

CYCLIZATION OF PHENYLPROPIOLIC ACID ON TITANOCENE. SYNTHESIS AND MOLECULAR STRUCTURE OF DI- η^5 -CYCLOPENTADIENYL(CINNAMYLATO- C^3,O)TITANIUM / PHENYLPROPIOLIC ACID (1/1), A NOVEL TITANACYCLE. SYNTHESIS OF DICYCLOPENTADIENYLBIS(PHENYLPROPIOLATO)TITANIUM

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Summary

Dimethyltitanocene reacts with phenylpropionic acid under hydrogen and with the assistance of light to yield the dark red titanium(IV) compound $[(\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{C}_6\text{H}_5\text{C}=\text{CH}\text{-COO}) \cdot \text{C}_6\text{H}_5\text{C}\equiv\text{CCOOH}]$. X-ray structure analysis showed the unit cell to be composed of a titanocene metallacycle in which titanium is η^5 -bonded to two cyclopentadienyl rings and to one carbon and one oxygen atom in a 5-membered metallacycle, the whole molecule being in a 1/1 hydrogen bonded association with phenylpropionic acid. The complex crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a 12.435(4), b 13.046(4), c 14.326(5) Å, β 92.50(4)°, and D_c 1.34 g cm⁻³ for $Z = 4$. Least-squares refinement based on 1812 independent observed reflections led to a final R value of 0.079.

Reaction of dimethyltitanocene with phenylpropionic acid in toluene gives the compound $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OOC}\text{-C}\equiv\text{C}\text{-C}_6\text{H}_5)_2]$ as an air stable orange crystalline solid.

Introduction

It is well known that reduced titanocene compounds are active catalysts in the hydrogenation of unsaturated hydrocarbons [1–4]. The active species is formed in situ as is usually the case in Ziegler systems by the use of reducing agents such as lithium or aluminum hydrides or alkyls which probably take part also as co-catalysts. Unfortunately, these systems are of limited value and interest because of their

failure to preserve their activity in hydrogenating functionalized olefins, mainly because of the "hard acid" nature of the active transition metal site.

Well defined cyclopentadienyltitanium(II) compounds as well as reduced titanocene species generated under hydrogen by photocleavage of titanium-carbon bonds in Cp_2TiR_2 compounds ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$) are also active in hydrogenating olefins [5]. It was during attempts to study the activity of the latter system in the hydrogenation of functionalized olefins and acetylenes that the metallacycle reported in the present work was isolated.

Experimental

Preparation of $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{C}_6\text{H}_5\text{C}=\text{CHCOO}\} \cdot \text{C}_6\text{H}_5\text{C}\equiv\text{CCOOH}]$ (1)

All solvents were thoroughly purified and dried by conventional methods. 50 mg of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ were dissolved in 5 ml of hexane and introduced in a pyrex glass round-bottomed flask. The apparatus was flushed with hydrogen and the solution was exposed to the light of a high pressure mercury radiation source (HANAU) emitting above 320 nm. Within a few minutes the orange color was discharged and a grey-black suspension was formed.

The solution was weakly paramagnetic and showed a broad signal by ESR due to a titanium(III) species. Photolysis was then stopped and a solution of 100 mg of phenylpropionic acid in 5 ml of toluene was added while stirring. The color became immediately violet and all the solid was dissolved. The solution became intensely paramagnetic and a sharp singlet was observed by ESR ($g = 1.9890$; $A(\text{iso, Ti}) 8.6$ G). Stirring was continued for another hour, then the solution was left standing for 48 h under hydrogen. Large air-stable red platelets which settled at the bottom of the flask (25 mg) were found suitable for the X-ray diffraction study.

IR: $\nu(\text{C}\equiv\text{C}) 2220 \text{ cm}^{-1}$ (s), $\nu(\text{C}=\text{O}) 1680 \text{ cm}^{-1}$ (m). $^1\text{H NMR}$ (CDCl_3 , TMS): δ 6.05 (vinylic proton); 6.53 (C_p protons); 6.75–7.00 (aromatic protons); 10.32 ppm (associated acid proton) (correct integrated intensities). The signal of the carboxylic proton is only slightly shifted in comparison with the free acid in the same solvent (δ 10.01 ppm). The mass spectrum exhibited molecular ion peaks of both the titanacycle ($M/e = 324$) and the associated acid ($M/e = 146$) with other principal peaks at 279 ($M - \text{CO}_2$), 178 (Cp_2Ti), 129 ($\text{C}_6\text{H}_5\text{C}\equiv\text{C} - \text{CO}$), 118 ($\text{C}_6\text{H}_5\text{C}\equiv\text{COH}$), and 102 ($\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$).

Preparation of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CCOO})_2]$ (2)

To a solution of 150 mg of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ in toluene was slowly added under argon 200 mg of diphenylpropionic acid in toluene. The reaction was immediately accompanied by vigorous gas evolution. Hexane was then added and the reaction flask was cooled to -30°C . An orange air-stable microcrystalline compound deposited, which was then recovered by filtration (230 mg). Analysis. Found: C, 71.39; H, 4.35; Ti, 10.14. $\text{C}_{18}\text{H}_{10}\text{O}_4$ calcd.: C, 71.79; H, 4.27; Ti, 10.25%. $^1\text{H NMR}$ (CDCl_3 , δ in ppm): 6.6 (10, $\text{C}_{10}\text{H}_{10}$); 7.1–7.7 (5, C_6H_5). IR: $\nu(\text{C}\equiv\text{C}) 2200 \text{ cm}^{-1}$ (s).

X-Ray data collection, structure determination, and refinement for 1

Crystals suitable for X-ray analysis were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement

TABLE 1
CRYSTAL DATA AND SUMMARY OF DATA COLLECTION FOR 1

Compound	TiO ₄ C ₂₈ H ₂₂
Mol. wt.	470.39
Space group	<i>P</i> 2 ₁ / <i>c</i>
Cell constants	
<i>a</i> , Å	12.435(4)
<i>b</i> , Å	13.046(4)
<i>c</i> , Å	14.326(5)
β, deg	92.50(5)
Cell vol. Å ³	2321.9
Molecules/unit cell	4
ρ(calc), g cm ⁻³	1.34
μ(calc), cm ⁻¹	4.18
Radiation	Mo-K _α
Max crystal dimensions, mm	0.35 × 0.25 × 0.20
Scan width	0.80 + 0.20 tan θ
Standard reflections	200, 040
Variation of standards	< 3%
2θ range	1–50
Reflections collected	1812
No. of parameters varied	214
GOF	1.25
<i>R</i>	0.079
<i>R</i> _w	0.083

of $(\sin \theta/\lambda)^2$ values for 25 reflections ($2\theta \geq 30^\circ$) accurately centered on the diffractometer are given in Table 1.

Data were collected on an Enraf–Nonius CAD-4 diffractometer by the $\omega/2\theta$ scan technique. The method has been previously described [6]. A summary of the data collection parameters is given in Table 1. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs [7]. Neutral atom scattering factors for Ti, O, and C were taken from Cromer and Waber [8], and the scattering factors for H were from [9]. The structure was solved by the application of the direct methods program MULTAN [10]. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.104$. The hydrogen atoms were placed at calculated positions 1.08 Å from the bonded carbon atoms of the phenyl and Cp groups and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.079$ and $R_w = 0.083$. A final difference Fourier showed no feature greater than 0.3 e/Å³. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 2 [11].

Results and discussion

The structure of the metallacycle is presented as Fig. 1, while that of the hydrogen-bonded neutral acid molecule is given as Fig. 2. Bond lengths and angles are listed in Table 3. The hydrogen bond is a very strong one between O(1) and

TABLE 2
FINAL FRACTIONAL COORDINATES FOR 1

Atom	x/a	y/b	z/c	U_{eqv}
Ti	0.0319(2)	0.4106(1)	0.7323(1)	0.045
O(1)	0.1769(6)	0.6619(5)	0.6338(5)	0.070
O(2)	0.0701(5)	0.5563(4)	0.7068(4)	0.055
C(1)	0.1493(8)	0.5723(7)	0.6523(6)	0.051
C(2)	0.2000(8)	0.4816(7)	0.6163(6)	0.053
C(3)	0.1657(7)	0.3890(6)	0.6408(6)	0.041
C(4)	0.2196(5)	0.2957(4)	0.6086(4)	0.046
C(5)	0.1752(5)	0.1974(4)	0.6259(4)	0.069
C(6)	0.2293(5)	0.1091(4)	0.5958(4)	0.078
C(7)	0.3234(5)	0.1131(4)	0.5489(4)	0.074
C(8)	0.3631(5)	0.2103(4)	0.5283(4)	0.094
C(9)	0.3126(5)	0.3021(4)	0.5588(4)	0.072
C(10)	0.060(1)	0.452(1)	0.8901(7)	0.087
C(11)	0.159(1)	0.436(1)	0.8566(8)	0.085
C(12)	0.165(1)	0.335(1)	0.8311(8)	0.085
C(13)	0.068(1)	0.2905(9)	0.8504(8)	0.081
C(14)	0.004(1)	0.363(1)	0.8877(8)	0.085
C(15)	-0.151(1)	0.359(1)	0.7253(8)	0.078
C(16)	-0.095(1)	0.2904(9)	0.6740(8)	0.068
C(17)	-0.053(1)	0.3427(9)	0.5958(8)	0.071
C(18)	-0.0869(9)	0.4426(9)	0.6030(7)	0.068
C(19)	-0.1449(9)	0.452(1)	0.6820(8)	0.075
O(3)	0.240(1)	0.8641(6)	0.5344(8)	0.165
O(4)	0.3023(6)	0.7125(5)	0.5068(5)	0.070
C(20)	0.295(1)	0.8102(8)	0.4914(8)	0.067
C(21)	0.3542(8)	0.8482(8)	0.4138(7)	0.062
C(22)	0.3988(8)	0.8864(8)	0.3521(7)	0.058
C(23)	0.4552(6)	0.9363(6)	0.2797(5)	0.058
C(24)	0.4888(6)	1.0379(6)	0.2911(5)	0.101
C(25)	0.5451(6)	1.0839(6)	0.2145(5)	0.116
C(26)	0.5674(6)	1.0366(6)	0.1424(5)	0.107
C(27)	0.5307(6)	0.9385(6)	0.1264(5)	0.158
C(28)	0.4705(6)	0.8842(6)	0.2006(5)	0.126

O(4): the separation is 2.53 Å. Although the hydrogen atom has not been located, any length less than 2.8 Å is diagnostic. Note also that the acid and the metallacycle form discrete hydrogen bonded pairs, with no significant association between such units.

Compound 1 is rather unusual in two respects. First, it is one of the very rare examples among the number of titanacycles known so far in which the metal is σ -bonded to only one carbon atom [12,13], so that the heterocyclic five-membered ring contains three different atomic species. Second, it is a 1/1 molecular adduct of a special type. In the family of titanocenes a few examples of such adducts are known, but they are usually solvates either in ionic structures [14,15] or in low-valent compounds such as $(\text{Cp}_2\text{Ti} \cdot \text{DME})(\text{Zn}_2\text{Cl}_6) \cdot \text{C}_6\text{H}_6$ (DME = dimethoxyethane) or $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_6$ [16]. In our example, the free carboxylic acid appears to be necessary to sustain the molecular edifice by imposing a suitable spatial arrangement. It is interesting to note that by dissolution of the solid even in an inert

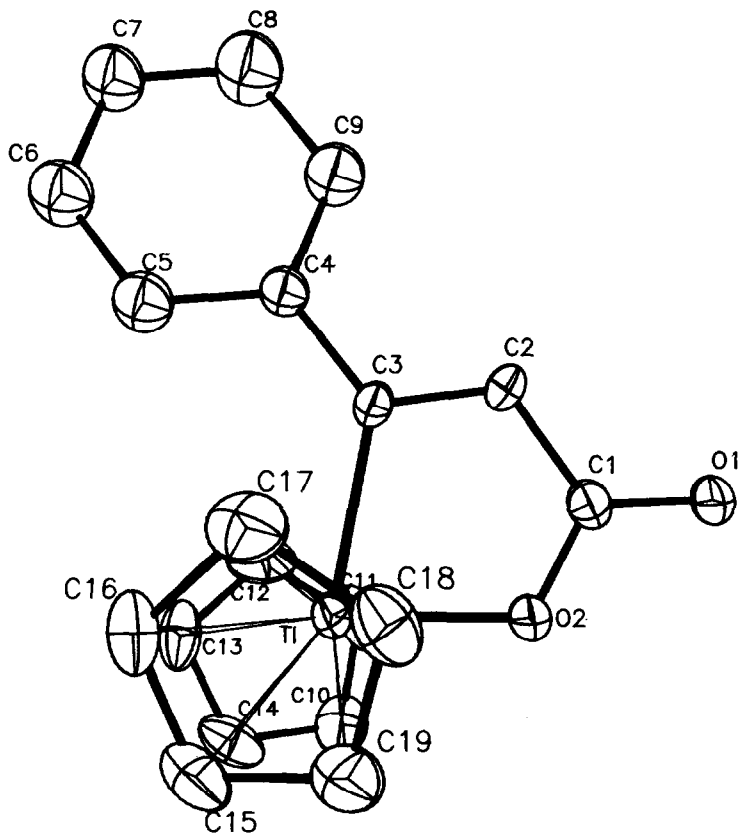


Fig. 1. Structure of the metallocycle.

solvent such as toluene, a breakdown of the edifice occurs and the compound can no longer be recovered by recrystallization nor can be the acid-free titanacycle metallocene.

We propose the following steps to account for the formation of the compound:

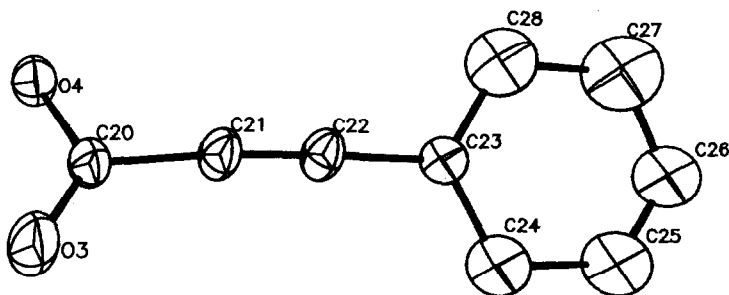
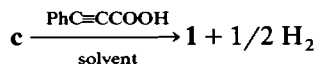
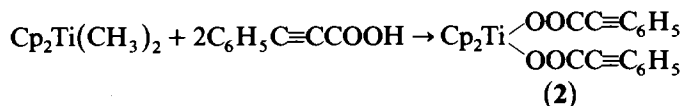


Fig. 2. Structure of the phenylpropionic acid molecule which is hydrogen bonded to the metallocycle through a hydrogen atom located between O(1) and O(4). In the crystal lattice the two molecules form discrete pairs, with no significant hydrogen bonding between such pairs.

addition of the substrate in the photolyzed titanocene suspension, mainly because of the isotropic titanium hyperfine interaction constant (8.6 G) which is of the same order of magnitude as in other titanocene(III) compounds containing Ti-C σ -bonds [17]. Formation of the titanium(IV) metallacycle in **1** is achieved by oxidative attack on titanium of the carboxylic extremity in **c** (or **d**) with loss of hydrogen. Catalytic activity on the metal center is thus inhibited:



During the course of these investigations, we found that phenyl propiolic acid reacts with dimethyltitanocene in toluene as follows:



Compound **2** precipitates as an air-stable yellow-red crystalline solid. It was characterized by elemental analysis, NMR and infrared spectra (see Experimental). This constitutes a new method for the preparation of carboxylato derivatives of titanocene [15].

Further work to elucidate the reactivity of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2/\text{H}_2$ systems in catalytic and stoichiometric reactions is in progress.

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