

# Synthesis and characterisation of quinonide bridged dinuclear complexes of titanium and zirconium

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Cyclopentadienyl-zirconium(IV) and -titanium(IV) halides and alkyls react with hydroquinones to give bridged dinuclear complexes. Such compounds are also formed upon treatment of titanium(III) precursors with benzoquinone. Various cyclopentadienyl derivatives were used [cyclopentadienyl ( $C_5H_5$ ), pentamethylcyclopentadienyl ( $C_5Me_5$ ), ethyltetramethylcyclopentadienyl ( $C_5Me_4Et$ ) and trimethylsilylcyclopentadienyl ( $C_5H_4SiMe_3$ )]. Several synthetic routes are described leading to the products [ $\{Zr(C_5H_5)_2Cl\}_2(\mu-OC_6H_4O)$ ] **1a**, [ $\{Zr(C_5H_5)_2Cl\}_2\{\mu-O(C_6H_3Bu^t-2)O\}$ ] **1b**, [ $\{Zr(C_5H_5)_2Cl\}_2\{\mu-O(C_6H_2Bu^t-2,5)O\}$ ] **1c**, [ $\{Zr(C_5Me_4Et)_2Cl\}_2(\mu-OC_6H_4O)$ ] **1d**, [ $\{Ti(C_5Me_4Et)Cl_2\}_2(\mu-OC_6H_4O)$ ] **2**, [ $\{Ti(C_5Me_5)_2Cl\}_2(\mu-OC_6H_4O)$ ] **3**, [ $\{Ti(C_5Me_5)F_2\}_2\{\mu-O(C_6H_2Bu^t-2,5)O\}$ ] **4**, [ $\{Zr(C_5Me_4Et)_2F_2\}_2(\mu-OC_6H_4O)$ ] **5**, [ $\{Ti(C_5Me_5)_2F_2\}_2(\mu-OC_6H_4O)$ ] **6a**, [ $\{Ti(C_5H_4SiMe_3)_2F_2\}_2(\mu-OC_6H_4O)$ ] **6b**, [ $\{Ti(C_5Me_5)Me_2\}_2\{\mu-O(C_6H_2Bu^t-2,5)O\}$ ] **7** and [ $\{Ti(C_5Me_5)Cl_2\}_2O$ ] **8**. Furthermore it is shown that the formation of the monobridged products is independent of the steric requirements of the substituents of the quinonide ring. The structures of [ $\{Zr(C_5Me_4Et)_2Cl\}_2(\mu-OC_6H_4O)$ ] **1d** and [ $\{Ti(C_5Me_5)_2Cl\}_2(\mu-OC_6H_4O)$ ] **3** were solved by X-ray diffraction analysis.

Compounds of Group 4 metal complexes containing oxygen have been the subject of interest for several decades. Tetraalkoxy metal complexes are thought of as promising precursors in chemical vapour deposition (CVD).<sup>1</sup> These compounds in general are interesting for industrial applications because of the wide use of these metal centres as catalysts in polymerisation reactions<sup>2</sup> and sometimes in hydroformylation reactions.<sup>3,4</sup> In the latter field the importance of cyclopentadienyl based complexes has grown in recent decades due to their use in homogeneous catalysis.<sup>2</sup>

However, publications dealing with the subject of cyclopentadienyl-based Group 4 metal complexes containing oxygen are restricted to only a few types of compounds mainly derived from structures A–E (Scheme 1).<sup>5</sup> Either one or more alkoxy groups are connected to a central metal atom<sup>3a,6</sup> (A) or bidentate ligands form metallaheterocycles (B).<sup>7</sup> Compounds containing more than one metal atom are known with one bridging oxygen as chain<sup>8</sup> (C) and ring systems<sup>9</sup> (e.g. D) or three-dimensional cages (e.g. E).<sup>10</sup>

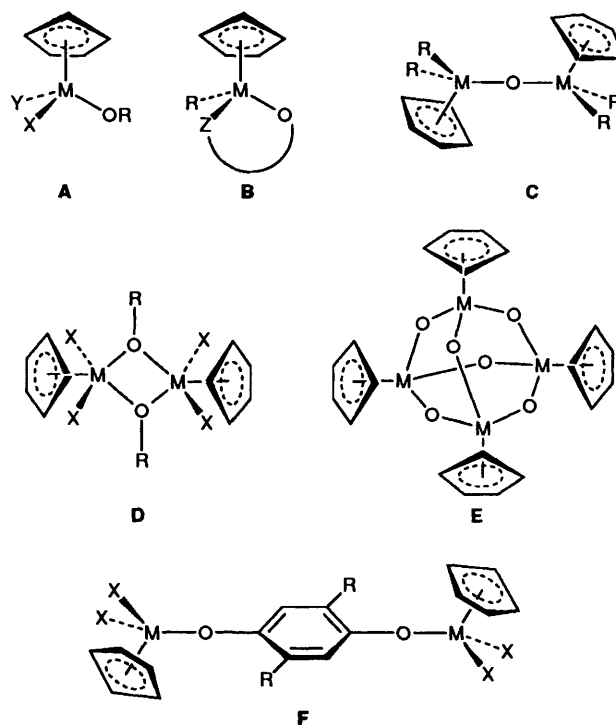
In this contribution, for the first time, a general route is presented to obtain the class of compounds that is structurally characterised by an  $M^{IV}-O-C_6H_{4-n}Bu^t_n-O-M^{IV}$  ( $M = Ti$  or  $Zr$ ,  $n = 0-2$ ) unit (F). A similar compound with  $OCH(CF_3)O$  as bridging unit, however, has been synthesised unexpectedly.<sup>11</sup> This family of complexes has been postulated earlier<sup>4</sup> to play a crucial role in hydroformylation catalysis. The only known quinonide bridged substance is reported with cerium.<sup>12</sup>

## Results and Discussion

### Synthetic procedures

Our investigations were directed towards the synthesis of compounds with the general formula F (Scheme 1). We were able to obtain those products with various ligands at  $Ti^{IV}$  and  $Zr^{IV}$  centres.

The complexes with chlorine substituents could be synthesised starting from the appropriate chlorides and ring substituted 1,4-hydroquinones. HCl formed during the reaction



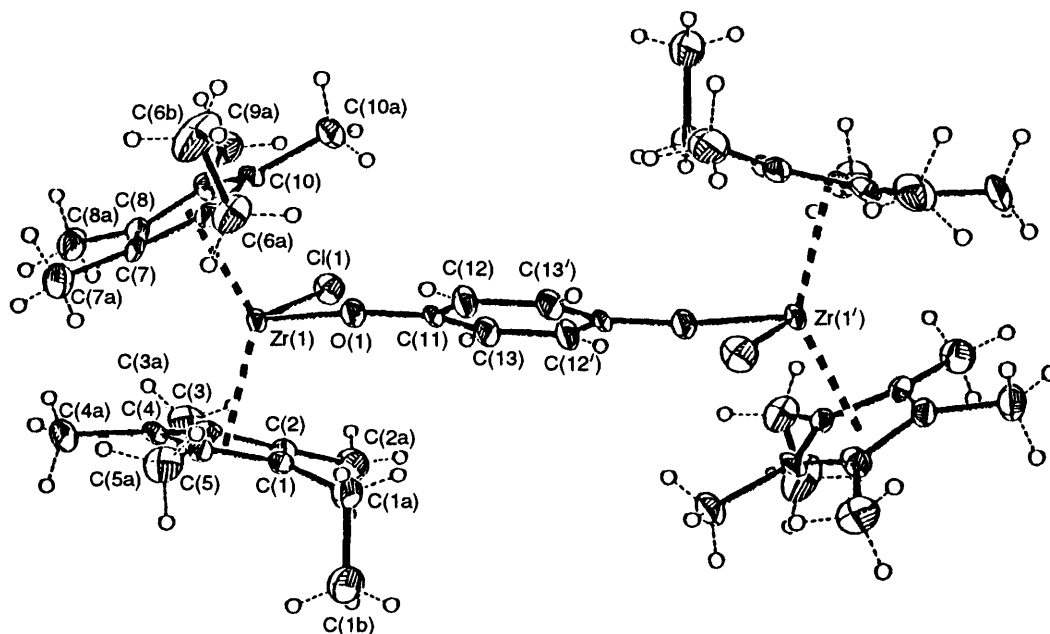
Scheme 1 Cyclopentadienyl based Group 4 metal complexes containing oxygen; R = H or alkyl, X, Y = halide

was separated as the adduct of triethylamine or pyridine (Scheme 2). Using this procedure we obtained compounds **1a–1c**. The compounds only differ in the spatial requirements of the bridge substituents showing that there are scarcely any steric restrictions. Compounds **1a–1c** were characterised by IR and <sup>1</sup>H NMR spectroscopy and mass spectrometry (Table 1). The molecular ions in the mass spectrum match the theoretically calculated isotope patterns. Structural information was

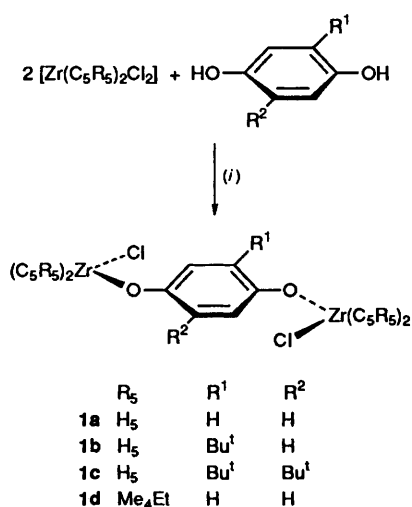
**Table 1** Physical and analytical data for the complexes

Complex	Colour	M.p./°C	Yield (%)	$M^+ m/z$ (%)	Analysis <sup>a</sup> (%)
<b>1a</b> [ $\{Zr(C_5H_5)_2Cl\}_2(\mu-OC_6H_4O)$ ]	Yellow	210 <sup>b</sup>	40	622 (2)	C 51.0 (50.2), H 4.3 (3.9), Cl 11.3 (11.4)
<b>1b</b> [ $\{Zr(C_5H_5)_2Cl\}_2(\mu-O(C_6H_3Bu^i-2)O)$ ]	Yellow	180 <sup>b</sup>	39	678 (30)	C 51.4 (53.1), H 4.9 (4.8), Cl 10.5 (10.1)
<b>1c</b> [ $\{Zr(C_5H_5)_2Cl\}_2(\mu-O(C_6H_2Bu^i-2,5)O)$ ]	Yellow	260 <sup>b</sup>	69	732 (24)	C 55.6 (55.6), H 5.8 (5.8)
<b>1d</b> [ $\{Zr(C_5Me_4Et)_2Cl\}_2(\mu-OC_6H_4O)$ ]	Yellow	210 <sup>b</sup>	40	958 (100)	C 62.4 (62.7), H 7.6 (7.6), Cl 7.8 (7.4)
<b>2</b> [ $\{Ti(C_5Me_4Et)Cl_2\}_2(\mu-OC_6H_4O)$ ]	Dark red	176	47	644 (30)	C 51.4 (52.2), H 6.7 (5.9)
<b>3</b> [ $\{Ti(C_5Me_5)_2Cl\}_2(\mu-OC_6H_4O)$ ]	Green-brown	233–235	88	678 (30)	C 67.6 (67.7), H 7.8 (7.9)
<b>4</b> [ $\{Ti(C_5Me_5)_2F\}_2(\mu-O(C_6H_2Bu^i-2,5)O)$ ]	Red	330 <sup>b</sup>	62	662 (20)	C 62.2 (61.6), H 7.7 (7.6)
<b>5</b> [ $\{Zr(C_5Me_4Et)_2F\}_2(\mu-OC_6H_4O)$ ]	Pale yellow	240 <sup>b</sup>	59	924 (100)	C 65.6 (64.9), H 8.7 (7.8)
<b>6a</b> [ $\{Ti(C_5Me_5)_2F\}_2(\mu-OC_6H_4O)$ ]	Green-brown	232 <sup>b</sup>	64	782 (19)	C 70.5 (70.6), H 8.1 (8.2), F 4.7 (4.9)
<b>6b</b> [ $\{Ti(C_5H_4SiMe_3)_2F\}_2(\mu-OC_6H_4O)$ ]	Green-brown	59–61	85	790 (15)	C 57.5 (57.7), H 6.9 (7.1), F 4.5 (4.8)
<b>7</b> [ $\{Ti(C_5Me_5)Me\}_2(\mu-O(C_6H_2Bu^i-2,5)O)$ ]	Yellow	202 <sup>b</sup>	66	647 (40)	
<b>8</b> [ $\{Ti(C_5Me_5)Cl_2\}_2O$ ]	Orange-red	226	59	524 (20)	C 46.4 (45.8), H 5.7 (5.2), Cl 27.0 (27.1)

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> With decomposition.



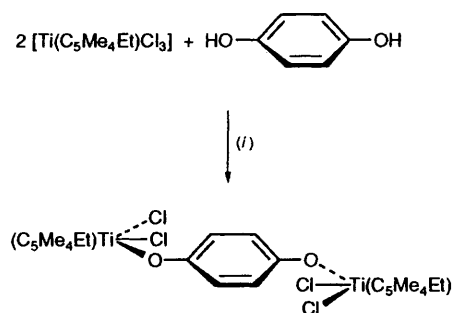
**Fig. 1** Crystal structure of complex **1d**



**Scheme 2** (i)  $2NEt_3$ ,  $-2NHEt_3Cl$

obtained by an X-ray crystal structure analysis of **1d** prepared analogously using [ $Zr(C_5Me_4Et)_2Cl_2$ ] (Fig. 1).

To demonstrate the wide applicability of the procedure, **2** was synthesised starting from a titanium complex (Scheme 3).



**Scheme 3** (i)  $2py$ ,  $-2py-HCl$

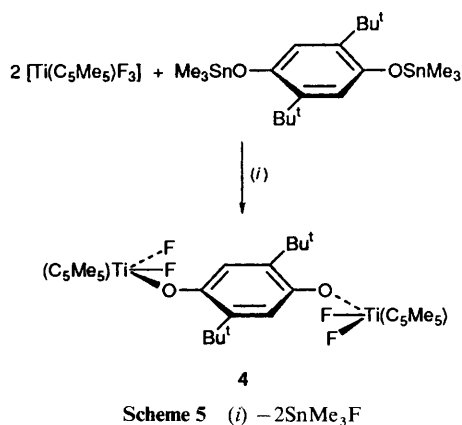
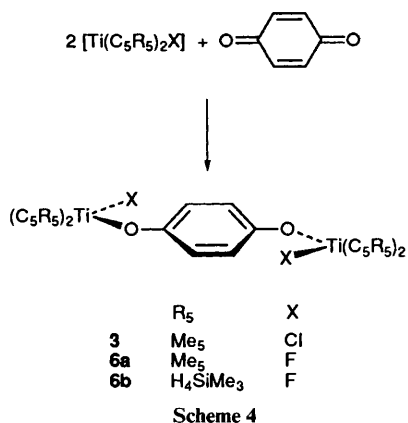
The synthetic route based on the redox potential of the starting materials, that has been used for the preparation of the cerium complex, is also applicable to titanium complexes (Scheme 4).

The quinonide bridged compound **3** was formed from [ $Ti(C_5H_5)_2Cl$ ] upon treatment with benzoquinone. The crystal structure was solved by X-ray structural analysis (Fig. 2).

Fluorine-substituted bridged complexes could be synthesised in three ways. The first is the straightforward synthesis using a fluorine complex with a substituted *O,O'*-bis(trimethylstannyl)-1,4-hydroquinone to eliminate the fluoride anion as  $SnMe_3F$  which can often be separated due to its low solubility (Scheme 5).

Both  $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{F}_2]$  and  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{F}_3]$  reacted in this manner, however, only the  $\text{C}_5\text{Me}_5$  substituted compound could be obtained as a pure complex (**4**). The analogous zirconium complexes do not react in this way. To obtain them we showed in one case, as an example, that fluorination of the bridged chlorine complex leads also to this series of compounds. Compound **5** was synthesised from **1d** using  $\text{SnMe}_3\text{F}$  as the fluorinating agent (Scheme 6).

Finally, fluorine-containing complexes can be prepared using titanium(III) complexes and benzoquinone analogously to the route described for the chlorine complexes (*cf.* Scheme 4). By this method complexes **6a** and **6b** were prepared. Methyl substituted compounds were accessible directly using methyl substituted titanium(IV) complexes and treating them with



hydroquinone, with evolution of methane being observed (Scheme 7). As an example, compound **7** was synthesised using  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$  and the 2,5-di-*tert*-butyl-1,4-hydroquinone.

Attempting to introduce electron rich aliphatic bridges between the two metal centres by reaction of the dilithium salt of tetraphenylethane-1,2-diol resulted in the formation of the already known compound **8** (Scheme 8).<sup>13</sup> As a by-product triphenylacetophenone could be detected by mass spectrometry.

These results allow conclusions on the mechanism of the reactions presented in this paper. We assume that the bridging of the metal centres takes place successively with intermediate formation of **9**.

In all reactions described we found that the expected products were formed whatever the stoichiometric ratios of the

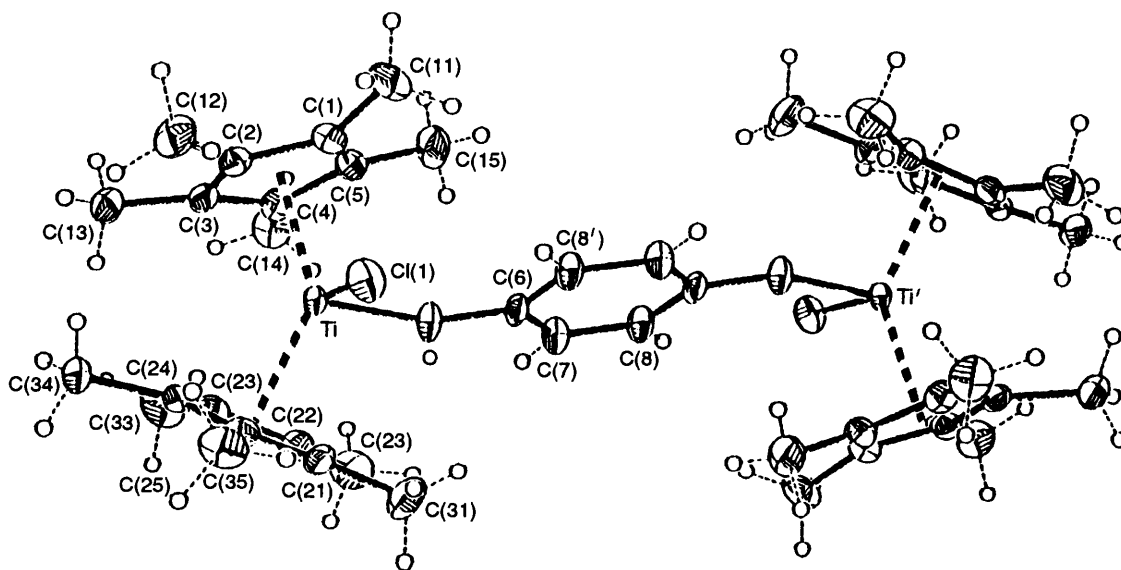
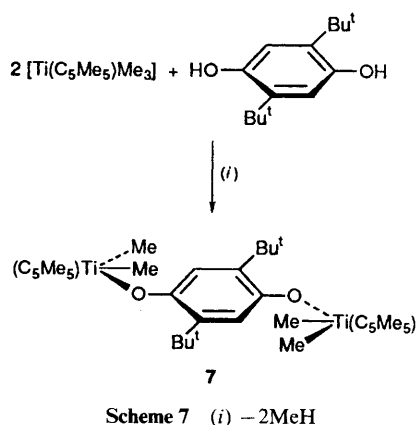
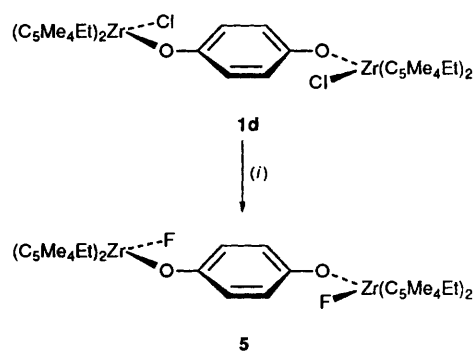
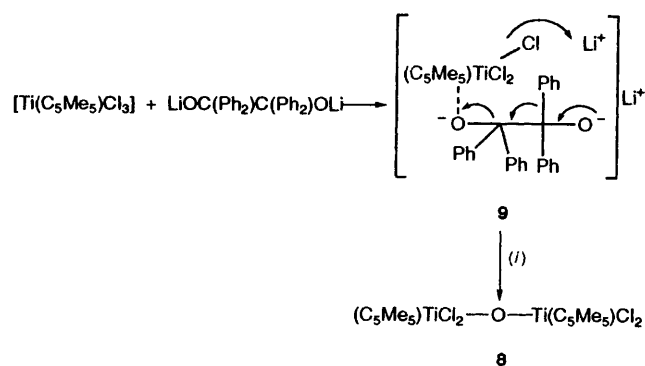


Fig. 2 Crystal structure of complex **3**



**Scheme 8** (i)  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]_2 - 2\text{LiCl}$

reagents. Multiply bridged complexes could not be formed with the employed starting materials. But there is evidence that, with longer aromatic dihydroxy compounds, the formation of multiply bridged metal centred complexes is favoured. These results will be presented in a subsequent paper.

### Spectroscopy

The  $^1\text{H}$  NMR spectra of the binuclear zirconium compounds **1a–1c** and the titanium compound **6b** show for the cyclopentadienyl hydrogen atoms signals in the range  $\delta$  6.4–6.3 (in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$ ) shifted to low field in  $\text{C}_6\text{D}_6$ . In complexes containing the  $\text{C}_5\text{Me}_5$  unit, the signals for the hydrogen atoms of the methyl substituents of the cyclopentadienyl moiety are found at *ca.*  $\delta$  1.9 (in  $\text{C}_6\text{D}_6$ ) for **3**, **4**, **6a** and **7**, and at  $\delta$  2.02 for **8**. The non-equivalence of the methyl moieties in  $\text{C}_5\text{Me}_4\text{Et}$  due to the ethyl substitution resulted in two signals from the methyl hydrogen atoms with a spacing that depends on the central metal atom (0.1 ppm in titanium compounds having one cyclopentadienyl ring and 0.05 ppm in the zirconium compounds **1a–1d** and **5**). Furthermore in the spectra of the zirconium complexes **1d** and **5** additional complexity arises from the orientational non-equivalence of the two  $\text{C}_5\text{Me}_4\text{Et}$  moieties attached to the same zirconium atom. This leads to the appearance of two pairs of signals ( $\delta$  1.90, 1.95 and 1.87, 1.94). The signals of the ethyl group ( $\text{C}_5\text{Me}_4\text{Et}$ ) are found in all cases as quadruplets and triplets at  $\delta$  *ca.* 2.5 and 0.9, respectively.

The signals of the aromatic protons in the spectra of **1a–1c** are located in the range  $\delta$  6.6–6.4. For complexes **1d** and **5** this signal shifts to  $\delta$  6.74. In  $\text{C}_6\text{D}_6$  the signal is shifted to low field ( $\delta$  6.9–6.7 for **2–4**, **6a**, **6b** and **7**). The protons of the  $\text{Bu}^1$  group are found at  $\delta$  *ca.* 1.3 (in  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$ ) or  $\delta$  1.6 (in  $\text{C}_6\text{D}_6$ ). In the case of doubly substituted hydroquinones different configurations account for the appearance of a multiplet.

The protons of the methyl group bound to titanium in **7** give rise to a singlet ( $\delta$  0.77). Those bound to silicon in **6b** appear at  $\delta$  0.28.

The  $^{19}\text{F}$  NMR spectra of **4** (**6b**) show two singlets [at  $\delta$  –63.99 (–64.04) and 90.4 (–54.5)] for the fluorine atoms, indicating their non-equivalence. In the spectrum of **5** the signal corresponding to the fluorine bound to zirconium appears at  $\delta$  17.3 in  $\text{C}_6\text{D}_6$ . The fluorine atoms in **6a** are found at  $\delta$  –65 as a broad peak.

The IR spectra show for all compounds similar absorptions (at *ca.* 1490, 1050 and  $860\text{ cm}^{-1}$ ) which can be assigned to the vibrations of the cyclopentadienyl ligands. Very strong C–O absorption peaks appear in the range  $1270$ – $1200\text{ cm}^{-1}$  and at *ca.*  $1000\text{ cm}^{-1}$ .

### Crystal structure

Single crystals of **1d** suitable for structure determination by X-ray diffraction were obtained from tetrahydrofuran (thf).

**Table 2** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for complex **1d**\*

Zr(1)–O(1)	1.973(3)	Zr(2)–O(2)	1.974(3)
Zr(1)–Cl(1)	2.471(2)	Zr(2)–Cl(2)	2.468(2)
Zr(1)–Cp(1a)	2.259(5)	Zr(2)–Cp(2a)	2.256(5)
Zr(1)–Cp(1b)	2.260(5)	Zr(2)–Cp(2b)	2.259(5)
Cp(1a)–Zr(1)–Cl(1)	104.9(13)	Cp(2a)–Zr(2)–Cl(2)	102.9(13)
Cp(1b)–Zr(1)–Cl(1)	104.3(12)	Cp(2b)–Zr(2)–Cl(2)	104.5(13)
Cp(1a)–Zr(1)–Cp(1b)	135.9(2)	Cp(2a)–Zr(2)–Cp(2b)	136.5(2)
Zr(1)–O(1)–C(11)	157.5(3)	Zr(2)–O(2)–C(31)	156.7(3)

\* Cp(1a), Cp(1b), Cp(2a) and Cp(2b) represent the centroids of the cyclopentadienyl rings C(1)–C(5), C(6)–C(10), C(21)–C(25) and C(26)–C(30), respectively.

**Table 3** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for compound **3**

Ti–O	1.865(2)	Ti–Cl(1)	2.393(7)
Ti–Cp(1a)	2.121(2)	Ti–Cp(1b)	2.134(2)
O–C(6)	1.352(3)		
Cp(1a)–Ti–Cl(1)	103.8(7)	Cp(1b)–Ti–Cl(1)	103.7(6)
Cp(1a)–Ti–Cp(1b)	135.7(6)	Ti–O–C(6)	155.1(2)

Cp(1a) and Cp(1b) represent the centroids of the cyclopentadienyl rings C(1)–C(5) and C(21)–C(25), respectively.

Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are presented in Table 2. The structural data show that **1d** crystallises as a monomer in the triclinic system, space group  $P\bar{1}$ . The asymmetric unit is composed of two separate half molecules related by an inversion centre. The steric shielding of the Zr atoms by the  $\text{C}_5\text{Me}_4\text{Et}$  moieties prevents **1d** from interacting with other molecules in the crystal. The chlorine atoms pointing in opposite directions introduce a centre of symmetry. The average Zr–Cl bond length is  $2.47\text{ \AA}$ . This is similar to the analogous distance found in  $[\text{Zr}(\text{C}_5\text{Me}_4\text{Et})_2(\text{Cl})\text{F}]$  ( $2.44\text{ \AA}$ )<sup>14</sup> but significantly longer than in  $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$  ( $2.31\text{ \AA}$ ).<sup>15</sup> The Zr atom forms an angle of  $136^\circ$  with the centres of the two  $\text{C}_5\text{Me}_4\text{Et}$  groups which lies between the corresponding angles found in  $[\text{Zr}(\text{C}_5\text{Me}_4\text{Et})_2(\text{Cl})\text{F}]$  ( $138^\circ$ ) and  $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$  ( $134^\circ$ ). This means that the molecule exhibits no additional steric stress by the bulky quinoide ligand. The Zr–O distance ( $1.97\text{ \AA}$ ) is characteristic of a typical single bond but is much smaller than the bond distance ( $2.23\text{ \AA}$ ) found in the four-membered ring unit  $(\text{Zr–O})_2$  of  $[\{\text{Zr}(\text{C}_5\text{H}_5)_2(\eta^2\text{-OCPh}_2)\}_2]$ .<sup>9a</sup> The oxygen is bent with Zr(1)–O(1)–C(11) and Zr(2)–O(2)–C(31) *ca.*  $157^\circ$ .

Compound **3** was crystallised from  $\text{CH}_2\text{Cl}_2$ –hexane and the single crystals studied by X-ray diffraction. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are presented in Table 3. The structural data show that **3** crystallises as a monomer in the orthorhombic system, space group  $Pbca$ . The inversion centre implicit in this space group was used to generate the second half molecule from the other one, representing the asymmetric unit. The overall appearance is quite similar to that of **1d**. Again, the metal atoms are shielded by  $\text{C}_5\text{Me}_5$  units with an angle of  $135.7^\circ$  at the titanium atom. Also the chlorine atoms are pointing in different directions. The angle Ti–O–C(6) [ $155.1(2)^\circ$ ] is only slightly smaller than the analogous angle in **1d** [ $157.5(3)^\circ$ ]. The Ti–Cl bond length [ $2.3938(7)\text{ \AA}$ ] is considerably longer than in comparable compounds [ $2.278(3)\text{ \AA}$  in  $[\{\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3(\mu\text{-O})_3\}]$ <sup>9b</sup> and  $2.239(2)\text{ \AA}$  in  $[\{\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2\}_2\text{O}]$ <sup>8c</sup>].

### Conclusion

There are various synthetic routes leading to compounds containing a  $\text{M}^{\text{IV}}\text{–O–C}_6\text{H}_{4-n}\text{Bu}_n\text{–O–M}^{\text{IV}}$  ( $\text{M} = \text{Ti}$  or  $\text{Zr}$ ,  $n = 0$ – $2$ ) unit. The stability of these complexes allows further reactions to be studied. Possibly they can be used as stepping stones to build up three-dimensional cages with similar properties to crown ethers.

**Table 4** Crystal data and structure refinement for **1d** and **3**\*

Complex	<b>1d</b>	<b>3</b>
Empirical formula	C <sub>50</sub> H <sub>72</sub> Cl <sub>2</sub> O <sub>2</sub> Zr <sub>2</sub>	C <sub>46</sub> H <sub>64</sub> Cl <sub>2</sub> O <sub>2</sub> Ti <sub>2</sub> ·2CH <sub>2</sub> Cl <sub>2</sub>
<i>M</i>	958.42	985.52
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> 1̄	<i>Pbca</i>
<i>a</i> /Å	9.358(2)	8.9224(12)
<i>b</i> /Å	16.912(3)	18.346(2)
<i>c</i> /Å	17.348(3)	29.265(3)
$\alpha$ /°	115.45(3)	90
$\beta$ /°	95.06(3)	90
$\gamma$ /°	104.39(3)	90
<i>V</i> /Å <sup>3</sup>	2340.9(8)	4790.3(10)
<i>Z</i>	2	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.360	1.366
Absorption coefficient (mm <sup>-1</sup> )	0.596	0.705
<i>F</i> (000)	1004	2072
Crystal size (mm)	0.70 × 0.70 × 0.30	0.50 × 0.50 × 0.25
$\theta$ Range for data collection/°	3.55–22.50	3.56–25.07
Index ranges, <i>hkl</i>	–10 to 10, –18 to 16, –18 to 18	–2 to 10, –21 to 21, –34 to 34
Reflections collected	8038	5129
Independent reflections ( <i>R</i> <sub>int</sub> )	6081 (0.1014)	4240 (0.0127)
Data/restraints/parameters	6081/0/525	4240/43/300
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.055	1.042
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0528, <i>wR</i> 2 = 0.1370	<i>R</i> 1 = 0.0384, <i>wR</i> 2 = 0.0861
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0596, <i>wR</i> 2 = 0.1443	<i>R</i> 1 = 0.0548, <i>wR</i> 2 = 0.0952
Largest difference peak and hole (e Å <sup>-3</sup> )	3.344, –0.786	0.258, –0.369

\* Details in common: *T* = 153(2) K;  $\lambda$  = 0.710 73 Å; full-matrix least-squares refinement on *F*<sup>2</sup>.

**Table 5** Atomic coordinates (× 10<sup>4</sup>) for **1d**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Zr(1)	1777(1)	–86(1)	2537(1)	Zr(2)	2875(1)	5227(1)	2613(1)
Cl(1)	696(2)	–1766(1)	1558(1)	Cl(2)	4282(1)	6890(1)	3498(1)
C(1)	4199(5)	497(4)	2088(3)	C(21)	3421(6)	3960(3)	1340(3)
C(2)	4058(6)	–405(4)	1912(3)	C(22)	3431(6)	4644(4)	1071(3)
C(3)	4243(6)	–437(4)	2726(3)	C(23)	4655(6)	5439(4)	1623(4)
C(4)	4534(5)	470(4)	3402(3)	C(24)	5458(6)	5242(4)	2221(4)
C(5)	4446(6)	1043(4)	3014(3)	C(25)	4706(6)	4331(4)	2043(3)
C(1a)	4254(6)	878(4)	1444(4)	C(21a)	2464(6)	2951(4)	865(4)
C(1b)	5858(7)	1184(5)	1324(4)	C(21b)	3245(7)	2368(4)	203(4)
C(2a)	3916(7)	–1198(4)	1017(4)	C(22a)	2525(7)	4504(4)	233(4)
C(3a)	4303(7)	–1262(4)	2842(4)	C(23a)	5136(8)	6307(4)	1525(4)
C(4a)	5189(6)	791(4)	4358(4)	C(24a)	6943(6)	5871(4)	2860(4)
C(5a)	4827(7)	2083(4)	3481(4)	C(25a)	5207(7)	3810(4)	2474(4)
C(6)	208(6)	868(3)	3387(3)	C(26)	119(5)	4623(3)	1759(3)
C(7)	1278(6)	887(4)	4034(3)	C(27)	558(5)	5596(3)	2142(3)
C(8)	950(6)	–21(4)	3937(3)	C(28)	757(5)	5939(3)	3070(3)
C(9)	–346(6)	–597(3)	3243(3)	C(29)	500(6)	5191(4)	3240(3)
C(10)	–786(5)	–50(4)	2896(3)	C(30)	142(6)	4371(4)	2432(3)
C(6a)	69(7)	1679(4)	3275(4)	C(26a)	–674(6)	3973(4)	802(3)
C(6b)	–989(9)	2110(5)	3801(5)	C(26b)	–2397(6)	3768(4)	706(4)
C(7a)	2294(7)	1768(4)	4814(4)	C(27a)	618(6)	6180(4)	1690(4)
C(8a)	1633(7)	–315(4)	4549(4)	C(28a)	1038(6)	6934(4)	3724(4)
C(9a)	–1230(7)	–1576(4)	3007(4)	C(29a)	520(8)	5239(5)	4137(4)
C(10a)	–2109(6)	–380(4)	2141(4)	C(30a)	–334(7)	3391(4)	2321(4)
O(1)	983(4)	227(2)	1650(2)	O(2)	3314(4)	4901(2)	3553(2)
C(11)	510(5)	121(4)	843(3)	C(31)	4147(6)	4949(3)	4266(3)
C(12)	64(6)	792(4)	734(3)	C(32)	3676(6)	4275(4)	4522(3)
C(13)	428(6)	–685(4)	93(3)	C(33)	5467(6)	5683(4)	4751(3)

These compounds may also be potential active catalysts for polymerisation reactions. Investigations will be discussed at a later stage.

## Experimental

All reactions were performed under dry nitrogen by Schlenk, vacuum-line and inert-atmosphere box techniques. Solvents were freshly distilled from sodium and degassed prior to use; CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, NEt<sub>3</sub> and pyridine were distilled using calcium hydride. Commercially available reagents were used as received. The hydroquinones were purchased from Aldrich.

Literature methods were used for the preparation of [Zr(C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Cl<sub>2</sub>],<sup>16</sup> [Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>3</sub>]<sup>17</sup> {and analogously [Ti(C<sub>5</sub>Me<sub>4</sub>Et)Cl<sub>3</sub>], [Ti(C<sub>5</sub>Me<sub>5</sub>)Me<sub>3</sub>],<sup>18</sup> [Ti(C<sub>5</sub>Me<sub>5</sub>)F<sub>3</sub>],<sup>19</sup> [Ti(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>F<sub>2</sub>],<sup>20</sup> [Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl]<sup>21</sup> and [Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>F]}.<sup>19</sup> NMR spectra were recorded on a Bruker AM 250 instrument with SiMe<sub>4</sub> (<sup>1</sup>H) and CFCl<sub>3</sub> (<sup>19</sup>F), respectively, used as internal standards. Electron impact (EI) mass spectra were measured on Finnigan MAT 8230 and Varian MAT CH5 instruments at 70 eV (≈ 1.12 × 10<sup>-17</sup> J). IR spectra were obtained on a Bio-Rad FTS 7 spectrophotometer as Nujol mulls between NaCl, KBr or CsI plates. Elemental analyses were performed at the Analytical Laboratory of the Institute

**Table 6** Atomic coordinates ( $\times 10^4$ ) for **3**

Atom	x	y	z
Ti	2373(1)	-3858(1)	6162(1)
Cl(1)	279(1)	-4302(1)	6590(1)
O	1543(2)	-4120(1)	5601(1)
C(6)	787(3)	-4558(1)	5309(1)
C(7)	994(3)	-4485(1)	4840(1)
C(8)	222(3)	-4926(1)	4536(1)
C(1)	3215(3)	-5071(1)	6404(1)
C(2)	3821(3)	-4550(1)	6719(1)
C(3)	4864(3)	-4125(1)	6486(1)
C(4)	4826(3)	-4330(1)	6016(1)
C(5)	3853(3)	-4934(1)	5978(1)
C(11)	2272(4)	-5715(2)	6525(1)
C(12)	3515(4)	-4545(2)	7225(1)
C(13)	6078(3)	-3676(1)	6701(1)
C(14)	5878(3)	-4083(2)	5646(1)
C(15)	3698(4)	-5389(2)	5556(1)
C(21)	867(3)	-2780(1)	6023(1)
C(22)	2206(3)	-2693(1)	5774(1)
C(23)	3403(3)	-2623(1)	6084(1)
C(24)	2799(3)	-2667(1)	6532(1)
C(25)	1243(3)	-2749(1)	6494(1)
C(31)	-666(3)	-2867(2)	5826(1)
C(32)	2330(4)	-2631(2)	5264(1)
C(33)	4909(3)	-2332(2)	5952(1)
C(34)	3558(3)	-2497(2)	6977(1)
C(35)	170(3)	-2700(2)	6886(1)
C(9)	7342(13)	-5651(3)	6749(2)
Cl(2)	8104(2)	-6283(1)	7127(1)
Cl(3)	6874(3)	-6046(2)	6230(1)
C(9')	7435(127)	-5592(29)	6669(10)
Cl(2')	6853(24)	-6022(8)	7168(4)
Cl(3')	7153(30)	-6166(17)	6206(6)

of Inorganic Chemistry of the University of Göttingen. Diffraction data were collected on Siemens-Stoe AED four-circle diffractometers at 153 K with Mo-K $\alpha$  radiation and were solved by direct methods with SHELXS 86<sup>22</sup> and refined by full-matrix least squares on  $F^2$  (SHELXL 93<sup>23</sup>). Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted in calculated positions. Crystal data for complexes **1d** and **3** are summarized in Table 4 and atomic coordinates in Tables 5 and 6.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

### Preparations

**[{Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>( $\mu$ -OC<sub>6</sub>H<sub>4</sub>O)] **1a**.** To a solution of [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] (1.00 g, 3.42 mmol) in thf (10 cm<sup>3</sup>) was added dropwise a solution of 1,4-hydroquinone (0.36 g, 3.27 mmol) and triethylamine (0.46 cm<sup>3</sup>) in thf (10 cm<sup>3</sup>). The suspension was stirred at room temperature for 18 h. After separating the voluminous white precipitate of NHEt<sub>3</sub>Cl by filtration the solvent was evaporated under reduced pressure. The oily residue was suspended in diethyl ether (20 cm<sup>3</sup>) and filtered off leading to pure **1a** (yield: 0.42 g) as a yellow solid.  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  6.67–6.39 (4 H, m, C<sub>6</sub>H<sub>4</sub>) and 6.00–5.86 (20 H, m, 4 C<sub>5</sub>H<sub>5</sub>). IR (Nujol, NaCl)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1491vs, 1248vs, 1230vs, 1092m, 1066m, 1013vs, 921w, 863vs, 844s, 831s, 803vs and 531m. Mass spectrum:  $m/z$  622 ( $M^+$ , 2%) and 227 (100).

**[{Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>( $\mu$ -O(C<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>-2)O)] **1b**.** A solution of 2-*tert*-butyl-1,4-hydroquinone (0.28 g, 1.68 mmol) and NEt<sub>3</sub> (0.46 cm<sup>3</sup>) in thf (10 cm<sup>3</sup>) was slowly added to a solution of [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] (1.00 g, 3.42 mmol) in thf (10 cm<sup>3</sup>). The resulting suspension was stirred at room temperature for 2 h. After filtration of the reaction mixture diethyl ether (20 cm<sup>3</sup>) was added to the filtrate, leading to a turbid solution. This

was filtered a second time using zeolites before evaporation to dryness of the solvents to give a yellow solid. Yield: 0.45 g.  $\delta_{\text{H}}(\text{CDCl}_3)$  6.73–6.47 (3 H, m, C<sub>6</sub>H<sub>3</sub>), 6.40–6.32 (20 H, m, 4 C<sub>5</sub>H<sub>5</sub>) and 1.3 (9 H, s, Bu<sup>t</sup>). IR (Nujol, NaCl)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1593w, 1557w, 1402m, 1290m, 1266s, 1244w, 1213vs, 1078m, 1014s, 956m, 858s, 806vs, 773m and 738s. Mass spectrum:  $m/z$  678 ( $M^+$ , 30%) and 227 (100).

**[{Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>( $\mu$ -O(C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,5)O)] **1c**.** To a solution of [Zr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.50 g, 1.71 mmol) in thf (10 cm<sup>3</sup>) was added dropwise a solution of 2,5-di-*tert*-butyl-1,4-hydroquinone (0.19 g, 0.86 mmol) and NEt<sub>3</sub> (0.23 cm<sup>3</sup>) in thf (10 cm<sup>3</sup>). After 2 h of stirring at room temperature NHEt<sub>3</sub>Cl was filtered off, and hexane (30 cm<sup>3</sup>) was added to the filtrate. After 12 h **1c** was separated from the solvent as a yellow solid and recrystallised from thf–hexane (1:1). Yield: 0.43 g.  $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$  6.6–6.45 (2 H, m, C<sub>6</sub>H<sub>2</sub>), 6.41–6.30 (20 H, m, 4 C<sub>5</sub>H<sub>5</sub>) and 1.40–1.10 (18 H, m, 2 Bu<sup>t</sup>). IR (Nujol, KBr)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1665m, 1491vs, 1204s, 1122s, 1019s, 888w, 809vs and 738s. Mass spectrum:  $m/z$  732 ( $M^+$ , 24%) and 225 (100).

**[{Zr(C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>( $\mu$ -OC<sub>6</sub>H<sub>4</sub>O)] **1d**.** A solution of 1,4-hydroquinone (0.07 g, 0.63 mmol) and NEt<sub>3</sub> (0.09 cm<sup>3</sup>) in thf (10 cm<sup>3</sup>) was slowly added to a solution of [Zr(C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Cl<sub>2</sub>] (0.60 g, 1.30 mmol) in thf (10 cm<sup>3</sup>). The solution was stirred for 4 h at room temperature. After removing the NHEt<sub>3</sub>Cl by filtration, the filtrate was concentrated to 5 cm<sup>3</sup>, and stored at –18 °C. After 12 h the yellow precipitate of **1d** was separated by filtration and recrystallised from hot toluene (5 cm<sup>3</sup>). Yield: 0.25 g.  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  6.70 (4 H, s, C<sub>6</sub>H<sub>4</sub>), 2.47 [8 H, q,  $J(\text{HH})$  7.4, 4 CH<sub>2</sub>], 2.00–1.80 (48 H, m, 4 C<sub>5</sub>Me<sub>4</sub>) and 0.82 [12 H, t,  $J(\text{HH})$  7.4 Hz, 4 Me]. IR (Nujol, CsI)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1484vs, 1260m, 1246s, 1097m, 1049m, 1023s, 966w, 948w, 866w, 828w, 726w, 458s, 380vs, 325vs and 313vs. Mass spectrum:  $m/z$  958 ( $M^+$ , 100%).

**[{Ti(C<sub>5</sub>Me<sub>4</sub>Et)Cl<sub>2</sub>]<sub>2</sub>( $\mu$ -OC<sub>6</sub>H<sub>4</sub>O)] **2**.** A solution of [Ti(C<sub>5</sub>Me<sub>4</sub>Et)Cl<sub>2</sub>] (0.44 g, 1.46 mmol) in thf (20 cm<sup>3</sup>) was treated with a solution of 1,4-hydroquinone (0.08 g, 0.73 mmol) and pyridine (0.11 cm<sup>3</sup>) in thf (10 cm<sup>3</sup>). After stirring for 4 h at room temperature the reaction mixture was filtered to remove py-HCl. After evaporation of the solvent the dark red solid **2** was washed with hexane (10 cm<sup>3</sup>) and recrystallised from thf (10 cm<sup>3</sup>). Yield: 0.22 g.  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  6.90–6.70 (4 H, m, C<sub>6</sub>H<sub>4</sub>), 2.75 [4 H, q,  $J(\text{HH})$  7.4, 2 CH<sub>2</sub>], 2.20–2.05 (24 H, m, 2 C<sub>5</sub>Me<sub>4</sub>) and 0.95 [6 H, t,  $J(\text{HH})$  7.4 Hz, 2 Me]. IR (Nujol, KBr)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1635w, 1608w, 1588w, 1538w, 1486vs, 1240s, 1216s, 1110w, 893s, 751vs, 724vs and 679m. Mass spectrum:  $m/z$  644 ( $M^+$ , 30%) and 149 (C<sub>5</sub>Me<sub>4</sub>Et<sup>+</sup>, 100).

**[{Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl]<sub>2</sub>( $\mu$ -OC<sub>6</sub>H<sub>4</sub>O)] **3**.** A solution of [Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl] (1.41 g, 4.00 mmol) in toluene (30 cm<sup>3</sup>) was added to a suspension of benzoquinone (0.22 g, 2.00 mmol) in toluene (20 cm<sup>3</sup>). The mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–hexane (1:1) to give **3** (yield: 2.87 g).  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  6.78 (4 H, s, C<sub>6</sub>H<sub>4</sub>) and 1.87 (60 H, s, 4 C<sub>5</sub>Me<sub>5</sub>). IR (Nujol, KBr)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1482s, 1239s, 1220m, 1021m, 871s and 828m.

**[{Ti(C<sub>5</sub>Me<sub>5</sub>)F<sub>2</sub>]<sub>2</sub>( $\mu$ -O(C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,5)O)] **4**.** A mixture of [(SnMe<sub>3</sub>)<sub>2</sub>( $\mu$ -O(C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,5)O)] (0.55 g, 1.00 mmol) and [Ti(C<sub>5</sub>Me<sub>5</sub>)F<sub>3</sub>] (0.48 g, 2.00 mmol) was treated with toluene (20 cm<sup>3</sup>) and stirred for 4 h at 80 °C. The resulting suspension was hot-filtered, and after evaporation of the solvent, the red solid was recrystallised from thf (10 cm<sup>3</sup>). Yield: 0.41 g.  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  6.75 (2 H, s, C<sub>6</sub>H<sub>2</sub>), 1.96 (15 H, s, C<sub>5</sub>Me<sub>5</sub>), 1.95 (15 H, s, C<sub>5</sub>Me<sub>5</sub>) and 1.45 (18 H, s, 2 Bu<sup>t</sup>).  $\delta_{\text{F}}(\text{C}_6\text{D}_6)$  –63.99 (s) and –64.04 (s). IR (Nujol, KBr)  $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$  1488s, 1394s, 1211vs, 1191s, 1123s, 1024m, 917vs, 891m, 835m, 757m, 742s, 734s,

609s and 509s. Mass spectrum:  $m/z$  662 ( $M^+$ , 20%) and 135 ( $C_5Me_5$ , 100).

$[Zr(C_5Me_4Et)_2F]_2(\mu-OC_6H_4O)$  **5**. A suspension of  $[Zr(C_5Me_4Et)_2Cl]_2(\mu-OC_6H_4O)$  (0.45 g, 0.50 mmol) and  $SnMe_3F$  (0.17 g, 1.00 mmol) in toluene (30 cm<sup>3</sup>) was heated to reflux for 2 days. All volatiles were removed under vacuum at 40 °C. The pale yellow precipitate of **5** was recrystallised from thf-hexane (1:1). Yield: 0.25 g.  $\delta_H(C_6D_6)$  6.74 (4 H, s,  $C_6H_4$ ), 2.47 [8 H, q,  $J(HH)$  7.4 Hz, 4  $CH_2$ ], 2.00–1.82 (48 H, m, 4  $C_5Me_4$ ) and 0.87 [12 H, t,  $J(HH)$  7.4 Hz, 4 Me].  $\delta_F(C_6D_6)$  17.30 (s). Mass spectrum:  $m/z$  924 ( $M^+$ , 100%).

$[Ti(C_5Me_5)_2F]_2(\mu-OC_6H_4O)$  **6a**. A solution of  $[Ti(C_5Me_5)_2F]$  (1.35 g, 4.00 mmol) in toluene (30 cm<sup>3</sup>) was added to a suspension of benzoquinone (0.22 g, 2.00 mmol) in toluene (20 cm<sup>3</sup>). The mixture was stirred overnight. The solvent was removed *in vacuo* and the residue was recrystallised from  $CH_2Cl_2$ -hexane (1:1) to give **6a** (yield: 1.00 g).  $\delta_H(C_6D_6)$  6.81 (4 H, s,  $C_6H_4$ ) and 1.88 (60 H, s, 4  $C_5Me_5$ ).  $\delta_F(C_6D_6)$  –64.5 (br s,  $w_3 = 92$  Hz). IR (Nujol, CsI)  $\tilde{\nu}_{max}/cm^{-1}$  1487s, 1239s, 1222m, 849s, 828m, 549m, 539m, 419m and 368m.

$[Ti(C_5H_4SiMe_3)_2F]_2(\mu-OC_6H_4O)$  **6b**. A solution of  $[Ti(C_5H_4SiMe_3)_2F]$  (1.44 g, 4.00 mmol) in thf (40 cm<sup>3</sup>) was added dropwise to sodium amalgam (15.30 g, 0.60%) in thf (20 cm<sup>3</sup>). After stirring overnight the solvent was removed *in vacuo*. The residue was extracted with hexane (70 cm<sup>3</sup>) and concentrated to 25 cm<sup>3</sup>. The solution was filtered at 0 °C to yield  $[Ti(C_5H_4SiMe_3)_2F]$  as a green solid (0.95 g, 70%), m.p. 138–139 °C (Found: C, 56.0, H, 7.4, F, 5.4.  $C_{16}H_{26}FSi_2Ti$  requires C, 56.3, H, 7.6, F, 5.6%). IR (Nujol, CsI)  $\tilde{\nu}_{max}/cm^{-1}$  3111w, 1243s, 1182s, 1052s, 913s, 872s, 843s, 801s, 751s, 692m, 628m, 421m and 392s. Mass spectrum:  $m/z$  341 ( $M^+$ , 80%) and 326 ( $M^+ - Me$ , 100%).

**6b** was then obtained by the same method as described for the preparation of **6a** using  $[Ti(C_5H_4SiMe_3)_2F]$  (yield: 1.67 g).  $\delta_H(C_6D_6)$  6.81 (4 H, s,  $C_6H_4$ ), 6.39–6.05 (16 H, m, 4  $C_5H_4$ ) and 0.28 (36 H, s, 4  $SiMe_3$ ).  $\delta_F(C_6D_6)$  –90.4 (s) and –54.5 (s). IR (Nujol, CsI)  $\tilde{\nu}_{max}/cm^{-1}$  3078w, 1487s, 1247s, 1227m, 1045m, 838s, 533m, 412m and 402m.

$[Ti(C_5Me_5)Me_2]_2(\mu-O(C_6H_2Bu^t-2,5)O)$  **7**. A solution of  $[Ti(C_5Me_5)Me_3]$  (0.46 g, 2.00 mmol) in hexane (7 cm<sup>3</sup>) was treated with a solution of 2,5-di-*tert*-butyl-1,4-hydroquinone (0.22 g, 1.00 mmol) in thf (8 cm<sup>3</sup>). After completion of gas evolution stirring was continued for 1 h at room temperature. The yellow solid obtained was separated and recrystallised from thf (5 cm<sup>3</sup>). Yield: 0.43 g.  $\delta_H(C_6D_6)$  6.75 (2 H, s,  $C_6H_2$ ), 1.85 (30 H, s, 2  $C_5Me_5$ ), 1.64 (18 H, s, 2  $Bu^t$ ) and 0.77 (12 H, s, 4  $CH_3$ ). IR (Nujol, KBr)  $\tilde{\nu}_{max}/cm^{-1}$  1489s, 1392s, 1358s, 1264w, 1244w, 1213s, 1190m, 1123s, 1111m, 921vs, 881m, 835m, 653m, 516s and 501s. Mass spectrum:  $m/z$  647 ( $M^+$ , 40%) and 44 (100).

$[Ti(C_5Me_5)Cl_2]_2O$  **8**. A suspension of  $[Ti(C_5Me_5)Cl_3]$  (0.58 g, 2.00 mmol) and dilithium tetraphenylethanediolate (0.38 g, 1.00 mmol) in toluene (30 cm<sup>3</sup>) was heated to reflux for 12 h. After filtration the solvent was evaporated and the resulting orange-red solid **8** recrystallised from hot hexane (15 cm<sup>3</sup>). Yield: 0.31 g.  $\delta_H(C_6D_6)$  2.02 [s, 2  $C_5Me_5$ ]. IR (Nujol, CsI)  $\tilde{\nu}_{max}/cm^{-1}$  1667m, 1600w, 1260s, 1092vs, 1022s, 800vs, 780vs, 762s, 699s, 619m, 452s, 399s and 344s. Mass spectrum:  $m/z$  524 ( $M^+$ , 20%) and 135 ( $C_5Me_5$ , 100).

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