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The Study of Redox Processes Involving $Cp_2V-CH_2SiMe_3$. 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 Cp_2VXY [1]. Cp_2VR- 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 Cp_2VR_2 mentioned in literature are limited to the following ones involving R = Me [2], Et [2, 3], CH_2Ph [2] and CH_2SiMe_3 [3]; among mixed compounds only $Cp_2(Cl)Me$ is known [4].

In this study we have investigated oxidation reactions of Cp_2VMe and $Cp_2VCH_2SiMe_3$ with non-organic halides $CuCl_2$, CuCl, AgCl and Cp_2VCl_2, using the electron paramagnetic resonance (EPR).

We have found that according to the ratio of reagents the interaction of Cp_2VMe 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 $Cp_2V(Cl)Me$

$$Cp_2VMe + Cu(Ag)Cl \longrightarrow Cp_2V(Cl)Me + Cu(Ag) \quad (1)$$

Using $CuCl_2$ as oxidizer produces $Cp_2V(Cl)Me$,

$$Cp_2VMe + CuCl_2 \longrightarrow Cp_2V(Cl)Me + CuCl \quad (2)$$

$$Cp_2VMe + CuCl \longrightarrow Cp_2V(Cl)Me + Cu \quad (3)$$

when the ratio is 1:1 as well as 2:1 owing to the possible step-by-step two-electron reduction of $CuCl_2$. When $CuCl_2$ is in excess, $Cp_2V(Cl)Me$ is oxidized to Cp_2VCl_2. $Cp_2V(Cl)Me$ 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_2VRR'	g_i [a]	A_i^{51V} [b] (gs)	$A_{H(R)}$ [b] (gs)
$Cp_2V(Cl)Me$	1.9900	69.2	3.6 (CH_3)
Cp_2VMe_2	1.9921	62.8	4.8 ($2CH_3$)
$Cp_2V(Cl)CH_2SiMe_3$	1.9900	70.0	–
$Cp_2V(CH_2SiMe_3)_2$	1.9916	64.3	–
$Cp_2V(Me)CH_2SiMe_3$	1.9926	63.7	3.9 (CH_3)

[a] Error 0.0005. [b] Error ±0.2 gs.

The increase of mol ratio of the reagents up to 2:1 with monohalides and up to 4:1 with $CuCl_2$ results in the formation of Cp_2VMe_2 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 Cp_2VMe with $Cp_2V(Cl)Me$ being formed on oxidation.

$$Cp_2VMe + Cp_2V(Cl)Me \longrightarrow Cp_2VMe_2 + Cp_2VCl \quad (4)$$

The reliability of this reaction was proved when we had carried it out independently using $Cp_2V(Cl)$-Me and Cp_2VMe as the initial reagents. Cp_2VMe_2 may be also obtained when Cp_2VMe interacts with Cp_2VCl_2 at 2:1 ratio:

$$2Cp_2VMe + Cp_2VCl_2 \longrightarrow Cp_2VMe_2 + 2Cp_2VCl \quad (5)$$

The reaction:

$$Cp_2VMe + Cp_2VCl_2 \longrightarrow Cp_2V(Cl)Me + Cp_2VCl \quad (6)$$

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

Similarly $Cp_2VCH_2SiMe_3$ reacts with copper and silver chlorides. In this case, however, the initial product of oxidation – $Cp_2V(Cl)CH_2SiMe_3$ – is much less stable as evidenced by the quick disappearance of EPR signal in solution. The parameters of isotropic EPR spectrum of $Cp_2V(Cl)CH_2SiMe_3$ (Table I) are very close to the corresponding parameters of the methyl analog.

$Cp_2V(CH_2SiMe_3)_2$ formed when $Cp_2VCH_2SiMe_3$ is in excess is more stable then $Cp_2V(Cl)CH_2SiMe_3$. 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 $Cp_2V(CH_2SiMe_3)_2$ occurs easily by the reaction similar to (5).

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*To whom correspondence should be addressed.

The reaction between $Cp_2V(Cl)Me$ and $Cp_2VCH_2SiMe_3$ is of special interest. The derivative of vanadocene (IV) $Cp_2V(Me)CH_2SiMe_3$ 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 $Cp_2V(Me)CH_2SiMe_3$ has been proved by the reaction with HCl in toluene which is completed in an hour at ~20 °C. The yields of Cp_2VCl_2, Me_4Si and CH_4 are 96,95 and 59%, respectively.

$$Cp_2V(Me)CH_2SiMe_3 + 2HCl \rightarrow Cp_2VCl_2 + Me_4Si + CH_4 \qquad (7)$$

High yields of the products in the reactions (1–5) make the latter convenient for preparative production of vanadocene alkyl-containing derivatives (IV) of $Cp_2V(X)R$, Cp_2VR_2 and Cp_2VRR' type. The experimental part gives the synthesis of $Cp_2V(Cl)Me$, Cp_2VMe_2 and $Cp_2V(Me)CH_2SiMe_3$ 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 solded 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 shaked during one hour at ~20 °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 $Cp_2V(Cl)Me$ 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 shaked 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 $Cp_2V(Cl)Me$

The mixture of 0.83 g (3.58 mmol) of $Cp_2V(Cl)Me$ 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 $Cp_2V(Cl)Me$ in 20 ml of cumene.

Reaction of $Cp_2V(Cl)Me$ with $Cp_2VCH_2SiMe_3$

The mixture of 0.74 g (32.1 mmol) of $Cp_2V(Cl)Me$ and 0.86 g (32.0 mmol) of $Cp_2VCH_2SiMe_3$ 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 $Cp_2V(Me)CH_2SiMe_3$ was isolated by low temperature crystallization. Insoluble residue is proved to be Cp_2VCl (0.68 g, 98.1%).

Reaction of $Cp_2V(Me)CH_2SiMe_3$ with HCl

The excess gaseous HCl was condensed into 0.88 g (31.0 mmol) of $Cp_2V(Me)CH_2SiMe_3$ 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).