

# Four- five- and six-co-ordinated pentafluorophenylthallium(III) complexes.

## Crystal structures of $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$ , $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)]_2$ and $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$

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### Abstract

$[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  or  $[\text{Ag}(\text{C}_6\text{F}_5)]$  act as arylating ligands able to transfer two or one pentafluorophenyl groups to  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  leading to  $[\text{NBu}_4][\text{Tl}(\text{C}_6\text{F}_5)_4]$  (**1**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (diox = 1,4 dioxane) (**2**) in an improved synthesis, the latter being a starting material for the synthesis of  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$  (**4**). However,  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  does not transfer the pentafluorophenyl group when reacted with  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  and the complexes  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{py})_2]$  (**5**),  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)]_2$  (**6**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$  (**7**) are obtained as the main products, which can be obtained in a better yield by the addition of the neutral ligands to  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$ . The X-ray structure of complexes **3**, **6** and **7** show thallium(III) centres in a tetrahedral, trigonal bipyramidal or octahedral arrangements, respectively.

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**Keywords:** Thallium; Silver; Aryl transfer; Phosphine oxide; Pentafluorophenyl complexes; Crystal structures

### 1. Introduction

The organometallic chemistry of thallium is of current interest because of its versatility in structural behaviour [1–6], because of its many metal–metal interactions with itself or with transition metals [7–13] and because of its relevance in environmental chemistry [14,15]. Thus, organometallic thallium complexes with the metal in different oxidation states such as I, II and III are known; oxidation state II being the least represented. It is noteworthy that the reported X-ray structures of thallium complexes reveal that this element presents

different structures for complexes with very similar stoichiometries, mainly due to interactions in solid state. This is both the source of beautiful structures and the reason behind a behaviour which is not easy to predict. Environmental concern has led to studies on the toxicity of thallium. These have led to the discovery of natural methylation resulting in  $\text{TlMe}_2$  derivatives which have been detected in the oceans [14,15]. This has underscored the importance of the studies on dimethylthallium(III) [16–18] complexes and on aryl thallium(III) derivatives which are poorly represented [1–4,19–21].

Continuing with our interest in both aryl–thallium chemistry and in the use of aryl–silver complexes as arylating agents [9,22–29], we report here the use of  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  and  $[\text{Ag}(\text{C}_6\text{F}_5)]$  as arylating agents capable of transferring one or two pentafluorophenyl groups to  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$ . This leads to a substantial

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improvement of the synthesis of  $[\text{NBu}_4][\text{Tl}(\text{C}_6\text{F}_5)_4]$  (**1**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (diox = 1,4-dioxane) (**2**) compared to the previously described method using the lithium derivative  $\text{LiC}_6\text{F}_5$  [23] or  $\text{HBF}_4$  [21]. Complex **2** is a precursor for the synthesis of  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$  (**4**). However,  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  does not behave as an arylating agent when reacted with  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  and only  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{L})]_2$  L = py (**5**);  $\text{OPPh}_3$  (**6**) and  $\text{OdppmO}$  (bis(diphenylphosphinemethane)dioxide) (**7**) are obtained as the main products of a complicated mixture. Complexes **5–7** can be obtained in a pure form by the reaction of  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  with the appropriate ligand. The lack of many structures in aryl thallium(III) chemistry—no  $[\text{TlR}_3(\text{L})]$  (R = aryl) has been totally characterised—and the above mentioned versatility of the thallium(III) centre forced us to resolve the structures of complexes  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**),  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)]_2$  (**6**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2]$ - $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$  (**7**), which show thallium(III) centres in such different surroundings as tetrahedral, trigonal bipyramidal or octahedral arrangements, respectively.

## 2. Results and discussion

The reaction of  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  with  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  in diethyl ether under inert atmosphere and in 1:1 molar ratio leads to  $[\text{NBu}_4][\text{Tl}(\text{C}_6\text{F}_5)_4]$  (**1**), with a very high yield, 93%, as an air-stable solid at room temperature whose properties coincide with those previously described for this complex [23,27] (Scheme 1, Eq. (i)). Previous procedures, such as the use of  $\text{TlCl}_3$  [23] or  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Br}]$  [27], require an excess of  $\text{LiC}_6\text{F}_5$  (6:1 or 4:1 molar ratio, respectively) to get the tetrakis(pentafluorophenyl)thallium(III) derivative and produce yields of only 60 or 54%, respectively, probably due to collateral reactions that take place because of the excess of lithium reagent. The good properties of polyhalophe-

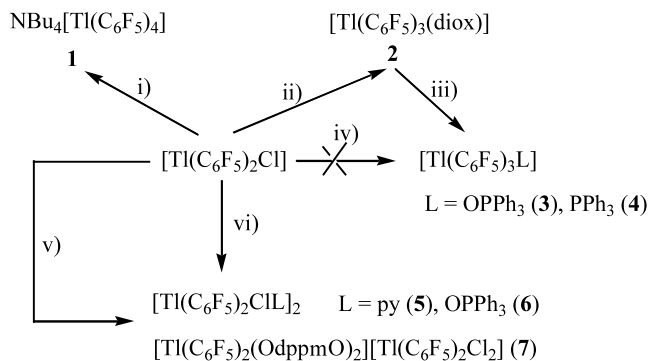
nylsilver(I) complexes as arylating agents are confirmed, as we have reported in previous papers [25,28]. Furthermore, this is one of the rare examples in which two  $\text{C}_6\text{F}_5$  groups are transferred between two metals. It is noteworthy that another complex able to transfer two  $\text{C}_6\text{F}_5$  groups is the starting material  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$ .

This result was determinant in the search for a similar reaction that would synthesise  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (**2**) from  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  whilst avoiding the use of excess corrosive  $\text{HBF}_4$  [21], required in the previous preparation of **2**. Thus, the reaction between  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  and  $[\text{Ag}(\text{C}_6\text{F}_5)]$  was carried out in a thallium–silver 1:1 molar ratio (Scheme 1, Eq. (ii)). The  $\text{AgCl}$  was filtered off and, adding dioxane, we managed to isolate a solid from the solution whose properties correspond to  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (**2**) with a yield of 91%.

The  $^{19}\text{F}$ -NMR spectra of **1** and **2** show the equivalence of pentafluorophenyl groups in each complex, which is consistent with the tetrahedral co-ordination of the thallium(III) centre proposed for these complexes. It is interesting to note that the presence of two active nuclei  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  (29.5 and 70.5% isotopic abundance) with similar gyromagnetic constants made the signals corresponding to  $F_o$ ,  $F_p$  and  $F_m$  atoms appear as doublets of multiplets, because of the additional coupling between them. These  $^{203,205}\text{Tl}-\text{F}$  coupling constants should be different depending on the co-ordination, as was observed in  $[\text{Tl}(2,4,6-\text{C}_6\text{F}_3\text{H}_2)_2]$ - $[\text{Tl}(2,4,6-\text{C}_6\text{F}_3\text{H}_2)\text{Cl}_3]$  (i.e.  $J_{203,205\text{Tl}-F_o} = 880.4$  and  $J_{203,205\text{Tl}-F_o'} = 913.1$  Hz), (i.e.  $J_{203,205\text{Tl}-H_m} = 187.7$  and  $J_{203,205\text{Tl}-H_m'} = 298.6$  Hz in  $^1\text{H}$ -NMR) or in the  $^{203,205}\text{Tl}-\text{H}$  constants in  $[\text{Tl}(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2]$ - $[\text{Tl}(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\text{Cl}_3]$  (i.e.  $J_{203,205\text{Tl}-H_m} = 168.0$  and  $J_{203,205\text{Tl}-H_m'} = 403.9$  Hz in the  $^1\text{H}$ -NMR) [26]. In these cases, based on the integration ratios, the largest constants correspond to the aromatic groups in a tetrahedral fashion and this information agrees with the solid state for the mesityl complex [25].

$[\text{TlR}_3(\text{diox})]$  complexes have been used as useful starting materials for the synthesis of new  $[\text{TlR}_3\text{L}]$  complexes, (R = 2,4,6- $\text{C}_6\text{F}_3\text{H}_2$  and L =  $\text{dppm}$ ,  $\text{OPPh}_3$ ,  $\text{PPh}_3$ ) [21] or (R =  $\text{C}_6\text{F}_5$  and L =  $\text{dppm}$ ,  $\text{OdppmO}$ ) [22] and so  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (**2**) reacts with  $\text{OPPh}_3$  or  $\text{PPh}_3$  leading to the new species  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**) or  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$  (**4**) (Scheme 1, Eq. (iii)).

Complexes **3** and **4** are non-conducting in acetone solutions and the IR spectra show absorptions due to the  $\text{C}_6\text{F}_5\text{-X}$ -sensitive mode at 961 (vs) (**3**), 962 (vs) (**4**)  $\text{cm}^{-1}$  and to the phosphine oxide  $\nu(\text{O}=\text{P})$  1160 (vs) (**3**)  $\text{cm}^{-1}$ . The last wave number suggests the co-ordination of the  $\text{OPPh}_3$  ligand because of the low energy displacement of  $\nu(\text{O}=\text{P})$   $\Delta = 33$   $\text{cm}^{-1}$  [30]. The  $^{19}\text{F}$ -NMR spectra at room temperature in  $\text{CDCl}_3$  of complexes **3** and **4** show the characteristic pattern, doublet of multiplets, doublet of triplets and doublet of multiplets, due to  $F_o$ ,  $F_p$  and  $F_m$  atoms in  $\text{C}_6\text{F}_5$  equivalent



i)  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$ , ii)  $[\text{Ag}(\text{C}_6\text{F}_5)]$ , iii) L, iv) and v)  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  or  $[\text{Ag}(\text{C}_6\text{F}_5)] + \text{L}$ , vi) L

Scheme 1.

groups. The field displacement of signals and the coupling  $^{203,205}\text{Tl}-\text{F}$  constants are similar for both complexes. The values of these constants are close to those found in  $[\text{NBu}_4][\text{Ti}(\text{C}_6\text{F}_5)_4]$  (**1**) and  $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (**2**) suggesting a similar structure for all these complexes in solution. The room temperature  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra show a singlet at 35.60 and 10.55 ppm for **3** and **4**, respectively. Cooling the solutions to  $-60^\circ\text{C}$  in (**3**) and  $-50^\circ\text{C}$  in (**4**) allows us to observe the splitting of the signal in a doublet of multiplets in both cases with  $J_{^{203,205}\text{Tl}-\text{P}} = 444.7$  (**3**) and 282.0 (**4**) Hz. These values are similar to those found in the few examples which have been described of  $[\text{TlR}_3\text{L}]$  stoichiometry,  $\text{L} = \text{CH}_2\text{PR}'_3$  [29], where monomer species are assumed, although none of them have been characterised by X-ray diffraction.

Since no structures of  $[\text{TlR}_3\text{L}]$  complexes are known, the molecular structure of the complex  $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**) has been established by X-ray diffraction. Single crystals were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of **3** at room temperature. The mononuclear species is shown in Fig. 1 and selected bond lengths and angles are given in Table 1.

The molecule of  $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**) displays a distorted tetrahedral arrangement for the thallium centre with angles ranging from  $122.23(14)^\circ$  ( $\text{C}(13)-\text{Ti}(1)-\text{C}(7)$ ) to  $90.59(12)^\circ$  ( $\text{O}(1)-\text{Ti}(1)-\text{C}(13)$ ). The  $\text{Ti}-\text{C}$  bond distances of 2.179(4), 2.190(4) and 2.193(4) Å are comparable to those found in  $[\text{Ti}\{\text{CH}_2\text{COMe}\}_2(\mu\text{-CF}_3\text{SO}_3)(\text{bipy})]_2$  [31] (2.16(8) and 2.171(7) Å) and  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}\{\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{PCH}_2\text{PPh}_2(\text{O}))\}_2]$  [32] (2.18(2) Å). Although the  $\text{Ti}(1)-\text{O}(1)-\text{P}(1)$  angle is very large [ $154.68(17)^\circ$ ] it is smaller than the corresponding angle ( $168.0^\circ$ ) of  $[\text{Ti}(2,3,5,6\text{-C}_6\text{F}_4\text{H})_2\text{Cl}(\text{OPPh}_3)]_2$

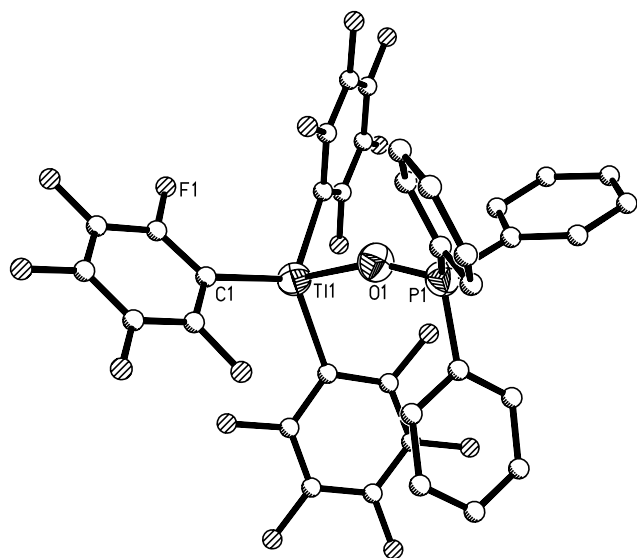


Fig. 1. View of the molecular structure of **3** (ellipsoids are drawn at 50% probability level). H atoms have been omitted for clarity.

Table 1  
Bond lengths (Å) and angles ( $^\circ$ ) for  $[\text{Ti}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**)

Bond lengths			
Ti(1)–C(1)	2.180(4)	Ti(1)–C(7)	2.192(4)
Ti(1)–C(13)	2.190(4)	Ti(1)–O(1)	2.300(3)
Bond angles			
C(1)–Ti(1)–C(13)	116.86(14)	C(2)–C(1)–Ti(1)	121.4(3)
C(1)–Ti(1)–C(7)	118.51(15)	C(6)–C(1)–Ti(1)	122.9(3)
C(13)–Ti(1)–C(7)	122.24(14)	C(8)–C(7)–Ti(1)	122.9(3)
C(1)–Ti(1)–O(1)	98.16(13)	C(12)–C(7)–Ti(1)	120.0(3)
C(13)–Ti(1)–O(1)	96.86(11)	C(18)–C(13)–Ti(1)	122.0(3)
C(7)–Ti(1)–O(1)	90.57(11)	C(14)–C(13)–Ti(1)	122.2(3)
P(1)–O(1)–Ti(1)	154.67(16)		

[**20**] and similar to that present in  $[(\text{C}_6\text{F}_5)_2\text{TlO}_2\text{CC}_6\text{F}_5(\text{OPPh}_3)]_2$  [**19**]. In our case this large angle can be attributed to steric factors. The  $\text{Ti}-\text{O}$  bond length of 2.300(3) Å is comparable to that found in  $[(\text{C}_6\text{F}_5)_2\text{TlO}_2\text{CC}_6\text{F}_5(\text{OPPh}_3)]_2$  [**19**] (2.391(9) Å).

The tetrahedral structure of **3** in the solid state is compatible with the NMR data in solution and, by extension, the spectroscopic data suggest that compounds **1–4** can be tetrahedral both in solution and in solid state.

Attempts to use  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$ , ( $\text{L} = \text{py}$ ), or mixtures of  $[\text{Ag}(\text{C}_6\text{F}_5)] + \text{L}'$  ( $\text{L}' = \text{OPPh}_3$  or  $\text{OdppmO}$ ) as arylating agents of  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]$ , capable of transferring one  $\text{C}_6\text{F}_5$  group as well as the ligand  $\text{L}$  or  $\text{L}'$ , failed and, instead of the expected  $[\text{Ti}(\text{C}_6\text{F}_5)_3\text{L}]$  complexes, different mixtures were obtained in which complexes of the type  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{CIL}]_2$  seem to be present as the main reaction products (Scheme 1, Eqs. (iv) and (v)). In order to confirm this point we have obtained these  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{CIL}]_2$  complexes ( $\text{L} = \text{py}$  (**5**);  $\text{OPPh}_3$  (**6**);  $\text{OdppmO}$  (**7**)) through the reaction of  $[\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}]$  with  $\text{L} = \text{py}$ ,  $\text{OPPh}_3$  or  $\text{OdppmO}$ , leading to complexes **5**, **6** and **7** with good yields as a result of the addition of the neutral ligand to the starting material (Scheme 1, Eq. (vi)).

The IR spectra show absorptions from the pentafluorophenyl group and no difference is observed in the  $\text{C}_6\text{F}_5\text{-X}$ -sensitive mode, 964 (vs) (**5**) 965 (vs) (**6**) and 962 (vs) (**7**)  $\text{cm}^{-1}$ . The  $\nu(\text{O}=\text{P})$  is assumed at 1171 (vs, br) (**6**) and 1184 (vs)  $\text{cm}^{-1}$  (**7**) [30], and the two ( $\text{Ti}-\text{Cl}$ ) bands at 226 (s), 260 (m)  $\text{cm}^{-1}$  in (**7**) change into a single band at 258 (m)  $\text{cm}^{-1}$  in (**5**) and 246 (m)  $\text{cm}^{-1}$  in (**6**). Although it was proposed [33] that when ( $\text{Ti}-\text{Cl}$ ) appears below 300  $\text{cm}^{-1}$  it is associated to polymer or dimer systems with halogen bridging, there are some examples of terminal ( $\text{Ti}-\text{Cl}$ ) bands below this value, such as in  $[\text{Ti}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2][\text{Ti}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{Cl}_3]$  [25]. The acetone solutions of complexes **5** and **6** show no electrolyte behaviour while that of **7** leads to lower values than those characteristic in 1:1 electrolytes [34].

The  $^1\text{H}$ -NMR spectra at room temperature of complexes **5–7** show the assignable resonances to the ligands in the aromatic region. In addition, complex **7** shows a

triplet at 3.59 ppm for two equivalent methylene protons with a  $J_{\text{P-H}} = 13.4$  Hz, which agrees with a symmetrical arrangement of the ligand. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra at room temperature in  $\text{CDCl}_3$  of complexes **6** and **7** show a singlet at 36.62 and 30.3 ppm, respectively. Lower temperatures do not provide a better resolution to understand the  $^{203,205}\text{Tl}$ -P coupling constants system and only in the former case is it possible to recognise a broadening in the signal that splits into a multiplet, centred at 32.90 ppm, when a  $(\text{CD}_3)_2\text{CO}$  solution is used and the experiment is recorded at  $-80$  °C. On the other hand, the  $^{19}\text{F}$ -NMR spectra of **5–7** show the signals corresponding to only one equivalent pentafluorophenyl group, which remains even if the temperature is lowered to  $-80$  °C, with  $^{203,205}\text{Tl}$ -F coupling constants for the  $F_o$ ,  $F_p$  and  $F_m$  of the same order of magnitude in all these complexes, although smaller than in complexes **1–4**. With all these data it is not easy to propose the structure of these complexes. This is because the molecular structures of complexes  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)]_2$  (**6**) and  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$  (**7**) have been established by X-ray diffraction (Figs. 2 and 3) on single suitable crystals obtained by slow diffusion from dichloromethane–diethyl ether. Selected bond lengths and angles are given in Tables 2 and 3.

The molecular structure of complex **6**, which exhibits a crystallographic centre of symmetry, comprises two distorted trigonal pyramidal  $\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)$  units linked through two different Tl–Cl bridging bonds. The apical positions are occupied by the two pentafluorophenyl rings giving an angle of  $139.41(17)^\circ$ . Two of these rings are close to perpendicular to each other, with a dihedral angle of about  $7.6^\circ$ . The  $\text{OPPh}_3$  and the two bridging chlorines occupy the equatorial sites. The Tl–O ( $2.380(3)$  Å) and Tl–C ( $2.168(5)$  and  $2.156(4)$  Å) bond

lengths are in the range of those found in complex **3**. The longer Tl–Cl distance ( $2.9498(12)$  Å) is similar to those found in thallium complexes with bridging chlorine atoms, such as  $[\text{Tl}_2(\text{CH}_2\text{SiMe}_3)_4(\mu\text{-Cl})_2]$  ( $2.993(3)$  Å) [35],  $[\text{Tl}_2(\text{C},\text{N}-\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2\text{Cl}_2(\mu\text{-Cl})_2]$  ( $2.936(3)$  Å) [36] and  $(\text{Pip})_2[\text{Tl}_2\text{Cl}_8(\mu\text{-Cl})_2]$  ( $2.893(4)$  Å) [37] and to the longer Tl–Cl distance in  $[\text{Tl}(\text{C}_6\text{F}_4\text{H})_2\text{Cl}(\text{OPPh}_3)]_2$  ( $2.936(3)$  Å) [20]. The shorter Tl–Cl distance ( $2.5339(13)$  Å) is similar to those found in terminal chloride atoms (see below), including those in complex **7** and to the shorter Tl–Cl distance in  $[\text{Tl}(\text{C}_6\text{F}_4\text{H})_2\text{Cl}(\text{OPPh}_3)]_2$  ( $2.541(3)$  Å) [20]. The main distortion from regular trigonal bipyramidal geometry is represented by the C–Tl–C  $139.41(17)^\circ$  angle. The very large value for the P–O–Tl  $164.1(2)^\circ$  angle is similar ( $168.0^\circ$ ) to that found in  $[\text{Tl}(\text{C}_6\text{F}_4\text{H})_2\text{Cl}(\text{OPPh}_3)]_2$  [20], where the large value was not attributed to any intramolecular steric factors but was rather based on the easy deformation of M–O–P angles that could be affected by crystal packing factors. Fig. 2 shows how pentafluorophenyl groups are contributing to this effect.

$[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{TlCl}_2(\text{C}_6\text{F}_5)_2]$  (**7**) crystallises in the  $P\bar{1}$  space group with both cation and anion being thallium complexes. The anion  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$  displays a distorted tetrahedral geometry where the main distortion comes from the C(11)–Tl(1)–C(21) angle of  $135.8(3)^\circ$ . The Tl–C bond distances ( $2.167(7)$  and  $2.177(7)$  Å) are similar to those found in complex **3** and the Tl–Cl bond lengths ( $2.4968(19)$  and  $2.567(2)$  Å) are in the range of the Tl–Cl terminal distances in complexes such as  $[\text{TlClBrI}(\text{OPPh}_3)_2]$  ( $2.469(1)$  Å) [38] and  $[\text{TlCl}_3(\text{C}_5\text{H}_5\text{N})_3] \cdot \text{C}_5\text{H}_5\text{N}$  ( $2.520(6)$  and  $2.498(4)$  Å) [39]. The co-ordination around the thallium in the cation  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2]$  can be rationalised as derived from a distorted octahedron with the penta-

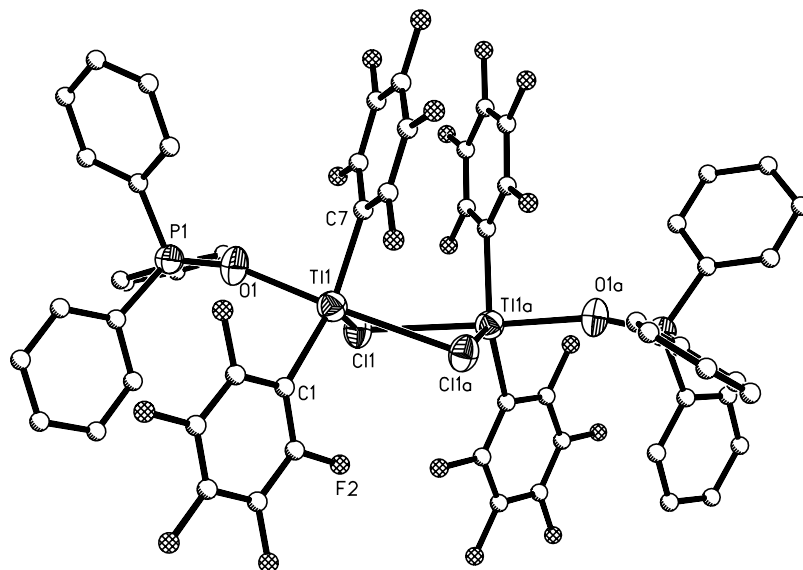


Fig. 2. Solid state molecular structure of **6**. Displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

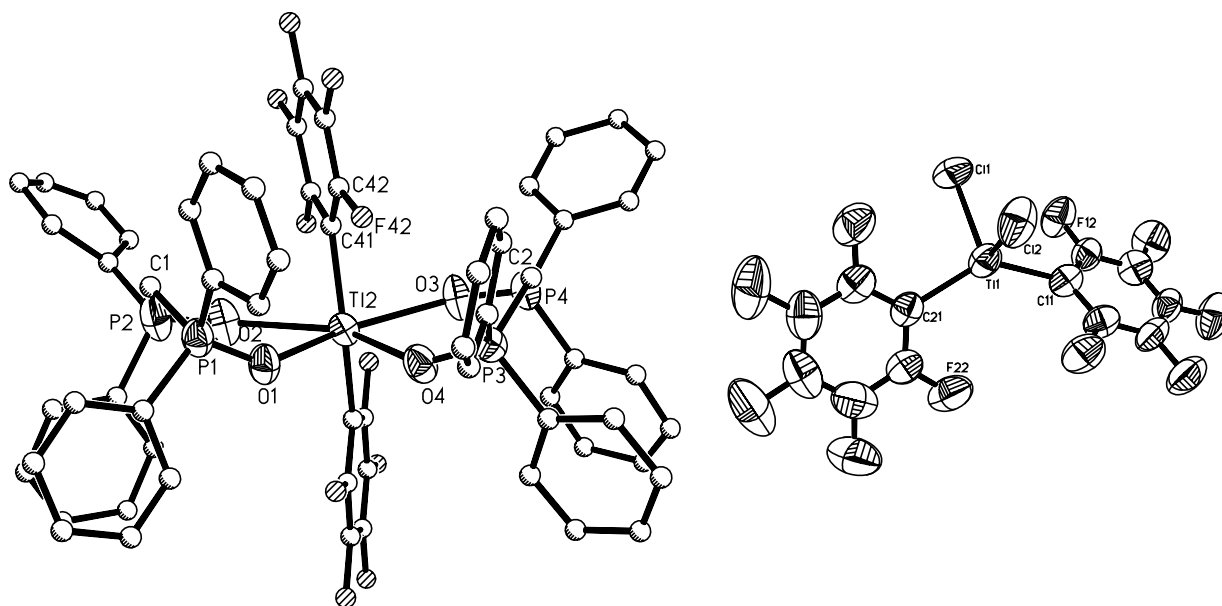


Fig. 3. Solid state structure of **7** showing the cation and the anion. Displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Table 2  
Bond lengths (Å) and angles (°) for  $[\text{Ti}_2(\text{C}_6\text{F}_5)_4(\mu\text{-Cl})_2(\text{OPPh}_3)_2]$  (**6**)

Bond lengths			
Ti(1)–C(1)	2.156(4)	Ti(1)–Cl(1)#1	2.9498(12)
Ti(1)–C(7)	2.168(5)	Cl(1)–Ti(1)#1	2.9498(12)
Ti(1)–O(1)	2.380(3)	O(1)–P(1)	1.496(3)
Ti(1)–Cl(1)	2.5339(13)		
Bond angles			
C(1)–Ti(1)–C(7)	139.41(17)	O(1)–Ti(1)–Cl(1)#1	169.19(9)
C(1)–Ti(1)–O(1)	91.32(15)	Cl(1)–Ti(1)–Cl(1)#	181.08(5)
C(7)–Ti(1)–O(1)	89.39(14)	Ti(1)–Cl(1)–Ti(1)#	194.10(4)
C(1)–Ti(1)–Cl(1)	111.44(13)	P(1)–O(1)–Ti(1)	164.1(2)
C(7)–Ti(1)–Cl(1)	109.15(12)	C(2)–C(1)–Ti(1)	125.3(3)
O(1)–Ti(1)–Cl(1)	88.90(9)	C(6)–C(1)–Ti(1)	117.2(4)
C(1)–Ti(1)–Cl(1)#1	96.09(12)	C(8)–C(7)–Ti(1)	123.9(4)
C(7)–Ti(1)–Cl(1)#1	90.08(11)	C(12)–C(7)–Ti(1)	119.3(3)

fluorophenyl groups occupying the *trans* positions ( $\text{C}(41)\text{--Ti}(2)\text{--C}(41) = 158.1(2)^\circ$ ). The two bis(diphenylphosphinmethane)dioxo molecules occupy the equatorial positions with  $\text{O--Ti--O}_{\text{cis}}$  angles ranging from  $72.96(13)$  to  $132.95(12)^\circ$  and  $\text{O--Ti--O}_{\text{trans}}$  with values of  $153.64(13)$  and  $150.51(13)^\circ$ . The Ti–C bond distances of  $2.111(6)$  and  $2.121(6)$  Å are shorter than the corresponding distances found in the anion. Two of the four Ti–O bond lengths ( $2.393(4)$  and  $2.406(4)$  Å) are slightly longer than those observed in complex **3**. However, the two remaining bond lengths are remarkably longer ( $2.559(4)$  and  $2.689(4)$  Å).

The structures of complexes **6** and **7** do not fit in perfectly with the solution data, mainly NMR, in which complexes **5–7** show similar behaviour. Complexes **5**

Table 3  
Bond lengths (Å) and angles (°) for  $[\text{Ti}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{TiCl}_2(\text{C}_6\text{F}_5)_2]$  (**7**)

Bond lengths			
Ti(1)–C(11)	2.167(7)	Ti(2)–O(3)	2.559(4)
Ti(1)–C(21)	2.177(7)	Ti(2)–O(2)	2.689(4)
Ti(1)–Cl(1)	2.4968(19)	P(1)–O(1)	1.496(4)
Ti(1)–Cl(2)	2.567(2)	P(2)–O(2)	1.491(4)
Ti(2)–C(31)	2.111(6)	P(3)–O(4)	1.498(4)
Ti(2)–C(41)	2.121(6)	P(4)–O(3)	1.486(4)
Ti(2)–O(1)	2.393(4)		
Ti(2)–O(4)	2.406(4)		
Bond angles			
C(11)–Ti(1)–C(21)	135.8(3)	O(4)–Ti(2)–O(3)	76.50(13)
C(11)–Ti(1)–Cl(1)	107.67(18)	C(31)–Ti(2)–O(2)	86.78(18)
C(21)–Ti(1)–Cl(1)	106.46(17)	C(41)–Ti(2)–O(2)	82.78(19)
C(11)–Ti(1)–Cl(2)	100.06(19)	O(1)–Ti(2)–O(2)	72.96(13)
C(21)–Ti(1)–Cl(2)	99.55(19)	O(4)–Ti(2)–O(2)	150.51(13)
Cl(1)–Ti(1)–Cl(2)	101.80(8)	O(3)–Ti(2)–O(2)	132.95(12)
C(31)–Ti(2)–C(41)	158.1(2)	P(1)–O(1)–Ti(2)	138.5(2)
C(31)–Ti(2)–O(1)	98.47(19)	P(2)–O(2)–Ti(2)	133.1(2)
C(41)–Ti(2)–O(1)	96.76(19)	P(4)–O(3)–Ti(2)	136.4(2)
C(31)–Ti(2)–O(4)	93.16(19)	P(3)–O(4)–Ti(2)	141.3(2)
C(41)–Ti(2)–O(4)	105.3(2)	C(12)–C(11)–Ti(1)	125.0(5)
O(1)–Ti(2)–O(4)	77.90(14)	C(16)–C(11)–Ti(1)	120.3(5)
C(31)–Ti(2)–O(3)	89.15(18)	C(22)–C(21)–Ti(1)	121.3(6)
C(41)–Ti(2)–O(3)	84.07(18)	C(26)–C(21)–Ti(1)	122.7(6)
O(1)–Ti(2)–O(3)	153.64(13)	C(36)–C(31)–Ti(2)	119.4(5)

and **6** should have dimer structures even in solution, because the data are compatible with this possibility and, in the case of **7**, some interchangeable equilibrium between the dimer and cation–anion structures exists in solution. The preparation of complexes **5–7** in a pure form allows us to confirm that these products are



present in the reaction mixtures of  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  with  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  (see above) although other pentafluorophenylthallium(III) complexes are present.

To conclude, we have described an improved synthesis of  $[\text{NBu}_4][\text{Tl}(\text{C}_6\text{F}_5)_4]$  and  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  proving the excellent behaviour of  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  and  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  as arylating ligands, the former being able to transfer even two  $\text{C}_6\text{F}_5$  groups to the same thallium(III) centre. The  $[\text{Ag}(\text{C}_6\text{F}_5)\text{L}]$  complexes failed to transfer the pentafluorophenyl group and  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  complexes were obtained as the main products of more complicated reactions. The synthesis of these complexes  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  through the addition of the appropriate ligand to  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  confirms this point. The X-ray structure determinations of three complexes once more show the versatility of the thallium(III) centre to adopt different co-ordination forms. In our case, using in all instances phosphine oxide ligands, the pentafluorophenyl derivatives resulted in tetrahedral  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$  (**3**), trigonal bipyramidal  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{OPPh}_3)_2]$  (**6**) or octahedral  $[\text{Tl}(\text{C}_6\text{F}_5)_2(\text{OdppmO})_2][\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$  (**7**) co-ordination of thallium(III) centres and, in the case of **7**, in a tetrahedral arrangement of the anion as well.

### 3. Experimental

#### 3.1. General procedures

IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range  $4000\text{--}200\text{ cm}^{-1}$ , using Nujol mulls between polyethylene sheets.  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{19}\text{F}$ -NMR spectra were recorded on a Varian UNITY 200 or 300 or BRUKER 300 in  $\text{CDCl}_3$  or  $(\text{CD}_3)_2\text{CO}$  solutions; chemical shifts are quoted relative to  $\text{SiMe}_4$  ( $^1\text{H}$ ),  $\text{H}_3\text{PO}_4$  (external  $^{31}\text{P}$ ) and  $\text{CFCl}_3$  (external,  $^{19}\text{F}$ ). The C, H, N analyses were performed with a Perkin–Elmer 2400 microanalyser.  $[\text{Ag}(\text{C}_6\text{F}_5)]$  [**40**],  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  [**40**],  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  [**41**] were prepared by established procedures.

#### 3.2. Synthesis

##### 3.2.1. Synthesis of $[\text{NBu}_4][\text{Tl}(\text{C}_6\text{F}_5)_4]$ (**1**)

To a solution of  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  (0.110 g, 0.19 mmol) in  $\text{Et}_2\text{O}$  (30 ml) was added  $[\text{NBu}_4][\text{Ag}(\text{C}_6\text{F}_5)_2]$  (0.131 g, 0.19 mmol) and the mixture was stirred at room temperature (r.t.) for 2 h under nitrogen. The insoluble  $\text{AgCl}$  was filtered off and the solution was concentrated in vacuum to 5 ml. The addition of  $\text{C}_6\text{H}_{14}$  (20 ml) led to the precipitation of the complex as colourless solid, which was filtered off, washed with  $\text{C}_6\text{H}_{14}$  and dried in vacuum. Yield (%): 93. Anal. Calc. for  $\text{C}_{36}\text{H}_{15}\text{F}_{15}\text{OPTl}$ : C, 43.08; H, 3.25; N, 1.26. Found for **1**: C, 43.66; H, 3.42; N, 1.38%. IR ( $\text{cm}^{-1}$ , Nujol):  $(\text{C}_6\text{F}_5) = 953, 1508,$

$1635$  (vs);  $(\text{NBu}_4) = 884$  (s).  $^{19}\text{F}$ -NMR ( $(\text{CD}_3)_2\text{CO}$ ):  $\delta -115.95$  (dd,  $J_{\text{Tl-F}_o} = 419.9$  Hz),  $-157.79$  (dt,  $J_{\text{Tl-F}_p} = 51.3$  Hz,  $J_{\text{F}_p-\text{F}_m} = 19.3$  Hz),  $-162.41$  (dm,  $J_{\text{Tl-F}_m} = 145.1$  Hz).

##### 3.2.2. Synthesis of $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$ (**2**)

To a solution of  $[\text{Tl}(\text{C}_6\text{F}_5)_2\text{Cl}]$  (0.203 g, 0.35 mmol) in hot  $\text{C}_6\text{H}_5\text{CH}_3$  (20 ml) was added  $[\text{Ag}(\text{C}_6\text{F}_5)]$  (0.096 g, 0.35 mmol) and the mixture was stirred in reflux for 5 h under nitrogen. The  $\text{AgCl}$  was filtered off and the solution was carried out to dryness dissolving the solid residue in  $\text{Et}_2\text{O}$  (15 ml). Addition of 1,4-dioxane (5 ml) and  $\text{C}_6\text{H}_{14}$  (20 ml) gave a white precipitate of  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$ . Yield (%): 91. Anal. Calc. for  $\text{C}_{22}\text{H}_8\text{F}_{15}\text{O}_2\text{Tl}$ : C, 33.30; H, 1.02. Found for **2**: C, 33.47; H, 1.15%. IR ( $\text{cm}^{-1}$ , Nujol):  $(\text{C}_6\text{F}_5) = 957, 1512, 1635$  (vs); (diox) = 862, 894 (vs).  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ ):  $\delta -117.62$  (dm,  $J_{\text{Tl-F}_o} = 531.2$  Hz),  $-153.39$  (dt,  $J_{\text{Tl-F}_p} = 57.3$  Hz,  $J_{\text{F}_p-\text{F}_m} = 19.3$  Hz),  $-160.19$  (dm,  $J_{\text{Tl-F}_m} = 187.2$  Hz).

##### 3.2.3. Synthesis of $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{OPPh}_3)]$ (**3**)

To a suspension of  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (0.194 g, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added  $\text{OPPh}_3$  (0.068 g, 0.25 mmol) and the dissolution of the thallium complex was immediately observed. After 1 h of stirring at r.t. the solution was concentrated to 5 ml and the addition of  $\text{C}_6\text{H}_{14}$  (20 ml) led to the precipitation of the new complex as colourless solid. It was filtered off, washed with  $\text{C}_6\text{H}_{14}$  and dried in vacuum. Yield (%): 60. Anal. Calc. for  $\text{C}_{36}\text{H}_{15}\text{F}_{15}\text{OPTl}$ : C, 43.95; H, 1.55. Found for **3**: C, 44.6; H, 1.35%. IR ( $\text{cm}^{-1}$ , Nujol):  $(\text{C}_6\text{F}_5) = 961, 1504, 1632$  (vs);  $(\text{OPPh}_3) = 471, 487, 515$  (m), 539 (vs), 601 (m), 693 (vs), 743, 753 (s), 780, 1160 (vs), 1592 (m).  $A_M$  ( $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ): 1.  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ ):  $\delta -118.48$  (dm,  $J_{\text{Tl-F}_o} = 551.1$  Hz),  $-153.51$  (dt,  $J_{\text{Tl-F}_p} = 57.9$  Hz,  $J_{\text{F}_p-\text{F}_m} = 19.3$  Hz),  $-160.24$  (dm,  $J_{\text{Tl-F}_m} = 208.1$  Hz).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $(\text{CDCl}_3, -60^\circ\text{C})$ :  $\delta 35.60$  (s);  $36.17$  (dm,  $J_{\text{Tl-P}} = 444.7$  Hz).

##### 3.2.4. Synthesis of $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{PPh}_3)]$ (**4**)

The same procedure as above was used starting from  $[\text{Tl}(\text{C}_6\text{F}_5)_3(\text{diox})]$  (0.095 g, 0.12 mmol) and  $\text{PPh}_3$  (0.031 g, 0.12 mmol). Yield (%): 72. Anal. Calc. for  $\text{C}_{36}\text{H}_{15}\text{F}_{15}\text{PTl}$ : C, 44.65; H, 1.55. Found for **4**: C, 44.2; H, 1.15%. IR ( $\text{cm}^{-1}$ , Nujol):  $(\text{C}_6\text{F}_5) = 962, 1504, 1634$  (vs);  $(\text{PPh}_3) = 501$ (s), 521, 694, 747 (vs), 777 (s).  $A_M$  ( $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ): 10.  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ ):  $\delta -117.02$  (dm,  $J_{\text{Tl-F}_o} = 536.3$  Hz),  $-153.48$  (dt,  $J_{\text{Tl-F}_p} = 57.9$  Hz,  $J_{\text{F}_p-\text{F}_m} = 19.3$  Hz),  $-160.24$  (dm,  $J_{\text{Tl-F}_m} = 186.1$  Hz).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta 10.55$  (s) ( $\text{CDCl}_3, -50^\circ\text{C}$ );  $10.66$  (dm,  $J_{\text{Tl-P}} = 282.0$  Hz).

### 3.2.5. Synthesis of $[Ti(C_6F_5)_2Cl(py)]_2$ (**5**)

To a solution of  $[Ti(C_6F_5)_2Cl]$  (0.143 g, 0.25 mmol) in  $Et_2O$  (30 ml) was added pyridine (0.020 g, 0.25 mmol) and a white precipitate appeared immediately. The suspension was stirred for 1 h at r.t. and the solid filtered off, washed with  $C_6H_{14}$  and dried in vacuum. Yield (%): 89. Anal. Calc. for  $C_{17}H_5ClF_{10}NTi$ : C, 31.3; H, 0.8; N, 2.15. Found for **5**: C, 31.8; H, 0.6; N, 2.25%. IR ( $cm^{-1}$  Nujol):  $(C_6F_5) = 964$  (vs), 1635 (vs);  $(Ti-Cl) = 258$  (m);  $(py) = 694, 754, 1509, 1604$  (vs).  $A_M$  ( $\Omega^{-1} cm^2 mol^{-1}$ ): 2.  $^{19}F$ -NMR ( $CDCl_3$ ):  $\delta -115.0$  (dm,  $J_{Ti-F} = 789.6$  Hz),  $-147.75$  (dt,  $J_{Ti-F} = 84.6$  Hz,  $J_{F-F} = 56.4$  Hz),  $-155.0$  (dm,  $J_{Ti-F} = 338.4$  Hz).

### 3.2.6. Synthesis of $[Ti(C_6F_5)_2Cl(OPPh_3)]_2$ (**6**)

The same procedure as above was used starting from  $[Ti(C_6F_5)_2Cl]$  (0.125 g, 0.22 mmol) and  $OPPh_3$  (0.061 g, 0.22 mmol). Yield (%): 90. Anal. Calc. for  $C_{30}H_{15}ClF_{10}OPTi$ : C, 42.28; H, 1.77. Found for **6**: C, 42.23; H, 1.46%. IR ( $cm^{-1}$ , Nujol):  $(C_6F_5) = 965, 1512, 1636$  (vs);  $(Ti-Cl) = 246$ (s);  $(OPPh_3) = 461$  (w), 490, 508 (vw), 540 (vs), 606 (w), 696, 746 (vs), 757, 791(s), 1171 (vs, br), 1590 (m).  $A_M$  ( $\Omega^{-1} cm^2 mol^{-1}$ ): 4.  $^{19}F$ -NMR ( $CDCl_3$ ):  $\delta -119.33$  (dd,  $J_{Ti-F} = 829.47$  Hz,  $J = 20.67$  Hz),  $-151.35$  (dt,  $J_{Ti-F} = 81.29$  Hz,  $J_{F-F} = 19.29$  Hz),  $-159.58$  (dt,  $J_{Ti-F} = 348.6$  Hz,  $J = 17.91$  Hz).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$ ):  $\delta 36.62$  (s);  $(CD_3)_2CO$ ,  $-80$  °C:  $\delta 32.90$  (s, br).

### 3.2.7. Synthesis of

#### $[Ti(C_6F_5)_2(OdppmO)_2][Ti(C_6F_5)_2Cl_2]$ (**7**)

The same procedure as above was used starting from  $[Ti(C_6F_5)_2Cl]$  (0.143 g, 0.25 mmol) and  $OdppmO$  (0.104 g, 0.25 mmol). Yield (%): 90. Anal. Calc. for  $C_{37}H_{22}ClF_{10}O_2P_2Ti$ : C, 44.85; H, 2.25. Found for **7**: C, 45.05; H, 2.30%. IR ( $cm^{-1}$ , Nujol):  $(C_6F_5) = 962, 1509, 1633$  (vs);  $(Ti-Cl) = 226$ (s), 260 (m);  $(OdppmO) = 506, 690, 740, 1184$  (vs).  $A_M$  ( $\Omega^{-1} cm^2 mol^{-1}$ ): 64.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta 3.59$  (t,  $J_{P-H} = 13.4$  Hz, 2H,  $-CH_2-$ ), 7–8 (m, 20H, Ph).  $^{19}F$ -NMR ( $CDCl_3$ ):  $\delta -119.10$  (dm,  $J_{Ti-F} = 877.7$  Hz),  $-152.20$  (dm,  $J_{Ti-F} = 68.9$  Hz),  $-159.80$  (dm,  $J_{Ti-F} = 373.4$  Hz).  $^{31}P\{^1H\}$ -NMR ( $CDCl_3$ ):  $\delta 30.30$ (s).

### 3.3. Crystal structure determination of compounds **3**, **6** and **7**

Single crystals were grown by diffusing  $C_6H_{14}$  into a  $CH_2Cl_2$  solution of complex  $[Ti(C_6F_5)_3(OPPh_3)]$  (**3**), or  $Et_2O$  into a  $CH_2Cl_2$  solution of complexes  $[Ti(C_6F_5)_2Cl(OPPh_3)]_2$  (**6**) and  $[Ti(C_6F_5)_2(OdppmO)_2][TiCl_2(C_6F_5)_2]$  (**7**), and mounted in inert oil. Crystals of **3**, **6** and **7** were mounted on a glass fibre on a Bruker–Siemens Smart CCD diffractometer using graphite monochromated Mo– $K_\alpha$  radiation ( $\lambda =$

0.71073) with a nominal crystal to detector distance of 4.0 cm.

#### 3.3.1. Crystal data and data collection parameters

Compound **3**  $C_{36}H_{15}F_{15}OPTi$ ,  $M = 983.82$ , monoclinic,  $a = 11.770(2)$ ,  $b = 12.931(3)$ ,  $c = 23.439(5)$  Å,  $\beta = 100.34(3)^\circ$ .  $V = 3509.5(12)$  Å<sup>3</sup>,  $T = 293(2)$  K, space group  $P2(1)/n$ ,  $Z = 4$ ,  $D_{calc} = 1.862$  mg m<sup>-3</sup>,  $F(000) = 1880$ , colourless prism with dimensions  $0.55 \times 0.4 \times 0.35$  mm,  $\mu = 4.757$  mm<sup>-1</sup>,  $\theta$  range for data collection  $1.77$ – $28.32^\circ$ ,  $-15 \leq h \leq 15$ ;  $-13 \leq k \leq 17$ ,  $-31 \leq l \leq 31$ ; 24 319 reflections collected, 8727 independent ( $R_{int} = 0.0468$ ).

Compound **6**  $C_{30}H_{15}ClF_{10}OPTi$ ,  $M = 852.21$ , monoclinic,  $a = 21.803(4)$ ,  $b = 15.535(3)$ ,  $c = 18.637(4)$  Å,  $\beta = 107.82(3)^\circ$ ,  $V = 6010(2)$  Å<sup>3</sup>,  $T = 298(2)$  K, space group  $C2/c$ ,  $Z = 8$ ,  $D_{calc} = 1.884$  mg m<sup>-3</sup>,  $F(000) = 3248$ , colourless prism with dimensions  $0.45 \times 0.35 \times 0.35$  mm,  $\mu = 5.603$  mm<sup>-1</sup>,  $\theta$  range for data collection  $1.64$ – $28.33^\circ$ ,  $-27 \leq h \leq 29$ ,  $-20 \leq k \leq 20$ ,  $-24 \leq l \leq 15$ ; 20 549 reflections collected, 7415 independent ( $R_{int} = 0.0469$ ).

Compound **7**  $C_{74}H_{44}Cl_2F_{20}O_4P_4Ti_2$ ,  $M = 1980.61$ , triclinic,  $a = 14.346(5)$ ,  $b = 16.239(5)$ ,  $c = 16.738(5)$  Å,  $\alpha = 91.338(5)$ ,  $\beta = 100.34(3)$ ,  $\gamma = 93.288(5)^\circ$ ,  $V = 3720(2)$  Å<sup>3</sup>,  $T = 298(2)$  K, space group  $P\bar{1}$ ,  $Z = 2$ ,  $D_{calc} = 1.768$  mg m<sup>-3</sup>,  $F(000) = 1912$ , colourless prism with dimensions  $0.45 \times 0.35 \times 0.35$  mm,  $\mu = 4.582$  mm<sup>-1</sup>,  $\theta$  range for data collection  $1.65$ – $28.38^\circ$ ,  $-18 \leq h \leq 19$ ,  $-17 \leq k \leq 21$ ,  $-22 \leq l \leq 21$ ; 26 705 reflections collected, 18 110 independent ( $R_{int} = 0.0450$ ).

#### 3.3.2. Structure solution and refinement

The structures were solved by direct methods (SHELXS-97) [42] and refined by full-matrix least-squares on  $F^2$ , using the program SHELXL-97 [43]. All data were corrected using the program SADABS [44]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeded to: **3**  $R = 0.031$ ,  $wR = 0.0677$  for 489 parameters, and  $R = 0.0544$   $wR = 0.0744$  for all data, electron density fluctuates in the range 0.723 and  $-1.102$  e Å<sup>-3</sup>. Compound **6**  $R = 0.0338$ ,  $wR = 0.0654$  for 393 parameters, and  $R = 0.0646$   $wR = 0.0760$  for all data, electron density fluctuates in the range 1.081 and  $-1.383$  e Å<sup>-3</sup>. Compound **7**  $R = 0.0489$ ,  $wR = 0.0947$  for 956 parameters, and  $R = 0.1095$   $wR = 0.1134$  for all data, electron density fluctuates in the range 1.270 and  $-1.171$  e Å<sup>-3</sup>.

## 4. Supplementary material

Tables of thermal parameters and observed and calculated structure factors for compounds **3**, **6** and **7** have been deposited at the Cambridge Crystallographic

Data Centre, CCDC nos. 190932–34 respectively. Any request for this material should quote a full literature citation which can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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