIRCONIUM AND HAFNIUM BOROHYDRIDE COMPLEXES

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Zirconium and hafnium tetrachlorides react with $NaBH_4$ in dimethoxyethane (DME) to give $[Na(DME)_3][M(BH_4)_5]$. These compounds react with Bu_4NBH_4 and Ph_4PBH_4 to give $(R_4E)[M(BH_4)_5]$. Bidentate and tridentate BH_4^- occur in $[M(BH_4)_5]^-$ according to IR spectroscopy. Data from ^1H and $^1H-\{^{11}B\}$ NMR spectra are consistent with intermolecular exchange of BH_4 ligands in solutions of complexes (I)-(VI). The BH_4 groups and the bridging and terminal protons in each BH_4 group equilibrate rapidly. Heating the complexes (I)-(VI) reduces the central atom, releases diborane, and decomposes the outer-sphere cation. The neutral borohydrides $M(BH_4)_4$ can be prepared by thermolysis of the sodium salts (I) and (II).

One method for preparing $M(BH_4)_4$ is the reaction of $LiBH_4$ with zirconium or hafnium tetrachloride in diethylether [1]. The reaction of $ZrCl_4$ and $HfCl_4$ in organic solvents has not been studied. We demonstrated that they react in 1,2-dimethoxyethane (DME) to give the anionic complexes $[Na(DME)_3][M(BH_4)_5](M = Zr, Hf)$. Tetraphenylphosphonium borohydride reacts with the tetrachlorides or directly with $M(BH_4)_4$ to give $(Ph_4P)[M(BH_4)_5]$. The compounds are characterized by chemical and thermal analysis and IR and NMR spectroscopies [2-4].

EXPERIMENTAL

Syntheses of the Zr and Hf borohydrides and sample preparation for physicochemical studies were carried out under dry Ar or N_2. Benzene, pentane, diethylether, THF, and DME were distilled over $LiAlH_4$; CH_2Cl_2 and 1,2-dichloroethane were distilled over P_2O_5.

Anhydrous Zr and Hf tetrachlorides (chemically pure) were sublimed in vacuum at 220°C before use. Sodium borohydride was recrystallized from diglyme and dried in vacuum with the temperature gradually rising from ∿20 to 100°C. Unsolvated $LiBH_4$ was obtained by dissolving commercial $LiBH_4$ in diethylether, adding an equal volume of toluene, filtering, and removing the solvent while keeping the temperature below 100°C. After cooling, the $LiBH_4$ crystals were filtered off and dried in vacuum. Tetrabutylammonium borohydride was recrystallized from benzene. Tetraphenylphosphonium borohydride was recrystallized from 10% aqueous $NaBH_4$ and dried in vacuum at 50°C. These borohydrides were at least 98% pure according to analysis for active hydrogen (H_H).

The compounds $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were prepared by reacting the corresponding tetrachlorides with $LiBH_4$ in diethylether or without solvent [1, 5]. The complexes $(Bu_4N)[M(BH_4)_5]$ were prepared by reacting tetrabutylammonium borohydride and $M(BH_4)_4$ in benzene [6] or by metathesis (see below). IR spectra of solutions or suspensions in mineral oil were recorded on UR-20 (400-4000 cm^{-1}) and IKS-22V (200-500 cm^{-1}) spectrophotometers. Thermal analysis was carried out on a Q-1000 derivatograph in a stream of Ar (5 liters/h) at a heating rate of 10 K/min and a sample mass of 0.1-0.3 g.

NMR spectra (^1H, $^1H-\{^{11}B\}$, ^{13}C, and $^{13}C-\{^1H\}$) were taken from a Varian XL-100-12 spectrometer (100.1 MHz working frequency). Chemical analyses were performed in the analytical chemistry laboratory of the Institute of New Chemical Problems of the Academy of Sciences of the USSR.

Tris(1,2-dimethoxyethane)sodium Pentakis(tetrahydridoborato)zirconate $[Na(DME)_3]\cdot$ $[Zr(BH_4)_5](I)$. To a suspension prepared by slow addition of 50 ml DME to $ZrCl_4$ (3.5 g, 0.015 mole) with cooling was added $NaBH_4$ (6.2 g, 0.164 mole). The mixture was stirred

for 10 h at ~20°C. Heating and gas evolution were not observed. A colorless solution that did not contain chlorine and a white precipitate were produced. The mixture was filtered. Solvent was removed in vacuum. The residue was dissolved in 50 ml diethylether. The solution was filtered. Ether was removed in vacuum. The residue was dried in vacuum at ~20°C. Yield of (I) as white crystals 6.2 g (90%). Found: Na, 5.1; Zr, 20.1; B, 11.2; H_H, 4.4%. $C_{12}H_{50}O_6B_5NaZr$. Calculated: Na, 5.0; Zr, 19.9; B, 11.8; H_H, 4.4%.

Tris(1,2-dimethoxyethane)sodium Pentakis(tetrahydridoborato)hafnate $[Na(DME)_3][Hf(BH_4)_5]$ (II). This was prepared by the same method from $HfCl_4$ and $NaBH_4$ as white crystals. Yield 85%. Found: Na, 4.2; Hf, 33.2; B, 9.4; H_H, 3.6%. $C_{12}H_{50}O_6B_5NaHf$. Calculated: Na, 4.2; Hf, 32.7; B, 9.9; H_H, 3.7%.

Reaction of $Zr(BH_4)_4$ with $NaBH_4$ in DME. To 0.9 g $Zr(BH_4)_4$ (0.006 mole) in 30 ml DME was added $NaBH_4$ (0.8 g, 0.021 mole). The mixture was stirred for 3 h at ~20°C and filtered. Solvent was removed in vacuum. The residue was extracted with 30 ml ether. After removal of ether, 2.1 g (I) (76% yield) was obtained.

Tetraphenylphosphonium Pentakis(tetrahydridoborato)zirconate $(Ph_4P)[Zr(BH_4)_5]$ (III). To 0.9 g $Zr(BH_4)_4$ (0.006 mole) in 20 ml THF were added 1.8 g Ph_4PBH_4 (0.005 mole). The mixture was stirred for 10 min and filtered. Solvent was removed in vacuum at ~20°C. Yield 2.2 g (73%) of white crystals (III). Found: Ph_4P, 70.2; Zr, 18.7; B, 10.4; H_H, 3.7%. $C_{24}H_{40}B_5PZr$. Calculated: Ph_4P, 67.2; Zr, 18.1; B, 10.7; H_H, 4.0%.

Tetraphenylphosphonium Pentakis(tetrahydridoborato)hafnate $(Ph_4P)[Hf(BH_4)_5]$ (IV). This was prepared by the same method from $Hf(BH_4)_4$ and Ph_4PBH_4. For the white crystals, found: Ph_4P, 57.4, Hf, 30.0; B, 8.8; H_H, 3.2%. $C_{24}H_{40}B_5PHf$. Calculated: Ph_4P, 57.3; Hf, 30.1; B, 9.1; H_H, 3.4%.

Reaction of (I) with Tetraphenylphosphonium Borohydride. To 2.6 g (I) (0.006 mole) in 30 ml CH_2Cl_2 were added 1.4 g Ph_4PBH_4 (0.004 mole). The mixture was stirred for 10 min and was then filtered. The filtrate was concentrated in vacuum to 10 ml and 30 ml ether was added to it. After 24 h the white crystalline precipitate was separated, washed with ether, and dried in vacuum. Yield 1.9 g (95% based on Ph_4PBH_4). The reaction product was identified by its IR spectrum and thermal analysis.

Reaction of (II) with Tetraphenylphosphonium borohydride gives $(Ph_4P)[Hf(BH_4)_5]$ (IV), which was identified by its IR spectrum and thermal analysis.

Reaction of (I) and (II) with Tetrabutylammonium borohydride was carried out by the same method. The product separated from benzene as an oil that crystallized on drying. The crystalline product was washed with pentane. The $(BU_4N)[Zr(BH_4)_5]$ (V) and $(Bu_4N)[Hf(BH_4)_5]$ (VI) obtained had spectral and thermal properties the same as those for the compounds prepared by the direct reaction [6].

Thermal Decomposition of (I) in Vacuum. One gram of (I) was placed in a Schlenk tube connected to a trap cooled to −196°C. A vacuum of ~100 Pa was pulled on the system. The tube was heated to 150°C. After the process was completed (~1 h), the residue was a pale gray powder identified as $NaBH_4$ from its IR spectrum, x-ray powder pattern, and active hydrogen analysis. A colorless liquid and white crystals that quickly dissolved in the liquid were found in the trap after warming to ~20°C. The solution contained $Zr(BH_4)_4$ in DME according to IR spectroscopy.

RESULTS AND DISCUSSION

The data presented show that $ZrCl_4$ and $HfCl_4$ react with excess $NaBH_4$ in DME to give the anionic complexes $[Na(DME)_3][M(BH_4)_5]$. These complexes can be metathesized with Ph_4PBH_4 in THF or CH_2Cl_2 to give the Ph_4P derivatives

$$[Na(DME)_3][M(BH_4)_5] + Ph_4PBH_4 \rightarrow (Ph_4P)[M(BH_4)_5] + NaBH_4 \downarrow$$

We prepared the complexes $(Bu_4N)[Zr(BH_4)_5]$ (V) and $(Bu_4N)[Hf(BH_4)_5]$ by an analogous reaction with Bu_4. Earlier, (V) and (VI) and the corresponding complexes with trioctylpropylammonium were prepared by reaction of $M(BH_4)_4$ and the tetraalkylammonium borohydrides [6]. Compounds (I)-(IV) also result from reaction of $M(BH_4)_4$ with the corresponding ionic borohydrides, for example

$$NaBH_4 + Zr(BH_4)_4 \xrightarrow{DME} [Na(DME)_3][Zr(BH_4)_5]$$
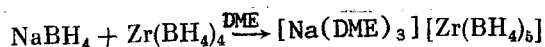
An excess of the $M(BH_4)_4$ can be used in the reaction with the ionic borohydrides since it is easily separated from the product due to its volatility and good solubility in organic solvents.

The data demonstrate that the compounds formed with the ionic borohydrides, the anionic borohydride complexes, are characteristic for $Zr(BH_4)_4$ and $Hf(BH_4)_4$ as well as for a number of other transition metal borohydrides [2]. In contrast to complexes of Zr and Hf borohydrides with simple ethers, which exist only in solutions or at low temperatures [7], complexes (I)-(VI) are isolated pure and decompose at elevated temperatures.

Complexes (I) and (II) gradually decompose on storage in an inert atmosphere at ∿20°C. They become gray. A new IR band at 2310 cm^{-1} appears and corresponds to νBH of $NaBH_4$ that forms through the decomposition. Compounds (III)-(VI) are stable at ∿20°C in an inert atmosphere for at least a month and gradually decompose in air. The Hf complexes are much more stable than the Zr complexes. The Ph_4P complexes are more stable than the $[Na(DME)_3]$ complexes. The tetrabutylammonium complexes are intermediate in stability.

Complexes (III) and (IV) are soluble in CH_2Cl_2, dichloroethane, and THF and insoluble in diethylether and aromatic and saturated hydrocarbons. Complexes (I) and (II) are soluble in chlorinated and aromatic hydrocarbons and simple ethers (diethyl ether, THF, and DME) and insoluble in saturated hydrocarbons.

Compounds (I)-(VI) were characterized by IR spectroscopy.* Based on the data of [8], the absorption bands (a.b.) of the BH_4 groups were assigned empirically (Table 1). The data of Table 1 and Fig. 1 show that the general nature of the $[M(BH_4)_5]^-$ spectrum is retained on changing the outer-sphere cation as well as the central metal.

Comparison of the data obtained with the vibrational spectra of $M(BH_4)_4$ [9-11] is interesting. These compounds in the solid and gas phase contain isolated $M(BH_4)_4$ molecules that have tetrahedral symmetry T_d. The BH_4 groups are bonded to the central atom by three bridging hydrogens. The IR spectra of $M(BH_4)_4$ have four groups of a.b. Stretching vibrations of terminal and bridging B—H bonds are located between 2000-2600 cm^{-1}. The HBH deformations and the MH_3 stretches lie in the region 1000-1300 cm^{-1}. The a.b. at ∿500 cm^{-1} is assigned to the M—B stretch. The a.b. at ∿210 cm^{-1} corresponds to M—H deformations [11].

Groups of a.b. that are not found in the organic cations and that are similar to the ones above occur in the spectra of (I)-(VI). The spectra of (I)-(VI) differ considerably from those of $M(BH_4)_4$ in the B—H stretching region. Instead of one $\nu(BH_t)$ band and two $\nu(BH_b)$ bands, the compounds studied have three $\nu(BH_t)$ bands and three $\nu(BH_b)$ bands. These are similar in number and position to the bands in $Sc(BH_4)_3(THF)_2$ [12], which according to an x-ray analysis has two tridentate and one bidentate BH_4 group [13]. This leads to the conclusion that bidentate and tridentate borohydrides occur in $[M(BH_4)_5]^-$. The nonequivalency of the BH_4 groups in $[M(BH_4)_5]^-$, in our opinion, is due to steric factors. A part of the BH_4 groups are bidentate so that they occupy a smaller volume in the coordination sphere.

One strong and several weak a.b. are seen for $M(BH_4)_4$ in the 1000-1300 cm^{-1} region. We could identify only one strong a.b. at ∿1110 cm^{-1} in the spectra of (I)-(VI) against the background of strong a.b. from the organic cations. This is probably due to δHBH deformations [8].

Two a.b. at lower frequencies are seen in the M—B stretching region (400-600 cm^{-1}) in the spectra of (I)-(VI) instead of one a.b. at ∿500 cm^{-1}. This is consistent with a lower symmetry for $[M(BH_4)_5]^-$ compared to $M(BH_4)_4$ and the presence of BH_4 groups of different denticities. The a.b. at ∿200 cm^{-1} in the spectra of (I)-(VI) is practically coincident in frequency to the δHMH vibration in $M(BH_4)_4$ [11].

The splitting of several a.b. for νBH in IR spectra of crystalline (III) and (IV) is evidently due to crystal lattice effects since the splitting is not seen in solution spectra of (III) and (IV) in noncoordinating solvents (dichloroethane). A similar effect was seen earlier for $(Ph_4P)[V(BH_4)_4]$ [14].

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*IR spectra of (V) and (VI) are presented in [6]. The authors note that the spectra obtained by them are not sufficiently resolved to determine the BH_4 coordination type. The νBH frequencies given by them differ from those obtained by us by the absence of absorption bands at ∿2530 and 1970 cm^{-1}.

TABLE 1. IR Absorption Bands of Anionic Zr and Hf Borohydride Complexes

| Compound (solvent)	νBH_t	νBH_b	δHBH	νMB	δHMH
$[Na(DME)_3][Zr(BH_4)_5]$ (suspension in mineral oil)	2525, 2470, 2410	2235, 2085, 1988	1115	447, 390	218
(DME)	2525, 2468, 2412	2232, 2088, 1985	1115	450, 392	218
(THF)	2525, 2468, 2411	2230, 2090, 1983	1116	452, 392	216
(DCE)	2525, 2468, 2410	2230, 2093, 1983	1118	450, 392	215
$(Bu_4N)[Zr(BH_4)_5]$ (suspension in mineral oil)	2543, 2465, 2410	2233, 2073, 1985	1113	445, 393	218
(THF)	2525, 2468, 2408	2228, 2085, 1981	1113	452, 392	219
$(Ph_4P)[Zr(BH_4)_5]$ (suspension in mineral oil)	2527, 2487, 2463, 2433, 2413	2233, 2097, 1995, 1975	1112	445, 400	220
(THF)	2525, 2468, 2410	2232, 2090, 1982	1116	452, 393	220
$[Na(DME)_3][Hf(BH_4)_5]$ (suspension in mineral oil)	2530, 2478, 2420	2248, 2100, 1995	1120	455, 380	212
(DCE)	2525, 2470, 2413	2240, 2103, 1988	1118	448, 382	216
$(Bu_4N)[Hf(BH_4)_5]$ (suspension in mineral oil)	2533, 2482, 2420	2243, 2105, 1990	1118	457, 380	212
(DME)	2525, 2468, 2412	2238, 2100, 1988	1117	453, 379	212
$(Ph_4P)[Hf(BH_4)_5]$ (suspension in mineral oil)	2528, 2487, 2466, 2435, 2415	2238, 2105, 1995, 1970	1118	449, 389	214
(THF)	2528, 2472, 2415	2242, 2100, 1988	1120	450, 381	214
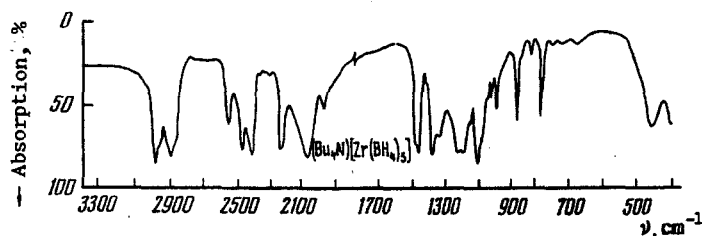
Fig. 1. IR spectrum of $(Bu_4N)[Zr(BH_4)_5]$.

Data on the state of complexes (I)-(VI) in solution (CH_2Cl_2 and DME) were obtained by NMR. The resonance from the BH_4 group in the ^1H spectra for all complexes appears as a quartet (1:1:1:1) with fine structure from $^1H-^{11}B$ coupling. Under $^1H-\{^{11}B\}$ double resonance conditions, the quartet changes into a singlet (Fig. 2). The ^1H, ^{13}C, and $^{13}C-\{^1H\}$ spectra of the organic part of the complexes correspond to those expected for DME, Ph_4P^+, and Bu_4N^+. The ratio of integrated intensities in the ^1H and $^1H-\{^{11}B\}$ spectra corresponds to that calculated for complexes of this composition. In the ^{11}B NMR spectra for (V) and (VI), a single quintet (1:4:6:4:1) is seen [6]. The nature of the NMR spectra of (I)-(VI) indicates that all H atoms of the BH_4 groups are equivalent and are coupled to one B nucleus. Also, the B nuclei are equivalent and coupled to four equivalent protons. Thus, the NMR spectra demonstrate that dynamic processes that are rapid on the NMR time scale at room temperature occur. These cause the BH_4 groups to be equivalent and average the bridging and terminal protons in each group.

Cooling the samples causes the quartet to broaden in the ^1H spectra. At a sufficiently low temperature, the $^1H-^{11}B$ fine structure disappears (Fig. 2). The initial singlet in the $^1H-\{^{11}B\}$ spectra narrows without splitting at low temperature. Analysis of these changes in the ^1H spectra suggests that these conversions cannot be explained by slow intramolecular exchange processes but are due to a strengthening of the quadrupolar relaxation of B and, as a result, to effective averaging of the $^1H-^{11}B$ coupling. The singlet in the $^1H-\{^{11}B\}$ spectra at −80°C indicates that the BH_4 groups and the protons in each group for the anionic complexes (I)-(VI) are equivalent, i.e., the rates of the exchange processes at −80°C are high enough to average the nonequivalency of the BH_4 groups in the ML_5 polyhedron. The
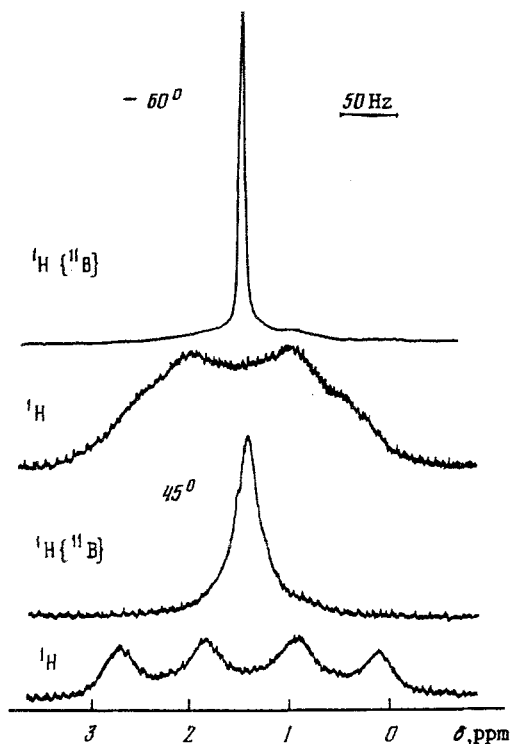
Fig. 2. ^1H and $^1H-\{^{11}B\}$ NMR spectra of $[Na(DME)_3]-[Zr(BH_4)_5]$ in CH_2Cl_2 at $-60°C$ and $45°C$.
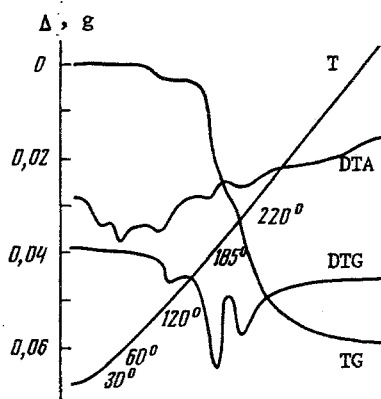
Fig. 3. Thermograms of $(Bu_4N)[Zr(BH_4)_5]$ from 20 to 500°C. Sample mass 0.1138 g.

differences in the line widths observed at room temperature in the $^1H-\{^{11}B\}$ spectra for the neutral and anionic borohydride complexes, in our opinion, are due to partial dissociation of the complex anions in solution

$$[M(BH_4)_5]^- \rightleftarrows M(BH_4)_4 + BH_4^-$$
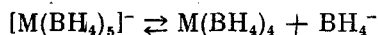
Due to the intermolecular exchange, the lifetime of the BH_4 group in the anionic complex is shortened. This causes the lines in the $^1H-\{^{11}B\}$ spectra to broaden. At low temperature, the degree of dissociation decreases and the lines narrow. The bulky cations Ph_4P^+ and Bu_4N^+ and coordinating solvent (DME for Na^+) stabilize the anionic complexes.

The proposed dissociation of $[M(BH_4)_5]^-$ in solution is consistent with the increased chemical shifts of the borohydride protons and the decreased $^1H-^{11}B$ spin—spin coupling constant for $[M(BH_4)_5]^-$ compared to $M(BH_4)_4$ (Table 2). This suggests increased ionic character for the bonds of the BH_4 groups in the ion. The chemical shifts and spin—spin coupling constants for the complexes studied by us were practically independent of the outer-sphere cation and solvent. Significant anion—cation or anion—solvent interactions that form more complicated particles are absent in solution.

TABLE 2. ^{1}H NMR Spectral Parameters of Zr and Hf
Borohydride Complexes (35°C, CH_2Cl_2 Solvent)

| Compound	δBH_4, ppm	J_{B-H}, Hz	$\Delta H_{1/2}$, Hz*
$Zr(BH_4)_4$	1,64	89	2
$[Na(DME)_3][Zr(BH_4)_5]$	1,50 **	87 **	7 **
	1,50	87	18
$(Ph_4P)[Zr(BH_4)_5]$	1,50	86	5
$(Bu_4N)[Zr(BH_4)_5]$	1,50	87	8
$Hf(BH_4)_4$	2,90	89	2
$[Na(DME)_3][Hf(BH_4)_5]$	2,48 **	85 **	5 **
	2,50	86	10
$(Ph_4P)[Hf(BH_4)_5]$	2,50	86	4
$(Bu_4N)[Hf(BH_4)_5]$	2,50	86	8
Ph_4PBH_4	−0,21	81	1

*$\Delta H_{1/2}$ is the line half-width for $^1H-\{^{11}B\}$.
**DME solvent.

In order to determine whether more complicated complexes ($[M(BH_4)_6]^{2-}$, $[M_2(BH_4)_9]^-$, etc.) were forming, we studied the ^{1}H and $^1H-\{^{11}B\}$ NMR spectra of the systems (cation)-$[M(BH_4)_5-M(BH_4)_4-CH_2Cl_2$ and (cation)$[M(BH_4)_5]-Ph_4PBH_4-CH_2Cl_2$. The ^{1}H spectra of these systems with a 1:1 ratio of components at 34°C contain a single 1:1:1:1 quartet. The $^1H-\{^{11}B\}$ spectra show a singlet. The spectral parameters of the systems differ from those of the starting compounds. However, the $^1H-\{^{11}B\}$ spectra at −34°C are a superposition of the spectra of the starting compounds without any additional lines assignable to new species. These data do not confirm that more complicated anions are forming in solution and demonstrate that intermolecular exchange of BH_4 groups occurs at room temperature (through a dissociative mechanism). This averages the NMR spectral parameters.

Thermal studies of (I) and (II) indicate that mass loss close to three moles of DME per one mole of complex occurs in one step between 70-150°C. An endo effect with a maximum at ∿120-130°C is seen. Near 100°C the samples become yellow and begin to melt. Above 150°C a black solid forms. Compounds (I) and (II) do not melt on heating up to 150°C in vacuum. $NaBH_4$ remains in the reaction vessel after thermolysis. $M(BH_4)_4$ and DME condense in the trap.

In contrast to (I) and (II), heating (III)-(VI) in vacuum does not give the corresponding $M(BH_4)_4$. We identified $Ph_3P \cdot BH_3$ and $Bu_3N \cdot BH_3$ among the thermolysis products. This indicates that a carbon-heteroatom bond breaks in the organic cation at elevated temperature. Nevertheless, some common features in the behavior of (I)-(VI) are seen. On heating >100°C, the samples change color and diborane, identified by its IR spectrum, condenses in the trap. The compounds (I)-(VI) explode on heating in air. These data suggest that the central atom is reduced on heating the $[M(BH_4)_5]^-$ anions

$$[M(BH_4)_5]^- \xrightarrow{\Delta} [M(BH_4)_4]^- + \tfrac{1}{2}B_2H_6 \uparrow + \tfrac{1}{2}H_2 \uparrow$$
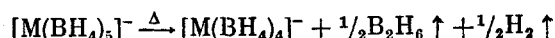
For complex (V), this process appears as a separate step in the thermogram. An endo effect with maximum at ∿120°C accompanied by a ∿3% mass loss occurs. This corresponds to loss of one BH_4 group (Fig. 3). A brown solid with covalently bound BH_4 groups forms as a result of this process. Above 150°C, it melts to form $Bu_3N \cdot BH_3$ and butane (∿20% mass loss). These effects are seen 10-15°C higher for complex (VI). For (III) and (IV), the central atom is reduced at a noticeable rate only at the temperature at which the complexes undergo extensive decomposition with release of the organic cations (>130°C). Therefore, it does not appear as a separate step in the thermograms. On the other hand, the outer-sphere cation $[Na(DME)_3]^+$ decomposes more quickly than the central metal is reduced (instability on storage, start of mass loss at ∿70°C). Devoid of a solvation sphere, the Na^+ cation strips a BH_4 group from $[M(BH_4)_5]^-$

$$[Na(DME)_3]^+ \rightarrow Na^+ + 3\,DME \uparrow$$
$$Na^+ + [M(BH_4)_5]^- \rightarrow NaBH_4 + M(BH_4)_4 \uparrow$$
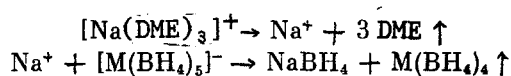
LITERATURE CITED

1. B. D. James and B. E. Smith, Synth. React. Inorg. Met.-Org. Chem., 4, 461 (1974).
2. V. D. Makhaev, A. P. Borisov, and K. N. Semenenko, in: Abstracts of Papers of the Fourth All-Union Conf. "Synthesis and Study of Inorganic Compounds in Nonaqueous Media" [in Russian], Ivanovo (1980), p. 92.

3. A. P. Borisov, V. D. Makhaev, G. N. Boiko, and K. N. Semenenko, in: Abstracts of Papers of the Sixteenth All-Union Chugaevskii Conf. on the Chemistry of Complex Compounds [in Russian], Krasnoyarsk (1987), Part 2, p. 372.
4. G. N. Boiko, A. P. Borisov, V. D. Makhaev, et al., in: Abstracts of Papers of the Sixth All-Union Conf. on the Chemistry of Nonaqueous Solutions of Inorganic and Complex Compounds [in Russian], Rostov-on-Don (1987), p. 210.
5. W. E. Reid, J. M. Bish, and A. Brenner, J. Electrochem. Soc., 104, 21 (1957).
6. H. Ehemann and H. Nöth, Z. Anorg. Allg. Chem., 386, 87 (1971).
7. V. V. Volkov, K. G. Myakishev, and G. I. Bagryantsev, Zh. Neorg. Khim., 15, 1941 (1970).
8. T. J. Marks and J. R. Kolb, Chem. Rev., 77, 263 (1977).
9. V. V. Volkov, E. V. Sobolev, Z. A. Grankina, and I. S. Kalinina, Zh. Neorg. Khim., 13, 659 (1968).
10. T. J. Marks, W. J. Kennely, J. R. Kolb, and L. A. Shimp, Inorg. Chem., 11, 2540 (1972).
11. T. A. Keiderling, W. T. Wozniak, G. D. Jurkowitz, et al., Inorg. Chem., 14, 576 (1975).
12. O. V. Kravchenko, S. E. Kravchenko, V. B. Polyakova, and K. N. Semenenko, Koord. Khim., 6, 76 (1980).
13. E. B. Lobkovskii, S. E. Kravchenko, and K. N. Semenenko, Zh. Strukt. Khim., 18, 389 (1977).
14. A. P. Borisov and V. D. Makhaev, Zh. Neorg. Khim., 33, 3030 (1988).