

The Study of Redox Processes Involving Cp₂V-CH₂SiMe₃. A New Route of Synthesis of Alkyl Vanadocene Derivatives (IV)

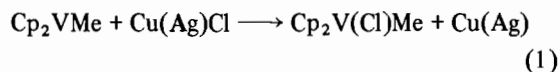
G. A. RAZUVAEV, P. YA. BAYUSHKIN, V. K. CHERKASOV, E. N. GLADYSHEV* and A. P. PHOKEEV
Institute of Chemistry, Academy of Sciences of the U.S.S.R., Gorky, U.S.S.R.

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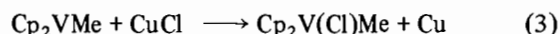
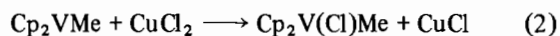
We have shown earlier that one-electron oxidation of vanadocene monohalides by different organic and non-organic halogen-containing oxidizers results in formation of paramagnetic dihalides of Cp₂VXY [1]. Cp₂VR- vanadocene monoalkyl derivatives behavior in such kinds of redox reactions is of particular interest because of vanadocene alkyl-containing derivatives (IV) being inaccessible. A number of compounds as Cp₂VR₂ mentioned in literature are limited to the following ones involving R = Me [2], Et [2, 3], CH₂Ph [2] and CH₂SiMe₃ [3]; among mixed compounds only Cp₂(Cl)Me is known [4].

In this study we have investigated oxidation reactions of Cp₂VMe and Cp₂VCH₂SiMe₃ with non-organic halides CuCl₂, CuCl, AgCl and Cp₂VCl₂, using the electron paramagnetic resonance (EPR).

We have found that according to the ratio of reagents the interaction of Cp₂VMe with oxidizers leads to different products. If organovanadium compound relates to the oxidizer (CuCl or AgCl) as 1:1 the reaction proceeds in the same way as the oxidation reaction of vanadocene monohalides and results in the formation of Cp₂V(Cl)Me



Using CuCl₂ as oxidizer produces Cp₂V(Cl)Me,



when the ratio is 1:1 as well as 2:1 owing to the possible step-by-step two-electron reduction of CuCl₂. When CuCl₂ is in excess, Cp₂V(Cl)Me is oxidized to Cp₂VCl₂. Cp₂V(Cl)Me has been identified by the EPR method. Isotropic spectrum parameters of the latter (Table I) are in a good agreement with the data of the work [4]. In highly diluted solutions we were first to establish the hyperfine splitting of each octet component into quartet (1:3:3:1) from three protons of the methyl group A_{H(Me)} being equal to 3.6 gs.

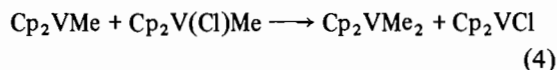
TABLE I. EPR Isotropic Spectrum Parameters of Vanadocene Alkyl Derivatives (IV).

Cp ₂ VRR'	g _i ^a	A _i ^{51V} ^b (gs)	A _{H(R)} ^b (gs)
Cp ₂ V(Cl)Me	1.9900	69.2	3.6 (CH ₃)
Cp ₂ VMe ₂	1.9921	62.8	4.8 (2CH ₃)
Cp ₂ V(Cl)CH ₂ SiMe ₃	1.9900	70.0	—
Cp ₂ V(CH ₂ SiMe ₃) ₂	1.9916	64.3	—
Cp ₂ V(Me)CH ₂ SiMe ₃	1.9926	63.7	3.9 (CH ₃)

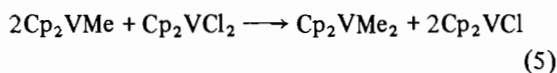
^aError 0.0005. ^bError ±0.2 gs.

The increase of mol ratio of the reagents up to 2:1 with monohalides and up to 4:1 with CuCl₂ results in the formation of Cp₂VMe₂ which is identified synonymously by EPR spectrum due to the hyperfine splitting on six equivalent protons of methyl groups [2].

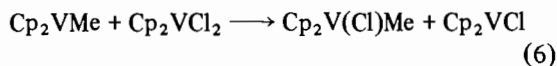
Unexpected formation of dialkyl derivative depends upon the reaction of excess Cp₂VMe with Cp₂V(Cl)Me being formed on oxidation.



The reliability of this reaction was proved when we had carried it out independently using Cp₂V(Cl)Me and Cp₂VMe as the initial reagents. Cp₂VMe₂ may be also obtained when Cp₂VMe interacts with Cp₂VCl₂ at 2:1 ratio:



The reaction:



takes place at the first stage of the two-step process, then (4) is realized.

Similarly Cp₂VCH₂SiMe₃ reacts with copper and silver chlorides. In this case, however, the initial product of oxidation – Cp₂V(Cl)CH₂SiMe₃ – is much less stable as evidenced by the quick disappearance of EPR signal in solution. The parameters of isotropic EPR spectrum of Cp₂V(Cl)CH₂SiMe₃ (Table I) are very close to the corresponding parameters of the methyl analog.

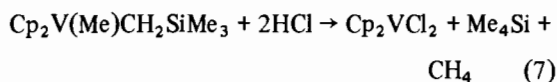
Cp₂V(CH₂SiMe₃)₂ formed when Cp₂VCH₂SiMe₃ is in excess is more stable than Cp₂V(Cl)CH₂SiMe₃. Its isotropic spectrum parameters are in perfect agreement with the recent work by Evans *et al.* [3].

It is impossible to carry out the reaction similar to (4) due to unstability of chloralkyl derivative. The synthesis of Cp₂V(CH₂SiMe₃)₂ occurs easily by the reaction similar to (5).

*To whom correspondence should be addressed.

The reaction between $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$ and $\text{Cp}_2\text{VCH}_2\text{-SiMe}_3$ is of special interest. The derivative of vanadocene (IV) $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ being formed here is the first asymmetric dialkyl compound of bis-(cyclopentadienyl)vanadium. The values of isotropic parameters of this complex, g_i 1.9926 and A_i 63.7 gs, are very close to the corresponding parameters of symmetric dialkyl derivatives (Table I) and that suggests their identical structure.

The composition of $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ has been proved by the reaction with HCl in toluene which is completed in an hour at $\sim 20^\circ\text{C}$. The yields of Cp_2VCl_2 , Me_4Si and CH_4 are 96,95 and 59%, respectively.



High yields of the products in the reactions (1–5) make the latter convenient for preparative production of vanadocene alkyl-containing derivatives (IV) of $\text{Cp}_2\text{V}(\text{X})\text{R}$, Cp_2VR_2 and $\text{Cp}_2\text{VRR}'$ type. The experimental part gives the synthesis of $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$, $\text{Cp}_2\text{-VMe}_2$ and $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ as an illustrative example.

It should be noted that the solvent affects the yield of both products (Cp_2VMe_2 and Cp_2VCl) in the reaction (4) as well as the formation of methane in the reactions (4) and (5). The decrease in the yield of vanadocene derivatives and the formation of methane – the product of V–Me bond homolysis in THF – is likely to associate with specific solvating ability of this solvent. At present the mechanism of reaction (5) is being examined in more detail.

Experimental

Reagent solutions were mixed in an evacuated two-necked ampoule. The reaction mixture was poured into the 4-mm diameter sanded glass branch which was then placed in the PZ-1301 spectrometer resonator.

Reaction of Cp_2VMe with CuCl_2

0.35 g (2.60 mmol) of CuCl_2 suspended in 30 ml of THF was added to 1.00 g (5.10 mmol) of Cp_2VMe in 20 ml of THF and shaken during one hour at $\sim 20^\circ\text{C}$. The colour of the reaction mixture changed from green to brown. THF was removed under reduced pressure and the residue was washed with toluene for several times. Toluene solution was decanted from the residue (0.15 g, 90.8% Cu). 1.08 g (92.2%) of $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$ was isolated by low-temperature crystallization from the solution.

Reaction of Cp_2VMe with Cp_2VCl_2

0.48 g (24.5 mmol) of Cp_2VMe in 10 ml of toluene was added to 0.26 g (10.3 mmol) suspension of Cp_2VCl_2 in 20 ml of THF. The mixture was shaken during 12 hours at room temperature. The colour of the solution changed from green to dark-blue. 5.0 mmol of methane was identified by GLC in gas phase. THF was removed under reduced pressure. 20 ml of hexane was added to the residue. Green crystals of Cp_2VMe_2 (0.21 g, 96.6%) were isolated by low temperature crystallization from hexane solution. Crystalline residue insoluble in hexane was identified as Cp_2VCl (0.35 g, 78.2%).

Reaction of Cp_2VMe with $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$

The mixture of 0.83 g (3.58 mmol) of $\text{Cp}_2\text{V}(\text{Cl})\text{-Me}$ and 0.72 g (3.67 mmol) of Cp_2VMe in 20 ml of THF was kept over night at room temperature. The colour of the solution changed from brown to green. Gas phase contains 0.45 mmol of methane. 0.65 g (86.0%) of Cp_2VMe_2 and 0.63 g (81.0%) of Cp_2VCl were isolated in the usual way.

Under comparable conditions 0.23 g (89.3%) of Cp_2VMe_2 and 0.24 g (1.11 mmol; 91.0%) of Cp_2VCl were isolated from 0.24 g (1.24 mmol) of Cp_2VMe and 0.30 g (1.29 mmol) of $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$ in 20 ml of cumene.

Reaction of $\text{Cp}_2\text{V}(\text{Cl})\text{Me}$ with $\text{Cp}_2\text{VCH}_2\text{SiMe}_3$

The mixture of 0.74 g (32.1 mmol) of $\text{Cp}_2\text{V}(\text{Cl})\text{-Me}$ and 0.86 g (32.0 mmol) of $\text{Cp}_2\text{VCH}_2\text{SiMe}_3$ in 20 ml of THF was kept over night at room temperature. THF was changed for hexane and the solution was decanted from the residue. 0.88 g (96.9%) of $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ was isolated by low temperature crystallization. Insoluble residue is proved to be Cp_2VCl (0.68 g, 98.1%).

Reaction of $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ with HCl

The excess gaseous HCl was condensed into 0.88 g (31.0 mmol) of $\text{Cp}_2\text{V}(\text{Me})\text{CH}_2\text{SiMe}_3$ in 30 ml of toluene. Green solid precipitated. The yield of Cp_2VCl_2 was 0.75 g (96.1%), 29.5 mmol (95.2%) of Me_4Si and 18.0 mmol (58.6%) of methane were identified by GLC.

References

- 1 E. N. Gladyshev, P. Ya. Bayuhkin, V. K. Cherkasov and V. S. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1144 (1979).
- 2 G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, V. K. Cherkasov, S. P. Korneva and N. N. Spiridonova, *J. Organometal. Chem.*, 129, 169 (1977).
- 3 A. G. Evans, Y. C. Evans, D. Y. C. Espley, P. H. Morgan and Y. Mortimer, *J. Chem. Soc. Dalton*, 57 (1978).
- 4 G. A. Razuvaev, S. P. Korneva, L. I. Vyshinskaya, V. P. Marjin and V. K. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 700 (1978).