Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. Razuvaev, V. N. Latyaeva,

1963

SovietRxiv

Abstract

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Corresponding Member of the Academy of Sciences of the USSR G. A. Razuvaev,
V. N. Latyaeva,
A. V. Malysheva, G. A. Kilyakova

NEW PHENYL DERIVATIVES OF TITANIUM

The chemistry of organic derivatives of transition elements is the subject of many works of theoretical and applied significance. For a long time it was considered that metals of the transition periods do not give stable true covalent compounds. This seemed to be further confirmed by the fact that the phenyl derivatives of chromium described by Hein in the 1920s proved in reality to be constructed according to the sandwich type. At the same time, suggestions were repeatedly made that metals of the transition periods can give unstable covalent organic derivatives which play an essential role as intermediate products of chemical reactions. Thus, for example, Kharasch suggested that, upon addition of chlorides of Co, Ni, Mn, etc. to organomagnesium compounds, unstable organometallic compounds of the indicated metals are formed, which readily decompose with formation of free radicals ([1]). As another example one may cite the numerous studies devoted to the extremely important system of new Ziegler-Natta type catalysts for the polymerization of α-olefins. It was firmly established that the radicals of an organometallic compound of one of the components (alkyl derivatives of aluminum, zinc, and a number of others) pass to titanium or vanadium with formation of a complex containing an organotitanium or organovanadium compound. In the interaction of $TiCl_4$ with AlK_3Al, AlK_4Pb, AlK_2Zn, it was possible to obtain a series of alkyl compounds of titanium. Highly reactive titanium compounds were obtained, containing different numbers of alkyl groups of the type AlK_4Ti, AlK_2TiX_2, $AlKTiX_3$ ([2]). Somewhat earlier, aromatic derivatives of the type $C_6H_5Ti(OR)_3$, containing the covalent phenyl-titanium bond, had been obtained ([3]). At the present time Hein has obtained "true" organochromium compounds with a phenyl-chromium bond ([4]).

Attempts to obtain phenyl derivatives of titanium were undertaken by Razuvaev and Bogdanov at the beginning of the 1930s by the reaction of $TiCl_4$ with diphenylmercury, with phenylmagnesium chloride, and with phenylsodium in various solvents and in the absence of a solvent upon heating the components ([5]). However, titanium compounds were not obtained, and the process could be expressed by the overall equation:

$$TiCl_4 + (C_6H_5)_2Hg \rightarrow C_6H_5HgCl + TiCl_3 + \tfrac{1}{2}(C_6H_5)_2. \qquad (1)$$

All experiments were carried out at comparatively high temperatures. Now, knowing some properties of organotitanium compounds, one may suppose that the synthesis was unsuccessful because heating was used, since titanium compounds readily decompose at elevated temperature. Therefore we decided to repeat the syntheses described in the above-mentioned work, but at considerably lower temperatures (~90°). In this case organotitanium compounds were obtained, but it was not possible to isolate them in pure form. Their formation was indicated by the appearance of phenol when the reactions were carried out in the presence of atmospheric oxygen. As is known, diphenylmercury is very resistant to oxidation and under the reaction conditions could not give phenol. The latter, evidently, could be formed only through oxidation of the phenyl derivative of titanium that had been formed.

If the reaction is carried out in the absence of oxygen, the reaction products will be the same as in equation (1). Taking into account the assumption about the formation of an organotitanium compound, it may be considered that the first act of interaction will be the reaction:

$$\mathrm{TiCl_4 + (C_6H_5)_2Hg \rightarrow C_6H_5HgCl + [C_6H_5TiCl_3]}.$$

To prove the formation of $C_6H_5TiCl_3$, we decided to use the widely applied reaction of exchange of phenyl radicals with sublimate. When a solution of sublimate was added to a solution of $C_6H_5TiCl_3$ in tetrahydrofuran, previously filtered from phenylmercury chloride (the amount of the latter corresponded to complete interaction of diphenylmercury with $TiCl_4$), phenylmercury chloride precipitated due to the organotitanium compound present in the solution:

$$\mathrm{[C_6H_5TiCl_3] + HgCl_2 \rightarrow C_6H_5HgCl + TiCl_4}.$$

On oxidation of the latter, phenolate is formed; decomposition leads to the evolution of diphenyl and $TiCl_3$. This process is observed in various solvents: benzene, CCl_4, chloroform, tetrahydrofuran, etc. It seemed interesting to establish how the decomposition of the organotitanium compound proceeds.

If free-radical decomposition with liberation of a phenyl radical in the bulk occurred, then the latter, in alcohols, chloroform, and tetrahydrofuran, should have formed benzene by abstraction of a hydrogen atom from the solvent. Upon abstraction of a chlorine atom from CCl_4, chlorobenzene should have been obtained. In our case, $C_6H_5TiCl_3$ in chloroform formed benzene together with considerable amounts of diphenyl. In reaction in CCl_4, chlorobenzene was not detected. Moreover, it was found that the diphenyl liberated upon decomposition of $C_6H_5TiCl_3$ in benzene labeled with C^{14} did not contain the solvent label, unlike other phenyl organometallic compounds decomposing according to a free-radical scheme. The formation of diphenyl was sharply accelerated in the presence of air. Whereas in the absence of oxygen the formation of phenylmercury chloride was observed on heating ($\sim$ 90°, 10–15 hours), in the presence of oxygen phenylmercury chloride began to precipitate from the solution at room temperature. When experiments were carried out in the presence of oxygen, oxidation of the organometallic compound occurs with formation of phenol; however, the main reaction proceeding simultaneously with oxidation is decomposition with formation of benzene and diphenyl in chloroform, and diphenyl in CCl_4 and benzene.

Thus, for example, in the reaction of 0.011 mole of diphenylmercury with 0.011 mole of $TiCl_4$ in an O_2 atmosphere, 0.0022 mole of O_2 was absorbed in 70 hours at room temperature; 0.0096 mole of C_6H_5HgCl, 0.0025 mole of diphenyl, 0.00018 mole of phenol, and 0.0064 mole of benzene were isolated. In the interaction of 0.0089 mole of diphenylmercury with $TiCl_4$ (1 : 1) in benzene under the same conditions, 0.0059 mole of O_2 was absorbed; 0.0086 mole of C_6H_5HgCl, 0.0018 mole of diphenyl, and 0.0019 mole of phenol were isolated. In a reaction carried out in labeled benzene, the diphenyl isolated did not contain the label from the solvent. It is more probable to assume that diphenyl is formed through a disproportionation reaction:

$$2C_6H_5TiCl_3 \rightarrow (C_6H_5)_2TiCl_2 + TiCl_4;$$

$(C_6H_5)_2TiCl_2$ decomposes intramolecularly into diphenyl and $TiCl_2$; the latter can form $TiCl_3$ with $TiCl_4$.

A reaction of this type was observed for vanadium compounds. When diphenylmercury acted on a solution of VCl_4 or $VOCl_3$, phenyl derivatives of vanadium were obtained, not isolated in pure form, which readily decomposed with liberation of diphenyl and vanadium chlorides of lower valence (^{6}).

The assumption that diphenyl is obtained through decomposition of diphenyldichlorotitanium led to a series of experiments carried out with varying ratios-

diphenylmercury and $TiCl_4$. It proved more convenient to carry out such reactions in tetrahydrofuran solutions. From the amount of C_6H_5HgCl liberated it was possible to judge that in $TiCl_4$ all 4 chlorine atoms are replaced by phenyl radicals. At the same time, the appearance was observed of a compound, extremely sensitive to atmospheric oxygen, having a deep black coloration.

Much more convenient for this purpose proved to be the reaction between phenyllithium and $TiCl_4$ in tetrahydrofuran. If the synthesis is carried out at ordinary temperature with a component ratio of 4 : 1, an intensely colored black solution is obtained. In this case an almost theoretical amount of LiCl is liberated (95—98%). If the reaction is carried out with strong cooling, to −70°, the formation of orange-red leaflets is observed, readily distinguishable among the LiCl precipitate. On warming to −30, −20°, an intense orange solution appears, which does not become decolorized on cooling. Thus, it may be considered that a profound change has occurred in the initially formed compound. We assumed that the orange-red crystals are tetraphenyltitanium:

$$TiCl_4 + 4C_6H_5Li \rightarrow (C_6H_5)_4Ti + 4LiCl.$$

In order to verify the correctness of our assumptions, we again used the reaction with sublimate. When a solution of sublimate in tetrahydrofuran was added to the reaction mixture at −70°, an exchange reaction occurred, and an almost calculated amount of phenylmercury chloride was isolated (98%):

$$(C_6H_5)_4Ti + 4HgCl_2 \rightarrow 4C_6H_5HgCl + TiCl_4.$$

We were unable to isolate pure tetraphenyltitanium because of its thermal instability. As indicated, its solutions in tetrahydrofuran sharply changed color from yellow to deep black, i.e., decomposition occurred. The reaction proceeded analogously in other solvents—benzene, ether. Saturated hydrocarbons practically do not dissolve the black substance. Therefore we decided to use the following method of work. After the interaction of $TiCl_4$ with C_6H_5Li, the reaction mixture was filtered from LiCl, and then the temperature was brought to room temperature. In this process a black coloration appeared. The solvent was removed in vacuo with careful exclusion of traces of oxygen. From the precipitate containing diphenyltitanium and diphenyl, the latter was washed out with petroleum ether, in which diphenyltitanium is completely insoluble. Diphenyltitanium dissolved in benzene, from which it was precipitated with a saturated hydrocarbon, for example, *n*-nonane, as a fine black precipitate that ignited spontaneously in air. Diphenyltitanium could be isolated by vacuum distillation of benzene in the form of black crystals with an anthracite luster. It is readily soluble in benzene, tetrahydrofuran, and ether. It is insoluble in aliphatic hydrocarbons. From comparison of the amount of diphenyl formed with the initial $TiCl_4$, it was always found exactly that per 1 mole of $TiCl_4$ consumed, 1 mole of diphenyl was liberated.

Thus, it may be considered that the initially formed $(C_6H_5)_4Ti$ decomposes according to the equation:

$$(C_6H_5)_4Ti \rightarrow (C_6H_5)_2Ti + (C_6H_5)_2$$

to diphenyl and a black residue—diphenyltitanium.

As far as we know, diphenyltitanium is the first covalent organometallic compound of divalent titanium. Therefore it seemed to us very interesting to investigate it in greater detail. We were struck by the thermal stability of the compound obtained. On heating in a sealed ampoule, deep decomposition begins at about 200° and proceeds rather slowly. In this process diphenyl is liberated (up to 80% of the theoretical amount) and a mirror of metallic titanium remains:

$$(C_6H_5)_2Ti \rightarrow (C_6H_5)_2 + Ti.$$

This reaction was used by us for analysis of the product.

Diphenyltitanium is exceptionally sensitive to oxygen. Attempts at elemental analysis of samples of $(C_6H_5)_2Ti$ did not give satisfactory results, since, despite all precautions, oxidation occurred during sampling. However, the atomic ratio in the oxidized weighed portions was always retained as $Ti : C = 1 : 12$. The analysis was carried out as follows. A weighed portion of diphenyltitanium in a sealed ampoule was heated until the product decomposed. After this the ampoule was opened, and the titanium content was determined by the usual methods. Found: Ti –23.2%; calculated for $C_{12}H_{10}Ti$ –23.7%.

It remains unclear whether diphenyltitanium is a monomeric compound or is a polymer.

The presence of phenyl groups bonded to titanium was demonstrated by reaction with sublimate. A benzene solution of $(C_6H_5)_2Ti$ reacted on heating with a solution of $HgCl_2$ in tetrahydrofuran. Phenylmercuric chloride was obtained, while at the same time reduction of sublimate to calomel and partly to metallic mercury was observed:

$$(C_6H_5)_2Ti + 2HgCl_2 \to 2C_6H_5HgCl + TiCl_2,$$

$$TiCl_2 + HgCl_2 \to TiCl_2 + HgCl.$$

This is explained by the fact that the titanium dichloride liberated in the first stage proves to be a strong reducing agent. Diphenyltitanium is decomposed at room temperature by chloroform and CCl_4. Alcoholysis with isopropyl alcohol, on heating on a water bath, leads to the formation of benzene, as well as biphenyl and phenol. Under the action of HCl (1 : 3), $(C_6H_5)_2Ti$ is decomposed, with evolution of hydrogen, benzene, and $TiCl_3$:

$$(C_6H_5)_2Ti + 2HCl \to 2C_6H_6 + TiCl_2,$$

$$TiCl_2 + HCl \to TiCl_3 + \tfrac{1}{2}H_2.$$

When iodine acts in benzene solution, the cleavage of phenyl groups occurs with formation of iodobenzene and TiJ_4.

All the reactions listed undoubtedly indicate the presence of phenyl groups bonded to titanium.

Received
16 II 1963

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