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# Synthesis of polymetallic Group 4 complexes bridged by benzenediolate and triolate ligands. X-ray crystal structure of $\{[Ti(C_5Me_5)Cl_2]_2\{\mu-1,4-O(2,3-C_6H_2Me_2)O-\}\}$

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## Abstract

This paper reports the synthesis of polymetallic complexes in which two or three Group 4 metals are linked to a benzene core through oxo groups. Four methods have been evaluated for the synthesis of such derivatives: from the appropriated alcohol with (a) methyl complexes via methane elimination, (b) chloride compounds in the presence of a Lewis base, or (c) a zirconium hydride, and (d) from the lithium salt of the alcohol and chloride complexes. Method a has been used for the synthesis of bimetallic and trimetallic (pentamethylcyclopentadienyl)titanium(IV) complexes  $\{[Ti(C_5Me_5)Cl_2]_2\{\mu-1,4-O(C_6H_2XY)O-\}\}$  (X = Y = H (1); X = H, Y = Me (2); X = Y = Me (3)),  $\{[Ti(C_5Me_5)Me_2]_2\{\mu-1,4-O(C_6H_2Me_2)O-\}\}$  (4), and  $\{[Ti(C_5Me_5)X_2]_3(\mu_3-1,3,5-C_6H_3O_3-)\}$  (X = Cl (7), Me (8)) from the corresponding hydroquinones 1,4-HO(2,3-C<sub>6</sub>H<sub>2</sub>XY)OH (X = Y = H, Me; X = H, Y = Me) or 1,3,5-trihydroxybenzene and  $[Ti(C_5Me_5)Cl_2Me]$  or  $[Ti(C_5Me_5)Me_3]$ , respectively. Bis(cyclopentadienyl)titanium bimetallic complex  $\{[Ti(C_5H_5)_2Cl]_2\{\mu-1,4-O(C_6H_2Me_2)O-\}\}$  (5) is better prepared by method d by treatment of the dilithium salt  $Li_2[1,4-O(2,3-C_6H_2Me_2)O-]$  with  $[Ti(C_5H_5)_2Cl_2]$  whereas the trimetallic compound  $\{[Ti(C_5H_5)_2Cl]_3(\mu_3-1,3,5-C_6H_3O_3-)\}$  (9) can be prepared directly from 1,3,5-trihydroxybenzene in the presence of  $NEt_3$  (method b). Finally, bis(cyclopentadienyl)zirconium complexes  $\{[Zr(C_5H_5)_2Cl]_2\{\mu-1,4-O(C_6H_2Me_2)O-\}\}$  (6) and  $\{[Zr(C_5H_5)_2Cl]_3(\mu_3-1,3,5-C_6H_3O_3-)\}$  (10) are obtained from  $[Zr(C_5H_5)_2ClH]$  (method c). The structure of complex 3 has been determined by X-ray diffraction methods.

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**Keywords:** Aryloxyde; Titanium; Zirconium; Cyclopentadienyl

## 1. Introduction

Group 4 metal complexes containing alkoxy or aryloxy ligands have been a subject of interest in the last decade. These compounds are interesting for industrial applications because of the wide use of these metal centres as catalysts in, for example, polymerisation [1], alkene epoxidation [2] or hydroformylation [3] reactions. In the polymerisation field the importance of cyclopentadienyl based complexes is especially significative due to their use in homogeneous catalysis [4].

A large number of mononuclear cyclopentadienyl titanium and zirconium complexes with aryloxy ligands have been described in the literature [5]. In contrast, there are very few examples of complexes in which benzenepolyolates are bridging two or more metal centres. Roesky et al. have described the first examples of Group 4 metal bimetallic complexes with quinonide bridged ligands using different synthetic routes depending on the metal complex precursor [6]. Lately, we have published the synthesis of some monocyclopentadienyl titanium complexes with quinonide bridged ligands starting from  $[Ti(C_5H_5)Cl_3]$  or  $[Ti(C_5Me_5)Cl_3]$  and different hydroquinones [7].

In this paper, we wish to present an extension of our previous work, describing new synthetic methodologies for some quinonide bridged bimetallic titanium com-

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plexes and reporting the synthesis and characterisation of new bimetallic and trimetallic cyclopentadienyl derivatives containing aryloxy bridged ligands. These compounds could be used as models and starting point for the study of the synthesis of rigid peripheral metal-dendrimers based on polyphenol skeleton, which is an area of interest in our research group.

## 2. Results and discussion

### 2.1. Synthesis and characterisation of bimetallic complexes

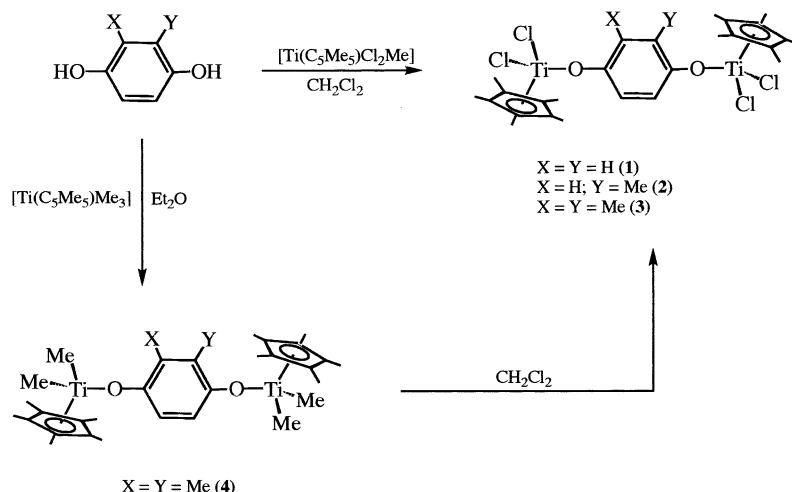
We have published recently that the reaction of 1,4-HO(2,3-C<sub>6</sub>H<sub>2</sub>XY)OH (X = Y = H, Me; X = H, Y = Me) with two equivalents of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] in diethyl ether at room temperature gives red–orange microcrystalline solids of bimetallic complexes [ $\{Ti(C_5H_5)Cl_2\}_2\{\mu-1,4-O(C_6H_2XY)O-\}$ ] in high yields [7]. However, for the compound [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>3</sub>] no reaction was observed with hydroquinones in analogous conditions and it was necessary the employment of the dilithium salts of such hydroquinones Li<sub>2</sub>[1,4-O(2,3-C<sub>6</sub>H<sub>2</sub>XY)O-] (X = Y = H, Me; X = H, Y = Me) to prepare the bimetallic derivatives [ $\{Ti(C_5Me_5)Cl_2\}_2\{\mu-1,4-O(C_6H_2XY)O-\}$ ] (X = Y = H (1); X = H, Y = Me (2); X = Y = Me (3)) [7].

Now we present here an alternative synthetic route for complexes 1–3 consisting in the reaction of hydroquinones 1,4-HO(2,3-C<sub>6</sub>H<sub>2</sub>XY)OH with two equivalents of [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>Me]. This synthetic procedure resulted to be more accurate and convenient than that using dilithium salts of hydroquinones because the methane subproduct was easily removed under vacuum conditions (Scheme 1).

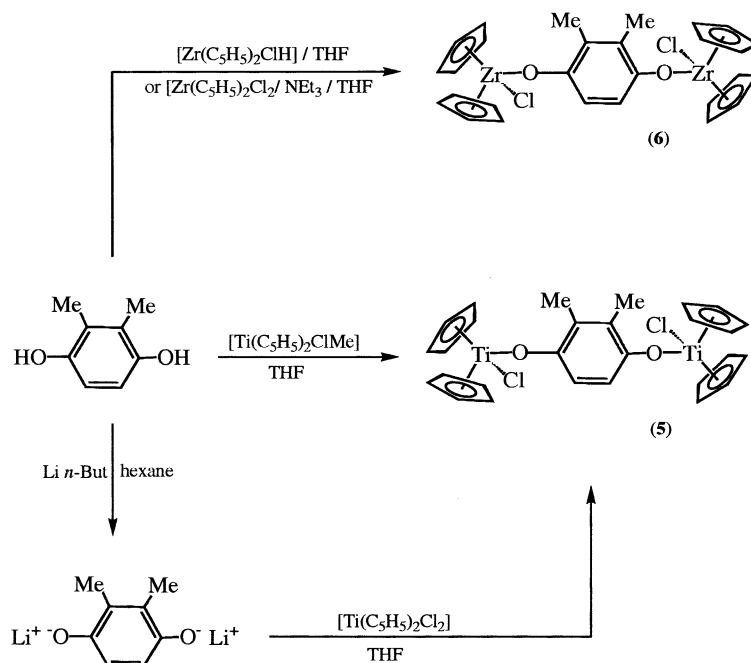
We have already published [7] that attempts to prepare methyl derivatives by reaction of complexes 1–3 with AlMe<sub>3</sub> were unsuccessful because the methyl-

ating agent reacts first with the aryloxy ligand than with the chlorine atoms. Nevertheless, methyl derivative [ $\{Ti(C_5Me_5)Me_2\}_2\{\mu-1,4-O(C_6H_2Me_2)O-\}$ ] (4) can be prepared by reaction of 1,4-HO(2,3-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>)OH with two equivalents of [Ti(C<sub>5</sub>Me<sub>5</sub>)Me<sub>3</sub>] (see Scheme 1). Complex 4 is a moisture sensitive yellow microcrystalline solid that is soluble in THF, Et<sub>2</sub>O, or toluene and scarcely soluble in hexane. This complex is also soluble in chlorinated solvents although a transformation of 4 into 3 was slowly occurred.

Phenolysis of titanium–methyl bonds can also be used to prepare bimetallic quinonide bridged complexes containing bis(cyclopentadienyl)titanium units although the synthetic procedure is less effective. According to this, we have prepared the compound [ $\{Ti(C_5H_5)_2Cl\}_2\{\mu-1,4-O(C_6H_2Me_2)O-\}$ ] (5) by reaction of the corresponding hydroquinone with [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ClMe] at 70 °C although low yields (37%) were achieved probably due to thermal decomposition. At room temperature, no reaction was observed indicating a strong Ti–Me bond. A more convenient method to prepare 5 consists in the reaction of two equivalents of [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] with the dilithium salt of the dimethylhydroquinone. The analogous zirconium complex [ $\{Zr(C_5H_5)_2Cl\}_2\{\mu-1,4-O(C_6H_2Me_2)O-\}$ ] (6) can be prepared by the method described by Roesky for a related bis(cyclopentadienyl)zirconium derivative [6], consisting in the reaction between two equivalents of [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] and 1,4-HO(2,3-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>)OH in the presence of two equivalents of triethylamine to separate the HCl formed during the reaction. Alternatively, treatment of the corresponding hydroquinone with [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ClH] affords compound 6 (see Scheme 2). Complexes 5 and 6 are air stable in the solid state but solutions of these compounds are partially hydrolysed to the corresponding  $\mu$ -oxo compounds [ $\{M(C_5H_5)_2Cl\}_2(\mu-O)$ ] where M = Ti or Zr [8], when they are opened to the air. Both of them are soluble in THF and chlorinated



Scheme 1.



solvents, partially soluble in toluene and completely insoluble in saturated hydrocarbons.

Compounds **4–6** were characterised by elemental analysis,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. These data (see details in Section 4) are consistent with the proposed formulation for these complexes. Spectroscopic data for complexes **1–3** obtained by phenolysis of a Ti–Me bond match perfectly with those previously reported by us [7]. X-ray analysis of compound **3** was carried out in order to provide precise structural details of this compound.

$^1\text{H}$ -NMR spectra of complexes **4–6** show one singlet for the hydrogen atoms of the  $\text{C}_5\text{Me}_5$  and  $\text{C}_5\text{H}_5$  ligands at  $\delta$  1.93 (30H), 6.32 (20H) and 6.36 (20H), respectively. The equivalence of both metal units in these bimetallic quinonide bridged complexes is also observed in the  $^1\text{H}$ -NMR signals of the quinonide group that appears for **4–6** as two different singlets, one corresponding to the methyl substituents at  $\delta$  2.23, 1.93 and 2.01, respectively, and another one corresponding to the two equivalent aromatic hydrogens at  $\delta$  6.56, 6.58 and 6.29.

These resonance patterns are in agreement with the symmetry of these compounds observed in the X-ray structure of **3** (see below), comparable to those shown by the analogous derivatives  $[\{\text{MoTp}(\text{NO})\text{X}\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_4)\text{O}-\}]$  [9],  $[\{\text{MoTp}(\text{O})\text{Cl}\}_2\{\mu\text{-}1,4\text{-N}(\text{C}_6\text{H}_4)\text{N}-\}]$  [10] or  $[\{\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}\}_2\{\mu\text{-}1,4\text{-N}(\text{C}_6\text{H}_4)\text{N}-\}]$  [11] ( $\text{M} = \text{Nb}, \text{Ta}$ ) and is expected for homobimetallic compounds bonding to the corresponding diphenoxide ligands.

Respecting to their  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra, an interesting feature is the chemical shift of the *ipso* carbons bonded directly to the oxygen atoms that are recorded at

$\delta$  157.0, 164.7 and 157.5 for **4–6**, respectively, which is indicative of the electronic density around the metal centre. Hence, for complex **4** the signal is shifted to high-field respecting to **3**, as consequence of the electrodonating properties of the methyl groups instead of the chloro atoms. Analogously, in complex **5** the resonance appears at lower field respecting to **6** due to the higher Lewis acidity of the titanium atom.

## 2.2. Crystal structure of **3**

Single crystals of **3** suitable for X-ray diffraction studies were obtained from a mixture of  $\text{Et}_2\text{O}$ –toluene cooled at  $-20^\circ\text{C}$ . An ORTEP draw of the molecular structure is shown in Fig. 1. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are listed in Table 1.

In the asymmetric unit of the unit cell a half molecule exists. The whole molecule consists in a bimetallic compound with the two half moieties related by a  $C_2$  symmetry axis located in the middle of the  $1,4\text{-O}(2,3\text{-C}_6\text{H}_2\text{Me}_2)\text{O}-$  system, in which the cyclopentadienyl rings present an *anti* conformation in the solid state. The molecular structure shows each titanium atom with a three-legged piano stool geometry. The Ti–Cl bond lengths (mean  $2.27 \text{ \AA}$ ) are analogous to that of comparable compounds such as  $[\{\text{Ti}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\}_2(\mu\text{-O})]$  [12] and considerably shorter than the distance reported for bis(cyclopentadienyl) quinonide bridged titanium complexes [6]. The Ti(1)–O(1)–C(7) angle ( $165.2(5)^\circ$ ) is opener than that observed in  $[\{\text{Ti}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\}_2(\mu\text{-}1,4\text{-OC}_6\text{H}_4\text{O}-)]$  [6] ( $155.1(2)^\circ$ ) and consequently the Ti(1)–O(1) bond length in **3** ( $1.784(5) \text{ \AA}$ ) is shorter than in such

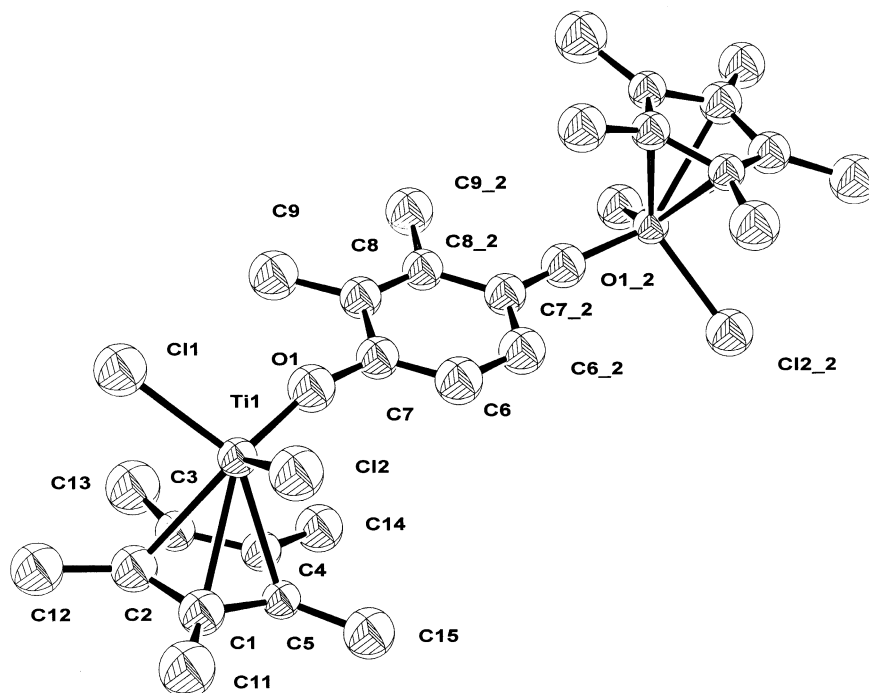


Fig. 1. ORTEP (50% thermal ellipsoids) view of the molecular structure of compound  $[\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_2\text{Me}_2)\text{O}-\}]$  (**3**) with atom-numbering scheme.

Table 1  
Bond lengths (Å) and angles (°) for compound **3**

Bond lengths			
Ti(1)–O(1)	1.784(5)	C(5)–C(15)	1.500(9)
Ti(1)–Cl(1)	2.266(2)	C(1)–C(11)	1.505(10)
Ti(1)–Cl(2)	2.271(2)	C(13)–C(3)	1.504(10)
Ti(1)–C(3)	2.342(8)	C(8)–C(7)	1.399(9)
Ti(1)–C(4)	2.346(7)	C(8)–C(8)#1	1.427(13)
Ti(1)–C(5)	2.358(8)	C(8)–C(9)	1.489(9)
Ti(1)–C(2)	2.385(7)	C(7)–C(6)	1.377(9)
Ti(1)–C(1)	2.397(7)	C(6)–C(6)#1	1.379(14)
O(1)–C(7)	1.360(8)	C(19)–C(23)	1.32(6)
C(4)–C(5)	1.408(10)	C(19)–C(18)	1.417(15)
C(4)–C(3)	1.419(10)	C(19)–C(18)#2	1.417(15)
C(4)–C(14)	1.499(10)	C(18)–C(17)	1.312(15)
C(2)–C(3)	1.406(10)	C(16)–C(24)	1.31(3)
C(2)–C(1)	1.421(10)	C(16)–C(17)#2	1.472(16)
C(2)–C(12)	1.505(9)	C(16)–C(17)	1.472(16)
C(5)–C(1)	1.424(10)	Ti(1)–Cp*	2.036
Bond angles			
O(1)–Ti(1)–Cl(1)	102.89(18)	O(1)–Ti(1)–Cp*	118.7
O(1)–Ti(1)–Cl(2)	101.66(18)	Cl(1)–Ti(1)–Cp*	114.5
Cl(1)–Ti(1)–Cl(2)	103.03(10)	Cl(2)–Ti(1)–Cp*	113.8
C(7)–O(1)–Ti(1)	165.2(5)		

Symmetry transformations used to generate equivalent atoms: #1  $-x+1/2, -y+1/2, z$ ; #2  $-x+1/2, -y+3/2, z$ . Cp\* is the centroid of C(1), C(2), C(3), C(4), C(5).

bis(pentamethylcyclopentadienyl) derivative (1.865(2) Å), this is usually invoked to be due to the better  $\pi$  electronic density donation from the oxygen atom to the titanium centre in **3**.

Complex **3** is the first dimetallic aryloxo monocyclopentadienyl compound reported so far. For this reason we are only able to compare their structural parameters with similar monometallic compounds. In Table 2 we show some structural parameters of monometallic Cp\* dichloro aryloxo species reported in the literature and obtained in the Cambridge Structural Database [13]. There, we can see that the Ti–O–C angle has important differences ranging between 157.6 and 179.4° although this is not reflected in really significant changes in the Ti–O distances that range from 1.772 to 1.817 Å. Every single titanium unit in **3** posses the Ti–O and Ti–O–C parameters almost identical to others similar monometallic complexes like  $[\text{Ti}(\text{C}_5\text{Me}_5)(O\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2]$  [14] or  $[\text{Ti}(\text{C}_5\text{Me}_5)\{O\text{-}2,6\text{-}(\text{OMe})_2\text{C}_6\text{H}_3\}\text{Cl}_2]$  [15] or the analogue containing the unsubstituted cyclopentadienyl ligand  $[\text{Ti}(\text{C}_5\text{H}_5)(O\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$  [5e,5f]. However, for a complex with bulkier ligands in the metal surroundings like in  $[\text{Ti}(\text{C}_5\text{Me}_5)(O\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$  [5e,5f], the Ti–O–C bond angle is more open (173°) than in **3** without any consequence in the Ti–O distance. For the case of  $[\text{Ti}(\text{C}_5\text{Me}_5)(O\text{-}2,6\text{-Ph}_2,3,5\text{-}^i\text{Bu}_2\text{C}_6\text{H})\text{Cl}_2]$  [5a] with a quasi linear system, Ti–O–C, the distance is longer than in **3** but of the same value than that in  $[\text{Ti}(\text{C}_5\text{Me}_5)(O\text{-}2,3,5,6\text{-Ph}_4\text{C}_6\text{H})\text{Cl}_2]$  [5a] which has a very close angle. These features describe that the change in the Ti–O–C bond angle and then a variation of the oxygen donation into the titanium atom is a compromise of electronic and steric influence of both cyclopentadienyl and substituted aryloxo ligands.

Table 2  
Structural parameters of Cp\*TiCl<sub>2</sub>(O–Ar)<sup>a</sup>

[Compound] <sup>ref</sup>	Ti–O	Ti–Cp	Ti–Cl	O–C	Ti–O–C	Cp–Ti–O	Cl–Ti–Cl
[Ti(C <sub>5</sub> Me <sub>5</sub> )Cl <sub>2</sub> (O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )] <sup>b</sup>	1.785	2.034	2.274	1.366	162.2	120.4	103.3
[Ti(C <sub>5</sub> Me <sub>5</sub> )Cl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )] <sup>c</sup>	1.772	2.035	2.304	1.366	172.9	120.4	103.4
[Ti(C <sub>5</sub> Me <sub>5</sub> )Cl <sub>2</sub> (O-2,6-Ph <sub>2</sub> -3,5' <i>i</i> -Bu <sub>2</sub> C <sub>6</sub> H)] <sup>d</sup>	1.803	2.052	2.258	1.369	176.8	123.1	100.4
[Ti(C <sub>5</sub> Me <sub>5</sub> )Cl <sub>2</sub> (O-2,3,5,6-Ph <sub>4</sub> C <sub>6</sub> H)] <sup>d</sup>	1.817	2.041	2.251	1.362	157.6	119.6	101.4
[{Ti(C <sub>5</sub> Me <sub>5</sub> )Cl <sub>2</sub> } <sub>2</sub> {μ-O(2,3-C <sub>6</sub> H <sub>2</sub> Me <sub>2</sub> )O-}] (3) <sup>e</sup>	1.784	2.036	2.269	1.360	165.2	118.7	103.0

Distances in (Å) and angles in (°).

<sup>a</sup> Data obtained from Cambridge Structural Database.

<sup>b</sup> From reference [13].

<sup>c</sup> From reference [5e].

<sup>d</sup> From reference [5a].

<sup>e</sup> This work.

### 2.3. Synthesis and characterisation of trimetallic complexes

Synthetic methodologies employed in the preparation of bimetallic quinonide bridged complexes were tested for the synthesis of trimetallic cyclopentadienyl Group 4 complexes with different results. Reaction of three equivalents of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] with one equivalent of 1,3,5-trihydroxybenzene failed to give the expected trimetallic complex under the experimental conditions used for complexes **1–3**. However, phenolysis of a titanium–methyl bond of [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>Me] or [Ti(C<sub>5</sub>-Me<sub>5</sub>)Me<sub>3</sub>] resulted to be an accurate method for the synthesis of two new trimetallic mono(pentamethylcyclopentadienyl)titanium derivatives [{Ti(C<sub>5</sub>-Me<sub>5</sub>)X<sub>2</sub>]<sub>3</sub>{μ<sub>3</sub>-1,3,5-C<sub>6</sub>H<sub>3</sub>O<sub>3</sub>-}] (X = Cl (**7**), Me (**8**)) (see Scheme 3).

In contrast, this method is not convenient for supporting bis(cyclopentadienyl)titanium derivatives over the previous trisphenolate ligand probably due again to the strength of the Ti–Me bond. Hence, the reaction of three equivalents of [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ClMe] with 1,3,5-trihydroxybenzene led to mixtures that we were not able to characterise. Fortunately, the desired complex [{Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl}<sub>3</sub>{μ<sub>3</sub>-1,3,5-C<sub>6</sub>H<sub>3</sub>O<sub>3</sub>-}] (**9**) was successfully prepared by reaction of [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] with 1,3,5-trihydroxybenzene in the presence of triethylamine (see Scheme 3). A similar reaction to the last one but using [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] failed to afford the analogous zirconium derivative of **9**. However, the use [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ClH] afforded [{Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl}<sub>3</sub>{μ<sub>3</sub>-1,3,5-C<sub>6</sub>H<sub>3</sub>O<sub>3</sub>-}] (**10**) as yellow microcrystals in high yield via dihydrogen evolution.

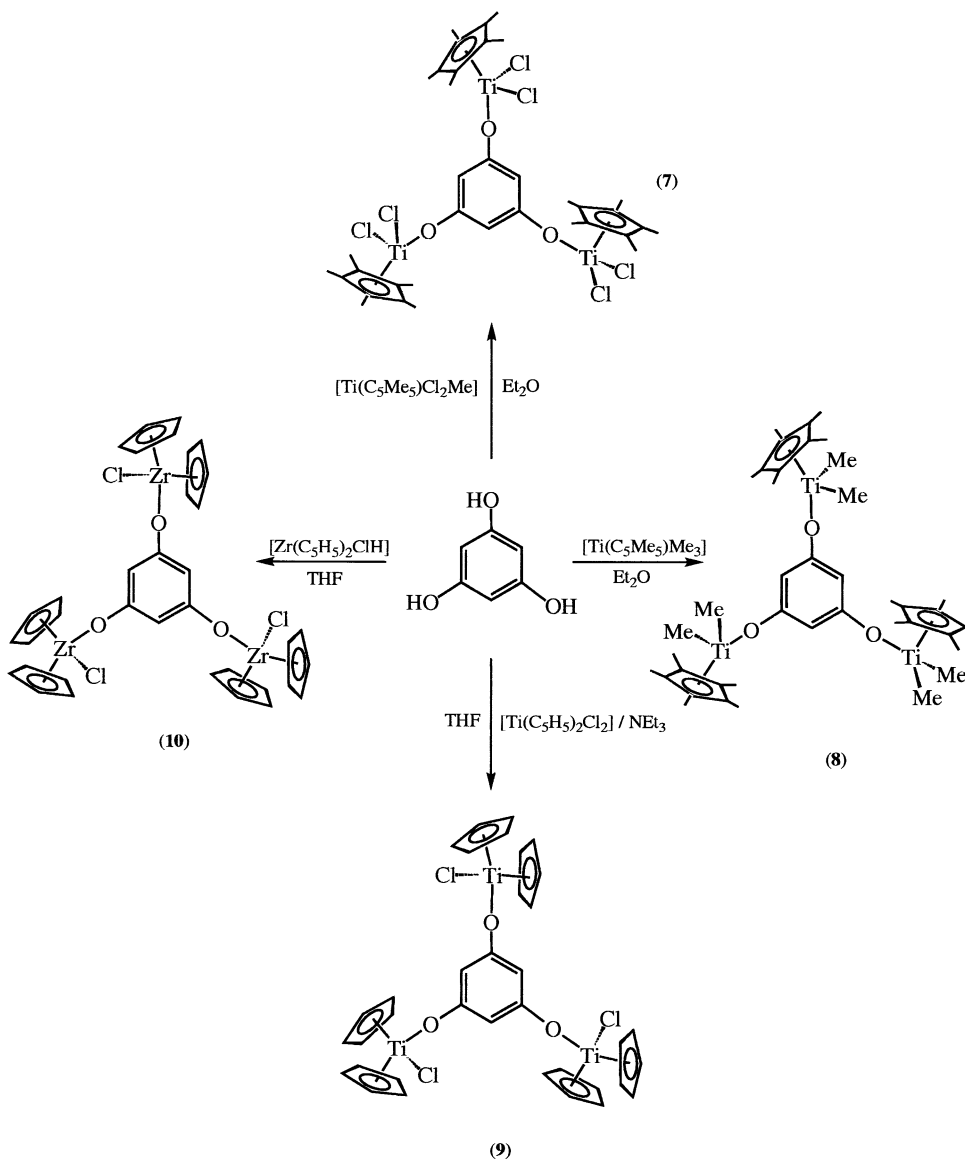
Trimetallic chloro derivatives **7**, **9** and **10** are soluble in THF and chlorinated solvents, partially soluble in toluene and insoluble in diethyl ether and hexane, whereas, compound **8** is soluble in all previous solvents except in hexane. All of four complexes can be stored under argon during long time periods but are moisture

sensitive and decompose in the presence of air to give different oxo derivatives. In the chloro complexes **7**, **9** and **10** the hydrolysis of Ti–OAr bond occurs before that of Ti–Cl bond producing well known oxo complexes [{Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub>(μ-O)] [12] and [M(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl]<sub>2</sub>(μ-O)] where M = Ti or Zr [8].

Structural characterisation of compounds **7–10** was carried out by elemental analysis, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy (see Section 4). <sup>1</sup>H-NMR spectra of these complexes show equivalence of the three metal fragments and consequently only one singlet is observed for the protons of the cyclopentadienyl rings at δ 2.23 (45H) for **7**, 1.94 (45H) for **8**, 6.39 (30H) for **9** and 6.39 (30H) for **10**. According to this, the three aromatic protons of the trisphenolate ligand are also equivalent and appear as a singlet at δ 6.24, 6.08, 5.44 and 5.44 for **7–10**, respectively. Besides these signals, complex **8** shows an additional singlet at δ 0.40 due to the methyl groups directly bonded to titanium. <sup>13</sup>C-NMR signals are in agreement with the data observed in the <sup>1</sup>H-NMR spectra. The chemical shift of the *ipso* carbons of the phenyl ring directly bonded to the oxygen atoms are recorded at δ 164.7, 165.6, 174.6 and 166.3 for **7–10**, respectively, which resonate at lower field compared with the analogous quinonide derivatives described before. This behaviour could be ascribed to the presence of three organometallic units in *meta* position instead of two in *para* position in the ariloxy fragment, which organises differently the electrodonating properties of both types of ligands.

### 3. Conclusions

Several synthetic methodologies have been employed to prepared aryloxy bridged bi- and trimetallic Group 4 derivatives. In the case of monocyclopentadienyl complexes the reaction of [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>Me] or [Ti(C<sub>5</sub>-Me<sub>5</sub>)Me<sub>3</sub>] with the hydroxy functionalities cleanly



Scheme 3.

introduce the metal fragment via liberation of inert methane. For bis(cyclopentadienyl) titanium complexes more standard procedures like the used of lithium salts of the hydroquinones or the employment of a Lewis base must be used. In the case of the zirconium analogues, the use of [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ClH] allows the synthesis of the corresponding complexes via dihydrogen formation. All these synthetic procedures, mainly those based on titanium, could be useful for the preparation of rigid peripheral metal-dendrimers based on polyphenol skeleton.

#### 4. Experimental

All manipulations were performed under an inert atmosphere of Ar using standard Schlenk techniques or

a dry box. Solvents were previously dried and freshly distilled under Ar as described elsewhere [16]. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Et<sub>3</sub>N was dried over calcium hydride and then distilled under Ar. [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>3</sub>] [17], [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>Me] [18] and [Ti(C<sub>5</sub>Me<sub>5</sub>)Me<sub>3</sub>] [19] were prepared according to reported methods.

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Varian Unity 200, Varian Unity VXR-300 or Varian Unity 500 Plus Instruments. Chemical shifts ( $\delta$  ppm) were measured relative to residual <sup>1</sup>H and <sup>13</sup>C resonances for chloroform-*d*<sub>1</sub> and benzene-*d*<sub>6</sub> used as solvent. C, H analyses were carried out with a Perkin–Elmer 240 C microanalyzer.

4.1. [ $\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_4)\text{O-}\}$ ] (**1**)

A solution of hydroquinone (0.30 g, 2.72 mmol) in  $\text{Et}_2\text{O}$  (20  $\text{cm}^3$ ) was slowly cannulated into a solution of  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$  (1.47 g, 5.45 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). The mixture was stirred overnight at room temperature (r.t.). Then, the solvent was evaporated under vacuum and the product was recrystallised in a mixture  $\text{Et}_2\text{O}$ –hexane leading to **1** as an orange microcrystalline solid (yield: 95%). For analytical and spectroscopic data see reference [7].

4.2. [ $\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_3\text{Me})\text{O-}\}$ ] (**2**)

A solution of methylhydroquinone (0.30 g, 2.42 mmol) in  $\text{Et}_2\text{O}$  (20  $\text{cm}^3$ ) was slowly cannulated into a solution of  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$  (1.30 g, 4.83 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). The mixture was stirred overnight at r.t. Then, the solvent was evaporated under vacuum and the product was recrystallised in a mixture  $\text{Et}_2\text{O}$ –hexane leading to **2** as an orange microcrystalline solid (yield: 95%). For analytical and spectroscopic data see reference [7].

4.3. [ $\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_2\text{Me}_2)\text{O-}\}$ ] (**3**)

A solution of 2,3-dimethylhydroquinone (0.30 g, 2.17 mmol) in  $\text{Et}_2\text{O}$  (20  $\text{cm}^3$ ) was slowly cannulated into a solution of  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$  (1.17 g, 4.34 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). The mixture was stirred overnight at r.t. Then, the solvent was evaporated under vacuum and the product was recrystallised in a mixture  $\text{Et}_2\text{O}$ –toluene leading to **3** as an orange microcrystalline solid (yield: 95%). For analytical and spectroscopic data see reference [7].

4.4. [ $\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_2\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_2\text{Me}_2)\text{O-}\}$ ] (**4**)

A solution of 2,3-dimethylhydroquinone (0.30 g, 2.17 mmol) in  $\text{Et}_2\text{O}$  (20  $\text{cm}^3$ ) was slowly cannulated into a solution of  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$  (1.04 g, 4.56 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). The mixture was stirred overnight at r.t., and then concentrated and cooled at  $-20^\circ\text{C}$ . After 24 h a yellow solid precipitated, which was filtered off and dried under vacuum affording **4** as a yellow microcrystalline solid (yield: 75%). Anal. Calc. for  $\text{C}_{32}\text{H}_{50}\text{O}_2\text{Ti}_2$ : C, 68.33; H, 8.96. Found: C, 68.49; H, 8.93%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.56 (s, 2H,  $\text{C}_6\text{H}_2\text{Me}_2$ ), 2.23 (s, 6H,  $\text{C}_6\text{H}_2\text{Me}_2$ ), 1.93 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 0.37 (s, 12H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  157.0 ( $\text{C}_{\text{ipso}}$  bonded to oxygen), 126.7 ( $\text{C}_{\text{ipso}}$  bonded to Me), 122.0 ( $\text{C}_5\text{Me}_5$ ), 117.6 ( $\text{C}_6\text{H}_2\text{Me}_2$ ), 52.6 ( $\text{CH}_3$ ), 13.4 ( $\text{C}_6\text{H}_2\text{Me}_2$ ), 11.5 ( $\text{C}_5\text{Me}_5$ ).

4.5. [ $\{\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_2\text{Me}_2)\text{O-}\}$ ] (**5**)

A solution of  $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$  (1.08 g, 4.34 mmol) in THF (40  $\text{cm}^3$ ) was cannulated into a Schlenk containing the dilithium salt of 2,3-dimethyl hydroquinone (0.32 g, 2.17 mmol). The mixture was stirred overnight at r.t., the solvent was removed under reduced pressure and the residue extracted with toluene ( $2 \times 15 \text{ cm}^3$ ). The filtrates were combined and volatiles removed in vacuo. The remaining solid was washed with hexane affording compound **5** as a dark brown microcrystalline solid (yield: 65%). Anal. Calc. for  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{Cl}_2\text{Ti}_2$ : C, 57.92; H, 5.23. Found: C, 58.38; H, 5.22%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.58 (s, 2H,  $\text{C}_6\text{H}_2\text{Me}_2$ ), 6.32 (s, 20H,  $\text{C}_5\text{H}_5$ ), 1.93 (s, 6H,  $\text{C}_6\text{H}_2\text{Me}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  164.7 ( $\text{C}_{\text{ipso}}$  bonded to oxygen), 122.0 ( $\text{C}_{\text{ipso}}$  bonded to Me), 117.1 ( $\text{C}_5\text{H}_5$ ), 114.4 ( $\text{C}_6\text{H}_2\text{Me}_2$ ), 13.6 ( $\text{C}_6\text{H}_2\text{Me}_2$ ).

4.6. [ $\{\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}\}_2\{\mu\text{-}1,4\text{-O}(\text{C}_6\text{H}_2\text{Me}_2)\text{O-}\}$ ] (**6**)

## 4.6.1. Method A

A solution of 2,3-dimethylhydroquinone (0.236 g, 1.71 mmol) in THF (20  $\text{cm}^3$ ) was cannulated into a solution of  $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$  (1.0 g, 3.42 mmol) in THF (20  $\text{cm}^3$ ) and then  $\text{Et}_3\text{N}$  (0.48  $\text{cm}^3$ , 3.42 mmol) was added. The mixture was stirred overnight at r.t., the solvent was removed under reduced pressure and the residue extracted with toluene ( $2 \times 15 \text{ cm}^3$ ). The filtrates were combined and volatiles removed in vacuo. The remaining solid was washed with hexane affording compound **6** as a yellow microcrystalline solid (yield: 70%).

## 4.6.2. Method B

A solution of 2,3-dimethylhydroquinone (0.08 g, 0.58 mmol) in THF (20  $\text{cm}^3$ ) was cannulated into a solution of  $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{HCl}]$  (0.3 g, 1.16 mmol) in THF (20  $\text{cm}^3$ ) and the mixture stirred for 1 h at r.t. Then, the solution was filtered and the solvent removed under reduced pressure affording **6** as yellow microcrystals (yield: 43%). Anal. Calc. for  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{Cl}_2\text{Zr}_2$ : C, 51.75; H, 4.34. Found: C, 51.52; H, 4.16%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.36 (s, 20H,  $\text{C}_5\text{H}_5$ ), 6.29 (s, 2H,  $\text{C}_6\text{H}_2\text{Me}_2$ ), 2.01 (s, 6H,  $\text{C}_6\text{H}_2\text{Me}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  157.5 ( $\text{C}_{\text{ipso}}$  bonded to oxygen), 124.8 ( $\text{C}_{\text{ipso}}$  bonded to Me), 114.2 ( $\text{C}_5\text{H}_5$ ), 112.9 ( $\text{C}_6\text{H}_2\text{Me}_2$ ), 13.4 ( $\text{C}_6\text{H}_2\text{Me}_2$ ).

4.7. [ $\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_3(\mu_3\text{-}1,3,5\text{-C}_6\text{H}_3\text{O}_3\text{-})$ ] (**7**)

A solution of 1,3,5-trihydroxybenzene (0.25 g, 1.98 mmol) in  $\text{Et}_2\text{O}$  (20  $\text{cm}^3$ ) was slowly cannulated into a solution of  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$  (1.65 g, 6.15 mmol) in  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ). The mixture was stirred overnight at  $60^\circ\text{C}$  in an ampoule and after this time an orange solid precipitated, which was filtered off, washed with  $\text{Et}_2\text{O}$  ( $3 \times 10 \text{ cm}^3$ ) and dried under vacuum to give **7** as an

orange microcrystalline solid (yield: 70%). Anal. Calc. for  $C_{36}H_{48}Cl_6O_3Ti_3$ : C, 48.85; H, 5.46. Found: C, 49.28; H, 5.53%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  6.24 (s, 3H,  $C_6H_3$ ), 2.23 (s, 45H,  $C_5Me_5$ ).  $^{13}C\{^1H\}$ -NMR ( $CDCl_3$ ):  $\delta$  164.7 ( $C_{ipso}$  bonded to oxygen), 133.6 ( $C_5Me_5$ ), 106.1 ( $C_6H_3$ ), 13.3 ( $C_5Me_5$ ).

#### 4.8. [ $\{Ti(C_5Me_5)Me_2\}_3(\mu_3-1,3,5-C_6H_3O_3-)$ ] (**8**)

A solution of 1,3,5-trihydroxybenzene (0.25 g, 1.98 mmol) in  $Et_2O$  ( $20\text{ cm}^3$ ) was slowly cannulated into a solution of  $[Ti(C_5Me_5)Me_3]$  (1.41 g, 6.15 mmol) and  $Et_2O$  ( $10\text{ cm}^3$ ). The mixture was stirred overnight at r.t. The solvent was removed under vacuum and the residue recrystallised in hexane giving **8** as a bright yellow microcrystalline solid (yield: 80%). Anal. Calc. for  $C_{42}H_{66}O_3Ti_3$ : C, 66.14; H, 8.72. Found: C, 65.52; H, 8.72%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  6.08 (s, 3H,  $C_6H_3$ ), 1.94 (s, 45H,  $C_5Me_5$ ), 0.40 (s, 18H,  $CH_3$ ).  $^{13}C\{^1H\}$ -NMR ( $C_6D_6$ ):  $\delta$  165.6 ( $C_{ipso}$  bonded to oxygen), 122.6 ( $C_5Me_5$ ), 105.8 ( $C_6H_3$ ), 54.6 ( $CH_3$ ), 11.7 ( $C_5Me_5$ ).

#### 4.9. [ $\{Ti(C_5H_5)_2Cl\}_3(\mu_3-1,3,5-C_6H_3O_3-)$ ] (**9**)

A solution of 1,3,5-trihydroxybenzene (0.07 g, 0.55 mmol) in THF ( $20\text{ cm}^3$ ) was cannulated into a solution of  $[Ti(C_5H_5)_2Cl_2]$  (0.41 g, 1.64 mmol) in THF ( $20\text{ cm}^3$ ) and then  $Et_3N$  ( $0.30\text{ cm}^3$ , 2.15 mmol) was added. The mixture was stirred overnight at r.t., the solvent was removed under reduced pressure and the residue extracted with toluene ( $2 \times 15\text{ cm}^3$ ). The filtrates were combined and volatiles removed in vacuum. The remaining solid was washed with hexane affording compound **9** as a red microcrystalline solid (yield: 80%). Anal. Calc. for  $C_{36}H_{33}O_3Cl_3Ti_3$ : C, 56.40; H, 4.73. Found: C, 56.75; H, 4.86%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  6.39 (s, 30H,  $C_5H_5$ ), 5.44 (s, 3H,  $C_6H_3$ ).  $^{13}C\{^1H\}$ -NMR ( $CDCl_3$ ):  $\delta$  171.6 ( $C_{ipso}$  bonded to oxygen), 117.5 ( $C_5H_5$ ), 97.5 ( $C_6H_3$ ).

#### 4.10. [ $\{Zr(C_5H_5)_2Cl\}_3(\mu_3-1,3,5-C_6H_3O_3-)$ ] (**10**)

A solution of 1,3,5-trihydroxybenzene (0.07 g, 0.55 mmol) in THF ( $20\text{ cm}^3$ ) was cannulated into a solution of  $[Zr(C_5H_5)_2HCl]$  (0.41 g, 1.64 mmol) in THF ( $20\text{ cm}^3$ ) and the mixture stirred during 1 h at r.t. Then, the solution was filtered and the volatiles removed under reduced pressure giving a white foam. This foam was washed with hexane affording compound **10** as a brown solid (yield: 52%). Anal. Calc. for  $C_{36}H_{33}O_3Cl_3Ti_3$ : C, 48.38; H, 3.72. Found: C, 48.22; H, 3.81%.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  6.39 (s, 30H,  $C_5H_5$ ), 5.44 (s, 3H,  $C_6H_3$ ).  $^{13}C\{^1H\}$ -NMR ( $CDCl_3$ ):  $\delta$  166.3 ( $C_{ipso}$  bonded to oxygen), 114.4 ( $C_5H_5$ ), 99.6 ( $C_6H_3$ ).

#### 4.11. Crystal structure determinations

Crystals of compound **3** were obtained by crystallisation from  $Et_2O$ –toluene. Suitable sized crystals sealed under Ar atmosphere in Lindemann tubes were mounted in an Enraf–Nonius CAD 4 automatic four-circle diffractometer white graphite monochromated Mo– $K_\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Crystallographic and experimental details of the structure are summarised in Table 3. Data were collected at r.t. Intensities were corrected for Lorentz and polarisation effects in the usual manner. No absorption or extinction correction were made. The structure was solved using the WINGX package [20], by direct methods (SHELXS-97) and refined by least-squares against  $F^2$  (SHELXL-97) [21]. When solved the structure, a disorder molecule of toluene was found. All non hydrogen atoms were refined anisotropically except those of the toluene molecule which were isotropically refined, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the carbon atom to which they are attached, except the hydrogen atoms of the methyl groups of the disorder toluene molecule.

The final coordinates the non hydrogen atom with the equivalent isotropic thermal parameters,  $U_{eq}$ , the co-

Table 3  
Crystal data and structure refinement for compound **3**

Empirical formula	$C_{28}H_{38}Cl_4O_2Ti_2 \cdot C_7H_8$
Formula weight	732.29
Temperature (K)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Orthorhombic
Space group	$Pccn$
Unit cell dimensions	
$a$ ( $\text{\AA}$ )	30.218(1)
$b$ ( $\text{\AA}$ )	7.605(1)
$c$ ( $\text{\AA}$ )	15.906(1)
$V$ ( $\text{\AA}^3$ )	3655.3(5)
$Z$	4
$D_{calc}$ ( $Mg\text{ m}^{-3}$ )	1.331
Absorption coefficient ( $mm^{-1}$ )	0.758
$F(000)$	1520
Crystal size ( $mm^3$ )	$0.34 \times 0.25 \times 0.21$
Theta range for data collection ( $^\circ$ )	2.56–24.96
Index ranges	$0 \leq h \leq 35, 0 \leq k \leq 9, 0 \leq l \leq 18$
Reflections collected	3198
Independent reflections	3198
Completeness to theta = $24.96^\circ$	99.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3198/0/179
Goodness-of-fit on $F^2$	0.915
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0667, wR_2 = 0.1510$
$R$ indices (all data)	$R_1 = 0.2222, wR_2 = 0.2021$
Largest difference peak and hole ( $e\text{\AA}^{-3}$ )	0.427 and $-0.280$



ordinates for the hydrogen atoms with the isotropic thermal parameters, anisotropic thermal parameters for the non hydrogen atoms, and a complete list of bond distances, angles and observed and calculated structure factors have been deposited in the Cambridge Crystallographic Data Center, CCDC No. 203509 for complex 3.

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