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Theoretical Studies on the Decomposition Mechanism of Tetraalkyl Titanium Complexes

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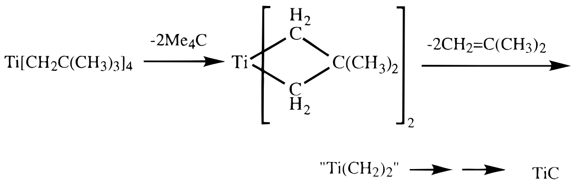
Abstract: Unimolecular and bimolecular methane eliminations of $TiMe_4$ have been studied using *ab initio* molecular orbital theory. Geometry optimizations were performed with the 3-21G and HW3 (equivalent to the 6−31G*) basis sets. The energies were further evaluated with the MP2/HW3 calculations. We predict a high activation energy for unimolecular methane elimination but a low activation energy for bimolecular methane elimination. For $Ti(CH_2CMe_3)_4$, neopentane elimination through α- and γ-hydrogen abstractions has been studied with the 3-21G basis set. We predict an intrinsic preference for α-hydrogen abstraction over γ-hydrogen abstraction. This preference is enhanced by the bulkiness of the alkyl ligands.

Introduction

Metal-organic chemical vapor deposition (MOCVD) is increasingly applied in growing high-quality thin films.[1] Recently, several reports on the MOCVD preparation of early-transition metal carbides using a single source of metal alkyl complex (MR_n) have appeared.[2−6] Most of these metal alkyl compounds are volatile and metastable and start to decompose under mild conditions. Titanium carbide, TiC, is an extremely hard material (Vickers hardness 2988 kgf mm^{-2}) with a high melting point (3340 K); it is corrosion resistant, highly conductive (specific resistivity 50 $\mu\Omega$ cm), and is essentially unaffected by acids and aqueous alkali.[7] Because of these physical properties, thin films of TiC have been used as first-wall coatings for fusion reactors, protective coatings for cutting tools,[8] and electrical contact materials.[9]

In 1987, Girolami *et al.* reported deposition of TiC at as low as 150 °C from tetraneopentyl titanium ($TiNp_4$) using a low pressure CVD method.[2] They obtained an amorphous solid with a Ti/C ratio of ca. 1:0.93. Smith *et al.* reported the CVD of TiC thin film from $TiNp_4$ at temperatures higher than 300 °C and found the Ti/C ratio of the film to be about 1:2.5.[3] In addition, a large amount of hydrogen (∼12%) was present in the film. They also found similar results for the CVD of ZrC and HfC thin films using $ZrNp_4$ and $HfNp_4$, respectively.[3]

It is important to understand the mechanism of the decomposition of metal alkyl complexes. The decomposition of many metal alkyl complexes has been studied in solution.[10] For example, $TiMe_4$ decomposes easily at room temperature in ether or hydrocarbon to afford less than a stoichiometric amount of methane (2 to 3 mol per mole of $TiMe_4$) as the major organic product. The residual black diamagnetic solid contains C, H, and Ti.[11] $TiNp_4$ decomposes in benzene at about 60 °C to give a black solid and Me_4C in which the hydrogens are not derived from the solvent.[12] It is generally accepted that the initial step in the decomposition of high-oxidation-state early-transition metal alkyl complexes is an α-hydrogen abstraction, either in an intramolecular or intermolecular fashion.[13] Initially, Girolami *et al.* proposed a mechanism with γ-hydrogen atom abstraction to rationalize the formation of the Ti−C thin film (eq 1).[2] Such a γ-hydrogen atom abstraction mechanism has been characterized for many organometallic systems[14] and in the decomposition of $CrNp_4$ based on the MS analysis of the products.[6c] However, more recent experiments by Girolami suggested neopentane elimination through α-hydrogen abstraction.[15]



(1)

In this paper, we report our *ab initio* quantum mechanics studies of alkane elimination from $TiMe_4$, Ti(n-Pr)Me_3, and

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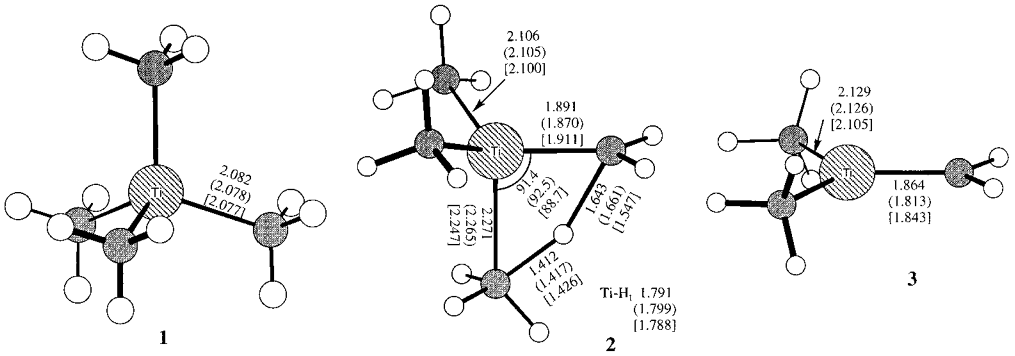
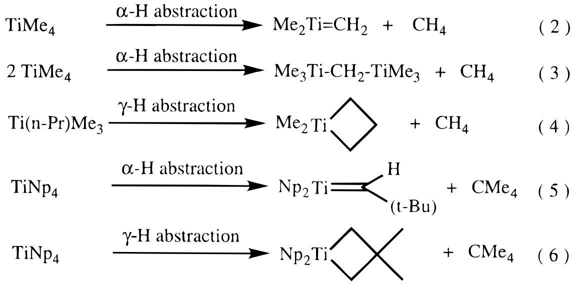


Figure 1. Calculated structure of $TiMe_4$ (**1**), transition structure of α-hydrogen abstraction (**2**), and methane elimination product (**3**) with the HF/HW3, HF/3-21G (in parentheses) and MP2/HW3 (in brackets) methods.

$TiNp_4$, as shown by eqs 2−6. We intend to address the following questions: (1) relative preferences for unimolecular and bimolecular alkane eliminations; (2) relative preference for α- and γ-hydrogen abstraction; and (3) steric effect on reaction mechanism.



Calculation Methods

All calculations were carried out with the GAUSSIAN 94 program of Pople.[16] For the $TiMe_4$ and $Ti(n\text{-}Pr)Me_3$ systems, geometries were fully optimized first with the closed-shell Hartree−Fock method and the all-electron 3-21G basis set of Hehre.[17] Harmonic vibration frequencies were calculated for each structure, based on which thermal energy and reaction entropy were calculated. The geometries were further optimized with the HW3 basis set according to Frenking's definition,[18] which was constructed by the contraction scheme [3311/2111/311] + ECP[19] on a 10-electron core for the titanium atom and the 6−31G* basis set for carbon and hydrogen atoms. The energy for each structure was also calculated by the MP2/HW3 method on the HF/HW3 geometries. The unimolecular methane elimination reaction of $TiMe_4$ was also studied with MP2/HW3 geometry optimizations. For the $TiNp_4$ system, geometries were first optimized with the HF/STO-3G method. Harmonic vibration frequencies, thermal energy, and reaction entropy were calculated based on these geometries. The geometries were further optimized with the HF/3-21G method.

Results and Discussion

The calculated total energies, thermal energies, and entropies of the reactants, transition structures, and the products of the reactions of $TiMe_4$, $Ti(n\text{-}Pr)Me_3$, and $TiNp_4$ are given in Table 1 of supporting information. Table 1 gives calculated reaction or activation energies, thermal energy ($T = 298$ K) corrections, and entropies of the decomposition reactions.

A. Unimolecular Mechanism for $TiMe_4$. Figure 1 shows the geometries of the reactant, transition structure, and alkylidene product of unimolecular methane elimination from $TiMe_4$. The optimization of $TiMe_4$ led to two different minima depending on the basis set: the 3-21G basis set yielded a structure which is in a gauche conformation with a dihedral angle H−C−Ti−C of 34.5° (T symmetry), while the HW3 basis set yielded a structure in staggered conformation (**1**) with a dihedral angle H−C−Ti−C of 60° (Td symmetry). The staggered conformation **1** calculated by the 3-21G basis set has four imaginary frequencies which correspond to the rotations of methyl groups and is higher in energy than the gauche conformation by 0.3 kcal/mol. This is in agreement with the result obtained by Frenking *et al.*[18a] But the calculated bond lengths and bond angles are very similar with both basis sets. We also calculated an eclipsed conformation of $TiMe_4$ (*Td* symmetry, dihedral angle H−C−Ti−C = 0°). It is 2.2 kcal/mol less stable than the staggered conformation **1** with the MP2/HW3 calculations.

The basic features of the transition structure (**2**) are very similar to those found for the small molecule activation/elimination process of transition metal complexes.[20] The four-centered structure is in a kite-like shape with an obtuse angle about H_t and three acute angles. The breaking Ti−C bond is about 0.2 Å longer than a normal Ti−C single bond. The ∠C−Ti−C angle is 91°, several degrees larger than in the transition structures of $NbMe_5$ and $TaMe_5$.[21] The distance between the metal (M) and the transferring hydrogen (H_t) is almost the same as the Ti−H bond length in $H_2Ti{=}CH_2$, indicating an important agostic interaction.[20b,c,22] The $Ti{=}C(H_2)$ bond is almost fully formed with the carbon center nearly planar. The breaking $C{-}H_t$ bond (1.64 Å) is very long, and is about 0.2 Å longer than the forming $C{-}H_t$ bond. In the Nb and Ta systems, however, the two C−H bonds have almost the same length.[21]

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Table 1. Calculated Changes in Energies (ΔE, kcal/mol), Changes in Enthalpies ($\Delta\Delta H°_{298}$, kcal/mol), and Entropies for the Formation of Transition Structures and Products for Alkane Elimination from TiMe$_4$, Ti(n-Pr)Me$_3$, and TiNp$_4$

		HF/3-21G			HF/HW3	MP2/HW3//HF/HW3
entry	reaction	ΔE	$\Delta\Delta H°_{298}$	ΔS_{298}	ΔE	ΔE
1	**(1) → (2)**	63.6	−2.6	−7.3	65.0	41.2 (40.7)^b
2	**(1) → (3) + CH$_4$**	51.0	−1.7	35.7	42.6	37.5 (36.7)^b
3	**(1) + (1) → (4)**	50.2	0.4	−54.0		
4	**(1) + (1) → (5)**	49.1	−0.1	−46.8	53.7	24.6
5	**(1) + (1) → (6) + CH$_4$**	−10.5	0.8	−11.0	−10.1	−20.5
6	**(7) → (8)**	62.0	−3.0	−9.3	66.1	43.4
7	**(7) → (9) + CH$_4$**	11.6	−2.8	21.1	12.9	6.7
8	**(10) → (11)**	55.2	−4.2^a	1.2^a		32.8^c
9	**(10) → (12)**	59.2	−3.4^a	−6.8^a		40.6^d
10	**(10) → (13) + CMe$_4$**	31.9	−3.2^a	47.5^a		18.4^e
11	**(10) → (14) + CMe$_4$**	2.0	−2.7^a	39.9^a		−2.9^f

[a] Calculated by the STO-3G basis set. [b] Calculated based on MP2/HW3 geometry optimizations. [c] Calculated based on comparison with entry 1: 41.2 − (63.6−55.2). [d] Calculated based on comparison with entry 6: 43.4 − (62.0−59.2). [e] Calculated based on comparison with entry 2: 37.5 − (51.0−31.9). [f] Calculated based on comparison with entry 7: 6.7 − (11.6−2.0).

Thus, the transition state is very late. This is reflected by the calculated high activation energy of 41 kcal/mol, which is larger than the activation energies of the NbMe$_5$ and TaMe$_5$ systems by about 5−7 kcal/mol. This may be due to the greater Ti−CH$_3$ bond energy.[23] The elimination is very endothermic (ΔE = 37.5 kcal/mol). For the NbMe$_5$ and TaMe$_5$ systems, the calculated corresponding reaction energies are 2.4 and 5.7 kcal/mol, respectively, more than 30 kcal/mol less endothermic. The high endothermicity and activation energy indicate that the monomeric mechanism of methane elimination from TiMe$_4$ is unlikely at room temperature.[11]

The alkylidene product **3** is slightly pyramidalized at the Ti atom (C$_1$ symmetry) with the 3-21G basis set,[24] but is "planar" with C_{2v} symmetry with the HW3 basis set, in agreement with the results of previous calculation on titanium alkylidene analogues.[25] The two methyls favor a staggered conformation with respect to the Ti═CH$_2$ bond.

Table 1 indicates that MP2 correlation energy significantly reduces the calculated reaction energy and activation energy. We therefore tested the effect of MP2/HW3 geometry optimization on the geometry and energetics. The MP2/HW3 geometries are only slightly different from those HF/HW3 and HF/3-21G geometries (Figure 1). The calculated MP2/HW3 reaction energies are slightly smaller than those calculated based on the HF/HW3 geometries. Therefore, MP2/HW3 geometry optimizations were not carried out for other reactions.

B. Bimolecular Mechanism for TiMe$_4$. Two transition structures **4** and **5** have been located with the 3-21G basis set for methane elimination with a bimolecular mechanism. Both transition structures are in an intermolecular mode. That is, the leaving methyl group abstracts a hydrogen from a methyl of the second TiMe$_4$. The two structures differ mainly in the orientation of the incoming TiMe$_4$ with respect to the leaving methyl group. In structure **4**, the relationship may be called anti, as indicated by a Ti$_2$−C$_t$−Ti$_1$−C$_l$ dihedral angle of 113.5° and an H$_t$−C$_t$−Ti$_2$ angle of 122°. In structure **5**, however, a syn relationship is found, as indicated by a Ti$_2$−C$_t$−Ti$_1$−C$_l$ dihedral angle of 0° and an H$_t$−C$_t$−Ti$_2$ angle of 98°. Compared to the monomeric transition structure **2**, some geometrical differences are apparent: (1) the length of the breaking C--H$_t$ bond (1.39 Å) is much shorter than that in structure **2** (1.64 Å); (2) the C--Ti--C angle is reduced from 92° in structure **2** to about 75°; and (3) the Ti--H$_t$ distance in the two structures is about 0.1 Å longer than that in structure **2**. With the HW3 basis set, we found that structure **4** collapsed into structure **5**.

The calculated activation energy (Table 1, $\Delta E_{\mathrm{MP2/HW3}}$) with structure **5** is 24.6 kcal/mol. Although structure **4** is about 1 kcal/mol less stable than **5** with the 3-21G basis set, and cannot be located with the HW3 basis set, we expect it to benefit from better correlation energy stabilization, because the C$_t$--H$_t$ is more anti to the C$_t$--Ti$_2$.[21] We therefore did an MP2/HW3 single point calculation on an HF/HW3 structure optimized with the constraint of the Ti$_2$−C$_t$−Ti$_1$−C$_l$ at 113.5° and found that it is about 3.4 kcal/mol more stable than structure **5**.[26] This means that if MP2/HW3 geometry optimization is carried out, structure **4** would have an activation energy of about 20 kcal/mol.

Therefore, the bimolecular mechanism of methane elimination has a significantly lower activation energy than the unimolecular mechanism.[27] We believe that this is mainly due to the formation of Ti−C−Ti bridging, which is reflected in the reaction energy. The calculated reaction energy is 37.5 kcal/mol for the unimolecular methane elimination but is −20.5 kcal/mol for the bimolecular mechanism.

Only one structure can be located for the product Me$_3$Ti(CH$_2$)TiMe$_3$ (**6**). It has a C_2 symmetry with the C_2 axis running along the bridging CH$_2$ group. The Ti−CH$_2$ single bond is shorter than the normal Ti−CH$_3$ bonds by 0.03 Å. The angle at the bridging group is 125°, somewhat larger than the tetrahedral value, possibly due to steric interactions between the two metal centers.

Tetramethyl titanium decomposes easily at 10−20 °C in benzene.[11] We believe that the decomposition in solution is through the bimolecular mechanism.[27] Such is the case in the decomposition of NbMe$_5$ and TaMe$_5$.[21]

C. Unimolecular γ-Hydrogen Abstraction Mechanism for Ti(n-Pr)Me$_3$. Metallacyclobutane has been proposed as a very

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(24) Pyramidilization at the titanium center of L$_2$Ti═CH$_2$ (L = H, Cl, Cp) structures was also found by the Extended Hückel (EH) molecular orbital method, see: Gregory, A. R.; Mintz, E. A. *J. Am. Chem. Soc.* **1985**, *107*, 2179.

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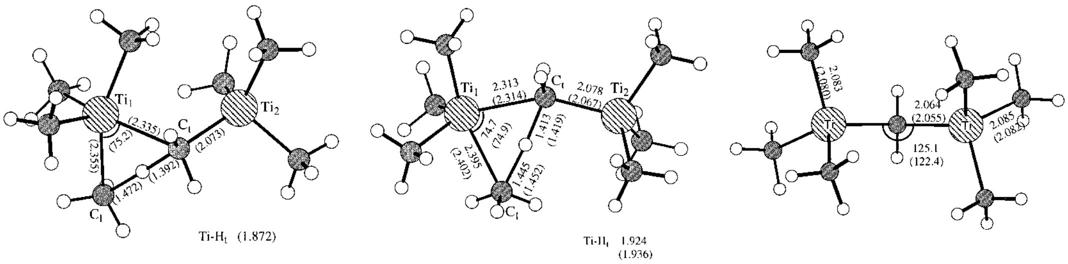
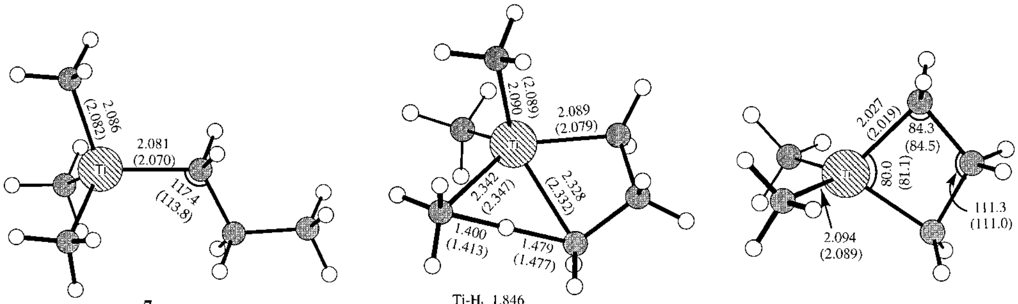
(26) This situation is very similar to the bimolecular methane elimination from ZrMe$_4$ where a stable structure **4** can be located with the HF/HW3 method, and it is 0.3 kcal/mol more stable than structure **5** with the HF/HW3 but becomes 7.0 kcal/mol more stable with the MP2/HW3 method: Wu, Y.-D.; Chan, K. W. K.; Peng, Z.-H., unpublished results.

(27) The calculated large loss of entropy in the bimolecular transition structures **4** and **5** are mainly contributed from the loss of translation and rotation and should not significantly contribute to the activation free energy for solution reactions. For related discussion, see: ref 21, p 9263.



4 **5** **6**

Figure 2. Transition structures (**4**, **5**) and product (**6**) for the bimolecular elimination from $TiMe_4$ calculated with HW3 and 3-21G (in parentheses) basis sets.



7 **8** **9**

Figure 3. Calculated structure of Ti(n-Pr)Me_3 (**7**), transition structure of γ-hydrogen abstraction (**8**), and the methane elimination product (**9**) with HW3 and 3-21G (in parentheses) basis sets.

important intermediate in olefin metathesis and other related catalytic reactions. Many theoretical[28] and experimental[29,30] studies on metallacyclobutane have confirmed this proposal. Bruno *et al.* carried out a detailed study on the cyclometalation of bis(pentamethylcyclopentadienyl)thorium dialkyl complexes and proposed that cyclometalation processes occur mostly through γ-hydrogen abstraction.[14] To test the possible involvement of titanium metallacyclobutane in the CVD of Ti−C from $TiNp_4$,[2] we first studied methane elimination from the model system of Ti(n-Pr)Me_3 with γ-hydrogen abstraction. Figure 3 shows the geometries of the reactant (**7**), transition structure (**8**), and titanacyclobutane product (**9**).

In the staggered conformation (**7**) of Ti(n-Pr)Me_3, the Ti−propyl carbon bond length is about 0.005 Å shorter than that of the other Ti−C bonds. The Ti−C−C angle in Ti−C_3H_7 is about 117°, several degrees larger than the tetrahedral value due to the steric interaction of the alkyl ligand.

The transition structure (**8**) has a kite-like shape, which is similar to that of the transition structure of bimolecular methane elimination of $TiMe_4$ (**5**). The breaking Ti−C bond and the forming Ti−C bond are almost the same length and are about 0.06 Å shorter than those in structure **5**. The ∠C−Ti−C is about 76°, almost the same as that in structure **5**. The two partially formed C−H bonds are slightly shorter than in the monomeric reaction and the Ti−H_t bond is 0.05 Å longer. The calculated activation energy (ΔE) is 43.4 kcal/mol, about 2.2 kcal/mol higher than that of the α-hydrogen abstraction in $TiMe_4$. With thermal energy and entropy included, the difference in activation free energy at room temperature is about 2.4 kcal/mol favoring α-hydrogen abstraction. This indicates that there is no intrinsic preference for γ-hydrogen abstraction, despite the avoidance of angle strain around the C−Ti−C. This is apparently caused by the angle strain in the metallacycle. The Ti−C−C angle is reduced to 94.7° from 117° in the reactant, while the C−C−C angle is 102.3°.

The titanacyclobutane product (**9**) is a planar ring with ∠C−Ti−C = 80°, ∠Ti−C−C = 84° (two), and ∠C−C−C = 111°, in agreement with experimental[29b] and theoretical data of similar compounds.[31] The Ti−C bond length in the ring is about 0.07 Å longer than that of a normal Ti−C single bond. Compared to the α-hydrogen abstraction in $TiMe_4$, the reaction is about 30 kcal/mol less endothermic, which reveals that the Ti−C σ-bond is much stronger than the Ti−C π-bond.

D. Neopentane Elimination from $TiNp_4$. Figure 4 shows the geometries of the reactant (**10**), α-hydrogen abstraction transition structure (**11**), γ-hydrogen abstraction transition structure (**12**), alkylidene product (**13**), and titanacyclobutane product (**14**).

The tetrahedral geometry of tetraneopentyl titanium (**10**) has an S_4 symmetry. All the methyl hydrogens, which are omitted in the drawing for clarity, have a staggered orientation. The Ti−C bond is longer than that in $TiMe_4$ by about 0.02 Å, presumably due to the steric crowding of neopentyl groups. The Ti−C−C angles are about 9° larger than those in Ti(n-Pr)Me_3 (**7**). As far as we know, there is no theoretical data on the

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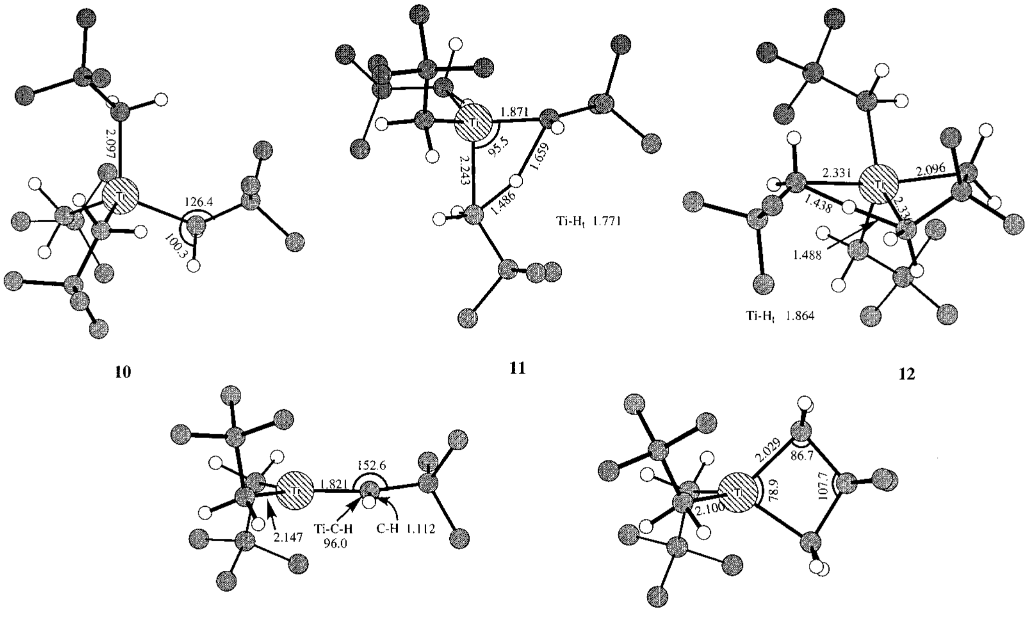

10

11

12

13

14

Figure 4. Calculated structure of TiNp$_4$ (**10**), transition structure of α-hydrogen abstraction (**11**), γ-hydrogen abstraction (**12**), and their CMe$_4$ elimination products (**13**, **14**) with 3-21G basis set (with methyl hydrogens omitted for clarity).

neopentyl metal complexes, but large Ti−C−C angles are generally observed in the X-ray crystal structures of transition metal complexes bearing a neopentyl group.[32] For example, the ∠Ti−C−C is 141.7° in (CMe$_3$CH$_2$)$_3$Ti-Si(SiMe$_3$)$_3$[32a] and the ∠Zr−C−C is 143° in (Cp′)$_2$ZrNp$_2$.[32b] Although the variation in the metal−C−C angle can be most conveniently attributed to steric crowding, we feel that agostic interaction involving the α-hydrogens also plays an important role.[22] Thus, more electron deficient metal centers should correspond to larger metal−C−C angles.

The α-hydrogen abstraction transition structure (**11**) is very similar to transition structure **2** for the unimolecular methane elimination of TiMe$_4$. The four *tert*-butyl groups adopt orientations which possess the lowest steric interactions. The transferring hydrogen is nearly on the same plane as Ti−C−C probably because the Ti−C−C is already large in the reactant and can be more easily opened up to accommodate the hydrogen. The γ-hydrogen abstraction transition structure **12** is very similar to structure **8**. The two intact neopentyl groups are in conformations which avoid steric interactions with the two reacting neopentyl groups.

The activation energies of the α- and γ-hydrogen abstraction processes calculated with the HF/3-21G method are 55.2 and 59.2 kcal/mol, respectively. The corresponding activation energies of α-hydrogen abstraction of TiMe$_4$ and γ-hydrogen abstraction of Ti(n-Pr)Me$_3$ at the HF/3-21G level are 63.6 and 62.0 kcal/mol, respectively. So the activation energies are reduced by about 8.4 kcal/mol for the α-hydrogen abstraction and by about 2.8 kal/mol for the γ-hydrogen abstraction. Presumably this is due to the release of the steric strain in the tetraneopentyl titanium complex. This steric effect on reactivity is widely recognized.[10,13] The fact that the α-hydrogen abstraction benefits more from the relief of steric interaction than the γ-hydrogen abstraction can be traced to the geometries of the two transition structures. The departure of a neopentyl group in structure **11** allows the two intact neopentyl groups to open up, leading to a less crowded environment, as indicated by the C−Ti−C angle of 117.9°; while in structure **12**, the pentacoordinated titanium center is still in a crowded environment, as evidenced by the near tetrahedral values for the C−Ti−C angles. For example, the C−Ti−C angle of the two intact neopentyls is 108.6°. The steric effect is also reflected in the reaction energies. The calculated reaction energy for the α-hydrogen abstraction process is about 19 kcal/mol less endothermic than that for the unimolecular reaction of TiMe$_4$, while for the γ-hydrogen abstraction process, the reaction energy is lowered by about 10 kcal/mol compared to that for the γ-hydrogen abstraction of Ti(n-Pr)Me$_3$.

Since the calculations indicate that the introduction of *tert*-butyl groups in TiNp$_4$ has little effect on geometries as compared to the geometries of TiMe$_4$ and Ti(n-Pr)Me$_3$, we can roughly estimate the MP2/HW3 reaction energies of the TiNp$_4$ system by adding the steric effects calculated by the HF/3-21G method (as just discussed above) to the corresponding MP2/HW3 values of the TiMe$_4$ and Ti(n-Pr)Me$_3$ systems. Thus, we estimate that at the MP2/HW3 level, the neopentane elimination of TiNp$_4$ through α-hydrogen abstraction has a lower activation energy by about 8 kcal/mol than the γ-hydrogen abstraction. In addition, the thermal energy correction calculated with the STO-3G basis set favors the α-hydrogen abstraction by about 1 kcal/mol, and the entropy favors the α-hydrogen abstraction by about 8 eu (see Table 1). Thus, for CVD of Ti−C from TiNp$_4$ at 150 °C, we estimate the activation free energy of initial neopentane elimination to be about 12 kcal/mol more favorable for α-hydrogen abstraction than for γ-hydrogen abstraction.

In benzene solution, TiNp$_4$ decomposes at 60 °C with a $t_{1/2}$ of 14 h.[12] Our calculated activation free energy for unimolecular neopentane elimination with α-hydrogen abstraction is about 27 kcal/mol. This is in accord with the experiment. A bimolecular mechanism would have higher activation free energy because of steric interactions between the two TiNp$_4$ units and the loss of entropy. The fact that the decomposition rates are in the order TiNp$_4$ > Ti(CH$_2$SiMe$_3$)$_4$ > Ti(CH$_2$SnMe$_3$)$_4$ is also in line with the unimolecular mechanism because the release of steric interaction decreases in the same order.[10]

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In the trigonal planar alkylidene product (**13**), the ∠Ti═C−C is very large (152.6°) and the ∠Ti═C−H is only about 96°. Such large deviation from an sp^2-hybridized carbon center has been generally found in isolated neopentylidene metal electron-deficient complexes.[33] This has been mainly attributed to the donation of the C−H bonding electron pair into the metal−carbon bond,[25d,33] i.e., hyperconjugation, as indicated by a long C−H bond length (1.112 Å) in structure **13**. Interestingly, the calculated $Ti-C_\alpha-C$ angle in the two neopentyl groups is about 109° (compared to 126° in structure **10**), and one of the $Ti-C_\alpha-H$ angles is about 105° while the other is about 117°; the above geometrical features indicate the importance of α-agostic interactions in the metal−alkylidene species. The geometry of the titanacyclobutane product (**14**) is very similar to that of structure **9**, and the four-membered ring is essentially planar.[29b,31] A C_{2v} structure with the two t-Bu groups bisecting the C−Ti−C angle is about 2 kcal/mol less stable than structure **14**.

D. Summary. Quantum mechanics *ab initio* calculations have been carried out for the unimolecular and bimolecular methane elimination from $TiMe_4$, methane elimination from Ti(n-Pr)Me_3 through γ-hydrogen abstraction, and neopentane elimination from $TiNp_4$ through α-hydrogen and γ-hydrogen abstractions. In agreement with Schrock's hypothesis and our previous study on $NbMe_5$ and $TaMe_5$, the first step in the decomposition of $TiMe_4$ is a bimolecular methane elimination through intermolecular hydrogen abstraction. For titanium alkyl complexes, there is an intrinsic preference for α-hydrogen abstraction over γ-hydrogen abstraction. This preference is increased when the alkyl group becomes bulkier. In support of Girolami's experiments, calculations suggest that the first step of CVD of TiC thin films is through intramolecular α-hydrogen abstraction to form alkylidene. The further detailed decomposition mechanism of $TiNp_4$ along with the decomposition of $ZrNp_4$ and $HfNp_4$ systems are currently being investigated.

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Supporting Information Available: Calculated energy, thermal energy, and entropy of the species involved in the decompositions of $TiMe_4$, Ti(n-Pr)Me_3, and $TiNp_4$ (1 page). See any current masthead page for ordering and Internet access instructions.

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