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THERMAL DECOMPOSITION OF ORGANO-BIELEMENTAL VANADIUM COMPOUNDS $Cp_2V(ER_3)$ ($ER_3 = GeEt_3, SnEt_3, CH_2SiMe_3, SeGeEt_3$) *

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Summary

The thermal decomposition of a number of organo-bielemental vanadium compounds with the general formula $Cp_2V(ER_3)$ ($ER_3 = GeEt_3, SnEt_3, CH_2SiMe_3, SeGeEt_3$) has been investigated in solids and in solutions. The main decomposition products of $Cp_2V(SnEt_3)$ are vanadocene and hexaethyldistannane. Et_3GeH, Et_3GeCp, Cp_2V and $CpV(C_5H_4GeEt_3)$ are formed from $Cp_2V(GeEt_3)$ decomposition. Isolated $CpV(C_5H_4GeEt_3)$ is characterized by IR and mass spectra. The decomposition of $Cp_2V(CH_2SiMe_3)$ is accompanied by Me_4Si, Cp_2V and $CpV(C_5H_4CH_2SiMe_3)$ formation, the latter is identified from the mass spectrum. Triethylgermane, vanadocene, and a diselenide of vanadium are isolated on decomposition of $Cp_2V(SeGeEt_3)$. Based upon the experimental data, mechanisms for the decomposition are proposed.

Introduction

Some bis-cyclopentadienylvanadium compounds such as Cp_2VR (R = alkyl, aryl, CH_2SiMe_3, $N(SiMe_3)_2$) were obtained in the reactions of Cp_2VCl with RMgX or RLi [1,2]. Organo-bimetallic compounds such as $Cp_2V(GeR_3)$ (R = Et, Ph) were obtained by oxidative addition of $(R_3Ge)_2Cd$ to vanadocene [3]. Sulfur and selenium are easily inserted into the vanadium—germanium bond giving $Cp_2V(SGeR_3)$ and $Cp_2V(SeGeR_3)$ [4]. $Cp_2V(SnEt_3)$ was obtained through Et_3SnH interaction with Cp_2VMe_2 or $Cp_2V(CH_2SiMe_3)$ [2,5]. All the compounds prepared are easily oxidized. Both the vanadium—carbon and vanadium—element bonds are cleaved by the action of alcohols and acids. All the compounds mentioned above are stable even at room temperature. Earlier, the ther-

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* In honor of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry.

mal decompositions of such compounds as Cp_2VR (R = alkyl, aryl) were investigated. It was established that decomposition of Cp_2VR results in the homolytical cleavage of the vanadium—carbon σ-bond with RH formation at the expense of the hydrogen of the cyclopentadienyl ring. The migration of a portion of the R ligands into cyclopentadienyl ring occurs also by thermolysis with the formation of "substituted vanadocenes" [1,6].

In this paper we report the thermal decomposition of some organo-bimetallic vanadium compounds. We wanted to establish the influence of the nature of the organo-element substituent upon the mode of thermal decomposition. $Cp_2V(CH_2SiMe_3)$, $Cp_2V(GeEt_3)$, $Cp_2V(GePh_3)$, $Cp_2V(SnEt_3)$, $Cp_2V[Sn(OPh)_3]$ and $Cp_2V(SeGeEt_3)$ were chosen as subjects of inquiry.

Results and discussion

The temperature intervals of the organo-element compound decomposition have been determined by of the DTA method. The DTA curve of $Cp_2V(SnEt_3)$ is characterized by two endothermic effects. The first reversible effect at 56°C is due to the melting of the compound. The decomposition starts at above 118°C, reaching a maximum at 139°C. $Cp_2V(GeEt_3)$ decomposition proceeds without prominent thermal effects in the temperature range of 130—150°C. The endothermic effect of $Cp_2V(CH_2SiMe_3)$ at 58°C is due to the melting of the compound. The wide exothermic effect corresponds to its decomposition at 130—170°C with a maximum at 145°C. $Cp_2V(GePh_3)$, $Cp_2V[Sn(OPh)_3]$ and $Cp_2V[N(SiMe_3)_2]$ decompose in the temperature range of 180—200°C without prominent thermal effects.

The thermal decomposition of Cp_2VER_3 is studied in solids and in toluene or tetrahydrofuran (THF) solutions.

The data of Table 1 indicate that $Cp_2V(SnEt_3)$ decomposition occurs in solids as well as in solutions with the quantitative formation of hexaethyldistannane and vanadocene.

It was interesting to clear up whether the nature of the substituent at a tin atom will influence upon the mode of thermal decomposition. For this purpose

TABLE 1

PRODUCTS OBTAINED FROM THE THERMAL DECOMPOSITION OF $Cp_2V(ER_3)$ ($ER_3 = SnEt_3$, $GeEt_3$, CH_2SiMe_3)

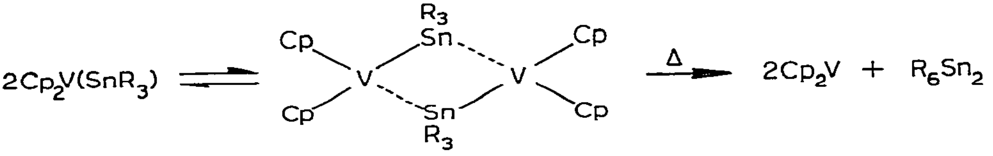
Compound	Decomposition conditions (°C, h)			Decomposition products [a]				
				$(R_3E)_2$	R_3EH	R_3ECp	Cp_2V	$CpV(C_5H_4ER_3)$
$Cp_2V(SnEt_3)$	vacuum,	140,	2	0.43	none	none	0.88	none
	toluene,	140,	2	0.45	traces	none	0.90	none
	THF,	140,	2	0.44	none	none	0.89	none
$Cp_2V(GeEt_3)$	vacuum,	150,	2	none	0.30	0.30	0.38	0.32
	toluene,	150,	2	none	0.31	0.30	0.40	0.33
	THF,	150,	2	none	0.32	0.10	0.48	0.27
$Cp_2V(CH_2SiMe_3)$	vacuum,	150,	2	traces	0.40	none	0.75 [b]	

[a] Here and further the yield is in moles per mole of initial organovanadium compound. [b] The total quantity of Cp_2V + $CpV(C_5H_4ER_3)$.

$Cp_2V[Sn(OPh)_3]$ was obtained as a result of Cp_2VCl interaction with $NaSn(OPh)_3$ in THF solution at 20°C and in a 1 : 1 molar ratio. $Cp_2V[Sn(OPh)_3]$ decomposes in vacuum at 180°C during two hours. The only vanadium-containing reaction product is vanadocene (0.88 mol). We were not successful in the identification of the organotin derivatives.

In our previous work the main decomposition products of $Cp_2M(SnEt_3)_2$ in THF solution were shown to be hexaethyldistannane and metallocene, Cp_2M (M = Ti, Zr). The bimolecular decomposition mode of the compounds indicated was proved by the ESR method [7].

Organotin compounds are capable of intermolecular association due to the presence of vacant *d*-orbitals on the outermost tin atom shell. This influences strongly the chemical reaction direction. It is beneficial for the thermal decomposition process of $Cp_2M(SnEt_3)_2$ (M = Ti, Zr) as well as $Cp_2V(SnR_3)$ to include a stage of binuclear intermediate complex formation:



(1)

It was ascertained that under certain conditions vanadocene reacts, resulting in oxidative addition with hexaalkyldistannane. By special experiments vanadocene was shown to react with an excess of hexabutyldistannane (1 : 10 molar ratio) in THF solution at 20°C. ESR spectra indicated the appearance of a tetravalent vanadium compound, $Cp_2V(SnBu_3)_2$, with isotropic parameters: g_i = 2.0030 and A_i^{51V} = 51.0 e in the reaction mixture. The tetravalent vanadium compound $Cp_2V(SnBu_3)_2$ proved to be unstable and attempts to isolate it led to the decomposition into the starting compounds: Cp_2V and Bu_6Sn_2. $Cp_2V(SnBu_3)_2$ may be supposed to decompose consecutively, including the formation of intermediate binuclear complexes. First, $Cp_2V(SnBu_3)$ is formed on decomposition of $Cp_2V(SnBu_3)_2$, which in turn decomposes to hexabutyldistannane and vanadocene. We did not succeed in isolating the compound $Cp_2V(SnBu_3)$ under the conditions of the reaction studied.

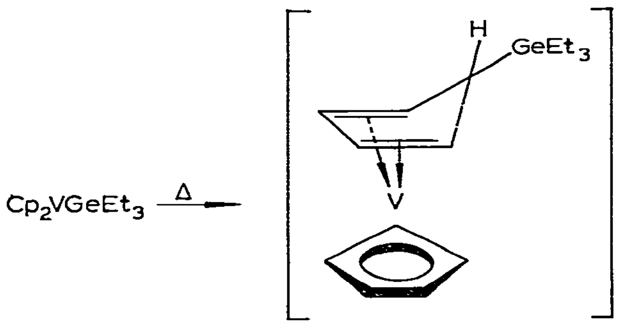
$$Cp_2V + R_3Sn{-}SnR_3 \rightleftharpoons Cp_2V(SnR_3)_2 \rightarrow \tfrac{1}{2}Sn_2R_6 + Cp_2V(SnR_3) \rightarrow \tfrac{1}{2}Sn_2R_6 + Cp_2V \tag{2}$$

The above leads to the conclusion that the only decomposition direction of organo-bielemental compounds with a vanadium—tin bond, $Cp_2V(SnR_3)_n$ (n = 1, 2; R = Et, Bu, OPh) is a bimolecular mode according to eq. 1.

It should be mentioned that vanadocene does not react even with a large excess of hexaalkyldigermanes and -disilanes in the range of temperature from 20 to 50°C and in THF solution.

The thermal decomposition of the triethylgermyl-vanadocene derivative, $Cp_2V(GeEt_3)$ resulted in the formation of a large number of products (Table 1). The isolation of substantial quantities of substituted vanadocene, $CpV(C_5H_4GeEt_3)$, points to the fact that the migration of the Et_3Ge group into cyclopentadienyl ring takes place during the thermal decomposition process of $Cp_2V(GeEt_3)$. The data of Table 1 show that the migration process does not depend upon the decomposition conditions. Such migration of an organo-element group is found for the first time in the thermal decomposition of organometallic compounds.

RH (0.50 mol), small quantities of CpR (up to 0.01 mol), Cp_2V (0.50 mol), $CpV(C_5H_4R)$ (0.30 mol) and $(C_5H_4R)_2V$ (0.10 mol) are know to be isolated from the solid and solution state thermal decomposition of Cp_2VR (R = alkyl, aryl). Therefore, alkyl and aryl groups σ-bonded to vanadium in the initial Cp_2VR migrate on thermal decomposition into the cyclopentadienyl ring with the formation of substituted vanadocene, $CpV(C_5H_4R)$ [1,6]. $CpV(C_5H_4GeEt_3)$ isolation points to the fact that on $Cp_2V(GeEt_3)$ decomposition, as well as in the case of Cp_2VR, intramolecular rearrangement occurs with transition of the σ-bonded Et_3Ge group into the cyclopentadienyl ring. In this case, an intermediate (η^5-cyclopentadienyl)(η^4-cyclopentadiene) complex (A) forms.

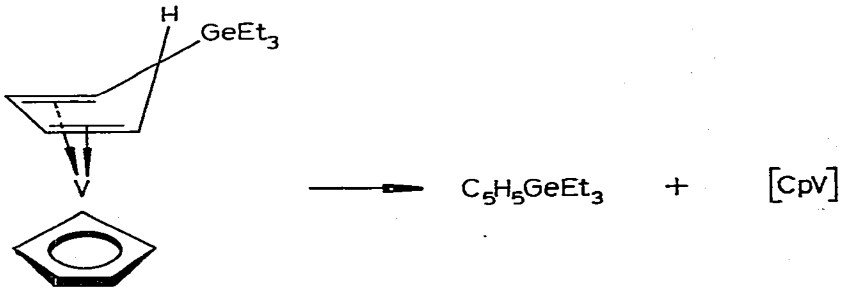


(A)

(3)

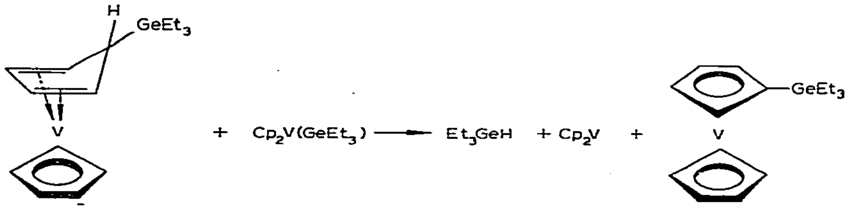
Similar additions to the cyclopentadienyl ring are known for bis-cyclopentadienyl compounds of nickel, cobalt, rhodium and iridium [8,11]. In these reactions one of the π-cyclopentadienyl ligands is transformed into a substituted cyclopentadiene one. For example, cobaltocene is capable of adding R radicals (R = CMe_2CN, CH_2Ph, C_6H_5 etc.) and giving a stable (π-cyclopentadienyl)cyclopentadienecobalt complex π-$C_5H_5CoC_5H_5R$ [8,9]. The cation $(\pi\text{-}C_5H_5)_2Rh^+$ reacts readily with RLi (R = C_5H_5, C_6H_5). In this case the addition of the R group to one of the π-cyclopentadienyl rings occurs with formation of a rhodium complex similar to complex A [10]. (π-Cyclopentadienyl)cyclopentadienenickel complexes are unstable and decompose readily to form substituted cyclopentadienes [11].

The composition and the yield of the $Cp_2V(GeEt_3)$ decomposition products indicate that complex A is unstable and decomposes in two directions under the conditions of the reactions studied. On the one hand, the isolation of triethyl(cyclopentadienyl)germanium indicates that complex A decomposes intramolecularly to form a substituted cyclopentadiene:



(4)

On the other hand the formation of triethylgermane, vanadocene and cyclopentadienyl(triethylgermylcyclopentadienyl)vanadium may be explained by the fact that complex A reacts with an initial molecule of $Cp_2V(GeEt_3)$ according to the to the total equation:

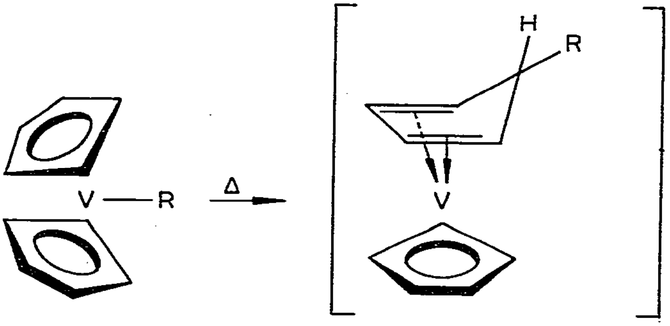


(5)

Thermal decomposition of $Cp_2V(CH_2SiMe_3)$ in the solid state yields tetramethylsilane (0.40 mol), vanadocene and $CpV(C_5H_4CH_2SiMe_3)$ (total quantity: 0.75 mol) at 180° during two hours. A change of the thermal decomposition conditions did not result in a substantial change in reaction products. So, the thermal decomposition of $Cp_2V(CH_2SiMe_3)$ gives first Me_4Si (0.16 mol) at 135°C during 0.7 h, then additionally 0.18 mol of Me_4Si at 180°C during 0.7 h; the total quantity of substituted and unsubstituted vanadocene did not exceed 0.75 mol. The monosubstituted vanadocene $CpV(C_5H_4CH_2SiMe_3)$ (*m/e* 267) is identified by mass spectrometry.

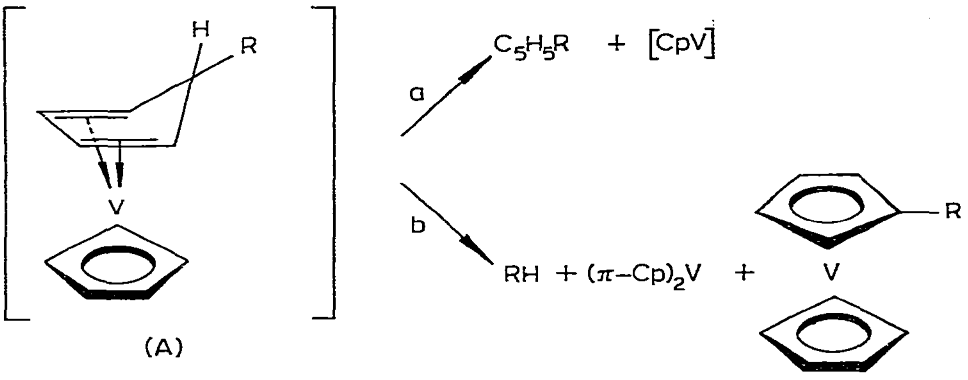
The data on the thermal decomposition of $Cp_2V(CH_2SiMe_3)$ were similar to the results of the methyl derivative decomposition: Cp_2VMe, Cp_2VMe_2 and Cp_2VMeCl under correlated conditions described earlier [6,12]. They include rearrangement with intermediate formation of a complex of type A.

The results obtained allow to compare the thermal decomposition of bis-cyclopentadienyl-vanadium derivatives to that of the organic and organoelemental substituents. In both cases the rearrangement occurs with formation of an intermediate complex (A).



(A)

Two decomposition directions of this complex are possible: a) monomolecular and b) bimolecular.



R = alkyl, aryl, CH_2SiMe_3, $GeEt_3$.

In the case of the monomolecular mechanism the abstraction of the substituted cyclopentadienyl ring and the formation of the substituted cyclopentadiene derivatives is observed. The bimolecular mode of the decomposition results in the isolation of RH, and substituted and unsubstituted vanadocenes.

Cp_2VR with organic substituents (alkyl, aryl) was earlier found to decompose through the bimolecular mechanism. Yet the monomolecular decomposition mode is observed too, but its part in the total process is small. For example, only small quantities of CpMe (up to 0.01 mol) were found on the decomposition of Cp_2VMe.

The experimental data show that for trimethylsilylmethyl-vanadocene derivative the main direction of the decomposition is bimolecular.

When passing to organo-bielemental vanadium compound $Cp_2V(GeEt_3)$ the contribution of the monomolecular mode increases considerably. This fact is confirmed by the formation of fairly high amounts of Cp_2VGeEt_3 (0.32 mol). The data of Table 1 show that in the decomposition of $Cp_2V(GeEt_3)$ the mono- and bimolecular mode of thermal degration are equivalent.

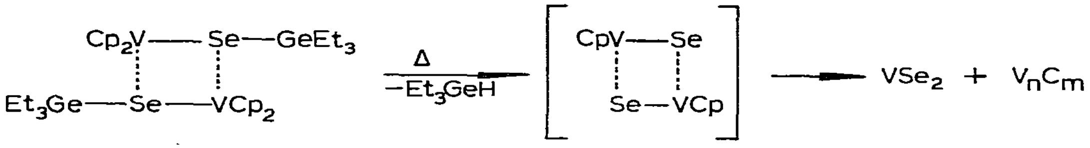
It should be noted further that monosubstituted vanadocene $CpV(C_5H_4R)$ may disproportionate according to eq. 6 under decomposition conditions, when R = alkyl, aryl:

$$CpV(C_5H_4R) \rightarrow Cp_2V + (C_5H_4R)_2V \qquad (6)$$

For example, 0.17 mol of $(C_5H_4Me)_2V$ was found from Cp_2VMe decomposition. In contrast, monosubstituted vanadocenes $CpV(C_5H_4R)$ (R = CH_2SiMe_3, $GeEt_3$) do not disproportionate according to eq. 6.

In the decomposition of stannyl-vanadocene derivatives $Cp_2V(SnR_3)$ the formation of the intermediate complex A accompanied by the migration of the σ-substituent into the cyclopentadienyl ring does not occur. The only decomposition direction is bimolecular, according to eq. 1. The thermal decomposition of the latter proceeded in a vacuum flow system at 400—450°C with the formation of triethylgermane and vanadocene, as well as vanadium carbide and diselenide, VSe_2. Unusual was the formation of diselenide, rather than vanadium selenide, in spite of the fact that in the initial compound the ratio V : Se = 1.1.

Based upon the thermal decomposition products and the solid phase composition the mechanism of the process was proposed as involving intermediate dimer complexes, in which elimination of triethylgermane, and then disproportion occurred.



In this case substituted vanadocene derivatives were not observed.

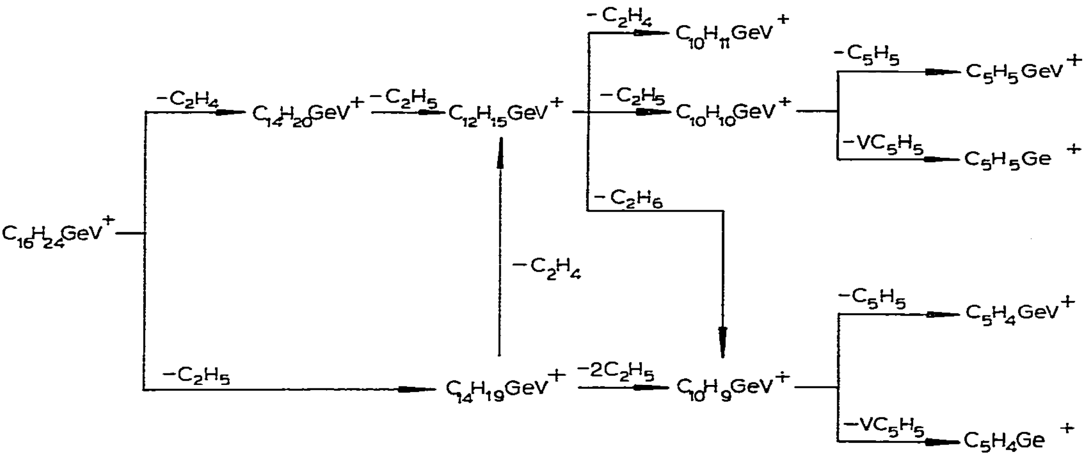
$CpV(C_5H_4GeEt_3)$, which we have obtained, was isolated individually by fractional distillation in vacuum (120°C) (10^{-3} mmHg). The complex is a dark blue, air-sensitive, viscous liquid. The compound is characterized by its IR and mass spectra (Table 2). Its IR spectrum shows the absorption bands at 810, 960, 1020, 1110 and 3100 cm^{-1}, characteristic of the substituted and unsubstituted η^5-cyclopentadienyl ring and at 700, 1380 and 1460 cm^{-1}, characteristic of the ethyl group of the Et_3Ge fragment. Its mass-spectrum has lines pertaining to a molecular ion of $C_5H_5(C_5H_4GeEt_3)V^+$ and its fragments. Based upon the lines of the respective ions in the mass-spectrum and the metastable transitions found the following mechanism is proposed for the molecular ion $(C_5H_5V\text{-}(C_5H_4GeEt_3)V^+$:

The main decomposition paths of the $C_{16}H_{24}GeV^+$ molecular ion are on the one hand elimination of ethyl groups bonded to germane, and on the other hand the elimination of the ethylene molecule. In the decomposition process of the fragment ions elimination of cyclopentadienyl ligand as well as of the C_5H_5V fragment occurs. It should be mentioned that the fragment ions, in addition to the fragmentation path considered, also lose hydrogen atoms.

TABLE 2

MASS SPECTRUM OF $(C_5H_5)V(C_5H_4GeEt_3)$ (I = relative intensity)

Ion	I(%)	Ion	I(%)
$C_{16}H_{24}GeV^+$	100.0	$C_{12}H_8GeV^+$	3.9
$C_{16}H_{23}GeV^+$	0.6	$C_{10}H_{11}GeV^+$	23.5
$C_{16}H_{22}GeV^+$	0.9	$C_{10}H_{10}GeV^+$	198.0
$C_{14}H_{20}GeV^+$	45.6	$C_{10}H_9GeV^+$	116.0
$C_{14}H_{19}GeV^+$	222.7	$C_{10}H_8GeV^+$	15.1
$C_{14}H_{17}GeV^+$	9.1	$C_{10}H_7GeV^+$	4.9
$C_{14}H_{16}GeV^+$	9.5	$C_{10}H_6GeV^+$	7.4
$C_{14}H_{15}GeV^+$	5.1	$C_{10}H_5GeV^+$	0.7
$C_{14}H_{14}GeV^+$	4.6	$C_{10}H_4GeV^+$	3.0
$C_{14}H_{12}GeV^+$	6.0	$C_8H_7GeV^+$	23.0
$C_{12}H_{15}GeV^+$	23.0	$C_8H_6GeV^+$	13.4
$C_{12}H_{14}GeV^+$	4.4	$C_5H_5GeV^+$	11.4
$C_{12}H_{13}GeV^+$	6.7	$C_5H_4GeV^+$	19.3
$C_{12}H_{12}GeV^+$	13.7	$C_6H_{15}Ge^+$	33.8
$C_{12}H_{11}GeV^+$	5.1	$C_5H_5Ge^+$	33.9
$C_{12}H_{10}GeV^+$	8.6	$C_5H_4Ge^+$	5.2



Experimental

All syntheses and reactions were carried out in an argon atmosphere or in vacuum using deoxygenated and dehydrated solvents. ESR spectra were determined with a ERA-2M radio spectrometer. Mn^{2+} in a MnO crystal lattice was used as a standard for calibration of the magnetic field. 2,2,6,6-Tetramethylpiperidinoxyl was used as a standard for defining the g factor. IR spectra were measured with a UR-20 spectrometer. The samples were prepared as suspensions in Nujol. Mass spectrometric measurements were carried out by means of a MY-1305, instrument with an accelerating voltage of 2 kV, an electron energy of 70 eV and an emission current of 1.5 mA. The differential-thermal analyses of compounds were carried out in the evacuated cells. The rate of temperature increase was 5°/min. Al_2O_3 was taken as a standard. The decomposition of compounds was carried out in evacuated ampoules equipped with a locking system for the sublimation of the decomposition products. Liquid and gaseous products were analyzed by GLC.

Preparation of bis(π-cyclopentadienyl)(triethylstannyl)vanadium

Et_3SnH (1.12 g, 5.4 mmol) in toluene (10 ml) was added to a Cp_2VMe_2 solution (0.56 g, 2.6 mmol) in toluene (20 ml). The reaction mixture was kept at room temperature for some hours. The colour of the solution changed from black-green to blue. The solvent was removed under vacuum. The residue was extracted with a toluene/hexane mixture (2/1). The solution was cooled to —78°C. Blue crystals precipitated, which were washed with cold hexane and dried under vacuum. (Yield, 0.70 g, 69%), m.p. 56°C. (Found: C, 49.92; H, 6.63; V, 12.98. $C_{16}H_{25}SnV$ calcd.: C, 49.68; H, 6.47; V, 13.17%).

Preparation of bis(π-cyclopentadienyl)(trisphenoxystannyl)vanadium

$NaSn(OPh)_3 \cdot THF$ (2.46 g, 4.9 mmol) in 100 ml of THF was added slowly to a Cp_2VCl solution (1.08 g, 4.9 mmol) in 50 ml of THF. The reaction mixture was stirred at 20°C for 5 hours. The colour of the reaction mixture changed from blue to green. The solution was filtered from the residue of NaCl. Then the solvent was completely removed under vacuum. The residue was solved in THF, the solution prepared was filtered out. Hexane was added to the filtrate. The green crystals which were precipitated were filtered out and dried under vacuum. (Yield, 2.25 g, 80%). (Found: C, 57.94; H, 5.37; V, 8.80. $C_{28}H_{25}OSnV$ calcd.: C, 57.07; H, 4.90; V, 9.01%).

Reaction of vanadocene with hexabutyldistannane

A mixture of Cp_2V (1.84 g, 10.6 mmol) and Bu_6Sn_2 (2.94 g, 5.3 mmol) was heated in an evacuated ampoule without solvent at 50°C for 15 hours. The colour of the reaction mixture changed from violet to black. At hourly intervals after beginning the heating an ESR signal was registered which was typical of Cp_2V. The ESR signal intensity of Cp_2V practically did not change in the course of the reaction. Bu_6Sn_2 (2.05 g, 69%) was isolated from the reaction mixture by vacuum distillation. The solid residue remained was sublimed at 160—165°C/10^{-1} mmHg to give violet crystals of Cp_2V (1.21 g, 66%). Mixing the sample with a pure sample did not result in a depression of melting point. The mixture of Cp_2V (0.06 g, 0.3 mmol) and Bu_6Sn_2 (2.00 g, 3.0 mmol) in 10 ml of THF was kept at 20°C for 20 hours. The colour of the reaction mixture changed gradually from violet to dark-green. A signal with $g_i = 2.0030$ and $A_i^{51V} = 51.0$ *e* appeared in the ESR spectrum. This signal may belong to $Cp_2V(ER_3)_2$ derivatives. The half-decomposition period of $Cp_2V(SnBu_3)_2$ was found to be equal to 0.5 h. After 20 hours the reaction solution consisted of a mixture of the initial products. V^{II} was determined by titration in the reaction solution. The initial Bu_6Sn_2 (1.65 g, 83%) was isolated by vacuum distillation at 168—170°C/1 mmHg.

Reaction of vanadocene with hexaethyldisilane

A mixture of Cp_2V (0.50 g, 2.7 mmol) and Et_6Si_2 (0.62 g, 2.7 mmol) was heated in an evacuated ampoule in toluene at 80°C for 3 hours. At hourly intervals after beginning the reaction an ESR signal was registered which was typical of Cp_2V. The ESR signal intensity of Cp_2V practically did not change in the course of the reaction. The initial Et_6Si_2 (0.56 g, 2.4 mmol) was found in the reaction solution by the GLC method. The remaining solid residue was sublimed at 160—165°C/10^{-1} mmHg, to give violet crystals of Cp_2V (0.40 g, 2.2 mmol).

Reaction of vanadocene with pentamethyl(butyl)disilane

A mixture of Cp_2V (0.50 g, 2.7 mmol) and $Me_3SiSiMe_2Bu$ (0.51 g, 2.7 mmol) was heated in an evacuated ampoule in toluene at 80°C for 30 hours. The analysis of the reaction mixture was conducted as in the previous experiment. According to the ESR spectra the signal intensity of Cp_2V does not change. The initial $Me_5(Bu)Si_2$ (0.46 g, 2.4 mmol) was identified by the GLC method in the reaction mixture. V^{II} (2.1 mmol) was titrated in the reaction solution.

Reaction of vanadocene with triethylgermanium hydride

Et_3GeH (1.50 g, 9.4 mmol) in 10 ml toluene was added to a Cp_2V solution 0.72 g, 4.0 mmol) in 20 ml of toluene. The reaction mixture was kept at 20°C for 20 hours. The ESR signal intensity for Cp_2V has not changed during this period of time. The initial Et_3GeH (1.35 g, 8.4 mmol) was identified in the reaction solution by the GLC method. The solvent was removed in vacuum. The solid residue was sublimed at 165°C/10^{-1} mmHg, to give Cp_2V (0.50 g, 2.7 mmol).

Preparation of bis(π-cyclopentadienyl)(triethylgermyl)vanadium

Cp_2V (2.14 g, 11.8 mmol) was dissolved in 100 ml of toluene and $(Et_3Ge)_2Cd$ (5.09 g, 11.8 mmol) in toluene was added dropwise. The mixture was kept in an ampoule for 48 hours at room temperature. The colour of the solution changed from black-green to violet. Metallic cadmium (1.31 g, 10.2 mmol) was precipitated from the reaction mixture. The solution was filtered and the solvent was removed under vacuum. The residue was extracted by hexane and the extract was filtered. The filtrate was concentrated under reduced pressure and cooled down to —78°C. The precipitated dark violet crystals were separated, washed out with cold hexane and dried in vacuum. (Yield, 2.13 g, 53%), m.p. 32°C. (Found: C, 56.40; H, 7.45; V, 14.75. $C_{16}H_{25}GeV$ calcd.: C, 56.37; H, 7.95; V, 14.90%).

Preparation of bis(π-cyclopentadienyl)(trimethylsilylmethyl)vanadium

Cp_2V (4.50 g, 24.8 mmol) was dissolved in 70 ml of hexane and Me_3SiCH_2Cl (1.52 g, 124 mmol) was added. The mixture was kept in an ampoule at 80°C for 3 hours. The colour of the solution changed from violet to dark blue. Cp_2VCl (1.62 g, 7.5 mmol) precipitated from the reaction mixture. The solution was filtered and the solvent was removed under vacuum. The residue was recrystallized from hexane. The precipitated black crystals were separated, washed with hexane and dried in vacuo. (Yield, 2.70 g, 81%), m.p. 56°C, (Found: C, 62.71; H, 8.11; V, 18.61. $C_{14}H_{21}SiV$ calcd.: C, 62.86; H, 7.85; V, 18.88%).

Thermal decomposition of bis(π-cyclopentadienyl)(triethylstannyl)vanadium

$Cp_2V(SnEt_3)$ (0.12 g, 0.30 mmol) was heated at 140°C for 2 hours. Then toluene (2 ml) was added in ampoule. Et_6Sn_2 (0.05 g, 0.13 mmol) was identified in the toluene solution by the GLC method. The solvent was removed under vacuum. The residue was sublimed at 80—100°C/10^{-3} mmHg, to give Cp_2V (0.05 g, 0.26 mmol).

Thermal decomposition of bis(π-cyclopentadienyl)(triethylstannyl)vanadium in toluene

$Cp_2V(SnEt_3)$ (0.20 g, 0.52 mmol) in 5 ml of toluene was heated at 140°C for 2 hours. Et_6Sn_2 (0.09 g, 0.22 mmol) was identified in the reaction solution by the GLC method. The solvent was removed under vacuum. The residue was sublimed at 80—100°C/10^{-3} mmHg, to give black-violet crystals of Cp_2V (0.09 g, 0.47 mmol). Vanadocene was identified from the mass-spectrum (M^+ m/e 181).

Thermal decomposition of bis(π-cyclopentadienyl)(triethylstannyl)vanadium in THF

$Cp_2V(SnEt_3)$ (0.13 g, 0.35 mmol) in 5 ml of THF was heated at 140°C for 2 hours. Et_6Sn_2 (0.06 g, 0.15 mmol) was identified in the reaction solution by the GLC method. The solvent was removed under vacuum. The residue was sublimed under vacuum at 100°C/10^{-3} mmHg, to give dark violet crystals. Vanadocene was identified by the mass-spectrum (M^+ m/e 181).

Thermal decomposition of (π-cyclopentadienyl)(trisphenoxyphenylstannyl)-vanadium

$Cp_2V[Sn(OPh)_3]$ (0.58 g, 1.0 mmol) was heated at 200°C for two hours. Then the solid residue was sublimed under vacuum at 80—100°C/10^{-3} mmHg to give bright dark violet crystals. Cp_2V (0.14 g, 0.8 mmol) was identified from the mass spectrum (M^+ *m/e* 181).

Thermal decomposition of bis(π-cyclopentadienyl)(triethylgermyl)vanadium

$Cp_2V(GeEt_3)$ (1.20 g, 3.5 mmol) was heated at 150°C for two hours. Then toluene (3 ml) was added into the ampoule. Et_3GeH (0.20 g, 1.2 mmol) and Et_3GeCp (0.20 g, 0.9 mmol) were detected in the reaction solution by the GLC method. The solvent was removed under vacuum. The solid residue was sublimed in vacuo. The violet crystals of Cp_2V were sublimed at 80—100°C/10^{-3} mmHg (yield, 0.20 g, 1.1 mmol). A blue viscous liquid was distilled off at 120°C/10^{-3} mmHg from the residue. The liquid was identified to be CpV-($C_5H_4GeEt_3$) (0.40 g, 1.1 mmol) by the mass-spectrometry method and analysis. (Found: V, 14.00. $C_{16}H_{24}GeV$ calcd.: V, 14.90%). Mass spectrum: M^+ *m/e* 341.

Thermal decomposition of bis(π-cyclopentadienyl)(triethylgermyl)vanadium in toluene

$Cp_2V(GeEt_3)$ (1.32 g, 3.8 mmol) in 20 ml of toluene was heated at 150°C for two hours. Et_3GeH (0.18 g, 1.1 mmol) and Et_3GeCp (0.25 g, 1.1 mmol) were detected in the reaction solution by the GLC method. The solvent was removed under vacuum. Cp_2V (0.28 g, 1.5 mmol) was sublimed from the residue at 100 100°C/10^{-3} mmHg. A blue viscous liquid was distilled off at 120°C/10^{-3} mmHg (Yield, 0.42 g, 1.2 mmol), and was identified as $CpV(C_5H_4GeEt_3)$ from its mass spectrum (M^+ *m/e* 341).

Thermal decomposition of bis(π-cyclopentadienyl)(triethylgermyl)vanadium in THF

$Cp_2V(GeEt_3)$ (1.32 g, 3.8 mmol) in 20 ml of THF was heated at 150°C for two hours. Et_3GeH (0.20 g, 1.2 mmol) and Et_3GeCp (0.09 g, 0.4 mmol) were detected in the reaction solution by the GLC method. The solvent was removed under vacuum. Cp_2V (0.33 g, 1.8 mmol) was sublimed from the residue at 80—100°C/10^{-3} mmHg. A blue viscous liquid (0.35 g, 1.0 mmol) was distilled off at 120°C/10^{-3} mmHg, and was identified as $CpV(C_5H_4GeEt_3)$ from its mass spectrum [M^+ *m/e* 341).

Thermal decomposition of bis(π-cyclopentadienyl)(trimethylsilylmethyl)vanadium

$Cp_2V(CH_2SiMe_3)$ (0.27 g, 1.0 mmol) was heated at 150°C for two hours. The evolved gas was identified as Me_4Si (0.4 mmol) by the GLC method. The solid residue was sublimed in vacuo at 100—110°C/10^{-3} mmHg. V^{II} (0.75 mmol) was determined by titration of the sublimate. According to the mass spectrometry analysis the sublimate consists of a mixture: Cp_2V (M^+ *m/e* 181) and CpV-($C_5H_4CH_2SiMe_3$) (M^+ *m/e* 267).

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