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Thermal decomposition and photodecomposition of biscyclopentadienyl complexes of titanium, vanadium, and their analogues

V P Mar'in, L I Vyshinskaya, G A Razuvaev (deceased)
Institute of Chemistry at the Lobachevskii Gorky State University

ABSTRACT. Data on the reactions involving the thermal decomposition and photodecomposition of the biscyclopentadienyl compounds Cp_2MR_n (M = Ti, Zr, Hf, V, or Nb) are surveyed. The pathways leading to the formation of RH as well as the rearrangement of the biscyclopentadienyl structure in the thermal and photochemical reactions are discussed. Processes involving hydrogen exchange and the exchange of the cyclopentadienyl rings are examined.

The bibliography includes 92 references.

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I. Introduction

Studies on the thermal decomposition of organometallic compounds (OMC) were published almost simultaneously with studies on their synthesis, but initially this was associated with the investigation of the theoretical aspects of the stability of the metal–carbon bond. Subsequently such investigations became of practical interest in relation to questions of analysis and, mainly, the preparation of metallic and inorganic coatings by the thermal decomposition of the corresponding OMC. Monographs[1,2] have been devoted to general problems of the study of the mechanism of the thermal decomposition of OMC and their practical use for the preparation of coatings.

Compounds of two types are most numerous among OMC of the titanium and vanadium subgroups: covalent, i.e. σ-alkyl or σ-aryl compounds, and sandwich-covalent compounds, i.e. π-cyclopentadienyl-σ-alkyl(aryl) complexes. The principal features of the thermal decomposition of the covalent derivatives have been examined in another review.[3]

The first studies on the thermal and photolytic decomposition of the sandwich-covalent compounds Cp_2TiR_2 (R = CH_3 or C_6H_5) were published at the end of the 1960's. These investigations established that the decomposition of Cp_2TiR_2 in solutions entails the homolytic cleavage of two Ti–R σ-bonds accompanied by the intermediate formation of paramagnetic trivalent titanium compounds, which has been demonstrated by EPR. When the reaction is carried out in CCl_4, the radicals formed react with metallic mercury. The interesting fact that the decomposition of Cp_2TiR_2 initiated the radical polymerisation of methacrylate, styrene, and vinyl chloride has been noted in addition. These studies have been surveyed.[4]

Various aspects of the thermal decomposition of the complexes Cp_2MR_n have been investigated in recent years. As the chemistry of the so called 'titanocene' developed, processes involving the cyclopentadienyl ligands, leading to a rearrangement of the initial biscyclopentadienyl structure of the compound, were examined. Such a rearrangement, inducing an increase in the coordinative unsaturation of the complex, leads to new applications of these compounds in processes involving the activation of the C–H bonds of hydrocarbons and the fixation of mercury or nitrogen, and also in organic synthesis.

Simultaneously with the investigation of the thermal decomposition of titanium subgroup compounds, studies were performed on the thermal decomposition of sandwich-covalent compounds of trivalent vanadium: Cp_2VR (R = CH_3 or C_6H_5). These studies demonstrated a sharp difference between the mechanisms of the decomposition of the reactions of the titanium and vanadium derivatives.

The first attempts at the synthesis of tetravalent vanadium compounds Cp_2VR_2 were unsuccessful, which helped to strengthen the concept that these derivatives are highly labile. However, in 1966 the compounds Cp_2VR_2 (R = CH_3, C_2H_5, or $C_6H_5CH_2$) were obtained and somewhat later their decomposition was also studied. The results made it possible to compare the decomposition reactions of titanium and vanadium compounds having the general formula Cp_2MR_2.

This review surveys the results of the thermal and photolytic decomposition of the sandwich-covalent compounds of titanium, vanadium, and their analogues having the general formula Cp_2MR_n as a function of the nature of the σ-substituents and the transition metals.

II. Thermal decomposition of titanium subgroup compounds

1. Thermal stability and decomposition products

The thermal stability of the majority of the compounds Cp_2MR_2 (M = Ti, Zr, or Hf) has been characterised by differential thermal analysis (DTA).[5–10] It has been established on the basis of DTA data that the compounds Cp_2TiR_2 (R = CH_3 or Ar) decompose exothermically in the temperature range from 80° to 160 °C. Among the compounds indicated, the methyl derivative, which decomposes appreciably even at room temperature, has the lowest thermal stability. The differences between the thermal stabilities of the aryl derivatives are insignificant. However, the increased stability of compounds containing methyl groups in the meta-position in the benzene ring compared with $Cp_2Ti(C_6H_5)_2$ is notable. This is probably caused by the steric effects of such ligands, which proved significant in the formation of the dehydrobenzene complex under the decomposition conditions.[6,7]

A kinetic study of the thermal decomposition of Cp_2TiR_2 [R = C_6H_5, $C_6H_5CH_2$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, or 3,4-$(CH_3)_2C_6H_3$] showed that the decomposition process is described by a first order equation. The calculated activation energy for the decomposition reaction is in the range 16–30 kcal mol^{-1} and decreases with decrease in the decomposition temperature of the compound Cp_2TiR_2. Depending on R, the decomposition temperature decreases in the following sequence:[8]

$$3,4\text{-}(CH_3)_2C_6H_3 > m\text{-}CH_3C_6H_4 > p\text{-}CH_3C_6H_4 > C_6H_5 > CH_2C_6H_5.$$

In the series of isotypical compounds Cp_2MR_2 (M = Ti, Zr, or Hf), the thermal stability rises from titanium to hafnium. Among all the compounds considered, $Cp_2Hf(CH_3)_2$ is the most stable (it decomposes above 250 °C).[9,10]

An increase in the stability of the biscyclopentadienyl compound on substitution of the hydrogen atoms by deuterium in the σ-substituents at the metal atom has been noted.[7,10] A similar substitution of hydrogen atoms by deuterium in the cyclopentadienyl rings does not increase significantly the thermal stability of the compounds. This fact shows that the rate-limiting stage of the decomposition process involves the rupture of the M–R bond or the abstraction of a hydrogen (deuterium) atom from the σ-linked group.

It has also been shown that the stability of the sandwich-covalent compound increases as the hydrogen atoms in the cyclopentadienyl rings are replaced by methyl groups.[11]

When the biscyclopentadienyl derivatives Cp_2MR_2 (M = Ti, Zr, or Hf; R = alkyl or aryl) are heated *in vacuo* or in hydrocarbon solvents at the decomposition temperatures, the M–R σ-bond is cleaved with liberation of 1.4–1.9 mol of RH (Table 1).[6,7,9,10] The dimerisation products are almost absent for all the compounds. The decomposition process can be formally represented by the scheme

$$(C_5H_5)_2MR_2 \rightarrow C_{10}H_8M + 2RH.$$

The decomposition of Cp_2MR_2 results in the formation of a residue, which has the approximate empirical formula $C_{10}H_8M$ according to analytical data. The IR spectra of this residue and its alcoholysis indicate the presence in it of η^5-Cp ligands.[6,7,9] The metal-containing residues formed on decomposition of Cp_2MR_2 (M = Ti, Zr, or Hf) react differently with hydrogen chloride. Thus Cp_2TiCl_2 is not formed when the titanium-containing residue is treated with HCl, treatment of the zirconium-containing residue with HCl affords a small amount of Cp_2ZrCl_2, while treatment of the hafnium-containing residue with HCl produces a yield of Cp_2HfCl_2 of 0.7 mol per mole of the initial compound. The different yields of the metallocene dichlorides in these reactions indicate differences between the compositions of the metal-contianing thermal decomposition products formed.[10]

Table 1. Thermal decomposition of the compounds Cp_2MR_2.

Compound	Decomposition conditions	Yield of RH after decomposition of Cp_2MR_2, mol mol^{-1}	Yield of products resulting from treatment of solid residue from decomposition of Cp_2MR_2 with HCl, mol mol^{-1}		Refs.
			RH	Cp_2MCl_2	
$Cp_2Ti(CH_3)_2$	vacuum, 100 °C, 15 min	1.65	0.10	—	[6]
$Cp_2Ti(C_6H_5)_2$	vacuum, 120 °C, 60 min	1.84	0.04	—	[7]
$Cp_2Ti(C_6H_5)_2$	toluene, 110 °C, 5 h	1.90	0.07	—	[7]
$Cp_2Ti(m\text{-}CH_3C_6H_4)_2$	vacuum, 134 °C, 60 min	1.88	—	—	[7]
$Cp_2Ti(p\text{-}CH_3C_6H_4)_2$	vacuum, 125 °C, 60 min	1.98	—	—	[7]
$Cp_2Ti[3,4\text{-}(CH_3)_2C_6H_3]_2$	vacuum, 136 °C, 60 min	1.92	—	—	[7]
$Cp_2Ti[3,4\text{-}(CH_3)_2C_6H_3]_2$	toluene, 110 °C, 5 h	1.84	0.02	—	[7]
$Cp_2Ti(CH_2C_6H_5)_2$	vacuum, 120 °C, 60 min	1.64	—	—	[6]
$Cp_2Zr(CH_3)_2$	vacuum, 220 °C, 30 min	1.83	0.10	0.17	[9]
$Cp_2Zr(C_6H_5)_2$	vacuum, 160 °C, 60 min	1.61	0.06	0.09	[9]
Cp_2ZrH_2	vacuum, 230 °C, 60 min	1.55	—	not determined	[9]
$Cp_2Hf(CH_3)_2$	vacum, 290 °C, 15 min	1.37	0.14	0.67	[10]
$Cp_2Hf(C_6H_5)_2$	vacuum, 200 °C, 3 h	1.30	0.32	0.59	[10]
$Cp_2Hf(C_6H_5)_2$	toluene, 180 °C, 3 h	1.33	0.10	0.70	[10]

2. Pathways leading to formation of RH

One of the important questions arising in the study of the thermal decomposition of Cp_2MR_2 is that of the source of hydrogen atoms for the formation of RH. The cyclopentadienyl rings, the σ-linked group, or the solvent can serve as sources of this kind. In order to answer this question, studies have been made using deuterium-labelled compounds. Deuterium was introduced either into the Cp rings or into the R groups, or deuteriated solvents were used.

Table 2. Thermal decomposition of deuteriated methyl derivatives of titanium subgroup metals *in vacuo*.

Compound	Decomposition conditions		Isotopic composition of methane, %					Refs.
	T, °C	*t*, min	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	
$Cp_2Ti(CH_3)_2\text{-}d_{10}$	90	30	54.0	41.0	4.1	0.9	—	[6]
$Cp_2Zr(CH_3)_2\text{-}d_{10}$	230	15	17.2	56.3	15.7	7.8	3.0	[9]
$Cp_2Hf(CH_3)_2\text{-}d_{10}$	290	30	48.7	33.4	14.2	2.9	0.8	[10]
$Cp_2Hf(CD_3)_2 + Cp_2Hf(CD_3)_2\text{-}d_{10}$ (1:1)	290	30	33.0	56.8	10.2	—	—	[10]

The thermal decomposition of $Cp_2M(CH_3)_2\text{-}d_{10}$ without a solvent involves the liberation of mainly CH_4, CH_3D, and CH_2D_2 (Table 2). The decomposition of the phenyl derivatives $Cp_2M(C_6H_5)_2\text{-}d_{10}$ under the same conditions affords C_6H_6, C_6H_5D, and $C_6H_4D_2$ (Table 3).

These data demonstrate unambiguously that in the decomposition of the titanium subgroup compounds there are two competing pathways leading to the formation of RH—both with participation of the hydrogen of the Cp rings and with participation of the hydrogen of the neighbouring group R.

Table 3. Thermal decomposition of deuteriated phenyl derivatives of titanium subgroup metals *in vacuo*.

Compound	Decomposition conditions		Isotopic composition of benzene, %							Refs.
	T, °C	t, min	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6	
$Cp_2Ti(C_6H_5)_2$-d_{10}	140	60	37.7	32.1	30.2	—	—	—	—	[6]
$Cp_2Ti(C_6D_5)_2$	137	60	—	—	—	—	32.4	35.6	32.0	[7]
$Cp_2Zr(C_6H_5)_2$-d_{10}	160	30	65.7	12.7	11.0	6.0	3.2	1.0	0.4	[9]
$Cp_2Hf(C_6H_5)_2$-d_{10}	200	30	85.0	15.0	—	—	—	—	—	[10]

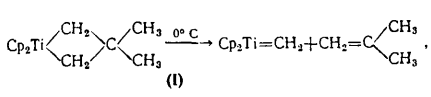
When hydrogen atoms are abstracted from the group R by an intramolecular pathway, intermediate complexes containing dehydrogenated groups R coordinated to the metal are formed:

$$Cp_2MR_2 \rightarrow RH + Cp_2M(R_{-H}). \quad (1)$$

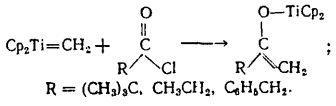
These complexes can decompose in their turn with liberation of RH as a result of the abstraction of hydrogen from the Cp or C_5H_4 groups via the reactions

$$Cp_2M(R_{-H}) \begin{cases} \rightarrow Cp(C_5H_3)M + RH \\ \rightarrow (C_5H_4)_2M + RH. \end{cases} \quad (2)$$

α-Elimination via reaction (1) from the methyl derivatives leads to the formation of carbene complexes of the type $Cp_2M = CH_2$ (I). The structural parameters of the complex (I) and the related carbene complexes have been calculated theoretically.[12] The Tebbe reagent $Cp_2Ti = CH_2AlCl(CH_3)_2$ is an example of compounds in which the methylene fragment has been stabilised by coordination to the metal. This complex participates in metathetical processes and is used to synthesise titanacyclobutanes[13–16] and other metallacycles.[17] The methylene complex (I), which is formed on decomposition of titanacyclobutanes, produces two stable titanium enolates in the presence of acid chlorides:[18,19]

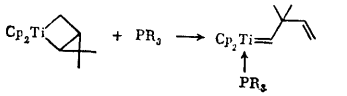


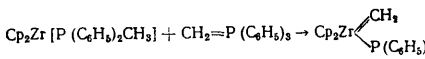
(I)



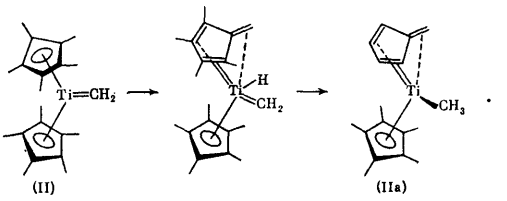
R = $(CH_3)_3C$, CH_3CH_2, $C_6H_5CH_2$.

The carbene complexes of titanocene and zirconocene can be stabilised by phosphines:[20,21]



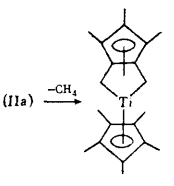


The thermal decomposition of the pentamethylcyclopentadienyl derivative $Cp^*_2Ti(CH_3)_2$ [$Cp^* = C_5(CH_3)_5$] involves the formation of the methylene complex $Cp^*_2Ti = CH_2$ (II) similar to compound (I). The methylene complex (II) is stabilised by the transfer of a hydrogen atom from a ring methyl group to the metal and then to the methylene group, which results in the formation of the complex (IIa):[22]

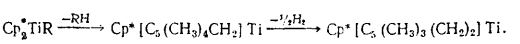


(II) (IIa)

Further heating of the complex (IIa) leads to the abstraction of a second methyl group from the metal atom, a methyl group of the cyclopentadienyl ring serving as a hydrogen donor in this process:[23]

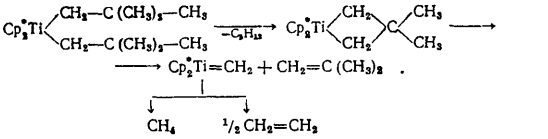


The thermal decomposition of Cp^*_2 leads to the same results:[23]



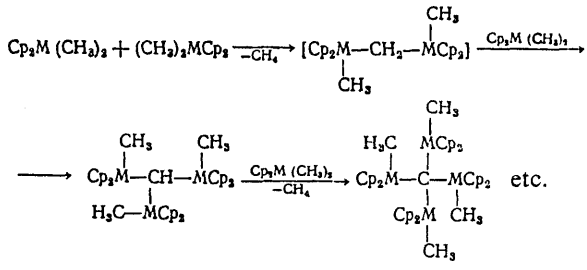
The synthesis of the ethylene complex $Cp^*_2Ti(CH_2=CH_2)$, which readily reacts with methylenecyclopropane forming the titanocyclopentane ring, has been described.[24]

γ-Elimination resulting in the formation of a metallacycle takes place in the thermal decomposition of $Cp^*_2Ti[CH_2C(CH_3)_3]_2$ in addition to the α-elimination, which leads to the liberation of neopentane and the formation of the carbene complex $Cp^*_2Ti = CH{-}C(CH_3)_3$ (main process). The cleavage of the bond in the metallacycle affords the carbene complex (II) and isobutene. The complex (II) generates methane as a result of the abstraction by the carbene of a hydrogen atom from the cyclopentadienyl rings or from the solvent. Ethylene is evolved on dimerisation of two carbene molecules. The unsubstituted norcarane has been detected among the decomposition products of $Cp^*_2Ti[CH_2C(CH_3)_3]_2$ in cyclohexane, which confirms the existence of compound (II):[25]



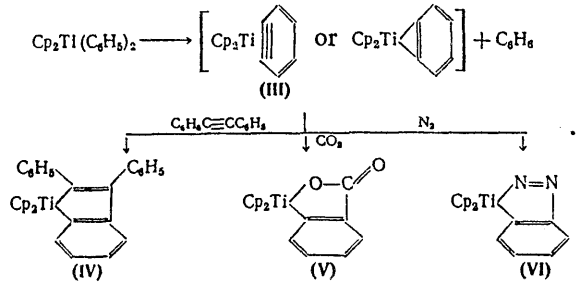
A similar γ-elimination process with formation of metallacycles takes place in the decomposition of the thorium complex $Cp^*_2Th.[CH_2Si(CH_3)_3]_2$.[26]

It has been suggested that the abstraction of hydrogen from the σ-linked ligand in the methyl derivatives $Cp_2M(CH_3)_2$ (M = Ti, Zr, or Hf) takes place also intermolecularly:

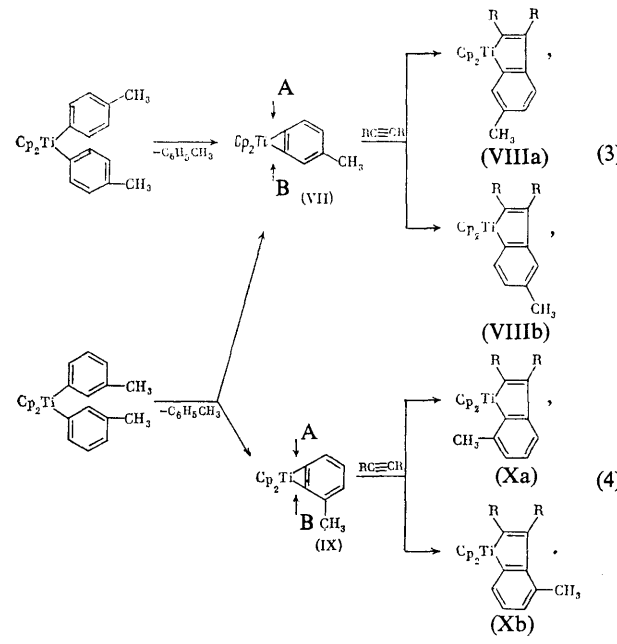


This pathway leading to the formation of RH has been confirmed by the hydrolysis of the decomposition products of $Cp_2M(CH_3)_2$ by deuteriated water. The evolution of CH_2D_2, CHD_3, and CD_4 indicates the presence of the [M–CH_2–M], [M–$\underset{\displaystyle M}{\overset{|}{C}}$H–M], and [C(M)]$_4$ groups in the decomposition products.[27]

The decomposition of the phenyl derivatives $Cp_2M(C_6H_5)_2$ via reaction (1) leads to the formation of benzene (as a result of the abstraction of the *ortho*-hydrogen atom from the neighbouring phenyl group) and of the intermediate complex (III). This decomposition mechanism has been confirmed in relation to the decomposition of $Cp_2Ti(C_6H_5)_2$ in the presence of tolane, CO_2 (80–90 °C), and N_2 (80–130 °C, 100 atm). In all three cases, the decomposition of $Cp_2Ti(C_6H_5)_2$ affords the intermediate complex (III), which then reacts with the above molecules, giving rise to the stable complexes (IV) and (V) and the unstable complex (VI) respectively:[28,29]



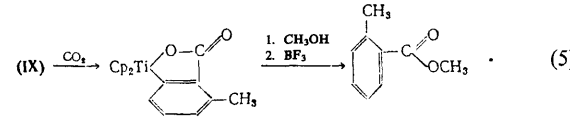
The thermal decomposition of the aryl derivatives of titanocene leads to the formation of similar intermediate complexes of titanium with substituted benzene rings, whose reactivity is determined by steric factors. The thermolysis of $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ [reaction (3)] proceeds via the formation of the intermediate complex (VII), which can react with the acetylenes RC≡CR (R = CH_3, CF_3, or C_6H_5), from the A or B side, producing the benzotitanoles (VIIIa) and (VIIIb) in approximately equal amounts:[30]



(3)

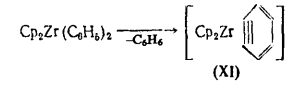
(4)

In the thermal decomposition of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ [reaction (4)] there is in principle a possibility of the formation of the intermediate complexes (VII) and (IX). There is no doubt that the steric influence of the methyl group in the *meta*-position in the benzene ring makes the formation of the complex (IX) less preferred than that of the complex (VII). If the decomposition of $Cp_2Ti(m\text{-}CH_3.C_6H_4)_2$ were accompanied by the formation of the intermediate (IX), then attack by the acetylene would be possible only from the A side, which would lead to the complex (Xa) but not (Xb).[30] However, this reaction pathway has been completely disproved[31] because, after carboxylation and alcoholysis, the orthoesters, which should have been formed via reaction (5), are absent from the products, and only the *para*- and *meta*-derivatives of benzoic acid esters are present in proportions of 1 : 3:



(5)

It has been shown[32–36] that, when $Cp_2Zr(C_6H_5)_2$ or its derivatives are heated (70–90 °C), the intermediate complex (XI) is formed:

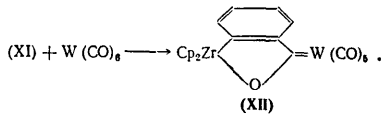


Similar complexes also serve as intermediates in the isomerisation reactions of the compound Cp_2ZrAr_2 and in the reaction with the solvent–benzene.[32]

The complex (XI) reacts with alkenes, affording high yields of zirconaindans.[33,34] The interaction of the complex (XI) with *cis*- and *trans*-stilbenes is stereospecific and gives rise to the formation of *cis*- and *trans* 2,3-diphenyl-1-zirconaindans respectively.[33] It has been shown that alkylzirconaindans decompose above 100 °C in saturated hydrocarbons with formation of phenylalkanes. It has been suggested that the decomposition proceeds via a stage involving

the formation of a phenylene complex via the transfer of a hydrogen atom from the aromatic ring to the metal. The thermolysis of 3-butylzirconaindan in the presence of an excess of norbornene entails the displacement of hexene and the formation of a zirconaindan complex containing the norbornane ring.[34]

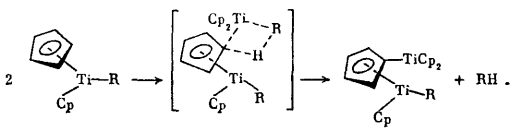
The reaction of the complex (XI) with $W(CO)_6$ yielded the carbene complex (XII):[35]



(XII)

The interaction of the complex (XI) with $CH_2 = P(C_6H_5)_3$ leads to the ylide $Cp_2Zr(C_6H_5)[CH = P(C_6H_5)_3]$.[36]

The cyclopentadienyl ligands together with the σ-linked groups R can serve as a source of hydrogen atoms in the formation of RH. The direct abstraction of hydrogen atoms by the group R from the Cp ring requires a high activation energy. Such a reaction proceeds more readily via an intermolecular pathway, in which the Cp ring is metallated by titanium, as suggested for the decomposition of trivalent titanium derivatives:[5]



However, it is more likely that hydrogen is abstracted from the Cp ring via the preliminary transfer of hydrogen to the metal. Such transfer was observed when the compounds Cp_2MR_2 (M = Ti, Zr, or Nb; R = Cl or CH_3) were treated with different reductants. Similar processes involving the transfer of hydrogen atoms to the metal occur also in the thermal decomposition of the derivatives Cp_2MR_2 (M = Ti, Zr, or Hf). One of the facts confirming such transfer is the isotopic composition of the hydrogen evolved on hydrolysis of the thermal decomposition products of Cp_2MR_2 (Table 4). When the products of the thermal decomposition of Cp_2MR_2-d_{10} are treated with HCl/H_2O, HD is formed preferentially, while treatment with DCl/D_2O leads to the preferential formation of D_2. The formation of HD in the former case and of D_2 in the latter shows that the decomposition products contain deuterium atoms which have been transferred from the Cp ligands to the metal.[10,27]

Table 4. Hydrolysis of the products of the thermal decomposition of Cp_2ZrR_2-d_{10}.[27]

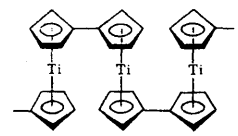
Initial compound	Agent	Isotopic composition of hydrogen
$Cp_2Zr(CH_3)_2$-d_{10}	HCl/H_2O	$H_2/HD/D_2 = 1/1.3/0.1$
	D_2O/DCl	$HD/D_2 = 1/5$
$Cp_2Zr(C_6H_5)_2$-d_{10}	HCl/H_2O	$H_2/HD/D_2 = 1/1.4/0.1$

The transfer of hydrogen to the metal takes place particularly readily after the abstraction of one group R and the liberation of a coordination site on the metal. The dehydrogenation of the cyclopentadienyl ring by the group R on formation of RH can proceed via the elimination of RH with participation of a hydrogen atom which has been transferred to the metal from the Cp ring:

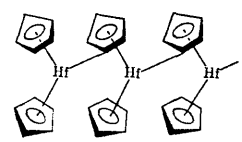
$$Cp_2MR \rightarrow Cp\,(C_5H_4)\,M\,(H)\,R \rightarrow Cp\,(C_5H_4)\,M + RH,$$
$$Cp_2MR_{-H} \rightarrow Cp\,(C_5H_4)\,M\,(H)\,R_{-H} \rightarrow Cp\,(C_5H_4)\,MR \rightarrow (C_5H_4)_2M + RH.$$

The donation of hydrogen atoms by the cyclopentadienyl ring for the formation of RH should lead to a rearrangement of the initial biscyclopentadienyl structure. The dimeric hydride forms of 'titanocene', having different structures, are known to react differently with HCl. Thus the 'titanocene' $[(\eta^5\text{-Cp})_2Ti_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]H_2$, having the fulvalene structure, does not afford Cp_2TiCl_2 on reaction with HCl.[37,28] However, the 'titanocene' containing the $\eta^5\text{:}\eta^1$-Cp ligands reacts with HCl to form Cp_2TiCl_2.[39]

These data permit the hypothesis that dimeric or polymeric chains with $\eta^5\text{:}\eta^5$-fulvalene ligands exist in the products of the thermal decomposition of the biscyclopentadienyl derivatives of titanium by analogy with the fulvalene form of 'titanocene':



A structure similar to the 'titanocene' with the $\eta^5\text{:}\eta^1$-cyclopentadienyl ligands is achieved in the products of the thermal decomposition of the hafnium derivatives:



The effect of the treatment of the product of the thermal decomposition of Cp_2HfR_2-d_{10} with HCl, which results in the formation (in 70% yield) of hafnocene dichloride whose isotopic composition is described predominantly by the formula Cp_2HfCl_2-d_{10}-d_7, serves as indirect proof of the existence of this structure in the hafnium products.[10] The existence of the Cp_2HfCl_2-d_9 and -d_{10} isotopic forms indicates the presence of ligands (C_5D_4) bound to the metal. The d_9 form corresponds to the $(C_5D_4)(C_5D_5)$Hf fragments, while the d_8 form corresponds to the $(C_5D_4)_2$Hf fragments in the decomposition products.

Thus the elimination of RH with participation of the hydrogen atoms of the Cp rings leads to a rearrangement of the initial biscyclopentadienyl structure, whose character is determined by the nature of the central atom.

3. The hydrogen exchange in the thermal decomposition of Cp_2MR_2

There exist a series of experimental data obtained in the thermal decomposition of deuteriated biscyclopentadienyl compounds of titanium, zirconium, and hafnium, which indicate the occurrence of hydrogen exchange between the groups Cp and R. The following must be included among them:

(1) The change in the isotopic composition of methane in the thermal decomposition of methyl derivatives of titanium and hafnium [it has been established that, with increase in the degree of decomposition of the compounds (after an increase in temperature and in the reaction time), the fraction of methane containing hydrogen derived from the Cp ring is found to increase[10,40,41]].

(2) The formation of protium-containing methane (CD_3H, CD_2H_2, and CH_3D) on treatment of the products of the thermal decomposition of $Cp_2M(CD_3)_2$ and deuterium-containing methane (CD_4, CD_3H, CDH_3) with DCl and on treatment of the products of the thermal decomposition of $Cp_2M(CH_3)_2$–d_{10} with HCl.[10]

(3) A clear-cut demonstration of the occurrence of hydrogen exchange has been obtained by detecting deuterium in the Cp rings in the Cp_2HfCl_2 formed on treatment of the $Cp_2Hf(CD_3)_2$ decomposition products with HCl:[10]

Isotopic forms of Cp ligands	d_0	d_1	d_2	d_3	d_4
Contents of these forms, %	85.3	12.3	1.5	0.7	0.2.

The hydrogen exchange between the Cp and R groups should entail two reactions—the reversible transfer of hydrogen from the methyl group to the metal [reaction (6)] and rapid exchange of hydride hydrogen and the hydrogen in the Cp or C_5H_4 ligands [reaction (7)]:

$$\rangle M{-}CH_3 \rightleftarrows \rangle M\langle^{CH_2}_{H}, \qquad (6)$$

$$Cp\,(C_5H_4)\,MH \rightleftarrows Cp\,(C_5H_5)\,M. \qquad (7)$$

The exchange is facilitated after the abstraction of one σ-linked group as a result of the liberation of a coordination site at the metal. The rate of exchange via reactions (6) and (7) must exceed the rate of elimination of the second methyl group. This in fact explains the finding that, on decomposition of $Cp_2M(CH_3)_2$, the fraction of methane containing hydrogen from the Cp rings increases with increasing reaction time. After the treatment of the $Cp_2Hf(CD_3)_2$ thermal decomposition products with HCl, Cp_2HfCl_2–d_1–d_4 compounds were isolated. These data indicate the presence in the decomposition products of the $(C_5H_5)(C_5H_3D)Hf$, $(C_5H_3D)_2Hf$, and other fragments containing one or several deuterium atoms. The dominant content of Cp_2HfCl_2-d_1 shows that the exchange involves only one ring.[10]

The transfer of the hydrogen atom from the ring to the metal takes place also via an intermolecular pathway. This is demonstrated by the composition of Cp_2MR_2 (M = Ti or Zr) in the presence of Cp_2V-d_{10}, in which there is H–D exchange between the hydride atoms of Cp_2MR_2 and vanadocene. The product of the thermal decomposition of Cp_2MR_2 also participates in the H–D exchange reaction with vanadocene. It has been shown that there exists a mobile equilibrium in which the hydrogen atoms of the Cp ligands in the initial compounds, the hydride hydrogen atoms, and the deuterium in the C_5D_5 ligands of vanadocene participate.[27]

The complexes $[Cp(C_5H_4)NbH]_2$ and Cp_2TaH_3 are known to be active catalysts of the H–D exchange in the D_2–C_6H_6 system.[42] It was found that the hydride complexes formed in the decomposition of the compounds Cp_2MR_2 are active in the hydrogen exchange of the hydrocarbons. Thus it has been established that hydrogen exchange takes place between C_6H_6 and D_2 under the conditions of the thermal decomposition of $Cp_2Ti(CH_3)_2$.[43] The thermal decomposition of $Cp_2Zr(C_6H_5)_2$-d_{10} in the presence of methane affords deuterium-containing methane. When the product of the thermal decomposition of $Cp_2Zr(CH_3)_2$-d_{10} is heated with C_2H_6, deuterium-containing propene and propane are produced (Table 5).[27] Deuteriomethane has been detected in the decomposition of $Cp_2Hf(CH_3)_2$ in C_6D_6.[10] It has been suggested that hydrogen exchange takes place under the thermal decomposition conditions between the hydride atoms of the cyclopentadienyl complex and the hydrogen atoms of the hydrocarbon.[10,27] The exchange proceeds via a stage involving the formation of σ-alkyl (or σ-aryl) intermediate transition metal complex:[44]

$$L_2M(R){-}H + R'D \longrightarrow \left[L_2M(R)(R'){-}D \right] \longrightarrow L_2M(R){-}D + R'H\ ;$$

L = Cp, C_5H_4.

Table 5. Thermal decomposition of Cp_2MR_2 in the presence of hydrocarbons (according to the results of Razuvaev and co-workers[10,27]).

System	Reaction conditions		Isotopic composition of hydrocarbons, %
	T, °C	t, min	
$Cp_2Zr(C_6H_5)_2$-d_{10} + CH_4	160	45	CH_4 96.0 CH_3D 4.0
Products of thermal decomposition of $Cp_2Zr(CH_3)_2$-d_{10} + C_3H_6	200	60	C_3H_6 17.5 C_3H_5D 86.3 C_3H_7D 39.5 C_3H_5D 13.7 $C_3H_6D_2$ 26.7 $C_3H_5D_3$ 16.3
$Cp_2Hf(CH_3)_2$ + C_6D_6	200	180	CH_4 95.1 CH_3D 4.9

Thus the thermal decomposition of biscyclopentadienyl compounds is accompanied by the hydrogen exchange between the hydrogen atoms of the Cp rings, the hydride atoms, the hydrogen atoms of the σ-linked group, and the hydrogen atoms of the hydrocarbon in the presence of which the decomposition takes place:

$$H_{Cp} \rightleftarrows H_M \rightleftarrows H_R\ .$$
$$\quad\ \uparrow\ \uparrow$$
$$\quad\ H_{ext}$$

If a compound containing an alkyl substituent in the cyclopentadienyl ring undergoes thermal decomposition, then the hydrogen exchange involves also the atoms in the alkyl group. Thus it has been shown on the basis of ^1H NMR and EPR data as well as the results of isotope analysis that H–D exchange takes place between the hydrogen atoms of the methyl groups and molecular deuterium in the thermolysis or photolysis of $[(C_5H_4CH_3)_2ZrH_2]_2$ in a D_2 atmosphere.[45]

It has been established that hydrogen is eliminated in the first stage with formation of a trivalent zirconium derivative:

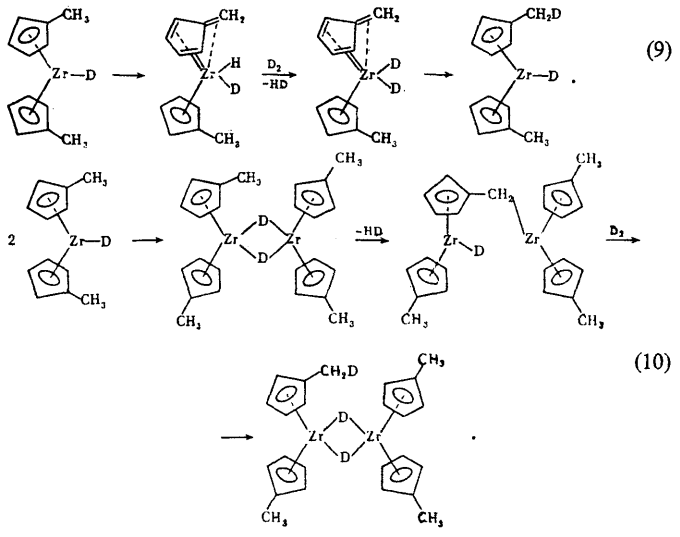
$$[(C_5H_4CH_3)_2ZrH_2]_2 \longrightarrow 2\,(C_5H_4CH_3)_2ZrH + H_2.$$

Next D_2 exchanges with hydride atoms. Such exchange can proceed via a four-centre transition state:

$$\rangle ZrH + D_2 \rightarrow \rangle Zr\langle^{H.}_{D.}D \rightarrow \rangle Zr{-}D + HD. \qquad (8)$$

It has been suggested that the exchange of hydride hydrogen with the hydrogen atoms of the alkyl group takes place intramolecularly with formation of zirconium-fulvene derivatives [reaction (9)] or via

an intermolecular pathway [reaction (10)]:



(9)

(10)

If the methyl group in the cyclopentadienyl ligand is replaced by the bulky silyl group SiR_3, then hydrogen exchange proceeds only via reaction (8) without involving the cyclopentadienyl rings of the hydride complex.[45]

4. The participation of the solvent in the decomposition of Cp_2MR_2

Comparison of the products of the thermal decomposition of Cp_2MR_2 without a solvent and in solutions in hydrocarbons (benzene, toluene) shows that the decomposition processes are similar.[6,10] Two pathways leading to the formation of RH are observed in both cases—with participation of the hydrogen atoms of the Cp rings and with participation of σ-linked groups. In the thermal decomposition of deuteriated Cp_2MR_2, both in solutions and in the solid state, the isotopic composition of RH is approximately the same. In most studies on the thermal decomposition of Cp_2MR_2 in deuterium-containing hydrocarbon solvents, it has been noted that the solvents do not participate in the RH formation process.[7,40] The small amounts of RD detected in this case may indicate the occurrence of hydrogen exchange between the solvent and RH.

The participation of oxygen-containing solvents in the decomposition of the complexes Cp_2MR_2 has been established and has been confirmed by the isolation of RD [for example, in the decomposition of Cp_2MR_2 in THF-d_8 or $(C_2D_5)_2O$ [7,40]] and also by the change in the isotopic composition of RH on passing from hydrocarbon solvents to ethers in the thermal decomposition of deuteriated compounds.[10] Solvents such as tetrahydrofuran (THF) and diethyl ether readily form adducts with various transition metal compounds. It has been established that the ligand bound in the complex is an additional donor of hydrogen in the formation of RH.

The products of the thermal decomposition of Cp_2MR_2 in chlorine-containing solvents such as CCl_4 and $CHCl_3$ differ from the decomposition products in hydrocarbons (Table 6). The thermal decomposition of Cp_2MR_2 in $CHCl_3$ and CCl_4 affords a high yield of RCl and Cp_2MCl_2 together with RH.[10,46]

Experimental data show that the thermal decomposition of Cp_2MR_2 in chlorine-containing solvents includes the stage involving the decomposition proper of the compounds (both in the decomposition without a solvent and in hydrocarbon solvents) and the stages involving the interaction of the chlorine-containing solvent with the initial compound or with its thermal decomposition product. It has been suggested that, together with the radical pathway, there exists a carbene decomposition pathway. The relative contributions of these pathways depend on the nature of the metal. The contribution of the carbene pathway is insignificant for M = Ti or Zr, increasing somewhat for M = Hf.[10,46]

Table 6. Thermal decomposition of Cp_2MR_2 in chlorine-containing solvents.

Compound	Decomposition conditions			Decomposition products, mol/mol of starting material				Refs.
	solvent	T, °C	t, h	RH	RCl	Cp_2MCl_2	$(CCl_3)_2$	
$Cp_2Ti(CH_3)_2$	$CHCl_3$	70	24	1.90	Нет	0.80	not determined	[4]
$Cp_2Ti(C_6H_5)_2$	$CHCl_3$	70	24	1.80	»	0.81	»	[4]
	CCl_4	80	20	1.20	0.60	0.24; 0.68 $CpTiCl_3$	nil	[7]
$Cp_2Zr(CH_3)_2$	$CHCl_3$	150	100	1.90	0.05	0.80	»	[46]
	CCl_4	150	100	1.30	0.65	0.72	»	[46]
$Cp_2Zr(C_6H_5)_2$	$CHCl_3$	150	100	1.20	0.62	0.73	»	[46]
	CCl_4	150	100	1.30	0.60	0.65	»	[46]
$Cp_2Hf(C_6H_5)_2$	CCl_4	150	8	0.72	0.22	0.81	0.41; 0.39 $(CHCl_3)$	[10]

III. Thermal decomposition of vanadium compounds

1. Thermal stability and decomposition products

The thermal stability of the biscyclopentadienyl compounds of trivalent vanadium Cp_2VR [R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or $CH_2C(CH_3)_3$] is determined by the nature of the σ-substituent.[47] Cp_2VCH_3 is the most stable. The presence of β-hydrogen atoms in the alkyl chain reduces sharply the stability of the compounds as a consequence of the ease of the elimination reaction with participation of these atoms.

In the series of tetravalent vanadium compounds Cp_2VR_2 (R = CH_3, C_2H_5, or $CH_2C_6H_5$), the benzyl derivative has the lowest stability, the half-life in toluene at 20 °C being 30 min. The highest thermal stability is shown by $Cp_2V(CH_3)_2$. This compound is thermally stable at room temperature for a long time. According to DTA data, the decomposition of the complex $Cp_2V(CH_3)_2$ is observed above 122 °C with an exothermic heat change,[48,49] In terms of its thermal stability, $Cp_2V(CH_3)_2$ resembles the monosubstituted derivative Cp_2VCH_3. The substitution of a methyl group in $Cp_2V(CH_3)_2$ by chlorine reduces sharply the stability of the compound. The mixed derivative $Cp_2V(CH_3)Cl$ begins to decompose at 87 °C (according to DTA data).[50]

The thermal decomposition of Cp_2VR (R = CH_3 or Ar), $Cp_2V(CH_3)Cl$, and $Cp_2V(CH_3)_2$ without a solvent and in solutions in hydrocarbons or THF leads to the elimination of approximately 0.5 mol of RH per σ-linked group. The principal vanadium-containing decomposition products of these compounds are biscyclopentadienyl compounds, whose yield is 0.6–0.8 mol per mole of the initial compound. The composition of the decomposition product has been established mass-spectrometrically. The decomposition products of Cp_2VR and Cp_2VR_2 are mixtures of vanadocene and its substituted derivatives $Cp(C_5H_4R)V$ and $(C_5H_4R)_2V$. [49,51] The decomposition of $Cp_2V(CH_3)Cl$ results in the formation of Cp_2VCl and its methyl derivatives.[50]

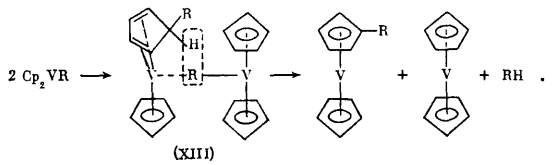
The migration of the bulky organoelemental group to the cyclopentadienyl ring has been demonstrated in the thermal decomposition of the biorganoelemental compound $Cp_2VGe(C_2H_5)_3$. The compound $Cp[C_5H_4Ge(C_5H_5)_3]V$ was isolated and characterised as a result of the reaction.[52]

2. Thermal decomposition pathways

Comparison of the compositions of the products of the thermal decomposition of the biscyclopentadienyl compounds of titanium and vanadium demonstrates a sharp difference between the decomposition pathways. In the decomposition of the vanadium compounds, the cleavage of the metal–carbon σ-bond takes place with retention of the sandwich structure, some of the σ-linked groups passing to the Cp ring.

In the thermal decomposition of vanadium compounds containing deuterium in the cyclopentadienyl rings, mainly RD and the vanadocenes $(C_5D_5)_2V$, $(RC_5D_4)(C_5D_5)V$, and $(RC_5D_4)_2V$ are formed.[49] The preferential involvement of the Cp rings as donors of hydrogen atoms in the formation of RH as well as the high yield of vanadocene and its substituted derivatives show that the formation of RH and the migration of the group R to the Cp ring are components of a single process.

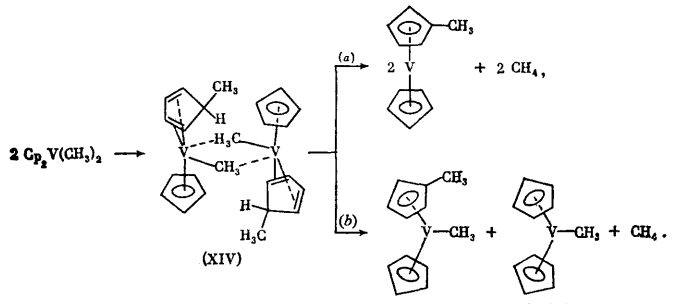
It has been suggested[49,52] that the decomposition of Cp_2VR is preceded by an intermolecular interaction leading to the dinuclear complex (XIII) with the η^4-alkyl(aryl)cyclopentadienyl ligand. The main pathway in the reaction of the complex (XIII) involves the elimination of RH, vanadocene, and its substituted derivative:



(XIII)

The isolation of small amounts of CpR indicates the occurrence of a side reaction of the complex (XIII) via a pathway involving the rupture of the V–η^4-CpR bond.

The decomposition of $Cp_2V(CH_3)_2$ is preceded by the formation of the dinuclear complex (XIV), which then decomposes via two pathways:[49]



(XIV) (XVa) (XVb)

The σ-derivatives formed via pathway (*b*) are unstable under the reaction conditions and decompose in accordance with the scheme presented above.

The formation of intermediate dinuclear complexes between the initial compounds and the vanadocene produced has also been postulated in the decomposition of Cp_2VR_n. This is indicated by the evolution of deuteriomethane in the thermolysis of an equimolar mixture of $Cp_2V(CH_3)_n$ + $Cp_2Vd\text{-}d_{10}$ and of products containing methyl groups in the deuteriated cyclopentadienyl ring.[49] The formation of di- and poly-methylvanadocenes in the thermolysis of $Cp_2V(CH_3)_n$ (n = 1,2) can be explained by the existence of the dinuclear complexes.

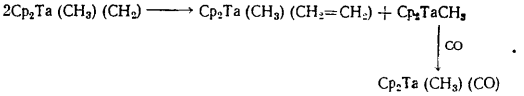
IV. Thermal decomposition of niobium and tantalum compounds

The thermal decomposition of the biscyclopentadienyl compounds of niobium and tantalum has been investigated for only a few examples. The compounds Cp_2NbR_2 (R = CH_3 or C_6H_5) decompose at temperatures close to those of the decomposition of compounds of the type Cp_2TiR_2.[53] The decomposition of Cp_2NbR_2 leads to the elimination of the σ–linked groups in the form of RH (1.3–1.8 mol). Treatment of the solid residue from the decomposition with HCl affords up to 10% of Cp_2NbCl_2.[53,54] The above products indicate the similarity of the thermal decomposition reactions of the niobium compounds and compounds of the titanium subgroup but not the vanadium subgroup elements.

The formation of C_6D_5H alone in the decomposition of $Cp_2Nb.(C_6D_5)_2$ shows that the cyclopentadienyl rings are the source of hydrogen atoms for the formation of RH. The abstraction of hydrogen from the Cp ring takes place mainly intramolecularly. This is indicated by the thermolysis of an equimolar mixture of $Cp_2Nb(C_6H_5)_2$ and $Cp_2Nb(C_6D_5)_2\text{-}d_{10}$. In contrast to the titanium analogue, the compound $Cp_2Nb(C_6H_5)_2$ does not react with tolane. This fact confirms that the decomposition of the niobium derivative does not involve the elimination of hydrogen from neighbouring phenyl groups and that a complex similar to the complex (III) is not formed.

Unfortunately there are as yet no experimental data indicating the pathway followed in the abstraction of hydrogen atoms from the cyclopentadienyl ring and in the elimination of RH. However, the existence of niobium hydride derivatives of the type $[Cp(C_5H_4)NbH]_2$ as well as the ease of the conversion of 'niobocene' into the hydride complex[55] show that in the case of titanium compounds too RH can be eliminated with participation of hydride hydrogen.

There are several examples of thermal decomposition reactions of tantalum and niobium complexes occurring with retention of the biscyclopentadienyl structure of the compounds. Thus it has been shown that the methyl complex of tantalum $Cp_2Ta(CH_3)(CH_2)$ decomposes slowly at room temperature via the mechanism



When $Cp_2Nb(C_2H_5)(C_2H_4)$ is heated, ethylene is readily split off. Subsequent β-elimination leads to the formation of $Cp_2Nb.(C_2H_4)H$.[56]

V. Photolytic decomposition of titanium and vanadium subgroup compounds

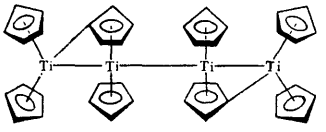
The photolytic decomposition of biscyclopentadienyl compounds of the titanium and vanadium subgroups differs from the thermal reactions already examined. EPR study of the photolysis of the methyl derivatives of titanium, zirconium, and hafnium $Cp_2M(CH_3)_2$

has led to the conclusion that the main stage of the photolysis is the homolytic cleavage of the M–CH_3 σ-bond with formation of intermediate compounds of the trivalent metal, which reacts both via the pathway involving the homolytic dissociation of a second M–CH_3 bond and via the pathway involving the intramolecular elimination of methane:[57–59]

$$Cp_2M(CH_3)_2 \xrightarrow{h\nu} Cp_2MCH_3 + {}^{\cdot}CH_3 ,$$
$$\downarrow \qquad\qquad \downarrow$$
$$\text{«}Cp_2M\text{»} + {}^{\cdot}CH_3 \qquad Cp(C_6H_4)M + CH_4 .$$

This course of the process has been confirmed by the isotopic composition of the methane evolved in the photolysis of $Cp_2Ti(CD_3)_2$ in C_6H_6 ($CD_3H : CD_4 = 2.5 : 1$).[60]

The photolysis of $Cp_2M(CH_3)_2$ (M = Ti or V) results in the formation of black pyrophoric oligomeric or polymeric products containing both cyclopentadienyl rings and C_5H_4 fragments. The so called 'titanocene', obtained in the photolysis of $Cp_2Ti(CH_3)_2$, has been most thoroughly investigated. Its treatment with gaseous HCl results in the formation of Cp_2TiCl_2 as the main product. In addition, $CpTiCl_3$ and $(C_5H_4Cl)_2TiCl$ were isolated. Its reaction with Br_2 affords predominantly $CpTiBr_3$ and Cp_2TiBr. Small amounts of $Cp(C_5H_4Br)_2TiBr$ and $Cp(C_5H_4Br)TiBr_2$ were obtained. On the basis of these data, it has been suggested that the 'titanocene' formed in the photolysis has the following structure:[61]



The photolysis of $Cp_2Ti(CH_3)_2$ initiates the free-radical polymerisation of methyl methacrylate. The low-valence complex (XVI) is formed in the first stage of the polymerisation reaction (via a cryptoradical mechanism or via the preliminary transfer of hydrogen from the Cp ring to the metal). In the presence of methyl methacrylate (MMA), the complex (VI) generates a radical:

$$Cp_2Ti(CH_3)_2 \xrightarrow{-CH_4} \underset{\textbf{(XVI)}}{Cp(C_5H_4)TiCH_3} \xrightarrow{MMA} Cp(C_5H_4)Ti + CH_3\dot{M}MA$$
$$\downarrow n\ MMA$$
$$\text{polymer} .$$

The polymer obtained in the photolysis of $Cp_2Ti(^{14}CH_3)_2$ in MMA contains on average about one ^{14}C atom per chain. It has also been established that the tritium atoms in the cyclopentadienyl rings of $Cp_2Ti(CH_3)_2$-t_{10} enter into the composition of the polymer formed as a result of the photolysis.[62]

In contrast to $Cp_2Ti(CH_3)_2$, biphenyl is formed in the photolysis of the phenyl analogue in benzene in an amount of 1.2 mol per mole of the initial compound.[63] This finding clearly demonstrates that the solvent participates in the formation of biphenyl. The photolysis of $Cp_2Ti(C_6H_5)_2$ in C_6D_6 yielded 46% of C_6H_5–C_6H_5 and 54% of Ph–Ph-d_5. The photolysis of $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ in benzene resulted in the formation of toluene (0.11 mol), 4-methylbiphenyl (0.11 mol), and 4,4-dimethylbiphenyl (0.36 mol) together with the 'titanocene'. Under analogous conditions, toluene (0.35 mol), 3-methylbiphenyl (0.35 mol), and 3,3-dimethylbiphenyl (0.21 mol) were obtained in the photolysis of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$. The data presented show that there are two completing pathways in the photolytic decomposition of aryltitanium compounds:

$$Cp_2TiAr_2 \xrightarrow{h\nu} \text{«}Cp_2Ti\text{»} + 2Ar^{\cdot} \xrightarrow[-H]{C_6H_6} Ar{-}C_6H_5 ,$$
$$\text{«}Cp_2Ti\text{»} + Ar{-}Ar .$$

The first pathway involves the homolytic cleavage of the Ti–Ar σ-bond and the generation of Ar radicals, which can abstract a hydrogen atom from the solvent or from the Cp ring or can enter into a homolytic substitution reaction with the solvent—benzene. The second pathway involves the reductive elimination reaction which leads to the formation of biaryls.[63]

In contrast to the titanium analogues, in the photolysis of diarylzirconocenes, the contribution of the reductive elimination reaction increases. This is confirmed by the high yield of 4,4-dimethylbiphenyl formed in the photolysis of $Cp_2Zr(p\text{-}CH_3C_6H_4)_2$ in benzene.[64]

The intermediate aryne complexes are not formed in the photolysis of titanium and zirconium compounds via the abstraction of an *ortho*-hydrogen atom from the aryl ligand, which is indicated by the absence of isomeric biphenyls among the reaction products.[64]

The study of the photolysis of the aryl derivatives Cp_2ZrAr_2 (Ar = C_6H_5 or $C_6H_5CH_2$) by the EPR method demonstrated the presence of a stage involving the homolytic cleavage of the Zr–Ar bond, as in the decomposition of the methyl derivatives. The compounds Cp_2ZrAr formed in this stage have been detected as complexes with phosphines.[65]

The photolysis of $Cp_2Ti(CH_3)_2$ and Cp_2TiAr_2 in the presence of CO leads to the formation of $Cp_2Ti(CO)_2$ in 50–60% yield.[63,66] The carbonyl groups in the complex $Cp_2Ti(CO)_2$ are capable of being exchanged for the molecules of gaseous carbon monoxide in hexane [reaction (11)].[67] The photolysis of $Cp_2Ti(CO)_2$ in the presence of an excess of PF_3 affords $Cp_2Ti(PF_3)_2$ [reaction (12)].

$Cp_2Ti(CO)PR_3$ is formed in the photolytic or thermal reaction of $Cp_2Ti(CO)_2$ with PR_3 (R = C_2H_5 or C_6H_5) in hydrocarbon solvents [reaction (13)]:[67]

$$Cp_2TiR_2 \xrightarrow{h\nu,\ CO} Cp_2Ti(CO)_2 \begin{cases} \xrightarrow[\leftarrow]{h\nu,\ C^{18}O} Cp_2Ti(CO)C^{18}O \xrightleftharpoons[-CO]{C^{18}O} Cp_2Ti(C^{18}O)_2 , & (11) \\ \xrightarrow[\leftarrow]{h\nu,\ PF_3} Cp_2Ti(CO)PF_3 \xrightleftharpoons[-CO]{PF_3} Cp_2Ti(PF_3)_2 , & (12) \\ \xrightarrow[\leftarrow]{h\nu \text{ or } \Delta,\ PR_3} Cp_2Ti(CO)PR_3 . & (13) \end{cases}$$

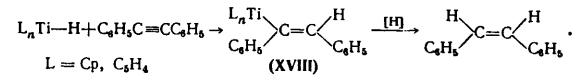
The photolysis of $Cp_2M(CH_3)_2$ and Cp_2MAr_2 (M = Ti or Zr) in the presence of diphenylacetylene leads to the metallacycles (XVII):[63,66,68]

$$Cp_2MR_2 \xrightarrow[C_6H_5C\equiv CC_6H_5]{h\nu} Cp_2M(C_6H_5)_4$$
$$\textbf{(XVII)}$$

A similar complex can be obtained by the reaction of Cp_2TiCl_2 with metallic magnesium and tolane.[68,70] In both cases an unstable metlalocene is formed in the first stage and then reacts with an alkyne, which leads to the complex (XVII).

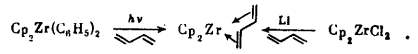
The photolysis of titanium and zirconium compounds differs from the thermal reaction, which leads to the formation of 1,1-bis-(cyclopentadienyl)-2,3-diphenylbenzotitanole or the analogous zirconole via an intermediate aryne complex.

Apart from compound (XVII), organic products such as diacetylenes and *cis*- and *trans*-stilbenes are formed in the photolysis of Cp_2TiAr_2 in the presence of diphenylacetylenes. Stilbenes are also formed in the photolysis of $Cp_2Ti(CH_3)_2$ in the presence of diphenylacetylene but in a lower yield. The formation of the reduction products, namely *cis*- and *trans*-stilbenes, indicates the presence of hydride intermediates in the photolysis process, which can be formed via the transfer of a hydrogen atom from the Cp ring to the metal:



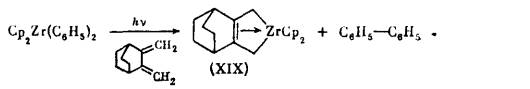
The first stage of the process involves the insertion of acetylene into the M–H bond with formation of the intermediate σ-complex (XVIII), which affords stilbene in the presence of a hydrogen donor.[63]

The stable complex $Cp_2Zr(\eta^4\text{-}trans\text{-}CH_2=CHCH=CH_2)$ is formed in the photolysis of $Cp_2Zr(C_6H_5)_2$ in the presence of *trans*-butadiene. It can also be obtained by reducing Cp_2ZrCl_2 with lithium in the presence of butadiene:[71]



When a solution of $Cp_2Zr(\eta^4\text{-}trans\text{-}CH_2\text{–}CHCH=CH_2)$ is irradiated or heated in C_6D_6, an equilibrium is established between the isomeric *trans*- and *cis*-forms of the diene complexes of zirconocene.[71]

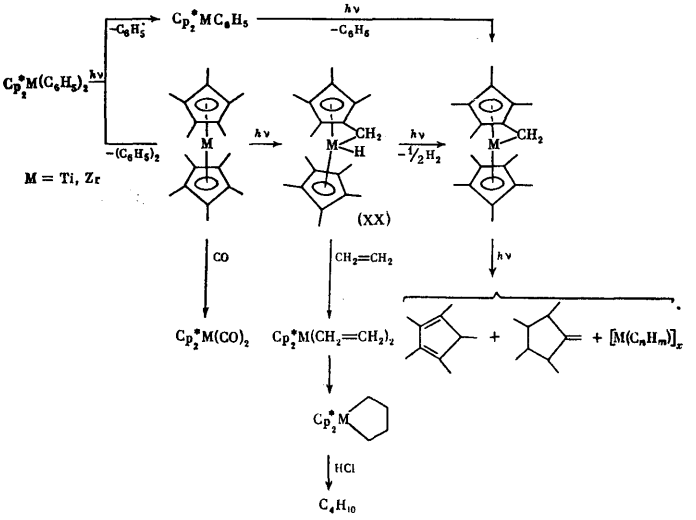
The photolysis of $Cp_2Zr(C_6H_5)_2$ in toluene in the presence of 2,3-bis(methylene)bi-cyclo[2.2.2]octane leads to the complex (XIX) in 65% yield:[72]



The photolysis of $Cp^*_2M(C_6H_5)_2$ (M = Ti or Zr)[73] as well as the unsubstituted derivatives proceeds via two main pathways: reductive elimination and homolysis. The isotopic composition of the biphenyl formed in the photolysis of $Cp^*_2M(C_6H_5)_2$ (M = Ti or Zr) in C_6D_6 established that the contribution by the reductive elimination is 97% for M = Ti and 25% for M = Zr.

The reductive elimination reaction of $Cp^*_2M(C_6H_5)_2$ leads to the unstable permethylmetallocene, which is converted into compound (XX) via the abstraction of hydrogen from the ring methyl group. Oligomeric metal-containing products as well as 2,3,4,5-tetramethylfulvene and pentamethylcyclopentadiene are formed ultimately.

A dicarbonylmetallocene is formed in the photolysis of the permethyl derivative in the presence of CO, as in the case of the unsubstituted compounds. The metallacycle is produced in the presence of ethylene (35 atm, –20 °C). The homolytic cleavage of the M–C_6H_5 σ-bond takes place to a slight extent even at low temperatures. The phenyl radicals formed have been detected by EPR as adducts with spin-trapping agents:



Comparison of the results of the photolysis of the permethyltitanocene derivatives and the unsubstituted compounds demonstrates an appreciable increase in the contribution of their reductive elimination with introduction of methyl substituents into the Cp ring. Such a change in the relative contributions of the photolytic pathways is due both to the steric influence of the bulky methyl group and to the absence from the rings of mobile hydrogen atoms capable of functioning as hydrogen donors in the homolytic decomposition. For the zirconium derivative, in which the central atom has a larger atomic radius compared with the titanium complex, the steric effect of the ligands is less significant.[73]

The photolysis of $Cp_2V(CH_3)_n$ (n = 1,2) and $Cp_2Nb(CH_3)_2$ in hydrocarbon solvents leads to the cleavage of the metal–carbon σ-bond. The main gaseous product is methane. Studies carried out with deuterium-containing compounds as well as C_6D_6 have shown that the source of hydrogen for the formation of methane may be the cyclopentadienyl rings, methyl groups, and solvents. As a result of the photolysis, the biscyclopentadienyl structure breaks down, which is indicated by the absence of vanadocene from the photolysis products.[74]

The photolysis of $Cp_2V(CH_3)_n$ (n = 1,2) and $Cp_2Nb(CH_3)_2$ in pentane in the presence of CO affords low yields of the carbonyl complexes $CpV(CO)_4$ and $CpNb(CH_3)(CO)$ respectively.[74]

VI. Exchange of cyclopentadienyl ligands

Under the conditions of photolysis in solution in toluene, the dichlorides of the biscyclopentadienyl derivatives of titanium, zirconium, and hafnium are capable of exchanging the cyclopentadienyl ligands:[75–77]

$$d_{10}\text{-}Cp_2MCl_2 + Cp_2MCl_2 \rightleftarrows 2Cp(d_5\text{-}Cp)MCl_2.$$

This process is not only photolytic but also thermal, its rate increasing with temperature.

The thermal exchange of the cyclopentadienyl ligands occurs also in the $Cp_2V\text{-}d_{10}\text{–}Cp_2M$ system:[78]

$$d_{10}\text{-}Cp_2V + Cp_2M \rightleftarrows d_5\text{-}CpVCp + d_5\text{-}CpMCp + d_{10}\text{-}Cp_2M + Cp_2V;$$
$$M = V, Cr, Mn.$$

The rate of this exchange depends on the nature of the metal in Cp_2M and increases in the sequence V < Cr < Mn.

The exchange of the cyclopentadienyl ligands can take place between metallocenes in different oxidation states. Thus the occurrence of the exchange in the Cp_2VCl–$(C_5H_4CH_3)_2VCl_2$, Cp_2V–$(C_5H_4CH_3)_2VCl_2$, and Cp_2V–$(C_5H_4CH_3)_2VCl$ systems has been demonstrated. The rate of exchange increases significantly on heating to 70 °C.[75]

Several mechanisms which can account for the exchange of the Cp ligands in metallocenes have been proposed.[75,78] In particular, a certain amount of ionic character of the bonds in the metallocenes Cp_2M (M = V, Cr, or Mn), manifested in the reactions with iron chloride and also in the rapid exchange with LiC_5D_5, indicates the possibility that the exchange reaction may proceed via an ionic pathway:

$$Cp_2M \rightleftarrows C_5H_5^- + CpM^+,$$

$$C_5H_5^- + d_{10}\text{-}Cp_2M \rightleftarrows d_5\text{-}CpMCp + C_5D_5^- .$$

The rate-determining stage of the exchange in the postulated mechanism is the dissociation into ions, whose rate is directly proportional to the amount of ionic character of the molecules. Comparison of the rates of exchange shows that the exchange process involving compounds with a more pronounced ionic character of the bonds is faster. Thus, in the systems Cp_2M-d_{10}–Cp_2M (M = V, Cr, or Mn), a faster exchange is observed in the case of manganocene, for which the ionic character of the bonding of the Cp ligands is more clearly manifested.

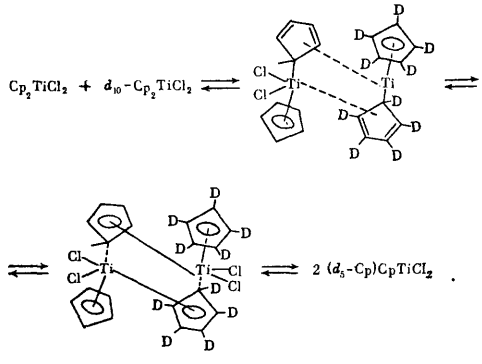
A radical pathway is possible for the photolytic ligand exchange:

$$(C_5H_5)_2V \rightleftarrows C_5H_5^{\cdot} + C_5H_5V^{\cdot},$$

$$C_5H_5^{\cdot} + (C_5D_5)_2V \rightleftarrows (C_5H_5)(C_5D_5)V + C_5D_5^{\cdot} .$$

The radical exchange of the Cp rings in Cp_2MCl_2 has been confirmed by experiments on the photolysis of Cp_2TiCl_2 by the EPR method, where the Cp radical was detected in the form of adducts with spin trapping agents.[76,80]

Together with the radical mechanism of the exchange, there exists an intermolecular bridge mechanism, which presupposes a change in the character of the bonding of the cyclopentadienyl ring during the exchange process:[77,79]



The exchange of the cyclopentadienyl ligands may be accompanied by the thermolysis of the compounds Cp_2MR_2. Such a process has been noted, for example, in the decomposition of the compounds $Cp_2V(CH_3)_n$.[49]

VII. Thermal decomposition with rupture of metal–cyclopentadienyl ring bonds

The thermal cleavage of the $(\eta^5\text{-}C_5H_5)$–M bonds occurs under more severe conditions than those leading to dissociation of the metal–carbon bond. The thermolysis of mixed sandwich-covalent titanium and vanadium derivatives takes place in the temperature range 100–200 °C. The contribution by the reactions involving the dissociation of the $M\text{–}C_5H_5$ bonds is then insignificant. The strength of this bond has also been measured thermochemically.[81] The average $M\text{–}C_5H_5$ dissociation energies in different titanium, zirconium, and vanadium compounds are in the range 63–88 kcal mol^{-1}.

The $M\text{–}C_5H_5$ bond dissociation energies of metallocenes of the 3*d* series have been estimated thermodynamically.[82] Similarly calculations have shown that dissociation in accordance with the equation

$$Cp_2M \rightarrow 2C_5H_5^{\cdot} + M \qquad (14)$$

is possible for vanadocene only at temperatures above 830 °C ($\Delta\overline{G} < 0$). In a real experiment, the thermal decomposition of metlalocenes occurs at a lower temperature (350–450 °C) and not via pathway (14) alone.

The study of the kinetics of the thermal decomposition of metallocenes Cp_2M (M = V, Cr, or Mn) made it possible to establish the following catalytic series:

$$Cp_2V > Cp_2Cr > Cp_2Mn.$$

The thermal stability diminishes in parallel with the decrease in the $M\text{–}C_5H_5$ bond strength.[83]

The thermal stability of bis(cyclopentadienyl)metal dichlorides Cp_2MCl_2 (M = Ti, Zr, or Hf) also depends on the nature of the central atom and increases in the sequence

$$Cp_2TiCl_2 < Cp_2ZrCl_2 < Cp_2HfCl_2.$$

The thermal decomposition of vanadocene has been examined in greatest detail.[84] The pyrolysis of Cp_2V in a static system (450–510 °C) takes place mainly with evolution of hydrogen and cyclopentadiene. Apart from the products indicated, methane, benzene, and naphthalene are formed in the pyrolysis of vanadocene. The composition of the volatile products depends on temperature and the duration of heating. Thus at low temperatures and for short heating, the formation of an appreciable amount of cyclopentadiene is observed. With increase in temperature and heating time, the yield of C_5H_6 falls and the main volatile products of the total pyrolysis of vanadocene are hydrogen and methane. In the pyrolysis of Cp_2V in a flow system (800–900 °C), considerable amounts of acetylene and ethylene are formed in addition to the products indicated.

The data presented show that the dehydrogenation of the cyclopentadienyl and the dissociation of a C–C bond are observed in the decomposition of vanadocene together with the metal–cyclopentadienyl bond cleavage reaction. The latter can occur via radical or molecular pathways. The radical pathway is more probable when the pyrolysis is carried out at low pressures and in the bulk of the reactor. In this case, the homolysis of the bond leads to the formation of the cyclopentadienyl radical, which abstracts a hydrogen atom from the initial molecule with the consequent evolution of C_5H_6.

In the decomposition via the molecular pathway, cyclopentadiene is formed intra- or inter-molecularly with participation of the Cp ligand and the hydrogen atom which had been transferred to the metal from another Cp group beforehand:

$$Cp_2V \rightarrow Cp(C_5H_4)VH \rightarrow C_5H_6 + (C_5H_4)V.$$

The elimination of hydrogen takes place either by the direct dissociation of a ring C–H bond or via the splitting off of a hydride atom:

$$Cp_2V \rightarrow Cp(C_5H_4)VH \rightarrow H_2 + (C_5H_4)_2V.$$

The final products of such reactions are polymeric species containing the metal and the dehydrogenated rings.

Analogous reactions occur also in the decomposition of the dichlorides Cp_2MCl_2 (M = Ti, Zr, or Hf). As a result of the presence of a strong M–Cl bond in these compounds, the main reaction in the range 400–800 °C is the dehydrogenation of a cyclopentadienyl ring with evolution of hydrogen.[6,85]

It is notable that the higher rate of dehydrogenation and dissociation of the C–C ring bond compared with the rate of the reaction involving dissociation of the M–Cp bond virtually precludes the segregation of the pure metal under the conditions of the thermal decomposition of the compounds indicated. This is confirmed by thermochemical data. The calculated thermodynamic functions (ΔG, ΔH, ΔS) for the most probable reactions show that the reaction leading to the formation of a carbide is most probable for Cp_2MCl_2.[82,86] Indeed, the carbides of the corresponding metals are formed in the high-temperature (900 °C) decomposition of Cp_2MCl_2 (M = Ti or Zr) in a hydrogen atmosphere. Titanium carbides are also formed in the high temperature decomposition of the sandwich-covalent compounds Cp_2TiR_2 (R = CH_2 or C_6H_5).[85]

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Analysis of the results of studies of the thermal and photochemical reactions of the sandwich-covlent derivatives of titanium and vanadium subgroup metals permitted the conclusion that the π-cyclopentadienyl ligands play an appreciable role in the splitting of the metal–carbon σ-bond. The processes occurring in the thermal and photochemical reactions can be regarded as model processes in the study of reduction or catalytic reactions with participation of these compounds.

During the preparation of the manuscript for the press, studies were published on the intermolecular activation of the C–H bonds of the substituents in the cyclopentadienyl rings in the thermolysis of the compounds $(C_5H_4R)_2Zr(C_6H_5)_2$ [R = $C(CH_3)_2C_6H_5$],[87] $(C_5H_3R_2)_2M(CH_3)_2$ (R = t-C_4H_9, M = Ti or Zr),[88] and $Cp^*_2Zr(C_6H_5)_2$.[89] It has been established that such activation of the C–H bonds of the alkyl groups of the Cp rings can occur as a result of low-temperature reactions of decamethylmetallocenes[90,91] and on dissociative ionisation of $(C_5H_4Alk)_2ZrCl_2$.[92]

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