Reaction of niobium pentachloride with bis(triethylgermyl)cadmium

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The reaction of niobium pentachloride with $Cd(GeEt_3)_2$ (1 : 1) in THF *in vacuo* has been studied. The reaction affords $Et_3GeNbCl_4 \cdot THF$, which was characterized by elemental analysis and IR spectroscopy. To refine the composition of the compound, the thermolysis of $Et_3GeNbCl_4 \cdot THF$ at 85 and 180 °C was studied.

Key words: niobium pentachloride, reaction with bis(triethylgermyl)cadmium; triethylgermylniobium pentachloride, monosolvate with THF; thermolysis, volatile and solid products.

Data on compounds of niobium with organic ligands, which are binuclear and trinuclear clusters, are available in the literature. As an example, we refer to the binuclear Nb^{IV} complexes $Nb_2Cl_4(OMe)_4(MeOH)_2 \cdot 2MeOH$; $Nb_2Cl_6(THF)_3$, and $[H(THF)_2][Nb_2Cl_3(CO)_8]$, in which the niobium atoms are bound together through three chloride bridges.[1–3] Binuclear complexes, in which the niobium atom is bonded to Group II—IV d-block elements, such as $Cp_2Nb(CO) \cdot SnR_nCl_{3-n}$ (R = Ph, $n = 3\div1$; R = Et, $n = 2$); $Cp_2NbH(ZnCp)_2$; Cp_2NbH_2ZnCp; and $Cp_2Nb(CO)HZn(BH_4)_2$, are also known.[4,5]

Previously[6] we have studied the reaction of Cp_2NbCl_2 with $(Et_3Ge)_2Cd$ in a THF—toluene mixture, and a volatile organometallic derivative with a Nb—Ge bond of formula $Cp_2Nb(Cl)GeEt_3$ was isolated. As part of a continuing study and with the aim of obtaining a polynuclear organometallic compound with a niobium—nontransition metal bond,[7] we studied the reaction of $NbCl_5$ with $(Et_3Ge)_2Cd$.

The reaction was carried out in THF *in vacuo* at 20 °C. The solvent was condensed on $(Et_3Ge)_2Cd$, and then it was added in small portions to a solution of $NbCl_5$ in THF for 1 h. An intense blue solution was obtained; this solution changed to brown after one day. The solvent was removed by condensation into a trap cooled with liquid nitrogen, the presence of Et_3GeCl (the major volatile germanium-containing reaction product), Et_3GeH, and Et_6Ge_2 were determined by GLC. After the addition of toluene to a dry residue, a small amount of a light-colored precipitate (which, according to X-ray powder analysis, consists of $CdCl_2$ and metallic cadmium) was isolated; the toluene solution was concentrated, and a diamagnetic fine-crystalline dark-brown powder (m.p. 152 °C) was precipitated with hexane. Based on elemental analysis data, the compound may be characterized as tetrachlorotriethylgermylniobium tetrahydrofuranate ($Et_3GeNbCl_4 \cdot THF$). It is readily soluble in THF, benzene, and toluene, and less soluble in benzene. The IR spectrum of the compound shows the following absorption bands (ν/cm⁻¹): 510 (Ge—C); 640, 850 (C—H); 1000 (C—C); 1360, 1410, 1440 (Me); 2760 (C—H).

Judging from the quantity of isolated Et_3GeCl and Cd (metallic), it may be suggested that the following reaction is the main route of the interaction between the starting reagents:

$$(Et_3Ge)_2Cd + NbCl_5 \rightarrow Et_3GeNbCl_4 + Et_3GeCdCl.$$

However, $Et_3GeCdCl$ was not found among the reaction products. This compound apparently reacts with $NbCl_5$:

$$Et_3GeCdCl + NbCl_5 \rightarrow Et_3GeNbCl_4 + CdCl_2$$

and partially decomposes

$$Et_3GeCdCl \rightarrow Et_3GeCl + Cd\ (\text{metallic.}).$$

The formation of small amounts of triethylgermane and hexaethylgermane is attributable to dimerization of the Et_3Ge fragments obtained due to a slight decomposition of $(Et_3Ge)_2Cd$ by light followed by abstraction of hydrogen atoms from solvent molecules.

The overall scheme of the formation of all characterized products is the following:

$$NbCl_5 + 2 \cdot (Et_3Ge)_2Cd \xrightarrow{THF} Et_3GeNbCl_4 \cdot THF +$$
$$+ 1.75\ Cd + 0.5\ Et_3GeCl + 0.5\ Et_6Ge_2 + 1.5\ Et_3GeH +$$
$$+ 0.25\ CdCl_2\ .$$

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To elucidate the composition of the obtained complex, we performed its thermal decomposition in a quasi-flow system *in vacuo*. The process was started at 60 °C, then the temperature was increased to 85 °C, and the compound was kept at this temperature for 10 h. Among the liquid products of thermal decomposition, Et_3GeCl and THF (in a quantitative yield) were determined. Further heating at 180 °C for 20 h results in elimination of Et_3GeCl and Et_2GeCl_2; the solid residue contained compounds of Ge and Nb.

Experimental

All manipulations with readily oxidized and hydrolyzed compounds were carried out under a dry argon atmosphere free of oxygen or *in vacuo*.

The obtained compounds were identified by elemental analysis and spectral methods. Highly volatile compounds were determined by GLC on a Tsvet-129 chromatograph with a thermal conductivity detector and a 100×0.3-cm column packed with OV-17 on Chromaton N-Super (0.160—0.200 mm, helium as the carrier gas, flow rate 33 $mL \cdot min^{-1}$). IR spectra were recorded on a Perkin-Elmer spectrophotometer in the region 400—3000 cm^{-1}. LiF, NaCl, and KBr prisms were used. Solid samples were prepared under argon as suspensions in vaseline oil.

Reaction of bis(triethylgermyl)cadmium with niobium pentachloride (1 : 1). A mixture of $NbCl_5$ (4.17 g, 0.015 mol) and $(Et_3Ge)_2Cd$ (6.63 g, 0.015 mol) in THF was stored for 48 h at 20 °C. Then the THF was condensed into a trap cooled with liquid nitrogen; Et_3GeCl (2.6 g, 53 % as referred to the initial amount of the Et_3Ge fragment) and small quantities of Et_3GeH and Et_6Ge_2 (3—5 %) were determined in the solution by GLC. After the solvent was changed to toluene, the solution was decanted from a precipitate (which, according to X-ray powder analysis, contained up to 80 mass % metallic Cd and 10 mass % $CdCl_2$). The toluene solution was concentrated and $Et_3GeNbCl_4 \cdot THF$ (6.12 g, 85 %), m.p. 152 °C, was precipitated with hexane. Calculated (%): C, 25.54; H, 4.79; Cl, 29.24. Found (%): C, 25.70; H, 4.94; Cl, 30.56.

Thermal decomposition of $Et_3GeNbCl_4 \cdot THF$. $Et_3GeNbCl_4 \cdot THF$ (0.63 g) was heated at 85 °C for 10 h. In the liquid products, THF (0.092 g, 100 %) and Et_3GeCl (0.04 g, 16 %) were determined. Then the compound was heated at 180 °C for 20 h. Et_3GeCl (0.05 g, 20 %) and Et_2GeCl_2 (0.03 g, 10 %) were isolated. The solid amorphous powder was washed with hexane and dried, and 0.37 g of a precipitate was obtained. The presence of Nb and Ge was qualitatively determined by X-ray fluorescence analysis.

Hence, the reaction of $(Et_3Ge)_2Cd$ with $NbCl_5$ in THF *in vacuo* affords $Et_3GeNbCl_4 \cdot THF$, which is unstable in air, readily soluble in THF, benzene, and toluene, and less soluble in saturated hydrocarbons. This compound was characterized by elemental analysis and IR spectra data. Thermal decomposition of this product affords triethylchlorogermane as the major volatile product.

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