

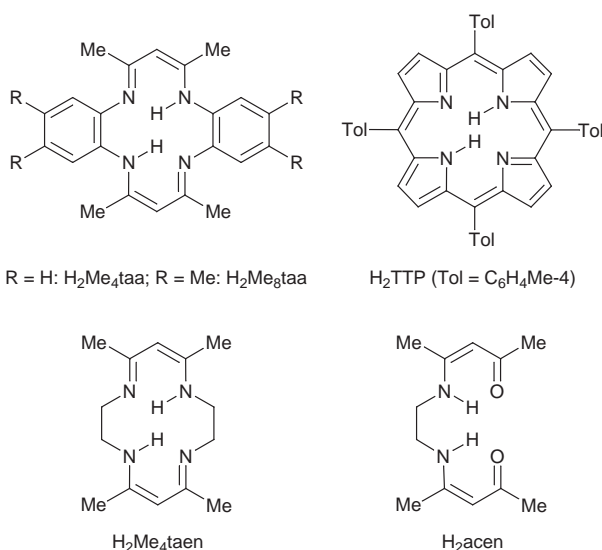
## Titanium imido complexes with tetraaza macrocyclic ligands

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Tetraaza macrocycle-supported *tert*-butyl titanium imido complexes [Ti(NBu<sup>t</sup>)(Me<sub>n</sub>taa)] (*n* = 4 **2** or 8 **3**; H<sub>2</sub>Me<sub>n</sub>taa = 6,8,15,17-tetra- or 2,3,6,8,11,12,17,18-octa-methyl-5,14-dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine, respectively), [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taen)] (**5**, H<sub>2</sub>Me<sub>4</sub>taen = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene) and [Ti(NBu<sup>t</sup>)(TTP)] (**6**, H<sub>2</sub>TTP = 5,10,15,20-tetratolylporphyrin) together with the N<sub>2</sub>O<sub>2</sub>-donor Schiff base analogue [Ti(NBu<sup>t</sup>)(acen)] (**7**, H<sub>2</sub>acen = 4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione) were prepared in good yield from the readily available [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] and the dilithium or disodium salts of the tetradentate ligands. The Ti=NBu<sup>t</sup> groups in **2** and **3** underwent imido group exchange reactions with anilines to form [Ti(NR)(Me<sub>n</sub>taa)] (*n* = 4, R = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **4**, Ph, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)-4, C<sub>6</sub>H<sub>4</sub>(NMe<sub>2</sub>)-4; *n* = 4 or 8, R = C<sub>6</sub>H<sub>4</sub>Me-4), and with H<sub>2</sub>E (E = O or S) to give the oxo and sulfido analogues [Ti(E)(Me<sub>4</sub>taa)]. Compound **4** was also prepared in good yield from [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>3</sub>] and Li<sub>2</sub>[Me<sub>4</sub>taa]. Reaction of **2** with 2 or 1 equivalents of ROH (R = Me or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) or pinacol afforded [Ti(OR)<sub>2</sub>(Me<sub>4</sub>taa)] and [Ti{OC(Me)<sub>2</sub>C(Me)<sub>2</sub>O}(Me<sub>4</sub>taa)] respectively. The crystal structures of **3** and **4** have been described.

Dianionic tetraaza macrocycles and N<sub>2</sub>O<sub>2</sub>-donor Schiff bases have received much attention in recent years as potential alternatives to the ubiquitous bis(cyclopentadienyl) ligand set in early transition-metal chemistry.<sup>1–18</sup> As part of an ongoing research program in transition-metal imido chemistry<sup>4,19–21</sup> we were interested to explore the opportunities that such ligands offer in this area. We were especially attracted by the dibenzotetraaza[14]annulene systems Me<sub>n</sub>taa (*n* = 4 or 8), the chemistry of which has been reviewed.<sup>2,3</sup> These tetraaza macrocycles are related to the porphyrins but differ in several important respects. For instance, their N<sub>4</sub> co-ordination cavity ‘hole size’ is *ca.* 0.1 Å smaller than that of porphyrins and they typically possess non-planar geometries.



It is relevant to note that dibenzotetraaza[14]annulene ligands have already provided supporting environments for a number of transition-metal- and main-group metal-ligand multiple bonds.<sup>4–8,22</sup> Cognisant of the very interesting reaction chemistry that Geoffroy and co-workers<sup>5</sup> found for the oxo-

titanium species [Ti(O)(Me<sub>n</sub>taa)] (*n* = 4<sup>22</sup> or 8), we prepared the isoelectronic imido analogues [Ti(NBu<sup>t</sup>)(Me<sub>n</sub>taa)] (*n* = 4 **2** or 8 **3**),<sup>23</sup> together with homologous tetraaza[14]annulene-supported zirconium imido compounds.<sup>4,24</sup> Since our preliminary communication<sup>23</sup> of a part of these initial studies, a number of other Group 4 macrocycle-supported imido derivatives have been described.<sup>25–27</sup> In this contribution we describe in full the synthesis, properties and imido group exchange reactions of titanium imido complexes with dibenzotetraaza[14]annulene ligands, together with synthetic routes to a number of other macrocycle- and Schiff base-supported analogues. A part of this work has been communicated.<sup>23,28</sup>

## Experimental

### General methods and instrumentation

Manipulations were carried out under an atmosphere of dinitrogen or argon using either standard Schlenk-line or dry-box techniques. Solvents were pre-dried over molecular sieves and refluxed over potassium (tetrahydrofuran, hexane), sodium-potassium alloy (pentane) or calcium hydride (dichloromethane) under an atmosphere of dinitrogen and collected by distillation. CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were dried over calcium hydride at room temperature (r.t.), distilled under reduced pressure and stored under N<sub>2</sub> in Young's ampoules in a dry-box. The NMR samples were prepared in a dry-box in Teflon valve (Young's) 5 mm tubes. Proton and <sup>13</sup>C NMR spectra were recorded on either a Bruker WM 250, Bruker AMX 500 or Bruker DPX 300 spectrometer at 298 K unless stated otherwise. The spectra were referenced internally to residual protio-solvent (<sup>1</sup>H) or solvent (<sup>13</sup>C) resonances and are reported relative to tetramethylsilane (δ = 0). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional, and NOE experiments as appropriate. Mass spectra were recorded on either a VG Micromass 7070E or a AEI MS902 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of this department or by Canadian Microanalytical Services Ltd.

The compounds Li<sub>2</sub>[(Me<sub>n</sub>taa)] (*n* = 4 or 8), Li<sub>2</sub>[Me<sub>4</sub>taen], Li<sub>2</sub>[TTP]·2THF, Na<sub>2</sub>[acen] and [Ti(NR)Cl<sub>2</sub>(py)<sub>3</sub>] (R = Bu<sup>t</sup> **1a** or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **1b**) were prepared as previously described.<sup>12,13,29–31</sup>

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## Syntheses

**[Ti(NBu)<sup>4</sup>(Me<sub>4</sub>taa)] 2.** A cold (0 °C) solution of Li<sub>2</sub>[Me<sub>4</sub>taa] (3.50 g, 9.83 mmol) in THF (40 ml) was added dropwise to a cold solution of [Ti(NBu)<sup>4</sup>Cl<sub>2</sub>(py)<sub>3</sub>] (4.18 g, 9.83 mmol) in THF (20 ml). The mixture was allowed to warm to r.t. and stirred for a further 12 h, after which the solvent was removed under reduced pressure. Dichloromethane (50 ml) was added, giving a red solution with a white precipitate (LiCl). The solution was filtered, reduced to *ca.* 20 ml and hexane (20 ml) was added. Compound **2** formed as a red solid that was washed with hexane (3 × 10 ml) and dried *in vacuo*. Yield: 3.18 g (70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz, 298 K): δ 7.32–7.36, 7.18–7.24 (2 × m, 2 × 4 H, C<sub>6</sub>H<sub>4</sub>), 5.13 [s, 2 H, NC(Me)CH], 2.40 [s, 12 H, NC(Me)CH], 0.26 (s, 9 H, Bu<sup>4</sup>). <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 62.5 MHz, 298 K): δ 160.1 [NC(Me)CH], 139.4 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 124.3, 123.3 (2 × CH of C<sub>6</sub>H<sub>4</sub>), 103.3 [NC(Me)CH], 67.2 (NCMe<sub>3</sub>), 31.6 (NCMe<sub>3</sub>), 22.7 [NC(Me)CH] [Found (Calc. for C<sub>26</sub>H<sub>31</sub>N<sub>5</sub>Ti·CH<sub>2</sub>Cl<sub>2</sub>): C, 60.2 (59.4); H, 6.0 (6.1); N, 12.6 (12.8)%].

**[Ti(NBu)<sup>4</sup>(Me<sub>8</sub>taa)] 3.** A THF (20 ml) solution of [Ti(NBu)<sup>4</sup>Cl<sub>2</sub>(py)<sub>3</sub>] (2.45 g, 5.70 mmol) was added dropwise to Li<sub>2</sub>[Me<sub>8</sub>taa] (2.40 g, 5.8 mmol) in THF (20 ml). The mixture was stirred for 16 h at r.t., after which the solvent was removed under reduced pressure. The red product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 ml), filtered through a pad of Celite to remove the LiCl and the solvent removed under reduced pressure. The resulting red-brown solid was recrystallised by solvent diffusion using CH<sub>2</sub>Cl<sub>2</sub> and pentane at –78 °C to afford the microcrystalline complex **3**, which was dried *in vacuo*. Yield: 2.50 g (70%). Diffraction quality crystals of **3** formed overnight at –30 °C from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with hexane. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.1 MHz): δ 7.13 (s, 4 H, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>), 5.07 [s, 2 H, NC(Me)CH], 2.39 [s, 12 H, NC(Me)CH], 2.32 (s, 12 H, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>), 0.29 (s, 9 H, Bu<sup>4</sup>). <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 125.7 MHz): δ 159.7 [NC(Me)CH], 137.1 (CN of C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub> of Me<sub>8</sub>taa), 132.5 (CMe of C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>), 124.2 (CH of C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>), 102.9 [NC(Me)CH], 67.0 (NCMe<sub>3</sub>), 31.8 (NCMe<sub>3</sub>), 22.7 [NC(Me)CH], 20.0 (C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>) [Found (Calc. for C<sub>30</sub>H<sub>39</sub>N<sub>5</sub>Ti): C, 69.6 (69.6); H, 7.6 (7.6); N, 13.4 (13.5)%].

**[Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(Me<sub>4</sub>taa)] 4.** *Method (a):* from **1b** and Li<sub>2</sub>[Me<sub>4</sub>taa]. To a cold (0 °C) solution of **1b** (0.200 g, 0.414 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added cold Li<sub>2</sub>[Me<sub>4</sub>taa] (0.140 g, 0.414 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was allowed to warm to r.t. and then stirred for 24 h. Filtration and removal of the volatiles under reduced pressure gave spectroscopically pure **4** as a brown solid. Yield: 0.150 g (71%).

*Method (b):* from **2** and 2,6-dimethylaniline. To a stirred solution of **2** (0.200 g, 0.433 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added 2,6-dimethylaniline (0.190 ml, 1.52 mmol, 3.5 equivalents). The solution changed from light red to dark red over 3 d at r.t. after which the volatiles were removed under reduced pressure. The residue was crystallised from hexane–CH<sub>2</sub>Cl<sub>2</sub> (6:1) at –25 °C overnight to give **4** as a brown solid that was washed with hexane–CH<sub>2</sub>Cl<sub>2</sub> and dried *in vacuo*. Yield: 0.170 g (77%). Diffraction quality crystals of 4·H<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 were grown at room temperature over several days from a CH<sub>2</sub>Cl<sub>2</sub> solution of crude **4** layered with hexane. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.47–7.43, 7.31–7.25 (2 × m, 2 × 4 H, C<sub>6</sub>H<sub>4</sub>), 6.39 (d, *J* 7.5, 2 H, *m*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 6.16 (t, *J* 7.2, 1 H, *p*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 5.32 [s, 2 H, NC(Me)CH], 2.48 [s, 12 H, NC(Me)CH], 1.10 (s, 6 H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 161.1 [NC(Me)CH], 139.7 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 129.5 (*o*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 126.3 (*m*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 125.4, 124.3 (2 × CH of C<sub>6</sub>H<sub>4</sub>), 117.9 (*p*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 105.0 [NC(Me)CH], 23.5 [NC(Me)CH], 18.1 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); note: the *ipso* carbon of the C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> group was not observed. EI mass spectrum: *m/z* = 509 {M<sup>+</sup>}, 406 {M<sup>+</sup> – C<sub>8</sub>H<sub>7</sub>}, 390 {M<sup>+</sup> – C<sub>8</sub>H<sub>9</sub>N} [Found (Calc. for C<sub>30</sub>H<sub>31</sub>N<sub>5</sub>Ti): C, 69.2 (70.7); H, 6.1 (6.1); N, 13.0 (13.7)%].

**[Ti(NBu)<sup>4</sup>(Me<sub>4</sub>taen)] 5.** To a cold (0 °C) solution of [Ti(NBu)<sup>4</sup>Cl<sub>2</sub>(py)<sub>3</sub>] (0.740 g, 1.73 mmol) in THF (30 ml) was added cold Li<sub>2</sub>[Me<sub>4</sub>taen] (0.450 g, 1.73 mmol) in THF (30 ml) dropwise to give a colour change from orange to red. After 24 h the volatiles were removed under reduced pressure and the residues were extracted into CH<sub>2</sub>Cl<sub>2</sub> (40 ml) and filtered. The volume was concentrated to 20 ml and hexane (20 ml) added. Compound **5** formed as a red solid, which was filtered, washed with hexane (2 × 10 ml), and dried *in vacuo*. Yield: 0.390 g (61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 4.70 [s, 2 H, NC(Me)CH], 4.21, 3.65 (2 × m, 2 × 2 H, NCH<sub>2</sub>), 1.98 [s, 12 H, NC(Me)CH], 0.89 (s, 9 H, Bu<sup>4</sup>). <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 163.0 [NC(Me)CH], 98.1 [NC(Me)CH], 67.1 (NCMe<sub>3</sub>), 50.7 (NCH<sub>2</sub>), 32.8 [NC(Me)CH], 21.2 (NCMe<sub>3</sub>). EI mass spectrum: *m/z* = 365 {M<sup>+</sup>}, 350 {M<sup>+</sup> – CH<sub>3</sub>} [Found (Calc. for C<sub>18</sub>H<sub>31</sub>N<sub>5</sub>Ti): C, 59.7 (59.2); H, 8.3 (8.5); N, 16.1 (19.2)%]; repeated analyses did not lead to improved %N found which may be low due to titanium nitride formation during combustion.

**[Ti(NBu)<sup>4</sup>(TTP)] 6.** To a cold (0 °C) solution of [Ti(NBu)<sup>4</sup>Cl<sub>2</sub>(py)<sub>3</sub>] (0.100 g, 0.234 mmol) in THF (30 ml) was added Li<sub>2</sub>[TTP]·2THF (0.200 g, 0.234 mmol) in THF (30 ml) dropwise. The mixture was allowed to warm to r.t. and then stirred for 24 h to give a red-purple solution. The volatiles were removed under reduced pressure, and the purple residue was extracted with toluene–hexane (1:1, 30 ml) and concentrated to give **6** as a spectroscopically pure, purple solid after cooling to –25 °C overnight. Yield: 0.130 g (71%). The compound was characterised by comparison with previously described data.<sup>27</sup>

**[Ti(NBu)<sup>4</sup>(acen)] 7.** To a cold (0 °C) solution of [Ti(NBu)<sup>4</sup>Cl<sub>2</sub>(py)<sub>3</sub>] (0.790 g, 1.8 mmol) in THF (20 ml) was added a slurry of Na<sub>2</sub>[acen] (0.500 g, 1.8 mmol) in THF (25 ml). On warming to r.t. the mixture turned a deep brown-red and was stirred at r.t. for a further 24 h. Volatiles were removed under reduced pressure and the dark brown-red residue was extracted into CH<sub>2</sub>Cl<sub>2</sub> (40 ml) and quickly filtered. The volume was reduced and **7** formed as a brown solid on the addition of hexane (20 ml). Yield: 0.310 g (52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.1 MHz): δ 5.19 [s, 2 H, MeC(O)CH(N)Me], 4.17, 3.67 (2 × m, 2 × 2 H, NCH<sub>2</sub>), 2.10, 2.08 [2 × s, 2 × 6 H, MeC(O)CH(N)Me and MeC(O)CH(N)Me], 0.85 (s, 9 H, Bu<sup>4</sup>). <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 178.1 [MeC(O)CH(N)CMe], 168.6 [MeC(O)CH(N)CMe], 101.9 [MeC(O)CH(N)CMe], 69.2 (NCMe<sub>3</sub>), 51.7 (NCH<sub>2</sub>), 31.8 (NCMe<sub>3</sub>), 24.9 [MeC(O)CH(N)CMe], 21.5 [MeC(O)CH(N)CMe]. Elemental analyses were not obtained for this compound which decomposed in solvents from which recrystallisation was attempted.

**[Ti(NPh)(Me<sub>4</sub>taa)] 8, [Ti(NC<sub>6</sub>H<sub>4</sub>Me-4)(Me<sub>4</sub>taa)] 9, [Ti{NC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)-4}(Me<sub>4</sub>taa)] 10, [Ti{NC<sub>6</sub>H<sub>4</sub>(NMe<sub>2</sub>)-4}(Me<sub>4</sub>taa)] 11 and [Ti(NC<sub>6</sub>H<sub>4</sub>Me-4)(Me<sub>8</sub>taa)] 12.** These compounds were prepared according to method (b) above for **4** from complex **2** (except for the synthesis of **12** for which benzene was used as solvent) and the corresponding aniline with reaction times of 3–24 h. Yields after crystallisation from CH<sub>2</sub>Cl<sub>2</sub>–hexane at r.t. or –25 °C: for **8**, 85; for **9**, 81; for **10**, 80; for **11**, 75; for **12**, 95%.

*Data for 8.* <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.50–7.46, 7.34–7.31 (2 × m, 2 × 4 H, C<sub>4</sub>H<sub>4</sub>), 6.55 (apparent t, apparent *J* 7.9, 2 H, *m*-Ph), 6.23 (t, *J* 7.2, 1 H, *p*-Ph), 5.33 (d, *J* 8.1, 2 H, *o*-Ph), 5.29 [s, 2 H, NC(Me)CH], 2.47 [s, 12 H, NC(Me)CH]. <sup>13</sup>C-<sup>1</sup>H NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 160.5 [NC(Me)CH], 138.2 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 127.2 (*m*-Ph), 125.2, 123.7 (2 × CH of C<sub>6</sub>H<sub>4</sub>), 120.7 (*o*-Ph), 117.2 (*p*-Ph), 104.5 [NC(Me)CH], 22.7 [NC(Me)CH]; note: the *ipso* carbon of the Ph group was not observed [Found (Calc. for C<sub>28</sub>H<sub>27</sub>N<sub>5</sub>Ti): C, 68.5 (69.8); H, 5.7 (5.6); N, 14.4 (14.6)%].

*Data for 9.* <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.49–7.45, 7.33–7.29 (2 × m, 2 × 4 H, C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 6.36 (d, *J* 8.0, 2 H, *m*-C<sub>6</sub>H<sub>4</sub>Me), 5.28 [s, 2 H, 2 × NC(Me)CH], 5.27 (d, *J* 8.0, 2 H,

*o*-C<sub>6</sub>H<sub>4</sub>Me), 2.46 [s, 12 H, NC(Me)CH], 1.94 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 160.4 [NC(Me)CH], 158.9 (*p*-C<sub>6</sub>H<sub>4</sub>Me), 138.3 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 127.7 (*m*-C<sub>6</sub>H<sub>4</sub>Me), 125.1, 123.7 (2 × CH of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 120.4 (*o*-C<sub>6</sub>H<sub>4</sub>Me), 104.4 [NC(Me)CH], 22.7 [NC(Me)CH], 20.5 (C<sub>6</sub>H<sub>4</sub>Me); note: the *ipso* carbon of the C<sub>6</sub>H<sub>4</sub>Me group was not observed [Found (Calc. for C<sub>29</sub>H<sub>29</sub>N<sub>5</sub>Ti): C, 69.9 (70.3); H, 5.8 (5.9); N, 14.0 (14.1)%].

**Data for 10.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.52–7.38 (overlapping 2 × *m* and *d*, 10 H, 2 × C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa and *m*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 5.43 [s, 2 H, NC(Me)CH], 5.07 (*d*, *J* 8.1, 2 H, *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 2.51 [s, 12 H, NC(Me)CH]. <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 165.2 (*p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 160.8 [NC(Me)CH], 137.2 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 126.1 (CH of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 124.7 (*m*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 123.8 (CH of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 120.3 (*o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 113.2 (*ipso*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), 105.5 [NC(Me)CH], 22.7 [4 × NC(Me)CH] [Found (Calc. for C<sub>28</sub>H<sub>26</sub>N<sub>6</sub>O<sub>2</sub>Ti): C, 64.0 (63.9); H, 5.3 (5.0); N, 16.0 (16.0)%].

**Data for 11.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.50–7.46, 7.33–7.29 (2 × *m*, 2 × 4 H, C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 6.12 (*d*, *J* 8.7, 2 H, *m*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 5.36 (*d*, *J* 8.7, 2 H, *o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 5.26 [s, 2 H, NC(Me)CH], 2.58 (s, 6 H, C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 2.46 [s, 12 H, NC(Me)CH]. <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 160.4 [NC(Me)CH], 155.1 (*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 143.3 (*ipso*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 138.5 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 125.0, 123.7 (2 × CH of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 121.2 (*m*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 113.8 (*o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 104.3 [NC(Me)CH], 42.1 (C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>), 22.7 [NC(Me)CH]. Satisfactory elemental analyses could not be obtained for this compound.

**Data for 12.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.37 (s, C<sub>6</sub>H<sub>6</sub>), 7.25 (s, 4 H, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub> of Me<sub>8</sub>taa), 6.33 (*d*, *J* 8.0, 2 H, *m*-C<sub>6</sub>H<sub>4</sub>Me), 5.33 (*d*, *J* 8.0, 2 H, *o*-C<sub>6</sub>H<sub>4</sub>Me), 5.32 [s, 2 H, 2 × NC(Me)CH], 2.46 [s, 12 H, NC(Me)CH], 2.37 (s, 12 H, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>), 1.98 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 160.3 (*ipso*-C<sub>6</sub>H<sub>4</sub>Me), 159.9 [NC(Me)CH], 136.0 (CN of C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub> of Me<sub>8</sub>taa), 134.2 (*p*-C<sub>6</sub>H<sub>4</sub>Me), 133.6 (CMe of C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub> of Me<sub>8</sub>taa), 127.7 (C<sub>6</sub>H<sub>6</sub>), 125.1 and 120.5 (*o*- and *m*-C<sub>6</sub>H<sub>4</sub>Me), 124.6 (4 × CH of Me<sub>8</sub>taa), 103.9 [2 × NC(Me)CH], 22.8 and 20.1 [NC(Me)CH and C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>, respectively], 20.6 (C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>) [Found (Calc. for C<sub>33</sub>H<sub>37</sub>N<sub>5</sub>Ti): C, 70.8 (71.9); H, 6.7 (6.8); N, 11.8 (12.7)%].

**[Ti(O)(Me<sub>4</sub>taa)] 13.** To a red solution of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] (0.100 g, 0.217 mmol) in THF (20 ml) at r.t. was added H<sub>2</sub>O (3.90 μl, 0.217 mmol). The colour changed instantly to yellow and a yellow solid precipitated which was filtered off after 30 min, washed with THF (2 × 5 ml) and dried to give spectroscopically pure **13**. Yield: 0.073 g (82%). The compound was characterised by comparison with previously described data.<sup>22</sup>

**[Ti(S)(Me<sub>4</sub>taa)] 14.** Dihydrogen sulfide was slowly passed through a stirred solution of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] (0.100 g, 0.217 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) for 1 min at r.t. to give **14** as a spectroscopically pure, orange solid. Yield: 0.080 g (87%). The compound was characterised by comparison with previously described data.<sup>22</sup>

**[Ti(OMe)<sub>2</sub>(Me<sub>4</sub>taa)] 15.** To a solution of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] (0.200 g, 0.433 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added methanol (0.10 ml, 2.5 mmol, 6 equivalents). After stirring for 24 h at r.t. the volume was reduced and hexane added. Cooling to –25 °C overnight gave **15** as a red solid which was washed with hexane (2 × 10 ml) and dried *in vacuo*. Yield: 0.12 g (62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.30–7.10 (overlapping 2 × *m*, 2 × 4 H, C<sub>6</sub>H<sub>4</sub>), 5.27 [s, 2 H, NC(Me)CH], 3.69 (s, 6 H, OMe), 2.39 [s, 12 H, NC(Me)CH]. <sup>13</sup>C-<sup>1</sup>H} DEPT-135 NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 124.9, 122.7 (CH of C<sub>6</sub>H<sub>4</sub>), 103.1 [NC(Me)CH], 62.6 (OMe), 23.6 [NC(Me)CH] [Found (Calc. for C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>Ti): C, 63.2 (63.7); H, 6.3 (6.2); N, 12.3 (12.4)%].

**[Ti(OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)<sub>2</sub>(Me<sub>4</sub>taa)] 16.** To a solution of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] (0.200 g, 0.433 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added 2,6-dimethylphenol (0.110 g, 0.866 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml). After 12 h at r.t. **16** formed as a red-brown microcrystalline CH<sub>2</sub>Cl<sub>2</sub> solvate (by <sup>1</sup>H NMR and elemental analysis) and was washed with a minimum volume of CH<sub>2</sub>Cl<sub>2</sub>–hexane (1 : 6) and dried *in vacuo*. Yield: 0.220 g (71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.22–7.11 (overlapping 2 × *m*, 2 × 4 H, C<sub>6</sub>H<sub>4</sub>), 6.48 (*d*, *J* 7.3, 4 H, *m*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 6.26 (*t*, *J* 7.3, 2 H, *p*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 5.50 [s, 2 H, NC(Me)CH], 2.43 [s, 12 H, C(Me)CH], 1.27 (s, 12 H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 165.7 (*ipso*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 158.5 [C(Me)CH], 140.4 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 127.2 (*m*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 125.5 (*o*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 124.9, 123.2 (2 × CH of C<sub>6</sub>H<sub>4</sub>), 117.5 (*p*-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 105.4 [NC(Me)CH], 24.4 [NC(Me)CH], 15.9 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) [Found (Calc. for C<sub>38</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>·Ti·CH<sub>2</sub>Cl<sub>2</sub>): C, 64.9 (65.3); H, 5.9 (5.9); N, 7.7 (7.8)%].

**[Ti{OC(Me)<sub>2</sub>C(Me)<sub>2</sub>O}(Me<sub>4</sub>taa)] 17.** To a solution of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] (0.100 g, 0.217 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added pinacol (0.026 g, 0.217 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml). The solution immediately changed from red to orange and was stirred for 24 h at r.t. The volume was reduced, hexane (15 ml) added and the solution cooled to –25 °C overnight to give microcrystalline **17** as an orange CH<sub>2</sub>Cl<sub>2</sub> hemi-solvate (by <sup>1</sup>H NMR and elemental analysis) that was washed with hexane (2 × 5 ml) and dried *in vacuo*. Yield: 0.10 g (81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250.1 MHz): δ 7.35–7.13 (overlapping 2 × *m*, 2 × 4 H, C<sub>6</sub>H<sub>4</sub>), 5.32 [s, 2 H, NC(Me)CH], 2.39 [s, 12 H, NC(Me)CH], 0.37 (s, 12 H, O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 62.5 MHz): δ 158.3 [NC(Me)CH], 141.5 (CN of C<sub>6</sub>H<sub>4</sub> of Me<sub>4</sub>taa), 123.9, 123.3 (2 × CH of C<sub>6</sub>H<sub>4</sub>), 104.5 [NC(Me)CH], 92.1 (O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>), 25.8 (O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>), 23.6 [NC(Me)CH] [Found (Calc. for C<sub>28</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>Ti·0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 62.7 (62.4); H, 6.6 (6.4); N, 10.4 (10.2)%].

## Results and Discussion

The ligand precursors used in this study are readily deprotonated with Bu<sup>n</sup>Li (for H<sub>2</sub>Me<sub>n</sub>taa and H<sub>2</sub>Me<sub>4</sub>taen),<sup>12,29</sup> LiN(SiMe<sub>2</sub>)<sub>2</sub> (for H<sub>2</sub>TTP),<sup>30</sup> or sodium hydride (H<sub>2</sub>acen)<sup>13</sup> to form the corresponding dilithium or disodium salts. In recent studies<sup>19</sup> we have found a number of different classes of titanium imido compound can be prepared *via* chloride and/or pyridine substitution reactions of the readily-available synthons [Ti(NR)Cl<sub>2</sub>(py)<sub>3</sub>] (R = Bu<sup>t</sup> **1a** or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **1b**).<sup>31</sup> The reactions of **1** with dianionic N<sub>4</sub>- and N<sub>2</sub>O<sub>2</sub>-donor ligands are summarised in Scheme 1 and details of the preparation and characterisation of all the compounds are given in the Experimental section.

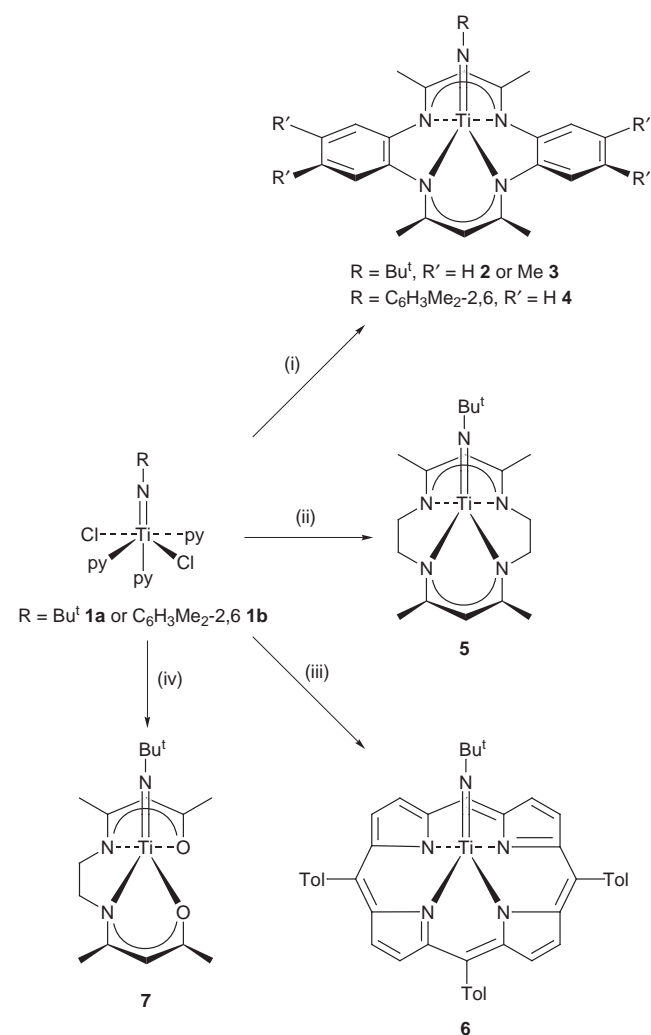
The reaction of [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>3</sub>] **1a** with Li<sub>2</sub>[Me<sub>n</sub>taa] (*n* = 4 or 8) in THF proceeds smoothly to afford good yields of the red tetraaza macrocyclic derivatives [Ti(NBu<sup>t</sup>)(Me<sub>n</sub>taa)] (*n* = 4 or 8). These compounds are also accessible from the bis(*tert*-butylpyridine) homologues [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(Bu<sup>t</sup>py)<sub>2</sub>] (Bu<sup>t</sup>py = *tert*-butylpyridine),<sup>23</sup> and are air- and moisture-sensitive in solution and the solid state. The arylimido analogue [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(Me<sub>4</sub>taa)] **4** was also prepared cleanly in an analogous fashion from [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>3</sub>] **1b** and Li<sub>2</sub>[Me<sub>4</sub>taa] in dichloromethane. However, use of dichloromethane as reaction solvent for **2** and **3** gave lower yields of isolated product. The compounds **2–4** are the first macrocycle-supported imido complexes of Group 4.

The NMR spectra for **2–4** are consistent with the proposed structures shown in Scheme 1. Interestingly, the <sup>1</sup>H chemical shifts for the NBu<sup>t</sup> group in **2** and **3** (δ 0.26 and 0.29 respectively) and the *ortho*-methyl substituents for NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 in **4** (δ 1.10) in CDCl<sub>3</sub> occur at significantly higher field compared with the corresponding resonances<sup>31</sup> for **1a** (δ 0.92) and **1b** (δ 2.40) respectively in the same solvent. We attribute this to

**Table 1** Selected distances (Å) and angles (°) for [Ti(NBu<sup>t</sup>)(Me<sub>n</sub>taa)] **3** and [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2-2,6</sub>)(Me<sub>4</sub>taa)] **4**<sup>23,28</sup>

	<b>3</b>	<b>4</b>
Ti–N <sub>imide</sub>	1.724(4)	1.720(4)
Ti···N <sub>4</sub> plane	0.76	0.75
Ti–N <sub>macrocycle</sub> *	2.070(4), 2.093(4), 2.089(4), 2.091(4)	2.064(4), 2.060(4), 2.084(4), 2.078(4)
Ti–N <sub>imide</sub> –C	164.3(3)	175.4(4)
N <sub>imide</sub> –Ti–N <sub>macrocycle</sub> *	107.0(2), 114.3(2), 108.7(2), 115.1(2)	109.7(2), 109.9(2), 113.0(2), 112.4(2)

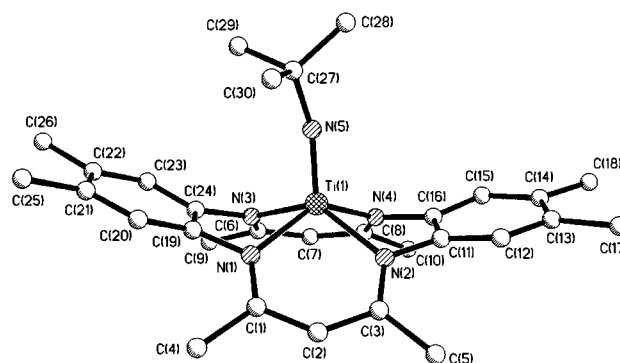
\* Values correspond to the atoms N(1), N(2), N(3), N(4) in that order in each instance.



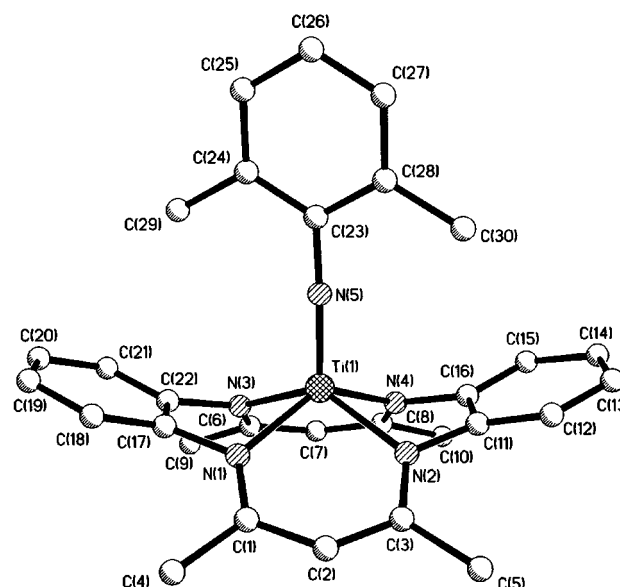
**Scheme 1** Synthesis of titanium imido complexes supported by tetraazamacrocyclic and acen ligands. (i) Li<sub>2</sub>[Me<sub>n</sub>taa] (*n* = 4 or 8), THF (for **2** and **3**) or CH<sub>2</sub>Cl<sub>2</sub>, 0 °C then r.t., 12–24 h, ca. 70%; (ii) Li<sub>2</sub>[Me<sub>4</sub>taen], THF, 0 °C then r.t., 24 h, 61%; (iii) Li<sub>2</sub>[TTP]·2THF, THF, 0 °C then r.t., 24 h, 71%; (iv) Na<sub>2</sub>[acen], THF, 0 °C then r.t., 24 h, 52%

shielding effects of the *o*-phenylene aromatic rings of the Me<sub>n</sub>taa ligand (see below).

The solid state structures<sup>23,28</sup> of **3** and **4** are shown in Figs. 1 and 2, and important molecular dimensions are summarised in Table 1. The structures contain approximately square-base pyramidal titanium centres with near-linear organoimido groups in the axial co-ordination sites. The macrocycle nitrogen donor atoms form the remainder of the co-ordination sphere and are effectively coplanar (the maximum deviation from the least squares macrocyclic N<sub>4</sub> plane is ca. 0.1 Å in both **3** and **4**), and the Ti lies 0.76 (for **3**) and 0.75 Å (for **4**) above the N<sub>4</sub> plane. The Ti≡N<sub>imide</sub> bond lengths of ca. 1.72 Å are at the longer end of the



**Fig. 1** Molecular structure of [Ti(NBu<sup>t</sup>)(Me<sub>8</sub>taa)] **3** with hydrogen atoms omitted<sup>23</sup>



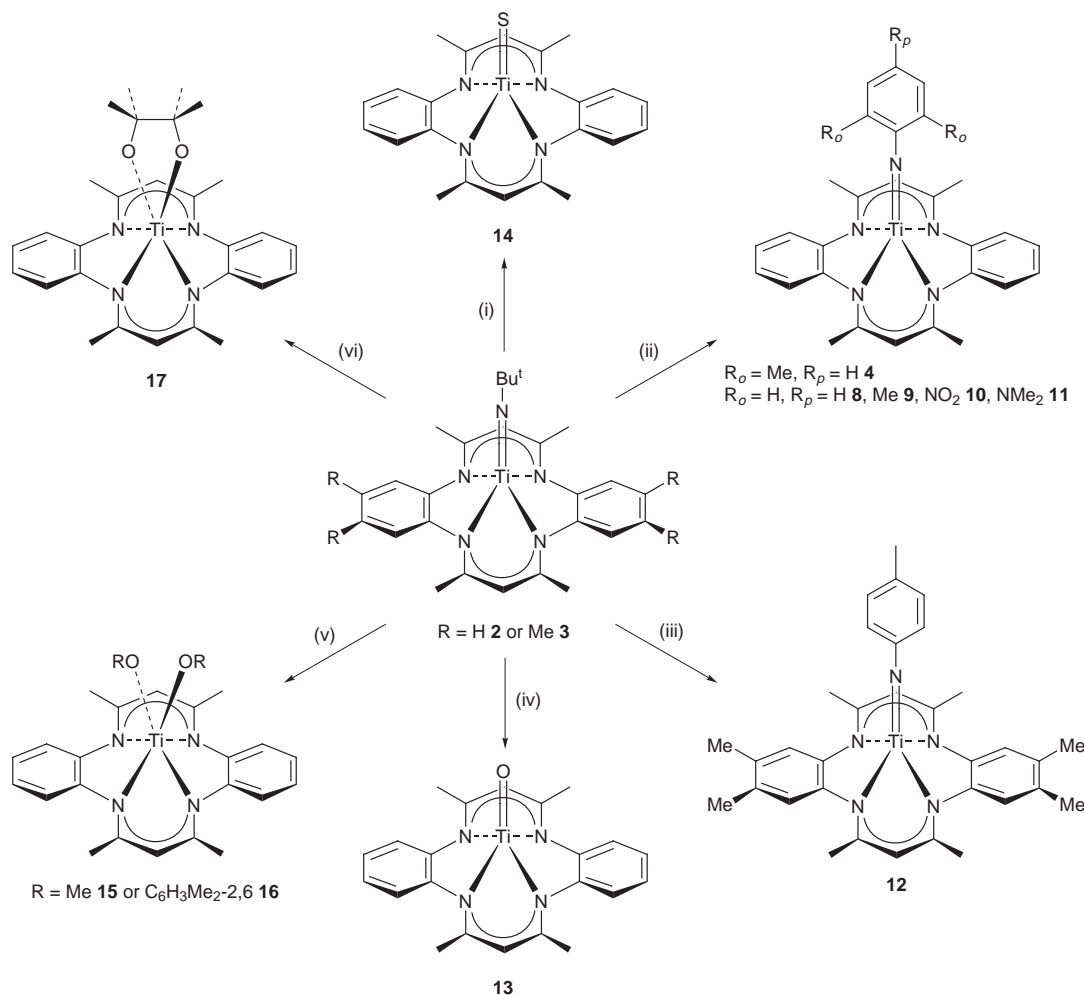
**Fig. 2** Molecular structure of [Ti(NC<sub>6</sub>H<sub>3</sub>Me<sub>2-2,6</sub>)(Me<sub>4</sub>taa)] **4** with hydrogen atoms omitted<sup>28</sup>

range for this linkage (range ca. 1.66–1.74 Å),<sup>19,32</sup> but still imply a formal Ti≡N<sub>imide</sub> triple bond.† The Me<sub>n</sub>taa ligands in **3** and **4** adopt the characteristic ‘saddle shape’,<sup>2,3</sup> and the folding of the *o*-phenylene rings ‘up’ towards the imido groups is consistent with the shielding effects seen in the <sup>1</sup>H NMR spectra.

The square-base pyramidal co-ordination geometry in **3** and **4** is well-established in titanium imido chemistry.<sup>19,32</sup> However, the macrocyclic compounds described here have unusually large average N≡Ti–N<sub>macrocycle</sub> bond angles (average 111.3° for both **3** and **4**) when compared with previous examples: [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(tmeda)] (tmeda = *N,N,N',N'*-tetramethylethylenediamine; average N≡Ti–L = 103.5°),<sup>33</sup> [Ti<sub>2</sub>(NBu<sup>t</sup>)<sub>2</sub>{μ-O<sub>2</sub>P(OSiMe<sub>3</sub>)<sub>2</sub>}<sub>4</sub>] (average N≡Ti–L = 107.1°),<sup>34</sup> [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(dipeda)] [dipeda = *N,N'*-diisopropylethylenediamine; average N≡Ti–L = 101.7(2)°],<sup>33</sup> [Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub>] [average N≡Ti–L = 105.4(3)°],<sup>35</sup> and [Ti(NPh)(TTP)] (average N≡Ti–N<sub>macrocycle</sub> = 104.3°).<sup>36</sup> This is apparently related to the small N<sub>4</sub> ‘hole size’ of Me<sub>n</sub>taa (see Introduction section) which leads to a relatively large displacement of Ti from the N<sub>4</sub> plane and so to larger average N≡Ti–N<sub>macrocycle</sub> bond angles. Possible electronic consequences of these structural constraints for [Ti(E)(Me<sub>n</sub>taa)] (E = NR or O) have been discussed by us elsewhere.<sup>28</sup>

We were interested to prepare other tetraaza macrocycle

† Although for ease of representation all titanium-imido linkages in Schemes 1 and 2 are drawn ‘Ti=NR’, the formal Ti–N bond order in the complexes [Ti(NR)(L)<sub>n</sub>] (R = Bu<sup>t</sup> or aryl, *n* = 1 or 2; L = dianionic tetradentate ligand) described herein is generally best thought of as three (pseudo-σ<sup>2</sup> π<sup>4</sup> triple bond) rather than as two.<sup>32</sup>



**Scheme 2** Imido ligand exchange and protonolysis reactions of  $[\text{Ti}(\text{NBu}^t)(\text{Me}_n\text{taa})]$  ( $n = 4$  **2** or **8** **3**). (i) Slow stream of  $\text{H}_2\text{S}$ ,  $\text{CH}_2\text{Cl}_2$ , r.t., 1 min, 87%; (ii)  $\text{H}_2\text{NC}_6\text{H}_2\{(\text{R}_o)_2(\text{R}_p)\}$ -2,4,6 (ca. 1–4 equivalents),  $\text{CH}_2\text{Cl}_2$ , 18 h–3 d, 75–85%; (iii) 4-methylaniline (1.1 equivalents),  $\text{C}_6\text{H}_6$ , r.t., 3 h, 95%; (iv)  $\text{H}_2\text{O}$ , THF, r.t., 30 min, 82%; (v) ROH (2 equivalents),  $\text{CH}_2\text{Cl}_2$ , r.t., 12–24 h, 62% (for **15**) or 71% (for **16**); (vi) pinacol,  $\text{CH}_2\text{Cl}_2$ , r.t., 24 h, 81%

titanium imido complexes (Scheme 1). Group 4 derivatives of  $\text{Me}_4\text{taen}$  have recently been reported by Jordan and co-workers but no imido derivatives were described.<sup>11,12</sup> We found that reaction of  $\text{Li}_2[\text{Me}_4\text{taen}]$  with  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  **1a** gave  $[\text{Ti}(\text{NBu}^t)(\text{Me}_4\text{taen})]$  **5** in 61% yield after standard work-up. The compound **5** is analogous to **2** and **3**, except that the *o*-phenylene rings have formally been replaced by ethylene linkages. The hydrogen atoms of these linkages appear as two mutually-coupled multiplets consistent with the proposed structure. The *tert*-butyl  $^1\text{H}$  NMR resonance for **5** appears at  $\delta = 0.89$ , somewhat upfield from the equivalent resonances for **2** and **3**; this lends support to our view that the upfield shifts of the imido N-substituents in the dibenzotetraaza[14]annulene derivatives can be attributed to effects of the *o*-phenylene rings.

While this work was in progress, Woo and co-workers<sup>27</sup> described the synthesis of the porphyrin titanium imido complex  $[\text{Ti}(\text{NBu}^t)(\text{TTP})]$  **6** from  $[\text{Ti}(\text{TTP})\text{Cl}_2]$  and  $\text{LiNHBU}^t$ . We have independently found that the same compound is accessible by treatment of  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  **1a** with  $\text{Li}_2[\text{TTP}]\cdot 2\text{THF}$  in 71% recrystallised yield from toluene–hexane. This compares with a crude yield (recrystallised yield not reported) of 94% using the previously published method.

There are only a few  $\text{N}_2\text{O}_2$  Schiff base-supported imido compounds known.<sup>37–41</sup> For comparison with the tetraaza macrocyclic systems we therefore prepared the complex  $[\text{Ti}(\text{NBu}^t)(\text{acen})]$  **7** from **1a** and  $\text{Na}_2[\text{acen}]$ . This compound was obtained as a spectroscopically pure, brown solid in 52% yield. Attempts to obtain analytically pure samples were unsuccessful. However, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are fully consistent with the structure proposed in Scheme 1. Thus the ethylene

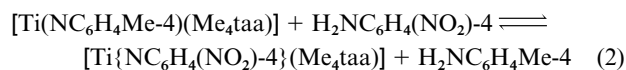
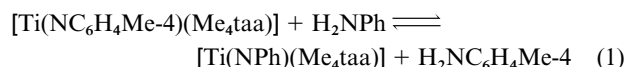
protons appear as a pair of mutually coupled multiplets, and the *tert*-butyl resonance occurs in the expected region ( $\delta$  0.85) for a terminal  $\text{Ti}\equiv\text{NBu}^t$  linkage.

Scheme 2 shows exchange and protonolysis reactions of the *tert*-butylimido ligand in  $[\text{Ti}(\text{NBu}^t)(\text{Me}_n\text{taa})]$  (**2** and **3**). Imide/amine exchange reactions of *tert*-butylimido compounds with certain anilines appears now to be a widely applicable route to the corresponding arylimido homologues.<sup>31,42–48</sup> We were interested to use this method for preparing dibenzotetraaza[14]-annulene-supported *o*-unsubstituted arylimido compounds since starting materials of the type  $[\text{Ti}(\text{NC}_6\text{H}_4\text{R}-4)\text{Cl}_2(\text{py})_3]$  ( $\text{R} = \text{H}$ , Me or  $\text{NO}_2$ )<sup>31</sup> are less convenient to use as synthons (due to their limited solubilities and stabilities) than  $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$  **1a** in reactions with  $\text{Li}_2[\text{Me}_n\text{taa}]$  (cf. Scheme 1).

Reaction of  $[\text{Ti}(\text{NBu}^t)(\text{Me}_4\text{taa})]$  **2** with 3.5 equivalents of 2,6-dimethylaniline in dichloromethane gave  $[\text{Ti}(\text{NC}_6\text{H}_3\text{Me}_2-2,6)(\text{Me}_4\text{taa})]$  **4** in 77% recrystallised yield (Scheme 2). The yield of **4** obtained this way is comparable to that from direct reaction of  $[\text{Ti}(\text{NC}_6\text{H}_3\text{Me}_2-2,6)\text{Cl}_2(\text{py})_3]$  with  $\text{Li}_2[\text{Me}_4\text{taa}]$  (71%, Scheme 1) and demonstrates the feasibility of the imide/aniline exchange route for these dibenzotetraaza[14]annulene derivatives. In a similar manner, reaction of **2** or **3** with either aniline itself or various 4-substituted anilines gave 75–95% yields of the corresponding arylimides, namely  $[\text{Ti}(\text{NC}_6\text{H}_4\text{R}-4)(\text{Me}_4\text{taa})]$  ( $\text{R} = \text{H}$  **8**, Me **9**,  $\text{NO}_2$  **10** or  $\text{NMe}_2$  **11**) or  $[\text{Ti}(\text{NC}_6\text{H}_4\text{Me}-4)(\text{Me}_4\text{taa})]$  **12**. The NMR spectroscopic data for **8–12** are fully consistent with the proposed structures. The  $^1\text{H}$  NMR spectra show doublets for the *o*-hydrogens of the phenyl rings in the range ca.  $\delta$  5.0–5.4 consistent with shielding effects from the macrocycle aromatic rings.

Bergman and co-workers<sup>46</sup> have reported mechanistic studies for *tert*-butylimide/2,6-dimethylaniline exchange reactions of [Os(NBu<sup>t</sup>)L] (L = η<sup>6</sup>-cymene). The reaction is proposed to go *via* a bis(amide) intermediate of the type [Os(NHBu<sup>t</sup>)(NHR)L] (R = C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) for which the rate of H-atom transfer to the most basic amide (in this case *to* NHBu<sup>t</sup> *from* NHR) is much larger than that from NHBu<sup>t</sup> back to NHR, leading to formation and release of Bu<sup>t</sup>NH<sub>2</sub>, giving [Os(NR)L]. A similar mechanism presumably operates for *tert*-butylimide/aniline exchange in Scheme 2 although we were unable (as was the case in Bergman's system) to observe equilibrium concentrations of the proposed bis(amide) intermediates [Ti(NHBu<sup>t</sup>)(NHR)-(Me<sub>4</sub>taa)] when the reactions were followed by <sup>1</sup>H NMR spectroscopy. For example, mixtures of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] **2** and 2,6-dimethylaniline show resonances only for the starting materials and (with time) products **4** and Bu<sup>t</sup>NH<sub>2</sub>. Similarly, mixtures of **4** and 2,6-dimethylaniline show no NMR spectroscopic evidence for the bis(amide) [Ti(NHC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)<sub>2</sub>(Me<sub>4</sub>taa)]. This contrasts with the chemistry of the zirconium analogue of **4**, namely [Zr(NC<sub>6</sub>H<sub>3</sub>Pr<sup>2</sup>-2,6)(Me<sub>4</sub>taa)(py)], which reacts rapidly and irreversibly with 2,6-diisopropylaniline to form [Zr(NHC<sub>6</sub>H<sub>3</sub>Pr<sup>2</sup>-2,6)<sub>2</sub>(Me<sub>4</sub>taa)].<sup>4</sup> The differing behaviour for Zr most likely reflects the larger covalent radius of the heavier congener.

In addition to *tert*-butylimide/aniline exchange we have also observed arylimide/aniline exchange by a series of NMR tube experiments in CDCl<sub>3</sub> [equations (1) and (2)]. Thus 1:1 mix-



tures of [Ti(NC<sub>6</sub>H<sub>4</sub>Me-4)(Me<sub>4</sub>taa)] **9** and aniline gave, after several days at ambient temperature, equimolar mixtures with [Ti(NPh)(Me<sub>4</sub>taa)] **8** and 4-methylaniline [equation (1)]. However, when the analogous experiment was carried out with [Ti(NC<sub>6</sub>H<sub>4</sub>Me-4)(Me<sub>4</sub>taa)] **9** and 4-nitroaniline [equation (2)] near-quantitative formation of [Ti{NC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)-4}(Me<sub>4</sub>taa)] **10** and 4-methylaniline was observed. The crossover experiments in equations (1) and (2) suggest that in the presence of anilines, arylimide/bis(arylamide) equilibria exist in solution, and also support Bergman's proposal that the relative basicities of the amide nitrogens in bis(amide) intermediates control the orientation of the equilibria.

Interestingly, the complex [Ti(NBu<sup>t</sup>)(TTP)] **6** prepared by Woo and co-workers<sup>27</sup> is reported not to undergo an imide exchange reaction with aniline, even though the expected product of such a process, namely [Ti(NBu<sup>t</sup>)(TTP)], can be prepared by an alternative route. This observation clearly contrasts with the behaviour of the dibenzotetraaza[14]annulene complexes and might imply a greater accessibility of the titanium centre in **2** and its homologues by virtue of Ti lying further out of the N<sub>4</sub> donor plane. It might also suggest a greater availability of the imido nitrogen lone pairs in the dibenzotetraaza[14]annulene systems, leading in turn to more facile amine to imide hydrogen transfer in the presumed first step of imide/aniline exchange.<sup>46</sup> Such a hypothesis is supported by our previous computational studies of model square-base pyramidal systems: these predict an increase in negative charge at the imido nitrogen as the N<sub>imide</sub>=Ti-N<sub>macrocycle</sub> angle (average 111.3° in **3** and **4**, and 104.3° in **6**) is increased.<sup>28</sup>

The imido ligand in [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] **2** also undergoes exchange reactions with H<sub>2</sub>O and H<sub>2</sub>S to form the previously described<sup>22</sup> oxo- and sulfido-titanium complexes [Ti(E)-(Me<sub>4</sub>taa)] (E = O **13** or S **14**) in excellent yield. Controlled conversion of the tetratolylporphyrin-supported phenylimido compound [Ti(NPh)(TTP)] to [Ti(O)(TTP)] has been described

previously.<sup>36</sup> The reaction of [Ti(NBu<sup>t</sup>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(py)] with H<sub>2</sub>S to form the bis(μ-sulfide) [Ti<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>(μ-S)<sub>2</sub>] has also recently been reported.<sup>49</sup> When the reaction of **2** with H<sub>2</sub>S was followed by <sup>1</sup>H NMR spectroscopy there was no evidence for any intermediates. As in the case for imide/aniline exchange, we infer that H-atom transfer to the amido nitrogen of the most likely intermediate {namely [Ti(NHBu<sup>t</sup>)(SH)(Me<sub>4</sub>taa)]} and subsequent elimination of RNH<sub>2</sub> is very fast.

In an attempt to prepare a model for the proposed amido intermediates [Ti(NHBu<sup>t</sup>)(X)(Me<sub>4</sub>taa)] (X = RNH, OH or SH) in the imide/EH<sub>2</sub> (E = RN, O or S) exchange process, the reaction of [Ti(NBu<sup>t</sup>)(Me<sub>4</sub>taa)] **2** with MeOH and 2,6-dimethylphenol was carried out. For comparison, the reaction of **2** with pinacol was also studied (Scheme 2). Thus reaction of **2** with 2 equivalents of ROH or one of pinacol gave [Ti(OR)<sub>2</sub>(Me<sub>4</sub>taa)] (R = Me **15** or C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 **16**) or [Ti{OC(Me)<sub>2</sub>C(Me)<sub>2</sub>O}(Me<sub>4</sub>taa)] **17** in good yield. The compounds **15** and **16** are proposed to possess *cis*-(OR)<sub>2</sub> geometries by analogy with the structurally characterised homologue [Ti(OSiMe<sub>3</sub>)<sub>2</sub>(Me<sub>4</sub>taa)].<sup>50</sup>

Addition of only 1 equivalent of 2,6-dimethylphenol to **2** did not give (by <sup>1</sup>H NMR spectroscopy) any observable quantities of the mono(amide)-mono(aryloxide) species [Ti(NHBu<sup>t</sup>)-(OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)(Me<sub>4</sub>taa)]; instead a *ca.* 50% conversion of **2** to **16** was observed. Since the proposed intermediate [Ti(NHBu<sup>t</sup>)-(OR)(Me<sub>4</sub>taa)] in these processes does not possess any hydrogens for *intramolecular* transfer to NHBu<sup>t</sup> (in contrast to that suggested in reactions of **2** with RNH<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S), we infer that *intermolecular* attack of a second equivalent of ROH at the NHBu<sup>t</sup> amido nitrogen to form **16** must be substantially more favourable than attack at the imido nitrogen of another molecule of **2**. This is consistent with previous work of Morrison and Wigley<sup>51</sup> who suggested that the nitrogen atoms in metal amides are much more basic than those of analogous imides.

## Conclusion

We have described a unified route to three classes of tetraaza macrocycle-supported *tert*-butylimido compounds along with a related N<sub>2</sub>O<sub>2</sub> Schiff base analogue. The imido/aniline, imido/H<sub>2</sub>O and imido/H<sub>2</sub>S exchange reactions of the new [Ti(NR)-(Me<sub>4</sub>taa)] complexes have revealed important similarities and differences to previous porphyrin-supported titanium imides and dibenzotetraaza[14]annulene-supported zirconium imides. Unsuccessful attempts to prepare a mono(amide)-mono(aryloxide) complex gave only the bis(aryloxide) **16**, and so support the view that amido nitrogen lone pairs are more accessible than those of analogous imides.

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