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Abstract

Full Text

Chemistry

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Preparation and Some Properties of the Complex of Methyltitanium Trichloride with Tetrahydrofuran

Recently increasing attention has been devoted to the study of the properties of alkyl derivatives of titanium, which are of considerable interest for organic synthesis. However, the broad application of these products is limited by the extremely low thermal stability of most known organotitanium compounds. The literature ([1]) indicates that complex compounds of titanium alkyl derivatives are more thermostable, in particular complexes of methyltitanium trichloride with dioxane and triphenylphosphorus. But the latter are practically insoluble in all indifferent solvents, which also greatly hampers their use.

In the present work we obtained a previously undescribed complex of methyltitanium trichloride with tetrahydrofuran (THF) and studied some of its properties. CH_3TiCl_3 was synthesized by the method described by us in a previous work ([2]). Before use, THF was carefully purified of impurities by distillation over solid KOH and metallic Na in an atmosphere of pure nitrogen.

When a solution of methyltitanium trichloride in hexane was cautiously mixed with THF cooled to $-40 \div -50^\circ$, formation of a homogeneous dark-cherry-colored solution was observed. After the solvent, together with excess THF, was distilled off under vacuum at low temperature ($-30 \div -40^\circ$), with the temperature raised to room temperature toward the end of the distillation, a solid product containing titanium was obtained, in the form of a very light cherry-colored powder. On interaction with absolute methanol it liberated methane (determined by chromatographic analysis), which indicated the presence of CH_3 groups in the product.

In composition the compound obtained was close to the complex $CH_3TiCl_3 \cdot 2C_4H_8O$.

Found, %:	Ti 15.2, 15.7;	Cl 34.7, 35.0;	CH_3 4.7, 4.9
$CH_3TiCl_3 \cdot 2C_4H_8O$. Calculated, %:	Ti 15.3;	Cl 34.0;	CH_3 4.8

This substance is very sensitive to the presence of oxygen and moisture, with which it reacts instantaneously.

The complex obtained by us was more thermostable in comparison with CH_3TiCl_3. In the absence of oxygen and moisture it was stored practically without change at temperatures below 0°, and was also fairly stable at room temperature. On heating in a sealed capillary it melted without noticeable decomposition at 107–108°.

The complex of methyltitanium trichloride with THF, in contrast to the previously known complexes of CH_3TiCl_3 with dioxane and $(C_6H_5)_3P$, dissolved in THF, benzene, alkylbenzenes, and some chlorinated hydrocarbons (CCl_4, $CHCl_3$), but practically did not dissolve in aliphatic hydrocarbons (hexane, heptane). It was noted that the complex is more stable in the solid state than in solution. On warming to room temperature, its solutions rapidly changed color from dark cherry to light yellow, and a decrease in the content of CH_3 groups in the organotitanium compound was observed. In some solvents (CCl_4, $CHCl_3$) an insoluble precipitate separated.

In the previously described work ([2]) we investigated the process of decomposition of methyltitanium trichloride on the surface of metallic mercury, and it was shown that in this case the decomposition of the alkyl derivative of titanium proceeds in two directions: without liberation and with liberation of free radicals. It was of interest to study the decomposition on the surface of metallic Hg of the complex of CH_3TiCl_3 with THF. To metallic Hg (50 g) in benzene, with vigorous stirring, a solution of the complex (0.0177 mole) in benzene was added. A rapid change in the color of the solution from dark cherry-red to yellow and the precipitation of a brown precipitate were observed. The reaction mixture was stirred for 6 h at room temperature.

The following compounds were identified: methane with a small admixture of methyl chloride (chromatographic analysis), CH_3HgCl–0.86 g (19.3 mole % of the starting material, calculated on the CH_3 group) (determined iodometrically ([3])), and titanium tetrachloride. In the precipitate the presence of trivalent titanium (by titration with ferric ammonium alum) and calomel was found. The reaction of the complex with metallic Hg was also carried out in THF medium, at a lower temperature. To metallic Hg (50 g) in THF, cooled with dry ice, a solution of the organotitanium compound (0.00636 mole) in THF was added. The temperature of the reaction mixture was raised to −2-−5° and at this temperature the reaction mixture was stirred for 5 h. During the reaction there occurred a gradual darkening of the solution and the evolution of gaseous products. On warming the reaction mass to room temperature the solution became clear, of a light-yellow color.

In the reaction products the following were determined: methane (0.0039 mole), CH_3HgCl (0.0022 mole, or 34.6 mole %), and calomel. No compounds of trivalent titanium were detected in the reaction mixture.

From the results obtained it is evident that decomposition of the complex on the surface of metallic Hg proceeds according to the same scheme as the decomposition of CH_3TiCl_3 in its presence, but in the case of decomposition of the

methyltitanium trichloride complex with THF the rate of the second process, with liberation of free radicals, is noticeably increased.

In the decomposition of methyltitanium trichloride on the surface of metallic mercury, about 10 mole % of methoxy groups was determined in the form of methylmercury chloride.

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Note: Figure translations are in progress. See original paper for figures.