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OXIDATIVE-REDUCTIVE TRANSMETALLATION REACTIONS OF GERMYLMERCURY COMPOUNDS WITH BIS(ETHYLBENZENE)VANADIUM AND VANADOCENE

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Summary

The ionic complex $[\{(C_6F_5)_3Ge\}_3Hg]^-[V(C_6H_5C_2H_5)_2]^+$ has been obtained in the reaction of $[(C_6F_5)_3Ge]_2Hg$ with bis(ethylbenzene)vanadium. Dicyclopentadienylvanadium displaces mercury in $[(C_6F_5)_3Ge]_2Hg$ to give the covalent product $Cp_2VGe(C_6F_5)_3$ ($Cp = \eta^5\text{-}C_5H_5$). The 4-nuclear product, $(C_6F_5)_3Ge\text{-}Hg\text{-}Cp_2V\text{-}Ge(C_6F_5)_3$, of the insertion of Cp_2V into the Ge-Hg bond, is formed in the first step of the reaction. It is thought that the next step of the process leads to an unstable divanadium complex with the Ge-V-Hg-V-Ge chain. $[(C_6F_5)_3Ge]_2Cd$ reacts similarly. Interaction of Cp_2V with the thallium mercurate $[(C_6F_5)_3Ge]_3HgTl \cdot 1.5DME$ (DME = 1,2-dimethoxyethane) gives Tl, Hg and $Cp_2VGe(C_6F_5)_3$. The germylvanadium complex $Cp_2VGe(C_6F_5)_3$ is readily oxidized by silver and mercury chlorides to give $Cp_2V(Cl)Ge(C_6F_5)_3$ derivatives. ESR spectra of vanadium d^1-complexes are presented.

Introduction

Reactions of the type, R-M + M′ ⇄ R-M′ + M, called oxidative-reductive transmetallation reactions [1], play an important part in the synthesis of polynuclear compounds. We have prepared a number of novel polynuclear compounds using 3- and 4-nuclear derivatives as R-M, and free metals and metallo-complexes (in which the metal is in the zero or a low valent state) as M′ [2]. It has been found that these reactions often stop at the intermediate stage and these intermediates are isolated as final products. They may be covalent products of insertion of M′ into R-M bonds or ionic compounds of ate-complex type. As a rule, when M or M′ have low values of the ionization potential *I* and electron affinity *E* (for example, alkali metals [3,4], magnesium [5], thallium [6], lanthanides [7], dibenzenechromium [8]), ionic products are formed. The formation of covalent R–M–M′ bonding becomes more probable when the values of *I* and *E* of the reacting M and M′ are larger. Thus, germyl-mercury and -cadmium compounds react with Pt^0 or Ni^{II} complexes, or with selenium, to give Ge–Pt–Hg–Ge–Ge–Hg–Pt–Ge, Ge–Ni–Cd–Ni–Ge and Ge–Hg–Se–Ge chains [9–11].

Vanadium compounds Cp_2V have been also used in transmetallation reactions. The interaction of dicyclopentadienylvanadium with $(C_6F_5)_2Hg$ results in precipitation of mercury and formation of $Cp_2V{-}C_6F_5$ [12]. The reaction of dicyclopentadienylvanadium with $(R_3Ge)_2Cd$ (R = Et, Ph) yields $Cp_2V{-}GeR_3$, metallic cadmium, R_3GeH and digermane R_6Ge_2 [13]. The formation of unstable covalent intermediates $R{-}Cp_2V{-}M{-}R$ ($R = C_6F_5$, M = Hg; $R = Et_3Ge$, M = Cd) was assumed in both cases, but this was not proven.

We have attempted to study the analogous reactions of vanadium derivatives with pentafluorophenyl compounds $(R^f_3Ge)_2Hg$ and $(R^f_3Ge)_2Cd$ ($R^f = C_6F_5$). Enhanced stability of most polynuclear derivatives with C_6F_5 substituents encouraged us to attempt to isolate intermediates and to define the scheme of these processes.

Results and discussion

It has been found that $(R^f_3Ge)_2Hg$ reacts with bis(ethylbenzene)vanadium in ether solution to give the ionic complex $[(R^f_3Ge)_3Hg]^-[V(PhEt)_2]^+$, the properties of which are similar to those of the dibenzenechromium, thallium and lanthanide

$$3\,(R^f_3Ge)_2Hg + 2\,V(PhEt)_2 \rightarrow 2\big[(R^f_3Ge)_3Hg\big]^-[V(PhEt)_2]^+ + Hg$$

complexes mentioned above. The tris[tris(pentafluorophenyl)germyl]mercurate of bis(ethylbenzene)vanadium is precipitated by pentane from toluene solution as a brown powder, which is unstable in air and decomposes on heating at 100°C. Electrolysis of the complex in THF leads to precipitation of metallic mercury and reduction of the vanadium cation to neutral $V(PhEt)_2$.

The reaction of $(R^f_3Ge)_2Hg$ with vanadocene results in the complete displacement of mercury and in the formation of the covalent germylvanadium compound $Cp_2VGeR^f_3$ (90% yield).

$$(R^f_3Ge)_2Hg + 2\,Cp_2V \rightarrow 2\,Cp_2VGeR^f_3 + Hg$$

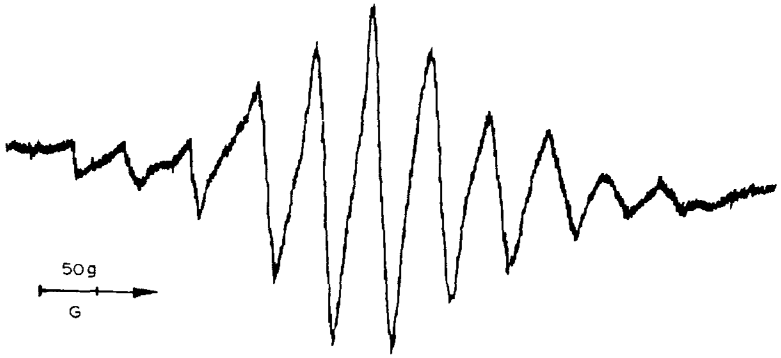
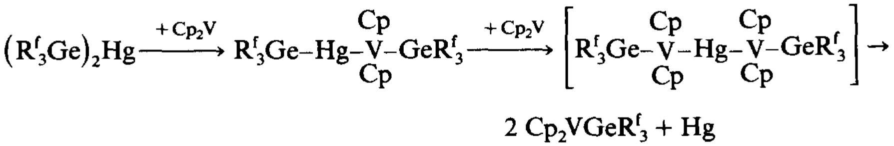


Fig. 1. ESR spectra of $R^f_3Ge{-}Hg{-}Cp_2V{-}GeR^f_3$.

At room temperature the reaction takes 3–5 min in THF, 30 min in DME, and more than 24 h in toluene solution. The colour of the reaction mixture changes gradually from violet to yellow-green. Then metallic mercury appears and the colour of the solution turns dark-violet. ESR spectroscopy indicates that the 4-valent vanadium derivative is formed at the intermediate stages of the process. It has been isolated in the reaction of germylmercury with an equimolar quantity of vanadocene in toluene solution. Its ESR spectrum ($g_{iso} = 1.978$, $A^{51V}_{iso} = 52.6$ G) (Fig. 1) is typical of Cp_2V d^1-complexes with two organometallic substituents σ-bonded to vanadium. The distinctive feature of the observed spectrum is the presence of additional components of hyperfine coupling $A = A^{51V}_{iso}$ in the lowfield region. The ratio between the intensities of the additional and original components in the spectrum (1/7) is in good agreement with the ratio between magnetic and non-magnetic mercury isotopes [14]. Thus, the existence of these components depends on the hyperfine coupling of the unpaired electron with ^{199}Hg ($\mu = 0.5027$, $J = 1/2$) and ^{201}Hg ($\mu = -0.5567$, $J = 3/2$). This indicates the presence of a V–Hg σ-bond in the complex. These data, together with those of elemental analysis and IR spectroscopy, testify to the fact that the isolated intermediate complex is a product of the insertion of Cp_2V into one Ge–Hg bond, i.e. $R^f_3Ge{-}VCp_2{-}Hg{-}GeR^f_3$. On cooling the toluene solution, the compound is precipitated as yellow-green crystals, which are unstable in air and decompose slowly at room temperature. On rapid heating, decomposition is observed at 100°C. Thermal decomposition in toluene solution is accompanied by the formation of $Cp_2VGeR^f_3$, R^f_3GeH, $R^f_6Ge_2$ and metallic mercury.

Tris(pentafluorophenyl)germane and the digermane are absent from the products of the reaction of vanadocene with $(R^f_3Ge)_2Hg$. Consequently, decomposition of the 4-nuclear intermediate does not occur in this case, and the formation of $Cp_2VGeR^f_3$ is a result of another process. It is assumed that after formation of $R^f_3GeHgCp_2VGeR^f_3$ the insertion of the second Cp_2V group takes place leading to the unstable divanadium intermediate $R^f_3Ge{-}Cp_2V{-}Hg{-}Cp_2V{-}GeR^f_3$. The complex decomposes immediately to give Hg and two molecules of $Cp_2VGeR^f_3$. Thus, the interaction of $(R^f_3Ge)_2Hg$ with vanadocene may be represented as follows:

SCHEME 1

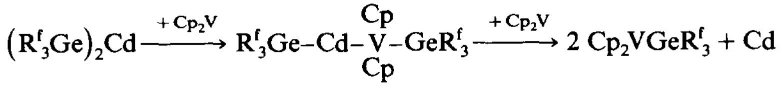


$$(R^f_3Ge)_2Hg \xrightarrow{+Cp_2V} R^f_3Ge{-}Hg{-}\overset{Cp}{\underset{Cp}{V}}{-}GeR^f_3 \xrightarrow{+Cp_2V} \left[R^f_3Ge{-}\overset{Cp}{\underset{Cp}{V}}{-}Hg{-}\overset{Cp}{\underset{Cp}{V}}{-}GeR^f_3\right] \rightarrow$$

$$2\,Cp_2VGeR^f_3 + Hg$$

Apparently, the 5-nuclear intermediate decomposes more quickly than it is formed. This is why we failed to get it in sufficient quantities for ESR spectroscopy.

Perfluorinated bis(triphenylgermyl)cadmium reacts with Cp_2V to give metallic cadmium (100%) and $Cp_2VGeR^f_3$ (79%). The intermediate complex was not isolated in this case, but its formation is shown by the ESR signal ($g_{iso} = 1.997$, $A^{51V}_{iso} = 45$ G).



$$(R^f_3Ge)_2Cd \xrightarrow{+Cp_2V} R^f_3Ge{-}Cd{-}\overset{Cp}{\underset{Cp}{V}}{-}GeR^f_3 \xrightarrow{+Cp_2V} 2\,Cp_2VGeR^f_3 + Cd$$

The non-fluorinated compound $(Ph_3Ge)_2Hg$ reacts with vanadocene much more slowly: 50% of the initial Cp_2V and the germylmercury were recovered, along with dicyclopentadienyl(triphenylgermyl)vanadium and metallic mercury after the reaction mixture in toluene had been left for 48 h at 20°C. An ESR signal of the intermediates has not been detected. Judging by the products obtained, the scheme of the process is no different from that given above.

The data obtained allow us to conclude that all the reactions of vanadocene with R_2Hg and R_2Cd involve the formation of the covalent intermediates $R-VCp_2-MR$. The intermediates decompose immediately to give Cp_2VR, M, RH and R–R ($R = C_6F_5$, M = Hg [12]; $R = Et_3Ge$, Ph_3Ge, M = Cd [13]), or after addition of the second equivalent of Cp_2V to give Cp_2VR and M ($R = GeR^f_3$, M = Cd, Hg). The difference in the reaction routes is obviously accounted for by the higher stability and acceptor abilities of pentafluorophenyl derivatives. As a result, the 4-nuclear intermediates $R^f_3Ge-VCp_2-M-GeR^f_3$ (M = Cd, Hg) add the second equivalent Cp_2V more quickly than they decompose.

The interaction of thallium germylmercurate with Cp_2V proceeds with displacement of metallic thallium. The solution is discoloured, probably due to formation of the ionic complex $[(R^f_3Ge)_3Hg]^- [VCp_2]^+$. It should be noted that all of the analogous complexes of titanium, manganese, nickel and chromium are weakly coloured [15]. Unlike these complexes and the arene derivatives mentioned above, tris[tris(pentafluorophenyl)germyl]mercurate of dicyclopentadienylvanadium is extremely labile and cannot be isolated from the reaction mixture. It decomposes to give the covalent products $(R^f_3Ge)_2Hg$ and $Cp_2VGeR^f_3$. The latter is a coloured product. Therefore the reaction mixture turns violet at the end of the reaction. With

$$(R^f_3Ge)_3HgTl \xrightarrow[-Tl]{+Cp_2V} \left[[(R^f_3Ge)_3Hg]^- [VCp_2]^+\right] \rightarrow Cp_2VGeR^f_3 + (R^f_3Ge)_2Hg$$

an excess of vanadocene the reduction of germylmercury formed proceeds according to Scheme 1.

It is interesting that vanadocene readily substitutes mercury and cadmium into the R^f_3Ge-M groups, but does not displace the less electropositive hydrogen in the hydride R^f_3GeH (THF, 95°C, 10 h). Dicyclopentadienyl[tris(pentafluorophenyl)-germyl]vanadium, formed in all the above-mentioned reactions, is isolated from a toluene/hexane mixture as dark-violet crystals which decompose at 145–146°C. The compound is readily oxidized in air and is well soluble in ethers and aromatic solvents. It is monomeric in benzene solution. Its IR spectrum contains bands characteristic of C_6F_5-Ge fragments (1650, 1530, 1480, 1390, 1290, 1090, 810, 720, 652 cm^{-1}) and of Cp–V groups (800, 830 cm^{-1}). The structure of $Cp_2VGeR^f_3$ is supported by the reaction with hydrogen chloride, which proceeds at 65°C to give vanadocene chloride, R^f_3GeH, vanadocene dichloride, R^f_3GeCl and hydrogen. The last three products result from the secondary reactions of hydrogen chloride with Cp_2VCl and R^f_3GeH. Similar processes were previously observed in the hydrochlorination of Cp_2VGePh_3 [13].

A convenient way of defining the structure of the derivatives of Cp_2VR is their oxidation by metal halides (AgCl, $CuCl_2$), which proceeds quantitatively in THF at room temperature [16]. The resulting d^1-complexes, $Cp_2V(X)R$, have characteristic parameters in their ESR spectra and are easily identified. In the case of oxidant deficiency, digermyl complexes $Cp_2V(GeR_3)_2$ are formed. This method, applied to $Cp_2VGeR^f_3$, makes it possible to obtain dicyclopentadienylchlorine[tris(pentafluoro-

$$Cp_2VGeR^f_3 + MCl \xrightarrow[(M = Ag,\ CuCl)]{} Cp_2V(Cl)GeR^f_3 + M$$

phenyl)germyl]vanadium ($g_{iso} = 1.9936$, $A_{iso}^{51V} = 64.7$ G). However, unlike the triethylgermyl analogue, this compound is not transformed into the digermyl complex $Cp_2V(GeR^f_3)_2$ under oxidant deficiency. The phenyl derivative, $Cp_2V(Cl)GePh_3$, in a similar reaction, does not form the digermyl complex either. Reaction of this complex with diethylcadmium results in formation of the product $Cp_2V(Et)GeR^f_3$ through substitution of Cl by Et. The product has an ESR spectrum with $g_{iso} = 1.9936$, $A_{iso}^{51V} = 60$ G.

$$Cp_2V(Cl)GeR^f_3 + Et_2Cd \rightarrow Cp_2V(Et)GeR^f_3 + EtCdCl$$

Experimental

All reactions were carried out in evacuated sealed tubes. GLC analyses of products were carried out on a Tsvet-104 chromatograph with a catarometer detector, using a 100 × 0.4 cm and a 50 × 0.4 cm column packed with Chromaton N-AW-ADMCS (T = 190°C), with helium as the carrier gas. LSC analyses were carried out on a Tsvet-304 liquid chromatograph with UV detector (254 nm) using a column (190 × 4 cm) made of steel packed with Silosorb 600 (5 m), hexane/isopropyl alcohol eluent, T = 23°C. IR spectra were recorded on a Perkin–Elmer-577 spectrophotometer. ESR data were obtained with an RE 1301 spectrometer. Melting points were determined using evacuated capillaries.

Reaction of bis(ethylbenzene)vanadium with bis[tris(pentafluorophenyl)germyl]mercury

A solution of $V(EtPh)_2$ (0.388 g, 1.48 mmol) in 8 ml of diethyl ether was added to a solution of $(R^f_3Ge)_2Hg$ (3 g, 2.22 mmol) in 10 ml of diethyl ether. The reaction proceeded for 5–10 h at 20°C with formation of 0.148 g of metallic mercury (33% of the total Hg). The organic layer was decanted from the mercury and the solvent was evaporated in vacuo. The brown residue was washed several times with pentane and dried in vacuo. The yield of $(R^f_3Ge)_3HgV(EtPh)_2$ was 2.8 g (86.6%). Found: C, 38.65; H, 0.90; V, 2.43. $C_{70}H_{20}F_{45}Ge_3HgV$ calcd.: C, 38.46; H, 0.92; V, 2.34%.

Reaction of bis[tris(pentafluorophenyl)germyl]mercury with vanadocene

To a solution of $(R^f_3Ge)_2Hg$ (0.787 g 0.58 mmol) in toluene (10 ml) was added a solution of Cp_2V (0.212 g, 1.17 mmol) in toluene (3 ml). Mercury (0.115 g, 99%) was isolated, after 20 h at 20°C, from the reaction mixture by centrifugation. The organic layer was decanted from the precipitate. A part of toluene was evaporated in vacuo, and 3 ml of hexane was added. After 24 h at −78°C 0.787 g (89%) of $Cp_2VGeR^f_3$, m.p. 145–146°C (dec), was isolated. Found: C, 43.71; H, 1.17; F, 38.62. $C_{28}H_{10}F_{15}GeV$ calcd.: C, 44.55; H, 0.13; F, 37.85%. Mol. wt. (cryoscopy). Found: 711; calcd.: 755.

Reaction of $(R^f_3Ge)_2Cd$ with vanadocene was carried out in a similar way.

Synthesis of $R^f_3GeVCp_2HgGeR^f_3$

To a solution of $(R^f_3Ge)_2Hg$ (0.216 g, 0.32 mmol) in toluene (10 ml) was added a solution of Cp_2V (0.058 g, 0.32 mmol) in toluene (3 ml). In 1 min the reaction mixture became yellow-green and an ESR signal for V^{IV} ($g_{iso} = 1.978$, $A_{iso}^{51V} = 52.6$ H) was detected. The solvent was partially evaporated in vacuo, and 0.2 g (81%) of the green crystalline $R^f_3GeCp_2VHgGeR^f_3$, m.p. 100°C (dec), was isolated in 30 min at −5°C. Found: C, 36.52; H, 1.63. $C_{46}H_{10}F_{30}Ge_2VHg$ calcd.: C, 36.14; H, 0.66%.

Reaction of bis(triphenylgermyl)mercury with vanadocene

A solution of $(Ph_3Ge)_2Hg$ (0.457 g, 0.57 mmol) in toluene (5 ml) was added to a solution of Cp_2V (0.205 g, 1.13 mmol) in toluene (3 ml). The reaction mixture was kept at 20°C for 48 h. The organic layer was decanted from the mercury precipitate (0.056 g, 50%). The solvent was removed in vacuo. Initially Cp_2V (0.085 g, 41%) was isolated by sublimation of the residue in vacuo at 70°C. The residue was then extracted with hexane. Cooling of the hexane solution to −78°C (24 h) gave violet crystals of Cp_2VGePh_3 (0.12 g, 88%), as identified by ESR spectroscopy after oxidation by $CuCl_2$ in THF.

Reaction of $(R^f_3Ge)_3HgTl \cdot 1.5DME$ with vanadocene

To a solution of $(R^f_3Ge)_3HgTl \cdot 1.5DME$ (0.469 g, 0.21 mmol) in THF (4 ml) was added a solution of Cp_2V (0.0375 g, 0.21 mmol) in THF (3 ml). Metallic thallium (0.04 g, 98%) was precipitated in 5 min at 20°C. The organic layer was decanted from the metal, and the THF was exchanged for toluene. $(R^f_3Ge)_2Hg$ (0.238 g, 82%), m.p. 226–228°C, was precipitated at 20°C in 24 h. It was identified by LSC. After addition of hexane, $Cp_2VGeR^f_3$ (0.095 g, 61%) was isolated from the mother liquor at −78°C in 24 h. It was identified by ESR spectroscopy after oxidation by $CuCl_2$ in THF.

Reaction of $Cp_2VGeR^f_3$ with hydrogen chloride

To a solution of $Cp_2VGeR^f_3$ (0.182 g, 0.24 mmol) in toluene (5 ml) was added gaseous hydrogen chloride (10 ml). The reaction mixture was kept at 65°C for 2 h. Toluene and the excess of HCl were removed by evaporation under vacuum. The residue was extracted with hexane. GLC analysis of the extract revealed R^f_3GeH (0.115 g, 80%) and R^f_3GeCl (0.017 g, 12%). According to ESR data the insoluble residue contained 0.061 g (95%) of dicyclopentadienylvanadium dichloride.

Reaction of $Cp_2VGeR^f_3$ with cupric chloride

A solution of $CuCl_2$ (0.022 g, 3 mmol) in THF (4 ml) was poured into an ampoule placed in an ESR-spectrometer and $Cp_2VGeR^f_3$ (0.248 g, 0.33 mmol) was added at room temperature. Immediately the ESR signal ($g_{iso} = 1.9936$, $A^{51V}_{iso} = 64.7$ G) for $Cp_2V(Cl)GeR^f_3$ appeared. A copper mirror was observed on the walls of the ampoule. After 1 h at 20°C the ESR signal of $Cp_2V(Cl)GeR^f_3$ disappeared and that of Cp_2VCl_2 appeared.

Reactions of $Cp_2VGeR^f_3$ with AgCl and of $Cp_2V(Cl)GeR^f_3$ with diethylcadmium were carried out in a similar way.

References

1 E.I. Negishi, Organometallics in Organic Synthesis, Willey, New York, 1980.

2 G.A. Razuvaev and M.N. Bochkarev, Organomet. Chem. Rev., 12 (1981) 241.

3 M.J. Albright, T.F. Schaaf, W.M. Butler, A.K. Hovland, M.D. Glick and J.P. Oliver, J. Am. Chem. Soc., 97 (1975) 6261.

4 T.F. Schaaf and J.P. Oliver, J. Am. Chem. Soc., 91 (1969) 4327.

5 E.A. Sadurski, W.H. Ilsley, R.D. Thomas, M.D. Glick and J.P. Oliver, J. Am. Chem. Soc., 100 (1978) 7761.

6 M.N. Bochkarev, N.I. Gur'ev, L.V. Pankratov and G.A. Razuvaev, Inorg. Chim. Acta, 44 (1980) L59.

7 L.N. Bochkarev, M.N. Bochkarev, G.S. Kalinina and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2589.

8 M.N. Bochkarev, L.V. Pankratov and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 2666.

9 M.N. Bochkarev, L.P. Maiorova and G.A. Razuvaev, Zh. Obshch. Khim., 50 (1980) 903.

10 S.N. Titova, V.T. Bychkov, G.A. Domrachev, G.A. Razuvaev, Yu.T. Struchkov and L.N. Zakharov, J. Organomet. Chem., 187 (1980) 167.

11 E.N. Gladyshev, V.S. Andreevichev, A.A. Klimov, N.S. Vyazankin and G.A. Razuvaev, Zh. Obshch. Khim., 42 (1972) 1077.

12 V.N. Latyaeva, A.N. Lineva and S.V. Zimina, Khim. Elementoorgan. Soedin., Mezhvuz. sb., Gorky, (1978) 35; Chem. Abstr., 91 (1979) 668.

13 G.A. Razuvaev, V.T. Bychkov, L.I. Vyshinskaya, V.N. Latyaeva and N.N. Spiridonova, Dokl. Acad. Nauk SSSR, 220 (1975) 854.

14 A. Gordon and R. Ford, Sputnik khimika, Moscow Mir, (1976) 123.

15 M.N. Bochkarev, L.V. Pankratov and G.A. Razuvaev, J. Organomet. Chem., 250 (1983) 135.

16 G.A. Razuvaev, V.K. Cherkasov, A.P. Fokeev, E.N. Gladyshev, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 1909.