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The crystal and molecular structure of $[(C_5HMe_4)TiBr(\mu\text{-}O)]_4$ and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$, by-products from the preparation of titanocene dibromides

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Abstract

The compounds $[(C_5HMe_4)TiBr(\mu\text{-}O]_4$ (I) and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$ (II) result from hydrolysis of $(C_5HMe_4)TiBr_3$ and $(C_5Me_5)TiBr_3$, respectively, in THF with aqueous HBr. They appear as byproducts if during the preparation of the corresponding titanocene dibromides air is accidentally introduced, or if substoichiometric amounts of reducing agents are present prior to addition of aqueous HBr. Such conditions cause formation of the cyclopentadienyltitanium dibromides or tribromides. The molecule of I forms a planar eight-membered titanoxane cycle with a two-fold symmetry axis perpendicular to the plane of the cycle. The Ti–O–Ti angles are alternately 149 and 176° whereas the O–Ti–O angles are nearly constant at 103–106°. The six-membered titanoxane cycle in II is planar except for the oxygen atom which connects the titanium atoms bearing those C_5Me_5 ligands orientated on the same side with respect to the plane; displacement of the oxygen atom is 0.4 Å.

Introduction

Low yields of titanocene dichloride, $\overline{Cp}_2TiCl_2$ ($\overline{Cp} = C_5H_{5-n}Me_n$; $n = 0$, 1, 3–5), and the formation of byproducts were observed [1] if the reaction mixtures were accidentally contaminated with air before the final preparative step, the addition of aqueous HCl. The byproducts were separated as yellow crystalline compounds after partial evaporation of THF from the mother liquor and after evaporation of methanol washings of crude $\overline{Cp}_2TiCl_2$ products. They contained, according to mass spectrometric analysis, mixtures of the following compounds: $(\overline{Cp}TiCl_2)_2(\mu\text{-}O)$, $[\overline{Cp}TiCl(\mu\text{-}O)]_m$ ($m = 3$, 4) and $(\overline{Cp}Ti)_4O_6$. Our studies on the effect of the Me groups on the properties of titanocene derivatives [1–3] were intended to establish the conditions for preparation of the pure compounds.

The conditions for obtaining pure (η^5-C_5Me_5)-substituted titanoxane compounds have recently been established mainly by Royo et al. [4] using the controlled hydrolysis of $(C_5Me_5)TiCl_3$ or $(C_5Me_5)TiBr_3$ in the presence of diethylamine (basic conditions) and by Babcock and Klemperer [5] exploring hydrolysis in wet acetone (acid conditions) or the reverse reaction of $[(C_5Me_5)Ti]_4O_6$ with HCl or $TiCl_4$. The crystal and molecular structures are known for the cyclopentadienyl(μ-oxo)titanium(IV) halides $[(C_5H_5)TiCl_2]_2(\mu\text{-}O)$ [6], $[(C_5H_5)TiCl(\mu\text{-}O)]_4$ (III) [7], $[(C_5H_4Me)TiCl(\mu\text{-}O)]_4$ (IV) [8], $[(C_5Me_5)TiBr(\mu\text{-}O)]_4$ (V) [4] and $[(C_5Me_5)Ti]_4(\mu\text{-}O)_6$ [9] and their derivatives $[(C_9H_7)TiCl(\mu\text{-}O)]_4$ (C_9H_7 = tetrahydroindenyl) (VI) [10], $[(C_5H_5)Ti(OR)(\mu\text{-}O)]_4$ (R = 2,4,6-trimethylphenyl) (VII) [11] and $[(C_5Me_5)Ti(Me)(\mu\text{-}O)]_3$ (VIII) [12].

Recently, we accidentally obtained the pure compounds $[(C_5HMe_4)TiBr(\mu\text{-}O)]_4$ (I) and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$ (II) as byproducts in the preparation of titanocene dibromides through using substoichiometric amounts of the cyclopentadienyllithium compounds with respect to $TiBr_3$. The conditions for their reproducible preparation and the crystal and molecular structures of these compounds are presented in this paper.

Experimental

$(C_5HMe_4)_2TiBr_2$ and $(C_5Me_5)TiBr_2$ were prepared by the published procedure [13] consisting of the following steps: (i) the reduction of $TiBr_4$ in THF by $(n\text{-}C_4H_9)Li$ in hexane to give $TiBr_3 \cdot THF$, (ii) addition of the latter to a suspension of $\overline{Cp}Li$ in ethyl ether (obtained from $(n\text{-}C_4H_9)Li$ and the corresponding cyclopentadiene), (iii) reflux in THF for 24 h and (iv) addition of an excess of aqueous 46–48% HBr (all steps under argon atmosphere). On standing overnight the compounds were separated as dark red crystals. The mother liquors contained compounds I and II if substoichiometric amounts of reducing agents were employed in steps (i) and (ii), if the reaction mixture was contaminated at any stage with air, and if both these conditions were met.

$(C_5HMe_4)TiBr_3$ and $(C_5Me_5)TiBr_3$ were obtained by the heating to 120 °C of equimolar mixtures of the corresponding titanocene dibromides and $TiBr_4$ in toluene. After heating for 4 h, toluene and traces of $TiBr_4$ were evaporated in vacuo and the products were distilled out in vacuo and dissolved in THF.

$[(C_5HMe_4)TiBr(\mu\text{-}O)]_4$ (I) and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$ (II) were crystallized from the mother liquors of experimental preparations which gave low yields of the titanocene dibromides. Alternatively, they were prepared by pouring aqueous HBr (46-48%, 50 ml) to a solution of the corresponding $\overline{Cp}TiBr_3$ compound (1 mmol in 20 ml of THF). The yellow crystals were separated overnight. They were dried and recrystallized from benzene. The yields were 0.15 g (55%) for I and 0.17 g (64%) for II.

Tetrakis(tetramethylcyclopentadienyl(μ-oxo)bromotitanium(IV)) (I). ^1H NMR (400 MHz, C_6D_6, TMS, 25 °C) 2.183 s, 2.278 s, 6.211 s (intensity ratio 6 : 6 : 1); ^{13}C NMR (100 MHz, C_6D_6, TMS, 25 °C) 12.83 q, 15.00 q, 119.59 d, 130.29 s, 131.10 s; IR (Nujol mull, cm^{-1}) 612 vw, 629 w, 773 vs, 813 s, 855 w, 872 vw.

Tris(pentamethylcyclopentadienyl(μ-oxo)bromotitanium(IV)) (II). ^1H NMR (400 MHz, C_6D_6, TMS, 25 °C) 2.151 s, 2.169 s (intensity ratio 1 : 2); ^{13}C NMR (100 MHz, C_6D_6, TMS, 25 °C) 12.74 q, 12.59 q (intensity ratio 1 : 2), 126.75 s, 129.53 s (int. ratio 2 : 1); IR (Nujol mull, cm^{-1}) 620 w, 772 vs. The NMR spectra indicate that the C_5HMe_4 ligands are equivalent in I and the C_5Me_5 ligands in II are not equivalent, by analogy to what is found in $[(C_5Me_5)TiCl(\mu\text{-}O)]_3$ [4,5].

Table 1

Details on the structure determination of I and II

	I	II
(a) *Crystal data*		
Chemical formula	$[(C_5HMe_4)TiBr(\mu\text{-}O)]_4$	$[(C_5Me_5)TiBr(\mu\text{-}O)]_3$
Crystal system	monoclinic	monoclinic
Space group, No.	$B2/b$, 15	$P2_1/b$, 14
a, Å	19.720(4)	16.594(2)
b, Å	26.440(6)	22.903(5)
c, Å	9.501(2)	9.158(2)
γ, deg	121.05(2)	92.01(2)
V, Å^3	4244	3478
Z	4	4
D_{calc}, g·cm^{-3}	1.659	1.598
μ, cm^{-1}	44.8	41.1
Approx. cryst. dimens., mm	0.15×0.30×0.40	0.20×0.40×0.50
(b) *Data collection and refinement*		
radiation	Mo-K_α	Mo-K_α
monochromator	graphite	graphite
temp, K	293	293
θ_{max}, deg	25	24
total data	4058	6008
unique observed data		
$F^2 \geqslant 3\sigma(F^2)$	2324	2905
No. of refined parameters	218	352
R	0.055	0.048
R_W	0.066	0.056
ESD of the unit weight	7.4	4.3

X-Ray structure determination

Single crystals were mounted in air in a four-circle automatic CAD-4 diffractometer (Mo-K_α radiation, graphite monochromator, $\theta_{max} = 25°$). Cell dimensions were refined from 20 reflections. Crystallographic data for compounds I and II are listed in Table 1. The intensities of reflections were corrected for the crystal absorption using the ψ-scanning of 8 reflections. The structures were solved by direct and Fourier methods. The atomic coordinates were refined by full-matrix least-squares methods in anisotropic approximation to give $R = 0.055$ for I and $R = 0.048$ for II; positions of hydrogen atoms were not determined.

Results and discussion

The hydrolysis of $(C_5HMe_4)TiBr_3$ and $(C_5Me_5)TiBr_3$ in THF by adding aqueous HBr in excess afforded I and II in 55 and 64% yields, respectively. These yields are low compared to the 80–90% yields obtained by controlled hydrolysis in the presence of diethylamine where the hydrolytic products depended on the stoichiometry of H_2O with respect to $(C_5Me_5)TiBr_3$ [4]; in that process, under basic conditions, $[(C_5Me_5)TiBr(\mu\text{-}O)]_4$ (V) and $[(C_5Me_5)TiCl(\mu\text{-}O)]_3$ were obtained [4] whereas under acid conditions, only the trimeric compounds II and $[(C_5Me_5)TiCl(\mu\text{-}O)]_3$ [5] resulted. Results so far show that under acid conditions, of the cyclic titanoxane

Table 2

Bond distances (Å) and bond angles (°) in the structure I

Ti(1)–Br(1)	2.447(2)	Ti(2)–Br(2)	2.447(2)
Ti(1)–O(1)	1.797(9)	Ti(2)–O(2)	1.799(7)
Ti(1)–O(2)	1.811(7)	Ti(2)–O(1′)	1.822(8)
Ti(1)–C(1)	2.309(11)	Ti(2)–C(6)	2.331(11)
Ti(1)–C(2)	2.394(11)	Ti(2)–C(7)	2.393(10)
Ti(1)–C(3)	2.408(10)	Ti(2)–C(8)	2.416(9)
Ti(1)–C(4)	2.414(11)	Ti(2)–C(9)	2.374(11)
Ti(1)–C(5)	2.353(12)	Ti(2)–C(10)	2.322(10)
C(1)–C(2)	1.46(2)	C(6)–C(7)	1.45(2)
C(1)–C(5)	1.41(2)	C(6)–C(10)	1.440(13)
C(2)–C(3)	1.43(2)	C(7)–C(8)	1.39(2)
C(3)–C(4)	1.43(2)	C(8)–C(9)	1.439(12)
C(4)–C(5)	1.425(15)	C(9)–C(10)	1.38(2)
C(1)–C(11)	1.523(15)	C(6)–C(61)	1.51(2)
C(2)–C(21)	1.47(2)	C(7)–C(71)	1.544(14)
C(3)–C(31)	1.55(2)	C(8)–C(81)	1.52(2)
C(4)–C(41)	1.50(2)	C(9)–C(91)	1.51(2)
O(1)Ti(1)O(2)	104.6(3)	O(1′)Ti(2)O(2)	105.3(3)
Br(1)Ti(1)O(1)	103.3(3)	Br(2)Ti(2)O(1′)	103.5(3)
Br(1)Ti(1)O(2)	101.7(3)	Br(2)Ti(2)O(2)	100.8(3)
Ti(1)O(1)Ti(2′)	149.3(5)	Ti(1)O(2)Ti(2)	175.7(5)

trimers are formed only from the C_5Me_5 derivatives while the less methylated compounds form cyclic tetramers as demonstrated for the compounds III [7], IV [8] and I. The existence of both trimer II and tetramer V demonstrates that there are no apparent sterical factors favouring formation of one or the other multimer, and this is inferred from their structures too.

Titanoxane byproducts of the preparation of titanocene dihalides were not a result of the hydrolysis of $\overline{Cp}_2TiX$ or $\overline{Cp}_2TiX_2$ compounds because in well conducted experiments these byproducts were not isolated even though the yields of the $\overline{Cp}_2TiX_2$ compounds have never exceeded 60% [1,13]. The byproducts could arise from the hydrolysis of either $\overline{Cp}TiX_2$ or $\overline{Cp}TiX_3$ compounds present in the reaction mixture before addition of the aqueous hydrogen halide. We have demonstrated the formation of I and II from the corresponding $\overline{Cp}TiBr_3$ compounds under analogous conditions.

X-Ray structures of I and II

Important bond distances and valence angles are listed in Tables 2 and 3, respectively; the atom coordinates for I and II are deposited in the Cambridge Crystallographic Data Centre *. The tetranuclear compound I contains a planar eight-membered $(-Ti-O-)_4$ cycle with a two-fold rotation axis perpendicular to the plane of the cycle (Fig. 1). The C_5HMe_4 ligands and bromine atoms lie alternately above and below the cycle plane. Similar tetrameric cycles have previously been found in the compounds III [7], IV [8], V [4], VI [10] and VII [11]. The compound V,

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Table 3

Bond distances (Å) [a] and bond angles (°) in the structure II

Ti(1)-Br(1)	2.431(2)	Ti(2)-Br(2)	2.446(2)	Ti(3)-Br(3)	2.425(2)
Ti(1)-O(1)	1.826(7)	Ti(2)-O(2)	1.811(7)	Ti(3)-O(1)	1.826(7)
Ti(1)-O(2)	1.820(7)	Ti(2)-O(3)	1.817(7)	Ti(3)-O(3)	1.813(7)
Ti(1)-C(1)	2.332(12)	Ti(2)-C(6)	2.337(12)	Ti(3)-C(11)	2.385(13)
Ti(1)-C(2)	2.327(12)	Ti(2)-C(7)	2.361(13)	Ti(3)-C(12)	2.328(13)
Ti(1)-C(3)	2.370(13)	Ti(2)-C(8)	2.384(12)	Ti(3)-C(13)	2.370(12)
Ti(1)-C(4)	2.410(13)	Ti(2)-C(9)	2.395(13)	Ti(3)-C(14)	2.403(11)
Ti(1)-C(5)	2.414(12)	Ti(2)-C(10)	2.389(12)	Ti(3)-C(15)	2.394(12)
C(1)-C(2)	1.40(2)	C(6)-C(7)	1.44(2)	C(11)-C(12)	1.42(2)
C(1)—C(5)	1.41(2)	C(6)-C(10)	1.39(2)	C(11)-C(15)	1.39(2)
C(2)-C(3)	1.41(2)	C(7)-C(8)	1.41(2)	C(12)-C(13)	1.41(2)
C(3)-C(4)	1.40(2)	C(8)-C(9)	1.40(2)	C(13)-C(14)	1.37(2)
C(4)-C(5)	1.41(2)	C(9)-C(10)	1.39(2)	C(14)-C(15)	1.41(2)
Br(1)Ti(1)O(1)	101.5(2)	Br(2)Ti(2)O(2)	104.0(3)	Br(3)Ti(3)O(3)	101.2(2)
Br(1)Ti(1)O(2)	103.4(2)	Br(2)Ti(2)O(3)	101.3(2)	Br(3)Ti(3)O(1)	104.6(2)
O(1)Ti(1)O(2)	102.7(3)	O(2)Ti(2)O(3)	104.1(3)	O(3)Ti(3)O(1)	103.2(3)
Ti(1)O(1)Ti(3)	132.4(4)	Ti(2)O(2)Ti(1)	135.6(4)	Ti(2)O(3)Ti(3)	135.0(4)

[a] All bonds of the C-C(Me) type are in the range 1.51-1.54 Å.

though containing one $CHCl_3$ molecule of crystallization, is the most similar to I in respect of chemical composition and because of the slight deviations from the plane of atoms in the $(-Ti-O-)_4$ cycle. A two-fold rotation axis in V passes through

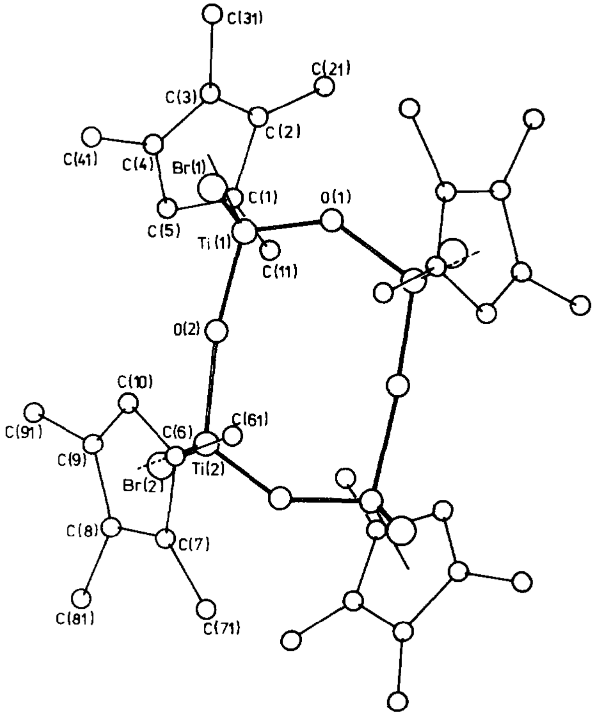

Fig. 1. Compound I with atoms individually numbered.

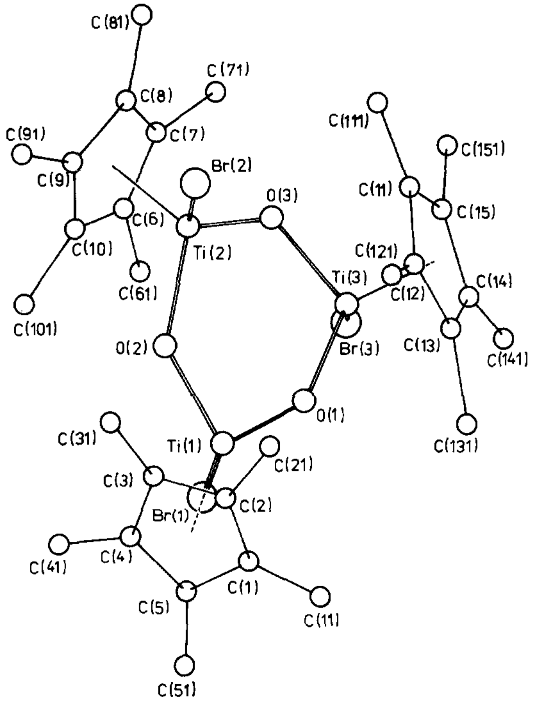

Fig. 2. Compound II with atoms individually numbered.

oxygen atoms that are opposite in the cycle [4]. The compound I has a maximum deviation from the plane of 0.06 Å whereas the compound V has the Ti atoms 0.2 Å above and below the plane formed by four oxygen atoms; the deviations from planarity in compounds III, IV, VI and VIII are larger with a maximum of 0.4 Å for VII [11]. The nearly perfect planarity of the cycle in I is associated with the maximum difference in the vicinal angles Ti–O–Ti, 149 and 176 °, the difference being 27 °. The analogous difference in the angles was about 15 ° in IV and VII, 5 ° in III and zero in VI. The Ti–O–Ti angles in V were within the range 163–164 °. The large difference in the oxygen bridge configurations in I is accompanied by only negligible changes in the Ti–O bond distances: the average Ti–O distance in the nearly linear oxygen bridges is 1.804 Å while in the bent bridges it is 1.811 Å. In contrast, the valence angles at the titanium atoms are almost constant: in I and III–VII the angles μ-O–Ti–μ-O are within the range 103–106 °. The average Ti–Br and Ti–C distances in I, 2.447 and 2.37 Å, respectively, are close to those found in V, 2.456 and 2.38 Å. The average distances Ti–$\overline{\text{Cp}}$-centroid are 2.04 Å for I and 2.05–2.06 Å for V. The connecting line Ti–$\overline{\text{Cp}}$-centroid is not exactly perpendicular to the C_5HMe_4 plane as follows from the continuous change in the Ti–C distances within each C_5HMe_4 ligand, differing at the most by 0.1 Å. The C_5HMe_4 ligands in I are planar within 0.01 Å and their methyl groups are slightly bent (by 0.05 Å) from the plane, further from the titanium atom. Orientation of the C_5HMe_4 ligands alternately above and below the $(-Ti-O-)_4$ plane is seen in Fig. 1.

The structure of II (Fig. 2) can be compared only to that of $[(C_5Me_5)Ti(Me)(\mu\text{-}O)]_3$ (VIII) [12]. The cycles $(-Ti-O-)_3$ in compounds II and VIII are not planar. In II, atom O(1) connecting two titanium atoms whose C_5Me_5 ligands are oriented the same way with respect to the $(\text{-Ti-O-})_3$ cycle is 0.4 Å distant from the plane containing all the titanium atoms and oxygen atoms O(2) and O(3). Analogous geometry was also found in VIII. The average Ti–O distances and average Ti–O–Ti and O–Ti–O angles in II and VIII were 1.819 and 1.823 Å, 134.3 and 132.9°, and 103.3 and 105.3°, respectively. The C_5Me_5 ligands in II are planar within 0.01 Å; the Ti–$\overline{\text{Cp}}$-centroid distance is in the range 2.045–2.054 Å. The methyl groups are slightly bent away from the plane further from titanium. The average distances Ti–Br and Ti–C in I and II are virtually the same. The differences in the average Ti–O bond lengths, 1.807 Å for I and 1.819 Å for II are brought about by the differences in the Ti–O–Ti angles, 149–176° for I and 132.5–135.5° for II: the valence angles should affect the bond orders in the Ti–O bonds. The formation of trimers from the C_5Me_5 derivatives and of tetramers from the less methylated $\overline{\text{Cp}}$ compounds has been tentatively explained by the steric effect of the C_5Me_5 ligand which would hinder the rapid hydrolytic dimerization of intermediate $(\overline{\text{Cp}}\text{TiX}_2)_2(\mu\text{-O})$ products, yielding the tetranuclear compounds [14]. Neither the recent [4,5] studies nor the research described here adequately support this view.

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