The chemical vapor deposition (CVD) of titanium nitride can be carried out with TiCl₄ or Ti(NR₂)₄ and NH₃. The present study uses molecular orbital methods to examine complexes of NH₃ with TiCl₄ and Ti(NH₂)₄ and the subsequent reaction paths for ligand exchange and elimination reactions which may occur in the gas phase. Geometry optimizations were carried out at the B3LYP/6-311G(d) level of density functional theory, and energies were calculated using a variety of levels of theory, up to G2 for systems with five or fewer heavy atoms. The TiCl₄-NH₃, TiCl₄(NH₂)₂, and Ti(NH₂)₄-NH₃ complexes are bound by 14.9, 30.9, and 7.9 kcal/mol, respectively. The barrier for TiCl₄ + NH₃ → TiCl₃NH₂ + HCl is 18.4 kcal/mol and is lowered by 23.1 kcal/mol with the introduction of a second NH₃. The present study uses molecular orbital methods to examine complexes of NH₃ with TiCl₄ and Ti(NH₂)₄ and the subsequent reaction paths for ligand exchange and elimination reactions which may occur in the gas phase. Geometry optimizations were carried out at the B3LYP/6-311G(d) level of density functional theory, and energies were calculated using a variety of levels of theory, up to G2 for systems with five or fewer heavy atoms. The TiCl₄-NH₃, TiCl₄(NH₂)₂, and Ti(NH₂)₄-NH₃ complexes are bound by 14.9, 30.9, and 7.9 kcal/mol, respectively. The barrier for TiCl₄ + NH₃ → TiCl₃NH₂ + HCl is 18.4 kcal/mol and is lowered by 23.1 kcal/mol with the introduction of a second NH₃. The computed barrier height of 8.4 kcal/mol for the Ti(NH₂)₄ + NH₃ ligand exchange reaction is in very good agreement with the experimental activation energy of 8 kcal/mol for Ti(NMe₂)₄ + NH₃ ligand exchange. The barrier for formation of Ti(NH₂)₂NH by elimination from Ti(NH₂)₄ is 33.5 kcal/mol and is reduced by 10 kcal/mol when assisted by an additional NH₃. However, examination of the free energies at CVD conditions indicates that the reactions without catalysis by an extra NH₃ are favored. Further elimination of NH₃ from Ti(NH₂)₂NH can yield a diimido product, Ti(NH₂)₂N, but the barriers and heats of reaction are sufficiently high to make these reactions unlikely in the gas phase during the CVD process.

Molecular Orbital Studies of Titanium Nitride Chemical Vapor Deposition: Gas Phase Complex Formation, Ligand Exchange, and Elimination Reactions

Jason B. Cross and H. Bernhard Schlegel*

Department of Chemistry, Wayne State University, Detroit, Michigan, 48202

Received February 8, 2000. Revised Manuscript Received June 6, 2000

The chemical vapor deposition (CVD) of titanium nitride can be carried out with TiCl₄ or Ti(NR₂)₄ and NH₃. The present study uses molecular orbital methods to examine complexes of NH₃ with TiCl₄ and Ti(NH₂)₄ and the subsequent reaction paths for ligand exchange and elimination reactions which may occur in the gas phase. Geometry optimizations were carried out at the B3LYP/6-311G(d) level of density functional theory, and energies were calculated using a variety of levels of theory, up to G2 for systems with five or fewer heavy atoms. The TiCl₄-NH₃, TiCl₄(NH₂)₂, and Ti(NH₂)₄-NH₃ complexes are bound by 14.9, 30.9, and 7.9 kcal/mol, respectively. The barrier for TiCl₄ + NH₃ → TiCl₃NH₂ + HCl is 18.4 kcal/mol and is lowered by 23.1 kcal/mol with the introduction of a second NH₃. The computed barrier height of 8.4 kcal/mol for the Ti(NH₂)₄ + NH₃ ligand exchange reaction is in very good agreement with the experimental activation energy of 8 kcal/mol for Ti(NMe₂)₄ + NH₃ ligand exchange. The barrier for formation of Ti(NH₂)₂NH by elimination from Ti(NH₂)₄ is 33.5 kcal/mol and is reduced by 10 kcal/mol when assisted by an additional NH₃. However, examination of the free energies at CVD conditions indicates that the reactions without catalysis by an extra NH₃ are favored. Further elimination of NH₃ from Ti(NH₂)₂NH can yield a diimido product, Ti(NH₂)₂N, but the barriers and heats of reaction are sufficiently high to make these reactions unlikely in the gas phase during the CVD process.

Introduction

Titanium nitride thin films have a variety of properties, such as extreme hardness, high chemical resistivity, good electrical conductivity, and optical properties similar to gold, which make them useful for a number of industrial and commercial applications, including wear-resistant coatings for tools, barrier materials and conductive coatings for microelectronics, and decorative coatings.¹–³ Chemical vapor deposition (CVD) is the preferred method for preparing thin films for semiconductor applications, because it produces good conformal coatings which are needed for submicron devices.² There are a number of methods for preparing Ti–N using CVD.⁴–¹¹ One of the primary challenges is to find a suitable low-temperature process for producing films that have the desired properties and are free of impurities.

High-quality Ti–N films can be deposited at high temperatures (900–1000 °C) using TiCl₄, N₂, and H₂.⁵,⁶ The temperature can be significantly reduced (500–700 °C) if ammonia is used as the nitrogen source:⁷

\[ \text{TiCl}_4 + \frac{3}{2}\text{NH}_3 \rightarrow \text{TiN} + 4\text{HCl} + \frac{3}{2}\text{N}_2 \]  (1)

However, if the temperature is too low, the films contain a mixture of TiN and TiNCl.⁸ Ti(IV) amido precursors, Ti(NR₂)₄, have been used to avoid chlorine impurities in the thin films.⁹,¹⁰,¹²,¹³ Deposition can then proceed at lower temperatures, but contamination from titanium carbide and organic carbon becomes a problem. Dubois¹⁴ has found evidence of Ti–N–C metallocycles that could be the source of the carbon contamination. These impurities can be overcome by using an excess of ammonia, resulting in high-quality films at relatively low temperatures (300–400 °C):¹¹,¹⁵,¹⁶,¹⁷

Titanium Nitride Chemical Vapor Deposition

\[ \text{Ti(NR}_2\text{)}_4 + \text{excess NH}_3 \rightarrow \text{TiN} + \text{volatile organics} \]

(2)

In low-pressure CVD of TiN films, reactions occur almost exclusively at the surface.\(^{17}\) However, gas-phase reactions are key components of atmospheric pressure TiN CVD.\(^{5}\) Through a combination of experimental and computational work, some of the details of this gas-phase chemistry are beginning to emerge. Relatively little is known about the thermochemistry of potential intermediates in Ti–N CVD. To fill this gap, we have calculated the gas-phase heats of formation of TiCl\(_4\), TiCl\(_3\)(NH\(_2\))\(_n\), TiCl\(_3\)(NH\(_2\))\(_n\)NH, and TiCl\(_4\)(NH\(_2\))\(_n\)N at the G2 level of theory.\(^{18}\) The results agree well with recent experimental values for TiCl\(_4\),\(^{19}\) and should yield theoretical bond dissociation energies accurate to \(\pm 2\) kcal/mol for the potential intermediates in titanium nitride CVD.

The reaction of NH\(_3\) with Ti complexes appears to be an essential first step for both process 1 and 2. Dubois and co-workers\(^{6,20}\) have shown that the nitrogen in TiN films produced from amido complexes is derived exclusively from NH\(_3\). Ammonia readily forms complexes with TiCl\(_4\) and with TiCl\(_2\)(NR\(_2\))\(_2\).\(^{21–23}\) Siodmiak, Frenking, and Korkin\(^{24}\) have studied ammonolysis of TiCl\(_4\) at the B3LYP, MP2, and CCSD(T) levels of theory using pseudopotentials and a split-valence basis set. The binding energy of TiCl\(_4\) + NH\(_3\) has been calculated to be ca. 12–24 kcal/mol,\(^{24,25}\) and the replacement of Cl by NH\(_3\) is computed to be endothermic by 10–20 kcal/mol per Cl.\(^{18,24}\) Experimentally, the reaction between Ti(NR\(_2\))\(_4\) and NH\(_3\) occurs readily,\(^{26–28}\) and activation energies of 8 and 12 kcal/mol have been measured for R = Me and Et, respectively. This reaction is inhibited by HNR\(_2\) and may be the rate-limiting step when CVD is controlled by gas-phase kinetics.\(^{26–28}\) Dubois\(^{5}\) has demonstrated that the hydrogen in HNR\(_2\) comes from the added ammonia.

The next step in the CVD process must be the elimination of either HCl or NH\(_3\) and can happen in the gas phase or on the surface. Gordon and co-workers\(^{5,13,34}\) have suggested imido complexes, TiX\(_2\) (X = NH, NH\(_2\)), are important gas-phase intermediates. Evidence for this has been provided by Winter and co-workers, who have produced high-quality TiN films using single source titanium amido precursors and have mass spectral evidence of titanium imido complexes as intermediates in the CVD.\(^{23,29}\) Also, by analyzing the kinetics of CVD, Wellier found that the reversible transamination reaction is followed by an irreversible reaction, most likely an elimination to form an imido complex.\(^{26–28}\) Dubois\(^{4}\) has evidence for the formation of large oligomeric clusters that decompose on the surface. Cundari et al.\(^{30–33}\) have calculated a number of decomposition reactions of model compounds for CVD intermediates. Using a modest level of theory, they found that reactions forming imido complexes from TiH\(_2\)(NH\(_2\))X had barriers of 30–35 kcal/mol for amine elimination and 50 kcal/mol for HCl elimination.

Ultimately, the Ti(IV) in the precursors must be reduced to Ti(III) in the film. Simple bond cleavage in the gas phase can probably be ruled out, since the bond dissociation energies are too high (75–120 kcal/mol calculated for Ti(IV) chloro, amido, imido, and nitrido compounds\(^{30}\)). No viable gas-phase mechanisms are apparent for other products of reduction such as N\(_2\). Most likely the reduction occurs at the surface, where reactive intermediates and transition states can be more readily stabilized.

In this paper we use computational methods to explore the initial gas-phase reactions of TiCl\(_4\) and Ti(NH\(_3\))\(_4\) with NH\(_3\) shown in Figures 1 and 2. The more extensive set of reactions examined and the significantly larger basis sets and higher levels of theory used in the present work should provide a more accurate description of gas-phase elimination reactions of the archetypal intermediates TiCl\(_3\)NH\(_2\) and Ti(NH\(_3\))\(_4\). These may also serve as models for nitride CVD processes for early transition metals other than titanium.\(^{33,34}\)

Method

Molecular orbital calculations were carried out using the GAUSSIAN 98\(^{35}\) series of programs. Equilibrium geometries were optimized by the B3LYP density functional method\(^{36–38}\) using the 6-311G(d) basis set.\(^{39–43}\)

For titanium, this corresponds to the 14s,9p,5d Wachters–Hay basis set\textsuperscript{41–43} contracted to 9s,5p,3d and augmented with an f-type Gaussian shell with an exponent of 0.690. Vibrational frequencies were computed at this level of theory and were used without scaling since the B3LYP frequencies agree quite well with experimental values for a wide range of second and third period compounds.\textsuperscript{44} (However, the zero point energies were scaled by 0.9826, as was done in our previous paper.\textsuperscript{18}) Thermal corrections to the energies were calculated by standard statistical thermodynamic methods\textsuperscript{45} using the unscaled B3LYP frequencies. As in our previous work,\textsuperscript{18} accurate energy differences were calculated using a modified G2 approach.\textsuperscript{46–49} 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. Correlated energies were calculated by fourth-order Møller–Plesset perturbation theory\textsuperscript{50,51} (MP4SDTQ, frozen core) and by quadratic configuration interaction with perturbative correction for triple excitations\textsuperscript{52} (QCISD(T), frozen core) using the B3LYP geometries. 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). (For titanium, the 6-311+G(3df,2p) basis corresponds to the Wachters–Hay basis set\textsuperscript{41,42} augmented with three sets of f functions and one set of g functions.)

For larger structures with six and seven heavy atoms (i.e., systems involving TiCl\textsubscript{4}N\textsubscript{3}H, TiCl\textsubscript{4}(N\textsubscript{3}H\textsubscript{3})\textsubscript{2} and Ti-(N\textsubscript{3}H\textsubscript{3})\textsubscript{2}+NH\textsubscript{3}), the G2 method was too costly, and energy differences were calculated at the B3LYP/6-311G(d) geometries, B3LYP/6-311+G(3df,2p), and MP2/6-311+G(3df,2p) levels of theory. When compared to the G2 level, B3LYP/6-311+G(3df,2p) performs significantly better than MP2/6-311+G(3df,2p) for heats of reaction [e.g., for TiCl\textsubscript{3}NH\textsubscript{2}→TiCl\textsubscript{2}NH+HCl (C9→C12): 59.9, 63.1,

\begin{thebibliography}{99}
\bibitem{44} Scott, A. P.; Radom, L. J. Phys. Chem. \textbf{1996}, 100, 16502–16513.
\end{thebibliography}
and 52.0 kcal/mol for G2, B3LYP, and MP2, respectively; for Ti(NH$_2$)$_4$ → Ti(NH$_2$)$_2$NH + NH$_3$ (C13 → C20): 46.4, 43.8, and 35.7 kcal/mol for G2, B3LYP, and MP2, respectively). Similarly, barrier heights at the B3LYP/6-311+G(3df,2p) level compare better with the G2 results [e.g., for TiCl$_3$NH$_2$ → TiCl$_2$NH + HCl (C9 → TS10): 44.7, 50.7, and 36.0 kcal/mol for G2, B3LYP, and MP2, respectively; for Ti(NH$_2$)$_4$ → Ti(NH$_2$)$_2$NH + NH$_3$ (C13 → TS18): 35.5, 34.9, and 29.6 kcal/mol for G2, B3LYP, and MP2, respectively]. Thus, the barriers for TiCl$_4$NH$_3$ → TiCl$_3$NH$_2$NH$_3$ (C2 → TS7) and Ti(NH$_2$)$_2$NH + NH$_3$ → Ti(NH$_2$)$_3$NH + NH$_3$ (C14 → TS15) were calculated at the B3LYP/6-311+G(3df,2p) level.

Unfortunately, B3LYP/6-311+G(3df,2p) underestimates NH$_3$ binding energies by 6–8 kcal/mol. Similar trends were observed by Frenking and co-workers. The MP2/6-311+G(3df,2p) and B3LYP/6-311G(d) results are in better agreement with G2 [e.g., for Ti(NH$_2$)$_2$NH + NH$_3$ (C20 → C19): 33.8, 33.9, 31.3, and 26.9 kcal/mol for G2, MP2/6-311+G(3df,2p), B3LYP/6-311G(d), and B3LYP/6-311+G(3df,2p), respectively]. Therefore, the MP2/6-311+G(3df,2p) values have been used for the NH$_3$ complexation energies for TiCl$_4$NH$_3$ (C1 → C2), TiCl$_3$NH$_2$NH$_3$ (C9 → C8), and Ti(NH$_2$)$_2$NH + NH$_3$ (C13 → C14).

For the seven heavy atom systems, the 6-311+G(3df,-2p) basis was too costly. The energy differences were calculated at B3LYP/6-311G(d), since this level of theory provided satisfactory NH$_3$ binding energies and barrier heights when compared to the G2 values. Specifically, the energetics for C2 → C4, C2 → C3 → TS5 → C6 and C13 → C14 → TS16 and C19 → C17 were calculated at B3LYP/6-311G(d).

Results and Discussion

Structures derived from reaction of TiCl$_4$ with NH$_3$ are found in Figure 1; relative energies are plotted in Figure 3. Structures derived from reaction of Ti(NH$_2$)$_4$ with NH$_3$ are found in Figure 2; relative energies are plotted in Figure 4. Transition-state structures are labeled with TS and complexes representing minima are labeled with C. Computed enthalpies, entropies, and free energies are listed in Table 1.

1. Complexation of Ammonia with Ti(IV) Compounds. The initial gas-phase reactions for processes
that this bond is composed of the nitrogen p-orbital (NH₂)₄, 1.904 Å. (Optimization at B3LYP/6-311G(d).

Energy profile for reaction paths starting with Ti(NH₂)₄ ᵃ. Relative enthalpies at 0 K in kcal/mol are included in parentheses.

1 and 2 appear to be the formation of complexes between TiCl₄ (C1) or Ti(NR₂)₄ (C13) and NH₃. The formation of the TiCl₄-NH₃ complex (C2) yields a trigonal-bipyramidal C₃ᵥ structure, with NH₃ occupying an axial position with respect to the Cl atoms. The Ti-Cl bond lengths increase from 2.173 Å in TiCl₄ to 2.222 and 2.213 Å for equatorial and axial positions, respectively, in TiCl₄-NH₃. As expected for a dative bond, the Ti-N bond length, 2.304 Å, is considerably longer than in Ti(NH₂)₄, 1.904 Å. (Optimization at B3LYP/6-311+G(3df,2p); C2 does not change these results significantly.) Similar geometry and trends were observed by Frenking and co-workers. Inspection of the molecular orbitals reveals that this bond is composed of the nitrogen p-orbital overlapping with the titanium d-orbital.

For the amido species, a model compound, Ti(NH₂)₄, was studied instead of Ti(NR₂)₄ in order to keep the cost of the calculations manageable. The formation of the

<table>
<thead>
<tr>
<th>C1</th>
<th>TiCl₄</th>
<th>ΔH₂₉₈ kcal/mol</th>
<th>entropy°C</th>
<th>rel enthalpy°C</th>
<th>rel free energy°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>TiCl₄-NH₃</td>
<td>-182.4</td>
<td>83.9</td>
<td>0.0</td>
<td>0.0-0.0</td>
</tr>
<tr>
<td>C3</td>
<td>trans-TiCl₄(NH₂)₃</td>
<td>-214.9</td>
<td>112.2</td>
<td>-32.5</td>
<td>55.5-97.6</td>
</tr>
<tr>
<td>C4</td>
<td>trans-TiCl₄(NH₂)₃</td>
<td>-212.3</td>
<td>121.3</td>
<td>-29.9</td>
<td>49.6-95.1</td>
</tr>
<tr>
<td>TS5</td>
<td>TiCl₄(NH₂)₄H⁺</td>
<td>-189.1</td>
<td>109.8</td>
<td>-6.7</td>
<td>83.7-64.6</td>
</tr>
<tr>
<td>TS7</td>
<td>TiCl₄(NH₂)₄Cl⁻</td>
<td>-165.0</td>
<td>101.0</td>
<td>-0.5</td>
<td>38.3-28.8</td>
</tr>
<tr>
<td>TS8</td>
<td>TiCl₄(NH₂)₃H⁺</td>
<td>-172.2</td>
<td>109.9</td>
<td>-10.8</td>
<td>42.7-33.2</td>
</tr>
<tr>
<td>TS9</td>
<td>TiCl₄(NH₂)₃H⁻</td>
<td>-169.9</td>
<td>93.4</td>
<td>12.5</td>
<td>0.9-0.9</td>
</tr>
<tr>
<td>TS10</td>
<td>TiCl₄(NH₂)H⁺</td>
<td>-125.2</td>
<td>92.3</td>
<td>57.2</td>
<td>40.4-40.4</td>
</tr>
<tr>
<td>TS11</td>
<td>TiCl₄(NH₂)H⁻</td>
<td>-125.2</td>
<td>95.8</td>
<td>57.2</td>
<td>43.1-43.1</td>
</tr>
<tr>
<td>TS12</td>
<td>TiCl₄NH⁺</td>
<td>-109.3</td>
<td>81.0</td>
<td>73.1</td>
<td>12.8-22.3</td>
</tr>
<tr>
<td>TS13</td>
<td>Ti(NH₂)₄</td>
<td>-66.3</td>
<td>93.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TS14</td>
<td>Ti(NH₂)₃NH⁻</td>
<td>-75.0</td>
<td>104.4</td>
<td>-8.7</td>
<td>14.8</td>
</tr>
<tr>
<td>TS15</td>
<td>Ti(NH₂)₂NH₃</td>
<td>-59.2</td>
<td>102.8</td>
<td>7.1</td>
<td>30.3</td>
</tr>
<tr>
<td>TS16</td>
<td>Ti(NH₂)NH₂NH₃</td>
<td>-43.9</td>
<td>103.7</td>
<td>22.4</td>
<td>45.4</td>
</tr>
<tr>
<td>TS17</td>
<td>Ti(NH₂)₂NH₃</td>
<td>-66.7</td>
<td>108.9</td>
<td>-0.4</td>
<td>23.8</td>
</tr>
<tr>
<td>TS18</td>
<td>Ti(NH₂)NHHNH₃</td>
<td>-33.3</td>
<td>90.0</td>
<td>33.0</td>
<td>35.4</td>
</tr>
<tr>
<td>TS19</td>
<td>Ti(NH₂)₂NH₃</td>
<td>-53.9</td>
<td>92.7</td>
<td>12.4</td>
<td>17.6</td>
</tr>
<tr>
<td>TS20</td>
<td>Ti(NH₂)₂NH</td>
<td>-19.4</td>
<td>79.5</td>
<td>46.9</td>
<td>25.6</td>
</tr>
<tr>
<td>TS21</td>
<td>Ti(NH₂)₂</td>
<td>24.3</td>
<td>75.5</td>
<td>90.6</td>
<td>70.0</td>
</tr>
<tr>
<td>TS22</td>
<td>Ti(NH₂)₂</td>
<td>10.2</td>
<td>78.9</td>
<td>76.5</td>
<td>57.5</td>
</tr>
<tr>
<td>TS23</td>
<td>Ti(NH₂)₂</td>
<td>45.3</td>
<td>64.1</td>
<td>111.6</td>
<td>69.9</td>
</tr>
<tr>
<td>TS24</td>
<td>Ti(NH₂)NHHNH₃</td>
<td>29.3</td>
<td>76.5</td>
<td>95.6</td>
<td>74.8</td>
</tr>
<tr>
<td>TS25</td>
<td>Ti(NH₂)NH₂</td>
<td>15.7</td>
<td>80.6</td>
<td>82.0</td>
<td>62.8</td>
</tr>
<tr>
<td>TS26</td>
<td>Ti(NH₂)N</td>
<td>46.9</td>
<td>66.1</td>
<td>113.2</td>
<td>70.2</td>
</tr>
</tbody>
</table>

ΔH₂₉₈ kcal/mol and NH₃ (-11.0 kcal/mol), calculated ΔH₂₉₈ for HCl (-22.4 kcal/mol), and the calculated enthalpy for TiCl₄ + 4NH₃ → Ti(NH₂)₄ + 4HCl (70.5 kcal/mol). Absolute enthalpies at 298.15 K and 1 atm. Relative enthalpies relative to C1 or C13 at 298.15 K and 1 atm; C1 → C9 → TS10 → C11 → C12 and C13 → C20 → TS21 → C22 → C23, C20 → TS24 → C25 → C26 calculated at G2; C1 → C2, C8 → C9 and C13 → C14 at MP2/6-311+G(3df,2p); C2 → TS7, C14 → TS15 at B3LYP/6-311+G(3df,2p); C1 → C4, C1 → C3 → TS5 → C6 and C13 → C14 → TS16 at B3LYP/6-311G(d). Absolute enthalpies relative to C1 or C13 at CVD conditions (for C1-C12 conditions are 903.15 K and 0.1-20 Torr; for C13-C26 conditions are 523.15 K and 20 Torr).
(3df,2p) and B3LYP/6-311G(d) results agree best with the G2 values (see the Methods section); hence, they should also be the most reliable for TiX4-NH3. The present calculations, as well as those of Frenking and co-workers, consistently predict that the binding energy for Ti(NH2)4-NH3 is 8−10 kcal/mol smaller than for TiCl4-NH3, which is in accord with the longer Ti−
NH3 bond. Inspection of the orbital energies of the TiCl4 and Ti(NH2)4 precursors shows that the d-orbitals are much lower in TiCl4 (−0.43 au vs −0.33 au), which leads to stronger binding of the NH3 ligand and a shorter Ti−
NH3 bond. This is also supported by the larger charge transfer from nitrogen to titanium computed for TiCl4−
NH3 compared to that for Ti(NH2)4-NH3.

For TiCl4, the calculated a1 and t2 Ti−Cl stretching frequencies, 389 and 501 cm−1, agree very well with the observed frequencies. In the TiCl4-NH3 complex, the computed Ti−Cl modes are shifted to lower frequencies, 370, 441, and 451 cm−1 for the symmetric equatorial, axial, and asymmetric equatorial stretches, respectively. The observed modes at 440 and 456 cm−1 correspond to the axial and asymmetric equatorial Ti−Cl stretches; the symmetric equatorial stretch is below the 400 cm−1 limit of the spectrometer. Other diagnostic frequencies include the NH3 rock, 683 cm−1 calculated vs 624 cm−1 exp, and the NH3 symmetric deformation, 1329 cm−1 calculated vs 1198 cm−1 exp.

There are no experimental vibrational frequencies published for Ti(NH2)4-NH3. The calculated Ti−NH3 stretching frequencies in Ti(NH2)4-NH3 are 629, 692, 715, and 719 cm−1, compared to 648 and 731 cm−1 calculated for the a1 and t2 modes in Ti(NH2)4. Other calculated diagnostic frequencies include 513 and 522 cm−1 for the NH3 rock and 1186 cm−1 for the NH3 symmetric deformation.

TiCl4-NH2 has been used as a single source precursor for deposition of Ti−N thin films. Mixing of TiCl4 and excess NH3 in solution or in the gas phase leads to a yellow solid, which can be sublimed at 120 °C, decomposes above 250 °C, and forms titanium nitride above 500 °C. This is consistent with the NH3 binding energy of ca. 30 kcal/mol computed at the B3LYP/6-311G(d) level. The cis isomer is calculated to be 2 kcal/mol more stable than the trans isomer, in agreement with previous calculations and the experimental preference for cis isomers in TiCl4-A2 in the absence of steric crowding. The cis-TiCl4-NH2 isomer (C4) has C2 symmetry, with the rotation axis bisecting the N−Ti−N angle. The lengths for Ti−N and Ti−Cl bonds that are in the same plane are similar to those in the TiCl4-NH3 complex; however, the Ti−Cl bonds perpendicular to this plane are elongated by ca. 0.1 Å. The trans-TiCl4-NH2 isomer (C3) is very close to C5 symmetry, but rotation of the NH3 groups by 12.5° breaks the symmetry. Compared to TiCl4-NH3, the Ti−
Cl bonds are 0.08 Å longer and the Ti−N bonds are 0.09 Å shorter. The geometric variations in the cis and trans isomers can be rationalized in terms of the trans influence. In the present case, this is manifested by a

lengthening of the bond trans to each Cl ligand. Similar trends have been seen experimentally in TiCl4-(THF)2, where crystal structures are available for both isomers.

The experimental vibrational data for TiCl4-NH3 are less detailed than for TiCl4-NH3. The calculated Ti−
Cl stretches are 360, 370, 414, and 416 cm−1 for cis and 371, 371, 382, and 428 cm−1 for trans. The band observed at 421 cm−1 could belong to either the cis or the trans isomer (400 cm−1 was the lower limit of the spectrometer). The calculated NH3 rocking modes (613, 679, 685, 722 cm−1 for cis, 676, 683, 708, 714 cm−1 for trans) correspond to the observed NH3 rocking mode at 678 cm−1. The NH3 symmetric deformations are calculated at 1312 and 1330 cm−1 for cis, and 1317 and 1322 cm−1 for trans, compared to the observed frequencies at 1238 and 1255 cm−1. The calculated splitting for the cis isomer is in much better agreement with the experimental splitting, suggesting that the observed structure is the cis isomer.

2. Ligand Exchange Reactions. For atmospheric pressure CVD of titanium nitride from TiCl4 or Ti(NR2)4 and NH3, one of the rate-limiting steps may be the formation of amido complexes in the gas phase. The stability of the TiCl4-NH2 (C2) and Ti(NH2)4-NH3 (C14) complexes described above suggests that this reaction occurs via these intermediate complexes. The first step in this process is one of the following reactions:

\[ \text{TiCl}_4 + \text{NH}_3 \rightarrow \text{TiCl}_3\text{NH}_2 + \text{HCl} \] (3)

\[ \text{Ti(NR}_2)_4 + \text{NH}_3 \rightarrow \text{Ti(NR}_2)_3\text{NH}_2 + \text{HNR}_2 \] (4)

An analogous step may occur on the surface for low-pressure CVD. Subsequent replacements of Cl or NR2 by NH3 in the gas phase or on the surface proceed in a similar fashion.

The structures along the TiCl4 + NH3 → TiCl3NH2 + HCl reaction path are labeled as uncatalyzed ligand exchange in the center of Figure 1. The reaction is calculated to be endothermic by 12.2 kcal/mol at the G2 level of theory. The transition state (TS7) can be characterized as late, which is consistent with an endothermic reaction. The Ti−Cl bond is nearly broken (elongated from 2.222 Å in the complex to 3.512 Å in the transition state), and the H−Cl bond is partially formed (1.653 vs 1.275 Å in HCl). The N−H bond is not yet broken (1.206 Å in the transition state), and the Ti−N bond length (2.001 Å) is approximately halfway between reactants and products. The transition state is ca. 33 kcal/mol above the complex at the B3LYP/6-311+G(3df,2p) level of theory, as illustrated in Figure 3. Frenking and co-workers found similar structures, but their barriers were somewhat higher because smaller basis sets were used. On the product side of the transition state, there is a weakly bound complex with a hydrogen bond between the hydrogen of HCl and the nitrogen of TiCl3NH2. The binding energy, 1.8 kcal/mol, is significantly less than H3N-HCl (11.8 kcal/mol) because the lone pair of the amido ligand is involved in bonding to the titanium. Nevertheless, the H−Cl bond shows the characteristic lengthening due to hydrogen...
bonding (1.315 Å in TiCl$_3$N$_2$H$_2$-HCl and 1.382 Å in H$_3$N-HCl vs 1.275 Å in HCl).

For titanium nitride CVD from Ti(NR$_2$)$_4$ and NH$_3$, the amido ligand exchange (transamination) reaction, Ti(NR$_2$)$_4$ + NH$_3$ → Ti(NR$_2$)$_3$NH$_2$ + HNR$_2$, appears to be the rate-determining step when the process is not mass transport limited.

Titanium amido complexes undergo transamination reactions readily in solution and in the gas phase. The kinetics for Ti(NR$_2$)$_4$ + NH$_3$ → Ti(NR$_2$)$_3$NH$_2$ + HNR$_2$ have been studied experimentally and in the gas phase. The reaction is calculated to be endothermic by 46.4 kcal/mol, and the transition state (TS18) lies 33.5 kcal/mol above the reactants. The reaction path has C$_5$ symmetry and occurs significantly earlier along the reaction path than HCl elimination from TiCl$_3$N$_2$H$_2$. The migrating hydrogen is almost equidistant between the two nitrogens (1.348 Å from the nitrogen it is leaving and 1.368 Å from the nitrogen it is approaching). One of the Ti−N bonds has elongated to 2.09 Å and another has shortened to 1.75 Å compared to the bond length of 1.90 Å in the reactant. Cundari et al. have found very similar transition states for NH$_3$ elimination from the model compounds TiH$_2$(NH$_2$)$_2$ and TiH$_2$(NHMe)NH$_2$ using a more modest level of theory. There is a complex (C19) on the product side of the transition state that lies 20.9 kcal/mol below the transition state and 33.8 kcal/mol below the products. It is characterized by a fully formed Ti−NH double bond (1.691 Å) and a strong dative bond between Ti and NH$_3$ (2.209 Å). Diagnostic vibrations for this complex are 1248 cm$^{-1}$ for the NH$_3$ symmetric deformation and 1008 cm$^{-1}$ for the Ti−NH stretch. The latter mode is at 1030 cm$^{-1}$ in the uncomplexed products.

The formation of uncomplexed imido species from either TiCl$_3$N$_2$H$_2$ or Ti(NH$_2$)$_4$ is rather endothermic.

\begin{align*}
\text{TiCl}_4 + 2\text{NH}_3 & \rightarrow \text{TiCl}_4(\text{NH}_2)_2 \rightarrow \text{TiCl}_3\text{NH}_2\cdot\text{NH}_3 + \text{HCl} \quad (5)
\end{align*}

The structures along this reaction path for elimination of HCl from trans-TiCl$_4$(NH$_2$)$_2$ are labeled as ligand exchange catalyzed by NH$_3$ in Figure 1. The presence of the second NH$_3$ ligand reduces the barrier height by 12.4 kcal/mol compared to the case of the TiCl$_4$NH$_3$ transition state where both are calculated at B3LYP/6-311++G(3df,2p). Frenking and co-workers did not observe as much stabilization because the conformation of their transition state did not facilitate hydrogen bonding between NH$_3$ and Cl. This transition state (TS5) lies ca. 24 kcal/mol above the trans-\text{TiCl}_4(\text{NH}_2)_2 complex at the B3LYP/6-311G(d) level of theory and occurs even later along the reaction path than the TiCl$_4$NH$_3$ transition state (TS7). The Ti−Cl bond is longer (3.833 vs 3.512 Å) and the H−Cl bond is shorter (1.502 vs 1.653 Å) than in the TiCl$_4$NH$_3$ transition state. The N−H bond is nearly broken (1.409 Å in the transition state), which causes the Ti−N bond length to decrease to 1.965 Å. There is likely to be a weakly bound complex on the product side of this reaction similar to that found for the TiCl$_4$NH$_3$ reaction, but this part of the reaction scheme was not pursued in this investigation.

3. Elimination Reactions Forming Imido Complexes. The amido compounds formed in the ligand exchange reactions can eliminate HCl or NH$_3$ to produce more reactive imido complexes:

\begin{align*}
\text{TiCl}_3\text{NH}_2 & \rightarrow \text{TiCl}_2\text{NH} + \text{HCl} \quad (6) \\
\text{Ti}(\text{NH}_2)_4 & \rightarrow \text{Ti}(\text{NH})_2\text{NH} + \text{NH}_3 \quad (7)
\end{align*}

The elimination of HCl from TiCl$_3$NH$_2$ (C9) is calculated to be endothermic by 59.9 kcal/mol at the G2 level of theory and has a transition state (TS10) of C$_5$ symmetry lying 44.7 kcal/mol above the reactants. Using a lower level of theory, Cundari and Gordon have found similar energetics for HCl elimination from the model compound TiClH$_2$NH$_2$ and found a transition state considerably earlier along the reaction path. In TS10 the N−H bond has completely dissociated (2.30 Å in the TiCl$_3$NH$_2$ TS vs 1.72 Å in the TiClH$_2$NH$_2$ TS), and the H−Cl bond is fully formed (3.11 Å in the TiCl$_3$NH$_2$ TS vs 1.39 Å in the TiClH$_2$NH$_2$ TS vs 1.28 Å in HCl). The transition state is followed by an adduct (C11) between the imido complex and HCl. This adduct is bound by less than 1 kcal/mol relative to the transition state, but by ca. 15.6 kcal/mol relative to the dissociated products, indicating a fairly strong donor−acceptor interaction between Ti and Cl. The Ti−NH stretching vibrational frequency of the product, 1055 cm$^{-1}$, is a potential probe for this imido intermediate.

Chemical vapor deposition from Ti(NR$_2$)$_4$ and NH$_3$ starts with a transamination reaction to form Ti(NR$_2$)$_3$NH$_2$. This system has been modeled with Ti(NH$_2$)$_4$ instead of Ti(NR$_2$)$_3$NH$_2$. Ti(NH$_2$)$_4$ can also be formed from TiCl$_4$ and NH$_3$ by exchanging all four Cl's for amido ligands. The elimination of NH$_3$ from Ti(NH$_2$)$_4$ proceeds by transferring a hydrogen atom from one amido group to another, followed by dissociation of NH$_3$. The reaction is calculated to be endothermic by 46.4 kcal/mol, and the transition state (TS18) lies 33.5 kcal/mol above the reactants. The reaction path has C$_5$ symmetry and occurs significantly earlier along the reaction path than HCl elimination from TiCl$_3$N$_2$H$_2$. The migrating hydrogen is almost equidistant between the two nitrogens (1.348 Å from the nitrogen it is leaving and 1.368 Å from the nitrogen it is approaching). One of the Ti−N bonds has elongated to 2.09 Å and another has shortened to 1.75 Å compared to the bond length of 1.90 Å in the reactant. Cundari et al. have found very similar transition states for NH$_3$ elimination from the model compounds TiH$_2$(NH$_2$)$_2$ and TiH$_2$(NHMe)NH$_2$ using a more modest level of theory. There is a complex (C19) on the product side of the transition state that lies 20.9 kcal/mol below the transition state and 33.8 kcal/mol below the products. It is characterized by a fully formed Ti−NH double bond (1.691 Å) and a strong dative bond between Ti and NH$_3$ (2.209 Å). Diagnostic vibrations for this complex are 1248 cm$^{-1}$ for the NH$_3$ symmetric deformation and 1008 cm$^{-1}$ for the Ti−NH stretch. The latter mode is at 1030 cm$^{-1}$ in the uncomplexed products.

The formation of uncomplexed imido species from either TiCl$_3$N$_2$H$_2$ or Ti(NH$_2$)$_4$ is rather endothermic.
However, the calculations described above show that the imido compounds readily form complexes and that the binding to ammonia is significantly stronger than the binding to HCl. Since excess ammonia is used in low-temperature CVD from Ti(NR2)4,11 complexation with NH3 could assist the elimination reaction to form the imido species:

\[
\text{Ti(NH}_2\text{)}_4\cdot\text{NH}_3 \rightarrow \text{Ti(NH}_2\text{)}_2\cdot\text{NH} \cdot (\text{NH}_3)_2
\] (8)

Geometries of the transition state and complexes are labeled as catalyzed imido formation in Figure 2. The complexation energies were computed at the B3LYP/6-311G(d) level, since these structures are too large to calculate expeditiously by the G2 protocol. For the smaller Ti(NH2)2NH-NH3 complex (C19), the NH3 binding energy computed at B3LYP/6-311G(d), 34.3 kcal/mol, is in good agreement with the G2 value, 33.8 kcal/mol. The reaction of the complexed species is more nearly thermoneutral, and the barrier is lowered by ca. 1 kcal/mol relative to Ti(NH2)2NH-NH3 but is reduced by ca. 9 kcal/mol relative to Ti(NH2)2NH + NH3. In the transition state (TS16), the migrating hydrogen remains nearly equidistant from the two nitrogens, but complexation makes the titanium less pyramidal and the inequivalent amido ligands break the symmetry. In the imido species complexed with two ammonias (C17), the titanium is planar, and the Ti=NH and Ti-NH3 bonds are elongated only slightly when compared to the complex with one ammonia. The small changes in the geometry are in keeping with the fact that the binding energy for the second ammonia, 12.7 kcal/mol, is much smaller than for the first ammonia, 33.8 kcal/mol. Characteristic frequencies are 1196 and 1201 cm\(^{-1}\) for the NH3 asymmetric and symmetric deformations and 990 cm\(^{-1}\) for the Ti=NH stretch, values slightly lower than for the complex with one ammonia.

4. Elimination of NH3 from Ti(NH2)2NH. If the elimination of one NH3 is possible, perhaps a second NH3 can also be removed. There are two pathways to consider. Migration of the imido hydrogen of Ti(NH2)2NH (C20) would yield a nitrido product, Ti(NH2)N (C26), and ammonia:

\[
\text{Ti(NH}_2\text{)}_2\cdot\text{NH} \rightarrow \text{Ti(NH}_2\text{)}\cdot\text{N} + \text{NH}_3
\] (9)

Alternatively, removal of an amido hydrogen from Ti(NH2)2NH results in a diimido species (C23) plus ammonia:

\[
\text{Ti(NH}_2\text{)}_2\cdot\text{NH} \rightarrow \text{Ti(NH}_2\text{)_2} + \text{NH}_3
\] (10)

The reactions are calculated to be nearly equally endothermic at the G2 level, 65.8 and 64.3 kcal/mol for the formation of the nitrido and diimido species, respectively. The corresponding barriers are also similar, 49.3 and 44.4 kcal/mol, with the diimido being slightly lower. In both cases, the migrating hydrogen is approximately halfway between the two nitrogens, and the Ti–N distance for the departing nitrogen has increased from 1.92 Å in the reactants to 2.10 Å in the transition state. The product side complexes lie ca. 14 kcal/mol below the transition states and consist of an NH3 forming a dative bond with Ti in the nitrido or diimido product. The Ti–NH3 bond lengths are comparable, 2.22–2.25 Å, and the nitrido or diimido fragments have geometries very similar to the products. Characteristic vibrational frequencies for the products include the Ti–N–H stretch, 677 cm\(^{-1}\), and Ti–N–H stretch, 1159 cm\(^{-1}\), for the nitrido species and asymmetric Ti–NH stretch, 971 cm\(^{-1}\), and symmetric Ti–NH stretch, 988 cm\(^{-1}\), for the diimido species.

Conclusions

The discussion above has focused on characterizing the gas-phase reaction paths for titanium nitride chemical vapor deposition in terms of computed structures, enthalpies, and vibrational frequencies of the most probable intermediates and transition states. Experimentally, these CVD reactions are carried out at high temperatures and low partial pressures. To interpret our calculated results for the experimental conditions, we need to examine the free energies. The heats of formation, absolute entropies, relative enthalpies, and relative free energies for the structures studied in this paper are collected in Table 1.

Ligand exchange reactions starting with the TiCl4 precursor are either endothermic or slightly exothermic. For ligand exchange with a single NH3 group the reaction is calculated to be endothermic by 12.2 kcal/mol, but \(\Delta G_{rxn} = 0.9\) kcal/mol at 0.1 Torr and 630 °C. This suggests that ligand exchange through complexation with a single NH3 group is thermodynamically feasible at CVD conditions. The transition state barrier is lowered by 9.4 kcal/mol, and the reaction becomes nearly thermoneutral (\(\Delta H_{rxn} = -2.0\) kcal/mol) for ligand exchange when a second NH3 group is added to the complex and TiCl3NH2-NH3 is formed, suggesting a catalyzed route to ligand exchange. However, calculations of the free energy reveal that \(\Delta G_{rxn} = 38.3–28.8\) kcal/mol at 0.1–20 Torr and 630 °C, making this route much less favorable than the pathway involving complexation of a single NH3.

Elimination reactions to form imido complexes are rather endothermic and have relatively high barriers at the G2 level. The direct elimination of HCl from TiCl3-NH3 is calculated to have \(\Delta G_{rxn} = 11.9\) kcal/mol at 0.1 Torr and 630 °C. Since elimination of NH3 is less exothermic, CVD from TiCl4 may involve multiple exchanges of NH2 for Cl before the elimination step. Multiple ligand exchanges, in turn, may require efficient removal of HCl to shift the equilibrium appropriately.

CVD from Ti(NR2)4 is carried out at lower temperatures and higher partial pressures. Elimination of NH3 from Ti(NH2)4 is calculated to have \(\Delta G_{rxn} = 25.6\) kcal/mol at 20 Torr and 250 °C. However, if ammonia remains complexed to the imide, the reaction is more favorable with \(\Delta G_{rxn} = 17.6\) kcal/mol. Complexation with one additional ammonia lowers the enthalpy of the reactants by 6.3 kcal/mol but raises the free energy by 14.8 kcal/mol. Complexation also decreases the enthalpy of the transition state and product side complex by 10.9 and 12.7 kcal/mol, respectively, but increases their free energy by 10.0 and 6.2 kcal/mol. Thus, complexation with additional ammonia does not facilitate the gas-phase reaction at 250 °C and 20 Torr. However, if complexation to a surface bound NH2 group is stronger than to a free NH3, the surface reaction could be more favorable than the gas-phase reaction.
The experimental kinetics indicates that the elimination reaction is slower than the transamination.\textsuperscript{26–28} The present work is consistent with this observation since the calculated free energy barrier for the elimination \( \text{Ti(NH}_2\text{)}_4 \rightarrow \text{Ti(NH}_2\text{)}_2\text{NH}\cdot\text{NH}_3 \) is 5.1 kcal/mol higher than for the transamination of \( \text{Ti(NH}_2\text{)}_4 \) at 250 °C and 20 Torr. The free energy barriers for the formation of the diimido and nitrido complexes are about 10 kcal/mol higher than the barrier for the formation of the imido complex; hence, these reactions are less likely in the gas phase.

\textbf{Acknowledgment.} We gratefully acknowledge support from the National Science Foundation (CHE 98-74005) and from the National Computational Science Alliance under CHE980042N utilizing the NCSA HP/Convex Exemplar SPP-2000.

\textbf{Supporting Information Available:} Tables of total energies, Cartesian coordinates, and vibrational frequencies of the structures described in this work. This material is available free of charge via the Internet at http://pubs.acs.org.