# Interaction of carbon dioxide with acetylene complexes of titanocene $\mathrm{Cp}_{2} \mathrm{Ti}\left(\mathrm{RC}_{2} \mathrm{R}\right)\left(\mathrm{R}=\mathrm{Ph}, \mathrm{SiMe}_{3}\right)$. Synthesis and structure of binuclear $\sigma$-alkenylcarboxylate complexes of titanium ( III) $\mathrm{Cp}_{2} \mathrm{TiC}(\mathrm{R})=\mathrm{C}(\mathrm{R}) \mathrm{COOTiCp}_{2}$ and unexpected transformation of these complexes into titanafuranone metallacycles under the action of air oxygen 

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#### Abstract

Absitract It has been shown that carbon dioxide reacts with acetylene complexes of titanocene $\mathbf{C p}, \operatorname{Ti}(\mathbb{R C}, \mathbf{R})(\mathbb{R}=\mathbf{P h}, \mathrm{SiMe}$ ) at room  COOTICp, comatning ino fined chelate cyeles and a tricoordinated oxygen atom. The imeraction of these binuclear carboxylate   Elevior Sclente S.A.


Renmeds: Tinamina: Acetylene complexes: Carbon dioxide

## 1. Introduction

Acetylene complexes of titanium react readily with carbon dioxide to give products the structure of which is dependent on the nature of the initial complex. In the case of tolane complex of pentamethyltitanocene $\mathrm{CpCp}{ }^{\text {Ti }}\left(\mathrm{PhC}_{2} \mathrm{Ph}\right)$ [1] and mixed phosphine-acetylene


[^0]Me) [2,3], the interaction with carbon dioxide results in the formation of titanafuranone metalacycles. e.g.:


The reaction of $\mathrm{CO}_{2}$ with bis(rimethylsilyl)acetylene complex of permethylitanocene $\mathrm{Cp}_{2} \mathrm{Tii}^{\left(\mathrm{Me}_{3} \mathrm{SiC}_{2} \mathrm{SiMe}_{3}\right) \text { is accompanied by displace }-~}$ ment of the acetylene ligand from the titanium coordination sphere and carbon dioxide undergoes disproportion-
ation yielding $\left.\mathrm{Cp}_{2} \mathrm{Ti}^{\mathrm{T}} \mathrm{CO}\right)_{2}$ and binuclear carbonate complex of titanium (III) ( $\mathrm{Cp}_{2}^{*} \mathrm{Ti}_{2} \mathrm{CO}_{3}$ [4].


Another type of carbon dioxide reaction is realized in the interaction of $\mathrm{CO}_{2}$ with tolane and bis(trimethylsilyl)acetylene complexes of titanocene $\mathrm{Cp}_{2} \mathrm{Ti}_{1}\left(\mathrm{PhC}_{2} \mathrm{Ph}\right)$ (I) [5] and $\mathrm{Cp}_{2} \mathrm{Ti}^{( } \mathrm{Me}_{3} \mathrm{SiC}_{2} \mathrm{SiMe}_{3}$ ) (II) [6,7]. Earlier [8] we have briefly reported that as a result of this reaction unusual binuclear $\sigma$-alkenylcarboxylate complexes of trivalent titanium $\mathrm{Cp}_{2} \mathrm{TiC}(\mathrm{R})=\mathrm{C}(\mathrm{R}) \cdot \mathrm{COOTiCp}_{2}(\mathrm{R}=\mathrm{Ph}$ (III), $\mathrm{SiMe}_{3}$ (IV)), containing two fused chelate cycles and a tricoordinated oxygen atom, are produced. In the present paper the synthesis, structure and some chemical properties of these carboxylate complexes are described in detail.

## 2. Results and discussion

The interaction of carbon dioxide with complexes 1 and II was studied in the solutions of aliphatic hydro ${ }^{-}$ carbons ( $n$-hexane, $n$-pentanc) at room temperature and atmospheric pressure. Under these conditions, 1 and 11 rapidly reacted with $\mathrm{CO}_{2}$ to give binuclear a alkenylcarboxylate complexes 111 and IV in $76=82 \%$ yields. As a result of the reaction corresponding free acetylene was also obtained.


The formation of carboxylate complex $\mathrm{CpCp}{ }^{*} \mathrm{TiC}(\mathrm{Ph})=\mathrm{C}(\mathrm{Ph})-\mathrm{COOTiCpCp}{ }^{*}$ of similar composition has been proposed earlier by Dixneuf et al. [1] in the reaction of $\mathrm{CO}_{2}$ with tolane complex of pentamethyltitanocene $\mathrm{CpCp}{ }^{*} \mathrm{Ti}^{\left(\mathrm{Ph}_{2}{ }_{2} \mathrm{Ph}\right) \text {, however this }}$ compound has not been isolated and characterized.

It is interesting that, in contrast to I and II, the analogous benzyne complex of titanocene $\mathrm{Cp}_{2}$ Tilo$\mathrm{C}_{6} \mathrm{H}_{4}$ ), produced during thermal decomposition of
$\mathrm{Cp}_{2} \mathrm{TiPh}_{2}$ [9], does not give the corresponding binuclear carboxylate complex in the reaction with $\mathrm{CO}_{2}$. In this case, the final reaction product is titanabenzofuranone metallacycle [10].

The structures of complexes III and IV have been established by spectral and chemical means as well as by X-ray diffraction studies.


Complex III is a grey- or black-coloured paramagnetic solid (m.p. $261-263^{\circ} \mathrm{C}$ (dec.) under Ar), complex IV is a dark green, paramagnetic crystalline solid (m.p. $214-216^{\circ} \mathrm{C}$ (dec.) under Ar ). Both complexes are readily soluble in THF and benzene and poorly soluble in aliphatic hydrocarbons. The complexes are stable under Ar at room temperature but decompose rapidly in the presence of air and moisture.

IR spectra of complexes within the range of 1300 $1600 \mathrm{~cm}^{-1}$ exhibit two strong absorption bands ( 1501 and $1385 \mathrm{~cm}^{-1}$ for III. 1481 and $1344 \mathrm{~cm}^{-1}$ for IV) that can be assigned to stretching vibrations of carboxylate group. The magnetic susceptibility of III and IV measured in the temperature range of $77-300 \mathrm{~K}$ obeys the Curie law (with the accuracy of $3 \%$ ). the magnetic moment of the complexes being equal to $1.6 \mu_{11}$ per titanium atom in both cases. This value is close to that of pute spin magnetic moment for Ti(1II) $\left(1.73 \mu_{n}\right)$ and indicates that each of the molecules of 111 and IV contains two unpaired electrons.

In accord with its alkenylcarboxylate structure, complex III readily reacts with HCl in ethanol at room temperature to give $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$, and trans- $\alpha$-phenylcinnamic acid in nearly quantitative yields.


Under similar conditions but on using DCl in $\mathrm{D}_{2} \mathrm{O}$, trans- $\alpha$-phenylcinnamic acid, containing two deuterium atoms, is produced.

The remarkable feature of complexes III and IV is that they are capable of rapidly reacting with air oxygen at room temperature, releasing one of titanocene units
and forming titanafuranone metallacycles (V) [11] and (VI).


The mechanism of this interesting reaction becomes understandable if one assumes that, along with the resonance form $\mathbb{A}$ (see below), the resonance form $\mathbb{B}$ (representing in fact the complex of corresponding titanafuranone ( $\mathbf{V}$ or VI) with titanocene) makes certain contribution into the electronic structure of $\sigma$-alkenylcarboxylates III and IV. In the resonance form B, the most sensitive site towards dioxygen attack is the $\mathrm{Cp}_{2} \mathrm{Ti}$ (II) unit whose oxidation results in degradation of binuclear $\sigma$-alkenylcarboxylate structure of III and IV producing titanafuranone.


Complexes III and IV are apparently formed via the step of displacement of acetylene ligand from 1 and III by $\mathrm{CO}_{2}$ followed by a rapid reaction of the intermediate carbon dioxide complex $\left[\mathrm{Cp}_{2} \mathrm{Ti} \cdot \mathrm{CO}_{2}\right]$ with an excess of the acetylene complex yet unreacted. An alternative mechanism involving an initial formation of the titanafuranone then acting as a ligand in displacing acetylene from the starting acetylene complex is not supported by the experimental data which show that complex $\mathbb{I}$ does not react with titanafuranone V in hexane at room temperature.

Complex V is an air stable, red crystalline solid (m.p. $261-262^{\circ} \mathrm{C}$ (dec.) under Ar), sparingly soluble in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and practically insoluble in ethereal and hydrocarbon solvents. Complex VI is a yellow solid, less stable than V . The structure of $\mathbf{V}$ has been proved by analytical and spectral methods and confirmed by an X-ray diffraction study (see below). In contrast to V . complex VI could not be isolated in the analytically pure state but the spectral data for this compound are in good agreement with its proposed titanafuranone structure.

Thus, IR spectra of both complexes V and VI within the range of $1600-1700 \mathrm{~cm}^{-1}$ show very strong absorp-
tion bands ( $1630 \mathrm{~cm}^{-1}$ for V and $1625 \mathrm{~cm}^{-1}$ for VI) that can be assigned to the stretching vibrations of carbonyl CO group. Analogous $\nu(\mathbf{C O})$ bands in this region are displayed by other known titana- and zirconafuranone metallacycles [ $1-3,12,13$ ]. The mass spectra of V and VI exhibit parent ion peaks at $\mathrm{m} / \mathrm{e} 400$ and 392, respectively. The ${ }^{1} \mathrm{H}$ NMR spectrum ( 200 $\mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) of complex $\mathbf{V}$ shows a singlet of cyclopentadienyl protons ( $\delta 6.51 \mathrm{ppm}$ ) and a multiplet of phenyl protons ( $\delta 6.82-7.14 \mathrm{ppm}$ ). The singlet-to-multiplet intensity ratio is close to the theoretical value for V.

For elucidation of the structural peculiarities of synthesized $\sigma$-alkenylcarboxylates and titanafuranones X ray diffraction studies of complexes $\mathbb{I V}$ and $\mathbf{V}$ have been carried out (see Figs. 1 and 2 and Tables 1-5).

Fig. 1 shows the structure of complex IV. One can see that the complex is indeed a binuclear $\sigma$-alkenylcarboxylate derivative of titanium. An interesting feature of the complex is that its molecule contains a tricoordinated oxygen atom and two fused chelate rings: a four-membered $\mathrm{TiO}_{2} \mathrm{C}$ ( $\mathrm{Ti}-\mathrm{O} 2.258$ (3) and 2.094(4) $\AA$ ) and a five-membered $\mathrm{TiOC}_{3}(\mathrm{Ti}-\mathrm{O} 2.178(3)$, Ti-C $2.256(6) \AA$ ). The tricoordinated oxygen atom forms longer $\mathrm{Ti}-\mathrm{O}$ bonds and a longer $\mathrm{C}-\mathrm{O}$ bond (1.310(6) $\AA$ ) than the two coordinated oxygen ( $\mathrm{C}-0$ 1.266(5) $\AA$ ).

The bicyclic system in IV exhibits as a whole only insignificant deviations from planarity: the $\mathrm{Ti}(1)$ and $\mathrm{Ti}(2)$ atoms are displaced to opposite sides of the mean $\mathrm{O}(2) \mathrm{C}(3) \mathrm{O}(6) \mathrm{C}(4) \mathrm{C}(5)$ plane (planar within $0.05 \AA$ ) by $0.143(5)$ and $0.146(5)$ A, respectively; both five-membered $\mathrm{Ti}(1) \mathrm{O}(2) \mathrm{C}(3) \mathrm{C}(4) \mathrm{C}(5)$ and the four-membered


Fig. I. Structure of complex IV.


Fig. 2. Structure of complex $V$.
$\mathrm{O}(2) \mathrm{C}(3) \mathrm{O}(6) \mathrm{Ti}(2)$ cycles are planar within $0.03 \AA$. Two bis(cyclopentadienyl)titanium fragments show noticeable geometric differences which are most probably due to different coordination environment of titanium atoms. Thus the $\mathrm{Ti}(1)=\mathrm{C}(\mathrm{Cp})$ bonds are on average slightly longer than the $\mathrm{Ti}(2)=\mathbf{C}(\mathbf{C p})$ distances (sec Table 2). The $\mathrm{Cp}_{2} \mathrm{Ti}(1)$ moiety in molecule IV has a nearly eclipsed conformation, whereas the conformation of the $\mathrm{Cp}_{2} \mathrm{Ti}(2)$ moiety is intermediate between the eclipsed and staggered (torsion angles $\mathrm{C}(17) \mathrm{Cp}(1) \mathrm{Cp}(2) \mathrm{C}(18)$ and $\mathrm{C}(23) \mathrm{Cp}(3) \mathrm{Cp}(4) \mathrm{C}(30)$ are equal to 8.6 and $24.0^{\circ}$ respectively) ${ }^{\text {I }}$. At the same time the difference in the dihedral angles between the planes of Cp ligands at the $\mathrm{Ti}(1)$ and $\mathrm{Ti}(2)$ atoms (135.2 and $133.2^{\circ}$. respectively) may hardly be considered significant. Complex III appears to have a similar structure.

An Xoray diffraction study of complex $\mathbf{V}^{3}$ (Fig. 2. Tables 4 and 5) has revealed that it is close in its geometric parameters to other known titanafuranones, e.g. VII [10,14] and VIII [12], as well as to the titanadihydrofurane complex (IX), which we have studied previously [15] (see Table 1). It should be noted, however. that. whereas the bond lengths and angles in metallacycle $\mathbf{V}$ do not differ significantly from those in VIII and

[^1]VIII, the conformation of $\mathrm{TiOC}_{3}$ cycle in V is rather close to that of metallacycle in IX.


(viI)

(vili)

(IX)

Indeed, the five-membered TiOC 3 cycle in $V$, as in IX. has an envelope conformation ${ }^{4}$ : the displacement of the Ti atom from the $\mathrm{O}(2) \mathrm{C}(3) \mathrm{C}(4) \mathrm{C}(5)$ plane (planar within $0.01 \AA$, plane $A$ ) is $0.224 \AA$; the folding angle along the line $\mathrm{O}(2) \cdots \mathrm{C}(5)$ is equal to $8.0^{\circ}$. The orientation of Ph rings in V does not essentially differ from that found in IX. As might be expected, the dihedral angles formed by the planes of these rings with plane $A$ are close to $90^{\circ}$ : they are equal to 100.7 and $103.9^{\circ}$ for the planes $\mathrm{Ph}_{7-12}$ and $\mathrm{Ph}_{19-18}$. respectively.

As already noted, the bond lengths and angles in $\mathbf{V}$ are very close to those in VIII and VIII. Thus, the values of the $T(1)-O(2)$ bond lengths in all three complexes ( $1.965(3) \AA$ in V, $1.945 \AA$ in VII, $1.997 \AA$ in

[^2]Table 1
Geometric parameters of five-membered metallacycles in complexes IV, V, VII-IX

| Complex | IV | V | VII | VIII | IX |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Bond lengths * |  |  |  |  |  |
| Tii(1)-O(2) | 2.178 | 1.965 | 1.945 | 1.997 | 1.830 |
| Ti(1)-C(5) | 2.256 | 2.201 | 2.201 | 2.181 | 2.190 |
| O(2)-C(3) | 1.310 | 1.327 | 1.338 | 1.300 | 1.434 |
| $C(3)=O(6)$ | 1.266 | 1.225 | 1.256 | 1.250 | - |
| C(3)-C(4) | 1.487 | 1.489 | 1.453 | 1.446 | 1.525 |
| C(4)-C(5) | 1.369 | 1.340 | 1.384 | 1.336 | 1.332 |
| Bond angles ${ }^{\text {a }}$ |  |  |  |  |  |
| $\mathrm{O}(2) \mathrm{Ti}(1) \mathrm{C}(5)$ | 75.8 | 78.0 | 78.6 | 79.6 | 78.7 |
| $\mathrm{Ti}(1) \mathrm{O}(2) \mathrm{C}(3)$ | 114.6 | 120.3 | 120.1 | 117.1 | 126.3 |
| $\mathrm{O}(2) \mathrm{C}(3) \mathrm{O}(6)$ | 115.0 | 121.7 | 119.8 | 120.0 | - |
| $\mathrm{O}(2) \mathrm{C}(3) \mathrm{C}(4)$ | 121.4 | 113.8 | 115.7 | 115.9 | 105.6 |
| $\mathrm{O}(6) \mathrm{C}(3) \mathrm{C}(4)$ | 123.6 | 124.4 | 124.2 | 124.2 | -- |
| C(3)C(4)C(5) | 113.6 | 116.8 | 115.5 | 119.9 | 118.9 |
| $\mathrm{Ti}(1) \mathrm{C}(5) \mathrm{C}(4)$ | 114.2 | 110.1 | 109.9 | 107.6 | 110.1 |
| Folding angle along the line $\mathrm{O}(2) \ldots \mathrm{C}(5)$ | 2.1 | 8.0 | 0.5 | 0.5 | 4.7 |

${ }^{\text {a }}$ Atomic numbering in all complexes corresponds to Fig. 1.
VIII) differ only slightly and correspond to an upper limit of a rather wide range $(1.75-1.96 \AA)$ found for this type of bonds in oxygen derivatives of bis(cyclopentadienyl)titanium [ $16-18$ ]. The lengthening of the Ti(1)-O(2) bond in V. VII and VIII is accompanied by shortening of the endocyclic $O(2)-\mathrm{C}(3)$ bond (1.327(5) $\AA$ in V. $1.338 \AA$ in VII, $1.300 \AA$ in VIIII) and is

Table 2
Bond lengths (A゙) for IV

| T(1) O\%2) | $2.178(3)$ | Si(2) C(5) | $1.890(6)$ |
| :---: | :---: | :---: | :---: |
| Ti(1) C(5) | 2.250(6) | $\mathrm{Si}(2) \mathrm{C}(10)$ | 1.878(8) |
| Ti(1) C(13) | $2.410(6)$ | Si(2) C(1I) | 1.859(6) |
| $\mathrm{Ti}(1)=\mathrm{C}(14)$ | 3.408(5) | $\mathrm{Si}(2)=\mathrm{C}(12)$ | 1.86507) |
| $\mathrm{Ti}(1)=\mathrm{C}(15)$ | 3.386(5) | $\mathrm{O}(2) \mathrm{C}(3)$ | $1.31006)$ |
| $\mathrm{Ti}(1)=\mathrm{C}(16)$ | $2.379(6)$ | $C(3)=O(6)$ | $1.266(5)$ |
| $\mathrm{Ti}(1)=\mathrm{C}(17)$ | $2.376(6)$ | $\mathrm{C}(3)=\mathrm{C}(4)$ | 1.487(7) |
| Ti(1)-C(18) | $2.395(6)$ | $\mathrm{C}(4)=\mathrm{C}(5)$ | $1.369(7)$ |
| Ti(1)-C(19) | $2.415(6)$ | C(13)-C(14) | $1.399(8)$ |
| Ti(1)-C(20) | $2.406(6)$ | $\mathrm{C}(13)-\mathrm{C}(17)$ | $1.389(7)$ |
| $\mathrm{Ti}(1)-\mathrm{C}(21)$ | 2.393(7) | C(14)-C(15) | $1.399(8)$ |
| $\mathrm{Ti}(1)-\mathrm{C}(22)$ | 2.373(7) | $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.402(8)$ |
| $\mathrm{Ti}(2)-\mathrm{O}(2)$ | 2.258(3) | C(16)-C(17) | 1.396(9) |
| Ti(2)-O(6) | 2.094(4) | C(18)-C(19) | 1.370(8) |
| Ti(2)-C(23) | 2.381(7) | C(18)-C(22) | 1.378(9) |
| $\mathrm{Ti}(2)=\mathrm{C}(24)$ | $2.388(7)$ | C(19)-C(20) | $1.395(8)$ |
| Ti(2) C (25) | 2.370)(6) | C(20) C (21) | 1.363(9) |
| Ti(2) $\omega$ C(26) | $2.383(6)$ | C(21)-C(22) | $1.386(9)$ |
| Ti(2)-C(27) | $2.373(6)$ | C(23) C (24) | $1.398(9)$ |
| Ti(2)- $\mathrm{C}(28)$ | $2.350(6)$ | C(23)-C(27) | $1.390(9)$ |
| $\mathrm{Ti}(2) \mathrm{C}(29)$ | $2.338(6)$ | C(24)-C(25) | 1.411(10) |
| $\mathrm{Ti}(2)-\mathrm{C}(30)$ | $2.365(6)$ | C(25)-C(26) | 1.389(9) |
| $\mathrm{Ti}(2)=\mathrm{C}(31)$ | 2.377(6) | C(26)-C(27) | $1.368(9)$ |
| $\mathrm{Ti}(2)=\mathbf{C}(32)$ | $2.394(6)$ | C(28)-C(29) | $1.383(9)$ |
| $\mathrm{Si}(1)-\mathrm{C}(4)$ | $1.908(6)$ | C(28) C (32) | $1.391(8)$ |
| $\mathrm{Si}(1)-\mathrm{C}(7)$ | $1.883(7)$ | C(29)-C(30) | $1.396(9)$ |
| $\mathrm{Si}(1)-\mathrm{C}(8)$ | 1.840(8) | $\mathbf{C ( 3 0 ) - C ( 3 1 ) ~}$ | 1.394(9) |
| $\mathbf{S i}(1)-\mathbf{C}(9)$ | 1.832(7) | C(31)-C(32) | 1.387(9) |

Table 3
Selected bond angles ( ${ }^{\circ}$ ) for IV

| $\mathrm{O}(2) \mathrm{Ti}(1) \mathrm{C}(5)$ | $75.8(2)$ | $\mathrm{C}(3) \mathrm{O}(2) \mathrm{Ti}(2)$ | $88.1(3)$ |
| :--- | :--- | :--- | ---: |
| $\mathrm{O}(6) \mathrm{Ti}(2) \mathrm{O}(2)$ | $59.77(13)$ | $\mathrm{Ti}(1) \mathrm{O}(2) \mathrm{Ti}(2)$ | $157.2(2)$ |
| $\mathrm{C}(9) \mathrm{Si}(1) \mathrm{C}(8)$ | $110.8(6)$ | $\mathrm{O}(6) \mathrm{C}(3) \mathrm{O}(2)$ | $115.0(5)$ |
| $\mathrm{C}(9) \mathrm{Si}(1) \mathrm{C}(7)$ | $101.4(5)$ | $\mathrm{O}(6) \mathrm{C}(3) \mathrm{C}(4)$ | $123.6(5)$ |
| $\mathrm{C}(8) \mathrm{Si}(1) \mathrm{C}(7)$ | $105.4(4)$ | $\mathrm{O}(2) \mathrm{C}(3) \mathrm{C}(4)$ | $121.4(5)$ |
| $\mathrm{C}(9) \mathrm{Si}(1) \mathrm{C}(4)$ | $117.5(3)$ | $\mathrm{O}(6) \mathrm{C}(3) \mathrm{Ti}(2)$ | $53.9(3)$ |
| $\mathrm{C}(8) \mathrm{Si}(1) \mathrm{C}(4)$ | $109.9(3)$ | $\mathrm{O}(2) \mathrm{C}(3) \mathrm{Ti}(2)$ | $61.3(3)$ |
| $\mathrm{C}(7) \mathrm{Si}(1) \mathrm{C}(4)$ | $111.0(3)$ | $\mathrm{C}(4) \mathrm{C}(3) \mathrm{Ti}(2)$ | $174.5(3)$ |
| $\mathrm{C}(11) \mathrm{Si}(2) \mathrm{C}(12)$ | $102.0(4)$ | $\mathrm{C}(5) \mathrm{C}(4) \mathrm{C}(3)$ | $113.6(5)$ |
| $\mathrm{C}(11) \mathrm{Si}(2) \mathrm{C}(10)$ | $111.1(4)$ | $\mathrm{C}(5) \mathrm{C}(4) \mathrm{Si}(1)$ | $136.9(4)$ |
| $\mathrm{C}(12) \mathrm{Si}(2) \mathrm{C}(10)$ | $104.2(4)$ | $\mathrm{C}(3) \mathrm{C}(4) \mathrm{Si}(1)$ | $109.5(4)$ |
| $\mathrm{C}(11) \mathrm{Si}(2) \mathrm{C}(5)$ | $112.2(3)$ | $\mathrm{C}(4) \mathrm{C}(5) \mathrm{Si}(2)$ | $123.6(4)$ |
| $\mathrm{C}(12) \mathrm{Si}(2) \mathrm{C}(5)$ | $114.8(3)$ | $\mathrm{C}(4) \mathrm{C}(5) \mathrm{Ti}(1)$ | $114.2(4)$ |
| $\mathrm{C}(10) \mathrm{Si}(2) \mathrm{C}(5)$ | $111.9(3)$ | $\mathrm{Si}(2) \mathrm{C}(5) \mathrm{Ti}(1)$ | $122.2(3)$ |
| $\mathrm{C}(3) \mathrm{O}(2) \mathrm{Ti}(1)$ | $114.6(3)$ | $\mathrm{C}(3) \mathrm{O}(6) \mathrm{Ti}(2)$ | $96.8(3)$ |

Table 4
Bond lengths ( $(\AA$ ) for $V$

| Ti(1)-O(2) | $1.965(3)$ | C(8)-C(9) | 1.401(6) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ti}(1)-\mathrm{C}(5)$ | $2.201(4)$ | C(9)-C(10) | 1.365(7) |
| $\mathrm{Ti}(1)-\mathrm{C}(19)$ | 2.37605 ) | C(10)-C(11) | 1.384(7) |
| $\mathrm{Ti}(1)-\mathrm{C}(20)$ | $2.376(5)$ | $\mathrm{C}(11)-\mathrm{C}(12)$ | $1.383(6)$ |
| T (1)-C(21) | $2.378(5)$ | $\mathrm{C}(13)-\mathrm{C}(14)$ | 1.380(5) |
| $\mathrm{Ti}(1) \mathrm{C}$ (22) | $2.346(5)$ | C(13)-C(18) | $1.385(6)$ |
| $\mathrm{Ti}(1)-\mathrm{C}(23)$ | $2.381(5)$ | $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.404(5) |
| Ti(1)-C(24) | $2.376(5)$ | C(15)-C(16) | $1.372(6)$ |
| Ti(1)-C(25) | 2.372(4) | $\mathrm{C}(16)-\mathrm{C}(17)$ | 1.379(6) |
| $\mathrm{Ti}(1) \mathrm{C}(26)$ | 2.389(4) | C(17)-C(18) | $1.387(5)$ |
| $\mathrm{Ti}(1)-\mathrm{C}(37)$ | $2.347(5)$ | $\mathrm{C}(19)=\mathrm{C}(20)$ | 1.380(6) |
| $\mathrm{Ti}(1) \mathrm{C}(28)$ | 2.369(5) | $\mathrm{C}(19) \mathrm{C}(23)$ | 1.378(7) |
| $\mathrm{O}(2) \mathrm{C}(3)$ | 1.327(5) | C(20)-C(2) | 1.354(7) |
| C(3) $0(6)$ | 1.225(5) | C(21)-C(22) | 1.378(7) |
| C(3) C(4) | 1.480(5) | C(25) $\mathbf{C ( 2 3 )}$ | $1.37088)$ |
| $\mathrm{C}(4) \mathrm{C}(5)$ | $1.34015)$ | $\mathrm{C}(24) \mathrm{C}(25)$ | 1.4(4)(6) |
| $C(4)=C(7)$ | $1.907(5)$ | C(24) - 2 (28) | $1.382(6)$ |
| $\mathrm{C}(5)=\mathrm{C}(13)$ | 1.499(5) | $\mathrm{C}(25)=\mathrm{C}(26)$ | 1.390(5) |
| C(7) $\mathrm{C}(8)$ | 1.388(6) | C(26)-C(27) | $1.392(6)$ |
| C(7)-C(12) | $1.38066)$ | C(27)-C(28) | 1.398(6) |

Table 5
Bond angles $\left({ }^{\circ}\right)$ for $V$

| O(2)Ti(1)C(5) | 78.04(13) | C(7)C(8)C(9) | $120.1(5)$ |
| :---: | :---: | :---: | :---: |
| C(3)O(2)Ti(1) | 120.3(3) | $\mathrm{C}(10) \mathrm{C}(9) \mathrm{C}(8)$ | $120.5(5)$ |
| $0(6) \mathrm{C}(3) \mathrm{O}(2)$ | $121.7(4)$ | $\mathrm{C}(9) \mathrm{C}(10) \mathrm{C}(11)$ | 120.195) |
| $\mathrm{O}(6) \mathrm{C}(3) \mathrm{C}(4)$ | 124.4(4) | C(12)C(11)C(10) | 119.0 (5) |
| $\mathrm{O}(2) \mathrm{C}(3) \mathrm{C}(4)$ | $113.8(4)$ | $\mathrm{C}(7) \mathrm{C}(12) \mathrm{C}(11)$ | 122.2(5) |
| $\mathrm{C}(5) \mathrm{C}(4) \mathrm{C}(3)$ | 116.8(4) | $\mathrm{C}(14) \mathrm{C}(13) \mathrm{C}(18)$ | 117.7(4) |
| $\mathrm{C}(5) \mathrm{C}(4) \mathrm{C}(7)$ | 126.1(3) | $\mathrm{C}(14) \mathrm{C}(13) \mathrm{C}(5)$ | 120.4(4) |
| $\mathrm{C}(3) \mathrm{C}(4) \mathrm{C}(7)$ | 116.9(4) | $\mathrm{C}(18) \mathrm{C}(13) \mathrm{C}(5)$ | 121.9(4) |
| $\mathrm{C}(4) \mathrm{C}(5) \mathrm{C}(13)$ | 121.3(4) | $\mathrm{C}(13) \mathrm{C}(14) \mathrm{C}(15)$ | $121.3(5)$ |
| C(4)C(5)Ti(1) | 110.1(3) | $\mathrm{C}(16) \mathrm{C}(15) \mathrm{C}(14)$ | 119.615 |
| $\mathrm{C}(13) \mathrm{C}(5) \mathrm{Ti}(1)$ | 128.4(3) | $\mathrm{C}(15) \mathrm{C}(16) \mathrm{C}(17)$ | 119.94) |
| $\mathrm{C}(12) \mathrm{C}(7) \mathrm{C}(8)$ | 118.0(4) | $\mathrm{C}(16) \mathrm{C}(17) \mathrm{C}(18)$ | 119.8(5) |
| C(12)C(7) C(4) | 119.6 (4) | $\mathrm{C}(13) \mathrm{C}(18) \mathrm{C}(17)$ | 121.7(4) |
| $\mathrm{C}(8) \mathrm{C}(7) \mathrm{C}(4)$ | 122.4(4) |  |  |

apparently caused by the proximity of carbonyl group: the $\mathrm{Ti}-\mathrm{O}(1.830 \AA)$ and $\mathrm{O}-\mathrm{C}(1.434 \AA)$ bonds in IX are shorter and longer, respectively, than in V, VII and VIII by $\sim 0.1 \AA$. A marked difference between the molecules of V, VII and VIII, on the one hand, and the molecule of IX, on the other hand, is also observed in the value of $\mathrm{Ti}(1) \mathrm{O}(2) \mathrm{C}(3)$ bond angle (120.3(3), 120.1, 117.1 and $126.3^{\circ}$ in V, VII, VIII and IX, respectively). At the same time the $\mathrm{Ti}(1)-\mathrm{C}(5)$ bond lengths and the endocyclic $\mathrm{Ti}(1) \mathrm{C}(5) \mathrm{C}(4)$ and $\mathrm{C}(3) \mathrm{C}(4) \mathrm{C}(5)$ bond angles are very close for all four molecules ( $\mathrm{Ti}(1)-\mathrm{C}(5)$ 2.201(4), 2.201, 2.181 and $2.190 \AA$; $\mathrm{Ti}(1) \mathrm{C}(5) \mathrm{C}(4)$ 110.1(3), 109.9. 107.6 and $110.1^{\circ} ; \quad C(3) C(4) C(5)$ 116.8(4), 115.5, 119.9 and $118.9^{\circ}$ in V. VII. VIII and IX. respectively) even though the $\mathbf{C}(4)=\mathbf{C}(5)$ double bonds in V. VIII and IX (1.340(5), 1.336 and $1.332 \AA$ ) are clearly shorter than the corresponding aromatic bond in VII ( $1.38 \AA$ ).

The bent $\mathrm{Cp}_{2} \mathrm{Ti}$ sandwich in $\mathbf{V}$ has the usual geometry: $\mathrm{Ti}-\mathrm{C}(\mathrm{Cp})$ distances range from 2.346 to $2.389 \AA$. the dihedral angle between the planes of the Cp ligands is $133.2^{\circ}$. Unlike complexes VII-IX, wherein the Cp ligands are in nearly perfectly eclipsed conformation. the conformation of Cp rings in $\mathbf{V}$ is intermediate: for example, the $\mathbf{C}(19) \mathrm{Cp}(1) \mathrm{Cp}(2) \mathrm{C}(24)$ torsion angle is equal to $20.9^{\circ}(\mathrm{Cp}(1), \mathrm{Cp}(2)$ are the centroids of the $\mathrm{C}(19=23)$ and $\mathrm{C}(24-28) \mathrm{Cp}$ rings, respectively).

According to current concepts, repeatedly confirmed by X -ray diffraction studies [19,2C], the $\mathrm{X}^{1}=\mathrm{Ti}=\mathrm{X}^{2}$ bond angle between equatorial $\sigma$-bonds in the bisector plane of acyclic derivatives of the bent sandwiches containing metal in $\mathrm{d}^{\circ}$ cofiguration lies generally in the tange of $94-97^{\circ}$. However, as noted in Ref. [15], this rule is violated on furmation of small metallacycles. Indeed, in all four molecules V. VII, VIII and IX the $\mathrm{O}(2) \mathrm{Ti}(1) \mathrm{C}(5)$ angles are nearly the same and equal to 78.0(1), 78.6, 79.6 and $78.71^{\circ}$, respectively.

A comparison of complexes IV and $\mathbf{V}$ shows (see Table 1) that the addition of $\mathrm{Cp}_{2} \mathrm{Ti}$ moiety to the OCO unit of titw afuranone ring primarily affects the geometric parameters of carboxylate part of the metallacycle: a significant lengthening of the $\mathrm{Ti}(1)=\mathrm{O}(2)$ bond, an increase in the $O(2) C(3) C(4)$ bond angle as well as a decrease in the $\mathrm{Ti}(1) \mathrm{O}(2) \mathrm{C}(3)$ and $\mathrm{O}(2) \mathrm{C}(3) \mathrm{O}(6)$ bond angles take place. At the same time, the conformation of the five-membered metallacycle as a whole varies insignificantly as a result of coordination of the $\mathrm{Cp}_{2} \mathrm{Ti}$ group.

## 3. Experimental details

Experiments were conducted under Ar with careful exclusion of air and moisture. Solvents were purified by conventional methods and distilled before use over sodium and calcium hydride ( $n$-hexane, $n$-pentane and

Table 6
Crystal data and data collection parameters for IV and $\mathbf{V}$

| Complex | $\mathrm{C}_{29} \mathrm{H}_{38} \mathrm{O}_{2} \mathrm{Si}_{2} \mathrm{Ti}_{2}-$ <br> (IV) | $\mathrm{C}_{25} \mathrm{H}_{20} \mathrm{O}_{2} \mathrm{Ti}-$ <br> (V) |
| :---: | :---: | :---: |
| Mol. wt. | 570.55 | 400.31 |
| Space group | Pbca | P $\overline{1}$ |
| a, $\AA$ | 10.336(2) | 8.833(2) |
| b, $\AA$ | 18.336(2) | 9.794(2) |
| c, $\AA$ | 31.656(4) | 12.804(2) |
| $\alpha$, ${ }^{\circ}$ ) | - | 78.08(1) |
| $\beta .{ }^{\circ}$ ) | - | 70.32(1) |
| $\gamma .\left({ }^{\circ}\right)$ | - | 63.85(1) |
| Cell vol., $\AA^{3}$ | 5999.5 | 934.0 |
| 2 | 8 | 2 |
| $d$ (calc.). $\mathrm{gcm}^{-3}$ | 1.263 | 1.423 |
| $\mu$ (calc.), $\mathrm{cm}^{-1}$ | 6.35 | 4.76 |
| Radiation | MoK $\alpha$ | MoK $\alpha$ |
| Temperature | $20^{\circ} \mathrm{C}$ | $20^{\circ} \mathrm{C}$ |
| Diffractometer | STOE-IPDS | STOE-IPDS |
| $2 \theta_{\text {max }}$ | 48.6 | 48.6 |
| Scan method | laser scanned imaging plate |  |
|  |  | laser scanned imaging plate |
| Total no. of unique refl. | 3549 | 2820 |
| No. of observed refl. | 1896 | 1539 |
| $R 1$ (on F for observed refl.) | 0.0517 | 0.0492 |
| $w R 2$ (on $F^{2}$ for all refl.) | 0.1328 | 0.1038 |

benzene) or over $\mathrm{P}_{2} \mathrm{O}_{5}$ (dichlormethane) under Ar. Carbon dioxide was recondensed in vacuum and passed through a column packed with $\mathrm{P}_{2} \mathrm{O}_{5}$ prior to its introduction into reaction. The IR spectra were measured on Nicolet Magna 550 and Nicolet 7199 FT.IR spectrometefs in fluorolube. Nujol or KBr pellets. The NMR spectra were recorded on Bruker WP.200-SY spectrometer. Magnetic susceptibility was measured by the Faram day method in the temperature range of $77-300 \mathrm{~K}$. The mass spectra were recorded on MS- 30 instrument at 70 eV.

### 3.1. X-pay diffraction sudies of complexes IV and V

The crystal data and experimental details for IV and V are presented in Table 6. All H atoms in IV and V were placed in the geometrically calculated positions and refined in the riding model approximation. All calculations were carried out on DEC 3000 AXP 400. DEC 3000 AXP 300 and IBM PC using SHELXS-86 [21]. SHELXL-93 [22] and SHELXTL. PLUS 5 (gamma version) programs. Atomic coordinates in the structures of IV and V are listed in Tables 7 and 8, respectively.

### 3.2. Symhesis of complex III

$0.516 \mathrm{~g}(1.45 \mathrm{mmol})$ of I was dissolved in 80 ml of $n$-hexane under Ar, and the resulting solution was fil-
tered. Argon was then carefully removed in vacuum, and the flask with solution of I was filled with pure $\mathrm{CO}_{2}$. Within 1-2 min grey powder or fine black crystals of III appeared on the bottom and walls of the flask. After 3 h the solution was decanted, and III was washed with $n$-hexane and dried in vacuum. The yield of IIII is $0.32 \mathrm{~g}(76 \%)$; m.p. $261-263^{\circ} \mathrm{C}$ (dec.) under Ar. Analysis: Found: C, 72.60; H, 5.26; Ti, 16.50\%; mol. wt. 527 (cryoscopically in $\mathrm{C}_{6} \mathrm{H}_{6}$ ) $\mathrm{C}_{35} \mathrm{H}_{30} \mathrm{Ti}_{2} \mathrm{O}_{2}$ requires: $\mathrm{C}, 72.68 ; \mathrm{H}, 5.23 ; \mathrm{Ti}, \mathbf{1 6 . 5 6 \%}$; mol.wt. 578 .

### 3.3. Synthesis of complex IV

$1.04 \mathrm{~g}(4.02 \mathrm{mmol})$ of II was dissolved in $15-20 \mathrm{ml}$ of $n$-pentane under Ar, the solution was filtered and (after removal of Ar in vacuum) was exposed to carbon dioxide. Within few minutes the reaction mixture turned green, and dark green crystals of IV appeared on the bottom and walls of the vessel. After 3 h the solution was decanted. Subsequent washing of the dark green

Table 7
Atomic coordinates $\left(\times 10^{4}\right)$ and equivalem isotropic displacement parameters $\left(\times 10^{3}\right)$ for IV

| Alom | $x$ | $y$ | : | $U(\mathrm{eq}) . \AA^{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| Ti(1) | -3970(1) | -1040(1) | -1532(1) | $43(1)$ |
| Ti(2) | - $5920(1)$ | 1035(1) | - $1724(1)$ | $43(1)$ |
| $\mathrm{Si}(1)$ | -762.4(2) | -496(1) | - 552(1) | 66(1) |
| Sil2) | - 5290(2) | - 2099(1) | -663(1) | $62(1)$ |
| O(2) | - $-5186(3)$ | - 7002) | - $=1521(1)$ | $39(1)$ |
| C(3) | - 603 $21(5)$ | $=49(3)$ | - $1210 \times 2)$ | $37(1)$ |
| C(4) | - $6212(4)$ | -685(3) | - $925(2)$ | $42(2)$ |
| C(5) | - $5346(5)$ | - $1238(3)$ | - 991( ${ }^{\text {a }}$ ) | $43(2)$ |
| $0(0)$ | $=0639 \times 3)$ | S4A(\%) | - $1175(1)$ | $45(1)$ |
| c(7) | $=9074(6)$ | - 152(9) | - 852(3) | $135(4)$ |
| C(8) | - $7194(7)$ | $243(5)$ | - $185(3)$ | $130(4)$ |
| C(9) | $=8317(11)$ | $-1273(5)$ | -267(4) | 224(8) |
| C(10) | $=5029(9)$ | $-1897(4)$ | ce 87(2) | 115(3) |
| C(11) | -6746(7) | -2678(3) | - $742(3)$ | 104(3) |
| C(12) | $-3054(7)$ | - 2739(4) | $\sim 801(3)$ | 12033) |
| C(13) | -2483(5) | - 1019(4) | -946(2) | $59(2)$ |
| C(14) | -1866(5) | - 1390(4) | -1276(3) | 64(2) |
| C(15) | -1688(5) | -880(4) | -16000(2) | 70(2) |
| C(16) | -2213(5) | -206(4) | -1480(3) | $61(2)$ |
| C(17) | -2704(5) | - 305(4) | - 1073(3) | $58(2)$ |
| C(18) | - 5574(6) | $-1387(4)$ | -2040(3) | 70(2) |
| C(19) | -5303(7) | -2006(4) | -1814(2) | $70(2)$ |
| C(20) | - $4018(8)$ | -2192(4) | -1896(3) | 76(2) |
| C(2) | $-3536(7)$ | - 1692(5) | -2172(3) | 75(2) |
| C(22) | -4482(8) | -1177(4) | -2259(2) | 70(2) |
| C(23) | -6512(7) | 1162(5) | -2447(2) | 78(2) |
| C(24) | -6633(9) | 422(5) | -2348(3) | $86(3)$ |
| C(25) | -7621(8) | 365(4) | --2042(3) | $76(2)$ |
| C(26) | - $8100(6)$ | 1061(5) | - 1969(3) | $75(2)$ |
| C(27) | -7415(7) | 1546(4) | -2209(3) | 73(2) |
| C(28) | $-4111(6)$ | 1455(3) | - 1345(3) | $61(2)$ |
| C(29) | $-3883(6)$ | 1585(4) | - 1769(3) | 74(2) |
| C(30) | -4773(8) | 2104(4) | - 1910(3) | $80(2)$ |
| C(31) | - $5549(6)$ | 2285(3) | - 1566(3) | 69(2) |
| C(32) | -5132(6) | 1894(3) | -1216(2) | 56(2) |

Table 8
Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\times 10^{3}\right)$ for $V$

| Atom | $x$ | $y$ | $z$ | $U(\mathrm{eq}),{ }^{\text {a }}$ ² |
| :---: | :---: | :---: | :---: | :---: |
| Ti(1) | -7770(1) | -7993(1) | -2287(1) | 27(1) |
| O(2) | - 9563(4) | -8786(3) | - 2046(2) | 35(1) |
| C(3) | -11192(6) | -7838(4) | -2054(4) | 36(1) |
| C(4) | -11427(5) | -6221(4) | -2367(4) | 27(1) |
| C(5) | -9988(5) | -5932(4) | - 2636(3) | 26(1) |
| O(6) | -12360(4) | -8292(3) | - 1845(3) | 64(1) |
| C(7) | -13279(5) | -5051(4) | -2266(4) | 29(1) |
| C(8) | -14129(6) | -4796(5) | -3068(4) | 42(1) |
| C(9) | -1585:(6) | -3692(5) | - 2936(5) | 52(2) |
| C(10) | -16716(6) | -2875(5) | -2014(5) | 50(2) |
| C(11) | -15900(6) | -3137(5) | -1196(5) | 52(2) |
| C(12) | -14198(6) | -4224(5) | -1335(4) | 40(1) |
| C(13) | -10059(5) | -4356(4) | -3013(4) | 26(1) |
| C(14) | -9420(6) | -3976(5) | -4124(4) | 36(1) |
| C(15) | -9466(6) | -2509(5) | -4493(4) | 44(1) |
| C(16) | - $10148(6)$ | -1430(5) | -3739(5) | 44(1) |
| C(17) | - 10814(6) | - 1782(4) | -2628(4) | 42(1) |
| C(18) | -10763(6) | -3235(4) | -2275(4) | 36(1) |
| C(19) | -9210(7) | -7195(7) | -447(4) | 53(2) |
| C(20) | -8143(8) | -6409(5) | -964(4) | 48(2) |
| C(21) | -6444(7) | -7422(8) | -1192(4) | $63(2)$ |
| C(22) | --6406(9) | -8864(7) | -849(5) | 78(2) |
| C(23) | -8106(11) | -8712(7) | -356(4) | $74(2)$ |
| C(24) | -6981(6) | -7971(5) | -4255(4) | 44(1) |
| C(25) | - 5936(6) | -7417(5) | - 3992(4) | 43(1) |
| C(26) | -4827(6) | -8604(5) | -3442(4) | 45(1) |
| C(27) | -5234(6) | -9858(5) | -3323(4) | 47(2) |
| C(28) | -6542(7) | -9474(5) | -3844(4) | 47(1) |

crystals with pentane and drying in vacuum gave 0.94 g ( $82 \%$ ) of complex IV. m.p. $214-216^{\circ} \mathrm{C}$ (dec.) under Ar. Analysis: Found: C. 59.60; H. 6.70; Ti, 16.71: Si, $10.01 \%, \mathrm{C}_{20} \mathrm{H}_{38} \mathrm{Si}_{2} \mathrm{Ti}_{2} \mathrm{O}_{2}$ requires: C. $61.05 ; \mathrm{H}, 6.71$ : Ti, 16.78, Si, $9.85 \%$. Mass spectrum (m/e, 70 eV ): 570 $(\mathrm{M})^{\dagger}$.

### 3.4. Reaction of complex III with HCl

$0.32 \mathrm{~g}(0.55 \mathrm{mmol})$ of IIII was dissolved in 5 ml of benzene under Ar , and 3 ml of 1.7 N solution of HCl in ethanol was added to the resulting solution under stirring. The solution rapidly became crimson. The reaction mixture was exposed to the air for 1 h , a red precipitate of $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$ formed was filtered off, washed with a small amount of benzene and dried. The yield of $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$ is $0.125 \mathrm{~g}(91 \%)$. The benzene filtrate, after separation from $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$, was evaporated to dryness, and the residue was treated with 10 ml of aqueous solution of 0.25 N NaOH . The obtained solution was filtered, HCl was added into the filtrate up to the acidic reaction, and the aqueous acidic solution was evaporated in vacuum to dryness. A solid residue was extracted with ether and the ether extract was evaporated to dryness again to give $0.11 \mathrm{~g}(89 \%)$ of trans- $\alpha$-phenylcinnamic acid with m.p. $173-174^{\circ} \mathrm{C}$ (lit. m.p. is $172-$
$174^{\circ} \mathrm{C}$ [23]). Analysis: Found: C. 80.27; H 5.59\%. $\mathrm{C}_{19} \mathrm{H}_{12} \mathrm{O}_{2}$ requires: $\mathrm{C}, 80.34 ; \mathrm{H}, \mathbf{5 . 3 9 \%}$. Mass spectrum (m/e, 70 eV ): 224 (M) ${ }^{+}$.

## 35. Reaction of complexes III and IV with air oxygen

$0.244 \mathrm{~g}(0.422 \mathrm{mmol})$ of IIII was dissolved in 10 ml of benzene under Ar, and the solution after filtration was exposed to dry air. Within 24 h , a mixture of red fine-crystalline complex $\mathbf{V}$ and a yellow powder of $\mathrm{Cp}_{2} \mathrm{Ti}$ oxidation products was formed. The solution was stirred and, along with the powder products, decanted from $\mathbf{V}$. Complex $\mathbf{V}$ was then dissolved in a mixture of 50 ml of dichloromethane and 10 ml of benzene. The subsequent slow evaporation of the filtered solution to $\sim 5 \mathrm{ml}$ under Ar produced red crystals of complex V which were washed with benzene and dried in vacuum. The yield of $V$ is $0.114 \mathrm{~g}(67 \%)$, m.p. $261-262^{\circ} \mathrm{C}$ (dec.) under Ar. Analysis: Found: C, 74.53; H, 5,13; Ti, $11.80 \% \mathrm{C}_{25} \mathrm{H}_{20} \mathrm{TiO}_{2}$ requires: $\mathrm{C}, 75.01 ; \mathrm{H}, 5.04 ; \mathrm{Ti}$. $11.96 \%{ }^{1} \mathrm{H} N M R$ spectrum $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta: 6.51$ (s, 10 H , Cp); 6.28-7.14 (m, 10H, Ph) ppm.

The oxidation of IV with air oxygen was performed in a similar way.

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[^1]:    ${ }^{7} \mathrm{Cp}(1), \mathrm{Cp}(2), \mathrm{Cp}(3)$ and $\mathrm{Cp}(4)$ are the centroids of Pp rings $\mathrm{C}(13-17), \mathrm{C}(18-22), \mathrm{C}(23-27)$ and $\mathrm{C}(28-32)$. respectively.
    'For preliminary communication, see Ref. (II).

[^2]:    ${ }^{3}$ In the molecules of ViI and ViII, the metallacyele is practically planar.

