THERMAL DECOMPOSITION OF BIS(CYCLOPENTADIENYL)HAFNIUM COMPOUNDS AND THEIR DEUTERATED ANALOGUES

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Summary

Thermal decomposition ranges of Cp_2HfR_2 (R = Me, Ph) have been found by the DTA method. The thermal stability of hafnium derivatives greatly exceeds the stability of analogous titanium and zirconium compounds. Decomposition of Cp_2HfR_2 occurs by abstraction of σ-bonded groups which convert into RH. Hydrogen donors for the RH formation are both π-cyclopentadienyl and σ-bonded groups. The initial π-Cp_2Hf structure rearranges to form the $(\eta^5$-Cp)-$(\eta^5,\eta^1$-$C_5H_4)Hf$ fragment. These react with HCl to produce Cp_2HfCl_2. It has been established that hydrogen exchange between cyclopentadienyl rings and methyl groups occurs during the thermal decomposition of Cp_2HfMe_2. As a result of the exchange process on thermal decomposition of Cp_2HfMe_2-d_6, deuterium insertion into the cyclopentadienyl ring has been shown. The participation of solvent during the decomposition process of the hafnium derivatives has been studied.

Introduction

The thermal decomposition of titanium and zirconium bis-cyclopentadienyl compounds has been studied in detail [1—3]. The hafnium analogues have been undeservedly neglected, with the exception of Rausch's work on the thermal decomposition of Cp_2MMe_2 (M = Ti, Zr, Hf) within the pyrolytic cell of a chromatograph [4]. The authors had qualitatively analysed the composition of the volatile products and showed that M—Cp bond homolysis with cyclopentadiene evolution along with M—CH_3 cleavage and methane formation takes place. However, the decomposition scheme of the hafnium compound was not ascertained.

This paper reports the study of the Cp_2HfR_2 decomposition process and compares the decomposition pathways with those of the titanium and zirconium derivatives which had been studied earlier. The emphasis is on the role of hydrogen exchange. Cp_2HfMe_2 and Cp_2HfPh_2 as well as their deuterated analogues were chosen as the object of investigation.

Result and discussion

Thermal stability

Cp_2HfMe_2 and Cp_2HfPh_2 were analysed by the DTA method. The DTA curve of Cp_2HfMe_2 shows two heat effects. The first effect is a reversible endothermic one. It was observed at 46°C. This effect is due to the rearrangement of the compound crystal lattice. The second effect is irreversible and exothermic. It is due to the decomposition of the compound. This decomposition process starts at a temperature greater than 260°C and reaches maximum at 310°C (Fig. 1).

The examination of the DTA curve of Cp_2HfPh_2 allowed us to conclude that the observable DTA curve is the result of two processes: melting (endothermic peak at 185°C) and compound decomposition. The latter process is characterized by an extensive exothermic effect within the temperature range of 175—210°C with maximum at 195°C. Measurement of the gas evolution rate showed that the maximum of the endothermic effect coincides with the maximum of the gas evolution rate. We have also noted the similar character of the decomposition of zirconium analogue [3].

The DTA data of Cp_2MR_2 (M = Ti, Zr, Hf; R = Me, Ph) compounds (Table 1) show that the thermal stability in the series of methyl and phenyl derivatives increases in the order Ti < Zr < Hf. In the series of methyl derivatives a more remarkable increase in stability is observed than in the series of phenyl compounds. Methyl derivatives of zirconium and hafnium are much more stable than their phenyl analogues. Cp_2HfMe_2 is the most stable compound among these derivatives. This compound shows surprising thermal stability for compounds containing a transition metal—carbon bond.

For comparison of the thermal stability of Cp_2HfMe_2 with that of its deuter-
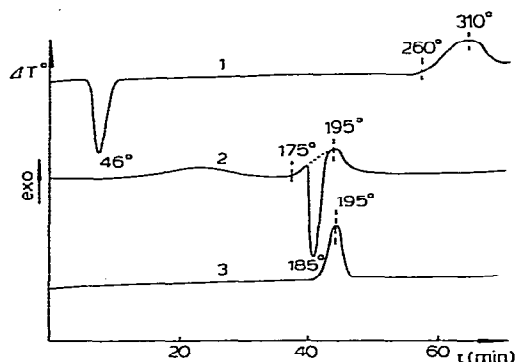

Fig. 1. Differential thermal analysis of Cp_2HfMe_2 (1), Cp_2HfPh_2 (2), and the rate of C_6H_6 evolution on the analysis of Cp_2HfPh_2 (3).

TABLE 1

THERMAL STABILITY OF TITANIUM SUBGROUP COMPOUNDS (ACCORDING TO DTA DATA)

Compound	Decomposition temperature (°C)	Compound	Decomposition temperature (°C)
Cp_2TiMe_2	90	Cp_2TiPh_2	146
Cp_2ZrMe_2	190	Cp_2ZrPh_2	150
Cp_2HfMe_2	>260	Cp_2HfPh_2	195

ated analogues the compound conversion degree (α) on decomposition under the same conditions was used. As can be seen from the result presented in Table 2 the thermal stability increases a little with substitution of hydrogen by deuterium in the cyclopentadienyl ligands.

The increase in stability upon deuteration of the methyl groups is remarkable. This fact indicates that a slow step in the decomposition of Cp_2HfMe_2 is due either to Hf—Me cleavage or to abstraction of a hydrogen (deuterium) atom from methyl groups. A similar trend in stability of deuterated compounds was noted by Boekel for titanium aryl derivatives [1].

Thermal decomposition products

The decomposition of Cp_2HfMe_2 occurs completely in 15 minutes at 290°C. Partial decomposition is observed at lower temperatures for the same period of time and undecomposed Cp_2HfMe_2 can be sublimed from the reaction mixture.

The main gaseous products from the thermal decomposition of Cp_2HfMe_2 are methane (1.4 mol) and hydrogen (0.3 mol) (Table 3). Cyclopentadiene was found in trace amounts. The considerable amounts of cyclopentadiene were found by Rausch [4] from the decomposition of Cp_2HfMe_2 are probably a result of the higher experimental temperature.

To determine the conservation of the cyclopentadienyl structure during the decomposition process the reaction with hydrogen chloride was used. It is known that this reaction depends on the experimental conditions. We used a hydrogen chloride solution in THF. It was established that when hydrogen chloride solution is added to Cp_2HfR_2 which is cooled to the temperature of liquid nitrogen and the temperature of the reaction mixture is raised to room temperature, formation of Cp_2HfCl_2 occurs quantitatively (Table 3). Treatment of the hafnium-containing residue of decomposed Cp_2HfMe_2 with HCl solution

TABLE 2

DEGREE (α) OF COMPOUND DECOMPOSITION AFTER 15 min AT $T = 250°C$

Compound	Evolved gas volume (mol/mol of initial compound)	α
Cp_2HfMe_2	0.35	0.26
$(Cp\text{-}d_5)_2HfMe_2$	0.28	0.20
$Cp_2HfMe_2\text{-}d_6$	0.06	0.04

TABLE 3

THERMAL DECOMPOSITION OF Cp_2HfR_2 (R = Me, Ph)

Compound	Experimental conditions	Products (mol/mol of initial compound)		
		Of thermal decomposition RH	Of reaction of hafnium residue with HCl	
			RH	Cp_2HfCl_2
Cp_2HfMe_2	Vacuum, 290°C, 15 min	1.37 [a]	0.14	0.67
	Vacuum, 220°C, 15 min ⎫	—		
	Vacuum, 250°C, 15 min ⎮	0.35 ⎫		
	Vacuum, 270°C, 15 min ⎬ [b]	0.60 ⎬ 1.35	0.03	0.50
	Vacuum, 270°C, 15 min ⎭	0.40 ⎭		
	Reaction with HCl [c]		2.00	0.90
Cp_2HfPh_2	Vacuum, 160—175°C, 30 min	0.92	0.61	0.68
	Vacuum, 200°C, 180 min	1.30	0.32	0.50
	Toluene, 180°C, 180 min	1.33	0.11	0.70
	Dioxan, 180°C, 180 min	0.82	0.30	0.65
	Reaction with HCl [c]		2.00	0.89

[a] Besides 0.30 mol of hydrogen. [b] Subsequent heating with selection of gaseous phase. [c] Initial compound reacts with HCl/THF solution.

produces Cp_2HfCl_2 (0.67 mol) and methane (0.14 mol). Thus, during the thermal decomposition of Cp_2HfMe_2 the cyclopentadienyl structure is largely preserved.

Benzene is the main product of Cp_2HfPh_2 thermal decomposition in vacuum, toluene and dioxan solution. During 30 minutes at 160—175°C the compound is decomposed partially and, as the result of action of HCl solution on the hafnium residue, a substantial amount of benzene is eliminated. About 1.3 mol of benzene is formed on complete decomposition of Cp_2HfPh_2 both in vacuum and toluene solution. The yield of benzene is somewhat decreased on decomposition in dioxan.

Treatment of the hafnium fraction of decomposed Cp_2HfPh_2 with HCl leads to the formation of 0.5—0.7 mol of Cp_2HfCl_2 and this indicates that upon decomposition of the phenyl derivatives the cyclopentadienyl structure is mainly preserved.

The comparison between the thermal decomposition products of hafnium derivatives and the titanium and zirconium compounds studied previously shows that there is a similarity and a distinction in the thermal decomposition of these compounds. The resemblance is the similar yield of RH, the distinction is in the fact that, unlike titanium compounds, the cyclopentadienyl structure is mainly preserved during the decomposition of the hafnium derivatives and that after the decomposition of the compound the Cp_2M fragment can be reconstructed by reaction with HCl.

Decomposition of deuterated compounds. RH formation reactions

To investigate RH formation and the participation of the cyclopentadienyl structure in the decomposition process the thermal decomposition of com-

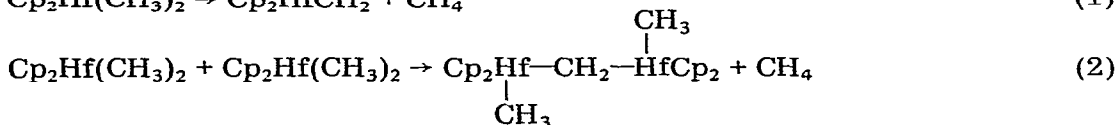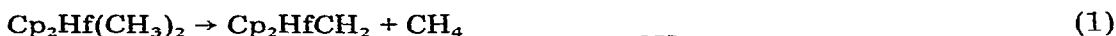pounds deuterated in the Cp rings and σ-bonded groups was studied. The results are given in Table 4.

On decomposition of Cp_2HfMe_2-d_6 under vacuum in toluene and dioxan, CD_3H, CD_4 and CD_2H_2 are formed but when $(Cp$-$d_5)_2HfMe_2$ decomposed, CH_3D, CH_4 and CH_2D_2 were evolved. The decomposition of $(Cp$-$d_5)_2HfPh_2$ gives benzene of isotopic composition: C_6H_6 (85%) and C_6H_5D (15%). According to these data, during decomposition of the hafnium compounds the Cp rings and R groups are hydrogen donors for the RH formation.

The thermal decomposition of Cp_2HfMe_2-d_6 and $(Cp$-$d_5)_2HfMe_2$ (Table 4, exp. 1, 2) under the same conditions shows a difference in the hydrogen abstraction from Cp rings and σ-bonded groups. The methane isotope composition in the decomposition of Cp_2HfMe_2-d_6 gives the ratio $CD_4/CD_3H = 1/1.7$ and in the decomposition of $(Cp$-$d_5)_2HfMe_2$ gives $CH_4/CH_3D = 1/0.7$ (Table 4, exp. 1, 2). Such a distinction in isotope composition is not due to a low degree of deuteration of the Cp rings and Me groups. According to mass spectrometric data the isotopic purity for Cp_2HfMe_2-d_6 is 99% and is 97% for $(Cp$-$d_5)_2HfMe_2$. The fact that deuteration of the Cp rings and Me groups differently influences the decomposition rate of these compounds probably results in the kinetic isotope effect observed.

During decomposition of the completely deuterated compound $(Cp$-$d_5)_2$-$HfMe_2$-d_6 89% of CD_4 and 11% of CD_3H are formed. The latter, however, exceeds the proton content of the Cp rings because of incompletely deuterated ligands. Such a discrepancy is due to the more rapid proton abstraction from Cp ring compared with that of deuterium. We have noted a similar isotope effect while investigating deuterated and undeuterated metallocenes under electron impact [5].

An equimolar mixture of $(Cp$-$d_5)_2HfMe_2$-d_6 and Cp_2HfMe_2 was decomposed to determine whether thermolysis was intra- or intermolecular in character. The formation of CD_3H, CH_2D_2 and CH_3D indicates unambiguously that the thermal decomposition of hafnium derivatives occurs via both intra- and intermolecular stages.

The initial stage of Cp_2HfMe_2 decomposition is hydrogen abstraction by a Me group with α-elimination (eq. 1) or intermolecular reaction (eq. 2).

$$Cp_2Hf(CH_3)_2 \rightarrow Cp_2HfCH_2 + CH_4 \tag{1}$$

$$Cp_2Hf(CH_3)_2 + Cp_2Hf(CH_3)_2 \rightarrow Cp_2Hf\!\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{-}}}}\!\!CH_2\!\!-\!\!HfCp_2 + CH_4 \tag{2}$$
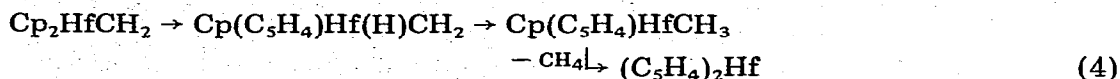
Carbene-like species are formed as a result of α-elimination. The intermolecular reaction is analogous to that proposed by Diachkovsky et al. for the decomposition of $TiMe_4$ [6].

It is of special interest to consider the participation of Cp rings in the decomposition process. From the result in Table 4 it follows that the Cp ring can be a hydrogen donor for RH formation. For hydrogen abstraction directly from the Cp ring a high activation energy is required. It is most probable to suppose that the hydrogen donation process occurs with preliminary rearrangement of the initial cyclopentadienyl structure by transfer of a hydrogen atom from the Cp ring to the metal. This process occurs especially readily after one methyl group
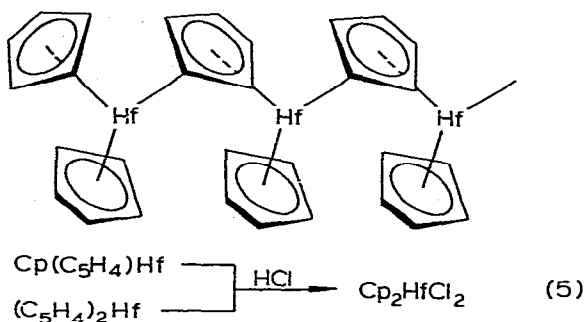
TABLE 4

THERMAL DECOMPOSITION OF DEUTERATED COMPOUNDS

Exp. No.	Compound	Experimental conditions	Isotope composition (%)				
			CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1	$Cp_2HfMe_2\text{-}d_6$	Vacuum, 290°C, 30 min (α = 0.8)	33.0	56.8	10.2	–	–
2	$(Cp\text{-}d_5)_2HfMe_2$	Vacuum, 290°C, 30 min (α = 1.0)	0.8	2.9	14.2	33.4	48.7
3	$Cp_2HfMo_2\text{-}d_6$	Toluene, 200°C, 40 h (α = 0.2)	30.1	57.2	12.7	–	–
4	$Cp_2HfMo_2\text{-}d_6$	Dioxan, 200°C, 40 h (α = 0.2)	21.3	56.8	7.4	–	–
5	$(Cd\text{-}d_5)_2HfMe_2\text{-}d_6$	Vacuum, 290°C, 30 min (α = 0.8)	89.3	10.7	–	–	–
6	Cp_2HfMe_2 + $(Cp\text{-}d_5)_2HfMe_2\text{-}d_6$	Vacuum, 290°C, 30 min	12.0	36.0	12.2	5.1	32.7
7	$Cp_2HfMe_2\text{-}d_6$	Vacuum, 250°C, 15 min (α < 0.1)	48.5	51.5	–	–	–
		Vacuum, 270°C, 40 min (α = 0.4)	30.7	61.8	7.5	–	–
8	$(Cp\text{-}d_5)_2HfMe_2$	Vacuum, 250°C, 15 min (α = 0.2)	0.1	0.9	12.2	16.5	70.5
		Vacuum, 290°C, 30 min (α = 1.0)	1.5	5.5	19.7	33.4	39.9
9	Decomposition product of $Cp_2HfMe_2\text{-}d_6$	Reaction with DCl	66.4	19.0	6.4	8.2	–
10	Decomposition product of $(Cp\text{-}d_5)_2HfMe_2$	Reaction with HCl	1.5	7.7	27.6	23.4	40.4

has been eliminated. This pathway is characteristic of titanium subgroup metallocenes and has been postulated previously [7,8].

$$Cp_2HfCH_3 \rightarrow Cp(C_5H_4)Hf(H)CH_3 \rightarrow Cp(C_5H_4)Hf + CH_4 \qquad (3)$$

$$Cp_2HfCH_2 \rightarrow Cp(C_5H_4)Hf(H)CH_2 \rightarrow Cp(C_5H_4)HfCH_3$$
$$\xrightarrow{-CH_4} (C_5H_4)_2Hf \qquad (4)$$

The rearrangement of the initial cyclopentadienyl structure should occur with conservation of the η^5-Cp ligands. This condition is necessary for the formation of Cp_2HfCl_2 by the action of HCl on the decomposition products of Cp_2HfR_2. Several structures for "titanocene" were previously suggested by Brintzinger [9], one of which is a dimeric structure with $(\eta^5, \eta^1\text{-}C_5H_4)$ ligands. There is an analogous polymer structure with η^5-Cp and $(\eta^5, \eta^1\text{-}C_5H_4)$ ligands in the thermal decomposition products of the hafnium compounds:

$$\left. \begin{array}{l} Cp(C_5H_4)Hf \\ (C_5H_4)_2Hf \end{array} \right\} \xrightarrow{HCl} Cp_2HfCl_2 \qquad (5)$$

An indirect proof for such a structure was acquired through the reaction of the hafnium residue of decomposed $(Cp\text{-}d_5)_2HfMe_2$ with HCl. Dichlorohafnocene of d_{10}–d_0 isotopic composition is formed with 70% yield in this reaction (Table 5).

The existence of the isotopic forms $(Cp\text{-}d_{4.5})_2HfCl_2$ and $(Cp\text{-}d_4)_2HfCl_2$ points to the presence of C_5D_4 ligands bonded to the metal. The d_9 isotopic form corresponds to a $(C_5D_4)(C_5D_5)Hf$ group and the d_8 isotopic form corresponds to

TABLE 5

ISOTOPIC COMPOSITION OF COMPOUNDS (ACCORDING TO MASS SPECTROMETRIC DATA)

Isotope forms of Cp ligands	Cp_2HfCl_2 [a] (%)	$(Cp\text{-}d_5)_2HfMe_2$ [b] (%)
d_{10}	22.9	75.2
d_9	37.1	21.7
d_8	19.2	2.1
d_7	18.7	0.9
d_{6-0}	2.1	0.1
Total deuterium content	86	97

[a] The compound is obtained by reaction of the decomposition product of $(Cp\text{-}d_5)_2HfMe_2$ with HCl (Table 4, exp. 8). [b] Initial compound.

$(C_5D_4)_2$Hf fragments in the decomposition products. The presence of $(Cp-d_5)_2$-$HfCl_2$ in the products of the reaction with HCl indicates that a part of the Cp_2HfMe_2 decomposes without participation of hydrogen atoms from Cp rings of its own molecules.

As has been noted, the treatment of the decomposition products of titanium cyclopentadienyl compounds with HCl gives no Cp_2TiCl_2. This fact is probably due to a fulvalene structure in the decomposition products of titanium compounds, in contrast to the hafnium ones [10,11].

Hydrogen exchange

The experimental data obtained from the decomposition of deuterated compounds points to hydrogen exchange between π-Cp rings and σ-R groups. The relevant data are:

1) Change in the methane isotope composition during the decomposition of Cp_2HfMe_2-d_6 (Table 4, exp. 7) and $(Cp-d_5)_2HfMe_2$ (Table 4, exp. 8). The amount of methane containing cyclopentadienyl hydrogen atoms rises with increasing decomposition degree of the compound (increase in temperature and time of process).

2) The formation of proton-containing methane (CD_3H, CD_2H_2 and CH_3D) as a result of the reaction of decomposed Cp_2HfMe_2-d_6 with DCl (Table 4, exp. 9) and formation of deuterated methane (CD_4, CD_3H, CDH_3) by the reaction of decomposed $(Cp-d_5)_2HfMe_2$ with HCl (Table 4, exp. 10).

3) The presence of d_7—d_0 isotopic forms in hafnocene dichloride formed when the decomposition product of $(Cp-d_5)_2HfMe_2$ reacts with HCl (Table 5).

4) The presence of methyl group deuterium in Cp rings after the decomposition of Cp_2HfMe_2-d_6 is evidence for hydrogen exchange. The initial compound Cp_2HfMe_2-d_6, without deuterium in the Cp rings, was decomposed for 60 minutes at 300°C. The decomposition product of this compound was subjected to a reaction with HCl to form the corresponding hafnocene dichloride which was analysed by mass spectrometry (Table 6). The analysis data points to the insertion of deuterium into the Cp ring.

The hydrogen exchange between Cp and σ-bonded ligands should involve two reactions. Firstly the reversible transfer of a hydrogen atom from the methyl group to the metal; secondly the rapid exchange of the hydrogen atom

TABLE 6

DEUTERIUM INSERTION INTO THE Cp RING DURING THERMAL DECOMPOSITION OF Cp_2HfMe_2-d_6

Isotopic forms of Cp ligands	Cp_2HfCl_2 [a]	Cp_2HfMe_2-d_6 [b]
d_0	85.3	100.0
d_1	12.3	—
d_2	1.5	—
d_3	0.7	—
d_4	0.2	—

[a] The compound is obtained by the reaction of decomposed Cp_2HfMe_2-d_6 with HCl. [b] Initial compound.

with hydrogen atoms of Cp rings or C_5H_4 ligands.

$$\begin{array}{c} \\ > \end{array}\text{Hf—CH}_3 \rightleftharpoons \begin{array}{c} \\ > \end{array}\text{Hf}\begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{H} \end{array} \tag{6}$$

$$Cp(C_5H_4)Hf(H) \rightleftharpoons Cp(C_5H_5)Hf \tag{7}$$

The exchange process occurs readily after one σ-bonded group is eliminated and the coordination vacancy at the hafnium atom is released. Not only a methyl group of the compound may participate in this process but a methylene group of the α-elimination product can also participate (eq. 1). Some literature data point to the possibility of reactions 6 and 7 occurring. The decomposition of methyl derivatives of transition metals supports reaction 6 [12]. Brintzinger's work on "titanocene" confirms the hydrogen transfer from the Cp ring to the metal [13,14]. For hafnium and zirconium tetrahydroborates rapid proton exchange between Cp rings and hydride atoms has been established [15]. Recently, it was shown that during decomposition of titanium and zirconium methyl derivatives reversible hydrogen transfer from the Cp ring to the metal does occur and that this is responsible for intra- and intermolecular exchange reactions [16,17].

The hydrogen exchange rate (according to eq. 6 and 7) should exceed the elimination rate of the second methyl group. This fact explains the increase in the amount of methane containing hydrogen atoms from the Cp ring with increasing time of heating Cp_2HfMe_2.

CH_4 and CH_3D formation in the decomposition of Cp_2HfMe_2-d_6 as well as CD_4 and CD_3H formation when $(Cp$-$d_5)_2HfMe_2$ decomposed is also a result of such an exchange. The hydrogen exchange in methyl groups leads to the hydrogen exchange in the Cp rings. The d_1—d_4 isotopic forms of hafnocene dichloride isolated after the decomposition of Cp_2HfMe_2-d_6 by reaction with HCl (Table 6) correspond to $(C_5H_5)C_5H_4D)Hf$, $(C_5H_4D)_2Hf$ and other fragments containing one or more deuterium atoms. The predominant content of the d_1 isotopic form indicates that the exchange concerns only one ring. The d_7—d_{10} isotopic forms of hafnocene dichloride formed as a result of reaction of decomposed $(Cp$-$d_5)_2$-$HfMe_2$ with HCl characterizes $(C_5D_5)(C_5HD_3)Hf$ and $(C_5HD_3)_2Hf$ and other fragments with one or more protons.

The observed hydrogen exchange during the decomposition of Cp_2HfMe_2 confirms the similarity of decomposition pathways for the titanium subgroup bis-cyclopentadienyl compounds.

The participation of solvent in the decomposition process

Comparison of decomposition products from Cp_2HfMe_2 under vacuum and in toluene and dioxan solutions (Table 3) shows the similarity of decomposition processes in vacuum and solutions. The isotopic composition of methane evolved in the decomposition of Cp_2HfMe_2-d_6 under vacuum, and in toluene and dioxan points to a decomposition pathway with participation of cyclo-pentadienyl and methyl hydrogen atoms in all cases.

On comparing the isotopic composition of methane formed during the decomposition of Cp_2HfMe_2-d_6 in toluene and dioxan (Table 4) it can be noted that the amount of undeuterated methane increases when the decomposition

TABLE 7

THE PRODUCTS OF THE INTERACTION OF Cp_2HfR_2 WITH SOLVENT

Compound	Thermal decomposition conditions	Interaction products
Cp_2HfMe_2	C_6D_6, 180°C, 20 h	CH_4, 95.1%; CH_3D, 4.9%
Cp_2HfPh_2	CCl_4, 150°C, 8 h	Cp_2HfCl_2, 0.81 mol; C_6H_6, 0.72 mol; C_6H_5Cl, 0.22 mol; $CHCl_3$, 0.39 mol; C_2Cl_6, 0.41 mol
Cp_2HfPh_2 + cyclohexene	CCl_4, 150°C, 8 h	7,7'-dichlornorcarane, 0.12 mol
Cp_2HfPh_2-d_{10}	CCl_4, 150°C, 8 h	$CHCl_3$, 91.0%; $CDCl_3$, 9.0%

proceeds in dioxan. Such a change in the isotopic composition in dioxan is probably caused by the fact that dioxan is an additional hydrogen donor for methane formation. Dioxan, with an unshared electron pair on the oxygen atom, is capable of coordinating to the hafnium atom and participating in the decomposition process. The participation of coordinated solvents in the decomposition of titanium compounds has been noted previously [1,18].

From the decomposition of Cp_2HfMe_2 in C_6D_6 deuteromethane was found (Table 7). The fact that hydrocarbons such as benzene and toluene do not participate on the decomposition of titanium compounds has been noted earlier. However, in a series of works which have appeared lately, the possibility of hydrogen exchange in the presence of transition metal complexes was pointed out. Thus hydrogen exchange was established to occur between C_6H_6 and D_2 when Cp_2TiMe_2 decomposed. This exchange is believed to proceed through the formation of titanium σ-arylhydride derivatives [19]. Bis-cyclopentadienyl compounds of tantalum and niobium are active catalysts of hydrogen exchange in the C_6H_6-D_2 system [20]. The interaction of CD_4 with complex catalysts occurring through the formation of carbene complexes has been discussed [21]. The formation of intermediate hydride complexes appears to be one of the conditions for exchange. We have shown that hydride complexes of zirconium formed during the thermal decomposition are active in hydrogen exchange reactions [17].

It is clear that the formation of deuteromethane during the thermal decomposition of Cp_2HfMe_2 in C_6D_6 is also a result of hydrogen exchange which takes place during the decomposition. The exchange is likely to occur via the stage of an intermediate hydride complex which is formed by hydrogen transfer from the Cp ring or the methyl group to the metal.
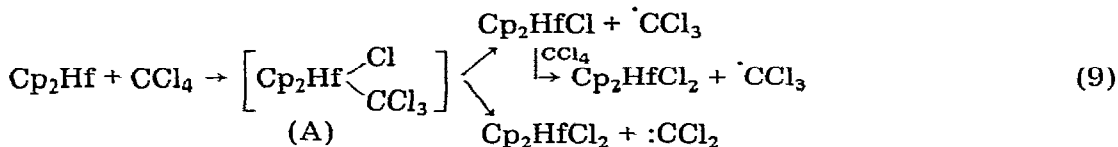

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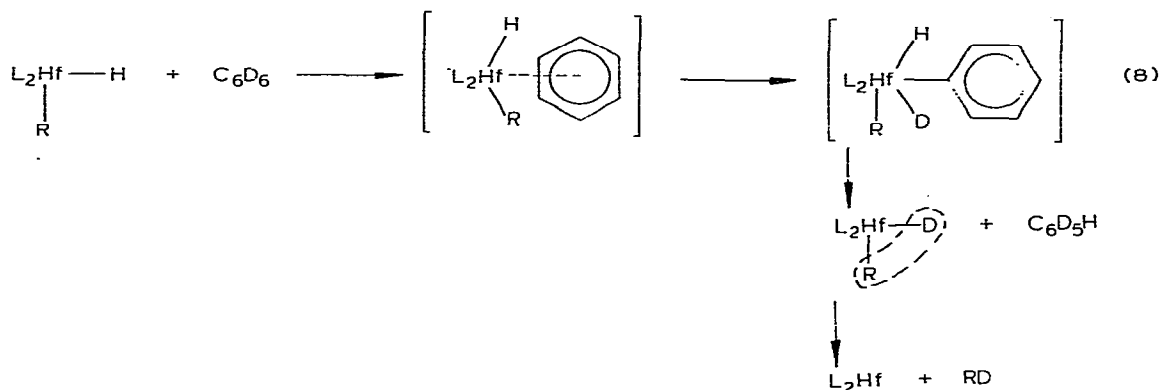
In the presence of a hafnium hydride complex, activation of a C—H bond in the benzene ring with deuterium transfer from the aromatic ring to the metal takes place. The similar metallation reaction of aromatic hydrocarbons with transition metal complexes was noted in the thermal decomposition of Cp_2ZrAr_2 ($Ar = o,m,p\text{-}CH_3C_6H_4$) in C_6H_6 [22] and in the reaction of the bis(monophosphine)complex of zirconocene with aromatic hydrocarbons [23]. The reversibility of reaction 8 produces the initial hydride complex containing deuterium and this complex further eliminates deuteromethane.

On transition from hydrocarbon solvent to a chlorine-containing one the direction of Cp_2HfR_2 decomposition changes. This is confirmed by the thermal decomposition products of Cp_2HfPh_2 in CCl_4: Cp_2HfCl_2, C_6H_6, C_6H_5Cl, $C_6H_5CCl_3$, $CHCl_3$ and C_2Cl_6 were identified in the thermal decomposition products (Table 7).

The presence of these compounds points to the participation CCl_4 in the decomposition of Cp_2HfPh_2. The participation of chlorine-containing solvents in the decomposition of titanium and zirconium compounds has been noted earlier [1,18,24].

The thermal decomposition of Cp_2HfPh_2 in CCl_4 occurs with cleavage of Hf—Ph bonds and the formation of benzene and chlorobenzene. As was shown above, benzene is formed because of hydrogen abstraction from an adjacent phenyl group with conservation of the Cp_2Hf fragment. A small part of the phenyl groups interact with solvent according to a well known reaction to form C_6H_5Cl and C_2Cl_6. The Cp_2Hf fragment undergoes oxidative addition with CCl_4 to give complex A which decomposes in two directions:

$$Cp_2Hf + CCl_4 \rightarrow \left[Cp_2Hf{<}^{Cl}_{CCl_3} \right] \begin{array}{l} Cp_2HfCl + {}^{\cdot}CCl_3 \\ \quad\quad\; |CCl_4 \\ \quad\quad\; {\hookrightarrow}\; Cp_2HfCl_2 + {}^{\cdot}CCl_3 \\ Cp_2HfCl_2 + :CCl_2 \end{array} \quad\quad (9)$$

(A)

The identification of 7,7'-dichloronorcarane from the decomposition of Cp_2HfPh_2 in the presence of cyclohexene confirms the formation of dichlorocarbene. The further pathway of $:CCl_2$ is insertion into the C—Cl bond of CCl_4 with the formation of C_2Cl_6; $^{\cdot}CCl_3$ is dimerized to C_2Cl_6 or converted into $CHCl_3$. The isotopic composition of chloroform obtained from $Cp_2HfPh_2\text{-}d_6$ decomposition indicates that $^{\cdot}CCl_3$ is able to remove a hydrogen atom from the Cp ring and the phenyl group.

The hafnium derivatives studied allowed us to find some common trends which are characteristic for bis-cyclopentadienyl compounds of the titanium subgroup. They are the following: 1) σ-bonded ligand cleavage occurs with the rearrangement of the initial bis-cyclopentadienyl structure without M—Cp bond cleavage, 2) hydrogen exchange reaction, 3) participation of coordinating and chloro-containing solvents in the decomposition process.

Experimental

Cp_2HfMe_2 and Cp_2HfPh_2 were obtained by procedures previously described [25]. For the synthesis of compounds deuterated in the Cp rings, C_5D_6 produced by reaction of C_5H_6 with D_2O was used [5]. The synthesis of com-

pounds with deuterium in the σ-bonded groups was realized with the use of CD_3I (99.8% D) and C_6D_5Br (99.8% D).

The isotopic purity of compounds was determined by mass spectrometry by placing them directly into the ion source. For $(Cp-d_5)_2HfMe_2$, $Cp_2HfMe_2-d_6$ and $(Cp-d_5)_2HfMe_2-d_6$ complete mass-spectra were obtained, on the basis of which the deuterium content in ligands was calculated. According to the analytical results the deuterium content in the Cp rings and methyl groups is not less than 97 and 99%, respectively. The analysis of methane isotopic composition was made by mass spectrometry.

All mass-spectrometric measurements were conducted using a MI model 1305 instrument at an accelerating voltage of 2 kV and electron energy of 70 eV.

DTA of Cp_2HfMe_2 was conducted in a cell, due to its volatility, but DTA of Cp_2HfPh_2 was performed in an argon atmosphere with recording of the elimination rates. The heating rate of the samples was 5°/min, the standard was Al_2O_3.

The decomposition of the compounds was studied in sealed ampules fitted with an outlet for selecting decomposition products. Samples of compounds (200—500 mg) were taken for the experiments. The experimental conditions are given in the Results and discussion.

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