Generation of the first representatives of the Schrock complexes of heavy carbene analogs

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The reaction of Cp^*_2V with 7-sila(germa)norbornadiene derivatives generated the first representatives of Schrock complexes of heavy carbene analogs with transition metals. Decamethylvanadocene Cp^*_2V can be used as a paramagnetic trap for short-lived dimethylgermylene.

Key words: carbene analogs, Schrock complexes of heavy carbene analogs, vanadocene, decamethylvanadocene, 1,1-dimethyl-7-silanorbornadiene, 1,1-dimethyl-7-germanorbornadiene, ESR spectra.

Vanadocene Cp_2V (**1**) and its substituted derivatives, for instance, decamethylvanadocene Cp^*_2V (**2**), are coordinatively unsaturated compounds and react readily with organics and organometallics *via* oxidative addition to form paramagnetic d^1-complexes.[1] In particular, the reactions of vanadocene with compounds containing a lone electron pair (carbon oxide, isonitriles, nitrenes) have been reported.[1—3] In the adducts formed, the added ligand is terminally linked to the vanadium atom. Parameters of isotropic and anisotropic ESR spectra of these complexes have characteristic values, due to which they can unambiguously be identified in solutions by ESR.[1]

Silylenes, germylenes, and stannylenes are known to form complexes with transition metal compounds (Cr, Mo, W, Fe, Ru, Ni, Pd, Pt), being similar in electronic structure to the Fischer carbene complexes.[4—6] The Schrock-type complexes of heavy carbene analogs are not described to date.

The purpose of this work is to synthesize the first representatives of the Schrock-type complexes of heavy carbene analogs and reveal a possibility of using vanadocenes as paramagnetic traps for derivatives of low-coordinate silicon, germanium, and tin (silylenes, germylenes, stannylenes, and others). Therefore, we used the ESR method to study the reactions of Cp_2V and Cp^*_2V with 7,7-dimethyl-7-silanorbornadiene (**3**) and 7,7-dimethyl-7-germanorbornadiene (**4**) derivatives in solution.

The reaction of Cp^*_2V with **3** in a toluene—THF mixture occurs only at 60—65 °C. It is accompanied by a change in the color of the solution and successive appearance in the ESR spectrum of several signals characteristic of the paramagnetic d^1-vanadium derivatives (^{51}V; 99.76%; $I = 7/2$; $\mu_N = 5.1392$).[7]

The intensity of the primary ESR spectrum of the reaction product of **2** with **3** (an octet with the parameters $g_i = 1.9853$; $A_i(^{51}V) = 2.54$ mT) primarily increases during the reaction, reaches a maximum, and then decreases gradually. This is accompanied by the appearance of a signal from another paramagnetic species in the ESR spectrum. This signal is also an octet but differs in parameters ($g_i = 1.9673$; $A_i(^{51}V) = 5.93$ mT) from the primary signal. Its intensity increases gradually in the reaction course, and after the reaction completion this signal remains to be the single in the ESR spectrum (Fig. 1).

It is known[1] that the magnetoresonance parameters (especially the isotropic constant $A_i(^{51}V)$) in the vanadocene complexes depend strongly on the complex type, whereas for the complexes of the same type they are virtually independent of the nature of the ligand (ligands). For the vanadocene complexes with two one-electron η^1-ligands, the $|A_i(^{51}V)|$ values range from 5.5 to 8.0 mT; for the complexes with η^2-ligands (alkenes, alkynes, *etc.*), they lie in a range of 4.0—4.5 mT; and for the complexes with two-electron terminal η^1-ligands (carbenes, nitrenes), these parameters range from 2.3 to 2.7 mT.

The isotropic $A_i(^{51}V)$ constant in the primary ESR spectrum of the reaction product of **2** with **3** (2.54 mT) indicates unambiguously that this product has a structure of the decamethylvanadocene complex with the two-electron terminal η^1-ligand. In the system under study, this ligand can be only a carbene analog: dimethylsilylene. Thus, the decamethylvanadocene complex de-

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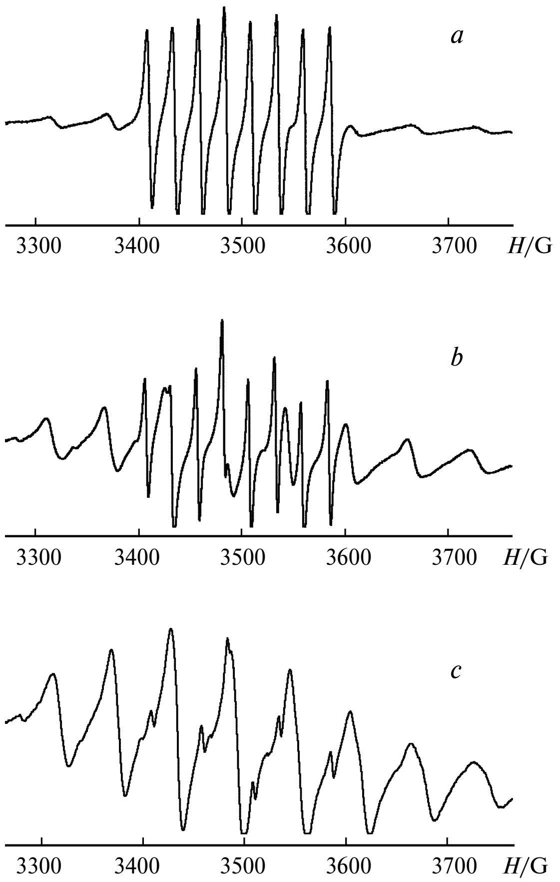


Fig. 1. Isotropic ESR spectrum of $Cp^*_2V{=}SiMe_2$ (toluene—THF, 23 °C) (*a*); $Cp^*_2V{=}SiMe_2$ after heating of the reaction mixture at 65 °C (1 h, toluene—THF) (*b*); and the final product after heating of the reaction mixture for 3 h at 65 °C (*c*).

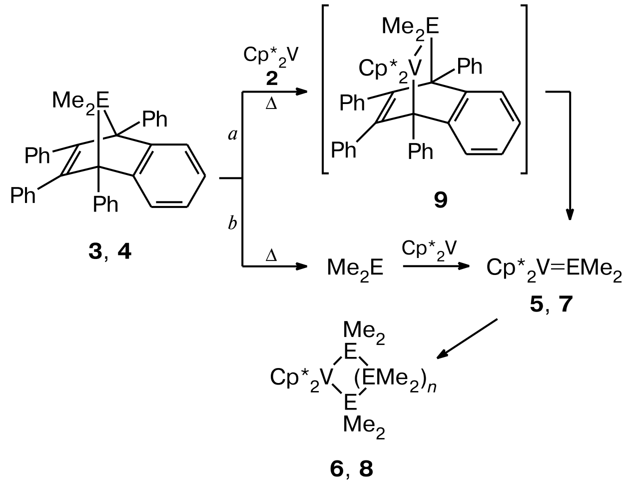
tected by us using ESR spectroscopy has a structure of $Cp^*_2V{=}SiMe_2$ (**5**). Note that no HFC constants with magnetic nuclei of the ligand (in the case of complex **5**, the ^{29}Si nucleus) are observed as in other earlier studied vanadocene complexes with two-electron terminal η^1-ligands.[1]

Based on the obtained values of magnetoresonance parameters, the second signal in the ESR spectrum of the final products of the reaction of **2** with **3** can be assigned to the d^1-complex Cp^*_2V containing two σ-bonded substituents. Probably, they belong to the cyclic vanadocene derivatives *cyclo*-$Cp^*_2V(SiMe_2)_n$ (**6**), which can be formed by the secondary disproportionation reactions of $Cp^*_2V{=}SiMe_2$. Additional experiments are needed to establish unambiguously the structure of these products.

A similar situation is observed by the ESR monitoring of the reaction of Cp^*_2V with a 7,7-dimethyl-7-germanorbornadiene derivative (**4**). This reaction also begins only on heating of the reaction mixture to 60—65 °C. In this case, the ESR spectra of the primary and final reaction products are close in parameters (g_i = 1.9671; $A_i(^{51}V)$ = 2.47 mT and g_i = 1.9763; $A_i(^{51}V)$ = 5.96 mT, respectively) to the ESR spectra of complexes **5** and **6**. Therefore, they can be assigned to the corresponding germanium analogs $Cp^*_2V{=}GeMe_2$ (**7**) and *cyclo*-$Cp^*_2V(GeMe_2)_n$ (**8**).

We can propose two routes of formation of the $Cp^*_2V{=}EMe_2$ complexes (E = Si, Ge) in the reactions of Cp^*_2V with 7-heteronorbornadienes **2** and **3** (route *a* or *b*, Scheme 1).

Scheme 1



Route *a* is the interaction of the starting reagents, which proceeds as the oxidative addition of Cp^*_2V to the strained endocyclic E—C bond with the intermediate formation of highly labile cycloadduct **9** decomposing to give complex **5** or **7** and tetraphenylnaphthalene. Note that the intermediate formation of labile cycloadducts of the type **9** has previously[8] been proposed for the reactions of **3** and **4** with the Pd^0 complexes.

Another reaction path (route *b*) is the direct trapping of the short-lived Me_2E (E = Si, Ge), formed by the thermolysis of **3** or **4**, with decamethylvanadocene Cp^*_2V.

Since 7-silanorbornadiene **3** does not decompose to Me_2Si and tetraphenylnaphthalene at temperatures lower than 200 °C,[9] the $Cp^*_2V{=}SiMe_2$ complex should form *via* route *a* (see Scheme 1). A more complicated pattern is observed for 7-germanorbornadiene **4**, which at 60—65 °C decomposes gradually to form Me_2Ge and tetraphenylnaphthalene.[10,11] In this case, the reaction proceeds, evidently, *via* two paths, and route *b* related to the direct trapping of Me_2Ge by decamethylvanadocene should contribute substantially to the formation of the $Cp^*_2V{=}GeMe_2$ complex.

Unlike Cp^*_2V, unsubstituted vanadocene **1** does not react with 7-heteronorbornadienes **3** and **4** under similar conditions (toluene—THF, 60—65 °C). Perhaps, this is associated with the difference in redox potentials of vanadocenes **1** and **2**.

We attempted to synthesize the Schrock complexes of germylenes and stannylenes by the reaction of Cp^*_2V with stable sterically strained $[(Me_3Si)_2N]_2E$ (E = Ge, Sn). However, in both cases, the reaction in toluene occurs neither at room, nor at elevated (65 °C) temperature. It is most likely that the reaction does not occur because of both the steric factors and high reduction potential of $[(Me_3Si)_2N]_2E$ ($E_{1/2} = -2.83$ (Ge) and -2.45 V (Sn)).[12]

Dichlorostannylene ($SnCl_2$) with a much lower reduction potential[13] reacts easily with Cp^*_2V at the temperature of THF melting. However, even under these conditions, the reaction proceeds as a redox process and produces not the decamethylvanadocene complex with dichlorostannylene but the products of dehalogenation of the latter, *viz.*, $Cp^*_2VCl_2$, and metallic tin. The formation of $Cp^*_2VCl_2$ was unambiguously proved by its ESR spectrum coinciding with that described in literature ($g_i = 1.9854$; $A_i(^{51}V) = 7.62$ mT).[14]

We attempted to use the pronounced reductive properties of vanadocene ($E_{ox} = 0.45$ V, $E_{red} = -2.70$ V)[15] to reduce compounds of the R_2SnX_2 type to stannylene R_2Sn followed by its trapping by vanadocene. For this purpose, we studied the reactions of vanadocenes **1** and **2** with Me_2SnBr_2 and Et_2SnCl_2 (toluene, 20 °C). It turned out that the reaction of Cp^*_2V with Me_2SnBr_2 results in the disappearance of the ESR signal of the starting vanadocene and appearance of a blue color. No ESR signal and characteristic color indicate the formation of Cp^*_2VBr.

The final products of the reaction of Cp_2V with Et_2SnCl_2 is also a similar d^2-derivative: Cp_2VCl. However, in this case, we observe the ESR spectrum of an intermediate product corresponding to the d^1-vanadocene complex. According to the parameters of its isotropic and anisotropic ESR spectra ($g_i = 1.9995$; $A_i(^{51}V) = 4.60$ mT; $A_i(^{117,119}Sn) = 18.0$ mT; $g_x = 1.985$; $g_y = 2.003$; $g_z = 2.000$; $|A_x(^{51}V)| = 7.70$ mT; $|A_y(^{51}V)| = 6.3$ mT; $|A_z(^{51}V)| \approx 0.10$ mT), we assigned this signal to the d^1-complex containing two tin atoms bonded to vanadium. The published data indicate[1] that the ESR spectrum of the three-membered metallocycle *cyclo*-$Cp_2V(SnEt_2)_2$ (**10**) can correspond to these parameters. The formation of **10** can be explained by the disproportionation of $Cp_2V{=}SnEt_2$, which is intermediately formed due to the trapping of dimethylstannylene by vanadocene. The dimethylstannylene is evidently generated by the reduction of Et_2SnCl_2 with vanadocene (Scheme 2).

Scheme 2

$$2\,Cp_2V + Et_2SnCl_2 \longrightarrow Et_2Sn + 2\,Cp_2VCl$$

$$Et_2Sn + Cp_2V \longrightarrow [Cp_2V{=}SnEt_2]$$

$$2\,[Cp_2V{=}SnEt_2] \longrightarrow \textit{cyclo}\text{-}Cp_2V(SnEt_2)_2 + Cp_2V$$

Thus, we obtained the first experimental proofs for the existence of the Schrock-type complexes of heavy carbene analogs and proposed methods for their generation.

Experimental

ESR spectra were recorded on a Bruker ER 200D—SRC spectrometer, equipped with an ER 4105DR double resonator (working frequency 9.5 GHz) and an ER 4111 VT thermocontrolling block, and a Bruker EMX 6/1 spectrometer equipped with an ER 4102ST resonator (9.8 GHz). Diphenylpycrylhydrazyl was used as standard for determination of the *g* factor.

Vanadocene,[16] decamethylvanadocene,[16] 7,7-dimethyl-7-silanorbornadiene,[9] 7,7-dimethyl-7-germanorbornadiene,[10] and $[(Me_3Si)_2N]_2E$ (E = Ge, Sn)[17] were synthesized according to known procedures. Commercial $SnCl_2$, Me_2SnBr_2, and Et_2SnCl_2 were additionally purified by recrystallization. All experiments were carried out in evacuated all-sealed systems fit for ESR spectra recording during the reaction.

An equimolar amount of a carbene analog (for example, **3** or **4**) or $[(Me_3Si)_2N]_2E$ (E = Ge, Sn) was placed into an all-sealed system equipped with a reaction flask, tube for ESR spectra recording, and ampule containing vanadocene or decamethylvanadocene (~0.25 mmol). Then anhydrous solvents (2 mL of toluene and, in some cases, 0.7 mL of THF) were frozen in a high vacuum ($<10^{-4}$ Torr). Then the system was sealed-off, and the ampule with vanadocene was broken with a pin. To dissolve vanadocene, a portion of the solvent was frozen on the vanadocene, and the resulting solution was slowly added to the second reagent on cooling to −60 °C. The reaction mixture was warmed to room temperature, and a portion of the mixture was transferred into the tube for thermolysis with simultaneous monitoring of ESR spectra.

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