

REACTION OF A TOLANE COMPLEX OF TITANOCENE WITH CARBONYL COMPOUNDS. SYNTHESIS OF TITANADIHYDROFURAN METALLACYCLES

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(Received June 5th, 1985)

Summary

The reaction of a THF solution of a tolane complex of titanocene [$\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)$] with benzaldehyde and acetone results in the formation of titanadihydrofuran metallacycles $\text{Cp}_2\text{TiC}(\text{Ph})=\text{C}(\text{Ph})\text{CH}(\text{Ph})\text{O}$ and $\text{Cp}_2\text{TiC}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{CH}_3)_2\text{O}$, respectively. The structure of the latter complex has been determined by X-ray analysis.

Introduction

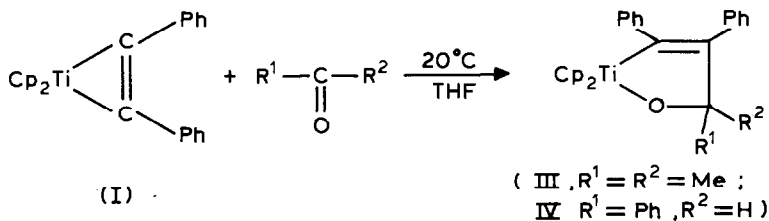
We have recently reported the synthesis of a tolane complex of titanocene [$\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)$] (I) by the interaction of titanocene dichloride with equimolar amounts of magnesium and tolane in THF under Ar [1-5]. The complex is a dark brown, crystalline solid with m.p. 117-119°C (dec.) and shows reactivity which is in good agreement with its proposed structure. When treated with HCl in ethanol, I yields *cis*-stilbene; when treated with water it gives the organometallic titanoxane [$\text{Cp}_2\text{TiC}(\text{Ph})=\text{CH}(\text{Ph})_2\text{O}$] (II) [1,2,4]; and when treated with acetylenes ($\text{R}^1\text{C}\equiv\text{CR}^2$), titanacyclopentadienes $\text{Cp}_2\text{TiC}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{R}^1)=\text{C}(\text{R}^2)$ [1-4]. In benzene solution the complex rapidly absorbs molecular hydrogen at 20°C to give dibenzyl, and it is a catalyst for homogeneous hydrogenation of unsaturated hydrocarbons under mild conditions [4].

Here we report that a THF solution of I reacts readily with aldehydes and ketones at room temperature to give titanadihydrofuran metallacycles*.

* For preliminary communications, see refs. 4 and 6.

Results and discussion

Upon addition of an equimolar amount of acetone to I in THF under Ar, the colour of the reaction mixture rapidly turns cherry-red. After work-up of the solution, a complex can be isolated which, according to X-ray and spectroscopic data (see below), has the structure of a titanadihydrofuran derivative (III). A similar complex (IV) has been obtained by treating benzaldehyde with a THF solution of I.



Complex III is an air-stable, bright red, crystalline solid with m.p. 238–240°C (dec.); complex IV is a dark red, crystalline solid with m.p. 177–178°C (dec.), somewhat less stable in air than III. Both complexes dissolve readily in benzene and THF but are poorly soluble in hexane.

The ^1H NMR spectrum of III in CS_2 (20°C, internal standard TMS) displays a singlet of methyl protons (δ 1.20 ppm), a singlet of cyclopentadienyl protons (δ 6.12 ppm), and a multiplet of phenyl protons (δ 6.63–6.88 ppm). The intensity ratio of the singlets to the multiplet coincides with the theoretical one for III (6/10/10).

The ^1H NMR spectrum of IV is more complicated. It shows a singlet of a methine proton of the PhCH group (δ 6.10 ppm), two singlets of cyclopentadienyl protons (δ 6.19 and 6.20 ppm) of equal intensity, and a multiplet of phenyl protons (δ 6.51–7.22 ppm). The signal intensity ratio is similar to that expected for IV (1/5/5/15).

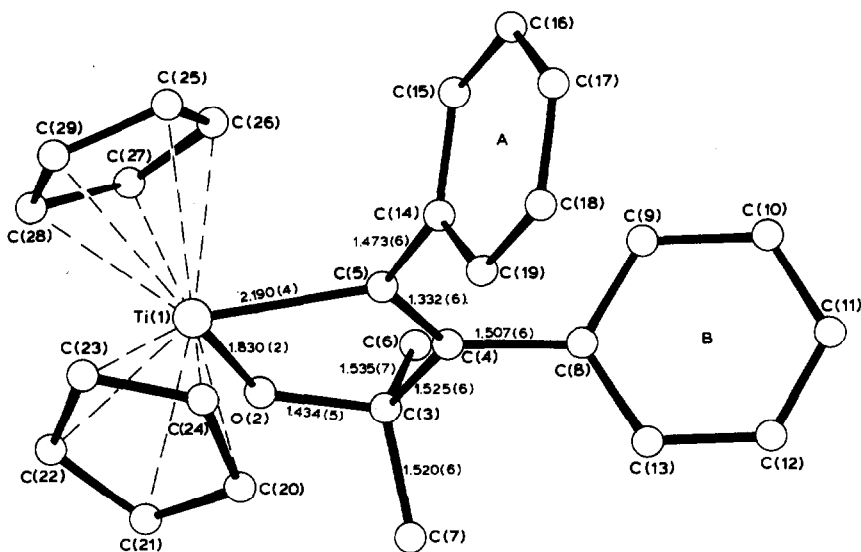
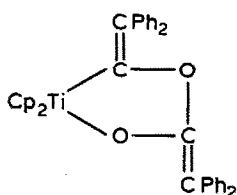


Fig. 1. Structure of complex III.

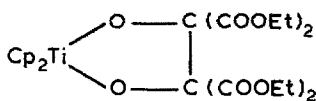
The mass spectrum of III (230°C, 70 eV) exhibits a parent ion peak at m/e 414 and characteristic peaks of fragmental ions at m/e 396 [$M - H_2O$]⁺, 381 [$M - H_2O - Me$]⁺, 356 [$M - Me_2CO$]⁺, 291 [$M - Me_2CO - Cp$]⁺, 236 [$M - C_2Ph_2$]⁺, 178 [Cp_2Ti]⁺ and [C_2Ph_2]⁺. A similar fragmentation pattern is observed in the mass spectrum of IV (170°C, 70 eV): m/e 462 [M]⁺, 444 [$M - H_2O$]⁺, 367 [$M - H_2O - Ph$]⁺, 356 [$M - PhCHO$]⁺, 291 [$M - PhCHO - Cp$]⁺, 284 [$M - C_2Ph_2$]⁺, 178 [Cp_2Ti]⁺ and [C_2Ph_2]⁺, which is indicative of the structural similarity of the two complexes.

The geometry of a molecule of III, together with the most important bond lengths is shown in Fig. 1. As can be seen, complex III is indeed a titanadihydrofuran derivative.

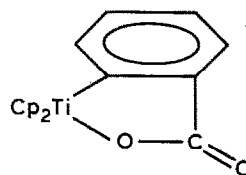
The five-membered metallacycle in III has a flattened envelope conformation: the displacement of the Ti atom from the C_3O plane is only 0.1243(1) Å; the ring is folded along the line O(2)··C(5) by 4.7(2)°. The structures of six bicyclopentadienyl titanium complexes (V–X) containing a five-membered metallacycle in the molecule were determined earlier [7–11]. Only in one case, in the molecule of V, were significant distortions of the ring from planarity observed: the displacement of the Ti atom from the COCO plane was 0.67 Å. In VI–X the metallacycles are practically planar.



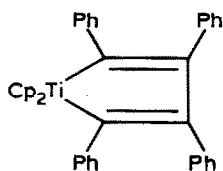
(V)



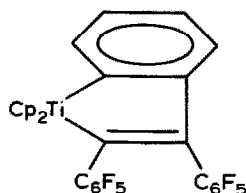
(VI)



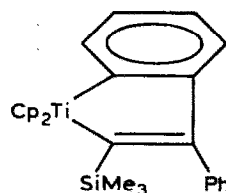
(VII)



(VIII)



(IX)



(X)

The Ti–O bond in III (1.830(2) Å) is substantially shorter than the corresponding bonds in V–VII (1.92, 1.91 and 1.95 Å, respectively); its length is close to the Ti–O bond lengths in the acyclic titanium derivatives $Cp_2Ti(OEt)Cl$ (XI) (1.855 and 1.85 Å) [12] and II (1.86 Å) [2]. An even shorter Ti–O distance than that in III has recently been found in a binuclear pinacol complex, $CpCl_2Ti(OCMe_2CMe_2O)-TiCl_2Cp$ (1.75 Å) [12].

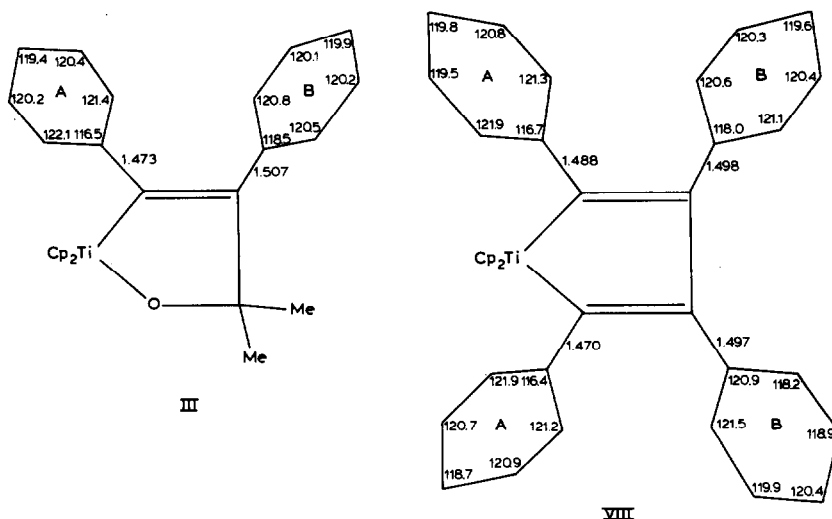
The Ti–C(sp^2) endocyclic bond length in III (2.190(4) Å) is within the range of values (2.13–2.22 Å) characteristic of the corresponding bonds in metallacycles V and VII–X; slightly longer Ti–C(sp^2) bonds are found in acyclic complexes of titanium: 2.27 Å in Cp_2TiPh_2 [13], 2.25 and 2.26 Å in II [2].

An interesting structural feature of titanium complexes with five-membered metallacycles is the significant distortion of the bond angles at the sp^2 -hybridized carbon atom bound to the metal atom. This feature is likely to be the most clearly pronounced in complex III: here, the endocyclic bond angle $Ti(1)C(5)C(4)$ is decreased to $110.1(3)^\circ$, whereas the endocyclic angle $C(3)C(4)C(5)$ at the other sp^2 -hybridized carbon atom of the metallacycle has the almost ideal value of $118.9(4)^\circ$. The difference in the exocyclic angles $Ti(1)C(5)C(14)$ ($128.5(3)^\circ$) and $C(14)C(5)C(4)$ ($121.4(4)^\circ$) is probably due to the repulsion of the phenyl ring A (see Fig. 1) from the cyclopentadienyl ligands (the shortest contacts are $C(14)\cdots C(24)$ $3.459(7)$, $C(14)\cdots C(25)$ $3.449(7)$, $C(15)\cdots C(25)$ $3.371(7)$, $C(19)\cdots C(24)$ $3.477(7)$ Å). Steric hindrance in the molecule also causes a small but significant ($0.093(4)$ Å) displacement of the $C(14)$ atom from the $O(2)C(3)C(4)C(5)$ plane towards the side opposite to the displacement of the Ti atom from this plane. The *ipso*-atom $C(8)$ of the second Ph-ring (**B**) in fact lies in the above-mentioned plane, its displacement being only $0.013(5)$ Å.

The difference between the exocyclic bond lengths $C(5)-C(14)$ ($1.473(6)$ Å) and $C(4)-C(8)$ ($1.507(6)$ Å), although small, still exceeds the experimental errors noticeably. This difference cannot be attributed to a different degree of π -conjugation of the phenyl rings with the $C(4)=C(5)$ double bond, since the planes of the Ph substituents form dihedral angles close to 90° (97.6 and 103.5° for cycles **A** and **B**, respectively) with the double-bond plane and, hence, in both cases the possibility of conjugation can be practically excluded. It should be noted that a similar, although less considerable, difference in the $C_{cycl}-C_{Ph}$ distances is also observed in the rather accurately determined structure of VIII, where both $C_{cycl}-C_{Ph}$ bonds involving metal-bonded atoms C_{cycl} are slightly shorter (1.470 and 1.488 Å) than the other two $C_{cycl}-C_{Ph}$ bonds (1.497 and 1.498 Å).

The nature of these differences in the $C_{cycl}-C_{Ph}$ bond length may become clearer if the distortions of the bond angles in the phenyl rings are taken into account. In III and VIII (see Scheme 1; the angles in the Ph rings of VIII were calculated from the atomic coordinates given in [9]), the bond angle in the ring at the *ipso*-atom $C(14)$ of phenyl ring **A** is decreased more significantly than the corresponding angle in the ring at $C(8)$ of phenyl ring **B**; the angles in the Ph rings at the C atoms adjacent to the *ipso*-atoms in ring **A** are also distorted slightly more than those in ring **B**. The relationship of the geometric distortions of a benzene ring with the electronic effects of substituents has been discussed in a number of papers [14,15]. As pointed out, for example, in [14], these distortions may be explained on the basis of Bent's concepts of bond rehybridization [16]. Thus, the bond between an *ipso*-atom of a benzene ring and an electron-donating substituent has a more pronounced *s*-character, while endocyclic bonds of this atom are characterized by a greater contribution of the *p*-component as compared to ideal sp^2 -hybridization. Consequently, the decrease of the endocyclic bond angle at the *ipso*-atom of ring **A** compared with the corresponding bond angle in ring **B**, as well as some shortening of the $C(5)-C(14)$ bond in comparison with the $C(4)-C(8)$ bond, may indicate that the $C(5)$ atom bound to the Ti atom exhibits a stronger electron-donating capacity than $C(4)$.

The geometry of the bent $(\eta^5-C_5H_5)_2Ti$ sandwich in III is not exceptional. As in XI [12] and in other biscyclopentadienyl titanium derivatives, variations of the $Ti-C(Cp)$ distance in complex III ($2.384-2.447$ Å) exceed the experimental errors considerably. The planes of the cyclopentadienyl rings form a dihedral angle of



Scheme 1

132.7°; the relative orientation of the rings is almost exactly eclipsed (e.g. the torsion angle C(20)–Cp¹–Cp²–C(26) * is –6.1°).

As in other bent sandwich complexes, the C(5)Ti(1)O(2) plane of the σ -ligands in III bisects the dihedral angle formed by the planes of the Cp rings. The C(5)Ti(1)O(2) bond angle in the five-membered metallacycle is considerably decreased (to 78.7(1)°) compared to the corresponding angles usually observed in wedge-like acyclic complexes with d^0 -configuration of the metal (94–97° [17,18]). An analogous decrease of the angle formed by the σ -bonds of the Ti atom (to 77–82°) has been observed in all the above-mentioned metallacyclic derivatives V–X.

Experimental

The reactions were conducted under Ar, with careful exclusion of atmospheric oxygen and moisture. The solvents were purified by conventional methods and distilled before use over sodium and lithium aluminium hydride (THF), or over sodium and calcium hydride (benzene, hexane) under argon. ¹H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200.13 MHz) in CS₂. Mass spectra were taken on an AEI MS-30 instrument.

Synthesis of complex III

1 g (4.02 mmol) of Cp₂TiCl₂, 0.1 g (4.1 mmol) of finely shaved magnesium and 0.72 g (4.04 mmol) of toluene in 35–40 ml of THF were stirred at room temperature under Ar for 3–3.5 h. To the resulting red-brown solution of I, 0.30 ml (4.1 mmol) of dry acetone was added and, after stirring at room temperature for 1 h, the cherry-red reaction mixture was evaporated to dryness in vacuum. The brown residue was dissolved in 25 ml of benzene at 50°C, and the benzene solution was filtered and

* Cp¹ and Cp² are the centroids of the Cp rings C(20)–C(24) and C(25)–C(29), respectively.

treated with 25 ml of hexane. The light-pink precipitate (1.19 g) was filtered-off, washed with 10 ml of hexane, and dried in vacuum. The filtered solution was placed in a refrigerator. After several days, 0.23 g of red crystalline complex III had formed in the solution. The light-pink product was dissolved in 20 ml of benzene at 50°C and separated from the undissolved residue. To the resulting cherry-red solution, 30 ml of hexane was added dropwise very slowly. After 1 day, a large amount of fine red crystals of III had formed in the solution. The solution was decanted, the crystals were washed with hexane and dried to give an additional 0.25 g of III. The mother liquors after separation of crystals of III were evaporated in vacuum and the residue was recrystallized in a similar manner from benzene/hexane. This gave an additional 0.19 g of III. The total yield of III was 0.67 g (40.5%). Final purification of III was carried out from THF/hexane and benzene/hexane mixtures. M.p. 238–240°C (dec.) under Ar. Found: C, 78.32; H, 6.30; Ti, 11.68. $C_{27}H_{26}OTi$ calcd.: C, 78.25; H, 6.32; Ti, 11.56%. For 1H NMR and mass spectral data, see Results and discussion.

Synthesis of complex IV

To a red-brown solution of I obtained as described above from 1 g of Cp_2TiCl_2 , 0.1 g of Mg and 0.72 g of toluene in 40 ml of THF, 0.40 ml (4.0 mmol) of freshly distilled benzaldehyde was added. The red colour of the solution deepened noticeably. The reaction mixture was stirred for 1 h at room temperature and was evaporated in vacuum. The residue was dissolved in 15 ml of benzene and filtered off. The benzene solution was treated with 70 ml of hexane, separated from the brown precipitate, and allowed to stand under Ar at room temperature. After 1 day, dark red crystals of IV covered by a light dingy-yellow precipitate had formed in the filtrate. The dingy-yellow precipitate was stirred up and carefully decanted together with the solution. The crystals of IV were washed with hexane and dried in vacuum. Yield 0.58 g (31.4%). Additional purification of IV was performed from a benzene/hexane mixture. M.p. 177–178°C (dec.) under Ar. Found: C, 80.33; H, 5.55; Ti, 10.33. $C_{31}H_{26}OTi$ calcd.: C, 80.51; H, 5.67; Ti, 10.36%. For 1H NMR and mass spectral data, see Results and discussion.

X-Ray structural analysis of III

Crystals of III are monoclinic: a 13.392(9), b 9.696(4), c 16.584(7) Å, β 104.81(4) $^\circ$, d_{calc} 1.322 g cm $^{-3}$ (at $-120^\circ C$), space group Cc , $Z = 4$. The unit cell parameters and intensities of 1882 reflections with $F^2 \geq 4\sigma$ were measured on a four-circle automatic Syntex P2 $_1$ diffractometer ($-120^\circ C$, $\lambda Mo-K_\alpha$, $\theta/2\theta$ scan, graphite monochromator, $\theta \leq 28^\circ$).

The structure was solved by the direct method using the MULTAN program. The Ti atom and the O and C atoms σ -bonded to it were located in the E -map. All other non-hydrogen atoms were found from subsequent synthesis of electron density. The structure was refined by the full-matrix least-squares technique, first in an isotropic and then in an anisotropic approximation. All H atoms were located in the difference Fourier synthesis and included in the refinement in the isotropic approximation. The final R factor was 0.0388; the weighted R_w factor was 0.0443. All calculations were performed with an Eclipse S/200 computer using the INEXTL program package [19]. The atomic coordinates are listed in Table 1; bond lengths and main bond angles are given in Tables 2 and 3, respectively.

TABLE 1
 ATOMIC COORDINATES ($\times 10^4$), for $\text{Ti} \times 10^3$, for $\text{H} \times 10^3$, AND THEIR TEMPERATURE FACTORS (isotropic for H atoms; equivalent isotropic a for non-hydrogen atoms)

Atom	X	Y	Z	B (\AA^2)	Atom	X	Y	Z	B (\AA^2)
Ti(1) ^b	0	18781(7)	0	1.45(1)	C(29)	-1345(4)	2869(6)	-1138(3)	2.8(1)
O(2)	255(2)	1724(3)	1134(2)	1.64(7)	H(61)	-30(4)	101(5)	248(3)	2(1)
C(3)	442(3)	469(4)	1606(3)	1.5(1)	H(62)	-106(3)	29(5)	168(3)	1.3(9)
C(4)	325(3)	-686(4)	965(3)	1.39(9)	H(63)	-36(4)	-54(6)	240(3)	3(1)
C(5)	52(4)	-365(4)	157(3)	1.5(1)	H(71)	169(3)	-24(5)	255(3)	1.3(8)
C(6)	-395(4)	323(5)	2084(3)	2.1(1)	H(72)	212(5)	70(7)	196(4)	4(1)
C(7)	1507(3)	561(5)	2207(3)	2.0(1)	H(73)	151(4)	129(5)	256(3)	2(1)
C(8)	469(3)	-2149(4)	1280(2)	1.7(1)	H(9)	-105(4)	-272(5)	93(3)	2(1)
C(9)	-393(4)	-2983(5)	1229(3)	2.2(1)	H(10)	-80(4)	-489(5)	142(3)	2(1)
C(10)	-280(4)	-4360(5)	1485(3)	2.8(1)	H(11)	87(5)	-583(7)	203(4)	6(2)
C(11)	684(5)	-4907(5)	1789(3)	2.8(1)	H(12)	219(4)	-440(5)	213(3)	2(1)
C(12)	1548(4)	-4089(5)	1853(3)	2.8(1)	H(13)	202(4)	-219(5)	166(3)	2(1)
C(13)	1438(4)	-2715(5)	1591(3)	2.1(1)	H(15)	-167(3)	-157(5)	-75(3)	1.1(9)
C(14)	-153(3)	-1441(4)	-491(2)	1.44(9)	H(16)	-195(4)	-321(6)	-172(3)	3(1)
C(15)	-1145(3)	-1922(5)	-856(3)	1.8(1)	H(17)	-69(4)	-424(5)	-209(3)	2(1)
C(16)	-1330(3)	-2977(5)	-1436(3)	2.0(1)	H(18)	106(4)	-354(6)	-147(3)	3(1)
C(17)	-515(4)	-3595(5)	-1674(3)	2.2(1)	H(19)	137(3)	-191(4)	-44(3)	1.2(9)
C(18)	477(3)	-3149(5)	-1326(3)	2.0(1)	H(20)	221(4)	75(6)	44(3)	3(1)
C(19)	662(3)	-2083(4)	-747(3)	1.8(1)	H(21)	200(3)	300(4)	86(3)	1.0(8)
C(20)	1810(3)	1442(5)	54(3)	2.1(1)	H(22)	88(5)	452(7)	-33(4)	5(2)
C(21)	1734(3)	2795(5)	341(3)	2.5(1)	H(23)	49(4)	286(5)	-160(3)	3(1)
C(22)	1155(4)	3562(5)	-311(4)	3.2(2)	H(24)	120(4)	57(5)	-117(3)	2(1)
C(23)	889(4)	2715(6)	-1022(4)	3.2(1)	H(25)	-175(4)	76(6)	-147(3)	4(1)
C(24)	1284(4)	1394(5)	-780(3)	2.5(1)	H(26)	-203(4)	54(5)	-6(3)	3(1)
C(25)	-1627(4)	1491(5)	-1038(3)	2.8(1)	H(27)	-146(3)	274(5)	77(3)	1.6(9)
C(26)	-1795(3)	1387(5)	-234(3)	2.4(1)	H(28)	-112(4)	455(6)	-23(4)	4(1)
C(27)	-1632(4)	2660(5)	153(3)	2.5(1)	H(29)	-132(5)	314(7)	-168(4)	5(2)
C(28)	-1308(4)	3592(5)	-397(3)	2.6(1)					

^a Equivalent isotropic temperature factors $B_{\text{iso}}^{\text{equiv}} = 1/3 \sum_i \sum_j B_{ij} (\bar{a}_i \bar{a}_j) a_i^* a_j^*$. ^b The X and Z coordinates of the Ti(1) atom fix the origin.

TABLE 2
BOND LENGTHS, d (Å), IN THE MOLECULE OF III

Bond	d	Bond	d	Bond	d
Ti(1)–O(2)	1.830(2)	C(7)–H(72)	1.01(6)	C(18)–H(18)	0.95(6)
Ti(1)–C(5)	2.190(4)	C(7)–H(73)	0.92(5)	C(19)–H(19)	0.97(4)
Ti(1)–C(20)	2.440(5)	C(8)–C(9)	1.394(7)	C(20)–C(21)	1.409(7)
Ti(1)–C(21)	2.414(5)	C(8)–C(13)	1.383(7)	C(20)–C(24)	1.383(7)
Ti(1)–C(22)	2.395(6)	C(9)–C(10)	1.398(7)	C(20)–H(20)	0.98(6)
Ti(1)–C(23)	2.446(6)	C(9)–H(9)	0.93(5)	C(21)–C(22)	1.377(8)
Ti(1)–C(24)	2.447(5)	C(10)–C(11)	1.367(8)	C(21)–H(21)	0.87(4)
Ti(1)–C(25)	2.436(5)	C(10)–H(10)	0.85(5)	C(22)–C(23)	1.405(9)
Ti(1)–C(26)	2.384(5)	C(11)–C(12)	1.384(8)	C(22)–H(22)	0.99(6)
Ti(1)–C(27)	2.387(5)	C(11)–H(11)	0.98(7)	C(23)–C(24)	1.405(8)
Ti(1)–C(28)	2.382(5)	C(12)–C(13)	1.397(7)	C(23)–H(23)	0.99(5)
Ti(1)–C(29)	2.448(5)	C(12)–H(12)	0.92(5)	C(24)–H(24)	1.02(5)
O(2)–C(3)	1.434(5)	C(13)–H(13)	0.92(5)	C(25)–C(26)	1.412(7)
C(3)–C(4)	1.525(6)	C(14)–C(15)	1.393(6)	C(25)–C(29)	1.409(8)
C(3)–C(6)	1.535(7)	C(14)–C(19)	1.412(6)	C(25)–H(25)	1.00(6)
C(3)–C(7)	1.520(6)	C(15)–C(16)	1.382(6)	C(26)–C(27)	1.383(7)
C(4)–C(5)	1.332(6)	C(15)–H(15)	0.84(5)	C(26)–H(26)	0.94(5)
C(4)–C(8)	1.507(6)	C(16)–C(17)	1.388(7)	C(27)–C(28)	1.428(7)
C(5)–C(14)	1.473(6)	C(16)–H(16)	0.88(6)	C(27)–H(27)	0.99(5)
C(6)–H(61)	0.92(5)	C(17)–C(18)	1.376(7)	C(28)–C(29)	1.406(8)
C(6)–H(62)	0.97(4)	C(17)–H(17)	0.92(5)	C(28)–H(28)	0.99(6)
C(6)–H(63)	0.99(6)	C(18)–C(19)	1.390(6)	C(29)–H(29)	0.95(7)
C(7)–H(71)	0.96(4)				

TABLE 3
MAIN BOND ANGLES, ω (°), IN THE MOLECULE OF III

Angle	ω	Angle	ω	Angle	ω
O(2)Ti(1)C(5)	78.7(1)	C(4)C(8)C(9)	119.7(4)	C(16)C(17)C(18)	119.4(4)
Ti(1)O(2)C(3)	126.3(3)	C(4)C(8)C(13)	121.8(4)	C(17)C(18)C(19)	120.4(4)
O(2)C(3)C(4)	105.6(3)	C(9)C(8)C(13)	118.5(4)	C(14)C(19)C(18)	121.4(4)
O(2)C(3)C(6)	108.1(3)	C(8)C(9)C(10)	120.8(4)	C(21)C(20)C(24)	107.9(4)
O(2)C(3)C(7)	108.2(3)	C(9)C(10)C(11)	120.1(5)	C(20)C(21)C(22)	108.2(5)
C(4)C(3)C(6)	109.5(3)	C(10)C(11)C(12)	119.9(5)	C(21)C(22)C(23)	108.3(5)
C(4)C(3)C(7)	114.3(4)	C(11)C(12)C(13)	120.2(5)	C(22)C(23)C(24)	107.3(5)
C(6)C(3)C(7)	110.7(4)	C(8)C(13)C(12)	120.5(4)	C(20)C(24)C(23)	108.3(5)
C(3)C(4)C(5)	118.9(4)	C(5)C(14)C(15)	122.2(4)	C(26)C(25)C(29)	106.9(5)
C(3)C(4)C(8)	117.9(3)	C(5)C(14)C(19)	121.2(4)	C(25)C(26)C(27)	109.3(5)
C(5)C(4)C(8)	123.2(4)	C(15)C(14)C(19)	116.5(4)	C(26)C(27)C(28)	107.9(5)
Ti(1)C(5)C(4)	110.1(3)	C(14)C(15)C(16)	122.1(4)	C(27)C(28)C(29)	107.1(5)
Ti(1)C(5)C(14)	128.5(3)	C(15)C(16)C(17)	120.2(4)	C(25)C(29)C(28)	108.7(5)
C(4)C(5)C(14)	121.4(4)				

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