brought up slowly to ∿20°, and it was let stand overnight. Then the precipitate was filtered, the solvent was distilled off, and the residue was vacuum distilled.

All of the experiments were run in an argon atmosphere.

CONCLUSIONS

Some esters of amidophosphorous acid, containing a vinyl group on the nitrogen atom, were obtained.

LITERATURE CITED

1. A. M. Kibardin, T. Kh. Gazizov, and A. N. Pudovik, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 2186.

STUDY OF OXIDATION–REDUCTION REACTIONS OF TRIETHYLGERMYL DERIVATIVES OF VANADOCENE BY EPR METHOD

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The oxidation reactions of halo [1] and alkyl [2] derivatives of vanadocene by chloro-containing inorganic and organic one-electron oxidizing agents were studied in previous papers.

$$Cp_2VX + MCl \rightarrow Cp_2V(X)Cl + M \qquad (1)$$

$$X = Cl,\ Br,\ CH_3,\ CH_2Si(CH_3)_3;\quad M = Ag,\ Cu,\ CuCl,\ Cp_2VCl,\ Ph_3C.$$

These reactions make it possible to obtain dialkyl and haloalkyl d^1 complexes of vanadocene, which are inaccessible when using conventional methods based on exchange reactions. An exceedingly convenient and efficient method when studying type (1) reactions is the EPR method, which permits checking the oxidation–reduction transitions between the d^2 and d^1 complexes of vanadocene in solution directly during reaction, which is especially important for the labile d^1 complexes of vanadocene.

The EPR method was used in the present paper to study the oxidation reactions of bis(cyclopentadienyl)triethylgermylvanadium (I) by cupric chloride and some chloro-containing d^1 complexes of Cp_2V. The oxidation of (I) by anhydrous $CuCl_2$ in THF or toluene leads to the appearance of an EPR spectrum with $g_i = 1.9956$, $A_i^{51V} = 66.8$ Oe. The simultaneous deposition of metallic copper as a mirror is also observed when a 2:1 ratio of the reactants is used.

$$\underset{(I)}{Cp_2VGeEt_3} + CuCl_2 \rightarrow \underset{(II)}{Cp_2V(Cl)GeEt_3} + CuCl \qquad (2)$$

$$(I) + CuCl \rightarrow (II) + Cu \qquad (3)$$

The parameters of the observed EPR spectrum are in agreement with theory (in harmony with the additivity rule) [3] for the d^1 complex (II), and testify to the fact that the oxidation of (I) proceeds in harmony with Eqs. (2) and (3). It is interesting that the EPR spectrum of (II) is identical with the spectrum observed previously in the reaction of Cp_2VCl_2 with $(Et_3Ge)_2Cd$ [4]. The identity of these two spectra testifies to the same coordination environment of the vanadium atom in both cases and serves to confirm the theory expressed in [4] that the chlorine atom on vanadium is replaced by the triethylgermyl group.

Compound (II) under the conditions of reactions (2) and (3) can be easily oxidized further to Cp_2VCl_2 if a stoichiometric ratio of the reactants is used.

$$(II) + CuCl_2 \rightarrow Cp_2VCl_2 + CuCl + Et_3GeCl \qquad (4)$$

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Besides $CuCl_2$ and CuCl, other oxidizing agents in reactions (2) and (3) can be the chloro-containing d^1 complexes of vanadocene.

The reaction of (I) with Cp_2VCl_2 is fast and is easily recorded by the EPR method. Here the EPR spectrum of Cp_2VCl_2, decreasing in intensity, is replaced by the EPR spectrum of (II) clear down to the complete disappearance of the former.

$$\text{(I)} + Cp_2VCl_2 \rightarrow \text{(II)} + Cp_2VCl \qquad (5)$$

Of special interest is the reaction of (I) with (II) when (I) is taken in excess relative to the oxidizing agent ($CuCl_2$, Cp_2VCl_2, etc.).

$$\text{(I)} + \text{(II)} \rightarrow \underset{\text{(III)}}{Cp_2V(GeEt_3)_2} + Cp_2VCl \qquad (6)$$

Reaction (6) leads to the first d^1 complex of vanadocene with two heteroorganic substituents (III). The parameters of the EPR spectrum of (III) ($g_i = 2.0025$, $A_i^{51V} = 55.2$ Oe) are extremal in the series of known d^1 complexes of vanadocene with two one-electron ligands, while the parameters of the EPR spectra of Cp_2VCl_2 and (II), taken for comparison, confirm the validity of the additivity rule for the parameters of the EPR spectra of the d^1 complexes of vanadocene with one-electron ligands.

Complex (III) can also be obtained by reaction (7), which has promise for the synthesis of (III).

$$Cp_2VCl_2 + 2\,(Et_3Ge)_2M \rightarrow \text{(III)} + 2M + 2Et_3GeCl \qquad (7)$$
$$M = Cd,\ Hg.$$

According to [4], reaction (7) proceeds in steps, and the intermediate product (II) can be obtained if the starting reactants are taken in an equimolar ratio.

Complex (II) can be obtained by the exchange oxidation–reduction reaction (8).

$$\text{(III)} + Cp_2VCl_2 \rightarrow 2\text{(II)} \qquad (8)$$

As a result, a definite analogy is observed in the behavior of (I), Cp_2VMe and $Cp_2VCH_2SiMe_3$ under the conditions of oxidation–reduction reactions. However, an attempt to obtain the mixed $Cp_2V(Me)GeEt_3$ derivatives by oxidizing (I) with $Cp_2V(Cl)Me$ unexpectedly led to the known (II) complex.

EXPERIMENTAL

The reactions were run in sealed evacuated ampuls in toluene at ∿20°. The EPR spectra were recorded on an instrument of the RE-1301 series.

CONCLUSIONS

1. It was established by the EPR method that Cp_2VGeEt_3 undergoes stepwise transformation under the conditions of oxidation–reduction reactions.

2. A d^1 complex of vanadocene with two heteroorganic substituents, and specifically $Cp_2V(GeEt_3)_2$, was obtained for the first time.

LITERATURE CITED

1. E. N. Gladyshev, P. Ya. Bayushkin, V. K. Cherkasov, and V. S. Sokolov, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 1144.
2. G. A. Razuvaev, P. Ya. Bayushkin, V. K. Cherkasov, E. N. Gladyshev, and A. P. Phokeev, Inorg. Chim. Acta, 44, L 103 (1980).
3. G. A. Razuvaev, S. P. Korneva, L. I. Vyshinskaya, V. P. Mar'in, and V. K. Cherkasov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 700.
4. L. I. Vyshinskaya, S. P. Korneva, and V. K. Cherkasov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 1405.