

# Structures and Energetics of Some Potential Intermediates in Titanium Nitride Chemical Vapor Deposition: $\text{TiCl}_m(\text{NH}_2)_n$ , $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ , and $\text{TiCl}_m(\text{NH}_2)_n\text{N}$ . An ab Initio Molecular Orbital Study

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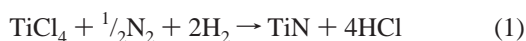
Received: February 11, 1998; In Final Form: April 20, 1998

The various potential intermediates in the chemical vapor deposition production of TiN films have been studied using a variant of the G2 level of theory. The structures of  $\text{TiCl}_m(\text{NH}_2)_n$ ,  $0 \leq m + n \leq 4$ ,  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ ,  $0 \leq m + n \leq 2$ , and  $\text{TiCl}_m(\text{NH}_2)_n\text{N}$ ,  $0 \leq m + n \leq 1$ , were optimized at B3LYP level of theory with the Wachters–Hay basis set for Ti and the 6-311G(d) basis set for H, N, and Cl. The energies were calculated at the MP4 and QCI levels with these basis sets augmented by multiple sets of polarization and diffuse functions using the B3LYP optimized geometries. Bond dissociation energies, heats of atomization, heats of formation, and entropies have been calculated at this modified G2 level of theory.

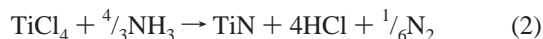
## Introduction

Titanium nitride thin films have a number of important uses because of attributes such as extreme hardness, high chemical resistivity, good electrical conductivity, and optical properties similar to gold.<sup>1</sup> Applications of titanium nitride films include wear-resistant coatings for tools, barrier materials, and conductive coatings for microelectronics, and decorative coatings for consumer goods. Titanium nitride films can be prepared by a number of chemical vapor deposition (CVD) processes; however, the temperature requirements and the purity of the films limit the utility of these CVD schemes. Current research efforts are directed toward lowering the application temperature and improving the purity of the coatings.

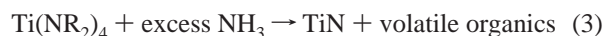
At high temperatures (900–1000 °C), high-quality titanium nitride films can be deposited using titanium tetrachloride, nitrogen, and hydrogen:<sup>2</sup>



Significantly milder conditions (500–700 °C) are possible using ammonia as the nitrogen source:<sup>3</sup>



However, both schemes yield HCl as a corrosive byproduct and produce films contaminated with traces of chlorine. To avoid these problems Gordon and co-workers<sup>4,5</sup> used Ti(IV) amido precursors,  $\text{Ti}(\text{NR}_2)_4$ , for CVD. Deposition can be carried out below 450 °C, but the films are contaminated with significant amounts of titanium carbide and organic carbon. However, in the presence of excess ammonia, high-quality coatings can be produced at temperatures of 300–400 °C.<sup>6</sup>



Transamination has been shown to occur rapidly under these conditions.<sup>7</sup> Gordon and co-workers<sup>4–6</sup> speculate that imido

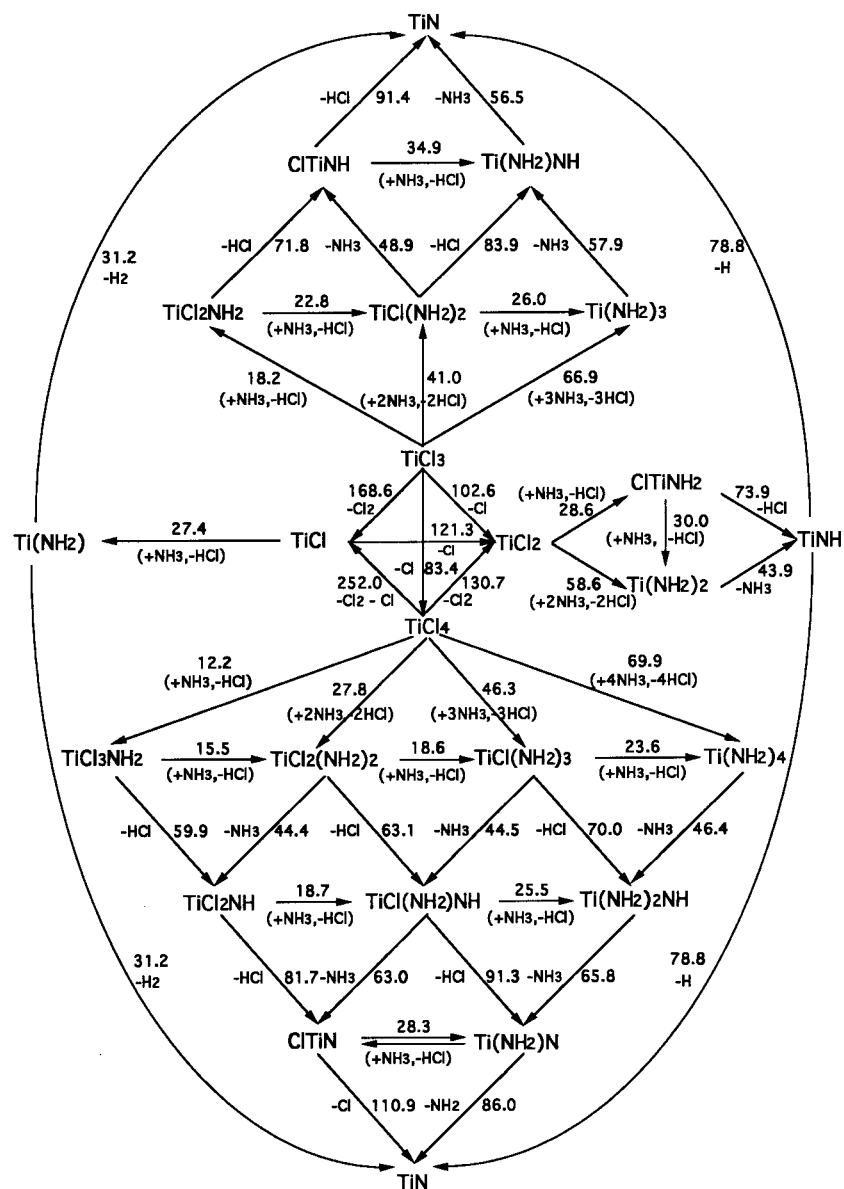
complexes,  $\text{Ti}(\text{NR}_2)_2\text{NH}$ , may be important intermediates in the deposition process. Winter and co-workers<sup>8</sup> have prepared a single-source imido precursor,  $\text{TiCl}_2(\text{NH}^t\text{Bu})_2(\text{NH}_2^i\text{Bu})_2$ . They found mass spectrometric evidence for an imido complex in the CVD process and obtained an X-ray structure of a phosphine oxide derivative of the imido complex.

Relatively little is known about the structure and thermochemistry of titanium nitride CVD intermediates, and even less is known about the mechanisms. Titanium tetrachloride has been well characterized for many years,<sup>9–11</sup> but the ground state of  $\text{TiCl}$  has just been reassigned based on new experimental<sup>12</sup> and theoretical data.<sup>13</sup> The heats of formation of  $\text{TiCl}_n$ ,  $n \leq 3$ , have been recently redetermined,<sup>14</sup> but only some of the necessary gas-phase spectroscopic and structural data have been measured.<sup>15,16</sup> Experimental thermochemical data for  $\text{Ti}(\text{NH}_2)_n$  are not available.<sup>9</sup> Some crystal structures are available for model amido<sup>17</sup> and imido complexes.<sup>8</sup> The diatomic TiN has been studied spectroscopically,<sup>18,19</sup> but the bond dissociation energy is known only approximately.<sup>20</sup> High-quality theoretical calculations have been carried out for the diatomics  $\text{TiCl}$ <sup>13</sup> and  $\text{TiN}$ <sup>13,21,22</sup> and for  $\text{TiCl}_4$ .<sup>23–25</sup> The heats of formation of  $\text{TiCl}_n$  and  $\text{Ti}(\text{NH}_2)_n$  have been estimated at the BAC-CCSD(T) level,<sup>26</sup> and some of the decomposition pathways for model titanium amido complexes have been examined.<sup>27</sup> The bonding in titanium amido and imido complexes has been discussed,<sup>27,28</sup> but little is available for the other potential intermediates. To contribute to the understanding of titanium nitride CVD processes, we have studied a number of precursors and intermediates by high-quality ab initio molecular orbital methods, as summarized in Figure 1. Specifically, we have used a modified version of the G2 level of theory<sup>29–31</sup> to calculate the structures, vibrational frequencies, atomization energies, heats of formation, and gas-phase entropies of  $\text{TiCl}_m(\text{NH}_2)_n$ ,  $0 \leq m + n \leq 4$ ,  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ ,  $0 \leq m + n \leq 2$ , and  $\text{TiCl}_m(\text{NH}_2)_n\text{N}$ ,  $0 \leq m + n \leq 1$ .

## Methods

Molecular orbital calculations were carried out with the GAUSSIAN 94<sup>32</sup> series of programs using a variety of basis

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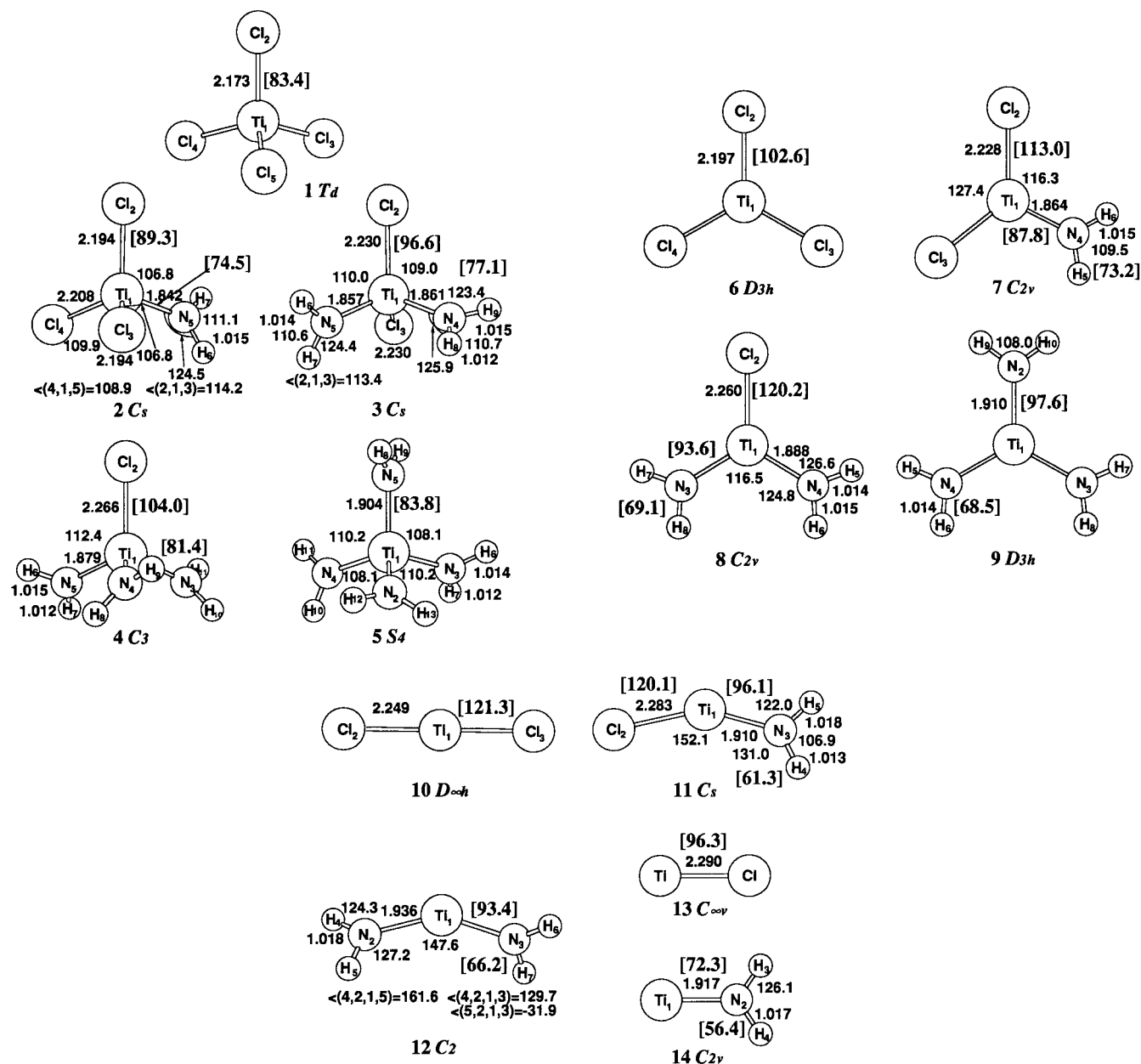
**Figure 1.** A general scheme for various gas-phase reactions that might participate the production of TiN films from  $\text{TiCl}_m$  and  $\text{Ti}(\text{NH}_2)_m$ ,  $0 < m \leq 4$  (calculated enthalpies of reaction at 0 K in kcal/mol).

sets of split valence quality or better, with multiple polarization and diffuse functions. Equilibrium geometries were optimized by the B3LYP density functional method<sup>33–35</sup> using the 6-311G(d) basis set<sup>36–38</sup> (for titanium, this corresponds to the Wachters–Hay basis set<sup>38</sup> augmented with an f-type Gaussian shell with an exponent of 0.690). Vibrational frequencies and zero-point energies were computed at the B3LYP/6-311G(d) level of theory. Thermal corrections to the energies were calculated by standard statistical thermodynamic methods<sup>39</sup> using the B3LYP frequencies. Since the B3LYP frequencies agree quite well with experimental values for a wide range of second- and third-period compounds,<sup>40</sup> the B3LYP/6-311G(d) frequencies were used without scaling. Correlated energies were calculated by fourth-order Møller–Plesset perturbation theory<sup>41</sup> (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations<sup>42</sup> (QCISD(T), frozen core) with the B3LYP optimized geometries. Atomization energies were computed by a modification of the G2 method based on the B3LYP geometries and frequencies.<sup>31</sup> The B3LYP/6-311G(d) optimized geometries and vibrational frequencies were used instead of the MP2/6-31G(d) geometries

and HF/6-31G(d) frequencies. The energy is computed in the usual fashion: the MP4/6-311G(d,p) energy is corrected for the effect of diffuse functions obtained at MP4/6-311+G(d,p), for the effect of higher polarization functions obtained at MP4/6-311G(2df,p), for the effect of electron correlation beyond fourth order obtained at QCISD(T)/6-311G(d,p), and for the inclusion of additional polarization functions at MP2/6-311+G(3df,2p). Higher level corrections (HLC) for deficiencies in the wave function are estimated empirically using the standard values.<sup>29</sup>

## Results and Discussion

The optimized geometries of the structures considered in the present work are shown in Figures 2–4. Total energies at the B3LYP/6-311G(d), QCISD(T)/6-311G(d,p), MP4SDTQ/6-311G(2df,p), and G2 levels are listed in Table S.1 of the Supporting Information, and the vibrational frequencies, zero-point energies, and moments of inertia are collected in Table S.2 of the Supporting Information. Heats of atomization, heats of formation, and entropies calculated at the modified G2 level of theory are listed in Table 1. Bond dissociation energies for Ti–Cl,



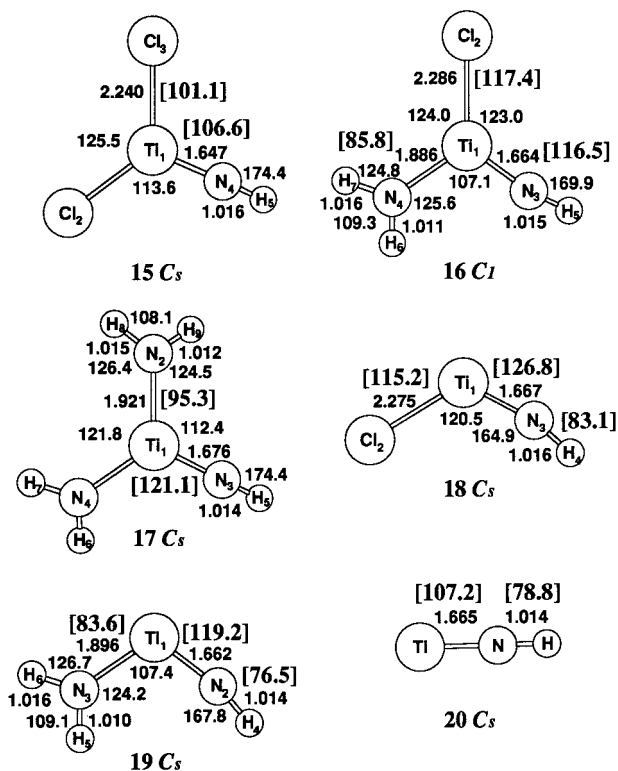
**Figure 2.** Equilibrium geometries (in Å and deg) for  $\text{TiCl}_m(\text{NH}_2)_n$ ,  $0 \leq m + n \leq 4$ , optimized at B3LYP/6-31G(d) level of theory. Bond dissociation energies (in kcal/mol) are in brackets.

$\text{Ti-NH}_2$ ,  $\text{Ti-NH}$ , and  $\text{TiN(H)-H}$ , and heats of reaction for addition–elimination and elimination reactions are given in Table 2.

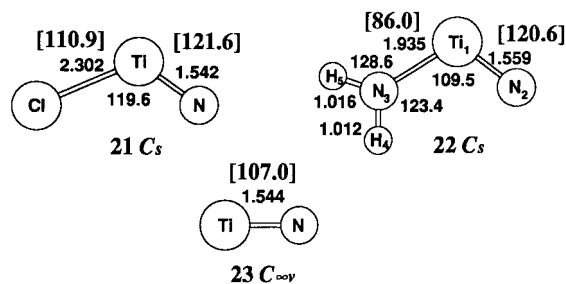
**$\text{TiCl}_{4-n}(\text{NH}_2)_n$ .** These titanium(IV) compounds are singlets with tetrahedral geometries. For  $\text{TiCl}_4$ , the calculated  $\text{Ti-Cl}$  bond length and vibrational frequencies are in excellent agreement with the experimental values (2.173 Å calc vs 2.170 Å expt;<sup>11</sup> 119, 143, 389, 501  $\text{cm}^{-1}$  calc vs 119, 139, 388, 499  $\text{cm}^{-1}$  expt<sup>10</sup>) and with previous calculations.<sup>23–26</sup> The calculated  $\text{Ti-N}$  bond lengths are good agreement experimental values in related monomeric titanium amido complexes (1.879 Å calc for  $\text{TiCl}(\text{NH}_2)_3$  vs 1.860–1.866 Å observed for  $\text{TiCl}(\text{NR}_2)_3$ ,  $\text{R} = \text{Me, Et}$ <sup>17</sup>). The amido groups are planar in both the calculations and the X-ray structures, indicating that the nitrogen  $p_\pi$  lone pairs participate in back-bonding to the empty d orbitals on titanium.<sup>28</sup> The calculated  $\text{Ti-Cl}$  bond lengths increase from 2.173 to 2.266 Å as the Cl's are replaced with  $\text{NH}_2$ 's. Normally bond lengthening is accompanied by a decrease in bond strength, but the calculated  $\text{Ti-Cl}$  bond strengths also increase, from 83

to 104 kcal/mol, as the Cl's are replaced with  $\text{NH}_2$ 's. A similar effect is seen in the  $\text{Ti-N}$  bonds: they lengthen and strengthen, from 1.842 Å and 75 kcal/mol in  $\text{TiCl}_3(\text{NH}_2)$  to 1.904 Å and 84 kcal/mol in  $\text{Ti}(\text{NH}_2)_4$ .

**$\text{TiCl}_{3-n}(\text{NH}_2)_n$ .** The calculations show that the tri-coordinated titanium(III) compounds are planar doublets with the unpaired electron in a  $d_{z^2}$  orbital. The titanium out-of-plane bending and the  $\text{NH}_2$  torsional modes occur at relatively low frequencies. The calculated vibrational frequencies in  $\text{TiCl}_3$  are in very good agreement with experiment for degenerate  $\text{T-Cl}$  stretching modes (499  $\text{cm}^{-1}$  calc vs 497  $\text{cm}^{-1}$  expt<sup>15,16</sup>) and support the estimates for the other modes used in the thermochemical analysis.<sup>14</sup> The  $\text{Ti-Cl}$  bonds are calculated to be nearly the same length but ca. 15 kcal/mol stronger than in the corresponding titanium(IV) compound with the same number of chlorines; likewise, the  $\text{Ti-N}$  bonds are ca. 10 kcal/mol stronger. This suggests stronger back-bonding in  $\text{Ti(III)}$  than in  $\text{Ti(IV)}$  complexes. The trends in the  $\text{Ti-Cl}$  and  $\text{Ti-N}$  bond



**Figure 3.** Equilibrium geometries (in Å and deg) for  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ ,  $0 \leq m + n \leq 2$ , optimized at B3LYP/6-31G(d) level of theory. Bond dissociation energies (in kcal/mol) are in brackets.



**Figure 4.** Equilibrium geometries (in Å and deg) for  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ ,  $0 \leq m + n \leq 1$ , optimized at B3LYP/6-31G(d) level of theory. Bond dissociation energies (in kcal/mol) are in brackets.

lengths and strengths are comparable to the tetracoordinated species—both lengthen and strengthen as the Cl's are replaced with  $\text{NH}_2$ 's.

**$\text{TiCl}_{2-n}(\text{NH}_2)_n$ .** In accord with experiment,<sup>15,16</sup>  $\text{TiCl}_2$  is linear; however, the calculated bending frequencies are very small ( $30 \text{ cm}^{-1}$ ). The calculated antisymmetric Ti–Cl stretching frequency agrees well with the observed value ( $475 \text{ cm}^{-1}$  calc vs  $486 \text{ cm}^{-1}$  expt<sup>15,16</sup>). Titanium dichloride is a triplet with the two unpaired electrons in  $\sigma$  and  $\delta$  orbitals;  $\text{TiClNH}_2$  and  $\text{Ti}(\text{NH}_2)_2$  have similar orbital occupancies, but are bent by ca.  $30^\circ$  due to Jahn–Teller effects. The  $\text{NH}_2$  group is planar in  $\text{TiClNH}_2$  and lies in the molecular plane. In  $\text{Ti}(\text{NH}_2)_2$  the  $\text{NH}_2$  groups are nearly planar but are twisted out of the N–Ti–N plane. The Ti–Cl and Ti–N bonds are slightly longer than in their titanium(III) counterparts and show smaller changes in bond strength as Cl is replaced by  $\text{NH}_2$ .

**TiCl and  $\text{TiNH}_2$ .** Both theory<sup>13</sup> and experiment<sup>12</sup> indicate that TiCl has a  $^4\Phi$  ground state, with the three unpaired electrons occupying  $\sigma$ ,  $\pi$ , and  $\delta$  orbitals. The  $^4\Phi$  state is calculated to be  $5.5 \text{ kcal/mol}$  lower than the  $^4\Sigma^-$  state at the CCSD(T)/6-311++G(2d2f) level of theory;<sup>13</sup> the same result is obtained at

**TABLE 1: States, Symmetries, Atomization Energies, Heats of Formation, and Entropies for  $\text{TiCl}_m(\text{NH}_2)_n$ ,  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ , and  $\text{TiCl}_m(\text{NH}_2)_n\text{N}$  Computed at the G2 Level of Theory<sup>a</sup>**

	structure	state	sym	heat of atomization	heat of formation	entropy
1	$\text{TiCl}_4$	$^1\text{A}_1$	$T_d$	403.6	−176.7	83.9
2	$\text{TiCl}_3\text{NH}_2$	$^1\text{A}'$	$C_s$	564.6	−151.9	93.4
3	$\text{TiCl}_2(\text{NH}_2)_2$	$^1\text{A}'$	$C_s$	722.3	−124.2	90.7
4	$\text{TiCl}(\text{NH}_2)_3$	$^1\text{A}'$	$C_s$	877.0	−93.4	90.0
5	$\text{Ti}(\text{NH}_2)_4$	$^1\text{A}$	$S_4$	1026.7	−57.1	93.0
6	$\text{TiCl}_3$	$^2\text{A}_1'$	$D_{3h}$	320.2	−121.7	80.6
7	$\text{TiCl}_2\text{NH}_2$	$^2\text{A}_1$	$C_{2v}$	475.3	−91.1	84.6
8	$\text{TiCl}(\text{NH}_2)_2$	$^2\text{A}_1$	$C_{2v}$	625.8	−55.7	86.5
9	$\text{Ti}(\text{NH}_2)_3$	$^2\text{A}_1'$	$D_{3h}$	773.0	−16.9	91.1
10	$\text{TiCl}_2$	$^3\Delta$	$D_{\infty h}$	217.6	−47.6	63.8
11	$\text{TiCl}(\text{NH}_2)$	$^3\text{A}'$	$C_s$	362.3	−6.7	75.0
12	$\text{Ti}(\text{NH}_2)_2$	$^3\text{A}$	$C_2$	505.5	36.0	76.7
13	TiCl	$^4\Phi$	$C_{\infty v}$	96.3	45.2	59.2
14	$\text{TiNH}_2$	$^4\text{B}_1$	$C_{2v}$	242.2	85.0	61.1
15	$\text{TiCl}_2(\text{NH})$	$^1\text{A}'$	$C_s$	402.1	−69.0	81.0
16	$\text{TiCl}(\text{NH}_2)\text{NH}$	$^1\text{A}$	$C_1$	556.7	−38.1	80.4
17	$\text{Ti}(\text{NH}_2)_2\text{NH}$	$^1\text{A}'$	$C_s$	704.5	−0.2	79.5
18	$\text{TiCl}(\text{NH})$	$^2\text{A}'$	$C_s$	301.0	3.6	70.8
19	$\text{Ti}(\text{NH}_2)\text{NH}$	$^2\text{A}'$	$C_s$	439.3	50.8	70.0
20	$\text{TiNH}$	$^3\Delta$	$C_{\infty v}$	185.8	90.6	47.0
21	TiClN	$^1\text{A}'$	$C_s$	217.9	35.8	67.3
22	$\text{Ti}(\text{NH}_2)\text{N}$	$^1\text{A}'$	$C_s$	362.8	76.3	66.1
23	TiN	$^2\Sigma$	$C_{\infty v}$	107.0	118.3	53.1

<sup>a</sup> G2 atomization energies in kcal/mol at 0 K, heats of formation in kcal/mol at 298 K, entropies in cal/deg mol at 298 K.

the G2 level used in the present work. The calculated bond length and vibrational frequency at the B3LYP/6-311G(d) level are in good agreement with experiment<sup>12</sup> ( $2.290 \text{ \AA}$  calc vs  $2.265 \text{ \AA}$  expt;  $387 \text{ cm}^{-1}$  calc vs  $404 \text{ cm}^{-1}$  expt) and with previous calculations.<sup>13</sup> The ground-state electronic structure of  $\text{TiNH}_2$  is  $^4\text{B}_1$  and corresponds to the same orbital occupancy as TiCl.

**$\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ .** The imido compounds have a Ti–N double bond with a length of  $1.65$ – $1.68 \text{ \AA}$  and a nearly linear Ti–N–H linkage. Similar geometries have been obtained for related imido complexes.<sup>27</sup> This is in excellent agreement with the X-ray structure of a related imido complex,  $\text{TiCl}_2\text{N}^t\text{Bu}$  ( $\text{OPPh}_3$ )<sub>2</sub> ( $R(\text{Ti}-\text{N}) = 1.672 \text{ \AA}$  and  $\text{Ti}-\text{N}-\text{C} = 174^\circ$ ).<sup>8</sup> The Ti–N double bond in these imido complexes is calculated to be ca.  $0.2 \text{ \AA}$  shorter and ca.  $40 \text{ kcal/mol}$  stronger than the Ti–N single bond in the corresponding  $\text{TiCl}_m(\text{NH}_2)_{n+1}$  complexes. The nature of the imido bond in  $\text{TiCl}_2\text{NH}$  and related complexes has been discussed previously.<sup>27</sup> The  $\text{TiCl}_{2-n}(\text{NH}_2)_n\text{NH}$  complexes are singlets and somewhat pyramidal (sum of the valence angles around titanium =  $345$ – $355^\circ$ ); as in the singly bonded species, the  $\text{NH}_2$  groups are nearly planar.  $\text{TiClNH}$  and  $\text{Ti}(\text{NH}_2)\text{NH}$  are bent and doublets with the unpaired electron in the plane of the heavy atoms;  $\text{TiNH}$  is a linear triplet with the unpaired electrons in  $\sigma$  and  $\delta$  orbitals.

**TiClN,  $\text{Ti}(\text{NH}_2)\text{N}$ , and TiN.** The electronic structure of TiN has been studied by Harrison<sup>21</sup> and is consistent with a triple bond. The  $\text{Ti}\equiv\text{N}$  triple bonds in these structures are  $0.1 \text{ \AA}$  shorter but not significantly stronger than the double bond in the corresponding  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$  complexes. However, in a fair comparison, cleavage of the triple bond in TiClN,  $\text{TiNH}_2\text{N}$ , and TiN would lead to excited states of TiCl,  $\text{TiNH}_2$ , and Ti. If these excited states were used in the computation of the bond strengths, the triple bonds would be, as expected, stronger than the double bonds. TiClN and  $\text{Ti}(\text{NH}_2)\text{N}$  are bent singlets. The ground state for TiN is  $^2\Sigma$ , and the calculated bond length and vibrational frequency at the B3LYP/6-311G(d) level are in fair agreement with experiment<sup>18,19</sup> ( $1.544 \text{ \AA}$  calc vs  $1.58 \text{ \AA}$  expt;

**TABLE 2: Energetics (in kcal/mol) for Bond Dissociations, Addition–Elimination Reactions, and Elimination for Reactions of  $\text{TiCl}_m(\text{NH}_2)_n$ ,  $\text{TiCl}_m(\text{NH}_2)_n\text{NH}$ , and  $\text{TiCl}_m(\text{NH}_2)_n\text{N}$  at the G2 Level of Theory at 0 K**

structure	bond dissociation				addn–elim	elim	
	Ti–Cl	Ti–NH <sub>2</sub>	Ti–NH	N–H	(NH <sub>3</sub> , HCl)	HCl	NH <sub>3</sub>
1	TiCl <sub>4</sub>	83.4			12.2		
2	TiCl <sub>3</sub> (NH <sub>2</sub> )	89.3	74.5		15.5	59.9	
3	TiCl <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub>	96.6	77.1		18.6	63.1	44.4
4	TiCl(NH <sub>2</sub> ) <sub>3</sub>	104.0	81.4		23.6	70.0	44.5
5	Ti(NH <sub>2</sub> ) <sub>4</sub>		83.8				46.4
6	TiCl <sub>3</sub>	102.6			18.2		
7	TiCl <sub>2</sub> (NH <sub>2</sub> )	113.0	87.8		22.8	71.8	
8	TiCl(NH <sub>2</sub> ) <sub>2</sub>	120.2	93.6		26.0	83.9	48.9
9	Ti(NH <sub>2</sub> ) <sub>3</sub>		97.6				57.9
10	TiCl <sub>2</sub>	121.3			28.6		
11	TiCl(NH <sub>2</sub> )	120.1	96.1		30.0	73.9	
12	Ti(NH <sub>2</sub> ) <sub>2</sub>		93.4				43.9
13	TiCl	96.3			27.4		
14	Ti(NH <sub>2</sub> )		72.3				
15	TiCl <sub>2</sub> (NH)	101.1		106.6	18.7	81.7	
16	TiCl(NH <sub>2</sub> )NH	117.4	85.8	116.5	25.5	91.3	63.0
17	Ti(NH <sub>2</sub> ) <sub>2</sub> NH		95.3	121.1			65.8
18	TiCl(NH)	115.2		126.8	34.9	91.4	
19	Ti(NH <sub>2</sub> )NH		83.6	119.2			56.5
20	TiNH			107.9			
21	TiClN	110.9		121.6 <sup>a</sup>	28.3		
22	Ti(NH <sub>2</sub> )N		86.0	120.6 <sup>a</sup>			
23	TiN			107.0 <sup>a</sup>			

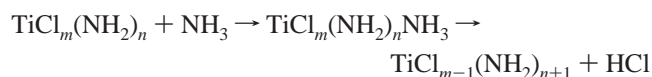
<sup>a</sup> Ti–N dissociation rather than Ti–NH. Other useful bond dissociation energies calculated at the same level include: NH<sub>3</sub> → NH<sub>2</sub> + H, 105.9; NH<sub>2</sub> → NH + H, 92.0; NH → N + H, 77.9; Cl<sub>2</sub> → 2 Cl, 55.3; HCl → H + Cl, 102.6; H<sub>2</sub> → 2 H, 104.1 kcal/mol.

1177 cm<sup>-1</sup> calc vs 1039 cm<sup>-1</sup> expt) and with previous calculations.<sup>21,22</sup>

**Thermochemistry.** Reliable bond energies and heats of formation for potential intermediates are an essential first step toward the understanding of the titanium nitride CVD process. Heats of formation were obtained by combining the calculated atomization enthalpies at 298 K with the experimental heats of formation for the atoms and are listed in Table 1. The titanium chlorides are well characterized and can be used to calibrate the calculated energetics. The computed heats of formation for TiCl, TiCl<sub>2</sub>, TiCl<sub>3</sub>, and TiCl<sub>4</sub> are 45.2, -47.6, -121.7, and -176.7 kcal/mol, compared to experimental value of 45.3 ± 2.5, -47.0 ± 3.5, -118.9 ± 4.3, and -182.4 ± 0.9 kcal/mol,<sup>9,14</sup> respectively. This is equivalent to an error of ca. ±2 kcal/mol per bond. While this error is somewhat larger than for compounds of second- and third-period elements,<sup>29–31</sup> it is quite satisfactory for the reactive intermediates considered here. To reduce the error, one would probably need to use larger basis sets, 3s,3p correlation in Ti, and correct for spin–orbit effects.

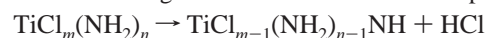
The calculated bond dissociation energies and heats of reaction for various processes are presented in Table 2. For TiCl<sub>n</sub> and Ti(NH<sub>2</sub>)<sub>n</sub>, Allendorf et al.<sup>26</sup> found similar trends at the BAC-CCSD(T) level: the strongest Ti–Cl bond is in TiCl<sub>2</sub> and the strongest Ti–N single bond is in Ti(NH<sub>2</sub>)<sub>3</sub>. For the mixed TiCl<sub>m</sub>(NH<sub>2</sub>)<sub>n</sub> and TiCl<sub>m</sub>(NH<sub>2</sub>)<sub>n</sub>NH compounds, we find the Ti–Cl bonds are 15–30 kcal/mol stronger than the Ti–NH<sub>2</sub> single bonds in the same molecule. The Ti–N multiple bonds are the strongest bonds in each molecule. An N–H bond can be the weakest bond in a complex if breaking this bond yields a Ti–N multiple bond in the product.

In addition to bond breaking, the CVD process can include ligand exchange and elimination reactions. Ligand exchange reactions for these titanium complexes can occur by an addition–elimination mechanism.



Replacing Cl by NH<sub>2</sub> is endothermic by ca. 15–35 kcal/mol, and the process becomes more difficult as more chlorines are replaced. Experiments show that amido ligand exchange occurs readily under CVD conditions and plays a significant role in the CVD process.<sup>4–8</sup>

Elimination reactions offer a lower energy pathway than bond dissociation for the degradation of the titanium complexes.



The heats of reaction for the elimination of NH<sub>3</sub> are endothermic, but are 20–30 kcal/mol lower than those for the elimination of HCl. This reflects the difference in the Ti–Cl and Ti–N bond strengths. Cundari et al.<sup>27</sup> have found similar trends in TiH<sub>2</sub>XNH<sub>2</sub> complexes (X = Cl, NH<sub>2</sub>) and calculate barriers of 35–50 kcal/mol for HX elimination.

Figure 1 summarizes the heats of reaction for some of the potential reactions in titanium nitride deposition. It should be kept in mind that reactions can have a considerable activation energy above the heat of the reaction. CVD from Ti(NR<sub>2</sub>)<sub>4</sub> occurs at lower temperatures than that from TiCl<sub>4</sub>. The present calculations support this since they show that Cl → NH<sub>2</sub> ligand exchange is endothermic and degradation by NH<sub>3</sub> elimination is less endothermic than HCl elimination. The present calculations also support imido complexes, TiCl<sub>2–n</sub>(NH<sub>2</sub>)<sub>n</sub>NH, as intermediates in the degradation since the ligand exchange and elimination reactions that lead to the imido complexes are less endothermic than simple bond dissociation. The calculations also suggest that titanium nitrides, RTiN, may be potential intermediates. An energetic bottleneck in processes that start with titanium(IV) complexes is the removal of the Cl or NH<sub>2</sub> from RTiN. If titanium(III) complexes were used as precursors, this step could be circumvented.

## Conclusions

The structures of 23 potential intermediates in titanium nitride CVD have been optimized at the B3LYP/6-311G(d) level.

Titanium (I), -(II), -(III), and -(IV) complexes have been considered, and a variety of structures with Ti–N single, double, and triple bonds have been found. The energetics of these structures were calculated by a modified G2 procedure that predicts average bond dissociation energies to within  $\pm 2$  kcal/mol. Bond dissociation reactions are calculated to be rather endothermic; however, ligand exchange and elimination reactions are fairly low-energy steps. The calculations support some of the observed trends in reactivity. In addition to the monomeric complexes and gas-phase reactions considered in the present work, dimeric species and surface reactions are probably needed to formulate a more complete picture of the titanium nitride CVD process.

**Acknowledgment.** H.B.S. would like to thank Jack Simons (U. of Utah) for his generous hospitality during the preparation of this paper. This work was supported by a grant from the National Science Foundation (CHE 94-00678).

**Supporting Information Available:** For the species considered in this paper, Table S.1 lists the total energies at the B3LYP/6-311G(d), QGISD(T)/6-311G(d), MP4SDTQ/6-311G-(2df,p), and G2 levels of theory and Table S.2 contains the zero-point energies, thermal correction to the energies, moment of inertia, and the harmonic vibrational frequencies (6 pages). See any current masthead page for ordering information.

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