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Article

Synthesis of Titanium(IV) Guanidinate Complexes and the Formation of Titanium Carbonitride via Low-Pressure Chemical Vapor Deposition

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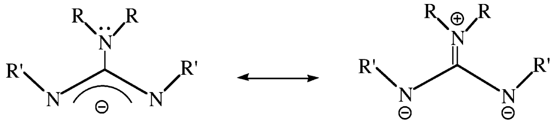
The mono(guanidinato) complex [Ti(NMe$_2$)$_2$Cl{*i*-PrNC[N(SiMe$_3$)$_2$]N-*i*-Pr}] (**1**) was prepared by reaction of [Ti(NMe$_2$)$_2$Cl$_2$] with 1 or 2 equiv of the lithium guanidinate salt [Li{*i*-PrNC[N(SiMe$_3$)$_2$]N-*i*-Pr}]. Compound **1** has been characterized by X-ray crystallography. Treatment of TiCl$_4$ with 2 equiv of [Li{*i*-PrNC[N(SiMe$_3$)$_2$]N-*i*-Pr}] resulted in the formation of dark red crystals. X-ray crystallography showed that these crystals consist of a 70:30 mixture of two bis(guanidinato) complexes, namely, [TiCl$_2${*i*-PrNC[N(SiMe$_3$)$_2$]N-*i*-Pr}{*i*-PrNC(N═CMe$_2$)N-*i*-Pr}] (**2**) and [TiCl$_2${*i*-PrNC[N(SiMe$_3$)$_2$]N-*i*-Pr}{*i*-PrNC[N(H)-*i*-Pr]N-*i*-Pr}] (**3**). Both compounds **2** and **3** possess a transformed guanidinate ligand. Low-pressure chemical vapor deposition of either compound **1** or [TiCl$_2${*i*-PrNC(NMe$_2$)N-*i*-Pr}] (**4**) at 600 °C results in thin films of titanium carbonitride.

Introduction

Guanidinate anions, $[R'NC(NR_2)NR']^-$, have recently attracted interest as ancillary ligands for transition and main group metals, due to their potential for steric and electronic tunability.[1] Guanidinate ligands can be modified by variation of the substituents R and R′. The presence of the NR$_2$ moiety in these ligands results in the possibility of a zwitterionic resonance structure (**I**), as shown in Scheme 1. Furthermore, it has been proposed that donation from the dialkylamido lone pair into the ligand could result in its metal complexes being electron rich when compared to other ligands, such as amidinates.[2]

The first transition-metal guanidinate complexes, reported in 1970 by Lappert et al., were prepared via the insertion of carbodiimides into homoleptic titanium and zirconium amides.[3] More recently, mono- and bis(guanidinate) complexes have been described for many elements of the periodic table, including alkali, transition, and main group metals and f block elements.[1] Recently, the chemistry of titanium guanidinate complexes has been investigated[2,4−6] including both bicyclic and covalently linked guanidinate ligands.[7−9]

Scheme 1



I

One of the driving forces for the interest in nitrogen-containing titanium complexes relates to their use as single-source precursors to titanium nitride (TiN) and titanium carbonitride (TiC$_x$N$_y$).[10] Thin films of TiN have found applications as diffusion barriers,[11] as solar control coatings,[12]

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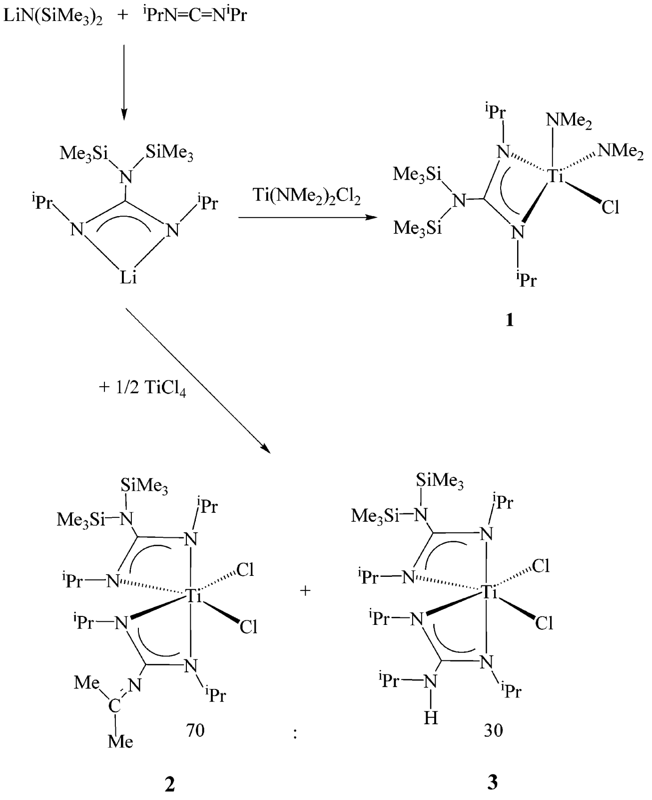
Scheme 2



and in jewelry and optics.[13] In addition, TiN and TiC_xN_y hard coatings are used to improve the hardness, corrosion resistance, and friction of surfaces in tool cutting and drilling.[14] Dual- and single-source chemical vapor deposition (CVD) techniques have been used to grow thin films of TiN from a variety of precursors.[15−23] We have been studying a range of nitrogen-containing titanium complexes and assessing their ability to form TiN thin films using low-pressure (LP)CVD.[24,25] We were interested in studying titanium guanidinate complexes as potential precursors to TiN or TiC_xN_y. In this Article, the synthesis and structural characterization of two new titanium guanidinate complexes is described. In addition, the formation of TiC_xN_y from two titanium guanidinate complexes is discussed.

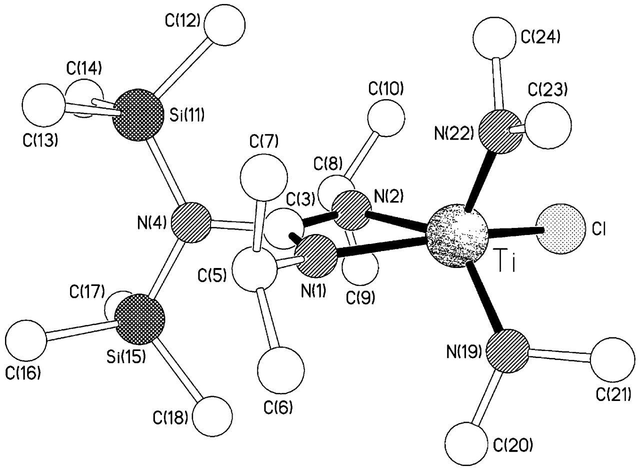


Figure 1. Molecular structure of **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ti−Cl	2.352(2)	Ti−N(1)	2.106(6)
Ti−N(2)	2.104(6)	Ti−N(19)	1.888(6)
Ti−N(22)	1.858(7)	N(1)−C(3)	1.319(9)
N(2)−C(3)	1.346(9)	C(3)−N(4)	1.416(9)
N(22)−Ti−N(19)	107.6(3)	N(22)−Ti−N(2)	117.0(3)
N(19)−Ti−N(2)	133.1(3)	N(22)−Ti−N(1)	101.9(3)
N(19)−Ti−N(1)	95.4(3)	N(2)−Ti−N(1)	62.6(2)
N(22)−Ti−Cl	99.7(2)	N(19)−Ti−Cl	95.0(2)
N(2)−Ti−Cl	91.4(2)	N(1)−Ti−Cl	151.8(2)

Results and Discussion

Treatment of $[Ti(NMe_2)_2Cl_2]$ with 1 equiv of $[Li\{i\text{-}PrNC[N(SiMe_3)_2]N\text{-}i\text{-}Pr\}]$ (generated in situ, according to ref 26) in diethyl ether at room temperature resulted in the isolation of red crystalline **1**. Analytical and spectroscopic data for **1** were consistent with the formation of the mono(guanidinate) complex $[Ti(NMe_2)_2Cl\{i\text{-}PrNC[N(SiMe_3)_2]N\text{-}i\text{-}Pr\}]$, **1** (Scheme 2). The room temperature ^1H NMR spectrum of **1** in $CDCl_3$ shows one set of broad resonances for the isopropyl groups and a single resonance for the $N(SiMe_3)_2$ ligand. A single resonance for the dimethylamido ligands is also observed. These results are consistent with compound **1** being fluxional on the NMR time scale, a feature which has been observed previously in some related titanium guanidinate complexes.[2] A single-crystal structure determination showed the complex (Figure 1) to have a distorted trigonal bipyramidal geometry at the titanium center, with the metal lying 0.171 Å out of the equatorial {N(2), N(19), N(22)} plane in the direction of Cl. The axial atoms Cl and N(1) subtend an angle of 151.8(2)° at the titanium, the departure from linearity being due to the restricted bite [62.6(2)°] of the axial/equatorial chelating guanidinato ligand. The Ti−N bond lengths to this ligand (Table 1) are typical of guanidinates bound to five-coordinate titanium(IV) centers.[2,5] The steric bulk of the two $SiMe_3$ substituents on N(4) results in a ca. 85° torsion angle about the C(3)−N(4) bond and an absence of conjugation

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between the p_π orbital on N(4) and the N(1)−C(3)−N(2) π system. Consequently, the C(3)−N(1) and C(3)−N(2) distances [1.319(9) and 1.346(9) Å, respectively] are markedly shorter than C(3)−N(4) [1.416(9) Å]. In the structures of other titanium(IV) guanidinato complexes with less sterically demanding substituents such as $(Me)_2$,[2,5] (*i*-Pr)(H),[5] and $(Et)_2$,[4] there is a fairly good correlation between the difference of the three C−N distances [Δ(C−N) 0.004−0.071 Å] and the $N_2C{-}NR_2$ torsion angle [ca. 30−42°]. The CN_3 unit itself is, however, coplanar to within 0.01 Å. The Ti−N(isopropylamine) and Ti−Cl distances are unexceptional. There are no intermolecular packing interactions of note.

In an attempt to obtain a TiN/TiC_xN_y precursor with an all-nitrogen coordination sphere, the reaction between $[Ti(NMe_2)_2Cl_2]$ and 2 equiv of [Li{*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}$_2$] (generated in situ) was carried out at room temperature in diethyl ether. After workup, compound **1** was the sole isolated compound from this reaction rather than the anticipated product [Ti($NMe_2)_2${*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}$_2$]. This result indicates that via the salt elimination route under the conditions employed (see the Experimental Section) the titanium bis(guanidinate) complex cannot be prepared. Related titanium bis(guanidinate) complexes, of the type [Ti($NMe_2)_2${RNC(NMe_2)NR}$_2$] (R = *p*-tolyl or cyclohexyl), were previously reported by Lappert et al in 1970. However, these complexes were prepared by a different route involving insertion of carbodiimides into $Ti(NMe_2)_4$ (2−4:1 ratio) and were characterized by IR and mass spectroscopy. Attempts to isolate [Ti($NMe_2)_2${*i*-PrNC(NMe_2)N-*i*-Pr}$_2$] from the reaction between $Ti(NMe_2)_4$ and 2 equiv of *i*-PrN═C═N-*i*-Pr were unsuccessful and only resulted in the formation of a mixture of products (by ^1H and $^{13}C\{^1H\}$ NMR).

The reaction of $TiCl_4$ with 2 equiv of [Li{*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}] was also investigated in an attempt to isolate a further TiN/TiC_xN_y precursor and compare the products to compound **1**. After workup of the reaction, red crystals were isolated, which were shown by a single-crystal structure determination to consist of a randomly distributed 70:30 mixture of the N(24)═C(Me)$_2$ species [$TiCl_2${*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}{*i*-PrNC(N═CMe_2)N-*i*-Pr}] (**2**) and the N(24)(H)−C(H)(Me)$_2$ species [$TiCl_2${*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}{*i*-PrNC[N(H)-*i*-Pr]N-*i*-Pr}] (**3**) (the major occupancy complex **2** is depicted in Figure 2). In each case the metal adopts a distorted octahedral geometry with two *cis* chloride ligands, the major angular distortions being associated with the bite of the chelating guanidinato ligands (Table 2). The Ti−N bond lengths, which are on average ca. 0.04 Å shorter than those seen in **1**, are unexceptional for guanidinates bound to six-coordinate titanium(IV) centers.[2,4] The Ti−Cl distances are also typical. The ($SiMe_3)_2$-substituted guanidinate ligand again has a nearly orthogonal relationship across the $N_2C{-}NR_2$ linkage [ca. 86°] with an associated Δ(C−N) of 0.078 Å. For the other guanidinate ligand in **2**, though the steric bulk is somewhat reduced [═C(Me)$_2$ vis-à-vis ($SiMe_3)_2$], the C(23)−N(24) torsion angle is still large at ca. 71° with a Δ(C−N) of 0.057 Å. Interestingly, contrary to the orientations seen for the N-*i*-Pr units in **1**, and for the other three such units in **2**/**3**, the N(21)-bound *i*-Pr moiety here is oriented so that the methyl groups point "away" from the metal center rather than toward it. Since this increases the steric congestion in the vicinity of N(24), it may have some role in the observed orientation of the substituent on N(24), though it is not immediately apparent how. There are no significant intercomplex interactions.

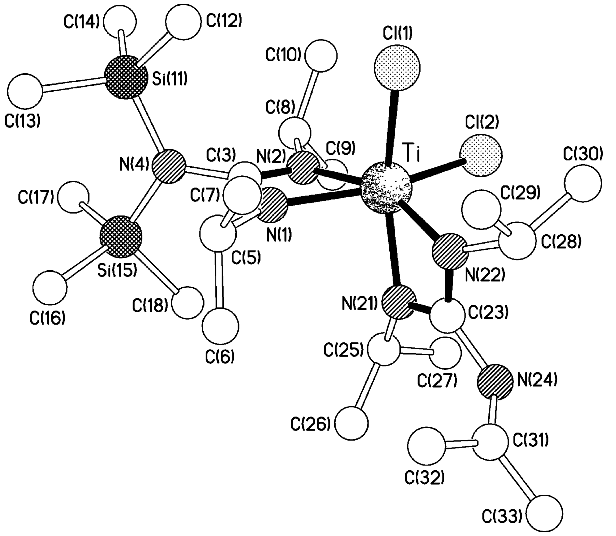

Figure 2. Molecular structure of **2** present in the mixed crystals of **2** and **3**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**/**3**

Ti−Cl(1)	2.3170(12)	Ti−Cl(2)	2.3234(13)
Ti−N(1)	2.094(4)	Ti−N(2)	2.051(4)
Ti−N(21)	2.045(4)	Ti−N(22)	2.071(4)
N(1)−C(3)	1.328(6)	N(2)−C(3)	1.343(5)
C(3)−N(4)	1.406(6)	N(21)−C(23)	1.325(6)
N(22)−C(23)	1.339(6)	C(23)−N(24)	1.382(6)
N(24)−C(31)	1.288(5)		
N(21)−Ti−N(2)	97.98(15)	N(21)−Ti−N(22)	64.23(16)
N(2)−Ti−N(22)	157.13(15)	N(21)−Ti−N(1)	91.44(15)
N(2)−Ti−N(1)	63.31(14)	N(22)−Ti−N(1)	101.11(15)
N(21)−Ti−Cl(1)	156.84(12)	N(2)−Ti−Cl(1)	103.99(10)
N(22)−Ti−Cl(1)	92.65(11)	N(1)−Ti−Cl(1)	91.90(11)
N(21)−Ti−Cl(2)	92.97(11)	N(2)−Ti−Cl(2)	94.19(10)
N(22)−Ti−Cl(2)	100.70(12)	N(1)−Ti−Cl(2)	157.48(11)
Cl(1)−Ti−Cl(2)	92.67(5)		

The ^1H and ^{13}C NMR of the red crystals (**2**/**3**) supports the formation of two complexes and shows a number of overlapping multiplets corresponding to the *i*-Pr group. A broad peak was also present at 4.00 ppm, corresponding to the NH group in compound **3**. However, a number of peaks in the 0.13−0.40 ppm region are observed for the $-SiMe_3$ protons, suggesting that another species is present or a fluxional process is taking place in solution. Both compounds **2** and **3** contain a transformed guanidinate ligand. The bisguanidinate complex [$TiCl_2${*i*-PrNC[N($SiMe_3)_2$]N-*i*-Pr}$_2$] was the expected product, and the mechanism for the formation of **2** and **3** was not investigated. However, it is likely that the formation of compounds **2** and **3** is the result of partial hydrolysis and/or oxidation of the guanidinate ligand. A previous report has shown that the reaction of [Ti(NAr′){*i*-PrNC(NMe_2)N-*i*-Pr}$_2$] (Ar′ = 2,6-$Me_2C_6H_3$) with Ar′NH_2 resulted in the isolation of [Ti(NAr′){*i*-PrNC[N(H)-*i*-Pr]NAr′}$_2$], which possesses transformed guanidinate ligands.[5] The transformation was described as a transamination

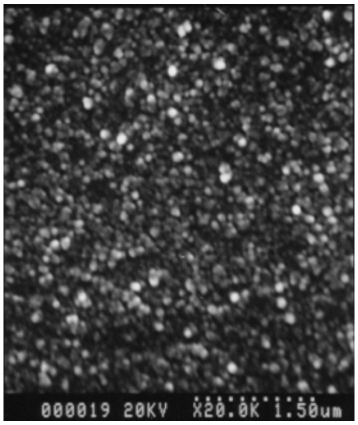

Figure 3. SEM image of a film grown from **4**.

reaction with exchange of a dimethylamine group, within the guanidinate ligand, for a dimethylaniline group.[5] The formation of **3** could be due to a similar transamination reaction where the bis(trimethylsilyl)amine group is exchanged for an isoproylamine group, resulting from the hydrolysis of *i*-PrN═C═N-*i*-Pr.

LPCVD of **1**, **2**/**3**, and [$TiCl_2$\{*i*-PrNC(NMe_2)N-*i*-Pr\}$_2$] (**4**) was investigated, the details of which are described in the Experimental Section.[24,25] Compound **4** was prepared according to literature procedures[2,5] from the reaction of [Ti(NMe_2)$_2$$Cl_2$] and 2 equiv of *i*-PrN═C═N-*i*-Pr. No film was deposited from compound **2**/**3**; instead the material decomposed to a black solid, and no carry over of organic products was noted. However, both **1** and **4** formed highly reflective, conducting gold-colored films on glass under LPCVD conditions at 600 °C. The films produced were analyzed by energy-dispersive analysis of X-rays (EDAX)/scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and powder X-ray diffraction (XRD). SEM analysis of the films showed that these films consist of islands of approximately 0.1 μm diameter (Figure 3). The thicknesses of the films produced were typically between 0.5 and 2 μm (cross-sectional SEM measurements). The EDAX analysis showed the presence of titanium and nitrogen in the films. Significant breakthrough of the excitation volume through the coating to the underlying glass was observed, so accurate quantitative analysis by EDAX was difficult. However, EDAX showed that chlorine contamination was below 0.1 atom %. XPS of the films confirmed this and revealed the presence of titanium, nitrogen, carbon, and oxygen. The surface of the film is principally oxide terminated; however, etching into the film surface massively reduced the oxide contamination. This oxygen could be due to diffusion of oxygen from the glass substrates as no barrier layer was present; however, XPS depth profiling indicated that the amount of oxide decreased with the depth in the sample. This indicates that the oxidation is most probably after film formation. The carbon concentration dropped on the first etch, indicating that this was surface bound. The N 1s binding energy shift was 396.6 and 397.2 eV for the films deposited from compounds **1** and **4**, respectively. The Ti 2p shifts were at 458.6 and 455.4 eV for films grown from compounds **1** and **4**, respectively. The C 1s shifts (282.8 eV) correspond to the formation of carbide,[26] and the N 1s, Ti 2p, and C 1s results are in agreement with the values reported for TiC_xN_y films (lit.[17,18] (TiN) 396.9 eV). Overall films grown from **1** have an approximate composition of $TiC_{0.3}N_{0.7}$, whereas those from **4** are $TiC_{0.5}N_{0.5}$. The Raman spectra of the thin films produced from **1** and **4** gave a broad feature at 500 cm^{-1}, matching those previously reported for TiN.[24] The films were amorphous according to powder XRD.

The films produced from both **1** and **4** are resistant to attack by common solvents (acetone, toluene, water, propan-2-ol). However, concentrated nitric acid digested the films in 48 h. The films passed the Scotch tape test and could not be abraded with a stainless steel scalpel or brass stylus. Thus, the films showed good chemical resistance and mechanical toughness; this is typical of titanium nitride and carbonitride films. The films produced were highly reflective and have some transmission in the visible region of the electromagnetic spectrum. The films have good heat mirror potential. Heat mirrors have high transmission in the visible (300−700 nm) while providing high reflectance in the infrared (beyond 800 nm). Thus, the films prepared from **1** and **4** have a maximum transmission in the visible at 580 nm while being reflective in the infrared. This behavior is characteristic of titanium nitride films which show metallic-like behavior.[13] The films grown from **1** and **4** further showed metallic-like behavior with a sheet resistance of 200 Ω per square.

The formation of titanium carbonitride films from **1** and **4** shows that titanium guanidinate complexes are suitable precursors for titanium carbonitride films. The coatings themselves show minimal reactivity with common solvents or acids. The films are hard and resistant to scratching, indicating that they are well adhered to the substrate. In addition, they show some interesting optical properties—such as high optical reflectance as heat mirrors (having less reflectance in the IR region). This is in contrast to titanium carbonitride coatings deposited from Ti(NMe_2)$_4$, which resulted in mat brown films at 500 °C or powdery coatings.[18,27]

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an MBraun Unilab glovebox. All solvents were distilled from appropriate drying agents prior to use (sodium−toluene and hexanes; sodium/benzophenone−THF; CaH_2 for CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. [Ti(NMe_2)$_2$$Cl_2$] and compound **4** were prepared according to literature procedures.[2,5,28] Microanalytical data were obtained at the University College London (UCL).

Physical Measurements. NMR spectra were recorded on Brüker AMX300 or DRX500 spectrometer at UCL. The NMR spectra are referenced to CD_2Cl_2, which was degassed and dried over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to the peak for $SiMe_4$ (0.00 ppm). Mass spectra (CI) were run on a micromass ZABSE instrument, and IR spectra on a Nicolet 205

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Table 3. Crystallographic Data for Compounds **1** and **2**/**3**[a]

	1	**2/3**
empirical formula	$C_{17}H_{44}ClN_5Si_2Ti$	$(C_{23}H_{52}Cl_2N_6Si_2Ti)_{0.7}$ $(C_{23}H_{54}Cl_2N_6Si_2Ti)_{0.3}$
fw	458.10	588.29
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
a (Å)	10.139(3)	8.9348(6)
b (Å)	14.614(3)	13.1922(12)
c (Å)	18.034(4)	13.9804(8)
β (deg)	99.81(2)	99.694(5)
V (Å^3)	2633.0(10)	1624.3(2)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.156	1.203
μ (mm^{-1})	4.634	4.612
R1[b]	0.075	0.037
wR2[c]	0.179	0.093

[a] Details in common: Bruker/Siemens rotating anode P4 diffractometer, graphite-monochromated Cu Kα radiation (λ = 1.54178 Å), 183 K, refinement based on F^2. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

instrument. Melting points were obtained in sealed glass capillaries under argon and are uncorrected. EDXA/SEM results were obtained on a Hitachi S570 instrument using the KEVEX system. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium−neon laser of wavelength 632.8 nm. Reflectance and transmission spectra were determined on a Zeiss miniature spectrometer. The Raman system was calibrated against the emission lines of neon. Glancing angle X-ray diffraction analysis of the films was obtained using a Siemens D5000 diffractometer in reflection mode (1.5° incidence) using Cu Kα (λ_1 = 1.5406 Å) radiation. X-ray photoelectron spectra were recorded using a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic Al Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging, and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Depth profile measurements were obtained by using argon beam sputtering. Film adherence to the glass was assessed using the Scotch tape test and by scratching the surface using brass and steel.

Synthesis of Compound 1. Following literature routes,[26] LiN($SiMe_3$)$_2$ (0.85 g, 5.1 mmol) was added to a solution of *i*-PrN═C═N-*i*-Pr (0.80 mL, 5.1 mmol) in diethyl ether (20 mL). A pale yellow solution resulted which was allowed to stir for 4 h. [Ti(NMe_2)$_2Cl_2$] (1.05 g, 5.1 mmol) was then added with stirring at room temperature, which resulted in a color change to dark red. The reaction mixture was allowed to stir for 6 h and filtered through Celite to give a dark red solution. Concentrating this solution to 5 mL and cooling to −20 °C for 24 h resulted in the formation of **1** in a 70% yield. Anal. Calcd for $C_{17}H_{44}N_5ClSi_2Ti$: C, 44.57; H, 9.68; N, 15.29. Found: C, 44.48; H, 9.46; N, 15.24. ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 18H, Si(CH_3)$_3$), 1.12 (br, 12H, CH(CH_3)$_2$), 3.11 (s, 12H, N(CH_3)$_2$), 3.70 (br, 2H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.2 (s, Si(CH_3)$_3$), 24.6 (s, CH(CH_3)$_2$), 45.0 (s, N(CH_3)$_2$), 47.4 (s, CH(CH$_3$)$_2$), 172.0 (CN$_3$).

Synthesis of Compound 2/3. Following modified literature routes,[26] LiN($SiMe_3$)$_2$ (0.85 g, 5.1 mmol) was added to a solution of *i*-PrN═C═N-*i*-Pr (0.80 mL, 5.1 mmol) in diethyl ether (20 mL). The reaction mixture was refluxed for 3 h, and a pale yellow solution resulted. On cooling of this solution to room temperature, a white precipitate formed. $TiCl_4$ (2.5 mL, 1.0 M solution in toluene) was then added with stirring at −78 °C, which resulted in a color change to dark red. The reaction mixture was allowed to stir for 2 h and slowly warmed to room temperature. After the mixture was filtered through Celite, a dark red solution resulted, and concentrating this solution to 5 mL and cooling to −20 °C for 24 h resulted in the formation of **2/3** (yield 34%). ^{1}H NMR ($CDCl_3$): δ 0.16, 0.18, 0.21, 0.23, 0.27 (s, Si(CH_3)$_3$), 1.15−1.38 (m, CH(CH_3)$_2$), 3.15 (sept, J = 6 Hz, CH(CH$_3$)$_2$), 3.50 (sept, J = 6 Hz, CH(CH$_3$)$_2$), 2.69 (s, C(CH_3)$_2$), 3.70−3.81 (m, CH(CH$_3$)$_2$), 4.00 (br, 1H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.99, 1.5, 1.9, 2.0, 3.22 (s, Si(CH_3)$_3$), 23.1, 23.3, 24.1, 24.3, 25.0 (s, CH(CH_3)$_2$), 43.7, 47.2 (s, CH(CH$_3$)$_2$), CN$_3$ not detected.

Low-Pressure CVD Experiments. Approximately 0.5 g of compound was loaded into the sealed end of a glass tube (400 mm length × 16 mm diameter) in the glovebox. Glass substrates (100 mm × 7 mm × 1 mm) were placed along the inside of the tube. The tube 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 tube was heated to a temperature of 600 °C under dynamic vacuum (0.1 Torr). The tube was slowly drawn into the furnace over a period of a few minutes until the sample started to melt. It was then held at that point until all of the precursor had decomposed. Once all of the compound had decomposed, the furnace was allowed to cool to room temperature. The total time for the whole process is in the region of 60 min. Compounds **1** and **4** produced gold films, which were deposited on the glass substrates. The films were analyzed by EDAX/SEM, reflectance/transmission measurements, Raman spectroscopy, and XPS.

X-ray Structure Determination of 1 and 2. Table 3 provides a summary of the crystallographic data for compounds **1** and **2/3**. The absolute structure of **2/3** was determined by a combination of R factor tests [$R_1^+ = 0.0367$, $R_1^- = 0.0536$] and by use of the Flack parameter [$x^+ = 0.000(16)$]. The CCDC numbers are 238379 and 238380.

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Supporting Information Available: ORTEP diagrams and X-ray crystallographic data in CIF format for the structures of compounds **1** and **2/3** and the optical transmittance spectrum of a film grown from **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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