Unusual Formation of Two New Titanium(IV) Tetraphenolates

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When the product of the reaction of 2,6-di-*tert*.-butylphenol with $TiCl_4$ in a 3:1 ratio is treated with $Na[HBEt_3]$, the isolated product is not $(2,6\text{-}tert.\text{-}Bu_2C_6H_3O)_3Ti(HBEt_3)$ but the isomerized ester $(2,4\text{-}tert.\text{-}Bu_2C_6H_3O)_4Ti$ with molecular S_4 symmetry. This rearrangement of the R substituents does not occur upon reacting 2,6-diisopropylphenol with $TiCl_4$ and $Na[HBEt_3]$. An unexpected result is also observed for the product of the reaction of tris(2,6-diisopropylphenolato)titanium(IV) chloride with lithium bis(pentafluorophenolato)dihydridoborate. The isolated product proved to be dimeric tris(pentafluorophenolato)(2,6-diisopropylphenolato)titanium(IV) with two bridging pentafluorophenolato groups generating pentacoordinated Ti atoms.

Key words: Tetrakis(2,4-di-*tert*.-butyl-phenolato)titanium(IV), Dimeric [Tris(pentafluorophenolato)(2,6-diisopropylphenolato)titanium(IV), X-Ray Structures

Introduction

Tetrakis(organyloxo)titanium(IV) compounds are generally prepared by reacting $TiCl_4$ with ROH compounds in a 1:4 ratio either at elevated temperatures to remove HCl or by trapping HCl with an amine base, generally Et_3N. Typical mononuclear species are $(2,6\text{-}i\text{Pr}_2C_6H_3O)_4Ti$ [1], $(2\text{-}tert.\text{-}BuC_6H_4O)_4Ti$ [2], $(2,3,5,6\text{-}Me_4C_6HO)_4Ti$ [3], $(2,6\text{-}Me_2C_6H_3O)_4Ti$ [1b], $(i\text{PrCH}_2O)_4Ti$ [1b], $(i\text{PrO})_4(i\text{PrOH})Ti$ [3] or $[(F_3C)_2C_6H_3O]_4Ti$ [4] having tetrahedrally coordinated Ti atoms, except for $(i\text{PrO})_4(i\text{PrOH})Ti$. Ti esters with small organyl groups are not monomeric but are either dimeric or even more highly associated, as shown for $[(2,6\text{-}i\text{Pr}_2C_6H_3O)(i\text{PrO})_2(\mu_2\text{-}i\text{PrO})]_2Ti_2$ [5], $[(tert.\text{-}BuCH_2O)_4Ti]_2$ [6], $[(F_5C_6O)_3(RO)Ti]_2$ (R = Et, *i*Pr) [7], $[(2,4,6\text{-}Me_3C_6H_2O)(i\text{PrO})_2(\mu_2\text{-}i\text{PrO})]_2Ti_2$ [8], $(i\text{PrO})_6(\mu_2\text{-}i\text{PrO})_3(\mu_3\text{-}i\text{PrO})_3Ti_3$ [9], $(MeO)_{12}Ti_3$ [10], $(EtO)_{16}Ti_4$ [11], $(EtO)_{12}(\mu_2\text{-}EtO)_8(\mu_3\text{-}O)_4Ti_7$, and $(EtO)_{12}(\mu_2\text{-}OEt)_{12}(\mu_3\text{-}O)_8Ti_{10}$ [12]. The multinuclear titanium esters show coordination numbers from 5 to 7 for the Ti atoms. We have shown that the reactions of $(2,6\text{-}i\text{Pr}_2C_6H_3O)_3TiCl$ with $M(H_2BR_2)$ generate only in a few cases the expected $[2,6\text{-}i\text{Pr}_2C_6H_3O]_3TiH_2BR_2$ compounds [13]. More often Ti-O bond cleavage occurs with formation of $ROBR_2$ as well as $(2,6\text{-}i\text{Pr}_2C_6H_3O)_4Ti$. For instance, $[2,6\text{-}i\text{Pr}_2C_6H_3O]_3TiMe$ reacts with catecholborane generating $MeB(O_2C_6H_4)$ and $ROB(O_2C_6H_4)$ [13]. Obviously the isopropyl group is not bulky enough to allow the synthesis of sufficiently stable $(RO)_3TiH_2BR_2$ compounds. Therefore, we assumed that the more bulky $(2,6\text{-di-}tert.\text{-}Bu_2C_6H_3O)_3TiCl$ might be a better starting material as has been shown for the reaction of 2,6-di(*tert*.-butyl)phenol with alane and hydridoaluminates which generate stable (2,6-di-*tert*.-butylphenolato)alanes and -hydridoaluminates [14].

Results

Reactions

We tried to prepare tris(2,6-di-*tert*.-butylphenolato)-titanium chloride (**1**) by the standard reaction shown in Eq. 1.

$$3\ 2,6\text{-}tert.\text{-}Bu_2C_6H_3OH + TiCl_4 \rightarrow \underset{\mathbf{1}}{(2,6\text{-}tert.\text{-}Bu_2C_6H_3O)_3TiCl} + 3\ HCl \qquad (1)$$

HCl was evaporated by heating the toluene solution at reflux for 5 h. After removing part of the solvent the ^1H NMR spectrum showed *two* signals for *tert*.-butyl groups and three signals for CH protons. This spectrum is, therefore, incompatible with 2,6-di-*tert*.-butylphenolato groups but in consonance with its 2,4-isomer, *i. e.* the reaction proceeds not according to Eq. 1 but according to Eq. 2. The dark-red solution of **2**

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$$3\ 2{,}6\text{-}\mathit{tert.}\text{-}Bu_2C_6H_3OH + TiCl_4 \rightarrow \underset{\mathbf{2}}{(2{,}4\text{-}\mathit{tert.}\text{-}Bu_2C_6H_3O)_3TiCl} + 3\ HCl \tag{2}$$

$$(2{,}4\text{-}\mathit{tert.}\text{-}Bu_2C_6H_3O)_3TiCl + Na(BHEt_3) \rightarrow \underset{\mathbf{3}}{(2{,}4\text{-}\mathit{tert.}\text{-}Bu)_2C_6H_3O)_3TiH} + NaCl + BEt_3 \tag{3}$$

$$4\ (2{,}4\text{-}\mathit{tert.}\text{-}Bu_2C_6H_3O)_3TiCl + 4\ Na(HBEt_3) \rightarrow \underset{\mathbf{4}}{3\ (2{,}4\text{-}\mathit{tert.}\text{-}Bu_2C_6H_3O)_4Ti} + 4\ NaCl + 4\ BEt_3 + 2\ H_2 \tag{4}$$

$$2\ F_5C_6OH + LiBH_4 \rightarrow \underset{\mathbf{5}}{Li[H_2B(OC_6F_5)_2]} + 2\ H_2 \tag{5}$$

$$[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3TiCl + \underset{\mathbf{5}}{Li[H_2B(OC_6F_5)_2]} \rightarrow \underset{\mathbf{6}}{[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3Ti[H_2B(OC_6F_5)_2]} + LiCl \tag{6}$$

$$\underset{\mathbf{6}}{[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3Ti[H_2B(OC_6F_5)_2]} \rightarrow \underset{\mathbf{7}}{[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3TiH} + \underset{\mathbf{8}}{HB(OC_6F_5)_2} \tag{7}$$

$$3\ HB(OC_6F_5)_2 + \underset{\mathbf{7}}{[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3TiH} \rightarrow \underset{\mathbf{9}}{2\ (F_5C_6O)_3B} + [(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3Ti[(H_2BH_2)] \tag{8}$$

$$[(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)]_3Ti[HB(OC_6F_5)_3] \rightarrow \underset{\mathbf{10}}{2{,}6\text{-}\mathit{i}Pr_2C_6H_3OTi(OC_6F_5)_3} + \underset{\mathbf{11}}{(2{,}6\text{-}\mathit{i}Pr_2C_6H_3O)_2BH} \tag{9}$$

was then treated with a toluene solution of $Na(HBEt_3)$. NaCl precipitated, and the filtrate showed the presence of BEt_3 by its ^{11}B NMR signal at 89 ppm [15]. This suggested a reaction according to Eq. 3. About 60 % of the solvent was then removed from the filtrate which was stored at −30 °C. Nice crystals settled within 4 days. These turned out to be the tetrakis(2,4-di-*tert.*-butyl-phenolato)titanium(IV), **4**. It showed ^1H NMR resonances at 1.29 (s, 36 H), and at 1.53 ppm (s, 36 H) for the *tert.*-butyl groups, a doublet of doublets at 6.98, a doublet at 7.12, and a doublet at 7.41 ppm, the latter in a 1:1:1 ratio for the $C_{arom}H$ hydrogen atoms. The ^{13}C NMR data are reported in the Experimental Section.

Another unexpected reaction, resulting in the formation of tris(pentafluorophenolato)(2,6-diisopropylphenolato)titanium(IV), occured when treating tris(2,6-diisopropylphenolato)titanium(IV) chloride with lithium bis(pentafluorophenolato)dihydridoborate, **5**. The latter compound has already been reported by Douthwaiter [17]. It was prepared from $LiBH_4$ and F_5C_6OH in Et_2O and isolated as $Li[H_2B(OC_6F_5)_2]\cdot OEt_2$. Its crystal structure has been characterized as a linear polymer with Li–F bonds.

We prepared the dihydroborate **5** as shown in Eq. 5.

The boron nucleus of **5** is quite deshielded as compared to $LiBH_4$, the $\delta^{11}B$ NMR signals appearing at 1.7 *versus* 41.1 ppm [15], the former being similar to that of $Li[B(OMe)_4]$ with $\delta^{11}B = 2.7$ ppm [15]. While a suspension of **5** is stable in hexane or benzene, this is not the case for a THF solution of **5**. A fresh THF solution showed within 20 min an ^{11}B NMR doublet at $\delta = 6.1$ ppm, (d, $^1J(^{11}B^1H) = 125$ Hz) which is due to $(F_5C_6O)_2BH\cdot THF$, **7**, besides the signal for **5** (1.7 ppm).

The reaction of the tris(2,6-diisopropylphenolato)titanium chloride with **5** in hexane or benzene was expected to proceed according to Eq. 6. The resulting dark-red solution showed two dominating ^{11}B NMR signals at $\delta = 17.6$ and 28.3 ppm. The signal for compound **5** ($\delta^{11}B = 1.7$ ppm) had vanished. The signal at $\delta^{11}B = 28.3$ ppm is typical for $(RO)_2BH$ compounds [15], in this case for $(F_5C_6O)_2BH$, **8**. The signal at 17.6 ppm agrees with $(F_5C_6O)_3B$ [15]. This signal is much weaker than the signal at 28.3 ppm, a compound that can result from an H/F_5C_6O ligand exchange (see Eq. 8).

From the solution dark-red single crystals separated that proved to be 2,6-diisopropylphenolato-tris(pentafluorophenolato)titanium, **10**. The route to its formation is still unknown, and Eq. 9 presents one possibility. However, it is reasonable to assume that the first step of the reaction occurs as shown in Eq. 7. A third step could then be the formation of **10**.

The mixed tetra(aryloxo)titanium ester **10** is so far unique. The closest relatives are the compounds

$Ti(OC_6F_5)_3(OiPr)$ and $Ti(OC_6F_5)_3OEt{\cdot}HOC_6F_5$ [8]. The X-ray structure determination of **10** showed it to be dimeric (see below).

Molecular structures

The ester **4** crystallizes in the tetragonal system, space group $P\bar{4}2_1c$. Fig. 1 shows its molecular structure. The Ti atom is located on a inversion center, *i. e.* the molecule has S_4 symmetry in analogy to tetrakis-(2-*tert.*-butyl-phenolato)titanium (**12**) [2]. Compound **4** shows comparatively long Ti–O and C–O bonds. The Ti–O–C bond angles are 141.0°, and the Ti–O–C–C torsion angles are almost 180°. The C1 to C6 plane is almost (0.5°) coplanar with its TiOC plane.

The molecular structure of the dimeric tetra(phenolato)titanium(IV) **10** is depicted in Fig. 2. The compound crystallizes in the triclinic space group $P\bar{1}$. The dominating feature is the four-membered Ti_2O_2 ring involving two bridging F_5C_6O groups as well as two pentacoordinated Ti atoms. The planar Ti_2O_2 ring shows an O–Ti–O bond angle of only 69.1(2)° which leads to a Ti···Ti distance of 3.394(6) Å. Its Ti–O–Ti bond angle is 110.9(3)°. Characteristic for the four-membered Ti_2O_2 is its inversion center. The exocyclic Ti–O bond length is 1.734(6) Å for the 2,6-$iPr_2C_6H_3O$ group. This is somewhat shorter than the Ti–O bonds of the two exocyclic F_5C_6O substituents with 1.802(6) and 1.817(6) Å. These longer bonds may be due to the less basic F_5C_6O groups. The O–Ti–O bond angles between these two exocyclic F_5C_6O ligands are 103.8(3)°, while the O4–Ti1–O2 bond angle is 156.7(3)°, and the O3–Ti1–O2 bond angle is 89.4(3)°. The angle O4–Ti–O2A is 89.4(3)°. These data show that the Ti atom is located in the center of a strongly distorted trigonal bipyramid (see Fig. 3).

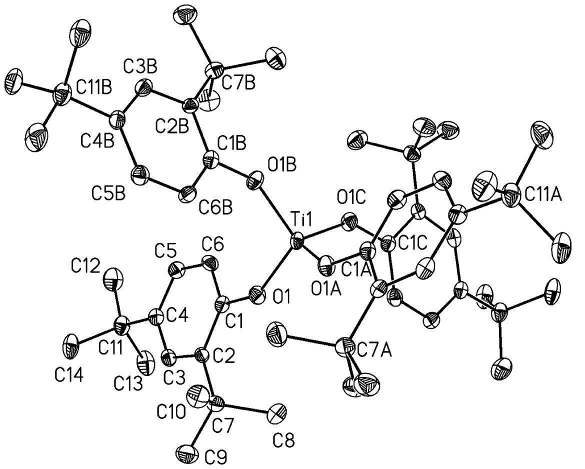

Fig. 1. Molecular structure of tetrakis(2,4-di-*tert.*-butylphenolato)titanium(IV), **4**. Displacement ellipsoids are drawn at the 25 % probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.796(2), C1–O1 1.383(3), C1–C2 1.400(4), C2–C3 1.406(3), C3–C4 1.384(4), C4–C5 1.377(4), C5–C6 1.394(3), C1–C6 1.373(43), C2–C7 1.509(4), C4–C11 1.533(3); O1–Ti1–O1A 106.8(1), O1–Ti1–O1B 110.82(6), C1–O1–Ti1 141.0(2), O1–C1–C6 117.8(2), O1–C1–C2 119.9(2).

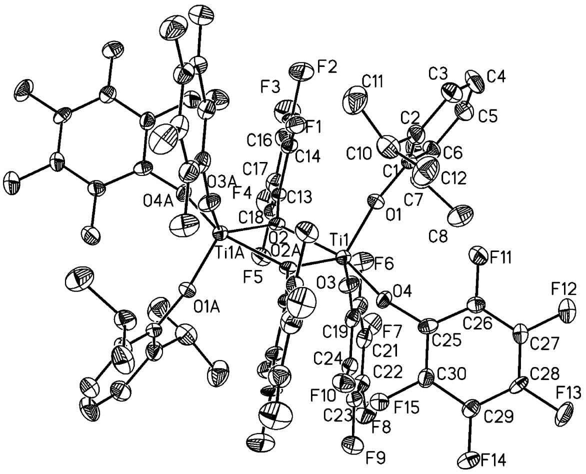

Fig. 2. Molecular structure of the dimeric tris(pentafluorophenolato)(2,6-diisopropylphenolato)titanium(IV), **10**. Displacement ellipsoids are drawn at the 25 % probability level. Selected bond lengths and angles are listed in Table 2.

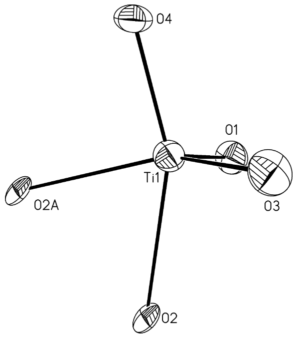

Fig. 3. The distorted trigonal-bipyramidal Ti coordination in complex **10**.

The C–O bond lengths of **10** span the range from 1.325(1) to 1.390(1) Å, with the longest bond to the O atom of the 2,6-diisopropylphenolato group. It is not surprising that the Ti–O bond to the bridging O atom of the F_5C_6O unit is significantly longer than the corresponding bonds to

Table 1. Relevant bonding parameters of compounds of the type $(ArO)_4Ti$ in Å and degrees. Only the substituents of the aryl groups are quoted.

Compound	2,4-*i*Pr (**4**)	2,6-*i*Pr [1a]	2,6-Me [1b]	2,3,5,6-Me [2]	2-*tert.*-Bu [2]
Ti–O	1.796	1.780	1.795	1.793	1.778
	1.796	1.781	1.783	1.761	1.778
	1.796	1.780	1.784	1.776	1.779
	1.796	1.781	1.794	1.760	1.778
C–O	1.383	1.366	1.374	1.346	1.328
	1.383	1.368	1.370	1.370	1.328
	1.383	1.368	1.362	1.310	1.328
	1.383	1.366	1.360	1.331	1.328
O–Ti–O	106.8	108.1	108.4	108.6	111.3
	110.8	110.2	109.7	108.1	108.6
	110.8	110.2	108.0	111.4	108.6
	106.8	108.1	108.4	108.1	108.6
	110.8	110.2	110.2	108.3	108.6
	110.8	110.1	106.5	110.3	111.3
Ti–O–C	141.0	164.5	154,8	170.2	151.9
	141.0	166.0	161.2	148.2	151.9
	141.0	166.0	152.6	148.9	151.9
	141.0	164.5	141.8	161.2	151.9
Ti–O–C–C	179.7	99.8	126.4	−166.6	140.9
	179.7	80.5	149.0	−96.7	
	179.7	137.1	128.4	69.3	
	179.7	139.9	77.4	103.4	

Table 2. Relevant structural data of compounds $[(F_5C_6O)_3(RO)(ROH)Ti]_2$ and related compounds[a].

	10	**12** [7]	**13** [7]	**14** [17]	**15** [17]	**16** [7]
Ti–O	2.117(5)	2.050	2.043(5)	2.051 r	2.053 r	2.001 r
	1.734(6)	2.166	2.054(5)	2.041 r	2.050 r	2.031 r
	1.802(6)	1.849	1.802(6)	1.809 f	1.806 f	1.856 rf
	1.817(6)	1.833	1.867(6)	1.800 f	1.799 f	1.894 f
		1.713 Pr	1.718(6)	1.879 f	1.886 f	1.723 f
		2.128 HOPr		2.182 pr	2.190 HPr	2.187 HOPr
C–O	1.390(1)	1.350 r	1.372Pr	1.354 fr	1.350 r	1.429 r
	1.344(1)	1.342 f	1.398	1.348 f	1.372 f	1.468 rf
	1.366(1)	1.343 f	1.342	1.333 f	1.368 f	1.491 f
	1.325(1)	1.453 HOPr	1.415Pr	1.341 f	1.351 f	1.428 f
		1.462 OPr		1.45 Pr	1.452 HOPr	1.369 f
						1.434 HOPr
Ti–O–Ti	110.9(2)	109.45	110.0(1)	108.36(2)	107.96(3)	107.2(2)
O–Ti–O	92.9(2) r	70.01 r	70.0 r	71.34 r	72.04 r	72.8 r
	103.8(3)	86.09 rf	89.6 rf	108.04 rf	81.52 fr	167.1 rf
	107.7(3)	90.80 rf	148.9 rf	93.04 rf	92.02 rf	79.9 fEt
	119.2(2)	157.13 rPr	106.1 rPr	81.99 rPr	162.7 rf	97.7 rf
	89.4.(3)	98.17 rHPr	97.3 ff	162.15 ff	91.4 fPr	90.5 rf
	108.6(3)	86.57 ff	101.0 fPr	98.59 rf	88.63 ff	82.3 rEt
		163.88 ff		81.99 rPr	99.35 ff	89.2 EtEt
				96.21 ff	98.04 fp	166.5 rEt
					165.58 fp	
					100.66 ff	
Ti–O–C	169.8(5)	128.8 r	123.3(4)	92.88	169.72 Pr	124.5(8) r
	119.4(4)	139.96 f	169.3(6)	86.68 rf	139.16 HOPr	127.0(9) Et
	159.5(7)	151.39 f	126.8(5)	127.39 rf	122.31 f	128.9(8) f
	154.7(6)	133.16 HPr	159.6(6)	165.32 ff	126.0 f	169.9(8) f
	128.5(5)	169.72 Pr	109.28	172.57 ff	151.39 f	
				132.42 Pr	139.36 f	
				124.9 rf		

[a] **12** = $[(F_5C_6O)_3(i\text{PrO})(i\text{PrOH})Ti]_2$, **13** = $[(2,6\text{-}F_2C_6CO)_3(i\text{PrO})Ti]_2$, **14** = $[(2\text{-}FC_6H_4O)_3(i\text{PrO})Ti]_2$, **15** = $[(4\text{-}FC_6H_4O)_4(i\text{PrOH})Ti]_2$, **16** = $[(F_3C)_2HCO)_2(EtO)_2Ti]_2$; abbreviations: r = ring, f = fluoroaryl ligand, ff = angle between two fluoroaryl groups, Pr = isopropyl group, HOPr = HO-isopropyl group, Et = ethyl group.

the exocyclic F_5C_6O ligand. Amongst the Ti–O–C bond angles, the Ti1–O1–C1 angle is close to linear (169.8(5)°), all others range from 119.4(4) to 159.5(7)° (Table 2).

Discussion and Conclusions

This study shows like that on tris(2,6-diisopropylphenolato)titanium(IV) dihydrido-diorganylborates [13] that there is a great tendency to form tetrakis(2,6-diorganylphenolato)-titanium compounds. In the case of the 2,6-di-*tert.*-butylphenolato compound the reaction of 3 equivalents of the corresponding phenol with $TiCl_4$ leads to an isomerization of the 2,6-species into the corresponding 2,4-isomer as shown by the isolation of tetrakis(2,4-di-*tert.*-butylphenolato)titanium(IV), **4**. A comparison of its molecular structure with that of tetrakis(2-*tert.*-butylphenolato)titanium(IV) **5** [2], which crystallizes in the same space group as compound **4**, shows similar Ti–O bond lengths and O–Ti–O bond angles (1.778 Å, 108.6 and 111.3°, *versus* 1.796 Å, 110.8 and 106.8° for **4**). The largest difference is associated with the Ti–O–C bond angles. These angles are 141.0° for compound **4**, but 151.9° for tetrakis(2-*tert.*-butylphenolato)titanium(IV) [2]. Compounds **10** to **16** show at least one obtuse Ti–O–C bond angle close to 170°, *e. g.* 178.2° for compound **14** (Table 2).

The reaction of 2,6-di-*tert.*-butylphenol with $TiCl_4$ in a 3:1 ratio leads to tris(2,4-di-*tert.*-$Bu_2C_6H_3O)_3TiCl$ which on reaction with $Na(BHEt_3)$ produces finally and unexpectedly compound **4**. This compound has the same symmetry (S_4) as (2-*tert.*-$BuC_6H_4O)_4Ti$, and Table 1 shows that it is exceptional as far as its Ti–O bonds are longer than observed for any other comparable tetrakis(phenolato)titanium(IV) species. More striking are the Ti–O–C bond angles which are more acute by about 10° compared with the other compounds in Table 1. The differences of the Ti–O–C bond angles of compounds **11** to **12** probably result from packing effects of the RO groups. These effects cannot be due to changes in Ti–O π bonding because the C–O bond lengths do not differ by more than 0.02 Å. Even more unusual is the result of the reaction of tris(2,6-diisopropylphenolato)titanium(IV) chloride with $Li[H_2B(OC_6F_5)_2]$ which affords $[(2,6\text{-}i\text{Pr}_2C_6H_3O)(F_5C_6O)_3Ti]_2$, **10**.

It is surprising that the pentafluorophenolato groups adopt the bridging position between two pentacoordinated Ti atoms each of which shows distorted trigonal-pyramidal coordination (see Fig. 3). The bridging Ti–O bonds (2.117(5) Å) are longer than the terminal Ti–O bonds as expected. In contrast to this normal behavior there is a significant difference between the Ti–O bond of the 2,6-diisopropylphenolato groups (1.734(6) Å) and the terminal pentafluorophenolato groups (1.802(6) and 1.817(6) Å). Moreover, the Ti–O–C bond angles to the F_5C_5O ligands are more acute (159.5 and 154.7°) than those to the 2,6-diisopropylphenolato groups (169.8°).

Significantly less open is the Ti–O–C bond angle to the bridging aryloxo group (119.4(4)°). Presently there are only two compounds that can be considered as close analogs to **10**. These are the compounds **12** and **13**. Compounds **13** to **16** need to be considered in comparing the influence of the fluorophenyl substituents on the Ti–O bond lengths and even more so on the Ti–O–C bond angles. These compounds were synthesized by the reaction of $Ti(OR)_4$ (R = *i*Pr) with fluorophenols or $(F_3C)_2CHOH$. In the majority of cases one of the HOR or RO groups or even both remain associated with the Ti atom. The Ti–O ring bonds of compound **10** are significantly longer than in all other comparable compounds. On the other hand, the Ti–O bonds to the exocyclic C_6F_5 groups are on average shorter. The Ti–O bond lengths to the O*i*Pr groups in compound **12** and **13** are somewhat shorter in contrast to the Ti–O bonds of the $O\text{-}CH(CF_3)_2$ groups. Compounds containing $TiOC_6F_5$ groups are generally dimeric usually with bridging F_5C_6O groups in the dimeric unit. This is, however, not the case for $[(F_3C)_2HCO)_2(OEt)_2Ti]_2$ [**13**] [7] where two OEt groups occupy bridging positions. Therefore, it is difficult to predict whether a fluorophenolate group, an isopropyloxy group or an EtO group will occupy bridging positions.

Experimental Section

All experiments were conducted in an atmosphere of nitrogen gas and by application of the Schlenk technique. Only H_2O-free solvents were used. $TiCl_4$, F_5C_6OH, *tert.*-BuOH and 2,6-$i\text{Pr}_2C_6H_3OH$ were commercial products. $H_3B{\cdot}THF$ was prepared from $LiBH_4$ and $BF_3{\cdot}OEt_2$ in Et_2O and dissolving the generated gas in THF. NMR: Bruker AC 300 (^{11}B), Jeol E 400 (^1H, ^{13}C, ^{11}B). Chemical shifts δ are given in ppm. ^{11}B NMR spectra were measured proton-coupled and proton-decoupled using $F_3B{\cdot}OEt_2$ as external standard. Elemental analyses were performed in the Microanalytical Laboratory of the Department.

*Tris(2,4-di-tert.-butylphenolato)titanium(IV) chloride, **2**, and tetrakis(2,4-di-tert.-butylphenolato)titanium(IV), **4***

2,6-Di-*tert.*-butylphenol (1.54 g, 7.46 mmol) was dissolved in toluene (30 mL). At ambient temperature this solution was added to a stirred toluene solution (30 mL) of $TiCl_4$ (0.47 g, 2.49 mmol). A dark-red solution resulted which was heated to 140 °C for 5 h to drive out all HCl. Afterwards, the toluene was removed at 60 °C *in vacuo*. The dark-red solid residue **2** had a m. p. of 125 – 127 °C. – ^{1}H NMR (C_6D_6): δ = 1.27 (s, 27 H, *p*-CMe_3), 1.52 (s, 27 H, *o*-CMe_3), 7.0 (dd, 3 H, ^3J(H,H) = 1.9 Hz, ^4J(H,H) = 1.9 Hz), 7.10 (d, 3 H, ^3J(H,H) = 7.8 Hz), 7.45 (d, 3 H, ^4J(H,H) = 1.9 Hz). – ^{13}C NMR (C_6D_6): δ = 31.22 (H_3CC), 31.9 (H_3CC), 34.33 (Me_3C), 34.74 (Me_3C), 122.33 (*p-C*), 135.12 (*m-C*), 139.86 (m-*C*), 141.53 (*o-C*), 146.31 (*o-C*), 169.58 (*i*-C). – $C_{42}H_{63}O_3ClTi$ (699.17): calcd. Cl 5.07; found Cl 5.4.

The residue was dissolved in toluene (40 mL) and the solution cooled to −78 °C. A solution of Na[$HBEt_3$] (2.49 mL, 1.0 M) in toluene (30 mL) was slowly added. After addition, the mixture was allowed to attain r. t. The solution showed an ^{11}B NMR signal at 89.0 ppm for BEt_3. The volatiles were removed *in vacuo* and the residue then treated with hexane (60 mL). After filtering the dark-red suspension the filtrate was reduced in volume to 20 mL and cooled to −30 °C. After several days dark-red crystals separated which were shown by X-ray crystallography to be tetrakis(2,4-di-*tert.*-butylphenolato)titanium(IV), **4**. – ^{1}H NMR (C_6D_6): δ = 1.29 (s, 36 H, $(CH_3)_3C$), 1.53 (s, 36 H, $(CH_3)_3C$), 6.98 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.9 Hz, *m*-C*H*), 7.12 (d, 3 H, ^3J(H,H) = 7.8 Hz, *o*-C*H*), 7.41 (d, ^{3}H, ^4J(H,H) = 1.9 Hz, *CH*). – ^{13}C NMR (C_6D_6): δ = 31.29 ($(H_3C)_3C$), 31.97 ($(H_3C)_3C$), 34.63 ($(H_3C)_3C$), 34.81 ($(H_3C)_3C$), 122.24 (*p-C*), 135.23 (*m*-C), 138.63 (*m*-C), 141.65 (*o*-C), 146.19 (*o*-C), 169.35 (*i*-C).

*Lithium-dihydrido-bis(pentafluorophenolato)borate, **5***

To a stirred suspension of $LiBH_4$ (240 mg, 11.2 mmol) in benzene (25 mL) was slowly added a benzene solution of F_5C_6OH (3.12 g, 22.4 mmol). H_2 evolved slowly. After 19 h the H_2 evolution had ceased. Afterwards, the solvent was removed *in vacuo* from the colorless suspension leaving a colorless solid. Yield: 3.4 g **5** (79 %); m. p. 129 – 132 °C. – ^{1}H NMR ($CDCl_3$): δ = no signals observed. – ^{13}C NMR: only a broad noise observed. – ^{11}B NMR ($CDCl_3$): δ = 1.7 (br.). – $C_{12}H_2O_2BF_{10}Li$ (385.89): calcd. C 37.35, H 0.52; found C 36.37, H 0.64.

*Tris(pentafluorophenolato)(2,6-diisopropylphenolato)titanium(IV), **10***

A suspension was prepared from $LiBH_2(OC_6F_5)_2$ (1.68 g, 4.4 mmol) and hexane (20 mL). While stirring, a solution of tris(2,6-diisopropylphenolato)titanium(IV) chloride (1.46 g, 2.32 mmol) in hexane (60 mL) was slowly added. There was some gas evolution. A yellow suspension formed at the beginning which slowly turned brown. After stirring over night the insoluble material was removed by filtration. About 70 % of the solvent was removed from the filtrate *in vacuo*. The filtrate was cooled to −30 °C. Red crystals separated within 6 d from the dark-red solution. Yield of **10**: 0.66 g, m. p. 104 °C. – ^{1}H NMR (C_6D_6): δ = 1.16 (d, ^3J(H,H) = 6.81 Hz, CHCH_3)$_2$, 3.57 (sept., ^3J(H,H) = 6.81 Hz, C*H*Me$_2$), 6.83 – 6.92 (m, *p*-C). – ^{19}F NMR (C_6D_6): δ = −175.2 (t, ^3J(F,F) = 20 Hz, *p*-F), −170.3 (^3J(F,F) = 20 Hz, *m*-F), −169.0 (^3J(F,F) = 20 Hz, *o*-F). – ^{11}B NMR (hexane): δ = 17.6 (br), 28.3 (d, $^1J(^{11}B^1H)$ = 162 Hz (2,6-*i*Pr$_2$C$_6$H$_3$O)(F$_6$C$_6$O)BH). – $C_{40}H_{17}O_4F_{15}Ti$ (894.44): calcd. C 53.71, H 1.92; found C 50.12, H 2.18.

Crystal structure determinations

X-Ray studies were performed with a Siemens P4 instrument equipped with a low-temperature device and an area detector. MoK_α radiation and a graphite monochromator were used and the data collected at −78 °C. The unit cell dimensions were calculated from the reflections collected on 8 different settings in ω and ϕ by changing ω in 2° steps and using the program SMART [18]. Data reduction was performed with SAINT [18], and the structures were solved and refined with SHELX programs [19]. Table 3 contains relevant crystallographic data.

CCDC 792546 (**4**) and 792547 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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