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Interaction of carbon dioxide with the bis(trimethylsilyl) acetylene complex of permethyltitanocene: synthesis and structure of the binuclear carbonate complex of permethyltitanocene $(Cp_2^* Ti)_2CO_3$

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Abstract

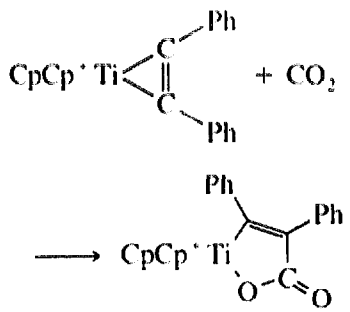
It has been shown that in the interaction of carbon dioxide with the bis(trimethylsilyl)acetylene complex of permethyltitanocene $Cp_2^* Ti(Me_3SiC_2SiMe_3)$, full displacement of bis(trimethylsilyl)acetylene from the titanium coordination sphere takes place and carbon dioxide undergoes disproportionation to form $Cp_2^* Ti(CO)_2$ and the binuclear carbonate complex of permethyltitanocene $(Cp_2^* Ti)_2CO_3$. The structure of $(Cp_2^* Ti)_2CO_3$ has been established by X-ray diffraction study. Structural data on the related chlorine-containing carbonate complex $Cp_2^* Ti(Cl)CO_3TiCp_2^*$ are also reported.

Keywords: Titanium; Alkyne complexes; Carbon dioxide; X-ray diffraction

1. Introduction

At present a number of acetylene complexes of titanocene, permethyltitanocene and pentamethyltitanocene containing no additional stabilizing ligands (CO or tertiary phosphine) are known [1–9]. All these complexes have a structure close to that of titanacyclopropene, but they differ markedly from each other in their reactivity, particularly manifested in their reactions with carbon dioxide.

Thus, in the interaction of the tolane complex of pentamethyltitanocene $CpCp^* Ti(PhC_2Ph)$ with carbon dioxide, the insertion of a CO_2 molecule into the Ti–C bond of the titanacyclopropene ring takes place with formation of a titanafuranone metallacycle [9].



The reaction of carbon dioxide with tolane, bis(trimethylsilyl)acetylene and phenyl(trimethylsilyl)acetylene complexes of titanocene $Cp_2Ti(R^1C_2R^2)$ ($R^1 = R^2 = Ph$; $R^1 = R^2 = SiMe_3$; $R^1 = Ph$, $R^2 = SiMe_3$) results in the displacement of approximately 0.5 mol of free acetylene and the formation of unusual binuclear σ-alkenylcarboxylate complexes of trivalent titanium, $Cp_2TiC(R^1)=C(R^2)-C(O)OTiCp_2$, containing two fused chelate cycles and a tricoordinated oxygen atom [6,7,10,11].

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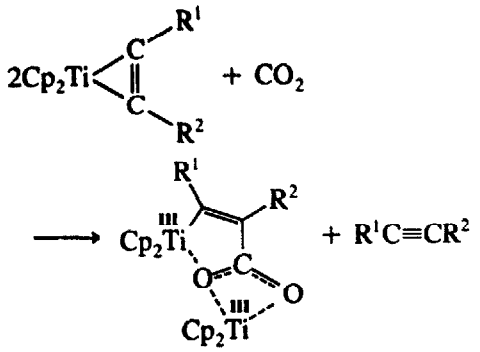
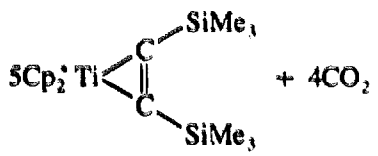


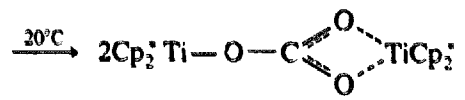
In the present paper one more type of carbon dioxide reaction is described, which we observed on studying the interaction of CO_2 with the bis(trimethylsilyl) acetylene complex of permethyltitanocene $Cp_2^*Ti(Me_3SiC_2SiMe_3)$ (**I**). It has been found that in the course of this reaction, full displacement of the acetylene ligand from the titanium coordination sphere takes place, and carbon dioxide undergoes disproportionation to give $Cp_2^*Ti(CO)_2$ and a binuclear carbonate complex of permethyltitanocene $(Cp_2^*Ti)_2CO_3$ (**II**). For preliminary results, see Refs. [6,12].

2. Results and discussion

On contact of the hexane solution of the acetylene complex **I** with carbon dioxide at room temperature, the reaction mixture rapidly darkens and dark green crystals of the carbonate complex **II** are precipitated. If the solution after separation of **II** is evaporated in vacuum, $Cp_2^*Ti(CO)_2$ can be found in the dry residue by means of IR spectroscopy (ν_{CO} = 1936 and 1855 cm^{-1}).



(**I**)



(**II**)

$$+ Cp_2^*Ti(CO)_2 + 5Me_3SiC{\equiv}CSiMe_3$$

Complex **II** can also be synthesized by bubbling CO_2 through the reaction mixture resulting from the interaction of $Cp_2^*TiCl_2$ with equimolar amounts of magnesium and bis(trimethylsilyl)acetylene in THF, but in this case small amounts of red–brown crystals of another carbonate complex, **III**, are obtained along with **II**. The X-ray structural data for **III** (see below), as well as the chemical implications, enable us to formulate it tentatively as the chlorine-containing carbonate complex $Cp_2^*Ti(Cl)CO_3TiCp_2^*$, apparently formed due to the presence of incompletely reduced Cp_2^*TiCl in the solution.

Complex **II** consists of dark green paramagnetic crystals (m.p. 294–296°C (dec.) under Ar), sensitive to air oxygen and moisture. The complex is readily soluble in THF and benzene and poorly soluble in n-hexane. The structure of **II** has been proved by spectral and chemical methods as well as by an X-ray diffraction study.

The measurements of magnetic susceptibility of the complex indicate that it contains two unpaired electrons. The molecular weight determination (cryoscopically in benzene) shows that the complex has a binuclear structure in the solution.

The IR spectra of **II** (in Fluorolube and KBr pellets) within the range of the stretching vibrations of the carbonate group (1300–1600 cm^{-1}) display a strong broad absorption band at 1413 cm^{-1} and two bands of medium intensity at 1376 and 1491 cm^{-1}. The latter two bands can also be assigned to the bending vibrations of the methyl groups in cyclopentadienyl rings.

The interaction of **II** with HCl in ethanol at 20°C leads to the rapid formation of CO_2 and $Cp_2^*TiCl_2$ (after the oxidation of resulting Cp_2^*TiCl in air) in the ratio 1 : 2 with quantitative yields.

$$(Cp_2^*Ti)_2CO_3 + 2HCl \xrightarrow{20°C} 2Cp_2^*TiCl + CO_2 + H_2O$$

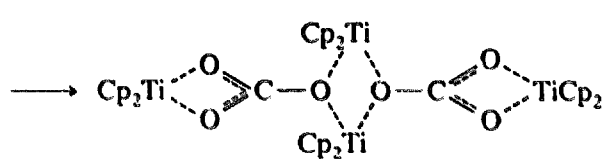
$$\downarrow{\scriptstyle 2HCl}\ \downarrow{\scriptstyle \frac{1}{2}O_2}$$

$$2Cp_2^*TiCl_2 + H_2O$$

All these data suggest that **II** is the binuclear carbonate complex of permethyltitanocene $(Cp_2^*Ti)_2CO_3$. An X-ray diffraction study of **II** has confirmed this conclusion (see below).

It is interesting that on studying the interaction of $Cp_2Ti(CO)_2$ with carbon dioxide, Floriani and coworkers [13] isolated titanocene carbonate of similar composition but of tetranuclear structure $[(Cp_2Ti)_2CO_3]_2$ (**IV**), as follows from X-ray diffraction data.

$$4Cp_2Ti(CO)_2 + 4CO_2$$



(**IV**)

$$+ 10CO$$

We recently obtained the same complex **IV** by reaction of the tert-butyl(trimethylsilyl)acetylene complex of titanocene $Cp_2Ti(^tBuC_2SiMe_3)$ with carbon dioxide in n-hexane [7].

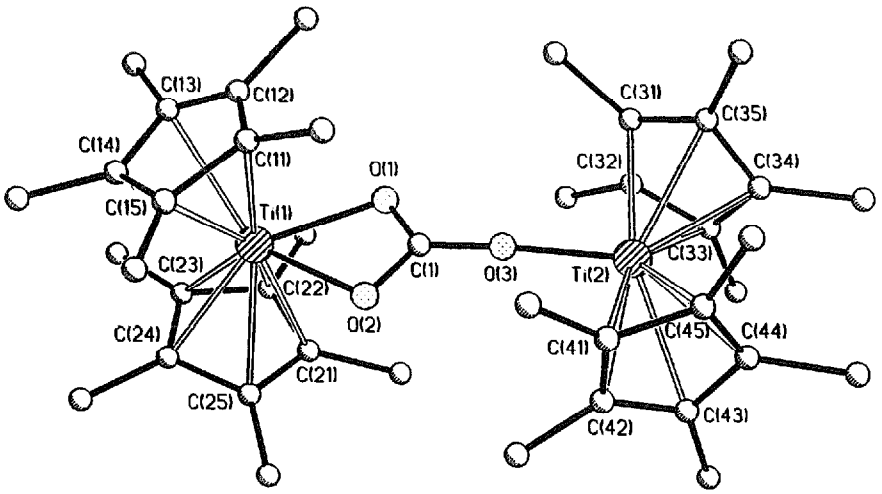


Fig. 1. Structure of the carbonate complex $(Cp_2^* Ti)_2CO_3$ (II).

In the IR spectrum of IV (Polytrichlorofluoroethylene mull), carbonate groups are characterized by absorption bands at 1475(m-s) and 1425(s) cm^{-1} [13]. On dissolving in THF or toluene, the light green complex IV forms dark blue solutions.

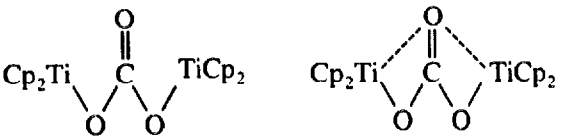
Subsequently, Bottomley et al. [14] have found that freshly prepared solutions of IV in THF or toluene are in reality green, and only turn blue with time; moreover, in blue solutions the IR bands of the carbonate group are observed at 1580 and 1355 cm^{-1} rather than at 1475 and 1425 cm^{-1} as in the solid complex. This result was explained by the dissociation of the tetranuclear complex IV in solution to form the binuclear carbonate complex V:

$$[(Cp_2Ti)_2CO_3]_2 \rightleftharpoons 2(Cp_2Ti)_2CO_3$$

(IV) (V)

The complex IV can be quantitatively obtained again by evaporation of the solvent to dryness.

Coutts and Wailes [15] have reported a blue carbonate complex of titanocene, to which a binuclear structure Va or Vb was ascribed.



(Va) (Vb)

The complex was prepared by the reaction of Cp_2TiCl with an aqueous solution of Na_2CO_3; it displays absorption bands at 1570(sh), 1530(s), and 1355(s) cm^{-1} in the IR spectrum (KBr pellet). According to Bottomley et al. [14], the samples of V, synthesized by the method of Ref. [15], contain solvent. Removal of the solvent in vacuum gives again the light green tetramer IV.

An X-ray diffraction study of complex II has shown that, unlike the carbonate complex of titanocene, it

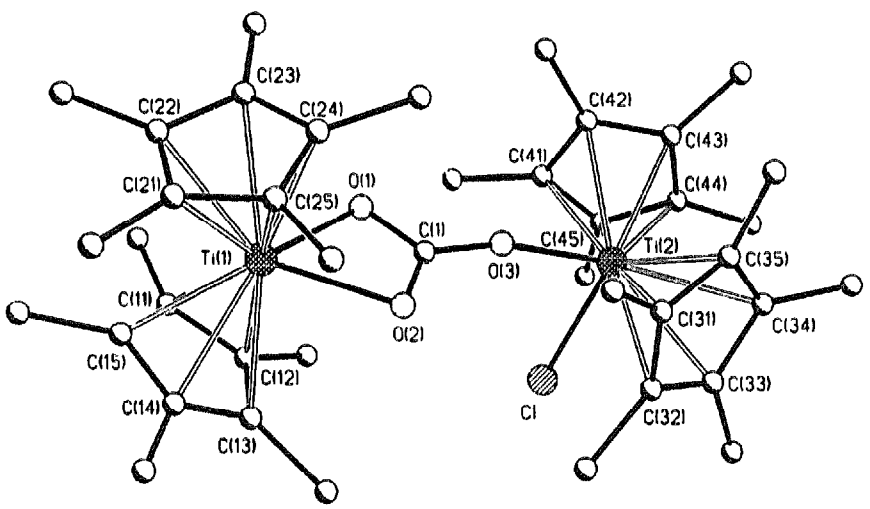


Fig. 2. Structure of the chlorine-containing carbonate complex $Cp_2^* Ti(Cl)CO_3TiCp_2^*$ (III).

retains the binuclear structure in solid state. The carbonate ligand in **II** forms a bridge between two Cp_2^*Ti units, one titanium atom (Ti(1)) in **II** being bonded to two oxygen atoms (O(1) and O(2)) of the carbonate group, whereas the other atom (Ti(2)) is bonded to only one oxygen atom (O(3)) (Fig. 1). Complex **III**, differing from **II** by the presence of the chloro ligand at the Ti(2) atom, has a similar structure (Fig. 2).

The structural and chemical resemblance of complexes **II** and **III** is also reflected in their geometric parameters, which differ in just a few details (Tables 1 and 2). Thus, the four-membered TiO_2C cycle is almost planar in both molecules (maximum deviations 0.001 and 0.020 Å for **II** and **III** respectively), and its mean plane practically coincides with the bisector plane of the bent sandwich at the Ti(1) atom (the dihedral angles Ti(1)O(1)C(1)C(2)/C(11)C(12)C(13)C(14)C(15), Ti(1)O(1)C(1)C(2)/C(21)C(22)C(23)C(24)C(25) are equal to 19.2, 17.5° and 21.5, 17.0° in **II** and **III** respectively). Both Cp_2^*Ti units in molecules **II** and **III** are roughly "orthogonal" to one another, i.e. the vectors connecting the centers of Cp^* rings form angles close to 90° (87.3 and 88.6° for **II** and **III** respectively).

In spite of the fact that complex **III** contains both Ti(III) and Ti(IV) atoms within one molecule (Ti(1) and Ti(2) atoms respectively), the geometrical parameters of their environments reveal no apparent peculiarities, which might be directly attributed to the difference in the oxidation state. The slight increase in the Ti(2)–C(Cp^*) average bond length value (2.426 Å) in **III** compared with those of Ti(1)–C(Cp^*) (2.391 Å) and Ti(2)–C(Cp^*) (2.409 Å) in **II** is hardly worth discussion taking into account the limited accuracy of both structures.

Table 1
Bond lengths (Å) and selected bond angles (°) for **II**

Bond lengths			
Ti(1)–O(1)	2.127(11)	C(14)–C(15)	1.486(24)
Ti(1)–O(2)	2.150(9)	C(14)–C(14′)	1.510(25)
Ti(1)–C(11)	2.377(16)	C(15)–C(15′)	1.437(35)
Ti(1)–C(12)	2.409(22)	C(21)–C(22)	1.380(21)
Ti(1)–C(13)	2.410(17)	C(21)–C(25)	1.389(21)
Ti(1)–C(14)	2.400(13)	C(21)–C(21′)	1.511(20)
Ti(1)–C(15)	2.386(15)	C(22)–C(23)	1.438(20)
Ti(1)–C(21)	2.403(12)	C(22)–C(22′)	1.521(27)
Ti(1)–C(22)	2.378(14)	C(23)–C(24)	1.384(22)
Ti(1)–C(23)	2.443(16)	C(23)–C(23′)	1.515(22)
Ti(1)–C(24)	2.463(17)	C(24)–C(25)	1.431(20)
Ti(1)–C(25)	2.424(17)	C(24)–C(24′)	1.496(22)
Ti(2)–O(3)	1.928(10)	C(25)–C(25′)	1.496(25)
Ti(2)–C(31)	2.387(19)	C(31)–C(32)	1.370(30)
Ti(2)–C(32)	2.390(16)	C(31)–C(35)	1.367(28)
Ti(2)–C(33)	2.384(16)	C(31)–C(31′)	1.527(24)
Ti(2)–C(34)	2.429(18)	C(32)–C(33)	1.408(20)
Ti(2)–C(35)	2.382(23)	C(32)–C(32′)	1.500(30)
Ti(2)–C(41)	2.380(20)	C(33)–C(34)	1.399(30)
Ti(2)–C(42)	2.358(20)	C(33)–C(33′)	1.498(26)
Ti(2)–C(43)	2.392(19)	C(34)–C(35)	1.425(25)
Ti(2)–C(44)	2.421(18)	C(34)–C(34′)	1.543(28)
Ti(2)–C(45)	2.388(22)	C(35)–C(35′)	1.513(27)
O(1)–C(1)	1.203(20)	C(41)–C(42)	1.344(35)
O(2)–C(1)	1.287(21)	C(41)–C(45)	1.408(43)
O(3)–C(1)	1.288(19)	C(41)–C(41′)	1.489(32)
C(11)–C(12)	1.346(28)	C(42)–C(43)	1.375(27)
C(11)–C(15)	1.476(27)	C(42)–C(42′)	1.494(43)
C(11)–C(11′)	1.489(26)	C(43)–C(44)	1.329(41)
C(12)–C(13)	1.290(29)	C(43)–C(43′)	1.527(31)
C(12)–C(12′)	1.552(33)	C(44)–C(45)	1.390(34)
C(13)–C(14)	1.365(27)	C(44)–C(44′)	1.579(30)
C(13)–C(13′)	1.545(25)	C(45)–C(45′)	1.488(44)

Bond angles			
O(1)–Ti(1)–O(2)	58.8(4)	Ti(1)–O(1)–C(1)	94.9(10)
O(1)–C(1)–O(2)	114.9(14)	Ti(1)–O(2)–C(1)	91.3(9)
O(1)–C(1)–O(3)	124.6(16)	Ti(2)–O(3)–C(1)	175.5(13)
O(2)–C(1)–O(3)	120.4(14)		

Primed atoms denote the C atoms of Me groups bonded to the corresponding atoms of the Cp ring.

Table 2
Bond lengths (Å) and selected bond angles (°) for **III**

Bond lengths			
Ti(1)–O(1)	2.151(4)	C(13)–C(13′)	1.509(12)
Ti(1)–O(2)	2.144(4)	C(14)–C(15)	1.387(8)
Ti(2)–Cl	2.415(2)	C(14)–C(14′)	1.520(11)
Ti(2)–O(3)	1.944(4)	C(15)–C(15′)	1.513(9)
O(1)–C(1)	1.277(7)	C(21)–C(22)	1.401(9)
O(2)–C(1)	1.290(7)	C(21)–C(25)	1.402(9)
O(3)–C(1)	1.280(7)	C(21)–C(21′)	1.523(10)
Ti(1)–C(11)	2.373(6)	C(22)–C(23)	1.399(8)
Ti(1)–C(12)	2.418(6)	C(22)–C(22′)	1.529(9)
Ti(1)–C(13)	2.448(7)	C(23)–C(24)	1.392(9)
Ti(1)–C(14)	2.416(6)	C(23)–C(23′)	1.499(10)
Ti(1)–C(15)	2.409(5)	C(24)–C(25)	1.419(9)
Ti(1)–C(21)	2.469(6)	C(24)–C(24′)	1.494(11)
Ti(1)–C(22)	2.471(6)	C(25)–C(25′)	1.486(12)
Ti(1)–C(23)	2.401(6)	C(31)–C(32)	1.397(8)
Ti(1)–C(24)	2.362(7)	C(31)–C(35)	1.400(9)
Ti(1)–C(25)	2.386(7)	C(31)–C(31′)	1.512(9)
Ti(2)–C(31)	2.433(6)	C(32)–C(33)	1.400(9)
Ti(2)–C(32)	2.407(6)	C(32)–C(32′)	1.531(10)
Ti(2)–C(33)	2.412(7)	C(33)–C(34)	1.412(9)
Ti(2)–C(34)	2.468(6)	C(33)–C(33′)	1.502(11)
Ti(2)–C(35)	2.425(6)	C(34)–C(35)	1.424(9)
Ti(2)–C(41)	2.410(7)	C(34)–C(34′)	1.507(10)
Ti(2)–C(42)	2.393(8)	C(35)–C(35′)	1.523(11)
Ti(2)–C(43)	2.434(7)	C(41)–C(42)	1.410(10)
Ti(2)–C(44)	2.444(7)	C(41)–C(45)	1.365(9)
Ti(2)–C(45)	2.438(7)	C(41)–C(41′)	1.499(12)
C(11)–C(12)	1.423(9)	C(42)–C(43)	1.382(10)
C(11)–C(15)	1.402(8)	C(42)–C(42′)	1.524(13)
C(11)–C(11′)	1.502(10)	C(43)–C(44)	1.402(10)
C(12)–C(13)	1.391(10)	C(43)–C(43′)	1.508(12)
C(12)–C(12′)	1.511(11)	C(44)–C(45)	1.369(10)
C(13)–C(14)	1.408(10)	C(44)–C(44′)	1.508(12)
C(45)–C(45′)	1.508(12)		

Bond angles			
O(1)–Ti(1)–O(2)	60.7(1)	O(1)–C(1)–O(3)	121.3(5)
Ti(1)–O(1)–C(1)	91.8(3)	O(2)–C(1)–O(3)	123.1(5)
Ti(1)–O(2)–C(1)	91.8(3)	Cl–Ti(2)–O(3)	87.3(1)
O(1)–C(1)–O(2)	115.6(5)	Ti(2)–O(3)–C(1)	164.6(4)

Primed atoms denote the C atoms of Me groups bonded to the corresponding atoms of the Cp ring.

The most important geometric difference between **II** and **III** is observed in the values of C(1)O(3)Ti(2) bond angles. In **II** this angle is equal to 175(1)°, i.e. the C(1)O(3)Ti(2) fragment is virtually linear here. In complex **III** this angle is noticeably smaller (164.6(4)°). As in the case of other bent sandwiches, the O(3)Ti(2)Cl plane of σ-ligands in **III** approximately coincides with the bisector plane of the dihedral angle formed by the C(31)–C(35) and C(41)–C(45) planes of Cp^* rings, the ClTi(2)O(3)/C(31)C(32)C(33)C(34)C(35) and ClTi(2)O(3)/C(41)C(42)C(43)C(44)C(45) dihedral angles being equal to 20.5 and 20.6° respectively. In both complexes Cp^*_2Ti sandwiches have nearly staggered conformations.

The bond lengths and angles in the carbonate ligand in the structures of **II** and **III** are quite close and agree relatively well with analogous structural parameters for the above-mentioned tetranuclear carbonate complex **IV** [13]. Some shortening of the C(1)–O(1) distance (to 1.20(2) Å) as compared with other C–O bonds in **II** appears to be due to general rather low accuracy of the structure of **II**, because such shortening lacks support from the more accurate structure of **III** and has no reasonable chemical substantiation.

The most notable feature of bond length distributions in complexes **II** and **III** is a significant shortening of the Ti(2)–O(3) bonds (1.93(1) Å in **II** and 1.946(4) Å in **III**) as compared with the Ti(1)–O(1) distances (2.13(1) Å in **II**, 2.151(4) Å in **III**), which can be indicative of increased multiplicity of Ti(2)–O(3) bonds. The latter assumption is in agreement with the fact that the C(1)O(3)Ti(2) bond angles in **II** and **III** are close to 180°. Such high values of the bond angles show that the O(3) atom in both complexes is in the state close to sp-hybridization.

3. Experimental details

Experiments were carried out under Ar with careful exclusion of air oxygen and moisture. n-Hexane and benzene were purified by conventional methods and twice distilled before use over sodium under Ar. Carbon dioxide was recondensed in vacuum and passed through a column packed with P_2O_5. The initial complex **I** was synthesized by the method described in Ref. [6]. The IR spectra were recorded on Nicolet Magna 550 and Nicolet 7199 FT-IR spectrometers in Nujol, Fluorolube or KBr pellets. Magnetic susceptibility was measured by the Faraday method in the temperature range 77–300 K.

3.1. X-ray diffraction studies of complexes II and III

Crystal data and X-ray experiment details for II. $C_{41}H_{60}Ti_2O_3$, $M = 696.7$, $F(000) = 748$, crystal dimensions $0.3 \times 0.2 \times 0.2$ mm^3, triclinic, space group $P\bar{1}$, at 23°C $a = 8.853(2)$, $b = 12.212(4)$, $c = 18.868(6)$ Å, $\alpha = 79.66(2)$, $\beta = 86.88(2)$, $\gamma = 74.90(2)°$, $V = 1937.4(9)$ Å^3, $Z = 2$, $d_{calc} = 1.194$ g cm^{-3}. The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer (23°C, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $\theta/2\theta$ scan technique, $\theta \leq 25°$, 5846 unique reflections collected, the value $\mu(\lambda$Mo K$\alpha) = 4.5$ cm^{-1} indicated no necessity for absorption correction).

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for **II**

Atom	x	y	z	U_{eq} *
Ti(1)	1997(3)	2949(2)	8501(1)	25(1)
Ti(2)	3034(3)	6933(2)	6612(1)	34(1)
O(1)	2115(12)	4694(8)	8321(6)	54(4)
O(2)	2672(11)	3759(8)	7468(5)	45(4)
O(3)	2791(17)	5595(8)	7279(5)	75(6)
C(1)	2523(18)	4711(14)	7701(9)	47(7)
C(11)	4760(18)	2492(14)	8624(9)	56(7)
C(12)	4179(23)	2812(15)	9251(12)	73(9)
C(13)	3406(22)	2130(16)	9609(10)	69(8)
C(14)	3439(18)	1240(12)	9257(9)	54(6)
C(15)	4328(20)	1420(14)	8573(10)	65(7)
C(11')	5828(19)	3012(19)	8114(11)	127(12)
C(12')	4547(26)	3853(18)	9507(12)	121(13)
C(13')	2720(24)	2147(21)	10378(10)	113(12)
C(14')	3044(24)	111(15)	9545(14)	144(13)
C(15')	4730(30)	705(25)	8029(14)	218(20)
C(21)	−566(14)	3857(11)	8014(8)	37(5)
C(22)	−692(16)	3719(13)	8755(8)	46(6)
C(23)	−410(17)	2503(12)	9015(8)	46(6)
C(24)	−44(17)	1935(12)	8432(8)	45(6)
C(25)	−123(17)	2789(13)	7798(8)	49(6)
C(21')	−985(21)	5011(14)	7522(10)	94(9)
C(22')	−1229(21)	4640(16)	9226(12)	104(11)
C(23')	−814(21)	1987(16)	9770(9)	88(9)
C(24')	43(22)	699(13)	8418(11)	88(9)
C(25')	56(21)	2590(17)	7035(10)	89(10)
C(31)	3260(27)	7656(13)	7685(9)	66(8)
C(32)	1702(22)	7975(12)	7518(8)	54(7)
C(33)	1522(22)	8748(13)	6860(9)	60(7)
C(34)	3000(26)	8915(13)	6656(8)	64(8)
C(35)	4108(20)	8167(15)	7163(13)	74(9)
C(31')	3976(32)	6851(17)	8366(10)	143(14)
C(32')	423(29)	7634(16)	7989(11)	130(13)
C(33')	−30(24)	9384(19)	6529(12)	132(13)
C(34')	3299(38)	9913(17)	6086(13)	202(21)
C(35')	5829(22)	8138(20)	7150(16)	153(16)
C(41)	4343(29)	5630(19)	5842(8)	80(10)
C(42)	2804(27)	5871(16)	5713(8)	64(9)
C(43)	2256(25)	7009(19)	5406(9)	78(10)
C(44)	3464(36)	7478(18)	5333(9)	85(11)
C(45)	4796(26)	6662(29)	5616(12)	98(14)
C(41')	5455(42)	4518(23)	6138(10)	284(26)
C(42')	1892(39)	4982(25)	5826(11)	202(24)
C(43')	618(28)	7583(27)	5106(13)	182(19)
C(44')	3361(45)	8655(21)	4806(12)	239(27)
C(45')	6401(35)	6835(37)	5598(14)	254(32)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Crystal data and X-ray experiment details for **III**. $C_{41}H_{60}ClTi_2O_3$, $M = 732.2$, $F(000) = 1564$, crystal dimensions $0.4 \times 0.2 \times 0.1$ mm^3, monoclinic, space group $P2_1/n$, at 23°C $a = 21.449(6)$, $b = 20.203(6)$, $c = 8.975(3)$ Å, $\beta = 96.37(3)$, $V = 3865(2)$ Å^3, $Z = 4$, $d_{calc} = 1.258$ g cm^{-3}. The X-ray diffraction experiment was carried out with a Philips-PW1100 diffractometer (23°C, graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\theta/2\theta$ scan technique, $\theta \leq 25°$, 6212 unique reflections collected, the value $\mu(\lambda$Mo K$\alpha) = 4.7$ cm^{-1} indicated no necessity for absorption correction).

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for **III**

Atom	x	y	z	U_{eq} *
Ti(1)	2939(0)	587(0)	1920(1)	35(1)
Ti(2)	4639(0)	2599(0)	402(1)	39(1)
Cl	3744(1)	3256(1)	898(2)	76(1)
O(1)	3721(2)	1225(2)	2609(4)	46(3)
O(2)	3311(2)	1203(2)	285(4)	45(3)
O(3)	4171(2)	1827(2)	944(4)	52(3)
C(1)	3742(3)	1430(3)	1269(6)	41(4)
C(11)	2325(2)	1010(3)	3746(7)	45(4)
C(12)	2407(3)	1549(3)	2765(8)	57(5)
C(13)	2097(3)	1397(4)	1362(8)	68(6)
C(14)	1821(3)	768(3)	1452(7)	54(5)
C(15)	1943(2)	547(3)	2919(7)	42(4)
C(11')	2561(3)	972(4)	5383(8)	83(7)
C(12')	2736(4)	2195(4)	3175(12)	109(9)
C(13')	2037(5)	1828(5)	−19(11)	146(12)
C(14')	1368(4)	461(5)	223(9)	100(9)
C(15')	1602(3)	−14(3)	3601(9)	75(6)
C(21)	2803(3)	−609(3)	1418(7)	53(4)
C(22)	3088(3)	−553(3)	2894(7)	49(4)
C(23)	3674(3)	−252(3)	2851(8)	50(4)
C(24)	3753(3)	−127(3)	1359(8)	60(4)
C(25)	3204(4)	−335(3)	452(8)	64(5)
C(21')	2222(3)	−1014(4)	884(10)	82(6)
C(22')	2880(3)	−895(3)	4276(8)	69(5)
C(23')	4139(3)	−135(4)	4199(10)	88(7)
C(24')	4344(4)	99(4)	779(11)	112(9)
C(25')	3108(5)	−304(4)	−1213(9)	107(9)
C(31)	4414(3)	2078(3)	−2042(6)	45(4)
C(32)	4031(3)	2636(3)	−2018(7)	49(4)
C(33)	4417(3)	3197(3)	−1923(7)	57(5)
C(34)	5045(3)	2984(3)	−1916(6)	52(5)
C(35)	5042(3)	2279(3)	−1913(7)	54(5)
C(31')	4210(3)	1367(3)	−2318(8)	70(6)
C(32')	3314(3)	2588(4)	−2215(10)	91(8)
C(33')	4210(5)	3906(4)	−2067(10)	105(8)
C(34')	5591(4)	3400(5)	−2278(8)	101(8)
C(35')	5592(4)	1832(5)	−2166(10)	96(8)
C(41)	4938(3)	2652(4)	3068(6)	61(5)
C(42)	5385(4)	2259(4)	2439(8)	74(6)
C(43)	5720(3)	2652(4)	1551(7)	62(5)
C(44)	5477(3)	3293(3)	1628(7)	60(5)
C(45)	5013(3)	3281(4)	2559(8)	62(5)
C(41')	4512(4)	2420(5)	4176(8)	120(9)
C(42')	5469(5)	1524(4)	2785(12)	155(11)
C(43')	6333(4)	2456(5)	1000(10)	120(11)
C(44')	5769(5)	3918(5)	1100(10)	120(11)
C(45')	4719(4)	3899(5)	3112(12)	131(10)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structures were solved by direct (**II**) and heavy atom (**III**) methods and refined by the full-matrix least-squares technique with anisotropic thermal displacement parameters assigned to all non-H atoms. The H atoms in both structures were placed in the calculated positions (with the sterically most favorable hypothetical orientation of Me groups) and included in the refinement in the riding model approximation with common refined (structure **II**; $U_{iso} = 0.187(15)$ Å^2) and fixed (**III**; $U_{iso} = 0.17$ Å^2) temperature factors. The refinement in both cases was carried out against the set of observed structure factors (2472 reflections with $F^2 \geq 3\sigma(F^2)$ for **II** and 4976 reflections with $F^2 \geq 2\sigma(F^2)$ for **III**) with the modified counting statistics weighting scheme $w = 1/[\sigma^2(F) + pF^2]$ ($p = 0.0004$ and 0 for **II** and **III** respectively); the $\Sigma w(|F_o| - |F_c|)^2$ functional was minimized. The final residuals were $R = 0.088$ and $R_w = 0.104$ for **II**, $R = 0.084$ and $R_w = 0.089$ for **III**. In both cases the rather low precision of the structures was caused by the poor quality and, especially in the case of **II**, weak diffraction of the single crystals. These peculiarities may well be attributed to the statistical or dynamic disorder of the Cp* groups, manifested in the high displacement parameters of the methyl C atoms. In spite of sustained efforts to resolve this disorder, no sensible alternative positions for the atoms of the Cp* ligands could be located in the difference syntheses.

All calculations for the structure of **II** were made with the program SHELXTL PLUS (PC version) [16] using an IBM PC computer. The solution and refinement of the structure of **III** were performed with the programs ULM-Programmsystem [17]. Bond lengths and selected bond angles in complexes **II** and **III** are listed in Tables 1 and 2 respectively. Coordinates of atoms in **II** and **III** are given in Tables 3 and 4.

3.2. Synthesis of complex II

1.80 g (3.68 mmol) of **I** was dissolved in 40 ml of n-hexane under Ar, the solution was filtered and (after removing Ar in vacuum) exposed to carbon dioxide at room temperature. Within a few minutes the solution turned dark, and in about 2.5 h dark green crystals of **II** appeared on the bottom and walls of the vessel. After 6 h the solution was decanted. Subsequent washing of the dark green crystals with cold hexane and drying in vacuum gave 0.55 g of **II**, m.p. 294–296°C (dec.) under Ar. After keeping the decanted solution overnight, an additional 0.24 g of **II** was precipitated. The total yield of **II** was approximately 0.79 g (75%). Anal. Found: C,

70.45; H, 8.86; Ti, 14.20 (mol. wt. 739, cryoscopically in C_6H_6). $C_{41}H_{60}Ti_2O_3$ Calc.: C, 70.68; H, 8.68; Ti, 13.75% (mol. wt. 697).

The mother liquor, obtained after separating crystals of **II**, was evaporated to dryness in vacuum. The resulting red–brown residue contained $Cp_2^*Ti(CO)_2$. IR spectrum (Nujol): ν_{co} 1936(vs) and 1855(vs) cm^{-1}. Lit. IR spectrum (n-hexane): ν_{co} 1940(vs) and 1855(vs) cm^{-1} [18].

3.3. Reaction of complex II with HCl

0.12 g (0.17 mmol) of **II** was dissolved in 3 ml of benzene under Ar in a Schlenk tube, which was then connected to a vacuum unit equipped with a gas burette and a Toepler pump. The benzene solution of **II** was frozen, degassed and mixed with 1 ml of previously degassed 6.5 N HCl solution in ethanol. Interaction with HCl led immediately to vigorous liberation of carbon dioxide which was transferred by the Toepler pump into the gas burette for the volume determination. The amount of CO_2 formed was 3.75 ml (STP) or 0.167 mmol (98%). All liberated gas was absorbed by an aqueous solution of $Ba(OH)_2$ to give a white precipitate of barium carbonate. The solution obtained after reaction with HCl and measurement of the amount of CO_2 was evaporated to dryness in vacuum and the solid residue extracted with chloroform in air. The evaporation of the extract in vacuum gave 0.13 g or 0.33 mmol (97%) of dark red crystalline $Cp_2^*TiCl_2$, m.p. 272–273°C (dec.). Lit. m.p. 273°C (dec.) [19].

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