Decomposition Pathways for a Model TiN Chemical Vapor Deposition Precursor

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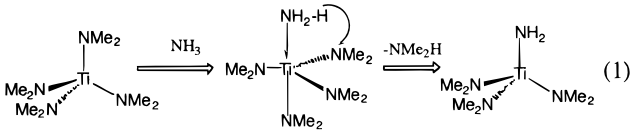
A computational study of small-molecule elimination, modeling chemical vapor deposition (CVD) pathways, from a model single-source precursor of titanium nitride is reported. A comparison of possible multiply bonded intermediates is made. Calculated geometries for all species agree well with experiment. Transition states for energetically favorable 1,2-elimination to form multiply bonded intermediates are four-centered geometries with a "kite-shape" (i.e., one obtuse and three acute angles). Processes involving the transfer of H from an amido (NHR) ligand to the leaving group (X) are predicted to be the most favorable. In cases where a group other than H (in this case, methyl) is transferred from the amido (NMeR) to X, the TS has a square shape and a much higher barrier to 1,2-elimination. Pathways to cyclic intermediates and β-H elimination pathways are also compared with 1,2-elimination. The β-H elimination process to form an organic imine and a Ti-amido is found to be kinetically and thermodynamically disfavored versus the lower energy 1,2-elimination processes. Pathways to the formation of cyclic products (η^2-imine complexes), recently suggested by experimentalists as a potential decomposition route for TiN precursors, have slightly higher barriers and may be competitive with 1,2-elimination processes under CVD conditions. Analysis of the data for all decomposition reactions suggests that interaction between the metal and the small molecule being eliminated plays an important role in stabilizing the transition state and making it energetically accessible. It is proposed that enhancing these interactions will result in lower activation barriers and potentially lower processing temepratures in CVD of transition-metal-containing materials in which such reactions are the rate-determining step.

Introduction

Complexes with transition metal (TM)−main group multiple bonds are of interest as intermediates in chemical vapor deposition (CVD),[1] a process that involves elimination of small molecules, such as methane or hydrogen, from organometallic precursors to form solid-state advanced materials.[1−5] TiN has many desirable properties, e.g., high hardness and melting point, good electrical conductivity, and chemical inertness.[6] Transition-metal nitrides are traditionally made by heating the metal in nitrogen or ammonia at high temperatures.[6] Nitrides can also be formed by reacting metal halide, nitrogen (or ammonia), and hydrogen at high temperatures (>1000 °C).[6] High-quality TiN films with low carbon content can be produced at ≈200−450 °C by reaction of $Ti(NMe_2)_4$ with ammonia in the gas phase.[2] In this case, ammonia seemingly helps by coordinating to Ti, transferring a proton to NMe_2, permitting dissociation of bulkier dimethylamine (eq 1).[3]



(1)

Recent work indicates that gas-phase reactions are important in depositing a high-quality TiN film.[2,3] In the case of reaction of $Ti(NMe_2)_4$ with ammonia, spectroscopic evidence suggests eventual formation of a polymeric intermediate containing amido and imido groups.[2] Evidence for imidos in TiN CVD is provided by Winter et al.[1] Reaction of $TiCl_4$ with *tert*-butylamine gave a compound of formula $[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_{0-2}]_n$. This oligomeric compound produced a TiN thin film when heated to 500 °C.

Computational studies of the deposition of main group materials, in particular Si, have contributed to a molecular level understanding of CVD of these materials.[7] Relatively few computational studies have focused on modeling CVD for TM-containing materials.[8,9] To this end we have performed quantum chemical studies to model processes proposed by experimentalists to occur

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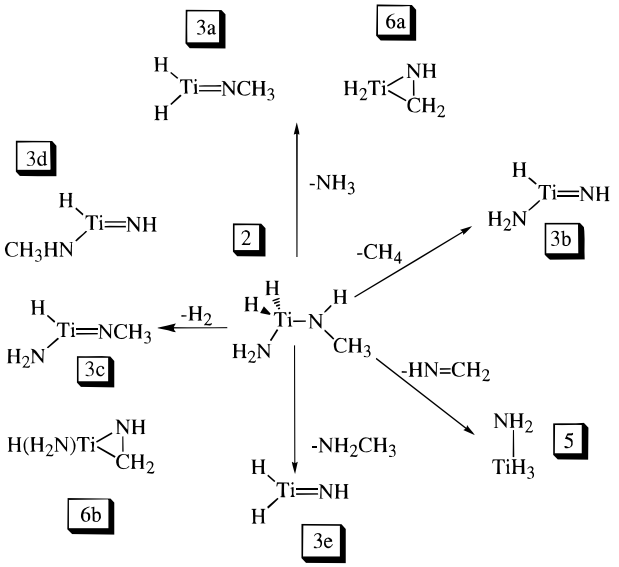
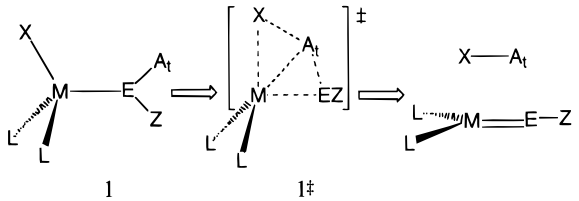


Figure 1. Decomposition pathways studied for model OMCVD precursor (**2**, $TiH_2(NHMe)(NH_2)$).

when an organometallic precursor is converted into a solid-state nitride.[8,9] Our main goal is to understand how the components in a hypothetical organometallic CVD (OMCVD) precursor (**1**), (metal (M), activating



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ligand (E), leaving group (X), ancillary ligands (L), donor group (A_t), substituent (Z)) affect the course of elimination reactions such as those in Figure 1. This paper reports the results of a computational study of $TiH_2(NH_2)(N(H)CH_3)$, a simple model of a single-source precursor for TiN. The use of H as an ancillary ligand helps maintain computational tractability. Previous computations[8,9] show ancillary ligands to have minimal influence, in the electronic sense, on the course of the reaction. However, one must be mindful of possible steric effects. Plausible decomposition pathways to pre-TiN intermediates are shown in Figure 1.

Computational Methods

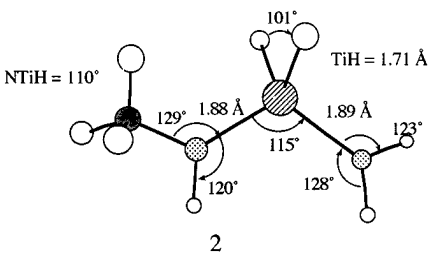
The results reported herein are obtained using the GAMESS program in both serial and parallel mode.[10] Chemically less important core orbitals are replaced with effective core potentials (ECPs). The ECPs and valence basis sets of Stevens et al.[11] are used to describe heavy atoms while the -31G basis set is used for H. For titanium, a 10-electron core is used.[11] A d polarization function is used to augment heavy main-group element basis sets.[11] A 2-electron core is used for C and N.[11] Geometry optimizations[12] are done at the restricted Hartree−Fock level for closed-shell singlets (RHF). This combination of ECPs, basis sets, and level of theory has been thoroughly tested on transition-metal (TM) complexes and reactions.[8,9,13] Minima and transition states are identified by calculating the energy Hessian at stationary points. The intrinsic reaction coordinate (IRC[14]) is used to confirm that a TS connects the appropriate products and reactants. Previous studies on related complexes and reactions were carried out at higher levels of theory, explicitly including electron correlation, and were found to have minimal effect on the geometries of stationary points, transition states included, and the shape of the IRC.[8,9]

Although electron correlation has a minimal effect on geometries, the same is typically not so for calculated energies. The correlation contribution can often be treated as a perturbation to the single configuration RHF energy, permitting the correlation energy to be calculated using second-order Møller−Plesset (MP2) theory.[15] Previous studies of similar systems using multiple configuration wave functions showed the RHF configuration to be dominant, supporting the viability of perturbation approaches for calculation of the correlation energy. Enthalpic data are determined using MP2 energies at RHF optimized geometries and corrected for zero-point energy and from absolute zero to 298.15 K. An RHF geometry/MP2 energy scheme yields good agreement with experiment, in both trends and relative activation barriers, for methane elimination from groups IVB and VB methyl(amido) complexes.[8,9,16,17] As the main goal of this work is to understand trends among related complexes and reactions, the RHF geometry/MP2 energy scheme provides an attractive, computationally efficient choice for this research.[8,9,16,17]

Results

All minima, transition states, and reaction coordinates corresponding to processes in Figure 1 were characterized by effective core potential methods. Amido and imido complexes are similar to those discussed previously and for which computational methods have been shown to accurately describe their bonding, structure, and energetics.[13,16,17] Pertinent bond lengths are discussed below; consideration of reaction energetics is primarily confined to the Discussion. Cartesian coordinates for optimized stationary points are available as supporting information; RHF energies, MP2 energies at RHF optimized stationary points, plus enthalpic corrections needed to convert energies to enthalpies are given in Table 1.

1. Bis(Amido) Reactant. The minimum energy geometry of $Ti(H)_2(N(H)Me)(NH_2)$, **2**,is slightly distorted



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from C_s symmetry (C−N−Ti−N dihedral = 173°). The geometry about Ti is approximately tetrahedral, with angles about the metal ranging from 101° (H−Ti−H)

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Table 1. Energetic Data for Stationary Points[a]

species	*E*(RHF)	*E*(MP2)	*H*(298.15 K)
2	−86.9309	−87.4976	64.910
2′	−86.9526	−87.5251	64.728
2‡	−86.8159	−87.4165	62.547
3a	−75.4381	−75.8686	38.699
3a−NH_3	−86.9066	−87.5057	66.327
3b	−79.1077	−79.5809	32.520
3c	−85.7551	−86.3500	52.760
3d	−85.7465	−86.3393	52.540
3e	−68.7893	−69.0973	18.482
3e−NH_2Me	−86.9021	−87.4968	66.159
3a‡	−86.8476	−87.4467	64.356
3b‡	−86.7951	−87.4041	63.263
3b′‡	−86.8653	−87.4843	62.810
3c‡	−86.8602	−87.4768	64.612
3d‡	−86.8532	−87.4685	62.633
3e‡	−86.8417	−87.4364	62.125
3e′‡	−86.7669	−87.3674	62.354
4‡	−85.6554	−86.2797	49.909
5	−86.8769	−87.4345	62.545
5‡	−86.8458	−87.4148	61.805
H_3TiNH_2	−69.9731	−70.2509	30.989
6a	−75.4376	−75.8349	37.998
6a−NH_3	−86.8909	−87.4660	65.573
6b	−85.7525	−86.3193	51.761
6a‡	−86.8289	−87.4256	61.253
6b‡	−86.8562	−87.4539	62.026
NH_3	−11.4099	−11.5719	25.161
NH_2Me	−18.0498	−18.3271	45.410
H_2	−1.1246	−1.1405	8.590
CH_4	−7.8034	−7.9278	31.911
$HN{=}CH_2$	−16.8721	−17.1398	29.295

[a] Energies (in hartrees) at RHF optimized stationary points (calculated at RHF and MP2 levels of theory) are given for all species discussed in text. Enthalpic (kcal mol^{-1}) corrections were calculated using RHF vibrational frequencies.

to 115° (N−Ti−N′). Reactant **2** has Ti−N(amido) = 1.89 Å and Ti−N(methylamido) = 1.88 Å, in good agreement with electron diffraction results for the Ti−N bonds of $Ti(NMe_2)_4$ (1.92 Å) and Cl_3TiNEt_2 (1.85 Å).[18] Amido coordination is planar, as expected,[18] suggestive of significant Ti dπ−N pπ bonding. Amido nitrogens show normal sp^2 coordination with no evidence of agostic bonding between N−H bonds and the Ti(IV) center. NMR and IR analyses of four-coordinated Ti− and Zr−amido complexes show no evidence of agostic interactions despite the low coordination number and electrophilic metal center.[19]

2. Products of 1,2-Elimination: Ti−Imidos. Six pathways leading to Ti−imidos (**3**, $L_nTi{=}NR$) were investigated (Figure 2). The imido products, which result from elimination of ammonia, methane, molecular hydrogen, or methylamine, are shown with their associated TSs in Figure 2. All imidos are roughly trigonal planar about Ti. Several Ti−imidos have been structurally characterized and possess Ti=N bond lengths ranging from 1.699(4) Å for $[Ti(TMEDA)(Cl)_2(=NC(Me)=)]_2$ to 1.723(2) Å for $(OAr)_2(py')_2Ti(=NPh)$ where Ar = 2,6-diisopropylphenyl and py′ = 4-pyrrolidinopyridine.[20] Calculated Ti=N bonds are 1.66 Å for $H_2Ti{=}NMe$ (**3a**) and $H_2Ti{=}NH$ (**3e**) and 1.67 Å for (H)$(NH_2)Ti{=}NH$ (**3b**), (H)$(NH_2)Ti{=}NMe$ (**3c**), and (H)(NHMe)Ti=NH (**3d**). Calculated Ti=N bond lengths are thus in good agreement with experiment, particularly if account is taken of the lower coordination numbers in the models. Two additional points are worthy of note. First, replacement of a hydride ligand (**3a** and **3e**) with an amido (**3b**−**d**) stretches the Ti=N bond by only 0.01 Å. Second, $Ti-N_{amido}$ bond lengths in **3b**−**d** are 1.92, 1.93, and 1.91 Å, respectively. This corresponds to an average lengthening versus **2** of the $Ti-N_{amido}$ bond of 0.04 ± 0.01 Å, despite a reduction in coordination number from four (**2**) to three (**3**). Hence, although the planarity of the amido suggests significant TiN π bonding, the latter two observations suggest that the amido does not effectively compete with the imido for Ti dπ−N pπ bonding and furthermore that the nature of the Ti=N bond is similar in all cases, despite changes in the substituents and ancillary ligands.

When eliminating a Lewis base, ammonia or methylamine, the extruded molecule remains coordinated to the metal to give a tetrahedral imido, **3a**−NH_3 and **3e**−NH_2Me. The Ti=N bonds lengthen upon amine coor-

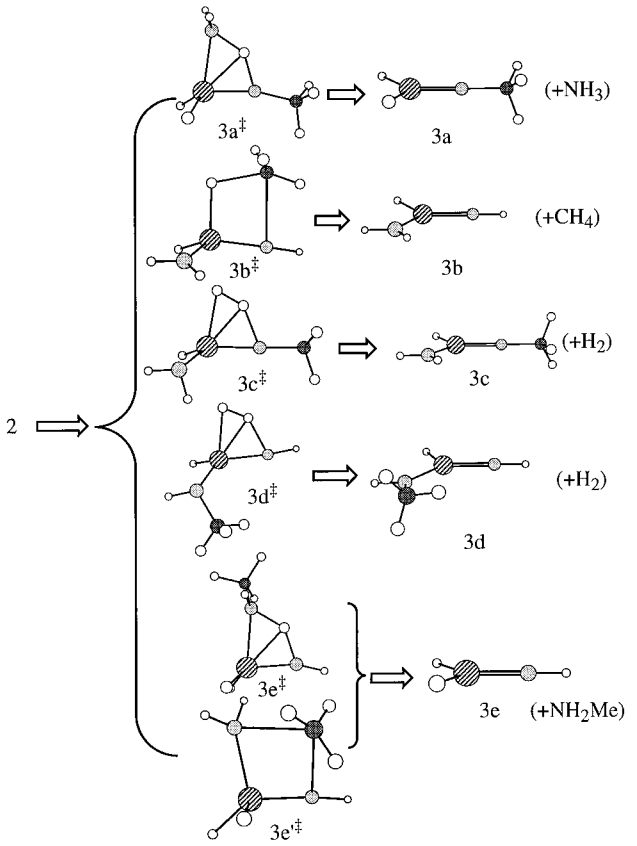

Figure 2. 1,2-Elimination pathways from **2** to imidos (**3**). In this and all subsequent structures, diagonal striped, open, light and dark circles correspond to Ti, H, N, and C atoms, respectively.

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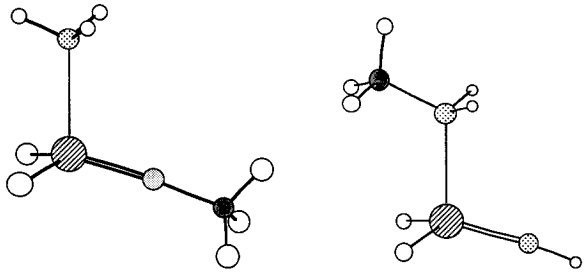
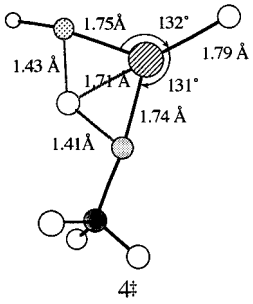


dination from 1.66 Å (**3a** and **3e**) to 1.67 Å (**3a**−**NH$_3$** and **3e**−**NH$_2$Me**). The Ti←N dative bonds are 2.23 Å (**3a**−**NH$_3$**) and 2.21 Å (**3e**−**NH$_2$Me**), nearly identical to Ti←N(py′) bonds in $(OAr)_2(py')_2Ti(=NPh)$.[20a] Amine binding enthalpies are 38 kcal mol^{-1} (**3a**−**NH$_3$**) and 43 kcal mol^{-1} (**3e**−**NH$_2$Me**). The ordering is consistent with methylamine being a stronger base than ammonia in the gas phase, with minimal steric interactions in these simple models. Both adducts are close in energy to reactant, **2**. Adducts **3a**−**NH$_3$** and **3e**−**NH$_2$Me** are 4 kcal mol^{-1} more stable and 2 kcal mol^{-1} less stable than **2**, respectively, and thus from a thermodynamic point of view their formation from **2** seems plausible.

Of the two isomeric imidos, **3c** and **3d**, the former is more stable by 6 kcal mol^{-1}. Hydrogen transfer among nitrogen ligands has been observed in high-valent transition-metal complexes, primarily from amino (NH_2R) to imido (=NR) ligands.[21] The conversion of **3c** → **3d** would involve transfer from an amido to imido ligand, a reaction, to our knowledge, which has not been observed experimentally. The transition state, **4**‡, for

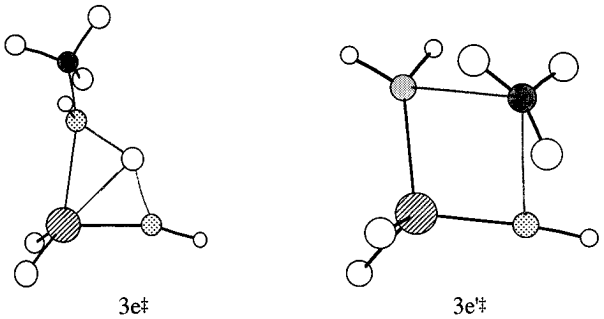


conversion of **3c** to **3d** was isolated. The enthalpic barrier for conversion of **3c** to **3d** is 41 kcal mol^{-1} and hence the barrier for the reverse reaction is 35 kcal mol^{-1}. Thus, interconversion between these isomeric imido products has a large intrinsic barrier for H-transfer and would occur, if at all, only at higher temperatures.

3. 1,2-Elimination Transition States. The geometry of TS **1**‡ engenders a short MA_t transannular distance, although there seems to be no consensus as to whether the short MA_t distance is indicative of bonding, in particular the magnitude of this interaction.[8b,22] Previous research from our lab on HX elimination (A_t = H) has shown that for a given metal (complexes of Ti, Zr, and Hf were investigated), a shorter MH_t distance correlates with a lower barrier to HX elimination.[9]

Transition states for each of the 1,2-elimination processes (Figure 2) were located. The transition states are four-centered (**1**‡), involving the metal (M = Ti), activating ligand (E = N), leaving group (X = H, NH_2, or NHMe), and donor group (A_t = H or Me), consistent with previous theoretical and experimental work on 1,2-elimination from d^0 transition-metal complexes.[8,9,23] The transition states can also be described as late (i.e., productlike) on the reaction coordinate for 1,2-elimination (e.g., the angle subtended by the Ti−N bond of the imido being formed and the N−Z bond, where Z is the spectator substituent on this N, is close to linear as in the imido product). Activation parameters determined from temperature dependent kinetics support the formulation of a late TS for hydrocarbon elimination from amidos to form imidos.[19,24] When the donor atom (A_t) is H, the angle about H_t is very large (≥150°) and the imaginary frequencies for TSs **3**‡ correspond to N−H_t bond breaking and H_t−X bond formation, a result consistent with the significant kinetic isotope effects which have been experimentally observed for small molecule elimination from high-valent amidos.[19,23,24] Calculation of intrinsic reaction coordinates[14] for 1,2-elimination (**2** → **3**‡ → **3**) confirms that calculated transition states connect the appropriate reactants (**2**) and products (**3**). Hence, in all respects the structural data for the 1,2-elimination TSs are consistent with indirect experimental evidence.[19,23,24]

For one reaction (**2** → **3e**) there are two isomeric transition states (**3e**‡ and **3e′**‡) through which the



transformation can take place. The transition states involve addition of the N−H (**3e**‡) or N−C (**3e′**‡) bond of methylamine across the Ti=N bond of H_2Ti=NH (**3e**). The kite shape of **3e**‡ is conducive to a short transannular TiH_t distance. The appreciably greater transannular distance of **3e′**‡ (TiC_t = 2.85 Å) versus **3e**‡ (TiH_t = 1.91 Å), even when differences in the covalent radii of C and H (r_{cov}(C) − r_{cov}(H) ≈ 0.4 Å) are figured in, is suggestive of greater transannular interaction in **3e**‡ than **3e′**‡. It is tempting to ascribe a large part of the difference in transition state enthalpies (44 kcal mol^{-1}) to the strength of the transannular interaction and its ability to keep the TSs energetically accessible, although one must consider other structural differences between **3e**‡ than **3e′**‡ and their effect on relative energies (e.g., $D°_{298}$(N−H) ≈ 103 kcal mol^{-1} and $D°_{298}$(C−N) ≈ 87 kcal mol^{-1}).

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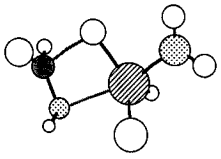
The TSs that involve H transfer during elimination of ammonia (**3a**‡) and methylamine (**3e**‡) have short Ti−H_t distances, ≈10% longer than the terminal Ti−H bond in **2**. The TSs for 1,2-H_2 elimination (**3c**‡ and **3d**‡) have TiH_t distances ≈4% and 5% longer, respectively, than the Ti−H bond lengths in **2**. For **3c**‡ and **3d**‡ the TiH_t distance is shorter than the Ti···H bond to the leaving group (X = H in **1**). The TiH_t distances suggest a weaker interaction in the TS for amine elimination than for H_2 elimination. It is of interest to see if structural changes in the TS correlate energetic differences for 1,2-elimination pathways.

4. Beta Elimination. In addition to 1,2-elimination another plausible decomposition route for **2** is β-H elimination.[25] This occurs by transfer of a β-hydrogen to the metal with concomitant formation of the doubly bonded species. Well characterized examples of β-H elimination by amides are not as common as β-H elimination by alkyls to form olefins.[26] A β-H elimination TS (**5**‡) was found which is 49 kcal mol^{-1} above **2**.



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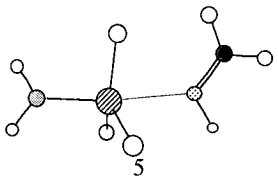
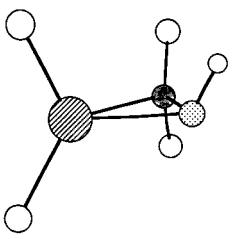
Calculation of the IRC shows that TS **5**‡ connects **2** and trigonal bipyramidal $Ti(H)_3(NH_2)(HN{=}CH_2)$, **5**, where



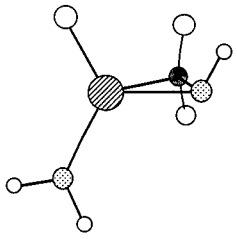
5

NH_2 and $HN{=}CH_2$ occupy axial coordination sites. The imine is coordinated through the N lone pair and not the π cloud. The Ti←N dative bond to the imine in **5** is 2.27 Å, and thus consistent with Ti←N bond lengths for **3a**−**NH_3** and **3e**−**NH_2Me** and experiment.[19] The Ti−N bond length is 1.89 Å, only 0.01 Å longer than the calculated Ti−N bond in $H_3Ti{-}NH_2$. The binding enthalpy of $HN{=}CH_2$ in **5** is 25 kcal mol^{-1}.

5. Intermediates Containing a Ti Metallacycle. Spectroscopic evidence obtained during the CVD of TiN from $Ti(NMe_2)_4$ and ammonia led Dubois et al. to postulate formation of η^2-imine complexes.[2a] Two imines (**6a** and **6b**) can be formed by elimination of

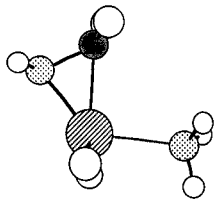


6a



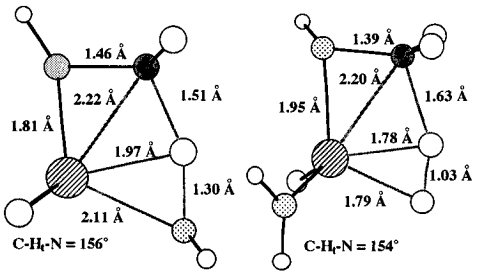
6b

ammonia or H_2, respectively. Ammonia remains coordinated to Ti upon ammonia elimination from **2** to yield **6a**−**NH_3**. This adduct is most comparable to the complex $Ti(OAr)_2$(4-phenylpyridine)(η^2-$Bz_2C{=}N$-*t*-Bu), characterized by Rothwell et al.[27] (calculated values in parentheses): Ti−N = 1.846(4) Å (1.90 Å); Ti−C = 2.158(5) Å (2.06 Å), C−N = 1.421(7) Å (1.40 Å), N−Ti−C = 40.6(2)° (41°). Thus, there is good agreement between experiment and model complex **6a**−**NH_3**. Complex **6a**−**NH_3** is isomeric to **2** and less stable by 21 kcal mol^{-1}.



6a-NH_3

The calculated five-centered TSs leading from **2** to imines **6a** and **6b** resulting from the elimination of ammonia (**6a**‡) and hydrogen (**6b**‡) are shown below. A



6a‡ 6b‡

notable difference between **6a**‡ and **6b**‡ is the considerably longer bond between Ti and the N in the latter TS. The five atoms which comprise the five-center TS are coplanar, even in **6b**‡ which is C_1, unlike **6a**‡ which is C_s. There is a large angle about the H being transferred in the TS, 154° and 156° for **6a**‡ and **6b**‡, respectively. Both TSs have relatively short metal−transannular hydrogen distances. In the case of ammonia elimination (**6a**‡), the Ti−H_t distance (1.98 Å) is 15% greater than a terminal Ti−hydride in **2**. For hydrogen elimination (**6b**‡), TiH_t is 1.78 Å or ≈4% greater than a terminal Ti−hydride. Both values are comparable to TiH_t distances in the TSs for 1,2-elimination of H_2 (**3c**‡ and **3d**‡) and amines (**3a**‡ and **3e**‡). In many of these properties the cyclization TSs thus resemble the 1,2-elimination TSs. In the next section we will compare the energetics of the 1,2-elimination and cyclization pathways.

Discussion

The energetics of the elimination processes play an important role in determining the preferred decomposition pathways of a CVD precursor. The energies of the TSs relative to model precursor **2** for each decomposition process studied are collected in Figure 3. Several points are of interest in connection with decomposition of single-source precursors to pre-TiN intermediates.

(25) Elschenbroich, C.; Salzer, A. Organometallics; VCH: Weinheim, 1992.
(26) (a) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein. (c) Koga, N.; Morokuma, K. *Chem. Mater.* **1991**, *91*, 823.
(27) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, K. *J. Am. Chem. Soc.* **1987**, *109*, 4770.

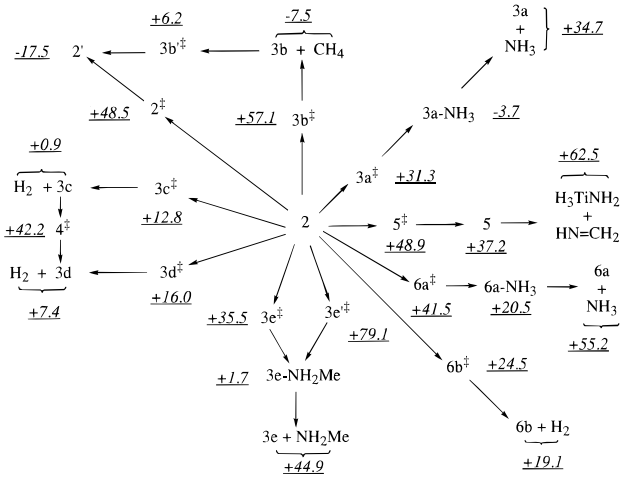
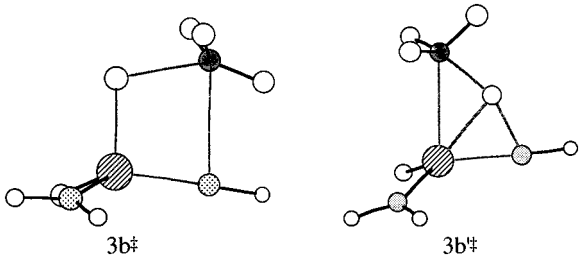


Figure 3. Enthalpies (kcal mol^{-1}) of species investigated. Values are calculated using MP2 energies at RHF stationary points are corrected for zero-point energy and from absolute zero to 298.15 K and are relative to model precursor **2** (H(**2**) ≡ 0.0 kcal mol^{-1}).

The β-H elimination process (**2** → **5**‡ → **5**) is endothermic by 37 kcal mol^{-1} and has an activation enthalpy of 49 kcal mol^{-1}. Therefore, the barrier for the microscopic reverse reaction, insertion of the C=N bond of HN=CH$_2$ into a Ti−H bond is a relatively facile process with only a 12 kcal mol^{-1} barrier. Buchwald and co-workers[28] have extensively investigated the use of chiral titanocene catalysts for asymmetric hydrogenation of organic imines, a primary step of which is presumably insertion of C=N into a Ti−H bond. However, well-characterized examples of the microscopic reverse, β-H elimination from TM-amidos are rare.[26] Calculations suggest that for the present system β-H elimination is not competitive, in a thermodynamic and kinetic sense, with the most favorable 1,2-elimination and cyclization processes for Ti(H)$_2$(NHMe)(NH$_2$), **2**.

Elimination processes that do not involve a transannular hydrogen (A$_t$ ≠ H) are clearly disfavored relative to those in which the donor group is hydrogen. The 1,2-elimination of methane from **2** (**2** → **3b**‡ → **3b** + CH$_4$) has a barrier of 57 kcal mol^{-1} while elimination of



methylamine by C−N formation (**2** → **3e′** ‡ → **3e**−**NH$_2$Me**) has an enthalpic barrier of 79 kcal mol^{-1}. The former barrier is 22 kcal mol^{-1} greater than the highest calculated barrier 1,2-elimination (**2** → **3e**‡ → **3e**−**NH$_2$Me**) in which A$_t$ = H. Methane elimination TS, **3b**‡, is particularly interesting since there is a large body of data for methane elimination and its microscopic reverse, methane activation by TM imidos.[17,19,21b,24,29] In all cases, activation of a methane C−H bond by the M=N bond of a high-valent imido occurs by formation of M−C and N−H bonds. Transition state **3b′** ‡ (X = CH$_3$, A$_t$ = H, **1**) is lower by 51 kcal mol^{-1} than **3b′** ‡ (X = H, A$_t$ = CH$_3$, **1**). Of course, **3b′** ‡ can only arise from methane elimination from Ti(H)(Me)(NH$_2$)$_2$, **2′**, an isomer of **2**.[30] The enthalpic difference between **3b**‡ and **3b′** ‡ (51 kcal mol^{-1}) is similar to that calculated for **3e**‡ and **3e′** ‡ (44 kcal mol^{-1}).

In processes involving H transfer (A$_t$ = H in **1**), for either 1,2-elimination (**2** → **3**‡ → **3**) or cyclization (**2** → **6**‡ → **6**) pathways, elimination of H$_2$ is favored (X = H) over the analogous process for extrusion of an amine (X = NH$_2$ or NHMe). For example, the enthalpic barrier to NH$_3$ elimination to form an imine (**2** → **6a**‡ → **6a**−**NH$_3$**) is 42 kcal mol^{-1}. Formation of imine by elimination of H$_2$ (**2** → **6b**‡ → **6b**) has an elimination barrier of 25 kcal mol^{-1}. As with 1,2-elimination, extrusion of H$_2$ is kinetically more favorable than ammonia elimination by ≈20 kcal mol^{-1}.

The elimination barriers to formation of imines **6** are slightly higher (by ≈10 kcal mol^{-1}) than analogous processes involving 1,2-elimination to form imidos **3**. Imine complexes fall in between imidos and **5** (formed by β-H elimination) in terms of thermodynamic stability. The 1,2-elimination reactions (**2** → **3**) are close to thermoneutral while β-H elimination (**2** → **5**) is endothermic by 37 kcal mol^{-1}. Cyclizations (**2** → **6**) are endothermic by ≈20 kcal mol^{-1}. The calculations thus suggest the following order of kinetic and thermodynamic accessibility: 1,2-elimination < cyclization < β-H elimination. However, at the current level of theory, the 1,2-elimination and cyclization pathways would seem to be competitive, particularly if higher deposition temperatures are used and multiple decomposition pathways occur.

A possible, albeit simple, gauge of the interaction between Ti and the atom being transferred in the TS is the distance Ti−A$_t$. When the transannular atom is hydrogen these distances are only slightly longer than a normal Ti−terminal hydride bond. For the two TSs in which A$_t$ = CH$_3$ (**3b**‡ and **3e′** ‡) the TiC$_t$ distances are considerably longer, even when MA$_t$ is normalized to subtract off a normal Ti−H and Ti−C single bond calculated from the sum of covalent radii (r_{cov}(C) = 0.76 Å; r_{cov}(H) = 0.35 Å; r_{cov}(Ti) = 1.32 Å; Ti−H ≈ 1.7 Å, Ti−C ≈ 2.1 Å). Clearly, in terms of having a 1,2-elimination TS with a large X−A$_t$−E angle and hence a short MA$_t$ distance, H is preferable to CH$_3$. The structure of compounds like Al$_2$Me$_6$ indicate that a methyl group does have some capacity for participating

(28) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11711.

(29) (a) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131. (b) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903. (c) Cundari, T. R. *Organometallics* **1994**, *13*, 2987. (d) Cundari, T. R. *Organometallics* **1993**, *12*, 4971.

(30) Although **2′** is more stable than **2** by 18 kcal mol^{-1}, the transition state for their interconversion, **2**‡, is very high, ≈49 kcal mol^{-1}.

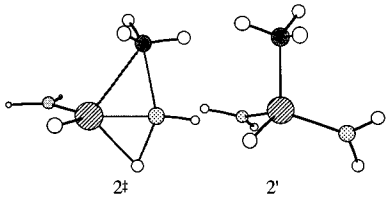


Table 2. Normalized TiA_t Distance versus Elimination Barrier

transition state	"Normalized" TiA_t (Å)[a]	$\Delta H^{\ddagger}_{elim}$ (kcal mol^{-1})[b]	X−A_t[c]
3c‡	0.11	13	H−H
3d‡	0.13	16	H−H
6b‡	0.11	25	H−H
3a‡	0.22	31	H_2N−H
3e‡	0.24	36	$CH_3(H)N$−H
6a‡	0.30	42	H_2N−H
3b‡	0.58	57	H−CH_3
3e′‡	0.77	79	H_2N−CH_3

[a] "Normalized" TiA_t distances were calculated for each 1,2-elimination (**3**‡) and cyclization (**6**‡) transition state. A typical Ti−H (**3c**‡, **3d**‡, **6b**‡, **3a**‡, **3e**‡, and **6a**‡) or Ti−C (**3b**‡ and **3e′**‡) single bond length was subtracted from the actual TiA_t distance to normalize the cases in which A_t = H and A_t = methyl. [b] Calculated enthalpies of elimination ($\Delta H^{\ddagger}_{elim}$) for 1,2-elimination (**2** → **3**‡ → **3**) and cyclization (**2** → **6**‡ → **6**). [c] The small molecule being eliminated in the decomposition pathways are given such that the leaving group (X in **1**) is denoted first and the donor group (A_t in **1**) is denoted second.

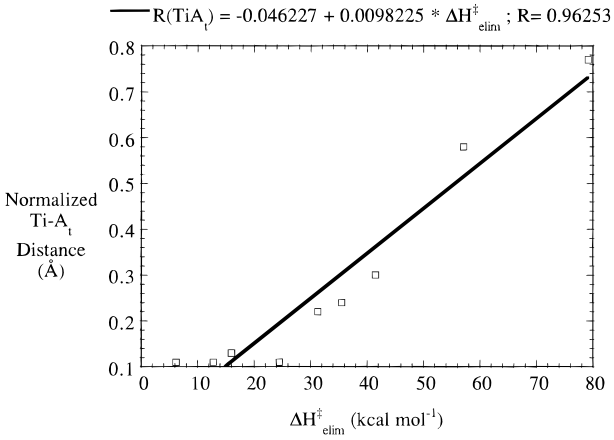


Figure 4. Plot of normalized Ti−A_t distances for TSs **3**‡ and **6**‡ versus $\Delta H^{\ddagger}_{elim}$ (HX). See text and footnotes to Table 2 for calculational details.

in multicentered interactions, but even in this case the Al−$C_{bridging}$−Al angle is very small (≈75°).[31] As first suggested by Bercaw et al.,[32] this is reasonable since the directed, sp^3 hybrid orbital of methyl cannot as easily span the obtuse angle of the "kite-shaped" TS in the same manner as the spherical H 1s orbital. It is unclear how significant these transannular interactions are in an energetic sense.

In Table 2 we have collected elimination barriers for all 1,2-elimination and cyclization processes leading from model precursor **2**. To facilitate comparison of different TiA_t interactions (A_t = H or methyl), the length of a "normal" Ti−H or Ti−C single bond (1.67 and 2.08 Å, respectively, as calculated from the sum of the appropriate covalent radii) is subtracted from these transannular distances to give normalized TiA_t distances in Table 2. Inspection of the data in Table 2 shows a general trend of increasing transannular distance with increasing elimination barrier. Plotting the data in Table 2 (Figure 4) shows a reasonable linear correlation between the normalized TiA_t distance and the elimination barrier. Shorter transannular distances in the TSs correlate with lower elimination barriers ($\Delta H^{\ddagger}_{elim}$).

Summary and Conclusions

Calculations have been performed on small-molecule elimination from $Ti(H)_2(NH_2)(N(H)Me)$, a model single-source OMCVD precursor of TiN. Reactions studied fall into three types: 1,2-elimination resulting in the formation of Ti−imidos, β-H elimination to form a five-coordinate, N-bound organic imine, and cyclization pathways leading to three-membered ring structures (i.e., η^2-imines). Several important results have been noted and are summarized below.

(1) The β-H elimination pathway from **2** is clearly thermodynamically and kinetically disfavored compared to other pathways. Formation of olefins through β-H elimination by TM−alkyls is well-known but comparatively rare for imine formation.[26] It is not clear if this is due to thermodynamic instability of imines or perhaps a kinetic disadvantage brought about by the electronegative N. To address this question, decomposition pathways for TiO and TiC precursors will compare β-H elimination to form carbonyl and olefin complexes, respectively, with imine formation by the same pathway.

(2) Elimination processes in which the atom being transferred is not a hydrogen are clearly kinetically disfavored. The present work, in particular the comparison of isomeric TSs **3e**‡/**3e′**‡ and **3b**‡/**3b′**‡, provides the first direct comparison of energetics.

(3) From a kinetic standpoint elimination of H_2 is favored over extrusion of amines. In a study of 1,2-HX elimination from group IVB amidos[9] (M = Ti, Zr, Hf) lower elimination barriers were found when X is electronegative (e.g., HX = NH_3 and HCl) versus electroneutral and electropositive (e.g., HX = H_2, CH_4, and SiH_4) leaving groups. From the viewpoint of designing single-source precursors with lower elimination barriers it is desirable to eliminate HX small molecules in which X is either electroneutral or electropositive (e.g., H_2, silanes and hydrocarbons).

(4) There are many similarities between the cyclization (**2** → **6**‡ → **6**) and 1,2-elimination pathways (**2** → **3**‡ → **3**). For example, H_2 elimination is favored over amine elimination. This suggests that the concepts developed with regard to rationalizing the relative favorability of 1,2-elimination processes may be applicable to cyclization pathways. Cyclization is slightly less favorable than analogous 1,2-elimination pathways, although differences are small enough and the limitations of the computational model suggest that at the conditions under which CVD of TiN takes place they may be competitive. One could justify this as being due to the larger coordination number, and hence greater steric crowding, in the cyclization TSs (**6**‡) than 1,2-elimination TSs (**3**‡) for the relatively small Ti. Studies are planned to further probe this question by analysis of Si and Zr analogues.

The results of this research suggest the importance of the metal−transannular interactions in modifying the energy of the TSs and hence the accessibility of reactions that pass through these TSs. It is important to reiterate that the short transannular distance results to some extent from the geometry of the TSs, and that there is no consensus as to whether the short MA_t distance is

(31) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Freeman: New York, 1990; p 316.

(32) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

indicative of bonding, in particular the energetic magnitude of this interaction.[22] The current calculations, in particular Figure 4, suggest the MA_t distance as a potentially useful design criterion for TM-containing, single-source, organometallic CVD precursors (**1**). Our research to date on quantum modeling of CVD suggests that L^8 and Z^{33} have somewhat less impact on the decomposition pathways, with X and A_t playing dominant roles (apart from M and E) in controlling the nature of the potential energy surfaces.[33]

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Supporting Information Available: Tables of Cartesian coordinates (in angstroms) for all stationary points determined in this study (10 pages). Ordering information is given on any current masthead page.

CM950314Z

(33) Substituent (*Z*) effects on model CVD reactions will be published in due course. Cundari, T. R.; Curtiss, S. *Int. J. Quantum Chem.*, in press.