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Catalytic activity of the titanocene complex with tolane in homogeneous hydrogenation of unsaturated hydrocarbons

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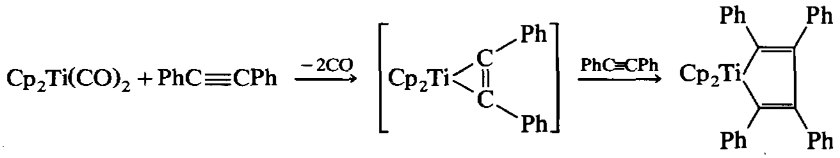
Abstract

The titanocene complex with tolane, $Cp_2Ti(C_2Ph_2)$, is an effective catalyst for homogeneous hydrogenation of olefins and acetylenes at room temperature and atmospheric pressure. In the absence of unsaturated substrate, the complex readily reacts with molecular hydrogen in benzene solution at 20°C to give dibenzyl.

Introduction

It is well known that titanium compounds may act as catalysts for homogeneous hydrogenation of olefins and acetylenes by molecular hydrogen (see *e.g.* refs. 1–6). In 1966 Sonogashira and Hagihara reported on the activity of titanocenedicarbonyl $Cp_2Ti(CO_2)$ in this process [2]. Hydrogenation was conducted in benzene solution at 50–65°C and H_2 pressure of 50 atm. It was supposed by the authors that acetylene hydrogenation proceeds *via* intermediate formation of acetylene complexes of titanocene $Cp_2Ti(C_2R_2)$. However, the attempts of Japanese authors to obtain such complexes by the interaction of $Cp_2Ti(CO)_2$ with tolane and some other acetylenes in benzene at 60°C in the absence of H_2 failed [2]. As a result of the reaction, corresponding titanacyclopentadiene derivatives rather than acetylene complexes $Cp_2Ti(C_2R_2)$ were formed.



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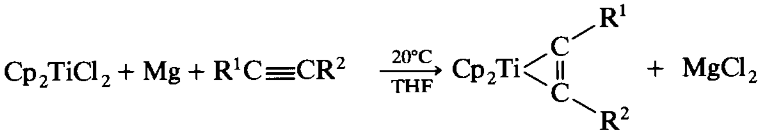
We have recently found [7–13] that acetylene complexes of titanocene $Cp_2Ti(C_2R_2)$ may be easily synthesized by a reaction of Cp_2TiCl_2 with equimolar amounts of Mg and appropriate acetylene in THF at room temperature under Ar.



$$Cp_2TiCl_2 + Mg + R^1C{\equiv}CR^2 \xrightarrow[THF]{20°C} Cp_2Ti(C(R^1){=}C(R^2)) + MgCl_2$$

$R^1 = R^2 = Ph$

$R^1 = R^2 = SiMe_3$

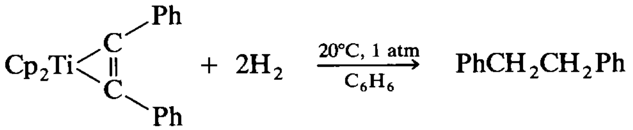
$R^1 = Ph, R^2 = SiMe_3$

In this way titanocene complexes with tolane and some other acetylenes were obtained. Spectral and chemical studies of the complexes showed that they have a structure close to that of titanacyclopropene. X-ray structural study of the complex $Cp_2Ti(PhC_2SiMe_3)$ confirmed this conclusion [13].

Here we report the reaction of one of the complexes obtained, namely the tolane complex of titanocene $Cp_2Ti(C_2Ph_2)$ (I), with dihydrogen as well as catalytic activity of this complex in homogeneous hydrogenation of olefins and acetylenes. For preliminary communications, see refs. 9, 14.

Results and discussion

Experiments on interaction of complex I with dihydrogen were conducted in benzene solution at room temperature and atmospheric pressure of H_2. Under such conditions the titanocene complex with tolane rapidly absorbed dihydrogen to form dibenzyl in nearly quantitative yield (90%).



$$Cp_2Ti(C(Ph){=}C(Ph)) + 2H_2 \xrightarrow[C_6H_6]{20°C,\ 1\ atm} PhCH_2CH_2Ph$$

It is of interest that dihydrogen may also interact with complex I in the absence of a solvent. However, in this case noticeable amounts of *cis*(8%)- and *trans*(25%)-stilbenes are formed besides dibenzyl (24%).

A study of the reaction of complex I with dihydrogen in the presence of excess tolane in benzene solution showed that under such conditions tolane undergoes catalytic hydrogenation to form dibenzyl. Reaction proceeds at room temperature and atmospheric pressure at a high rate. Thus, if the tolane to I ratio is 100 : 1 and initial I concentration is 2×10^{-3} *M*, hydrogenation of tolane is completed in several minutes, dibenzyl yield being close to 100% (Table 1).

Besides tolane, 3-hexyne also undergoes catalytic hydrogenation at room temperature under the action of complex I though at a lower rate (Table 1). As a result of the reaction, n-hexane is formed. Thus, as with tolane, both π-bonds of acetylene group of 3-hexyne are involved in the process of hydrogenation.

Similar to acetylenes, various olefins both with terminal and internal double bonds readily react with dihydrogen in benzene solution at 20°C in the presence of catalytic amounts of complex I. As can be seen from Table 1, *cis*- and *trans*-stil-

Table 1

Hydrogenation of unsaturated hydrocarbons catalyzed by complex I [a]

Substrate	[I], $M \cdot 10^3$	Molar ratio substrate : I	Time of H_2 uptake min [b]	Reaction product	Yield of the product (%)
tolane	2.6	35 : 1	5	dibenzyl	99
tolane	2.0	102 : 1	5–7	dibenzyl	96
trans-stilbene	2.0	45 : 1	5	dibenzyl	99
cis-stilbene	2.0	46 : 1	5–7	dibenzyl	97
styrene	1.9	47 : 1	2–3	ethylbenzene	98
3-hexyne	2.2	40 : 1	20–25	hexane	96
1-heptene	2.2	40 : 1	5–7	heptane	100
cyclohexene	2.2	41 : 1	20–25	cyclohexane	100
1,4-diphenylbutadiene	7.5	36 : 1	13–15	1,4-diphenylbutane	94

[a] 20°C, $P(H_2) = 1$ atm; benzene as a solvent. [b] In all experiments amount of absorbed dihydrogen corresponded well to the yield of hydrogenation product determined by GLC.

benes form dibenzyl under such conditions, styrene is transformed into ethylbenzene, 1-heptene is transformed into n-heptane, cyclohexene gives cyclohexane. It should be noted that although hydrogenation in nearly all cases is practically quantitative, reaction rate depends to a considerable extent on the nature of the olefin. Thus, olefins with phenyl substituents at the double bond are more active in hydrogenation when compared with non-activated aliphatic and alicyclic olefins. For instance, hydrogenation of *cis*- and *trans*-stilbenes containing an internal C=C bond proceeds quantitatively for 5–7 min while complete transformation of cyclohexene into cyclohexane takes 20–25 min under the same conditions. Retardation of the reaction (from 2–3 to 5–7 min) is also observed on going from styrene to 1-heptene *i.e.* for terminal olefins. It also follows from the data obtained that both in the case of olefins with phenyl substituents (styrene, *cis*- and *trans*-stilbenes) and in the case of the usual non-activated olefins (1-heptene, cyclohexene), terminal C=C bonds are hydrogenated more rapidly than internal C=C bonds.

A study of the ability of conjugated dienes to undergo catalytic hydrogenation was conducted on the example of trans-, trans-1,4-diphenyl-1,3-butadiene. The results showed that benzene solution of this diene containing catalytic amounts of complex I readily absorbs dihydrogen at room temperature and atmospheric pressure to give 1,4-diphenylbutane in a substantially quantitative yield.

As it has been pointed out, complexes of the type I were postulated earlier as intermediates in the reaction of homogeneous hydrogenation of acetylenes under the action of titanocenedicarbonyl [2]. However, in the presence of this carbonyl complex the reaction requires considerably more drastic conditions (50–65°C, $P(H_2) = 50$ atm) than on using individual complex I as a catalyst. Both complexes differ markedly from each other also in their catalytic activity towards concrete substrates. Thus, although $Cp_2Ti(CO)_2$ is capable like I of catalyzing tolane hydrogenation to dibenzyl, usual aliphatic acetylenes with internal C≡C bonds (*e.g.* 3-heptyne) are not hydrogenated in the presence of $Cp_2Ti(CO)_2$. Despite I, $Cp_2Ti(CO)_2$ does not catalyze hydrogenation of *trans*-stilbene and styrene hydrogenation proceeds at a considerably lower rate than in the presence of I.

Inactivity of $Cp_2Ti(CO)_2$ in hydrogenation of 3-heptyne and *trans*-stilbene can be explained by the fact that under the conditions reported [2] these unsaturated substrates are not capable of displacing CO ligands from $Cp_2Ti(CO)_2$ and thus of being activated as a result of complexation with titanium. On the other hand, however, it cannot be excluded that the above-mentioned differences in behaviour of complex I and $Cp_2Ti(CO)_2$ are due to differing natures of active species responsible for catalytic hydrogenation under the action of these two complexes.

Much closer to I in its catalytic activity in hydrogenation of acetylenes and olefins is a mixed tolane-carbonyl complex of titanocene $Cp_2Ti(CO)(C_2Ph_2)$ (II) synthesized by Fachinetti *et al.* [3] by the interaction of $Cp_2Ti(CO)_2$ with tolane in n-heptane at room temperature under conditions of continuous removal of carbon monoxide formed:

$$Cp_2Ti(CO)_2 + PhC{\equiv}CPh \rightleftharpoons Cp_2Ti(CO)(C_2Ph_2) + CO$$

Similar to I, complex II exhibits high catalytic activity at 20°C and 1 atm of H_2 in homogeneous hydrogenation of tolane and *trans*-stilbene to dibenzyl, styrene to ethylbenzene, terminal aliphatic olefins (1-octene) to alkanes and 1,4-diphenyl-1,3-butadiene to 1,4-diphenylbutane. Apparently, hydrogenation caused by these complexes proceeds under the action of one and the same catalytically active species.

Experimental

All manipulations with complex I were conducted under Ar using standard Schlenk techniques. Argon and dihydrogen were purified of traces of dioxygen and of moisture by passing through columns with active γ-alumina, reduced Ni/Cr catalyst and zeolites NaA and NaX (5 Å). Benzene was purified by conventional methods and distilled before use under Ar over sodium and calcium hydride. The initial complex I was prepared by a published method [10].

Hydrogenation products were determined by GLC on Chrom-42 and LHM-8MD instruments (flame ionization detector: carrier gas N_2). Analysis of dibenzyl and *cis*- and *trans*-stilbenes was carried out on a column (2.5 m × 4 mm) with 10% SKTFT-50-X on Chromaton N-AW-DMCS (internal standard phenathrene) under temperature programming conditions (120–170°C, 3°C/min, 170–200°C, 20°C/min, 200°C, isothermal). Ethylbenzene was analyzed at 62°C on a column (2 m × 4 mm) with 15% Reoplex-400 on Chromaton N-AW-HMDS (internal standard *o*-xylene). Quantitative determination of n-hexane, n-heptane and cyclohexane was conducted on a column (2.8 m × 4 mm) with 30% β,β'-oxydipropionitrile on Celyte C-22 at 44°C (internal standards cyclohexane, n-octane and n-hexane, respectively). Mass spectra were recorded on an AEI MS-30 instrument.

Reaction of dihydrogen with complex I in benzene solution

0.040 g (0.11 mmol) of complex I was dissolved under argon in 15 ml of benzene. Then the argon was carefully removed by evacuating and replaced by dihydrogen. The magnetic stirrer was switched on simultaneously and the red-brown solution of the complex rapidly deepened. The mixture was stirred at room temperature for 0.5 h and the resulting solution was brought into contact with dry air. The mixture was kept at 20°C overnight, the yellow precipitate was filtered off and the filtrate was analyzed by GLC. The yield of dibenzyl was 89%. Neither tolane nor *trans-* or *cis*-stilbenes were detected.

Reaction of complex I with dihydrogen in the absence of a solvent

0.033 g (0.094 mmol) of complex I was placed under argon in a Schlenk tube and after evacuation dihydrogen was introduced at room temperature. As a result of the reaction with dihydrogen the complex instantly deepened in colour. After a period of 3 h, 2 ml of n-heptane was added to the reaction products. The analysis of the heptane extract by GLC showed the presence of dibenzyl (24%), *trans*-stilbene (25%) and *cis*-stilbene (8%).

Catalytic hydrogenation of olefins and acetylenes

0.03–0.04 g of complex I and 35 ml of benzene were placed under Ar into a two-necked flask connected to a mercury burette filled with dihydrogen. After dissolving the complex in benzene, argon was carefully removed under vacuum, and dihydrogen was introduced into the flask from the mercury burette. Then 10 ml of 0.4 *M* benzene solution of substrate was rapidly added to a solution of I in benzene and the mixture was intensively stirred at room temperature under a dihydrogen atmosphere. When dihydrogen absorption stopped, the solution was stirred at 20°C for an additional 20–25 min and analyzed by GLC.

Catalytic hydrogenation of trans,trans-*1,4-diphenyl-1,3-butadiene*

0.04 g (0.11 mmol) of complex I was dissolved under Ar in 15 ml of benzene and the resulting solution was rapidly added to 0.83 g (4.0 mmol) of *trans,trans*-1,4-diphenyl-1,3-butadiene kept in a dihydrogen atmosphere. Then the mixture was intensively stirred at room temperature under dihydrogen. After 15 min dihydrogen absorption was terminated. The solution was stirred at 20°C in H_2 atmosphere for an additional hour and oxidized by dry air dioxygen as described above. After separation from a yellow precipitate, the solution was passed through a small column with Al_2O_3 and evaporated in vacuum to dryness. The solid residue of 1,4-diphenylbutane was recrystallized from ethanol. The yield of 1,4-diphenylbutane was *ca.* 0.79 g (93.9%). M.p. 52.5–53°C (Lit. 53°C, 52.5°C, 52–52.5°C [15]). Found: C, 91.33; H, 8.67. $C_{16}H_{18}$ calcd.: C, 91.37; H, 8.63. Mass spectrum: m/e 210 (M^+).

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