

Synthesis, Structure, Coordination Expansion and Theoretical Modelling of Dichlorobis(phenoxo) Titanium(IV) Complexes

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Thermalisation of TiCl_4 and two equivalents of a phenol in toluene is found to be the best preparative method for quantitative yields of a variety of dichlorobis(phenoxo) complexes. $[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3-4)_2]$ (**1**) is monomeric in benzene, a phenoxo-bridged dimer in the solid state and undergoes coordination expansion with 4,4'-dimethyl-2,2'-bipyridine (dmbipy) to give $[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3-4)_2(\text{dmbipy})]$ (**2**). Also monomeric are $[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2]$ (**3**) and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Pr}_2-2,6)_2]$ (**5**) which expand their coordination with dmbipy to give $[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2(\text{dmbipy})]$ (**4**) and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Pr}_2-2,6)_2(\text{dmbipy})]$ (**6**). In contrast $[\text{TiCl}_2(\text{OC}_6\text{H}_2(\text{CMe}_3)_2-2,6-\text{Me}-4)_2]$ (**7**) is only partially formed by the thermolysis reaction and does not coordinatively expand with dmbipy. $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,4)_2]$ (**8**) is monomeric in benzene and reacts to form $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,4)_2(\text{dmbipy})]$ (**9**). $[\text{TiCl}_2(\text{OC}_6\text{H}_3(\text{CMe}_3)_2-2,4)_2]$ (**10**) forms along with the tri-phenoxo complex $[\text{TiCl}(\text{OC}_6\text{H}_3(\text{CMe}_3)_2-2,4)_3]$.

$[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$ (**11**) is monomeric in benzene and forms $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2(\text{dmbipy})]$ (**12**). 2-Phenylphenol and 1-naphthol form $[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{Ph}-2)_2]$ (**13**) and $[\text{TiCl}_2(\text{OC}_{10}\text{H}_9)_2]$ (**14**) which are monomeric in benzene. DFT calculations give structural parameters for monomeric $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ (**15**) in good agreement with the X-ray data for $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$. Each oxygen of the phenoxo ligand in **15** acts essentially as a 2π donor to titanium and there is substantial $p_\pi(\text{O})-p_\pi^*(\text{C}=\text{C})$ backbonding with the phenyl ring, which is absent in $[\text{TiCl}_2(\text{OCH}_3)_2]$ (**16**). The global minimum for the dimer $[(\text{TiCl}_2(\text{OC}_6\text{H}_5)\{\mu\text{-OC}_6\text{H}_5\})_2]$ is in almost perfect agreement with the crystal structure obtained for $[(\text{TiCl}_2(\text{OC}_6\text{H}_5)\{\mu\text{-OC}_6\text{H}_5\})_2]$ or $[(\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3-4)\{\mu\text{-OC}_6\text{H}_4\text{CMe}_3-4\})_2]$ (**1**). The dimerisation energy for **15** is $-26.2 \text{ kJ}\cdot\text{mol}^{-1}$.

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Introduction

The relationship between dichlorobis(phenoxo) complexes $[\text{TiCl}_2(\text{OAr})_2]$ and titanium metallocenes $[\text{TiCl}_2\text{Cp}_2]$ is now very apparent^[1,2] with the phenoxo complexes emerging as promising synthons and catalysts for organic reactions^[2,3,4] and catalysts for olefin polymerisation.^[5] Alkoxo complexes of titanium often form higher associates than monomers in solution^[6] but the solution behavior of the bis(phenoxo) complexes and the coordination expansion properties have not been studied.^[7] From the synthetic point of view, complexes containing *tert*-butyl or phenyl groups in the 2,6- positions of the aryloxo ring have received the most attention.^[5,8–10] However, little is known about bis(phenoxo) complexes containing ligands which are less sterically demanding. For example, $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ has a dimeric structure in the solid state^[11] and there is conflicting evidence for the structure in solution.^[12,13] $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$ has a monomeric solid-state structure,^[9] and $[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2]$ is monomeric in benzene and expands its co-ordination sphere forming the bis-adducts $[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2(\text{L})_2]$ ($\text{L} = \text{pyridine}$,

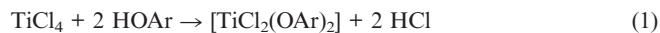
ArNH_2 and tetrahydrofuran) which have been characterised only by analytical data and IR spectroscopy.^[14] We have reported^[15] a comprehensive systematic study of the mono-(phenoxo) complexes $[\text{TiCl}_3(\text{OAr})]$ ($\text{Ar} = \text{unsubstituted or substituted phenyl group}$) which included aspects of best synthetic method, co-ordination expansion and theoretical modelling. We report here a similar investigation for complexes of the type $[\text{TiCl}_2(\text{OAr})_2]$ where changes are made to the size of the *ortho*-substituents of the phenyl rings. In particular we investigate the nature of the complexes in non-coordinating solvents to ascertain if co-ordinative unsaturation is maintained in solution. Some general comparisons of the bis(phenoxo) complexes with $[\text{TiCl}_2\text{Cp}_2]$ ($\text{Cp} = \text{cyclopentadienyl}$) are also made.

Results and Discussion

Synthetic Studies

Bis(phenoxide) complexes have been prepared by thermalising TiCl_4 and the phenol in a non-coordinating solvent^[14,16] or more commonly by reacting the lithium phenolate with TiCl_4 in diethyl ether.^[2–10] We have found that thermalisation in toluene of TiCl_4 and the phenol in 1:2 ratio is the best procedure for most phenols [Equation (1)].

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HOAr = $\text{HOC}_6\text{H}_4\text{CMe}_3$ -4, $\text{HOC}_6\text{H}_2\text{Me}_3$ -2,4,6, $\text{HOC}_6\text{H}_3\text{iPr}_2$ -2,6, $\text{HOC}_6\text{H}_3\text{Me}_2$ -2,4, $\text{HOC}_6\text{H}_3(\text{CMe}_3)_2$ -2,4, $\text{HOC}_6\text{H}_3\text{CMe}_3$ -2-Me-6, $\text{HOC}_6\text{H}_4\text{Ph}$ -2, $\text{HOC}_{10}\text{H}_9$ (naphthyl)

If the reaction is carried out to completion, then solid complexes can be obtained in virtually quantitative yield and in an analytically pure form. It is important to determine the end point of the reaction otherwise gummy materials often result which are difficult to purify. The last traces of HCl gas produced in the reaction are easily detected by a simple but very sensitive test which involves passing the exhaust gases close to concentrated ammonia solution or a liquid organic amine and observing any white hydrochloride cloud. On a 5–10 g scale in vigorously boiling toluene, the reactions are usually complete in less than 14 h and on a 50–100 g scale the reaction times are not much longer.

The crystal structure of $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ has been determined,^[11] but we have found the complex is not suitably soluble in benzene for an accurate cryoscopic molecular weight determination. However, reaction of TiCl_4 with 4-*tert*-butylphenol gave highly soluble $[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3)_2]$ (**1**) and an X-ray crystal structure determination of the product crystallised from benzene showed a dimeric complex containing a phenoxo bridge in which each titanium atom adopts a distorted pentagonal bipyramidal coordination geometry (Figure 1). The titanium atoms each have two *cis*-coordinated chloro ligands and two *cis*-coordinated phenoxo ligands, one of which bridges to the adjacent titanium atom where it lies *trans* to a terminal phenoxo ligand.

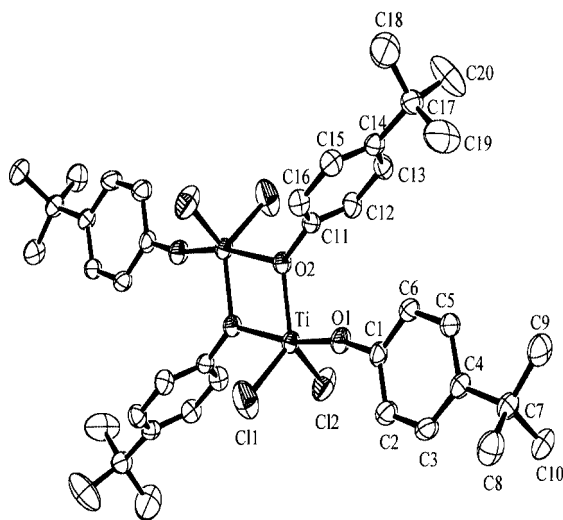


Figure 1. Thermal ellipsoid diagram (at the 50% probability level) for (**1**) showing the numbering system. Hydrogen atoms have been omitted for clarity.

The structure of **1** is essentially similar to that found for dimeric $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$,^[11] but is described now in terms of modern bonding concepts. Selected bond lengths and angles are given in Table 1. The Ti–O(1) and O(1)–C(1) bond lengths [1.749(2) and 1.369(3) Å, respectively] and the

Ti–O(1)–C(1) bond angle [165.2(2)°] are similar to those found for the mono(phenoxo) complex $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3)_2]$ [1.750(2), 1.390(2) Å and 163.1°, respectively^[15]]. Theoretical calculations on the model complex $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3)_2]$ show that the terminal phenoxo ligand oxygen atom acts essentially as a 1-σ, 2-π donor to titanium but that there is also some O(2p) donation to the phenyl ring C=C(π*) orbital.^[15] The Ti–O(2) bond length in **1** [1.912(2) Å], is significantly longer than the Ti–O(1) bond length [1.749(2) Å] as a consequence of O(2) forming a dative bond to the other titanium atom [Ti–O(2)′ bond length 2.142(2) Å] in the unsymmetrical bridge. The O(2) lone pair donation to Ti occurs *trans* to the strongly π-donating terminal phenoxo ligand so that the potentially π-donating chloro ligands do not have to compete for the same d orbitals. The increased length of the Ti–O(2) bond indicates that O(2)-to-Ti π-donation is much less than for the Ti–O(1) bond. Also the bridging phenoxo ligand O–C bond [O(2)–C(11) bond length 1.406(3) Å] is significantly longer than the terminal phenoxo ligand O–C bond [O(1)–C(1) bond length 1.369(3) Å] indicating there is less O(2p) donation to the phenyl ring C=C(π*) orbital for the bridging mode. This may be a consequence of the phenyl ring π-orbitals being unable to overlap to any significant extent with oxygen orbitals when the two oxygen lone pairs on O(2) are otherwise involved with bonding to Ti [possible O(2)p-to-Ti(1)d π-donation and O(2)p-to-Ti(2)d σ-donation].

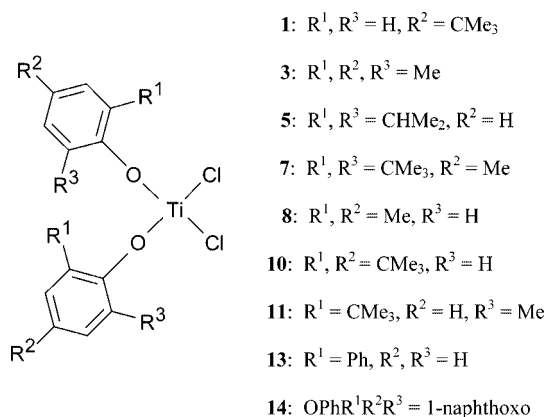
Table 1. Selected bond lengths [Å] and angles [°] for **1**. Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y + 1, -z + 1$.

Ti–O(1)	1.749(2)
Ti–O(2)	1.912(2)
Ti–O(2)#1	2.142(2)
Ti–Cl(1)	2.2186(11)
Ti–Cl(2)	2.2256(11)
Ti–Ti#1	3.282(2)
O(1)–C(1)	1.369(3)
O(2)–C(11)	1.406(3)
O(2)–Ti#1	2.142(2)
O(1)–Ti–O(2)	96.03(9)
O(1)–Ti–O(2)#1	167.96(9)
O(2)–Ti–O(2)#1	71.99(9)
O(1)–Ti–Cl(1)	96.52(8)
O(2)–Ti–Cl(1)	122.74(8)
O(2)#1–Ti–Cl(1)	89.25(6)
O(1)–Ti–Cl(2)	97.43(8)
O(2)–Ti–Cl(2)	119.23(7)
O(2)#1–Ti–Cl(2)	89.78(7)
Cl(1)–Ti–Cl(2)	114.06(5)
O(1)–Ti–Ti#1	134.38(7)
O(2)–Ti–Ti#1	38.36(6)
Cl(1)–Ti–Ti#1	107.85(4)
Cl(2)–Ti–Ti#1	106.38(4)
C(1)–O(1)–Ti	165.2(2)
C(11)–O(2)–Ti	123.5(2)
Ti–O(1)	1.749(2)
Ti–O(2)–Ti#1	108.01(9)

The Ti–Cl(1) and Ti–Cl(2) bond lengths in complex **1** [2.2186(11) and 2.2256(11) Å] are not very different from each other but are slightly longer than those found for

[TiCl₃(OC₆H₂{CMe₃}_{2-2,6-Me-4})] [Ti–Cl bond lengths 2.1822(8), 2.1913(8) and 2.1945(9) Å] where π -donation from chloro ligands is needed to increase the overall electron count. The theoretical calculations made on the model complex [TiCl₃(OC₆H₂Me_{3-2,4,6})] show that significant Cl(2p) to Ti(3d) π -donation occurs in these tetrahedral molecules.^[15] Assuming that O(2) in complex **1** makes a single π -donor interaction with the titanium atom then the overall (formal) electron count for the complex is 16 so an 18-electron count can be attained if Cl(2p) to Ti(3d) donation occurs.

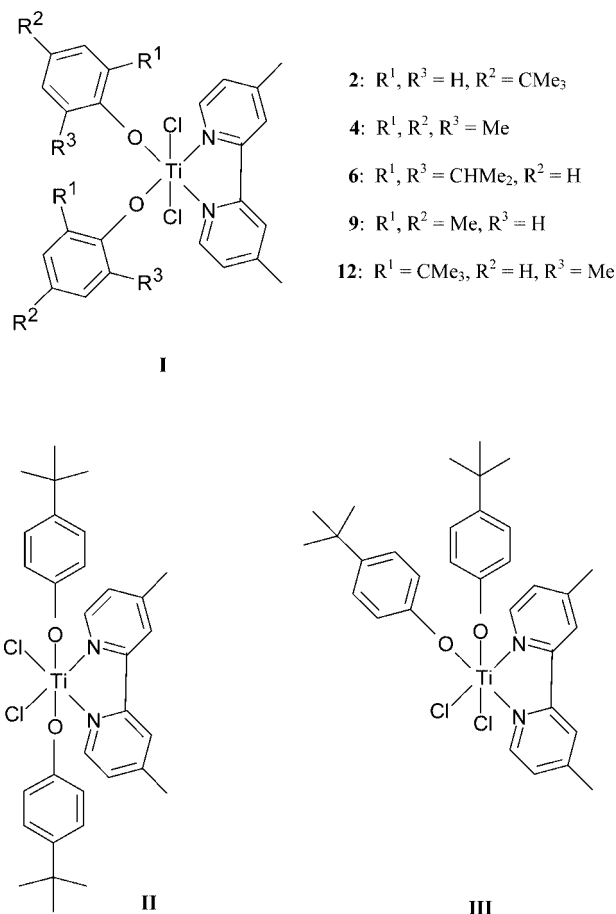
The X-ray crystal structure indicates complex **1** exists in the solid state as a dimer but a molecular weight determination in benzene, the solvent from which the dimer crystallised, indicates a monomer (Scheme 1). The ¹H NMR spectrum in C₆D₆ shows a single resonance for the *tert*-butyl groups, a doublet for the *meta*-protons of the phenyl ring but a broadened resonance for the *ortho*-protons. In the ¹³C{¹H} NMR spectrum the *tert*-butyl group methyl and quaternary carbons appear as single sharp resonances but the aromatic ring C resonances are somewhat broadened. Identical spectra are obtained for the complexes reported here whether the solvent is C₆D₆ or CDCl₃ but the resonances are slightly sharper in CDCl₃. Cooling CDCl₃ or [D₈]toluene solutions of **1** produced little change in the broadening observed leaving unclear the nature of any solution dynamics. The spectra are thus consistent with the monomeric structure shown by the molecular weight determination and not the dimer found in the solid state. The *ipso*-C resonance occurs at δ = 166.3 ppm, which lies slightly upfield to that observed for [TiCl₃(OC₆H₄CMe₃₋₄)] (δ = 169.6 ppm^[15]) and this may represent a small change in the O(2p)–C=C(π^*) bonding system associated with the smaller need for tight O(2)p-to-Ti(1)d orbital donation on addition of the second phenoxide ligand which is a better π -bonder than Cl.^[15]



Scheme 1.

The coordination expansion properties of complex **1** were studied using 4,4'-dimethyl-2,2'-bipyridine (dmbipy), as this ligand is useful in determining isomer structure by NMR spectroscopy.^[15] [TiCl₂(OC₆H₄CMe₃₋₄)₂(dmbipy)] (**2**) was readily formed in CH₂Cl₂ and the NMR spectra

showed the presence of only one isomer. Both the ¹H and ¹³C{¹H} NMR spectra indicate a symmetrical molecule based on a single set of resonances for the relevant position of the phenoxo and dmbipy ligands. Structure **I** (Scheme 2) is the preferred isomer since structure **II** contains *trans*-orientated phenoxo ligands, which would lead to an unfavourable competition for d-metal orbitals and structure **III** is an unsymmetrical molecule. A *trans*-chloro-*cis*-phenoxo configuration has been observed in the X-ray crystal structures [TiCl₂(OC₆H₃Me_{2-2,6})₂(THF)₂]^[17] [i.e. consistent with structure **I**, Scheme 2], where the THF ligands coordinate *cis* to each other and *trans* to the strongly π -donating phenoxo ligands. The NMR spectra for **2** show sharp resonances, which suggests that solution dynamics are not prevalent. The *ipso*-C resonance occurs at δ = 164.8 ppm, which lies slightly upfield to that observed for complex **1** (δ = 166.3 ppm) and again this may represent a small change in the O(2p)–C=C(π^*) bonding system associated with the smaller need for tight O(2)p-to-Ti(1)d orbital donation on addition of the 4-electron donor bipy chelate. (see Table 2 for comparisons of the ¹³C{¹H} spectra *ipso*-C resonance positions for complexes of the type [TiCl₃(OAr)], [TiCl₂(OAr)₂] and [TiCl₂(OAr)₂(dmbipy)]).



Scheme 2.

Thermalisation of 2,4,6-trimethylphenol and TiCl₄ gave [TiCl₂(OC₆H₂Me_{3-2,4,6})₂]^[14] (**3**) which is monomeric in

Table 2. Comparison of $^{13}\text{C}\{^1\text{H}\}$ spectra *ipso*-C resonance positions for complexes of the type $[\text{TiCl}_3(\text{OAr})]$, $[\text{TiCl}_2(\text{OAr})_2]$ and $[\text{TiCl}_2(\text{OAr})_2(\text{dmbipy})]$.

Ligand (OAr)	$[\text{TiCl}_3(\text{OAr})]^{[b]}$	Complex ^[a] $[\text{TiCl}_2(\text{OAr})_2]$	$[\text{TiCl}_2(\text{OAr})_2(\text{dmbipy})]$
(OC ₆ H ₄ CM ₃ -4)	169.6	166.3 (1)	164.8 (2)
(OC ₆ H ₃ Me ₃ -2,4,6)	^[c]	166.4 (3)	164.5 (4)
(OC ₆ H ₃ <i>i</i> Pr ₂ -2,6)	170.5	165.7 (5)	162.6 (6)
(OC ₆ H ₃ Me ₂ -2,4)	169.9	165.2 (8)	164.3 (9)
(OC ₆ H ₃ CM ₃ -2-Me-6)	172.8	168.3 (11)	166.4 (12)
(OC ₆ H ₃ {CM ₃ } ₂ -2,6-Me-4)	174.9	170.0	^[d]

[a] Spectra obtained in CDCl₃. [b] Data taken from ref.^[15]. [c] *ipso*-C resonance not observed due to long relaxation times.^[15] [d] Dmbipy complex does not form.

benzene and shows sharper NMR spectra than complex **1** suggesting again that solution dynamics are not prevalent. The complex reacts with dmbipy to give $[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2(\text{dmbipy})]$ (**4**) for which the NMR spectra indicate one isomer with a similar structure to **2**. The *ipso*-C resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** occurs at $\delta = 164.5$ ppm compared with $\delta = 166.4$ ppm in the parent complex **3** (Table 2). Both complexes **3** and **4** did not crystallise, so that comparisons of *ipso*-C resonance position with solid state bond length data cannot be made. However, complex **3** is closely related to $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$ for which an X-ray crystal structure determination has shown a monomeric tetrahedral structure with Ti–O bond lengths of 1.734(7) and 1.736(8) Å, Ti–Cl bond lengths of 2.192(4) and 2.211(4) Å^[9] and an *ipso*-C resonance in the ^{13}C NMR spectrum at $\delta = 167.8$ ppm.^[8] In the octahedral adduct $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2(\text{dpda})]$ [dpda = (1*S*,2*S*)-diphenylethylenediamine] the Ti–O bond lengths increase to 1.804(4) and 1.787(4) Å, the Ti–Cl bond lengths to 2.353(2) Å and the *ipso*-C resonance is at $\delta = 166.0$ ppm.^[7] The standard deviations for the C–O bond lengths do not allow reliable bond length comparisons to be made for these complexes.

The reaction of 2,6-diisopropylphenol with TiCl₄ gave an oil which failed to form a solid^[9,18,19] but was identified as $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Pr}_2-2,6)_2]$ (**5**) on the basis of its NMR spectra (*ipso*-C resonance $\delta = 165.7$, cf. $\delta = 170.5$ ppm for $[\text{TiCl}_3(\text{OC}_6\text{H}_3\text{Pr}_2-2,6)]$,^[15] Table 2) being identical to an authentic sample.^[19] Reaction of complex **5** with dmbipy gave $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Pr}_2-2,6)_2(\text{dmbipy})]$ (**6**) for which the NMR spectra showed one isomer with a similar structure to **2** [structure **I**, Scheme 2] and the *ipso*-C resonance at $\delta = 162.6$ ppm. Refluxing a solution of 2,6-di-*tert*-butyl-4-methylphenol with TiCl₄ in toluene for 18 h, at which time HCl production had essentially ceased, gave a gum which NMR spectroscopy showed to be a mixture of $[\text{TiCl}_3(\text{OC}_6\text{H}_2\{\text{CMe}_3\}_2-2,6-\text{Me}-4)]$,^[15] $[\text{TiCl}_2(\text{OC}_6\text{H}_2\{\text{CMe}_3\}_2-2,6-\text{Me}-4)_2]$ ^[8] (**7**) and unreacted phenol. This indicated that the thermalisation reaction is not successful with this sterically demanding phenol.^[8] A sample of $[\text{TiCl}_2(\text{OC}_6\text{H}_2\{\text{CMe}_3\}_2-2,6-\text{Me}-4)_2]$ prepared by the reaction of TiCl₄ and LiOC₆H₂(CMe₃)₂-2,6-Me-4^[8] did not react with dmbipy and is reported not to react with pyridine.^[8] These results indicate that 2,6-di-*tert*-butyl substitu-

ents represent the steric limit for coordination expansion about the titanium centre.

Several unsymmetrically substituted phenols were also thermalised with TiCl₄ in toluene giving bis(phenoxo) complexes which have not been reported before. $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,4)_2]$ (**8**) (*ipso*-C resonance at $\delta = 165.2$ ppm, cf. $\delta = 169.9$ ppm for $[\text{TiCl}_3(\text{OC}_6\text{H}_3\text{Me}_2-2,4)]$,^[15] Table 2) is monomeric in benzene and reacts with dmbipy to give $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,4)_2(\text{dmbipy})]$ (**9**) for which the NMR spectra show a single isomer similar to structure **I**, Scheme 2 and an *ipso*-C resonance at $\delta = 164.3$ ppm. Reaction of 2,4-di-*tert*-butylphenol and TiCl₄ gave a mixture of $[\text{TiCl}_2(\text{OC}_6\text{H}_3\{\text{CMe}_3\}_2-2,4)_2]$ (**10**) (identified as a monomer by NMR spectroscopy, one set of resonances in the NMR spectra, *ipso*-C resonance at $\delta = 165.7$ ppm) and the tris(phenoxo) complex $[\text{TiCl}(\text{OC}_6\text{H}_3\{\text{CMe}_3\}_2-2,4)_3]$, which could be crystallised from the solution and has a distinctly different *ipso*-C resonance position ($\delta = 163.2$ ppm). NMR spectroscopy showed that a reaction of two equivalents of LiOC₆H₃(CMe₃)₂-2,4 with TiCl₄ in benzene also gave the tris(phenoxo) complex as the major product. The reason for the ease of formation of this tris-product in these reactions is unclear but appears to be related to the presence of the *para-tert*-butyl substituent. NMR spectral analysis of the reaction of two equivalents of 2-*tert*-butyl-4-methylphenol with TiCl₄ shows the product is exclusively the bis(phenoxo) complex (*ipso*-C resonance at $\delta = 165.8$ ppm).

Reaction of 2-*tert*-butyl-6-methylphenol and TiCl₄ gave $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$ (**11**) (*ipso*-C resonance at $\delta = 169.3$ ppm, cf. $\delta = 172.8$ ppm for $[\text{TiCl}_3(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)]$,^[15] Table 2) which is monomeric in benzene. The complex is reported to be a liquid when prepared by thermolysis in CH₂Cl₂^[18] and is formed in only 50% yield when $[\text{Ti}(\text{NEt}_2)_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$ is reacted with SiCl₄.^[4b] Using the present thermolysis method, production of HCl appeared to have ceased after approximately 8 h of vigorous refluxing, but NMR spectroscopy indicated that the reaction was only about 80% complete. Starting the cooled solution refluxing again led to resumption of HCl gas production and further NMR spectral analysis at intervals showed that another 10 h of reaction time was needed for completion. On removing the solvent an oil remained but this solidified on standing. The reaction time can be compared with that when using 2,6-di-*tert*-butyl-4-methylphe-

nol where HCl gas production appeared to cease after about 18 h but NMR spectral analysis showed the presence of $[\text{TiCl}_3(\text{OC}_6\text{H}_2\{\text{CMe}_3\}_2\text{-2,6-Me-4})]$, $[\text{TiCl}_2(\text{OC}_6\text{H}_2\{\text{CMe}_3\}_2\text{-2,6-Me-4})_2]$ (**7**) and unreacted phenol. This result emphasises the need to correctly identify the end-point of these reactions, especially in cases where the size of both *ortho*-substituents becomes larger. The X-ray crystal structure of **11** shows a distorted tetrahedral structure in the solid state with bond lengths and angles that are not significantly different from those found for $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2]$ except for the O–Ti–O bond angle which widens by ca. 3.5° in **11**.^[4a] Complex **11** reacts readily with dmbipy to form $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3\text{-2-Me-6})_2(\text{dmbipy})]$ (**12**) for which the NMR spectra indicate a similar structure to complex (**2**). The *ipso*-C resonance occurs at $\delta = 166.4$ ppm. $[\text{TiCl}_2(\text{OC}_2\text{H}_4\text{Ph-2})_2]$ (**13**) and the 1-naphthoxo complex $[\text{TiCl}_2(\text{OC}_{10}\text{H}_9)_2]$ (**14**) were also prepared and found to be monomeric in benzene.

Theoretical Studies

Density functional theory (DFT) calculations were carried out on model complexes to study the electronic properties of the phenoxo and chloro ligand interactions with the titanium centre in the monomeric and dimeric complexes shown by the solution and solid-state structures. Unsubstituted phenoxo ligands were used in the models to simplify the calculations. The optimised geometry for the monomers $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ (**15**) and $[\text{TiCl}_2(\text{OCH}_3)_2]$ (**16**) (used for comparisons) are shown in Figure 2. Bond lengths and angles for these two structures are given in Table 3 where they are compared with data obtained from the X-ray structure of the monomeric complexes $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2]$ ^[9] and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3\text{-2-Me-6})_2]$.^[3]

As expected, the ligands in **15** are tetrahedrally coordinated to titanium with the O–Ti–Cl, Cl–Ti–Cl and O–Ti–O bond angles (108.7° , 111.1° , and 111.0° , respectively) being very close to those found in the two X-ray structures. The Ti–O bond lengths in **15** [$1.753 \text{ \AA}$] are also similar to

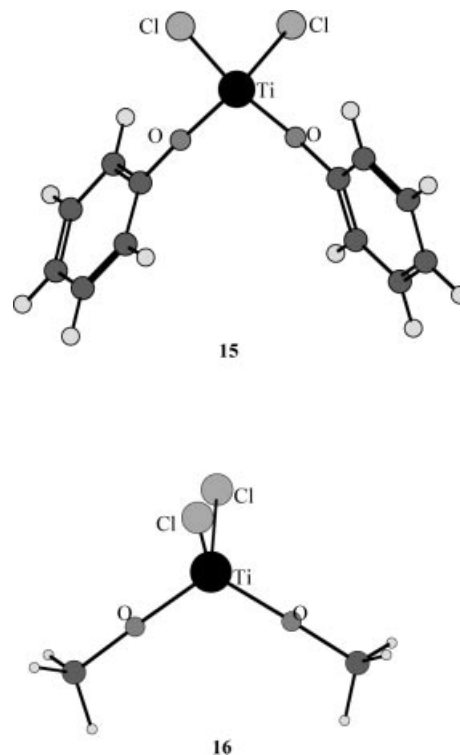


Figure 2. Optimized B3LYP structures of $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ (**15**) and $[\text{TiCl}_2(\text{OCH}_3)_2]$ (**16**).

those found in the X-ray structures [Ti–O bond lengths $1.734(7)$ and $1.753(4) \text{ \AA}$, respectively]. The model structures, however, indicate that the Ti–O bond lengths are longer in phenoxo model **15** ($1.753 \text{ \AA}$) than in the alkoxo model **16** ($1.740 \text{ \AA}$). Theoretical calculations have shown previously that a short Ti–O bond length of $1.750(2) \text{ \AA}$ in $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3\text{-2,4,6})]$ corresponds to a phenoxo ligand acting formally as a 2π -donor to $\text{Ti}^{[1.5]}$ but the Ti–O bonding is clearly stronger in **16**, where there is no $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ backbonding with a phenyl ring (the C–O bond lengths in **15** and $[\text{TiCl}_2(\text{OMe})_2]$ (**16**) are 1.384 and $1.436 \text{ \AA}$,

Table 3. Comparison of the bond lengths [$\text{\AA}$] and angles [$^\circ$] for the X-ray structure of $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2]$ and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3\text{-2-Me-6})_2]$ with the calculated structures $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ (**15**) and $[\text{TiCl}_2(\text{OCH}_3)_2]$ (**16**).

	$[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2]$ (X-ray) ^[9]	$[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3\text{-2-Me-6})_2]$ (X-ray) ^[5]	$[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ (15) (calcd.)	$[\text{TiCl}_2(\text{OCH}_3)_2]$ (16) (calcd.)
Ti–O(1)	1.734(7)	1.753(4)	1.753	1.740
Ti–O(2)	1.736(8)	1.752(5)	1.753	1.740
Ti–Cl(1)	2.192(4)	2.217(3)	2.249	2.257
Ti–Cl(2)	2.211(4)	2.207(3)	2.249	2.257
C–O(1)	1.353(12)	1.403(7)	1.384	1.436
C–O(2)	1.365(15)	1.401(9)	1.384	1.436
O(1)–Ti–O(2)	109.1(4)	112.6(2)	111.1	112.2
O(1)–Ti–Cl(1)	109.4(3)	109.2(2)	108.7	108.6
O(1)–Ti–Cl(2)	108.1(3)	107.8(2)	108.7	108.2
O(2)–Ti–Cl(1)	109.2(3)	107.0(2)	108.7	108.6
O(2)–Ti–Cl(2)	110.1(3)	110.0(2)	108.7	108.3
Cl(1)–Ti–Cl(2)	111.0(2)	110.3(1)	111.1	111.1
Ti–O(1)–C(11)	167.3(7)	162.2(4)	175.8	178.3
Ti–O(2)–C(21)	168.9(8)	163.4(4)	175.8	178.3

respectively). A similar situation was found for the models $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)]$ and $[\text{TiCl}_3(\text{OMe})]$.^[15]

The Ti–Cl bond lengths in **15** [2.249 Å] are somewhat longer than in $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$ [2.192(4) and 2.211(4) Å] and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$ [2.217(3) and 2.207(3) Å], but this is to be expected from the level of theory applied, and they compare with 2.257 Å in $[\text{TiCl}_2(\text{OMe})_2]$ where the strong Ti–O bonding allows the Ti–Cl bond to relax its π -bonding component somewhat when the electron count is maximised.

The Ti–O–C bond angle in model **15** [175.8°] is close to being linear which is also the case in the calculated structure of $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)]$ [177.7°]^[15] but the angles are smaller in the X-ray structures [e.g. 167.3(7)° in $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$ and 163.2(4)° in $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$. Ti–O–C bond angle linearity is also favoured by $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ back bonding with the phenyl ring. However, the Ti–O–C bond angle in the model $[\text{TiCl}_2(\text{OMe})_2]$ (**16**) in which there is no $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ back bonding with a phenyl ring is 178.3°. In this molecule the bond angles about the titanium atom are similar to those in **15**, but more importantly the Ti–O bond lengths are slightly shorter in $[\text{TiCl}_2(\text{OMe})_2]$ (1.740 Å, 1.753 Å in **15**), where the oxygen atom can bind to the metal without the influence of π -bonding to an aromatic ring. An angle scan reveals, however, that for the Ti–O–C bond angle in $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)]$ the energy difference between the calculated angle (177.7°) and the experimental value in the crystal [163.1(1)°] is only 3 kJ·mol^{−1}.^[15] The reduced bond angle in the crystal structure is thus due to intermolecular effects similar to those apparent in the related organoimido complexes, where M–N–C bond angles can be as low as 150° without greatly effecting the electronic nature of the multiple bond.^[20]

Interestingly, the phenyl rings in **15** face each other with the faces of the phenyl rings inclined to each other at an angle of 92.6°. This fact can be easily explained from electronic arguments. As there is strong π -overlap with both the Ti centre and the phenyl ring carbon atom (cummulene type arrangement), one oxygen atom overlaps with the d_{xz} orbital whilst the other overlaps with the d_{yz} orbital resulting in phenyl rings perpendicular to each other (Figure 3). The $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ interaction extends the π system in the complexes which accounts for the deep red coloration observed. In comparison, bis(alkoxo) complexes which do not contain this feature are usually colourless.^[6]

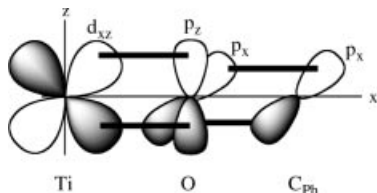


Figure 3. $\text{O}p_z$ – $\text{Ti}d_{xz}$ and $\text{O}p_x$ – $\text{C}p_x$ orbital overlaps in the Ti–O–Ar system.

A natural bond orbital (NBO) analysis^[21] of **15** using second order perturbation analysis of the Fock matrix,

which allows assignment of energetic contributions to individual donor acceptor pairs, shows there is substantial donation from the two oxygen 2p lone pairs on the phenoxo ligands to both the phenyl C=C (π^*) orbital ($E_2 = 104.6 \text{ kJ mol}^{-1}$) and more importantly to the unoccupied titanium 3d orbitals ($E_2 = 376.6 \text{ kJ mol}^{-1}$). Both the $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ and the $p_\pi(\text{O})$ –Ti interactions are stronger than that in the mono(phenoxo) model $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)]$ ($E_2 = 54.4 \text{ kJ mol}^{-1}$ and 230 kJ mol^{-1} per lone pair, respectively). Even so these values in **15** are clearly overestimated by the NBO procedure, but nevertheless it clearly points towards Ti–O multiple bonding. The O_{2p} –phenyl C=C (π^*) back-bonding is also sufficiently strong to prevent rotation, so that at ambient temperatures the configuration of the two phenoxo ligands is essentially locked. A decrease in the Ti–O–C bond angle diminishes the backbonding into the Ti 3d-orbitals. This bonding situation would leave no orbitals available for π -donation from the two chloro ligands, which could build the electron count formally to 18. However, the perturbation analysis reveals that this picture is too simple as there is some orbital mixing of the Cl(3p) lone-pair on both chlorines via back donation into unoccupied titanium 3d orbitals. In comparison, for the complex $[\text{TiCl}_3(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)]$ in which there is only one phenoxo ligand and thus a greater need for Cl_p –Ti π -donation, calculations show that two of the lone pairs donate more strongly ($E_2 = 108.8 \text{ kcal mol}^{-1}$).^[15] In $[\text{TiCl}_2(\text{OMe})_2]$ (**16**) the calculations show that the contribution from the chloro ligands is much less than in **15** as without the $p_\pi(\text{O})$ – $p_\pi^*(\text{C}=\text{C})$ interaction the strong Ti–O bonding allows the Ti–Cl bond to relax its π -bonding component and this is reflected in the longer Ti–Cl bond length in **16**.

Calculations were also carried out on models of the dimeric complex $[(\text{TiCl}_2\{\text{OC}_6\text{H}_4\text{CMe}_3-4\}\{\mu\text{-OC}_6\text{H}_4\text{-CMe}_3-4\})_2]$. For each titanium centre a trigonal bipyramidal arrangement for the ligands with the bridging oxygen atoms in the equatorial position was chosen in agreement with the crystal structure. With the 4-*tert*-butyl substituent replaced by H for computational convenience, a number of different structures according to all possible permutations was obtained. However, all the possible starting geometries optimised to only three different structures and these are shown in Figure 4. The global minimum (Figure 4A) is in almost perfect agreement with the crystal structures $[(\text{TiCl}_2\{\text{OC}_6\text{H}_4\text{CMe}_3-4\}\{\mu\text{-OC}_6\text{H}_4\text{-CMe}_3-4\})_2]$ (complex **1**) and $[(\text{TiCl}_2\{\text{OC}_6\text{H}_5\}\{\mu\text{-OC}_6\text{H}_5\})_2]$ ^[11] (see Table 4). In particular the terminal Ti–O bond lengths are 1.747, 1.749 and 1.744 Å, respectively, and the Ti–O bridging bond lengths are 1.908, 1.912 and 1.910 Å, respectively. The C–O_{br}–Ti bond angles are also in reasonable agreement with experimental data (169.9, 165.2 and 165.9°, respectively) as are the C–O_b–Ti bond angles (126.6, 123.5 and 128.3°, respectively). It is clear that solid state effects and limitations in the computational procedure accounts for the small differences in the geometries. The other two structures (Figure 4 B and C) are 13.2 and 23.3 kJ·mol^{−1} above the global minimum (Figure 4, A). The dimerization energy for the reaction

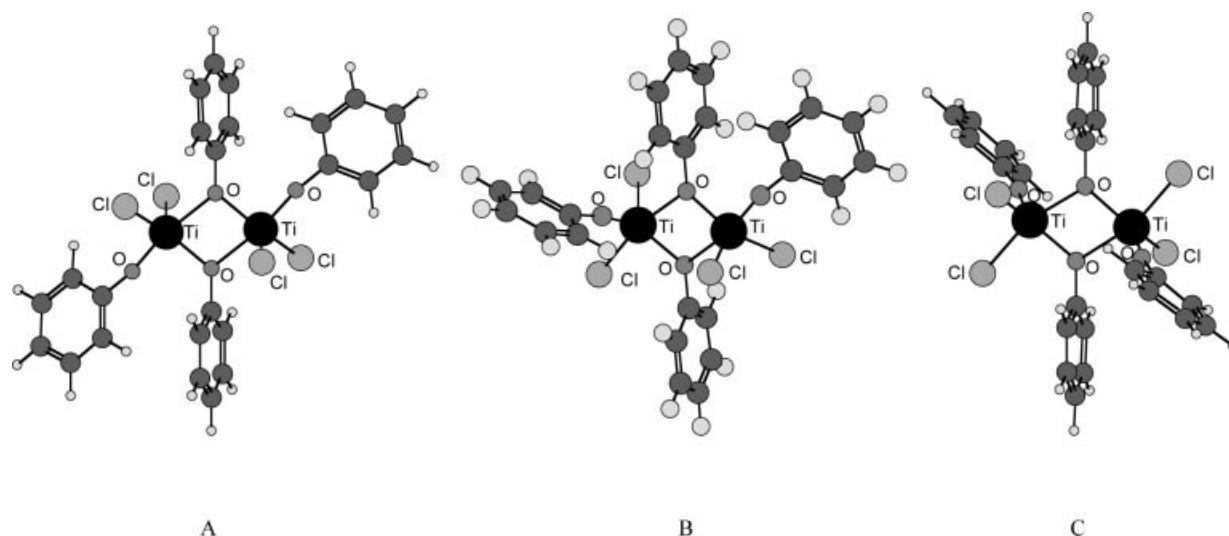


Figure 4. Optimized B3LYP structures of the dimeric titanium compound, $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]_2$. (A) global minimum; (B); $[\Delta E = 13.2 \text{ kJ}\cdot\text{mol}^{-1}]$ compared to (A); (C) $[\Delta E = 23.3 \text{ kJ}\cdot\text{mol}^{-1}]$ compared to (A).

Table 4. Comparison of the bond lengths [$\text{\AA}$] and angles [$^\circ$] for the calculated structure $[(\text{TiCl}_2\{\text{OC}_6\text{H}_5\}\{\mu\text{-OC}_6\text{H}_5\})_2]$ with the X-ray structures $[(\text{TiCl}_2\{\text{OC}_6\text{H}_5\}\{\mu\text{-OC}_6\text{H}_5\})_2]^{[11]}$ and $[(\text{TiCl}_2\{\text{OC}_6\text{H}_4\text{CMe}_3\text{-4}\}\{\mu\text{-OC}_6\text{H}_4\text{CMe}_3\text{-4}\})_2]$ (**1**).

Bond/angle ^[a]	$[(\text{TiCl}_2\{\text{OC}_6\text{H}_5\}\{\mu\text{-OC}_6\text{H}_5\})_2]$ (calcd.)	$[(\text{TiCl}_2\{\text{OC}_6\text{H}_5\}\{\mu\text{-OC}_6\text{H}_5\})_2]$ (X-ray ^[11])	$[(\text{TiCl}_2\{\text{OC}_6\text{H}_4\text{CMe}_3\text{-4}\}\{\mu\text{-OC}_6\text{H}_4\text{CMe}_3\text{-4}\})_2]$ (1) (X-ray)
Ti–O _b	2.151	2.122(9)	2.142(2)
Ti–O _t	1.747	1.744(10)	1.749(2)
Ti–O _b	1.908	1.910(9)	1.912(2)
Ti–Cl	2.270	2.209(6)	2.219(1)
Ti–Cl	2.276	2.219(6)	2.226(1)
C–O _t	1.382	1.359(19)	1.369(3)
C–O _b	1.423	1.422(14)	1.406(3)
C–O _t –Ti	169.9	165.9(6)	165.2(2)
C–O _b –Ti	126.6	128.3(4)	123.5(2)

[a] b = bridging, t = terminal.



[i.e. for dimer (A)] is only $-26.2 \text{ kJ mol}^{-1}$. This supports the results obtained here indicating complex (**1**) is monomeric in solution but a dimer in the solid state and also gives insight as to why molecular weight studies could indicate either monomeric or dimeric structures in solution.^[12,13] In the gas phase only the monomeric compound was found from mass spectroscopic studies.^[13]

Conclusions

The results of this work show that a range of dichlorobis(phenoxo)titanium(IV) complexes can be prepared in essentially pure form and in quantitative yield if the end-point of thermalising TiCl_4 and two equivalents of a phenol in toluene is determined. This represents a major advance in the ease of preparing these complexes when larger quantities are required. In a non coordinating solvent such as benzene the complexes are monomeric and thus have a four-coordinate geometry typical of $[\text{Cp}_2\text{TiCl}_2]$ complexes. When

there are no substituents in both *ortho*-positions of the phenoxo ligand phenyl rings, a dimeric phenoxo-bridged structure is possible in the solid state. Coordination expansion occurs where a ligand such as dmbipy is used but this ceases when both *ortho*-positions of the phenoxo ligand phenyl ring contain *tert*-butyl substituents. This compares with the dicyclopentadienyl complex $[\text{Cp}_2\text{TiCl}_2]$ which is not known to undergo coordination expansion easily and can be prepared in the presence of coordinating solvents.^[22] The chloro ligands in the six-coordinate bis(phenoxo) adducts are expected to lie *trans* to each other which is not the orientation required for many catalytic reactions. It is thus important to keep potentially coordinating ligands away from the complexes if a *cis*-dichloro geometry is to be maintained. The *ipso*-C resonance position in the ^{13}C NMR spectra of the phenoxo ligand phenyl rings indicate that there is a trend towards less $\text{O}(2p)\text{-C}=\text{C}(\pi^*)$ bonding component through the series $[\text{TiCl}_3(\text{OAr})]$, $[\text{TiCl}_2(\text{OAr})_2]$ and $[\text{TiCl}_2(\text{OAr})_2(\text{dmbipy})]$ and this would appear to be a sensitive probe for determining $\text{O}_\pi\text{-orbital-Ti}_d$ orbital bonding tightness. The comparable feature in cyclopentadienyl complexes is ring slippage which is uncommon and is only found in circumstances where a strong π -donating ligand is

able to compete for available metal orbitals.^[23] DFT calculations on the model $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ show that the structural parameters compare well with the X-ray structures of $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{Me}_2-2,6)_2]$ and $[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{CMe}_3-2-\text{Me}-6)_2]$ and as already discussed, an NBO analysis indicates substantial donation from the two oxygen 2p lone pairs on the phenoxo ligands to the unoccupied titanium 3d orbitals. This is consistent with each ligand acting formally as a 5-electron donor and gives credence to the analogy with the 5-electron donor Cp ligand.^[1] There is also sufficient $\text{O}(2p)-\text{C}=\text{C}(\pi^*)$ interaction to prevent rotation of the phenyl rings about the C–O bond at room temperature. The calculations also show that there is only a small dimerisation energy for $[\text{TiCl}_2(\text{OC}_6\text{H}_5)_2]$ and the global minimum structure is the one observed in the solid state. Overall the bis(phenoxo) complexes show a range of differences compared with $[\text{Cp}_2\text{TiCl}_2]$ and in the absence of cyclometallation involving the *ortho*-substituents on the aromatic rings^[24] these differences may be exploited in tuning stoichiometric and catalytic reactions in organic synthesis. Such metal-mediated reactions are now emerging.^[3]

Experimental Section

Syntheses: 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. 4,4'-Dimethyl-2,2'-bipyridine (dmbipy) was dried under vacuum before use. Light petroleum (b.p. 40–60 °C) and toluene were distilled from sodium wire and dichloromethane from freshly ground CaH_2 . ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 400 and 100 MHz respectively with a Bruker AM400 spectrometer. CDCl_3 and CD_2Cl_2 were dried with, and distilled from, freshly ground CaH_2 and $[\text{D}_6]\text{benzene}$ from sodium wire. Molecular mass values were determined cryoscopically in benzene with a Knauer molecular weight determination apparatus under N_2 gas conditions using concentrations in the vicinity of $5.3 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$. C, H and N analyses were determined by Dr A. Cunningham and associates, University of Otago, New Zealand. Chlorine was determined by gravimetric measurements. The production of HCl gas in the thermalisation reactions was monitored by passing the exhaust gases from the nitrogen bubbler over N,N,N',N' -teramethylethylenediamine and observing the white cloud produced.

$[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3-4)_2]$ (1): 4-*tert*-Butylphenol (4.75 g, 31.6 mmol) in toluene (50 cm³) was added to TiCl_4 (3.0 g, 15.8 mmol) in toluene (50 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (9 h). The solution was cooled, filtered and the solvent removed to give a deep red microcrystalline solid which was pumped on for several hours. Yield: 6.57 g, 100%. $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{O}_2\text{Ti}$: calcd. C 57.6, H 6.3, Cl 17.0; found C 57.5, H 6.3, Cl 17.3. Cryoscopic mol. mass: found 420.6; required: 417.2. ^1H NMR: δ = 1.25 (s, 18 H, CMe_3), 6.92 (b, 4 H, *o*-H), 7.18 (d, $^3J(\text{H,H})$ = 7.7 Hz, 4 H, *m*-H) ppm. ^{13}C NMR: δ = 31.4 (CMe_3), 34.4 (C), 118.8 (*o*-C), 125.8 (*m*-C), 148.2 (*p*-C), 166.3 (*ipso*-C) ppm. Recrystallisation of a portion of the solid from benzene gave well formed crystals. $[\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{O}_2\text{Ti}]$: calcd. C 57.6, H 6.3; found C 57.5, H 6.5. One of these crystals was used in the X-ray analysis.

$[\text{TiCl}_2(\text{OC}_6\text{H}_4\text{CMe}_3-4)_2(\text{dmbipy})]$ (2): Dmbipy (0.24 g, 1.3 mmol) in CH_2Cl_2 (25 cm³) was added to complex **1** (0.54 g, 1.3 mmol) in

CH_2Cl_2 (30 cm³) and the mixture was stirred for 2 h. The solution was filtered, the solvent removed and the residue allowed to stand under petroleum ether (20 cm³) overnight giving the complex as a noncrystalline orange solid. Yield: 0.75 g, 97%. $\text{C}_{32}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$: calcd. C 63.6, H 6.3, N 4.6; found C 63.5, H 6.2, N 4.9. ^1H NMR: δ = 1.30 (s, 18 H, CMe_3), 2.39 (s, 6 H, Me-dmbipy), 7.23 and 7.27 [2d, (AB quartet), $^3J_{\text{H,H}}$ = 8.8 Hz, 8 H, *o*,*m*-H], 7.27 (d, obs., H^2 -dmbipy), 7.93 (br. s, 2 H, H^4 -dmbipy), 8.96 (d, $^3J_{\text{H,H}}$ = 5.6 Hz, 2 H, H^1 -dmbipy) ppm. ^{13}C NMR: δ = 21.5 (Me-dmbipy), 31.4 (CMe_3), 34.3 (C), 118.5 (*o*-C), 122.5 (C^2 -dmbipy), 125.8 (*m*-C), 126.9 (C^4 -dmbipy), 145.5 (*p*-C), 148.7 (C^1 -dmbipy), 150.4 (C^3 or C^5 -dmbipy), 152.4 (C^5 or C^3 -dmbipy), 164.8 (*ipso*-C) ppm.

$[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2]$ (3): 2,4,6-Trimethylphenol (4.31 g, 31.6 mmol) in toluene (50 cm³) was added to TiCl_4 (3.0 g, 15.8 mmol) in toluene (50 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (10 h). The solution was cooled, filtered and the solvent removed to give the complex as a noncrystalline deep red solid. Yield: 5.97 g, 97%. $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{O}_2\text{Ti}$: calcd. C 55.6, H 6.1, Cl 18.2; found C 55.6, H 6.1, Cl 18.8. Cryoscopic mol. mass: found 395.4; required: 389.1. ^1H NMR: δ = 2.22 (s, 6 H, *p*-Me), 2.29 (s, 12 H, *o*-Me), 6.75 (s, 4 H, *m*-H) ppm. ^{13}C NMR: δ = 16.8 (*o*-Me), 20.8 (*p*-Me), 127.3 (*o*-C), 128.6 (*m*-C), 134.1 (*p*-C), 166.4 (*ipso*-C) ppm.

$[\text{TiCl}_2(\text{OC}_6\text{H}_2\text{Me}_3-2,4,6)_2(\text{dmbipy})]$ (4): Dmbipy (0.33 g, 1.79 mmol) in CH_2Cl_2 (30 cm³) was added to complex **3** (0.69 g, 1.78 mmol) in CH_2Cl_2 (30 cm³) and the mixture was stirred for 3 h. The solution was filtered, the solvent removed and the residue allowed to stand under petroleum ether (20 cm³) overnight giving the complex as a noncrystalline orange solid. Yield: 1.02 g, 100%. $\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$: calcd. C 62.8, H 6.4, N 4.9; found C 62.4, H 6.4, N 4.8. ^1H NMR: δ = 2.23 (s, 6 H, *p*-Me), 2.38 (s, 6 H, Me-dmbipy), 2.51 (s, 12 H, *o*-Me), 6.75 (s, 4 H, *m*-H), 7.22 (d, $^3J_{\text{H,H}}$ = 5.5 Hz, 2 H, H^2 -dmbipy), 7.90 (br. s, 2 H, H^4 -dmbipy), 8.99 (d, $^3J_{\text{H,H}}$ = 5.5 Hz, 2 H, H^1 -dmbipy) ppm. ^{13}C NMR: δ = 18.1 (*o*-Me), 20.6 (*p*-Me), 21.4 (Me-dmbipy), 122.6 (C^2 -dmbipy), 126.5 (C^4 -dmbipy), 128.9 (*m*-C), 129.3 (*o*-C), 131.6 (*p*-C), 148.6 (C^1 -dmbipy), 150.4 (C^3 or C^5 -dmbipy), 151.9 (C^5 or C^3 -dmbipy), 164.5 (*ipso*-C) ppm.

$[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{iPr}_2-2,6)_2]$ (5): 2,6-Diisopropylphenol (3.76 g, 21.1 mmol) in toluene (50 cm³) was added to TiCl_4 (2.0 g, 10.5 mmol) in toluene (50 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (13 h). The solution was cooled, filtered and the solvent removed to give an oil which failed to solidify over time. Yield: 4.96 g. The product gave an identical NMR spectra to a literature complex.^[19]

$[\text{TiCl}_2(\text{OC}_6\text{H}_3\text{iPr}_2-2,6)_2(\text{dmbipy})]$ (6): Dmbipy (0.31 g, 1.79 mmol) in CH_2Cl_2 (30 cm³) was added to complex **5** (0.8 g, 1.79 mmol) in CH_2Cl_2 (30 cm³) and the mixture was stirred for 3 h. The solution was filtered, the solvent removed and the residue allowed to stand under diethyl ether (50 cm³) overnight giving the complex as a noncrystalline deep red solid. Yield: 1.03 g, 88%. $\text{C}_{36}\text{H}_{46}\text{Cl}_2\text{N}_2\text{O}_2\text{Ti}$: calcd. C 65.8, H 7.1, N 4.3; found C 65.9, H 7.0, N 4.8. ^1H NMR: δ = 1.10 (d, $^3J_{\text{H,H}}$ = 6.7 Hz, 24 H, CMe_2), 2.43 (s, 6 H, Me-dmbipy), 4.20 (sept, $^3J_{\text{H,H}}$ = 6.7 Hz, 4 H, CH), 7.07 (m, 6 H, *m*,*p*-H), 7.25 (d, $^3J_{\text{H,H}}$ = 5.4 Hz, 2 H, H^2 -dmbipy), 7.92 (br. s, 2 H, H^4 -dmbipy), 8.89 (d, $^3J_{\text{H,H}}$ = 5.4 Hz, 2 H, H^1 -dmbipy) ppm. ^{13}C NMR: δ = 21.6 (Me-dmbipy), 24.5 (CMe_2), 26.1 (CH), 122.7 (C^2 -dmbipy), 122.9 (*p*-C), 123.6 (*m*-C), 126.4 (C^4 -dmbipy), 140.2 (*o*-C), 148.5 (C^1 -dmbipy), 150.4 (C^3 or C^5 -dmbipy), 151.8 (C^5 or C^3 -dmbipy), 162.6 (*ipso*-C) ppm. The complex is slightly soluble in diethyl ether.

[TiCl₂(OC₆H₃Me₂-2,4)₂] (8): 2,4-Dimethylphenol (5.15 g, 42.2 mmol) in toluene (50 cm³) was added to TiCl₄ (4.0 g, 21.1 mmol) in toluene (50 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (10 h). The solution was cooled, filtered and the solvent removed to give the complex as a noncrystalline deep red solid. Yield: 7.28 g, 96%. C₁₆H₁₈Cl₂O₂Ti: calcd. C 54.6, H 5.2, Cl 19.0; found C 54.6, H 5.4, Cl 19.4. Cryoscopic mol. mass: found 376.5; required: 360.0. ¹H NMR: δ = 2.23 (s, 6 H, Me), 2.25 (s, 6 H, Me), 6.82 (m, 4 H, *m*-H), 6.98 (d, ³J_{H,H} = 7.2 Hz, 2 H *o*-H) ppm. ¹³C NMR: δ = 16.5 (Me), 20.8 (Me), 119.3 (*o*-CH), 126.4 (*p*-C), 127.0 and 131.0 (*m*-CH), 134.2 (*o*-C), 165.2 (*ipso*-C) ppm.

[TiCl₂(OC₆H₃Me-2,4)₂(dmbipy)] (9): Dmbipy (0.25 g, 1.36 mmol) in CH₂Cl₂ (20 cm³) was added to complex **7** (0.49 g, 1.78 mmol) in CH₂Cl₂ (20 cm³) and the mixture was stirred for 2 h. The solution was filtered, the solvent removed and the residue allowed to stand under petroleum ether (20 cm³) overnight giving the complex as a noncrystalline orange solid. Yield: 0.69 g, 93%. C₂₈H₃₀Cl₂N₂O₂Ti: calcd. C 61.8, H 5.6, N 5.1; found C 61.4, H 5.9, N 4.9. ¹H NMR: δ = 2.27 (s, 6 H, Me), 2.42 (s, 6 H, Me), 2.43 (s, 6 H, Me-dmbipy), 6.74 (d, ³J_{H,H} = 8.1 Hz, ⁴J_{H,H} = 1.2, 2 H, *m*-H), 6.85 (br. s, 2 H, *m*-H), 7.23 (d, ³J_{H,H} = 5.5 Hz, 2 H, H²-dmbipy), 7.46 (d, ³J_{H,H} = 8.1 Hz, 2 H, *o*-H), 7.92 (br. s, 2 H, H⁴-dmbipy), 8.88 (d, ³J_{H,H} = 5.5 Hz, 2 H, H¹-dmbipy) ppm. ¹³C NMR: δ = 17.0 (Me), 20.8 (Me), 21.5 (Me-dmbipy), 119.7 (*o*-CH), 122.5 (C²-dmbipy), 126.9 (C⁴-dmbipy), 127.0 (*m*-C), 127.2 (*p*-C), 130.8 (*m*-C), 131.9 (*o*-C), 148.5 (C¹-dmbipy), 150.4 (C³ or C⁵-dmbipy), 152.2 (C⁵ or C³-dmbipy), 164.3 (*ipso*-C) ppm.

[TiCl₂(OC₆H₃{CMe₃}₂-2,4)₂] (10) and [TiCl(OC₆H₃{CMe₃}₂-2,4)₃]. **Procedure A:** 2,4-Di-*tert*-butylphenol (6.53 g, 31.6 mmol) in toluene (60 cm³) was added to TiCl₄ (3.0 g, 15.8 mmol) in toluene (50 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (12 h). The solution was cooled, filtered and the solvent removed to give an oil which solidified on standing overnight. NMR spectroscopy showed the product consisted of complex **10** [¹H NMR: δ = 1.33 (s, 18 H, CMe₃), 1.52 (s, 18 H, CMe₃), 7.14–7.25 (m, 4 H, *o*,*m*-H), 7.34 (d, ⁴J_{H,H} 2.1 Hz, 2 H, *m*-H) ppm. ¹³C NMR: δ = 30.3 (CMe₃), 31.4 (CMe₃), 34.7 (C), 35.1 (C), 123.3 (*o*-CH), 123.4 (*m*-CH), 124.2 (*m*-CH), 135.8 (*p*-C), 148.0 (*o*-C), 165.7 (*ipso*-C) ppm], and [TiCl(OC₆H₃{CMe₃}₂-2,4)₃], which was crystallised from the mixture by dissolving the reaction product in petroleum ether (100 cm³), reducing the volume to ca. 50 cm³ while keeping the solution hot, then allowing it to stand and cool. [C₄₂H₆₃ClO₃Ti: calcd. C 72.1, H 9.1; found C 72.7, H 9.4].

Procedure B: A solution of *n*-butyllithium (13.2 cm³, 1.6 mol L⁻¹) in hexane was added dropwise to a solution of 2,4-di-*tert*-butylphenol (4.35 g, 21.1 mmol) in benzene (50 cm³) chilled with ice-water. The cooling bath was removed and the mixture stirred for 1 h. The solution and precipitated solid was added slowly to TiCl₄ (2.0 g, 10.5 mmol) in benzene (50 cm³) via a cannula and the mixture stirred overnight. The mixture was allowed to stand for 24 hours to settle the precipitated LiCl, the solution was filtered and the solvent removed to give a red solid which was shown to be a mixture of complex **10** and [TiCl(OC₆H₃{CMe₃}₂-2,4)₃] by NMR spectroscopy. Crystallisation of the mixture as for procedure A, gave [TiCl(OC₆H₃{CMe₃}₂-2,4)₃] [C₄₂H₆₃ClO₃Ti: calcd. C 72.1, H 9.1; found C 71.1, H 9.9] which had identical NMR spectra with the sample prepared under procedure A.

[TiCl₂(OC₆H₃CMe₃-2-Me-6)₂] (11): 2-*tert*-Butyl-6-methylphenol (5.2 g, 31.7 mmol) in toluene (40 cm³) was added to TiCl₄ (3.0 g, 15.8 mmol) in toluene (30 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (18 h). The solution

was cooled, filtered from a small amount of solid and the solvent removed to give the complex as an oil which turned into a noncrystalline orange-red solid on standing. Yield: 6.80 g, 96%. C₂₂H₃₀Cl₂O₂Ti: calcd. C 59.3, H 6.8, Cl 15.9; found C 59.3, H 6.7, Cl 15.8. Cryoscopic mol. mass: found 454.4; required: 445.3. ¹H NMR: δ = 1.52 (s, 18 H, CMe₃), 2.29 (s, 6 H, Me), 6.93 (t, ³J_{H,H} = 7.6 Hz, 2 H, *p*-H), 7.00 (d, ³J_{H,H} = 7.6, ⁴J_{H,H} = 1.2 Hz, 2 H, *m*-H), 7.17 (d, ³J_{H,H} = 7.6, ⁴J_{H,H} = 1.2 Hz, 2 H, *m*-H) ppm. ¹³C NMR: δ = 18.5 (Me), 30.3 (CMe₃), 35.0 (C), 124.6 (*m*-C), 124.7 (*m*-C), 129.1 (*p*-C), 131.1 [*o*-C(methyl)], 137.7 [*o*-C(*tert*-butyl)], 169.3 (*ipso*-C) ppm.

[TiCl₂(OC₆H₃CMe₃-2-Me-6)₂(dmbipy)] (12): Dmbipy (0.32 g, 1.75 mmol) in CH₂Cl₂ (25 cm³) was added to complex **11** (0.78 g, 1.75 mmol) in CH₂Cl₂ (30 cm³) and the mixture was stirred for 3 h. The solution was filtered, the solvent removed and the residue allowed to stand under petroleum ether (20 cm³) overnight giving the complex as a noncrystalline orange solid. Yield: 0.60 g, 55%. C₃₄H₄₂Cl₂N₂O₂Ti: calcd. C 64.9, H 6.7, N 4.5; found C 64.5, H 7.0, N 4.5. ¹H NMR: δ = 1.48 (s, 18 H, CMe₃), 2.46 (s, 6 H, Me-dmbipy), 2.76 (s, 6 H, Me-phenoxo), 6.84 (t, ³J_{H,H} = 7.4 Hz, 2 H, *p*-H), 6.99 (bd, 2 H, *m*-H), 7.17 (bd, 2 H, *m*-H), 7.22 (d, ³J_{H,H} 5.5 Hz, 2 H, H²-dmbipy), 7.93 (br. s, 2 H, H⁴-dmbipy), 8.84 (d, ³J_{H,H} 5.5 Hz, 2 H, H¹-dmbipy) ppm. ¹³C NMR: δ = 21.5 (Me-dmbipy), 21.8 (Me), 31.7 (CMe₃), 35.6 (C), 122.1 (CH), 124.5 (CH), 129.8 (CH), 133.0 [*o*-C(methyl)], 140.8 [*o*-C(*tert*-butyl)], 148.6 (C¹-dmbipy), 150.6 (C³ or C⁵-dmbipy), 151.5 (C⁵ or C³-dmbipy), 166.4 (*ipso*-C) ppm. The complex is slightly soluble in petroleum ether.

[TiCl₂(OC₆H₄Ph-2)₂] (13): 2-Phenylphenol (5.38 g, 31.6 mmol) in CH₂Cl₂ (60 cm³) was added to TiCl₄ (3.0 g, 15.8 mmol) in CH₂Cl₂ (40 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (12 h). The solution was cooled, filtered and the solvent removed to give the complex as an oil which turned into a noncrystalline deep red solid on standing for several days. Yield: 7.21 g, 100%. C₂₄H₁₈Cl₂O₂Ti: calcd. C 63.1, H 4.0, Cl 15.5; found C 63.4, H 4.1, Cl 15.5. Cryoscopic mol. mass: found 471.3; required: 457.2. ¹H NMR: δ = 6.91–7.49 (m, 18 H, aromatic-H's) ppm. ¹³C NMR: δ = 115.9, 120.3, 124.3, 127.5, 128.4, 128.5, 129.0, 129.3, 130.1, 137.0 (*o*-C), 161.9 (*ipso*-C) ppm.

[TiCl₂(OC₁₀H₉)₂] (14): 1-Naphthol (4.56 g, 31.6 mmol) in toluene (60 cm³) was added to TiCl₄ (3.0 g, 15.8 mmol) in toluene (30 cm³) and the mixture was refluxed vigorously until the production of HCl gas ceased (12 h). The solution was cooled, filtered and the solvent removed to give the complex as a noncrystalline solid. Yield: 6.8 g, 100%. C₂₀H₁₄Cl₂O₂Ti: calcd. C 61.3, H 3.9, Cl 16.4; found C 61.4, H 4.1, Cl 15.9. Cryoscopic mol. mass: found 426.9; required: 405.0. The ¹H NMR spectrum shows the product contains a small amount of toluene which is difficult to remove by pumping.

Theoretical: Density functional (DFT) calculations were carried out on the model compound [TiCl₂(OC₆H₅)₂] and its possible dimeric structures using a hybrid Becke three parameter function together with the Lee–Yang–Parr correlation function (B3LYP).^[25,26] For H, C and O a Dunning/Huzinaga valence double-zeta set was used.^[27] For Ti and Cl we applied the pseudopotential approximation using the Hay–Wadt parametrization together with valence double-zeta basis.^[28] This resulted in 934 basis functions contracted to 368 for the dimeric species. The geometries were fully optimized until the gradients were below 10⁻⁵ a.u. which took several months of supercomputer time on a 16-processor SGI. The structures are shown in Figure 2 and Figure 4. All calculations were performed with a parallel version of Gaussian98^[29] The bonding situation has

been examined using the natural bond orbital (NBO) partitioning of Weinhold and Reed.^[21]

X-ray Crystallography: Data were collected with a Siemens Bruker CCD instrument with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 203(2) \text{ K}$. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. This was negligible. Unit cell parameters were obtained by a least-squares fit of all data with $I > 10 \sigma(I)$. Data were corrected for Lorentz, polarisation and absorption effects.^[30] The structures were solved by direct methods and refined on all F^2 by the full-matrix least-squares technique. All non-hydrogen atoms were allowed to assume anisotropic thermal motion. Hydrogen atoms were in calculated positions (C–H, $0.94 \text{ \AA}$ for phenyl ring H and $0.97 \text{ \AA}$ for *tert*-butyl H) and refined with a riding model with $U_{\text{iso}} = 0.08$. Programs used were SHELXS^[31] for structure solution and SHELXL^[32] for refinement. Diagrams were prepared with ORTEP-3 for Windows[®].^[33]

Crystal Data: $[\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{O}_2\text{Ti}]$, $M = 417.21$, monoclinic, space group $P 2_1/c$, $a = 11.265(2)$, $b = 18.603(3)$, $c = 11.491(2) \text{ \AA}$, $\beta = 116.59(3)^\circ$, $V = 2153.4(6) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd.}} = 1.287 \text{ mg m}^{-3}$, $\mu (\text{Mo-}K_{\alpha}) = 0.655 \text{ mm}^{-1}$, crystal size $0.23 \times 0.22 \times 0.14 \text{ mm}$, ω scans, $\theta_{\text{max.}} = 28.19^\circ$, $F(000) = 872$, 12833 reflections measured, 4783 unique ($R_{\text{int.}} = 0.0381$), $I_{\text{min.}}/I_{\text{max.}} = 0.8639/0.9139$, $R_1 = 0.0547$ [$I > 2\sigma(I)$], $wR_2 = 0.1210$ (all data).

CCDC-249718 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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