Synthesis and characterisation of a bridging nitrido complex of titanium

Letter

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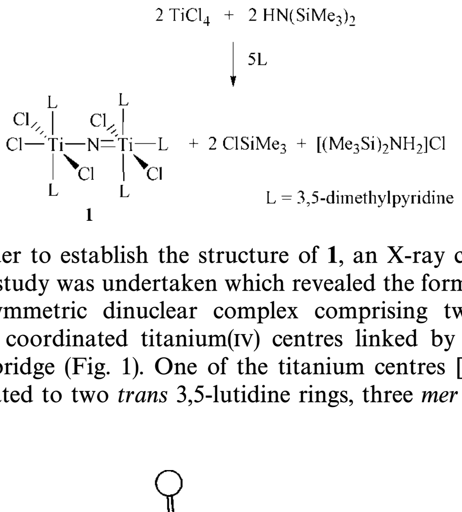
Titanium tetrachloride reacts with hexamethyldisilazane in the presence of 3,5-dimethylpyridine (L) to form a bridging nitrido species, $[\{Ti_2Cl_5(L)_5\}(\mu\text{-}N)]$, the structure of which has been established by X-ray crystallography.

Transition metal nitrido complexes have received significant attention in recent years because of their potential applications in catalytic reactions and as heart and brain imaging agents.[1–3] However, titanium nitrido species are rare and are only stabilised by the presence of bulky ligands in the complex, for example $[\{Ti(\eta^5\text{-}C_5Me_5)(NH)\}_3(\mu_3\text{-}N)]$,[4] $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}N)\}_4]$,[5] $[\{N(CH_2CH_2NPr^i)_3Ti\}_2(\mu_3\text{-}N)\text{-}Na(thf)]$[6] and $[\{Ti_2(\eta^5\text{-}C_5Me_5)_2Cl_3(NH_3)\}(\mu\text{-}N)]$.[7] More recently, two complexes with nitrido bridges between rhenium and titanium, of the type Re≡N–Ti, have been reported, namely $[\{Re(PMe_2Ph)_3(MeCN)Cl\}(\mu\text{-}N)TiCl_5]$ and $[\{Re(Me_2PhP)_3Cl_2N\}_2TiCl_4]$.[8]

An emerging application of nitrido chemistry is in the field of electronic materials. The high metallic conductivity and refractory nature of transition metal nitrides results in these metals being well suited for use as diffusion barriers.[9] Titanium nitride (TiN) is the most extensively used because of its low resistivity, excellent thermal stability and high tolerance to chemical etching.[9] The traditional preparation of TiN involves the chemical vapour deposition (CVD) reaction of either $TiCl_4$[10] or $Ti(NR_2)_4$[11] (R = Me, Et) with NH_3. More recently, attention has turned to the development of single-source precursors to TiN that feature preformed titanium–nitrogen bonds and labile leaving groups.[12,13] A promising precursor to TiN, using a single dipcoat-fire sequence, is $[Ti\{N(H)SiMe_3\}Cl_3]$ which was reportedly formed *via* the reaction of hexamethyldisilazane (HMDS) with $TiCl_4$.[14] However, a more detailed investigation has shown that the same reaction (under similar conditions) results in the formation of red crystals of $[Ti(NSiMe_3)Cl_2]_8$ and not the aforementioned complex.[15,16] Nevertheless, both complexes are attractive single-source precursors to TiN owing to the presence of the labile silyl leaving groups, although a disadvantage of such species is their modest volatility which stems, in the case of $[Ti(NSiMe_3)Cl_2]_8$, from its oligomeric nature.

With a view to isolating mononuclear, monomeric TiN precursors, we reacted $TiCl_4$ with HMDS in the presence of excess 3,5-dimethylpyridine (3,5-lutidine, L) at −78 °C. Surprisingly, work-up of the reaction mixture resulted in an 83% yield of the bridging nitrido complex, $[\{Ti_2Cl_5(L)_5\}(\mu\text{-}N)]$ **1**.† It is presumed that **1** arises from the reaction given in eqn. (1) with chlorotrimethylsilane and bis(trimethylsilyl)ammonium chloride ($[(Me_3Si)_2NH_2]Cl$) also being produced.

The stoichiometry observed in eqn. (1) supports the formation of $[(Me_3Si)_2NH_2]Cl$, although it is possible that some L·HCl is also produced. It is interesting that the reaction between $TiCl_4$ and HMDS (with no ligand present) was reported to produce the bis(trimethylsilyl)ammonium salt, $[(Me_3Si)_2NH_2][Ti_2Cl_9]$ as a by-product.[15] Related reactions between MCl_5 (M = Nb, Ta), HMDS and pyridine, were reported to result in the formation of silylimido complexes of the type $[M(NSiMe_3)Cl_3L_2]$ rather than nitrido complexes.[17]



1

(1)

In order to establish the structure of **1**, an X-ray crystallographic study was undertaken which revealed the formation of a C_2 symmetric dinuclear complex comprising two octahedrally coordinated titanium(IV) centres linked by a linear nitrido bridge (Fig. 1). One of the titanium centres [Ti(1)] is coordinated to two *trans* 3,5-lutidine rings, three *mer* chloride

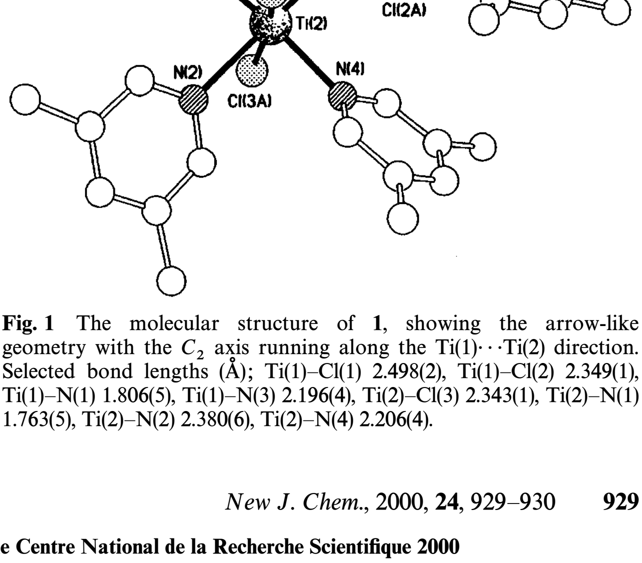


Fig. 1 The molecular structure of **1**, showing the arrow-like geometry with the C_2 axis running along the Ti(1)···Ti(2) direction. Selected bond lengths (Å); Ti(1)–Cl(1) 2.498(2), Ti(1)–Cl(2) 2.349(1), Ti(1)–N(1) 1.806(5), Ti(1)–N(3) 2.196(4), Ti(2)–Cl(3) 2.343(1), Ti(2)–N(1) 1.763(5), Ti(2)–N(2) 2.380(6), Ti(2)–N(4) 2.206(4).

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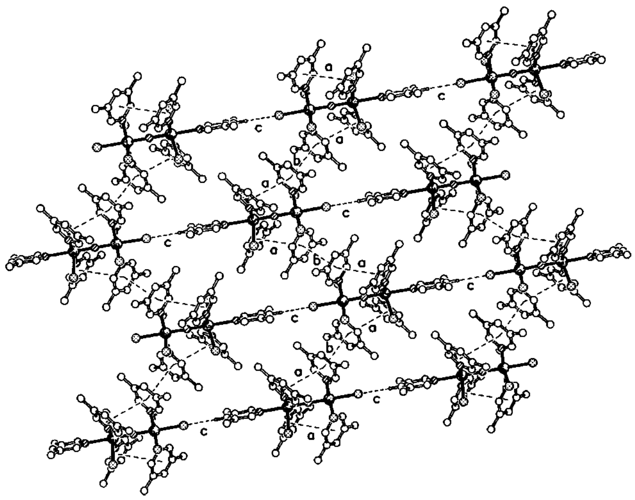

Fig. 2 Part of one of the two-dimensional sheets of linked zigzag chains of molecules present in the structure of **1**. The mean interplanar and centroid···centroid separations are (a) 3.62 and 3.93, and (b) 3.46 and 3.61 Å, respectively. The [C···Cl] and [H···Cl] distances and C–H···Cl angle are (c) 3.70, 2.74 Å, 180°.

ions and the bridging nitrido whereas the other [Ti(2)] is coordinated to three *mer* 3,5-lutidine rings, two *trans* chloride ions and the bridging nitrido. The distortions from octahedral geometry at Ti(1) are small with the titanium atom being displaced out of the equatorial plane by 0.07 Å in the direction of N(1), the Ti–Cl(1) distance [2.498(2) Å] being substantially longer than that to Cl(2) [2.349(1) Å] reflecting the *trans* influence of the nitrido ligand [Ti(1)–N(1) 1.806(5) Å]. In contrast, the geometry at Ti(2) is much more distorted with the titanium atom lying 0.20 Å out of its equatorial plane in the direction of N(1) [Ti(2)–N(1) 1.763(5) Å]; the other axial 3,5-lutidine ligand is only weakly bound with a Ti(2)–N(2) distance of 2.380(6) Å *cf.* 2.206(4) Å to N(4). The Ti–N(1) bond lengths observed here are comparable with those in, for example, $[\{Ti_2(\eta^5\text{-}C_5Me_5)_2Cl_3(NH_3)\}(\mu\text{-}N)]$ [av. Ti–N(nitrido) 1.788 Å][7] and $[\{N(CH_2CH_2N^iPr_2)_3Ti\}_2(\mu_3\text{-}N)Na(thf)]$ [av. Ti–N(nitrido) 1.832 Å],[6] and indicate the presence of a Ti=N=Ti bridging unit in **1**. There is a *ca.* 26° torsional twist between the *trans* dichlorides on the two metal centres, a twist that facilitates a weak intramolecular π–π interaction between adjacent approximately parallelly aligned (*ca.* 15°) 3,5-lutidine rings. The molecules pack to form π–π stacked zigzag chains which are linked to their neighbours by weak C–H···Cl interactions creating two-dimensional sheets (Fig. 2).

Preliminary experiments indicate that **1** is not a suitable single-source precursor to TiN. However, it is likely that other group(IV) nitrido complexes are accessible using the methodology described herein and the synthesis of these complexes is currently under investigation.

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Notes and references

† *Experimental procedure*: 3,5-dimethylpyridine (0.63 cm^3) was added slowly to a solution of $TiCl_4$ (2 cm^3, 1 M solution in toluene) in CH_2Cl_2 (25 cm^3) at −78 °C resulting in a yellow slurry. HMDS (0.42 cm^3, 2.60 mmol) was added dropwise to the foregoing solution and the mixture was allowed to warm slowly to room temperature. The reaction mixture was stirred overnight and then filtered through Celite resulting in a dark orange/red solution which was reduced *in vacuo* to a volume of *ca.* 10 cm^3. Cooling of the resulting solution to −20 °C overnight afforded an 83% yield of orange, crystalline **1** [mp 180–185 °C decomp.].

‡ *Selected spectroscopic data* for **1**: ^1H NMR (CD_2Cl_2): δ 2.18 [s, 30H, $NC_6H_3(CH_3)_2$], 6.85–9.10 [m, 15H, $NC_6H_3(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.3 [$NC_6H_3(CH_3)_2$], 159.9 [s, *o*-$NC_6H_3(CH_3)_2$], 140.6 [s, *m*-$NC_6H_3(CH_3)_2$], 133.4 [s, *p*-$NC_6H_3(CH_3)_2$]. FTIR: ν 939 cm^{-1} (μ-N). Anal. Calc. for $C_{35.5}H_{46}N_6Cl_6Ti_2$ ($\mathbf{1}\cdot 0.5CH_2Cl_2$): C, 49.28; H, 5.36; N, 9.71, Cl, 24.58. Found: C, 49.19; H, 5.35; N, 9.50; Cl, 23.49%.

§ *Crystal data* for **1**: $C_{35}H_{45}N_6Cl_5Ti_2\cdot 4CH_2Cl_2\cdot C_7H_8$, $M = 1254.7$, monoclinic, space group $C2/c$ (no. 15), $a = 25.101(6)$, $b = 14.916(3)$, $c = 17.108(4)$ Å, $\beta = 107.11(2)°$, $V = 6122(2)$ Å^3, $Z = 4$ (the complex has crystallographic C_2 symmetry), $D_c = 1.361$ g cm^{-3}, μ(Cu-Kα) = 7.72 mm^{-1}, $F(000) = 2576$, $T = 173$ K; yellow hexagonal needles, 0.47 × 0.37 × 0.17 mm, Siemens P4/RA diffractometer, ω-scans, 4490 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give $R_1 = 0.066$, $wR_2 = 0.170$ for 3653 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 120°$] and 320 parameters.

CCDC reference number 440/221. See http://www.rsc.org/suppdata/nj/b0/b008211m/ for crystallographic files in .cif format

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