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Complex of titanocene with tolane. Isolation, spectral characteristics, reactivity

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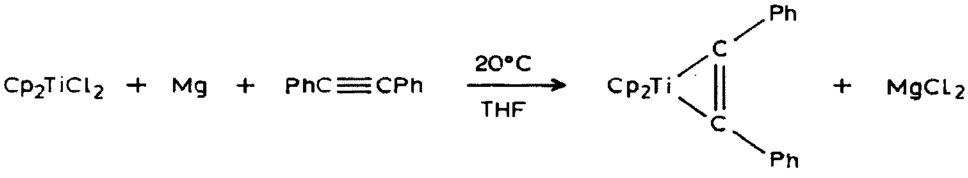
Abstract

The interaction of Cp_2TiCl_2 with equimolar amounts of Mg and tolane in THF results in the formation of a tolan complex of titanocene $Cp_2Ti(C_2Ph_2)$. The complex has been isolated from the reaction mixture as a definite compound and identified by spectral and chemical means. From the data obtained the conclusion has been made that the complex has a structure close to that of titanacyclopropene.

Introduction

Despite the high activity of titanium compounds in various catalytic transformations of acetylenes and an assumed participation of acetylene complexes in these reactions, the first evidence for the existence of stable titanium complexes with acetylenes has been obtained only relatively recently. In 1974 Fachinetti and Floriani reported [1] that the reaction of $Cp_2Ti(CO)_2$ with tolan in heptane at room temperature results in the formation of a mixed tolane-carbonyl complex of titanocene $Cp_2Ti(CO)(C_2Ph_2)$. We have found that in the interaction of titanocene dichloride with equimolar amounts of magnesium and tolan in THF under Ar, a titanocene complex with tolan $Cp_2Ti(C_2Ph_2)$ (I) is formed [2–4] *.



(I)

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* For other acetylene complexes of titanium obtained in recent years, see refs. 5–10.

Initial proofs of the formation of complex I were obtained from the study of the reactivity of its solutions [2–4, 11–14]. Subsequently, however, we managed to isolate I from the reaction mixture as a definite compound and to identify it [4,14].

Here we describe spectral and some chemical properties of complex I, as well as the procedure for its isolation from solution and purification.

Results and discussion

The isolation and purification of complex I are complicated by the high sensitivity of its solutions to air and moisture. The attempt to isolate I from the reaction mixture by chromatography on alumina resulted, as has already been reported [3], in the formation of titanoxane $[Cp_2TiC(Ph){=}CH(Ph)]_2O$ (II) due to the presence of water as an impurity in Al_2O_3. An isolated complex I was obtained by slow cooling of its hexane solution under Ar to -40– -45 °C followed by keeping the mixture at this temperature for several hours. A repetition of this procedure gives an analytically pure crystalline product. If cooling of the hexane solution of I is conducted rapidly and to a lower temperature (-70– -80 °C), I precipitates as a powder and contains a greater amount of impurities.

Complex I is a dark brown, fine-crystalline substance (m.p. 117–119 °C (dec.) under Ar) readily soluble in benzene and THF and less soluble in hexane. In the solid state the complex is stable under Ar at room temperature, but in the presence of air and moisture it rapidly decomposes. The structure of the complex was proved by elemental analysis, molecular weight determination, NMR and IR spectroscopy data, as well as by investigation of its chemical properties.

The molecular weight determination (cryoscopically, in benzene) has shown that complex I is monomeric.

The IR spectrum of I within the range of 1600–2300 cm^{-1} displays a single absorption band at 1712 cm^{-1} which can be assigned to stretching vibrations of the coordinated CC bond of the acetylene group. Such a low value of $\nu(C\equiv C)$ shows that I has a structure close to that of titanacyclopropene.

Table 1

Frequences $\nu(C\equiv C)$ for acetylene complexes of titanium and free acetylenes

Complex	$\nu(C\equiv C)$ (cm^{-1})		$\Delta\nu(C\equiv C)$ (cm^{-1})	Refs. [a]
	free acetylene	acetylene in complex		
$(\eta^5\text{-}C_5Me_5)_2Ti(PhC\equiv CPh)$	2223	1647	576	8
$(\eta^5\text{-}C_5Me_5)_2Ti(MeC\equiv CMe)$	2233	1683	550	8
$(\eta^5\text{-}C_5H_5)_2Ti(PhC\equiv CPh)$	2233	1712	511	this work
$(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)(PhC\equiv CPh)$	2223	1740	483	5
$(\eta^5\text{-}C_5H_5)_2Ti(CO)(C_6F_5C\equiv CC_6F_5)$	2246	1770	476	6
$(\eta^5\text{-}C_5H_5)_2Ti(CO)(PhC\equiv CPh)$	2223	1780 [b]	443	1
$(\eta^5\text{-}C_5H_5)_2Ti(PMe_3)(HC\equiv CH)$	1974	1618	356	9

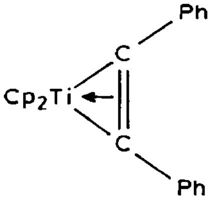
[a] The listed references relate to $\nu(C\equiv C)$ for acetylene complexes; values of $\nu(C\equiv C)$ for free acetylenes, except $C_6F_5C\equiv CC_6F_5$, are taken from ref. 15, $\nu(C\equiv C)$ for $C_6F_5C\equiv CC_6F_5$ is taken from ref. 16.

[b] In ref. 6 the value of $\nu(C\equiv C)$ equal to 1785 cm^{-1} is given.

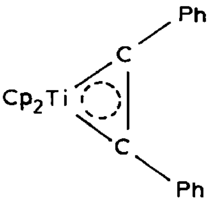
The data on $\nu(C\equiv C)$ frequences observed in IR spectra of acetylenetitanium complexes described up to the present time are given in the Table 1. As can be seen from Table 1, on passing from I to its pentamethylcyclopentadienyl analogue $(\eta^5\text{-}C_5Me_5)_2Ti(C_2Ph_2)$ [8] the value of $\nu(C\equiv C)$ is lowered even more which is apparently due to an increase in efficiency of the electron transfer from titanium to the acetylene ligand as a result of the replacement of both $\eta^5\text{-}C_5H_5$ rings in I with considerably more electron-donating $\eta^5\text{-}C_5Me_5$ groups. The appearance of an additional carbonyl or phosphine ligand at the titanium atom in I results in a shift of the $\nu(C\equiv C)$ band towards higher frequences.

The ^1H NMR spectrum of I in THF-d_8 shows a singlet of cyclopentadienyl protons (δ 6.51 ppm, internal standard TMS) and a multiplet of phenyl protons (δ 6.37–7.06 ppm). The intensity ratio of the singlet to the multiplet is close to the theoretical one for I (1/1).

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of I in C_6H_6 in addition to the signals of cyclopentadienyl (δ 115.9 s ppm) and phenyl (δ 125.7 s ppm; 127.2 s ppm; 142.8 s ppm) * atoms of C displays a sole singlet of acetylene carbon atoms with δ 196.01 ppm. Such a value of $\delta(C\equiv C)$ indicates that the coordinated molecule of tolane in I is formally a four-electron ligand (see [17–19]) **. The four electrons donated by tolane to the vacant orbitals of titanium enable the latter to fill up its external shell to 18-electrons. Thus, the π-electrons of the double bond of the titanacyclopropene ring in complex I are likely to be delocalized at the titanium atom. This feature of the complex can be expressed by the structure **A** or identical structure **B**, in which the complex resembles the aromatic system of diphenylcyclopropenylium (cf. [20,21]).



(A)



(B)

Further studies have to show whether this analogy with the cyclopropenylium system is formal, or whether the titanacyclopropene ring in such acetylene complexes indeed has an aromatic character.

Chemical shifts of acetylene carbon atoms close to that in I were observed in ^{13}C NMR spectra of the complexes $(\eta^5\text{-}C_5Me_5)_2Ti(C_2Ph_2)$ and $(\eta^5\text{-}C_5Me_5)_2Ti(C_2Me_2)$ [8]. Apparently, the acetylene ligand in these complexes is also the donor of four electrons.

The isolated complex I has also been characterized chemically.

Upon heating to 130 °C under Ar, the solid I decomposes to give *trans*-stilbene (70%). *cis*-Stilbene and tolane are not detected in the products of thermodecomposition of I. It may be assumed that the cyclopentadienyl rings are the source of

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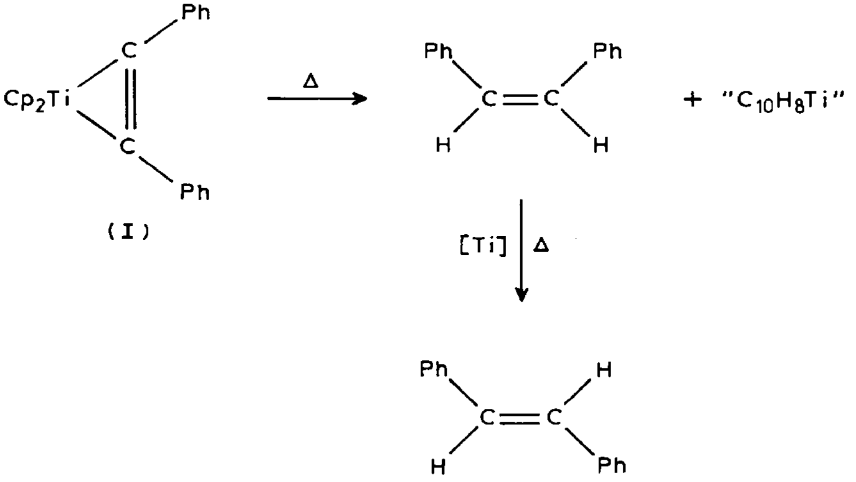
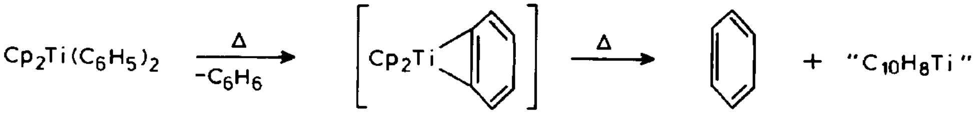
* The observed signals correspond respectively to *para-*, *meta-* and the key carbon atoms of phenyl rings. The singlet of *ortho*-carbon atoms is shielded by the signal from C_6H_6.

** For complexes where acetylene is a two-electron ligand, the $\delta(C\equiv C)$ value is within the range of ~100–120 ppm [17,19].

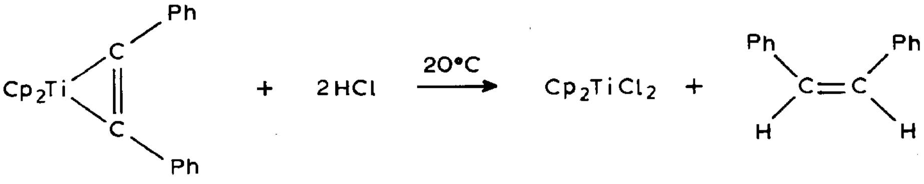

(I)

hydrogen in the formation of *trans*-stilbene. Evidently, the thermolysis of I initially yields *cis*-stilbene which is further isomerized into *trans*-stilbene in the presence of titanium compounds.

According to Boekel et al. [22], the benzyne complex of titanocene formed as an intermediate during thermolysis of Cp_2TiPh_2 is decomposed in a similar manner.

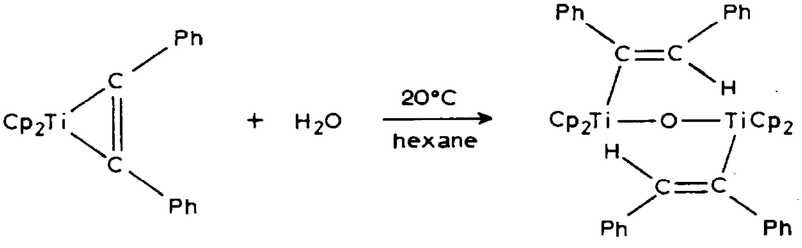


The protolysis of complex I with HCl in ethanol gives *cis*-stilbene and titanocene dichloride in nearly quantitative yields.

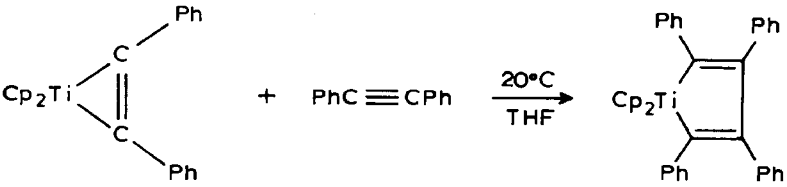

(I)

Such specificity of the formation of *cis*-stilbene in the protolysis and the absence of tolan are in agreement with the titanacyclopropene structure of complex I.

The interaction of the isolated I with water in hexane results in the formation of the above mentioned titanoxane II [2,3] (yield 81%).

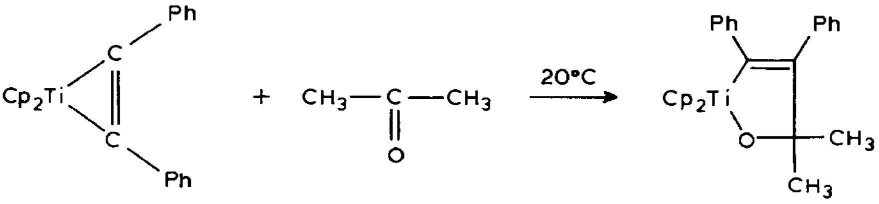

(I) (II)

The reaction of I with tolan affords the well known titanacyclopentadiene (III) in a yield of 73%.



(I) (III)

The addition of an excess of dry acetone to solid I results in the instant formation of a bright red titanadihydrofuran metallacycle (IV) [12,13] in a substantially quantitative yield.



(I) (IV)

Most of these reactions, as we have shown earlier [2–4,11–13], can be carried out without isolation of I from the reaction mixture, although yields of the products under such conditions are lower in some cases. For instance, if the interaction of acetone with complex I is conducted without isolation of I from the solution in THF, the final titanadihydrofuran (IV) can only be obtained in a yield of 40% [13].

Thus, all the above data show that the compound isolated by us from the reaction of Cp_2TiCl_2 with magnesium and tolan in THF is indeed a complex of titanocene with tolan.

Experimental

The experiments were conducted under Ar with careful exclusion of air and moisture. The solvents were purified by conventional methods and distilled before use over sodium and lithium aluminium hydride (THF), or over sodium and calcium hydride (benzene, hexane) under argon. IR spectra of I were recorded on a Specord M80 spectrometer in Apiezon-grease M, IR spectra of II and III were obtained on a UR-20 instrument in KBr. NMR spectra were taken on a Bruker WP-200-SY spectrometer (200.13 MHz); internal standard TMS. Mass spectra were recorded on an AEI MS-30 spectrometer at 70 eV. *Cis*- and *trans*-stilbenes were determined by GLC on a column (2.5 m × 4 mm) with 10% SKTFT-50-X on Chromaton N-AW-DMCS (Chrom-42 instrument with flame ionization detector; carrier gas N_2; internal standard phenanthrene). The analysis was carried out under temperature programming conditions (120–170 °C, 3 °C/min; 170–200 °C, 20 °C/min; 200 °C, isothermal) ensuring the separation of *cis*- and *trans*-stilbenes, tolan and dibenzyl.

Synthesis of complex I

1 g (4.0 mmol) of Cp_2TiCl_2, 0.1 g (4.1 mmol) of finely shaved magnesium and

0.72 g (4.0 mmol) of tolane in 35 ml of THF were stirred at room temperature under argon for 3.5 h and the resulting red-brown solution was evaporated in vacuo to dryness at room temperature. The residue was dissolved in 120 ml of n-hexane and filtered off. The filtered solution was gradually cooled for one hour to -40–-45 °C under argon and kept at this temperature for 5–6 h. On the bottom and walls of the vessel dark-brown crystalline aggregates of complex I were slowly formed. The solution was decanted and the remaining crystals were dried in vacuo at room temperature. The yield of I is 0.38–0.52 g (27–36%). A repeated crystallization from hexane by the method described above gives analytically pure I, m.p. 117–119 °C (dec.) under argon (Found: C, 80.66; H, 5.86; Ti, 13.16; mol.wt. 361 (cryoscopically, in benzene). $C_{24}H_{20}Ti$ calcd.: C, 80.90; H, 5.66; Ti, 13.44%; mol.wt. 356.) For NMR and IR spectra, see "Results and discussion".

Thermolysis of complex I

0.024 g of complex I was heated in a Schlenk tube for 3 min at 130 °C under argon and the resulting dark resinous mass was dissolved (after cooling to room temperature) in 1 ml of benzene. The analysis of the benzene solution by GLC showed the presence of *trans*-stilbene (yield 71%). *cis*-Stilbene, as well as tolan and dibenzyl were absent.

Protolysis of complex I

0.065 g of complex I was dissolved in 5 ml of benzene under argon and the resulting solution was treated with stirring with an excess of a 6.8 *N* HCl in ethanol (0.3 ml). The colour of the reaction mixture instantly changed to crimson and a red precipitate of Cp_2TiCl_2 was formed. The GLC analysis of the solution revealed the presence of *cis*-stilbene (91%). The mixture was then evaporated to dryness and the residue containing Cp_2TiCl_2 was washed with hexane and recrystallized from benzene/n-octane. Yield of pure Cp_2TiCl_2 0.026 g (57%), m.p. 288–289 °C. Lit. m.p. of Cp_2TiCl_2 289–291 °C.

Reaction of I with water

0.12 g of complex I was dissolved in 60 ml of hexane under argon and 0.1 ml of deaerated water was added to the solution. The mixture was stirred at room temperature under argon for 20–30 min. In the course of the reaction the brown colour of the solution disappeared and an orange-yellow precipitate of the titanoxane complex II was formed [3]. The complex was filtered, washed with hexane and dried in vacuo. The yield of II is 0.10 g (81%). The IR spectrum of the product is identical to that of an authentic sample of II [3]. M.p. 164–166 °C (dec.) under argon after recrystallization from benzene/hexane. Lit. m.p. of II 165–167 °C (dec.) [3].

Reaction of I with tolan

To 0.22 g (0.63 mmol) of complex I, a solution of 0.11 g (0.63 mmol) of tolan in 10 ml of THF was added under argon and the mixture was stirred under argon for 8 h. The resulting solution was evaporated to dryness in vacuo and the residue was chromatographed on a column with Al_2O_3 under argon using benzene as an eluent. The subsequent removal of the solvent from the collected dark green fraction gave 0.24 g (72.7%) of titanacyclopentadiene III which was recrystallized from hexane. M.p. 150–152 °C (dec.) under argon. Lit. m.p. 150 °C (dec.) [23,24] and 157–159 °C (dec.) [25]. The IR spectrum of the product is identical to that of an authentic sample of III. The mass spectrum contains a peak of the molecular ion at *m/e* 534.

Reaction of I with acetone

To 0.074 g of complex I, 1 ml of dry acetone was added under argon and the mixture was stirred for several minutes. The solution immediately became a red-orange colour, and a red-orange precipitate was formed. Acetone was evaporated in vacuo at room temperature, the residue was dissolved in benzene and the slightly turbid red solution was filtered off. Subsequent removal of the solvent gave 0.079 g (92%) of the bright red complex IV with m.p. 235–237 °C (dec.) under argon. Lit. m.p. 238–240 °C (dec.) under argon [12,13].

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