

SYNTHESIS AND X-RAY STRUCTURE DETERMINATION OF AN ORGANOMETALLIC TITANOXANE $[\text{Cp}_2\text{TiC}(\text{Ph})=\text{CH}(\text{Ph})]_2\text{O}$. EVIDENCE FOR THE FORMATION OF A TITANOCENE COMPLEX WITH TOLANE

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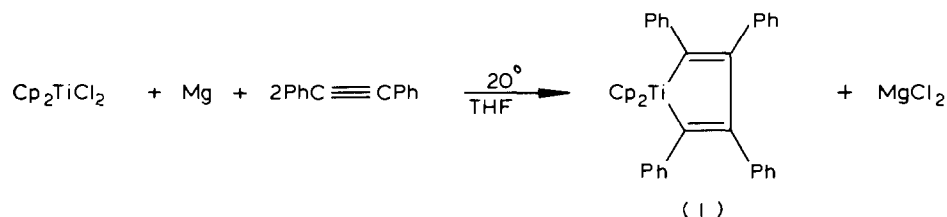
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Summary

The reaction of Cp_2TiCl_2 with magnesium in THF in the presence of tolane at a $\text{Cp}_2\text{TiCl}_2 : \text{Mg} : \text{Ph}_2\text{C}_2$ ratio of 1:1:1 results in formation of a dark red-brown solution which yields cis-stilbene when treated with HCl in ethanol, the titanacyclopentadiene complex $\text{Cp}_2\text{TiC}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{Ph})$ when treated with tolane, and the organometallic titanoxane $[\text{Cp}_2\text{TiC}(\text{Ph})=\text{CH}(\text{Ph})]_2\text{O}$ when treated with water. It is suggested that in the solution the titanocene complex with tolane $[\text{Cp}_2\text{Ti}(\text{Ph}_2\text{C}_2)]$, postulated previously as an intermediate in the catalytic hydrogenation of tolane to dibenzyl under the action of $\text{Cp}_2\text{Ti}(\text{CO})_2$ is present. The structure of $[\text{Cp}_2\text{TiC}(\text{Ph})=\text{CH}(\text{Ph})]_2\text{O}$ has been established by an X-ray analysis.

Introduction

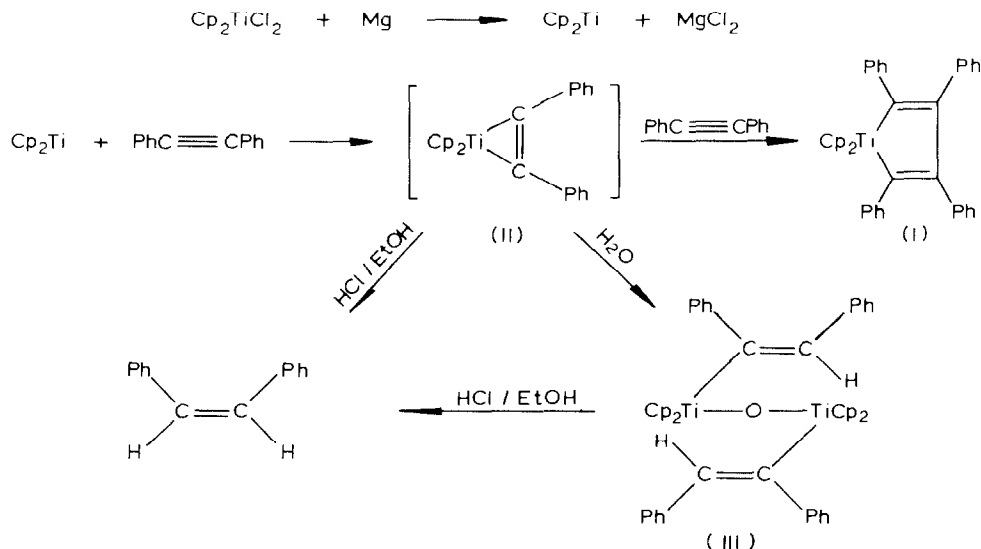
Recently, we have found [1] that in the interaction of titanocene dichloride with magnesium in THF in the presence of tolane at a $\text{Cp}_2\text{TiCl}_2 : \text{Mg} : \text{Ph}_2\text{C}_2$ ratio of 1:1:2, a dark green solution is formed from which a well known titanacyclopentadiene (I) [2–6] can be isolated. The reaction proceeds at room temperature with a good yield.



Here we report evidence which suggests that if this reaction is carried out at a $\text{Cp}_2\text{TiCl}_2:\text{Mg}:\text{Ph}_2\text{C}_2$ ratio of 1:1:1, the titanocene complex with tolane $[\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)]$ (II) is formed as the end product. Although we have not yet been able to isolate II in a pure state, a study of the reactivity of its solutions has led to synthesis of organometallic titanoxane, $[\text{Cp}_2\text{TiC}(\text{Ph})=\text{CH}(\text{Ph})]_2\text{O}$ (III), whose structure and some properties are described in detail below see also ref. [10].

Results and discussion

The reaction of Cp_2TiCl_2 with equimolar amounts of magnesium and tolane in THF produces a dark red-brown solution containing, according to the data from chromatography on alumina, only traces of I. When HCl in ethanol is added to the solution, *cis*-stilbene is formed (ca. 70%), while addition of tolane gradually turns the colour of the mixture to dark green, yielding I (ca. 76%). This is indicative of the presence in the solution of complex II, which is thus an intermediate in the formation of I from Cp_2TiCl_2 , Mg, and tolane at a ratio of 1:1:2.



Further evidence for the existence of II was provided by studying the reaction of the dark red-brown solution with water. It turned out that treatment by water leads to rapid formation of a complex having, according to X-ray and spectroscopic data (see below), the structure of the organometallic titanoxane III. The same complex III was obtained during an attempt to isolate II from the solution by chromatography on alumina under argon. Evidently, II is highly sensitive to hydrolysis and so during chromatography it reacts rapidly with the traces of water adsorbed on alumina, yielding III. Recently, Rausch et al. reported the isolation of a similar titanoxane, $[\text{Cp}_2\text{TiC}(\text{CF}_3)=\text{CH}(\text{CF}_3)]_2\text{O}$ (IV), from the reaction of $\text{Cp}_2\text{Ti}(\text{CO})_2$ with perfluoro-2-butyne [7]; however, the mechanism of formation of this compound remained obscure. Taking our data into account it may be assumed that the source of IV is the complex of titanocene with perfluorobutyne hydrolyzed in the course of the reaction by traces of water present in the reagents used.

Complex III is an air-stable orange crystalline solid (m.p. 165–167°C (dec.) under Ar) readily soluble in benzene, THF, and CS₂, less readily in acetone and ether, and poorly soluble or insoluble in alcohols or aliphatic hydrocarbons. Unlike II, complex III does not react with toluene in THF at room temperature but it yields *cis*-stilbene (ca. 70%) in a reaction with HCl in ethanol.

The IR spectrum of III (KBr pellets), besides the absorption bands of η^5 -C₅H₅ ligands and Ph rings, contains a broad, intense band at ~ 675 cm⁻¹, which can be assigned to vibrations of the Ti–O–Ti group. A similar band (at 665 cm⁻¹) is observed in the spectrum of titanoxane IV, described by Rausch et al. [7]. In the range of 1500–1600 cm⁻¹, the IR spectrum of III exhibits three bands: at 1593s, 1569mw and 1556w cm⁻¹. The latter band is intense in the Raman spectrum, which allows it to be assigned to the C=C stretching vibrations of the phenyl-substituted σ -vinylic groups. The band at 1600 cm⁻¹ is ascribed to similar vibrations in the spectrum of IV [7].

The ¹H NMR spectrum of III in CS₂ (300 MHz, 23°C, internal standard TMS) displays a singlet of cyclopentadienyl protons (δ 6.00 ppm) and a complex multiplet (13 lines with δ 7.26, 7.23, 7.21, 7.04, 7.01, 6.98, 6.95, 6.86, 6.83, 6.80, 6.77, 6.68, and 6.66 ppm) of phenylic and vinylic protons. The intensity ratio of the singlet to multiplet is close to the theoretical one for III (1 : 1.1). In the ¹H NMR spectrum of dideutero-III, [Cp₂TiC(Ph)=CD(Ph)]₂O, obtained by treating a THF solution of II with D₂O and containing deuterium at vinylic positions, one of the multiplet components (with δ 6.77 ppm) disappears whereas the rest of the lines are retained. In this case, the intensity ratio of the multiplet to the singlet is 1 : 1. Thus, the line with δ 6.77 ppm in the spectrum of III belongs to the vinylic protons of the PhCH=C(Ph) groups.

Figure 1 shows the X-ray structure of III together with the most essential bond distances and angles. In terms of the structural parameters, complex III is closely similar to the above-mentioned titanoxane IV [7]. The lengths of the Ti–O bonds in III (1.85 and 1.86(1) Å) practically coincide with those observed in IV (1.853 and 1.860 Å) and slightly exceed the Ti–O bond lengths (1.78–1.83 Å) in the previously

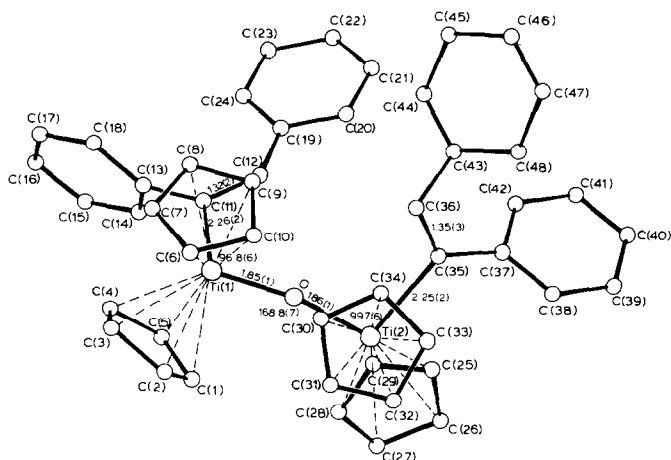


Fig. 1. Structure of the complex III.

investigated complexes containing the Ti–O–Ti group (see the references cited in [7]). Just as in III, in IV the Ti–O–Ti angle ($168.8(7)^\circ$ in III; 171.0 and 169.1° in two independent molecules of IV) differs from 180° to a greater extent than in other titanoxane complexes for which structural information is available [7]. In discussing the structure of IV, Rausch et al. note that the Ti–C(sp^2) σ -bonds in IV (2.239 \AA) are somewhat longer than the similar bonds in the titanacyclopentadiene ring of I (2.141 and 2.172 \AA [8]). Such lengthening is also exhibited by both Ti–C(sp^2) σ -bonds in III (2.25 and $2.26(2) \text{ \AA}$). The C(sp^2)Ti \cdots TiC(sp^2) torsion angle in III ($68(1)^\circ$) is, however, considerably greater than the corresponding angle in IV (53.7 and 54.1°)*, which must be due to the different shape and volume of the substituted σ -vinyl ligands in these compounds.

The $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}$ fragments in III have a typically bent sandwich geometry. The Ti–C bond lengths in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}$ groups range from 2.31 to 2.49 \AA ; the dihedral angles between the planes of the Cp rings are 126.5 and 130.7° ; the sandwiches are in a staggered conformation. The OTi(1)C(11) (A) and OTi(2)C(35) (B) planes bisect the dihedral angles formed by the pairs of Cp-ring planes. The dihedral angles formed by the planes A and B with the planes of the corresponding Cp rings are 23.3 – 26.9° .

Thus, the titanocene formed in the course of reduction of Cp_2TiCl_2 with metallic magnesium in THF is capable of reacting with toluene to yield a complex II which is sufficiently stable in solution for its chemical properties to be studied. The formation of II was postulated earlier as an intermediate in the catalytic hydrogenation of toluene to dibenzyl in the presence of $\text{Cp}_2\text{Ti}(\text{CO})_2$ [3]. Recently, Fachinetti et al. reported the synthesis of a mixed toluene-carbonyl complex, $\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)(\text{CO})$, from the interaction of toluene with $\text{Cp}_2\text{Ti}(\text{CO})_2$ at room temperature [9].

At present, we are trying to isolate II in a pure state and to investigate the structure and properties of this compound.

Experimental

The reactions were conducted under Ar with careful exclusion of atmospheric oxygen and moisture. The solvents were purified by conventional methods and distilled before use over sodium and LiAlH_4 (THF) or twice over sodium (benzene, hexane) under argon. The IR spectra were recorded on a UR-20 spectrometer. The Raman spectra were taken on a Coderg PHO instrument. The ^1H NMR spectra were obtained on RYa-2309 (90 MHz) and SC-300 Varian spectrometers. *cis*-Stilbene was determined by GLC on a column ($2.6 \text{ m} \times 4 \text{ mm}$) with 10% SKTFT-50-X on Chromaton N-AW-DMCS (chromatograph Chrom-42 with flame ionization detector; carrier gas N_2 ; internal standard phenanthrene). The analysis was performed with temperature programming (120 – 170°C , $3^\circ\text{C}/\text{min}$; 170 – 200°C , $20^\circ\text{C}/\text{min}$; 200°C , isothermal) ensuring the separation of *cis*- and *trans*-stilbenes, toluene, and

* In ref. 7 it is claimed that two independent molecules in the crystal of IV have different conformations since the C(sp^2)Ti \cdots TiC(sp^2) torsion angles in these molecules differ in sign (-53.7 and 54.1°). If, however, it is borne in mind that IV crystallizes in the centrosymmetric space group $P\bar{1}$ ($Z = 4$), the differences in the sign of the torsion angles obviously do not imply the differences in conformations. Therefore, both independent molecules of IV have in fact the same conformation.

TABLE I
 ATOMIC COORDINATES ($\times 10^4$) IN THE STRUCTURE OF III

Atom	X	Y	Z	Atom	X	Y	Z
Ti(1)	7903(2)	1087(3)	6694(2)	C(26)	9370(11)	1916(17)	9094(8)
Ti(2)	9155(2)	2349(3)	8083(2)	C(27)	9408(16)	814(17)	8792(10)
O	8452(7)	1841(8)	7378(5)	C(28)	8594(15)	560(16)	8423(10)
C(1)	8987(12)	-448(14)	7118(8)	C(29)	7976(14)	1468(20)	8421(10)
C(2)	8145(12)	-989(14)	6983(10)	C(30)	10120(10)	2454(16)	7510(8)
C(3)	7773(12)	-1048(17)	6378(9)	C(31)	10490(11)	1675(16)	7947(9)
C(4)	8403(17)	-483(14)	6172(10)	C(32)	10723(12)	2238(19)	8463(9)
C(5)	9139(14)	-67(15)	6625(10)	C(33)	10517(10)	3492(16)	8352(9)
C(6)	6485(13)	576(20)	6610(11)	C(34)	10118(11)	3568(17)	7761(9)
C(7)	6477(15)	826(17)	6063(10)	C(35)	8612(12)	4216(13)	8113(7)
C(8)	6652(13)	2010(17)	6035(10)	C(36)	7820(9)	4402(15)	7743(8)
C(9)	6739(14)	2498(17)	6566(10)	C(37)	9094(12)	5200(15)	8481(8)
C(10)	6628(13)	1600(21)	6934(11)	C(38)	9336(15)	5203(16)	9072(10)
C(11)	8409(12)	2321(13)	6133(8)	C(39)	9749(15)	6204(19)	9398(9)
C(12)	8546(11)	3414(14)	6356(8)	C(40)	9987(15)	7239(20)	9133(10)
C(13)	8597(11)	1944(12)	5602(7)	C(41)	9756(14)	7219(16)	8551(10)
C(14)	9460(11)	1821(13)	5631(8)	C(42)	9348(15)	6233(16)	9227(9)
C(15)	9658(12)	1449(15)	5168(9)	C(43)	7313(11)	5529(16)	7713(8)
C(16)	9033(12)	1249(16)	4650(9)	C(44)	6873(14)	5898(16)	7194(10)
C(17)	8131(15)	1387(16)	4613(8)	C(45)	6276(14)	6888(18)	7064(9)
C(18)	7895(12)	1763(17)	5071(8)	C(46)	6255(16)	7565(18)	7520(11)
C(19)	8897(13)	4563(14)	6160(9)	C(47)	6661(14)	7243(19)	8035(10)
C(20)	8970(11)	5553(14)	6523(8)	C(48)	7304(17)	6252(23)	8172(10)
C(21)	9240(13)	6681(14)	6374(9)	THF(1) ^a	1770(23)	1124(34)	199(16)
C(22)	9477(13)	6798(16)	5889(9)	THF(2) ^a	2730(23)	743(34)	491(16)
C(23)	9385(14)	5835(15)	5526(8)	THF(3) ^a	2702(25)	-475(38)	121(17)
C(24)	9117(14)	4714(13)	5671(9)	THF(4) ^a	2398(31)	400(46)	-304(20)
C(25)	8459(10)	2221(16)	8817(8)	THF(5) ^a	1523(23)	221(34)	-301(16)

^a The atoms of the solvating THF molecule.

dibenzyl. Column chromatography was carried out under Ar on alumina from which adsorbed air was removed by evacuation for several hours at room temperature.

Synthesis of complex III

1 g (4.02 mmol) of Cp_2TiCl_2 , 0.1 g (4.1 mmol) of finely shaved magnesium, and 0.72 g (4.04 mmol) of toluene in 40 ml of THF were stirred at room temperature under Ar for 2.5–3.5 h, and the resulting dark red-brown solution was evaporated to dryness in vacuum. The residue was chromatographed under Ar on a column with Al_2O_3 . The elution with benzene brought down first the pale greenish band containing traces of I, then the yellow-orange band corresponding to III. Subsequent removal of the solvent in vacuum and crystallization from benzene-hexane gave 0.3–0.7 g of III, m.p. 165–167°C (dec.) under Ar. Found: C, 77.81; H, 5.81; Ti, 12.99. $\text{C}_{48}\text{H}_{42}\text{OTi}_2$ calcd.: C, 78.90; H, 5.80; Ti, 13.11%.

In a similar experiment, 0.3 ml of H_2O was added under Ar to the dark red-brown solution obtained from 1 g of Cp_2TiCl_2 , 0.1 g of Mg, and 0.72 g of toluene in 40 ml of THF. The solution immediately turned dark yellowish orange. The mixture was stirred at room temperature for 30–40 min and evaporated in vacuum. The residue was dissolved in benzene, the benzene solution was filtered and treated with hexane. The precipitated orange powder of III was separated, washed with hexane, and dried in vacuum. Yield 0.86 g (57.1%). The additional purification of III was carried out from THF-hexane. M.p. 165–166°C (dec.) under Ar. The IR and ^1H NMR spectra of the product (see Results and discussion) are identical to those of III obtained by chromatography of a THF solution of II on alumina. The reaction with D_2O was conducted in a similar manner.

X-Ray analysis of III

The crystals of III were obtained from a THF-petroleum ether mixture. The unit cell parameters and intensities of 2221 unique reflections with $F^2 \geq 2\sigma$ were measured on a four-circle automatic Hilger-Watts diffractometer (20°C, $\lambda\text{Cu-K}\alpha$, graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 57^\circ$); no correction for absorption was applied. The gradual decay of the crystal during data collection led to a decrease in the intensity of two standard reflections which were measured after each 50 reflection batch. In the course of data collection (5 days), the intensity of one of the standard reflections decreased almost two-fold, while that of the other decreased four-fold. During data reduction a correction for decrease of intensities, averaged over both standard reflections, was applied. However, the disregard for the difference in individual intensity decrease curves (i.e. radiation decay anisotropy) had an adverse effect on the accuracy of the final results.

The crystals of III are monoclinic, $a = 16.192(2)$, $b = 11.041(1)$, $c = 24.575(3)$ Å, $\beta = 106.99(1)^\circ$, $V = 4202(2)$ Å³, $d_{\text{calc}} = 1.275$ g/cm³ (at 20°C), $Z = 4$, space group $P2_1/a$. The structure was solved by direct methods (MULTAN program). In the *E*-synthesis, the Ti atoms were localized and all non-hydrogen atoms were found in a series of subsequent *F*-syntheses. In addition to the peaks corresponding to the atoms of III the electron density syntheses revealed five peaks located at the vertices of a five-membered cycle with edges of 1.40–1.62 Å. These peaks correspond to the atoms of a solvating THF molecule, however, the localisation of the oxygen atom in this molecule proved impossible.

The structure of III was refined first in an isotropic, then in an anisotropic (for all

non-hydrogen atoms of the complex) approximation. The solvating THF molecule was refined isotropically, all of its atoms being treated as carbons. The final discrepancy indices are $R = 0.114$, $R_w = 0.122$. All calculations were made using an Eclipse S/200 computer with modified EXTL programs. The atomic coordinates are listed in Table 1.

Reaction of a THF solution of II with tolane

A solution of 0.72 g (4.04 mmol) of tolane in 10 ml of THF was added to the dark red-brown solution of II obtained, as was described above, from 1 g of Cp_2TiCl_2 , 0.1 g of Mg, and 0.72 g of tolane in 35 ml of THF, and the mixture was stirred at room temperature under Ar for 6 h. The resulting dark green solution was evaporated in vacuum, and the residue was chromatographed under Ar on a column with Al_2O_3 . The elution with benzene of the dark green band with subsequent removal of the solvent in vacuum gave 1.63 g (ca. 76%) of dark green I. M.p. 150–152°C (dec.) under Ar (after recrystallization from hexane). Lit. m.p. 150°C (dec.) [2–4] and 157–159°C (dec.) [5]. The 1H NMR spectrum of the product in CCl_4 (90 MHz) is identical to that described in the literature [3]. The mass spectrum contains a weak peak of the molecular ion at m/e 534.

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