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Abstract

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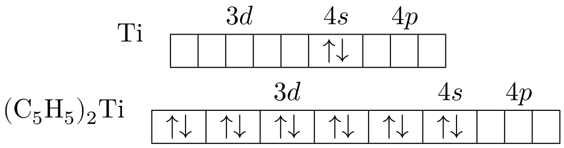
M. E. VOL' PIN, V. A. DUBOVITSKII, O. V. NOGINA,
Corresponding Member of the USSR Academy of Sciences D. N. KURSANOV

THE COMPOUND OF TITANOCENE WITH TOLANE

As was shown earlier (¹), divalent derivatives of silicon and germanium possess "carbenoid"properties, i.e., they are capable of entering into reactions of the same type as compounds of divalent carbon—carbenes. We assumed that compounds of transition elements may also possess analogous carbenoid properties, provided that the following basic conditions are fulfilled*:
a) the "inner" vacant *d*-levels (with a smaller principal quantum number than that of the valence *s*- and *p*-electrons) must be occupied through the formation of chemical bonds; b) the central atom must have at least one free pair of *s*- or *p*-electrons (or two unpaired electrons); c) there must be at least one free *p*-orbital (or two unpaired electrons in two *p*-orbitals).

From this point of view, dicyclopentadienyltitanium in particular should possess a "carbenoid" character, since the electronic configuration of titanium in this compound satisfies all the conditions given above:



It could be expected that this compound would be capable, like carbenes, of reacting with unsaturated compounds with the formation of two or four new titanium—carbon bonds. Proceeding from these considerations, we studied the reaction of dicyclopentadienyltitanium (at the moment of its formation) with diphenylacetylene. For this purpose titanium tetrachloride was introduced into a reaction with an excess of sodium cyclopentadienide in the presence of tolane. It indeed turned out that under these conditions two molecules of tolane were added to a molecule of titanocene. A probable scheme of this reaction is as follows:

$$\mathrm{TiCl_4 + 4\,C_5H_5Na \rightarrow (C_5H_5)_2Ti}$$

$$\mathrm{(C_5H_5)_2Ti + 2\,PhC \equiv CPh \rightarrow (C_5H_5)_2Ti(PhC_2Ph)_2}.$$

Structural formulas A—G for titanoceneditolan

Figure 1: Structural formulas A—G for titanoceneditolan

The substance obtained, titanocenedithiolane, consists of dark-green, almost black crystals, quite stable in air and comparatively readily soluble in benzene, dioxane, and tetrahydrofuran; poorly soluble in petroleum ether, heptane, and alcohol. The benzene solution is stable in air; however, the solution in tetrahydrofuran is rapidly oxidized (apparently through the action of peroxides). The substance does not add hydrogen over platinum (Adams) in alcoholic solution.

When a solution of bromine in carbon tetrachloride acts on titanocenedithiolane, addition of two moles of Br_2 occurs, with formation of dibromotitanocene amide and bromide not containing titanium:

$$(C_5H_5)_2Ti(PhC_2Ph)_2 + 2Br_2 \rightarrow (C_5H_5)_2TiBr_2 + C_{28}H_{20}Br_2.$$

Titanoceneditolan slowly decomposes on heating with an alcoholic solution of sodium ethoxide; in this process cyclopentadiene is evolved and 1,2,3,4-tetraphenylbutadiene is formed:

$$(C_5H_5)_2Ti(PhC_2Ph)_2{+}4C_2H_5OH \xrightarrow{C_2H_5ONa} 2C_5H_6{+}Ti(OC_2H_5)_4{+}HC(Ph) = C(Ph){-}C(Ph) = CH(Ph).$$

No tolane could be detected in the reaction products.

The same tetraphenylbutadiene is readily formed even without heating when dilute acid solutions act on titanoceneditolan:

$$(C_5H_5)_2Ti(PhC_2Ph)_2{+}HCl \rightarrow (C_5H_5)_2TiCl_2{+}HC(Ph) = C(Ph){-}C(Ph) = CH(Ph).$$

In this case also, no appreciable amounts of tolane are formed.

On the basis of the composition, molecular weight, and chemical properties of titanoceneditolan, four possible structures A—G may be proposed for it (everywhere $R = C_6H_5$).

The properties of titanoceneditolan and, in particular, the formation of tetraphenylbutadiene on acid and alkaline cleavage agree best with structure A.

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* They are formulated here schematically, as applied to the electronic structure of a chemically unbound atom.

Schematic electronic structure of $(Ph_3P)_2Pt$

Figure 2: Schematic electronic structure of $(Ph_3P)_2Pt$

However, the same reactions can also be explained by the complex cyclobutadiene structure B, since it is known that the cyclobutadiene ring, upon liberation from a complex, can readily rupture with formation of butadiene derivatives (cf. (^{2})). The π-complex structure V is unlikely, since the IR spectrum of the compound obtained shows no absorption in the region characteristic of triple $C \equiv C$ bonds. Moreover, the chemical properties of the substance also argue against this structure. Structure G is likewise unlikely, since upon cleavage of three-membered rings one would expect the formation of tolane or of stilbene derivatives.

Thus, in the reaction of dicyclopentadienyltitanium with tolane, two molecules of tolane add to form an adduct of probable structure A. However, the structure of the compound obtained must be subjected to further investigation.

It should be noted that, from the standpoint of the concept of carbenoid character, it is possible to explain not only the reaction of titanocene described above, but also data that have recently appeared in the literature on reactions of compounds of other transition elements with acetylenes and olefins.

Thus, Chatt and co-workers (^{3}) obtained platinum complexes of acetylene by the reaction:

$$2(Ph_3P)_2PtCl_2 + N_2H_4 + 2RC \equiv CR \rightarrow 2(Ph_3P)_2Pt(C_2R_2) + N_2 + 4HCl.$$

Here one may think that the compound $(Ph_3P)_2Pt$, having a carbenoid structure, is formed initially

and then reacts with acetylenes, similarly to carbenes.

An analogous reaction occurs in the interaction of cyclopentadienylmanganese tricarbonyl with tolane $^{(4)}$:

$$C_5H_5Mn(CO)_3 \xrightarrow{-CO} C_5H_5Mn(CO)_2 \xrightarrow{+\ PhC\equiv CPh} C_5H_5Mn(CO)_2(PhC_2Ph).$$

The cyclopentadienylmanganese dicarbonyl formed as an intermediate has a carbenoid structure:

$$C_5H_5Mn(CO)_2 \qquad 3d \qquad 4s$$

Reactions of the same type, with formation of alkyl derivatives, have also been described for cobalt carbonyls $^{(5)}$.

Consequently, derivatives of a series of transition metals having a carbenoid electronic configuration, including titanocene, are capable of adding acetylenes with formation of cyclic compounds.

Experimental Part

Preparation of titanocenetolane. To a solution of cyclopentadienylsodium, prepared from 18.4 g (0.8 g-atom) of sodium and 52.8 g of freshly distilled cyclopentadiene in 350 ml of tetrahydrofuran (freshly distilled over $LiAlH_4$), there were added, in a stream of argon, 28.4 g of titanium tetrachloride (0.15 mole) and 50 g of tolane (0.28 mole). The mixture was boiled in an atmosphere of argon for 4 hours and left overnight. Then tetrahydrofuran was distilled off from the reaction mixture in vacuo in a stream of argon, and the residue was treated with absolute benzene (∼ 300 ml). By centrifugation the solution was separated from the precipitate and diluted with a 3-4-fold amount of heptane. A brownish-yellow precipitate separated; after standing for 2 days in a refrigerator, black-green crystals formed on the bottom and walls of the flask. The solution and the readily suspended yellow precipitate were decanted from the crystals; the crystals were washed several times with petroleum ether and dried in a vacuum desiccator. Practically pure titanocenetolane was thus obtained (8.35 g), m.p. 150°; after recrystallization from toluene, m.p. 150°. By evaporation of the filtrates a further 3.4 g of substance was isolated. Total yield 11.75 g (16%, calculated on tolane). Molecular weight (cryoscopically, in benzene) 490; calculated 534.5.

Found %: C 85.28; 85.21; H 5.70; 5.77; Ti 8.79; 9.08
$C_{38}H_{30}Ti$. Calculated %: C 85.38; H 5.66; Ti 8.96

Bromination of titanocenetolane. To a solution of 0.9514 g (0.0016 mole) of titanocenetolane in 8 ml of dry carbon tetrachloride, a solution of bromine in carbon tetrachloride was added dropwise until a persistent excess of bromine remained in the solution. In all, 0.00365 mole of Br was taken up (2.3 moles per mole of substance). The red precipitate that separated (0.22 g) was dissolved in benzene and the solution was evaporated. Red crystals of titanocene dibromide were obtained, m.p. 300°; according to the literature, m.p. 309–310° (6). It does not depress the melting point with an authentic sample of titanocene dibromide.

By evaporation of the filtrate and recrystallization of the precipitate from alcohol, a yellow substance was obtained, m.p. 146–150°. After repeated crystallizations from alcohol and heptane, m.p. 173°.

Found %: C 65.67; 65.90; H 4.03; 4.03; Br 30.21; 29.89
$C_{28}H_{20}Br_2$. Calculated %: C 65.14; H 3.91; Br 30.96

This substance was not subjected to further investigation.

Reaction of titanocenetolane with alkalis and acids. Titanocenetolane does not react to any appreciable extent at room temperature with aqueous or alcoholic-benzene solution of caustic po—

However, upon boiling titanocenediphenylacetylene (2 g) with an alcoholic-benzene solution of caustic potash, cyclopentadiene is liberated (identified as C_5H_5Tl). The solution remaining after distillation of the cyclopentadiene was evaporated in vacuo; the residue was extracted with cold benzene and the solution evaporated. This gave 1.254 g of 1,2,3,4-tetraphenylbutadiene, yield 94%, m.p. 181–182° (from heptane); according to the literature, m.p. 182.5–183° (7).

Found, %:	C 93.35; 93.31;	H 6.22; 6.30
$C_{28}H_{22}$. Calculated, %:	C 93.81;	H 6.19

The substance gives no depression of the melting point with an authentic sample of tetraphenylbutadiene obtained by the reaction of diphenylacetylene with lithium (7).

When an aqueous solution of hydrochloric acid is added to a benzene or alcoholic solution of titanocenediphenylacetylene, the solution rapidly changes color from dark green to red; upon alkalization of the solution the original color is not restored. Chromatography on alumina plates showed that, as a result of the reaction, 1,2,3,4-tetraphenylbutadiene is formed.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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