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Terminal and Bridging Imido Complexes from Titanium Tetrachloride and Primary Amines. Implications for the Chemical Vapor Deposition of Titanium Nitride Films

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Reaction of titanium tetrachloride with *tert*-butylamine (≥5 equiv) in dichloromethane affords the trimeric imido complex $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$ in 90% yield. Treatment of $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$ with *tert*-butylamine in chloroform or dichloromethane affords $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$ in 87% yield as orange crystals. Solid $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$ evolves *tert*-butylamine upon standing at 23 °C for 12−24 h to reform $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$. In solution, $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$ exists as a complex mixture of compounds. Sublimation of $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$ or $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$ affords the hexameric imido complex $\{[\mathrm{TiCl_2(NtBu)}]_3\}_2\cdot 2.4\mathrm{tBuNH_2}$, in which most of the *tert*-butylamine was lost during the sublimation process. Other primary alkyl- and arylamines react with titanium tetrachloride in dichloromethane to afford complexes of the general formula $[\mathrm{TiCl_2(NR)(NH_2R)_2}]$. Treatment of $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$, $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$, or $\{[\mathrm{TiCl_2(NtBu)}]_3\}_2\cdot 2.4\mathrm{tBuNH_2}$ with triphenylphosphine oxide (2 equiv per titanium), tetramethylethylenediamine (TMEDA, 1 equiv per titanium), or *N,N′*-diisopropylethylenediamine (DIPEDA, 1 equiv per titanium) affords monomeric imido complexes of the formula $[\mathrm{TiCl_2(NtBu)L_2}]$ in 42−65% yields. These complexes contain very short titanium−nitrogen triple bonds and possess essentially linear imido linkages. $[\mathrm{TiCl_2(NtBu)(TMEDA)}]$ crystallizes in the space group $P2_1/n$ with $a = 16.355(9)$ Å, $b = 8.794(3)$ Å, $c = 23.052(6)$ Å, $\beta = 92.97(4)^\circ$, $V = 3311(2)$ Å^3, and $Z = 4$. $[\mathrm{TiCl_2(NtBu)(DIPEDA)}]$ crystallizes in the space group $P2_1/c$ with cell dimensions $a = 8.113(2)$ Å, $b = 12.049(3)$ Å, $c = 18.598(5)$ Å, $\beta = 99.48(2)^\circ$, $V = 1793.2(8)$ Å^3, and $Z = 4$. The mass spectra of $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_3}]$, $[\mathrm{TiCl_2(NtBu)(NH_2tBu)_2}]_3$, $\{[\mathrm{TiCl_2(NtBu)}]_3\}_2\cdot 2.4\mathrm{tBuNH_2}$, $[\mathrm{TiCl_2(NnBu)(NH_2nBu)_2}]$, and $[\mathrm{TiCl_2(NtBu)(TMEDA)}]$ were studied in order to understand the types of gas phase species that might be present during the chemical vapor deposition of titanium nitride films from these precursors. In general, ions and fragments derived from $[\mathrm{TiCl_2(NtBu)}]_3$, $[\mathrm{TiCl_2(NtBu)}]_2$, $[\mathrm{TiCl_3(NHR)}]$, and $[\mathrm{TiCl_2(NtBu)}]$ were observed. These results imply that monomeric and dimeric imido complexes are significant gas phase species derived from the above precursors, and such imido complexes are probably important intermediates in the deposition of titanium nitride films.

Introduction

The rational design of precursors to binary inorganic materials implies a detailed understanding of the path that leads to the final product. Chemical Vapor Deposition (CVD), in which gas phase species react to form a film on a surface, has become a very attractive method to prepare thin films of early transition metal chalcogenides, pnictogenides, and carbides.[2] Despite such wide use of CVD to fabricate thin films, very little is known about the chemical reactions that are involved in these processes. Recently, we initiated a research program to investigate ligand intermediates in CVD processes to the above mentioned materials.[3] A particular goal was to assess the possible intermediacy of metal−ligand multiple bonded compounds in CVD processes, since such species have been widely proposed in film deposition mechanisms.[4] Proscia has reported that the atmospheric pressure chemical vapor deposition (APCVD) reaction between titanium tetrachloride and alkylamines at ≥475 °C leads to the formation of excellent quality thin films of titanium nitride.[5] This process represented an excellent starting point for mechanistic studies due to the high reactivity between titanium tetrachloride and alkylamines over a large temperature

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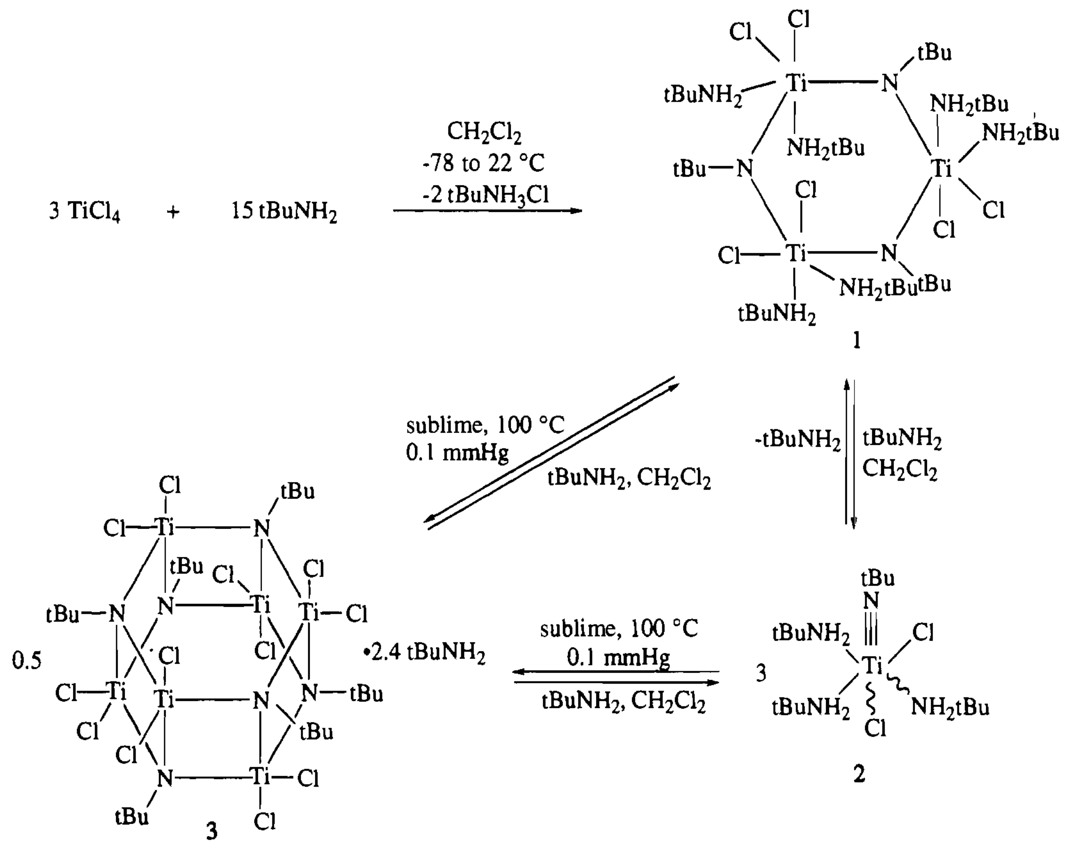
Scheme 1. Preparation and Reactions of **1**



range, the ability of titanium to stabilize a variety of nitrogen ligand types, and the presence of an alkyl group on nitrogen (e.g., imparts solubility to complexes, allows use of ^{1}H and ^{13}C NMR, increases volatility by reducing oligomerization, etc.). As part of our studies, the solution chemistry of titanium tetrachloride and primary amines was investigated in attempts to synthesize single-source precursors to titanium nitride thin films and to understand the chemical species that might be present during the CVD process.

The reaction between titanium tetrachloride and amines has been previously studied.[6,7] Fowles reported that titanium tetrachloride undergoes aminolysis when treated with six or more equivalents of aliphatic amines to afford the complexes of the type $[TiCl_2(NHR)_2(NH_2R)_{0-4}]$.[6] The amount of coordinated amine present in these complexes was dependent on the alkyl group of the amine and on the length of time the complex was dried under vacuum. Nielson recently suggested that these complexes are better depicted by the general formula $[TiCl_2(NR)(NH_2R)_2]$, where the two amide groups are replaced by an imido functionality.[7] The generation of an imido linkage from a bis(amide) complex by hydrogen abstraction from one of the amide groups is common for group 4 metal diamides.[8]

Recently, we reported that the complex derived from the solution reaction of titanium tetrachloride and *tert*-butylamine constitutes the first successful single-source precursor to high quality titanium nitride thin films under CVD conditions, although the structure of this material was not conclusively established.[3a] Also, we showed that the monomeric titanium imido complex $[TiCl_2(NtBu)(O{=}PPh_3)_2]$ could be prepared by treatment of the single-source precursor with two equivalents of triphenylphosphine oxide. Herein, we provide detailed chemical insight into the reaction of titanium tetrachloride with primary amines. The relationship between these results and the deposition of titanium nitride films from the molecular precursors is discussed.

Results

Reaction of Titanium Tetrachloride with Primary Alkylamines. Treatment of titanium tetrachloride with *tert*-butylamine ($\geq$6 equiv) in dichloromethane at -78 °C immediately afforded an orange solution. Warming to ambient temperature, followed by removal of the solvent, extraction of the resultant residue with hexane, filtration, and vacuum drying, afforded orange crystals of $[TiCl_2(NtBu)(NH_2tBu)_2]_n$ (**1**, 90%, Scheme 1). Complex **1** was characterized by microanalysis, IR spectroscopy, and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. The microanalytical data were consistent with the proposed formulation. The infrared spectrum showed strong N$-$H absorptions at 3320, 3268, 3216, 3187, 3147, and 3112 cm^{-1}. Such absorptions are consistent with strong N$-$H$\cdots$Cl hydrogen bonding.[9,10] N$-$H bending modes were observed at 1605, 1576, and 1559 cm^{-1}. Complex **1** displayed IR absorptions at 1230 (vs) and 1207 (vs) cm^{-1} characteristic of an imido complex, although these bands could be assigned either to Ti$-$N or C$-$N

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stretches.[11] The ^1H NMR spectrum of **1** showed three equal intensity *tert*-butyl methyl resonances at δ 1.51, 1.42, and 1.01 and two broad resonances centered at δ 3.21 and 6.83 due to NH_2 protons. The $^{13}C\{^1H\}$ NMR spectrum of **1** revealed singlets attributable to imido (72.64 ppm) and amine (53.82, 51.84 ppm) functionalities, as well as resonances from the *tert*-butyl methyls at 31.20, 30.37, and 27.98 ppm. Carbon resonances due to a *tert*-butylamide quaternary carbon (should appear at ca. 60–64 ppm) were not observed. An osmometric solution molecular weight determination of **1** in dichloromethane at 27 °C afforded a value of 1011, which is consistent with a trimeric formulation $[TiCl_2(NtBu)(NH_2tBu)_2]_3$ (molecular weight = 1008; deviation of experimental value from calculated value = 0.3%). We propose that **1** exists as a cyclic six-membered ring, with bridging imido ligands. The simple NMR spectra suggest either a single isomer for **1** in solution or rapid interconversion of isomers on the NMR time scale.

Treatment of **1** with *tert*-butylamine (2–3 equiv) in dichloromethane, followed by crystallization from hexane at −20 °C, afforded a quantitative yield of orange crystals with the proposed formulation $[TiCl_2(NtBu)(NH_2tBu)_3]$ (**2**, Scheme 1). Complex **2** could also be prepared in 87% yield by reaction of titanium tetrachloride with *tert*-butylamine ($\geq$6 equiv) in dichloromethane, followed by crystallization from hexane at −20 °C. Upon isolation and warming to 23 °C, the orange crystals of **2** powdered (with evolution *tert*-butylamine) over 12–24 h to give back a quantitative yield of **1**. Hence, one of the *tert*-butylamine ligands per titanium in **2** is very weakly coordinated. C, H, N microanalytical data were consistent with the formulation $[TiCl_2(NtBu)(NH_2tBu)_3]$. The infrared spectrum of **2** was nearly identical to that of **1** and exhibited N–H stretches at 3320, 3265, 3226, 3181, 3142, 3126, and 3048 cm^{-1}, which are indicative of strong N–H••Cl hydrogen bonding.[9,10] Imido absorptions were observed at 1259 (vs), 1237 (vs), and 1209 (vs) cm^{-1}. A difference between the infrared spectra of **1** and **2** was that a strong intesity 1259 cm^{-1} band was present in **2** but was absent in **1**. Since the 1259 cm^{-1} absorption is associated with the imido band, **1** and **2** probably differ in their imido linkages. The ^1H NMR spectrum of **2** in chloroform-*d* was complicated and exhibited N–H resonances at δ 4.58 (d, $J = 12.6$ Hz), 4.35 (m), 3.41 (br s), and 2.71 (d, $J = 12.9$ Hz). Methyl resonances from the *tert*-butyl groups were observed at δ 1.54, 1.46, 1.31, 1.15, and 0.96. At −80 °C in dichloromethane-d_2, the ^1H NMR revealed equal intensity N–H resonances at δ 4.93 (d), 4.44 (q), 4.25 (d), 3.43 (d), 3.24 (s), 2.60 (m), and 2.32 (s). Methyl resonances were observed at δ 1.49, 1.34, 1.24, 1.07, and 0.96. The $^{13}C\{^1H\}$ NMR spectrum of **2** showed resonances due to imido carbons at 73.95 and 72.20 ppm, which suggested that two different imido complexes were present. Peaks due to amine carbons were observed at 52.60, 52.23, and 51.81 ppm, while the *tert*-butyl methyl carbons resonated at 31.53, 31.37, 31.21, 31.00, and 30.74 ppm. The relatively rapid evolution of *tert*-butylamine from **2** precluded a molecular weight determination by vapor phase osmometry.

The NMR data for **2** were not consistent with a pure, single compound in solution, but rather implied a mixture of two or more different compounds. In particular, the ^{13}C NMR spectrum showed two different imido carbons, neither of which corresponded to **1**. While the available data do not establish a solution structure, we propose that **2** consists of an equilibrium mixture of **1**, *tert*-butylamine, and the limiting monomeric imido complex $[TiCl_2(NtBu)(NH_2tBu)_3]$. Alternatively, **2** may consist of a mixture of geometric isomers. In the solid state, the microanalytical data are consistent with $[TiCl_2(NtBu)(NH_2tBu)_3]$.

Sublimation of **1** or **2** (110 °C, 0.1 mmHg) afforded the red-orange complex **3** (Scheme 1). Unlike **1** and **2**, which were quite soluble in hexane, **3** was insoluble in hexane and required more polar organic solvents (e.g., dichloromethane, benzene, etc.) for dissolution. The C, H, N microanalysis was consistent with a formulation of $[TiCl_2(NtBu)(NH_2tBu)_{0.4}]$, in which most of the *tert*-butylamine had been lost during the sublimation. The infrared spectrum of **3** showed strong N–H absorptions at 3211, 3115, and 3054 cm^{-1}, an N–H bending mode at 1586 cm^{-1}, and strong imido stretches at 1240 and 1206 cm^{-1}. The 1259 cm^{-1} band that was present in **2** was absent in **3**. The ^1H NMR spectrum of **3** showed a broad hump arising from NH_2 groups centered at δ 6.25 as well as two methyl resonances at δ 1.08 and 1.00. The ratio of the methyl and NH_2 resonances was ca. 13:1, which is relatively close to a value of 15.8 calculated for the formulation $[TiCl_2(NtBu)(NH_2tBu)_{0.4}]$ derived from a microanalysis. Also observed in the sublimate was a small amount of *tert*-butylammonium chloride (δ 6.8 ($N\boldsymbol{H}_3C(CH_3)_3$), 1.45 ($NH_3C(C\boldsymbol{H}_3)_3$)), which was easily separated from **3** by extraction with benzene (in which *tert*-butylammonium chloride is sparingly soluble). The $^{13}C\{^1H\}$ NMR spectrum revealed resonances at 75.39 ($TiN\boldsymbol{C}(CH_3)_3$), 54.20 ($TiNH_2\boldsymbol{C}(CH_3)_3$), 29.61 ($TiNC(\boldsymbol{C}H_3)_3$), and 28.09 ($TiNH_2C(\boldsymbol{C}H_3)_3$) ppm. An osmometric molecular weight determination of **3** in dichloromethane at 27 °C afforded a value of 1086, which is consistent with a hexameric formulation $[TiCl_2(NtBu)]_6$ (molecular weight = 1140; deviation of experimental value from calculated value = −4.7%). A reasonable structure for **3** is one in which two trimeric $[TiCl_2(NtBu)]_3$ units bond together to form a drum structure, as depicted in Scheme 1. Addition of 2.5–3.0 equiv of *tert*-butylamine (per titanium) to a sample of **3** dissolved in chloroform-*d* regenerated **2** (Scheme 1).

A variety of other primary amines reacted with titanium tetrachloride, in a fashion similar to the preparation of **1**, to afford imido complexes of the formula $[TiCl_2(NR)(NH_2R)_2]_x$ (**4–9**, eq 1). The structures were assigned on the basis of

$$TiCl_4 \quad + \quad 5\,RNH_2 \xrightarrow[-2\,RNH_3Cl]{\substack{CH_2Cl_2 \\ -78\text{ to }22\ ^\circ C}} [TiCl_2(NR)(NH_2R)_2]_x \qquad (1)$$

4, R = n-Bu, 81%
5, R = i-Bu, 82%
6, R = i-Pr, 74%
7, R = CH_2CH_2Ph, 89%
8, R = $CH(C_2H_5)_2$, 86%
9, R = 2,6-$(CH(CH_3)_2)_2$-C_6H_3, 83%

infrared, ^1H NMR, and $^{13}C\{^1H\}$ NMR spectroscopy and microanalyses. The C, H, N microanalyses for **4–9** were close to the values expected for the $[TiCl_2(NR)(NH_2R)_2]$ formulation, although none were within the ±0.4% limit. In the case of **7–9**, the ^1H and $^{13}C\{^1H\}$ NMR spectra could be easily interpreted in terms of one imido group and two chemically identical amine ligands. However, **4–6** gave complicated ^1H and $^{13}C\{^1H\}$ NMR spectra that could not be obviously assigned to $[TiCl_2(NR)(NH_2R)_2]$. It is likely that **4–6** are mixtures containing complexes analogous to **2** and **3**, which would lead to the complicated NMR spectra. No attempts were made to determine solution molecular weights of **4–9**, although it is reasonable to assume that the structures and chemical behavior are similar to that of **1**. All attempts to probe the solid state

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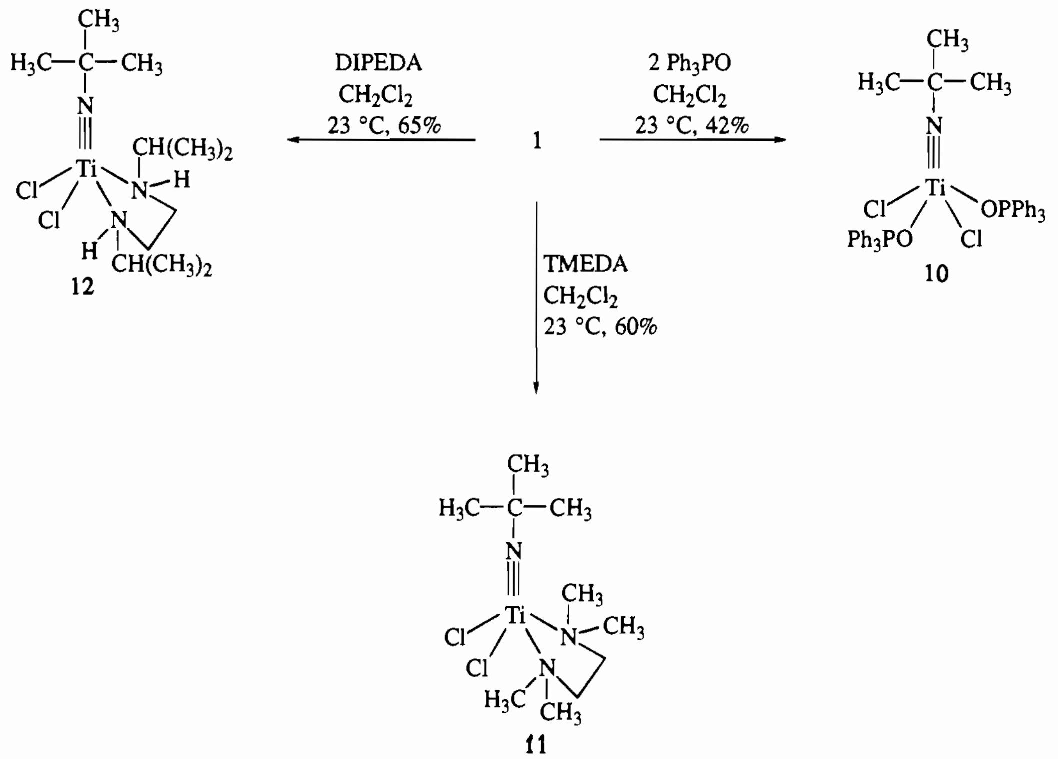
Scheme 2. Preparation of Monomeric Imido Complexes



structure of complexes **1**−**8** failed due to either poor crystal quality or crystal decomposition.

Synthesis of Monomeric Imido Complexes. It was envisaged that the reaction between **1** and donor ligands might provide a route to stable, crystalline derivatives for which X-ray structures could be obtained. Such structural data could be used to infer the structures of **1**−**3**. Accordingly, **1** was treated with triphenylphosphine oxide, N,N,N′,N′-tetramethylethylenediamine (TMEDA), and N,N′-diisopropylethylenediamine (DIPEDA) in dichloromethane at 23 °C (Scheme 2). Color changes from bright orange to bright yellow were observed after addition of the ligands. Workup afforded [$TiCl_2(NtBu)(OPPh_3)_2$] (**10**, 60%), [$TiCl_2$(NtBu)(TMEDA)] (**11**, 60%), and [$TiCl_2$(NtBu)(DIPEDA)] (**12**, 65%) as yellow crystalline solids.

The structures of **10**−**12** were assigned based upon spectral and analytical data and from X-ray crystallographic structure determinations (vide infra). In the infrared spectra, medium to strong absorptions characteristic of the $Ti{\equiv}NC(CH_3)_3$ group were observed at 1252 (**10**), 1260 (**11**), and 1233 (**12**) cm^{-1}. The *tert*-butyl methyl groups showed singlets in the ^1H NMR at δ 0.58 (**10**), 1.05 (**11**), and 1.00 (**12**). The highly shielded methyl resonance for **10** was particularly unusual, since **11** and **12** showed more normal chemical shifts values for *tert*-butyl methyls. We have previously reported the crystal structure of **10**,[3a] which showed that the methyl groups of the *tert*-butylimido ligand were constrained a "pocket" formed by the two triphenylphosphine oxide ligands. The configuration of the phosphine oxide ligands places the methyl hydrogens above the shielding region of the phosphorus-bound phenyl rings, which results in the observed upfield shift. Complexes **11** and **12**, wherein such shielding interactions are not possible, showed normal chemical shifts for the *tert*-butyl methyl hydrogens. In the $^{13}C\{^1H\}$ NMR spectra, the imido carbons resonated at 72.14 (**10**), 73.85 (**11**), and 72.14 (**12**) ppm.

Interestingly, the reaction between **1** and TMEDA was very slow in dichloromethane at 23 °C. However, removal of the volatiles from the reaction medium resulted in the rapid formation of **11**, due to the removal of *tert*-butylamine expelled during the generation of **11**. By contrast, complex **3** reacted immediately with one equivalent of TMEDA in dichloromethane-d_2 to afford **11** quantitatively in an NMR tube experiment, due to the absence of the equilibrium that was operant in the reaction between **1** and TMEDA.

Table 1. Experimental Crystallographic Data for **11** and **12**

	11	**12**
chem formula	$C_{10}H_{26}Cl_2N_3Ti$	$C_{12}H_{29}Cl_2N_3Ti$
fw	305.8	334.2
space group	$P2_1/n$	$P2_1/c$
a (Å)	16.355(9)	8.113(2)
b (Å)	8.794(3)	12.049(3)
c (Å)	23.053(6)	18.598(5)
β (deg)	92.97	99.48(2)
V (Å^3)	3311(2)	1893.2(8)
Z	8	4
T (K)	295	299
λ (Å)	0.710 73	0.710 73
ϱ_{calcd} (g·cm^{-3})	1.23	1.238
μ (cm^{-1})	8.4	7.65
transm coeff	0.706−0.670	1.08
$R(F)^a$ (%)	5.0	6.41
$R_w(F)^a$ (%)	5.0	8.32

[a] $R = (\Sigma|\Delta F|)/\Sigma|F_o|$; $R_w = [(\Sigma w|\Delta F|^2)/\Sigma w F_o^2]^{1/2}$.

X-ray Crystal Structures of 11 and 12. The crystal structures of **11** and **12** were determined in order to establish their nuclearities and molecular geometries. X-ray data were collected under the conditions summarized in Table 1. Bond lengths, bond angles, and positional parameters are provided in Tables 2−5. Perspective views of **11** and **12** are shown in Figures 1 and 2.

Complex **11** crystallized as a monomeric imido complex with a TMEDA ligand and cis-chloride ligands. There were two independent molecules in the unit cell, which were identical within experimental error. Data are only presented for molecule 1; complete data for both molecules are contained in the supplementary material. The geometry about the titanium atom was approximately square pyramidal, with the imido linkage comprising the apex. The unusual square pyramidal geometry

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **11**

Ti(1)−Cl(1)	2.325(2)	Ti(1)−C(2)	2.338(2)
Ti(1)−N(1)	1.662(4)	Ti(1)−N(2)	2.230(5)
Ti(1)−N(3)	2.278(5)	N(1)−C(1)	1.464(7)
N(2)−C(5)	1.46(1)	N(2)−C(6)	1.460(8)
N(2)−C(7)	1.41(1)	N(3)−C(8)	1.50(1)
N(3)−C(9)	1.44(1)	N(3)−C(10)	1.499(9)
C(1)−C(2)	1.515(9)	C(1)−C(3)	1.519(8)
C(1)−C(4)	1.48(1)	C(7)−C(8)	1.32(2)
Ti(1)−N(1)−C(1)	164.1(4)	C(6)−N(2)−C(7)	109.8(7)
Ti(1)−N(2)−C(5)	111.9(4)	C(8)−N(3)−C(9)	108.7(7)
Ti(1)−N(2)−C(6)	111.4(4)	C(8)−N(3)−C(10)	107.8(6)
Ti(1)−N(2)−C(7)	107.7(6)	C(9)−N(3)−C(10)	108.2(6)
Ti(1)−N(3)−C(8)	107.5(5)	Ti(1)−N(3)−C(9)	110.1(4)
Ti(1)−N(3)−C(10)	114.3(4)	Cl(1)−Ti(1)−Cl(2)	93.92(7)
Cl(1)−Ti(1)−N(1)	107.1(1)	Cl(1)−Ti(1)−N(2)	150.6(1)
Cl(1)−Ti(1)−N(3)	87.6(1)	Cl(2)−Ti(1)−N(1)	104.5(1)
Cl(2)−Ti(1)−N(2)	87.9(2)	Cl(2)−Ti(1)−N(3)	151.8(1)
N(1)−Ti(1)−N(2)	100.7(2)	N(1)−Ti(1)−N(3)	101.9(2)
N(1)−C(1)−C(2)	109.7(5)	N(1)−C(1)−C(3)	107.9(5)
N(1)−C(1)−C(4)	109.9(5)	N(2)−Ti(1)−N(3)	77.5(2)
N(2)−C(7)−C(8)	123.3(9)	N(3)−C(8)−C(7)	118.0(9)
C(2)−C(1)−C(3)	109.0(5)	C(2)−C(1)−C(4)	110.3(6)
C(3)−C(1)−C(4)	110.1(6)	C(5)−N(2)−C(6)	108.5(6)
C(5)−N(2)−C(7)	107.5(7)		

Table 3. Bond Lengths (Å) and Angles (deg) for **12**

Ti−Cl(1)	2.411(2)	Ti−Cl(2)	2.373(2)
Ti−N(1)	1.681(7)	Ti−N(2)	2.257(6)
Ti−N(3)	2.236(7)	N(1)−C(1)	1.440(11)
N(2)−C(5)	1.475(11)	N(2)−C(7)	1.493(10)
N(3)−C(6)	1.476(11)	N(3)−C(10)	1.493(12)
C(1)−C(2)	1.501(15)	C(1)−C(3)	1.499(15)
C(1)−C(4)	1.483(14)	C(5)−C(6)	1.363(15)
C(7)−C(8)	1.501(13)	C(7)−C(9)	1.518(13)
C(10)−C(11)	1.474(19)	C(10)−C(12)	1.478(19)
Cl(1)−Ti−Cl(2)	95.4(1)	Cl(1)−Ti−N(1)	99.4(2)
Cl(2)−Ti−N(1)	100.9(2)	Cl(1)−Ti−N(2)	88.1(2)
Cl(2)−Ti−N(2)	155.9(2)	N(1)−Ti−N(2)	102.0(2)
Cl(1)−Ti−N(3)	153.9(2)	Cl(2)−Ti−N(3)	89.9(2)
N(1)−Ti−N(3)	104.6(3)	N(2)−Ti−N(3)	77.2(2)
Ti−N(1)−C(1)	163.5(5)	Ti−N(2)−C(5)	110.3(5)
Ti−N(2)−C(7)	119.3(5)	C(5)−N(2)−C(7)	114.7(6)
Ti−N(3)−C(6)	107.6(6)	Ti−N(3)−C(10)	121.5(6)
C(6)−N(3)−C(10)	113.4(7)	N(1)−C(1)−C(2)	108.4(8)
N(1)−C(1)−C(3)	108.7(7)	C(2)−C(1)−C(3)	108.8(9)
N(1)−C(1)−C(4)	112.5(8)	C(2)−C(1)−C(4)	108.0(8)
C(3)−C(1)−C(4)	110.4(9)	N(2)−C(5)−C(6)	115.3(8)
N(3)−C(6)−C(5)	116.3(8)	N(2)−C(7)−C(8)	112.3(8)
N(2)−C(7)−C(9)	112.4(7)	C(8)−C(7)−C(9)	109.4(7)
N(3)−C(10)−C(11)	113.2(9)	N(3)−C(10)−C(12)	113.0(9)
C(11)−C(10)−C(12)	112.1(10)		

Table 4. Atomic Positional Parameters for **11**

atom	*x*	*y*	*z*
Ti(1)	0.86006(5)	0.1273(1)	0.91905(4)
Cl(1)	0.8155(1)	0.0316(2)	1.00594(7)
Cl(2)	0.9010(1)	0.3608(2)	0.95960(8)
N(1)	0.7770(2)	0.1680(4)	0.8773(2)
N(2)	0.9576(3)	0.1557(7)	0.8558(2)
N(3)	0.8859(3)	−0.1173(6)	0.8928(2)
C(1)	0.6979(3)	0.2275(7)	0.8548(3)
C(2)	0.6661(4)	0.1315(9)	0.8039(3)
C(3)	0.6382(4)	0.217(1)	0.9030(3)
C(4)	0.7070(5)	0.388(1)	0.8367(4)
C(5)	0.9409(5)	0.284(1)	0.8166(4)
C(6)	1.0378(4)	0.179(1)	0.8854(3)
C(7)	0.9588(7)	0.023(2)	0.8216(5)
C(8)	0.9353(8)	−0.112(1)	0.8400(4)
C(9)	0.8099(6)	−0.1958(9)	0.8783(4)
C(10)	0.9331(5)	−0.2081(8)	0.9382(4)
Ti(2)	0.15257(5)	0.0425(1)	0.66769(3)
Cl(3)	0.17536(9)	0.1328(2)	0.76282(5)
Cl(4)	0.05973(9)	−0.1451(2)	0.69304(6)
N(4)	0.0975(2)	0.1788(4)	0.6341(2)
N(5)	0.2830(2)	0.1155(5)	0.6516(2)
N(6)	0.1817(3)	−0.0961(5)	0.5891(2)
C(11)	0.0391(4)	0.2980(6)	0.6177(2)
C(12)	0.0495(4)	0.4258(7)	0.6622(3)
C(13)	0.0559(5)	0.3568(8)	0.5575(3)
C(14)	−0.0477(4)	0.2302(8)	0.6192(3)
C(15)	0.2857(4)	0.2845(7)	0.6499(3)
C(16)	0.3445(3)	0.0660(7)	0.6970(3)
C(17)	0.3073(4)	0.050(1)	0.5956(3)
C(18)	0.2475(6)	−0.014(1)	0.5620(3)
C(19)	0.2042(5)	−0.2545(8)	0.6036(3)
C(20)	0.1117(5)	−0.1035(8)	0.5464(3)

Table 5. Atomic Positional Parameters ($\times 10^4$) for **12**

atom	*x*	*y*	*z*
Ti	5536(1)	1409(1)	640(1)
Cl(1)	4079(2)	−313(2)	743(1)
Cl(2)	3281(3)	2296(2)	−119(1)
N(1)	5380(7)	1971(5)	1453(3)
N(2)	7957(7)	456(5)	894(3)
N(3)	7339(7)	2506(5)	187(4)
C(1)	4747(10)	2387(8)	2080(5)
C(2)	4272(17)	1417(10)	2509(6)
C(3)	3214(15)	3065(12)	1824(6)
C(4)	6000(15)	3056(11)	2567(6)
C(5)	9320(10)	1076(8)	640(5)
C(6)	9040(11)	2183(9)	533(8)
C(7)	8421(10)	−76(8)	1624(5)
C(8)	9089(13)	745(10)	2206(5)
C(9)	9674(12)	−1010(8)	1618(6)
C(10)	7090(12)	3732(8)	129(7)
C(11)	7561(21)	4314(10)	830(8)
C(12)	7871(17)	4235(10)	−457(7)

is common for many group 4 monomeric imido complexes.[12] The titanium−nitrogen bond distance of the imido fragment was 1.662(4) Å with a Ti(1)−N(1)−C(1) bond angle of 164.1(4)°. This is the shortest known titanium−nitrogen bond. The nearly linear Ti−N(1)−C(1) bond angle is consistent with the lone pair on nitrogen being donated to an acceptor orbital on titanium. Hence, the titanium−nitrogen imido bond can be considered a triple bond. The titanium−nitrogen bond lengths associated with the TMEDA ligand (Ti−N(2) 2.230(5) Å, Ti−N(3) 2.278(5) Å) were 0.57−0.60 Å longer than the imido titanium−nitrogen bond length. The titanium−chlorine bond lengths (Ti−Cl(1) 2.325(2) Å, Ti−Cl(2) 2.338(2) Å) were in the normal range for such linkages.

Complex **12** also crystallized as a monomeric imido complex with approximate square pyramidal geometry. The gross structural features were very similar to those of **11**. The titanium−nitrogen imido distance was 1.681(7) Å, which is 0.019 Å longer than the analogous value in **11**. The Ti−N(1)−C(1) angle (163.5(5)°) was nearly linear. The titanium−nitrogen bond lengths for the DIPEDA ligand were 2.257(6) Å (Ti−N(2)) and 2.236(7) Å (Ti−N(3)), which were 0.56−0.58 Å longer than the imido bond length. The titanium−chlorine bond lengths were 2.411(2) Å (Ti−Cl(1)) and 2.373(2) Å (Ti−Cl(2)), which were considerably longer than those observed in **11**. The longer titanium−chlorine bonds in **11** may be due to steric interactions between the isopropyl groups and the

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(12) (a) Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669. (b) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (c) Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689. (d) Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863. (e) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143. (f) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

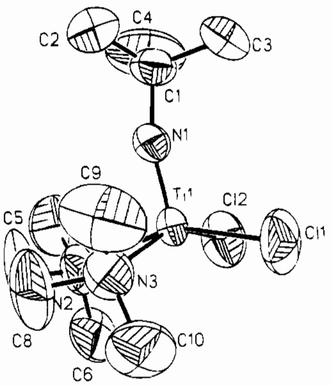

Figure 1. Perspective view for molecule 1 of $[TiCl_2(NtBu)(TMEDA)]$ (**11**) with thermal ellipsoids at the 35% probability level. The second molecule shows a virtually identical coordination sphere.

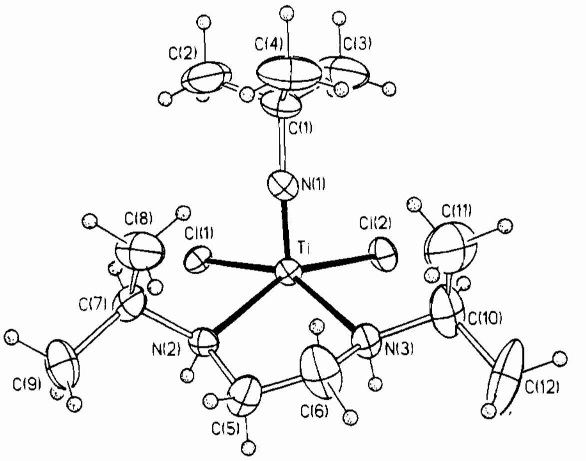

Figure 2. Perspective view of $[TiCl_2(NtBu)(DIPEDA)]$ (**12**) with thermal ellipsoids at the 50% probability level.

Table 6. Mass Spectral Data for Imido Complexes[a]

mass fragment	proposed structure	**1**	**2**[c]	**3**	**4**	**11**
512	$[TiCl_2(NR)]_3^{\bullet -} - R$	0.5			0.1	
380	$[TiCl_2(NR)]_2^{\bullet -}$	27			20	40
363	$[TiCl_2(NR)]_2^{\bullet -} - CH_3$			9.1		1.9
349	$[TiCl_2(NR)]_2^{\bullet -} - 2CH_3$		33			
323	$[TiCl_2(NR)]_2^{\bullet -} - R$	100			62.5	100
309	$[TiCl_2(NR)]_2^{\bullet -} - 2Cl$	2.1		72		
225	$[TiCl_3(NHR)]^{\bullet -}$	71			100	28
210	$[TiCl_3(NHR)]^{\bullet -} - CH_3$	41	26	100		16
190[b]	$[TiCl_2(NR)]^{\bullet -}$ or $TiCl_4^{\bullet -}$	50	49	26	14	19
174	$[TiCl_2(NR)]^{\bullet -} - CH_3$		19	58		
167	$[TiCl_3(CH_3)]^{\bullet -}$	40			49	
153	$[TiCl(NR)]^{\bullet -}$	9	95	43		

[a] Mass spectra were determined using negative chemical ionization conditions with butane as the bath gas. The data are presented as percent intensity versus the base peak. The elemental composition of all mass envelopes was verified by computer simulation. Peaks were observed either as the ions M^- or MH^-. [b] It was not possible to distinguish between $[TiCl_2(NR)]^-$ and $TiCl_4^-$ using computer simulation of the mass envelope. For discussion, see text. [c] Base peak = 91.

chlorines. Steric crowding between the isopropyl groups and the *tert*-butyl group may also account for the slightly longer imido titanium–nitrogen bond length in **12**. The NMR inequivalence of the two methyl groups on the isopropyl skeleton (^{1}H NMR δ 1.46, 1.34 ppm; $^{13}C\{^1H\}$NMR 22.15, 19.90 ppm) of **12** is consistent with hindered isopropyl rotation and suggests a high degree of crowding. The lack of isopropyl rotation also implies that the solid state structure is maintained in solution.

The structural parameters of **11** and **12** can be compared with those of other monomeric titanium imido complexes whose structures have been determined. We have previously reported the molecular structure of **10**,[3a] which was monomeric with approximate square pyramidal geometry. The imido titanium–nitrogen bond length in **10** was 1.672(7) Å while the imido Ti–N–C angle was 174.0(6)°. These values are very close to the related values in **11** and **12**. The slightly more linear Ti–N–C angle in **10** (174°), relative to **11** (164.1°) and **12** (163.5°), is probably a consequence of steric interactions between the *tert*-butyl group and phenyl groups of the triphenylphosphine oxide groups. The titanium–nitrogen bond lengths and titanium–nitrogen–carbon angles in **10**–**12** can be compared to the related values in $[TiCl_2(NP(S)Ph_2)(py)_3]$ (Ti–N 1.720 Å, Ti–N–P 172.5°),[12a] $[Ti(OAr)_2(NPh)(py')_2]$ (Ti–N 1.72 Å, Ti–N–C 173.1°),[12b] [*trans*-NC(Me)=(Me)CN]$[TiCl_2(TMEDA)]_2 \cdot CH_3CN$ (Ti–N 1.702 Å, Ti–N–C, 164.2°),[12d] and $[TiCl_2(NPh)(TMEDA)]$ (Ti–N 1.699 Å, Ti–N–C 175.2°).[12d] All of these structurally characterized imido complexes contain a phenyl or unsaturated group on the imido nitrogen and have imido titanium–nitrogen bond lengths that are ca. 0.02–0.06 Å longer than in the *tert*-butylimido complexes **10**–**12**. It is clear that the longer titanium–nitrogen imido bond lengths in linkages containing unsaturated groups results from partial delocalization of the lone pair onto the organic group, which reduces the bond order between titanium and nitrogen.

Mass Spectral Data. We have previously reported that complexes **1**–**9** constitute single-source precursors to titanium nitride thin films.[3a,c] It is well established that the decomposition pathways of precursors under CVD conditions can be predicted from mass spectral data.[13a,b] Therefore the fragmentation patterns of complexes **1**–**4** and **11** were carefully analyzed by mass spectrometry. Table 6 lists the mass fragments generated from these complexes under negative chemical ionization conditions.[13d] The use of the negative chemical ionization mode was important, since positive chemical ionization or electron impact mass spectra of **1**–**4** and **11** led to considerably more fragmentation (with concomitant loss of information), apparently due to the low stability of the positively charged ions containing titanium(IV). There are several caveats that must be considered in evaluation of the mass spectral data. The intensities of the various mass envelopes reflect the electron-capture cross sections for the neutral species and therefore the peak intensities may not be a reliable estimate of the gas phase concentrations. Also, the CVD processes using **1**–**9** rely upon thermal fragmentation of the precursors, while the mass spectrometer uses ionization. Hence, the fragmentation modes observed in the mass spectra may not necessarily correlate with those of neutral species in a CVD process. Finally, daughter ion analysis has not been carried out due to lack of appropriate equipment. Therefore, it was not possible to determine the evolution of the various ions. However, the data suggest structures that have analogies in condensed phases and may therefore help to understand the gas phase chemistry.

The mass spectra of complexes **1** and **4** showed very weak mass envelopes centered at *m/e* 512, which might correspond to the loss of an R group from the trimer $[TiCl_2(NR)]_3$. The presence of this peak, albeit of weak intensity, suggests the volatilization of **1** and **4** as $[TiCl_2(NR)]_3$. This is important, since we demonstrated that **2** is trimeric in solution. Furthermore, we proposed that **3** exists as the hexamer $\{[TiCl_2(NR)]_3\}_2$, from which a trimeric fragment $[TiCl_2(NR)]_3$ could be easily

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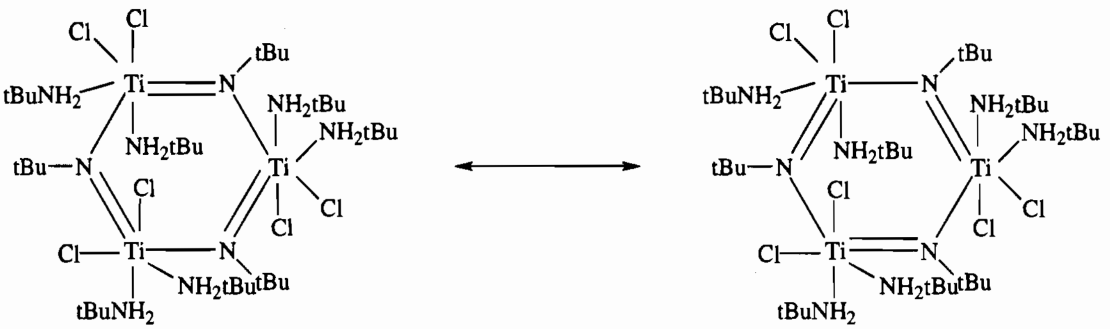
(13) (a) Amato, C. C.; Hudson, J. B.; Interrante, L. V. *Mater. Res. Soc. Symp. Proc.* **1990**, *168*, 119. (b) Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252. (c) MacInnes, A. N.; Power, M. B.; Hepp, A. F.; Barron, A. R. *J. Organomet. Chem.* **1993**, *449*, 95. (d) Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1992.

Scheme 3. Resonance Structures of **1**



dissociated. The next highest mass envelopes for **1** and **4** corresponded to 380, for which a dimeric formulation was suggested by simulation of the isotope pattern. We propose that this mass corresponds to the dimeric imido complex $[TiCl_2(NR)]_2$, which could be accessed by expulsion of a $[TiCl_2(NR)]$ fragment from the trimer $[TiCl_2(NR)]_3$. The dimeric imido complex probably exists as a bridging imido complex, in analogy with $\{[TiCl_2(NSi(CH_3)_3)]_2\}_n$, which has been structurally characterized and contains a Ti_2N_2 ring as the central structural element.[14] The next major fragment observed in **1** and **4** was at *m/e* 323 and corresponded to loss of an alkyl group from the $[TiCl_2(NR)]_2$ fragment. This is a significant cleavage pattern, since nitrogen-carbon bond cleavage is required in the formation of titanium nitride films. Another intense fragment for **1** and **4** was observed at *m/e* 225. Simulation of the mass envelopes suggested the formulation $[TiCl_3(NHR)]$. An important mass envelope was centered at *m/e* 190. Computer simulations could not distinguish between a monomeric imido formulation $[TiCl_2(NR)]$ or $TiCl_4$. However, the fragments at lower mass did not correspond to those observed in the mass spectrum of titanium tetrachloride taken under similar conditions. These fragments, however, could be correlated to the $[TiCl_2(NR)]$ structure (174 ($[TiCl_2(NR)]^{\bullet-}$ − CH_3), 153 ($[TiCl_2(NR)]^{\bullet-}$ − Cl)). Hence, we suggest that the mass envelope at *m/e* 190 corresponds to the monomeric imido formulation $[TiCl_2(NR)]$. Possible origins for this fragment include the splitting of $[TiCl_2(NR)]_3$ or $\{[TiCl_2(NR)]_3\}_2$ into $[TiCl_2(NR)]_2$ and $[TiCl_2(NR)]$, cleavage of $[TiCl_2(NR)]_2$, or loss of HCl from the $[TiCl_3(NHR)]$ fragment. The mass spectra of **1** and **4** provide strong evidence for monomeric and dimeric imido complexes as significant gas phase species.

The mass spectra of **2** and **3** were similar to those of **1** and **4**, but showed several differences. The 380 mass envelope, which was of strong intensity in **1** and **4**, was absent in **2** and **3**. However, **2** and **3** revealed peaks derived from the fragment $[TiCl_2(NR)]_2$ (**2**, 349 ($[TiCl_2(NR)]_2^{\bullet-}$ − $2CH_3$); **3**, 363 ($[TiCl_2(NR)]_2^{\bullet-}$ − CH_3), 309 ($[TiCl_2(NR)]_2^{\bullet-}$ − 2Cl)). The next intense mass envelope was centered at *m/e* 210 and corresponded to $[TiCl_3(NHR)]^{\bullet-}$ − CH_3. This fragment was also observed in the mass spectrum of **1**, but not in that of **4**, and probably reflects the stabilized radical that can be formed by loss of a methyl group from a *tert*-butyl group, but not from an *n*-butyl group. A fragment that could be attributed to $[TiCl_2(NR)]$ or $TiCl_4$ was observed at *m/e* 190. Again, we propose that this mass envelope corresponds to $[TiCl_2(NR)]$, since fragments derived from $[TiCl_2(NR)]$ were observed at lower mass (174 ($[TiCl_2(NR)]^{\bullet-}$ − CH_3), 153 ($[TiCl_2(NR)]^{\bullet-}$ − Cl)).

The mass spectrum of the monomeric imido complex **11** was determined in order to compare it to those of **1**−**4**. Surprisingly, no evidence was obtained for retention of the monomeric structure of **11** in the gas phase. Instead, the mass spectrum of **11** was similar to that of **1**. Hence, moderate to strong intensity fragments were observed at 380 ($[TiCl_2(NtBu)]_2^{\bullet-}$), 323 ($[TiCl_2(NtBu)]_2^{\bullet-}$ − R), 225 ($[TiCl_3(NHtBu)]^{\bullet-}$), 210 ($[TiCl_3(NHtBu)]^{\bullet-}$ − CH_3), and 190 ($[TiCl_2(NtBu)]^{\bullet-}$ or $TiCl_4^{\bullet-}$). These data are consistent with the liberation of monomeric and dimeric imido complexes from **11**. Since **11** can be sublimed without decomposition, these reactions most probably occur in the gas phase and not in the solid state upon sublimation into the ionization chamber of the mass spectrometer.

Discussion

The complicated nature of the reaction between titanium tetrachloride and primary alkylamines is illustrated by *tert*-butylamine. Treatment of titanium tetrachloride with *tert*-butylamine in dichloromethane, followed by extraction with hexane and vacuum drying of the resultant powder, results in the trimeric imido complex $[TiCl_2(NtBu)(NH_2tBu)_2]_3$ (**1**). The trimeric formulation for **1** was established by an osmometric solution molecular determination in dichloromethane. We propose that **1** exists as a cyclic six-membered ring structure, with bridging imido ligands. While a cyclic, trimeric titanium imido complex has not been reported, several related complexes have been prepared for other metals. For example, $[Cp^*Ta(N)Cl]_3$[15] and $[Cp^*Ta(N)CH_3]_3$[16] have been crystallographically characterized and possess nearly planar six-membered Ta_3N_3 rings. Borazine is also a prominent example of a compound that contains a six-membered conjugated ring. The complex $[\{Cp^*Ti(NH)\}_3N]$ contains a Ti_3N_3 ring,[17] except that it is nonplanar and the three titaniums are bonded to a triply-bridging nitride ligand, in addition to the bridging imido ligands. It has been suggested that planar, trimeric nitride complexes $(L_nMN)_3$ should be particularly stable, due to cyclic delocalization of their in-plane π electrons.[18] We suggest that **1** should also enjoy such stabilization, since three formal titanium-nitrogen double bonds would be present in each trimer (Scheme 3). This structural arrangement would make **1** a benzene analog. While the energy associated with π-electron delocalization in **1** is probably very small, it appears to be enough to favor the trimeric structure over other possibilities.

Sublimation of either **1** or **2** gave a red-orange solid of the apparent formula $[TiCl_2(NtBu)(NH_2tBu)_{0.4}]$ (**3**), as determined by microanalysis. Thus, **3** corresponds to loss of most of the coordinated *tert*-butylamine ligands from **1** and **2**. An osmo-

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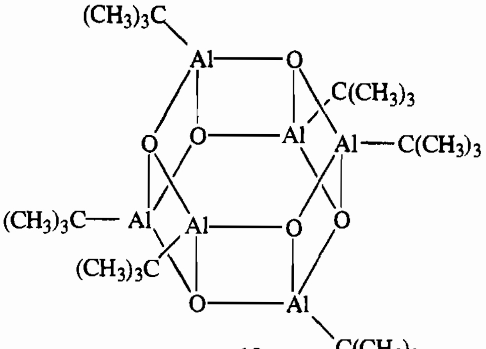
metric solution molecular weight determination of **3** in dichloromethane suggested the hexameric formulation $[TiCl_2(NtBu)]_6$. A reasonable structure for **3** is one in which two cyclic $[TiCl_2(NtBu)]_3$ units are fused together to form the drum compound $\{[TiCl_2(NtBu)]_3\}_2$ via triply-bridging imido linkages. Again, there are no known titanium imido complexes that adopt such a structure. However, hexameric drum structures are precedented in other systems. For example, Barron has characterized the alkoxide $[tBuAl(\mu_3\text{-}O)]_6$ (**13**),[19a] which adopts a drum structure similar to that proposed for **3**. Other related complexes with hexameric drum structures are known.[19b-d]

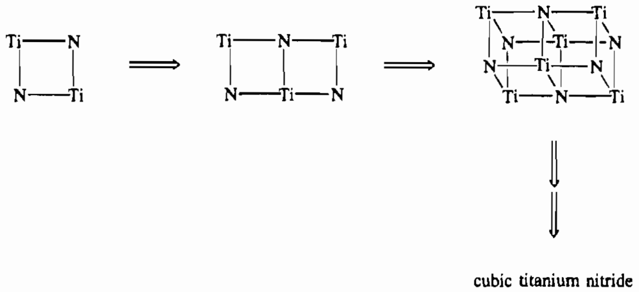


13

A priori, one might expect the imido linkage in **10**−**12** to be reactive toward a variety of unsaturated organic molecules. Surprisingly, **10** is unreactive toward diphenylacetylene, acetonitrile, and benzophenone at room temperature in dichloromethane and is unaffected by reflux in benzene for 12 h. Apparently, the phosphine oxide ligands in **10** protect the imido linkage from attack and do not appear to dissociate to open up an open coordination site. By contrast, **11** reacts with a wide variety of unsaturated organic compounds to afford new titanium amide complexes.[24] The TMEDA ligand is considerably more labile than the triphenylphosphine ligands and thus allows other ligands to access the titanium center.

The mass spectral data for **1**−**4** and **11** provide information about the types of gas phase species that might be present during the deposition of titanium nitride films in a CVD reactor. In complexes **1** and **4**, weak intensity mass envelopes were observed at *m*/*e* 512, which could correspond to loss of a *tert*-butyl group from trimeric **1**. This peak suggests that **1** and **4** sublime as trimers, but the trimers are not robust enough to survive under the ionizing conditions. In **1**, **4**, and **11**, strong mass envelopes were centered at *m*/*e* 380, which corresponds to the ion of the dimeric imido complex $[TiCl_2(NR)]_2$. We suggest that this fragment has a dimeric Ti_2N_2 core formed by bridging imido ligands. The dimeric bridging imido core is one of the most commonly observed structural modes for titanium imido complexes. For example, the complexes $\{TiCl_2(NSi(CH_3)_3)]_2\}_n$,[14] $[((CH_3)_2N)_2Ti]_2(\mu\text{-}tBuN)_2$,[20] $[Cp'TiCl(NSn(CH_3)_3)]_2$,[21] and $[CpTiCl(NPh)]_2$[22] are all dimeric, with Ti_2N_2 rings. The monomeric imido fragment $[TiCl_2(NR)]$ is another significant fragment that was present in the mass spectra of **1**−**4** and **11**. While we were unable to differentiate between $[TiCl_2(NR)]$ and $TiCl_4$ based upon calculation of the expected isotope distribution for this mass envelope, the lower mass peaks were logical fragments of $[TiCl_2(NR)]$ and did not match the fragmentation pattern of $TiCl_4$. The monomeric imido complexes **10**−**12** represent structural models for $[TiCl_2(NR)]$. In analogy with **10**, we expect that $[TiCl_2(NR)]$ is trigonal planar, with a very short (ca. 1.60−1.68 Å) titanium−nitrogen bond length. The final mass envelope that corresponds to a reasonable neutral fragment is at 225, which has a formulation of $[TiCl_3(NHR)]^{\bullet-}$ based on simulation of the isotope distribution. This ion, which is intense for **1**, **4**, and **11**, may originate from the reaction of HCl and $[TiCl_2(NR)]$, followed by electron capture. Loss of HCl would generate $[TiCl_2(NR)]$.

Scheme 4. Formation of Cubic Titanium Nitride from a Ti_2N_2 Fragment



Unfortunately, our mass spectral data do not allow us to assess the relative importance of each of the ions derived from **1**−**4** in the deposition of titanium nitride films. However, the data suggest that monomeric and dimeric imido complexes are the significant gas phase species derived from the precursors **1**−**4** and **11**. The identification of the $[TiCl_2(NR)]$ fragment is significant, since it is direct evidence for the formation of unsaturated titanium-nitrogen linkages in a film deposition. Such unsaturated complexes have been frequently proposed as intermediates in CVD processes,[4] although little evidence has been presented to back up these claims. It is interesting to note that fragments containing Ti_2N_2 rings are building blocks for the preparation of cubic titanium nitride, since titanium nitride crystallizes in the NaCl structure (Scheme 4). In a particularly relevant study, Castleman prepared titanium nitride clusters in the gas phase and found that clusters $(TiN)_x$ were particularly stable when they corresponded to a piece of the cubic NaCl structure.[23] Significantly, $(TiN)_2$ and $(TiN)_3$ (in addition to $(TiN)_x$, $x = 4, 6, 9, 18, 24, 32, 40, 50, 75, 90, 108, 126$) were "magic numbers", indicating that they are energy minima and probably represent fragments of the cubic titanium nitride lattice. Thus, the proposed dimeric structure of $[TiCl_2(NR)]_2$ may lead to the $(TiN)_2$ building block needed to form the cubic titanium nitride structure (depositions with **1**−**9** afford exclusively *cubic* titanium nitride films[24]). We stress that higher oligomers of $[TiCl_2(NR)]_x$ ($x > 3$) were not observed in the mass spectra, probably due to their fragile nature under the ionizing conditions of the mass spectrometer. It is possible that a whole range of cage compounds are present in depositions using **1**−**9** and play important roles in the transition between gas phase and surface chemistry.[25] The limitations of our mass spectrometry study have not allowed us to probe beyond $[TiCl_2(NR)]_3$.

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Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere using either glovebox or Schlenk line techniques. Benzene, hexane, and toluene were distilled from purple solutions of sodium/benzophenone. Dichloromethane was distilled over calcium hydride. All NMR solvents were purified by vacuum transfer from activated 4 Å molecular sieves. All chemicals were purchased from Aldrich Chemical Co. and were used as received.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75 MHz, respectively, in chloroform-*d*, dichloromethane-d_2, or benzene-d_6. Infrared spectra were obtained on a Nicolet DX20 spectrophotometer using Nujol mulls. Mass spectra were obtained on Kratos MS-50 or MS-80 spectrometers in the electron impact mode or negative chemical ionization (using butane gas) mode. Simulations of the isotope patterns were carried out on a SPARK workstation using programs supplied by Kratos. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Osmometric solution molecular weight analyses were performed by Galbraith Laboratories, Knoxville, TN, and have uncertainties of ±5%. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $\mathbf{[TiCl_2(NtBu)(NH_2tBu)_2]_3}$ (1). A 200-mL Schlenk flask was charged with *tert*-butylamine (4.8 mL, 45.6 mmol), dichloromethane (120 mL), and a stir bar and was fitted with a rubber septum. The solution was cooled to −78 °C, and titanium tetrachloride (1.0 mL, 9.12 mmol) was added via a syringe to afford an orange solution. The solution was allowed to warm to ambient temperature and was stirred for 5 h. The volatiles were pumped off, and the resultant orange solid was extracted with hexane (200 mL). The hexane extract was filtered through a 2-cm pad of Celite to give a clear, orange solution. The solvent was removed, and the resultant orange solid was vacuum dried for 72 h to afford **1** (2.76 g, 90% based on titanium tetrachloride): mp 150−156 °C (dec); IR (Nujol, cm^{-1}) 3320 (w), 3268 (w), 3216 (s), 3187 (s), 3147 (w), 3112 (s), 2587 (m), 2489 (m), 2072 (m), 1605 (m), 1576 (s), 1559 (s), 1513 (s), 1478 (s), 1403 (s), 1351 (m), 1288 (s), 1276 (m), 1230 (s), 1207 (s), 1155 (m), 1138 (s), 1120 (s), 1109 (m), 1091 (w), 1016 (s), 923 (m), 895 (s), 797 (m), 739 (m), 687 (s), 647 (s), 601 (w); ^{1}H NMR (CDCl$_3$, 21 °C, δ) 6.83 (br s, $\mathrm{N}\mathit{H}_2$), 3.00−3.50 (2 br s, $\mathrm{N}\mathit{H}_2$), 1.51 (s, $\mathrm{Ti{=}NC(C}\mathit{H}_3)_3$), 1.42 (s, $\mathrm{Ti{-}NH_2C(C}\mathit{H}_3)_3$), 1.01 (s, $\mathrm{Ti{-}NH_2C(C}\mathit{H}_3)_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 21 °C, ppm) 72.64 (s, $\mathrm{Ti{=}N}\mathit{C}\mathrm{(CH_3)_3}$), 53.82 (s, $\mathrm{Ti{-}NH_2}\mathit{C}\mathrm{(CH_3)_3}$), 51.84 (s, $\mathrm{Ti{-}NH_2}\mathit{C}\mathrm{(CH_3)_3}$), 31.20 (s, $\mathrm{Ti{=}NC(}\mathit{C}\mathrm{H_3)_3}$), 30.37 (s, $\mathrm{Ti{-}NH_2C(}\mathit{C}\mathrm{H_3)_3}$), 27.98 (s, $\mathrm{Ti{-}NH_2C(}\mathit{C}\mathrm{H_3)_3}$).

Anal. Calcd for $\mathrm{C_{12}H_{31}N_3Cl_2Ti}$: C, 42.87; H, 9.29; N, 12.50. Found: C, 42.16; H, 9.98; N, 11.75 (not obtained analytically pure).

Preparation of $\mathbf{[TiCl_2(NtBu)(NH_2tBu)_3]}$ (2). A 200-mL Schlenk flask was charged with *tert*-butylamine (2.3 mL, 21.90 mmol), dichloromethane (30 mL), a stir bar and was fitted with a rubber septum. The solution was cooled to −78 °C, and titanium tetrachloride (0.30 mL, 2.74 mmol) was added via a syringe to afford an orange solution. The solution was allowed to warm to ambient temperature and was stirred for 5 h. The volatiles were pumped off, and the resultant orange solid was taken up with hexane (50 mL). The hexane extract was filtered through a 2-cm pad of Celite to give a clear solution. This solution was placed at −30 °C to afford orange crystals. The solvent was decanted, and the crystals were vacuum dried to afford **1** (0.98 g, 87% based on titanium tetrachloride): mp 184 °C (dec); IR (Nujol, cm^{-1}) 3222 (s), 3189 (s), 3148 (m), 3115 (m), 3050 (s), 2598 (m), 2500 (m), 1606 (m), 1581 (m), 1524 (m), 1401 (s), 1355 (w), 1294 (m), 1259 (s), 1230 (s), 1213 (s), 1155 (m), 1144 (m), 1110 (m), 1026 (w), 928 (w), 902 (w), 805 (w), 752 (w), 722 (w), 659 (m), 605 (w); ^{1}H NMR (CDCl$_3$, 23 °C, δ) 4.58 (d, J = 12.6 Hz, $\mathrm{TiN}\mathit{H}\mathrm{tBu}$), 4.35 (m, $\mathrm{TiN}\mathit{H}\mathrm{tBu}$), 3.41 (br s, $\mathrm{TiN}\mathit{H}_2\mathrm{tBu}$), 2.71 (d, J = 12.9 Hz, $\mathrm{TiN}\mathit{H}_2\mathrm{tBu}$), 1.54 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.46 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.31 (br s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.15 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 0.96 (s, $\mathrm{C(C}\mathit{H}_3)_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C, ppm) 73.95 (s, $\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 72.20 (s, $\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 52.60, 52.23 and 51.81 (s, $\mathrm{NH_2}\mathit{C}\mathrm{(CH_3)_3}$), 31.53, 31.37, 31.21, 30.99 and 30.74 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$).

Anal. Calcd for $\mathrm{C_{16}H_{42}C_{12}N_4Ti}$: C, 46.95; H, 10.34. Found: C, 46.86; H, 10.79.

Preparation of $\mathbf{\{[TiCl_2(NtBu)]_3\}_2{\cdot}2.4tBuNH_2}$ (3). A vial (0.5 in. diameter) was charged with **1** (0.1 g, 0.24 mmol), and a plug of glass wool was placed above the compound. This vial was placed in a sublimation tube (1 in. diameter) and was connected to the vacuum line. The tube was evacuated and was placed in a sublimation apparatus, and the contents were sublimed (110 °C, 0.01 mmHg) to afford **3** as a deep orange sublimate (0.042 g, 79% based on complex **1**): mp 176 °C (dec); IR (Nujol, cm^{-1}) 3174 (s), 3140 (s), 3061 (s), 2678 (m, br), 2568 (m, br), 2472 (m, br), 2047 (w), 1934 (w), 1576 (s), 1492 (s), 1407 (m), 1350 (m), 1293 (m), 1242 (s), 1209 (s), 1158 (w), 1078 (w), 1022 (w), 987 (w), 976 (w), 965 (w), 931 (w), 888 (w), 801 (w); 712 (w), 608 (w); ^{1}H NMR (CDCl$_3$, 23 °C, δ) 6.10 (br s, $\mathrm{N}\mathit{H}_2$), 1.08 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.00 (s, $\mathrm{C(C}\mathit{H}_3)_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C, ppm) 75.39 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 54.20 (s, $\mathrm{NH_2}\mathit{C}\mathrm{(CH_3)_3}$), 29.61 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 28.09 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$).

Anal. Calcd for $\mathrm{\{[TiCl_2(NtBu)]_3\}_2{\cdot}2.4tBuNH_2}$: C, 30.42; H, 6.05; N, 8.88. Found: C, 30.34; H, 6.46; N, 8.61.

Reaction between $\mathbf{[TiCl_2(NtBu)(NH_2tBu)_{0.4}]}$ (3) and *tert*-Butylamine. A 5-mm NMR tube was charged with **3** (60 mg, 0.23 mmol) and chloroform-*d* (0.5 mL) and was fitted with a rubber septum. To this solution was added via syringe *tert*-butylamine (0.07 mL, 0.69 mmol). The NMR tube was shaken vigorously for 5 min, and both ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded: ^{1}H NMR (CDCl$_3$, 23 °C, δ) 4.58 (d, J = 12.0 Hz, $\mathrm{TiN}\mathit{H}\mathrm{tBu}$), 4.35 (m, $\mathrm{TiN}\mathit{H}\mathrm{tBu}$), 3.41 (br s, $\mathrm{TiN}\mathit{H}_2\mathrm{tBu}$), 2.71 (d, J = 12.6 Hz, $\mathrm{TiN}\mathit{H}_2\mathrm{tBu}$), 1.54 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.46 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.31 (br s, $\mathrm{C(C}\mathit{H}_3)_3$), 1.15 (s, $\mathrm{C(C}\mathit{H}_3)_3$), 0.96 (s, $\mathrm{C(C}\mathit{H}_3)_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C, ppm) 73.95 (s, $\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 72.20 (s, $\mathrm{N}\mathit{C}\mathrm{(CH_3)_3}$), 52.60, 52.23 and 51.81 (s, $\mathrm{NH}\mathit{C}\mathrm{(CH_3)_3}$ and $\mathrm{NH_2}\mathit{C}\mathrm{(CH_3)_3}$), 31.53, 31.37, 31.21, 30.99 and 30.74 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$).

Preparation of $\mathbf{[TiCl_2(NH(CH_2)_3CH_3)_2(NH_2(CH_2)_3CH_3)_2]}$ (4). A 200-mL Schlenk flask was charged with *n*-butylamine (9.02 mL, 91.3 mmol), benzene (30 mL), and a stir bar and was fitted with a rubber septum. The contents were cooled to −78 °C, and titanium tetrachloride (1.0 mL, 9.13 mmol) was added via a syringe to give an orange solution. The solution was allowed to warm to ambient temperature over 0.5 h and was stirred for 6 h. The volatiles were pumped off, the resultant orange solid was extracted with hexane (60 mL), and the extract was filtered through a 2-cm pad of Celite on a medium glass frit to afford a clear, orange solution. This solution was concentrated (30 mL) and was placed at −30 °C for 24 h. The solvent was decanted by a cannula, and crystals were vacuum dried to afford **4** as opaque, orange crystals (3.03 g, 81% based on titanium tetrachloride): mp 147 °C (dec); IR (Nujol, cm^{-1}) 3270 (m), 3207 (m), 3120 (m), 3080 (m), 2649 (w), 2511 (w), 2407 (w), 1585 (s), 1568 (s), 1493 (m), 1321 (w), 1240 (w), 1211 (w), 1165 (s), 1067 (s), 1016 (m), 970 (w), 947 (w), 907 (w), 884 (w), 786 (m), 728 (m), 631 (m); ^{1}H NMR (CDCl$_3$, 21 °C, δ) 6.9 (br s, $\mathrm{N}\mathit{H}_2$), 4.36 (br s, $\mathrm{N}\mathit{H}_2$), 4.09 (br s, $\mathrm{C}\mathit{H}_2$), 3.20 (br m, $\mathrm{C}\mathit{H}_2$), 2.98 (m, $\mathrm{C}\mathit{H}_2$), 2.88 (br m, $\mathrm{C}\mathit{H}_2$), 1.65 (br m, $\mathrm{C}\mathit{H}_2$), 1.33 (br m, $\mathrm{C}\mathit{H}_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 21 °C, ppm) 74.35 and 72.18 (s, $\mathrm{N}\mathit{C}\mathrm{H_2C_3H_7}$), 47.57 and 45.97 (s, $\mathrm{NH_2}\mathit{C}\mathrm{H_2C_3H_7}$), 40.64 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2C_2H_5}$), 35.19, 34.54, 33.69, 33.13 and 30.66 (s, $\mathrm{NHCH_2}\mathit{C}\mathrm{H_2C_2H_5}$ and $\mathrm{NH_2CH_2}\mathit{C}\mathrm{H_2C_2H_5}$), 20.39, 20.15 and 19.78 (s, $\mathrm{NH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$, $\mathrm{NHCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$, and $\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 13.81, 13.69 and 13.49 (s, $\mathit{C}\mathrm{H_3}$).

Anal. Calcd for $\mathrm{C_{12}H_{31}Cl_2N_3Ti}$: C, 42.87; H, 9.29. Found: C, 45.13; H, 9.66 (not obtained analytically pure).

Preparation of $\mathbf{[TiCl_2(NCH_2CH(CH_3)_2)(NH_2CH_2CH(CH_3)_2)]}$ (5). A 200-mL Schlenk flask was charged with isobutylamine (7.25 mL, 72.96 mmol), dichloromethane (30 mL), and a stir bar and was fitted with a rubber septum. The solution was cooled to −78 °C and titanium tetrachloride (1.0 mL, 9.12 mmol) was added via a syringe. A vigorous reaction was observed with fuming, and an orange solution resulted. The solution was allowed to warm to ambient temperature and was stirred for 5 h. The volatiles were pumped off, the resultant orange solid was taken up with hexane (50 mL), and the extract was filtered through a 2-cm pad of Celite to give a clear solution. This solution was placed at −30 °C to afford orange crystals. The solvent was decanted, and the crystals were vacuum dried to afford **5** (2.5 g, 82%, based on titanium tetrachloride): mp 88−90 °C (dec); IR (Nujol, cm^{-1}) 3315 (s), 3242 (s), 3181 (w), 3126 (m), 3096 (m), 1577 (s), 1507 (m), 1371 (s), 1307 (w), 1238 (s), 1182 (m), 1161 (s), 1100 (s), 1023 (s), 935 (m), 889 (w), 813 (w), 720 (w), 668 (w); ^{1}H NMR (CDCl$_3$, 23 °C, δ) 4.27−1.76 (br humps, $\mathrm{C}\mathit{H}$, $\mathrm{C}\mathit{H}_2$, $\mathrm{N}\mathit{H}_2$), 1.02 (d, J = 6.9 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 0.95 (d, J = 6.3 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 0.90 (d, J = 6.9 Hz, $\mathrm{C(C}\mathit{H}_3)_2$), 0.85 (d, J = 6.6 Hz, $\mathrm{C(C}\mathit{H}_3)_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C, ppm)

66.78 (s, NCH_2), 55.51, 53.60, 53.49 (s, NH_2CH_2), 31.74 (br s, NCH_2CH), 31.04, 30.23, 30.14 (br s, NH_2CH_2CH), 20.98, 20.54, 20.35, 19.87 (s, CH_3).

Anal. Calcd for $C_{12}H_{31}Cl_2N_3Ti$: C, 42.87; H, 9.29; N, 12.50. Found: C, 42.16; H, 9.98; N, 11.75 (not obtained analytically pure).

Preparation of [$TiCl_2(NCH(CH_3)_2)(NH_2CH(CH_3)_2)_2$] (6). A 200-mL Schlenk flask was charged with isopropylamine (15.2 mL, 178.1 mmol), dichloromethane (100 mL), and a stir bar and was fitted with a rubber septum. The solution was cooled to 0 °C, and titanium tetrachloride (3.0 mL, 27.4 mmol) was added via a syringe to afford a red solution. The solution was allowed to reach ambient temperature and was stirred for 6 h. The volatiles were pumped off to afford a red solid, which was subsequently extracted with hexane (30 mL). The extract was filtered through a 2-cm pad of Celite, and the solvent was removed to give spectroscopically pure **6** (5.96 g, 74% based on titanium tetrachloride): mp 64−65 °C (dec); IR (Nujol, cm^{-1}) 3192 (s), 3114 (s), 3081 (s), 3008 (s), 2709 (m), 2604 (w), 2498 (w), 2016 (w), 1592 (s), 1465 (s), 1394 (s), 1379 (s), 1337 (m), 1303 (m), 1229 (s), 1165 (s), 1067 (s, br), 1010 (w), 943 (m), 877 (m), 815 (s), 720 (w), 642 (m, br); ^1H NMR ($CDCl_3$, 23 °C, δ) 7.86 (br s, NH), 3.00−5.00 (several broad humps, NH, $CH(CH_3)_2$, NH_2), 1.41 (br m, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 68.39, 67.53 (s, $NCH(CH_3)_2$), 49.45, 48.38, 47.52 (s, $NH_2CH(CH_3)_2$), 25.11, 25.09, 24.61, 23.79, 21.24 (s, CH_3).

Anal. Calcd for $C_9H_{25}Cl_2N_3Ti$: C, 36.75; H, 8.57; N, 14.29. Found: C, 34.25; H, 8.64; N, 13.70 (not obtained analytically pure).

Preparation of [$TiCl_2(NCH_2CH_2Ph)(NH_2CH_2CH_2Ph)_2$] (7). A 200-mL Schlenk flask was charged with phenylethylamine (6.80 mL, 54.80 mmol), and a stir bar and was fitted with a rubber septum. This solution was cooled to 0 °C, and titanium tetrachloride (1.0 mL, 9.12 mmol) was added via a syringe. The resultant red solution was allowed to reach ambient temperature over a period of 0.5 h and was stirred for 6 h. The volatiles were pumped off, the red solid was extracted with benzene (30 mL), and the extract was filtered through a 2-cm pad of Celite to afford a clear, red solution. The solvent was pumped off to give 7 as a red powder (3.92 g, 89% based upon titanium tetrachloride): mp 59−60 °C; IR (Nujol, cm^{-1}) 3101 (m), 3057 (m), 3024 (m), 1591 (m), 1494 (w), 1260 (s), 1152 (w), 1095 (m, br), 1073 (w), 1021 (s, br), 933 (w), 873 (w), 840 (w), 799 (m), 743 (w), 720 (w), 694 (w); ^1H NMR ($CDCl_3$, 21 °C, ppm) 7.23 (m, C_6H_5), 7.12 (m, C_6H_5), 6.96 (m, C_6H_5), 4.13 (m, $NH_2CH_2CH_2Ph$), 3.53 (m, NCH_2CH_2Ph), 3.09 (br s, NH_2), 2.98 (m, NCH_2CH_2Ph), 2.86 (m, NH_2), 2.72 (m, $NH_2CH_2CH_2Ph$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 139.02 (s, C_6H_5), 137.70 (s, C_6H_5), 128.88 (m, C_6H_5), 128.69 (s, C_6H_5), 128.41 (s, C_6H_5), 128.19 (s, C_6H_5), 126.77 (s, C_6H_5), 126.59 (s, C_6H_5), 126.34 (s, C_6H_5), 126.03 (s, C_6H_5), 73.23 (s, NCH_2CH_2Ph), 47.07 (s, $NH_2CH_2CH_2Ph$), 43.83 (br s, $NH_2CH_2CH_2Ph$), 38.94 (s, NCH_2CH_2Ph), 38.49 (br s, $NH_2CH_2CH_2Ph$), 37.77 (s, $NH_2CH_2CH_2Ph$).

Anal. Calcd for $C_{24}H_{31}Cl_2N_3Ti$: C, 60.01; H, 6.51. Found: C, 59.18; H, 6.51 (not obtained analytically pure).

Preparation of [$TiCl_2(NCH(C_2H_5)_2)(NH_2CH(C_2H_5)_2)_2$] (8). A 200-mL Schlenk flask was charged with 3-pentylamine (6.91 mL, 59.28 mmol), hexane (30 mL), and a stir bar and was fitted with a rubber septum. This solution was cooled to 0 °C, and titanium tetrachloride (1.0 mL, 9.12 mmol) was added via a syringe to form a red precipitate. The mixture was allowed to reach ambient temperature and was stirred for 1.5 h. During this time the color of the precipitate turned deep yellow; the mixture was then stirred for 3 h. The solvent was pumped off to give a pale yellow solid, which was extracted with hexane (30 mL). The resultant yellow solution was filtered through a 2-cm pad of Celite, and the solvent was pumped off to afford spectroscopically pure **8** (2.95 g, 86% based on titanium tetrachloride): mp 82 °C (dec); IR (Nujol, cm^{-1}) 3275 (s), 3236 (s), 3225 (s), 3130 (s), 1570 (s), 1324 (m), 1279 (w), 1256 (w), 1240 (w), 1217 (s), 1172 (m), 1144 (w), 1105 (m), 1088 (s), 1066 (m), 1032 (w), 1004 (w), 954 (s), 914 (m), 875 (w), 836 (w), 780 (m), 752 (w), 718 (w); ^1H NMR ($CDCl_3$, 23 °C, δ) 3.17 (broad singlet overlapped with a multiplet, NH_2 and $NCH(CH_2CH_3)_2$), 2.79 (m, $NCH(CH_2CH_3)_2$), 1.66 (m, $NH_2CH(CH_2CH_3)_2$), 1.24 (m, $NH_2CH(CH_2CH_3)_2$), 1.13 (m, $NH_2CH(CH_2CH_3)_2$), 1.01 (t, $J = 6.3$ Hz, $NCH(CH_2CH_3)_2$), 0.93 (t, $J = 6.9$ Hz, $NCH(CH_2CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 83.40 (s, $NCH(CH_2CH_3)_2$), 56.97 (s, $NH_2CH(CH_2CH_3)_2$), 30.37 (s, $NCH(CH_2CH_3)_2$), 27.03 (s, $NH_2CH(CH_2CH_3)_2$), 11.44 (s, $NCH(CH_2CH_3)_2$), 9.35 (s, $NH_2CH(CH_2CH_3)_2$).

Anal. Calcd for $C_{15}H_{37}Cl_2N_3Ti$: C, 47.63; H, 9.86; N, 11.11. Found: C, 46.74; H, 9.46; N, 10.44 (not obtained analytically pure).

Preparation of [$TiCl_2(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)(NH_2(2,6\text{-}(CH(CH_3)_2)_2\text{-}C_6H_3)_2$] (9). A 200-mL Schlenk flask was charged with 2,6-diisopropylaniline (10.32 mL, 54.72 mmol), hexane (40 mL), and a stir bar and was fitted with a rubber septum. The flask was cooled to 0 °C, and titanium tetrachloride (1.0 mL, 9.12 mmol) was added via a syringe to give a green-brown mixture. This suspension was allowed to reach ambient temperature over a period of 0.5 h and was stirred for 6 h. The solvent was pumped off, the resultant solid was taken up in hexane (50 mL), and the mixture was filtered through a 2-cm pad of Celite to give a clear, brown solution. This solution was kept at −30 °C to effect crystallization. Cannulation of the solvent and subsequent vacuum drying afforded opaque, green-yellow crystals of **11** (4.91 g, 83% based on titanium tetrachloride): mp 149 °C; IR (Nujol, cm^{-1}) 3387 (w), 3337 (w), 3286 (w), 3189 (m, br), 3052 (m, br), 3035 (m, br), 2564 (w), 1616 (m), 1599 (w), 1553 (m), 1514 (s), 1435 (s), 1417 (m), 1360 (m), 1344 (m), 1315 (m), 1270 (m), 1253 (w), 1111 (w), 1094 (w), 1054 (s), 1031 (s), 975 (w), 856 (m), 810 (m), 793 (m), 782 (m), 748 (m), 742 (s), 731 (m); ^1H NMR ($CDCl_3$, 23 °C, δ) 7.14 (m, $Ti{-}NH_2C_6H_3(i\text{-}C_3H_7)$), 6.78 (m, $Ti{=}NC_6H_3(i\text{-}C_3H_7)$), 6.41 (br s, NH_2), 5.96 (d, $J = 11.1$ Hz, NH_2), 5.72 (d, $J = 11.4$ Hz, NH_2), 4.04 (septet, $J = 6.6$ Hz, $CH(CH_3)_2$), 3.86 (septet, $J = 6.6$ Hz, $CH(CH_3)_2$), 3.08 (septet, $J = 6.6$ Hz, $CH(CH_3)_2$), 1.36 (d, $J = 6.6$ Hz, CH_3), 1.32 (d, $J = 6.6$ Hz, CH_3), 1.20 (d, $J = 6.9$ Hz, CH_3), 0.97 (d, $J = 6.9$ Hz, CH_3), 0.93 (d, $J = 6.9$ Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 158.31 (s, $Ti{=}N{-}C_{1,ipso}$), 145.72 (s, $Ti{-}NH_2{-}C_{1,ipso}$), 138.64 (s, $Ti{-}NH_2{-}C_{1,ipso}$), 136.96 (s, $Ti{-}NH_2{-}Ar\ C_2,\ C_6$), 136.65 (s, $Ti{-}NH_2{-}Ar\ C_2,\ C_6$), 133.34 (s, $Ti{=}N{-}Ar\ C_2,\ C_6$), 125.46 (s, $Ti{=}N{-}Ar\ C_3,\ C_5$), 123.54 (s, $Ti{-}NH_2{-}Ar\ C_3,\ C_5$), 123.18 (s, $Ti{=}N{-}Ar\ C_{4,ipso}$), 121.69 (s, $Ti{-}NH_2{-}Ar\ C_4,ipso$), 28.20 (s, $CH(CH_3)_2$), 27.74 (s, $CH(CH_3)_2$), 27.55 (s, $CH(CH_3)_2$), 24.76 (s, CH_3), 23.82 (s, CH_3), 23.20 (s, CH_3), 22.83 (s, CH_3), 22.68 (s, CH_3).

Anal. Calcd for $C_{36}H_{55}Cl_2N_3Ti$: C, 66.66; H, 8.55; N, 6.48. Found: C, 65.49; H, 8.55; N, 6.44 (not obtained analytically pure).

Preparation of [$TiCl_2(NtBu)(O{=}PPh_3)_2$] (10). A 150-mL Schlenk flask was charged with **1** (0.15 g, 0.37 mmol), dichloromethane (15 mL), and a stir bar and was fitted with a rubber septum. A solution of triphenylphosphine oxide (0.21 g, 0.75 mmol) was cannulated into the above solution to afford a lemon yellow solution. The resultant solution was stirred for 0.5 h, and the volatiles were pumped off to give a yellow compound. This was redissolved in dichloromethane (10 mL), and the mixture was filtered through a 2-cm pad of Celite to give a clear, yellow solution. Hexane (75 mL) was carefully layered on this solution, and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the deep yellow crystals of **10** were vacuum dried (0.12 g, 42% based on complex **1**): mp 175−185 °C (dec); IR (Nujol, cm^{-1}) 3074 (w), 3056 (w), 3026 (w), 1437 (s), 1252 (m), 1151 (s), 1117 (s), 1089 (m), 1032 (m), 999 (w), 807 (w), 768 (w), 745 (m), 723 (s), 695 (s); ^1H NMR ($CDCl_3$, δ, 23 °C) 7.93 (br s, o Ar CH), 7.48 (m, m,p Ar CH), 0.58 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 133.10−132.58 (m, o,p C_6H_5 overlapping), 129.75 (br s, $P{-}C$), 128.49 (d, $J_{CP} = 12.9$ Hz, m C_6H_5), 72.14 (s, $C(CH_3)_3$), 30.58 (s, $C(CH_3)_3$).

Anal. Calcd for $C_{40}H_{39}Cl_2NO_2P_2Ti$: C, 64.36; H, 5.27; N, 1.88. Found: C, 63.97; H, 5.06; N, 1.72.

Preparation of [$TiCl_2(NtBu)(TMEDA)$] (11). A 150-mL Schlenk flask was charged with **1** (0.6 g, 1.78 mmol), dichloromethane (15 mL), and a stir bar and was fitted with a rubber septum. A solution of *N,N,N′,N′*-tetramethylethylenediamine (0.37 mL, 2.44 mmol) was cannulated into the above solution to afford a lemon-yellow solution. The resultant solution was stirred for 0.5 h, and the volatiles were pumped off to give a yellow compound. This solid was redissolved in a minimum amount of dichloromethane (10 mL), and the mixture was filtered through a 2-cm pad of Celite to give a clear, yellow solution. Hexane (75 mL) was carefully layered on this solution, and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the deep yellow crystals of **11** were vacuum dried (0.32 g, 60% based on complex **1**): mp 194−195 °C (dec); IR (Nujol, cm^{-1}) 2992 (m), 2802 (m), 2598 (w), 2492 (w), 1379 (m), 1344 (s), 1281 (m), 1239 (s), 1203 (m), 1160 (w), 1126 (w), 1112 (w), 1062 (m), 1041 (m), 1013 (m), 985 (m), 929 (m), 795 (m), 767 (m); ^{1}H NMR ($CDCl_3$, 23 °C, δ) 3.10 (s, $\mathrm{C}H_2\mathrm{C}H_2$), 2.85 (s, $\mathrm{N(C}H_3)_2$), 1.05 (s, $\mathrm{C(C}H_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 73.85 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 58.80 (s, $\mathrm{Me_2N}C\mathrm{H_2}C\mathrm{H_2}$-$NMe_2$), 51.51 (s, $\mathrm{N(}C\mathrm{H_3)_2}$), 30.90 (s, $\mathrm{C(}C\mathrm{H_3)_3}$).

Anal. Calcd for $C_{10}H_{25}Cl_2N_3Ti$: C, 39.20; H, 8.17; N, 13.70. Found: C, 37.80; H, 7.89; N, 13.06 (not obtained analytically pure).

Reaction between [$TiCl_2(NtBu)(NH_2tBu)_{0.4}$] (3) and TMEDA. A 5-mm NMR tube was charged with **3** (60 mg, 0.22 mmol) and $CDCl_3$ (0.5 mL) in the glovebox and capped with a rubber septum. TMEDA (0.035 mL, 0.23 mmol) was added via a syringe, and the contents of the NMR tube were shaken vigorously for 3 min. An immediate color change of the solution from orange to lemon yellow occurred during this time, and ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded at 23 °C: ^{1}H NMR ($CDCl_3$, 23 °C, δ) 6.01 (br s, $\mathrm{N}H_2\mathrm{tBu}$), 3.11 (s, $\mathrm{C}H_2\mathrm{C}H_2$), 2.81 (s, TMEDA $\mathrm{C}H_3$), 1.27 (s, $\mathrm{(C}H_3\mathrm{)_3CNH_2}$), 1.00 (s, $\mathrm{NC(C}H_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 73.85 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 58.53 (s, TMEDA $C\mathrm{H_3}$), 51.08 (s, $C\mathrm{H_2}C\mathrm{H_2}$), 30.50 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$).

Preparation of [$TiCl_2(NtBu)(DIPEDA)$] (12). A 150-mL Schlenk flask was charged with **1** (0.15 g, 0.37 mmol), dichloromethane (15 mL), and a stir bar and was fitted with a rubber septum. A solution of *N,N'*-diisopropylethylenediamine (0.13 mL, 0.74 mmol) was cannulated into the above solution to afford a lemon yellow solution. The resultant solution was stirred for 0.5 h, and the volatiles were pumped off to give a yellow compound. This was redissolved in dichloromethane (10 mL), and the mixture was filtered through a 2-cm pad of Celite to give a clear, yellow solution. Hexane (75 mL) was carefully layered on this solution, and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the deep yellow crystals of **12** were vacuum dried (0.08 g, 65% based on complex **1**): mp 156−157 °C (dec); IR (Nujol, cm^{-1}) 3266 (w), 3239 (m), 3211 (s), 2716 (w, br), 2601 (w), 2520 (w), 2449 (w), 2400 (w), 1649 (w), 1600 (w), 1578 (w), 1456 (s), 1432 (m), 1421 (m), 1369 (m), 1355 (m), 1338 (m), 1318 (w), 1301 (w), 1272 (w), 1245 (m), 1233 (s), 1208 (m), 1168 (m), 1160 (m), 1139 (m), 1119 (m), 1071 (w), 1063 (w), 1032 (s), 1015 (m), 992 (m), 974 (w), 945 (w), 936 (w), 931 (w), 887 (m), 808 (w), 796 (m), 746 (m), 721 (w), 611 (w); ^{1}H NMR ($CDCl_3$, δ, 23 °C) 4.02 (m, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.82 (br s, $\mathrm{N}H$), 3.12 (s, $\mathrm{C}H_2\mathrm{C}H_2$), 1.46 (d, J = 6.7 Hz, $\mathrm{CH(C}H_3)_2$), 1.34 (d, J = 6.3 Hz, $\mathrm{CH(C}H_3)_2$), 1.04 (s, $\mathrm{NC(C}H_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 72.14 (s, $C\mathrm{(CH_3)_3}$), 50.88 (s, $C\mathrm{H_2}C\mathrm{H_2}$), 42.31 (s, $C\mathrm{H(CH_3)_2}$), 30.62 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 22.15 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 19.90 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$).

Anal. Calcd for $C_{12}H_{27}Cl_2N_3Ti$: C, 43.39; H, 8.19. Found: C, 41.86; H, 8.93 (not obtained analytically pure).

Reaction between 3 and Triphenylphosphine Oxide. A 150-mL Schlenk flask was charged with **3** (0.60 g, 2.20 mmol), dichloromethane (15 mL), a stir bar and was fitted with a rubber septum. A solution of triphenylphosphine oxide (1.14 g, 4.10 mmol in 5 mL of dichloromethane) was cannulated into the above solution to afford a lemon yellow solution. The resultant solution was stirred for 2 h, and the volatiles were pumped off to give a yellow compound. This solid was redissolved in a minimum amount of dichloromethane (12 mL), and the mixture was filtered through a 2-cm pad of Celite to give a clear, yellow solution. Hexane (70 mL) was carefully layered on this solution, and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the deep yellow crystals of **11** were vacuum dried (1.46 g, 89% based on **3**).

X-ray Crystal Structure Determination of 11. The single crystal X-ray diffraction experiment was performed on a Nicolet R3 automated diffractometer with Mo K_α radiation and graphite monochromator at ambient temperature. $\theta/2\theta$ scans were used for data collection. The structures were refined with the programs of SHELX-76. Absorption corrections were made by empirical methods. All non-hydrogen atoms are described anisotropically. Neutral atom scattering factors and corrections for anomalous dispersion were from *International Tables for X-Ray Crystallography*, Vol. 4. Further data are contained in the supplementary material.

X-ray Crystal Structure Determination of 12. The single crystal X-ray diffraction experiment was conducted on a Siemens P4 diffractometer with Mo K_α radiation and graphite monochromator at ambient temperature. The crystal was found to belong to the $2/m$ Laue symmetry group by photographic methods, and systematic absences in the diffraction data allowed a unique space group assignment. ψ-Scan data revealed an insignificant variation in the azimuthal intensities, and a correction for absorption was ignored. The structure was solved by direct methods. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL-PC program library (G. Sheldrick, ver. 4.2, Siemens XRD, Madison, WI). Further data are contained in the supplementary material.

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Supplementary Material Available: Tables S1−S8, giving numbered perspective views of **11** and full experimental details for data collection and refinement, bond lengths and angles, anisotropic thermal parameters, and hydrogen positional and isotropic thermal parameters for **11** and **12** (12 pages). Ordering information is given on any current masthead page.