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Abstract

Full Text

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SOME REACTIONS OF BIS(CYCLOPENTADIENYL)DIPHENYL

Bis(cyclopentadienyl) derivatives of titanium of the type $(C_5H_5)_2TiX_2$, where X is a halide, form complexes with alkyl or aryl aluminum compounds, which are used as Ziegler-type catalysts for the polymerization of α-olefins. The halogen atom in these compounds is labile, as evidenced by halogen-exchange reactions (^{1}), and also by replacement of the latter by a hydrocarbon radical, which is bound by a σ-bond to the titanium atom. Alkyl compounds are unstable and are obtained with great difficulty (^{2}). Aryl derivatives are more stable (^{3}), but their chemical properties have still not been completely studied.

It seemed of interest to us to compare some chemical properties of $(C_5H_5)_2TiAr_2$, in which the group $(C_5H_5)_2Ti$ may be equated with a metal, with those of other organometallic compounds. For comparing the reactivity of the latter, the radical-halide exchange reaction is widely used. We decided to carry out such an exchange reaction for $(C_5H_5)_2TiCl_2$ and $(C_6H_5)_2Hg$, on the one hand, and for $(C_5H_5)_2Ti(C_6H_5)_2$ and $HgCl_2$, on the other.

The first system was studied by heating the components in boiling benzene or methylene chloride for 6 h. During this time, from the benzene solution $\sim 20\%$ of the expected phenylmercuric chloride was isolated; in methylene chloride solution, despite the fact that the reaction temperature was considerably lower, the yield of the latter reached almost the theoretical value:

$$(C_5H_5)_2TiCl_2 + 2(C_6H_5)_2Hg \rightarrow (C_5H_5)_2Ti(C_6H_5)_2 + 2C_6H_5HgCl. \qquad (1)$$

The second product—$(C_5H_5)_2Ti(C_6H_5)_2$—under the experimental conditions reacted further and therefore could not be isolated.

The interaction of bis(cyclopentadienyl)diphenyltitanium with mercuric chloride was carried out in a solution of CCl_4 or benzene at 80° with stirring in a nitrogen atmosphere. The ratio of the initial components $(C_5H_5)_2Ti(C_6H_5)_2 : HgCl_2$ was varied from $1 : 1$ to $1 : 2$; in the latter case the yield of reaction products was higher. The main products isolated were bis(cyclopentadienyl)titanium dichloride and phenylmercuric chloride; moreover, in all experiments the ratio of the isolated products was maintained as $1 : 2$. In the best case, in carbon tetrachloride solution, from 0.021 mole of $(C_5H_5)_2Ti(C_6H_5)_2$ and 0.042 mole of $HgCl_2$, 0.0145 mole of $(C_5H_5)_2TiCl_2$ and 0.0281 mole of C_6H_5HgCl were obtained. Hence it may be concluded that, essentially (~ 70%), an exchange reaction takes place between bis(cyclopentadienyl)diphenyltitanium and mercuric chloride according to the equation:

$$(C_5H_5)_2Ti(C_6H_5)_2 + 2HgCl_2 \rightarrow (C_5H_5)_2TiCl_2 + 2C_6H_5HgCl. \tag{2}$$

In benzene solutions the amount of these products changed sharply: the yield of bis(cyclopentadienyl)titanium dichloride fell to 24%, while the amount of phenylmercuric chloride formed increased to 90%. The quantitative determination of the organotitanium compound was carried out by a spectrophotometric method.

In addition to the main products of the reaction carried out in a CCl_4 medium, chlorobenzene, diphenyl, and calomel were isolated. In the presence of atmospheric oxygen, phenol was detected. In benzene solutions chlorobenzene was not found; at the same time, the yield of diphenyl increased. The formation of the indicated products can be explained by the parallel interaction of the starting organotitanium compound with the solvent. Processes of this kind explain the absence of $(C_5H_5)_2Ti(C_6H_5)_2$ among the products of reaction (1), as well as the sharp increase in the yield of phenylmercuric chloride in methylene chloride medium.

This led us to carry out decomposition reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ in various solvents. The reaction of biscyclopentadienyldiphenyltitanium in benzene, carried out with careful removal of atmospheric oxygen, proved especially interesting. On heating ampoules sealed under vacuum with the initial solution, a sharp color change was observed, from the original yellow to dark green, characteristic of titanium compounds of lower valency. As is known, the dark-green color is possessed by the paramagnetic form of bisdicyclopentadienyltitanium briefly described in the literature ([4]). In our case, paramagnetism was demonstrated by the EPR spectrum. As a result of the reaction with CCl_4, biscyclopentadienyltitanium dichloride, chlorobenzene, and small amounts of diphenyl were isolated. The formation of chlorobenzene and diphenyl is usual for reactions of phenyl radicals in carbon tetrachloride medium ([5]). It may be assumed that initial homolysis of the Ti—C_6H_5 bond occurs, with formation of a free phenyl radical.

To verify this assumption, reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ with alcohols (methyl and isopropyl) and chloroform were carried out. In the first case benzene and the products of alcohol dehydrogenation by the phenyl radical (formaldehyde or acetone) were isolated quantitatively. At the same time an intensely green-colored solution of $(C_5H_5)_2Ti$ was obtained. As a result of thermal and photoreactions in chloroform, benzene and almost quantitative $(C_5H_5)_2TiCl_2$, as well as a small amount of diphenyl, were isolated.

On the basis of the results obtained, the following mechanism may be accepted for the reactions of biscyclopentadienyldiphenyltitanium. On heating or irradiation with UV light, the initial titanium compound decomposes with liberation of a phenyl radical and formation of dark-green paramagnetic biscyclopentadienyltitanium:

$$(C_5H_5)_2Ti(C_6H_5)_2 \rightarrow (C_5H_5)_2Ti + 2C_6H_5\cdot$$

This stage resembles the decomposition of diphenylmercury, with the difference that the role of metallic mercury here is played by an extremely reactive divalent titanium compound.

The behavior of the phenyl radicals formed depends on the solvent; in benzene phenyl radicals give diphenyl, while in alcoholic solutions or chloroform they abstract hydrogen with formation of benzene:

$$2C_6H_5\cdot + CH_3OH \rightarrow 2C_6H_6 + CH_2O;$$

$$2C_6H_5\cdot + CH_3CHOHCH_3 \rightarrow 2C_6H_6 + CH_3COCH_3;$$

$$C_6H_5\cdot + CHCl_3 \rightarrow C_6H_6 + \cdot CCl_3.$$

In a CCl_4 solution, phenyl radicals form chlorobenzene:

$$C_6H_5\cdot + CCl_4 \rightarrow C_6H_5Cl + \cdot CCl_3.$$

Biscyclopentadienyltitanium remains unchanged in benzene or alcohols in the absence of atmospheric oxygen.

In the presence of CCl_4 or chloroform it is rapidly oxidized to the dichloride:

$$(C_5H_5)_2Ti + 2CCl_4 \rightarrow (C_5H_5)_2TiCl_2 + 2\cdot CCl_3.$$

We carried out this reaction by adding CCl_4 to a green benzene solution of $(C_5H_5)_2Ti$. In this process the green color rapidly changed to red, characteristic of the dichloride. The latter was isolated from the solution and

has been characterized. An analogous reaction takes place under the action of sublimate on $(C_5H_5)_2Ti$.

$$(C_5H_5)_2Ti + 2HgCl_2 \rightarrow (C_5H_5)_2TiCl_2 + Hg_2Cl_2.$$

The formation of calomel in exchange reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ with sublimate must be explained by this process. The conversion of $(C_5H_5)_2Ti$ into the dichloride under the action of HCl on it in the absence of air has been described in the literature (^{4}).

All the reactions listed are very reminiscent of the thermal and photoreactions of diphenylmercury with alcohols, carbon tetrachloride, and chloroform, which proceed by a free-radical mechanism.

The presence of phenyl radicals during the decomposition of dicyclopentadienyldiphenyltitanium was confirmed by reaction with metallic mercury in a carbon tetrachloride medium. The phenylmercuric chloride obtained in this case can serve as reliable proof of the formation of phenyl radicals on the surface of metallic mercury:

$$(C_5H_5)_2Ti(C_6H_5)_2 + Hg + CCl_4 \rightarrow C_6H_5HgCl + (C_5H_5)_2TiCl_2 + C_6H_5Cl.$$

In addition, the presence of free phenyl radicals was confirmed by the decolorization of solutions of α,α-diphenyl-β-picrylhydrazyl in benzene, alcohol, and carbon tetrachloride in the presence of $(C_5H_5)_2Ti(C_6H_5)_2$. In carrying out the experiments, careful removal of oxygen from the air is extremely important. The dark-green color of solutions of dicyclopentadienyltitanium in the presence of even traces of oxygen disappeared instantaneously; the faintly colored noncrystalline precipitates formed in this process, containing titanium and cyclopentadienyl groups, are evidently products of oxidation of the latter.

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