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New titanium imido complexes containing piperazine-based diamido–diamine ligands

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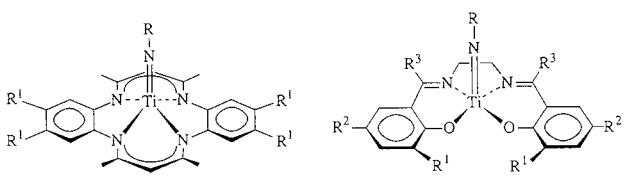
Abstract

Syntheses of the new piperazine derivatives 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine (**2**) and 1,4-bis(2-trimethylsilylamino-4-R-benzyl)piperazine (R = H **3** or Bu^t **4**; H_2L^1 and H_2L^2, respectively) are described along with the X-ray crystal structure of **2**. Treatment of H_2L^1 and H_2L^2 with *n*-butyl lithium gives the amido derivatives Li_2L^1 (**5**) and Li_2L^2 (**6**), which react with $[Ti(NBu^t)Cl_2(py)_3]$ to form $[Ti(NBu^t)(L^1)]$ (**7**) and $[Ti(NBu^t)(L^2)]$ (**8**). Reaction of Li_2L^1 with $[Ti(N\text{-}4\text{-}C_6H_4Me)Cl_2(py)_3]$ gives the corresponding arylimido homologue $[Ti(N\text{-}4\text{-}C_6H_4Me)(L^1)]$ (**9**). The X-ray structure of **8** shows a strongly *transoid* disposition of the aryl rings of the L^1 ligand and this geometry is maintained in solution. Somewhat surprisingly **7** does not undergo *tert*-butylimide/arylamine exchange with 4-methylphenylamine to form **9**. The related compound *N*,*N*′-bis(2-trimethylsilyl-aminobenzyl)-*N*,*N*′-dimethyl-1,3-diaminopropane (**12**, H_2L^3) and its lithium salt Li_2L^3 (**13**) are also described. However, reaction of **13** with $[Ti(NBu^t)Cl_2(py)_3]$ affords no tractable product.

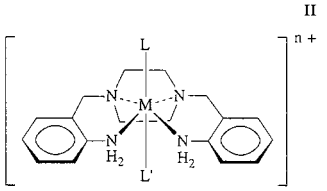
Keywords: Titanium; Imide; Amide; Polydentate ligand; X-ray diffraction

1. Introduction

As part of an ongoing research programme in early transition metal imido chemistry [1–9], we recently described the syntheses, structures and reactivity of titanium imido complexes supported by dianionic, tetradentate N_4-donor dibenzotetraaza [14]annulene (**I**) [10] and N_2O_2-donor Schiff base (**II**) [11] ligands[2]. These polydentate ligands provide a useful supporting environment that directs reactivity towards the Ti=NR linkage [6]. In the context of this previous work we noted with interest new complexes of tetradentate piperazine-based ligands (**III**) recently developed by Wieghardt and co-workers [12].



I II



III

M = Ni, Pd, Cu; L = L′ = none; n = 2
M = Cu; L = H_2O; L′ = none; n = 2
M = Ni; L = L′ = NCS; n = 0

Although the ligands in **III** are neutral for the complexes shown, we thought it likely that appropriate

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[2] Note that although for ease of representation all titanium–imido linkages are drawn Ti=NR, the formal Ti–N bond order in the complexes [Ti(NR)(tetradenate-ligand)] (R = Bu^t or aryl) described herein is generally best thought of as three (pseudo-$\sigma^2\pi^4$ triple bond) rather than as two [7,39,40].

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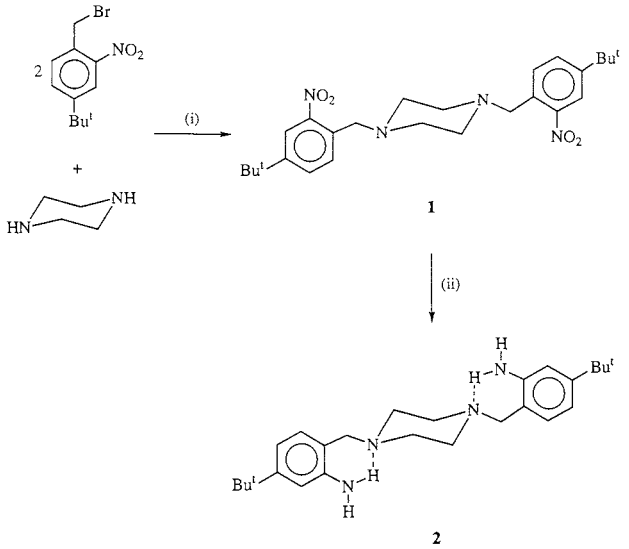
N-derivatisation could provide precursors to dianionic ligands suitable for early transition metal chemistry. A second interesting feature of the ligands in **III** was the non-planar, *pseudo*-C_2 symmetric conformation that they adopt (with one phenyl ring tilted up and one down), even for the four-coordinate complexes with no additional axial donor ligand(s). We envisaged that such a conformation might, in the long term, allow for asymmetric synthetic applications of metal–ligand multiply bonded complexes containing such ligands. Finally, we noted that the coordination chemistry of piperazines [13,14] and their open-chain [12,15–19] and macrocyclic [20–26] derivatives has only been developed for later transition metals, and we were therefore interested to see if analogous complexes of early transition metals could be prepared.

2. Results and discussion

The compound 1,4-bis(2-aminobenzyl)piperazine (as shown in complexes **III** above) was prepared according to the method of Wieghardt and co-workers [12]. In the previously studied systems **I** and **II** we found that the introduction of ligand aryl ring methyl or *tert*-butyl substituents frequently aided solubility and crystallisation, and could also provide useful NMR handles. We therefore prepared *tert*-butyl substituted analogues of the Wieghardt systems as shown in Scheme 1.

Coupling of 1-bromomethyl-4-*tert*-butyl-2-nitrobenzene [27] with piperazine afforded the nitrobenzyl compound **1** as a pale yellow solid in 19% yield. The yield for the formation of **1** is significantly lower than that reported by Weighardt and co-workers for the non-*tert*-butyl substituted homologue, 1,4-bis(2-nitrobenzyl)piperazine (98%) [12]. We attribute the reduced yield of **1** to a lower electrophilicity of the benzylic methlene in 1-bromomethyl-4-*tert*-butyl-2-nitrobenzene compared to that of 1-bromomethyl-2-nitrobenzene. Subsequent graphite-catalysed reduction of **1** with hydrazine monohydrate gave 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine (**2**) as a colourless, crystalline solid in



Scheme 1. Reagents and conditions: (i) KOH (two equivalents), toluene, 60°C, 20 h, 19%; (ii) hydrazine monohydrate, graphite catalyst, refluxing ethanol, 68 h, 69%.

69% yield after recrystallisation from ethanol. Single crystals of 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine·4 $CHCl_3$ (**2**·4 $CHCl_3$) suitable for X-ray diffraction were grown from an ethanol–chloroform (1:1) mixture at room temperature. The molecular structure is shown in Fig. 1, data collection and processing parameters are listed in Table 1, and selected bond lengths and angles are given in Table 2.

Molecules of **2** lie across crystallographic inversion centres, and the crystals contain four $CHCl_3$ molecules of crystallisation for each molecule of **2**. There are no unusual contacts between **2** and $CHCl_3$, with the molecules of **2** and $CHCl_3$ forming alternating sheets in the crystal structure. The piperazine ring adopts a thermodynamically favourable chair conformation with the benzyl substituents occupying equatorial positions as expected [28]. There are, in addition, weak intramolecular hydrogen bonds [NH···N = 2.4(1) Å] between the piperazine nitrogen atoms and one of the

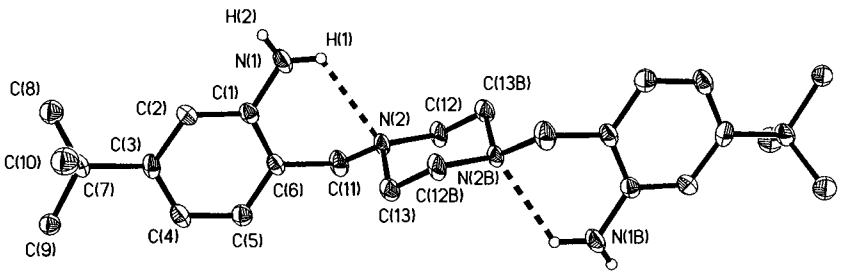


Fig. 1. Displacement ellipsoid plot of 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine (**2**). Displacement ellipsoids are drawn at the 35% probablility level and H atoms are drawn as spheres of arbitrary radius. Carbon-bonded hydrogen atoms and the chloroform molecules of crystallisation are omitted. Atoms carrying the suffix B are related to their non-suffixed counterparts by the symmetry operator $[-x+3/2, -y+1/2, -z]$.

Table 1
X-ray data collection and processing parameters for 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine·4 $CHCl_3$ (**2**·4 $CHCl_3$) and [Ti(NBu^t)(L^1)] (**8**)

	2·4 $CHCl_3$	**8**
Molecular formula	$C_{26}H_{40}N_4$·4 $CHCl_3$	$C_{36}H_{63}N_5Si_2Ti$
Formula weight	886.14	670.01
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Wavelength	0.71069	0.71069
Unit cell dimensions		
a (Å)	40.63(2)	16.114(1)
b (Å)	6.137(5)	10.7550(8)
c (Å)	17.367(10)	23.204(1)
β (°)	108.26(6)	101.824(4)
V (Å^3)	4112.6	2936.1
Z	4	4
Absorption coefficient (mm^{-1})	0.84	0.30
Crystal description	Colourless column	Yellow plate
Crystal size (mm)	$0.62\times0.29\times0.20$	$0.60\times0.52\times0.17$
Theta range for data collection (°)	2.70–25.06	1.72–26.52
Scan type	ω-scans with profile fitting	ω-scans
Index ranges	$-48\le h\le45,\ 0\le k\le7,\ 0\le l\le20$	$0\le h\le20,\ 0\le k\le13,\ -28\le l\le28$
Reflections collected	3612	54927
Independent reflections	3612	8227
R_{merge}	No reflections to be merged	0.052
Observed reflections	2360 [$I>2\sigma(I)$]	5092 [$I>3\sigma(I)$]
Absorption correction	Integration	Multi-scan
T_{min}, T_{max}	0.777, 0.851	0.856, 0.950
Variation in standard reflections	Random ± 4.5%	–
No. of data used in refinement	2360	5092
No. of restraints applied	21	0
No. of parameters refined	212	420
Refinement method	Blocked-matrix,	Full-matrix,
Weighting scheme	Chebychev polynomial	Chebychev polynomial
Final R indices [a]	$R_1=0.0963$, $vR_w=0.1165$ [$I>2\sigma(I)$]	$R_1=0.0627$, $R_w=0.0472$ [$I>3\sigma(I)$]
Goodness-of-fit	0.968	1.155
Final $(\Delta/\sigma)_{max}$	0.013	0.001
Largest residual peaks (e Å^{-3})	0.97 and −0.86	0.95 and −0.64

[a] $R=R_1=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; $R_w=\sqrt{\{\Sigma\,w(|F_o|-|F_c|)^2/\Sigma\,w|F_o|^2\}}$.

2-amino group hydrogen atoms. Similar solid-state geometries were recently reported for phenolic analogues 1,4-bis(2-hydroxybenzyl)piperazine [16] and 1,4-bis-(2-hydroxy-3-formyl-5-bromobenzyl)piperazine [29] which contain intramolecular OH···N hydrogen bonds.

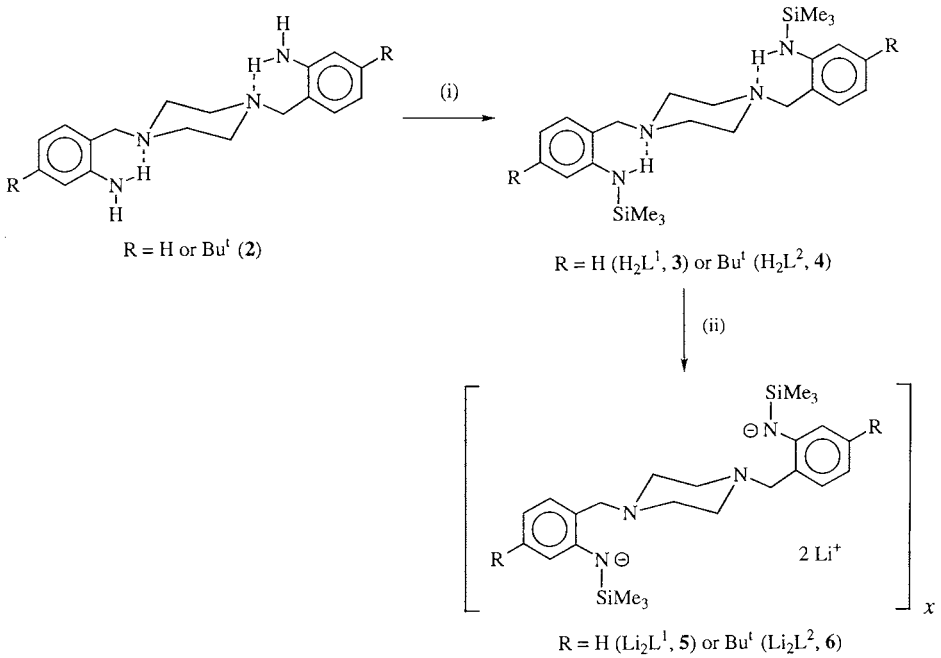
In $CDCl_3$ solution the ^{1}H-NMR spectrum of **2** shows a broad resonance at ca. 2.4 ppm for the piperazine methylene hydrogen atoms, indicating that this compound is fluxional in solution. The corresponding signals for the nitrobenzyl analogue **1** appear as a considerably sharper signal, suggesting that the activation energy barrier to chair↔boat↔chair interconversion in this case is lower as would be expected since **1** cannot form intramolecular NH···N bonds.

Reaction of 1,4-bis(2-aminobenzyl)piperazine with chlorotrimethylsilane in THF in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded 1,4-bis(2-trimethylsilylaminobenzyl)piperazine (H_2L^1 **3**) as a cream solid in 75% yield after recrystallisation from hexane (Scheme 2). The homologous proligand 1,4-bis(2-trimethylsilylamino-4-*tert*-butylbenzyl)piperazine

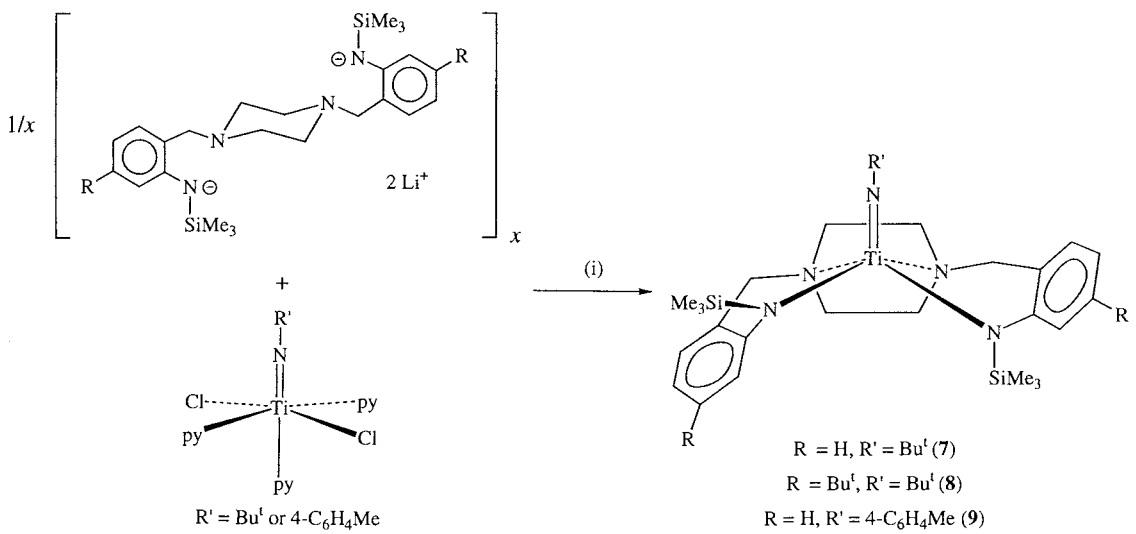
Table 2
Selected bond distances (Å) and angles (°) for 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine (**2**) [a]

Bond distances		Bond angles	
N(1)–C(1)	1.39(1)	C(1)–N(1)–H(1)	125(6)
N(1)–H(1)	0.91(9)	C(1)–N(1)–H(2)	108(7)
N(1)–H(2)	0.8(1)	H(1)–N(1)–H(2)	107(9)
N(2)···H(1)	2.4(1)	C(11)–N(2)–C(12)	109.9(6)
N(2)–C(11)	1.47(1)	C(11)–N(2)–C(13)	111.3(6)
N(2)–C(12)	1.468(8)	C(12)–N(2)–C(13)	108.9(5)
N(2)–C(13)	1.470(8)	C(11)–N(2)···H(1)	90.4(23)
C(1)–C(2)	1.394(9)	C(12)–N(2)···H(1)	118.0(22)
C(1)–C(6)	1.40(1)	C(13)–N(2)···H(1)	116.8(22)
C(2)–C(3)	1.39(1)	N(1)–H(1)···N(2)	115(8)
C(3)–C(4)	1.37(1)	N(2)–C(11)–C(6)	111.6(7)
C(3)–C(7)	1.552(8)	N(2)–C(12)–C(13B)	109.5(7)
C(4)–C(5)	1.41(1)	N(2)–C(13)–C(12B)	109.5(6)
C(5)–C(6)	1.40(1)		
C(6)–C(11)	1.537(9)		
C(12)–C(13B)	1.51(1)		

[a] Atoms carrying the suffix B are related to their counterparts by the symmetry operator [$-x+3/2,\ -y+1/2,\ -z$].



Scheme 2. Reagents and conditions: (i) DABCO (two equivalents) and Me_3SiCl (2.2 equivalents), THF or Et_2O, r.t., 18–24 h, 75 or 64% for **3** and **4**, respectively; (ii) ^{n}BuLi (2.2 equivalents), toluene or hexane, ca. −70°C then r.t., 17–18 h, 90 or 78% for **5** and **6**, respectively.



Scheme 3. Reagents and conditions: (i) THF (for **7**, **8**) or benzene (for **9**), r.t., 17–23 h, 31 (for **7**, **8**) or 22% (for **9**).

(H_2L^2 **4**) was prepared in 64% yield in an analogous manner. The compounds are expected to possess similar structures to those proposed for 1,4-bis(2-amino-4-R-benzyl)piperazine (R = H or Bu^t **2**) with intramolecular NH···H hydrogen bonds. The remaining aniline hydrogen atoms of H_2L^1 and H_2L^2 are readily removed by reaction with *n*-butyl lithium in toluene (for **3**) or hexane to form the corresponding dilithium diamido derivatives Li_2L^1 (**5**) and Li_2L^2 (**6**) in 90 and 78% yields, respectively. The compounds **5** and **6** are air- and moisture-sensitive, highly insoluble pale yellow powders; they were characterised by elemental analysis and infrared spectroscopy only. Their low solubility is attributed to the thermodynamic tendency of piperazine and its derivatives to adopt a chair conformation which can result in the formation of oligomeric derivatives.

In previous studies we found that the compounds [Ti(NR)Cl_2(py)$_3$] (R = Bu^t or aryl) [30] are extremely useful precursors to new imido–titanium chemistry via salt-elimination reactions with metallated reagents [1,10,11]. Reaction of the dilithium amides Li_2L^1 (**5**) or Li_2L^2 (**6**) with [Ti(NBu^t)Cl_2(py)$_3$] in THF gave the yellow–orange derivatives [Ti(NBu^t)(L^1)] (**7**) or [Ti(NBu^t)(L^2)] (**8**) in ca. 30% yield after recrystallisation from pentane (Scheme 3). Similarly, reaction of Li_2Li^1 (**5**) with [Ti(N-4-C_6H_4Me)Cl_2(py)$_3$] in benzene afforded

the arylimido homologue [Ti(N-4-C_6H_4Me)(L^1)] (**9**) as an orange, microcrystalline solid in 21% yield.

The low isolated yields of **7**–**9** warrant further comment. When the crude reaction mixtures were examined by NMR spectroscopy a number of relatively intense, broad resonances were observed; similar resonances were seen for NMR tube-scale reactions in C_6D_6. The work-up of the mixtures separated oily, poorly soluble side-products from the desired complexes. These side-products are most likely to be oligomeric in nature, again reflecting the tendency of piperazine to adopt a thermodynamically favourable chair conformation [16,17,28]. The inclination of the piperazine moiety of L^1 and L^2 to bind via a bidentate, boat conformation to a single Ti centre is presumably further diminished by the steric crowding (see below) around Ti in **7**–**9**.

Slow cooling of a sub-saturated pentane solution of **8** to -35°C gave diffraction-quality crystals. The molecular structure is shown in Fig. 2, data collection and processing parameters are listed in Table 1, and selected bond lengths and angles are given in Table 3.

The molecular structure of [Ti(NBu^t)(L^2)] (**8**) consists of a dianionic, tetradentate L^2 moiety coordinated to a Ti=NBu^t fragment. The Ti=N-Bu^t angle [176.4(2)°] and Ti=NBu^t bond length [1.716(2) Å] are comparable to those found in compounds of the type **I** (dibenzotetraaza[14]annulene complexes) [10] and **II** (Schiff base complexes) [11] and are consistent with a formal Ti=N_{imide} triple bond. The titanium atom lies 0.59 Å out of the least squares plane defined by N(1)–N(4) (maximum deviation of these atoms from the least-squares N_4 plane = 0.003 Å). This is similar to the value found (0.56 Å) for [Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] (**II** where R = 2,6-$C_6H_3Me_2$, $R^1 = R^2 = H$, R^3 = Et) but somewhat less than for the two crystallographically characterised compounds of the type **I** (Ti···N_4 plane = 0.75–0.76 Å). The Ti–N_{amide} [2.027(2), 2.032(2) Å] and Ti–$N_{piperazine}$ [2.259(2), 2.267(2) Å] bond lengths are consistent with their description as amido– and amino–titanium linkages; the sums of the angles subtended at N(3) (357.9°) and N(4) (359.9°) reveal nearly trigonal planar (sp^2-hybridised) centres, indicating the potential for N(p_π)–Ti(d_π) interactions in this otherwise 14 valence electron system. The piperazine fragment adopts a boat conformation as required for bidentate coordination; the dihedral angles N(1)–C(1)–C(2)–N(2) and N(1)–C(3)–C(4)–N(2) are 6.1 and 8.4°, respectively. The N(1)–Ti(1)–N(2) and N(3)–Ti(1)–N(4) bite angles [65.07(9) and 106.41(9)°, respectively] differ from the corresponding N_{imine}–Ti–N_{imine} [77.97(9)°] and O–Ti–O [97.17(8)°] angles in [Ti(N–2,6-$C_6H_3Me_2$)(Et_2salen)] by ca. $\pm$ 11–13°.

Perhaps the most striking feature of the molecular structure of **8** is the strongly *transoid* arrangement of the aryl rings of the L^2 ligand. These rings are inclined down and up (with respect to the imido ligand) by ca.

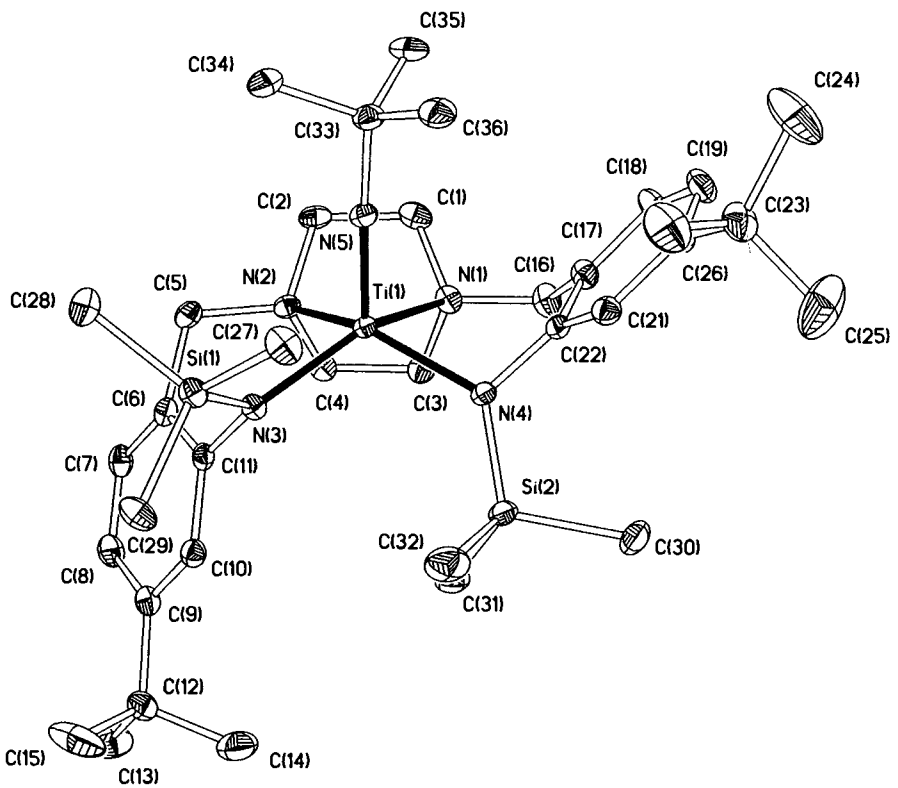


Fig. 2. Displacement ellipsoid plot of [Ti(NBu^t)(L^2)] (**8**). Displacement ellipsoids are drawn at the 25% probability level. Hydrogen atoms are omitted.

Table 3
Selected distances (Å) and angles (°) for [Ti(NBu^t)(L^1)] (**8**)

Bond distances			
Ti(1)–N(1)	2.259(2)		
Ti(1)–N(2)	2.267(2)		
Ti(1)–N(3)	2.032(2)		
Ti(1)–N(4)	2.027(2)		
Ti(1)–N(5)	1.716(2)		
N(5)–C(33)	1.456(3)		
Ti(1)···(N$_4$ plane)	0.59		
Bond angles			
N(1)–Ti(1)–N(2)	65.07(9)	Ti(1)–N(1)–C(1)	105.7(2)
N(1)–Ti(1)–N(3)	141.81(9)	Ti(1)–N(1)–C(3)	104.6(2)
N(2)–Ti(1)–N(3)	86.64(9)	Ti(1)–N(3)–Si(1)	122.0(1)
N(1)–Ti(1)–N(4)	83.23(9)	Ti(1)–N(3)–C(11)	120.4(2)
N(2)–Ti(1)–N(4)	139.41(9)	Si(1)–N(3)–C(11)	115.5(2)
N(3)–Ti(1)–N(4)	106.41(9)	Ti(1)–N(4)–Si(2)	129.8(1)
N(1)–Ti(1)–N(5)	99.3(1)	Ti(1)–N(4)–C(22)	110.0(2)
N(2)–Ti(1)–N(5)	102.2(1)	Si(2)–N(4)–C(22)	120.1(2)
N(3)–Ti(1)–N(5)	111.9(1)	Ti(1)–N(5)–C(33)	76.4(2)
N(4)–Ti(1)–N(5)	107.7(1)		
Angles between least-squares mean planes			
[C(6), C(7), C(8), C(9), C(10), C(11)] to [N(1), N(2), N(3), N(4)]			64.2
[C(17), C(18), C(19), C(20), C(21), C(22)] to [N(1), N(2), N(3), N(4)]			45.7
[C(6), C(7), C(8), C(9), C(10), C(11)] to[C(17), C(18), C(19), C(20), C(21), C(22)]			141.5

64.2 and 47.7° from the N_4 plane. In the Schiff base complex [Ti(N-2,6-$C_6H_3Me_2$)(Et_2salen)] the corresponding angles (which are in fact typical of complexes of these types of ligand [31,32]) are 26.7 and 9.1°. Surprisingly, given the apparent steric crowding imposed by the $SiMe_3$ substituents, the inclination of the aryl rings in **8** with respect to the N_4 plane are not substantially different to that found for the compounds **III** described by Wieghardt and co-workers. In these five complexes the average inclination from the N_4 plane is 51.3° with a range of values spanning 46.0–58.9°.

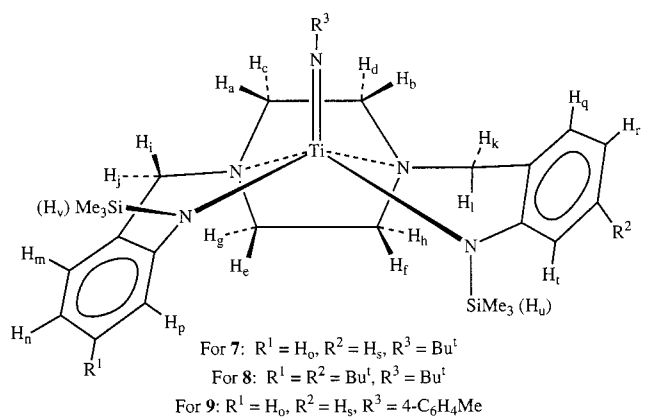


Fig. 3. The NMR labelling scheme used for the imido complexes [Ti(NBu^t)(L^1)] (**7**), [Ti(NBu^t)(L^2)] (**8**) and [Ti(N-4-C_6H_4Me)(L^1)] (**9**). See Section 4 for further details.

The solution ^{1}H- and ^{13}C-NMR data for [Ti(NBu^t)(L^1)] (**7**), [Ti(NBu^t)(L^2)] (**8**), and [Ti(N-4-C_6H_4Me)(L^1)] (**9**) are consistent with the solid-state structure found for **8**, and the overall pattern and distribution of NMR resonances for the three compounds is consistent with them possessing analogous solution structures. The NMR spectra have been fully assigned as far as possible using a combination of ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectroscopy, and phase-sensitive nuclear Overhauser effect spectroscopy (NOESY). Full details of the assignments (provided in Section 4) are made with reference to Fig. 3 which shows the H atom labelling scheme adopted.

The ^{1}H-NMR spectra of **7**–**9** thus reveal eight inequivalent environments for the methylene H atoms of the piperazine ring, two $SiMe_3$ signals, four signals for the benzyl group diastereotopic H atoms, and two different environments for the aryl rings (and their Bu^t substituents for **8**) of the L^1 or L^2 ligands. The unusual high-field shift (6.06 ppm) for the *ortho*-H atoms of the 4-methylphenylimido ligand in **9** is attributed to shielding effects of the up aryl ring of the L^1 ligand. For all three compounds the H_a, H_b and H_i resonances consistently appear at relatively low fields compared to the other piperazine and benzyl methylene resonances. We attribute this to the deshielding effects of the titanium–imido nitrogen multiple bond. In contrast, H_e of the piperazine ligand is consistently observed at relatively high field because of the shielding influence of the down aryl ring of L^1 or L^2. Further examination of the NOESY spectrum for [Ti(NBu^t)(L^1)] (**7**) showed negative cross peaks between the two $SiMe_3$ group resonances and also between certain other pairs of signals. This indicates slow (on the NMR timescale) chemical exchange between the up and down rings of the L^1 ligand in **7**, as confirmed by qualitative spin saturation transfer (SST) experiments. We expect that the homologous compounds **8** and **9** also undergo slow exchange in this manner.

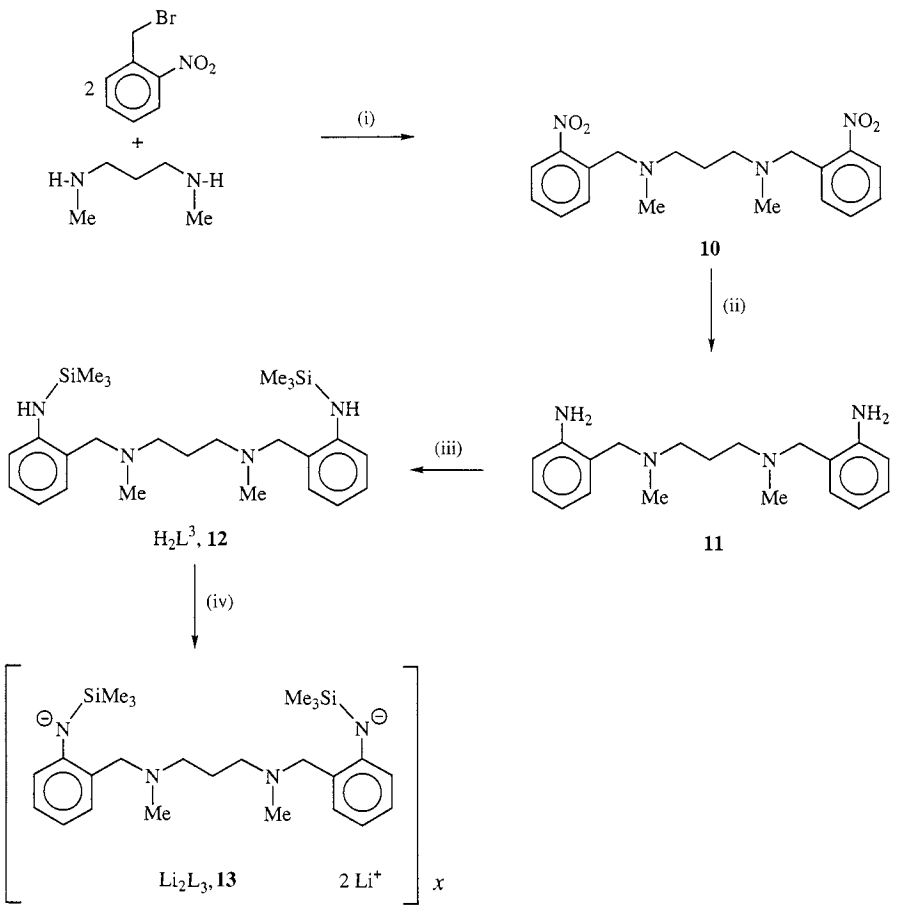
The Ti=NR linkages in the compounds **7**–**9** appear to be very sterically protected by the up aryl ring and one of the $SiMe_3$ groups of the L^1 or L^2 ligand. Consistent with this we found that [Ti(NBu^t)(L^1)] (**7**) does not undergo *tert*-butylimide/arylamine exchange with H_2N-4-C_6H_4Me even after prolonged heating. This type of exchange reaction is facile for many of the imido–titanium complexes we have described [1,10,11,30], including the dibenzotetraaza[14]annulene (**I**) and Schiff base (**II** for R^1, R^2 ≠ Bu^t) complexes. The expected products of the reaction between **7** and H_2N-4-C_6H_4Me are free Bu^{t}NH$_2$ and **9**, which can clearly be prepared via the metathetical route shown in Scheme 3. However, attempts to make arylimido complexes of titanium with 2,6-substituents in the aryl ring by analogous metathetical routes (e.g. from Li_2L^1 and [Ti(N-2,6-$C_6H_3Me_2$)Cl_2(py)$_3$]) were unsuccessful, possi-

bly due to intolerable steric interactions in the desired product. An NMR tube-scale reaction between Li_2L^1 and $[Zr(N\text{-}2,6\text{-}C_6H_3Pr^i_2)Cl_2(THF)_2]$ [33] appeared to be promising, but we were unable to separate a single product on scale-up. The reaction of Li_2L^1 with other metal complexes including $[Nb(NBu^t)Cl_3(py)_2]$ [34] and $[ZrCl_4(THF)_2]$ also failed to yield tractable products.

In an attempt to obtain a more versatile ligand system, while retaining some of the principal features of the piperazine-based ligands L^1 and L^2, we prepared the new compounds **10**–**12** (Scheme 4). We hoped that incorporation of the more flexible $CH_2CH_2CH_2$ linkage into the backbone would allow the ligand to adopt less sterically crowded conformations. Reaction of H_2L^3 (**12**) with *n*-butyl lithium gave the dilithiated derivative Li_2L^3 (**13**) in 72% yield. In contrast to the highly insoluble (and presumably polymeric) piperazine analogues Li_2L^1 (**5**) and Li_2L^2 (**6**), compound **13** is readily soluble in hydrocarbon solvents. Unfortunately, reaction of **13** (and the protio-analogue **12**) with a number of early transition metal imido substrates including $[Ti(NR)Cl_2(py)_3]$ and $[Zr(N\text{-}2,6,C_6H_3Pr^i_2)Cl_2(THF)_2]$ failed to yield any tractable product. NMR tube-scale reactions (in C_6D_6) of **13** showed very complex mixtures with these substrates. It is possible that the greater bite angle of the 1,3-diaminopropane moiety in the backbone of L^3 forces the two trimethylsilyamido donor groups closer together, thereby increasing steric hinderance between these groups.

3. Summary and conclusions

We have described syntheses of two new dianionic, tetradentate ligand systems incorporating piperazine rings into their backbones, along with an analogue containing a $CH_2CH_2CH_2$ link in place of the piperazine ring. The ligand precursor 1,4-bis(2-amino-4-*tert*-butylbenzyl)piperazine (**2**) was crystallographically characterised. Three new imidotitanium derivatives of the piperazine-based ligands were prepared and fully characterised; the X-ray structure of **8** is consistent with the solution structures of **7**–**9** determined by NMR spectroscopy. The geometries of the dianionic L^1 and L^2 ligands when complexed to Ti=NR are similar to that found for their neutral analogues in the previously described complexes **III**. The phase-sensitive NOESY spectra for **7** shows that slow exchange of up and down



Scheme 4. Reagents and conditions: (i) KOH (two equivalents), toluene, 60°C, 24 h, 98%; (ii) hydrazine monohydrate, graphite catalyst, refluxing ethanol, 48 h, 68%; (iii) DABCO (two equivalents) and Me_3SiCl (2.2 equivalents), Et_2O, r.t., 20 h, 89%; (iv) ^{n}BuLi (2.2 equivalents), pentane, −73°C then r.t., 4 h, 72%.

resonances occurs in solution on the NMR timescale. The ligands L^1 and L^2 lead to sterically crowded metal centres in the complexes **7**–**9**.

4. Experimental

4.1. General

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. All protio-solvents and commercially available reagents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over freshly ground calcium hydride at room temperature (r.t.) ($CDCl_3$) or molten potassium (C_6D_6), distilled under reduced pressure and stored under N_2 in J. Young ampoules. NMR samples of air- and moisture-sensitive compounds were prepared in the dry-box in 5 mm Wilmad tubes, generally equipped with a Young's Teflon valve.

^{1}H- and ^{13}C-NMR spectra were recorded on either a Bruker DPX 300 or a Varian Unity Plus 500 spectrometer and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$ ppm) 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 experiments as appropriate. IR spectra were recorded on either a Perkin–Elmer 1600 Series or a Mattson Polaris FT-IR spectrometer in the range 4000–400 cm^{-1}. Samples were prepared in the dry-box between KBr plates as Nujol mulls or as KBr discs and data are quoted in wavenumbers (ν, cm^{-1}). Mass spectra were recorded on a AEI MS902 or Micomass Autospec 500 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of this department.

$[Ti(NR)Cl_2(py)_3]$ ($R = Bu^t$ or 4-C_6H_4Me) [30], 1,4-bis(2-aminobenzyl)piperazine [12] and 1-bromomethyl-4-*tert*-butyl-2-nitrobenzene [27] were prepared according to literature methods.

4.2. 1,4-Bis(2-nitro-4-tert-butylbenzyl)piperazine (1)

1-Bromomethyl-4-*tert*-butyl-2-nitrobenzene (60 g, 0.22 mol) and powdered potassium hydroxide (13 g, 0.23 mol) were added to a stirred solution of piperazine (9.50 g, 0.11 mol) in toluene (350 ml). The mixture was heated to 60°C for 20 h and the contents of the flask were then allowed to cool to r.t., yielding a red–orange solution with solid precipitate. The mixture was filtered and the residue extracted with toluene (2×50 ml), before combining the toluene filtrates and drying ($MgSO_4$). The volatiles were removed by rotary evaporation to yield an oily orange–yellow solid. This solid was thoroughly washed with diethyl ether (ca. 350 ml in total) and dried in vacuo, giving the desired product (**1**) as a pale yellow powder. Yield: 9.85 g (19%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz): 7.79 (d, $J = 1.8$, 2H, 3-C_6H_3), 7.52 (d of d, $J = 8.1$ and 1.9, 2H, 5-C_6H_3), 7.47 (d, $J = 8.1$, 2H, 6-C_6H_4), 3.73 (s, 4H, ArCH_2N), 2.41 (br s, 8H, NCH_2CH_2N), 1.33 (s, 18H, CMe_3). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): 151.7 (4-C_6H_3), 149.8 (2-C_6H_3), 130.7 (CH of C_6H_3), 129.4 (1-C_6H_3), 121.3, 109.6 ($2 \times$ CH of C_6H_3), 58.6, (ArCH_2N), 53.2 (NCH_2CH_2N), 34.8 (CMe_3), 31.1 (CMe_3). Anal. Found (Anal. Calc. for $C_{26}H_{36}N_4O_4$): C 66.1 (66.6); H 8.2 (7.7); N 11.7 (12.0)%. EI-MS: 468 [M^+].

4.3. 1,4-bis(2-amino-4-tert-butylbenzyl)piperazine (2)

A stirred mixture of 1,4-bis(2-nitro-4-*tert*-butylbenzyl)piperazine (**1**) (9.85 g, 0.02 mol) and graphite catalyst (3 g, Sigma-Aldrich) in ethanol (200 ml) was purged with argon. Oxygen-free hydrazine monohydrate (22.53 g, 0.45 mol) was added and the mixture heated to reflux under an argon atmosphere for 68 h. The hot mixture was filtered and the residue extracted with chloroform (3×50 ml). Upon cooling to r.t., colourless crystals of **2** grew from the ethanol filtrate and were isolated. The ethanol and chloroform solutions were combined and the volatiles removed by rotary evaporation to yield an oily solid, which was recrystallised from hot ethanol (150 ml) to yield a second batch of **2** as colourless crystals. The product in each case was dried in vacuo. Total yield: 5.91 g (69%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz): 6.89 (d, $J = 7.5$, 2H, 6-C_6H_3), 6.69–6.66 (m, 4H, overlapping 3- and 5-C_6H_3), 4.71 (br s, 4H, NH_2), 3.46 (s, 4H, ArCH_2N), 2.41 (br s, 8H, NCH_2CH_2N), 1.28 (s, 18H, CMe_3). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): 151.6 (4-C_6H_3), 146.5 (2-C_6H_3), 130.1 (6-C_6H_3), 119.5 (1-C_6H_3), 114.7 (5-C_6H_3), 112.8 (3-C_6H_3), 61.6 (ArCH_2N), 53.0 (NCH_2CH_2N), 34.4 (CMe_3), 31.4 (CMe_3). Anal. Found (Anal. Calc. for $C_{26}H_{40}N_4$): C 76.3 (76.4); H 10.0 (9.9); N 13.5 (13.7)%. IR (KBr disc): 3443 [s, ν(N–H)], 3325 [s, ν(N–H)], 2960 (vs), 2903 (m), 2868 (m), 2804 (vs), 2765 (m), 1618 (s), 1576 (m), 1511 (m), 1480 (w), 1451 (m), 1427 (vs), 1386 (m), 1368 (m), 1340 (s), 1296 (vs), 1261 (m), 1245 (w), 1215 (w), 1203 (w), 1173 (w), 1150 (s), 1136 (m), 1082 (w), 1006 (vs), 951 (m), 917 (w), 870 (m), 836 (m), 804 (s), 724 (m), 682 (m), 656–425 (series of weak peaks) cm^{-1}. EI-MS: 408 [M^+].

4.4. 1,4-bis(2-trimethylsilylaminobenzyl)piperazine (H_2L^1, 3)

To a stirred solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.70 g, 15.18 mmol) in THF (30 ml) was

added chlorotrimethylsilane (1.81 g, 16.70 mmol) over 5 min. There was an immediate formation of a white precipitate and the mixture was left to stir for a further 1 h. A solution of 1,4-bis(2-aminobenzyl)piperazine (2.25 g, 7.59 mmol) in THF (80 ml) was added, resulting in a thickening of the white precipitate. After a further ca. 24 h the solution was filtered and the residue (white powder) extracted with further THF (30 ml). The filtrates were combined and the volatiles removed under reduced pressure to yield a waxy yellow–white solid, which was recrystallised from hexane and dried in vacuo to yield **3** as a cream solid. Yield: 2.50 g (75%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz): 7.10 (apparent t, apparent $J = 7.7$, 2H, 4-C_6H_4), 6.97 (d, $J = 7.4$, 2H, 6-C_6H_4), 6.71 (d, $J = 8.0$, 2H, 3-C_6H_4), 6.62 (apparent t, apparent $J = 7.4$, 2H, 5-C_6H_4), 6.34 (br s, 2H, NH), 3.50 (s, 4H, ArCH_2N), 2.42 (br s, 8H, NCH_2CH_2N), 0.28 (s, 18H, $SiMe_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): 148.3 (2-C_6H_4), 130.5 (6-C_6H_4), 128.2 (4-C_6H_4), 123.3 (1-C_6H_4), 116.5 (5-C_6H_4), 115.5 (3-C_6H_4), 62.7, (ArCH_2N), 52.7 (NCH_2CH_2N), 0.3 ($SiMe_3$). Anal. Found (Anal. Calc. for $C_{24}H_{40}N_4Si_2$): C 65.4 (65.4); H 9.5 (9.2); N 13.1 (12.7)%. IR (KBr plates, Nujol mull): 3223 [br m, ν(N–H)], 1606 (m), 1583 (m), 1499 (s), 1342 (m), 1318 (w), 1299 (s), 1262 (m), 1250 (s), 1147 (w), 1104 (w), 1049 (w), 1006 (m), 939 (w), 913 (s), 838 (s), 754 (m), 689 (w) 668 (w) cm^{-1}. EI-MS: 440 [M$^+$].

4.5. 1,4-bis(2-trimethylsilylamino-4-tert-butylbenzyl)piperazine (H_2L^2, **4**)

To a stirred solution of 1,4-diazabicyclo[2.2.2]octane (0.54 g, 4.80 mmol) in diethyl ether (15 ml) was added chlorotrimethylsilane (0.52 g, 4.80 mmol) over 5 min giving an immediate formation of a pale white precipitate. After 1 h a solution of **2** (0.98 g, 2.40 mmol) in diethyl ether (30 ml) was added, resulting in a thickening of the white precipitate. After ca. 18 h the mixture was filtered and the residue (white powder) extracted with further diethyl ether (30 ml). The ether filtrates were combined and the volatiles removed under reduced pressure to yield a waxy white solid, which was recrystallised from pentane and dried in vacuo, to give **4**. Yield: 0.84 g (64%).

^{1}H-NMR ($CDCl_3$, 300.1 MHz): 6.91 (d, $J = 7.8$, 2H, 6-C_6H_3), 6.77 (d, $J = 1.9$, 2H, 3-C_6H_3), 6.66 (d of d, $J = 7.8$ and 1.9, 2H, 5-C_6H_4), 6.30 (br s, 2H, NH), 3.49 (s, 4H, ArCH_2N), 2.43 (br s, 8H, NCH_2CH_2N), 1.32 (s, 18H, CMe_3), 0.30 (s, 18H, $SiMe_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): 151.1 (4-C_6H_3), 147.8 (2-C_6H_3), 130.0 (6-C_6H_3), 120.4 (1-C_6H_3), 113.5 (5-C_6H_3), 113.1 (3-C_6H_3), 62.3, (ArCH_2N), 52.8 (NCH_2CH_2N), 34.4 (CMe_3), 31.4 (CMe_3), 0.3 ($SiMe_3$). Anal. Found (Anal. Calc. for $C_{32}H_{56}N_4Si_2$): C 70.0 (69.5); H 10.4 (10.2); N 10.4 (10.1)%. IR (KBr plates, Nujol mull): 3212 [br m, ν(N–H)], 1614 (m), 1573 (s), 1507 (w), 1341 (m), 1301 (s), 1250 (vs), 1154 (m), 1128 (m), 1096 (w), 1009 (s), 969 (vs), 931 (m), 885 (s), 856 (m), 838 (vs), 795 (m), 746 (m), 689 (w), 658 (w), 616 (w) cm^{-1}. EI-MS: 552 [M$^+$].

4.6. Dilithium 1,4-bis(2-trimethylsilylamidobenzyl)-piperazine (Li_2L^1, **5**)

To a cold (ca. −68°C), stirred solution of H_2L^1 (**3**, 1.50 g, 3.40 mmol) in toluene (40 ml) was added a 2.5 M solution of *n*-butyl lithium in hexanes (2.99 ml, 7.49 mmol = 2.2 equivalents) over 5 min. The reaction was allowed to warm to r.t. and the resulting yellow mixture stirred for a further 18 h to give a colourless solution containing a volumous oily yellow precipitate. The mixture was filtered and the solid washed with toluene (35 ml) and hexane (2 × 35 ml) before drying in vacuo, to yield **5** as a pale yellow powder. Yield: 1.39 g (90%).

Anal. Found (Anal. Calc. for $C_{24}H_{38}N_4Si_2Li_2$): C 64.1 (63.7); H 8.4 (8.5); N 11.9 (12.4)%. IR (KBr plates, Nujol mull): 1590 (m), 1556 (w), 1346 (w), 1320 (w), 1290 (m), 1260 (s), 1241 (s), 1153 (w), 1103 (m), 1044 (w), 988 (m), 937 (s), 917 (s), 848 (s), 825 (vs), 777 (m), 739 (s), 663 (w), 588 (w) cm^{-1}.

4.7. Dilithium 1,4-bis(2-trimethylsilylamido-4-tert-butylbenzyl)piperazine (Li_2L^2, **6**)

To a cold (ca. −73°C) stirred solution of H_2L^2 (**4**, 0.60 g, 1.09 mmol) in hexane (35 ml) was added a 2.5 M solution of *n*-butyl lithium in hexanes (0.95 ml, 2.39 mmol = 2.2 equivalents) over 5 min. The mixture was allowed to warm to r.t., a further 15 ml of hexane was added and the mixture was stirred for a further 17 h giving a colourless solution, together with large amounts of yellow precipitate. The mixture was filtered and the solid washed with hexane (20 ml) before drying in vacuo, to yield **6** as a pale yellow powder. Yield: 0.48 g (78%).

Anal. Found (Anal. Calc. for $C_{32}H_{54}N_4Si_2Li_2$): C 68.2 (68.0); H 9.9 (9.6); N 9.9 (9.9)%. IR (KBr plates, Nujol mull): 1594 (m), 1552 (w), 1342 (m), 1320 (m), 1280 (vs), 1253 (s), 1236 (vs), 1200 (m), 1096 (m), 986 (vs), 939 (w), 919 (w), 883 (vs), 866 (s), 826 (vs), 737 (m), 676 (w), 658 (w), 580 (m), 549 (m), 500 (w), 478 (m), 452 (m) cm^{-1}.

4.8. Tert-butylimido-{1,4-bis(2-trimethylsilylamidobenzyl)piperazine}-titanium (**7**)

A pale orange solution of [Ti(NBu^t)Cl_2(py)$_3$] (0.52 g, 1.16 mmol) in THF (30 ml) was added to a stirred yellow slurry of (Li_2L^1, **5**) (0.53 g, 1.16 mmol) in THF (40 ml). An immediate colour change was observed, giving a brown solution which gradually became more red as stirring continued. After ca. 23 h the volatiles

were removed under reduced pressure to yield a brown–yellow solid which was extracted into hexane (4 × 40 ml). The combined extracts were filtered through a bed of Celite and the pale orange filtrate was evaporated to dryness, yielding a yellow–orange solid. Recrystallisation (twice) from pentane and drying in vacuo yielded **7** as a yellow–orange powder. Yield: 0.20 g (31%).

The following assignments refer to the labelling scheme in Fig. 3. ^{1}H-NMR (C_6D_6, 300.1 MHz): 7.37 (d, $J = 7.8$, 1H, H_t), 7.32 (apparent t, apparent $J = 7.4$, 1H, H_s), 7.26–7.22 (overlapping 2 × m, 2H, H_o and H_p), 6.97 (d, $J = 6.0$, 1H, H_q), 6.90–6.85 (overlapping 2 × m, 2H, H_m and H_r), 6.78 (m, 1H, H_n), 4.60 (d, $J = 11.1$, 1H, H_i), 3.73 (m, 1H, H_a), 3.63 (m, 1H, H_b), 3.34 (d, $J = 13.1$, 1H, H_l), 2.68 (d, $J = 13.1$, 1H, H_k), 2.52 (d, $J = 11.1$, 1H, H_j), 2.20 (m, 1H, H_f), 1.99 (m, 1H, H_g), 1.71 (overlapping 2 × m, 2H, H_c and H_d), 1.48 (m, 1H, H_h), 0.92 (m, 1H, H_e), 0.84 (s, 9H, $NCMe_3$), 0.68 (s, 9H, H_v), 0.25 (s, 9H, H_u). ^{13}C-{^{1}H} (C_6D_6, 75.5 MHz): 159.8, 156.0 (2 × 2-C_6H_4), 131.6 (one of 1-C_6H_4), 130.0 (two signals overlapping, CH_m or CH_r, and one of CH_o, CH_p, CH_s) 129.4, 129.2 (two of CH_o, CH_p, CH_s), 128.8 (one of 1-C_6H_4), 128.1 (CH_q), 126.2 (CH_t), 118.8 (CH_r or CH_m), 118.7 (CH_n), 70.1 ($NCMe_3$), 61.9 ($CH_{k,l}$), 59.2 ($CH_{i,j}$), 56.3 ($CH_{a,c}$), 52.7 ($CH_{b,d}$), 52.3 ($CH_{f,h}$), 46.3 ($CH_{e,g}$), 32.4 ($NCMe_3$), 5.1 (CH_v), 3.2 (CH_u). Anal. Found (Anal. Calc. for $C_{28}H_{47}N_5Si_2Ti$): C 60.3 (60.3); H 8.9 (8.5); N 12.4 (12.6)%. IR (KBr plates, Nujol mull): 1607 (w), 1592 (m), 1560 (w), 1298 (m), 1252 (s), 1227 (s), 1151 (w), 1088 (s), 1069 (s), 1035 (s), 935 (m), 922 (m), 902 (m), 856 (s), 837 (vs), 816 (s), 802 (s), 745 (m), 668 (m), 633 (w), 591 (w), 524 (w), 498 (w) cm^{-1}. FAB-MS: 558 [MH^+].

4.9. Tert-butylimido-{1,4-bis(2-trimethylsilylamido-4-tert-butylbenzyl)piperazine}-titanium (8)

A pale orange solution of [Ti(NBu^t)$Cl_2(py)_3$] (0.24g, 0.53 mmol) in THF (20 ml) was added to a stirred yellow slurry of (Li_2L^2, **6**) (0.30 g, 0.53 mmol) in THF (25 ml). A pale orange solution was obtained, which gradually became darker as stirring continued. After ca. 18 h, the volatiles were removed under reduced pressure to yield a brown–yellow solid which was extracted into hexane (4 × 30 ml). The combined extracts were filtered through a bed of Celite and the pale orange–yellow filtrate was evaporated to dryness, yielding a yellow–orange solid. The product was purified by recrystallisation from pentane to yield **8** as yellow–orange crystals. Yield: 0.11 g (31%).

The following assignments refer to the labelling scheme in Fig. 3. ^{1}H-NMR (C_6D_6, 300.1 MHz): 7.49 (s, 1H, H_t), 7.30 (s, 1H, H_p), 6.97 (overlapping 2 × m, 2H, H_q and H_r), 6.90 (overlapping 2 × m, 2H, H_m and H_n), 4.56 (d, $J = 11.0$, 1H, H_i), 3.75 (m, 1H, H_a), 3.67 (m, 1H, H_b), 3.33 (d, $J = 13.3$, 1H, H_l), 2.72 (d, $J = 13.3$, 1H, H_k), 2.53 (d, $J = 11.0$, 1H, H_j), 2.22 (m, 1H, H_f), 2.03 (m, 1H, H_g), 1.73 (overlapping 2 × m, 2H, H_c and H_d), 1.47 (m, 1H, H_h), 1.46 (s, 9H, ArCMe_3), 1.41 (s, 9H, ArCMe_3), 0.91 (m, 1H, H_e), 0.84 (s, 9H, $NCMe_3$), 0.71 (s, 9H, H_v), 0.28 (s, 9H, H_u). ^{13}C-{^{1}H} (C_6D_6, 75.5 MHz): 158.9, 155.2 (2 × 2-C_6H_4), 152.2, 151.6 (2 × 4-C_6H_4), 129.6 (CH_m or CH_n), 128.7 (one of 1-C_6H_4), 127.5 (two signals overlapping, CH_p and CH_q or CH_r), 126.1 (one of 1-C_6H_4), 123.5 (CH_t), 115.7 (CH_r or CH_q), 115.6 (CH_n or CH_m), 70.0 ($NCMe_3$), 61.6 ($CH_{k,l}$), 58.8 ($CH_{i,j}$), 56.1 ($CH_{a,c}$), 52.9 ($CH_{b,d}$), 52.4 ($CH_{f,h}$), 46.4 ($CH_{e,g}$), 34.7, 34.4 (2 × ArCMe_3), 32.6($NCMe_3$), 31.8, 31.6 (2 × ArCMe_3), 5.2 (CH_v), 3.3 (CH_u). Anal. Found (Anal. Calc. for $C_{36}H_{63}N_5Si_2Ti$): 64.4 (64.5); 9.9 (9.5); 10.5 (10.5)%. IR (KBr plates, Nujol mull): 1596 (m), 1574 (m), 1302 (m), 1282 (m), 1252 (s), 1235 (s), 1224 (s), 1151 (w), 1136 (w), 1116 (w), 1088 (m), 1069 (m), 1009 (w), 969 (vs), 949 (w), 934 (w), 907 (m), 891 (s), 858 (s), 837 (vs), 799 (s), 678 (w), 620 (w), 602 (m), 566 (w), 521 (w), 496 (w), 469 (w), 424 (w) cm^{-1}. FAB-MS: 670 [MH^+].

4.10. 4-Methylphenylimido-{1,4-bis(2-trimethylsilylamidobenzyl)piperazine}-titanium (9)

A slurry of [Ti(N-4-C_6H_4Me)$Cl_2(py)_3$] (0.61 g, 1.33 mmol) in benzene (80 ml) was added to a stirred yellow suspension of (Li_2L^1, **5**) (0.60 g, 1.33 mmol) in benzene (40 ml). A dark brown solution was formed which became more orange in colour after 17 h. The volatiles were removed under reduced pressure to yield an oily brown–red solid which was extracted into hexane (4 × 40 ml). The combined extracts were filtered through a bed of Celite and evaporated to dryness, yielding an orange–red solid. The product recrystallised from pentane at −35°C and dried in vacuo, giving **9** as an orange microcrystalline solid. Yield: 0.17 g (22%). Repeated fractional recrystallisations from pentane afforded an analytically pure sample.

The following assignments refer to the labelling scheme in Fig. 3. ^{1}H-NMR (C_6D_6, 500.0 MHz): 7.41–7.36 (overlapping 2 × m, 2H, H_s and H_t), 7.26–7.21 (overlapping 2 × m, 2H, H_o and H_p), 7.00 (d, $J = 6.5$, 1H, H_q), 6.95 (apparent t, apparent $J = 6.9$, 1H, H_r), 6.89 (d, $J = 6.5$, 1H, H_m), 6.83 (d, $J = 8.0$, 2H, 3-C_6H_4Me), 6.81 (apparent t, apparent $J = 7.0$, 1H, H_n), 6.06 (d, $J = 8.5$, 2H, 2-C_6H_4Me), 4.49 (d, $J = 11.0$, 1H, H_i), 3.55 (m, 1H, H_a or H_b), 3.37 (m, 1H, H_b or H_a), 3.33 (d, $J = 13.5$, 1H, H_l), 2.68 (d, $J = 13.0$, 1H, H_k), 2.50 (d, $J = 11.5$, 1H, H_j), 2.29 (m, 1H, H_f), 2.15 (m, 1H, H_g), 2.09 (s, 3H, C_6H_4Me), 1.63 (m, 1H, H_c or H_d), 1.48 (overlapping 2 × m, 2H, H_h and H_c or H_d), 0.98 (m, 1H, H_e), 0.58 (s, 9H, H_v), 0.25 (s, 9H, H_u). ^{13}C-{^{1}H} (C_6D_6, 125.7 MHz): 159.2, 158.8, 154.9 (2 × 2-C_6H_4 of L^1 and 1-C_6H_4Me), 130.5 (one of 1-C_6H_4 of L^1

or 4-C_6H_4Me), 130.2 (CH_m) 130.0 (CH_s or CH_t), 129.6 (CH_o or CH_p), 129.4 (CH_p or CH_o), 128.8 (one of 1-C_6H_4 or 4-C_6H_4Me), 128.7, (two signals overlapping, 3-C_6H_4Me and CH_q), 124.7 (CH_t or CH_s), 123.4 (2-C_6H_4Me), 119.5 (CH_n), 118.9 (CH_r), 62.0 ($CH_{k,l}$), 59.5 ($CH_{i,j}$), 55.7 ($CH_{a,c}$ or $CH_{b,d}$), 52.3 ($CH_{b,d}$ or $CH_{a,c}$), 52.0 ($CH_{f,h}$), 46.8 ($CH_{e,g}$), 21.0 (C_6H_4Me), 3.9 (CH_v), 2.9 (CH_u). One resonance for one of 1-C_6H_4 or 4-C_6H_4Me was not observed. Anal. Found (Anal. Calc. for $C_{31}H_{45}N_5Si_2Ti$): C 62.0 (62.9); H 8.0 (7.7); N 11.5 (11.8)%. IR (KBr plates, Nujol mull): 1609 (w), 1585 (w), 1492 (s), 1341 (m), 1328 (m), 1298 (s), 1251 (s), 1149 (w), 1105 (w), 1088 (w), 1071 (w), 1046 (w), 1007 (w), 928 (s), 915 (s), 854 (s), 839 (vs), 805 (m), 750 (s), 636 (w), 518 (w), 481 (w), 436 (w), 431 (w) cm^{-1}. EI-MS: 591 [M^+].

4.11. *N,N′-Bis(2-nitrobenzyl)-N,N′-dimethyl-1,3-diaminopropane* (**10**)

1-Bromomethyl-2-nitrobenzene (12.94 g, 0.06 mol) and powdered potassium hydroxide (3.93 g, 0.07 mol) were added to a solution of oxygen-free *N,N′*-dimethyl-1,3-diaminopropane (3.06 g, 0.03 mol) in toluene (250 ml). The resultant yellow slurry was heated to 60°C under an argon atmosphere for 24 h. The mixture was allowed to cool to r.t., giving a golden yellow solution with orange precipitate. The mixture was filtered and the residue extracted with toluene (2×100 ml). The filtrates were combined and the volatiles removed by rotary evaporation to yield **10** as an orange–yellow oil, which was dried in vacuo (2×10^{-3} mbar) to remove residual solvent. Yield: 10.93 g (98%).

^{1}H-NMR ($CDCl_3$, 500.0 MHz): 7.77 (d, $J = 8.0$, 2H, 3-C_6H_4), 7.56 (d, $J = 7.5$, 2H, 6-C_6H_4), 7.49 (apparent t, apparent $J = 7.6$, 2H, 4-C_6H_4), 7.34 (apparent t, apparent $J = 7.6$, 2H, 5-C_6H_4), 3.73 (s, 4H, ArCH_2N), 2.35 (t, $J = 7.3$, 4H, N$CH_2$$CH_2$), 2.11 (s, 6H, NMe), 1.59 (quin, $J = 7.1$, 2H, N$CH_2$$CH_2$). ^{13}C-{^{1}H} ($CDCl_3$, 125.7 MHz): 149.6 (2-$C_6H_4$), 134.9 (1-$C_6H_4$), 132.3, 130.9, 127.6, 124.1 ($4 \times$ CH of C_6H_4), 58.8 (ArCH_2N), 55.4 (N$CH_2$$CH_2$), 42.1 (NMe), 25.2 (N$CH_2$$CH_2$). CI-MS: 373 [$MH^+$].

4.12. *N,N′-Bis(2-aminobenzyl)N,N′-dimethyl-1,3-diaminopropane* (**11**)

A stirred mixture of *N,N′*-bis(2-nitrobenzyl)-*N,N′*-dimethyl-1,3-diaminopropane (**10**) (11.10 g, 0.03 mol) and graphite catalyst (3 g, Sigma-Aldrich) in ethanol (400 ml) was purged with nitrogen. Oxygen-free hydrazine monohydrate (31.34 g, 0.63 mol) was added and the mixture heated to reflux under a nitrogen atmosphere for 48 h. The hot mixture was filtered, yielding a pale yellow solution and the residue was extracted with chloroform (250 ml). The filtrates were combined and the volatiles removed by rotary evaporation, giving a pale yellow oily solid, which was dried in vacuo and then dissolved in chloroform (275 ml) and dried ($MgSO_4$). The solvent was removed by rotary evaporation to give a yellow–white oil. This solidified on standing in the cold (ca. 5°C) and was dried in vacuo. Recrystallisation from ethanol afforded **11** as a white crystalline solid. Yield: 6.35 g (68%).

^{1}H-NMR ($CDCl_3$, 500.0 MHz): 7.08 (apparent t, apparent $J = 7.8$, 2H, 4-C_6H_4), 6.95 (d, $J = 7.5$, 2H, 6-C_6H_4), 6.66 (apparent t, apparent $J = 7.4$, 2H, 5-C_6H_4), 6.61 (d, $J = 8.0$, 2H, 3-C_6H_4), 4.45 (br s, 4H, NH_2), 3.45 (s, 4H, ArCH_2N), 2.33 (t, 4H, $J = 7.3$, N$CH_2$$CH_2$), 2.12 (s, 6H, NMe), 1.68 (quin, 2H, $J = 7.1$, N$CH_2$$CH_2$). ^{13}C-{^{1}H} ($CDCl_3$, 125.7 MHz): 147.0 (2-$C_6H_4$), 130.3, 128.2 (4- and 6-C_6H_4), 123.1 (1-C_6H_4), 117.4, 115.4 (3- and 5-C_6H_4), 62.1 (ArCH_2N), 55.1 (N$CH_2$$CH_2$), 41.6 (NMe), 25.1 (N$CH_2$$CH_2$). Anal. Found (Anal. Calc. for $C_{19}H_{28}N_4$): C 72.8 (73.0); H 9.2 (9.0); N 17.8 (17.9)%. IR (Nujol mull, KBr plates): 3341[br s, ν(N–H)], 3263 [br s, ν(N–H)], 2789 (vs), 1618 (s), 1492 (vs), 1363 (vs), 1271 (s), 1250 (w), 1220 (w), 1156 (m), 1137 (w), 1115 (w), 1077 (w), 1050 (m), 1041 (w), 1024 (w), 1005 (s), 966 (m), 927 (w), 883 (m), 854 (m), 790 (w), 747 (vs), 728 (s), 628 (m), 540 (w), 449 (w), 437 (m) cm^{-1}. CI-MS: 313 [MH^+].

4.13. *N,N′-Bis(2-trimethylsilylaminobenzyl)-N,N′-dimethyl-1,3-diaminopropane* (H_2L^3, **12**)

To a stirred solution of 1,4-diazabicyclo[2.2.2]octane (1.62 g, 14.40 mmol) in diethyl ether (40 ml) was added chlorotrimethylsilane (1.72 g, 15.84 mmol) over 5 min giving immediate formation of a pale white precipitate. After a further 80 min a solution of **11** (2.25 g, 7.20 mmol) in diethyl ether (50 ml) was added resulting in a thickening of the precipitate. After a further ca. 20 h the mixture was filtered and the residue (white powder) extracted with diethyl ether (50 ml). The filtrates were combined and the volatiles removed under reduced pressure to yield a cream–white oil. Crystallisation from pentane at −80°C for several days afforded **12** as a pale yellow–white solid. Yield: 2.92 g (89%).

^{1}H-NMR ($CDCl_3$, 500.0 MHz): 7.11 (apparent t, apparent $J = 7.6$, 2H, 4-C_6H_4), 6.96 (d, $J = 7.5$, 2H, 6-C_6H_4), 6.72 (d, $J = 8.0$, 2H, 3-C_6H_4), 6.63 (apparent t, apparent $J = 7.3$, 2H, 5-C_6H_4), 6.15 (br s, 2H, NH), 3.45 (s, 4H, ArCH_2N), 2.37 (t, $J = 7.5$, 4H, N$CH_2$$CH_2$), 2.13 (s, 6H, NMe), 1.73 (quin, 2H, $J = 7.1$, N$CH_2$$CH_2$), 0.27 (s, 18H, $SiMe_3$). ^{13}C-{^{1}H} ($CDCl_3$, 125.7 MHz): 148.2 (2-C_6H_4), 130.4, 128.0 (4- and 6-C_6H_4), 124.4 (1-C_6H_4), 116.5, 115.5 (3- and 5-C_6H_4), 62.9 (ArCH_2N), 55.3 (N$CH_2$$CH_2$), 41.1 (NMe), 25.3 (N$CH_2$$CH_2$), 0.3 ($SiMe_3$). Anal. Found (Anal. Calc. for $C_{25}H_{44}N_4Si_2$): C 65.7 (65.7); H 10.1 (9.7); N 12.2 (12.3)%. IR (KBr

plates, Nujol mull): 3265 [br m, ν(N–H)], 1606 (s), 1583 (s), 1496 (s), 1421 (w), 1402 (w), 1297 (s), 1249 (s), 1207 (w), 1167 (w), 1101 (m), 1066 (w), 1049 (m), 1033 (m), 920 (s), 843 (s), 746 (s), 630 (w), 476–428 (series of weak peaks) cm^{-1}. CI-MS: 457 [MH^+].

4.14. Dilithium N,N′-bis(2-trimethylsilylamidobenzyl)-N,N′-dimethyl-1,3-diaminopropane (Li_2L^3, **13**)

To a cold (ca. −73°C), stirred solution of (H_2L^3, **12**) (1 g, 2.19 mmol) in pentane (25 ml) was added a 2.5 M solution of *n*-butyl lithium in hexanes (1.93 ml, 4.82 mmol = 2.2 equivalents) over 5 min. After a further 5 min the yellow–white mixture was allowed to warm to r.t. and was stirred for a further 4 h. The resulting yellow–white suspension was filtered and the solid dried in vacuo, to give **13** as a yellow–orange powder. A further batch of **13** (as a pale yellow powder) was obtained by cooling the filtrate at −80°C over several days. Total yield: 0.74 g (72%).

^{1}H-NMR (C_6D_6, 500.0 MHz): 7.19 (apparent t, apparent $J = 7.5$, 2H, 4-C_6H_4), 7.08 (d, $J = 7.3$, 2H, 6-C_6H_4), 6.82 (apparent t, apparent $J = 7.4$, 2H, 5-C_6H_4), 6.25 (d, $J = 7.5$, 3-C_6H_4), 3.96 (d, $J = 11.5$, 2H, ArCH_aH_b), 2.60 (m, 2H, N$CH_cH_dCH_2CH_{c'}H_{d'}$N), 2.28 (d, $J = 11.5$, 2H, ArCH_aH_b), 1.89 (s, 6H, NMe), 1.79 (m, 2H, N$CH_cH_dCH_2CH_{c'}H_{d'}$N), 1.25 (m, 2H, NCH_2CH_2), −0.11 (s, 18H, $SiMe_3$). ^{13}C-{^{1}H} (C_6D_6, 125.7 MHz): 159.2 (2-C_6H_4), 133.8 (1-C_6H_4), 132.9, 130.6, 124.0, 117.7 (4 × CH of C_6H_4), 64.0 (ArCH_2), 55.0 (NCH_2CH_2), 40.4 (NMe), 22.9 (NCH_2CH_2), 3.0 ($SiMe_3$). Anal. Found (Anal. Calc. for $C_{25}H_{42}N_4Si_2Li_2$): C 63.8 (64.1); H 8.7 (9.0); N 11.9 (12.0)%. IR (KBr plates, Nujol mull): 1590 (m), 1444 (vs), 1420 (m), 1365 (m), 1326 (w), 1275 (vs), 1262 (vs), 1240 (s), 1154 (w), 1103 (m), 1045 (m), 1021 (w), 989 (w), 958 (s), 935 (m), 878 (m), 846 (s), 827 (vs), 784 (m), 756 (m), 734 (m), 661 (w), 586 (w), 538 (w), 446 (w) cm^{-1}.

4.15. Crystal structure determination of 1,4-bis(2-amino-4-tert-butylbenzyl)piperazine·4$CHCl_3$ (**2**·4 $CHCl_3$) and [Ti(NBu^t)(L^2)] (**8**)

Diffraction quality crystals of **2**·4 $CHCl_3$ were grown at r.t. from an ethanol–chloroform (1:1) mixture; those of **8** were grown from a pentane solution at −35°C. Crystal data collection and processing parameters are given in Table 1. The crystals were immersed in a film of perfluoropolyether oil on a glass fibre and transferred to a Stoë Stadi-4 four-circle (for **2**·4 $CHCl_3$) or Enraf–Nonius DIP2000 image plate diffractometer (for **8**) equipped with an Oxford Cryosystems low-temperature device [35]. Data were collected at 150 K using Mo–K_a radiation. For **8** equivalent reflections were merged and the images were processed with the DENZO and SCALEPACK programs [36]. Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using SIR92 [37]. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The methyl carbons of the ring *tert*-butyl groups for **2** (molecules of which lie across crystallographic inversion centres) are disordered over two sites of equal occupancy. Residual electron density for **2** was modelled as two $CHCl_3$ molecules of crystallisation per asymmetric unit (there are four $CHCl_3$ molecules per molecule of **2**). Similarity restraints were applied to the bond angles and/or distances of one of the $CHCl_3$ molecules and the disordered *tert*-butyl groups. Carbon-bound hydrogen atoms for both structures were placed geometrically and their positions allowed to vary using a riding model. H atoms of the amino group in **2** were located from Fourier difference syntheses and positionally refined. All H atoms for **2** were assigned fixed $U_{[iso]}$ values 1.3 times the $U_{[iso]}$ or $U_{equivalent}$ of the supporting atom; for **8** common $U_{[iso]}$ parameters of chemically related groups of H atoms were refined. Examination of the refined extinction parameters and agreement analyses suggested that no extinction correction was required. The relatively high final *R*-values for **2** are attributed to the disorder in the *tert*-butyl substituents and the presence of two $CHCl_3$ molecules of crystallisation. All crystallographic calculations were performed using SIR92 and CRYSTALS-PC [38].

5. Crystallographic data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, nos. 127479 (compound **2**) and 127480 (compound **8**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ. Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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