# Reactivity of boranes with a titanium(IV) amine tris(phenolate) alkoxide complex; formation of a Ti(IV) tetrahydroborate complex, a Ti(III) dimer and a Ti(IV) hydroxide Lewis acid adduct<sup>†</sup>‡

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Treatment of the titanium(IV) alkoxide complex  $[Ti(O'Pr)(OC_6Me_2H_2CH_2)_3N]$  (2) with BH<sub>3</sub>·THF, as part of a study into the utility and reactivity of (2) in the metal mediated borane reduction of acetophenone, results in alkoxide–hydride exchange and formation of the structurally characterised titanium(IV) tetrahydroborate complex  $[Ti{BH_4}(OC_6Me_2H_2CH_2)_3N]$  (3). Complex (3) readily undergoes reduction to form the isolable titanium(III) species  $[Ti(OC_6Me_2H_2CH_2)_3N]_2$  (4). Reaction of (2) with  $B(C_6F_5)_3$  results in formation of the Lewis acid adduct  $[Ti(OC_6Me_2H_2CH_2)_3N]_[HO \cdot B(C_6F_5)_3]$ (5). In comparison, treatment of the less sterically encumbered alkoxide  $Ti(O'Pr)_4$  with  $B(C_6F_5)_3$  results in alkoxide–aryl exchange and formation of the organometallic titanium complex  $[Ti(O'Pr)_3(C_6F_5)]_2$  (6). The molecular structures of 3, 4, 5 and 6 have been determined by X-ray diffraction.

# Introduction

The first reported reaction of the simple borane  $BH_3$ ·THF, with the group(IV) alkoxide complex, Ti(O'Bu)<sub>4</sub>, to form the tetrahydroborate complex Ti(BH<sub>4</sub>)<sub>2</sub>(O'Bu), was published in 1966 by James and Wallbridge.<sup>1</sup> Since then, the reaction of boranes such as  $BH_3$ ·L and  $B_2H_6$  with metal alkoxides has provided a method for the synthesis of metal tetrahydroborate systems.<sup>2</sup> The variable coordination modes of  $[BH_4]^-$  ( $\eta^1$ ,  $\eta^2$  and  $\eta^3$ ) have led to descriptions of tetrahydroborate as a 'gate-keeper' ligand,<sup>3</sup> with exploitation of the variable bonding to moderate the coordinative saturation at the metal. As such, many compounds containing tetrahydroborate ligands (and other B–H groups) have been, and continue to be, investigated for their potential catalytic activity in areas such as olefin polymerisation,<sup>3</sup> ring-opening polymerisation of cyclic esters,<sup>4</sup> hydrogenation,<sup>5</sup> hydroboration<sup>6</sup> and reduction reactions.<sup>7</sup>

Unfortunately, reactions between transition metal alkoxides and boranes often result in reduction of the metal centre to a lower oxidation state; however, in the very few cases that this method has been used successfully, the physical and chemical data for such products is sparse.<sup>1,2,8</sup>

More recently the reactive chemistry of the strongly Lewis acidic borane  $B(C_6F_5)_3$ , which has been extensively studied for its application in catalytic processes,<sup>9</sup> has attracted considerable interest, and reactions with metal-oxo,<sup>10</sup> metal-acyl,<sup>11</sup> metal-alkoxide<sup>12</sup> and metal-carbonyl<sup>13</sup> sytems have all been reported.

We have recently been interested in the utility of the tris-(phenolamine) ligand  $(LH_3)$ , 1 (Fig. 1), as scaffolds for the

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production of stable titanium(IV) complexes and their utility in catalytic applications.<sup>14</sup> Here we report the reactivity of the amine tris(phenolate) titanium isopropoxide, **2**, with BH<sub>3</sub>·THF, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and BPh<sub>3</sub> respectively and describe the differing reactivity of these boranes towards the titanium species. As part of this study we also describe the reactivity of Ti(O'Pr)<sub>4</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and formation of alkoxide–aryl exchange products.



Fig. 1 Tris(phenolamine) ligand (LH<sub>3</sub>), 1.

# **Results and discussion**

Titanium alkoxide compounds have been known for some time to mediate reactions such as hydroboration<sup>6</sup> and carbonyl reduction<sup>7</sup> in the presence of boranes, and while many of these reactions are complicated, metal hydrides and metal borohydrides have been suggested as potentially reactive species.<sup>3-7</sup> For this reason we have been interested in the utility of the metal alkoxide complex, **2**, as a catalyst in the reduction of carbonyl species, and the general reactivity of such alkoxide complexes with other borane systems.

It has previously been shown that the uncatalysed room temperature reaction of borohydrides with acetophenone requires *ca.* 24 h for complete reduction; the addition of  $Ti(O'Pr)_4$  reduces this reaction time to 30 min with a 93% yield.<sup>7b</sup> Preliminary screening experiments showed that **2** is a moderately effective precatalyst for the reduction of acetophenone at room temperature

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<sup>&</sup>lt;sup>†</sup> Dedicated to Prof. Ken Wade, a friend and mentor, on the occasion of his 75th birthday.

(2 h, 94% isolated yield) (Scheme 1). However, due the inherent racemic nature of 2, no enantioselectivity was observed.<sup>14a</sup>



Scheme 1 Reduction of acetophenone by  $BH_3$ . THF in the presence of metal alkoxide catalyst, 2.

Addition of  $BH_3$ ·THF (or  $BH_3$ ·SMe<sub>2</sub>) to a THF solution of **2**, in the presence of substrate (1 : 10.1 : 10) results in an immediate colour change of the solution from pale yellow to red. However, in the absence of ketone the reaction mixture slowly (several hours) undergoes further colour changes at room temperature from red– orange, through green, to a dark blue–purple solution, indicating the production of a Ti(III) species, the production of which is enhanced at elevated temperatures.

#### (i) Reaction of 2 with BH<sub>3</sub>

In an attempt to elucidate the role of the metal alkoxide complex 2 in the borane reduction, the reaction between the metal alkoxide and BH<sub>3</sub> was investigated. The reaction of 2, in toluene, with excess BH<sub>3</sub>·THF at -20 °C results in an immediate colour change from pale yellow to deep red. On standing overnight, at -60 °C, highly air-sensitive crystals of the titanium(IV) tetrahydroborate complex, (L)Ti{BH<sub>4</sub>} 3, were formed, the identity of which was established spectroscopically and confirmed by single crystal X-ray diffraction (Fig. 2).

The monomeric,  $C_3$ -symmetric complex contains an approximately trigonal bipyramidal Ti centre, which sits slightly out of the 'pocket' of the equatorial phenolate-O atoms compared to  $2^{14a}$  [distance of Ti atom above the plane of the three phenolate-O atoms: 0.251(1), 0.247(1) Å for 2 and 0.276(2) Å for 3]. The axial sites around the metal are occupied by the neutral nitrogen atom of the ligand, and the  $\{BH_4\}$  unit which is bound to the central metal in a  $\eta^3$ -fashion (via three hydride bridges) [Ti(1)-B(1) 2.230(7) Å.]. A superficial comparison between 3 and the parent titanium complex 2, shows that despite replacement of the terminal alkoxide ligand for a  $\{BH_4\}$  group there is little change in the coordination of the amine tris(phenolate) ligand to titanium [average Ti-O(phenolate) distance: 1.850 Å for 2 and 1.823(2) Å for 3] [Ti–N distances: 2.303(2), 2.295(2) Å for 2 and 2.393(4) Å for 3]. As for 2, complex 3 shows 'propeller' chirality, evidenced by the P and M enantiomers inherent in the crystallographic classification, and the two resonances at  $\delta$  2.84 and 3.91 ppm observed in the <sup>1</sup>H NMR spectra assigned to the diastereotopic N-



Fig. 2 ORTEP (50% probability ellipsoids) diagram of 3. Selected bond lengths (Å): Ti(1)-O(1) 1.823(2), Ti(1)-N(1) 2.393(4), Ti(1)-B(1) 2.230(7), Ti(1)-H(2B) 2.05(5), O(1)-C(1) 1.367(4); Bond angles (°): Ti(1)-O(1)-C(1) 137.8(2), N(1)-Ti(1)-O(1) 81.29(7), O(1)-Ti(1)-B(1) 98.71(7), H(1B)-B(1)-H(2B) 114.0(2). Toluene of crystallisation and non-{BH} hydrogen atoms have been omitted for clarity.

CH<sub>2</sub> protons of the tripodal ligand. The <sup>1</sup>H{<sup>11</sup>B} NMR spectrum of compound **3** reveals the presence of a single resonance for the {BH<sub>4</sub>} ligand which is consistent with the rapid exchange of terminal and bridging hydrogen atoms at ambient temperatures, resulting in magnetic degeneracy. <sup>11</sup>B NMR spectroscopy confirms this fluxional behaviour with the appearance of a quintet at  $\delta$ 16.3 ppm ( $J_{B-H} = 86$  Hz) in the <sup>11</sup>B NMR spectrum at room temperature.<sup>2b</sup>

To our knowledge, there exist only seven other examples of crystallographically characterised titanium(IV) tetrahydroborate complexes.<sup>15</sup> Therefore complex **3** represents a rare example of a structurally characterised titanium(IV) tetrahydroborate derivative. Moreover, **3** represents the first structurally characterised product of an alkoxide–hydride exchange reaction, as the more common synthetic route to tetrahydroborate derivatives is *via* the reaction of metal halides with Li[BH<sub>4</sub>].<sup>2</sup> Interestingly, a common feature of **3** and other crystallographically characterised tetrahydroborate complexes is the use of bulky ligand systems which presumably lend a significant kinetic stability to the system.

The mode of formation (Scheme 2) of the complex can be inferred from *in situ* <sup>11</sup>B NMR studies performed on the reaction mixture. Addition of excess BH<sub>3</sub>·THF to **2** results in the immediate formation of **3** ( $\delta$  = 16.3 ppm ( $J_{B-H}$  = 86 Hz)), along with HB(O'Pr)<sub>2</sub> ( $\delta$  = 27.3 ppm)<sup>16</sup> which presumably arises from a rapid exchange process between two molecules of the unobserved



Scheme 2 Reaction schemes for the production of the titanium tetrahydroborate 3 from the metal alkoxide 2, showing the proposed intermediates.

H<sub>2</sub>BO<sup>*i*</sup>Pr. This observation is entirely consistent with other reports on the relative exchange rates in alkoxyboron hydride species.<sup>17</sup> Similar reactions between BH<sub>3</sub>. THF and metal chloride complexes have been recorded and NMR studies have shown conclusively that reactions proceed with the loss of BH<sub>2</sub>Cl.<sup>18</sup> We therefore suggest that the formation of 3 proceeds in an analogous manner. In particular, product formation is initiated by BH<sub>3</sub> coordination to the Lewis basic alkoxide group, followed by elimination of mono-alkoxyborane and the formation of a transient titanium hydride species. This short-lived metal hydride has the potential to react with a suitable substrate (as in Scheme 1), or alternatively, is trapped by reaction with excess BH<sub>3</sub> and results in the formation and isolation of the metal borahydride complex 3 (Scheme 2). Indeed, comparable exchange reactions between boron trihalides e.g. BCl<sub>3</sub> with metal alkoxides and metal amides have been known for some time.<sup>19</sup> It is interesting to note that although 2 reacts rapidly with both BH<sub>3</sub>·THF and BH<sub>3</sub>·SMe<sub>2</sub>, the system was found to be inactive when catecholborane and pinacolborane were used. Similarly, when BH<sub>3</sub>·N(H)Me<sub>2</sub> was used the reaction was found to be much slower. We believe these observations to be consistent with the formation of a metal alkoxide-borane adduct, with the less Lewis acidic of the boranes (either through slow adduct dissociation or by virtue of electron donation from ligands) resulting in slower or impaired reactions.

Titanium(IV) hydride species are a highly reactive class of compounds that have been implicated in a number of catalytic reaction processes,<sup>2b</sup> but despite their importance only a few examples are known.<sup>20</sup> In many cases metal tetrahydroborate complexes have been viewed as 'protected' metal hydride systems in which the first step in the activation pathway is the loss of BH<sub>3</sub> and the formation of a transient metal hydride species. In an effort to isolate the proposed titanium(IV) hydride complex (Scheme 2), a toluene solution of 3 was treated with two molar equivalents of PMe<sub>3</sub>, at -78 °C in the expectation that either the hydride species, or a PMe<sub>3</sub> adduct, (Scheme 3) could be isolated in an analogous reaction to those previously reported by Nöth involving  $(ArO)_{3}Ti\{BH_{4}\}$  (ArO = 2,6-di-*iso*-propylphenyl).<sup>21</sup> The resulting immediate colour change from red through green to purple-blue indicated that any hydride intermediate that might be forming in the reaction rapidly decomposes to yield a highly reactive Ti(III) species. Crystals of 4 were grown from a toluene solution at -20 °C, in order to undertake structural characterisation.



Scheme 3 Proposed reaction scheme for the synthesis of Ti(IV) hydride species.

An X-ray crystallographic study of **4** reveals it to be a dimeric complex, with two inversion related  $\{(L)Ti^{(III)}\}\$  units bridged by a phenoxide unit of the tris(phenolate) ligand (Fig. 3), which is reminiscent of the related Al(III) tris(phenolate) complex  $\{(L)Al\}_2$ , recently reported by Verkade.<sup>22</sup> The geometry about each titanium atom is best described as distorted trigonal bipyramidal, with



Fig. 3 ORTEP (50% probability ellipsoids) diagram of **4**. Selected bond lengths (Å): Ti(1)–O(1) 1.8724(13), Ti(1)–O(2) 1.8724(13), Ti(1)–O(3) 1.9801(12), Ti(1)–O(3A) 2.0361(13), Ti(1)–N(1) 2.2412(15), O(1)–C(1) 1.352(2), O(2)–C(21) 1.349(2), O(3)–C(31) 1.379(2); Bond angles (°): Ti(1)–O(1)–C(1) 135.61(12), Ti(1)–O(2)–C(21) 139.61(12), Ti(1)–O(3)–C(31) 135.98(11), N(1)–Ti(1)–O(3a) 176.08(5). Toluene of crystallisation and hydrogen atoms have been omitted for clarity. The symmetry operator (1 - x, 1 - y, 1 - z) generates the equivalent atoms denoted with 'A'.

the nitrogen atom [Ti(1)–N(1): 2.241(2) Å] and the phenolic oxygen of the neighbouring Ti(III) unit occupying axial positions [Ti(1)–O(3A): 2.0361(13) Å]. As expected, the Ti–O bridging bond is slightly elongated compared to the other equatorial Ti–O contacts [Ti–O distances: 1.872(2), 1.873(2) Å (non bridging) and 1.980(2) Å (bridging)]. The relatively long Ti–Ti distance of 2.6616(6) Å rules out the possibility of metal–metal bonding interactions, and is consistent with the paramagnetic nature of **4**. Although the precise mechanism of Ti(IV) tetrahydroborate decomposition is not clearly understood, is most likely proceeds *via* loss of BH<sub>3</sub> (as BH<sub>3</sub>·PMe<sub>3</sub>) and formation of a Ti(IV) hydride that, in the absence of substrate with which to react, is unstable towards loss of H<sub>2</sub> and reduction of the metal centre to Ti(III) (Fig. 3).<sup>21</sup>

#### (ii) Reaction of 2 with BPh<sub>3</sub> and $B(C_6F_5)_3$

As previously stated, initial reaction between **2** and BH<sub>3</sub>·THF proceeded with a significant excess of borane present in the reaction mixture. Attempts to isolate the proposed borane adduct (Scheme 2) by stoichiometric reactions between **2** and BH<sub>3</sub>·THF were unsuccessful, yielding an equimolar mixture of compounds **2** and **3**. It was hoped that treatment of **2** with a stronger, less labile Lewis acid such as BPh<sub>3</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, where there would be no possibility of alkoxide–hydride exchange, might yield isolable adducts which would (in turn) serve as models for the proposed borane adduct.

Reaction of complex 2 with  $B(C_6F_5)_3$  resulted in an instant colour change from yellow to red and the isolation of red

crystals upon standing overnight, which were characterised and identified as the titanium(IV) hydroxy–Lewis acid adduct  $(L)Ti\{(H)O\cdot B(C_6F_5)_3\}$  (5).

An X-ray crystallographic study of **5** reveals it to be a rare example of a titanium(IV) hydroxide complex in which the titanium hydroxide moiety is coordinated to the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> *via* the oxygen of the hydroxide group (Fig. 4).



Fig. 4 ORTEP (50% probability ellipsoids) diagram of 5. Selected bond lengths (Å): Ti(1)–O(1) 1.9436(16), Ti(1)–O(2) 1.819(3), Ti(1)–O(3) 1.804(3), Ti(1)–O(4) 2.034(3), Ti(1)–N(1) 2.227(3), B(1)–O(4) 1.528(5), B(1)–C(41) 1.640(6), B(1)–C(51) 1.655(6), B(1)–C(61) 1.653(5), O(4)–F(62) 2.691(4), O(4)–H(4) 0.82(3), H(4)–F(62) 1.97(3), O(1)–C(11) 1.388(4), O(2)–C(21) 1.378(5), O(3)–C(31) 1.386(5); Bond angles (°): Ti(1)–O(4)–B(1) 143.5(3), Ti(1)–O(1)–C(11) 141.1(2), Ti(1)–O(2)–C(21) 140.9(2), Ti(1)–O(3)–C(31) 141.6(2), N(1)–Ti(1)–O(4) 170.98(13), O(4)–H(4)–F(62) 147(3). Toluene of crystallisation and hydrogen atoms [except for H(4)] have been omitted for clarity.

The molecular structure of **5** shows a similar coordination mode of the tris(phenolate) ligand to that observed in complexes **2** and **3**, excepting replacement by a { $(H)O \cdot B(C_6F_5)_3$ } unit in an axial site of the pseudo trigonal bipyramidal titanium centre. Coordination of the hydroxyl group by the { $B(C_6F_5)_3$ } [B(1)–O(4): 1.528(5) Å] fragment results in a lengthening of the Ti–O(H) bond and a concomitant shortening of the axial Ti–N bond in comparison to the *tert*-butyl substituted tris(phenolamine) Ti–OH complex reported by Brown *et al.*<sup>23</sup> [Ti(1)–O(4): 2.034(2) Å, Ti(1)–N(1): 2.227(3) Å (*cf.* Ti–O: 1.810(3) and Ti–N: 2.364(3) Å)].

The hydrogen atom of the hydroxide group, which was not observed in the <sup>1</sup>H NMR spectrum, was located by the X-ray structure determination and shown to be involved in a short O–H…F hydrogen bonding interaction with one of the *ortho*-F atoms on an adjacent { $C_6F_5$ } ring of the { $B(C_6F_5)_3$ } unit [O(4)–F(62) 2.691(4) Å; H(4)–F(62) 1.97(3) Å; O(4)–H(4)–F(62)

 $147(3)^{\circ}$ ], which may well account for its absence in the <sup>1</sup>H NMR spectrum.

Previous studies have shown that reaction of  $B(C_6F_5)_3$  with alkoxides have resulted in aryl-alkoxide exchange,12 which is presumably prohibited in the case of 2 by the steric bulk of the amine tris(phenolate) ligand. Indeed reaction of Ti(O'Pr)<sub>4</sub> with  $B(C_6F_5)_3$ , which was conducted as part of this study, results in the formation of the dimeric organometallic complex  ${Ti}(\mu$ - $O'Pr(O'Pr)_2(C_6F_5)$  6, as shown in Fig. 5, the synthesis of which, by reaction of TiCl(O'Pr)<sub>3</sub> with LiC<sub>6</sub>F<sub>5</sub>, has previously been reported.<sup>24</sup> The molecular structure (Fig. 5) establishes that 6 is a dimeric complex with five coordinate distorted trigonal bipyramidal geometry at the metal centres, with each  $\mu^2$ -O'Pr group occupying an axial equatorial site on adjacent metal centres (Fig. 5), such that the ligands bridge the two metal centres asymmetrically, with the equatorial Ti-O bonds [Ti(1)-O(1), 1.9436(15) Å] being shorter than the axial [Ti(1A)–O(1), 2.0852(14) Å]. The C-ipso atom of the perfluorophenyl group occupies a terminal equatorial site [Ti(1)-C(1) 2.177(2) Å] and both ligands are arranged transoid to each other such that the molecule has crystallographic C<sub>i</sub> symmetry. The terminal Ti-O'Pr bond lengths [Ti(1)–O(2), 1.7595(14) Å (axial); Ti(1)–O(3), 1.7656(16) Å (equatorial)] are unsurprisingly shorter than the bridging Ti-O bonds, with very little variation between the axial and equatorial positions.



**Fig. 5** ORTEP (50% probability ellipsoids) diagram of **6**. Selected bond lengths (Å): Ti(1)–O(1A) 2.0852(14), Ti(1)–O(2) 1.7595(14), Ti(1)–C(1) 2.177(2), Ti(1)–O(1) 1.9436(15), Ti(1)–O(3) 1.7656(16); Bond angles (°): O(1A)–Ti(1)–O(2) 167.75(7), O(1)–Ti(1)–C(1) 127.07(8), O(1)–Ti(1)–O(3) 118.87(7), C(1)–Ti(1)–O(3) 108.65(8). Hydrogen atoms have been omitted for clarity. The symmetry operator (1 - x, -y, -z) generates the equivalent atoms denoted with 'A'.

In comparison with the reaction of  $B(C_6F_5)_3$ , treatment of **2** with one molar equivalent of BPh<sub>3</sub> in toluene resulted in a colour change from pale yellow to orange. Allowing the solution to stand at -25 °C overnight resulted in the isolation of a crop of yellow micro-crystals, which were identified by NMR, elemental analysis and mass spectrometry as the previously reported oxo-bridged species (L)Ti–O–Ti(L) (7).<sup>25</sup>

The reactions of BPh<sub>3</sub> and  $B(C_6F_5)_3$  with 2 are consistent with the formation of intermediate alkoxide-borane adducts. In both cases we propose that coordination of the borane results in a Lewis acid promoted loss of alkene (specifically propene in the case of 4 and 5) rather than aryl-exchange which is presumably inhibited by the steric bulk of the amine tris(phenolate) ligand. In the case of the more strongly bound  $B(C_6F_5)_3$ , the steric bulk of the borane adduct inhibits further reaction, facilitating isolation of the reactive hydroxy system 5. For the more weakly coordinated BPh<sub>3</sub> containing system, the lability of the borane allows the hydroxy complex to react further with a second molecule of alkoxide 2, to form the bridged oxo complex 7 and free isopropanol. The absence of H<sub>2</sub>O in the <sup>1</sup>H NMR spectrum of the reaction between  $BPh_3$  and 2, suggests that formation of the oxo complex 7 by a condensation of two molecules of the hydroxide complex is less likely. While we cannot completely exclude the possibility of adventitious hydrolysis to yield 5 and 7, reproducible high yields of these compounds under rigorous anhydrous conditions, in our opinion, suggest alkene elimination from the alkoxide as a more likely source of hydroxyl and oxo functionalities.

# Conclusions

We have demonstrated the reactivity of the boranes  $BH_3 \cdot THF$ ,  $BPh_3$  and  $B(C_6F_5)_3$  with  $\{L\}TiO'Pr$ , and provided insight into the reactive pathways and catalytic role of the metal alkoxide species in borane reductions. Coordination of the borane to the metal alkoxide facilitates exchange between the borane and the metal alkoxide, where sterics permit. In instances where exchange is prohibited by steric bulk, activation of the metal alkoxide by coordination of the borane results in reduction of the alkoxide group, by loss of alkene, and the formation of metal-hydroxy and -oxo species.

## Experimental

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk and glove-box techniques. Solvents were purified by conventional procedures and distilled prior to use. BPh<sub>3</sub>, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, BH<sub>3</sub>·THF and Ti(O'Pr)<sub>4</sub> were purchased from Aldrich and used as received, without further purification. The complex **2** was prepared using literature procedure.<sup>14a</sup>

Solution <sup>1</sup>H and <sup>13</sup>C NMR experiments were performed at ambient temperature using a Bruker Avance-300. <sup>1</sup>H NMR data are referenced to residual non-deuterated solvent.

#### Syntheses of complexes

[Ti{BH<sub>4</sub>}(OC<sub>6</sub>Me<sub>2</sub>H<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] **3.** To a stirred solution of **2** (4 mmol, 2 g) in toluene (15 ml), 8 ml of a 1.0 M solution of BH<sub>3</sub>. THF in THF (8 mmol) was added dropwise by syringe, at 0 °C. The reaction mixture was allowed to warm to room temperature, with stirring, during which time the solution changed colour from orange to a deep red colour. The mixture was allowed to stir at room temperature for 2 h, after which, removal of solvent under reduced pressure resulted in the precipitation of a red residue, which was re-dissolved in a minimum of fresh toluene (10 ml), with gentle heating. The solution has filtered hot to remove insoluble residues. A red crystalline solid was obtained on standing

for 3 h at -20 °C. The solid was collected by filtration, washed with cold hexane, and dried *in vacuo*. Yield: 1.59 g, 83%. Anal. Calcd for C<sub>27</sub>H<sub>34</sub>B<sub>1</sub>N<sub>1</sub>O<sub>3</sub>Ti (C<sub>7</sub>H<sub>8</sub>)<sub>1</sub>: C, 71.5; H, 7.41; N, 2.45: Found: C, 71.1; H, 7.94; N, 2.4; <sup>1</sup>H NMR (300 MHz, 23 °C), CD<sub>2</sub>Cl<sub>2</sub> (ppm):  $\delta$  1.84 (d, 4H, BH<sub>4</sub>) 2.11 (s, 9H, L(*Me*/Me)), 2.14 (s, 9H, L(Me/Me)), 2.97 (m, 3H, CH<sub>2</sub> (AB system)), 3.91 (m, 3H, CH<sub>2</sub> (BA system)), 6.68 (s, 3H, CH arom), 6.81 (s, 3H, CH arom); <sup>11</sup>B NMR (96 MHz, 23 °C) – 16.3 (quint, <sup>1</sup>*J*(B–H) = 84 Hz); <sup>13</sup>C{1H} NMR (100 MHz)  $\delta$  16.3, 21.2, 59.0, 123.7, 124.7, 128.0, 131.6, 132.0, 161.5.3.

**[Ti(OC<sub>6</sub>Me<sub>2</sub>H<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub> 4.** To a stirred solution of **3** (1 mmol, 0.5 g) in toluene (15 ml), 2 ml of a 1.0 M solution of PMe<sub>3</sub> in THF (2 mmol) was added dropwise by syringe, at -15 °C. The reaction mixture was allowed to warm to room temperature, with stirring, during which time the solution changed colour from orange to blue. The mixture was allowed to stir at room temperature for 2 h, after which, removal of solvent under reduced pressure resulted in the precipitation of a blue residue, which was re-dissolved in a minimum of fresh toluene (10 ml), with gentle heating. The solution has filtered warm to remove insoluble residues. A blue–purple crystalline solid was obtained on standing at -20 °C. The solid was collected by filtration, washed with cold hexane, and dried *in vacuo*. Yield: 0.34 g, 74%. Anal. Calcd for C<sub>54</sub>H<sub>60</sub>N<sub>2</sub>O<sub>6</sub>Ti<sub>2</sub>(C<sub>7</sub>H<sub>8</sub>)<sub>3</sub>: C, 74.74; H, 7.02; N, 2.23: Found: C, 74.6; H, 7.9; N, 2.2. FAB MS: m/z 928 [M<sub>2</sub><sup>+</sup>], 464 [M<sup>+</sup>], 416 [M<sup>+</sup> – Ti]

 $[Ti(OC_6Me_2H_2CH_2)_3N][HO \cdot B(C_6F_5)_3]$  5. To a stirred solution of 2 (2 mmol, 1 g) in toluene (15 ml), 2 mmol of  $B(C_6F_5)_3$  (1 g) in toluene (5 ml) was added dropwise at -75 °C. The reaction mixture was allowed to warm to -20 °C, during which time the solution changed colour from orange to a deep red colour. The reaction was allowed to warm to room temperature after which removal of solvent under reduced pressure resulted in the precipitation of a red residue, which was re-dissolved in a minimum of fresh toluene (10 ml), with gentle heating. The solution has filtered warm to remove insoluble residues. A red crystalline solid was obtained on standing for 3 h at -20 °C. The solid was collected by filtration, washed with cold hexane, and dried in vacuo. Yield: 1.43 g, 72%. Anal. Calcd for C<sub>45</sub>H<sub>31</sub>B<sub>1</sub>F<sub>15</sub>N<sub>1</sub>O<sub>4</sub>Ti (C<sub>7</sub>H<sub>8</sub>)<sub>1.5</sub>: C, 58.91; H, 3.83; N, 1.24: Found: C, 58.29; H, 3.81; N, 1.25; <sup>1</sup>H NMR (300 MHz, 23 °C), CD<sub>2</sub>Cl<sub>2</sub> (ppm):  $\delta$  1.73 (s, 9H, L(Me/Me)), 2.17 (s, 9H, L(Me/Me)), 3.09 (m, 3H, CH<sub>2</sub> (AB system)), 4.01 (m, 3H, CH<sub>2</sub> (BA system)), 6.74 (s, 3H, CH arom), 6.79 (s, 3H, CH arom); <sup>11</sup>B NMR (96 MHz, 23 °C) -1.17 (s,  $B(C_6F_6)_3$ ); <sup>13</sup>C{1H} NMR  $(75.5 \text{ MHz}) \ \delta \ 15.7, \ 21.1, \ 59.2, \ 123.4, \ 124.1, \ 128.2, \ 132.2, \ 133.3,$ 160.9; <sup>19</sup>F NMR (376 MHz)  $\delta$  -134.6 (m), -158.8 (m), -164.6 (m).

**[Ti(O'Pr)<sub>3</sub>(C<sub>6</sub>F<sub>5</sub>)]<sub>2</sub> 6.** To a stirred solution of Ti(O'Pr)<sub>4</sub> (1 mmol, 0.3 g) in toluene (15 ml), 1 mmol of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.5 g) in toluene (5 ml) was added dropwise at -75 °C. The reaction was allowed to warm to room temperature, and on standing a colourless crystalline solid was obtained. The solid was collected by filtration, washed with cold hexane, and dried *in vacuo*. A second crop of crystals was obtained from the filtrate by cooling to -20 °C Yield: 0.14 g, 61%. Anal. Calcd for C<sub>30</sub>H<sub>42</sub>F<sub>10</sub>O<sub>6</sub>Ti<sub>2</sub> : C, 45.93; H, 5.40; Found: C, 46.31; H, 5.98; <sup>1</sup>H NMR (300 MHz, 23 °C), CD<sub>2</sub>Cl<sub>2</sub> (ppm): δ1.18 (d, <sup>3</sup>J = 12 Hz, 36H, CH(*CH*<sub>3</sub>)<sub>2</sub>) 4.77 (br m, 6H, *CH*(CH<sub>3</sub>)<sub>2</sub>) <sup>13</sup>C{1H} NMR (75.5 MHz) δ 23.9, 84.8.

Compound	3	4	5	6
Formula	C <sub>34</sub> H <sub>42</sub> BNO <sub>3</sub> Ti	$C_{75}H_{84}N_2O_6Ti_2$	C55.5H42.5BF15NO4Ti	$C_{30}H_{42}F_{10}O_6Ti_2$
Formula weight	571.40	1205.24	1131.1	784.44
T/K	150(2)	150(2)	150(2)	150(2)
Crystal system	Trigonal	Triclinic	Triclinic	Monoclinic
Space group	R3	$P\overline{1}$	$P\overline{1}$	$P2_1/n$
a/Å	14.1580(2)	10.1340(2)	11.8900(5)	8.8980(3)
b/Å		13.3940(2)	14.5430(4)	16.8170(5)
c/Å	26.3930(6)	13.7670(3)	16.4190(7)	12.0480(5)
$a/^{\circ}$	90	66.7420(10)	108.3880(10)	90
β/°	90	70.8950(10)	100.7370(10)	96.5380(10)
y/°	120	80.5040(10)	99.759(3)	90
V/Å <sup>3</sup>	4581.66(14)	1620.87(5)	2566.42(17)	1791.11(11)
Ζ	6	1	2	2
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.243	1.235	1.464	1.455
$\mu/\mathrm{mm}^{-1}$	0.314	0.300	0.269	0.536
F(000)	1824	639	1154	808
Crystal size/mm	$0.175\times0.125\times0.50$	$0.28 \times 0.25 \times 0.15$	$0.3 \times 0.25 \times 0.17$	$0.35 \times 0.3 \times 0.22$
$\theta$ range/°	3.69 to 27.46	3.76 to 27.12	3.55 to 27.26	3.87 to 27.48
Reflections collected	23 103	30 318	48 049	31754
Independent reflections	2311 [R(int) = 0.0547]	7110 [R(int) = 0.0560]	11290[R(int) = 0.0932]	4084 [R(int) = 0.0942]
Reflections $[I > 2\sigma((I)]]$	1803	5402	6259	2765
Data/restraints/parameters	2311/16/137	7110/0/433	11 290/7/695	4084/0/224
Goodness-of-fit on $F^2$	1.047	1.017	1.022	1.058
Final $R1$ , $wR2 [I > 2\sigma(I)]$	0.0481, 0.1232	0.0461, 0.1102	0.0733, 0.1727	0.0446, 0.0879
Final $R1$ , $wR2$ (all data)	0.0670, 0.1343	0.0700, 0.1215	0.148, 0.2095	0.0866, 0.1037
Max, min diff./e Å <sup>-3</sup>	0.330, -0.366	0.496, -0.481	0.755, -0.532	0.258, -0.389

 Table 1
 Crystal data and structure refinement for compounds 3, 4, 5 and 6

[{Ti(OC<sub>6</sub>Me<sub>2</sub>H<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N}( $\mu^2$ -O)] 7. To a stirred solution of of 2 (2 mmol, 1 g) in toluene (15 ml), 2 mmol of BPh<sub>3</sub> (0.48 g) in toluene (5 ml) was added dropwise at -75 °C. The reaction mixture was allowed to warm to room temperature after which removal of solvent under reduced pressure resulted in the precipitation of a yellow–orange residue, which was re-dissolved in a minimum of fresh toluene (10 ml), with gentle heating. The solution has filtered warm to remove insoluble residues. An orange micro-crystalline solid was obtained on standing overnight at -20 °C. The solid was collected by filtration, washed with cold hexane, and dried *in vacuo*. Yield: 0.74 g, 84%. Data for 7 is consistent with that previously reported.<sup>25</sup>

### X-Ray crystallography‡

Crystallographic data for compounds **3**, **4**, **5** and **6** are summarised in Table 1. All data collections were implemented on a Nonius KappaCCD diffractometer, using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were corrected for Lorentz and polarization effects, and structure refinement was by full-matrix least squares on  $F^2$ . Structure solution and refinement was performed using SHELX-86<sup>26</sup> and SHELXL-97<sup>27</sup> software, respectively. Data were uniformly corrected for Lorentz and polarisation. Hydrogen atoms involved in hydrogen bonding and M–H bonding were detected in the penultimate difference Fourier maps and freely refined. All other hydrogen atoms were included at calculated positions throughout, and refined using a riding model.

In **3**, in addition to 1/3 of the complex molecule, the asymmetric unit also contains a fraction of disordered solvent. Maximum convergence was attained by treating this latter volume of the electron density map as 5 carbon atoms bearing 0.5 occupancy. Consideration of the crystallographic symmetry in the solvent

region reveals a resemblance to toluene. However, no solvent hydrogens were included in the refinement. In complex 4, the asymmetric unit consists of one half of the dimeric species. One and half molecules of disordered toluene was also seen to present in the ASU. One molecule of toluene was partitioned over two sites such that C(101)-C(107) and C(201)-C(207) and their associated hydrogens show a 60 : 40 occupancy respectively. The residual electron density was modelled as one half of a molecule of toluene, with a disordered methyl group. As well as one molecule of the titanium complex, the ASU of 5 also contains one and a half molecules of toluene. The half molecule of toluene (a solvent fragment at 50% occupancy) is modelled as a rigid hexagon and refined isotropically with hydrogens in calculated positions using a riding model.

CCDC reference numbers 648697-648700.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708378e

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