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Abstract

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New Monocyclopentadienyl Derivatives of Titanium

Recently, many diverse organotitanium compounds (TiOC) have been obtained; in particular, tetramethyltitanium and tetraphenyltitanium have been described, existing at low temperatures (-78°) ([1,2]). More stable are compounds in which, along with alkyl or aryl substituents, cyclopentadienyl groups are present. Of the mono-π-cyclopentadienyl derivatives, only cyclopentadienyltrimethyltitanium is known; it forms yellow needle-like crystals which, in an inert atmosphere, decompose at temperatures below 20° ([3]). Expansion of the range of such compounds and the study of their chemical properties are of definite theoretical interest.

In the present work, reactions involving exchange of chlorine atoms in monocyclopentadienyltitanium trichloride for phenyl groups were studied. Earlier ([2]) it was shown that, upon interaction of titanium tetrachloride with diphenylmercury, all four chlorine atoms are replaced by phenyl radicals. Therefore we first investigated the exchange reaction of diphenylmercury with $C_5H_5TiCl_3$ in a ratio of $3:1$, carried out in benzene solution at room temperature. The reaction mixture was stirred in a sealed ampoule for 100 hours. Phenylmercury chloride was isolated as the main product (70% calculated on the diphenylmercury taken). Formation of cyclopentadiene in the reaction was not observed. Hydrolysis of the reaction products gave benzene, and when the reaction was carried out in the presence of oxygen, considerable amounts of phenol were isolated. Diphenylmercury and phenylmercury chloride are stable compounds and, under the experimental conditions, could not have given benzene and phenol. All this permits one to assume the formation in this reaction of an organotitanium compound having a titanium—phenyl bond:

$$C_5H_5TiCl_3 + 3(C_6H_5)_2Hg \rightarrow 3C_6H_5HgCl + [C_5H_5Ti(C_6H_5)_3]. \tag{1}$$

It proved impossible to isolate an individual titanium compound in this case, since, as will be shown below, it decomposes under the conditions of the reaction under consideration.

Replacement of diphenylmercury by the more reactive phenyllithium proved convenient and effective; the reaction with it proceeds under mild conditions.

When $C_5H_5TiCl_3$ (0.016 mole) was treated with phenyllithium (0.048 mole) in ether at $-78°$ in a nitrogen atmosphere, a precipitate of LiCl separated. The color of the solution did not change, remaining yellow. In the precipitate, 0.047 g-atom of Cl' was determined, which amounts to 98% calculated on the initial $C_5H_5TiCl_3$. Decomposition of the substance with formation of cyclopentadiene and benzene at $-78°$ was not observed. All this permits one to assume that the reaction proceeds according to the equation:

$$C_5H_5TiCl_3 + 3C_6H_5Li \rightarrow C_5H_5Ti(C_6H_5)_3 + 3LiCl. \tag{2}$$

If the ethereal solution of the compound obtained is filtered at $-78°$ into a previously cooled ampoule and the ether is then removed in vacuo, orange lustrous crystals appear on the walls of the ampoule; they are sensitive to the action of light and decompose with blackening when the temperature is raised to room temperature.

To confirm the formation of cyclopentadienyltriphenyltitanium, we used the widely applied exchange reaction of phenyl radicals with mercuric chloride. As a result of the interaction of 0.007 mole of $C_5H_5Ti(C_6H_5)_3$ with 0.028 mole of $HgCl_2$ at $-78°$, 0.020 mole of C_6H_5HgCl was isolated (95%, determined iodometrically (4)) and 0.003 mole of $C_5H_5TiCl_3$, which corresponds to the equation:

$$C_5H_5Ti(C_6H_5)_3 + 3HgCl_2 \rightarrow 3C_6H_5HgCl + C_5H_5TiCl_3. \tag{3}$$

Owing to the thermal instability of cyclopentadienyltriphenyltitanium, we did not work with the solid substance, but investigated the ethereal solutions obtained.

Alcoholysis of 0.0073 mole of $C_5H_5Ti(C_6H_5)_3$ with absolute isopropyl alcohol at $-78°$ leads to the formation of 0.0210 mole of benzene (96%) and small amounts of acetone (0.0028 mole).

The determination of benzene and acetone in this reaction and in all subsequent ones was carried out spectrometrically in the IR region. The sample analyzed was dissolved in *n*-heptane. The concentrations of benzene and acetone in the resulting solution were determined from the intensity of the absorption bands: C_6H_6–671 cm^{-1}, acetone–1730 cm^{-1}. The initial concentrations were calculated taking into account the volume of the sample and of the solutions. The relative error of the determination does not exceed 5%.

Cyclopentadiene was not detected in the reaction products. On this basis it was logical to assume that the reaction proceeded according to the equation:

$$C_5H_5Ti(C_6H_5)_3 + \text{iso-}C_3H_7OH \rightarrow 3C_6H_6 + C_5H_5Ti(\text{o-iso-}C_3H_7)_3. \tag{4}$$

The $C_5H_5Ti(\text{o-iso-}C_3H_7)_3$ formed, upon treatment of the reaction mixture first with hydrochloric acid and then with gaseous hydrogen chloride, was converted into $C_5H_5TiCl_3$ (0.002 mole):

$$C_5H_5Ti(\text{o-iso-}C_3H_7)_3 + 3HCl \rightarrow C_5H_5TiCl_3 + 3\,\text{iso-}C_3H_7OH. \tag{5}$$

Regeneration of $C_5H_5TiCl_3$ according to reaction (5) is convincing proof that, upon interaction with isopropyl alcohol, the cyclopentadienyl group is not cleaved off. However, it is not possible to obtain a quantitative yield of cyclopentadienyltitanium trichloride, since carrying out the indicated operations is always accompanied by considerable resinification of the substance.

Cyclopentadienyltriphenyltitanium is cleaved under mild conditions by the action of chloroform. Interaction of 0.012 mole of $C_5H_5Ti(C_6H_5)_3$ with chloroform at -78° leads to the formation of 0.020 mole of benzene and 0.0045 mole of $C_5H_5TiCl_3$.

Thus, all the reactions of $C_5H_5Ti(C_6H_5)_3$ considered by us proceed under mild conditions. Another feature of them is that the changes occurring with TiOC do not affect the C_5H_5Ti group, but are associated with homolytic cleavage of the $Ti{-}C_6H_5$ bond. In this respect cyclopentadienyltriphenyltitanium is similar to bis-cyclopentadienyldiphenyltitanium. In the decomposition and exchange reactions of the latter, carried out at the boiling temperature of the solvents, the $(C_5H_5)_2Ti$ group remains unchanged (5).

As noted above, $C_5H_5Ti(C_6H_5)_3$ is a thermally unstable compound. On decomposition of 0.011 mole of an ethereal solution of cyclopentadienyltriphenyltitanium, 0.0082 mole of benzene, 0.0042 mole of diphenyl, and a black substance containing 0.0088 g-atom of titanium are formed. Cyclopentadiene was not detected among the reaction products. The amount of diphenyl and benzene corresponds to the detachment of two phenyl radicals from $C_5H_5Ti(C_6H_5)_3$, at the expense of which reduction of the initial TiOC occurs. The observed picture is analogous to the decomposition of tetraphenyltitanium at -20°, leading to quantitative formation of diphenyl and of a divalent titanium compound—diphenyltitanium (2). It may therefore be assumed that, in the decomposition of $C_5H_5Ti(C_6H_5)_3$, cyclopentadienylphenyltitanium is formed:

$$C_5H_5Ti(C_6H_5)_3 \xrightarrow[t<-20^\circ]{\text{ether}} C_5H_5TiC_6H_5 + C_6H_6 + \tfrac{1}{2}C_6H_5{-}C_6H_5. \tag{6}$$

The method used for isolating $C_5H_5TiC_6H_5$ is analogous to that described earlier for diphenyltitanium. This compound is a black substance, sensitive to oxygen and moisture. An attempt to isolate $C_5H_5TiC_6H_5$ in crystalline form was unsuccessful. After removal of the solvent from the ampoule, the residue does not crystallize even on prolonged standing in vacuum.

The compound is thermally stable. When heated in a sealed ampoule to 170°, its decomposition proceeds rather slowly. In the reaction products metallic titanium was detected in the form of a mirror, as well as benzene, isolated by vacuum transfer (90% of the theoretical amount). In addition, there is a resinous residue, washed off the titanium with ether and containing unsaturated bonds:

$$C_5H_5TiC_6H_5 \rightarrow C_6H_6 + Ti + [C_5H_4]. \tag{7}$$

The presence of a phenyl group bound to titanium was proved by reaction with mercuric chloride. Phenylmercuric chloride was isolated (89% of theoretical); at the same time mercuric chloride is reduced to calomel and Ti^{2+} is oxidized to Ti^{4+} with formation of $C_5H_5TiCl_3$:

$$C_5H_5TiC_6H_5 + HgCl_2 \rightarrow C_6H_5HgCl + [C_5H_5TiCl], \tag{8}$$

$$[C_5H_5TiCl] + 2HgCl_2 \rightarrow C_5H_5TiCl_3 + Hg_2Cl_2. \tag{9}$$

On treatment of cyclopentadienylphenyltitanium with 1 N HCl, evolution of hydrogen and a green coloration of the solution were observed. This reaction is characteristic of divalent titanium compounds. Benzene was found in the reaction products (82% of theory); cyclopentadiene (86% as C_5H_5Tl) is liberated only when the reaction mixture is boiled:

$$C_5H_5TiC_6H_5 + 2HCl \rightarrow C_5H_6 + C_6H_6 + TiCl_2, \tag{10}$$

$$TiCl_2 + HCl \rightarrow {}^1/{}_2H_2 + TiCl_3. \tag{11}$$

The trivalent titanium formed according to reaction (11) is precipitated as a black precipitate of titanium hydroxide $Ti(OH)_3$.

As a result of alcoholysis in absolute isopropyl alcohol, 0.006 mole of $C_5H_5TiC_6H_5$ gives 0.0046 mole of benzene (77%). Cyclopentadiene was not detected. On subsequent treatment of the residue with hydrochloric acid in air, $C_5H_5TiCl_3$ was isolated qualitatively. Oxidation of the ethereal solution of $C_5H_5TiC_6H_5$ with oxygen leads to the formation of phenol in the reaction mixture.

To clarify the nature of the bond between the metal and the cyclopentadienyl ring in the newly obtained compounds, a reaction with $FeCl_2$ was carried out. Interaction of the starting $C_5H_5TiCl_3$ does not lead to the formation of ferrocene. However, when $FeCl_2$ was allowed to act on $C_5H_5Ti(C_6H_5)_3$ and $C_5H_5TiC_6H_5$, small amounts of ferrocene (of the order of 1%) were detected. The reaction was carried out at room temperature in tetrahydrofuran solution. The solvent was removed from the reaction mixture in vacuum and the residue was extracted with petroleum ether. The petroleum ether was distilled off. On treatment of the residue sublimed in vacuum with $4N$ HNO_3, the appearance of a blue color, characteristic of the ferricinium ion, was observed.

Thus, it may be assumed that the bond of the titanium atom with the cyclopentadienyl ring in the compounds studied is, to a considerable extent, similar to the bond in ferrocene.

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