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Paramagnetic d^1-Complexes of Biscyclopentadienylvanadium

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Electron paramagnetic resonance data for the Cp_2V d^1-complexes are surveyed and the dependence of the EPR parameters for the complexes on their molecular and electronic structure is discussed. Examples of the use of the EPR method for the determination of the structures of labile Cp_2V d^1-complexes, formed as intermediates in various reactions, are considered. The bibliography includes 59 references.

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I. INTRODUCTION

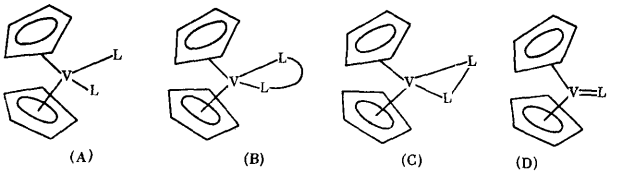
The electron paramagnetic resonance method is widely used for the solution of various problems in the chemistry of organometallic compounds (OMC), including the determination of their molecular and electronic structures. We believe that this aspect of the application of the EPR method to the OMC chemistry is most important and interesting. Unfortunately, the EPR study of paramagnetic OMC is frequently undertaken with the utilitarian aim of obtaining the spectroscopic characteristics of the given specific compounds. For this reason, most of the available EPR information obtained in OMC chemistry is concerned with specific species, is of an unrelated character, and is relatively unsuitable for the solution of problems involving the determination of the electronic and molecular structures of OMC because success in research of this kind is impossible without the elucidation of the influence of the ligand environment on the EPR parameters.

In the present review an attempt is made to survey EPR data obtained for the Cp_2V d^1-complexes: the spectroscopic parameters are compared with the available information about the molecular and electronic structures of these complexes; certain rules governing the variation of the EPR parameters as a function of the nature of additional ligands attached to Cp_2V are discussed; the relations found between the EPR parameters and the structure are used to determine the structures of labile Cp_2V d^1-complexes formed as intermediates in various reactions involving Cp_2V and its derivatives.

II. THE EPR SPECTRA OF Cp_2V d^1-COMPLEXES

1. Types of Cp_2V d^1-Complexes. General Information about the Molecular and Electronic Structures

A paramagnetic 17-electron vanadium d^1-complex incorporating Cp_2V can be formally produced from the 15-electron complex Cp_2V by adding to the latter either two one-electron ligands or one two-electron ligand. The first variant can be achieved in only one way—as a result of the formation of two σ-bonds between Cp_2V and two one-electron ligands (A).



(A) (B) (C) (D)

Depending on their nature (structure), the two-electron ligand can be linked to vanadium in three different ways. Bidentate chelate ligands (formally η^2-ligands), in which the atoms bound directly to vanadium are not linked to one another, form complexes of type (B) which differ little from complexes of type (A) (in terms of the character of the V–L bond) and can be regarded as d^1-complexes with two one-electron η^1-ligands. Bidentate ligands in which the atoms bound to vanadium are linked directly to one another form on addition to Cp_2V a three-membered metallocycle. In the resulting d^1-complex a two-electron η^2-ligand (C) is bound to Cp_2V. The third "terminal" type of binding of the two-electron ligand to Cp_2V leads to d^1-complexes with a two-electron η^1-ligand (D).

The majority of the known Cp_2V d^1-complexes belong to the first two types [(A) and (B)]. The one-electron η^1-ligand which enters into the composition of type (A) complexes can be of a wide variety of types: the halogens (Cl, Br, and I), the pseudohalogens (CN, OCN, SCN, SeCN, and N_3), carboxy-compounds (OCOPh), alkyls (Me, Et, CH_2Ph, and CH_2SiMe_3), hydrogen, element-containing groups (SiR_3, GeR_3, SnR_3, and SR), etc. The complex can contain both two identical and two different additional ligands. In complexes of type (B) the ligands bound to vanadium may be various chelate species forming four-, five-, and six-membered rings; their coordinating atoms may be C, O, N, and S.

The two-electron ligands in the main react with Cp_2V to form complexes of type (C) (η^2-ligands). A fairly large number of such complexes are known in which the ligands are alkenes $EtOC(O)C(H) = C(H)C(O)OEt$, $F_3CFC = CFCF_3$), alkynes ($PhC{\equiv}CPh$, $C_6F_5C{\equiv}CC_6F_5$, etc.), diazenes ($PhN{=}NPh$), heterocumulenes ($Ph_2C{=}C{=}O$, $Ph{-}N{=}C{=}O$, $S{=}C{=}S$). Among complexes of type (D) described in the literature, one may refer to compounds with carbon monoxide, isonitriles, and nitrenes.

The classification of complexes of type (C) and (D) as d^1-complexes still remains controversial. Thus the authors of a review[1] regard Cp_2V complexes with ligands of this kind as d^3-complexes, assuming that the ligands in them are neutral and that the formal oxidation state of vanadium in the complexes is +2. This view has been confirmed by the results of quantum-chemical calculations, from which it follows that the highest fully occupied molecular orbital in the complexes involves a large contribution by the *d* orbitals of the atom.[2] On the other hand, the results of calculations indicate an appreciable decrease of the energy of this orbital compared with the initial d^3-complex (Cp_2V), i.e. the transformation of this orbital from non-bonding to bonding. The available data concerning the molecular structure of certain d^1-complexes with η^2-ligands[3-5] also show that the alkene and alkyne molecules coordinated to Cp_2V undergo appreciable deformations, the resulting structures approaching those of alkanes and alkenes respectively. The V–C bond lengths in these complexes are comparable to those of the normal V–C σ-bonds. Thus the binding of vanadium to the carbon atoms in the complexes of type (C) differs little in its character from the σ-binding in complexes of types (A) and (B). In order to compare the properties of different 17-electron Cp_2V complexes, in the present review compounds of types (C) and (D) will be considered together with those of types (A) and (B) and will be classified as d^1-complexes.

The general features of the molecular and electronic structures of the Cp_2V d^1-complexes are well known. Admittedly, this claim refers to a large extent to complexes of type (A) (with two one-electron ligands), for which fairly reliable quantum-chemical calculations have been performed,[6,7] whose results agree well with EPR experimental data for diamagnetically diluted single crystals.[8,9] As regards complexes of the other three types, their electronic structures can be inferred on the basis of a qualitative "angular sandwich" structural model[2] and also on the basis of the available data for the molecular structure of such complexes. Here one should naturally take into account the similarities and differences in the structures of complexes of different types and the character of the bond linking the additional ligand to Cp_2V.

In conformity with the available data, the general features of the structure of Cp_2V d^1-complexes are as follows. Their molecular geometry is described in an idealised manner by C_{2v} symmetry with a twofold symmetry axis, which coincides with the *X* axis (for the arrangement of the coordinate axes illustrated in Fig.1). In the presence of different additional ligands, the symmetry of the complex decreases to C_2.[2] For the arrangement of coordinate axes shown in Fig.1, the lines joining vanadium to the centres of the Cp ligands are in the *xy* plane and the bonding to the additional ligands L is in the *xz* plane. In this case the unpaired electron is located in the molecular orbital with a_1 symmetry. In terms of its character, this orbital is non-bonding with a dominant contribution from the d_{z^2} orbital of vanadium. Taking into account the ligand contribution, the expression for the molecular orbital of the electron (MO_e) can be formulated as follows:

$$\varphi^{\circ}_{a_1} = \alpha(d_{z^2},\ d_{x^2-y^2}) + (1-\alpha)^{1/2}\varphi_L, \qquad (1)$$

where α and $(1-\alpha)^{1/2}$ are the coefficients of the orbitals forming part of the composition of MO_e and ϕ_L is the combined orbital of the ligands with a^1 symmetry.

According to the results of quantum-chemical calculations,[6,7] the contribution of the vanadium orbitals (*d* orbitals) is from 58 to 72% depending on the nature of the additional ligands, the contribution of the ligand orbitals (p_π orbitals) is 23–37%, and the contribution of the orbitals of the Cp ligand does not exceed 5%. It is striking that MO_e contains virtually no contribution from the *s* orbitals of the ligands (< 1%). An interesting feature of the Cp_2V d^1-complexes is the dependence of the relative contributions of the d_{z^2} and $d_{x^2-y^2}$ orbitals of vanadium on the nature of the additional ligands. This dependence is manifested very distinctly in the anisotropic EPR spectra and will be discussed in detail when such spectra are considered.

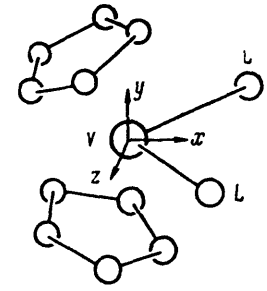


Figure 1. The molecular geometry and disposition of the coordinate axes in Cp_2V d^1-complexes.[20]

Table 1. Parameters of the isotropic EPR spectra of Cp_2V d^1-complexes.

No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
1	Cp_2VCl_2	1.9876	74.2	[9]
	Cp_2VCl_2	1.9880	74.3	[10]
2	Cp_2VBr_2	1.999	67.0	[11]
	Cp_2VBr_2	2.0212	65.3	[12]
3	Cp_2VClBr	—	—	[12]
4	Cp_2VI_2	1.998	59.4	[11]
5	Cp_2VBrI	1.990	64.0	[11]
6	Cp_2VClI	1.989	66.0	[11]
7	$Cp_2V(OCN)_2$	1.985	76.1	[10]
8	$Cp_2V(NCS)_2$	1.991	73.0	[10]
	$Cp_2V(NCS)_2$	1.982	73.4	[13]
9	$Cp_2V(NCSe)_2$	1.990	73.6	[10]
	$Cp_2V(NCSe)_2$	1.981	73.0	[13]
10	$Cp_2V(N_3)_2$	1.985	72.0	[10]
11	$Cp_2V(CN)_2$	1.999	60.3	[10]
12	$Cp_2V(CN)(NCS)$	1.981	59.4	[13]
13	$Cp_2V(CN)(NCSe)$	1.983	57.5	[13]
14	$Cp_2V(NO)(Cl)$	1.993	72.0	[14]
15	$Cp_2V(NO)(Br)$	1.991	66.0	[14]
16	$Cp_2V(OCOPh)_2$	1.967	80.0	[15]
17	$Cp_2V(Me)_2$	1.9915	63.0; 4.8 (6H)	[16]
18	$Cp_2V(CH_2Me)_2$	1.995	62.4	[17]
	$Cp_2V(CH_2Me)_2$	1.9920	62.7	[16]
19	$Cp_2V(CH_2Ph)_2$	1.9910	64.0	[16]
20	$Cp_2V(CH_2SiMe_3)_2$	1.990	64.5; 3.0 (4H)	[17]
	$Cp_2V(CH_2SiMe_3)_2$	1.9916	64.3	[18]
21	$Cp_2V(Me)(CH_2SiMe_3)$	1.9926	63.7; 3.9 (3H)	[18]
22	$Cp_2V(Me)Cl$	1.9900	69.2; 3.6 (3H)	[19]
23	$Cp_2V(CH_2SiMe_3)Cl$	1.9900	70.0	[18]
24	$Cp_2V(CH_2SiMe_3)Br$	2.0223	64.5	[20]
25	$Cp_2V(SPh)_2$	2.00	62.6	[21]
26	$Cp_2V(SiEt_3)_2$	2.0047	53.4	[20]
27	$Cp_2V(GeEt_3)_2$	2.0025	55.2	[22]
28	$Cp_2(SnEt_3)_2$	2.0032	50.7; 154 (2Sn)	[23]
29	$Cp_2V(SiCl_2Me)Cl$	1.9954	62.6	[20]
30	$Cp_2V(Cl)GeEt_3$	1.9956	66.8	[22]
31	$Cp_2V(Br)GeEt_3$	2.0167	61.7	[22]
32	$Cp_2V(Cl)Ge(C_6F_5)_3$	1.9936	64.7	[24]
33	$Cp_2V(CH_2Me)Ge(C_6F_5)_3$	1.9936	60.0	[24]
34	$Cp_2V(Cl)Ge(C_6F_5)_2H$	1.9946	64.4	[20]
35	$Cp_2V(H)SnEt_3$	2.0007	41.6; 14.6 (1H); 143 (1Sn)	[23]
36	$Cp_2V(Cl)SnEt_3$	1.9946	62.0; 188 (1Sn)	[23]
37	$Cp_2V(Br)SnEt_3$	2.0170	61.5; 145 (1Sn)	[23]
38	$Cp_2V(CH_2Me)SnEt_3$	1.9964	60.8; 143 (1Sn)	[23]
39	$Cp_2V(CH_2SiMe_3)SnEt_3$	1.9964	60.8; 5.2 (2H); 143 (1Sn)	[23]
40	$Cp_2VGe(C_6F_5)_3HgGe(C_6F_5)_3$	1.978	52.6; 116 (1Hg)	[24]
41	Cp_2VS_5	2.00	61.4	[25]
	Cp_2VS_5	—	64.8	[8]

Table 1. (continued)

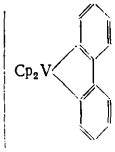
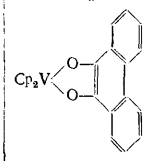
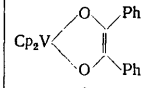
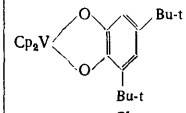
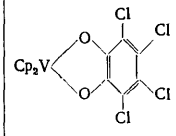
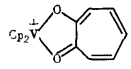
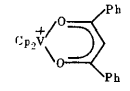
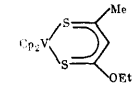
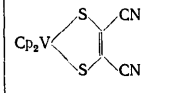
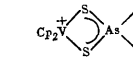
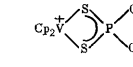
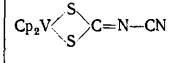
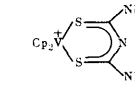
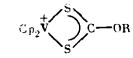
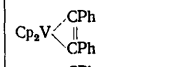
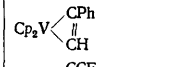
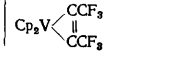
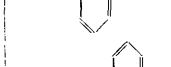
No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
42		2.00	47	[26]
43		1.9795	70.0	[27]
44		1.9760	71.7	[27]
45		1.9797	70.2	[28]
46		1.9812	68.9	[28]
47		1.983	65.9	[10]
48		1.985	74.6	[10]
49		1.982	60.5	[29]
50		1.985	59.4	[29]
51		1.985	65.7; 40.3 (1As)	[29]
52		1.98	63.6; 44.5 (1P)	[30]
53		1.990	60.5	[29]
54		1.990	60.5	[29]
55	 R = Me, Et, Pr, iso-Pr, cyclo-C_6H_{11}	1.985—1.990	60.5—62.5	[31]
56		1.9968 1.9970	43.1 42.6	[5] [28]
57		1.9968 1.9966	44.8 42.9	[5] [28]
58		1.9968 1.9971	44.6 46.0	[5] [52]

Table 1. (continued)

No.	Complex	g_i	$-A(^{51}V)$, G	Refs.
59		1.9983	44.6	[3]
60		1.9976 1.9968	44.0 43.3	[32] [5]
61		1.9968	45.0	[5]
62		1.9968 1.9970	45.2 45.4	[5] [28]
63		2.0009	43.6	[33]
64		1.9976	45.5	[34]
65		1.9961	43.7	[28]
66	$Cp_2V[N_2C(HC(O)OEt)_2]$	1.9942	41	[35]
67	$Cp_2V(N_2CPh_2)$	1.9918	23	[35]
68		1.9953	41	[35]
69	Cp_2VCO	2.0015	27.7	[28]
70	Cp_2V (CN-t-Bu)	2.0022	27.0	[20]
71	Cp_2V (CN-cyclo-C_6H_{11})	2.0019	27.3	[20]

2. Isotropic EPR Spectra of Cp_2V d^1-Complexes

The isotropic parameters of the EPR spectra of d^1-complexes of various types are presented in Table 1. The data in this table show that, depending on the nature of the additional ligands bound to vanadium, the isotropic parameters vary within wide limits. The constants for the hyperfine interaction with the ^{51}V nucleus (99.9%; $J = 7/2$; $\mu = 5.1392$) $A_i(V)$ vary from -23 to -80 G and the g_i range from 1.965 to 2.025. Comparative analysis of the isotropic parameters of the spectra of the Cp_2V d^1-complexes makes it possible to discover certain relations governing their variation as a function of the properties of the additional ligand. These relations are clearly illustrated by the "field" of the values of g_i and $A_i(^{51}V)$ in which the majority of the known Cp_2V d^1-complexes are represented (Fig.2).

Virtually all d^1-complexes of type (A) (two one-electron ligands) fit on a straight line (linear correlation between g_i and A_i), constituting one group. An analogous relation has been observed for d^1-complexes of type (B) (chelating two-electron ligands); the straight line combining these complexes has approximately the same slope but differs in the linear term. For complexes of type (C) (two-electron η^2-ligand), the hyperfine interaction constant A_i varies very slightly with L, remaining virtually invariant. An analogous tendency has been noted for complexes of type (D) (two-electron η^1-ligand), but the number of examples of complexes of this type is small. Cp_2V complexes with carbon-containing additional ligands, in which the coordination is via carbon atoms [dialkyl derivatives of type (A), alkene and alkyne complexes of type (C), and carbonyl and isonitrile complexes of type (D)] constitute yet another group of d^1-complexes with its own linear relation between the isotropic parameters.

The groups enumerated include almost all Cp_2V d^1-complexes for which the parameters of the isotropic EPR spectra are known.

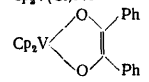
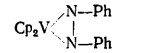
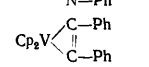
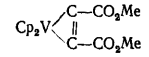
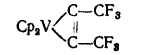
It is striking that the composition of the groups combining complexes in terms of the isotropic parameters of the EPR spectra is consistent with the formal types of these complexes based on the nature of the binding of the additional ligands to Cp_2V (see Section I). This indicates, on the one hand, the similarity of the molecular and electronic structures of isotypical complexes within each group and, on the other hand, differences between the complexes in different groups (different types). The correlation between the parameters of the carbon-containing d^1-complexes of different types emphasises common features in the electronic structures of all the Cp_2V d^1-complexes. The relation between the spectroscopic parameters and molecular electronic structures of Cp_2V d^1-complexes appears most distinctly in the analysis of anisotropic EPR spectra.

3. Anisotropic EPR Spectra of Cp_2V d^1-Complexes

Anisotropic EPR spectra have been investigated for a much smaller number of Cp_2V d^1-complexes than the isotropic spectra although the information obtained from the analysis of the former makes it possible to understand certain important details of the electronic and molecular structures of these complexes (the composition of the molecular orbital of the unpaired electron, the relative energy of the lowest occupied and unoccupied MO, and the geometry of the complex). Table 2 presents anisotropic EPR spectroscopic parameters of Cp_2V d^1-complexes. The majority of the data quoted were found in the study of "vitrified" solutions and only the data concerning Cp_2VCl_2 and Cp_2VS_5 have been obtained in experiments with diamagnetically diluted single crystals.[8,9]

It follows from Table 2 that the $\bar{g}$ and $\bar{T}$ tensors for all the d^1-complexes have orthorhombic symmetry (the principal components of the $\bar{g}$ and $\bar{T}$ tensors are not the same). The anisotropic EPR spectra of the series of Cp_2V d^1-complexes were interpreted incorrectly in a number of studies[29,31,36] based on the hypothesis of axial symmetry of the $\bar{g}$ and $\bar{T}$ tensors, the authors failing to take into account the z components of the two tensors.

Table 2. Parameters of the anisotropic EPR spectra of Cp_2V d^1-complexes.

Complex	g_x	g_y	g_z	T_x, G	T_y, G	T_z, G	Refs.
Cp_2VCl_2	—	—	—	—80.1	—127.2	—28.6	[37]
Cp_2VCl_2	1.986	1.971	2.000	—79.2	—125.2	—16.3	[6]
$(C_5H_4Me)_2VCl_2$	1.9802	1.9895	2.0013	—80.6	—125.5	—20.5	[9]
Cp_2VS_5	1.9964	1.9997	1.9889	—66.6	—111.3	—23.5	[8]
$Cp_2V(SCN)_2$	1.988	1.958	2.000	—76.2	—123.3	—20.5	[6]
$Cp_2V(OCN)_2$	1.985	1.957	2.000	—78.5	—127.7	—19.9	[6]
$Cp_2V(CN)_2$	1.994	1.986	2.000	—62.8	—106.0	—11.8	[6]
Cp_2VMe_2	1.986	2.005	1.984	—66	—111	—12	[28]
Cp_2VEt_2	1.977	2.000	1.993	—67.0	—108.0	—13.9	[17]
$Cp_2V(CH_2SiMe_3)_2$	1.997	1.999	1.999	—66.0	—114.5	—12.06	[17]
$Cp_2V(Cl)Me$	1.985	1.992	1.992	—73	—121	—14	[28]
	1.982	1.964	1.982	—82	—118	—15	[28]
$Cp_2V(H)SnEt_3$	1.984	2.009	2.006	—70	—58	+4	[20]
$Cp_2V(CH)(NCSe)$	1.982	1.970	2.000	—64.0	—109.8	—11.9	[13]
$Cp_2V(NCSe)_2$	1.985	1.957	2.000	—74.0	—114.6	—33.6	[13]
$Cp_2V(NCS)_2$	1.988	1.958	2.000	—75.8	—123.0	—20.4	[13]
$Cp_2V(CN)(NCS)$	1.988	1.958	2.000	—62.0	—108.2	—12.9	[13]
	1.978	2.000	1.995	—80	—64	+8	[28]
	1.9815	2.0000	2.0020	—77.5	—65.5	—2	[5]
	1.978	2.018	1.995	—80	—58	+10	[28]
	1.9815	2.0130	2.0020	—77	—58.5	—2.0	[5]
	1.9810	2.0090	2.0020	—77.5	—62.5	—2.0	[5]
$Cp_2V(CO)$	1.984	2.027	1.995	—72	—27	+16	[28]

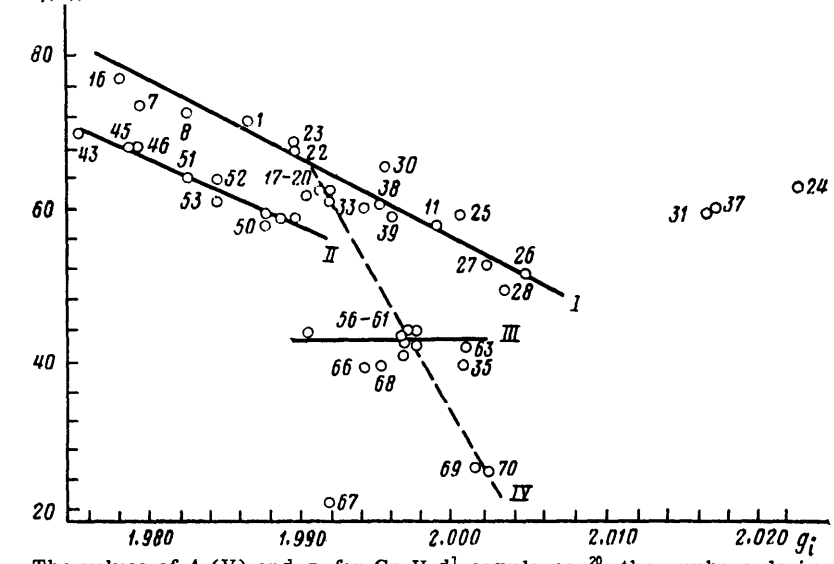


Figure 2. The values of A_i(V) and g_i for Cp_2V d^1-complexes;[20] the numbers designating the circles correspond to the numbers of the complexes in Table 1.

The interpretation of the anisotropic EPR spectra using a quantum-chemical model was first achieved for Cp_2VCl_2 in a study[37] whose authors established that the unpaired electron in Cp_2VCl_2 is located in a molecular orbital with a_1 symmetry, comprising the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals of the metal atom. However, since the crystal structure of the matrix (Cp_2TiCl_2) was unknown at the time, it was impossible to determine the correct orientation of the axes of the $\bar{g}$ and $\bar{T}$ tensors relative to the crystal. Somewhat later a complete analysis of the anisotropic EPR spectra was carried out for a series of Cp_2V and Cp_2Nb d^1-complexes obtained in vitrified solutions.[6] Despite the fact that the initial orientation of the axes of the $\bar{g}$ and $\bar{T}$ tensors in the above investigation was selected incorrectly (the z axis coincided with the C_{2v} symmetry axis), the data obtained by the authors for the composition of the unpaired electron orbital and other details of the electronic structure differ little from the more accurate results obtained later[8,9] and based on a comparison of the parameters of the anisotropic EPR spectra of a diamagnetically diluted Cp_2VCl_2 single crystal with the quantum-chemical calculations for this complex by the Fenske–Hall method.[7] A somewhat simplified model, based on the conclusions reached in the studies listed above, as well as the investigation of Lauher and Hoffman[2] devoted to a qualitative consideration of the binding of ligands of different types in "angular sandwiches", has been used in the present review for the interpretation of the anisotropic EPR spectra of Cp_2V d^1-complexes with different ligands.

If one uses Eqn.(1) for the unpaired electron MO, then, resorting to the ligand field approximation and assuming that the contributions of the orbitals and additional ligands to the ground state are small, the principal components of the $\bar{g}$ and $\bar{T}$ tensors for the Cp_2V d^1-complexes with C_{2v} symmetry can be expressed as follows:[6,7]

$$g_x = g_0 - 2\lambda(a\cdot 3^{1/2} + b)^2\left[\frac{P^*_{b_1}}{\Delta E(\varphi^*_{b_1} \leftarrow \varphi^e_{a_1})} - \frac{1-P^*_{b_1}}{\Delta E(\varphi^e_{a_1} \leftarrow \varphi_{b_1})}\right], \quad (2a)$$

$$g_y = g_0 - 2\lambda(a\cdot 3^{1/2} - b)^2\left[\frac{P^*_{b_2}}{\Delta E(\varphi^*_{b_2} \leftarrow \varphi^e_{a_1})} - \frac{1-P^*_{b_2}}{\Delta E(\varphi^e_{a_1} \leftarrow \varphi_{b_2})}\right], \quad (2b)$$

$$g_z = g_0 \quad (2c)$$

$$T_x = -K + P\left[-\frac{2}{7}(a^2-b^2) + \frac{4\cdot 3^{1/2}}{7}ab\right], \quad (3a)$$

$$T_y = -K + P\left[-\frac{2}{7}(a^2-b^2) + \frac{4\cdot 3^{1/2}}{7}ab\right], \quad (3b)$$

$$T_z = -K + P\left[\frac{4}{7}(a^2-b^2)\right], \quad (3c)$$

where $P = g_0 q^{51}_N \beta\beta_N \langle r^{-3}\rangle$ is the dipolar contribution, $K = -g_0 g^{51}_N \beta\beta_n \times 2/3\chi$ the contact contribution to the hyperfine interaction (HFI) with the ^{51}V nucleus, λ the spin–spin orbit coupling constant for ^{51}V, $g_0 = 2.0023$ the g-factor for the free electron, $\phi^e_{a_1}$ the molecular orbital of the unpaired electron, ϕ_{b_1} and ϕ_{b_2} are the highest fully occupied orbitals with b_1 and b_2 symmetry, $\phi^*_{b_1}$ and $\phi^*_{b_2}$ the lowest unoccupied orbitals with the same symmetries, and a and b are coefficients of the d_{z^2} and $d_{x^2-y^2}$ vanadium orbitals. The form of Eqns.(3a)–(3c) for different values of the components of the $\bar{T}$ tensor has been simplified for their more complete expression,[7] omitting small terms whose contribution to T_x, T_y, and T_z is less than 1%. On the other hand, additional terms, taking into account the spin–orbit coupling between $\phi^e_{a_1}$ and the highest fully occupied orbitals ϕ_{b_1} and ϕ_{b_2} have been introduced into the expressions for g_x and g_y, as was done by Stewart and Porte.[6] The discussion below will make clear the importance of these terms for the explanation of the values of the $\bar{g}$ tensor, especially in the case of the Cp_2V d^1-complexes with neutral η^1- and η^2-ligands.

According to Eqn.(2c), the g_z component for the Cp_2V d^1-complexes should be close to $g_0 = 2.0023$ and the T_z component should be largest, bearing in mind that all the quantities T_x, T_y, T_z, and A_i are negative. In view of these features of the z components of the $\bar{g}$ and $\bar{T}$ tensors, their assignment in the experimental spectra does not present major difficulties. The assignment of two other components, based solely on EPR spectra, is impossible, since the signs of the coefficients a and b for the metal d orbitals incorporated in $\phi^e_{a_1}$ cannot be determined from the EPR experiment. The quantum-chemical calculations[6,7] for Cp_2V d^1-complexes of types (A) and (B) yield the opposite signs for a and b, i.e. for complexes of these types $T_x > T_y$. The relative values of g_x and g_y are determined not only by the signs of the coefficients a and b but also by the relative magnitudes of the terms expressing the spin–orbital coupling of $\phi^e_{a_1}$ for the lowest unoccupied and highest fully occupied MO ($\phi^*_{b_1}$, $\phi^*_{b_2}$, ϕ_{b_1}, ϕ_{b_2}).

III. THE EPR PARAMETERS AND STRUCTURE OF Cp_2V d^1-COMPLEXES

1. Dependence of the Components of the $\bar{g}$ and $\bar{T}$ Tensors on the Structure of the Cp_2V d^1-Complexes

When use is made of the qualitative scheme proposed by Lauher and Hoffman[2] for the description of the binding of the Cp_2M fragment to the additional ligands in "angular sandwiches", then comparison of the molecular diagrams for complexes of types (A), (C), and (D) (Fig.3) can reveal significant differences, which determine the electronic structure of these complexes and hence also the parameters of the anisotropic EPR spectra.

(1) In conformity with C_{2v} molecular symmetry (with the choice of coordinate axes shown in Fig.1), the highest fully occupied MO in the complexes of all three types is an orbital with b_2 symmetry consisting mainly of contributions from the dxz orbital of vanadium and the b_2 orbital of the ligand (or ligands) and virtually lacking any contribution from the Cp ligands.

(2) The highest fully occupied and lowest unoccupied MO with b_1 symmetry consists predominantly of the d_{yz} orbital of the vanadium atom and the b_1 group orbitals of the Cp ligands and have virtually no contribution due to the orbitals of the additional ligands.

(3) In contrast to complexes of type (A), in which the b_2 orbital of the ligands is a b_2 group orbital consisting of the σ orbitals (p or s) of the ligands, in complexes of types (C) and (D) the b_2 orbital of the ligand is an antibonding orbital of a neutral ligand. As a consequence, both its energy and the energy of the b_2 orbital of the complex produced from it on formation of a bond is significantly higher than the energy of the initial σ orbitals of the one-electron ligands and the MO of the same symmetry in complexes of type (A).

The factors noted above entail two conclusions concerning the properties of the principal components of the $\bar{g}$ tensor of Cp_2V d^1-complexes. Firstly the g_x component of the $\bar{g}$ tensor must show very little sensitivity to the nature of the

additional ligands, since, as a consequence of spin–orbit coupling, the a_1 orbital of the unpaired electron becomes mixed in this instance with the MO having b_1 symmetry, which contains no contribution from the additional ligands and therefore both its energy and its composition change little when such ligands are replaced. Conversely, the g_y component must be very sensitive to changes in the properties of additional ligands, because the angular momentum operator L_y mixes the a_1 orbital of the unpaired electron with the b_2 orbital, whose energy and composition are determined by the interactions of the d_{xz} orbital of vanadium with the b_2 orbital of the ligand (or ligands). Secondly the g_y component may be greater than $g_0 = 2.0023$, since the appreciable difference between the energies of the initial b_2 orbitals of the ligands should lead to a significant difference between the energies of the MO with b_2 symmetry (ϕ_{b_2} and $\phi^*_{b_2}$) depending on the type of ligands.

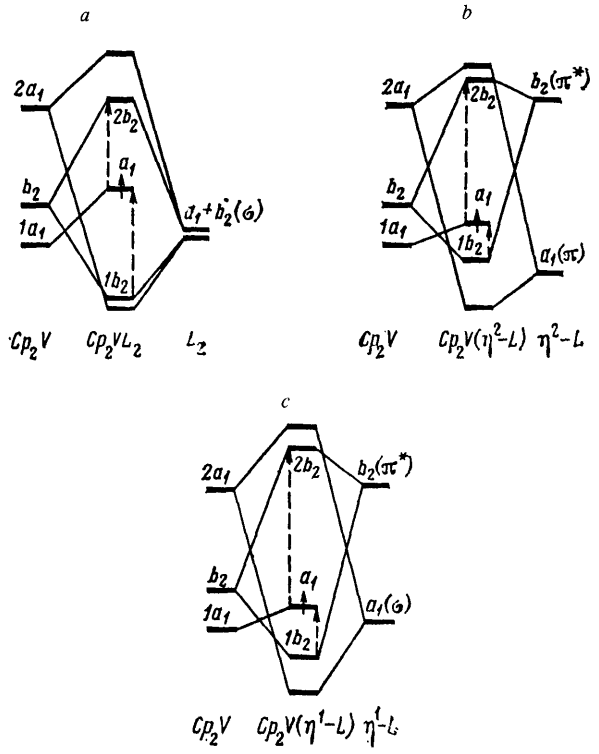


Figure 3. A qualitative energy level diagram for molecular orbitals with a_1 and b_2 symmetry in Cp_2V d^1-complexes: *a*) complexes of type (A); *b*) complexes of type (C); *c*) complexes of type (D).[20,28]

In complexes of type (A) the energy of the initial b_2 group orbital of the ligands is lower than the energy of the d_{xz} orbital of the Cp_2V complex (see Fig.3), as a result of which the energy difference ΔE between $\phi^e_{a_1}$ and ϕ_{b_2} is greater than that between $\phi^e_{a_1}$ and $\phi^*_{b_2}$, i.e. the electronic transitions predominate in the spin–orbit coupling over the "hole" transitions. Another situation arises in complexes of types (C) and (D). The high energy of the antibonding b_2 orbitals in the neutral alkene, alkyne, and CO ligands causes a shift of the energy of the b_2 and b^*_2 MO relative to the MO of the unpaired electron such that ΔE between $\phi^e_{a_1}$ and $\phi^*_{b_2}$ becomes greater than that between $\phi^e_{a_1}$ and ϕ_{b_2}, as a result of which the "hole" transitions make a greater contribution to g_y than the electronic transitions.

Unfortunately there are no literature data on the photoelectron spectra of the Cp_2V d^1-complexes of different types but such information does exist for the analogous Cp_2Mo complexes. It follows from the data of Green et al.[38] that the energy difference ΔE between the MO with a_1 symmetry, occupied in the given instance by a pair of electrons, and the orbital with b_2 symmetry (in the original study this orbital was assigned to b_1 symmetry as a result of a different type of indexing of the coordinate axes) in the complexes $Cp_2Mo(CO)$ and $Cp_2Mo(C_2H_4)$ is 0.9 eV, while in the complexes Cp_2MoMe_2 and Cp_2MoH_2 the energy differences are 2.5 and 2.2 eV respectively. At the same time, the long-wavelength transition in the electronic spectrum of Cp_2VCl_2, for example, corresponding to the excitation of the unpaired electron from the a_1 orbital to the b^*_2 orbital, is characterised by an intermediate energy of approximately 1.5 eV.[9]

On the basis of the model for binding of the additional ligands in the Cp_2V d^1-complexes considered above, the component of the $\bar{g}$ tensor greater than g_0 can be defined as the g_y component. This fact was taken into account in the compilation of Table 2, where, in contrast to the original communication,[5] the g_x and g_y components have been assigned in conformity with the model described above. Here the corresponding components of the $\bar{T}$ tensor naturally also undergo a change in indexing in such a way that $|T_x| > |T_y|$, in contrast to $|T_x| < |T_y|$ for the Cp_2V d^1-complexes of type (A). It follows from Eqns.(3a) and (3b) that the relative values of the components T_x and T_y depend only on the relative signs of the coefficients *a* and *b* defining the contribution of the vanadium d_{z^2} and $d_{x^2-y^2}$ orbitals to the MO of the unpaired electron.

Quantum-chemical calculations for the Cp_2V d^1-complexes of types (C) and (D) have not been made. As mentioned previously, calculations for the type (A) complexes lead to the conclusion that *a* and *b* have opposite signs, which is responsible for the relation $|T_x| < |T_y|$. The authors of a study[5] devoted to the analysis of the anisotropic EPR spectra of Cp_2V d^1-complexes with alkenes, alkynes, and azobenzene assume that the coefficients *a* and *b* for complexes of this type also have the opposite signs, whence follows the relation $|T_x| < |T_y|$. However, the authors[5] fail to give a correct explanation of the relation $g_x > g_y$ which follows from the preceding relation.

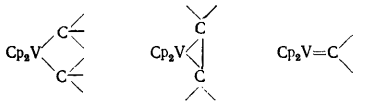
As shown above, the relation $g_y > g_0 > g_x$ between the components of the $\bar{g}$ tensor agrees best with the electronic structure of the d^1-complexes of types (C) and (D). In order to account for the relation $|T_x| > |T_y|$ associated with the above relation, one must assume that in complexes of these types the coefficients *a* and *b* have the same sign. This hypothesis agrees well with the dependence of the L–V–L valence angle on the population of the MO with a_1 symmetry known for "angular sandwiches".

The change in the relative signs of the coefficients *a* and *b* has the simple physical significance of a change in the spatial distribution of the electron density in the a_1 MO. As was correctly noted by Petersen and Dahl,[8] when $a < 0$ and $b > 0$, a small positive contribution of the $d_{x^2-y^2}$ orbital corresponds to an increase of the electron density within the L–V–L angle (along the *x* axis) and to its corresponding

decrease in the direction of the normal to the L–V–L plane (along the y axis) compared with the "pure" d_{z^2} orbital (Fig.1). The dependence of the L–M–L valence angle on the population of the MO with a_1 symmetry has been established for the Cp_2M d^0-, d^1-, and d^2-complexes: the angle L–M–L diminishes with increasing population, i.e. in this case the electronic factor (the population of the non-bonding orbital) influences the parameter of the molecular structure (the valence angle). It is natural to expect that this influence should be reciprocal, i.e. that a change in the valence angle should entail a redistribution of the spatial electron density in the a_1 MO.

It has been shown[7–9] that a simple criterion of the spatial distribution of electron density in this orbital in the transition metal d^1-complexes, especially for Cp_2V, may be the quantity a^2/b^2 determined from the anisotropic parameters of the EPR spectra. For a series of Cp_2V d^1-complexes of type (A), these quantities have been calculated.[7] Their values, which vary in the range 7.7–20, indicate the predominant contribution of the d_{z^2} orbital with a small admixture of the $d_{x^2-y^2}$ orbital. Later,[5,28] in the analysis of the EPR spectra recorded in "vitrified" toluene, it was established that the contribution of the small $d_{x^2-y^2}$ orbital for complexes of type (C) with two-electron η^2-ligands is significantly reduced ($a^2/b^2 = 70–250$), i.e. the MO of the unpaired electron is an almost pure d_{z^2} orbital.

Comparison with the available X-ray diffraction data for the structures of complexes of both types enabled the authors[5,28] to formulate a conclusion concerning the molecular structure of the complex (the L–V–L valence angle) and its electronic structure (the spatial distribution of the electron density in the a_1 MO). However for complexes of type (D) (for example, Cp_2VCO and Cp_2VCNR) a discrepancy is observed between a^2/b^2 and the L–V–L angle within the framework of this simple relation. Indeed complexes of type (D) can be regarded as limiting in the series established in accordance with a decreasing C–V–C valence angle:



(A); ~ 87° (C); 35 – 39° (D); 0°.

For complexes of type (D), in which the η-ligand is located on the x axis, the C–V–C valence angle can be regarded as zero, whence it follows that $a^2/b^2 \to \infty$, in conflict with experiment [for example, $a^2/b^2 = 13.4$ for $Cp_2V(CO)$].[28]

The conflict can be readily resolved if it is assumed that a and b have the same sign in conformity with the model of the binding of the ligands in complexes of type (C) and (D). Despite the identical values of a^2/b^2 for complexes of types (A) and (D), here the spatial distribution of electron density in the MO of the unpaired electron is significantly different. The positive sign of the $d_{x^2-y^2}$ orbital would then correspond to a decrease of electron density along the x axis and its corresponding increase along the y axis, as should be also the case under the conditions of the limiting decrease of the L–V–L valence angle.

2. Dependence of the Isotropic Hyperfine Interaction Constant A_i(V) on the Nature of the Ligand

As already mentioned, the Cp_2V d^1-complexes of types (A) and (B) differ from the complexes of types (C) and (D) by the dependence of the hyperfine interaction (HFI) constant on the nature of the additional one-electron ligands. The change in the quantity A_i(M) in transition metal complexes, where the unpaired electron is in a d orbital, has been attributed in EPR theory to the possible operation of two mechanisms: (1) the spin polarisation of the inner s orbitals and (2) the mixing of the MO_e with a MO of the complex having a suitable symmetry, in which there is a large contribution by the s orbital of the metal. In those cases where spin polarisation predominates, a correlation is observed between the change in the effective charge on the central atom (or the charge in the covalence of the metal–ligand bonds) and the quantity A_i;[99] under these conditions, an increase of the covalence of the bond entails an increase in the positive contribution to the A_i for transition elements of the first series. Bearing in mind the negative sign of A_i, for ^{51}V this should entail a decrease of $|A_i(V)|$. This type of linear relation had been noted earlier for titanium, vanadium, etc. complexes.[1] In the Cp_2V d^1-complexes of type (A), this mechanism is likewise the main one, since a linear correlation has been observed for such complexes between $|A_i(V)|$ and the sum $\sum_L (\chi_V - \chi_L)$ (Fig.4), which characterises the amount of ionic character (the covalence) of the V–L bonds. One should note that the correlation under discussion is observed when a rough approximation is used: the values of χ for the ligand atoms directly linked to vanadium are employed as the χ_L.

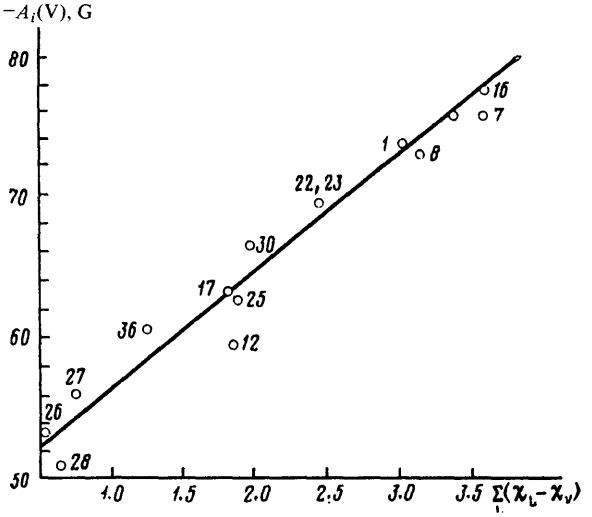


Figure 4. Dependence of the constant A_i(V) for Cp_2V d^1-complexes on the electronegativity of the ligands χ_L (χ is the Pauling electronegativity)[20] (for the significance of the numbering of the circles, see Table 1).

The linear relation between $\sum_L (\chi_V - \chi_L)$ and $|A_i|$ in a series of isostructural (within the limits of the immediate coordination environment of the vanadium atom) d^1-complexes of type (A) permits the conclusion that the HFI A_i(V) constants are additive. This makes it possible, in turn, to identify the ligands bound to vanadium in the complex from its EPR spectrum. As an illustration, Table 3 presents the experimental and calculated A_i(V) for certain mixed complexes

of the type $Cp_2VL_1L_2$; these values agree well with one another. As an example of the application of the rule of the additivity of the $A_i(V)$ for the identification of the Cp_2V d^1-complexes, one may consider the complex $Cp_2V(CN)(NCS)$ described by Morán and Fernandez.[13] The authors assumed that the complex has a structure corresponding to the presence of the isothiocyanato-ligand with a V–N bond. However, the value $|A_i(V)| = 59.43$ for this complex corresponds much better to the thiocyanato-complex $Cp_2V(CN)(SCN)$ with a V–S bond.

Table 3. Experimental isotropic parameters of the EPR spectra of certain Cp_2V d^1-complexes and the spectra calculated assuming additivity.[20]

Complex	g_i^e	$\|A_i(^{51}V)\|^e$	g_i^c	$\|A_i(^{51}V)\|^c$
$Cp_2V(Cl)Me$	1.9900	69.2	1.9898	68.7
$Cp_2V(Cl)CH_2SiMe_3$	1.9900	70.0	1.9896	69.4
$Cp_2V(Cl)SnEt_3$	1.9946	62.0	1.9954	62.2
$Cp_2V(Cl)GeEt_3$	1.9956	66.8	1.9950	64.9
$Cp_2V(CN)(NCS)$	1.9810	59.4	1.9900	66.7
$Cp_2V(CN)(SCN)$	—	—	1.9970	61.4
$Cp_2V(CH_2SiMe_3)SnEt_3$	1.9964	60 8	1.9979	57.5

*The experimental and calculated parameters are designated by the superscripts e and c respectively.

The additivity rule holds also for g_i for type (A) d^1-complexes, but with a lower degree of precision. The explanation is that, apart from the influence of the effective charge on vanadium, which alters the spin–orbit coupling constant, the quantity g_i is acted upon by at least two [sic] further factors: the contribution to g_i by the spin–orbit coupling. Both these factors also change on passing from one ligand to another and, although the overall trend in the variation of g_i is maintained (Fig.2), the overall operation of the three factors enumerated above complicates the character of the dependence of g_i on $\sum_L(\chi_V - \chi_L)$.

On passing from complexes of type (A) to those of types (C) and (D), the quantity $A_i(^{51}V)$ increases in succession and there is also a successive rise in g_i.[20] These changes are particularly clear in the carbon-containing d^1-complexes $Cp_2V(Alk)_2$, $Cp_2V(en)$, $Cp_2V(CO)$. Bearing in mind the negative sign of $A_i(V)$, its increase can be accounted for either by a decrease of spin density in the inner *s* orbitals of the vanadium or by an increase in the positive sign of the contribution of the 4*s* orbital to $A_i(V)$.

The amount of ionic character (covalence) of the V–L bonds can change on replacement of two one-electron ligands by one two-electron ligand with the same coordinating atom (carbon), but it is not possible to estimate it by a simple procedure, as has been done for complexes of type (A). One should only note that the approximation based on the use of the electronegativities of the coordinating atoms lacks significance in the given instance.

The most probable cause of the decrease of $|A_i(^{51}V)|$ on passing from complexes of type (A) to those of type (C) and further to complexes of type (D) may be the increase of the contribution of the 4s orbital to MO_e as a consequence of the mixing of the latter with a MO orbital of the same symmetry in which there is a large contribution by the 4*s* orbital. In the Cp_2V d^1-complexes there exist orbitals with a_1 symmetry, which are involved in the binding of the ligands L to Cp_2V and whose energies are close to that of MO_e. The effectiveness of their mixing with MO_e depends on the energy difference between the orbitals $\phi^e_{a_1}$ and ϕ_{a_1}, which should change following the replacement of ligands. If one takes into account the fact that, according to the results of quantum-chemical calculations[7] for the complex Cp_2VCl_2, the contribution of the 4*s* orbital of vanadium to MO_e is less than 1%, then the observed change in A_i for complexes of type (C) must be due to the increase of this contribution up to 2%, while that for the complexes of type (D) is caused by an increase up to 4%. (The value of A_i in the case of one unpaired electron in the 4*s* orbital of ^{51}V, quoted by Goodman and Raynor,[1] was used to calculate the amount of the admixture of the 4*s* orbital).

3. Hyperfine Interaction with Magnetic Nuclei of the Ligands in the Cp_2V d^1-Complexes

The idea of the transfer of spin density to the ligands in paramagnetic transition metal complexes has long been adopted in coordination chemistry. The fact that hyperfine interaction with the magnetic nuclei of the ligands has been observed by EPR has considerably promoted the development of this concept. Quantum-chemical calculations for the Cp_2V d^1-complexes yield high contributions of the ligands to MO_e. For the p_π orbitals of Cl or SH in Cp_2VCl_2 and $Cp_2V(SH)_2$, the contribution is approximately 22%.[7] However, hyperfine interaction with the magnetic ^{35}Cl and ^{37}Cl nuclei in the EPR spectrum of Cp_2VCl_2 as well as with the ^{79}Br and ^{81}Br nuclei in the Cp_2VBr_2 spectrum has not been observed,[9–12] but in a whole series of other complexes, where L = H, Me, Et, CH_2SiME_3, $SnET_3$, or $HgGe(C_6F_5)_3$ (Table 1), the change in spin density on the ligands has been confirmed experimentally by the presence of a signal due to the hyperfine interaction with the ^1H, ^{117}Sn, ^{119}Sn, ^{199}Hg, and ^{201}Hg nuclei in the EPR spectra. The hyperfine interaction with the ^{31}P and ^{75}As nuclei has been observed[29,30] in type (B) complexes, where the ligands were dialkyl phosphorodithioates and dialkyl arsenodithioates. For complexes of types (C) and (D), hyperfine interaction with the magnetic nuclei of the ligands was not observed. One should note that the additional hyperfine interaction with the magnetic nuclei of the ligands makes it possible to identify Cp_2V d^1-complexes with a high degree of reliability on the basis of their isotropic EPR spectra as a consequence of the highly characteristic nature of the latter. As an example, Fig.5 presents the isotropic EPR spectra of certain Cp_2V d^1-complexes.

The spin densities in the *s* orbitals of the ligands calculated from the experimental HFI constants are 2.9% (H), 2.7% (Me), and 1.9–2.5% ($SnEt_3$). Thus the overall spin density should not exceed 6% in the presence of two such ligands at the vanadium atom. According to the results of quantum-chemical calculations by a number of workers[6,7] for the Cp_2Ti, Cp_2V, Cp_2Cr, and Cp_2MO d^1-complexes, the contribution of the ligand *s* and *p* orbitals to MO_e is very insignificant. When these data are used as the starting point, one may conclude that the principal mechanism of the transfer of spin density to the α-atoms of the σ-bonded ligands is the

spin polarisation of the V–L–σ bonds under the influence of the unpaired electron in the *d* orbitals (the d_{z^2} orbital) of vanadium.

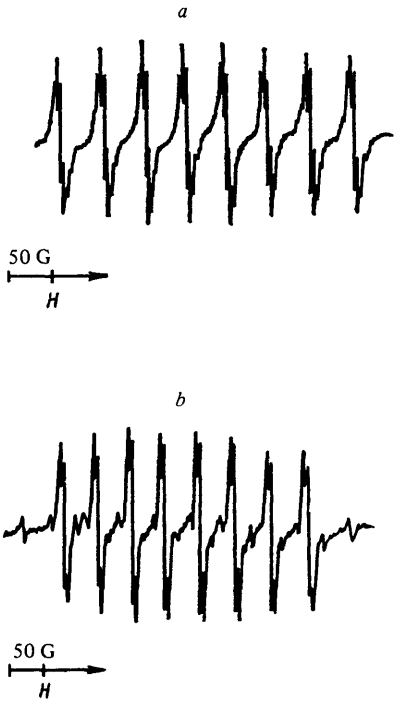


Figure 5. Isotropic EPR spectra of Cp_2V d^1-complexes: *a*) Cp_2VMe_2; *b*) $Cp_2V(CH_2SiMe_3)(SnEt_3)$ (toluene, 25 °C).[23]

In those cases where the α-atom of the ligands have p_π orbitals with a symmetry suitable for interaction with MO_e, a spin density should appear at the nucleus of the ligand atom as a result of the direct interaction between the ligand orbitals and the d_{z^2} orbital of the metal. Since in this case the binding to the metal is also achieved via the p_σ orbitals, the isotropic constant for the hyperfine interaction with the magnetic nuclei of the ligands is determined by the overall spin density of two different *p* orbitals of the ligand: p_π and p_σ. The two contributions have the opposite signs, because the direct delocalisation of the unpaired electron over the ligand leads to the appearance of a positive spin density in the p_π orbital, while spin polarisation induces a negative spin density in the p_σ orbital. An appreciable hyperfine interaction with the ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br nuclei is absent in the complexes Cp_2VCl_2 and Cp_2VBr_2,[9–12] which indicates a low overall spin density in the *p* orbitals of these ligands, i.e. approximately equal contributions by each mechanism. If it is assumed (and this assumption is fairly valid) that the spin polarisation of the σ-bonds induces approximately equal spin densities in the orbitals (*s* and *p*) involved in the binding regardless of their nature, then it follows from the equality $\rho_{p_\pi} = \rho_{p_\sigma}$ that the overall contribution of the p_π orbitals of the ligands to the MO_e for the Cp_2V d^1-complexes should not exceed 6%. This differs significantly from the calculated data for Cp_2VCl_2 (22%) and Cp_2VS_5 (21%) obtained by Petersen et al.,[7] but agrees with the calculated data for the series of Cp_2V d^1-complexes quoted by Stewart and Porte.[6]

It is noteworthy that hyperfine interaction with the magnetic Cl and Br nuclei has been observed experimentally in the EPR spectra of the isoelectronic cationic complexes Cp_2Mo^+ and Cp_2W^+ and is appreciable: $A(Cl) = 3.1$ G and $A(Br) = 15.0$ and 21.9 G.[40] The spin polarisation contribution should not change significantly on passing from Cp_2V to the Cp_2Mo^+ and Cp_2W^+ complexes and the increase of $A(Cl)$ and $A(Br)$ should therefore be attributed to an increase in the direct contribution of the p_π orbitals of the halogens to MO_e. This conclusion agrees with the results of a calculation[7] indicating an increase in the contribution of the p_π ligand orbitals to MO_e for Cp_2MoCl_2 relative to Cp_2VCl_2.

Spin density can be transferred to the β-atoms of the ligands (the protons of the methyl and methylene groups in alkyl ligands) from the central atom via a mechanism similar to that of hyperconjugation in organic π-radicals.[41] This is indicated by the values of $A(H_\beta)$ which are comparable to $A(H_\alpha)$ for the hydride complex; in the case of the spin polarisation mechanism, the $A(H_\beta)$ must be much smaller, because the spin polarisation rapidly decays with increase of the number of "spin polarised" σ-bonds.

IV. EPR STUDY OF Cp_2V d^1-COMPLEXES IN SOLUTION

The data presented show that there is a close relation between EPR spectroscopic parameters and the structure of the Cp_2V d^1-complexes, which in some cases has a simple significance. This permits the EPR identification of the relatively unstable Cp_2V d^1-complexes formed as intermediates in various reactions and also determination of their structures.

1. Oxidative Addition to Cp_2V ($d^3 \rightarrow d^1$ Reactions)

Oxidative addition is the most typical reaction for Cp_2V. A wide variety of reagents, namely variable-valence metal salts, alkyl halides, chalcogenides, organic disulphides, alkynes, alkenes, and many other compounds interact with Cp_2V to form d^1-complexes (sometimes d^2-complexes). We may note that a large number of Cp_2V d^1-complexes with heterocumulenes have been synthesised and investigated during the last ten years by Floriani and co-workers (see, for example, Pasquali et al.[42]).

One of the first reactions involving oxidative addition to Cp_2V investigated was that with alkyl halides. A study[43] of the interaction of Cp_2V with MeI, EtBr, and $PhCH_2Cl$ led to the conclusion that the reaction proceeds in accordance with the equation

$$2Cp_2V + X-R \rightarrow Cp_2V-R + Cp_2V-X,$$

possibly via the intermediate formation of the extremely unstable complex $Cp_2V\begin{smallmatrix}R\\X\end{smallmatrix}$. Treatment of Cp_2V–R with an excess of R–X for a long time led to the appearance of Cp_2VX and R–R. The authors did not use the EPR method in their investigations, which apparently retarded for more than ten years the synthesis of dialkyl and alkyl halide Cp_2V d^1-complexes. The results of the above study[43] also apparently promoted the firm establishment of the idea that the high lability of such Cp_2V derivatives is due to the steric strain at the central atom.[44]

In reality, as shown[45] by monitoring the reaction of Cp_2V with RX with the aid of EPR, the latter proceeds in a more complex manner (Scheme 1):

Scheme 1

$$Cp_2V\langle^{R}_{R} + Cp_2VX;$$

$$(c)\uparrow Cp_2VR$$

$$Cp_2V + X{-}R \xrightarrow{(a)} Cp_2V\langle^{R}_{X} \xrightarrow[(b)]{Cp_2V} Cp_2V{-}R + Cp_2V{-}X;$$

$$(d)\downarrow$$

$$Cp_2V{-}X + [\dot{R}].$$

The first stage of the reaction is the synchronous oxidative addition of a molecule of RX to Cp_2V with formation of the alkyl halide d^1-complex $Cp_2V\langle^{R}_{X}$, which is stable. The difficulty of detecting it in solution by traditional methods is due to the reaction conditions and not to its increased lability. The presence in solution of Cp_2V, with which $Cp_2V\langle^{R}_{X}$ reacts very rapidly yielding Cp_2VR and Cp_2VX, is the main cause of the extremely low stationary concentration of $Cp_2V\langle^{R}_{X}$.[45] Under specially selected conditions, all the stages of the reaction can be realised separately. Thus slow dropwise addition at reduced temperatures (between -30° and -50 °C) of a solution of Cp_2V to a solution of RX taken in a large excess (more than 100-fold) makes it possible to reduce significantly the rate of the second stage (*b*) and promotes a steady detection of $Cp_2V\langle^{R}_{X}$ in solution by EPR.

We may note that, when alkyl iodides (MeI and Me_3SiCH_2I) are employed under the usual conditions, the interaction of Cp_2V with RX in stoichiometric proportions leads to the formation of appreciable amounts of the dialkyl complex Cp_2VR, which can be unambiguously identified from the EPR spectrum. It has been established, also by EPR, that it is formed as a result of the interaction of $Cp_2V\langle^{R}_{X}$ with Cp_2VR [stage (*c*)], accumulating in solution in the course of the reaction. The observation of this reaction made it possible to develop a new method of synthesis of dialkyl Cp_2V d^1-complexes, previously difficult to obtain, using Cp_2V and an alkyl halide as the starting materials.[45]

Another example of oxidative addition to Cp_2V, the understanding of the detailed mechanism of which would be impossible without the application of the EPR method, is provided by the interaction of Cp_2V with organic and organoelemental derivatives of cadmium and mercury. As early as 1975, it was shown[46] that the reaction of Cp_2V with $Cd(GeR_3)_2$ leads to the formation of Cp_2VGeR_3. The reaction mechanisms were assumed to involve the insertion of Cp_2V in the Cd–Ge bond (which is equivalent to oxidative addition to Cp_2V) with subsequent elimination of metallic cadmium and GeR_3. In a study[16] of the interaction of Cp_2V with $CdMe_2$, $CdEt_2$, $Cd(CH_2Ph)_2$, and $CdPh_2$ by EPR, the formation of Cp_2V d^1-complexes of the type Cp_2VR_2 was recorded. One of the complexes, namely dimethylvanadocene Cp_2VMe_2, was isolated in a crystalline form and thus proved to be the first reliably demonstrated dialkyl Cp_2V d^1-complex. Together with the data of Razuvaev et al.,[46] the results of this study led to the establishment of a scheme for the interaction of Cp_2V with organic and organoelemental derivatives of cadmium (Scheme 2):

Scheme 2

$$Cp_2V + X{-}Cd{-}X \rightarrow \left[Cp_2V\langle^{CdX}_{X}\right] \begin{cases} \rightarrow Cp_2V{-}X + Cd + [\dot{X}]; \\ \rightarrow Cp_2V\langle^{X}_{X} + Cd. \end{cases}$$

The primary product, a d^1-complex with a V–Cd bond, is merely a tentative intermediate in the above scheme. The final proof of the mechanism illustrated in Scheme 2 has been obtained recently[24] in a study of the reaction of Cp_2V with $Hg[Ge(C_6F_5)_3]_2$. As in the case of the reaction with Cp_2VGeR_3, the final product in this instance is the d^2-complex $Cp_2VGe(C_6F_5)_3$. A d^1-complex, which is a product of the oxidative addition of the organobimetallic derivative to Cp_2V, was detected by EPR in the course of the reaction. The presence of the mercury-containing substituent in this complex follows unambiguously from the analysis of the hyperfine structure of the EPR spectrum, which contains "satellite" components due to the interaction of the unpaired electron with magnetic Hg isotopes (Fig.6).

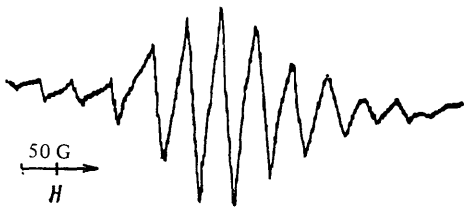


Figure 6. Isotropic EPR spectrum of $Cp_2V[Ge(C_6F_5)_3]$. $.HgGe(C_6F_5)_3$ (toluene, 10 °C).[24]

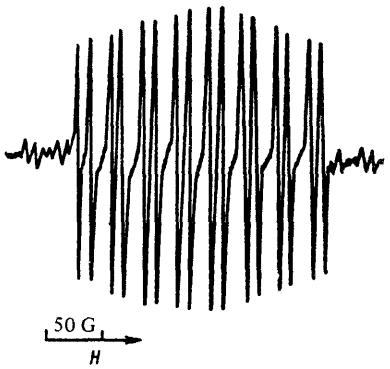


Figure 7. Isotropic EPR spectrum of $Cp_2V(H)SnEt_3$ (toluene, 25 °C).[23]

The first hydride d^1-complex $Cp_2V{-}Cp_2V(H)SnEt_3$, obtained as an intermediate in the reaction of Cp_2V with $HSnEt_3$, was detected by EPR.[23] The parameters of the observed EPR spectrum (Fig.7) [g_i = 2.0007; A_i(V) = -41.6 G; A_H = 14.6 G; A_{Sn} = 143 G] define unambiguously

the composition of the complex. Judging from the parameters of the anisotropic EPR spectrum, its structure is unusual for d^1-complexes with two η^1-ligands. The principal components of the $\bar{g}$ and $\bar{T}$ tensors of this complex differ appreciably from values typical for type (A) d^1-complexes and are close to the corresponding parameters of the type (C) d^1-complexes.

As mentioned above (in Section III), there is a relation between the spectroscopic parameters of the Cp_2V d^1-complexes and the structure, in particular the L–V–L valence angle. The d^1-complexes of type (C) usually differ from the d^1-complexes of type (A) by significantly smaller L–V–L valence angles. Judging from the EPR parameters, the compound $Cp_2V(H)SnEt_2$ should also differ in its structure from the usual d^1-complexes with two one-electron ligands, having a reduced L–V–L valence angle. This may be caused by the formation of an intramolecular bridging hydride bond H...Sn. The conclusions concerning the structure of the complex $Cp_2V(H)SnEt_3$, derived from the analysis of the spectroscopic data, cannot be tested by X-ray diffraction, since the complex investigated cannot be isolated from the reaction medium. However, a similar intramolecular hydride bond, leading to a decrease of the H–Nb–Sn valence angle to 58°, has been recently observed in a study of the complex $(Cp_2NbH)_2SnClEt$ by X-ray diffraction.[47]

In the presence of $HSnEt_3$ the hydride Cp_2V d^1-complex is converted, as shown by EPR, into a new d^1-complex containing two $SnEt_3$ groups, namely $Cp_2V(SnEt_3)$. This is indicated by the hyperfine structure of the EPR spectrum, corresponding to the interaction of the unpaired electron with the two equivalent tin nuclei.[23] The complex $Cp_2V.(SnEt_3)_2$ is also unstable and is converted after a time into Cp_2VSnEt_3 and hexaethyldistannane.[23]

The reaction of Cp_2V with $HSnEt_3$, investigated by EPR, is also of interest, because its mechanism may be similar in many details to the mechanism of the reaction of Cp_2V with alkanes (activation of C–H bonds[48]). Intermediates, with a structure analogous to that of the hydride complex $Cp_2V(H).SnEt_3$, have been postulated[48] in the reaction

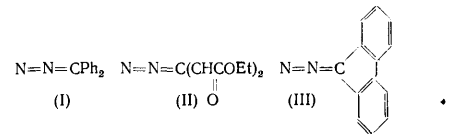
$$Cp_2V + CH_4 \rightarrow Cp_2V\begin{matrix}H\\Me\end{matrix}.$$

The existence of the fairly stable complex $Cp_2V(H)SnEt_3$ makes this hypothesis quite probable. We may note that the reaction of Cp_2V with $HSiCl_3$ described by Cardoso et al.,[49] which leads to the formation of a d^1-complex, can also proceed via the intermediate formation of a hydride silyl d^1-complex.

As already mentioned, the carbene-like properties of Cp^2V are very strikingly manifested in reactions with various substrates containing double and triple bonds. Many d^1-complexes of this type have been isolated in a pure state and their structures have been determined by X-ray diffraction. In all cases where the structure and EPR parameters of the complexes are known, complete agreement between them has been found. On the other hand, in certain EPR investigations of Cp_2V d^1-complexes the conclusions reached concerning the structure of the complexes are not entirely correct. Some of these controversial conclusions are discussed below.

It has been demonstrated convincingly[50] that the conclusions reached in an earlier investigation[51] of the structure of Cp_2V were based on an erroneous experiment. The isotropic EPR spectrum with $g_i = 2.00$ and $A_i(^{51}V) = 27.4$ G observed by the authors,[51] could not have been due to Cp_2V and must have been caused by the presence of an impurity. However, Prins[50] was also unable to assign the given spectrum to any one complex. On the basis of the conclusions reached in the present review, one may decide that the impurity signal, erroneously attributed to Cp_2V, referred to the Cp_2V d^1-complex of type (C) containing a two-electron η^2-ligand. It is difficult to arrive at conclusions about the nature of this ligand, since the experimental conditions are not fully known; it is quite likely that it might have been a carbene or a carbene-like ligand.

In considering reactions involving the oxidative addition of neutral ligands to Cp_2V one must deal with the study[35] of the interaction of Cp_2V with substituted diazomethanes:

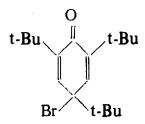


(I) (II) (III)

Depending on the diazomethane employed, EPR spectra of two types were observed: a spectrum with $g_i = 1.9918$ and $A_i(^{51}V) = 23$ G for (I) and one with $g_i = 1.9942$ (II) and 1.9953 (III) and $A_i(V) = 41$ G for (II) and (III). Despite the difference between the parameters, the authors[35] assigned the observed EPR spectra to g^1-complexes of one type, explaining the difference indicated in the spectra by the different degrees of delocalisation of the unpaired electron over the ligand. However, as shown above (Section II), the nature of the ligand in Cp_2V d^1-complexes of types (C) and (D) does not influence their EPR parameters to such a great extent (particularly as regards A_i). The observed difference between the constants $A_i(V)$ therefore requires a different explanation. The most natural cause of the difference between the EPR spectra is, in our view, the fact that they arise from complexes of different types. Judging from the value of $A_i(V)$, compound (I) is a type (D) d^1-complex with a two-electron η^1-ligand. Compounds (II) and (III) are type (C) d^1-complexes with a two-electron η^2-ligand.

2. Oxidation Reactions of Cp_2V d^2-Complexes ($d^2 \rightarrow d^1$ Reactions

The EPR method has been used particularly successfully in the study of reactions of the type $d^2 \rightarrow d^1$, namely reactions involving the oxidation of Cp_2V d^2-complexes. Compounds of the type Cp_2VX, where X = Cl, Br, alkyl, GeR_3, SnR_3, etc., are readily oxidised to Cp_2V d^1-complexes by various halogen-containing reagents, both inorganic and organic. The formal oxidation state of vanadium then increases from +3 to +4. The oxidation of Cp_2VCl, Cp_2VBr, Cp_2VMe, $Cp_2VCH_2SiMe_3$, Cp_2VGeEt_3, Cp_2VSnEt_3, and other Cp_2V d^2-complexes by reagents such as Ph_3CCl,

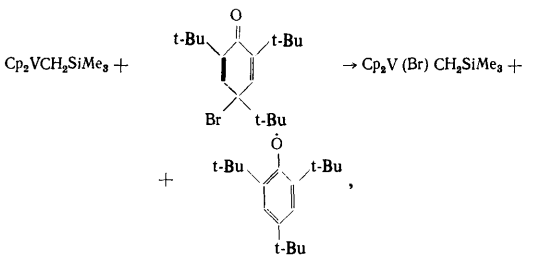


CuCl, $CuCl_2$, AgCl, AgBr, and Cp_2VCl_2 with formation of the corresponding Cp_2V d^1-complexes has been investigated[12,18,23] by EPR:

$$Cp_2VCl + Ph_3CCl \rightarrow Cp_2VCl_2 + Ph_3\dot{C}, \quad (4)$$

$$Cp_2VBr + CuCl \rightarrow Cp_2VBrCl + Cu, \quad (5)$$

$$Cp_2VMe + AgCl \rightarrow Cp_2V(Cl)Me + Ag, \quad (6)$$

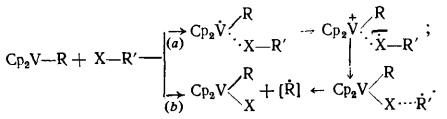


(7)

$$Cp_2VGeEt_3 + Cp_2VCl_2 \rightarrow Cp_2V(Cl)GeEt_3 + Cp_2VCl. \quad (8)$$

The occurrence of reactions (4) and (7), in which the oxidant is reduced to an organic free radical, clearly indicates a one-electron mechanism of the oxidation reaction. The oxidation-reduction reaction via a mechanism involving inner-sphere (bridge-type) one-electron transfer (with transfer of the bridging ligand) appears to be the most likely. This mechanism is formally equivalent to the transfer of a halogen atom [Scheme 3, pathway (*b*)].

Scheme 3



Reactions (4)–(8) indicate a high "affinity" of the Cp_2V d^2-complexes for one-electron reagents; free radicals may also be included among them. Hitherto there has been virtually no information in the literature about the reactions of Cp_2V d^2-complexes with free radicals. An exception is the study of Morán and Gayoso,[14] who showed that nitric oxide (NO), which is a stable radical, reacts with Cp_2VCl and Cp_2VBr, forming the d^1-complexes $Cp_2V(Cl)NO$ and $Cp_2V(Br)NO$ respectively. The study of the interaction of the Cp_2V d^2-complexes with free radicals is of undoubted interest, since reactions of this kind have been little investigated.

The oxidation-reduction reactions between Cp_2V d^2- and d^1-complexes, for example reaction (8), occupy a special place among the $d^2 \rightarrow d^1$ reactions. The complex Cp_2VCl_2 can also oxidise monoalkyl derivatives of the type Cp_2VR.[18] The mechanism of these reactions is evidently similar to that illustrated in Scheme 3. Mixed alkyl halide Cp_2V d^1-complexes can also participate in the oxidation-reduction $d^2 \rightarrow d^1$ reactions as oxidants. For example, $Cp_2V(Cl)Me$ can oxidise Cp_2VGeEt_3 and Cp_2VSnEt_3 to the corresponding d^1-complexes, being reduced at the same time to Cp_2VMe:[23]

$$Cp_2V\begin{matrix}Me\\Cl\end{matrix} + Cp_2V{-}R' \rightarrow Cp_2V{-}Me + Cp_2V\begin{matrix}R'\\Cl\end{matrix}. \quad (9)$$

The reaction between Cp_2V and alkyl halide d^1-complexes and alkyl d^2-complexes, which results in the formation of dialkyl d^1-complexes and monohalide d^2-complexes, proceeds differently:[18]

$$Cp_2V\begin{matrix}Cl\\R\end{matrix} + Cp_2V{-}R' \rightarrow Cp_2V\begin{matrix}R'\\R\end{matrix} + Cp_2VCl. \quad (10)$$

In terms of its formal features, reaction (10) is an exchange reaction in which the halogen in the d^1-complex is replaced by an alkyl group. However, its mechanism is evidently more complex and requires additional study.

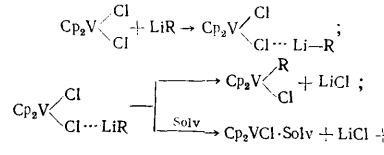
Investigation of reactions (4)–(10) by EPR showed that they are in many instances quantitative and can be used as preparative methods for the synthesis of mixed alkyl halide and dialkyl Cp_2V d^1-complex.[18] In the EPR variant, reactions of the type $d^2 \rightarrow d^1$ can be used as tests for the detection of Cp_2V d^2-complexes in solution. In particular, the formation of $Cp_2VGe(C_6F_5)_3$ and Cp_2VGePh_3 in the reactions of Cp_2V with $Hg[Ge(C_6F_5)_3]_2$ and $Hg(GePh_3)_2$ has been demonstrated in this way.[24]

3. Cp_2 d^1-Complexes in Exchange Reactions ($d^1 \rightarrow d^1$ Reactions)

The reactions of Cp_2VCl_2 with organometallic compounds, in particular with lithium, cadmium and aluminium compounds, have been most thoroughly investigated among processes of the type $d^1 \rightarrow d^1$ studied by EPR. Attempts to employ organolithium compounds for the synthesis of dialkyl complexes in solvating solvents have been frequently undertaken by various groups of investigators,[52] but they all gave a negative result—the reaction products were Cp_2V d^2-complexes, i.e. Cp_2VCl was reduced by LiR. These data served as a basis for the idea that the dialkyl Cp_2V d^1-complexes are unstable due to the steric hindrance around the central atom.[44]

The synthesis of Cp_2VMe_2, Cp_2VEt_2, and $Cp_2V(CH_2Ph)_2$ by the reaction of Cp_2V with organocadmium compounds showed that this concept is erroneous, after which Cp_2VMe_2 was also obtained by the exchange reaction from Cp_2VCl_2 and MeLi but in toluene instead of tetrahydrofuran.[53] There is no explanation in the literature of this type of strong dependence of the reaction pathway on the nature of the solvent. We believe that the main cause may be the influence of the solvating solvent on the intermediate complex formed in the first reaction stage (see Scheme 4).

Scheme 4



A second pathway, involving the oxidation-reduction reaction leading to the reduction of Cp_2VCl_2 to Cp_2VCl, competes in the presence of a solvating solvent, for example THF, with the "normal" pathway corresponding to the formal substitution of Cl^- by R^-. The solvation of the vanadium atom in the resulting d^2-complex by the solvent, which undoubtedly enters into the composition of the outer coordination sphere also of the initial compound Cp_2VCl_2, should play an important role in this process. Use of non-solvating solvents (for example toluene, as in the study of Foust and Rausch[53]) promotes the "normal" course of reaction.

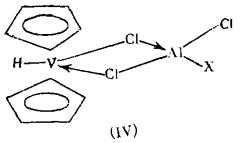
The OMC of cadmium and aluminium are also capable of interacting with Cp_2VCl_2, forming exchange products. The reaction of Cp_2VCl_2 with Et_2AlCl and other aluminium OMC has been studied in greatest detail. The EPR spectrum of the dialkyl vanadocene derivative has in fact been observed for the first time in one of these reactions. This concerns an EPR study[54] of a catalytic system based on Cp_2VCl_2 and an organoaluminium compound in which EPR spectra with a parameter $g_i = 1.992$ and $A_i \cong 62$ G, which evidently refer, as is now evident, to Cp_2VMe_2 and Cp_2VEt_2, were recorded. These products are obtained following the complete ligand exchange between Cp_2VCl_2 and the organoaluminium compound:

$$Cp_2VCl_2 + 2R_2AlCl \rightarrow Cp_2VR_2 + RAlCl_2. \quad (11)$$

Mixed alkyl halide Cp_2V d^1-complexes are also formed in such

reactions after the replacement of one halogen atom by an alkyl group.

A study of the reaction of Cp_2VCl_2 with Et_2AlCl led[54] to the observation of yet another unidentified EPR spectrum with the parameters $g_i = 1.997$ and $A_i = -39.5$ G. The same signal was later recorded in another study.[55] Having investigated in detail the isotropic and anisotropic EPR spectra, the authors[55] concluded that the EPR spectrum refers to a hydrido Cp_2V complex having the following structure:



(IV)

This hypothesis of such an unusual structure with parallel cyclopentadienyl rings is based on the "anomalous", from the authors' points of view,[55] parameters of the EPR spectrum of this complex compared with other Cp_2V d^1-complexes ($Cp_2.VCl_2$ and Cp_2VR_2). The disappearance of the isotropic EPR spectrum of the complex (IV) on treatment with THF or pyridine and the appearance of a new EPR spectrum with the parameters $g_i = 1.988$ and $A_i(^{51}V) = 70.3$ G was explained[55] by the conversion of compound (IV) into the hydrochloride d^1-complex $Cp_2V(H)Cl$ and was also regarded as evidence in support of the structure (IV), which the authors proposed. Treatment of a solution containing $Cp_2V(H)Cl$ with HCl led to the appearance of the spectrum of Cp_2VCl_2, while treatment with Et_2AlCl led to the spectrum of Cp_2VEt_2.

Comparison of the spectroscopic parameters quoted by Evans et al.[55] and the corresponding parameters of the EPR spectra of d^1-complexes of type (C) (with one two-electron η^2-ligand) and the known hydride Cp_2V and Cp_2Nb d^1-complexes, as well as the analysis of the chemical behaviour of the complexes showed that the interpretation of the two EPR spectra observed initially was erroneous.

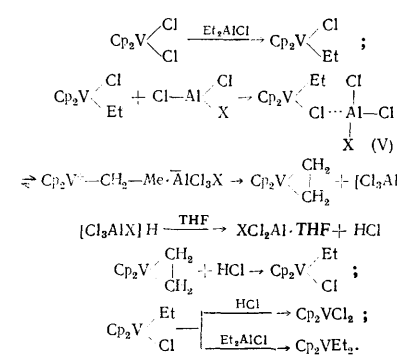
In the first place, in terms of their isotropic and anisotropic parameters [$g_i = 1.996$, $A_i(V) = -41.1$ G, $g_x = 2.001$, $g_y = 1.987$, $g_z = 2.000$, $T_x = -63.7$ G, $T_y = -70.5$ G, and $T_z = +1.09$ G], the primary EPR spectrum corresponds most closely to a Cp_2V d^1-complex with a two-electron η^2-ligand. Furthermore, one can assume that in the complex (IV) the hyperfine interaction with the hydrogen atom is weak and is therefore not manifested in the EPR spectrum (complexes of this type are unknown). As regards the complex $Cp_2V(H)Cl$, the absence from its spectrum of evidence for its hyperfine interaction with the ^1H nucleus is difficult to account for, since the $A(H)$ constants for the EPR spectra of other similar complexes [$Cp_2V(H)SnEt_3$ [23] and $Cp_2Nb(H)Cl$ [56]] are fairly large (>10 G) and the corresponding hyperfine structure should have been observed.

The absence of such hyperfine structure in the EPR spectra indicates an incorrect interpretation of the latter. The parameters of this spectrum correspond exactly to those of the spectrum of the known $Cp_2V(Cl)Et$ d^1-complex within the limits of the error of the measurement.

The new interpretation of the EPR spectra observed in the reaction of Cp_2VCl_2 with Et_2AlCl leads to a different mechanism for this reaction (Scheme 5), which differs from that proposed by Evans et al.[55]

The interaction of the reactants in the first stage of the reaction (the presence of small amounts of Et_2AlCl) leads to the replacement of one chlorine atom at the vanadium atom by the ethyl group with formation of the complex $Cp_2V(Cl)Et$, which can exist in solution both in a free state and in the form of a complex with an $XAlCl_2$ molecule. (The ability of Cp_2VCl_2 to form complexes with $AlCl_3$ is known[54]). An analogous complex, consisting of the reaction products, is formed on interaction of Cp_2VCl_2 with $Cd(GeR_3)_2$.[57] It is noteworthy that in solution $Cp_2V(Cl)GeR_3$ and its complex $Cp_2V(Cl)GeR_3.Cd(Cl)GeR_3$ are spectroscopically indistinguishable. Under the reaction conditions (with a hexane–CH_2Cl_2 mixture as the solvent), the complex (V) undergoes partial dissociation; proton transfer from $Cp_2V^+-CH_2-Me$ to $AlCl_3X^-$, which is evidently a stronger Lewis base than the ethylene complex formed, completes the process. In our view the "anomalous" EPR spectrum is in fact due to the ethylene Cp_2V d^1-complex.

Scheme 5



Under the influence of THF and the solution, the hydrogen chloride bound in the complex is liberated and reacts with the ethylene complex, converting it into $Cp_2V(Cl)Et$. Subsequent treatment with HCl converts $Cp_2V(Cl)Et$ into Cp_2VCl_2, while on interaction with Et_2AlCl alkylation proceeds further with formation of Cp_2VEt_2. The proposed mechanism undoubtedly requires special experimental confirmation, but it is much more consistent with the EPR data.[54,55] The results of a study[58] in which analogous reactions were observed between Cp_2MoCl_2 and Et_2AlCl may serve as its indirect confirmation.

Yet another interesting variety of $d^1 \rightarrow d^1$ reactions has been discovered[23] by EPR in a study of the interaction of Cp_2VEt_2 and $Cp_2V(CH_2SiMe_3)_2$ with $HSnEt_3$. This interaction leads to the formation of mixed d^1-complexes of the type $Cp_2V(R)SnEt_3$ under mild conditions. The second alkyl group is also not substituted under more severe conditions (−20 °C)—up to the decomposition temperatures of the initial dialkyl complexes. The mechanism of this reaction is still obscure and requires further study.

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In conclusion one should note that the EPR method will undoubtedly prove useful in the study of the structures of new Cp_2V d^1-complexes, whose chemistry is at present developing vigorously. Thus, much interesting information can be obtained from the study of the reactions, mentioned in this review, of Cp_2V with heterocumulenes which are coordinated to vanadium and in many cases undergo a series of consecutive reactions of the type $d^1 \rightarrow d^1$. Another interesting aspect of the chemistry of Cp_2V, involving reactions with unsaturated compounds containing Si=C, Si=Si, and Ge=Ge bonds, has so far been almost completely uninvestigated. It is to be expected that the high reactivity of Cp_2V with respect to multiple bonds will lead in this instance to the formation of complexes of type (C) with η^2-coordinated two-electron ligands, whose structure can be determined from the EPR parameters.

In the methodological sense, the conclusions reached in this review concerning the relation between the EPR parameters of the Cp_2V d^1-complexes and their structure can also be used in the study of the d^1-complexes of other transition metals (Ti, Zr, Hf, Nb, Ta, Mo, and W).

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