

**REACTIONS OF DOUBLY TUCKED-IN PERMETHYLTITANOCENE WITH *tert*-BUTANOL AND PROPARGYL ALCOHOL. THE CRYSTAL STRUCTURES OF UNUSUAL HYDROLYTIC BYPRODUCTS**

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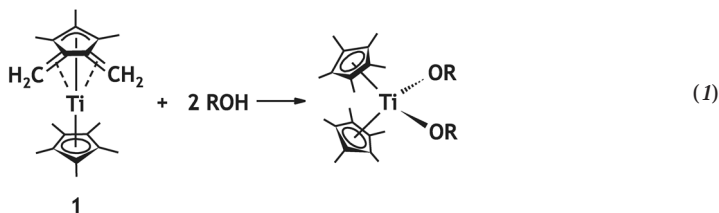
Reactions of double tucked-in permethyltitanocene  $[\text{Ti}\{\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\eta^5\text{-C}_5\text{Me}_5)]$  (**1**) with *tert*-butanol or propargyl alcohol in toluene proceeded sluggishly even with excess of the alcohol and at elevated temperature. The alcoholysis of **1** with *tert*-butanol afforded  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ot-Bu})_3]$  (**3**) as the major product and  $\text{Ti}(\text{Ot-Bu})_4$  as the minor one. The other product of the alcoholysis was pentamethylcyclopentadiene. The only isolated crystalline product was the very minor hydrolytic byproduct  $[\{\text{Ti}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)_2\}(\mu\text{-O})\{\text{Ti}^{\text{IV}}(\text{Ot-Bu})_3\}]$  (**2**). The alcoholysis of **1** containing traces of LiI with  $\text{HOCH}_2\text{C}\equiv\text{CH}$ , containing apparently more water than *t*-BuOH, gave an inseparable mixture of oily products from which several crystals of an unintended hydrolytic byproduct  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})(\mu\text{-O})\}_3\text{LiI}]$  (**4**) were isolated. X-ray crystal structures of **2** and **4** were determined.

**Keywords:** Titanium; Double tucked-in titanocene; Allyl-diene ligand; Alcoholysis; *tert*-Butanol; Propargyl alcohol; NMR spectra; Hydrolysis byproduct; Crystal structures

Double tucked-in permethyltitanocene complex  $[\text{Ti}\{\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}(\eta^5\text{-C}_5\text{Me}_5)]$  (**1**) contains one allyl-diene ligand whose vicinal exomethylene groups are, as follows from NMR and IR spectra,  $\pi$ -coordinated to the metal, whilst the remaining three ring carbon atoms are bonded as a  $\pi$ -allyl<sup>1</sup>. The crystal structure of **1** has never been published because of an extensive disorder. However, crystal structures of a number of derivatives having one methyl group on each ring replaced with another substituent were deter-

mined showing that the diene plane is inclined to the metal which is close to the allyl side of planar cyclopentadienyl ring<sup>2</sup>. EHT<sup>3a</sup> as well as recent DFT<sup>3b</sup> calculations revealed a strong mixing of d orbitals with carbon sp<sup>2</sup> orbitals which makes difficult to describe the electronic structure of **1** in a classical manner.

The blue compound **1** is available by thermolysis of decamethyltitanocene derivatives whose leaving ligands abstract hydrogen atoms from two vicinal methyl substituents of one cyclopentadienyl ligand. Examples are [TiMe<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] liberating methane<sup>1</sup> or [Ti(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] evolving Me<sub>3</sub>SiCH=CHSiMe<sub>3</sub> (ref.<sup>4</sup>). Particularly, the latter method affords **1** in nearly quantitative yield from the starting [TiCl<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]. Compound **1** could thus serve as a readily available starting material for the synthesis of numerous titanocene derivatives, provided the titanium–methylene bonds undergo a smooth acidolysis, e.g., according to Eq. (1). Our previous study of reactions of **1** with substituted propargylic alcohols FcC≡CCMe<sub>2</sub>(OH) (Fc = ferrocenyl) and PhC≡CCH<sub>2</sub>OH revealed that products of the [Ti(OR)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)] type were mainly formed. Methanolysis of **1** gave, in addition to the same product type crystalline dinuclear complex {(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(OMe)<sub>2</sub>(μ-OMe)}<sub>2</sub> and some other minor products<sup>5</sup>.



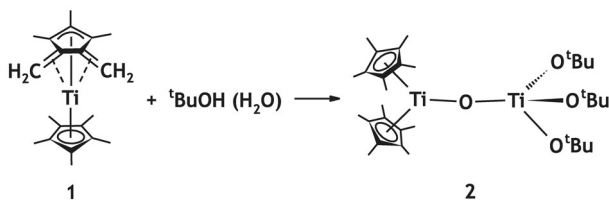
Here we report the reaction of **1** with *tert*-butanol and propargyl alcohol, and crystal structures of unusual products arising from partial hydrolysis.

## RESULTS AND DISCUSSION

### Reaction of **1** with *tert*-Butanol

A toluene solution of **1** reacted very slowly with a ten-fold molar excess of *tert*-butanol at room temperature, and surprisingly, even after heating to 100 °C for 5 h the blue color of the solution still indicated the presence of a considerable amount of unreacted **1**. Only heating to 110 °C for 5 h resulted in the color change from blue to pale reddish brown. After cooling to ambient temperature all volatiles (toluene and *tert*-butanol) were distilled

off in vacuum into another ampule, to be used for another experiment with **1**. The dirty brown oily distillation residue was dissolved in minimum hexane, and the solution cooled to  $-18\text{ }^{\circ}\text{C}$  for crystallization. Pale purple crystals were separated from the mother liquor and identified to be paramagnetic binuclear complex  $\{[\text{Ti}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-O})\{\text{Ti}^{\text{IV}}(\text{O}t\text{-Bu})_3\}\}$  (**2**) (Scheme 1). Even so, a further concentration and cooling of the mother liquor resulted in obtaining several blue crystals that were identified by EI MS to be unreacted **1** (ca. 5 mg). Finally, a complete evaporation of hexane from the mother liquor gave a yellow-brown oil containing according to  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra mainly  $[\text{Ti}(\text{O}t\text{-Bu})_3(\eta^5\text{-C}_5\text{Me}_5)]$  (**3**) and a number of other minor unidentified products. To obtain pure **3** the toluene and *tert*-butanol recovered from the above experiment were used again in the reaction with a new portion of **1** (heated to  $110\text{ }^{\circ}\text{C}$  for 6 h). After cooling to ambient temperature this reaction mixture did not display any signal in ESR spectra. The volatiles were evaporated in vacuum, rising the temperature gradually to  $50\text{ }^{\circ}\text{C}$ , and the yellow oily residue was subsequently evaporated in a high vacuum at  $90\text{ }^{\circ}\text{C}$  until no product was condensing in a trap cooled by liquid nitrogen. The yellow oily residue was identified by EI MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra to be **3** (>95% based on NMR data), and the distilled fraction contained  $\text{Ti}(\text{O}t\text{-Bu})_4$ , pentamethylcyclopentadiene, and a very trace of **1**.



SCHEME 1

The molecular structure of **2** was determined by X-ray diffraction analysis (see below) and corroborated by its EI MS spectra showing a molecular ion as the second most abundant peak and the molecular ion of single tucked-in titanocene ( $m/z$  317) as the base peak. This indicated that compound **2** dissociated under electron impact into two mononuclear species with the bridging oxygen atom abstracting one hydrogen atom from the permethyltitanocene moiety and joining the more electropositive trialkoxytitanium moiety as the OH group. The ESR spectra of **2** confirmed the presence of one  $\text{Ti}^{\text{III}}$  moiety  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiO}$ , displaying a very narrow signal at  $g = 1.972$  ( $\Delta H = 3.2\text{ G}$ ) flanked with side wings of ca. 20 times less intense

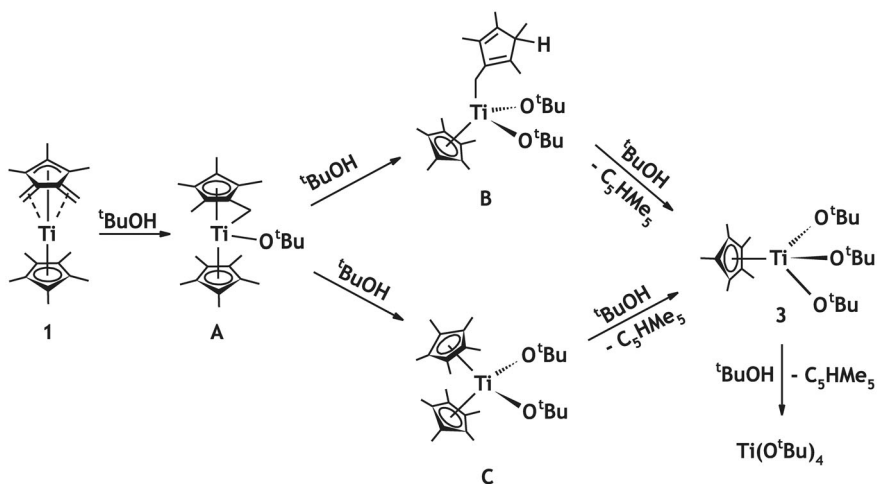
multiplets typical for the unpaired electron interaction with  $^{47}\text{Ti}$  ( $I_N = 5/2$ ) and  $^{49}\text{Ti}$  ( $I_N = 7/2$ ) nuclei in their natural abundance ( $a_{\text{Ti}} = 8.7$  G). Very similar spectra were reported previously for titanocene alkoxides  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Ti}(\text{O}t\text{-Bu})]^6$ ,  $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Ti}(\text{O}t\text{-Bu})]^7$ ,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{OMe})]^8$ , the hydroxide  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiOH}]^9$ , and the metal oxide  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiOLi}(\text{THF})_2]$  (ref.<sup>10</sup>). A somewhat lower  $g$ -value of **2** compared to a range of  $g = 1.977\text{--}1.982$  is apparently due to a lower extent of Ti–O  $\pi$ -bonding exerted by the bridging oxygen atom.

The origin of **2** is to be sought in the presence of water traces after apparently insufficient dehydration of *tert*-butanol with  $\text{LiAlH}_4$ . Elimination of isobutene from the  $[\text{Cp}_2\text{Zr}(\text{O}t\text{-Bu})]^+$  cation resulting in the formation of poly(isobutene) and  $[\text{Cp}_2\text{Zr}(\mu\text{-OH})_2]^{2+}$  is known<sup>11</sup>; however, this reason for the formation of **2** would not be compatible with the absence of **2** in the second experiment where all the water was surely removed during the previous experiment. It is probable that **1** reacted with water much faster than with *tert*-butanol to give  $[\text{Ti}(\text{OH})_2(\eta^5\text{-C}_5\text{Me}_5)_2]^{12}$  or coordinatively unsaturated  $[\text{TiO}(\eta^5\text{-C}_5\text{Me}_5)_2]^{13}$  as reaction intermediates. However, their reduction to Ti(III) is difficult to specify. An expected elimination of hydrogen was not experimentally confirmed due to a low yield of **2**.

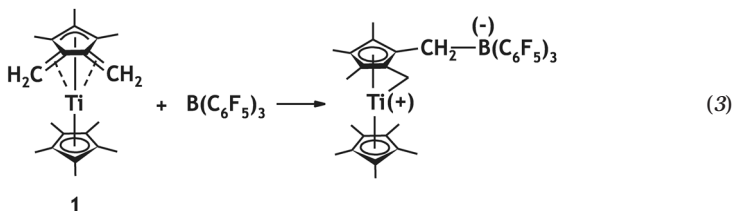
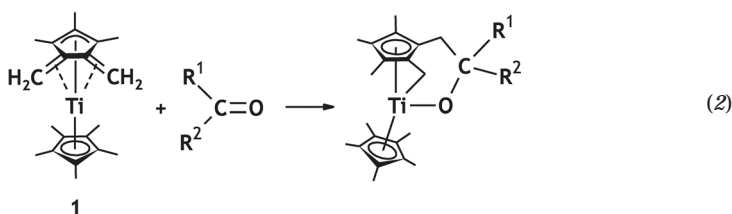
Compound **3** was abundant in the first experiment using a not completely dehydrated *tert*-butanol as well as in the second experiment where the reaction between **1** and anhydrous *tert*-butanol was cleaner. The compound was unequivocally identified by NMR and EI MS spectra. In EI MS spectra the molecular ion  $m/z$  402 (24%) fragmented in two competitive ways losing BuOH to give the most abundant ionic species, or the  $\text{C}_5\text{Me}_5$  ligand to give the second most abundant fragment peak. In addition to **3** a minor, ultimate alcoholysis product,  $[\text{Ti}(\text{O}t\text{-Bu})_4]$ , was also detected by NMR and EI MS. The distillate from the isolation of **3** consisted of the latter together with overwhelming pentamethylcyclopentadiene (see Experimental).

The above results show that **1** reacts with *t*-BuOH very sluggishly while the subsequent steps leading to **3** run faster since no anticipated intermediates were detected (Scheme 2). The presence of **1** in the reaction mixture even when  $[\text{Ti}(\text{O}t\text{-Bu})_4]$  was already formed indicates that the first step leading to anticipated intermediate **A** requires a comparable or stronger thermal treatment than the final step leading to  $[\text{Ti}(\text{O}t\text{-Bu})_4]$ . The next alcoholysis of **A** apparently involves the tucked-in cyclopentadienyl ligand yielding **B** or **C** intermediates which precede the formation of **3**. No evidence for the formation of intermediates **A–C** could be obtained due to their low concentration. However the intermediate **A** should be a rather stable compound

since it is known that cyclopentadienyl ring-tethered alkoxides are formed from the reaction of **1** with ketones (Eq. (2)), and these do not react at the remaining exo-methylene moiety with an excess of ketones<sup>1,14</sup>. Likewise, compound **1** was shown to react with an excess of  $B(C_6F_5)_3$  via only one of the available exo-methylene groups (Eq. (3))<sup>15</sup>.

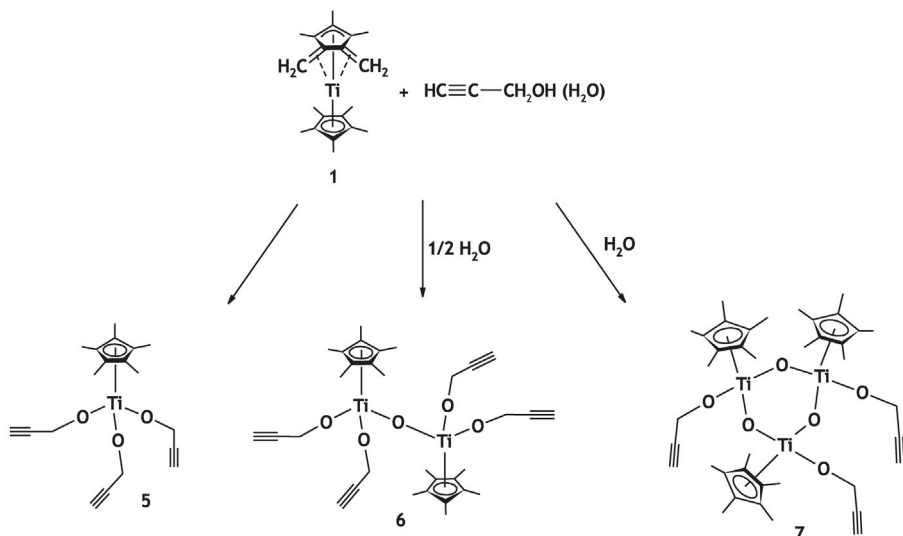
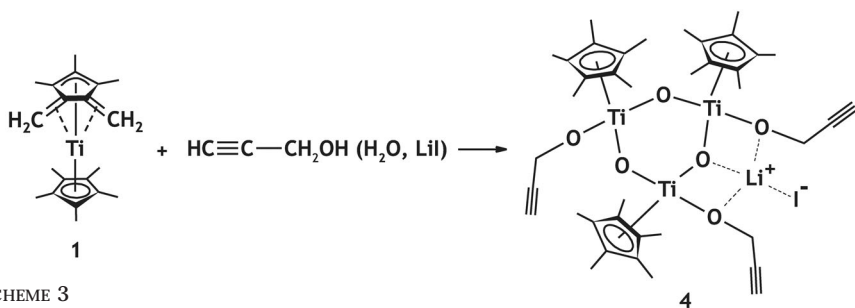


SCHEME 2



### Reaction of **1** with Propargyl Alcohol

Analogous reaction of **1** and  $\text{HC}\equiv\text{CCH}_2\text{OH}$  was hampered by two unintended circumstances. First, compound **1** used for the reaction was prepared by thermolysis of  $[\text{TiMe}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  obtained from  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  and commercial  $\text{LiMe}$  which contained considerable amount of the  $\text{LiMe-LiI}$  complex. Traces of  $\text{LiI}$  were thus introduced into the system with **1**. Second, the composition of the only solid isolated product  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})(\mu\text{-O})\}_3\text{LiI}]$  (**4**) indicated that the propargyl alcohol was not entirely dehydrated with  $\text{LiAlH}_4$  (no warming was used to prevent hydrogenation of the triple bond) (Scheme 3). The NMR analysis of prod-



ucts revealed a mixture of three products which could be tentatively formulated as  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})_3]$  (**5**) (an analogue of **3**),  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})\}_2(\mu\text{-O})]$  (**6**), and  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}(\text{CH})(\mu\text{-O}))\}_3]$  (**7**) (partial hydrolytic products) (Scheme 4). Since the complete removal of water from the alcohol was not attainable this research was confined to determining the crystal structure of **4**.

### Crystal Structure of **2**

Compound **2** crystallizes in monoclinic space group  $P2_1/c$ . The molecule of **2** is shown in Fig. 1, and the relevant geometric parameters are listed in Table I. The oxo-bridged titanocene moiety contains the trigonally coordinated titanium(III) atom whereas the  $(\mu\text{-oxo})\text{tri}(\text{tert-butoxy})\text{titanium(IV)}$  part comprises pseudotetrahedrally coordinated titanium atom. Of the bridging Ti–O bonds the titanocene-binding Ti–O distance (1.9158(18) Å) is by about 0.14 Å longer than that linking the titanium alkoxide (1.7734(17) Å). The former distance is even longer than the Ti–O bond in  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{-Ti}^{\text{III}}(\text{O}t\text{-Bu})]$  (1.8425(14) Å)<sup>16</sup>, while the latter is yet shorter than the bridg-

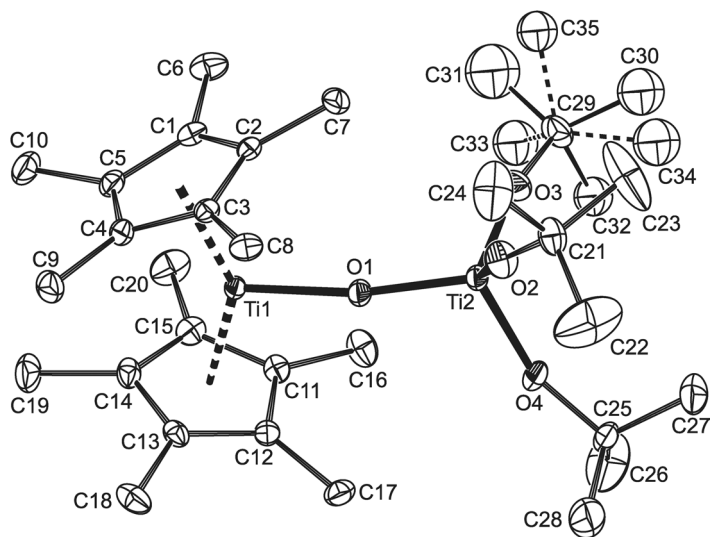


FIG. 1

PLATON drawing of compound **2** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

ing Ti–O bond in  $[\{(\eta^5\text{-C}_5\text{Me}_4t\text{-Bu})\text{TiCl}_2\}_2\text{O}]$  (1.8170(4) Å)<sup>17</sup>,  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{-TiCl}_2\}_2\text{O}]$  (1.803(3)–1.809(6) Å; three independent molecules in the unit cell)<sup>18</sup>, or the shortest Ti–O bridging bond in **4** (vide infra). The Ti–O bonds binding *tert*-butoxy groups in **2** (1.788–1.799(2) Å) are markedly elongated compared to the Ti–O bonds in  $[(t\text{-BuO})_3\text{TiCo}(\text{CO})_3]$  (av. 1.74 Å)<sup>19</sup>.

The permethyltitanocene moiety adopts a staggered conformation with the methyl groups in hinge positions most declined from the least-squares plane of their parent cyclopentadienyl ring (C(10) 0.337(5) Å and C(19) 0.368(5) Å). The Cg(1)–Ti(1)–Cg(2) angle of 142.59(5)° falls into the range of the angles found for trigonal  $[\text{TiL}(\eta^5\text{-C}_5\text{Me}_5)_2]$  derivatives, where L = Cl (143.6(2)°, ref.<sup>6</sup>), CH<sub>2</sub>CMe<sub>3</sub> (139.4(3)°, ref.<sup>20a</sup>), OH (143.79(5)°, ref.<sup>9</sup>), N=CMe<sub>2</sub> (145.7(2)°, ref.<sup>20b</sup>), NHMe (141.7°, ref.<sup>8</sup>), and F (av. 144.9°, ref.<sup>8</sup>). The Ti(1)–O(1)–Ti(2) angle of 167.04(12)° falls in the range of angles found for symmetrical titanoxane compounds  $[\{(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\}_2\text{O}]$  (180°, ref.<sup>21</sup>),  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2\}_2\text{O}]$  (154–159°, three independent molecules in the unit

TABLE I  
Selected bond lengths (in Å) and angles (in °) for complex **2**

Bond distance			
Ti(1)–Cg(1) <sup>a</sup>	2.0729(12)	Ti(1)–Cg(2) <sup>a</sup>	2.0788(13)
Ti–C(Cp)	2.375(2)–2.435(3)	C–C(Cp)	1.409(4)–1.424(4)
C(Cp)–C(Me)	1.494(4)–1.509(4)	Ti(1)–O(1)	1.9158(18)
Ti(2)–O(1)	1.7734(17)	Ti(2)–O(2)	1.799(2)
Ti(2)–O(3)	1.788(2)	Ti(2)–O(4)	1.796(2)
O(2)–C(21)	1.417(3)	O(3)–C(29)	1.405(3)
O(4)–C(25)	1.407(3)		
Bond angles			
Cg(1)–Ti(1)–Cg(2) <sup>a</sup>	142.59(5)	Ti(1)–O(1)–Ti(2)	168.04(12)
Cg(1)–Ti(1)–O(1)	108.87(7)	Cg(2)–Ti(1)–O(1)	108.51(6)
O(1)–Ti(2)–O(2)	109.07(9)	O(1)–Ti(2)–O(3)	110.08(10)
O(1)–Ti(2)–O(4)	109.59(9)	O(2)–Ti(2)–O(3)	111.10(10)
O(2)–Ti(2)–O(4)	109.80(10)	O(3)–Ti(2)–O(4)	107.17(10)
φ <sup>b</sup>	35.66(13)		

<sup>a</sup> Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(11–15) cyclopentadienyl rings, respectively. <sup>b</sup> Dihedral angle subtended by the cyclopentadienyl ring least-squares planes.



cell; ref.<sup>18</sup>), and  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OSiPh}_2)_2\text{O}\}_2\text{O}]$  ( $161.6(3)^\circ$ , ref.<sup>22</sup>). The plane of this angle is nearly perpendicular to the plane defined by the Cg(1)–Ti(1)–Cg(2) angle, not raising a steric strain between the two titanium ligands.

### Crystal Structure of **4**

The molecule of **4** is shown in Fig. 2, and the selected geometric data are given in Table II. The structure of **4** is essentially very similar to cyclic titanoxane trimers  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{L})(\mu\text{-O})]_3$  bearing simple monoanionic ligands (L = Cl<sup>18</sup>, Br<sup>23</sup>, and Me<sup>24</sup>). In all cases the titanoxane skeletons are neither planar nor crystallographically symmetrical. The two units whose ligands L are directed to the same side of the titanoxane least-squares plane differ from the third one with the group L directed to the opposite side.

In compound **4** the two oxygen atoms of one-side oriented propargyloxy groups, O(5) and O(6), and the bridging oxygen between the concerned

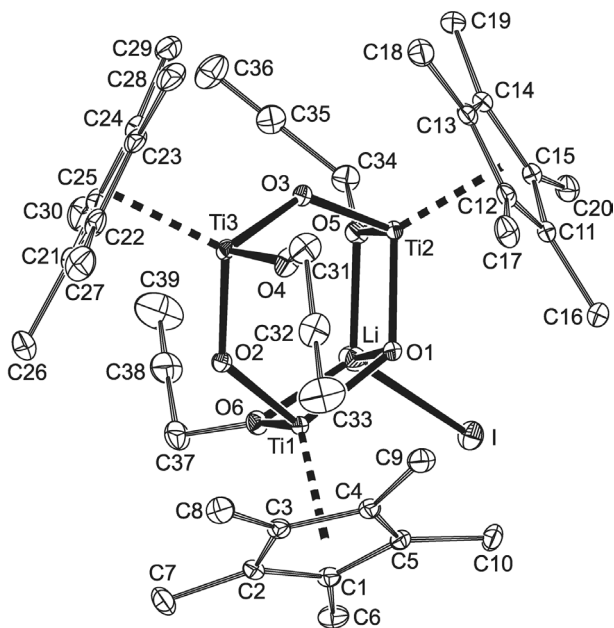


FIG. 2

PLATON drawing of compound **4** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

TABLE II  
Selected bond lengths (in Å) and angles (in °) for complex 4

Bond distance			
Ti(1)–Cg(1) <sup>a</sup>	2.0399(9)	Ti(2)–Cg(2) <sup>a</sup>	2.0484(8)
Ti(3)–Cg(3) <sup>a</sup>	2.0389(9)	Ti–C(Cp)	2.345(2)–2.404(2)
Ti(1)–O(1)	1.8517(12)	Ti(1)–O(2)	1.8094(13)
Ti(2)–O(1)	1.8559(12)	Ti(2)–O(3)	1.8145(12)
Ti(3)–O(3)	1.8420(13)	Ti(3)–O(2)	1.8475(13)
Ti(1)–O(6)	1.8717(13)	Ti(2)–O(5)	1.8726(13)
Ti(3)–O(4)	1.8301(13)	O(4)–C(31)	1.398(2)
O(5)–C(34)	1.419(2)	O(6)–C(37)	1.415(2)
C–C <sup>b</sup>	1.458(3)–1.466(3)	C≡C <sup>c</sup>	1.171(4)–1.179(4)
Li–I	2.655(4)	Li–O(1)	2.316(4)
Li–O(5)	1.950(4)	Li–O(6)	1.952(4)
Bond angles			
Cg(1) <sup>a</sup> –Ti(1)–O(1)	118.13(5)	Cg(1) <sup>a</sup> –Ti(1)–O(2)	113.75(5)
Cg(1) <sup>a</sup> –Ti(1)–O(6)	117.51(5)	Cg(2) <sup>a</sup> –Ti(2)–O(1)	119.38(5)
Cg(2) <sup>a</sup> –Ti(2)–O(3)	113.53(5)	Cg(2) <sup>a</sup> –Ti(2)–O(5)	116.50(5)
Cg(3) <sup>a</sup> –Ti(3)–O(2)	114.00(5)	Cg(3) <sup>a</sup> –Ti(3)–O(3)	113.99(5)
Cg(3) <sup>a</sup> –Ti(3)–O(4)	117.33(5)	Ti(1)–O(6)–C(37)	138.80(13)
Ti(2)–O(5)–C(34)	142.60(13)	Ti(3)–O(4)–C(31)	155.34(14)
O–C–C <sup>d</sup>	109.7(2)–112.5(2)	C–C≡C <sup>e</sup>	177.5(3)–179.3(3)
O(1)–Ti(1)–O(2)	105.84(6)	O(2)–Ti(1)–O(6)	104.61(6)
O(1)–Ti(1)–O(6)	94.56(6)	O(1)–Ti(2)–O(3)	102.96(6)
O(1)–Ti(2)–O(5)	94.35(6)	O(3)–Ti(2)–O(5)	107.74(6)
O(2)–Ti(3)–O(3)	102.12(6)	O(2)–Ti(3)–O(4)	103.46(6)
O(3)–Ti(3)–O(4)	104.20(6)	Ti(1)–O(1)–Ti(2)	129.94(7)
Ti(1)–O(2)–Ti(3)	132.23(7)	Ti(2)–O(3)–Ti(3)	135.34(7)
O(1)–Li–O(5)	79.24(14)	O(1)–Li–O(6)	79.22(13)
O(5)–Li–O(6)	117.69(19)	O(1)–Li–I	114.34(15)
O(5)–Li–I	119.80(16)	O(6)–Li–I	122.41(17)
Ti(1)–O(6)–Li	98.26(12)	Ti(2)–O(5)–Li	98.81(12)
Ti(1)–O(1)–Li	87.15(10)	Ti(2)–O(1)–Li	87.46(10)

<sup>a</sup> Cg(1), Cg(2), and Cg(3) denote the centroids of the C(1–5), C(11–15), and C(21–25) cyclopentadienyl rings, respectively. <sup>b</sup> Propargyl C–C single bond. <sup>c</sup> Propargyl C≡C triple bond. <sup>d</sup> Propargyl alkoxide group. <sup>e</sup> Propargyl group.

titanium atoms O(1) coordinate the Li<sup>+</sup> cation. The bond lengths Li–O (Table II) indicate that coordinating ability of the bridging O(1) atom is lower than that of O(5) and O(6). Consequently, the Ti(1)–O(6) and Ti(2)–O(5) bonds are distinctly longer than the Ti(3)–O(4) bond, and Ti(1)–O(1) and Ti(2)–O(1) are longer than Ti(1)–O(2) and Ti(2)–O(3) bond lengths. A difference of ca. 0.04 Å indicates that the bridging O(1) atom significantly participates in binding Li<sup>+</sup> cation. The binding of Li<sup>+</sup> by O(5) and O(6) atoms led to a discernible prolongation of the O–C bonds compared to the non-involved O(4)–C(31) bond. The bonds in the concerned propargyl groups and ( $\eta^5$ -pentamethylcyclopentadienyl) titanium moieties do not differ significantly. The Li<sup>+</sup> coordination is reflected also in respective valence angles; however, the differences are in no way dramatic (see Table II). The Li–I distance is moderately longer than in the LiI crystal (3.0128 Å)<sup>25</sup>.

### Conclusions

The bulky and low acidic *tert*-butanol is not able to react with double tucked-in titanocene **1** via Eq. (1). The compounds react with a reasonable rate at 110 °C affording compound **3** and [Ti(Ot-Bu)<sub>4</sub>] under elimination of pentamethylcyclopentadiene. The presence of water traces in *tert*-butanol resulted in obtaining crystalline Ti<sup>III</sup>/Ti<sup>IV</sup> complex **2**. Reaction of propargyl alcohol containing water with **1** containing traces of LiI afforded crystalline **4**. Its formation and separation from main reaction products of alcoholysis/hydrolysis, which did not crystallize, opened a way to a new class of cyclic titanoxane–alkali metal halide coordination complexes.

### EXPERIMENTAL

#### General

All manipulations with **1** and its reaction with *tert*-butanol or propargyl alcohol were performed under vacuum in sealed all-glass devices equipped with breakable seals. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C<sub>6</sub>D<sub>6</sub> solutions at 25 °C. Chemical shifts ( $\delta$ , ppm) are given relative to the solvent signals ( $\delta_{\text{H}}$  7.15,  $\delta_{\text{C}}$  128.00); coupling constants, *J*, are given in Hz. EI MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 7% and by important peaks of lower intensity. Crystals of **2** for EI-MS measurements and melting point determinations were placed in glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). The liquid samples of **3** and Ti(Ot-Bu)<sub>4</sub> for EI-MS measurements were prepared by evaporating their hexane solutions in capillary tips

in vacuo. A sample of **2** in KBr pellet was prepared in a glovebox Labmaster 130 (mBraun), and its IR spectrum in the range of 400–4000  $\text{cm}^{-1}$  was recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer. GC MS measurements were performed on a Thermo Focus DSQ using the capillary column Thermo TR-5MS (15 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu\text{m}$ ). UV-VIS measurements were performed on a Varian Quartz 17 D spectrometer in the range 300–800 nm using a device equipped with a pair of quartz cuvettes (10.0 mm and 1.0 mm, Hellma). ESR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) equipped with a magnet controlling and data acquisition CU1 unit (Magnettech, Berlin, Germany) in the X-band.  $g$ -Values were determined using an  $\text{Mn}^{2+}$  ( $M_1 = -1/2$  line) standard at  $g = 1.9860$ . An STT-3 variable temperature unit was used for the measurement in the range from  $-140$  to  $+22$   $^{\circ}\text{C}$ . Single crystals of **2** and **4** were mounted into capillaries under purified nitrogen in the glovebox and sealed with a wax.

### Chemicals

The solvents toluene and hexane were dried by refluxing over  $\text{LiAlH}_4$  and stored as solutions of dimeric titanocene  $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)(\mu\text{-H})_2\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\}_2]$ <sup>26</sup>. *tert*-Butanol and propargyl alcohol (Aldrich) were degassed on a vacuum line and distilled onto subequivalent amount of powdery  $\text{LiAlH}_4$  (Aldrich). When the evolution of hydrogen ceased the formed slurry was degassed and the alcohols distilled into ampules. Crystalline blue **1** prepared according to ref.<sup>4</sup> was used for reaction with *tert*-butanol. It was weighed in the glovebox, distributed into ampules equipped with a breakable seal and sealed off with flame. A sample of crystalline **1** obtained previously according to (ref.<sup>1</sup>) was used for reaction with propargyl alcohol. A 1.6 M solution of methylolithium in diethyl ether (0.05 M LiI) used for preparation of  $[\text{TiMe}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  was purchased from Aldrich.

### Preparation of $[\{\text{Ti}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)_2\}(\mu\text{-O})\{\text{Ti}^{\text{IV}}(\text{O}t\text{-Bu})_3\}]$ (**2**)

Compound **1** (0.316 g, 1.0 mmol) was dissolved in toluene (15 ml). *tert*-Butanol (1.0 ml, 10 mmol) was added by distillation on a vacuum line, and the mixture in an ampule equipped with two breakable seals was sealed off. The mixture was successively heated until the blue color of the solution began to fade. This became observable at 110  $^{\circ}\text{C}$  whereupon it was held for 4 h. After cooling, all volatiles were distilled in vacuo into an ampule that was used for the further experiment. A solid residue was dissolved in hexane. The fraction crystallization afforded purple prisms of **2**, and from the mother liquor after its concentration blue crystals of **1** (ca. 0.005 g, 1.6%; identified by EI MS) were obtained. Recrystallization of purple **2** from hexane afforded brownish green crystals that gave the same IR spectrum and crystal structure. Yield of **2** 0.054 g (18% related to Ti). M.p. 142  $^{\circ}\text{C}$  (decomposes with gas evolution).

EI MS (direct inlet, 70 eV, 200  $^{\circ}\text{C}$ ),  $m/z$  (relative abundance, %): 604 (7), 603 (19), 602 (36), 601 ( $\text{M}^{+}$ ; 73), 600 (21), 599 (16), 586 ( $[\text{M} - \text{Me}]^{+}$ ; 6), 528 ( $[\text{M} - \text{OBu}]^{+}$ ; 8), 472 (7), 471 ( $[\text{M} - \text{OBu} - \text{Bu}]^{+}$ ; 16), 466 ( $[\text{M} - \text{C}_5\text{Me}_5]^{+}$ ; 6), 413 (12), 411 (10), 410 (15), 409 ( $[\text{M} - \text{C}_5\text{Me}_5 - \text{Bu}]^{+}$ ; 28), 408 (9), 399 (9), 398 (18), 397 ( $[\text{M} - \text{OBu} - \text{Bu} - \text{BuOH}]^{+}$ ; 20), 396 (9), 354 (12), 353 ( $[\text{M} - \text{C}_5\text{Me}_5 - \text{Bu} - \text{C}_4\text{H}_8]^{+}$ ; 19), 319 (13), 318 (34), 317 ( $[\text{Ti}(\text{C}_5\text{Me}_5)_2 - \text{H}]^{+}$ ; 100), 316 (15), 315 (13), 299 (12), 298 (18), 297 (38), 296 (16), 295 (17), 281 (13), 280 (33), 279 (36), 278 (19), 277 (12), 263 (12), 262 (16), 261 (13), 237 (9), 228 (17), 199 (18), 69 (20), 59 (19), 57 (10). IR (KBr): 2969 (vs), 2902 (s), 2863 (m), 1491 (vw), 1453 (w), 1380 (m), 1357 (s),

1228 (m), 1213 (s), 1182 (s), 1043 (m), 1006 (vs), 768 (vs), 586 (m), 480 (vw), 436 (w). ESR (toluene, 22 °C):  $g = 1.972$ ,  $\Delta H = 3.2$  G,  $a_{\text{Ti}} = 8.7$  G; (toluene, -140 °C):  $g_1 = 2.000$ ,  $g_2 = 1.982$ ,  $g_3 = 1.935$ ,  $g_{\text{av}} = 1.972$ . UV-VIS (toluene, 22 °C): 516 > 645 (sh).

#### Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_3]$ (**3**)

Volatiles from the above experiment (toluene and ca. 7 mmol of *tert*-butanol) were used as a solvent for crystalline **1** (0.20 g, 0.63 mmol). The solution was heated to 110 °C for 6 h when the solution turned yellow. All volatiles were distilled off in vacuo at 60 °C, and the remaining yellow oil was evaporated in high vacuum at 90 °C with the vapors collected in a liquid nitrogen-cooled trap. When no more vapors were condensing the yellow distillation residue (0.21 g, 0.52 mmol, 83%) was collected for analysis.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra revealed it is **3** (purity > 95% according to the NMR spectra). The distillate in the trap (30 mg) was identified by EI MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra to be  $[\text{Ti}(\text{O}t\text{-Bu})_4]$  and some pentamethylcyclopentadiene.

**Data for 3.**  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ): 1.34 (s, 9 H,  $\text{OCMe}_3$ ); 2.06 (s, 5 H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ): 12.41 ( $\text{C}_5\text{Me}_5$ ); 33.22 ( $\text{OCMe}_3$ ); 80.07 ( $\text{OCMe}_3$ ); 120.71 ( $\text{C}_5\text{Me}_5$ ). EI MS (direct inlet, 70 eV, 70 °C):  $m/z$  (relative abundance, %): 403 (9), 402 ( $\text{M}^{++}$ ); 24), 330 (18), 329 (45), 328 ( $[\text{M} - \text{BuOH}]^+$ ; 100), 327 (15), 326 (12), 272 ( $[\text{M} - \text{BuOH} - \text{C}_4\text{H}_8]^+$ ; 14), 269 (8), 268 (13), 267 ( $[\text{M} - \text{C}_5\text{Me}_5]^+$ ; 58), 266 (8), 257 (10), 255 ( $[\text{M} - \text{BuOH} - \text{BuO}]^+$ ; 9), 217 (15), 216 ( $[\text{M} - \text{BuOH} - 2 \text{C}_4\text{H}_8]^+$ ; 16), 212 (7), 211 ( $[\text{M} - \text{C}_5\text{Me}_5 - \text{C}_4\text{H}_8]^+$ ; 21), 200 (9), 199 ( $[\text{M} - \text{BuOH} - \text{BuO} - \text{C}_4\text{H}_8]^+$ ; 33), 198 (15), 197 (10), 196 (8), 195 (20), 181 ( $[\text{M} - 2 \text{BuOH} - \text{BuO}]^+$ ; 11), 156 (12), 155 ( $[\text{M} - \text{C}_5\text{Me}_5 - 2 \text{C}_4\text{H}_8]^+$ ; 50), 139 ( $[\text{M} - \text{C}_5\text{Me}_5 - \text{Bu} - \text{Me} - \text{C}_4\text{H}_8]^+$ ; 35), 137 (9), 135 ( $[\text{C}_5\text{Me}_5]^+$ ; 23), 122 (13), 121 (20), 119 (16), 105 (13), 99 ( $[\text{M} - \text{C}_5\text{Me}_5 - 3 \text{C}_4\text{H}_8]^+$ ; 34), 59 (24), 57 (47).

**Data for  $[\text{Ti}(\text{O}t\text{-Bu})_4]$ .**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 1.34 (s,  $\text{CMe}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): 32.44 ( $\text{CMe}_3$ ); 79.98 ( $\text{CMe}_3$ ). EI MS (direct inlet, 70 eV, 70 °C):  $m/z$  (relative abundance, %) 340 ( $\text{M}^{++}$ ; not observed), 327 (10), 326 (22), 325 ( $[\text{M} - \text{Me}]^+$ ; 86), 324 (11), 323 (10), 269 ( $[\text{M} - \text{Me} - \text{C}_4\text{H}_8]^+$ ; 11), 252 ( $[\text{M} - \text{Me} - \text{OBu}]^+$ ; 10), 213 ( $[\text{M} - \text{Me} - 2 \text{C}_4\text{H}_8]^+$ ; 11), 157 ( $[\text{M} - \text{Me} - 3 \text{C}_4\text{H}_8]^+$ ; 18), 139 (15), 121 (59), 105 (18), 91 (10), 85 (20), 84 (100), 83 (8), 82 (21), 69 (34).

The volatiles distilled off at 60 °C in vacuo contained mostly 1,2,3,4,5-pentamethylcyclopentadiene identified by EI MS ( $m/z$  136) and NMR spectra.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ): 0.98(d,  $^3J_{\text{HH}} = 7.5$ ,  $\text{CHMe}$ ); 1.73, 1.79 (2  $\times$  s, 2  $\times$  6 H, =CMe); 2.40 (m,  $\text{CHMe}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ): 11.20, 11.69 (=CMe); 14.25 ( $\text{CHMe}$ ); 51.78 ( $\text{CHMe}$ ); 134.40, 137.47 (=CMe).

#### Preparation of $\{[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})(\mu\text{-O})]_3\cdot\text{LiI}\}$ (**4**)

Compound **1** (prepared by thermolysis of  $[\text{TiMe}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ )<sup>1</sup> (0.18 g, 0.57 mmol) was dissolved in toluene (15 ml), propargyl alcohol (0.5 g, 9.0 mmol) added, and the mixture was heated to 110 °C for 3 h. A yellow solution was evaporated in vacuum at 90 °C, and the oily residue was dissolved in toluene (2 ml). After cooling in refrigerator for one week a few yellow-orange crystals of **4** grew up, and were collected for X-ray single crystal diffraction analysis. Attempts to obtain more crystals of **4** or other crystalline products were unsuccessful. The only source of LiI in the system can be sought in the synthesis of **1** via thermolysis of  $[\text{TiMe}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  obtained from  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  and commercial LiMe solution containing LiI.

**Data for 4.** Yield 8 mg (5% on Ti). The compound was analyzed by X-ray single crystal diffraction only, and characterized by its IR spectrum. IR (KBr): 3308 (m), 3223 (m), 2974

(m), 2909 (s), 2857 (m), 2114 (w), 1493 (w), 1435 (m), 1378 (m), 1355 (m), 1237 (vw), 1120 (s, b), 1063 (vs, b), 992 (w), 926 (w), 740–790 (vs, b), 654 (s), 625 (s), 560 (vw), 544 (vw), 470 (s), 426 (m).

The mother liquor was evaporated in vacuum at 90 °C, the yellow residue was dissolved in C<sub>6</sub>D<sub>6</sub> and examined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the sample consist mainly two sets of signals attributable to the permethylcyclopentadienyl

TABLE III  
Crystal and structure refinement data for **2** and **4**

Parameter	<b>2</b>	<b>4</b>
Empirical formula	C <sub>32</sub> H <sub>57</sub> O <sub>4</sub> Ti <sub>2</sub>	C <sub>39</sub> H <sub>54</sub> ILiO <sub>6</sub> Ti <sub>3</sub>
Formula weight	601.58	896.36
Crystal system	monoclinic	monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>c</i> (No.14)	<i>P2</i> <sub>1</sub> / <i>c</i> (No.14)
<i>a</i> , Å	14.0220(3)	15.6450(2)
<i>b</i> , Å	14.9200(2)	16.2500(3)
<i>c</i> , Å	16.8630(3)	16.6380(3)
β, °	94.6060(11)	97.2290(9)
<i>V</i> , Å <sup>3</sup>	3516.48(11)	4196.28(12)
<i>Z</i>	4	4
Calculated density, g cm <sup>-3</sup>	1.252	1.419
μ(MoKα), mm <sup>-1</sup>	0.490	1.334
<i>F</i> (000), e	1404	1832
Crystal habit	red, plate	orange, prism
Crystal size, mm <sup>3</sup>	0.35 × 0.30 × 0.20	0.55 × 0.40 × 0.33
Θ range, °	2.00–27.48	2.51, 30.07
Range of <i>hkl</i>	–18/18; –19/19; –21/21	–20/22; –22/22; –23/23
Reflections collected	15780	68402
Independent reflections	6062	10062
Data/parameters	6062/362	10062/466
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.070	1.033
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0745, 0.1471	0.0439, 0.0800
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0516, 0.1339	0.0313, 0.0732
Max. and min. residual density, e Å <sup>-3</sup>	0.695, –0.488	0.666, –1.050

ligands and  $\text{HC}\equiv\text{CCH}_2\text{O}$  moieties. In view of the composition of **4** requiring an equimolar quantity of **1** and water, a mixture of major compounds was suggested to consist of  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})_3]$  (**5**) (75%) and  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})_2(\mu\text{-O})\}]$  (**6**) (20%). Some minor signals can belong to **4** or its titanoxane precursor  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{OCH}_2\text{C}\equiv\text{CH})(\mu\text{-O})\}_3]$  (**7**).

*Data for 5.*  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ): 1.97 (s, 15 H,  $\text{C}_5\text{Me}_5$ ); 2.08 (t,  $^4J_{\text{HH}} = 2.1$ , 3 H,  $\equiv\text{CH}$ ); 4.80 (d,  $^4J_{\text{HH}} = 2.1$ , 6 H,  $\text{OCH}_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ): 11.23 ( $\text{C}_5\text{Me}_5$ ); 60.84 ( $\text{OCH}_2$ ); 72.48 ( $\text{C}\equiv\text{CH}$ ); 84.25 ( $\text{C}\equiv\text{CH}$ ); 124.31 ( $\text{C}_5\text{Me}_5$ ).

*Data for 6.*  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ): 2.04 (s, 15 H,  $\text{C}_5\text{Me}_5$ ); 2.11 (t,  $^4J_{\text{HH}} = 2.1$ , 2 H,  $\equiv\text{CH}$ ); 4.91 (d,  $^4J_{\text{HH}} = 2.1$ , 4 H,  $\text{OCH}_2$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ): 11.42 ( $\text{C}_5\text{Me}_5$ ); 60.55 ( $\text{OCH}_2$ ); 72.30 ( $\text{C}\equiv\text{CH}$ ); 84.57 ( $\text{C}\equiv\text{CH}$ ); 123.71 ( $\text{C}_5\text{Me}_5$ ).

### X-ray Crystal Structure Determination

A purple crystal fragment of **2** and an orange prism of **4** were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox and the capillaries were sealed with flame. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed with HKL program package<sup>27</sup>. The structures were solved by direct methods (SIR97)<sup>28</sup>, followed by consecutive Fourier syntheses and refined by full-matrix least-squares on  $F^2$  (SHELX97)<sup>29</sup>. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. The *tert*-butyl groups in **2** are disordered, however, only for the C(29)-centered group two sets of corresponding atoms (C(30–32) and C(33–35)) were distinguished. The disorder of the other two groups is witnessed by large thermal parameters for the methyl carbon atoms. Relevant crystallographic data for both the compounds are given in Table III. CCDC 684319 (for **2**) and 682753 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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