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FULL PAPER

Trichloro monophenoxide complexes of titanium(IV)

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Thermalisation of $TiCl_4$ and phenol (1 : 1) in toluene gave $[TiCl_3(OC_6H_5)]$ **1**. The more soluble complex $[TiCl_3(OC_6H_4CMe_3\text{-}4)]$ **2** is monomeric in benzene and reacts with 4,4′-dimethyl-2,2′-bipyridyl (dmbipy) to give *mer*-$[TiCl_3(OC_6H_4CMe_3\text{-}4)(dmbipy)]$ **3** and the disproportionation product $[TiCl_2(OC_6H_4CMe_3\text{-}4)_2(dmbipy)]$. The complex $[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)]$ **4** is monomeric in benzene whereas $[TiCl_3(OC_6H_3Pr^i_2\text{-}2,6)]$ **5** partially disproportionates in solution into $[TiCl_2(OC_6H_3Pr^i_2\text{-}2,6)_2]$ and reacts with dmbipy to give *mer*-$[TiCl_3(OC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ **6** and $[TiCl_2(OC_6H_3Pr^i_2\text{-}2,6)_2(dmbipy)]$. Thermalisation of 2,6-di-*tert*-butyl-4-methylphenol and $TiCl_4$ in toluene caused debutylation but $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4\}]$ **7** forms in light petroleum (bp range 40–60 °C). Complex **7** is monomeric in benzene and does not form adducts with dmbipy or other sigma donors. A crystal structure determination of **7** showed a monomer with distorted tetrahedral co-ordination, a Ti–O bond length of 1.750(2) Å and Ti–Cl bonds longer than in $TiCl_4$ but shorter than in $[TiCl_3(C_5H_5)]$ or $[TiCl_3\{C_5H_3(CMe_3)_2\text{-}1,3\}]$. 2,4,6-Tri-*tert*-butylphenol debutylates when thermalised with $TiCl_4$ in toluene giving $[TiCl_3\{OC_6H_4(CMe_3)_2\text{-}2,4\}]$ **8**. The complexes $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}OMe\text{-}4\}]$ **9**, $[TiCl_3(OC_6H_3CMe_3\text{-}2\text{-}Me\text{-}4)]$ **10**, $[TiCl_3(OC_6H_4Ph\text{-}2)]$ **11** and the 1-naphthoxide complex $[TiCl_3(OC_{10}H_7)]$ **12** were also prepared. Density functional calculations performed on the models **4** and $[TiCl_3(OMe)]$ showed both lone pairs on oxygen donate electron density to titanium but O(2p)-to-C=C (π*) donation weakens the Ti–O interaction in the phenoxide complex; Cl(2p)-to-Ti(3d) donation is much reduced in the methoxide complex. The system $[TiCl_3(OC_6H_4CMe_3\text{-}4)]/AlMe_3$ is 280 times more active than $[TiCl_3Cp]$ (Cp = cyclopentadienyl)/$AlMe_3$ for low pressure (6 psi) ethylene polymerisation but $\frac{1}{3}$ less active than $TiCl_4/AlMe_3$.

Currently there is intense interest in finding replacements for the cyclopentadienyl ligand in Group 4 transition metal chemistry due mainly to the impact metallocenes have had on olefin polymerisations.[1] A major challenge is finding replacements that allow the metal to remain co-ordinatively and electronically unsaturated.[2]

Monocyclopentadienyl complexes $[TiCl_3Cp]$ (Cp = unsubstituted or substituted cyclopentadienide) and their derivatives are known as active catalysts for polymerisations of ethylene and propene,[3] conjugated dienes,[4] and the syndiospecific polymerisation of styrene[5] but there have been few studies directed towards replacing the 1σ, 2π donor ligand in this type of complex. Both alkoxide (RO) and phenoxide ligands (ArO)[6] are capable of 1σ, 2π donation[7] to transition metals with the latter ligand being especially attractive since electronic and steric properties can easily be assessed because of the commercial availability of a wide range of substituted phenols.

The chemistry of the monophenoxides, $[TiCl_3(OAr)]$, is poorly developed. For example, $[TiCl_3(OC_6H_5)]$ has been known for many years[8] but few of its properties have been described.[9] The complex $[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)]$ has been shown to be monomeric in non-co-ordinating solvents and the bis adducts $[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)(L)_2]$ (L = pyridine, 2-, 3-, 4-methylpyridine, $PhNH_2$, tetrahydrofuran, $\frac{1}{2}$ $Ph_2PCH_2CH_2PPh_2$ or $\frac{1}{2}$ 2,2′-bipyridyl) have been characterised by analytical data and IR spectroscopy.[10] Uncharacterised $[TiCl_3(OC_6H_4CMe_3\text{-}2)]$ has been evaluated for regioselective *ortho*-acylation[11] and the 3,3′,5,5′ tetrasubstituted biphenolate (tsb) complexes $[\{TiCl_3(L)\}_2(tsb)]$ (L = diethyl ether or tetrahydrofuran) prepared.[12] The complex $[TiCl_3\{OC_6H_3(CMe_3)_2\text{-}2,6\}]$ has been tested in the presence of methylaluminoxane [$(MeAlO)_n$, MAO] co-catalyst for the co-polymerisation of styrene and ethylene[13] and its crystal structure determined.[14]

We report here a comprehensive study of the monophenoxides $[TiCl_3(OAr)]$ (Ar = unsubstituted or substituted phenyl group) prepared for use in catalytic applications. In particular we have investigated the influence of steric factors on molecular structure and on expansion of the co-ordination sphere. We also present a fully optimised Density Functional Theory (DFT) study of the bonding in the model complex $[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)]$ and compare it with the alkoxide model $[TiCl_3(OMe)]$. These studies represent the first detailed theoretical description of phenoxide and alkoxide bonding in an early transition metal complex.

Results and discussion

Synthetic studies

The synthetic strategy employed in preparing the complexes was dictated by the requirement to produce multigram quantities of a pure product in high yield without recrystallisation, *via* a simple and cheap method using commercially available starting materials as supplied. This was best achieved by thermalisation,[10] eqn. (1). This method gave good yields of

$$TiCl_4 + ArOH \xrightarrow[\text{toluene}]{\text{reflux}} [TiCl_3(OAr)] + HCl \qquad (1)$$

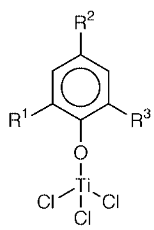
solid complexes if the reactions were thermalised to completion whereas incomplete thermalisation gave gums which proved difficult to purify. Generally the complexes were obtained as non-crystalline solids. Attempted recrystallisations mostly gave gums of various composition and in some cases partial disproportionation to the bis-phenoxide, $[TiCl_2(OAr)_2]$, occurred especially after extended periods of solvent contact. In general the complexes were best isolated by filtering the reflux solution and pumping off the solvent. In some instances this procedure

Table 1 Yields and analytical data

Complex		Crude yield (%)	Analysis[a] (%) C	H	Cl
1	$[TiCl_3(OC_6H_5)]^{b,c}$	90	37.6 (37.7)	2.9 (3.0)	37.5 (37.1)
2	$[TiCl_3(OC_6H_4CMe_3\text{-}4)]^{b\text{–}d}$	87	45.6 (45.5)	5.2 (4.9)	31.3 (31.0)
4	$[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)]^{c,e,f}$	97	38.1 (38.1)	4.2 (3.9)	36.2 (36.3)
5	$[TiCl_3(OC_6H_3Pr^i{}_2\text{-}2,6)]$	94	43.9 (43.5)	5.5 (5.2)	32.4 (32.1)
7	$[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4\}]^{g}$	95	48.2 (48.5)	6.2 (5.7)	27.8 (28.6)
8	$[TiCl_3\{OC_6H_3(CMe_3)_2\text{-}2,4\}]$	96	45.6 (46.7)	6.2 (5.9)	29.5 (29.6)
9	$[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}OMe\text{-}4\}]$	99	47.7 (47.7)	6.1 (6.0)	26.9 (26.4)
10	$[TiCl_3(OC_6H_3CMe_3\text{-}2\text{-}Me\text{-}4)]$	100	42.2 (41.6)	5.4 (4.8)	33.5 (33.5)
11	$[TiCl_3(OC_6H_4Ph\text{-}2)]$	100	44.5 (44.6)	3.3 (2.8)	32.2 (32.9)
12	$[TiCl_3(OC_{10}H_7)]^{c,h}$	96	48.7 (48.0)	3.3 (3.5)	30.3 (30.4)

[a] Calculated values given in parentheses. [b] Calculated analytical data include 0.43 C_7H_8. [c] Solvent supported by NMR spectra. [d] *M* 317, calc. 303.5. [e] Calculated analytical data include 0.041 C_7H_8. [f] *M* 284, calc. 289.3. [g] *M* 375, calc. 371.0. [h] Calculated data include 0.57 C_7H_8.

left toluene in the sample which was difficult to remove by pumping. Washing introduced further solvent. Analytical data are contained in Table 1 which indicates the solvent content. The presence of solvent in the complexes was confirmed by NMR spectroscopy.



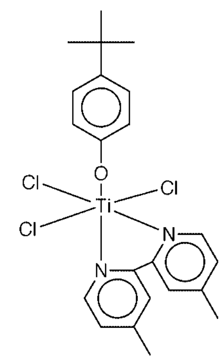
1 $R^1 – R^3 = H$
2 $R^1,R^3 = H$; $R^2 = CMe_3$
4 $R^1,R^2,R^3 = Me$
5 $R^1,R^3 = CHMe_2$; $R^2 = H$
7 $R^1,R^3 = CMe_3$; $R^2 = Me$
8 $R^1,R^2 = CMe_3$; $R^3 = H$
9 $R^1,R^3 = CMe_3$; $R^2 = OMe$
10 $R^1 = CMe_3$; $R^2 = Me$, $R^3 = H$
11 $R^1 = Ph$; $R^2,R^3 = H$

The reaction of $TiCl_4$ and phenol in a 1 : 1 ratio produced HCl gas for 12 h giving rise to $[TiCl_3(OC_6H_5)]$[8] **1** for which the ^1H NMR spectrum (Table 2) showed the absence of the phenolic proton and the $^{13}C\text{-}\{^1H\}$ NMR spectrum showed a phenoxide ligand *ipso*-carbon at δ 169.65. The more soluble complex $[TiCl_3(OC_6H_4CMe_3\text{-}4)]$ **2** is monomeric in benzene solution and also shows an *ipso*-carbon resonance in this region (δ 169.6, $CDCl_3$; 170.53, C_6D_6). Recrystallisations did not give crystals suitable for X-ray analysis and contact with solvent over time led to disproportionation, eqn. (2). Thus, if a solution

$$2[TiCl_3(OC_6H_4CMe_3\text{-}4)] \longrightarrow [TiCl_2(OC_6H_4CMe_3\text{-}4)_2] + TiCl_4 \quad (2)$$

of **2** in light petroleum is allowed to stand to give slow crystallisation over several days, crystals of the dichlorobis(phenoxide) are formed and the solution fumes characteristically for $TiCl_4$. However, after a series of such crystallisations, if the solution is concentrated sufficiently then complex **2** is deposited and fuming does not occur. We have recently reported a much more rapid disproportionation for a series of tungsten monophenoxide complexes.[15] Based on the *ipso*-carbon resonance position in the $^{13}C\text{-}\{^1H\}$ NMR spectra of **1** and **2** and the monomeric nature of **2**, tetrahedral coordination geometry is predicted for these two complexes. This allows the electron count to be maximised by π donation from the chloro and phenoxide ligands. A theoretical model for this type of bonding is discussed later.

Owing to the relevance of co-ordination expansion in titanium chemistry and, in particular, the importance of bidentate σ-donor ligands in stereospecific Ziegler–Natta catalysis,[16] a variety of such ligands was treated with complex **2** but were found to produce mixtures which were difficult to distinguish by NMR spectroscopy. However, complex **2** reacts with 4,4′-dimethyl-2,2′-bipyridyl (dmbipy) in CH_2Cl_2 to give an orange solid which analysed as $[TiCl_3(OC_6H_4CMe_3\text{-}4)(dmbipy)]$ when the solvent was removed from the reaction mixture. The NMR spectra showed, however, that the $CDCl_3$ solubles consisted of a mixture of *mer*-$[TiCl_3(OC_6H_4CMe_3\text{-}4)(dmbipy)]$ **3** (63%) and the bis-phenoxide $[TiCl_2(OC_6H_4\text{-}CMe_3\text{-}4)_2(dmbipy)]$ (34%).† The ^1H NMR spectrum shows inequivalent dmbipy rings for **3** (see structure **I**) with widely



I

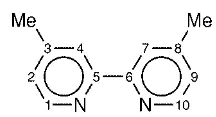
separated doublets for the C^1 and C^{10} hydrogens (δ 9.69 and 8.70; see dmbipy numbering scheme, Table 2), two singlets for the C^4 and C^7 hydrogens (δ 8.02 and 7.96; *meta* coupling not resolved), doublets for the C^2 and C^9 hydrogens (δ 7.47 and 7.35) and a broadened resonance containing the C^3 and C^8 methyl groups. Similarly, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum there are individual resonances for each of the carbons in the two dmbipy rings and a broadened resonance for the C^3 and C^8 methyl groups. The phenoxide *ipso*-carbon resonance (δ 166.40) lies to slightly higher field than for the four-co-ordinate parent

† The bis-phenoxide complexes mentioned in this work were independently prepared and will be reported elsewhere.

Table 2 Selected NMR spectral data (*J*/Hz)[a]

Complex	^{1}H[b]	^{13}C-{^{1}H}
1	7.16 (m, 3 H, *m*, *p*-H); 7.29 [d, ^3J(HH) 7.1, 2 H, *o*-H]	118.77 (*o*-C); 126.24 (*p*-C); 129.38 (*m*-C); 169.65 (*ipso*-C)
2	1.28 (s, 9 H, CMe_3); 7.12 [d, ^3J(HH) 8.4, 2 H, *o*-H]; 7.27 [d, ^3J(HH) 8.4, 2 H, *m*-H]	31.31 (Me); 34.80 (C); 118.14 (*o*-C); 126.15 (*m*-C); 150.07 (*p*-C); 169.60 (*ipso*-C)
3[c]	1.31 (s, 9 H, CMe_3); 2.52 [s, 3 H, Me (dmbipy)]; 7.35 [d, ^3J(HH) 5.6, 1 H, H^2 or H^9 (dmbipy)]; 7.38 [d, ^3J(HH) 8.7, 2 H, *o*-H]; 7.47 [d, ^3J(HH) 5.6, 1 H, H^9 or H^2 (dmbipy)]; 7.54 [d, ^3J(HH) 8.7, 2 H, *m*-H]; 7.96 [s, 1 H, H^4 or H^7 (dmbipy)]; 8.02 [s, 1 H, H^7 or H^4 (dmbipy)]; 8.70 [d, ^3J(HH) 5.6, H^1 or H^{10} (dmbipy)]; 9.69 [d, ^3J(HH) 5.6, H^{10} or H^1 (dmbipy)]	21.77 (Me); 31.52 (CMe_3); 34.67 (C); 119.53 [*o*-C (phenoxide)]; 122.73 and 122.88 [C^2 and C^9 (dmbipy)]; 126.16 [*m*-C (phenoxide)]; 127.18 and 127.47 [C^4 and C^7 (dmbipy)]; 148.22 (C^1 or C^{10} (dmbipy)]; 148.36 [*p*-C (phenoxide)]; 150.64 and 151.12 [C^3 and C^8 or C^5 and C^6 (dmbipy)]; 151.27 [C^{10} or C^1 (dmbipy)]; 152.52 and 153.28 [C^6 and C^5 or C^8 and C^3 (dmbipy)]; 166.40 [*ipso*-C (phenoxide)]
4	2.30 (s, 3 H, *p*-Me); 2.47 (bs, 6 H, *o*-Me); 6.83 (s, 2 H, *m*-H)	16.96 (*o*-Me); 20.95 (*p*-Me); 128.70 (*m*-C); *o*-C, *p*-C and *ipso*-C not observed
5[d]	1.38 [d, ^3J(HH) 6.8, 6 H, CMe_2]; 3.70 [sept, ^3J(HH) 6.8, 1 H, CH]; 7.18 [m, 3 H, *m*, *p*-H]	23.31 [CMe_2]; 27.59 [CH]; 123.41 [*m*-C]; 126.93 [*p*-C]; 139.32 [*o*-C]; 170.50 [*ipso*-C]
6[c]	1.22 [d, ^3J(HH) 6.6, 12 H, CMe_2]; 2.56 and 2.59 [2s, 6 H, Me (dmbipy)]; 4.50 [sept, ^3J(HH) 6.6, 2 H, CH]; 7.13 [m, 1 H, *p*-H]; 7.20 [m, 2 H, *m*-H]; 7.27 [d, ^3J(HH) 5.2, 1 H, H^2 or H^9 (dmbipy)]; 7.47 [d, ^3J(HH) 5.2, 1 H, H^9 or H^2 (dmbipy)]; 8.00 [bs, 2 H, H^4 or H^7 (dmbipy)]; 8.53 [d, ^3J(HH) 5.2, 1 H, C^1 or C^{10} (dmbipy)]; 9.72 [d, ^3J(HH) 5.2, 1 H, C^{10} or C^1 (dmbipy)]	21.78 [Me(dmbipy)]; 24.54 (CMe_2); 26.51 (CH); 122.81 [*p*-C (phenoxide)]; 124.08 [*m*-C (phenoxide)]; 125.31 and 125.55 [C^2 and C^9 (dmbipy)]; 127.02 and 125.55 [C^4 and C^7 (dmbipy)]; 142.91 [*o*-C (phenoxide)]; 148.22 [C^1 or C^{10} (dmbipy)]; 150.80 and 150.94 [C^3 and C^8 or C^5 and C^6 (dmbipy)]; 151.01 [C^{10} or C^1 (dmbipy)]; 152.04 and 153.30 [C^6 and C^5 or C^8 and C^3 (dmbipy)]; 164.60 [*ipso*-C (phenoxide)]
7	1.56 (s, 18 H, CMe_3); 2.34 (s, 3 H, Me); 7.06 (s, 2 H, *m*-H)	21.69 (Me); 31.69 (CMe_3); 45.06 (C); 125.51 (*m*-C); 135.67 (*p*-C); 140.40 (*o*-C); 174.87 (*ipso*-C)
8[d]	1.35 (s, 9 H, *p*-CMe_3); 1.55 (s, 9 H, *o*-CMe); 7.27 and 7.29 [dd, ^3J(HH) 8.5, ^4J(HH) 2.3, 1 H, *m*-H]; 7.37 [d, ^4J(HH) 2.3, 1H, *m*-H]; 7.50 [d, ^3J(HH) 8.5, 1 H, *o*-H]	30.47 (*p*-CMe_3); 31.33 (*o*-CMe_3); 35.00 (C); 35.26 (C); 123.26, 123.35 and 124.26 (*o*, *m*-CH); 136.05 (*p*-C); 150.02 (*o*-C); 169.90 (*ipso*-C)
9	1.57 (s, 18 H, CMe_3); 3.82 (s, 3 H, OMe); 6.76 (s, 2 H, *m*-H)	31.51 (CMe_3); 35.42 (C); 55.36 (OMe); 109.67 (*m*-C); 141.57 (*o*-C); 155.95 (*p*-C); 173.17 (*ipso*-C)
10[d]	1.49 (s, 9 H, CMe_3); 2.36 (s, 3 H, Me); 7.02 [d, ^3J(HH) 8.2, 1 H, *m*-H]; 7.10 (bs, 1 H, *m*-H); 7.41 [d, ^3J(HH) 8.2, 1 H, *o*-H]	21.42 (Me); 30.45 (CMe_3); 34.96 (C); 124.23 (*o*-CH); 127.01 (*m*-CH); 127.99 (*m*-CH); 136.53 (*p*-C); 136.92 (*o*-C); 170.21 (*ipso*-C)
11	6.90–7.18 [m, 2 H, *o*-H(phenoxide), *p*-H(phenyl)]; 7.22 [td, ^3J(HH) 7.6, ^4J(HH) 1.6, 1 H, *p*-H (phenoxide)]; 7.30 [td, ^3J(HH) 7.6, ^4J(HH) 1.6, 2 H, *m*-H (phenoxide)]; 7.36 [bt, ^3J(HH) 7.1, 2 H, *m*-H (phenyl)]; 7.44 [d, ^3J(HH) 7.1, ^4J(HH) 1.3, 2 H, *o*-H (phenyl)]	120.36, 125.80, 127.90, 128.34, 128.62, 129.38, 130.25 (CH); 131.49 [C(phenyl)]; 136.49 [C(phenoxide)]; 166.63 (*ipso*-C)

[a] Spectra obtained in dry $CDCl_3$ solution. [b] bs = Broad singlet, bt = broad triplet, d = doublet, dd = doublet of doublets, m = multiplet, s = singlet, sept = septet, td = triplet of doublets. [c] Spectra also contain resonances characteristic of [$TiCl_2(OAr)_2$(dmbipy)]. [d] Spectra also contain resonances characteristic of [$TiCl_2(OAr)_2$].



complex **2** (δ 169.6), most likely as a result of decreased π-electron donation from the phenoxide ligand in the six-co-ordinate dmbipy adduct.

The appearance in the NMR spectra of the bis-phenoxide complex (identified by comparison with an authentic sample) suggests that addition of dmbipy to the monophenoxide complex **2** in CH_2Cl_2 solution involves a disproportionation, eqn. (3). The presence of [$TiCl_4$(dmbipy)] has not been

$$3[TiCl_3(OC_6H_4CMe_3\text{-}4)] + 3\text{dmbipy} \longrightarrow [TiCl_3(OC_6H_4CMe_3\text{-}4)(\text{dmbipy})] + [TiCl_2(OC_6H_4CMe_3\text{-}4)_2(\text{dmbipy})] + [TiCl_4(\text{dmbipy})] \quad (3)$$

confirmed since it is extremely insoluble and remains contaminated when the mono- and bis-phenoxide complexes are extracted. Whether the disproportionation involves an acceleration of the solution dynamics observed for **2** is unclear but the reaction does explain the overall analysis as [$TiCl_3(OC_6H_4$-CMe_3-4)(dmbipy)] and the observed NMR spectra.

Further to understand this process and also to determine the capacity of the analysed material to carry aromatic solvent, dmbipy in light petroleum–benzene (80:20) was added to complex **2** in light petroleum and the orange precipitate collected. After repeated washings with light petroleum and drying *in vacuo*, the complex analysed as [$TiCl_3(OC_6H_4CMe_3$-4)(dmbipy)]·0.33C_6H_6. Only with strong heating under vacuum the solvent was driven off. The integrity of this material is unknown but the process of dissolving in $CDCl_3$ apparently sets off solution dynamics. The material initially dissolves but a precipitate rapidly forms and the ^{1}H NMR spectrum shows more of a variety of products than was observed for the reaction in CH_2Cl_2 although the mono- and bis-phenoxide products still dominate.

Reactions of $TiCl_4$ were carried out with other phenols which contain substituents in the 2,6 positions of the phenyl ring, in order to assess the effect of increasing steric size. The complex [$TiCl_3(OC_6H_2Me_3$-2,4,6)] **4** is monomeric in benzene; the ^{1}H NMR spectrum shows a broadened resonance for the 2,6-dimethyl groups and in the ^{13}C-{^{1}H} NMR spectrum the quaternary carbons of the aromatic ring were not observed due to slow relaxation times. Octahedral adducts of this complex have been described[10] but NMR spectral characteristics have not been reported. The complex [$TiCl_3(OC_6H_3Pr^i_2$-2,6)] **5** can be obtained as a solid product from the thermalisation reaction but the composition indicated by the NMR spectra differs from that indicated by the analytical figures, and this suggests that dynamic processes occur in solution. In $CDCl_3$ disproportionation apparently occurs giving a mixture of complex **5** (74%) (*ipso*-carbon resonance δ 170.50) and [$TiCl_2(OC_6H_3Pr^i_2$-2,6$)_2$] (26%) whereas in C_6D_6–$CDCl_3$ (1:1) the proportions are 60 and 40% respectively. The solution dynamics apparently occur rapidly on dissolving the solid since the mixture proportions do not change with time after the initial ^{1}H NMR spectrum is run. When **5** is dissolved on a larger scale in $CHCl_3$ the solution fumes characteristically for $TiCl_4$. Complex **5** reacts with dmbipy in CH_2Cl_2 solution to give an orange solid which analyses as $[TiCl_3(OC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ but which NMR spectra show to be a mixture of *mer*-trichloro $[TiCl_3(OC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]$ **6** (55%) (*ipso*-carbon resonance δ 164.6) and the bis-phenoxide $[TiCl_2(OC_6H_3Pr^i_2\text{-}2,6)_2(dmbipy)]$ (45%). When the reaction was carried out in light petroleum–benzene (as for complex **2**) an orange solid was obtained analysing as $[TiCl_3(OC_6H_3Pr^i_2\text{-}2,6)(dmbipy)]\cdot 0.83C_6H_6$ and which gave up benzene only on heating under vacuum. This material, which initially dissolves in $CDCl_3$ and then produces a precipitate, shows more products in the NMR spectra than does the original CH_2Cl_2 reaction but the mono- and bis-phenoxide dmbipy products still dominate.

When 2,6-di-*tert*-butyl-4-methylphenol was refluxed with $TiCl_4$ in a 1 : 1 ratio in toluene NMR spectroscopy showed that a significant amount of debutylation occurred. However $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4\}]$ **7** was prepared in almost quantitative yield by refluxing $TiCl_4$ and the phenol in light petroleum (bp 40–60 °C) until the production of HCl ceased. The complex $[TiCl_3\{OC_6H_3(CMe_3)_2\text{-}2,6\}]$ has been synthesized[13,14] by treating $LiOC_6H_3(CMe_3)_2\text{-}2,6$ with $TiCl_4$ in benzene but the reflux method represents a cheaper and more convenient synthesis for this type of complex. A 50 g preparation of complex **7** is easily obtainable using this method.

A molecular weight determination showed that complex **7** is monomeric in benzene. The NMR spectrum shows a single resonance for each of the appropriate protons and carbons with the phenoxide ligand *ipso* carbon positioned in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 174.87. This is further downfield than that observed for all the other complexes and may represent an increase in π donation from the phenoxide ligand with the electron donating *tert*-butyl groups present. The NMR spectra do not show any evidence for disproportionation to the bis-phenoxide suggesting that, although the *tert*-butyl groups are more electron donating than the isopropyl groups in complex **5**, steric influences may now be important. Preliminary studies show that even after extended refluxing of $TiCl_4$ and 2 equivalents of 2,6-di-*tert*-butyl-4-methylphenol in toluene there is more of the monophenoxide present than the bis-phenoxide. In comparison with complexes **2** and **5** the di-*tert*-butyl complex **7** does not react with dmbipy to expand its co-ordination sphere nor does it react with a variety of other σ-donor ligands such as tetrahydrofuran, pyridine or PMe_3.

Reaction of 2,6-diphenylphenol with $TiCl_4$ gave a mixture of two complexes which the NMR data suggest are $[TiCl_3(OC_6H_3Ph_2\text{-}2,6)]$ and the bis-phenoxide $[TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2]$.[17] Owing to the expense of this phenol, in comparison with the others used here, we have not yet persevered with the monophenoxide preparation although a comparison of its steric properties with those of the 2,6-di-*tert*-butyl substituted phenoxide in complex **7** are of interest.

When 2,4,6-tri-*tert*-butylphenol was refluxed in toluene with $TiCl_4$ debutylation of one of the *tert*-butyl groups occurred giving $[TiCl_3\{OC_6H_3(OCMe_3)_2\text{-}2,4\}]$ **8**. In a preliminary study on the electronic effect of substituents on the 2,6-di-*tert*-butylphenoxide system 2,6-di-*tert*-butyl-4-methoxyphenol gave $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}OMe\text{-}4\}]$ **9** (*ipso*-carbon resonance, δ 173.17), whereas the reaction with 2,6-di-*tert*-butyl-4-nitrophenol generated HCl only very slowly and did not produce a characterisable product.

A single-crystal structure determination confirmed the solid state monomeric nature of $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4\}]$ **7**. The co-ordination geometry of the Ti is that of a distorted tetrahedron with three chloro ligands and a phenoxide oxygen as donor atoms (Fig. 1) and is similar to that reported recently for $[TiCl_3\{OC_6H_3(CMe_3)_2\text{-}2,6\}]$.[14] Owing to the importance of this type of complex in olefin polymerisations[13] we compare the

Table 3 Selected bond lengths [Å] and angles [°] for $[TiCl_3\{OC_6H_2(CMe_3)_2\text{-}2,6\text{-}Me\text{-}4\}]$

Ti–O(1)	1.750(2)	Ti–Cl(1)	2.1945(9)
Ti–Cl(3)	2.1822(8)	O(1)–C(1)	1.390(2)
Ti–Cl(2)	2.1913(8)		
O(1)–Ti–Cl(3)	112.66(6)	Cl(3)–Ti–Cl(1)	105.78(4)
O(1)–Ti–Cl(2)	109.18(6)	Cl(2)–Ti–Cl(1)	107.58(3)
Cl(3)–Ti–Cl(2)	108.57(3)	C(1)–O(1)–Ti	163.08(14)
O(1)–Ti–Cl(1)	112.84(5)		

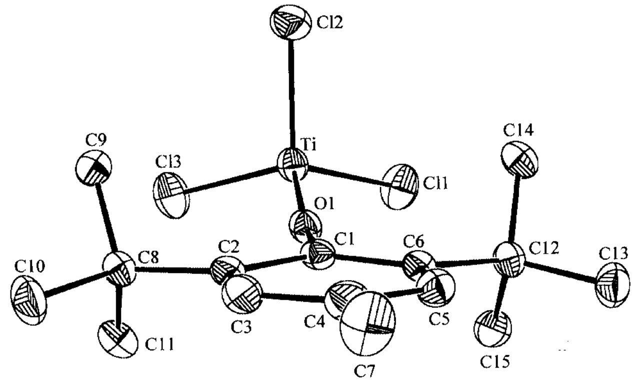


Fig. 1 Molecular structure of complex **7**; atoms are depicted as 50% probability surfaces. Hydrogen atoms have been omitted for clarity.

structural features of **7** with other related complexes which carry out this function. Selected bond lengths and angles for **7** are given in Table 3; comparable data for $TiCl_4$[18] and the monocyclopentadienyl complexes $[TiCl_3Cp]$ [$Cp = C_5H_5$,[19] $C_5H_3(SiMe_3)_2$[20] or $C_5H_3(CMe_3)_2$[21]] are given in Table 4.

The Ti–O(1) bond length in complex **7** [1.750(2) Å] is longer than that found for the tetrahedral bis-phenoxide complex $[TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2]$ [1.726(2) Å][17] and a range of neutral octahedral monoisopropoxide complexes of titanium [range 1.702(4)–1.726(4) Å][22] all of which require strong π donation from oxygen to maximise the electron count on Ti. However, it is shorter than the Ti–O distances found in the tris-phenoxide complex $[TiCl\{OC_6H_3(CMe_3)_2\text{-}2,6\}_3]$ [1.810(9), 1.802(7) and 1.782(8) Å][23] where three phenoxide oxygens are able to π-donate to the metal. The Ti–O–C bond angle in **7** [163.1(1)°] is smaller than that in $[TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2]$ (168.5(2)°)[17] but larger than those found for the octahedral isopropoxide complexes [range 153.7(4)–157.5(6)°][22] suggesting that the M–O–C bond angle is not greatly affected by the π nature of the ligand to metal bonding.

In complex **7** the phenyl ring is oriented so that the *tert*-butyl groups are positioned over Cl(1) and Cl(3) leaving Cl(2) exposed. The 3 Ti–Cl bond lengths are all similar (range 2.1822(8)–2.1945(9) Å but are longer than those found in $TiCl_4$ [2.170(2) Å][18] where each chloride must π-donate 2 electrons to attain an electron count of 16 for the metal. However, on average they are shorter than in the $[TiCl_3Cp]$ complexes (Table 4) where the π-donor ability of the Cp ligands appears to reduce the amount of π donation needed from chlorine. This is especially so with the 1,3-di-*tert*-butylcyclopentadienyl ligand where the Ti–Cl bond lengths increase to *ca*. 2.240(1) Å when the electron donating *tert*-butyl substituents are present. In **7** the two chloro ligands lying closer to the *tert*-butyl groups [Cl(1) and Cl(3)] are directed away from the phenoxide ligand more than is the more isolated chloro ligand [O(1)–Ti–Cl(1), 112.84(5); O(1)–Ti–Cl(2), 109.18(6); O(1)–Ti–Cl(3), 112.66(6)°]. Overall, however, the ligand is less sterically demanding than its Cp counterparts of Table 4 where the Cp(centroid)–Ti–Cl angles widen to 117°. As a result the Cl–Ti–Cl angles of **7** are all larger than those for the Cp complexes of Table 4.

Table 4 Comparative bond length (Å) and bond angle (°) data

	$[TiCl_3\{OC_6H_2(CMe_3)_2$-2,6-Me-4$\}]$	$TiCl_4$ [a]	$[TiCl_3(C_5H_5)]$ [b]	$[TiCl_3\{C_5H_3(SiMe_3)_2$-1,3$\}]$ [c]	$[TiCl_3\{C_5H_3(CMe_3)_2$-1,3$\}]$ [d]
Ti–Cl(1)	2.1945(9)	2.170(2)	2.201(3)	2.232(3)	2.240(1)
Ti–Cl(2)	2.1913(8)	2.170(2)	2.248(5)	2.229(3)	2.243(1)
Ti–Cl(3)	2.1822(8)	2.170(2)	2.221(2)	2.229(3)	2.243(1)
Ti–O	1.750(2)	2.170(2) [e]	[2.01] [f]	[2.007(8)] [f]	[2.022] [f]
Cl(1)–Ti–Cl(2)	105.78(4)	109	102.0	102.0(1)	100.4(1)
Cl(2)–Ti–Cl(3)	108.57(3)	109	104.1(2)	102.6(1)	101.9(1)
Cl(1)–Ti–Cl(3)	107.58(3)	109	102.3(3)	102.0(1)	100.4(1)
O–Ti–Cl(1)	112.84(5)	109 [g]	117.2 [h]	116.4(2) [h]	—
O–Ti–Cl(3)	112.66(6)	109 [g]	114.3 [h]	116.4(2) [h]	—
O–Ti–Cl(2)	108.57(3)	109 [g]	115.0 [h]	115.3(3) [h]	—

[a] Gas diffraction data taken from ref. 18. [b] X-Ray data taken from ref. 19. [c] X-Ray data taken from ref. 20. [d] X-Ray data taken from ref. 21. [e] Ti–Cl bond length. [f] Ti–Cp centroid distance. [g] Cl–Ti–Cl bond angle. [h] Cp centroid–Ti–Cl bond angle.

The phenoxide ligand in complex **7** bends towards Cl(2) [Ti–O(1)–C(1) is 163.1(1)°] which allows the *tert*-butyl group methyls to maximise their distances from Cl(1) and Cl(3). However, it is unlikely that the Ti–O(1)–C(1) bond angle is substantially influenced by such steric contacts since small rotations of the bulky groups can minimise the interactions. The angles subtended at C(8) and C(12) by the *tert*-butyl carbon atoms facing Cl(1) and Cl(3) widen [C(9)–C(8)–C(11), 111.9(2); C(14)–C(12)–C(15), 112.1(2)°] compressing the other C–C–C bond angles of the *tert*-butyl group [range 105.9(2)–106.4(2)°] and, as well, the angles C(1)–C(2)–C(8) and C(1)–C(6)–C(12) [123.7(2) and 123.4(2)° respectively] are increased slightly above the ideal angle of 120° to relieve the steric pressures.

The unsymmetrically substituted phenols 2-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butylphenol on refluxing with $TiCl_4$ gave $[TiCl_3(OC_6H_3CMe_3$-2-Me-4$)]$ **10** and $[TiCl_3\{OC_6H_3(CMe_3)_2$-2,4$\}]$ **8** the latter complex having previously been prepared by debutylation of 2,4,6-tri-*tert*-butylphenol. NMR spectra show disproportionation occurs in $CDCl_3$ solution for these complexes. The monophenoxides (composition 70% for **10**, 61% for **8**) show *ipso*-carbon resonances at δ 170.21 for **10** and 169.90 for **8** and there are NMR resonances characteristic of the bis-phenoxides (composition 30 and 39% respectively).

Refluxing 2-*tert*-butyl-6-methylphenol with $TiCl_4$ in toluene gave a mixture of monophenoxide $[TiCl_3(OC_6H_3CMe_3$-2-Me-6$)]$ [tentatively identified in the ^{13}C-$\{^1H\}$ NMR spectrum from its *ipso*-carbon position (δ 172.61)], and the bis-phenoxide $[TiCl_2(OC_6H_3CMe_3$-2-Me-6$)_2]$. The toluene reflux reaction using 2-phenylphenol gave $[TiCl_3(OC_6H_4Ph$-2$)]$ **11** (*ipso*-carbon resonance δ 166.63) and with 1-naphthol $[TiCl_3(OC_{10}H_7)]$ **12** (*ipso*-carbon resonance δ 166.62). Complexes **11** and **12** are relatively insoluble and have not been characterised further.

Theoretical studies

Density-functional calculations (DFT) were carried out on the model complex $[TiCl_3(OC_6H_2Me_3$-2,4,6$)]$ **4** to obtain an understanding of the chloro and phenoxide ligand bonding to the titanium centre. In the absence of π donation from any of the ligands the complex has an overall electron count of 8. This increases to 12 if the phenoxide oxygen makes 2 π-donor interactions and to 16 if chloro ligands add 2 extra π-donor interactions.

Fig. 2 shows the fully optimised B3LYP structure of complex **4**. From a comparison with the crystal structure of **7** we see that the geometry of the model compound is generally in good agreement with the crystallographic interatom distances and angles. For example, the calculated Ti–O and the Ti–Cl bond lengths of 1.73 and 2.23 Å, respectively, are close to those obtained from the crystal structure (1.75 and 2.19 Å). The only large deviation observed is the Ti–O–C bond angle (177.7° at

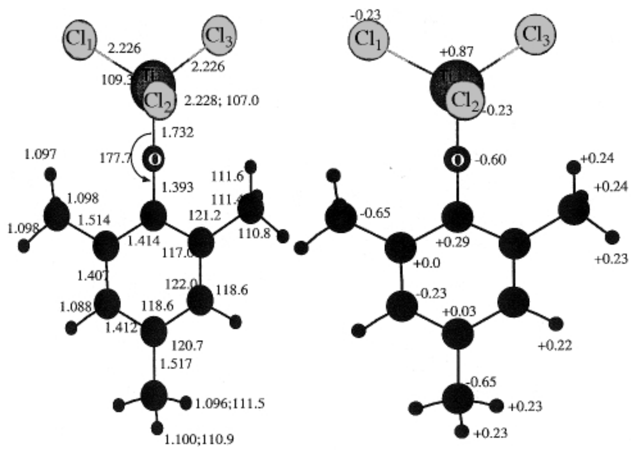


Fig. 2 DFT (B3LYP) optimised structure (left) and DFT (B3LYP) natural charges (right) for $[TiCl_3(OC_6H_2Me_3$-2,4,6$)]$ **4**. All bond distances (in Å) and angles (in °) are indicated in the drawing. The important optimised torsion angles τ are as follows: τ (CCOTi) = 90.0; τ (COTiCl^1) = 119.3; τ (COTiCl^2) = 2.6°.

the B3LYP level), which in the crystal structure is 163.1°. However, the calculation does not take into account the effect of the bulky CMe_3 substituents in the 2,6 positions of the phenyl ring or any crystal packing forces. In addition, approximations in the basis sets, pseudopotentials, *etc.* may overestimate the oxygen lone-pair back bonding into the unoccupied Ti(3d) or phenyl C=C(π*) orbitals (see discussion below). Nevertheless, we confirm an approximately linear arrangement of the Ti–O–C unit as an angle scan demonstrates (Fig. 3). This figure shows that the minimum at α = 177.7° is shallow, and the difference between both geometries (the B3LYP minimum at α = 177.7° and the crystal structure at α = 177.7°) is only 3 kJ mol^{-1}.

There appear to be no crystal structure determinations of the alkoxide complexes $[TiCl_3(OR)]$ (R = alkyl group) but molecular weight determinations indicate monomeric structures in solution.[24] Therefore a DFT calculation was carried out on the model $[TiCl_3(OMe)]$ (Fig. 4) for comparison with the model of **4**. Whereas the Ti–Cl bond distances are almost identical with those of compound **4**, the Ti–O bond distance is shortened significantly and the C–O bond distance increases. The latter effect is understandable since bonding to an sp^2 hybridised carbon should lead to a smaller bond distance compared with an sp^3 hybridised carbon. In addition, the π bonding between the oxygen and the phenyl π system is eliminated in $[TiCl_3(OMe)]$. This should also lead to an increase in the oxygen 2p lone-pair back donation into the empty titanium d orbitals. Indeed, the Ti–O bond distance in $[TiCl_3(OMe)]$ (1.718 Å) is considerably shorter than that in the model of **4**

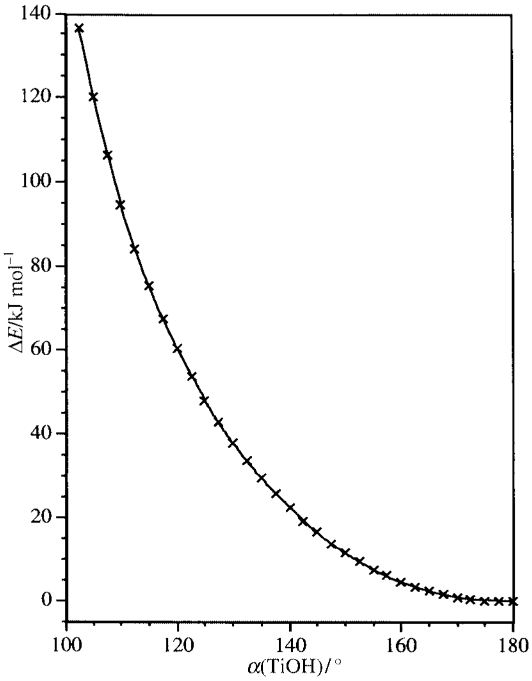


Fig. 3 Ti–O–C angle scan from the linear arrangement (α = 180°) to a Ti–O–C angle of 100°. The calculations were carried out at the B3LYP level of theory.

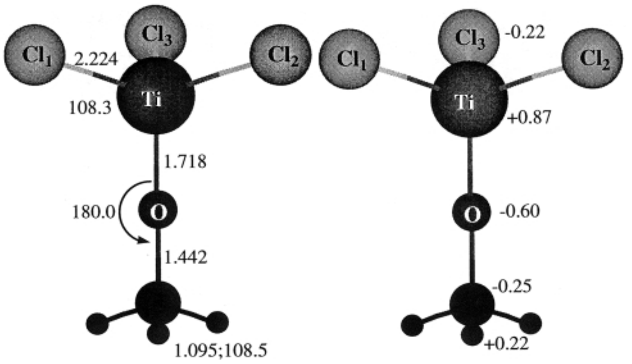


Fig. 4 DFT (B3LYP) optimised structure (left) and DFT (B3LYP) natural charges (right) for [$TiCl_3$(OMe)]. All bond distances (in Å) and angles (in °) are indicated in the drawing.

(1.732 Å). Interestingly, the Ti–O–C bond is now linear which also indicates a substantially increased oxygen 2p lone-pair donation to titanium.

Second order perturbation theory analysis of the Fock matrix within the natural bond order (NBO) basis assigns energetic contributions E_2 to individual donor–acceptor bonding pairs. The analysis for complex **4** reveals substantial donation from the oxygen 2p lone pairs into both the phenyl C=C (π*) orbital (E_2 = 13 kcal mol^{-1} per lone pair) as shown in Fig. 5A, and the unoccupied titanium 3d orbitals (E_2 = 55 kcal mol^{-1} per lone pair) as shown in Fig. 5B. This explains the slightly increased bond length of 1.414 Å of the first C=C unit in the phenyl ring system compared with the other C=C bonds. The two oxygen lone-pair donations to titanium are approximately equal in size. The perturbation analysis further reveals very strong lone-pair Cl(3p) back donation into unoccupied titanium 3d orbitals which vary between the different lone pairs (one of the three lone pairs shows only weak donation, the other two donate more strongly with a maximum E_2 = 26 kcal mol^{-1}). One of these lone pairs is shown in Fig. 5C. In contrast, [$TiCl_3$(OMe)] shows only little Cl(3p) back donation to titanium (maximum E_2 = 7 kcal mol^{-1}).

Fig. 6A clearly demonstrates this showing almost pure Cl(p) lone-pair character. This is probably due to the increased

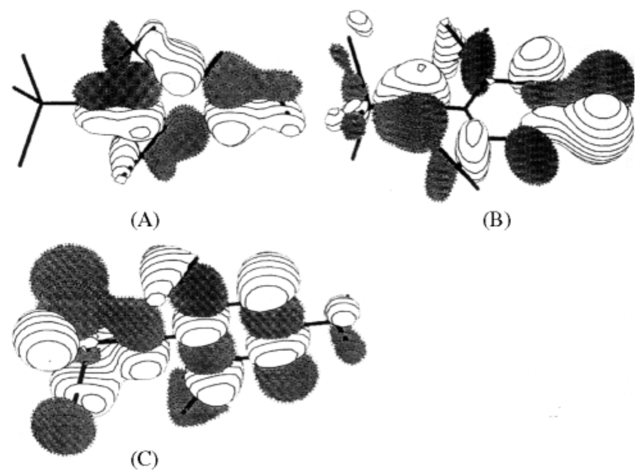


Fig. 5 Occupied MOs for [$TiCl_3(OC_6H_2Me_3$-2,4,6)] **4** showing (A) the overlap between the O(p_π) and $C_{Ph}(p_\pi)$, (B) the overlap between the O(p_π) and Ti(d_π), (C) the interaction between the Cl(p) lone pair with O(p) and Ti(d) orbitals.

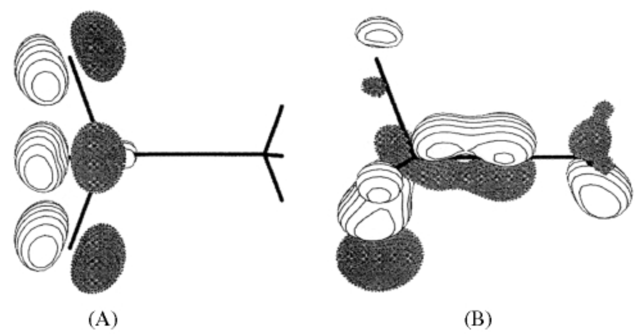


Fig. 6 Occupied MOs for [$TiCl_3$(OMe)] showing (A) one of the Cl(p) lone pairs, (B) the overlap between the O(p_π) and Ti(d_π).

2p oxygen lone-pair back donation to titanium for this compound. Indeed, the NBO analysis for [$TiCl_3$(OMe)] does not show oxygen lone pairs but rather identifies two oxygen–titanium π bonds with 88% oxygen and 12% titanium character as shown in Fig. 6B. This explains the linear Ti–O–C arrangement.

The NBO atomic charges for both compounds are shown in Figs. 2 and 4. Both the Mulliken (q_{Ti} = +0.77) and the NBO analysis (q_{Ti} = +0.87) for compound **4** assign a much smaller atomic charge compared with the titanium in $TiCl_3Me$ (q_{Ti} = +1.27).[25] The difference is large between the two compounds and can mostly be attributed to differences in the basis sets used. Indeed, the structure of $TiCl_3Me$ at the B3LYP level was optimised using the same basis sets and pseudopotentials as in complex **4**. For the optimised C_{3v} structure (Ti–Cl, 2.210; Ti–C, 2.08; C–H, 1.098 Å; C–Ti–Cl, 106.0; C–Ti–Cl, 108.7°), the NBO charges are similar, *i.e.* q_{Ti} = +0.73, q_{Cl} = −0.19. It is expected that the more electronegative oxygen atom would result in a much higher atomic charge for titanium but this is not the case and again indicates strong back donation of the oxygen lone-pair 2p orbitals into the unoccupied titanium 3d orbitals. Interestingly, the NBO analysis for $TiCl_3Me$ shows only a small lone-pair Cl(3p) back donation into the unoccupied titanium 3d orbitals in accordance with that found for [$TiCl_3$(OMe)].

Catalytic activity studies

Preliminary results are reported for catalytic activity. The complex [$TiCl_3(OC_6H_4CMe_3$-4)] **2** was tested as a catalyst in a low-pressure (6 psi) polymerisation of ethylene. The various runs (Table 5) were conducted in toluene solution, each with similar mole quantities of catalyst, similar pressure of ethylene, a

Table 5 Ethene polymerisation[a]

Run	Complex	10^6 concentration/ mol dm^{-3} × 10^{-6}	Solvent	Pressure[b]	Yield/g	Activity[c]
1	**2**	7.4	Toluene	6	0.768	5.1797
2	$TiCl_4$	6.3	Toluene	6	1.900	15.0
3	[$TiCl_3Cp$]	7.3	Toluene	6	0.0027	0.0185
4	**2**	6.3	Light petroleum	6	0.227	1.8130
5	**2**	7.7	Light petroleum	20	1.128	7.2840
6	**2**	5.9	Toluene	20	0.550	4.6368
7	**9**	6.5	Toluene	6	0.353	2.7328

[a] 21 °C; 0.12 to 0.16 mmol of catalyst; 50 cm^3 total solvent volume; approximately 7 mol equivalents of $AlMe_3$; 1 h reaction period. [b] psi (lbf in^{-2} ≈ 6895 Pa). [c] kg polyethylene (mol cat)$^{-1}$ h^{-1}.

7-fold excess of $AlMe_3$, and reaction times of 1 h so that catalyst activity could be directly compared by the production of polyethylene.

Based on the yield of polyethylene, complex **2** is approximately 3 times less active than $TiCl_4$/$AlMe_3$ (Ziegler–Natta catalysis) but 280 times more active than [$TiCl_3Cp$]/$AlMe_3$ where minimal polyethylene was formed. When the polymerisation was carried out in light petroleum (bp 40–60 °C) (run 4) polyethylene production dropped to 30% of the toluene reaction (run 1). At 20 psi the production in light petroleum (run 5) was 1.4 times that of run 1 whereas in toluene (run 6) production dropped to about 90% of run 1. The 2,6-di-*tert*-butylphenoxide complex **9** had approximately only $\frac{1}{2}$ the activity at 6 psi (run 7) found for complex **2** in run 1.

Conclusion

The results of these studies show that whereas monophenoxide complexes, [$TiCl_3(OAr)$], can be prepared by a simple thermalisation reaction, dynamic processes complicate the solution chemistry, especially where the phenyl substituents are 2,6-diisopropyl or 2,4-di-*tert*-butyl substituents, but more importantly when a bidentate donor such as dmbipy is added. The complex [$TiCl_3\{OC_6H_2(CMe_3)_2$-2,6-Me-4\}] **7**, in which the phenoxide ligand has structural similarities longitudinally to the 1,3-bis-*tert*-butylcyclopentadienyl ligand, remains unchanged in solution and is unaffected by dmbipy. Theoretical studies show that O(2p) lone pair donation to the phenyl ring C=C (π*) orbital reduces electron donation to the metal and structural comparisons of complex **7** and [$TiCl_3Cp$] complexes reflect this in the longer Ti–Cl bonds in the Cp complexes. Whereas a phenoxide ligand can be regarded as a 1σ, 2π donor, it is likely to create a more electron deficient titanium centre than does a Cp ligand when chloro ligands are replaced by methyl ligands. This may be reflected by the higher catalytic activity of complex **2** towards ethylene polymerisation than [$TiCl_3Cp$] when $AlMe_3$ co-catalyst is used.

Preliminary studies indicate that the [$TiCl_3(OAr)$] complexes are more easily reduced than [$TiCl_3Cp$] and this, coupled with the solution dynamics, suggests the co-ordination chemistry of the monophenoxides will be complicated. However, the potential of the less highly substituted phenoxide complexes, and in particular **7**, to act as catalysts in a variety of situations should not be underestimated. Studies are at present underway to establish the wider applicability of these systems.

Experimental

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard bench-top techniques for air sensitive substances. Titanium tetrachloride and the phenols were used as received from commercial sources. 4,4′-Dimethyl-2,2′-bipyridine and phenanthroline were dried under vacuum before use. Light petroleum (bp 40–60 °C) and toluene were distilled from sodium wire and dichloromethane from freshly ground CaH_2. Proton and ^{13}C-{^1H} NMR spectra were recorded at 400 and 100 MHz respectively in $CDCl_3$ solution on a Bruker AM400 spectrometer; $CDCl_3$ was dried over, and distilled from, freshly ground CaH_2. Molecular weights were determined cryoscopically in benzene with a Knauer molecular weight determination apparatus under N_2 gas conditions using concentrations in the vicinity of 0.065 mol dm^{-3}. The C, H and N analyses were determined by Dr A Cunninghame and associates, University of Otago, New Zealand. Chlorine was gravimetrically determined.

Syntheses

[$TiCl_3(OC_6H_5)$] 1. Phenol (1.5 g, 15.9 mmol) in toluene (30 cm^3) was added *via* a cannula to $TiCl_4$ (3.1 g, 16.3 mmol) in toluene (40 cm^3) and the solution refluxed until the exhaust gases no longer produced a white cloud when passed over *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (8 h). The solution was filtered, the solvent removed and the residue washed with light petroleum (5 × 20 cm^3) and dried under vacuum for several hours. This procedure leaves traces of toluene in the dark red sample (see analytical data, Table 1). A solvent-free product has been obtained by preparing the complex in a mixture of $CHCl_3$ and light petroleum and boiling off the $CHCl_3$.[8]

[$TiCl_3(OC_6H_4CMe_3$-4)] 2. *p*-*tert*-Butylphenol (4.75 g, 31.6 mmol) in toluene (50 cm^3) was added *via* a cannula to $TiCl_4$ (6.0 g, 31.6 mmol) in toluene (60 cm^3) and the mixture refluxed until HCl gas was no longer produced (12–18 h). The solution was filtered and the solvent removed to give the complex as a deep red solid which was dried under vacuum for 3 h. This procedure leaves traces of toluene in the sample (see analytical data, Table 1). When smaller quantities (*ca.* 1–2 g) were allowed to stand in light petroleum for crystallisation during long periods (*e.g.* several days) in more dilute solution red crystals of [$TiCl_2(OC_6H_4CMe_3$-4$)_2$] were slowly formed and the remaining solution fumed vigorously in moist air as $TiCl_4$ hydrolysed. Found: C, 58.0; H, 6.5. $C_{20}H_{26}Cl_2O_2Ti$ requires C, 57.6; H, 6.3%. After several such crystallisations the solution was then concentrated and [$TiCl_3(OC_6H_4CMe_3$-4)] formed within several hours. Found: C, 40.2; H, 4.7. $C_{10}H_{13}Cl_3OTi$ requires C, 39.7; H, 4.3%. NMR (C_6D_6): ^1H, δ 1.19 (s, 9 H, CMe_3); 6.94 [d, ^3J(HH) 8.2, 2 H, *o*-H] and 7.00 [d, ^3J(HH) 8.2 Hz, 2 H, *m*-H]; ^{13}C-{^1H} δ 31.69 (CMe_3); 35.05 (C); 118.82 (*o*-C); 126.75 (*m*-C); 150.35 (*p*-C) and 170.53 (*ipso*-C).

Reaction of complex 2 with dmbipy. *Procedure A.* 4,4′-Dimethyl-2,2′-bipyridine (0.61 g, 3.3 mmol) in CH_2Cl_2 (30 cm^3) was added to a rapidly stirred solution of complex **2** (1.0 g, 3.3 mmol) in CH_2Cl_2 (20 cm^3) *via* a cannula and the stirring continued for 2 h. The solution was filtered and the solvent removed to give an orange solid which was then allowed to stand under light petroleum overnight to give an orange powder [Found: C, 57.1; H, 5.5; N, 5.3. $C_{22}H_{25}Cl_3NOTi$

requires C, 57.0; H, 5.4; N, 5.3%]. The ^{1}H NMR spectrum in $CDCl_3$ shows the presence of *mer*-[$TiCl_3(OC_6H_4CMe_3$-4)-(dmbipy)] **3** and [$TiCl_2(OC_6H_4CMe_3$-4$)_2$(dmbipy)] in a ratio of 63 : 34.

Procedure B. Complex **2** (0.45 g, 1.5 mmol) was dissolved in light petroleum (70 cm^3) and the solution filtered from a small amount of solid. To this rapidly stirred solution was added dmbipy (0.28 g, 1.52 mmol) in light petroleum (10 cm^3) and benzene (20 cm^3) to give an immediate orange precipitate. After stirring for 1 h the solution was filtered and the solid washed with light petroleum (5 × 20 cm^3) and held under vacuum for 1 h [Found: C, 55.7; H, 5.4; N, 5.8. $C_{22}H_{25}Cl_3NOTi\cdot0.33C_6H_6$ requires C, 56.1; H, 5.4; N, 5.5%]. The solid dissolves in $CDCl_3$ and then produces a precipitate. A ^{1}H NMR spectrum shows *mer*-[$TiCl_3(OC_6H_4CMe_3$-4)(dmbipy)] **3** and [$TiCl_2(OC_6H_4$-CMe_3-4$)_2$(dmbipy)] in a ratio of 20 : 80. Benzene solvent (δ 7.28) decreased after heating the solid under vacuum.

[$TiCl_3(OC_6H_2Me_3$-2,4,6)] 4. 2,4,6-Trimethylphenol (2.1 g, 15.4 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene and the mixture refluxed until the production of HCl ceased (10 h). The solution was filtered, the solvent removed and the dark red solid washed with light petroleum (5 × 20 cm^3). The residue was then dried under vacuum for several hours. This procedure leaves a trace of toluene in the sample (see analytical data, Table 1).

[$TiCl_3(OC_6H_3Pr^i_2$-2,6)] 5. 2,6-Diisopropylphenol (4.7 g, 26.4 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (5.0 g, 26.4 mmol) in toluene (50 cm^3) and the mixture refluxed until the production of HCl ceased (12 h). The solution was filtered and the solvent removed to give a deep red gum which solidified on gentle heating (water bath 60–70 °C) under vacuum for several hours.

Reaction of complex 5 with dmbipy. *Procedure A.* The compound dmbipy (0.47 g, 2.6 mmol) in CH_2Cl_2 (30 cm^3) was added to a rapidly stirred solution of complex **2** (0.85 g, 2.6 mmol) *via* a cannula and stirring continued for 2 h. The orange solution was filtered, the solvent removed and the residue allowed to stand under light petroleum (50 cm^3) for 2 d. Filtration gave an orange powder [Found: C, 56.4; H, 5.8; N, 5.3. $C_{24}H_{29}Cl_3NOTi$ requires C, 55.9; H, 5.7; N, 5.4%]. The ^{1}H NMR spectrum in $CDCl_3$ shows the presence of *mer*-[$TiCl_3(OC_6H_3Pr^i_2$-2,6)-(dmbipy)] **6** and [$TiCl_2(OC_6H_3Pr^i_2$-2,6$)_2$(dmbipy)] in a ratio of 55 : 45.

Procedure B. The compound dmbipy (0.35 g, 1.9 mmol) in benzene (25 cm^3) was added rapidly to complex **5** (0.63 g, 1.9 mmol) in light petroleum (70 cm^3) and the mixture stirred for 1 h. The orange solid was filtered off, washed with light petroleum (2 × 30 cm^3) and held under vacuum for 2 h [Found: C, 60.5; H, 6.2; N, 5.4. $C_{24}H_{29}Cl_3NOTi\cdot0.83C_6H_6$ requires C, 60.7; H, 6.0; N, 4.7%]. The solid dissolves in $CDCl_3$ and then produces a precipitate. A ^{1}H NMR spectrum shows *mer*-[$TiCl_3(OC_6H_3Pr^i_2$-2,6)(dmbipy)] **6** and [$TiCl_2(OC_6H_3Pr^i_2$-2,6$)_2$-(dmbipy)] in a ratio of 55 : 45. Benzene solvent (δ 7.28) decreases after heating the solid in vacuum.

[$TiCl_3\{OC_6H_2(CMe_3)_2$-2,6-Me-4\}] 7. 2,6-Di-*tert*-butyl-4-methylphenol (2.3 g, 10.5 mmol) in light petroleum (50 cm^3) was added to $TiCl_4$ (2.0 g, 10.5 mmol) in light petroleum (30 cm^3) and the mixture refluxed until the production of HCl ceased (12–15 h). The solution was filtered and the solvent removed to give a solid which is essentially pure (NMR spectroscopy). An analytically pure crystalline sample was obtained by dissolving a portion of the bulk sample in hot light petroleum and allowing the sample to stand.

[$TiCl_3\{OC_6H_3(CMe_3)_2$-2,4\}] 8. *Procedure A.* 2,4-Di-*tert*-butylphenol (3.25 g, 15.8 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene (30 cm^3) and the mixture refluxed until the production of HCl ceased (14 h). The solution was filtered and the solvent removed to give a deep red solid which, on dissolving in light petroleum (100 cm^3) and reducing the volume, was washed with light petroleum (20 × 30 cm^3) and dried under vacuum.

Procedure B. 2,4,6-Tri-*tert*-butylphenol (4.2 g, 16.0 mmol) in toluene (40 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene (50 cm^3) and the mixture refluxed until the production of HCl ceased (*ca.* 16 h). The solution was filtered and the solvent removed to give a dark red solid which, on dissolving in light petroleum (100 cm^3) and reducing the volume, gave the complex as dark red microcrystals (yield 3.4 g, 60%) [Found: C, 47.2; H, 6.1. $C_{14}H_{21}Cl_3OTi$ requires C, 46.7; H, 5.9%]. The product showed identical ^{1}H and ^{13}C-{^{1}H} NMR spectra to the sample prepared under A.

[$TiCl_3\{OC_6H_2(CMe_3)_2$-2,6-OMe-4\}] 9. 2,6-Di-*tert*-butyl-4-methoxyphenol (3.72 g, 15.7 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene (50 cm^3) and the mixture refluxed until the production of HCl ceased (11 h). The solution was filtered and the solvent removed to give a gum which gave the complex as a purple crystalline mass after extended drying under vacuum (5 h).

[$TiCl_3(OC_6H_3CMe_3$-2-Me-4)] 10. 2-*tert*-Butyl-4-methylphenol (2.6 g, 15.8 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene (30 cm^3) and the mixture refluxed until production of HCl gas ceased (13 h). The solution was filtered and the solvent removed to give a deep red solid which was dried under vacuum for 4 h [Found: C, 42.6; H, 5.4. $C_{11}H_{15}Cl_3OTi\cdot0.0625C_7H_8$ requires C, 42.6; H, 4.9%]. The solid was dissolved in boiling light petroleum (120 cm^3), the solution filtered while hot and the volume reduced while keeping the solution hot to give an analytically pure sample as a deep red solid.

[$TiCl_3(OC_6H_4Ph$-2)] 11. 2-Phenylphenol (1.8 g, 10.6 mmol) in CH_2Cl_2 (25 cm^3) was added to $TiCl_4$ (2.0 g, 10.6 mmol) in CH_2Cl_2 (25 cm^3) and the mixture refluxed until the production of HCl gas ceased (12.5 h). The solution was filtered, the solvent removed and the residue held under vacuum for 4 h giving the complex as a deep red solid. The complex is partially soluble in $CHCl_3$, less so in benzene or toluene and only slightly soluble in light petroleum.

[$TiCl_3(OC_{10}H_7)$] 12. 1-Naphthol (2.25 g, 15.6 mmol) in toluene (50 cm^3) was added to $TiCl_4$ (3.0 g, 15.8 mmol) in toluene (20 cm^3) and the mixture refluxed for 11.5 h. The solution was filtered, the solvent removed and the product held under vacuum for 4 h. This procedure leaves toluene in the sample (see analytical data, Table 1). The solid is only slightly soluble in $CDCl_3$ but the ^{1}H NMR shows the presence of extracted toluene.

Polymerisations

Polymerisations were performed in a 400 cm^3 flame-dried pressure bottle equipped with a head containing inlet and outlet taps and a pressure gauge. Toluene (20 cm^3) and $AlMe_3$ in toluene [1 cm^3 of a 0.072 g cm^{-3} solution (approximately 7 mol equivalents)] were added *via* a syringe to the vessel which contained a Teflon stirring bar and the mixture was saturated with ethylene until the head pressure remained at 6 psi. Complex **2** (0.045 g, 1.5 mmol) in toluene (29 cm^3) was added *via* a cannula under nitrogen keeping a stream of ethylene flowing from the pressure bottle during the addition. The mixture was stirred vigorously for 1 h at 21 °C while maintaining the head pressure at 6 psi. The polymerisation was terminated by degassing the solution (bubbling N_2 through the solution) and adding methanol (100 cm^3) containing 5% HCl solution. The polyethylene was filtered off, broken into small pieces, washed extensively with methanol to remove impurities and dried under vacuum to constant weight.

X-Ray crystallography

Crystals of complex **7** were grown from a light petroleum solution. Data were collected on a Siemens SMART diffractometer. The collection covered a nominal sphere of reciprocal space, by a combination of four sets of exposures. Each set had a different φ angle for the crystal and each exposure covered 0.3° in α. Coverage of the unique data set is at least 98% complete to 56° in 2θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. 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. The structure was solved by direct methods and refined 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, 0.96 Å) and refined with a riding model with $U_{iso} = 0.05$. Programs used were SHELXS[26] for structure solution and SHELXL[27] for refinement. Diagrams were prepared with ORTEP 3.[28]

Crystal data. $C_{15}H_{23}Cl_3OTi$, $M = 373.58$, monoclinic, space group $P2_1/c$, $a = 17.294(3)$, $b = 6.1220(10)$, $c = 17.833(4)$ Å, $\beta = 108.36(3)°$, $U = 1791.9(6)$ Å^3, $T = 203$ K, $Z = 4$, μ(Mo-Kα) = 0.918 mm^{-1}, 3416 observed reflections, final $wR(F^2)$ for all 4032 data 0.1024, $R1 = 0.0466$.

CCDC reference number 186/1795.

See http://www.rsc.org/suppdata/dt/a9/a908435e/ for crystallographic files in .cif format.

Theoretical

Density functional calculations[29] were carried out on the complexes $[TiCl_3(OC_6H_2Me_3\text{-}2,4,6)]$ **4**, $[TiCl_3(OMe)]$ and $TiCl_3Me$. The hybrid Becke-3 parameter functional (B3)[30] together with the Lee–Yang–Parr correlation functional (LYP)[31] has been used in all calculations. Owing to the large size of molecule **4** the basis set was restricted to a Dunning/Huzinaga valence double-zeta set for H, C and O[32] using Hay–Wadt pseudo-potentials with valence double-zeta basis sets for Cl and Ti.[33] This resulted in 378 basis functions contracted to 158 and the geometry optimisation required several days on a 16-processor R10000 SGI supercomputer. At the optimised geometry a subsequent natural bond orbital analysis was carried out.

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References

1 H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger and R. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1998, 1413; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 429.

2 T. V. Lubben, P. T. Wolczanski and G. D. Van Duyne, *Organometallics*, 1984, **3**, 977.

3 K. Soga, J. R. Park and Y. Shiono, *Polym. Commun.*, 1989, **22**, 2126; J. R. Park, T. Shiono and K. Soga, *Macromolecules*, 1992, **25**, 521; C. Pellecchia, A. Immirzi, A. Grassi and A. Zambelli, *Organometallics*, 1993, **12**, 4473; R. Quyoum, Q. Wang, M. J. Tudoret, M. C. Baird and D. J. Gillis, *J. Am. Chem. Soc.*, 1994, **116**, 6435; D. Jeremic, Q. Wang, R. Quyoum and M. C. Baird, *J. Organomet. Chem.*, 1995, **497**, 143; S. W. Ewart, M. J. Sarsfield, D. Jeremic, T. L. Tremblay and M. C. Baird, *Organometallics*, 1998, **17**, 1502.

4 G. Ricci and L. Porri, *Macromolecules*, 1994, **27**, 868.

5 N. Ishichara, T. Seimiya, M. Kuramoto and M. Uoi, *Macromolecules*, 1986, **19**, 2464; N. Ishihara, M. Kuramoto and M. Uoi, *Macromolecules*, 1988, **21**, 3356; A. Zambelli, L. Oliva and C. Pellecchia, *Macromolecules*, 1989, **22**, 2129; J. C. W. Chien, Z. Salajka and S. Dong, *Macromolecules*, 1992, **25**, 3199; T. E. Ready, R. O. Day, J. C. W. Chien and M. D. Rausch, *Macromolecules*, 1993, **26**, 5822; D. J. Duncalf, H. J. Wade, C. Waterson, P. J. Derrick, D. M. Haddleton and A. McCamley, *Macromolecules*, 1996, **29**, 6399; W. Kaminsky, S. Lenk, V. Scholz, H. W. Roesky and A. Herzog, *Macromolecules*, 1997, **30**, 7647.

6 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978; K. C. Malhotra and R. L. Martin, *J. Organomet. Chem.*, 1982, **239**, 159.

7 M. H. Chisholm, *Chemtracts*, 1992, **4**, 273.

8 G. P. Lutschinsky and E. S. Al'tman, *Z. Anorg. Allg. Chem.*, 1935, **225**, 321.

9 R. W. Crowe and A. N. Caughlan, *J. Am. Chem. Soc.*, 1950, **72**, 1694.

10 S. Shah, A. Singh and R. C. Mehrotra, *Polyhedron*, 1986, **3**, 1285.

11 G. Sartori, G. Casnati, F. Bigi and G. Predieri, *J. Org. Chem*, 1990, **55**, 4371.

12 D. L. Barnes, N. W. Eilerts and J. A. Heppert, *Polyhedron*, 1994, **13**, 743.

13 P. Aaltonen, J. Seppala, L. Matilainen and M. Leskela, *Macromolecules*, 1994, **27**, 3136.

14 L. Matilainen, M. Klinga and M. Leskela, *Polyhedron*, 1996, **15**, 153.

15 M. W. Glenny, A. J. Nielson and C. E. F. Richard, *Polyhedron*, 1998, **17**, 851.

16 P. Sobota and S. Szafert, *Inorg. Chem.*, 1996, **35**, 1778; G. Morini, E. Albizzati, G. Balbontin, I. Mingozzi, M. C. Sacchi, F. Forlini and I. Tritto, *Macromolecules*, 1996, **29**, 5770; P. Sobota and S. Szafert, *Inorg. Chem.*, 1996, **35**, 1778; J. Xu, L. Feng, S. Yang, Y. Yang and X. Kong, *Macromolecules*, 1997, **30**, 7655.

17 J. R. Dilworth, J. Hanich and M. Krestel, *J. Organomet. Chem.*, 1986, **315**, C9.

18 Y. Morino and H. Uehara, *J. Chem. Phys.*, 1966, **45**, 4543.

19 L. M. Engelhardt, R. I. Papasergio, C. L. Raston and A. H. White, *Organometallics*, 1984, **3**, 18.

20 C. H. Winter, X.-X. Zhou, D. A. Dobbs and J. Heeg, *Organometallics*, 1991, **10**, 210.

21 I. Jibril, S. Abu-Orabi, S. A. Klaib, W. Imhof and G. Huttner, *J. Organomet. Chem.*, 1992, **433**, 253.

22 H.-M. Gau, C.-S. Lee, C.-C. Lin, M.-K. Jiang, Y.-C. Ho and C.-N. Kuo, *J. Am. Chem. Soc.*, 1996, **118**, 2936.

23 S. L. Latesky, J. Keddington, A. K. McMullen, I. P. Rothwell and J. C. Huffman, *Inorg. Chem.*, 1985, **24**, 995.

24 R. L. Martin and G. Winter, *J. Chem. Soc.*, 1961, 2947.

25 C. N. Field, J. C. Green, N. Kaltsoyannis, G. S. McGrady, A. N. Moody, M. Siggel and M. De Simone, *J. Chem. Soc., Dalton Trans.*, 1997, 213.

26 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

27 G. M. Sheldrick, SHELXL 93, Program for the refinement of crystal structures, University of Göttingen, 1993.

28 ORTEP 3 for WINDOWS, Based on ORTEP III, C. K. Johnson and M. N. Burnette, Report ORNL-6895, modified by L. J. Farrugia, University of Glasgow, 1996.

29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN 94, Revision D.1, Gaussian, Inc., Pittsburgh, PA, 1996.

30 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

31 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

32 T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H. F. Schaefer III, Plenum, New York, 1976, pp. 1–28.

33 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

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