Investigation of the reaction of bis(triethylgermyl)cadmium with titanium tetrachloride

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The reaction between $(Et_3Ge)_2Cd$ and $TiCl_4$ in the presence of α,α′-bipyridyl afforded a compound with a Ge—Cd—Ti group. This compound was characterized by IR and ESR spectroscopy. Thermal decomposition of this compound at 130 and 160 °C and its interaction with gaseous HCl were studied. A novel complex, $(Et_3Ge)_2Cd \cdot bpy$, was obtained as a by-product of the reaction, and some its physicochemical characteristics were determined. Based on the experimental results, a scheme for the interaction of $(Et_3Ge)_2Cd$ with $TiCl_4$ has been suggested.

Key words: mixed organo-Cd, Ge, Ti compounds.

We have examined the possibility of synthesizing triethylgermyl derivatives by the reaction of $(Et_3Ge)_2Cd$ with $TiCl_4$. This reaction is of interest as a method for preparing organopolymetallic compounds containing bonds between transition and nontransition metals.

Results and Discussion

We believed that the replacement of halogen atoms bound with titanium by triethylgermyl fragments might afford new compounds containing Ge—Ti bonds. Unlike derivatives of the type $Cp_2Ti(Cl)GeR_3$ (R = Et, Ph), these titanium compounds would contain no stabilizing cyclopentadienyl substituent. We chose THF, which is able to stabilize organotitanium compounds with σ-bonds to a certain extent, as the solvent.

Titanium chloride $TiCl_4$ was preliminarily converted to the corresponding tetrahydrofuranate, $TiCl_4 \cdot 2THF$. The first step of the process involves substitution of the Et_3Ge moiety for a chlorine atom.

$$TiCl_4 + (Et_3Ge)_2Cd \xrightarrow[THF]{-20\ °C} Et_3GeCdCl + Et_3GeTiCl_3$$

Triethylgermylcadmium chloride is a stable compound. As was reported previously,[1] it can be readily prepared from $(Et_3Ge)_2Cd$ and $CdCl_2$ in THF.

We could not isolate the triethylgermyl derivative of Ti^{IV}. We believe that it reacted with excess titanium tetrachloride.

$$TiCl_4 + Et_3GeTiCl_3 \rightarrow Et_3GeCl + 2TiCl_3$$

Similar processes have been described previously[2] for alkyl organotitanium(IV) derivatives.

As titanium trichloride, which is formed in the reaction as the $TiCl_3 \cdot 3THF$ complex, accumulated, it partly precipitated and partly reacted with new portions of $(Et_3Ge)_2Cd$ to give (triethylgermyl)cadmiumtitanium dichloride (**1**).

$$TiCl_3 + (Et_3Ge)_2Cd \rightarrow \underset{\mathbf{1}}{Et_3GeCdTiCl_2} + Et_3GeCl$$

Exchange reactions are typical of $TiCl_3$. In particular, its reactions with methyllithium and Grignard reagents yielding σ-derivatives of titanium(III) have been reported.[3,4]

Compound **1** is stable as a THF solution for several days. It was identified as a stable crystalline complex, $(Et_3GeCdTiCl_2 \cdot bpy)_2$ (**2**), obtained in 45 % yield. In addition, we isolated the titanium-free complex $(Et_3Ge)_2Cd \cdot bpy$ (**3**).

Taking into account the resulting compounds, the overall reaction of $TiCl_4$ with $(Et_3Ge)_2Cd$ may be written as follows:

$$TiCl_4 + (Et_3Ge)_2Cd \xrightarrow{THF} TiCl_3 \cdot 3THF + \mathbf{A}$$

$$\mathbf{A} + bpy \longrightarrow \underset{\mathbf{2}}{(Et_3GeCdTiCl_2 \cdot bpy)_2} + Et_3GeCl +$$

$$+ \underset{\mathbf{3}}{(Et_3Ge)_2Cd \cdot bpy} + TiCl_{1.7} \cdot 1.5bpy + Cd.$$

A denotes a mixture of the reaction products dissolved in THF including Et_3GeCl and $Et_3GeCdTiCl_2$. Isolated compound **2** is extremely sensitive to oxygen and moisture. It is practically insoluble in toluene and hexane and is soluble in THF. The IR spectrum exhibits the following absorption bands (ν/cm^{-1}): 520, 545 (Ge—C);

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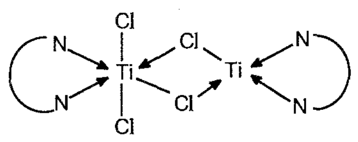
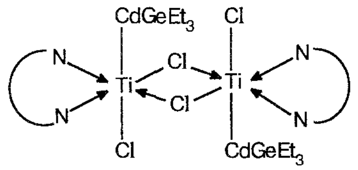
1365, 1450 (CH_3); 1585 (C—N). The absorption band at 1585 cm^{-1} is shifted to the high-frequency spectral region with respect to the corresponding band in the spectrum of free bpy by 15 cm^{-1}. This attests to the donor character of the nitrogen atom in this compound. Compound **2** is paramagnetic, and its ESR spectrum is typical of Ti^{III} derivatives, $g = 1.969$. To determine the fragment composition of compound **2** more precisely we investigated its reaction with gaseous HCl and its thermal decomposition. We found that compound **2** incorporates Et_3Ge, bpy, Cd, and Ti fragments in a 1 : 1 : 1 : 1 ratio.

Based on the above-presented data from IR and ESR spectroscopy, the results of the study of the fragment composition of compound **2**, and the literature[5] data that solid titanium trichloride is a crystalline polymer with halogen bridges and a Ti^{III} coordination number of 6, one may suggest that compound **2** exists as a dimer with bridging chlorine atoms. For the $(TiCl_3 \cdot bpy)_2$ complex the following structure has been proposed.[6]



Compound **2** contains Et_3GeCd moieties instead of two axial chlorine atoms. Two isomers of this compound are possible. The fact that the products of thermal decomposition of **2** (see below) contain Et_3GeCl and no Et_6Ge_2 allows one to give preference to the *trans*-isomer.



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In a THF solution, formation of the monomer coordinated with a THF molecule, *viz.*, $Et_3GeCdTiCl_2 \cdot bpy \cdot THF$, would also be expected.

Thermal decomposition of **2** was carried out at 130 °C in toluene. As shown by GLC, the resulting solution contained bpy in a quantitative yield and Et_3GeCl.

When thermal decomposition of **2** was carried out under more drastic conditions (160 °C), the yield of Et_3GeCl increased. In the solid residue, Cd was detected, which was formed in a quantitative yield. Most of the triethylgermyl moieties were eliminated as Et_3GeCl. In addition, the residue contained halides of low-valence titanium, amorphous to X-rays.

Based on the products of the thermal decomposition, one may assume that this process begins with abstraction of bpy. The arising vacant sites in the coordination environment of Ti^{III} facilitate intramolecular disproportionation.

The reaction of compound **2** with gaseous HCl in toluene at ambient temperatures and a 1 : 1 ratio between the reactants did not result in the decomposition of the starting complex. When the amount of HCl taken for the reaction was increased to four moles per mole of compound **2**, the reaction afforded Et_3GeH and a precipitate of the composition $ClCdTiCl_2 \cdot bpy \cdot HCl$ (**4**). The fact that Et_3GeH is formed in the reaction of compound **2** with HCl attests to the cleavage of the Ge—Cd bond.

A tenfold increase in the amount of HCl taken for the reaction did not result in a higher degree of decomposition. The complex salt **4** was still the major reaction product.

When we studied the interaction of $TiCl_4$ with $(Et_3Ge)_2Cd$ with the addition of bpy, some of the starting germylcadmium compound did not react and was isolated as complex **3**. To confirm the structure of compound **3** we prepared it specially by the reaction of $(Et_3Ge)_2Cd$ with bpy (1 : 1) in hexane. The product was readily soluble in toluene and hexane and very sensitive to oxygen and air moisture. The IR spectrum of this compound exhibited the following absorption bands (ν/cm^{-1}): 510, 550 (Ge—C); 1000 (C—C); 1360, 1410, 1440 (CH_3); 1580 (C—N).

Experimental

All of the operations with readily oxidizable and hydrolyzable compounds were carried out under dry argon (freed from oxygen) or under a vacuum.

The resulting compounds were identified by elemental analysis, determination of functional groups, and spectroscopy. Volatile compounds were identified on a Tsvet-129 chromatograph with a heat-conductivity detector; a 100×0.3 cm column packed with OV-17 on Chromaton N-Super, granulation 0.160—0.200; helium as the carrier gas (33 mL min^{-1}). IR spectra were recorded on a Perkin Elmer spectrophotometer in the region 400—3000 cm^{-1}. NaCl, LiF, and KBr prisms were used. Samples of solid compounds as suspensions in vaseline oil were prepared under argon.

The reaction of bis(triethylgermyl)cadmium with titanium tetrachloride in THF. THF (20 mL) was added to $TiCl_4$ (2.20 g), and a solution of $(Et_3Ge)_2Cd$ (4.74 g) in THF (10 mL) was added at −20 °C to the resulting tetrahydrofuranate, $TiCl_4 \cdot 2THF$, over a period of 1 h. A blue-colored suspension of $TiCl_3 \cdot 3THF$ formed. The temperature was raised to ~20 °C, and after 20 h the solution of compound **1** was decanted from the precipitate. 0.07 g (5.0 %) of Cd and 2.36 g (55 %) of $TiCl_3 \cdot 3THF$ were found in the precipitate. Found (%): Ti, 12.60. Calculated (%): Ti, 12.97. α,α′-Bipyridyl (1.66 g) was added to the THF solution of **1** left, and the mixture was kept for 24 h at ~20 °C. The solution was decanted from the dark-blue precipitate insoluble in THF. The precipitate contained 0.1 g (2.0 %) of $TiCl_{1.7} \cdot 1.5bpy$. Found (%): Ti, 13.50; Cl, 17.0. $C_{15}H_{12}N_3Cl_{1.7}Ti$. Calculated (%): Ti, 14.00; Cl, 17.6. THF was removed *in vacuo*, and the residue was washed with hexane and dried to give 2.70 g (44.6 %) of bis(triethylgermylcadmiumtitanium bipyridyl dichloride) $(Et_3GeCdTiCl_2 \cdot bpy)_2$ (**2**), m.p. 124 °C (dec.); g = 1.969. Found (%): C, 36.00; H, 4.36; Cl, 11.80; Cd, 20.11. $C_{32}H_{46}N_4Cd_2Cl_4Ge_2Ti_2$. Calculated (%): C, 35.11; H, 4.21; Cl, 12.98; Cd, 20.48.

The reaction of bis(triethylgermyl)cadmium with α,α′-bipyridyl. A mixture of $(Et_3Ge)_2Cd$ (1.00 g) and α,α′-bipyridyl (0.36 g) in 30 mL of hexane was kept for 4 h at ~20 °C. The solution was cooled to −78 °C and kept for 12 h, and bis(triethylgermyl)(dipyridyl)cadmium $(Et_3Ge)_2Cd$ bpy (**3**) (0.95 g, 70.0 %) was isolated at ~20 °C as red needle crystals, m.p. 45—46 °C. Found (%): C, 45.37; H, 6.43; Ge, 24.61; Cd, 19.09. $C_{22}H_{38}N_2Ge_2Cd$. Calculated (%): C, 45.00; H, 6.47; Ge, 24.70; Cd, 19.10.

Thermal decomposition of compound 2. ***A.*** Thermal decomposition was carried out in toluene in evacuated sealed tubes. Compound **2** (0.61 g) was kept for 10 h at 130 °C. The solution was decanted from the precipitate. As shown by GLC, the solution contained bpy (0.17 g, 98 %) and Et_3GeCl (0.08 g, 36.7 %). The dark-blue precipitate (0.25 g) of an unknown structure contained (%): Cd, 40.2; C, 15.3; Cl, 13.0; Ti, 13.5.

B. Compound **2** (0.48 g) was kept for 10 h at 160 °C and filtered. According to GLC, the filtrate contained bpy (0.12 g, 90 %) and Et_3GeCl (0.12 g, 70 %). The dark-blue precipitate was a mixture of Cd (0.1 g, 100 %) (X-ray phase analysis) and compounds of low-valent titanium (0.07 g). The variation in the valency of titanium in the course of thermal decomposition was monitored in a separate run using an RE-1301 ESR spectrometer. The ESR spectrum was a singlet with g_i = 1.969 typical of Ti^{III}.

The reaction of compound 2 with gaseous HCl. A mixture of compound **2** (0.61 g) and anhydrous HCl (the ratio between the reactants was 1 : 4) in 20 mL of toluene was kept for 24 h at ~20 °C. The resulting light-grey precipitate was filtered off, washed with THF, and dried to give 0.40 g (78.3 %) of $ClCdTiCl_2 \cdot bpy \cdot HCl$ (**4**), m.p. 120—130 °C (dec.). Found (%): C, 27.06; H, 2.27; Cl, 32.16; Cd, 24.34. $C_{10}H_9N_2Cl_4CdTi$. Calculated (%): C, 26.05; H, 1.96; Cl, 30.80; Cd, 24.40. Et_3GeH (0.13 g, 72.3 %) was detected in the volatile products by GLC.

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