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Titanium imido complexes as precursors to titanium nitride

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Treatment of $TiCl_4$ with 2–4 fold excess of $Bu^tN(H)SiMe_3$ in CH_2Cl_2 resulted in the formation of orange crystals of $[TiCl_2(NBu^t)(NH_2Bu^t)]_4$, the X-ray crystal structure of which has been determined. In the presence of excess pyridine, the reaction of $TiCl_4$ with 1 equivalent of $Bu^tN(H)SiMe_3$ resulted in the isolation of the monomeric complex $[TiCl_2(NBu^t)(py)_3]$. Low pressure chemical vapour deposition of $[TiCl_2(NBu^t)(py)_3]$ forms thin films of titanium nitride ($a = 4.23(1)$ Å, XPS $TiN_{0.75}$) at 600 °C.

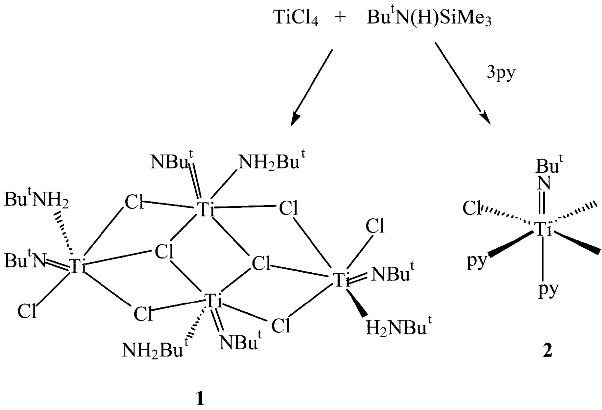
Introduction

Transition metal nitrides constitute a diverse class of materials with many interesting applications.[1] Of the many nitrides known, titanium nitride (TiN) has received significant attention because of its diffusion barrier and solar control properties.[1–4] In turn, there has been heightened interest in titanium imido complexes either as single-source TiN precursors,[5–8] or as proposed intermediates in the conversion of titanium–nitrogen derivatives to TiN.[9] In addition, a range of stable titanium imido complexes, of the type $[TiCl_2(NR)(L)_n]$ (*e.g.* $n = 3$, L = py, R = Bu^t, Ph, C_6H_4Me-4, $C_6H_4NO_2$-4, $P(S)Ph_2$, $P(S)Pr^i_2$; $n = 2$, L = *tert*-butylpyridine, R = Bu^t; $n = 1$, L = TMEDA, R = Ph) have been described.[10–15] A number of single-source precursors to TiN have been reported. The list includes $[Ti(NR_2)_4]$ (R = Me, Et),[16] $[Ti(NMe_2)_2(N_3)_2(py)_2]$ (py = pyridine),[5,17] $[TiCl_2(NHBu^t)_2(NH_2Bu^t)_2]_n$,[7] $[TiCp_2(N_3)_2]$ (Cp = η^5-C_5H_5),[18] $[Ti(\mu\text{-}NBu^t)(NMe_2)_2]_2$,[16] $[TiCl_4(NH_3)_2]$[19] and $[TiCl_3\{N(H)SiMe_3\}]$.[20] There are problems associated with all of these compounds, in particular contamination from other species (C, H and halide) and in some cases a lack of volatility. The $[Ti(NR_2)_4]$ complexes have received the most attention and have excellent volatility, unfortunately carbon contamination can exceed 20 atom%.[16] This can be overcome but requires the use of a secondary nitrogen source such as ammonia.

We have been studying the reactivity of metal halides with silylamines in an attempt to isolate volatile single-source precursors to metal nitrides.[21,22] Herein we describe the reactivity of $TiCl_4$ with $Bu^tN(H)SiMe_3$ under various conditions. The crystal structure of a new complex $[TiCl_2(NBu^t)(NH_2Bu^t)]_4$ is described. Vapour phase thin-film experiments on the complexes are described, enabling assessment of their potential as precursors for the formation of titanium nitride thin films.

Results and discussion

Treatment of $TiCl_4$ with four equivalents of $Bu^tN(H)SiMe_3$, resulted in the formation of orange crystalline $[TiCl_2(NBu^t)(NH_2Bu^t)]_4$ **1** (Scheme 1). Interestingly, regardless of the $TiCl_4$: $Bu^tN(H)SiMe_3$ reactant mole ratio employed (1 : 1, 1 : 2 or 1 : 4), the sole isolated solid product is compound **1**. Analytical data (CHN) for **1** was consistent with the formation of $[TiCl_2(NBu^t)(NH_2Bu^t)]_4$. However, in order to establish both the degree of oligomerisation and the stereochemistry at titanium, an X-ray crystallographic study was carried out. This study showed the compound to be the tetranuclear centrosymmetric complex **1** (Fig. 1). The structure comprises four $TiCl_4(NBu^t)(NH_2Bu^t)$ units with a combination of μ and μ_3 chlorides forming a Ti_4Cl_6 "core" having a geometry directly analogous to that seen in $[Fe_4(\mu_3\text{-}Cl_2)(\mu\text{-}Cl)_4Cl_2(thf)_6]$[23] and $[Nb_4(\mu_3\text{-}Cl)\text{-}$



Scheme 1

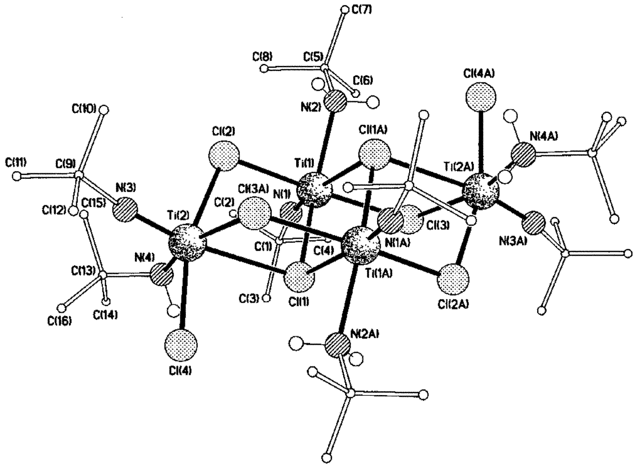


Fig. 1 The molecular structure of the centrosymmetric tetranuclear titanium complex **1**.

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Table 1 Selected bond lengths (Å) and angles (°) for **1**

Ti(1)–Cl(1)	2.4672(12)	Ti(1)–Cl(1A)	2.8429(12)
Ti(1)–Cl(2)	2.4828(12)	Ti(1)–Cl(3)	2.4205(13)
Ti(1)–N(1)	1.671(3)	Ti(1)–N(2)	2.217(4)
Ti(2)–Cl(1)	2.8206(13)	Ti(2)–Cl(2)	2.5125(13)
Ti(2)–Cl(3A)	2.4659(12)	Ti(2)–Cl(4)	2.3927(14)
Ti(2)–N(3)	1.677(3)	Ti(2)–N(4)	2.226(4)
N(1)–Ti(1)–N(2)	106.6(2)	N(1)–Ti(1)–Cl(3)	92.40(12)
N(2)–Ti(1)–Cl(3)	92.38(10)	N(1)–Ti(1)–Cl(1)	99.66(12)
N(2)–Ti(1)–Cl(1)	153.32(10)	Cl(3)–Ti(1)–Cl(1)	90.93(4)
N(1)–Ti(1)–Cl(2)	101.99(12)	N(2)–Ti(1)–Cl(2)	86.71(10)
Cl(3)–Ti(1)–Cl(2)	165.24(4)	Cl(1)–Ti(1)–Cl(2)	83.48(4)
N(1)–Ti(1)–Cl(1A)	171.79(12)	N(2)–Ti(1)–Cl(1A)	74.54(9)
Cl(3)–Ti(1)–Cl(1A)	79.40(4)	Cl(1)–Ti(1)–Cl(1A)	80.09(4)
Cl(2)–Ti(1)–Cl(1A)	86.17(4)	N(3)–Ti(2)–N(4)	106.5(2)
N(3)–Ti(2)–Cl(4)	102.76(13)	N(4)–Ti(2)–Cl(4)	88.32(10)
N(3)–Ti(2)–Cl(3A)	92.57(12)	N(4)–Ti(2)–Cl(3A)	160.67(11)
Cl(4)–Ti(2)–Cl(3A)	90.64(4)	N(3)–Ti(2)–Cl(2)	97.13(13)
N(4)–Ti(2)–Cl(2)	84.91(10)	Cl(4)–Ti(2)–Cl(2)	160.08(5)
Cl(3A)–Ti(2)–Cl(2)	89.63(4)	N(3)–Ti(2)–Cl(1)	169.18(13)
N(4)–Ti(2)–Cl(1)	81.57(10)	Cl(4)–Ti(2)–Cl(1)	84.41(4)
Cl(3A)–Ti(2)–Cl(1)	79.12(4)	Cl(2)–Ti(2)–Cl(1)	76.08(4)
Ti(1)–Cl(1)–Ti(2)	96.03(4)	Ti(1)–Cl(1)–Ti(1A)	99.91(4)
Ti(2)–Cl(1)–Ti(1A)	90.48(3)	Ti(1)–Cl(2)–Ti(2)	104.05(4)
Ti(1)–Cl(3)–Ti(2A)	110.76(4)	C(1)–N(1)–Ti(1)	168.1(3)
C(5)–N(2)–Ti(1)	129.8(3)	C(9)–N(3)–Ti(2)	165.2(3)
C(13)–N(4)–Ti(2)	127.0(3)		

$(\mu\text{-}Cl)_4(Cl)_6(PhCCPh)_4]$.[24] A search of the Cambridge Structural Database revealed that there do not appear to be any comparable titanium species, though there are several similar Ti_4X_6 "core" structures with oxygen bridges.[25] The geometry at each independent titanium centre in **1** is distorted octahedral with, in each case, the titanium atom being displaced out of the $N_{(amino)}Cl_3$ plane in the direction of the imido nitrogen atom (by 0.42 and 0.40 Å for Ti(1) and Ti(2) respectively), a geometry essentially the same as that seen in, for example, $[TiCl(\mu\text{-}Cl)(MeCN)(NBu^t)(NH_2Bu^t)]_2$ where the deviation is 0.39 Å.[26] The Ti–Cl bond lengths are distinctive with those to the μ-chlorides being symmetric whereas those to the μ_3-chlorides have one short and two long Ti–Cl bond lengths (Table 1), an asymmetry that is also seen – with similar M–Cl distances – in the above mentioned niobium[24] and titanium[26] complexes. The Ti–Cl bonds *trans* to the imido ligands are significantly longer than those *trans* to amido groups, a pattern present in $[TiCl(\mu\text{-}Cl)(MeCN)(NBu^t)(NH_2Bu^t)]_2$, which also has virtually identical angles at the imido and amido nitrogen atoms.[26] The Ti–N distances clearly reflect their formal single and double bond character with those to N(1) and N(3) being substantially shorter than those to N(2) and N(4). The non-bonded Ti ··· Ti separations within the Ti_2Cl_2 rings are in the range 3.94 to 4.07 Å, lengths very similar to the Nb ··· Nb distances in the aforementioned niobium complex.[24] There are no intermolecular packing interactions of note.

The ^1H and ^{13}C NMR of **1** in CD_2Cl_2 show a number of peaks corresponding to the *tert*-butyl groups. These data suggest either that the tetrameric structure does not stay intact in solution at room temperature or that fluxional exchange processes (such as intramolecular N–H migration) are rapid at room temperature. Notable integration of the NH_2 region and the Bu^tH region give the required 8 : 72 relative intensities. The NH_2 peaks are made up of both broad singlets at $\delta = 2.90$ and 3.40 ppm as well as a number of small doublets at between 2.8 and 4.1 ppm. It is likely that these are due to diastereotopic NH_2 protons. In the Bu^t region 12 main resonances are seen clustered around $\delta = 1.05$ ppm assigned to NBu^t protons and $\delta = 1.46$ ppm due to NH_2Bu^t protons. Notably the integration of these Bu^t peaks is 1 : 2 rather than the expected 1 : 1. Thus the assignment is not straightforward indicating complicated exchange and/or fragmentation.

Interestingly, the reaction between $TiCl_4$ and *tert*-butylamine has been described previously and resulted in the isolation of the trimeric complex $[TiCl_2(NBu^t)(NH_2Bu^t)_2]_3$, the structure of which was not described.[7] However, the compound did serve as a single-source precursor to titanium nitride films.[7]

As outlined in Scheme 1, the addition of pyridine to the reaction mixture of $TiCl_4$ and $Bu^tN(H)SiMe_3$ resulted in the formation of $[TiCl_2(NBu^t)(py)_3]$ **2**. Compound **2** has been reported previously[10] from the reaction of $TiCl_4$ with NH_2Bu^t in the presence of pyridine. An X-ray structure of **2** showed that, as in the previous report, the complex had crystallised with two crystallographically independent molecules in the asymmetric unit, but here with the inclusion of a molecule of dichloromethane; both the unit cell and space group of the CH_2Cl_2 solvate are different from the reported non-solvated complex. Geometric details do not differ significantly between the two determinations with their being a characteristic deviation of *ca.* 0.27 Å of the titanium centre out of the plane of the equatorial substituents in the direction of the imido nitrogen atom.

In order to study the decomposition pathway of compounds **1** and **2** thermal analyses were carried out in aluminium pans under a flow of nitrogen. The TGA (thermal gravimetric analysis) of **1** (10 °C min^{-1} from 20 to 500 °C) shows a weight loss of 64.8% (calculated weight loss 76.5% for TiN formation from **1**). This behaviour indicates an incomplete decomposition to TiN up to 500 °C. The TGA of **2** indicates that this compound may be a suitable single-source precursor for the deposition of TiN thin-films. Thus, the TGA of **2** (Fig. 2) is clean and shows a total weight loss of 79.2% (calculated weight loss 85% from **2** for the formation of TiN).

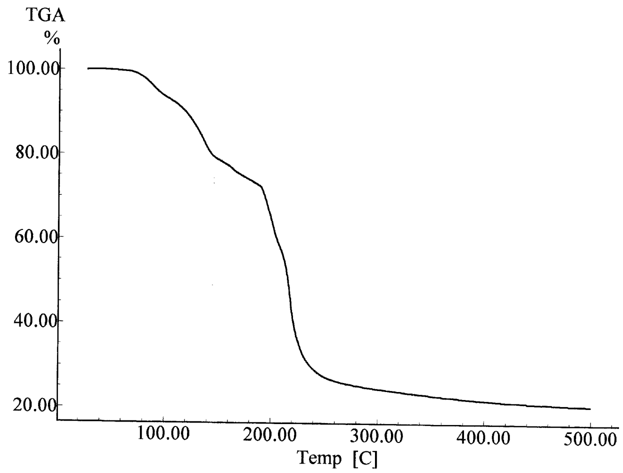

Fig. 2 TGA of **2**.

Low pressure CVD of **1** and **2** were investigated, the details of which are described in the Experimental section.[27] No film was deposited from compound **1** instead the material decomposed to a black solid; no carry over of condensable organic products was noted. However, from compound **2** a gold-coloured film was deposited on glass substrates at 600 °C. The film produced was analysed by EDAX/SEM, electron probe and reflectance/transmission measurements. The EDAX and electron probe data showed the presence of titanium and nitrogen in the film. Significant breakthrough of the excitation volume through the coating to the underlying glass was observed and so accurate quantitative analysis by EDAX was difficult. However, EDAX data showed that chlorine contamination was below 0.1%. By scanning electron microscopy (SEM) the titanium nitride films were seen to consist of agglomerates of approximately 0.1 μm (Fig. 3).

The film produced showed a maximum transmission in the visible region (450–700 nm) and an increase in reflectivity in the IR region (> 850 nm). This behaviour is characteristic of titanium nitride films which show metallic like behaviour.[28] The

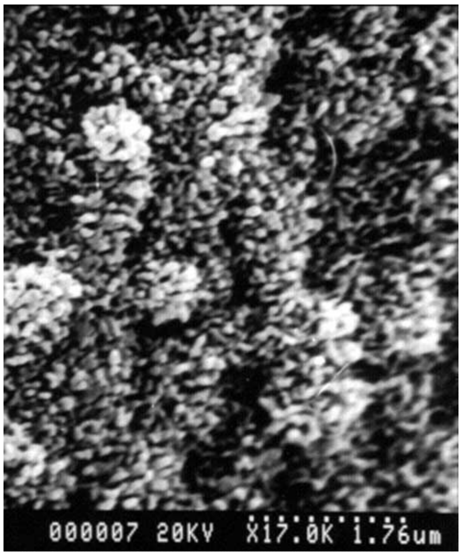

Fig. 3 SEM of a film grown from **2** under low pressure CVD conditions.

TiN films from **2** further showed metallic like behaviour with a sheet resistance of 200 Ω per square. The TiN films showed Raman absorptions at *ca.* 500 cm^{-1}. This matched with a bulk powder of TiN purchased from Aldrich Chemical Co.

The titanium nitride film produced from **2** is resistant to attack by common solvents (water, acetone, toluene, propan-2-ol, petroleum ether). However, concentrated nitric acid digested the film from **2** in 48 hours. The contact angle of the film was found to be 95°, which is the same as titanium nitride film produced *via* dual-source CVD in our laboratories.[29] The TiN films passed the Scotch tape test and could not be abraded with a brass stylus or stainless steel scapel – this is again typical of TiN.

X-Ray powder diffraction of the film obtained from **2** showed a broad diffraction pattern for TiN consistent with a NaCl (*Fm*3*m*) structure, Fig. 4. Determination of the lattice constant by Win-Index (version 1.2, Sigma C GmbH, 1991) gave a value of $a = 4.23(1)$ Å, this can be compared with a literature value of $a = 4.241$ Å for bulk $TiN_{1.0}$.[30] The TiN lattice parameter is known to decrease linearly from $TiN_{1.0}$ to $TiN_{0.45}$ all with the same NaCl cubic pattern.[30] The lattice parameter observed here indicates a composition of $TiN_{0.70}$. Crystallite size determination from line broadening studies of the (2 0 0) peak, ignoring strain effects, gave a value of *ca.* 200 Å. Notably the TiN formed in the study did not show any preferred orientation. This is unlike the dual source APCVD reactions of $TiCl_4/NH_3$ or $TiCl_4$/hexamethyldisilazane on glass which showed marked growth in the (2 0 0) peak.

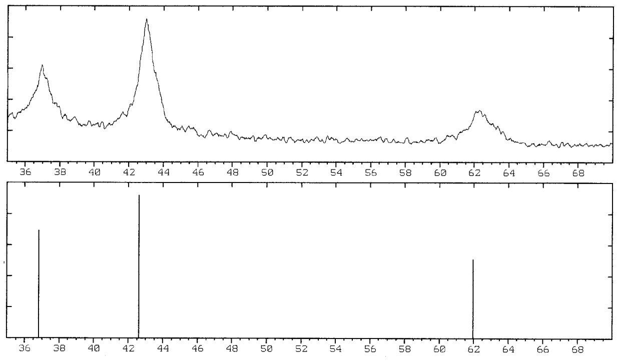

Fig. 4 XRD data pattern of TiN film from the low pressure CVD of **2**.

The XPS depth profiles analysis of the film formed from **2** showed the presence of Ti, C, N and O. The carbon concentration dropped dramatically on the first etch, indicating that this was surface bound. The titanium and nitrogen concentration followed each other in abundance through the film. At the second etch the relative ratio was $TiN_{0.75}$. The oxygen content was lowest at the surface and increased on depth profiling. Notably the increase in oxygen content with depth was accompanied by growth of a Si peak and is due to sputtering through to the underlying SiO_2. The $Ti2P_{3/2}$ peak at the second etch had a binding energy of 459.0 eV and N_{1s} peak at 398 eV. These are consistent with other thin-film studies of TiN.[31] No chlorine contamination of the film was observed by XPS (less than 0.5 atom%).

In comparison with the work performed on forming titanium nitride films from $[Ti(NR_2)_4]$ (R = Me, Et)[16] the use of **2** has some distinct advantages, in particular the fact that the as-formed films have negligible carbon contents. This is probably because **2** has an easy release mechanism for loss of the Bu^t groups *via* formation of isobutylene, whereas Me and Et groups are less easily eliminated from $[Ti(NR_2)_4]$ leading to carbon contamination. Furthermore, **2** has in place a strong Ti–N multiple bond, which remains intact during the CVD in forming the TiN film. Notably despite **2** containing chlorine, no chlorine is detected in the TiN film by either XPS or EDAX analysis, indicating that this precursor could be used in microelectronic applications.

Conclusions

The tetrameric complex, $[TiCl_2(NBu^t)(NH_2Bu^t)]_4$, has been synthesised and structurally characterised. Low pressure CVD indicates that $[TiCl_2(NBu^t)(py)_3]$ is an effective titanium nitride precursor.

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium/benzophenone: toluene, THF and hexanes; CaH_2 for CH_2Cl_2). All other reagents were obtained from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL). BDH microscope slides were used for the CVD experiments.

Physical measurements

^1H and ^{13}C NMR spectra were recorded on a Brüker AMX400 spectrometer at UCL. The NMR spectra are referenced to $CDCl_3$, which was degassed and dried over molecular sieves prior to use; ^1H chemical shifts are reported relative to $SiMe_4$ (0.00 ppm). IR spectra were recorded on a Nicolet 205 instrument. EDAX/SEM results were obtained on a JEOL 35-CF instrument using ISIS software (revision 3.2, series 300 configuration, Oxford Instruments, 1992–1997). Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. Electron probe data were measured on a JXZ 8600 instrument calibrated using a PET crystal (88.03). TGA of the compounds were obtained from the Thermal Methods Laboratory at Birkbeck College (ULIRS) by Dr M. Odlyha. The TGA experiments were performed in aluminium pans at atmospheric pressure under a flow of dry nitrogen gas.

Preparations

$[TiCl_2(NBu^t)(NH_2Bu^t)]_4$ 1. $TiCl_4$ (1.0 cm^3, 1 mmol, 1.0 M solution in toluene) was added to a solution of $Bu^tN(H)SiMe_3$ (0.75 cm^3, 3.94 mmol) in CH_2Cl_2 (20 cm^3) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature with stirring. After stirring at room temperature for 3 hours, an orange solution resulted which was filtered through Celite. Cooling of this solution to −20 °C overnight afforded a 44% yield (0.12 g, 0.11 mmol) of orange crystalline **1**. Anal. Calc. for $C_{32}H_{80}Cl_8N_8Ti_4$: C, 36.53; H, 7.06; N, 10.65. Found C, 38.40; H, 8.71; N, 9.82%. ^{1}H NMR ($CDCl_3$): δ 0.93 (s, NBu^t), 0.94 (s, NBu^t), 1.04 (s, NBu^t), 1.07 (s, NBu^t), 1.1 (s, NBu^t), 1.38 (s, $NH_2$$Bu^t$), 1.46 (s, $NH_2$$Bu^t$), 1.47 (s, $NH_2$$Bu^t$), 1.51 (s, $NH_2$$Bu^t$), 1.52 (s, $NH_2$$Bu^t$), 1.53 (s, $NH_2$$Bu^t$), 1.55 (s, $NH_2$$Bu^t$), 2.9 (s, N$H_2$$\mathrm{Bu}^t$), 3.4 (s, N$H_2$$\mathrm{Bu}^t$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.9 (N–C(CH_3)$_3$), 31.4 (N–C(CH_3)$_3$). N–*C*(CH_3)$_3$ not detected. FT-IR 2879s, 2701m, 2595w, 2500w, 2395 sh, 2061 br, 1609w, 1560m, 1507w, 1477w, 1459w, 1400m, 1375s, 1355w, 1294w, 1261s, 1211s, 1093 br, 1022s, 927w, 901w, 799m, 751w, 653w, 587w cm^{-1}.

[$TiCl_2(NBu^t)(py)_3$] 2. $TiCl_4$ (1.0 cm^3, 1 mmol, 1.0 M solution in toluene) was added to a solution of Bu^tN(H)$SiMe_3$ (0.75 cm^3, 3.94 mmol) in pyridine (0.5 cm^3) and CH_2Cl_2 (20 cm^3) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature with stirring. After stirring at room temperature for 3 hours, a dark orange solution resulted which was filtered through Celite. Cooling of this solution to −20 °C overnight afforded a 50% yield (0.22 g, 0.5 mmol) of orange crystalline **2**. Anal. Calc. for $C_{19}H_{24}Cl_2N_4Ti(CH_2Cl_2)_{0.5}$ C, 49.87; H, 5.36; N, 11.93. Found C, 50.16; H, 5.48; N, 11.69%. ^{1}H NMR ($CDCl_3$): δ 0.89 (s, 9H, NBu^t), 7.15 (t, 2H, *m*-C_5H_5N), 7.43 (t, 4H, *m*-C_5H_5N), 7.55 (t, 2H, *p*-C_5H_5N), 7.78 (t, 2H, *p*-C_5H_5N), 8.59 (br, 2H, *o*-C_5H_5N), 9.19 (d, 4H, *o*-C_5H_5N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.2 (N–C(CH_3)$_3$), 72.5 (N–*C*(CH_3)$_3$), 123.5 (*m*-C_5H_5N), 123.5 (*m*-C_5H_5N), 123.9 (*m*-C_5H_5N), 138.5 (*p*-C_5H_5N), 150.3 (*o*-C_5H_5N), 151.9 (*o*-C_5H_5N). FT-IR 1393w, 1373w, 1353w, 1302w, 1245m, 1223m, 1213m, 1151w, 1070 br, 1042s, 1011m, 998m, 978w, 803w, 768m, 761m, 712m, 705m, 697s, 667s, 658w, 635s, 616m, 541 br cm^{-1}.

Low pressure CVD experiments

The same procedure was carried out for both compounds **1** and **2** and is described here for **2**. A sample of compound **2** (0.3 g) was loaded into the end of a glass ampoule (40 cm length × 16 mm diameter) in the glovebox. Glass substrates (10 cm × 7 mm × 1mm) were placed carefully along the whole length of the inside the ampoule. The ampoule was then placed in a furnace such that 30 cm was inside the furnace and the end containing the sample protruded by 4 cm. The ampoule was heated to a temperature of 600 °C under dynamic vacuum, except for the section of the tube containing the sample. The ampoule was slowly drawn into the furnace over a period of a few minutes until the sample started to melt, *ca* 170 °C. Once all of the compound had decomposed the furnace was allowed to cool to room temperature. A gold film, deposited on the glass substrate, was analysed by EDAX/SEM, electron probe and UV/visible/NIR reflectance/transmission measurements.

X-Ray crystallography

Crystals of **1** and **2** were grown from CH_2Cl_2 at −20 °C.

Crystal data for 1. $C_{32}H_{80}N_8Cl_8Ti_4\cdot 4CH_2Cl_2$, $M = 1391.9$, triclinic, $P\bar{1}$ (no. 2), $a = 12.400(1)$, $b = 12.952(3)$, $c = 13.509(1)$ Å, $\alpha = 63.13(1)$, $\beta = 63.23(1)$, $\gamma = 87.77(1)°$, $V = 1690.7(4)$ Å^3, $Z = 1$ (C_i symmetry), $D_c = 1.367$ g cm^{-3}, μ(Cu-Kα) = 9.94 mm^{-1}, T = 183 K, yellow prisms; 4759 independent measured reflections, F^2 refinement, $R_1 = 0.047$, $wR_2 = 0.112$, 3879 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$], 318 parameters.

Crystal data for 2. $C_{19}H_{24}N_4Cl_2Ti\cdot 0.5CH_2Cl_2$, $M = 469.7$, orthorhombic, $Pna2_1$ (no. 33), $a = 16.880(1)$, $b = 9.215(1)$, $c = 29.000(1)$ Å, $V = 4510.9(3)$ Å^3, $Z = 8$, $D_c = 1.383$ g cm^{-3}, μ(Cu-Kα) = 6.58 mm^{-1}, T = 183 K, orange prisms; 3421 independent measured reflections, F^2 refinement, $R_1 = 0.037$, $wR_2 = 0.081$, 3063 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$], 497 parameters. The absolute structure was determined by a combination of R-factor tests [$R_1^+ = 0.0374$, $R_1^- = 0.0462$] and by use of the Flack parameter [$x^+ = +0.01(2)$, $x^- = +0.99(2)$].

CCDC reference numbers 190026 and 190027.

See http://www.rsc.org/suppdata/dt/b2/b204027c/ for crystallographic data in CIF or other electronic format.

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