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Steric influences in cyclopentadienyl-monophenoxide complexes of titanium(iv) arising from *ortho*-substitution of the phenoxide ligand

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Abstract

Reaction of [$CpTiCl_3$] with 1 equiv. of $Me_3SiOC_6H_4CMe_3$-4 in benzene or thermalisation with an excess of neat $Me_3SiOC_6H_4CMe_3$-4 gives good yields of crystalline [$CpTiCl_2(OC_6H_4CMe_3$-4)] (**1**) for which an X-ray crystal structure determination shows a distorted tetrahedral geometry. Reaction of [$CpTiCl_3$] and $Me_3SiOC_6H_3CMe_3$-2-Me-4 via the benzene solvent method or the direct thermalisation gives rise to crystalline [$CpTiCl_2(OC_6H_3CMe_3$-2-Me-4)] (**2**) for which an X-ray crystal structure determination shows a distorted tetrahedral geometry little changed from complex **1** but with the phenoxide ligand ring rotated so that two of the *tert*-butyl group methyls straddle one chloro ligand. Refluxing [$CpTiCl_3$] and $Me_3SiOC_6H_4Ph$-4 in toluene gave crystalline [$CpTiCl_2(OC_6H_4Ph$-2)] (**3**) which X-ray crystallography shows has a distorted tetrahedral geometry little changed from **1** or **2**. The phenoxide ligand ring is rotated less in **1** than in **2** or **3** with the 2-phenyl substituent sited between the chloro and Cp ligands. The complexes differ only in the interplanar angle between the Cp and phenoxide ligand phenyl rings [6.4(1)° for **1**, 29.4(1)° for **2** and 22.2(1)° for **3**]. DFT calculations carried out on **2** are in good agreement with the X-ray crystal structure. A relaxed PES scan shows that the *tert*-butyl group in the complex cannot freely rotate past the adjacent chloro ligand and is essentially locked in close proximity to it. There is a shallow minimum (2 kJ/mol within a range of 60 degrees) for the Ti–O–C–C dihedral angle indicating there is sufficient torsional motion within the molecule to accommodate the *tert*-butyl group in the observed position.

Keywords: Ti(iv); Cyclopentadienyl-monophenoxides; Steric influences; Crystal structures

1. Introduction

Cyclopentadienyl-monophenoxide complexes of titanium(iv), [$CpTiCl_2(OAr)$], which have been known for some time [1] have found use in inorganic synthesis [2] olefin polymerizations [3] and organic synthesis [4]. In all these applications the nature of the phenoxide ligand plays an important role in whether the reaction is successful or not. For example, in olefin polymerizations when a cocatalyst such as MAO (methyl aluminoxane) is present, the activity is highest when the 2,6-diisopropylphenoxide ligand is used in conjunction with Cp* (pentamethyl cyclopentadiene). Ligand-based steric influences of phenoxide ligands may also be important in tuning stoichiometric and catalytic reactions in organic synthesis [5]. We have therefore looked at producing [$CpTiCl_2(OAr)$], complexes in which the phenoxide ligand is capable of exerting a steric influence on one of the chloro ligands. As the cost of preparing potential catalysts is another important factor influencing usage [6], in order to prepare bulk quantities of complexes for catalytic studies we have chosen 2-*tert*-butyl or 2-phenyl substituted phenols which are obtainable cheaply from commercial sources. We report here results of preparative and structural studies for complexes containing these ligands and indicate through DFT calculations how a *tert*-butyl group in the *ortho* position of the phenyl ring sterically influences the molecule.

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2. Results and discussion

2.1. Syntheses and X-ray crystallography

We have concentrated our studies on cyclopentadienyl complexes since the Cp ligand is easily prepared in comparison with pentamethylCp (Cp*). The normal starting material for titanium Cp complexes is [$CpTiCl_3$], which can be prepared by the reaction of $CpSiMe_3$ with $TiCl_4$ in dichloromethane [7]. We have found that to obtain good yields of pure product using this method, high purity $TiCl_4$ must be used otherwise the reaction material is contaminated with a dark product which is difficult to remove. Rather than distill the $TiCl_4$ we have opted to purify the [$CpTiCl_3$] which can be easily carried out by sublimation (see Section 4).

[$CpTiCl_2(OAr)$] complexes are reported to be prepared in good yield by the addition of 1 equiv. of LiOAr (Ar = $OC_6H_2Me_3$-2,4,6; $OC_6H_3{}^iPr_2$-2,6; $OC_6H_2CMe_3$-2-Me_2-4,6) to [$CpTiCl_3$] in diethyl ether (Eq. (1)) [3k,l]

$$[CpTiCl_3] + LiOAr \longrightarrow [CpTiCl_2(OAr)] + LiCl \qquad (1)$$

However in developing a high yield route to [$CpTiCl_2(OC_6H_4CMe_3$-4)] (**1**) which was to be used for comparative studies, it was found that the reaction of $LiOC_6H_4CMe_3$-4 and [$CpTiCl_3$] did give the complex but two minor products were always present even when the reaction was carried out under carefully controlled conditions. Further, the complex proved very difficult to crystallize when prepared in this manner. Thermalisation using the phenol (Eq. (2)) also gave a similar result.

$$[CpTiCl_3] + HOAr \longrightarrow [CpTiCl_2(OAr)] + HCl \qquad (2)$$

When the phenol was reacted with [$CpTiCl_2Me$)] generated in situ from [$CpTiCl_3$] and 1 equiv. of MeLi in diethyl ether there was one major contaminating product but the desired complex still proved difficult to crystallise. Reaction of LiCp with [$TiCl_3(OC_6H_4CMe_3$-4)] [8] produced the complex but the reaction also formed another product which reduced the yield. We have found that use of the *O*-trimethyl silyl (TMS) phenol in a thermalisation reaction (Eq. (3)) gives a better result, producing initially a red oil which solidifies after pumping to give the required crystalline solid in high yield.

$$\begin{aligned}&[CpTiCl_3] + Me_3SiOC_6H_4CMe_3\text{-}4\\&\quad\longrightarrow [CpTiCl_2(OC_6H_4CMe_3\text{-}4)]\,(\mathbf{1}) + Me_3SiCl \qquad (3)\end{aligned}$$

The reaction is best carried out by stirring a slight excess of the TMS phenol with [$CpTiCl_3$] in benzene solution for ca. 18 h after which the solvent is removed and the residue pumped on or washed with cold petroleum spirit to remove the unreacted TMS phenol. The complex then crystallises to a solid mass. NMR spectroscopy indicated that only 10% of the [$CpTiCl_3$] remained at this stage and that a short period of reflux (ca. 2 h) removed essentially all the [$CpTiCl_3$]. Only very small amounts of another product were formed if the refluxing period was extended to 6–8 h. Even in this case the product crystallises to a solid mass when the first formed oil is pumped on or washed with petroleum spirit and then allowed to stand.

We have also looked at producing complex **1** directly from $TiCl_4$ using a one-pot reaction. $CpSiMe_3$ and $TiCl_4$ were reacted in CH_2Cl_2 to produce [$CpTiCl_3$] and the reaction solution treated with $Me_3SiOC_6H_4CMe_3$-4. However, NMR spectroscopy indicated that the reaction did not go to completion with more than 50% of the reaction mixture being [$CpTiCl_3$].

An X-ray crystal structure determination of **1** was carried out in order to establish the structural features present in the complex when no *ortho*-substituent is present on the phenoxide ligand aromatic ring. The structure shows a distorted tetrahedral geometry (Fig. 1). The Ti–O bond length [1.772(2) Å] (Table 1) is similar to that found in [$CpTiCl_2(OC_6H_3(CHMe_2)_2$-2,6)] [1.760(4) Å] [31] and the more bulky pentamethylcyclopentadienyl complexes [Cp^*TiCl_2-

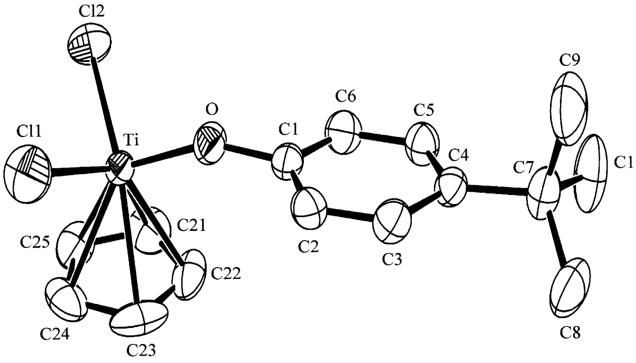

Fig. 1. ORTEP diagram, at the 50% probability level, of the molecular structure of [$CpTiCl_2(OC_6H_4CMe_3$-4)] (**1**). Hydrogen atoms have been omitted for clarity. Selected bond distances and angles are given in Table 1.

Table 1
Selected bond distances (Å) and angles (°) for **1**, **2** and **3**

Complex	**1**	**2**	**3**
Bond distances (Å)			
Ti–O	1.7718(18)	1.7805(15)	1.7824(12)
Ti–Cl(1)	2.2542(9)	2.2581(8)	2.2572(6)
Ti–Cl(2)	2.2594(8)	2.2517(8)	2.2631(6)
O–C(1)	1.368(3)	1.372(2)	1.366(2)
Bond angles (°)			
Ti–O–C(1)	153.77(16)	152.75(14)	155.84(11)
O–Ti–Cl(1)	103.84(7)	101.82(6)	102.91(5)
O–Ti–Cl(2)	104.39(7)	103.47(5)	102.56(4)
Cl(1)–Ti–Cl(2)	102.89(4)	104.02(3)	102.73(2)
O–C(1)–C(2)	119.8(2)	117.35(19)	117.82(16)
O–C(1)–C(6)	119.9(2)	120.79(19)	120.56(15)
C(1)–C(6)–C(7)		122.82(19)	121.74(15)
C(5)–C(6)–C(7)		122.0(2)	120.90(16)
C(6)–C(7)–C(8)		110.13(19)	120.87(16)
C(6)–C(7)–C(9)		110.90(18)	
C(6)–C(7)–C(10)		111.28(19)	
C(8)–C(7)–C(9)	109.2(4)	110.0(2)	
C(8)–C(7)–C(10)	110.5(4)	106.7(2)	
C(9)–C(7)–C(10)	104.7(4)	107.71(19)	

$(OC_6H_3Me_2\text{-}2,6)]$ and $[Cp^*TiCl_2(OC_6H_3(CHMe_2)_2\text{-}2,6)]$ [Ti–O bond lengths 1.786(2) and 1.773(3) Å, respectively] [31] and $\{(1,3\text{-}Bu^t_2Cp)TiCl_2[OC_6H_3(CHMe_2)_2\text{-}2,6]\}$ [Ti–O bond length 1.773(2) Å] [9]. The Ti–Cl bond lengths in **1** [2.254(1) and 2.259(1) Å] are not significantly different from one another and are also the same length as in $[CpTiCl_2(OC_6H_3(CHMe_2)_2\text{-}2,6)]$ [Ti–Cl bond lengths 2.261(1) Å]. Also the C–O bond length in **1** [1.368(3) Å] is no different to the other phenoxide complexes [range 1.366(3)–1.368(6) Å]. It can thus be seen that based on the bond length data, there is little electronic or steric effect in this type of complex whether *ortho*-substituents such as *iso*-propyl groups are present or not. In the mono phenoxide complex $\{TiCl_3[OC_6H_3(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4]\}$ where the phenoxide ligand is the dominant π-donor and has no competition from a π-donor Cp ligand, the Ti–O bond length has the shorter value of 1.750(2) Å [8] showing stronger phenoxide π-donation than would be expected for the Cp-phenoxide complexes. The Ti–O–C bond angle in **1** [153.8(2)°] (Table 1) is significantly smaller than those found in the 2,6-dimethyl or diisopropyl complexes quoted above [range 162.3(2)–173.6(3)°] so that the 2,6-substituents do have an effect on this angle but where they are not present, this angle can go down to ca. 154° without having any electronic effect on the Ti–O bond as indicated by the similar Ti–O bond lengths.

In **1** the phenoxide ligand phenyl ring is rotated so that the interplanar angle between the Cp and phenyl rings is only 6.4(1)° which apparently allows maximum π-overlap in the Ti–O–C system [5]. Some comparison of the strength of the π-bonding component in the phenoxide ligand can be obtained from the ^{13}C NMR spectrum which shows the *ipso*-carbon resonance at δ 166.2. This is further upfield from that observed in the monophenoxide complex $[TiCl_3(OC_6H_4CMe_3\text{-}4)]$ (δ 169.6) and for a variety of this type of complex (δ range 169.6–174.9) where there is a need for tight O(2p)-to-Ti(d) orbital donation in the presence of three chloro ligands which are less efficient π-donors than a phenoxide ligand [8]. However in the bis-phenoxide complex $[TiCl_2(OC_6H_4CMe_3\text{-}4)_2]$ where this need is relaxed, the *ipso*-carbon resonance is at a similar position (δ 166.3 [5]) to that observed for **1** indicating that the π-donor requirement is similar whether the other ligand is Cp or OAr. This would then give some experimental evidence for the "isolobal" analogy [10] used to compare these different type of ligands systems [11].

The reaction of $[CpTiCl_3]$ and a slight excess of $Me_3SiOC_6H_3CMe_3\text{-}2\text{-}Me\text{-}4$ in benzene does not go to completion when the reaction is stirred at room temperature, but does so when the mixture is refluxed for a short period (ca. 2 h) giving rise to $[CpTiCl_2(OC_6H_3CMe_3\text{-}2\text{-}Me\text{-}4)]$ (**2**). The complex forms as a solid mass on standing after the excess of TMS phenol is pumped off or removed by washing. It can then be crystallised from petroleum spirit. The NMR spectra show a single set of resonances for the Cp and phenoxide ligands and in the ^{13}C NMR spectrum the *ipso*-carbon resonance appears at δ 166.4 which is similar to that shown by complex **1** and suggests that the phenoxides are electronically equivalent in both complexes.

An X-ray crystal structure determination of **2** shows a distorted tetrahedral geometry similar to complex **1** with the phenoxide phenyl ring rotated so that two of the 2-*tert*-butyl substituent methyl groups straddle Cl(2) (Fig. 2). The Ti–O bond length [1.781(2) Å], C–O bond length [1.372(2) Å] and Ti–Cl bond lengths [2.252(1) and 2.258(1) Å] are no different from those found in complex **1** which indicates that the 2-*tert*-butyl substituent does not cause significant steric pressure and force an electronic change to the Ti–O or Ti–Cl bonds in the solid state. Similarly the O–Ti–Cl(1), O–Ti–Cl(2) and Cl(1)–Ti–Cl(2) bond angles in the molecule are also little different from those for complex **1** (see Table 1) and there is little difference in the Ti–O–C bond angles [152.8(1)° for **2**, 153.8(2)° for **1**]. However the interplanar angle between the Cp and phenyl rings in **2** [29.4(1)°] is now larger than in **1** [6.4(1)°] and this would appear to be a consequence of the *tert*-butyl methyls moving away from the Cp ligand to avoid a clash and to also be accommodated about the Cl ligand.

The Cl(2)···C(8) and Cl(2)···C(9) contacts in **2** are 3.98 and 4.12 Å, respectively, so that with this frozen structure, the *tert*-butyl group would have difficulty passing over Cl(2). However the ^1H NMR spectrum shows a singlet for the *tert*-butyl methyl groups indicating rotation or at least some movement so that there is clearly some flexibility in the molecule in solution. For example, in the configuration shown by the crystal structure, bending back of the Ti–O–C bond further than observed [152.8(1)°] would clearly allow the *tert*-butyl methyls to rotate but angles smaller than this may be difficult to attain [8]. There is nothing unusual about the angles associated with the *tert*-butyl group either. The O–C(1)–C(6) and C(5)–C(6)–C(7) angles [120.8(2)° and 122.0(2)°] are little different from the ideal sp^2 angle and all the angles associated with C(7) are close to the ideal sp^3 angle. In particular the C(8)–C(7)–C(9) angle which might be expected to widen if

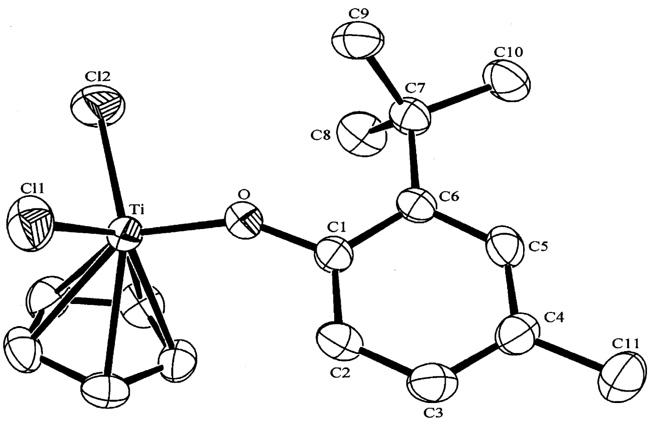

Fig. 2. ORTEP diagram, at the 50% probability level, of the molecular structure of $[CpTiCl_2(OC_6H_3CMe_3\text{-}2\text{-}Me\text{-}4)]$ (**2**). Hydrogen atoms have been omitted for clarity. Selected bond distances and angles are given in Table 1.

seriously effected by proximity to Cl(2) is 110.0(2)°. As to whether the phenoxide ring can rotate so that the *tert*-butyl group passes over the two chloro ligands and also allow rotation as it does so (geared rotation [12]), is further complicated as there would be an interaction of the phenoxide ring *ortho*-proton with the Cp ligand hydrogens to restrict Ti–O–C bond bending. This effect would be even more pronounced if there were a methyl group in the phenoxide ring *ortho*-position or if pentamethyl Cp were present.

NMR spectral analysis of the reaction between [$CpTiCl_3$] and $Me_3SiOC_6H_4Ph$-4 showed that after 4 h of refluxing only 8% of the [$CpTiCl_3$] remained and [$CpTiCl_2(OC_6H_4Ph$-2)] (**3**) could be obtained as a crystalline solid in high yield.

The complex had a single set of resonances for the various hydrogens and carbons in the NMR spectra with the *ipso*-carbon resonance of the phenoxide ring at δ 165.4 which is the same as *tert*-butyl complex **2**. An X-ray crystal structure determination showed a distorted tetrahedral array (Fig. 3.) with bond length and bond angle features little different from those found in complexes **1** and **2** (see Table 1).

The phenoxide ligand phenyl ring is rotated so that the phenyl substituent sits over and between Cl(1) and the Cp ring so that the interplanar angle between the Cp and phenoxide ligand phenyl ring is 22.2(1)°. This compares with 29.4(1)° for 2-*tert*-butylcomplex **2** indicating there is less need for rotation for the phenyl substituent which does not need to position itself about Cl(1) as does the *tert*-butyl group.The phenyl substituent thus covers Cl(1) to a much lesser extent than the *tert*-butyl group in complex **2** where the two of the methyl groups straddle Cl(1) to minimize interactions.

Given the high yield route to complexes **1**, **2** and **3** using the TMS phenols, we have looked at carrying out the reaction in the absence of solvent to see if 'green chemistry' principles could be applied to the reactions. When [$CpTiCl_3$] and $Me_3SiOC_6H_4CMe_3$-4 were heated together at 100 °C for 6 h. NMR spectroscopy indicated that only about 7% of the [$CpTiCl_3$] remained unconverted and complex **1** could also be obtained as a crystalline solid. Similarly, a reaction between [$CpTiCl_3$] and neat Me_3SiO-$C_6H_3CMe_3$-2-Me-4 at 90 °C for 6 h gave a high conversion of the [$CpTiCl_3$] and a good yield of complex **2**. However with $Me_3SiOC_6H_4Ph$-2 at 160–170 °C the [$CpTiCl_3$] conversion was only about 40% whereas the [$CpTiCl_3$] conversion in benzene solution was 80% after work-up.

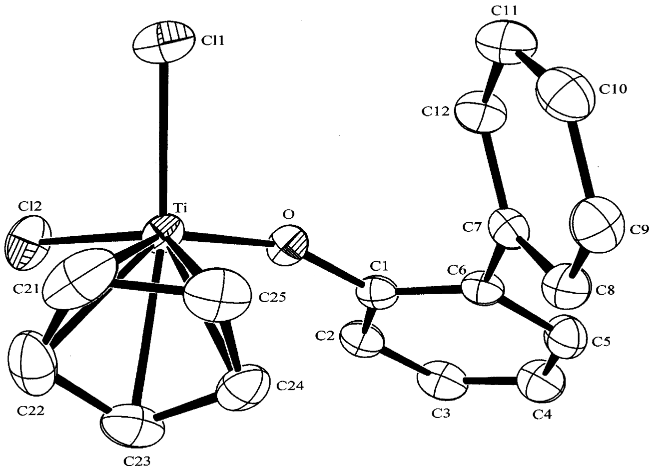

Fig. 3. ORTEP diagram, at the 50% probability level, of the molecular structure of [$CpTiCl_2(OC_6H_4Ph$-2)] (**3**). Hydrogen atoms have been omitted for clarity. Selected bond distances and angles are given in Table 1.

2.2. Theoretical calculations

Complexes **2** and **3** are asymmetric (C_s symmetry) in the solid state with one of the chloro ligands biased by the substituent at the 2-position of the phenoxide ligand ring. DFT calculations [13] were carried out to assess the ability of the phenoxide ligands to rotate over the Cp or chloro ligands and maintain the asymmetry. In particular the structure of [$CpTiCl_2(OC_6H_3CMe_3$-2-Me-4)] (**2**) was investigated as the X-ray structure indicated the greater degree of influence of the *ortho*-substituent. The calculations gave good agreement with the crystal structure with the greatest deviation occurring for the Cp–Ti parameters as the Cp ligand was rotated slightly (4°) in comparison with the experimental structure. Bond distances between the heavy elements (i.e., excluding H) for the other degrees of freedom (i.e., non Cp–Ti bond distances) were all within 1% of the crystal structure parameters and the angles agreed within 2% or better.

An NBO analysis [14] was performed. The NBO analysis estimates the interaction [$E(2)$] between each donor and acceptor NBO by second order perturbation theory. This allows a qualitative understanding of the energetic importance of the delocalisation of electrons from the various filled (i.e., high occupancy) orbitals into the empty (i.e., low occupancy) orbitals. Using this analysis one can assess the relative importance of the various ligand (donor) to metal (acceptor) interactions. Analysis of the NBO's according to this procedure for the ligand to metal interactions indicates that there is strong interaction between the lone pairs on the Cl atoms and the metal d orbitals (ranging up to 268 kJ/mol). The Cp to Ti interactions are dominated [$E(2) = 1224$ kJ/mol] by the interaction between a lone pair (3% 2s 97% 2p character) orbital on C25 with one of the partially occupied 3d orbitals on the Ti. A number of interactions [$E(2)$ ranging up to 108 kJ/mol] between the C21–C22 and C23–C24 π-bonds (donors) and the Ti 3d orbitals (acceptors) are also clearly evident.

There are a total of nine interactions with an $E(2)$ in the range between 41 and 214 kJ/mol between the various oxygen valence orbitals and the partially occupied Ti 3d orbitals. The results clearly imply that a simple interpretation in terms of a single lone pair donation to the Ti centre is an inadequate one. Similarly, a first principles model might predict a strong donor–acceptor interaction between the oxygen valence orbitals and the C1–C2, C1–C6 π-antibonding orbitals, and this indeed seems to be the case with the O lone pair/C1–C2 π* $E(2)$ calculated to be 90 kJ/mol and the O lone pair/C1–C6 $E(2)$ weaker at 30 kJ/mol. There are also weaker interactions between a lone pair on each of the Cl1 and Cl2 atoms (donor) with empty O (predominantly 3s/3p: 12%s, 88%p character) orbitals with $E(2) = 21$ kJ/mol for each of these interactions.

The Ti to ligand interactions are dominated by the interaction between the partially filled valence 4s (88%) + 3d (12%) Ti hybrid with the empty O 3s(12%) + 3p(88%) hybrid with an $E(2)$ of 95 kJ/mol. Other significant interactions occur between this Ti orbital and the antibonding O–C orbital ($E(2) = 39$ kJ/mol) and one of the vacant O hybrid (involving 4s, 4p, 3d O basis functions) orbitals ($E(2) = 37$ kJ/mol). The only other significant Ti to ligand interactions are between the partially occupied valence 3d orbitals (on Ti) and the π*-antibonding orbitals between C21/C22 ($E(2) = 75$ kJ/mol) and C23/C24 ($E(2) = 60$ kJ/mol).

Examination of the charges calculated from the Natural Population Analysis (NPA) for the two protons closest to the Cl atom (+0.23 and +0.25) indicates that there is no significant difference to the other protons on these two methyl groups (+0.23). The NPA analysis yields for the other atoms of interest: +1.26 for Ti, −0.32 for Cl1, −0.31 for Cl2, and −0.71 for the O atom.

A potential energy surface (PES) scan was performed by scanning the Ti–O–C1–C6 dihedral angle and allowing all of the other internal degrees of freedom to relax to their minimum energy values. The results of this relaxed PES scan are shown in Fig. 4 for a variation of the dihedral angle from +15° to −95° (minimum at −27°). Outside this range the calculations failed to converge. The results indicate that there is a shallow minimum where the energy change is a mere 2 kJ/mol within a range of 60° for the dihedral. Further inspection indicates that despite the large change in angle the *tert*-butyl group does not rotate past the Cl2 atom, but moreover, the change in dihedral is accompanied by a distortion in other dihedral coordinates. The most noticeable change being that as the Ti–O–C1–C6 angle is displaced away from its equilibrium value the Cl atom straddled by the two *tert*-butyl CH_3 groups is pushed further toward the *tert*-butyl group central C. This occurs as a consequence of a twisting motion of the $(Cl)_2$–Ti–Cp group which is coupled to the change in Ti–O–C1–C6 dihedral. Examination of the normal mode harmonic vibrational frequencies calculated for **2** yields six frequencies lower than 100 cm^{-1}, at least three of which involve a significant component of Ti–O–C1-C6 torsion. Despite this, these motions are bounded at one extreme by the difficulty of rotating the Cl atom past the *tert*-butyl group methyls and at the other by the decrease in distance between the phenoxide ring *ortho*-proton with the Cp protons (the distance decreases from an average of 3.00 Å at the minimum energy structure to 2.77 Å at +15°) as suggested above. The net result of this discussion is that the motion of Cl2 appears to be sterically encumbered by the close proximity of the *tert*-butyl group rather than by any electronic constraints

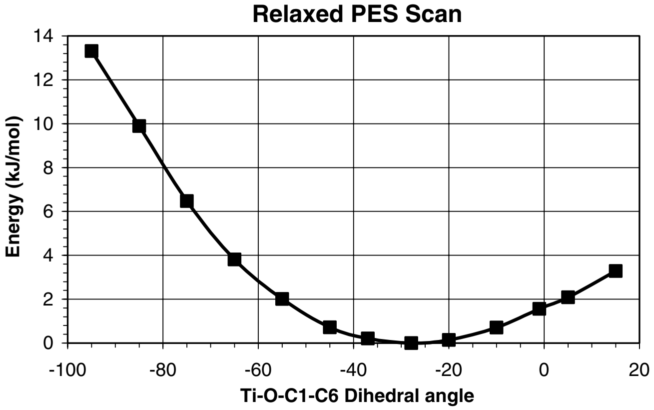

Fig. 4. Relaxed PES scan for the Ti–O–C1–C6 dihedral.

3. Conclusion

The complexes [CpTiCl(OAr)] [Ar = $C_6H_4CMe_3$-4 (**1**), $C_6H_4CMe_3$-2-Me-4 (**2**) and C_6H_4Ph-2 (**3**)] are conveniently prepared by the reaction of the relative TMS phenol with $[CpTiCl_3]$. X-ray crystallography shows that there is not much difference in the structural parameters for the three complexes indicating that 2-*tert*-butyl or 2-phenyl substituents on the phenyl ring of the phenoxide ligand are easily accommodated. The main effect of the substituent is to change the interplanar angle between the Cp and phenoxide ligand phenyl rings. For complex **1** in which there is no *ortho*-substituent, the angle is only 6.4(1)° which most likely allows a maximum of O(2p)-to-Ti(d) and O(2p)-to-C(π) orbital interaction if intermolecular effects in the crystal structure are not important. For complex **2** (*ortho*-*tert*-butyl group), the angle increases to 29.4(1)° and for complex **3** (*ortho*-phenyl group) the effect is somewhat smaller at 22.2(1)°. DFT calculations indicate that for **2** the *tert*-butyl group cannot freely rotate past the adjacent chloro ligand and is essentially locked in the position shown by the solid state structure. However, there is a shallow minimum associated with the Ti–O–C–C dihedral angle (2 kJ/mol within a range of 60°) so that there is sufficient flexibility in the molecule to allow torsional motion which accommodates the *tert*-butyl group in the observed position.

4. Experimental

4.1. General methods and materials

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard bench-top techniques for air-sensitive substances. $TiCl_4$ and the phenols were used as received from commercial sources. $CpSiMe_3$ was prepared by the reaction of CpNa with Me_3SiCl in [15]. Light petroleum (b.p. 40–60 °C) and toluene were distilled from sodium wire and dichloromethane from freshly ground CaH_2. ^1H and ^{13}C–{^1H} NMR spectra were recorded at 400 and 100 MHz, respectively, on a

Bruker AM400 spectrometer. $CDCl_3$ was dried over, and distilled from freshly ground CaH_2 and benzene-d_6 from sodium wire. C, H and N analyses were determined by Dr. A. Cunninghame and associates, University of Otago, New Zealand.

4.2. Synthesis

4.2.1. Preparation of [$CpTiCl_3$]

This complex was prepared by the reaction of $CpSiMe_3$ and $TiCl_4$ in CH_2Cl_2 [7]. The resulting grey-green solid was purified prior to use by subliming some of the material from a 250-cm^3 round-bottom flask into an unjacketed air condenser and scraping the required amount of sublimate into another flask.

4.2.2. $Me_3SiOC_6H_4CMe_3$-4

Triethylamine (6.5 cm^3, 46.6 mmol) was added dropwise to 4-*tert*-butylphenol (5.0 g, 33.3 mmol) in diethyl ether (80 cm^3), the mixture was cooled to 0 °C and chlorotrimethylsilane (5 cm^3, 39.4 mmol) added dropwise via a syringe. The mixture was stirred for 14 h, refluxed for 3 h, the solution filtered and the remaining triethylamine hydrochloride washed with diethyl ether (50 cm^3). The solvent was removed from the combined filtrate and extract to give the TMS phenol as a colourless oil. Yield 7.2 g, (97%). ^{1}H NMR δ: 0.41 (s, 9H, $SiMe_3$); 1.44 (s, 9H, CMe_3); 6.92 [d, ^3J(HH) 8.8, 2H, *o*-Hs]; 7.38 [d, ^3J(HH) 8.8, 2H, *m*-Hs]. ^{13}C NMR δ: 0.27 ($SiMe_3$), 31.6 (CMe_3), 34.0 (C), 119.3 (*o*-C), 126.1 (*m*-C), 143.8 (*p*-C), 152.8 (*ipso*-C).

*4.2.3. [$CpTiCl_2(OC_6H_4CMe_3$-4)] (**1**)*

Method A: $Me_3SiOC_6H_4CMe_3$-4 (0.90 g, 4.0 mmol) in benzene (30 cm^3) was added dropwise over 20 m to [$CpTiCl_3$] (0.86 g, 3.9 mmol) in benzene (25 cm^3) and the mixture was stirred for 18 h and refluxed for 2 h. The solution was filtered and the solvent removed to give a gum (1.4 g) which formed a crystalline mass on standing. The solid was broken-up and washed with chilled (0 °C) petroleum spirit (30 cm^3) and dried under vacuum. Yield 1.22 g, (94%). The complex was characterized by X-ray crystallography using a single crystal from the mass. ^{1}H NMR δ: 1.24 (s, 9H, CMe_3); 6.70 (s, 5H, Cp); 6.86 [d, ^3J(HH) 8.4, 2H, *o*-Hs]; 7.23 [d, ^3J(HH) 8.4, 2H, *m*-Hs]. ^{13}C NMR δ; 31.4 (CMe_3), 34.5 (C), 117.8 (*o*-C), 120.7 (Cp), 126.1 (*m*-C), 147.6 (*p*-C), 166.2 (*ipso*-C).

Method B: $Me_3SiOC_6H_4CMe_3$-4 (0.96 g, 4.4 mmol) was added to [$CpTiCl_3$] (0.97 g, 4.4 mmol) and the mixture was stirred at 100 °C for 6 h. On cooling and standing a solid crystalline mass was formed which was washed with chilled (0 °C) petroleum spirit to give the orange-red complex which had identical NMR spectra to the sample prepared under by Method A.

4.2.4. $Me_3SiOC_6H_4CMe_3$-2-Me-4

Triethylamine (6.0 cm^3, 43.0 mmol) was added dropwise to 2-phenylphenol (7.2 g, 42.4 mmol) in diethyl ether (80 cm^3), and chlorotrimethylsilane (5.5 cm^3, 39.4 mmol) added dropwise as for the reaction with to 4-*tert*-butylphenol described above. Yield 7.85 g, (91%). ^{1}H NMR δ: 0.32 (s, 9H, $SiMe_3$); 1.35 (s, 9H, CMe_3); 2.26 (s, 3H, Me); 6.71 [d, ^3J(HH) 8.0, 1H, *o*-H]; 6.93 [dd, ^3J(HH) 8.0, ^4J(HH) 1.8,1H, *m*-H]; 7.13 [d, ^4J(HH) 1.8, 1H, *m*-H]. ^{13}C NMR δ; 0.7 ($SiMe_3$); 20.8 (Me); 29.6 (CMe_3); 34.4 (C); 118.3 (*o*-C); 126.9 and 127.7 (*m*-Cs); 151.9 (*ipso*-C).

*4.2.5. [$CpTiCl_2(OC_6H_3CMe_3$-2-Me-4)] (**2**)*

Method A: $Me_3SiOC_6H_3CMe_3$-2-Me-4 (0.93 g, 3.93 mmol) in benzene (25 cm^3) was added to [$CpTiCl_3$] (0.86 g, 3.9 mmol) in benzene (25 cm^3) and the mixture stirred for 1 h and then refluxed for 3 h. The solution was filtered and the solvent removed to give an oil which formed a crystalline mass on standing. Crude yield 1.28 g (94%) The solid was dissolved in hot petroleum spirit (120 cm^3), the solution filtered and the volume reduced giving the complex as long orange-yellow crystals on standing. Yield 0.85 g, (62.4%). The complex was characterized by X-ray crystallography using a single crystal of this product. ^{1}H NMR δ: 1.39 (s, 9H, CMe_3); 2.33 (s, 3H, Me); 6.78 (s, 5H, Cp); 6.83 [d, ^3J(HH) 7.8, 1H, *o*-H]; 6.97 [bd, ^3J(HH) 7.8, 1H, *m*-H]; 7.08 [m, ^3J(HH) 7.8, 1H, *m*-H]. ^{13}C NMR δ; 21.2 (Me); 29.9 (CMe_3); 34.7 (C); 123.5 (*o*-CH); 127.0 (*m*-CH); 127.8 (*m*-CH); 134.1 (*p*-C); 137.1 (*o*-C); 165.4 (*ipso*-C).

Method B: $Me_3SiOC_6H_3CMe_3$-2-Me-4 (1.1 g, 4.6 mmol) was added to [$CpTiCl_3$] (1.0 g, 4.6 mmol) the mixture stirred at 90 °C for 6 h and then allowed to stand at room temperature overnight. On standing further, a solid crystalline mass was formed which was washed with chilled (0 °C) petroleum spirit to give the complex as an orange solid which had identical NMR spectra with the sample prepared under method A.

4.2.6. $Me_3SiOC_6H_4Ph$-2

Triethylamine (6.0 cm^3, 43.0 mmol) was added dropwise to 2-phenylphenol (7.2 g, 42.4 mmol) in diethyl ether (80 cm^3), and chlorotrimethylsilane (5.5 cm^3, 39.4 mmol) added dropwise as for the reaction with 4-*tert*-butylphenol described above. The oil obtained was dissolved in petroleum spirit (50 cm^3), the solution filtered to remove a small amount of white solid and the solvent removed giving the TMS phenol as a colourless liquid. Yield 9.6 g, (93%). ^{1}H NMR δ: 0.10 (s, 9H, $SiMe_3$); 6.98 [dd, ^3J(HH) 7.2, ^4J(HH) 1.1, 1H, *o*-H]; 7.11 [td, ^3J(HH) 7.2, ^4J(HH) 1.1, 1H, *m*-H]; 7.20 [td, ^3J(HH) 7.2, ^4J(HH) 1.1, 1H, *m*-H]; 7.25-7.61 [m, 6H, aromatic-Hs]. ^{13}C NMR δ: 120.6 (CH); 121.9 (CH); 126.7 (CH); 127.8 (*m*-CHs); 128.4 (CH); 129.6 (*o*-CHs); 130.7 (CH); 133.3 (C); 139.0 (*o*-C); 152.4 (*ipso*-C).

*4.2.7. [$CpTiCl_2(OC_6H_4Ph$-2)] (**3**)*

$Me_3SiOC_6H_4Ph$-2 (1 g, 4.13 mmol) in toluene (25 cm^3) was added to [$CpTiCl_3$] (0.88 g, 4.0 mmol) in toluene (25 cm^3) and the mixture stirred for 1 h and then refluxed

Table 2
Crystallographic data for complexes **1**, **2** and **3**

Empirical formula	$C_{15}H_{18}Cl_2OTi$	$C_{16}H_{20}Cl_2OTi$	$C_{17}H_{14}Cl_2OTi$
Colour, habit	orange, plate	orange, plate	yellow, plate
Crystal size (mm)	0.44 × 0.18 × 0.11	0.38 × 0.22 × 0.07	0.42 × 0.16 × 0.08
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	6.5596(1)	10.1346(2)	15.3821(2)
b (Å)	10.9940(3)	10.3240(3)	7.2149(1)
c (Å)	22.4839(6)	16.7649(3)	15.563(1)
α (°)	90	90	90
β (°)	93.259(1)	104.777(1)	111.783(1)
γ (°)	90	90	90
V (Å^3)	1618.83(7)	1697.60(7)	1603.97(3)
Z	4	4	4
λ (Å)	0.71073	0.71073	0.71073
T (K)	203(2)	200(2)	150(2)
θ Range for data collection	1.81–27.50	2.14–26.74	1.43–27.10
No. of data collected	9875	9935	9605
No. of unique data, R_{int}	3562, 0.0371	3535, 0.0213	3407, 0.0166
Completeness to θ_{max} (%)	95.8	98.1	96.5
No. of parameters refined	182	181	190
R_1, data with $I > 2\sigma(I)$	0.0542, 2730	0.0380, 2806	0.0291, 2904
wR_2, all data	0.1354, 3562	0.0908, 3535	0.0770, 3407

for 3 h. The solution was filtered and the solvent removed to give a gum which solidified to a crystalline mass on standing. The solid was broken up and washed with hot light petroleum spirit (50 cm^3) leaving a crystalline solid. Yield 1.15 g (80%). The complex was characterized by X-ray crystallography using a single crystal from the solid. ^{1}H NMR δ: 6.30 (s, 5H, Cp); 7.13 [dd, ^3J(HH) 8.1, ^4J(HH) 1.2, 1H, *o*-H]; 7.17 [td, ^3J(HH) 7.6, ^4J(HH) 1.2, 1H, *m*-H]; 7.23-7.33 (m, 2H, *m*, *p*-Hs); 7.47 (2t, 3H, *m*-and *p*-Hs); 7.56 [dd, ^3J(HH) 8.1, ^4J(HH) 1.2, 2H, *o*-H]. ^{13}C NMR δ: 120.0 (CH); 121.0 (Cp); 124.7 (CH); 127.5 (CH); 128.5 (*m*-CHs); 130.2 (*o*-CHs); 130.4 (CH); 130.7 (C); 152.4 (*o*-CH)); 165.4 (*ipso*-C).

4.3. X-ray crystallography

Crystallographic and refinement data are given in Table 2. Data collected, with graphite monochromated Mo Kα X-radiation, were measured on a Siemens SMART CCD area detector diffractometer with the omega scan method. The data were corrected for Lorentz and polarisation effects and for absorption by the multi scan method [16]. The structures were solved by direct methods [17] and refined by full-matrix least-squares methods [18] on F^2. Hydrogen atoms were placed in calculated positions (phenyl ring C–H 0.94, ^{t}Bu C–H 0.97 Å) and were refined with a riding model ($U_{iso} = 0.08$). Some disorder was noted for the *tert*-butyl group in **1** (with a site occupancy ratio of ca. 8:2). Diagrams were prepared by ORTEP [19].

4.4. Theoretical calculations

All structures were fully optimized using GAUSSIAN 98 [13] at the B3LYP [20] level utilising the 6-311 + G(d) basis set for Ti, O, and Cl in conjunction with the 6–31G(d) basis set for C and H. This resulted in 404 basis functions contracted from the 764 primitive Gaussians. Vibrational frequency calculations yielded sets of all real frequencies for the minimum energy structure.

5. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 272194–272196 for compounds **1**, **2** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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