

Interaction of carbon dioxide with acetylene complexes of titanocene $\text{Cp}_2\text{Ti}(\text{RC}_2\text{R})$ ($\text{R} = \text{Ph}, \text{SiMe}_3$). Synthesis and structure of binuclear σ -alkenylcarboxylate complexes of titanium (III) $\text{Cp}_2\text{TiC}(\text{R})=\text{C}(\text{R})\text{COOTiCp}_2$ and unexpected transformation of these complexes into titanafuranone metallacycles under the action of air oxygen

V.V. Burlakov ^a, A.I. Yanovsky ^a, Yu.T. Struchkov ^{a,1}, U. Rosenthal ^b, A. Spannenberg ^b,
R. Kempe ^b, O.G. Ellert ^c, V.B. Shur ^{a,*}

^a A.N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 117813, Russian Federation

^b Max-Planck-Gesellschaft, Arbeitsgruppe Komplexkatalyse an der Universität Rostock, Buchbinderstraße 5–6, D-18055 Rostock, Germany

^c N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninskii 31, Moscow 117907, Russian Federation

Received 1 February 1997; revised 10 May 1997; accepted 10 May 1997

Abstract

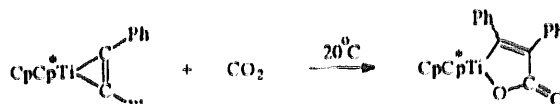
It has been shown that carbon dioxide reacts with acetylene complexes of titanocene $\text{Cp}_2\text{Ti}(\text{RC}_2\text{R})$ ($\text{R} = \text{Ph}, \text{SiMe}_3$) at room temperature and atmospheric pressure to form binuclear σ -alkenylcarboxylate complexes of trivalent titanium $\text{Cp}_2\text{TiC}(\text{R})=\text{C}(\text{R})\text{COOTiCp}_2$ containing two fused chelate cycles and a tricoordinated oxygen atom. The interaction of these binuclear carboxylate complexes with air oxygen at 20°C results in rapid formation of titanafuranone metallacycles $\text{Cp}_2\text{TiC}(\text{R})=\text{C}(\text{R})\text{C}(\text{O})\text{O}$. X-ray diffraction studies of complexes $\text{Cp}_2\text{TiC}(\text{SiMe}_3)=\text{C}(\text{SiMe}_3)\text{COOTiCp}_2$ and $\text{Cp}_2\text{TiC}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{O})\text{O}$ have been carried out. © 1997 Elsevier Science S.A.

Keywords: Titanium; 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 $\text{CpCp}^*\text{Ti}(\text{PhC}_2\text{Ph})$ [1] and mixed phosphine–acetylene complexes of titanocene $\text{Cp}_2\text{Ti}(\text{RC}_2\text{R})(\text{PMe}_3)$ ($\text{R} = \text{H},$

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



The reaction of CO_2 with bis(trimethylsilyl)acetylene complex of permethyltitanocene $\text{Cp}_2^*\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$ is accompanied by displacement of the acetylene ligand from the titanium coordination sphere and carbon dioxide undergoes disproportionation

* Corresponding author.

¹ Deceased on August 16, 1995.

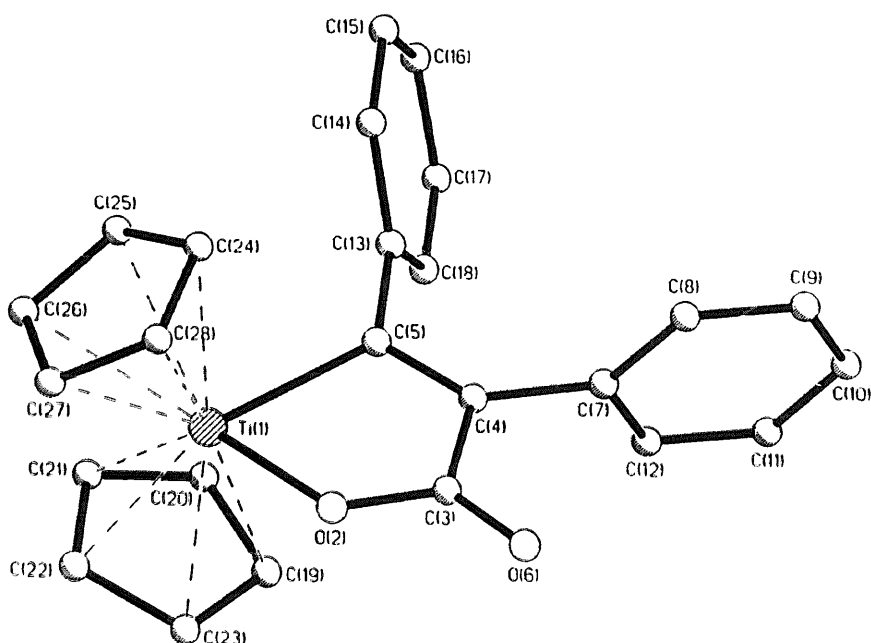
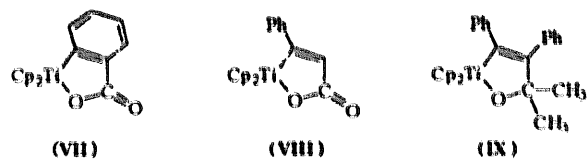


Fig. 2. Structure of complex V.

O(2)C(3)O(6)Ti(2) cycles are planar within 0.03 Å. Two bis(cyclopentadienyl)titanium fragments show noticeable geometric differences which are most probably due to different coordination environment of titanium atoms. Thus, the Ti(1)–C(Cp) bonds are on average slightly longer than the Ti(2)–C(Cp) distances (see Table 2). The Cp₂Ti(1) moiety in molecule IV has a nearly eclipsed conformation, whereas the conformation of the Cp₂Ti(2) moiety is intermediate between the eclipsed and staggered (torsion angles C(17)Cp(1)Cp(2)C(18) and C(23)Cp(3)Cp(4)C(30) are equal to 8.6 and 24.0° respectively)². At the same time the difference in the dihedral angles between the planes of Cp ligands at the Ti(1) and Ti(2) atoms (135.2 and 133.2°, respectively) may hardly be considered significant. Complex III appears to have a similar structure.

An X-ray diffraction study of complex V³ (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 titanadihydrofuranone 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 V do not differ significantly from those in VII and

VIII, the conformation of TiOC₃ cycle in V is rather close to that of metallacycle in IX.



Indeed, the five-membered TiOC₃ cycle in V, as in IX, has an envelope conformation⁴: the displacement of the Ti atom from the O(2)C(3)C(4)C(5) plane (planar within 0.01 Å, plane A) is 0.224 Å; the folding angle along the line O(2)···C(5) is equal to 8.0°. 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°: they are equal to 100.7 and 103.9° for the planes Ph₇₋₁₂ and Ph₁₃₋₁₈, respectively.

As already noted, the bond lengths and angles in V are very close to those in VII and VIII. Thus, the values of the Ti(1)–O(2) bond lengths in all three complexes (1.965(3) Å in V, 1.945 Å in VII, 1.997 Å in

² Cp(1), Cp(2), Cp(3) and Cp(4) are the centroids of Cp rings C(13–17), C(18–22), C(23–27) and C(28–32), respectively.

³ For preliminary communication, see Ref. [11].

⁴ In the molecules of VII and VIII, the metallacycle is practically planar.

Table 1
Geometric parameters of five-membered metallacycles in complexes IV, V, VII–IX

Complex	IV	V	VII	VIII	IX
Bond lengths^a					
Ti(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^a					
O(2)Ti(1)C(5)	75.8	78.0	78.6	79.6	78.7
Ti(1)O(2)C(3)	114.6	120.3	120.1	117.1	126.3
O(2)C(3)O(6)	115.0	121.7	119.8	120.0	–
O(2)C(3)C(4)	121.4	113.8	115.7	115.9	105.6
O(6)C(3)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
Ti(1)C(5)C(4)	114.2	110.1	109.9	107.6	110.1
Folding angle along the line O(2)...C(5)					
	2.1	8.0	0.5	0.5	4.7

^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 Å) 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)–C(3) bond (1.327(5) Å in V, 1.338 Å in VII, 1.300 Å in VIII) and is

Table 2
Bond lengths (Å) for IV

Ti(1)–O(2)	2.178(3)	Si(2)–C(5)	1.890(6)
Ti(1)–C(5)	2.256(6)	Si(2)–C(10)	1.878(8)
Ti(1)–C(13)	2.410(6)	Si(2)–C(11)	1.859(6)
Ti(1)–C(14)	2.408(5)	Si(2)–C(12)	1.865(7)
Ti(1)–C(15)	2.386(5)	O(2)–C(3)	1.310(6)
Ti(1)–C(16)	2.379(6)	C(3)–O(6)	1.266(5)
Ti(1)–C(17)	2.376(6)	C(3)–C(4)	1.487(7)
Ti(1)–C(18)	2.395(6)	C(4)–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)	C(13)–C(17)	1.389(7)
Ti(1)–C(21)	2.393(7)	C(14)–C(15)	1.399(8)
Ti(1)–C(22)	2.373(7)	C(15)–C(16)	1.402(8)
Ti(2)–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)
Ti(2)–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)–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)–C(28)	2.350(6)	C(23)–C(27)	1.390(9)
Ti(2)–C(29)	2.338(6)	C(24)–C(25)	1.411(10)
Ti(2)–C(30)	2.365(6)	C(25)–C(26)	1.389(9)
Ti(2)–C(31)	2.377(6)	C(26)–C(27)	1.368(9)
Ti(2)–C(32)	2.394(6)	C(28)–C(29)	1.383(9)
Si(1)–C(4)	1.908(6)	C(28)–C(32)	1.391(8)
Si(1)–C(7)	1.883(7)	C(29)–C(30)	1.396(9)
Si(1)–C(8)	1.840(8)	C(30)–C(31)	1.394(9)
Si(1)–C(9)	1.832(7)	C(31)–C(32)	1.387(9)

Table 3
Selected bond angles (°) for IV

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

Table 4
Bond lengths (Å) for V

Ti(1)–O(2)	1.965(3)	C(8)–C(9)	1.401(6)
Ti(1)–C(5)	2.201(4)	C(9)–C(10)	1.365(7)
Ti(1)–C(19)	2.376(5)	C(10)–C(11)	1.384(7)
Ti(1)–C(20)	2.376(5)	C(11)–C(12)	1.383(6)
Ti(1)–C(21)	2.378(5)	C(13)–C(14)	1.380(5)
Ti(1)–C(22)	2.346(5)	C(13)–C(18)	1.385(6)
Ti(1)–C(23)	2.381(5)	C(14)–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)	C(16)–C(17)	1.379(6)
Ti(1)–C(26)	2.389(4)	C(17)–C(18)	1.387(5)
Ti(1)–C(27)	2.347(5)	C(19)–C(20)	1.389(6)
Ti(1)–C(28)	2.369(5)	C(19)–C(23)	1.378(7)
O(2)–C(3)	1.327(5)	C(20)–C(21)	1.354(7)
C(3)–O(6)	1.225(5)	C(21)–C(22)	1.378(7)
C(3)–C(4)	1.489(5)	C(22)–C(23)	1.370(8)
C(4)–C(5)	1.340(5)	C(24)–C(25)	1.409(6)
C(4)–C(7)	1.507(5)	C(24)–C(28)	1.382(6)
C(5)–C(13)	1.499(5)	C(25)–C(26)	1.390(5)
C(7)–C(8)	1.388(6)	C(26)–C(27)	1.392(6)
C(7)–C(12)	1.380(6)	C(27)–C(28)	1.398(6)

Table 5
Bond angles (°) 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)	C(10)C(9)C(8)	120.5(5)
O(6)C(3)O(2)	121.7(4)	C(9)C(10)C(11)	120.1(5)
O(6)C(3)C(4)	124.4(4)	C(12)C(11)C(10)	119.0(5)
O(2)C(3)C(4)	113.8(4)	C(7)C(12)C(11)	122.2(5)
C(5)C(4)C(3)	116.8(4)	C(14)C(13)C(18)	117.7(4)
C(5)C(4)C(7)	126.1(3)	C(14)C(13)C(5)	120.4(4)
C(3)C(4)C(7)	116.9(4)	C(18)C(13)C(5)	121.9(4)
C(4)C(5)C(13)	121.3(4)	C(13)C(14)C(15)	121.3(5)
C(4)C(5)Ti(1)	110.1(3)	C(16)C(15)C(14)	119.6(5)
C(13)C(5)Ti(1)	128.4(3)	C(15)C(16)C(17)	119.9(4)
C(12)C(7)C(8)	118.0(4)	C(16)C(17)C(18)	119.8(5)
C(12)C(7)C(4)	119.6(4)	C(13)C(18)C(17)	121.7(4)
C(8)C(7)C(4)	122.4(4)		

apparently caused by the proximity of carbonyl group: the Ti–O (1.830 Å) and O–C (1.434 Å) bonds in IX are shorter and longer, respectively, than in V, VII and VIII by ~0.1 Å. 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 Ti(1)O(2)C(3) bond angle (120.3(3), 120.1, 117.1 and 126.3° in V, VII, VIII and IX, respectively). At the same time the Ti(1)–C(5) bond lengths and the endocyclic Ti(1)C(5)C(4) and C(3)C(4)C(5) bond angles are very close for all four molecules (Ti(1)–C(5) 2.201(4), 2.201, 2.181 and 2.190 Å; Ti(1)C(5)C(4) 110.1(3), 109.9, 107.6 and 110.1°; C(3)C(4)C(5) 116.8(4), 115.5, 119.9 and 118.9° in V, VII, VIII and IX, respectively) even though the C(4)=C(5) double bonds in V, VIII and IX (1.340(5), 1.336 and 1.332 Å) are clearly shorter than the corresponding aromatic bond in VII (1.38 Å).

The bent Cp₂Ti sandwich in V has the usual geometry: Ti–C(Cp) distances range from 2.346 to 2.389 Å, the dihedral angle between the planes of the Cp ligands is 133.2°. Unlike complexes VII–IX, wherein the Cp ligands are in nearly perfectly eclipsed conformation, the conformation of Cp rings in V is intermediate: for example, the C(19)Cp(1)Cp(2)C(24) torsion angle is equal to 20.9° (Cp(1), Cp(2) are the centroids of the C(19–23) and C(24–28) Cp rings, respectively).

According to current concepts, repeatedly confirmed by X-ray diffraction studies [19,20], the X¹–Ti–X² bond angle between equatorial σ-bonds in the bisector plane of acyclic derivatives of the bent sandwiches containing metal in d⁰-configuration lies generally in the range of 94–97°. However, as noted in Ref. [15], this rule is violated on formation of small metallacycles. Indeed, in all four molecules V, VII, VIII and IX the O(2)Ti(1)C(5) angles are nearly the same and equal to 78.0(1), 78.6, 79.6 and 78.71°, respectively.

A comparison of complexes IV and V shows (see Table 1) that the addition of Cp₂Ti moiety to the OCO unit of titanafuranone ring primarily affects the geometric parameters of carboxylate part of the metallacycle: a significant lengthening of the Ti(1)–O(2) bond, an increase in the O(2)C(3)C(4) bond angle as well as a decrease in the Ti(1)O(2)C(3) and O(2)C(3)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 Cp₂Ti 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 V

Complex	C ₂₉ H ₃₈ O ₂ Si ₂ Ti ₂ (IV)	C ₂₅ H ₂₀ O ₂ Ti (V)
Mol. wt.	570.55	400.31
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.336(2)	8.833(2)
<i>b</i> , Å	18.336(2)	9.794(2)
<i>c</i> , Å	31.656(4)	12.804(2)
α , (°)	–	78.08(1)
β , (°)	–	70.32(1)
γ , (°)	–	63.85(1)
Cell vol., Å ³	5999.5	934.0
<i>Z</i>	8	2
<i>d</i> (calc.), g cm ⁻³	1.263	1.423
μ (calc.), cm ⁻¹	6.35	4.76
Radiation	MoK α	MoK α
Temperature	20°C	20°C
Diffractometer	STOE-IPDS	STOE-IPDS
2 θ_{\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
<i>R</i> 1 (on <i>F</i> for observed refl.)	0.0517	0.0492
<i>wR</i> 2 (on <i>F</i> ² for all refl.)	0.1328	0.1038

benzene) or over P₂O₅ (dichloromethane) under Ar. Carbon dioxide was recondensed in vacuum and passed through a column packed with P₂O₅ prior to its introduction into reaction. The IR spectra were measured on Nicolet Magna 550 and Nicolet 7199 FT-IR spectrometers in fluorolube, Nujol or KBr pellets. The NMR spectra were recorded on Bruker WP-200-SY spectrometer. Magnetic susceptibility was measured by the Faraday method in the temperature range of 77–300 K. The mass spectra were recorded on MS-30 instrument at 70 eV.

3.1. X-ray diffraction studies 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. Synthesis of complex III

0.516 g (1.45 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 CO₂. 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 III is 0.32 g (76%); m.p. 261–263°C (dec.) under Ar. Analysis: Found: C, 72.60; H, 5.26; Ti, 16.50%; mol. wt. 527 (cryoscopically in C₆H₆). C₃₅H₃₀Ti₂O₂ requires: C, 72.68; H, 5.23; Ti, 16.56%; mol. wt. 578.

3.3. Synthesis of complex IV

1.04 g (4.02 mmol) of II was dissolved in 15–20 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 ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for IV

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), Å ²
Ti(1)	–3970(1)	–1040(1)	–1532(1)	43(1)
Ti(2)	–5920(1)	1035(1)	–1724(1)	43(1)
Si(1)	–7624(2)	–496(1)	–552(1)	66(1)
Si(2)	–5290(2)	–2099(1)	–663(1)	62(1)
O(2)	–5186(3)	–70(2)	–1521(1)	39(1)
C(3)	–6021(5)	–49(3)	–1210(2)	37(1)
C(4)	–6212(4)	–685(3)	–925(2)	42(2)
C(5)	–5346(5)	–1238(3)	–991(2)	43(2)
O(6)	–6639(3)	544(2)	–1175(1)	45(1)
C(7)	–9074(6)	–152(5)	–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)	–87(2)	115(3)
C(11)	–6746(7)	–2678(3)	–742(3)	104(3)
C(12)	–3954(7)	–2739(4)	–801(3)	120(3)
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)	–1600(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(21)	–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)	89(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 ($\times 10^3$) for V

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), Å 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)	–15851(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°C (dec.) under Ar. Analysis: Found: C, 59.60; H, 6.70; Ti, 16.71; Si, 10.01%. C₂₀H₁₈Si₂Ti₂O₂ requires: C, 61.05; H, 6.71; Ti, 16.78; Si, 9.85%. Mass spectrum (*m/e*, 70 eV): 570 (M)⁺.

3.4. Reaction of complex III with HCl

0.32 g (0.55 mmol) of III 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 Cp₂TiCl₂ formed was filtered off, washed with a small amount of benzene and dried. The yield of Cp₂TiCl₂ is 0.125 g (91%). The benzene filtrate, after separation from Cp₂TiCl₂, 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 g (89%) of *trans*- α -phenylcinnamic acid with m.p. 173–174°C (lit. m.p. is 172–

174°C [23]). Analysis: Found: C, 80.27; H 5.59%. $C_{15}H_{12}O_2$ requires: C, 80.34; H, 5.39%. Mass spectrum (m/e, 70 eV): 224 (M)⁺.

3.5. Reaction of complexes III and IV with air oxygen

0.244 g (0.422 mmol) of III 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 V and a yellow powder of Cp₂Ti oxidation products was formed. The solution was stirred and, along with the powder products, decanted from V. Complex 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 ~5 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 g (67%), m.p. 261–262°C (dec.) under Ar. Analysis: Found: C, 74.53; H, 5.13; Ti, 11.80%. $C_{25}H_{20}TiO_2$ requires: C, 75.01; H, 5.04; Ti, 11.96%. ¹H NMR spectrum (CD₂Cl₂) δ: 6.51 (s, 10H, Cp); 6.28–7.14 (m, 10H, Ph) ppm.

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

Acknowledgements

The work was supported by the Russian Foundation for Basic Research (RFBR, project codes 95-03-08800a and 94-03-08338). The financial support of the RFBR for the partial covering of the License fee for the use of Cambridge Structural Database is also gratefully acknowledged (project No. 96-07-89187). The authors wish to thank Prof. B.V. Lokshin for help in interpretation of the IR spectra.

References

[1] B. Demerseman, R. Mahé, P.H. Dixneuf, *J. Chem. Soc. Chem. Commun.* (1984) 1394.

- [2] H.G. Alt, G.S. Herrmann, *J. Organomet. Chem.* 390 (1990) 159.
 [3] H.G. Alt, G.S. Herrmann, M.D. Rausch, T.D. Mallin, *J. Organomet. Chem.* 356 (1988) C53.
 [4] V.V. Burlakov, U. Rosenthal, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, O.G. Ellert, V.B. Shur, M.E. Vol'pin, *Metalloorg. Khim.* 5 (1992) 1213; *Organomet. Chem. USSR* 5 (1992) 593.
 [5] V.B. Shur, V.V. Burlakov, M.E. Vol'pin, *J. Organomet. Chem.* 347 (1988) 77.
 [6] V.V. Burlakov, U. Rosenthal, P.V. Petrovskii, V.B. Shur, M.E. Vol'pin, *Metalloorg. Khim.* 1 (1988) 953; *Organomet. Chem. USSR* 1 (1988) 526.
 [7] V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur, M.E. Vol'pin, U. Rosenthal, H. Görts, *J. Organomet. Chem.* 476 (1994) 197.
 [8] V.V. Burlakov, U. Rosenthal, A.I. Yanovsky, Yu.T. Struchkov, O.G. Ellert, V.B. Shur, M.E. Vol'pin, *Metalloorg. Khim.* 2 (1989) 1193; *Organomet. Chem. USSR* 2 (1989) 633.
 [9] J. Dvorak, R.J. O'Brien, W. Santo, *J. Chem. Soc. Chem. Commun.* (1970) 411.
 [10] I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaja, G.G. Alexandrov, Yu.T. Struchkov, M.E. Vol'pin, *J. Chem. Soc. Chem. Commun.* (1971) 972.
 [11] V.B. Shur, V.V. Burlakov, A.I. Yanovsky, Yu.T. Struchkov, M.E. Vol'pin, *Metalloorg. Khim.* 1 (1988) 475; *Organomet. Chem. USSR* 1 (1988) 261.
 [12] E. Samuel, J.L. Atwood, W.E. Hunter, *J. Organomet. Chem.* 311 (1986) 325.
 [13] U. Rosenthal, A. Ohff, M. Michalik, H. Görts, V.V. Burlakov, V.B. Shur, *Organometallics* 12 (1993) 5016.
 [14] G.G. Alexandrov, Yu.T. Struchkov, *Zh. Strukt. Khim.* 12 (1971) 307.
 [15] V.B. Shur, V.V. Burlakov, A.I. Yanovsky, P.V. Petrovskii, Yu.T. Struchkov, M.E. Vol'pin, *J. Organomet. Chem.* 297 (1985) 51.
 [16] J.C. Huffmann, K.G. Moloy, J.A. Marsella, K.G. Caulton, *J. Am. Chem. Soc.* 102 (1980) 3009.
 [17] J.L. Atwood, W.E. Hunter, H. Alt, M.D. Rausch, *J. Am. Chem. Soc.* 98 (1976) 2454.
 [18] M. Pasquali, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* 20 (1981) 349.
 [19] J.C. Green, M.L.H. Green, C.K. Prout, *J. Chem. Soc. Chem. Commun.* (1972) 421.
 [20] K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, V.G. Rees, *Acta Crystallogr., Sect. B* 30 (1974) 2290.
 [21] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467.
 [22] G.M. Sheldrick, to be published.
 [23] Beilsteins Handbuch der Organischen Chemie, Bd. 9, Teil 3, 3414.