DALTON
FULL PAPER

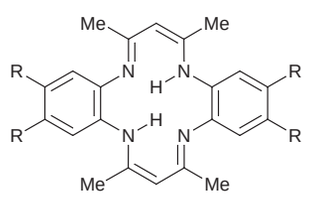
Titanium imido complexes with tetraaza macrocyclic ligands

Daniel Swallow, Jacqueline M. McInnes and Philip Mountford *,†

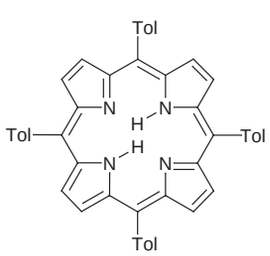
Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD

Tetraaza macrocycle-supported *tert*-butyl titanium imido complexes [Ti(NBu^t)(Me$_n$taa)] (n = 4 **2** or 8 **3**; H_2Me_ntaa = 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^t)(Me$_4$taen)] (**5**, H_2Me_4taen = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene) and [Ti(NBu^t)(TTP)] (**6**, H_2TTP = 5,10,15,20-tetratolylporphyrin) together with the N_2O_2-donor Schiff base analogue [Ti(NBu^t)(acen)] (**7**, H_2acen = 4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione) were prepared in good yield from the readily available [Ti(NBu^t)Cl$_2$(py)$_3$] and the dilithium or disodium salts of the tetradentate ligands. The Ti=NBu^t groups in **2** and **3** underwent imido group exchange reactions with anilines to form [Ti(NR)(Me$_n$taa)] (n = 4, R = $C_6H_3Me_2$-2,6 **4**, Ph, $C_6H_4(NO_2)$-4, $C_6H_4(NMe_2)$-4; n = 4 or 8, R = C_6H_4Me-4), and with H_2E (E = O or S) to give the oxo and sulfido analogues [Ti(E)(Me$_4$taa)]. Compound **4** was also prepared in good yield from [Ti(NC$_6$H$_3$Me$_2$-2,6)Cl$_2$(py)$_3$] and Li$_2$[Me$_4$taa]. Reaction of **2** with 2 or 1 equivalents of ROH (R = Me or $C_6H_3Me_2$-2,6) or pinacol afforded [Ti(OR)$_2$(Me$_4$taa)] and [Ti{OC(Me)$_2$C(Me)$_2$O}(Me$_4$taa)] respectively. The crystal structures of **3** and **4** have been described.

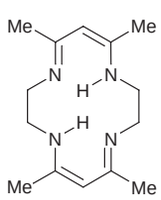
Dianionic tetraaza macrocycles and N_2O_2-donor Schiff bases have received much attention in recent years as potential alternatives to the ubiquitous bis(cyclopentadienyl) ligand set in early transition-metal chemistry.[1–18] As part of an ongoing research program in transition-metal imido chemistry[4,19–21] 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$_n$taa (n = 4 or 8), the chemistry of which has been reviewed.[2,3] These tetraaza macrocycles are related to the porphyrins but differ in several important respects. For instance, their N_4 co-ordination cavity 'hole size' is *ca.* 0.1 Å smaller than that of porphyrins and they typically possess non-planar geometries.



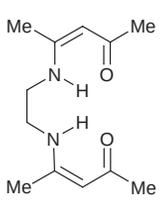
R = H: H_2Me_4taa; R = Me: H_2Me_8taa



H_2TTP (Tol = C_6H_4Me-4)



H_2Me_4taen



H_2acen

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.[4–8,22] Cognisant of the very interesting reaction chemistry that Geoffroy and co-workers[5] found for the oxo-titanium species [Ti(O)(Me$_n$taa)] (n = 4[22] or 8), we prepared the isoelectronic imido analogues [Ti(NBu^t)(Me$_n$taa)] (n = 4 **2** or 8 **3**),[23] together with homologous tetraaza[14]annulene-supported zirconium imido compounds.[4,24] Since our preliminary communication[23] of a part of these initial studies, a number of other Group 4 macrocycle-supported imido derivatives have been described.[25–27] 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.[23,28]

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, $CDCl_3$ and CD_2Cl_2 were dried over calcium hydride at room temperature (r.t.), distilled under reduced pressure and stored under N_2 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 ^{13}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 (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$). 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$_2$[(Me$_n$taa)] (n = 4 or 8), Li$_2$[Me$_4$taen], Li$_2$[TTP]·2THF, Na$_2$[acen] and [Ti(NR)Cl$_2$(py)$_3$] (R = Bu^t **1a** or $C_6H_3Me_2$-2,6 **1b**) were prepared as previously described.[12,13,29–31]

† P. Mountford is the Royal Society of Chemistry Sir Edward Frankland Fellow. E-Mail: Philip.Mountford@Nottingham.ac.uk (http://www.nottingham.ac.uk/~pczwww/Inorganic/PMount.html).

Syntheses

[Ti(NBu^t)(Me$_4$taa)] 2. A cold (0 °C) solution of Li_2[Me$_4$taa] (3.50 g, 9.83 mmol) in THF (40 ml) was added dropwise to a cold solution of [Ti(NBu^t)Cl$_2$(py)$_3$] (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%). ^{1}H NMR ($CDCl_3$, 250.1 MHz, 298 K): δ 7.32–7.36, 7.18–7.24 (2 × m, 2 × 4 H, C_6H_4), 5.13 [s, 2 H, NC(Me)C*H*], 2.40 [s, 12 H, NC(*Me*)CH], 0.26 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz, 298 K): δ 160.1 [N*C*(Me)CH], 139.4 (*C*N of C_6H_4 of Me$_4$taa), 124.3, 123.3 (2 × *C*H of C_6H_4), 103.3 [NC(Me)*C*H], 67.2 (N*C*Me$_3$), 31.6 (NC*Me*$_3$), 22.7 [NC(*Me*)CH] [Found (Calc. for $C_{26}H_{31}N_5Ti\cdot CH_2Cl_2$): C, 60.2 (59.4); H, 6.0 (6.1); N, 12.6 (12.8)%].

[Ti(NBu^t)(Me$_8$taa)] 3. A THF (20 ml) solution of [Ti(NBu^t)-Cl$_2$(py)$_3$] (2.45 g, 5.70 mmol) was added dropwise to Li_2[Me$_8$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_2Cl_2 (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_2Cl_2 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_2Cl_2 solution layered with hexane. ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.13 (s, 4 H, $C_6H_2Me_2$), 5.07 [s, 2 H, NC(Me)-C*H*], 2.39 [s, 12 H, NC(*Me*)CH], 2.32 (s, 12 H, $C_6H_2Me_2$), 0.29 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.7 MHz): δ 159.7 [N*C*(Me)CH], 137.1 (CN of $C_6H_2Me_2$ of Me$_8$taa), 132.5 (*C*Me of $C_6H_2Me_2$), 124.2 (*C*H of $C_6H_2Me_2$), 102.9 [NC(Me)*C*H], 67.0 (N*C*Me$_3$), 31.8 (NC*Me*$_3$), 22.7 [NC(*Me*)CH], 20.0 ($C_6H_2Me_2$) [Found (Calc. for $C_{30}H_{39}N_5Ti$): C, 69.6 (69.6); H, 7.6 (7.6); N, 13.4 (13.5)%].

[Ti(NC$_6$H$_3$Me$_2$-2,6)(Me$_4$taa)] 4. *Method* (*a*): *from* **1b** *and* Li_2[Me$_4$taa]. To a cold (0 °C) solution of **1b** (0.200 g, 0.414 mmol) in CH_2Cl_2 (20 ml) was added cold Li_2[Me$_4$taa] (0.140 g, 0.414 mmol) in CH_2Cl_2 (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_2Cl_2 (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_2Cl_2 (6:1) at −25 °C overnight to give **4** as a brown solid that was washed with hexane–CH_2Cl_2 and dried *in vacuo*. Yield: 0.170 g (77%). Diffraction quality crystals of **4**·$H_2NC_6H_3Me_2$-2,6 were grown at room temperature over several days from a CH_2Cl_2 solution of crude **4** layered with hexane. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.47–7.43, 7.31–7.25 (2 × m, 2 × 4 H, C_6H_4), 6.39 (d, *J* 7.5, 2 H, *m*-$C_6H_3Me_2$), 6.16 (t, *J* 7.2, 1 H, *p*-$C_6H_3Me_2$), 5.32 [s, 2 H, NC(Me)C*H*], 2.48 [s, 12 H, NC(*Me*)CH], 1.10 (s, 6 H, $C_6H_3Me_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 161.1 [N*C*(Me)CH], 139.7 (CN of C_6H_4 of Me$_4$taa), 129.5 (*o*-$C_6H_3Me_2$), 126.3 (*m*-$C_6H_3Me_2$), 125.4, 124.3 (2 × *C*H of C_6H_4), 117.9 (*p*-$C_6H_3Me_2$), 105.0 [NC(Me)*C*H], 23.5 [NC(*Me*)CH], 18.1 ($C_6H_3Me_2$); note: the *ipso* carbon of the $C_6H_3Me_2$ group was not observed. EI mass spectrum: *m*/*z* = 509 {M^+}, 406 {$M^+ - C_8H_7$}, 390 {$M^+ - C_8H_9N$} [Found (Calc. for $C_{30}H_{31}N_5Ti$): C, 69.2 (70.7); H, 6.1 (6.1); N, 13.0 (13.7)%].

[Ti(NBu^t)(Me$_4$taen)] 5. To a cold (0 °C) solution of [Ti-(NBu^t)Cl$_2$(py)$_3$] (0.740 g, 1.73 mmol) in THF (30 ml) was added cold Li_2[Me$_4$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_2Cl_2 (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%). ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 4.70 [s, 2 H, NC(Me)C*H*], 4.21, 3.65 (2 × m, 2 × 2 H, NCH_2), 1.98 [s, 12 H, NC(*Me*)CH], 0.89 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 163.0 [N*C*(Me)CH], 98.1 [NC(Me)*C*H], 67.1 (N*C*Me$_3$), 50.7 (NCH$_2$), 32.8 [NC(*Me*)CH], 21.2 (NC*Me*$_3$). EI mass spectrum: *m*/*z* = 365 {M^+}, 350 {$M^+ - CH_3$} [Found (Calc. for $C_{18}H_{31}N_5Ti$): 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^t)(TTP)] 6. To a cold (0 °C) solution of [Ti(NBu^t)-Cl$_2$(py)$_3$] (0.100 g, 0.234 mmol) in THF (30 ml) was added Li_2[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.[27]

[Ti(NBu^t)(acen)] 7. To a cold (0 °C) solution of [Ti(NBu^t)-Cl$_2$(py)$_3$] (0.790 g, 1.8 mmol) in THF (20 ml) was added a slurry of Na_2[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_2Cl_2 (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%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 5.19 [s, 2 H, MeC(O)C*H*(N)Me], 4.17, 3.67 (2 × m, 2 × 2 H, NCH$_2$), 2.10, 2.08 [2 × s, 2 × 6 H, *Me*C(O)CH(N)Me and MeC(O)CH(N)*Me*], 0.85 (s, 9 H, Bu^t). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 178.1 [Me*C*(O)CH(N)CMe], 168.6 [MeC(O)-CH(N)*C*Me], 101.9 [MeC(O)*C*H(N)CMe], 69.2 (N*C*Me$_3$), 51.7 (NCH$_2$), 31.8 (NC*Me*$_3$), 24.9 [*Me*C(O)CH(N)CMe], 21.5 [MeC(O)CH(N)C*Me*]. Elemental analyses were not obtained for this compound which decomposed in solvents from which recrystallisation was attempted.

[Ti(NPh)(Me$_4$taa)] 8, [Ti(NC$_6$H$_4$Me-4)(Me$_4$taa)] 9, [Ti{NC$_6$-H$_4$(NO$_2$)-4}(Me$_4$taa)] 10, [Ti{NC$_6$H$_4$(NMe$_2$)-4}(Me$_4$taa)] 11 and [Ti(NC$_6$H$_4$Me-4)(Me$_8$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_2Cl_2–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**. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.50–7.46, 7.34–7.31 (2 × m, 2 × 4 H, C_4H_4), 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)C*H*], 2.47 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 160.5 [N*C*(Me)CH], 138.2 (CN of C_6H_4 of Me$_4$taa), 127.2 (*m*-Ph), 125.2, 123.7 (2 × CH of C_6H_4), 120.7 (*o*-Ph), 117.2 (*p*-Ph), 104.5 [NC(Me)*C*H], 22.7 [NC(*Me*)CH]; note: the *ipso* carbon of the Ph group was not observed [Found (Calc. for $C_{28}H_{27}N_5Ti$): C, 68.5 (69.8); H, 5.7 (5.6); N, 14.4 (14.6)%].

Data for **9**. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.49–7.45, 7.33–7.29 (2 × m, 2 × 4 H, C_6H_4 of Me$_4$taa), 6.36 (d, *J* 8.0, 2 H, *m*-C_6H_4Me), 5.28 [s, 2 H, 2 × NC(Me)C*H*], 5.27 (d, *J* 8.0, 2 H,

o-C_6H_4Me), 2.46 [s, 12 H, NC(*Me*)CH], 1.94 (s, 3 H, C_6H_4*Me*). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 160.4 [N*C*(Me)CH], 158.9 (*p*-C_6H_4Me), 138.3 (CN of C_6H_4 of Me_4taa), 127.7 (*m*-C_6H_4Me), 125.1, 123.7 (2 × CH of C_6H_4 of Me_4taa), 120.4 (*o*-C_6H_4Me), 104.4 [NC(Me)*C*H], 22.7 [NC(*Me*)CH], 20.5 (C_6H_4*Me*); note: the *ipso* carbon of the C_6H_4Me group was not observed [Found (Calc. for $C_{29}H_{29}N_5Ti$): C, 69.9 (70.3); H, 5.8 (5.9); N, 14.0 (14.1)%].

Data for **10**. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.52–7.38 (overlapping 2 × m and d, 10 H, 2 × C_6H_4 of Me_4taa and *m*-$C_6H_4NO_2$), 5.43 [s, 2 H, NC(Me)C*H*], 5.07 (d, *J* 8.1, 2 H, *o*-$C_6H_4NO_2$), 2.51 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 165.2 (*p*-$C_6H_4NO_2$), 160.8 [N*C*(Me)CH], 137.2 (CN of C_6H_4 of Me_4taa), 126.1 (CH of C_6H_4 of Me_4taa), 124.7 (*m*-$C_6H_4NO_2$), 123.8 (CH of C_6H_4 of Me_4taa), 120.3 (*o*-$C_6H_4NO_2$), 113.2 (*ipso*-$C_6H_4NO_2$), 105.5 [NC(Me)CH], 22.7 [4 × NC(Me)CH] [Found (Calc. for $C_{28}H_{26}N_6O_2Ti$): C, 64.0 (63.9); H, 5.3 (5.0); N, 16.0 (16.0)%].

Data for **11**. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.50–7.46, 7.33–7.29 (2 × m, 2 × 4 H, C_6H_4 of Me_4taa), 6.12 (d, *J* 8.7, 2 H, *m*-$C_6H_4NMe_2$), 5.36 (d, *J* 8.7, 2 H, *o*-$C_6H_4NMe_2$), 5.26 [s, 2 H, NC(Me)C*H*], 2.58 (s, 6 H, $C_6H_4NMe_2$), 2.46 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 160.4 [N*C*(Me)CH], 155.1 (*p*-$C_6H_4NMe_2$), 143.3 (*ipso*-$C_6H_4NMe_2$), 138.5 (CN of C_6H_4 of Me_4taa), 125.0, 123.7 (2 × CH of C_6H_4 of Me_4taa), 121.2 (*m*-$C_6H_4NMe_2$), 113.8 (*o*-$C_6H_4NMe_2$), 104.3 [NC(Me)*C*H], 42.1 ($C_6H_4NMe_2$), 22.7 [NC(*Me*)CH]. Satisfactory elemental analyses could not be obtained for this compound.

Data for **12**. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.37 (s, C_6H_6), 7.25 (s, 4 H, $C_6H_2Me_2$ of Me_8taa), 6.33 (d, *J* 8.0, 2 H, *m*-C_6H_4Me), 5.33 (d, *J* 8.0, 2 H, *o*-C_6H_4Me), 5.32 [s, 2 H, 2 × NC(Me)C*H*], 2.46 [s, 12 H, NC(*Me*)CH], 2.37 (s, 12 H, $C_6H_2Me_2$), 1.98 (s, 3 H, C_6H_4*Me*). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 160.3 (*ipso*-C_6H_4Me), 159.9 [N*C*(Me)CH], 136.0 (CN of $C_6H_2Me_2$ of Me_8taa), 134.2 (*p*-C_6H_4Me), 133.6 (CMe of $C_6H_2Me_2$ of Me_8taa), 127.7 (C_6H_6), 125.1 and 120.5 (*o*- and *m*-C_6H_4Me), 124.6 (4 × CH of Me_8taa), 103.9 [2 × NC(Me)-*C*H], 22.8 and 20.1 [NC(*Me*)CH and $C_6H_2Me_2$, respectively], 20.6 ($C_6H_2Me_2$) [Found (Calc. for $C_{33}H_{37}N_5Ti$): C, 70.8 (71.9); H, 6.7 (6.8); N, 11.8 (12.7)%].

[Ti(O)(Me_4taa)] 13. To a red solution of [Ti(NBu^t)(Me_4taa)] (0.100 g, 0.217 mmol) in THF (20 ml) at r.t. was added H_2O (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.[22]

[Ti(S)(Me_4taa)] 14. Dihydrogen sulfide was slowly passed through a stirred solution of [Ti(NBu^t)(Me_4taa)] (0.100 g, 0.217 mmol) in CH_2Cl_2 (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.[22]

[Ti(OMe)$_2$(Me_4taa)] 15. To a solution of [Ti(NBu^t)(Me_4taa)] (0.200 g, 0.433 mmol) in CH_2Cl_2 (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%). ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.30–7.10 (overlapping 2 × m, 2 × 4 H, C_6H_4), 5.27 [s, 2 H, NC(Me)C*H*], 3.69 (s, 6 H, OMe), 2.39 [s, 12 H, NC(*Me*)CH]. ^{13}C-{^{1}H} DEPT-135 NMR ($CDCl_3$, 62.5 MHz): δ 124.9, 122.7 (CH of C_6H_4), 103.1 [NC(Me)*C*H], 62.6 (OMe), 23.6 [NC(*Me*)CH] [Found (Calc. for $C_{24}H_{28}N_4O_2Ti$): C, 63.2 (63.7); H, 6.3 (6.2); N, 12.3 (12.4)%].

[Ti($OC_6H_3Me_2$-2,6)$_2$(Me_4taa)] 16. To a solution of [Ti(NBu^t)(Me_4taa)] (0.200 g, 0.433 mmol) in CH_2Cl_2 (15 ml) was added 2,6-dimethylphenol (0.110 g, 0.866 mmol) in CH_2Cl_2 (15 ml). After 12 h at r.t. **16** formed as a red-brown microcrystalline CH_2Cl_2 solvate (by ^{1}H NMR and elemental analysis) and was washed with a minimum volume of CH_2Cl_2–hexane (1:6) and dried *in vacuo*. Yield: 0.220 g (71%). ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.22–7.11 (overlapping 2 × m, 2 × 4 H, C_6H_4), 6.48 (d, *J* 7.3, 4 H, *m*-$C_6H_3Me_2$), 6.26 (t, *J* 7.3, 2 H, *p*-$C_6H_3Me_2$), 5.50 [s, 2 H, NC(Me)C*H*], 2.43 [s, 12 H, C(*Me*)CH], 1.27 (s, 12 H, $C_6H_3Me_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 165.7 (*ipso*-$C_6H_3Me_2$), 158.5 [*C*(Me)CH], 140.4 (CN of C_6H_4 of Me_4taa), 127.2 (*m*-$C_6H_3Me_2$), 125.5 (*o*-$C_6H_3Me_2$), 124.9, 123.2 (2 × CH of C_6H_4), 117.5 (*p*-$C_6H_3Me_2$), 105.4 [NC(Me)*C*H], 24.4 [NC(*Me*)CH], 15.9 ($C_6H_3Me_2$) [Found (Calc. for $C_{38}H_{40}N_4O_2Ti\cdot CH_2Cl_2$): C, 64.9 (65.3); H, 5.9 (5.9); N, 7.7 (7.8)%].

[Ti{OC(Me)$_2$C(Me)$_2$O}(Me_4taa)] 17. To a solution of [Ti(NBu^t)(Me_4taa)] (0.100 g, 0.217 mmol) in CH_2Cl_2 (15 ml) was added pinacol (0.026 g, 0.217 mmol) in CH_2Cl_2 (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_2Cl_2 hemi-solvate (by ^{1}H NMR and elemental analysis) that was washed with hexane (2 × 5 ml) and dried *in vacuo*. Yield: 0.10 g (81%). ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 7.35–7.13 (overlapping 2 × m, 2 × 4 H, C_6H_4), 5.32 [s, 2 H, NC(Me)C*H*], 2.39 [s, 12 H, NC(*Me*)CH], 0.37 (s, 12 H, $O_2C_2Me_4$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 62.5 MHz): δ 158.3 [N*C*(Me)CH], 141.5 (CN of C_6H_4 of Me_4taa), 123.9, 123.3 (2 × CH of C_6H_4), 104.5 [NC(Me)*C*H], 92.1 ($O_2C_2Me_4$), 25.8 ($O_2C_2Me_4$), 23.6 [NC(*Me*)CH] [Found (Calc. for $C_{28}H_{34}N_4O_2Ti\cdot 0.5CH_2Cl_2$): 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^{n}Li (for H_2Me_ntaa and H_2Me_4taen),[12,29] LiN(SiMe$_3$)$_2$ (for H_2TTP),[30] or sodium hydride (H_2acen)[13] to form the corresponding dilithium or disodium salts. In recent studies[19] 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_2(py)$_3$] (R = Bu^t **1a** or $C_6H_3Me_2$-2,6 **1b**).[31] The reactions of **1** with dianionic N_4- and N_2O_2-donor ligands are summarised in Scheme 1 and details of the preparation and characterisation of all the compounds are given in the Experimental section.

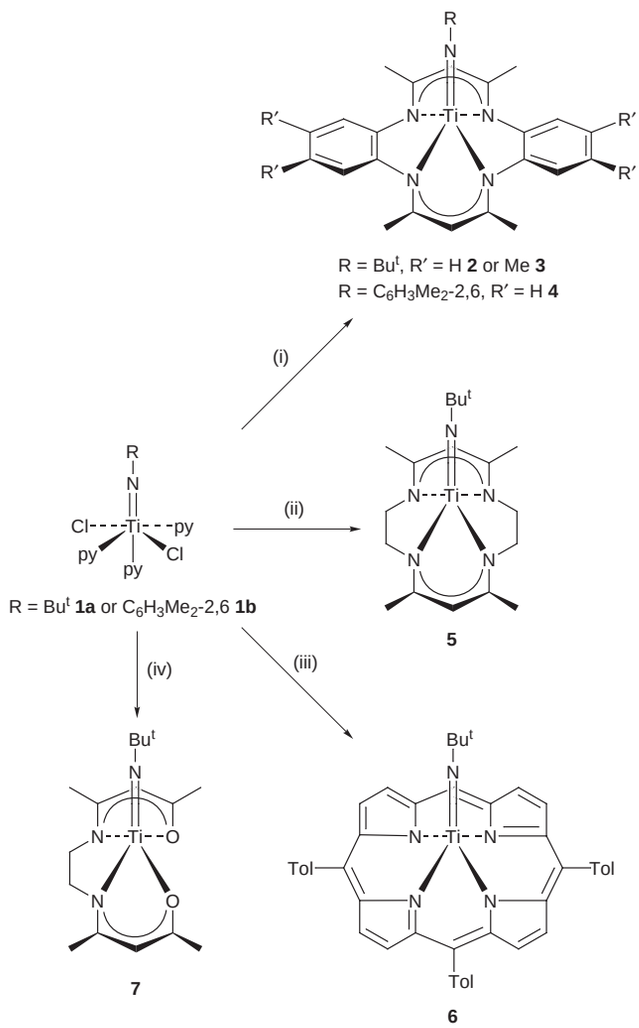
The reaction of [Ti(NBu^t)Cl_2(py)$_3$] **1a** with Li_2[Me_ntaa] (n = 4 or 8) in THF procedes smoothly to afford good yields of the red tetraaza macrocyclic derivatives [Ti(NBu^t)(Me_ntaa)] (n = 4 **2** or 8 **3**). These compounds are also accessible from the bis(*tert*-butylpyridine) homologues [Ti(NBu^t)Cl_2(Bu^{t}py)$_2$] (Bu^{t}py = *tert*-butylpyridine),[23] and are air- and moisture-sensitive in solution and the solid state. The arylimido analogue [Ti($NC_6H_3Me_2$-2,6)(Me_4taa)] **4** was also prepared cleanly in an analogous fashion from [Ti($NC_6H_3Me_2$-2,6)Cl_2(py)$_3$] **1b** and Li_2[Me_4taa] 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 ^{1}H chemical shifts for the NBu^t group in **2** and **3** (δ 0.26 and 0.29 respectively) and the *ortho*-methyl substituents for $NC_6H_3Me_2$-2,6 in **4** (δ 1.10) in $CDCl_3$ occur at significantly higher field compared with the corresponding resonances[31] 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^t)(Me$_8$taa)] **3** and [Ti(NC$_6$H$_3$Me$_2$-2,6)(Me$_4$taa)] **4**[23,28]

	3	**4**
Ti–N$_{imide}$	1.724(4)	1.720(4)
Ti · · · N$_4$ plane	0.76	0.75
Ti–N$_{macrocycle}$*	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$_{imide}$–C	164.3(3)	175.4(4)
N$_{imide}$–Ti–N$_{macrocycle}$*	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$_2$[Me$_n$taa] (n = 4 or 8), THF (for **2** and **3**) or CH_2Cl_2, 0 °C then r.t., 12–24 h, *ca.* 70%; (ii) Li$_2$[Me$_4$taen], THF, 0 °C then r.t., 24 h, 61%; (iii) Li$_2$[TTP]·2THF, THF, 0 °C then r.t., 24 h, 71%; (iv) Na$_2$[acen], THF, 0 °C then r.t., 24 h, 52%

shielding effects of the *o*-phenylene aromatic rings of the Me$_n$taa ligand (see below).

The solid state structures[23,28] 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$_4$ 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$_4$ plane. The Ti≡N$_{imide}$ bond lengths of *ca.* 1.72 Å are at the longer end of the

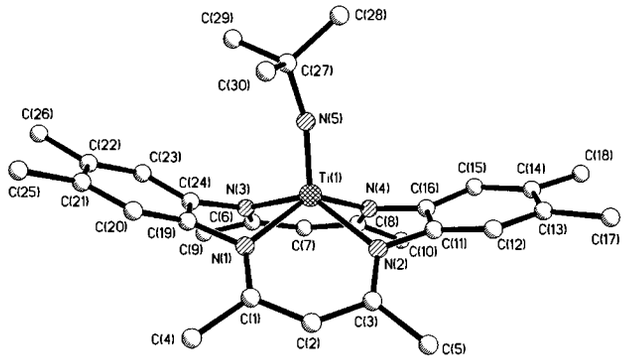


Fig. 1 Molecular structure of [Ti(NBu^t)(Me$_8$taa)] **3** with hydrogen atoms omitted[23]

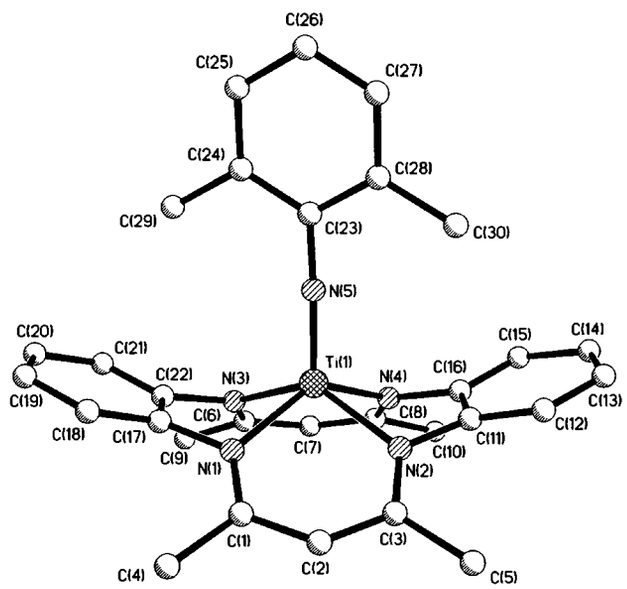


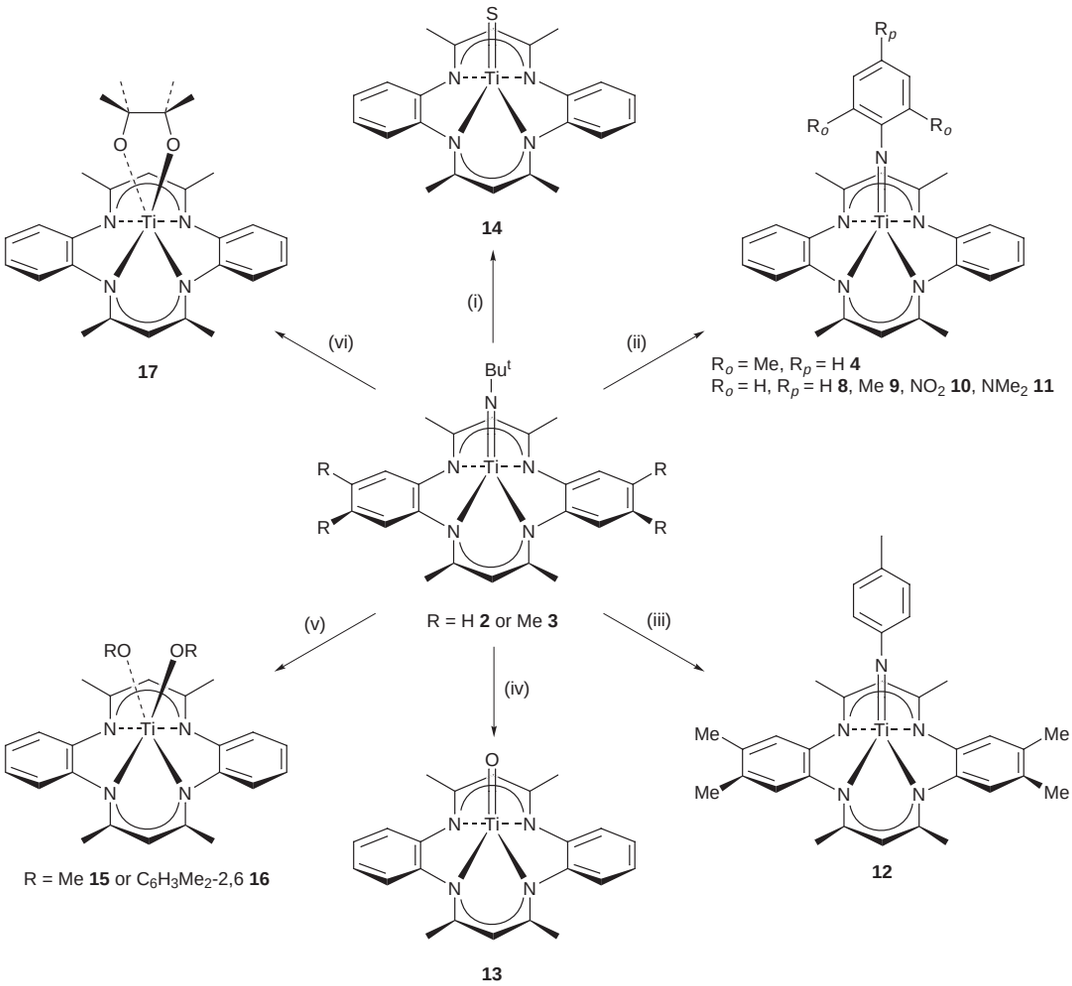
Fig. 2 Molecular structure of [Ti(NC$_6$H$_3$Me$_2$-2,6)(Me$_4$taa)] **4** with hydrogen atoms omitted[28]

range for this linkage (range *ca.* 1.66–1.74 Å),[19,32] but still imply a formal Ti≡N$_{imide}$ triple bond.‡ The Me$_n$taa ligands in **3** and **4** adopt the characteristic 'saddle shape',[2,3] and the folding of the *o*-phenylene rings 'up' towards the imido groups is consistent with the shielding effects seen in the ^{1}H NMR spectra.

The square-base pyramidal co-ordination geometry in **3** and **4** is well-established in titanium imido chemistry.[19,32] However, the macrocyclic compounds described here have unusually large average N≡Ti–N$_{macrocycle}$ bond angles (average 111.3° for both **3** and **4**) when compared with previous examples: [Ti(NBu^t)Cl$_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; average N≡Ti–L = 103.5°),[33] [Ti$_2$(NBu^t)$_2${μ-O$_2$P(OSiMe$_3$)$_2$}$_4$] (average N≡Ti–L = 107.1°),[34] [Ti(NBu^t)Cl$_2$(dipeda)] [dipeda = *N*,*N*′-diisopropylethylenediamine; average N≡Ti–L = 101.7(2)°],[33] [Ti(NBu^t)Cl$_2$(OPPh$_3$)$_2$] [average N≡Ti–L = 105.4(3)°],[35] and [Ti(NPh)(TTP)] (average N≡Ti–N$_{macrocycle}$ = 104.3°).[36] This is apparently related to the small N$_4$ 'hole size' of Me$_n$taa (see Introduction section) which leads to a relatively large displacement of Ti from the N$_4$ plane and so to larger average N≡Ti–N$_{macrocycle}$ bond angles. Possible electronic consequences of these structural constraints for [Ti(E)(Me$_n$taa)] (E = NR or O) have been discussed by us elsewhere.[28]

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)$_n$] (R = Bu^t or aryl, n = 1 or 2; L = dianionic tetradentate ligand) described herein is generally best thought of as three (pseudo-σ^2 π^4 triple bond) rather than as two.[32]



Scheme 2 Imido ligand exchange and protonolysis reactions of [Ti(NBu^t)(Me$_n$taa)] (n = 4 **2** or 8 **3**). (i) Slow stream of H_2S, CH_2Cl_2, r.t., 1 min, 87%; (ii) $H_2NC_6H_2\{(R_o)_2(R_p)\}$-2,4,6 (*ca.* 1–4 equivalents), CH_2Cl_2, 18 h–3 d, 75–85%; (iii) 4-methylaniline (1.1 equivalents), C_6H_6, r.t., 3 h, 95%; (iv) H_2O, THF, r.t., 30 min, 82%; (v) ROH (2 equivalents), CH_2Cl_2, r.t., 12–24 h, 62% (for **15**) or 71% (for **16**); (vi) pinacol, CH_2Cl_2, r.t., 24 h, 81%

titanium imido complexes (Scheme 1). Group 4 derivatives of Me$_4$taen have recently been reported by Jordan and co-workers but no imido derivatives were described.[11,12] We found that reaction of Li$_2$[Me$_4$taen] with [Ti(NBu^t)Cl$_2$(py)$_3$] **1a** gave [Ti(NBu^t)(Me$_4$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}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[27] described the synthesis of the porphyrin titanium imido complex [Ti(NBu^t)(TTP)] **6** from [Ti(TTP)Cl$_2$] and LiNHBu^t. We have independently found that the same compound is accessible by treatment of [Ti(NBu^t)Cl$_2$(py)$_3$] **1a** with Li$_2$[TTP]·2THF 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 N_2O_2 Schiff base-supported imido compounds known.[37–41] For comparison with the tetraaza macrocyclic systems we therefore prepared the complex [Ti(NBu^t)(acen)] **7** from **1a** and Na$_2$[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}H and ^{13}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 (δ 0.85) for a terminal Ti≡NBu^t linkage.

Scheme 2 shows exchange and protonolysis reactions of the *tert*-butylimido ligand in [Ti(NBu^t)(Me$_n$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.[31,42–48] We were interested to use this method for preparing dibenzotetraaza[14]annulene-supported *o*-unsubstituted arylimido compounds since starting materials of the type [Ti(NC$_6$H$_4$R-4)Cl$_2$(py)$_3$] (R = H, Me or NO$_2$)[31] are less convenient to use as synthons (due to their limited solubilities and stabilities) than [Ti(NBu^t)Cl$_2$(py)$_3$] **1a** in reactions with Li$_2$[Me$_n$taa] (*cf.* Scheme 1).

Reaction of [Ti(NBu^t)(Me$_4$taa)] **2** with 3.5 equivalents of 2,6-dimethylaniline in dichloromethane gave [Ti(NC$_6$H$_3$Me$_2$-2,6)(Me$_4$taa)] **4** in 77% recrystallised yield (Scheme 2). The yield of **4** obtained this way is comparable to that from direct reaction of [Ti(NC$_6$H$_3$Me$_2$-2,6)Cl$_2$(py)$_3$] with Li$_2$[Me$_4$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 [Ti(NC$_6$H$_4$R-4)(Me$_4$taa)] (R = H **8**, Me **9**, NO$_2$ **10** or NMe$_2$ **11**) or [Ti(NC$_6$H$_4$Me-4)(Me$_8$taa)] **12**. The NMR spectroscopic data for **8**–**12** are fully consistent with the proposed structures. The ^{1}H NMR spectra show doublets for the *o*-hydrogens of the phenyl rings in the range *ca.* δ 5.0–5.4 consistent with shielding effects from the macrocycle aromatic rings.

Bergman and co-workers[46] have reported mechanistic studies for *tert*-butylimide/2,6-dimethylaniline exchange reactions of [Os(NBu^t)L] (L = η^6-cymene). The reaction is proposed to go *via* a bis(amide) intermediate of the type [Os(NHBu^t)(NHR)L] (R = $C_6H_3Me_2$-2,6) for which the rate of H-atom transfer to the most basic amide (in this case *to* NHBu^t *from* NHR) is much larger than that from NHBu^t back to NHR, leading to formation and release of Bu^{t}NH$_2$, 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^t)(NHR)(Me$_4$taa)] when the reactions were followed by ^{1}H NMR spectroscopy. For example, mixtures of [Ti(NBu^t)(Me$_4$taa)] **2** and 2,6-dimethylaniline show resonances only for the starting materials and (with time) products **4** and Bu^{t}NH$_2$. Similarly, mixtures of **4** and 2,6-dimethylaniline show no NMR spectroscopic evidence for the bis(amide) [Ti(NHC$_6$H$_3$Me$_2$-2,6)$_2$(Me$_4$taa)]. This contrasts with the chemistry of the zirconium analogue of **4**, namely [Zr(NC$_6$H$_3$Pr^i-2,6)(Me$_4$taa)(py)], which reacts rapidly and irreversibly with 2,6-diisopropylaniline to form [Zr(NHC$_6$H$_3$Pr^i-2,6)$_2$(Me$_4$taa)].[4] 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 $CDCl_3$ [equations (1) and (2)]. Thus 1:1 mixtures of [Ti(NC$_6$H$_4$Me-4)(Me$_4$taa)] **9** and aniline gave, after several days at ambient temperature, equimolar mixtures with [Ti(NPh)(Me$_4$taa)] **8** and 4-methylaniline [equation (1)]. However, when the analogous experiment was carried out with [Ti(NC$_6$H$_4$Me-4)(Me$_4$taa)] **9** and 4-nitroaniline [equation (2)] near-quantitative formation of [Ti{NC$_6$H$_4$(NO$_2$)-4}(Me$_4$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.

$$[Ti(NC_6H_4Me\text{-}4)(Me_4taa)] + H_2NPh \rightleftharpoons [Ti(NPh)(Me_4taa)] + H_2NC_6H_4Me\text{-}4 \quad (1)$$

$$[Ti(NC_6H_4Me\text{-}4)(Me_4taa)] + H_2NC_6H_4(NO_2)\text{-}4 \rightleftharpoons [Ti\{NC_6H_4(NO_2)\text{-}4\}(Me_4taa)] + H_2NC_6H_4Me\text{-}4 \quad (2)$$

Interestingly, the complex [Ti(NBu^t)(TTP)] **6** prepared by Woo and co-workers[27] is reported not to undergo an imide exchange reaction with aniline, even though the expected product of such a process, namely [Ti(NBu^t)(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_4 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.[46] 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 $N_{imide}{\equiv}Ti{-}N_{macrocycle}$ angle (average 111.3° in **3** and **4**, and 104.3° in **6**) is increased.[28]

The imido ligand in [Ti(NBu^t)(Me$_4$taa)] **2** also undergoes exchange reactions with H_2O and H_2S to form the previously described[22] oxo– and sulfido–titanium complexes [Ti(E)(Me$_4$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.[36] The reaction of [Ti(NBu^t)(η^5-C$_5$H$_5$)$_2$(py)] with H_2S to form the bis(μ-sulfide) [Ti$_2$(η^5-C$_5$H$_5$)$_4$(μ-S)$_2$] has also recently been reported.[49] When the reaction of **2** with H_2S was followed by ^{1}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^t)(SH)(Me$_4$taa)]} and subsequent elimination of RNH$_2$ is very fast.

In an attempt to prepare a model for the proposed amido intermediates [Ti(NHBu^t)(X)(Me$_4$taa)] (X = RNH, OH or SH) in the imide/EH$_2$ (E = RN, O or S) exchange process, the reaction of [Ti(NBu^t)(Me$_4$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)$_2$(Me$_4$taa)] (R = Me **15** or C$_6$H$_3$Me$_2$-2,6 **16**) or [Ti{OC(Me)$_2$C(Me)$_2$O}(Me$_4$taa)] **17** in good yield. The compounds **15** and **16** are proposed to possess *cis*-(OR)$_2$ geometries by analogy with the structurally characterised homologue [Ti(OSiMe$_3$)$_2$(Me$_4$taa)].[50]

Addition of only 1 equivalent of 2,6-dimethylphenol to **2** did not give (by ^{1}H NMR spectroscopy) any observable quantities of the mono(amide)–mono(aryloxide) species [Ti(NHBu^t)(OC$_6$H$_3$Me$_2$-2,6)(Me$_4$taa)]; instead a *ca.* 50% conversion of **2** to **16** was observed. Since the proposed intermediate [Ti(NHBu^t)(OR)(Me$_4$taa)] in these processes does not possess any hydrogens for *intra*molecular transfer to NHBu^t (in contrast to that suggested in reactions of **2** with RNH$_2$, H_2O and H_2S), we infer that *inter*molecular attack of a second equivalent of ROH at the NHBu^t 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[51] 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_2O_2 Schiff base analogue. The imido/aniline, imido/H_2O and imido/H_2S exchange reactions of the new [Ti(NR)(Me$_n$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.

Acknowledgements

This work was supported by grants (to P. M.) from the EPSRC, Leverhulme Trust and Royal Society. We thank the EPSRC also for a studentship (to D. S.) and the provision of an X-ray diffractometer. We also thank Professor K. L. Woo (Iowa State University) and Dr. S. D. Gray for helpful discussions and disclosure of results prior to publication. We acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory.

References

1 H. Brand and J. Arnold, *Coord. Chem. Rev.*, 1995, **140**, 137.
2 F. A. Cotton and J. Czuchajowska, *Polyhedron*, 1990, **9**, 2553.
3 P. Mountford, *Chem. Soc. Rev.*, 1998, **27**, 105.
4 G. I. Nikonov, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 1107.
5 C. E. Housemekerides, D. L. Ramage, C. M. Kretz, J. T. Shontz, R. S. Pilato, G. L. Geoffroy, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.*, 1992, **31**, 4453.

6 J. L. Kisko, T. Hascall and G. Parkin, *J. Am. Chem. Soc.*, 1997, **119**, 7609.
7 A. Klose, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Chem. Commun.*, 1997, 2297.
8 H. Schumann, *Inorg. Chem.*, 1996, **35**, 1808.
9 L. Giannini, E. Solari, S. De Angelis, T. R. Ward, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 5801.
10 A. Martin, R. Uhrhammer, T. G. Gardner, R. F. Jordan and R. D. Rogers, *Organometallics*, 1998, **17**, 382.
11 D. G. Black, R. F. Jordan and R. D. Rogers, *Inorg. Chem.*, 1997, **36**, 103.
12 D. G. Black, D. C. Swenson, R. F. Jordan and R. D. Rogers, *Organometallics*, 1995, **14**, 3539.
13 E. B. Tjaden, D. C. Swenson, R. F. Jordan and J. L. Petersen, *Organometallics*, 1995, **14**, 371.
14 P. G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1995, **14**, 4994.
15 E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 367.
16 F. Franceschi, E. Gallo, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Eur. J. Chem.*, 1996, **2**, 1466.
17 F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1335.
18 J.-M. Rosset, C. Floriani, M. Mazzanti, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1990, **29**, 3991.
19 P. Mountford, *Chem. Commun.*, 1997, 2127 (Feature Article).
20 P. J. Stewart, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 1982.
21 P. J. Wilson, A. J. Blake, P. Mountford and M. Schröder, *Chem. Commun.*, 1998, 1007.
22 V. L. Goedken and J. A. Ladd, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 142.
23 S. C. Dunn, A. S. Batsanov and P. Mountford, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2007.
24 A. J. Blake, P. Mountford, G. I. Nikonov and D. Swallow, *Chem. Commun.*, 1996, 1835.
25 M. J. Scott and S. J. Lippard, *Organometallics*, 1997, **16**, 5857.
26 M. D. Fryzuk, J. B. Love and S. J. Rettig, *Organometallics*, 1998, **17**, 846.
27 S. D. Gray, J. L. Thorman, L. M. Berreau and L. K. Woo, *Inorg. Chem.*, 1997, **36**, 278.
28 P. Mountford and D. Swallow, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2357.
29 S. de Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520.
30 S. D. Gray and L. K. Woo, personal communication.
31 A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1549.
32 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
33 T. S. Lewkebandra, P. H. Sheridan, M. J. Heeg, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1994, **33**, 5879.
34 D. L. Thorn and R. L. Harlow, *Inorg. Chem.*, 1992, **31**, 3917.
35 C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg and J. W. Proscia, *J. Am. Chem. Soc.*, 1992, **114**, 1095.
36 L. M. Berreau, V. G. Young and L. K. Woo, *Inorg. Chem.*, 1995, **34**, 527.
37 R. L. Elliott, P. J. Nichols and B. O. West, *Polyhedron*, 1987, **6**, 2191.
38 P. J. Nichols, G. D. Fallon, K. S. Murray and B. O. West, *Inorg. Chem.*, 1988, **27**, 2795.
39 W.-H. Leung, A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2051.
40 W.-H. Leung, M.-C. Wu, K.-Y. Wong and Y. Wang, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1659.
41 We have recently reported complexes of the type $[Ti(NR)L]_n$ ($R = Bu^t$ or 2,6-$C_6H_3Me_2$-2,6; L = substituted salen; $n = 1$ or 2): J. M. McInnes, D. Swallow, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1998, submitted.
42 P. J. Stewart, A. J. Blake and P. Mountford, *Inorg. Chem.*, 1997, **36**, 3616.
43 M. C. W. Chan, J. M. Cole, V. C. Gibson and J. K. Howard, *Chem. Commun.*, 1997, 2345.
44 A. Bell, W. Clegg, P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L. Marshall, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2547.
45 A. Bell, W. Clegg, P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L. Marshall, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2247.
46 R. I. Michelman, R. G. Bergman and R. A. Andersen, *Organometallics*, 1993, **12**, 2741.
47 M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1995, **14**, 2455.
48 D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041.
49 P. Mountford, *J. Organomet. Chem.*, 1997, **528**, 15.
50 C.-H. Yang, J. A. Ladd and V. L. Goedken, *J. Coord. Chem.*, 1988, **19**, 235.
51 D. L. Morrison and D. E. Wigley, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 79.

Received 8*th April* 1998; *Paper* 8/02686F