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Reaction of *N,N'*-Bis(trimethylsilyl)dicyandiamide with Bis(η^5-cyclopentadienylvanadium) Dichloride

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Abstract—1,3,5-Tris[bis(η^5-cyclopentadienyl)chlorovanadium]melamin is prepared in high yield by the reaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with bis(η^5-cyclopentadienylvanadium) dichloride in tetrahydrofuran. As side products, trimethylchlorosilane and cyclopentadiene formed. Reaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with benzoyl chloride results in the formation of tris(benzoyl)melamin.

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Earlier we have shown that the reaction of dicyandiamide with hexamethyldisilazane in THF affords in high yield *N,N'*-bis(trimethylsilyl)dicyandiamide, and its further thermal decomposition leads to the formation of *N,N'*-bis(trimethylsilyl)carbodiimide and *N,N',N''*-tris(trimethylsilyl)melamin as major products [1]. On the other hand, studying the reactions of bis(η^5-cyclopentadienyl)vanadium (Cp_2V) with phenyl isocyanate, monophenylurea, and the cyanamide derivatives allowed the preparation of the series of potentially promising nitrogen-containing vanadium complexes [2–4].

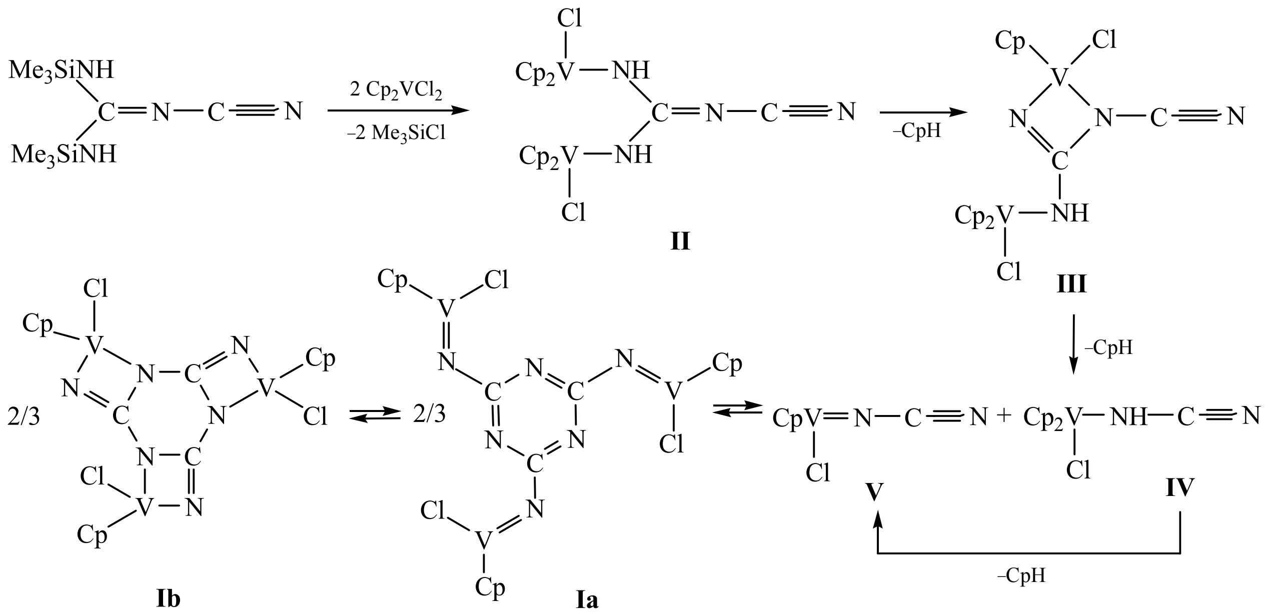
In order to expand the array of biologically and catalytically active nitrogen-containing compounds, in this work we have studied the reaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with bis(η^5-cyclopentadienylvanadium) dichloride (Cp_2VCl_2). The reaction turned out to proceed upon heating of the reagents in THF in an evacuated tube (100°C, 48 h) giving rise to 1,3,5-tris[bis(η^5-cyclopentadienyl)chlorovanadium]-melamin **I** as the main product in the form of fine-dispersed green powder in 68–82% yield. In the filtrate, trimethylchlorosilane and cyclopentadiene were found (yields up to 80%). The replacement of THF by toluene substantially decreases the yield of the reaction products. ESR monitoring has shown that without heating the reaction does not proceed at all: Only the intense signal of Cp_2VCl_2 was detected [$A_i(^{51}V)$ = 74.0 Oe, g_i = 1.9880] [5]. In the course of the reaction, this signal is weakened, and the signals of the earlier unknown paramagnetic vanadium compounds appear and grow in intensity, whose formation can be explained by scheme (1).

As follows from scheme (1), first the dicyandiamide derivative **II** is formed, which is converted into metallocycle **III** similar to those described earlier in [2, 5]. Compound **III**, apparently, decomposes to cyanamide **IV** (A_i = 81.0 Oe, g_i = 1.9730) and cyanamide **V** (A_i = 109.4 Oe, g_i = 1.9697).

Note that compounds **II, III** themselves do not give signals in the ESR spectra, and the parameters of the ESR spectrum of compound **V** are close to those in the spectrum of vanadyl of the type $Cl_2V{=}O$ (A_i = 108 Oe [6]), which is a model system for complexes CpClV=NX. The formation of cyanamides **IV, V** is also confirmed by the presence in the IR spectra of the reaction mixtures the absorption bands ν_{as}(N–C≡N) with maxima at 2220, 2180 cm^{-1}.

Since the signals of compound **IV** appear only in the ESR spectra of the freshly prepared reaction mixtures, while the signals of compound **V** are always observed, it can be concluded that during the transformations under consideration cyanamide **IV** is fully converted into **V**.

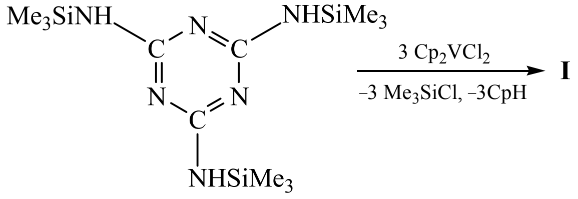
Finally, the reaction system is stabilized by trimerization of the cyanamide derivative **V** into


(1)

iminomelamin **Ia** and its isomer **Ib** similar to the triphenyliminomelamin and its isomer triphenylmelamin described in the literature [7].

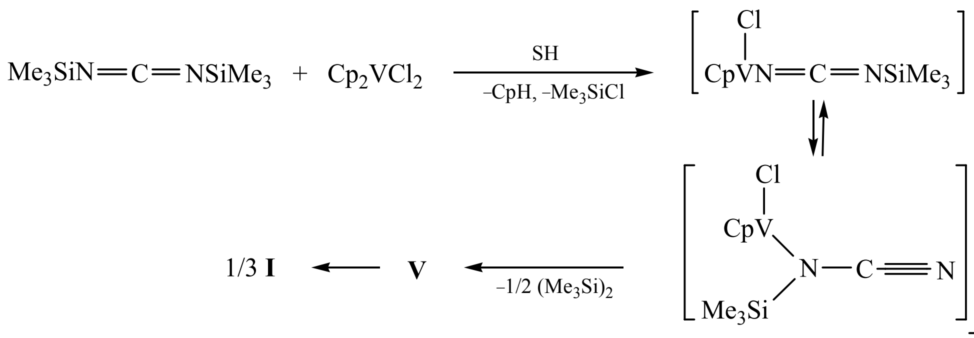
The hydrolysis of the reaction mixtures (1) results in the formation of melamin as the main product, which proves the *symm*-triazine structure of the target product **I**. The IR spectra of the products of hydrolysis show the presence of a small admixture of the cyanamide derivatives.

Since it could not be ruled out that compound **I** was formed by the reaction of Cp_2VCl_2 with the products of thermal decomposition of the starting *N,N'*-bis(trimethylsilyl)dicyandiamide, we have studied the reaction of vanadocene dichloride with *N,N',N''*-tris(trimethylsilyl)melamin and *N,N'*-bis(trimethylsilyl)carbodiimide [1]. Special experiments have shown that, indeed, upon heating *N,N',N''*-tris(trimethylsilyl)melamin with Cp_2VCl_2 under the conditions of reaction (1) results in the formation of compound **I**. Moreover, in the ESR spectra of the reaction mixtures, signals of cyanamide **V** of low intensity were found, which is indicative of reversibility of the process of trimerization of organovanadium cyanamides of this type. The increased duration of the heating to 96 h or more leads only to a small increase in the yield of the target product (less than 45%). The most pure product was synthesized at the use of the three-fold excess of *N,N',N''*-bis(trimethylsilyl)melamin since it was impossible to separate compound **I** and the unreacted Cp_2VCl_2, whereas the starting organosilicon melamin is easily washed out by organic solvents. As side products of the reaction, trimethylchlorosilane and cyclopentadiene were detected (the latter was identified by the GLC method) [scheme (2)].


(2)

In the ESR spectra of the reaction mixtures of *N,N'*-bis(trimethylsilyl)carbodiimide and Cp_2VCl_2 [the conditions were similar to reactions (1) and (2)] only weak signals of compound **V** were detected, and the starting vanadocene dichloride was practically completely recovered. However, the IR spectroscopy showed the presence of melamin in the products of hydrolysis suggesting the principal possibility for the reaction to occur by scheme (3).

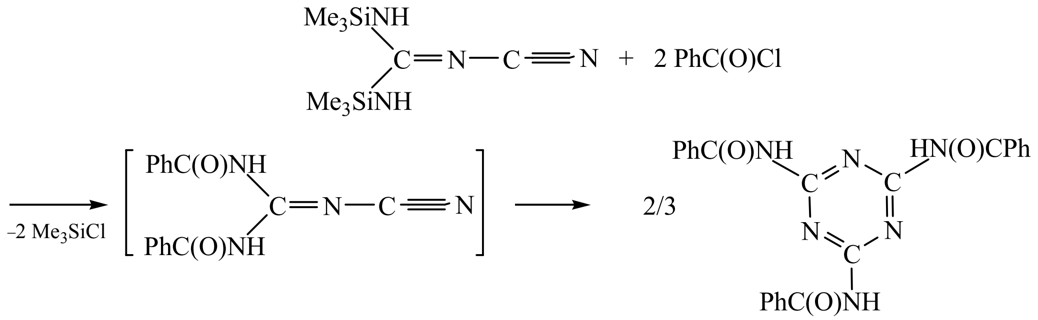
Therefore, the main route of the studied reaction is the direct interaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with vanadocene dichloride [scheme (1)], whereas the reactions of the latter with the products of thermolysis (2), (3) should be considered as secondary. This allows an assumption that in the reaction with Cp_2VCl_2 the Me_3SiNH groups in the linear nitrogen-containing compounds are more reactive than in their cyclic analogs.



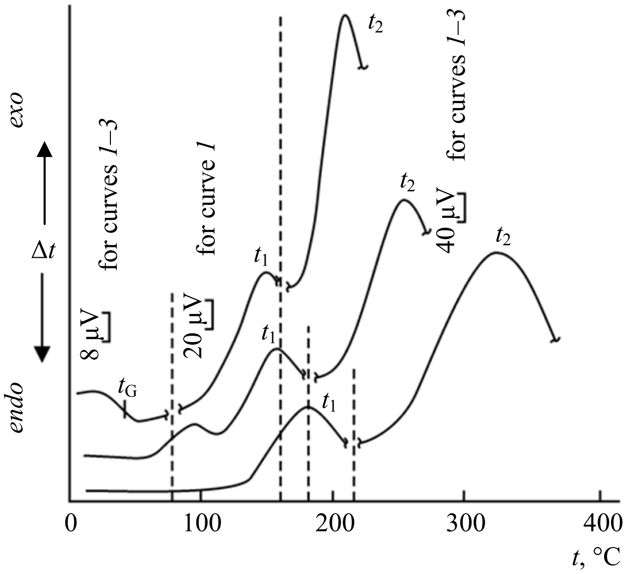
(3)

The IR spectra of the isomeric **Ia, Ib** contain the following principal characteristic absorption bands, cm^{-1}: 3300–3280 (N–H), 3090–3080, 1005, 815–805 (cyclopentadienyl), 1630–1620, 1470–1460, 830–820 (skeletal vibrations of the triazine ring).

In order to prove the main direction of chemical transformations of *N,N'*- bis(trimethylsilyl)dicyandiamide presented in scheme (1), we have for the first time investigated its reaction with organic halide, benzoyl chloride (reflux, 100–120°C, 8–10 h). It turned out that the replacement of Cp_2VCl_2 by benzoyl chloride resulted in the formation of tris(benzoyl) melamin as the main product of the reaction in up to 80% yield [scheme (4)]. The same compound was obtained by us earlier by the reaction of benzoyl chloride with *N,N',N''*-tris(trimethylsilyl)melamin [8], which is consistent with the above Eqs. (1)–(3).



(4)



Thermograms of the studied sample: (*1*) first run of heating; (*2*) second run of heating; and (*3*) third run of heating.

Compound **I** was studied by the differential thermal analysis (DTA). The sample was placed in a thermal chamber, cooled with liquid nitrogen to –190°C, and then heated at the rate 5 deg min^{-1}. After the first run of heating (see the figure, curve *1*) an anomaly of endothermic nature appeared on the thermogram in the range 30–50°C (the middle point of the transition t_G = 41.5°C), relatively sharp deviation of the base line from the zero level towards the temperature axis. This can be explained by the increase of the heat capacity by analogy with the data of [9], where the so-called G-type glass-like transitions were found in the crystals, which are connected with the increase in the heat capacity due to cooperative torsional vibrations of the molecules in the nodes of the crystal lattice, for example, in glycine [10]. At ~90°C, an exothermic process started to appear, which reached the extremum value at t_1 = 147°C. Further on, another exothermic process (larger in amplitude) was observed, which started at ~170°C, with maximum at t_2 = 208°C. After heating the sample to 220°C and subsequent cooling to room temperature the powder turned gray-black and became non free-flowing. Apparently, the transitions followed by evolution of energy are related to the formation of new chemical bonds. This becomes possible after the molecules acquire mobility in the temperature range of the G-type transition.

The sample was again cooled to –190°C and heated to 270°C. In the course of the second run of heating, two exothermic peaks with maxima at $t_1 = 155°C$ and $t_2 = 252.5°C$ appeared on the thermogram (see the figure, curve *2*). The amplitude of the transitions became substantially smaller and the temperature slightly increased as compared to the first run of heating. It can be assumed that with the chosen rate of heating the processes have no time to be completed and upon the repeated run of heating proceeds at a higher temperature. Therewith, the sample turned dark-brown and retained the powder consistence.

The third run of heating to 370°C (see the figure, curve *3*) also resulted in appearance of two exothermic peaks on the thermogram at $t_1 = 178°C$ and $t_2 = 324.5°C$. The color of the sample did not change after heating.

The high-temperature *exo*-effect (170–208°C) is, apparently, connected with the reversible transition of the two forms **Ia** and **Ib** in the solid state. The low-temperature transition can be assigned to the conversion of small amounts of compound **V** into one of isomeric forms of **I**. The analysis of thermograms suggests the absence of the starting compounds in the products of synthesis.

Therefore, the DTA data also confirm the suggested scheme of interconversions.

EXPERIMENTAL

IR spectra were obtained on Specord IR-75 and Specord M-80 spectrophotometers in thin layer for pure compounds or in mineral oil using KBr or ZnSe windows. ESR spectra were recorded on a Bruker EMX spectrometer. As a standard for determination of the *g*-factor, diphenylpicrylhydrazyl (DPPG, g_i = 2.0037) was used. Chromatographic studies were performed on a Tsvet-69A gas chromatograph with 2 m columns, detector catharometer, stationary phase Reoplex-400 on Chromaton N-AW, the temperature of columns 70°C, of catharometer, 120°C, of injector, 150°C. All chemical operations with organovanadium compounds were performed in vacuum. DTA in the range from –190 to +400°C was performed on a device whose construction and operation were described in [11]. The thermal chamber was filled with helium, quartz was used as a standard. The sample and the standard of ~0.35 g mass were placed into hermetic evacuated glass crucibles. The temperature of the sample and the temperature difference between the sample and the standard was measured by the chromel-copel thermocouple with the accuracy to 0.5°C. The sample in the thermal chamber was cooled by liquid nitrogen to –190°C, then heated at the rate of 5 deg min^{-1}. Deviation from linearity did not exceed 1%. The operation of the DTA device was checked by determination of the melting point of the standard *n*-heptane and the glass temperature of the purified glycerol. The obtained results coincided with the literature data for *n*-heptane [12] and glycerol [13] to 0.2 and 1°C, respectively.

Reaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with vanadocene dichloride. The mixture of 0.80 g of *N,N'*-bis(trimethylsilyl)dicyandiamide and 0.88 g of Cp_2VCl_2 (the ratio of the reagents 1:2) in 30 ml of THF was kept for 48 h in a sealed evacuated tube at 100°C. After cooling, the precipitate of green color was washed with the solvent, filtered, and dried in a vacuum to obtain 1.1 g (82%) of 1,3,5-tris[bis(η^5-cyclopentadienyl)chlorovanadium]melamin **I**. Found, %: C 37.94; H 3.01; Cl 18.43; V 26.02. $C_{18}H_{15}N_6Cl_3V_3$. Calculatedd, %: C 37.63; H 2.63; Cl 18.51; V 26.60. In the filtrate, Me_3SiCl and CpH were identified by the GC method (yields up to 80%). The reaction solution of yellow-green color was analyzed by the ESR method.

Reaction of *N,N',N''*-tris(trimethylsilyl)melamin with vanadocene dichloride. The mixture of 0.26 g of *N,N',N''*-tris(trimethylsilyl)melamin and 0.58 g of Cp_2VCl_2 (the ratio of the reagents 1:3) in 30 ml of toluene was kept for 100 h in a sealed evacuated tube at 100°C. After cooling, the precipitate of green color was washed with the solvent, filtered, and dried in a vacuum to obtain 0.20 g (45%) of 1,3,5-tris[bis(η^5-cyclopentadienyl)chlorovanadium]melamin **I**. In the filtrate, Me_3SiCl and CpH were identified by the GLC method (yields up to 80%). The reaction solution of yellow-green color was analyzed by the ESR method.

Reaction of *N,N'*-bis(trimethylsilyl)dicyandiamide with benzoyl chloride. The mixture of 2.0 g of *N,N'*-bis(trimethylsilyl)dicyandiamide and 2.46 g of benzoyl chloride (the calculated ratio of the reagents 1 : 2, eight-fold excess of benzoyl chloride, 9.7 g, was taken) was heated with a reflux condenser for 10 h at 100°C.

After cooling, diethyl ether was added to the reaction mixture. The formed yellowish precipitate was filtered off and dried in vacuum to obtain 1.98 g (78%) of tris (benzoyl)melamin, mp 203–204°C (mp 203–204°C [8]). In the filtrate, the corresponding amount of Me_3SiCl was found.

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