

17 β -Acetoxy-16 α -²H-5 α ,14 α -androstan (24). Smp.: 76°. – NMR.: 0,80/s, CH₃(18), CH₃(19); 2,05/s, 17-OCOCH₃; 4,57/d, J_{16,17} = 6, CH(17). – IR.: 2930, 2860, 2195, 1725, 1450, 1375, 1260, 1030. – MS.: 3% d₀, 97% d₁.

17 α -Acetoxy-16-²H-5 α ,14 α -androstan (19). Smp.: 97°. – NMR.: 0,74/s, 0,80/s, CH₃(18), CH₃(19); 2,05/s, 17-OCOCH₃; 4,79/s, CH(17). – IR.: 2930, 2860, 2195, 2150, 1725, 1450, 1375, 1260, 1030. – MS.: 2% d₁, 98% d₂.

17 β -Acetoxy-16-²H-5 α ,14 α -androstan (15). Smp.: 76°. – NMR.: 0,79/s, 0,80/s, CH₃(18), CH₃(19); 2,05/s, 17-OCOCH₃; 4,60/s, CH(17). – IR.: 2930, 2860, 2210, 2130, 1725, 1450, 1375, 1260, 1030. – MS.: 2% d₁, 98% d₂.

17 β -Acetoxy-17 α -²H-5 α ,14 α -androstan (28). Smp.: 76°. – NMR.: 0,79/s, 0,80/s, CH₃(18), CH₃(19); 2,05/s, 17-OCOCH₃. – IR.: 2930, 2860, 2170, 1730, 1450, 1375, 1030. – MS.: 1% d₀, 99% d₁.

Diese Arbeit wurde vom Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung unterstützt.

LITERATURVERZEICHNIS

- [1] W. Benz & K. Biemann, J. Amer. chem. Soc. 86, 2375 (1964).
- [2] C. Djerassi & W. S. Briggs, J. org. Chemistry 33, 1612 (1968).
- [3] C. G. McDonald, J. S. Shannon & G. Sugowdz, Tetrahedron Letters 1963, 807.
- [4] R. Robbiani & J. Seibl, Org. Mass. Spectrom. 7, 1153 (1973).
- [5] K. Biemann & J. Seibl, J. Amer. chem. Soc. 81, 3149 (1959).
- [6] J. L. Courtney & J. S. Shannon, Tetrahedron Letters 1963, 13.
- [7] A. N. H. Yeo, R. G. Cooks & D. H. Williams, Chem. Commun. 1969, 1269.
- [8] K. Meier & J. Seibl, Int. J. Mass. Spectrom. Ion. Phys., im Druck.
- [9] E. Tajima & J. Seibl, Int. J. Mass. Spectrom. Ion. Phys. 3, 245 (1969).
- [10] F. W. McLafferty, Chem. Commun., 1966, 78.
- [11] C. Djerassi, M. Fischer & J. B. Thomson; Chem. Commun., 1966, 12.
- [12] F. W. McLafferty & M. M. Bursey, Chem. Commun., 1967, 533.
- [13] M. Kraft & G. Spiteller, Chem. Commun., 1967, 943.
- [14] H. Budzikiewicz & F. G. v. D. Haar, Org. Mass. Spectrom. 1, 323 (1968).
- [15] T. Nambara, M. Usui & H. Hosoda, Chem. Pharm. Bull. 17, 1611 (1969).
- [16] L. Cagliotti, Tetrahedron 22, 487 (1966).

76. Studies of Organometallic Compounds XV¹⁾ The Crystal Structure of Bis(tribenzyl-titanium(IV))- μ -oxo

by Helen Stoeckli-Evans

Institut de Chimie, Université de Neuchâtel, Switzerland

(13. II. 74)

Summary. The crystal and molecular structure of bis(tribenzyl-titanium(IV))- μ -oxo, [(PhCH₂)₃-Ti]₂O, has been determined from analysis of X-ray photographic data. The crystal system is rhombohedral, $a = 9.58(2)$ Å, $\alpha = 83.6(2)^\circ$, space group $R\bar{3}$, $Z = 1$.

1. Introduction. – Interest in tetra-alkyl and tetra-aryl compounds of titanium has developed owing to their catalytic properties in the polymerization of ethylene [1] and α -olefins [2] [3]. Tetrabenzyl-titanium (PhCH₂)₄Ti, has been prepared in several

¹⁾ A series of studies of organometallic compounds pursued under the direction of Prof. A. Jacot-Guillarmod, in the same institute.

ways [4–6]. Two crystal structure analyses of this compound, one at room temperature [7] and the other at -40° [8], have revealed a distorted tetrahedral coordination of the titanium atom.

In part XII [9] of this series, it was suggested that the product of the reaction between $\text{TiCl}_4 \cdot 2\text{pyridine}$ and PhCH_2MgCl in diethyl ether was an ether adduct of $(\text{PhCH}_2)_4\text{Ti}$, thought to be stable in boiling ether [10]. On refluxing the reaction mixture dark orange crystals were left on the walls of the reaction vessel. The present analysis establishes the structure to be bis(tribenzyl-titanium(IV))- μ -oxo, $[(\text{PhCH}_2)_3\text{Ti}]_2\text{O}$.

Later, the same compound was prepared again by refluxing $(\text{PhCH}_2)_4\text{Ti}$ (prepared in pentane [4]) in diethyl ether. Further investigations of this reaction, which involves oxygen abstraction from ether, are in progress [11].

2. Experimental Part. – The crystals were dark orange and of rectangular shape. No molecular weight or precise molecular formula were available. Owing to the sensitivity to oxygen and moisture, no density determination could be made. For the X-ray analysis the crystals were sealed in *Lindemann* glass capillaries under nitrogen.

Preliminary oscillation, *Weissenberg* and precession photographs indicated a C-centred triclinic cell:

$$a_{\text{T}} = 14.27(3), b_{\text{T}} = 12.77(2), c_{\text{T}} = 9.55(3) \text{ \AA},$$

$$\alpha_{\text{T}} = \gamma_{\text{T}} = 90^\circ, \beta_{\text{T}} = 98.3(2)^\circ, V_{\text{T}} = 1757.8 \text{ \AA}^3,$$

Space group C1 or C1.

The transformation $a_{\text{R}} = \frac{1}{2}(a_{\text{T}} + b_{\text{T}})$, $b_{\text{R}} = \frac{1}{2}(a_{\text{T}} - b_{\text{T}})$, $c_{\text{R}} = -c_{\text{T}}$ leads to a rhombohedral cell ($a_{\text{R}} = 9.58(2) \text{ \AA}$, $\alpha_{\text{R}} = 83.6(2)^\circ$, $Z = 1$), as later verified directly when a new crystal preparation became available.

Owing to practical difficulties, however, the initial crystal, oriented with $[110]_{\text{R}}$ as rotation axis, could not be re-orientated, and the data were therefore collected in the triclinic setting. The layers $(h0l)_{\text{T}}$ to $(h11)_{\text{T}}$ were recorded by the equi-inclination *Weissenberg* method, using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), on multiple film packs. Intensities were estimated visually by comparison with a standard calibration strip. A total of 2779 reflections were measured and corrected for *Lorentz*-polarization effects, to give relative F_o -values; 2234 reflections had $F_o \geq 2.5$ and were taken as observed.

3. Structure Analysis and Refinement. – The relative F_o -values were put on an absolute scale by *Wilson's* method. The E distribution indicated a centrosymmetric space group. A three-dimensional *Patterson* synthesis revealed a dominant peak in the section $y_{\text{T}} = 0$ at a distance of 3.6 \AA from the origin. If this peak is identified as a Ti-Ti vector, then the molecule must be binuclear with a centre of inversion at the origin. A F_o -synthesis phased on the Ti atom coordinates ($R = 43\%$) revealed three benzyl groups attached to each Ti atom. A peak at the origin, $1.0 - 1.6 \text{ e.\AA}^{-3}$, higher than the peaks of the benzyl groups, was taken to be an oxygen atom, leading to a bis(tribenzyl-titanium(IV))- μ -oxo structure, with a linear Ti-O-Ti bridge.

After four rounds of block-diagonal least-squares (BDLS), with isotropic vibrational parameters and unit weights, R was 16%. The $(F_o - F_c)$ -synthesis indicated no further atomic positions. Refinement was continued, using isotropic full-matrix least-squares (FMLS) with unit weights and including refinement of layer scales. After six such rounds R was 12%.

At this stage a new preparation of crystals became available, and the rhombohedral symmetry of the crystals was confirmed from new precession photographs.

The reflections were re-indexed in terms of the rhombohedral cell, and intensities of symmetry-equivalent reflections averaged, leading to 841 'observed' reflections with $F_o \geq 2.5$. In the rhombohedral coordinate system, the oxygen atom is located at (0,0,0), and the Ti atom is on the three-fold axis.

After one round of FMLS refinement with unit weights, R was 13.7%. Two further rounds of BDLS with anisotropic vibrational parameters reduced R to 12.6%. All the hydrogen atoms could now be located in a $(F_o - F_c)$ -synthesis. In the final BDLS cycles they were included at calculated positions with $B = 3.5 \text{ \AA}^2$, but not refined. Between each round, new hydrogen positions were calculated. Refinement

Table 1. *Final positional parameters* (estimated standard deviations $\times 10^4$ in parentheses)

Atom	x/a	y/b	z/c
Ti	0.0983(0)	0.0983(0)	0.0983(0)
O	0	0	0
C(1)	-0.1371(8)	0.3258(8)	0.1328(8)
C(2)	-0.2255(9)	0.3381(9)	0.0218(9)
C(3)	-0.3714(10)	0.3534(10)	0.0488(10)
C(4)	-0.4351(10)	0.3547(9)	0.1841(10)
C(5)	-0.3492(10)	0.3375(9)	0.2972(9)
C(6)	-0.2024(10)	0.3254(9)	0.2685(9)
C(7)	0.0168(10)	0.3077(10)	0.1035(10)

Table 2. *Anisotropic vibrational parameters, expressed in the form $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot hk + 2\beta_{13} \cdot hl + 2\beta_{23} \cdot kl)]$*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.0082	0.0082	0.0082	-0.0007	-0.0007	-0.0007
O	0.0115	0.0115	0.0115	-0.0010	-0.0010	-0.0010
C(1)	0.0113	0.0077	0.0090	-0.0006	0.0002	-0.0008
C(2)	0.0134	0.0098	0.0094	0.0004	-0.0012	0.0003
C(3)	0.0148	0.0120	0.0124	0.0010	-0.0038	-0.0001
C(4)	0.0162	0.0101	0.0134	-0.0012	0.0000	-0.0012
C(5)	0.0162	0.0108	0.0101	-0.0011	0.0008	-0.0025
C(6)	0.0132	0.0107	0.0121	-0.0006	-0.0034	-0.0018
C(7)	0.0129	0.0133	0.0146	-0.0017	0.0012	-0.0014

Table 3. *Calculated positional parameters for the hydrogen atoms*

Atom	x/a	y/b	z/c
H(2)	-0.1787	0.3353	-0.0856
H(3)	-0.4358	0.3644	-0.0379
H(4)	-0.5484	0.3687	0.2037
H(5)	-0.3969	0.3340	0.4046
H(6)	-0.1383	0.3152	0.3554
H(71)	0.0457	0.3646	0.0030
H(72)	0.0631	0.3525	0.1840

Hydrogen atoms were calculated at their respective trigonal and tetrahedral positions at a distance C-H = 1.075 Å to a given atomic position, with two other atoms fixing the orientation of the group.

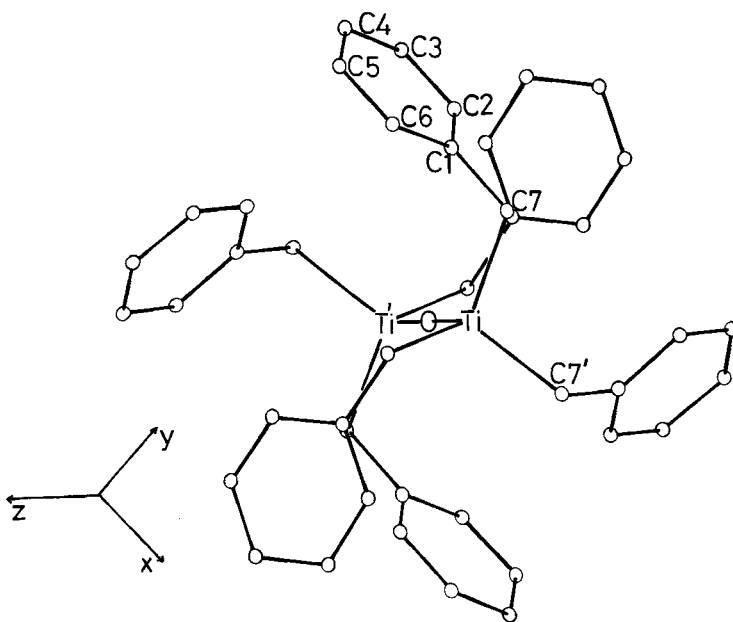


Figure 1. *Projection of the molecule on the (121) plane*

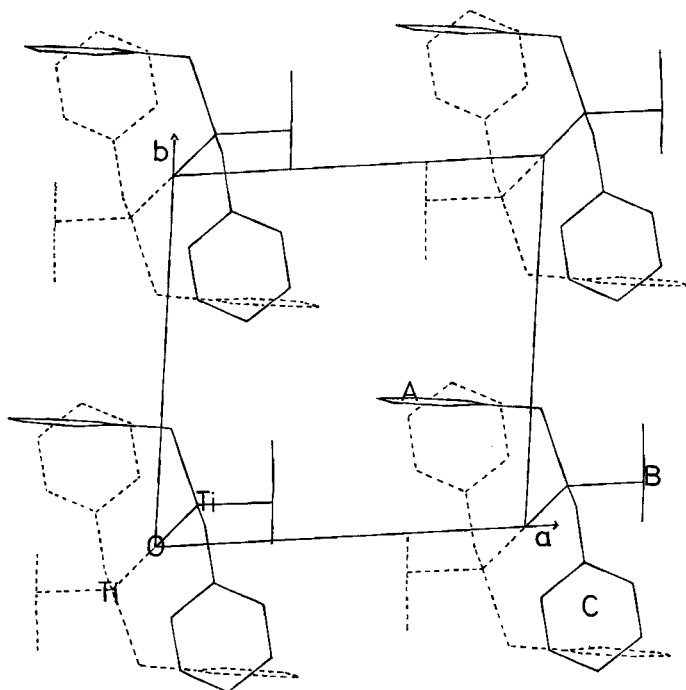


Figure 2. *Projection of the structure on the (001) plane, the part of the molecule marked --- is below the plane of the paper, and the part marked — is above*

was terminated when the majority of parameters shifts were less than 0.4 e.s.d., with a final R value of 11.2%. Unit weights were used throughout, as seemed justified by the uniform distribution of the quantity $\langle w(F_o - F_c)^2 \rangle$. Final positional and vibrational parameters are given in Tables 1 and 2. Table 3 gives the calculated hydrogen positions. Observed and calculated structure factors may be obtained in tabular form from the author.

4. Results and Discussion. – The atomic labelling system used is illustrated in Fig. 1. The molecule has $\bar{3}$ (S_6) symmetry. Interatomic distances and angles are given in Tables 4 and 5.

Table 4. *Bond lengths* (Å) with estimated standard deviations $\times 10^3$ in parentheses

Ti...C(7)	2.979(7)		
Ti–O	1.798(0)	C(3)–C(4)	1.372(13)
Ti–C(7)	2.076(9)	C(4)–C(5)	1.415(15)
C(1)–C(2)	1.417(12)	C(5)–C(6)	1.398(13)
C(2)–C(3)	1.388(13)	C(6)–C(1)	1.379(11)

Table 5. *Bond angles* (degrees) with estimated standard deviations $\times 10$ in parentheses

Ti–O–Ti	180.0(0)	C(6)–C(1)–C(2)	117.1(3)
O–Ti–C(7)	113.0(1)	C(1)–C(2)–C(3)	121.2(0)
C(7)–Ti–C(7')	105.7(1)	C(2)–C(3)–C(4)	121.2(4)
Ti–C(7)–C(1)	113.4(4)	C(3)–C(4)–C(5)	118.7(5)
C(7)–C(1)–C(2)	120.8(2)	C(4)–C(5)–C(6)	119.5(3)
C(7)–C(1)–C(6)	122.1(1)	C(5)–C(6)–C(1)	122.2(2)

The benzyl group is planar (Table 6), the planes of groups related by the three-fold axis (A, B, C, Fig. 2) being nearly perpendicular (92.7°) to one another.

Table 6. *Least-squares plane of benzyl group*

Equation of plane for atoms C(1)–C(7); $0.108x + 0.992y - 0.061z - 3.016 = 0$. Deviation in Å: C(1), 0.018; C(2), -0.008 ; C(3), -0.005 ; C(4), 0.008; C(5), -0.016 ; C(6), 0.008; C(7), -0.009

The linear Ti–O–Ti bridge present in this compound is also found in the binuclear complex $(C_5H_5TiCl_2)_2O$ [12]. The distance Ti–O (1.80 Å) is short, compared with 1.95 and 1.99 Å in rutile [15], but long compared with 1.73 Å in the complex mentioned above [12]. In a binuclear acetylacetonate complex of octahedrally coordinated Ti(IV) [13], the Ti–O distances were 1.79 and 1.81 Å, with a bridging angle of 167.5° . In a chelated binuclear peroxy compound of seven-fold coordinated Ti(IV) [14], the Ti–O distances were both 1.825 Å with a bridging angle of 178.1° .

The O–Ti–CH₂ angles (113.0°) are larger than the CH₂–Ti–CH₂ angles (105.7°). This reflects the influence of the benzyl groups on the packing in the crystal. The two halves of the molecule are in a staggered arrangement with the benzyl groups folding inwards and towards one another. To minimise the repulsion energy between the benzyl groups there is an opening of the O–Ti–CH₂ angle (from the normal tetrahedral value of 109°) which results in a closing of the CH₂–Ti–CH₂ angle. The Ti–CH₂–C _{β} angles are 113.4° , which is normal for a σ -bonded arrangement. The Ti–CH₂ distance is 2.08 Å, the same, within experimental error, as in $(PhCH_2)_4Ti$ (Table 7). All C–C

bond lengths and C–C–C bond angles are close to average values observed in other compounds containing similar groups.

Table 7. Comparison of some distances and angles in $[(PhCH_2)_3Ti]_2O$ and $(PhCH_2)_4Ti$

	$[(PhCH_2)_3Ti]_2O$	ref. [7]	$(PhCH_2)_4Ti$	ref. [8]
O–Ti–CH ₂ (°)	113.0(1)			
CH ₂ –Ti–CH ₂ (°)	105.7(1)	123, 118, 102, 106, 100, 107	104, 105, 105, 109, 115, 119	
Ti–CH ₂ –C _β (°)	113.4(4)	88, 116, 98, 107	92, 98, 109, 115	
Ti–CH ₂ (Å, mean)	2.08(1)	2.14(4)	2.13(4)	
Ti...C _β (Å)	2.98(1)	2.61, 3.16, 2.81, 2.95	not given	
Torsion angle (°)				
O–Ti–CH ₂ –C _β	44.9			
C–Ti–CH ₂ –C _β		not given	–2, 40, –52, –52	

Table 7 compares bond distances and angles for the title compound and $(PhCH_2)_4Ti$ [7] [8]. In the title compound the distance Ti...C_β is 2.98 Å, the Ti–CH₂–C_β angle is 113.4°. In $(PhCH_2)_4Ti$ two distinct sets of distances and angles are found: two short distances (2.6 and 2.8 Å) with angles of 88° and 98°, and two longer distances (2.9 and 3.2 Å) with angles of 116° and 107°. The shorter distances and smaller angles were ascribed to interaction between filled π -orbitals of the benzene rings and empty orbitals of the Ti atom [7].

It should be pointed out that only two tetrahedrally coordinated binuclear Ti(IV) compounds with linear Ti–O–Ti bridges are known so far: the title compound and $(C_5H_5TiCl_2)_2O$ [12]. Most other Ti(IV) binuclear compounds with linear or non-linear Ti–O–Ti bridges involve the Ti atom in seven- or eight-fold coordination.

We wish to thank Prof. A. Jacot-Guillarmod for suggesting the problem and Mr. D. Roulet for supplying the crystals; Prof. J. D. Dunitz and Dr. P. Murray-Rust (ETH Zurich) for stimulating discussions; Prof. M. Truter (Rothamsted Experimental Station, London) for supplying the set of crystallographic programs XRAC (IBM 1130), and finally the *Fonds national suisse de la recherche scientifique* for financial support.

REFERENCES

- [1] U. Giannini & U. Zucchini, Chem. Commun. 1968, 940.
- [2] G. Natta, P. Pino, G. Mazzanti & R. Lanzo, Chimica e Industria 39, 1032 (1957).
- [3] C. Beermann & H. Bastine, Angew. Chem. 71, 618 (1959).
- [4] A. Jacot-Guillarmod, R. Tabacchi & J. Porret, Helv. 53, 1494 (1970).
- [5] K. S. Boustany, K. Bernhauer & A. Jacot-Guillarmod, Helv. 50, 1080, 1305 (1967).
- [6] P. Zdzunneck & K.-H. Thiele, J. Organometal. Chemistry 22, 695 (1970).
- [7] I. W. Bassi, G. Allegra, R. Scordamaglia & G. Chioccola, J. Am. chem. Soc. 93, 3787 (1971).
- [8] G. R. Davies, J. A. Jarvis & B. T. Kilbourn, Chem. Commun. 1971, 1511.
- [9] R. Tabacchi & A. Jacot-Guillarmod, Helv. 53, 1977 (1970).
- [10] R. Tabacchi & A. Jacot-Guillarmod, Chimia 25, 326 (1971).
- [11] A. Jacot-Guillarmod & D. Roulet, Chimia 28, 15 (1974).
- [12] P. Corradini & G. Allegra, J. Am. chem. Soc. 81, 5510 (1959); G. Allegra & P. Ganis, Atti. Accad. Naz. Lincei. Sci. Fis. Mat. Nat. 33, 438 (1962).
- [13] K. Waijenpaugh & C. N. Caughlan, Inorg. Chemistry 6, 963 (1967).
- [14] D. Schwarzenbach, J. Am. chem. Soc. 9, 2391 (1970).
- [15] W. H. Baur, Acta. Cryst. 9, 515 (1956).