Molecular Precursor Chemistry for TiN: Synthesis and Structure of [Ti(NMe$_2$)(N$_3$)(μ-NMe$_2$)]$_3$(μ_3-N$_3$)(μ_3-NH)

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TiN is a refractory, gold-colored material that has found use in decorative and mechanical wear-resistant coatings and, most recently, in microelectronic circuits. With an electrical resistivity of about 50 $\mu\Omega$ cm and the ability to act as a diffusion barrier for Al, TiN is being introduced into VLSI (very large scale integration) integrated circuits to protect increasingly shallow junctions in Si. It also serves as an adhesion layer for Al and as a nucleation and protection layer for W CVD. Line-of-sight physical vapor deposition techniques, such as reactive sputtering of Ti in N$_2$, are not capable of achieving adequate coverage in increasingly higher aspect ratio contact windows and vias. Therefore, the conformal coverages achievable through chemical vapor deposition (CVD) are considered critical to a successful metallization scheme.

CVD TiN processes based on NH$_3$ reduction of TiCl$_4$[1–3] and Ti(NMe$_2$)$_4$[4,5] have been studied. Although the TiCl$_4$ process has been commercialized, deposition temperatures of about 650 °C limit the application to the contact level, before any Al has been deposited. The high temperatures are needed to reduce the content of potentially corrosive Cl below 0.5%. A lower temperature metal–organic CVD (MOCVD) process using Ti(NMe$_2$)$_4$ has been used to deposit TiN at about 400 °C, but high density films were only achieved at atmospheric pressure.[4,5] A low-pressure process is considered more desirable, however, for integration into multichamber manufacturing tools. Both of these CVD processes rely on NH$_3$ not only as the reducing agent but also as the source of N in the TiN. Rapid gas phase reactions in both systems complicate control of these processes and may affect the ability to achieve conformal coverage.

Brown,[6] and Ikeda, et al.[7] recently reported the thermal and photoassisted decomposition of (η^5-C$_5$H$_5$)$_2$Ti(N$_3$)$_2$ to deposit TiN. Although films were contaminated with varying amounts of graphitic C, the azide ligand proved to be a viable intramolecular source of N. Combining the attributes of Ti(NMe$_2$)$_4$ and (η^5-C$_5$H$_5$)$_2$Ti(N$_3$)$_2$, we pursued the synthesis of azide derivatives of Ti(NMe$_2$)$_4$, the results of which are reported herein.

Results and Discussion

Direct substitution of azide for dimethylamide was attempted by reacting a stoichiometric amount of azidotrimethylsilane with Ti(NMe$_2$)$_4$. When this reaction was carried out in benzene at ~5 °C, the solution changed color from orange to deep red. After being warmed to room temperature and being stirred for 1 h, the reaction mixture was pumped to dryness to leave a thick brick red oil. Solvent and other volatile reaction products were collected in a liquid N$_2$ trap and analysis of the colorless liquid by ^{1}H NMR revealed the presence of (dimethylamino)trimeth-

ylsilane and no unreacted azidotrimethylsilane. The brick red oil was extracted with toluene, filtered through a glass frit in the drybox, and recrystallized by addition of hexane to give air-sensitive red-orange crystals, **1**. Subsequent repetition of the reaction using an Me$_3$SiN$_3$:Ti(NMe$_2$)$_4$ ratio of 1.67:1 led to direct isolation of a brick red solid. Attempts to sublime **1** were unsuccessful, and we were surprised to find that **1** exhibits remarkable thermal stability, with a slight darkening on heating to 125 °C in vacuum. Despite this *apparent* stability, *extreme care should be exercised in handling all transition metal azides*.

Intense absorptions at 2110 and 2090 cm^{-1} in the infrared (IR) spectrum of **1** confirmed the presence of azide ligands, and a weak absorption at 3348 cm^{-1} was assigned to an N–H vibration. The ^{1}H NMR spectrum showed a single resonance for the N(CH$_3$)$_2$ groups at δ 3.12 and a resonance due to NH at δ 12.81 (C$_6$D$_6$). The elemental analysis could not be rationalized on the basis of a simple substitution of azide for dimethylamide and thus suggested that the product might be an oligomer.

A single-crystal X-ray structure determination established **1** to be a trimer with the composition [Ti(NMe$_2$)(N$_3$)(μ-NMe$_2$)]$_3$-(μ_3-N$_3$)(μ_3-NH). The molecular structure is shown in Figure 1 and bond lengths and angles of interest are listed in Table I. The structure consists of a six-membered (TiNMe$_2$)$_3$ titanacycle in a pseudo-chair configuration with a mirror plane passing through Ti(1) and bisecting the Ti(2)–Ti(2') bond. The six-coordinate Ti atoms are connected through bridging dimethylamide groups, which are bent towards a triply bridging azide cap on one side of the titanacycle. The other face of the ring is capped by a triply bridging imide group. Although the crystal structure does not allow differentiation between an imide and a nitride, the IR and ^{1}H NMR spectra confirm the cap to be an imide. The coordination sphere of the Ti is completed by singly bonded dimethylamide and azide ligands. The terminal azide ligands are all bent away from the Ti plane in the direction of the azide cap.

It is interesting to note the presence of terminal and triply bridging bonding modes for the azides and the absence of doubly bridging azides.[8] To our knowledge this is the first Ti complex containing a triply bridging azide. The Ti–N$_3$(cap) bond length of 2.30 Å is significantly longer than the terminal Ti–N$_3$(terminal) bond lengths of 1.91 and 2.01 Å, reflecting the weaker Ti–N interactions in the four-center bond. The Ti–N$_3$(terminal) bond lengths are comparable to the Ti–N$_3$ bond length of 2.03 Å in (η^5-C$_5$H$_5$)$_2$Ti(N$_3$)$_2$.[9] The Ti–NH(cap) bond length of 1.94 Å is comparable to the Ti–NH bond length of 1.93 Å in [(η^5-C$_5$-Me$_5$)Ti(μ-NH)]$_3$(μ_3-N) and is slightly longer than the 1.91 Å Ti–N bond.[10] The slight deviation from planarity of the titanacycle toward a chair configuration is reflected in the 0.16-Å separation between the planes formed by the Ti (Ti(1)–Ti(2)–Ti(2')) and the NMe$_2$ (N(9)–N(9')–N(14)) centers, with a dihedral angle of 177.5 (4)° between them.

The mechanism for formation of the imide has not been fully established, but is likely derived from a capping azide ligand. The fact that we could not isolate a molecule with one azide substitution per Ti reflects the tendency of Ti complexes to oligomerize when not constrained by steric effects. The tendency of metal–organic Ti complexes to oligomerize is well-known. Bradley et al. reported the transamination reactions of Ti(NMe$_2$)$_4$ with primary alkylamines to produce polymers with Ti(μ-NR)$_2$ repeat units.[11] Only when the sterically bulky *tert*-butylamine was used could the dimer Ti$_2$(μ-N^{t}Bu)$_2$(NMe$_2$)$_4$ be isolated.[11] The N-containing heterotitanacycles reported herein, along with [(η^5-C$_5$Me$_5$)Ti-(μ-NH)]$_3$(μ_3-N),[10] can be viewed as building blocks in the

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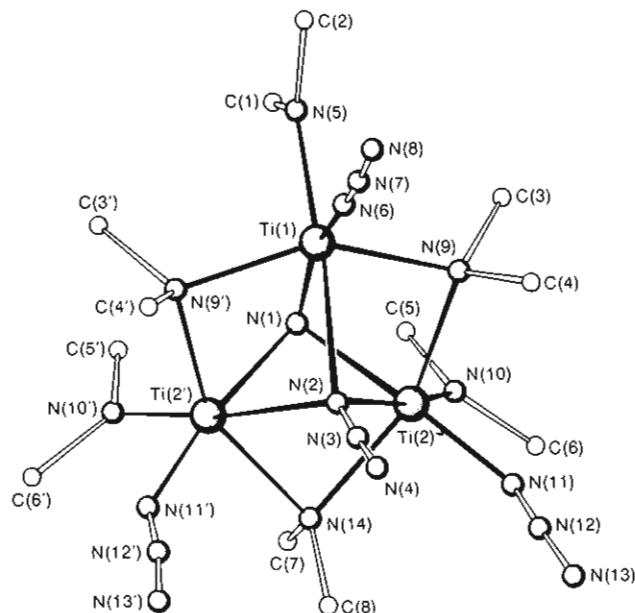(11) Bradley, D. C.; Torrible, E. G. *Can. J. Chem.* **1963**, *41*, 134.

Figure 1. Molecular structure of 1.

Table I. Selected Bond Lengths and Angles for Compound 1

Bond Lengths (Å)

Ti(1)–N(1)	1.94 (2)	Ti(2)–N(1)	1.97 (1)
Ti(1)–N(2)	2.31 (2)	Ti(2)–N(2)	2.31 (2)
Ti(1)–N(9)	2.17 (2)	Ti(2)–N(9)	2.15 (2)
Ti(1)–N(6)	1.92 (5)	Ti(2)–N(11)	1.90 (2)
Ti(1)–N(5)	2.00 (3)	Ti(2)–N(10)	1.88 (2)
		Ti(2)–N(14)	2.18 (2)

Bond Angles (deg)

N(9)–Ti(1)–N(9')	151.4 (8)	N(9)–Ti(2)–N(14)	150.4 (7)
Ti(1)–N(9)–Ti(2)	87.7 (8)	Ti(2)–N(14)–Ti(2')	87.2 (8)
Ti(1)–N(6)–N(7)	173 (5)	Ti(2)–N(11)–N(12)	142 (2)

formation of TiN. The lack of volatility of these compounds rules out their use as MOCVD precursors, but the structures do begin to offer interesting insights into the formation of TiN. We are continuing to explore the synthesis of related precursors with the goal of isolating volatile monomeric species.

Experimental Section

Table II. Crystallographic Data for
$[Ti(NMe_2)(N_3)(\mu\text{-}NMe_2)]_3(\mu_3\text{-}N_3)(\mu_3\text{-}NH)$

$C_{12}H_{37}N_{19}Ti_3$	MW = 590.2
$a = 9.282$ (2) Å	monoclinic, $P2_1/m$
$b = 18.880$ (4) Å	$T = 25$ °C
$c = 10.337$ (2) Å	$\lambda = 0.709\ 30$ Å
$\beta = 108.96$ (2)°	$\rho = 1.146$ g cm^{-3}
$V = 1713.2$ (6) Å^3	$R_F = 0.112^a$
$Z = 2$	$R_{wF} = 0.083^b$
cryst dimens: $0.11 \times 0.10 \times 0.08$ mm	

$^a R_F = \sum(F_o - F_c)/\sum F_o.$ $^b R_{wF} = [\sum(w(F_o - F_c)^2)/\sum wF_o^2].^{1/2}$

Synthesis of 1. A solution of Me_3SiN_3 (4.25 g, 36.9 mmol) in toluene (5 mL) was added dropwise to a solution of $Ti(NMe_2)_4$ (5.0 g, 22.3 mmol) in toluene (15 mL) with stirring and cooling in an ice bath at 0 °C. The dark red mixture was allowed to warm to room temperature and was stirred overnight. Solvent and volatile components were condensed in a liquid-nitrogen-cooled flask and analyzed by ^{1}H NMR. The remaining solid was extracted with hexane.

Multiple attempts to obtain accurate elemental analysis of 1 were apparently subject to some decomposition during handling. Anal. Calcd for $C_{12}H_{37}N_{19}Ti_3$ (1): C, 24.38; H, 6.31; N, 45.01; Ti, 24.30. Found: C, 25.59; H, 6.58; N, 42.96; Ti, 24.95.

Structure Determination. X-ray quality crystals were obtained by slow diffusion of hexane into a concentrated toluene solution of 1 at –35 °C. The size of the crystal used in the structural determination was limited by severe twinning in all of the larger crystals that were investigated. Crystallographic data are listed in Table II. The crystal of 1 was mounted in a standard X-ray capillary due to extreme sensitivity to air. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.709\ 30$ Å), ω scan mode with $2\theta_{max} = 45$ °C, hkl ranges –9 to 9, 0 to 19, and 0 to 11, respectively. A total of 2627 reflections were measured, with 2275 belonging to the unique set, of which 589 with $I > 2.5\sigma(I)$ were used in the refinement. A Gaussian absorption correction was applied. Three standard reflections were measured every hour to correct for the crystal decay (overall decay 25%). Systematic extinctions gave the possible space groups P_c and $P2_1/m$. The structure was solved using direct methods, locating the heavy (Ti) atoms; the lighter atoms were subsequently located using Fourier maps.[12] The solution showed $P2_1/m$ to be the correct space group. Full-matrix least-squares refinement was carried out; however, only the metal atoms were refined with anisotropic thermal parameters due to the large number of unobserved reflections. Final refinement factors were $R_F = 0.112$ and $R_{wF} = 0.083$.

Supplementary Material Available: ORTEP view and stereoscopic view of 1 and tables of data collection details, final atomic parameters, anisotropic and isotropic thermal parameters, symmetry equivalents, intramolecular bond distances and angles, and distances to least-squares planes (17 pages). Ordering information is given on any current masthead page.

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