Tris(dimethylamido)bis(dimethyl-amine)titanium(IV) chlorido-bis(dimethylamine)[tris(pentafluoro-phenyl)boron–amido][tris(penta-fluorophenyl)boron–nitrido]-titanate(IV) toluene solvate

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The title ionic solid, $[Ti(C_2H_6N)_3(C_2H_7N)_2][Ti(C_{18}BF_{15}N)(C_{18}H_2BF_{15}N)Cl(C_2H_7N)_2]\cdot C_7H_8$, (I), comprises a cation with three dimethylamide ligands in the equatorial plane and two dimethylamine ligands positioned axially in a trigonal–bipyramidal geometry about the central Ti^{IV} atom. The anion has a highly distorted octahedral structure. The two dimethylamine ligands are coordinated mutually *trans*. The chloride is *trans* to the tris(pentafluorophenyl)boron–amide, while the sixth coordination site is occupied by an *ortho*-F atom of the tris(pentafluorophenyl)boron–amide group in a *trans* disposition with respect to the tris(pentafluorophenyl)boron–nitride ligand. The most significant feature of the anion is the presence of an unprecedented terminal Ti≡N moiety [1.665 (2) Å], stabilized by coordination to B(C$_6$F$_5$)$_3$, with a Ti≡N—B angle of 169.50 (19)°.

Comment

The reaction with ammonia is employed to promote the controlled chemical deposition of the technologically important metal nitride material [TiN] from tetrakis(dimethylamido)titanium. The species formed intially is believed to be [(NMe$_2$)$_3$Ti(NH$_2$)] and intermediates involving NH$_2$, NH and N ligands have been postulated (Dubois, 1994; Hoffman, 1994; Toth, 1971; Weiller, 1996). Interest in this process has driven a number of investigations into the course of reactions between Brønsted basic group 4 metal compounds and ammonia. Typically, they react with one or more of the weakly acidic NH groups to give polynuclear products with bridging amide, imide and nitride ligands, even where sterically demanding ancillary ligands are employed (Abarca *et al.*, 2000; Carmalt *et*

al., 2000; Duan & Verkade, 1996; García-Castro *et al.*, 2006; Gómez-Sal *et al.*, 1995; Roesky *et al.*, 1989).

Complexation of NH$_3$ with a strong Lewis acid profoundly moderates its reactivity, not only by preventing it from functioning as a Lewis base and providing steric protection, but also through polarization of the N—H bonds, rendering it more Brønsted acidic (Ronan & Gilje, 1971). Tris(pentafluorophenyl)borane has proven utility as a Lewis acidic activator for polymerization catalysts and in applications as diverse as organic synthesis and materials (Erker, 2005; Piers, 2005). The ammonia adduct of tris(pentafluorophenyl)borane was amongst the first derivatives reported (Massey *et al.*, 1963; Massey & Park, 1964, 1966), but prior to our investigations its chemistry has been largely neglected.

We have recently shown that H$_3$N·B(C$_6$F$_5$)$_3$, (I), reacts with strong Brønsted bases to give complexes of the tris(pentafluorophenyl)boratoamide (amidoborate) ligand, [NH$_2${B-(C$_6$F$_5$)$_3$}]$^-$. For example, the reaction between (I) and (NMe$_2$)$_4$Ti yields {NH$_2$B(C$_6$F$_5$)$_3$}(NMe$_2$)$_3$Ti, (II) (Mountford, Clegg *et al.*, 2005; Mountford *et al.*, 2007). During the course of these investigations, we attempted to repeat the preparation of complex (II), using what appears to have been a chloride-contaminated sample of '(NMe$_2$)$_4$Ti'. Cooling the resulting solution gave a low yield of yellow plate-like crystals of the title compound, (III), and a viscous colourless oil. The low yield and adhering oil precluded satisfactory characterization by spectroscopic or elemental analysis methods.

(III)
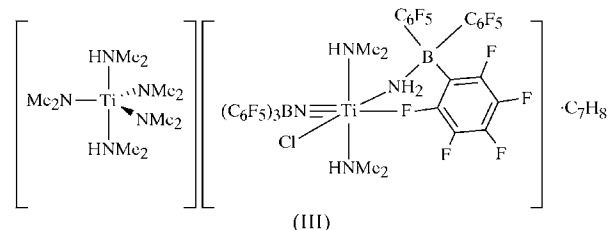
The structure of (III) consists of the ion pair [Ti(NMe$_2$)$_3$(NMe$_2$H)$_2$]$^+$[TiCl{NB(C$_6$F$_5$)$_3$}{NH$_2$B(C$_6$F$_5$)$_3$}(NMe$_2$H)$_2$]$^-$. The geometry of the cation in (III) (Fig. 1) closely resembles that of the previously reported salt [Ti(NMe$_2$)$_3$(NC$_5$H$_5$)$_2$]$^+$[BPh$_4$]$^-$, with the amide ligands arranged in the equatorial and the amine ligands in the axial positions of a trigonal bipyramid (Boisson *et al.*, 1997). At 1.89 [range 1.879 (3)–1.899 (3) Å in (I)] and 1.87 Å, respectively, the average titanium–amide bond lengths in the cations of (III) and Boisson's salt are very similar.

The anion in (III) has a highly distorted octahedral structure (Fig. 2). The most significant feature of the anion is the presence of a terminal Ti≡N moiety, stabilized by coordination to B(C$_6$F$_5$)$_3$. The triple bond was confirmed by the short Ti1—N4 bond length of 1.665 (2) Å and approximately linear Ti1—N4—B2 bond angle [169.50 (19)°] {comparable Ti—N bond lengths have been observed for imide complexes, for example, in [Ti(salophen)(═NCPh$_3$)], Ti═N = 1.686 (4) Å (Franceschi *et al.*, 1999)}. The B2—N4 distance of 1.532 (4) Å is significantly shorter than those observed in the amidoborate ligands of (II) and (III) [1.605 (4) and 1.575 (4) Å, respectively] and in the amidodiborate anion (1.63 Å; Lancaster *et*

metal-organic compounds

al., 2002). Terminal nitrides, with or without borane stabilization, are unprecedented for titanium. However, there are related later transition metal complexes, for example, [Re{NB(C$_6$F$_5$)$_3$}(PMePh$_2$)(S$_2$CNEt$_2$)$_2$] [1.548 (7) Å; Doerrer *et al.*, 1998]. The two NMe$_2$H ligands are mutually *trans*, while the Cl atom is located opposite the amidoborate ligand. An *ortho*-F atom of the amidoborate ligand occupies the final coordination site *trans* to the nitridoborate ligand. The Ti—N3 bond length in the amidoborate ligand [2.189 (2) Å] is slightly longer in octahedral complex (III) than in tetrahedral complex (II), presumably as a result of steric factors (Mountford *et al.*, 2007).

The most significant cation–anion interaction in (III) is a hydrogen bond between an amino H atom of the cation and the chloride ligand of the anion (Table 1). Solid-state structures of primary amine adducts of tris(pentafluorophenyl)boron and related amidoborate complexes, such as (II), normally exhibit a bifurcated hydrogen-bonding interaction in which one N—H group interacts strongly with two *ortho*-F atoms, while the second N—H group has only a rather longer contact to a third *o*-F atom (Mountford, Clegg *et al.*, 2005; Mountford *et al.*, 2007) (Fig. 3*a*). A similar arrangement is not possible for the amidoborate ligand in the anion of (III) because of the restraint imposed by the donor interaction between an *o*-F atom and the Ti centre. Instead, each N—H group is engaged in a short-to-medium length hydrogen-bonding interaction with one *o*-F atom (Fig. 3*b*).

Whilst complex (II) can be regarded as a B(C$_6$F$_5$)$_3$-stabilized [(NMe$_2$)Ti(NH$_2$)], the first intermediate in the stepwise ammonolysis of [(NMe$_2$)$_4$Ti], the formation of the [N≡B-

(C$_6$F$_5$)$_3$] ligand in compound (III) formally requires three consecutive ammonia deprotonation steps. Nitridoborate ligands have been reported for later transition metals, such as the rhenium example given above. However, this is the first instance in which an [N≡B(C$_6$F$_5$)$_3$] ligand has been prepared by a method other than complexation between a metal nitride and B(C$_6$F$_5$)$_3$.

All attempts to reproduce the synthesis of (III) in order to present a full spectroscopic characterization have been hampered by ignorance of the exact composition of the 'tita-
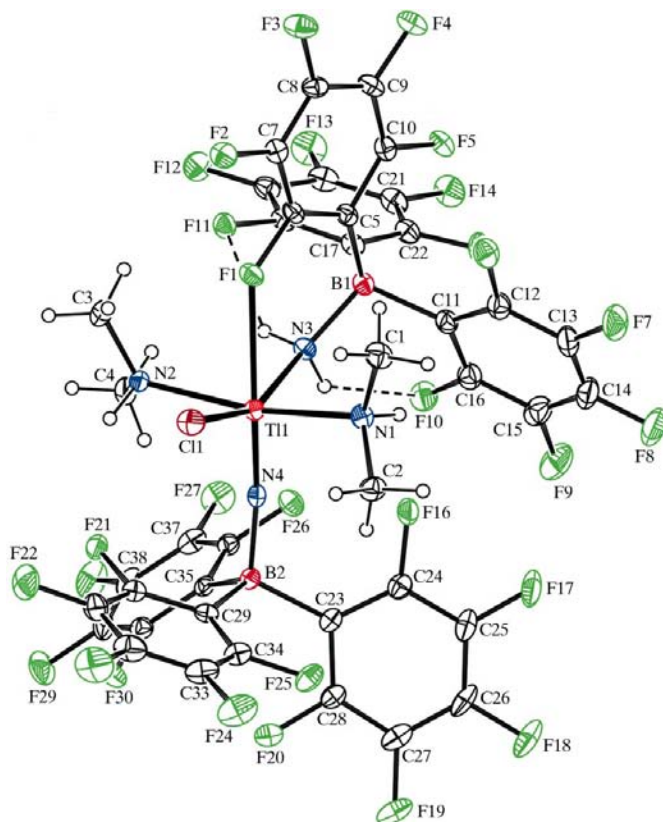

Figure 2
A view of the anion in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure 1
A view of the cation in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
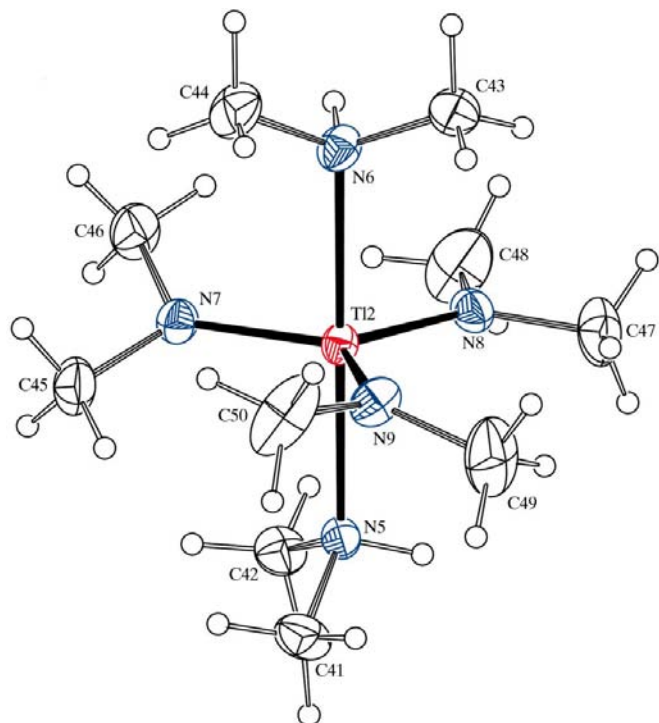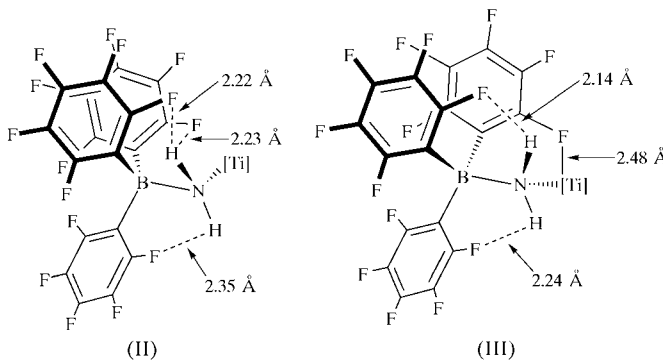

Figure 3
A comparison between the intramolecular hydrogen-bonding arrangement in neutral amidoborate complexes, such as (II), and in the anion of (III).

nium amide' sample employed. Clearly, there needs to be chloride present, and the product composition corresponds precisely to that expected for the reaction of [(NMe$_2$)$_4$Ti]:[(Cl)(NMe$_2$)$_3$Ti]:(H$_3$N·B(C$_6$F$_5$)$_3$) as a 1:1:2 reactant mixture. However, employing the conditions used to prepare (III), these reactants resulted only in the formation of (II), while treating (I) with [(Cl)(NMe$_2$)$_3$Ti] gave no discernible reaction.

Despite our difficulties repeating its synthesis, we consider the structural characterization of (III) to be an extremely significant result, since it demonstrates that mononuclear titanium nitrides, stabilized by B(C$_6$F$_5$)$_3$, are accessible. We are currently exploring means to promote consecutive deprotonation of (I) as a general route to such compounds.

Experimental

All manipulations were conducted using Schlenk-line techniques under a dry nitrogen atmosphere with anhydrous solvents, following procedures described in detail elsewhere (Mountford *et al.*, 2007). H$_3$N·B(C$_6$F$_5$)$_3$, (I), was prepared according to a literature procedure (Mountford, Lancaster *et al.*, 2005). (NMe$_2$)$_4$Ti (0.439 g, 2.0 mmol) was added to a suspension of (I) (1.036 g, 2.0 mmol) in light petroleum (15 ml) at 253 K. The mixture was warmed to 273 K and the reactants dissolved, affording a homogeneous yellow solution. Yellow plates of (III) and a viscous oil were isolated by filtration after cooling the solution to 248 K overnight.

Crystal data

[Ti(C$_2$H$_6$N)$_3$(C$_2$H$_7$N)$_2$]-
  [Ti(C$_18$BF$_{15}$N)(C$_18$H$_2$BF$_{15}$N)-
  Cl(C$_2$H$_7$N)$_2$]·C$_7$H$_8$
M_r = 3178.95
Triclinic, $P\bar{1}$
a = 12.8980 (12) Å
b = 14.5217 (15) Å
c = 19.470 (2) Å
α = 70.482 (9)°

β = 78.890 (7)°
γ = 77.513 (9)°
V = 3327.1 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 120 (2) K
0.30 × 0.14 × 0.02 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.888, T_{max} = 0.992

61684 measured reflections
15240 independent reflections
10096 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.144
S = 1.03
15240 reflections

902 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$F16	0.93	2.42	3.000 (3)	120
N2—H2$\cdots$F21	0.93	2.32	3.113 (3)	143
N3—H3$D\cdots$F10	0.92	2.24	2.961 (3)	135
N3—H3$D\cdots$F26	0.92	2.50	3.277 (3)	143
N3—H3$E\cdots$F11	0.92	2.14	2.885 (3)	137
N5—H5$\cdots$Cl1	0.93	2.41	3.281 (3)	156
C1—H1$B\cdots$F6	0.98	2.50	3.186 (4)	127
C2—H2$B\cdots$F16	0.98	2.52	3.114 (3)	119
C42—H42$B\cdots$F29^i	0.98	2.44	3.224 (5)	136

Symmetry code: (i) $x + 1, y, z$.

All H atoms were positioned using geometric constraints and refined as riding on their parent C or N atoms, with aromatic C—H, Csp^3—H and N—H distances of 0.95, 0.98 and 0.92–0.93 Å, respectively, and with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(parent). A toluene solvent molecule was located with crystallographic disorder refined over two sites. A large amount of residual electron density was still left unaccounted for in the lattice and was presumed to be another toluene solvent molecule, but it was too disordered to refine a chemically sensible model. The program *PLATON* (Spek, 2003) determined a total solvent-accessible volume of 205.5 Å^3 for this region, which is equivalent to a toluene solvent molecule. Therefore, the SQUEEZE (van der Sluis & Spek, 1990) function of *PLATON* was used to eliminate the contribution of the electron density in the solvent region from the intensity data. The *PLATON* suite was used to generate a new reflection file, which was used for the final refinement.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Version 1.05; Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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