

# Mechanistic Studies of the Thermolysis of Tetraneopentyltitanium(IV). 1. Solution Evidence That Titanium Alkylidenes Activate Saturated Hydrocarbons

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**Abstract:** Studies of the thermolysis of  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$  in solution have been carried out in parallel with studies of the chemical mechanism responsible for its conversion to titanium carbide under CVD conditions. In hydrocarbon solutions, the neopentyl complex thermolyzes to eliminate 2.1 equiv of neopentane as the principal organic product. A deuterium kinetic isotope effect ( $k_{\alpha(\text{H})}/k_{\alpha(\text{D})} = 5.2 \pm 0.4$ ) upon deuterating the alkyl groups at the  $\alpha$  positions provides clear evidence that the initial step in the thermolysis is an  $\alpha$ -hydrogen abstraction reaction to form neopentane. The activation parameters for this  $\alpha$ -hydrogen abstraction process are  $\Delta H^\ddagger = 21.5 \pm 1.4$  kcal/mol and  $\Delta S^\ddagger = -16.6 \pm 3.8$  cal/(mol K). The titanium-containing product of this reaction is a titanium alkylidene, which in solution activates C–H bonds of both saturated and unsaturated hydrocarbon solvents such as benzene and cyclohexane. No activation of the C–F bonds of hexafluorobenzene is seen, however. Under special circumstances, a second thermolysis pathway for  $\text{TiNp}_4$  can be detected,  $\gamma$ -hydrogen activation, but this pathway is intrinsically about 25 times slower than the  $\alpha$ -hydrogen abstraction process.

In 1987, we reported a metal–organic chemical vapor deposition (MOCVD) method for the deposition of amorphous thin films of titanium carbide at temperatures some 1000 °C lower than those characteristic of CVD processes that use  $\text{TiCl}_4$  and methane as starting materials.<sup>1,2</sup> The organometallic precursor used, tetraneopentyltitanium ( $\text{TiNp}_4$ ), reacts at temperatures as low as 150 °C to deposit TiC as pure, adherent films on a variety of substrates. In the course of the CVD process,  $\text{TiNp}_4$  undergoes selective thermolysis to lose 19 of the 20 carbon atoms and essentially all of the 44 hydrogen atoms to give a single solid-state product.<sup>3</sup>

We have been interested in determining the mechanism by which this remarkable transformation takes place. The mechanisms of the thermal decomposition of transition metal alkyls have been intensively studied in solution,<sup>4–6</sup> and an important issue to be addressed is whether these same mechanisms can operate under CVD conditions as well. In solution,  $\beta$ -stabilized alkyl complexes of  $d^0$  early transition metals (of which  $\text{TiNp}_4$  is an example) do not all thermolyze via similar mechanisms. For some early transition metal alkyl complexes, e.g.  $\text{TiMe}_4$ ,<sup>7–9</sup>  $\text{NbMe}_5$ ,<sup>10</sup> and  $\text{TaMe}_5$ ,<sup>10</sup> the evolution of alkane as a function of time follows an “S” shape that is characteristic of an auto-

catalytic mechanism. However, other early transition metal alkyls such as  $\text{Cp}_2\text{TiMe}_2$ ,<sup>11–14</sup>  $\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})_2$ ,<sup>15</sup>  $\text{Cp}_2\text{TiNp}_2$ ,<sup>16</sup>  $\text{Cp}^*\text{TiMe}_2$ ,<sup>17</sup>  $\text{Cp}^*\text{Hf}(\text{CH}_2\text{Ph})_2$ ,<sup>18</sup>  $\text{Ta}(\text{CH}_2\text{Ph})_5$ ,<sup>19</sup>  $\text{TaNp}_5$ ,<sup>20,21</sup>  $\text{CpTaNp}_2\text{X}_2$ ,<sup>22</sup> and  $\text{Cp}^*\text{TaNp}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ )<sup>22</sup> have been shown to decompose in solution via non-autocatalytic mechanisms involving intramolecular  $\alpha$ -hydrogen abstraction processes. In the above studies, however, only for the group 5 neopentyl compounds  $\text{TaNp}_5$ ,  $\text{CpTaNp}_2\text{X}_2$ , and  $\text{Cp}^*\text{TaNp}_2\text{X}_2$  could an alkylidene complex be isolated as the direct organometallic product.

We note in passing that while  $\alpha$ -hydrogen abstraction is well-known for the alkyl derivatives of the group 5 and 6 metals, it is rare for group 4 alkyls. There are a few reports of the generation of group 4 alkylidene compounds in situ,<sup>23,24</sup> and recently the first such compound has been isolated

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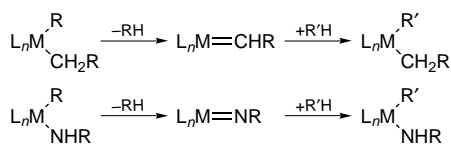
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and fully characterized.<sup>25</sup> Group 4 alkylidenes remain very elusive.<sup>26–31</sup>

Early transition metal alkylidenes are of interest in another context. High-valent (e.g., d<sup>0</sup>) metal compounds with M=C or M=N double bonds can effect the intermolecular activation of saturated hydrocarbons. For example, alkylidene or imido intermediates such as (RO)<sub>2</sub>M=CHR, Cp<sub>2</sub>M=CHR, and Cp<sub>2</sub>M=NR, where M can be Ti, Zr, V, or Ta, generated by 1,2 alkane elimination from dialkyl or alkylamido precursors, can add a second hydrocarbon R'-H across the double bond.<sup>17,18,32–39</sup>

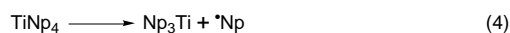
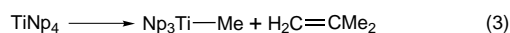
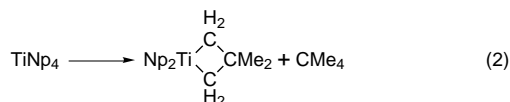


Intermolecular addition of a hydrocarbon across an M=CHR (or M=NR) bond constitutes the microscopic reverse of  $\alpha$ -hydrogen abstraction from metal-dialkyl (or metal-alkylamido) complexes.

The thermolysis of TiNp<sub>4</sub> in solution has been reported to follow first order kinetics to give neopentane, but full details have not been described.<sup>4,40,41</sup> We now present our studies of the thermolysis of TiNp<sub>4</sub> in solution; analogous studies under CVD conditions are described elsewhere.<sup>42</sup> Our results clearly demonstrate that TiNp<sub>4</sub> thermolyzes via a unimolecular  $\alpha$ -hydrogen abstraction process to give a titanium alkylidene complex irrespective of the medium. Interestingly, in solution the titanium alkylidene reacts with the hydrocarbon solvent: even saturated hydrocarbons such as cyclohexane add across the Ti=C double bond to give what we believe is an unstable Ti-(c-Hx)Np<sub>3</sub> intermediate.

## Results and Discussion

**Preliminary Evaluation of the Possible Thermolysis Mechanisms.** The thermolysis of TiNp<sub>4</sub> could occur via one of at least four different mechanisms:  $\alpha$ -hydrogen abstraction to give a titanium alkylidene and neopentane (eq 1),  $\gamma$ -hydrogen abstraction to give a titanacyclobutane and neopentane (eq 2),  $\beta$ -methyl elimination to give a Ti-Me complex and isobutylene (eq 3), or homolytic cleavage of the Ti-C bond to give a Ti<sup>III</sup> intermediate and a neopentyl radical (eq 4). Neopentyl radicals are known to scavenge hydrogen efficiently to form neopentane; they can also couple to form dineopentyl, eliminate a hydrogen atom to yield 1,1-dimethylcyclopropane, or eliminate a methyl group to form isobutylene.<sup>43,44</sup>



We find, in agreement with a previous report,<sup>40</sup> that the thermolysis of TiNp<sub>4</sub> both in solution and under CVD conditions (250 °C, 10<sup>-4</sup> Torr) gives neopentane as the predominant organic product. The absence of significant amounts of isobutylene among the products immediately suggests that the  $\beta$ -methyl elimination mechanism (eq 3) is not the pathway by which TiNp<sub>4</sub> thermolyzes. The other three mechanisms, however, all predict that neopentane should be a major component of the organic byproducts, and cannot be distinguished on this basis.

**Kinetic Isotope Effects in Solution.** In order to determine which of the other three mechanisms accounts for the early stages of the decomposition process, deuterium-labeling studies have been carried out. Specifically, only the  $\alpha$ -hydrogen abstraction mechanism predicts that the three molecules Ti(CH<sub>2</sub>-CMe<sub>3</sub>)<sub>4</sub> (TiNp<sub>4</sub>-d<sub>0</sub>), Ti(CHDCMe<sub>3</sub>)<sub>4</sub> (TiNp<sub>4</sub>-d<sub>4</sub>), and Ti(CD<sub>2</sub>-CMe<sub>3</sub>)<sub>4</sub> (TiNp<sub>4</sub>-d<sub>8</sub>) should thermolyze at significantly different rates.

The thermal decompositions of these three isotopically-labeled compounds have been followed by <sup>1</sup>H NMR spectroscopy in benzene-d<sub>6</sub> at 80 °C in sealed NMR tubes. Over a period of about a day, the solutions darken and a black precipitate appears. The <sup>1</sup>H and <sup>13</sup>C NMR spectra show that neopentane is the only organic byproduct formed. No organometallic species other than the starting material are evident at any time.

The reaction rates were determined from the disappearance of TiNp<sub>4</sub>. The thermolyses of TiNp<sub>4</sub>-d<sub>0</sub>, -d<sub>4</sub>, and -d<sub>8</sub> at 80 °C in C<sub>6</sub>D<sub>6</sub> all follow first-order kinetics over 3 half-lives (Figure 1), and the rate constants are independent of the initial concentration (Table 1). In no case was there evidence of an induction period that would suggest an autocatalytic mechanism for these thermolyses.

The rates of thermolysis of the different deuterated complexes are clearly different. Whereas TiNp<sub>4</sub>-d<sub>0</sub> decomposes with a half-life of approximately 2.2 h at 80 °C, TiNp<sub>4</sub>-d<sub>8</sub> decomposes with a half life of approximately 11.3 h. The rate constants for thermolysis at 80 °C in C<sub>6</sub>D<sub>6</sub> are 8.8 × 10<sup>-5</sup>, 5.2 × 10<sup>-5</sup>, and 1.7 × 10<sup>-5</sup> s<sup>-1</sup> for the TiNp<sub>4</sub>-d<sub>0</sub>, -d<sub>4</sub>, and -d<sub>8</sub> compounds, respectively. As expected on statistical grounds, the rate constant for thermolysis of the d<sub>4</sub> compound is almost exactly

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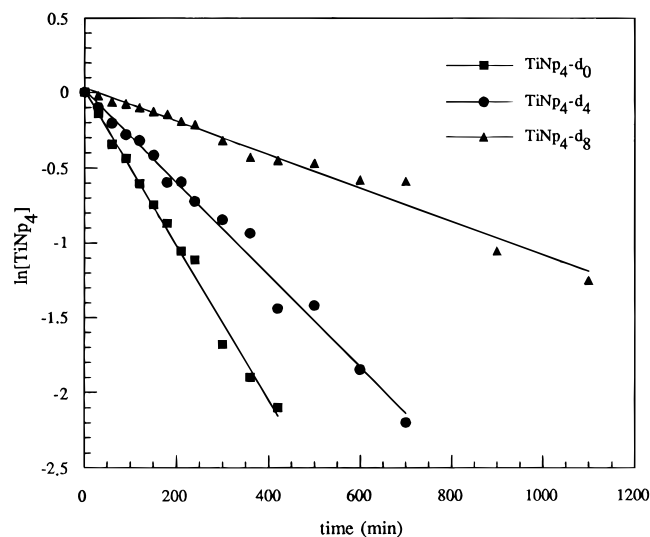
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**Figure 1.** First-order kinetic plots of the thermolysis of  $\text{TiNp}_4$ - $d_0$ , - $d_4$ , and - $d_8$  in  $\text{C}_6\text{D}_6$  at 80 °C.

**Table 1.** Summary of Rate Constants of Thermolysis of  $\text{TiNp}_4$  at 80 °C

compd	solv	conc, $10^{-2}$ M	rate const, $10^{-5}$ s $^{-1}$
$\text{TiNp}_4$ - $d_0$	$\text{C}_6\text{D}_6$	0.5	$9.0 \pm 0.2$
	$\text{C}_6\text{D}_6$	2.5	$8.5 \pm 0.2$
	$\text{C}_6\text{D}_6$	8.0	$8.9 \pm 0.2$
	$\text{C}_6\text{F}_6$	3.0	$10.1 \pm 0.3$
	$\text{C}_6\text{F}_6$	6.0	$11.0 \pm 0.3$
	$\text{C}_6\text{D}_{12}$	2.9	$9.7 \pm 0.6$
$\text{TiNp}_4$ - $d_4$	$\text{C}_6\text{D}_6$	6.0	$10.6 \pm 0.6$
	$\text{C}_6\text{D}_6$	2.8	$4.9 \pm 0.1$
	$\text{C}_6\text{D}_6$	6.0	$5.5 \pm 0.1$
$\text{TiNp}_4$ - $d_8$	$\text{C}_6\text{D}_6$	9.1	$5.2 \pm 0.1$
	$\text{C}_6\text{D}_6$	2.5	$1.3 \pm 0.06$
	$\text{C}_6\text{D}_6$	8.9	$1.9 \pm 0.06$
	$\text{C}_6\text{D}_6$	16.2	$1.7 \pm 0.06$
	$\text{C}_6\text{F}_6$	3.0	$1.8 \pm 0.12$

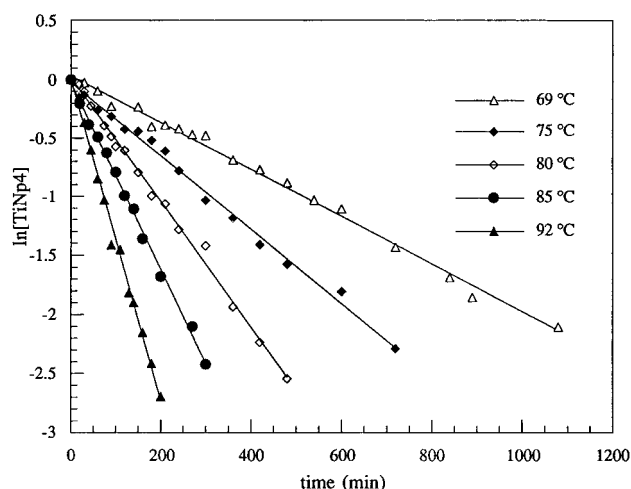
the arithmetic mean of the rate constants for thermolysis of the  $d_0$  and  $d_8$  species. From a comparison of the thermolysis rates of the  $d_0$  and  $d_8$  compounds, a kinetic isotope effect  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})}$  of  $5.2 \pm 0.4$  can be derived. This result clearly indicates that a methylene C–H bond is broken in the rate-determining step. Such a large kinetic isotope effect rules out the  $\gamma$ -hydrogen abstraction and radical pathways and is only consistent with an  $\alpha$ -hydrogen abstraction mechanism.

Studies in cyclohexane- $d_{12}$  and hexafluorobenzene showed that thermolysis of  $\text{TiNp}_4$  followed first-order kinetics in these solvents also, with rate constants that are very similar to those measured in benzene- $d_6$  (Table 1). This observation rules out the possibility that the thermolysis of  $\text{TiNp}_4$  is a pseudo-first-order reaction involving participation of the solvent in the rate-determining step. The thermolysis of  $\text{TiNp}_4$  at 80 °C in  $\text{C}_6\text{D}_6$  is also unaffected by the presence of phosphines such as 1,2-bis(dimethylphosphino)ethane. A rate of  $10.5 \times 10^{-5}$  s $^{-1}$  was measured in the presence of 1.3 equiv of this chelating phosphine.

Kinetic isotope effects have been measured for a few other  $\alpha$ -hydrogen abstraction processes involving early transition metal alkyls and aryls. Schrock measured a kinetic isotope effect of 2.7 for the  $\alpha$ -hydrogen abstraction process that converts  $\text{TaNP}_5$  (formed in situ from the reaction of  $\text{TaNP}_3\text{Cl}_2$  with  $\text{LiNp}$ ) to the alkylidene  $\text{Ta}(\text{=CHCMe}_3)\text{Np}_3$ .<sup>20</sup> The thermal decomposition of  $\text{Ta}(\text{CH}_2\text{Ph})_5$  exhibited a similar kinetic isotope effect of 2–3 for the  $\alpha$ -hydrogen abstraction process.<sup>19</sup>

**Table 2.** Rate Constants for Thermolysis of 0.03 M Solutions of  $\text{TiNp}_4$ - $d_0$  in  $\text{C}_6\text{D}_6$  at Different Temperatures

$T$ , °C	rate const, $10^{-5}$ s $^{-1}$
69	$3.1 \pm 0.06$
75	$5.4 \pm 0.1$
80	$8.6 \pm 0.2$
85	$13.7 \pm 0.2$
92	$22.9 \pm 0.5$



**Figure 2.** First-order kinetic plots of the thermolysis of  $\text{TiNp}_4$ - $d_0$  in  $\text{C}_6\text{D}_6$  at different temperatures. These data gave the rates listed in Table 2.

In contrast, the thermal decomposition of  $\text{Cp}^*\text{TaNP}_2\text{X}_2$  and  $\text{Cp}^*\text{TaNP}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) showed a large kinetic deuterium isotope effect of ca. 6 in the rate determining  $\alpha$ -hydrogen abstraction step.<sup>22</sup> There are two studies of  $\alpha$ -hydrogen abstraction processes in group 4 alkyls: Bercaw determined kinetic isotope effects of 2.9 and 3.1 for thermolysis of  $\text{Cp}^*_2\text{TiMe}_2$ <sup>17</sup> and  $\text{Cp}^*_2\text{Hf}(\text{CH}_2\text{Ph})_2$ ,<sup>18</sup> respectively. In addition, a kinetic isotope effect of 5.1 has been measured for an  $\alpha$ -hydrogen migration reaction in the tungsten alkyl/alkylidyne complex  $\text{W}(\text{=CSiMe}_3)\text{Np}_3$ .<sup>45</sup>

The kinetic isotope effect  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})}$  of  $5.2 \pm 0.4$  observed for  $\text{TiNp}_4$  is larger than most of those measured for  $\alpha$ -hydrogen abstraction processes in other group 4 and 5 transition metal alkyls, but is similar to the KIE's seen in  $\text{Cp}^*\text{TaNP}_2\text{X}_2$ ,  $\text{Cp}^*\text{TaNP}_2\text{X}_2$ , and the group 6 alkyl  $\text{W}(\text{=CSiMe}_3)\text{Np}_3$ .<sup>22,45</sup> The large isotope effect suggests that the transition state for  $\alpha$ -hydrogen abstraction in  $\text{TiNp}_4$  must lie near the half-way point along the reaction coordinate that connects the reactant and products. Symmetric transition states are known to deliver the maximum kinetic isotope effect.<sup>46–51</sup>

**Activation Parameters in Solution.** The activation parameters for the thermolysis of  $\text{TiNp}_4$ - $d_0$  in  $\text{C}_6\text{D}_6$  have been determined from the temperature dependence of the rate constant (Table 2). The resulting first-order plots are shown in Figure 2. From these data, the activation parameters  $\Delta H^\ddagger = 21.5 \pm 1.4$  kcal/mol and  $\Delta S^\ddagger = -16.6 \pm 3.8$  cal/(mol K) have been

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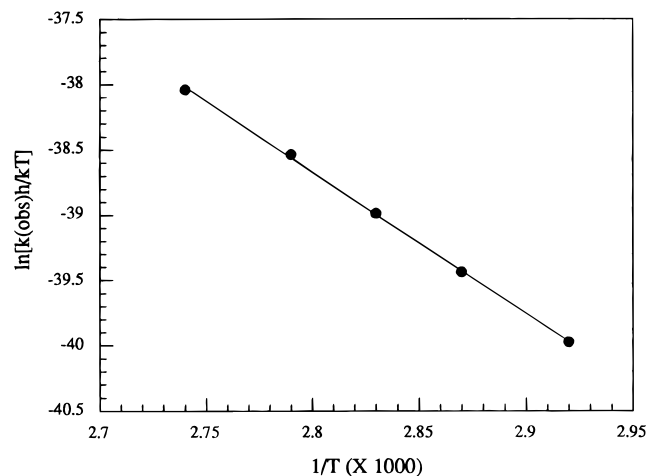
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**Figure 3.** Eyring plot of the thermolysis of  $\text{TiNp}_4\text{-}d_0$  in  $\text{C}_6\text{D}_6$ . The derived activation parameters are  $\Delta H^\ddagger = 21.5 \pm 1.4$  kcal/mol and  $\Delta S^\ddagger = -16 \pm 4$  eu.

calculated from an Eyring plot (Figure 3). The free energy of activation,  $\Delta G^\ddagger$ , is  $27.4 \pm 3.9$  kcal/mol at  $80^\circ\text{C}$ .<sup>52–55</sup>

In comparison, activation parameters of  $\Delta H^\ddagger = 27.6 \pm 0.3$  kcal/mol and  $\Delta S^\ddagger = -2.9 \pm 0.7$  eu were found for the thermal decomposition of  $\text{Cp}^*\text{TiMe}_2$ <sup>17</sup> and  $\Delta H^\ddagger = 34 \pm 1$  kcal/mol and  $\Delta S^\ddagger = 1 \pm 3$  eu for thermolysis of  $\text{Cp}^*\text{Hf}(\text{CH}_2\text{Ph})_2$ .<sup>18</sup> Similar activation parameters of  $\Delta H^\ddagger = 27.5 \pm 0.6$  kcal/mol and  $\Delta S^\ddagger = -2.0 \pm 1.7$  eu have been measured for migration of an  $\alpha$ -hydrogen atom in  $\text{W}(\equiv\text{CSiMe}_3)\text{Np}_3$ .<sup>45</sup> Activation parameters for the group 5 compounds  $\text{CpTa}\text{Np}_2\text{X}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are solvent dependent due to the differing populations of its *cis* and *trans* isomers in different solvents. In chloroform the activation parameters are  $\Delta H^\ddagger = 10.7 \pm 0.5$  kcal/mol and  $\Delta S^\ddagger = -36 \pm 2$  eu, whereas in benzene the activation parameters are  $\Delta H^\ddagger = 21 \pm 2$  kcal/mol and  $\Delta S^\ddagger = -4 \pm 10$  eu.<sup>22</sup>

The relatively large and negative  $\Delta S^\ddagger$  of  $-16$  eu for  $\text{TiNp}_4$  indicates that the transition state is highly ordered. This may be the result of steric crowding: the neopentyl groups may have to move closer to one another to allow one of the  $\alpha$ -hydrogen atoms to approach the  $\alpha$ -carbon atom of a neighboring neopentyl group. The resulting increase in steric crowding may reduce the rotational degrees of freedom of the neopentyl groups in the transition state. Similarly large entropies of activation are seen for some cyclometalation processes at  $d^0$  metal centers.<sup>56–60</sup>

**Titanium Alkylidene Trapping Experiments.** The conclusion that  $\text{TiNp}_4$  decomposes via an intramolecular  $\alpha$ -hydrogen abstraction process implies that the first step in the thermolysis of  $\text{TiNp}_4$  results in the liberation of 1 equiv of neopentane and the formation of a titanium alkylidene intermediate “ $\text{Ti}(=\text{CHCMe}_3)\text{Np}_2$ ”:

(52) For comparison, the strength of the  $\text{Ti}-\text{C}(\text{neopentyl})$  bond has been measured thermochemically to be 44 kcal/mol.<sup>53,54</sup>

(53) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830–831.

(54) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110.

(55) Activation free energies ( $\Delta G^\ddagger$ ) of 20–30 kcal/mol for  $\text{Cp}_2\text{TiR}_2$  complexes have also been measured. However, the activation entropies were not determined.<sup>15</sup>

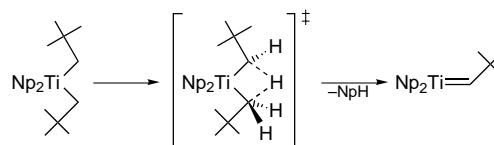
(56) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56.

(57) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6807.

(58) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246.

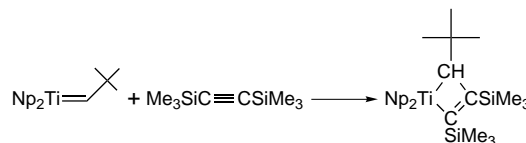
(59) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232–241.

(60) Chamberlain, L. R.; Rothwell, J. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502–1509.



The thermolysis of  $\text{TiNp}_4$  in the presence of dmpe (see above) did not result in the trapping of the proposed alkylidene intermediate. Tebbe has shown, however, that titanium alkylidene intermediates can sometimes be trapped by alkynes as stable metallacyclobutene complexes.<sup>61</sup> Accordingly, the thermolysis of  $\text{TiNp}_4$  was carried out in the presence of the alkyne bis(trimethylsilyl)acetylene (BTMSA), and the reaction was monitored by NMR spectroscopy.

When a solution of  $\text{TiNp}_4$  and 1 equiv of BTMSA in  $\text{C}_6\text{D}_6$  was heated to  $55^\circ\text{C}$  for 6 h, new  $^1\text{H}$  NMR peaks at  $\delta$  0.33, 0.37, 0.97, 1.08, 1.41, and 5.26 appeared with relative intensities of 9:9:9:9:9:1. The  $^{13}\text{C}$  NMR spectrum featured new peaks at  $\delta$  1.7, 2.4, 34.9, 33.6, 33.0, 101.4, 104.3, and 111.9. These peaks may be assigned to a bis(trimethylsilyl)*tert*-butyltitanacyclobutene complex that is formed by trapping of the titanium neopentylidene intermediate:



Peak assignments are given in the Experimental Section. The chemical shifts seen are very similar to those of the known titanacyclobutene complex  $\text{Cp}_2\text{Ti}[\text{CH}_2\text{C}(\text{SiMe}_3)=\text{CSiMe}_3]$ .<sup>61</sup> For example, the methylene group in  $\text{Cp}_2\text{Ti}[\text{CH}_2\text{C}(\text{SiMe}_3)=\text{CSiMe}_3]$  appears at  $\delta$  4.64 in the  $^1\text{H}$  NMR spectrum and at  $\delta$  107.1 in the  $^{13}\text{C}$  NMR spectrum, while the corresponding  $\text{CH}(t\text{-Bu})$  group in the metallacyclobutane derived from  $\text{TiNp}_4$  and BTMSA resonates at  $\delta$  5.26 in the  $^1\text{H}$  NMR spectrum and at  $\delta$  111.9 in the  $^{13}\text{C}$  NMR spectrum.

Unfortunately, the peaks due to the titanacyclobutene complex are always relatively small and do not persist. Evidently this species decomposes almost as fast as it is generated, and we have been unable to isolate the titanacyclobutene complex from the partly thermolyzed solutions.

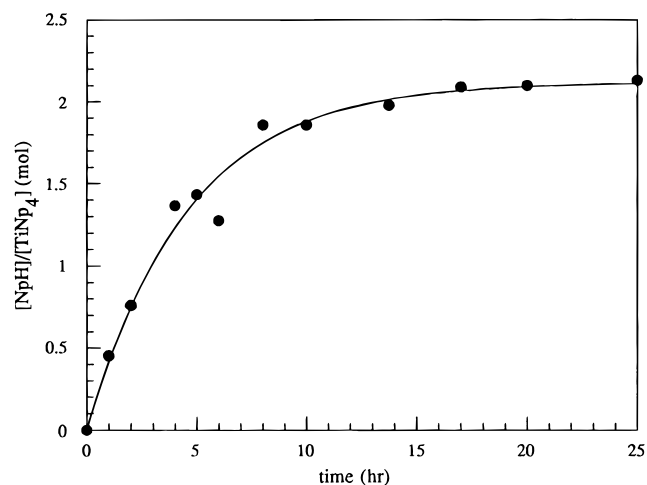
We now turn to studies of the fate of the titanium alkylidene intermediate in the *absence* of trapping agents.

**Stoichiometry of the Thermolysis Process.** In most cases,  $\alpha$ -hydrogen abstraction from a transition metal alkyl results in the liberation of 1 equiv of alkane. Occasionally, however, the resulting organometallic product is itself unstable and liberates further equivalents of alkane. Such behavior is exhibited by, for example, the permethyl complexes  $\text{TiMe}_4$ ,  $\text{NbMe}_5$ ,  $\text{TaMe}_5$ , and  $\text{WMe}_6$ , all of which lose more than 1 equiv of methane when they decompose.<sup>7–10,62</sup>

$^1\text{H}$  NMR spectroscopy was used to determine the amount of neopentane liberated per mole of  $\text{TiNp}_4\text{-}d_0$  or  $\text{-}d_8$  originally present as a function of time (Figure 4). The resulting curves could be fit to the first-order equation  $[\text{NpH}]_t/[\text{TiNp}_4]_0 = n(1 - e^{-kt})$ , where  $n$  is the number of moles of neopentane generated per mole of  $\text{TiNp}_4$  consumed. Both  $n$  and  $k$  were varied to give the best least-squares fit to the data.

(61) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149–6151.

(62) Shortland, A. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 872–876.



**Figure 4.** Plot of formation of neopentane during the thermolysis of  $\text{TiNp}_4\text{-}d_0$  in  $\text{C}_6\text{D}_6$  at  $80^\circ\text{C}$ . The data were fit by using a non-linear least-squares algorithm to the equation  $y = n(1 - e^{-kt})$ , and the best-fit curve is shown.

For both the  $\text{TiNp}_4\text{-}d_0$  and  $\text{-}d_8$  complexes, the fits were good and the first-order rate constants deduced from the *generation* of NpH ( $6.1 \times 10^{-5}$  and  $1.4 \times 10^{-5} \text{ s}^{-1}$ , respectively) were very similar to those measured from the *consumption* of  $\text{TiNp}_4$  (Table 1). As before, the rate of evolution of NpH from  $\text{TiNp}_4\text{-}d_0$  is much faster than that from  $\text{TiNp}_4\text{-}d_8$ . The kinetic isotope effect  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})}$  of 4.3 deduced from these experiments differs somewhat from the value of 5.2 measured previously. The thermolysis rates and kinetic isotope effects determined from the evolution of neopentane, however, are not as accurate as those determined from the disappearance of  $\text{TiNp}_4$ , because the neopentane peaks are small and hard to integrate accurately during the early stages of the thermolysis when most of the reaction is taking place.

For the  $\text{TiNp}_4\text{-}d_0$  complex, the best-fit value for  $n$  showed that  $2.1 \pm 0.2$  equiv of neopentane were generated per mole of  $\text{TiNp}_4$  consumed (Figure 4).<sup>63</sup> This result clearly reveals that the initial  $\text{TiNp}_4$  thermolysis product, “ $\text{Ti}(\text{=CHCMe}_3)\text{Np}_2$ ”, is indeed thermally unstable at  $80^\circ\text{C}$ , and decomposes to liberate a second equivalent of neopentane. Evidently, this second hydrogen abstraction reaction gives rise to the black precipitate that forms during the thermolysis.

Since *both* equivalents of neopentane are eliminated at the same rate, the decomposition of “ $\text{Ti}(\text{=CHCMe}_3)\text{Np}_2$ ” must be *fast* compared with the rate of decomposition of  $\text{TiNp}_4$ . This conclusion is consistent with the absence of resonances due to this proposed alkylidene intermediate in the  $^1\text{H}$  NMR spectra taken during thermolysis.

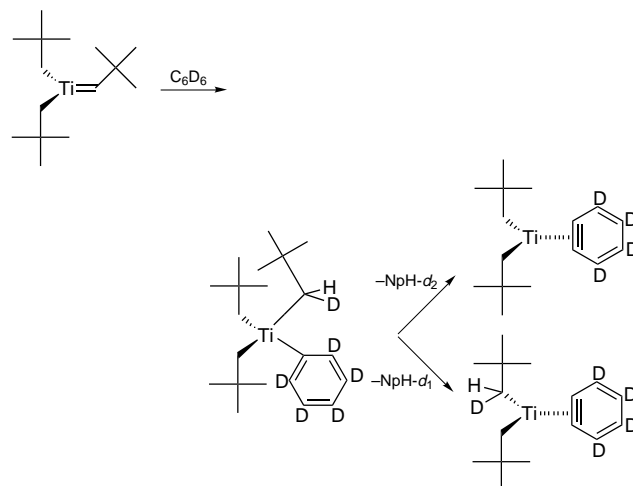
**Fate of the Titanium Alkylidene Intermediate and the Intermolecular Activation of Solvent C–H Bonds.** Although kinetic isotope studies were successful in establishing the mechanism of the first step in the thermolysis sequence, rate studies cannot be used to determine the nature of any of the subsequent steps because they are not rate limiting. The mechanism of the second step in the sequence, the fate of “ $\text{Ti}(\text{=CHCMe}_3)\text{Np}_2$ ”, must therefore be established by other means. We will show in this section that the mechanism of this second step can be deduced from an analysis of the distribution of deuterium labels in the neopentane liberated from the variously deuterated  $\text{TiNp}_4$  molecules.<sup>64</sup>

The first question to address is what is the source of the 12th hydrogen atom that appears in the second equivalent of evolved

neopentane? There are at least three possibilities:  $\alpha$ -hydrogen atoms in the titanium alkylidene,  $\gamma$ -hydrogens in the titanium alkylidene, and solvent. The last possibility can be tested by examining the neopentane evolved from the thermolysis of  $\text{TiNp}_4\text{-}d_0$  in benzene- $d_6$ . In this experiment, the first equivalent of neopentane evolved (as a result of the  $\alpha$ -hydrogen abstraction process) must be completely undeuterated. Therefore, if any deuterated neopentanes are found among the products, they must be produced by a subsequent solvent-assisted decomposition of “ $\text{Ti}(\text{=CHCMe}_3)\text{Np}_2$ ”.

Thermolysis of  $\text{TiNp}_4\text{-}d_0$  in  $\text{C}_6\text{D}_6$  at  $80^\circ\text{C}$  was carried out to completion in a sealed NMR tube, and then the tube was broken and the gases analyzed by GC/MS. Analysis of the neopentane evolved (Table 3) showed that only 50% was neopentane- $d_0$ , and that significant amounts of neopentane- $d_1$  and  $-d_2$  were also present (36% and 14%, respectively). No neopentane- $d_3$  was detected.<sup>65</sup> This result strongly suggests that the second equivalent of neopentane liberated during the thermolysis of  $\text{TiNp}_4$  in  $\text{C}_6\text{D}_6$  consists almost exclusively of neopentane- $d_1$  and  $-d_2$ .<sup>66</sup> Therefore, the titanium alkylidene intermediate must be reacting essentially quantitatively with the solvent, and the second equivalent of neopentane results from the activation of solvent C–D bonds.

The amounts of deuterated neopentanes formed can be accounted for almost exactly if benzene- $d_6$  adds across the  $\text{Ti}=\text{C}$  bond of the titanium alkylidene intermediate to give a titanium phenyl complex. In this process, a benzene deuterium atom adds to the neopentylidene ligand to convert the latter back to a neopentyl group; the stoichiometry of the resulting organometallic product would be  $\text{Ti}(\text{C}_6\text{D}_5)(\text{CHDCMe}_3)(\text{CH}_2\text{CMe}_3)_2$ .<sup>67</sup> In a subsequent step, ortho metalation of the phenyl group in this phenyltrineopentyltitanium species gives the second equivalent of neopentane.



Statistically, ortho metalation of the phenyl ring in  $\text{Ti}(\text{C}_6\text{D}_5)(\text{CHDCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  should liberate  $2/3$  equiv of neopentane- $d_1$  and  $1/3$  equiv of neopentane- $d_2$ . When these products

(64) The line of reasoning is as follows: (1) 2 equiv of neopentane are liberated when the variously deuterated  $\text{TiNp}_4$  molecules decompose—1 equiv from the  $\alpha$ -hydrogen abstraction process and 1 equiv from the subsequent decomposition of the titanium alkylidene intermediate; (2) the distribution of deuterated isotopologs in the first equivalent of neopentane can be calculated from the known  $k_{\text{H}}/k_{\text{D}}$  ratio of the  $\alpha$ -hydrogen abstraction process; and (3) the distribution of deuterium in the second equivalent of neopentane can be determined by measuring the total amounts of neopentane- $d_0$ ,  $-d_1$ ,  $-d_2$ , and  $-d_3$  liberated and subtracting the amounts of neopentane isotopologs calculated to result from the  $\alpha$ -hydrogen abstraction process. As we will see, different mechanisms predict different distributions of deuterium in the neopentane evolved in the second step of the thermolysis sequence.

(63) These values have been corrected for the deuterium content of the neopentane.

are added to the 1 equiv of neopentane- $d_0$  generated in the  $\alpha$ -hydrogen abstraction step, the 2 equiv of neopentane evolved from the thermolysis of  $\text{TiNp}_4-d_0$  in  $\text{C}_6\text{D}_6$  should have the following isotopolog distribution: 50%  $d_0$ , 33%  $d_1$ , 17%  $d_2$ , and 0%  $d_3$ . This prediction very closely matches the observed distribution of 50%  $d_0$ , 36%  $d_1$ , 14%  $d_2$ , and 0%  $d_3$ .<sup>68</sup>

Ortho metalation and loss of neopentane from  $\text{Ti}(\text{C}_6\text{D}_5)$ - $(\text{CHDCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  should result in the formation of a benzyne complex of stoichiometry “ $\text{Ti}(\text{C}_6\text{D}_4)(\text{CH}_2\text{CMe}_3)_2$ ”.<sup>69</sup> This process has precedent in the thermolysis of the niobium and tantalum phenyl complexes  $\text{Cp}^*\text{M}(\text{Ph})\text{Me}_3$ , which are known to undergo ortho metalation to yield methane and the metal-benzyne species  $\text{Cp}^*\text{M}(\text{C}_6\text{H}_4)\text{Me}_2$ .<sup>70</sup> Similarly, thermolysis of group 4  $\text{Cp}_2\text{MPh}_2$  complexes results in loss of benzene and formation of benzyne complexes of stoichiometry  $\text{Cp}_2\text{M}(\text{C}_6\text{H}_4)$ .<sup>59,71–77</sup> Metal-benzyne complexes have also been proposed to be reactive intermediates in the thermal decomposition of perphenyl derivatives of early transition metals.<sup>78–80</sup>

This titanium benzyne intermediate is probably the immediate precursor to the black precipitate that is the ultimate organometallic product formed upon thermolysis of  $\text{TiNp}_4$  in benzene at 80 °C. This conclusion is supported by analyses of the organic products obtained upon hydrolysis of the black precipitate (see below).

**Neopentane Isotopologs Evolved from  $\text{TiNp}_4-d_4$  and  $\text{TiNp}_4-d_8$ .** We have carried out analyses of the neopentane evolved from the thermolysis of  $\text{TiNp}_4-d_4$  and  $\text{TiNp}_4-d_8$  in  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  to determine whether the isotopolog distributions also agree with those predicted from the  $\alpha$ -hydrogen abstraction/solvent activation/ortho metalation sequence. In this case, the calculated distributions must take into account the kinetic isotope

(65) The determination of the isotopic composition of mixtures of deuterated neopentanes can be accomplished by mass spectroscopy provided that some care is taken (see the Experimental Section). We made only one assumption: that in the mixtures of deuterated neopentanes, the deuterium labels present in any one molecule were all attached to the same carbon atom. As long as scrambling of deuterium labels into the  $\gamma$ -hydrogen positions (i.e., the methyl groups) of the neopentyl ligands is slow, this will be a reasonable assumption. The satisfactory analyses of the neopentane isotopolog distributions from the observed spectrometric cracking patterns suggest that the assumption does in fact hold true.

(66) A similar experiment with  $\text{TiNp}_4-d_8$  in  $\text{C}_6\text{H}_6$  showed that neopentane- $d_1$  and  $-d_2$  are formed along with the expected neopentane- $d_3$ .

(67) Note Added in Proof: A similar reaction of a tungsten alkylidene has recently been reported: Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071–5072.

(68) Conceivably, the second equivalent of neopentane could have been generated via a second  $\alpha$ -hydrogen abstraction process involving two neopentyl ligands, but this possibility can be ruled out since the calculated distribution of neopentanes should be 80%  $d_0$  and 20%  $d_1$ . It is evident that abstraction of neopentyl  $\alpha$ -hydrogen atoms is *not* a significant pathway for the decomposition of  $\text{Ti}(\text{C}_6\text{D}_5)(\text{CHDCMe}_3)(\text{CH}_2\text{CMe}_3)_2$ .

(69) Or “ $\text{Ti}(\text{C}_6\text{D}_4)(\text{CHDCMe}_3)(\text{CH}_2\text{CMe}_3)$ ” depending on whether neopentane- $d_1$  or  $-d_2$  is eliminated.

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**Table 3.** Observed and Calculated Distributions of Neopentane Isotopologs Obtained upon Thermolysis of  $\text{TiNp}_4$  in Benzene at 80 °C<sup>a</sup>

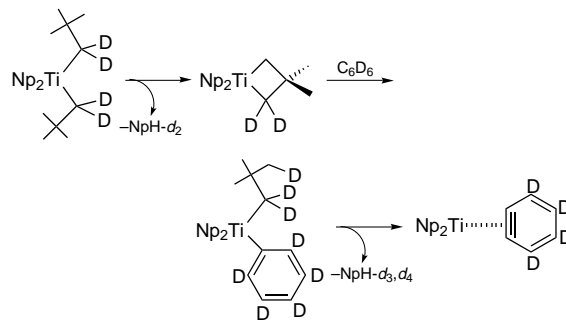
compd	solv	neopentane isotopolog distribution (%)				
		$d_0$	$d_1$	$d_2$	$d_3$	$d_4$
$\text{TiNp}_4-d_0$	$\text{C}_6\text{H}_6$	100 (100)	0 (0)	0 (0)	0 (0)	0 (0)
	$\text{C}_6\text{D}_6$	50 (50)	36 (33)	14 (17)	0 (0)	0 (0)
$\text{TiNp}_4-d_4$	$\text{C}_6\text{H}_6$	7 (3)	86 (89)	7 (8)	0 (0)	0 (0)
	$\text{C}_6\text{D}_6$	0 (0)	40 (42)	44 (44)	16 (14)	0 (0)
$\text{TiNp}_4-d_8$	$\text{C}_6\text{H}_6$	0 (0)	22 (8)	52 (67)	26 (25)	0 (0)
	$\text{C}_6\text{D}_6$	0 (0)	2 (0)	33 (25)	53 (67)	12 (8)

<sup>a</sup> The calculated distributions (shown in parentheses) are obtained from Scheme 1, taking  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})} = 5.2$  and  $k_{\alpha(\text{H})}/k_{\gamma(\text{H})} \approx 25$ . For  $\text{TiNp}_4-d_8$ , the calculated distributions given in the table are not corrected for the presence of residual hydrogen in the deuterated sites (i.e.,  $\text{TiNp}_4-d_7$ ).

effect for the  $\alpha$ -hydrogen abstraction step (i.e., about 85% of the  $\text{TiNp}_4-d_4$  molecules will decompose by means of  $\alpha$ -hydrogen rather than  $\alpha$ -deuterium abstraction). For the thermolysis of  $\text{TiNp}_4-d_4$  in both  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$ , the predicted distributions of neopentane isotopologs agree very closely with the distributions actually observed (Table 3). These results provide further support for the contention that the titanium alkylidene intermediate quantitatively activates solvent C–H and C–D bonds to form a  $\text{TiPhNp}_3$  intermediate that subsequently loses a second equivalent of neopentane by ortho metalation.

For the thermolysis of  $\text{TiNp}_4-d_8$  in  $\text{C}_6\text{H}_6$  and in  $\text{C}_6\text{D}_6$ , the observed distributions of neopentane isotopologs differ somewhat from those calculated from the  $\alpha$ -hydrogen abstraction/solvent activation/ortho metalation sequence. In both cases, the  $d_1$  and  $d_2$  isotopologs are more prevalent, and the  $d_3$  isotopolog less prevalent, than predicted. In part, these differences are consequences of the fact that the extent of deuteration at each  $\alpha$ -position in  $\text{TiNp}_4$  is not 100% but ca. 98%, so that the samples of “ $\text{TiNp}_4-d_8$ ” actually consist of a distribution of  $\text{TiNp}_4$  isotopologs: 85%  $d_8$ , 14%  $d_7$ , and 1%  $d_6$ , assuming that the labels are distributed randomly.<sup>81</sup> The amount of  $\text{TiNp}_4-d_7$  present is, however, insufficient to account for the amounts of neopentane- $d_1$  and  $-d_2$  isotopologs actually generated upon thermolysis of “ $\text{TiNp}_4-d_8$ ”.

Instead, we propose that  $\gamma$ -hydrogen abstraction is important for  $\text{TiNp}_4-d_8$  (but not for the  $d_0$  isotopolog) because the  $\alpha$ -hydrogen abstraction process is five times slower than it is in the  $d_0$  complex. A  $\gamma$ -hydrogen abstraction process would generate a titanacyclobutane complex and liberate 1 equiv of neopentane; reaction of the titanacyclobutane complex with benzene and subsequent ortho metalation would produce a second equivalent of neopentane:



This reaction sequence has a precedent: Marks has shown that the thorium dineopentyl complex  $\text{Cp}^*_2\text{ThNp}_2$  thermolyzes to give the thoracyclobutane  $\text{Cp}^*_2\text{Th}[(\text{CH}_2)_2\text{CMe}_2]$  and that the latter complex reacts with benzene to give neopentane and  $\text{Cp}^*_2\text{ThPh}_2$ .<sup>82–84</sup>

**Table 4.** Observed Distributions of Neopentane Isotopologs Obtained upon Addition of HCl to the Black Precipitate Formed by Thermolysis of TiNp<sub>4</sub>

compd	solv	neopentane isotopolog distribution (%)				
		d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>
TiNp <sub>4</sub> -d <sub>0</sub>	C <sub>6</sub> D <sub>6</sub>	44	38	12	7	0
	C <sub>6</sub> D <sub>12</sub>	57	33	8	2	0
TiNp <sub>4</sub> -d <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	10	88	2	0	0
	C <sub>6</sub> H <sub>12</sub>	19	77	4	0	0

The reaction sequence above predicts that thermolysis of TiNp<sub>4</sub>-d<sub>8</sub> in C<sub>6</sub>D<sub>6</sub> should generate some neopentane-d<sub>4</sub>. In fact, about 12% of the neopentane generated in this experiment is neopentane-d<sub>4</sub>. The distribution of neopentane isotopologs obtained from the thermolysis of TiNp<sub>4</sub>-d<sub>8</sub> in both C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> can be accounted for reasonably well if about half of the TiNp<sub>4</sub>-d<sub>8</sub> reacts via  $\alpha$ -deuterium abstraction and half by  $\gamma$ -hydrogen abstraction (Table 3). After being corrected for statistical factors (8  $\alpha$ -deuterium atoms vs 36  $\gamma$ -hydrogens) and for the known kinetic isotope effect for  $\alpha$ -hydrogen abstraction ( $k_{\alpha(H)}/k_{\alpha(D)} = 5.2$ ), the ratio of the *intrinsic*  $\alpha$ -hydrogen abstraction and  $\gamma$ -hydrogen abstraction rates,  $k_{\alpha(H)}/k_{\gamma(H)}$ , can be calculated to be approximately 25.

**Nature of the Black Precipitate.** Additional evidence that the titanium alkylidene intermediate reacts with benzene can be obtained from an analysis of the black precipitate formed from the thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> in C<sub>6</sub>H<sub>6</sub>. The identities of the organic groups present in the black precipitate were determined by GC/MS analyses of the gases produced upon deuterolysis of the precipitate with 1 M DCl in D<sub>2</sub>O. Both neopentane and benzene are liberated, and GC/MS showed the following distribution of neopentane isotopologs: 20% d<sub>0</sub>, 72% d<sub>1</sub>, 5% d<sub>2</sub>, and 3% d<sub>3</sub>. The evolution of substantial amounts of neopentane-d<sub>1</sub> upon deuterolysis clearly shows that neopentyl groups remain in the black precipitate, but the absence of appreciable amounts of neopentane-d<sub>2</sub> clearly shows that no neopentylidene (or neopentylidene-derived) groups are present. In a similar experiment, TiNp<sub>4</sub>-d<sub>0</sub> was thermolyzed in C<sub>6</sub>D<sub>6</sub>, and the resulting black precipitate was hydrolyzed with HCl. GC/MS analysis of the neopentane (Table 4) showed that substantial H/D exchange had occurred during thermolysis (43% d<sub>0</sub>, 38% d<sub>1</sub>, 12% d<sub>2</sub>, and 7% d<sub>3</sub>). This result supports the contention that the titanium alkylidene intermediate reacts with C<sub>6</sub>D<sub>6</sub> to give a Ti(C<sub>6</sub>D<sub>5</sub>)(CHDCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> species containing deuterated neopentyl groups, and that this species subsequently thermolyzes to give the black precipitate.

The presence of fragments derived from solvent molecules is also confirmed by these hydrolysis experiments. Deuterolysis of the black precipitate obtained from TiNp<sub>4</sub>-d<sub>0</sub> in C<sub>6</sub>H<sub>6</sub> gives three benzene isotopologs: 45% d<sub>0</sub>, 38% d<sub>1</sub>, and 16% d<sub>2</sub>. The presence of benzene-d<sub>2</sub> is consistent with the presence of benzyne (or benzyne-derived) groups in the black precipitate;

(81) The presence of residual hydrogen atoms in the  $\alpha$ -positions of the neopentyl groups affects the neopentane isotopolog distributions because of the large kinetic isotope effect. For example, the first equivalent of neopentane evolved from TiNp<sub>4</sub>-d<sub>7</sub> will be predominantly (57%) the d<sub>2</sub> isotopolog rather than the d<sub>3</sub> isotopolog. In contrast, the deuteration efficiency has little effect on the neopentane isotopologs obtained from TiNp<sub>4</sub>-d<sub>4</sub> because fewer deuterated sites are involved, and because the four sites that are 100% hydrogen labeled dominate the thermolysis process. For a discussion of the effect of residual hydrogen on the isotopologs generated upon thermolysis of "perdeuterated" compounds, see ref 17.

(82) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214–2216.

(83) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425–437.

(84) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832.

**Table 5.** Observed Distributions of Neopentane Isotopologs Obtained upon Thermolysis of TiNp<sub>4</sub> in Other Solvents

compd	solv	neopentane isotopolog distribution (%)				
		d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>
TiNp <sub>4</sub> -d <sub>0</sub>	C <sub>6</sub> D <sub>12</sub>	70	24	4	0	0
	C <sub>6</sub> F <sub>6</sub>	100	0	0	0	0
	<i>n</i> -C <sub>7</sub> F <sub>16</sub>	100	0	0	0	0
TiNp <sub>4</sub> -d <sub>4</sub>	C <sub>6</sub> H <sub>12</sub>	7	81	12	0	0
	C <sub>6</sub> D <sub>12</sub>	1	71	26	2	0
TiNp <sub>4</sub> -d <sub>8</sub>	C <sub>6</sub> H <sub>12</sub>	0	16	55	29	0
	C <sub>6</sub> D <sub>12</sub>	0	14	43	45	0
	C <sub>6</sub> F <sub>6</sub>	0	5	41	57	0

some benzene-d<sub>1</sub> (derived from phenyl groups) and benzene-d<sub>0</sub> (due to trapped C<sub>6</sub>H<sub>6</sub> molecules) are also present. These results confirm that multiple activation of benzene C–D bonds has occurred. Thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> in C<sub>6</sub>D<sub>6</sub> followed by hydrolysis with HCl gives a benzene isotopolog distribution (28% d<sub>6</sub>, 35% d<sub>5</sub>, 25% d<sub>4</sub>, and 12% d<sub>3</sub>) that is also consistent with this view.

**Thermolysis of TiNp<sub>4</sub> in Cyclohexane.** Since the activation of aliphatic C–H bonds is usually more difficult to accomplish than the activation of aromatic C–H bonds, it is of interest to determine whether thermolysis of TiNp<sub>4</sub> in saturated hydrocarbons also effects intermolecular C–H activation. Analysis of the neopentane evolved upon thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> in cyclohexane-d<sub>12</sub> clearly shows that even *saturated* hydrocarbons add across the Ti=C double bond of the titanium alkylidene intermediate. The distribution of deuterated neopentanes seen (Table 5) contains more neopentane-d<sub>0</sub> and less neopentane-d<sub>1</sub> than observed from the thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> in benzene-d<sub>6</sub>; this result suggests that the alkylidene species is somewhat less reactive toward saturated hydrocarbons than toward aromatic hydrocarbons. In cyclohexane, the titanium alkylidene intermediate evidently can react in one of two ways: by a solvent-assisted pathway in which cyclohexane molecules add intermolecularly across the Ti=C double bond, or by a solvent-independent pathway in which the titanium alkylidene intermediate activates its own C–H bonds.

Hydrolysis of the black precipitate obtained upon thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> in C<sub>6</sub>D<sub>12</sub> yields various deuterated cyclohexane isotopologs (41% d<sub>12</sub>, 38% d<sub>11</sub>, 16% d<sub>10</sub>, and 5% d<sub>9</sub>). This result confirms that cyclohexane is being activated and that cyclohexyl (or cyclohexyl-derived) groups are present as titanium-bound substituents in the black precipitate. As expected, neopentyl groups are also present in this black precipitate (Table 4).

Detailed labeling studies of the thermolysis mechanism in cyclohexane are impractical owing to the complexities associated with unraveling the two competing reaction pathways (i.e., solvent-dependent and solvent-independent).

**Thermolysis of TiNp<sub>4</sub> in Fluorocarbon Solvents.** We became interested in the possibility that more information about the solvent-independent pathway could be obtained by studying the thermolysis of TiNp<sub>4</sub> in fluorocarbon solvents. Thermolysis of TiNp<sub>4</sub>-d<sub>0</sub> at 80 °C was carried out in two fluorocarbon solvents, hexafluorobenzene and perfluoro-*n*-heptane; in both cases neopentane was the exclusive organic product as detected by GC/MS. No neopentyl fluoride was generated.

The fate of the titanium alkylidene intermediate in fluorocarbon solvents is not clear. Thermolyses of TiNp<sub>4</sub>-d<sub>0</sub> and TiNp<sub>4</sub>-d<sub>4</sub> in C<sub>6</sub>F<sub>6</sub> give essentially no mechanistic information, since neopentane-d<sub>0</sub> is expected to be (and is) the exclusive or predominant product irrespective of the mechanism. Thermolysis of TiNp<sub>4</sub>-d<sub>8</sub>, however, is more informative. The major neopentane isotopolog (57%) evolved is neopentane-d<sub>3</sub> (Table

5), which is the result of  $\alpha$ -deuterium abstraction. The remainder of the neopentane evolved consists largely of the  $d_2$  isotopolog (41%), which evidently arises from competing  $\gamma$ -hydrogen abstraction processes as noted above. The relative amounts of neopentane- $d_2$  and - $d_3$  in this experiment provide further evidence that, for  $\text{TiNp}_4$ - $d_8$ , about half thermolyzes via  $\alpha$ -deuterium abstraction, and about half by  $\gamma$ -hydrogen abstraction.

The neopentane isotopologs evolved in subsequent steps depend on the subsequent fate of the titanium alkylidene and titanacyclobutane complexes.<sup>85</sup> In any case, the appearance of neopentane- $d_2$  from the thermolysis of  $\text{TiNp}_4$ - $d_8$  necessarily implies that the  $\gamma$ -hydrogens of the neopentyl ligands (which are the only source of hydrogen atoms) become involved in the thermolytic chemistry at 80 °C in the absence of reactive solvents. Similar  $\gamma$ -hydrogen activation processes have been shown to occur when  $\text{TiNp}_4$ - $d_8$  is thermolyzed on a surface.<sup>42</sup>

**Comparison with Theoretical Studies of  $\text{TiNp}_4$  Thermolysis.** *Ab initio* molecular orbital studies of  $\text{TiNp}_4$  have recently shown that  $\alpha$ -hydrogen abstraction has a significantly lower barrier than  $\gamma$ -hydrogen abstraction.<sup>86</sup> The stabilization of the transition state for  $\alpha$ -hydrogen abstraction relative to that for  $\gamma$ -hydrogen abstraction is steric in origin: the latter transition state is severely crowded. In agreement with our results, the transition state for  $\alpha$ -hydrogen abstraction is computed to be relatively symmetric, since the calculated C–H bond lengths in the  $\text{C}\cdots\text{H}\cdots\text{C}$  unit are 1.49 and 1.66 Å.

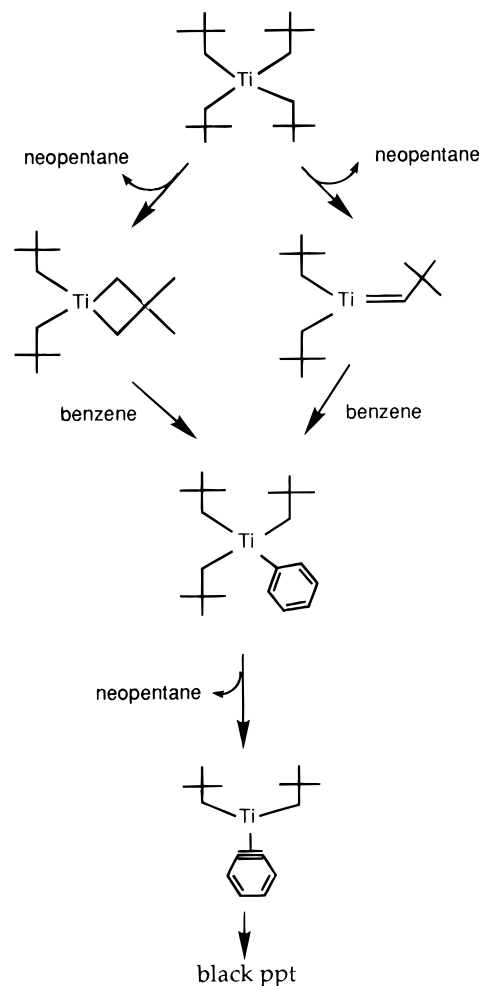
### Concluding Remarks

The investigations above have given us considerable insight into the pathways responsible for the thermolysis of  $\text{TiNp}_4$  at 80 °C in solution (Scheme 1). The first step involves elimination of 1 equiv of neopentane by  $\alpha$ -hydrogen abstraction. The kinetic isotope effect for this step is  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})} = 5.2$ . In contrast,  $\gamma$ -hydrogen abstraction is slow and we estimate that  $k_{\alpha(\text{H})}/k_{\gamma(\text{H})} \approx 25$ . The first step in the thermolysis sequence generates the titanium alkylidene  $\text{Ti}(=\text{CHCMe}_3)\text{Np}_2$ . In reactive solvents such as benzene (and to some extent in cyclohexane) the alkylidene intermediate activates solvent C–H bonds intermolecularly by addition across the  $\text{Ti}=\text{C}$  bond. In contrast, in inert solvents such as fluorocarbons the titanium alkylidene activates its own  $\alpha$ - and  $\gamma$ -C–H bonds.

Although we would have liked to have carried out more detailed mechanistic studies in cyclohexane and fluorocarbons, the results of isotopic labeling experiments in these solvents are difficult to interpret owing to the competition between solvent-dependent, solvent-independent,  $\alpha$ -hydrogen-abstraction, and  $\gamma$ -hydrogen-abstraction pathways. In contrast, the results of the isotopic studies in benzene are easier to interpret because the chemistry is simpler: the solvent-assisted and  $\alpha$ -hydrogen-abstraction pathways can be studied in the absence of competing processes. This is because benzene serves as a quantitative trap for the titanium alkylidene intermediate whereas the other solvents do not.

Our parallel studies of the reactions responsible for the growth of TiC films from  $\text{TiNp}_4$  under CVD conditions at 250 °C are described elsewhere.<sup>42</sup> Interestingly, under these conditions the first step is the same as that in solution:  $\alpha$ -hydrogen abstraction. Subsequent reactions are similar to those that occur when  $\text{TiNp}_4$  is thermolyzed in fluorocarbon solvents. These results dem-

**Scheme 1.** Proposed Thermolysis Pathways for  $\text{TiNp}_4$  in Benzene<sup>a</sup>



<sup>a</sup> The first step is rate limiting and subsequent steps are fast. The relative rates for the first step are  $k_{\alpha(\text{H})}/k_{\gamma(\text{H})} \approx 25$  and  $k_{\alpha(\text{H})}/k_{\alpha(\text{D})} = 5.2$ ; these intrinsic rate constants must be combined with the relative populations of the  $\alpha$ - and  $\gamma$ -hydrogen or deuterium atoms to obtain the branching ratio for the first step.

onstrate that, under the right circumstances, the chemistry of organometallic molecules in solution can afford important insight into the chemistry behind CVD processes.

### Experimental Section

**General Methods.** All manipulations were carried out with Schlenk and cannula techniques under argon or in vacuum. Pentane, benzene, cyclohexane, and diethyl ether were distilled from sodium benzophenone ketyl under  $\text{N}_2$  before use. Benzene- $d_6$  (Cambridge Isotopes, 99.6% D) and cyclohexane- $d_{12}$  (Cambridge Isotopes, 99.7% D) were distilled from sodium.  $\text{C}_6\text{F}_6$  and  $n\text{-C}_7\text{F}_{16}$  were washed with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ , dried over  $\text{P}_2\text{O}_5$ , and fractionally distilled.  $\text{Ti}(\text{OEt})_4$  (Strem) was distilled before use (60 °C,  $10^{-2}$  Torr). Neopentyl chloride (Fairfield), trimethylacetyl chloride (Aldrich), and trimethylacetaldehyde (Aldrich) were dried over 4A molecular sieves and distilled. Dimethylformamide was dried over 13X molecular sieves (Linde) and distilled.  $\text{LiAlD}_4$  (Cambridge Isotopes, 98% D),  $\text{D}_2\text{O}$  (Sigma, 99.9% D), and  $\text{PCl}_5$  (Aldrich) were used as received. Neopentyllithium<sup>20</sup> was prepared by a literature procedure.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a General Electric QE 300 instrument at 300 and 75.44 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in  $\delta$  units (positive chemical shifts to higher frequency). A Hewlett Packard 5890 gas chromatograph with a 5970 series mass selective detector was used to obtain GC/MS data. The mass selective detector was calibrated by using the 31, 50, and 69 amu peaks of perfluorotributylamine. The column used was a 30-m

(85) While some 2,2-dimethyltitanacyclobutanes can eliminate isobutylene (Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880–4890), essentially no isobutylene is formed upon thermolysis of  $\text{TiNp}_4$  in fluorocarbons.

(86) Wu, Y.-D.; Peng, Z.-H.; Xue, Z. *J. Am. Chem. Soc.* **1996**, *118*, 9772–9777.



RSL-160 (5  $\mu\text{m}$  thick poly(dimethylsiloxane) film, 0.32-mm, i.d., Alltech). Elemental analyses were performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois.

**Tetraneopentyltitanium,  $\text{Ti}(\text{CH}_2\text{CMe}_3)_4$ .** This procedure is an improvement over literature methods;<sup>40,87,88</sup> the use of tetraethoxytitanium<sup>1</sup> in place of titanium tetrachloride minimizes reduction to lower valent titanium byproducts. To a solution of neopentyltitanium in pentane (50 mL of a 0.65 M solution, 32.5 mmol) was added  $\text{Ti}(\text{OEt})_4$  (1.5 mL, 7.3 mmol) in pentane (20 mL) dropwise over 45 min at  $-78^\circ\text{C}$  in a foil-covered flask. After the addition was complete, the reaction mixture was stirred for 1.5 h at  $-78^\circ\text{C}$  and then for 6 h at room temperature. The solution was filtered, and the solvent was removed under vacuum to leave an oily brown solid. The brown solid was purified by sublimation ( $55^\circ\text{C}$ ,  $10^{-3}$  Torr) over 10 h to give the product as yellow crystals. Yield: 1.20 g (49%). Anal. Calcd for  $\text{C}_{20}\text{H}_{44}\text{Ti}$ : C, 72.3; H, 13.3; Ti, 14.4. Found: C, 72.1; H, 13.6; Ti, 14.3.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  2.22 (s,  $\text{CH}_2\text{CMe}_3$ ), 1.17 (s,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  118.9 (triplet of decets,  $^1J_{\text{CH}} = 109.6$  Hz,  $^3J_{\text{CH}} = 4.6$  Hz,  $\text{CH}_2\text{CMe}_3$ ), 34.1 (m,  $\text{CH}_2\text{CMe}_3$ ), 33.9 (quartet of nonets,  $^1J_{\text{CH}} = 124.1$  Hz,  $^3J_{\text{CH}} = 4.6$  Hz,  $\text{CH}_2\text{CMe}_3$ ). IR ( $\text{cm}^{-1}$ ): 2773 w, 2694 w, 1376 m, 1254 w, 1225 s, 1146 w, 1111 m, 1069 w, 932 m, 908 w, 800 w, 747 s, 716 w, 544 m, 510 m, 495 sh, 450 w, 367 w.

**Tetraneopentyltitanium- $d_4$ ,  $\text{Ti}(\text{CHDCMe}_3)_4$ .** This complex was prepared as above but from  $\text{LiNp-}d_1$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{40}\text{D}_4\text{Ti}$ : C, 71.4; H/D, 13.2; Ti, 14.2. Found: C, 71.5; H/D, 13.1; Ti, 14.4.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  2.18 (s,  $\text{CHDCMe}_3$ ), 1.16 (s,  $\text{CHDCMe}_3$ ). The  $\text{TiNp-}d_4$  was determined to be  $\sim 98\%$  monodeuterated in the methylene positions by  $^1\text{H}$  NMR spectroscopy and GC/MS of the neopentane evolved upon alcoholysis with methanol.

**Tetraneopentyltitanium- $d_8$ ,  $\text{Ti}(\text{CD}_2\text{CMe}_3)_4$ .** This complex was prepared as above but from  $\text{LiNp-}d_2$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{36}\text{D}_8\text{Ti}$ : C, 70.6; H/D, 13.0; Ti, 14.1. Found: C, 70.4; H/D, 12.1; Ti, 14.3.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.17 (s,  $\text{CD}_2\text{CMe}_3$ ). The  $\text{TiNp-}d_8$  was determined to be  $\sim 98\%$  deuterated in the methylene positions by  $^1\text{H}$  NMR spectroscopy and GC/MS of the neopentane evolved upon alcoholysis with methanol.

**Neopentyl- $d_1$  Alcohol,  $\text{HOCHDCMe}_3$ .**<sup>56</sup> To a suspension of  $\text{LiAlD}_4$  (7.95 g, 0.189 mol) in diethyl ether (30 mL) was added trimethylacetaldehyde,  $\text{Me}_3\text{CCHO}$  (63.5 g, 0.63 mol) dropwise over 2 h at  $0^\circ\text{C}$ . The solution was stirred for another 30 h at room temperature. The reaction mixture was hydrolyzed with distilled water (100 mL) and 10%  $\text{H}_2\text{SO}_4$  (250 mL). The diethyl ether layer was separated and dried over  $\text{CaCl}_2$ , and the ether was removed by distillation. The remaining white gelatinous solid was purified by sublimation ( $0^\circ\text{C}$ ,  $10^{-3}$  Torr) to afford the product as a white solid. Yield: 35 g (70%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  3.26 (s, CHD), 1.48 (s, OH), 0.90 (s,  $\text{CMe}_3$ ). The  $\text{CMe}_3\text{:CH}$  peak intensity ratio was 9:1.

**Neopentyl- $d_2$  Alcohol,  $\text{HOCD}_2\text{CMe}_3$ .**<sup>56</sup> To a suspension of  $\text{LiAlD}_4$  (3.27 g, 0.08 mol) in diethyl ether (40 mL) was added trimethylacetyl chloride,  $\text{Me}_3\text{CCOCl}$  (19.58 g, 0.16 mol), dropwise over 45 min at  $0^\circ\text{C}$ . The solution was stirred for another 40 h at room temperature. The reaction mixture was hydrolyzed with distilled water (80 mL) and 10%  $\text{H}_2\text{SO}_4$  (250 mL). The diethyl ether layer was separated and dried over  $\text{CaCl}_2$ , and the ether was removed by distillation. The residue was purified by sublimation ( $0^\circ\text{C}$ ,  $10^{-3}$  Torr) to afford the product as a white crystalline solid. Yield: 10.4 g (75%). Anal. Calcd for  $\text{C}_5\text{H}_{10}\text{D}_2\text{O}$ : C, 66.6; H/D, 13.4. Found: C, 66.5; H/D, 13.3.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.74 (s, OH), 0.89 (s,  $\text{CMe}_3$ ).

**Vielsmeier Reagent,  $[\text{Me}_2\text{N}=\text{CHCl}]\text{Cl}$ .**<sup>89</sup> To dimethylformamide (100 mL) was added  $\text{PCl}_5$  (26.76 g, 0.13 mol) over 1 h. After being stirred for 20 h at  $25^\circ\text{C}$ , the clear orange solution had turned yellow and a large amount of solid had formed. The yellow reaction product was collected by filtration, washed with cold DMF (15 mL) and cold

diethyl ether (30 mL), and dried to give the product as a light tan solid. Yield: 16.0 g (96%).

**Neopentyl- $d_1$  chloride,  $\text{ClCHDCMe}_3$ .**<sup>89</sup> To a solution of Vielsmeier reagent (13.0 g, 0.20 mol) in dimethylformamide (15 mL) was added  $\text{NpOH-}d_1$  (8.2 g, 0.18 mol) in dimethylformamide (10 mL) dropwise over 45 min. The reaction mixture was then refluxed for 15 h. The brown solution was filtered and the product was purified by distillation at atmospheric pressure (bp  $84^\circ\text{C}$ ). Yield: 6.7 g (67%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  3.30 (t,  $J_{\text{HD}} = 1.3$  Hz, CHD), 0.99 (s,  $\text{CMe}_3$ ). The  $\text{CMe}_3\text{:CH}$  peak intensity ratio was 9:1.

**Neopentyl- $d_2$  chloride,  $\text{ClCD}_2\text{CMe}_3$ .**<sup>89</sup>  $\text{NpCl-}d_2$  was prepared by the same procedure as for  $\text{NpCl-}d_1$  except that  $\text{NpOH-}d_2$  was used as the starting material. Anal. Calcd for  $\text{C}_5\text{H}_9\text{D}_2\text{Cl}$ : C, 55.3; H/D, 10.2; Cl, 32.6. Found: C, 55.3; H/D, 10.2; Cl, 32.5.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  0.99 (s,  $\text{CMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  56.3 (quintet,  $J_{\text{CD}} = 91.2$  Hz,  $\text{CD}_2\text{CMe}_3$ ), 32.4 (s,  $\text{CD}_2\text{CMe}_3$ ), 26.9 (s,  $\text{CD}_2\text{CMe}_3$ ).

**Neopentyltitanium- $d_1$ ,  $\text{Li}(\text{CHDCMe}_3)_5$ .**<sup>56</sup> To a suspension of finely-cut chips of lithium (2.1 g, 0.3 mol) and sodium (0.5 g) in hexane (250 mL) was added  $\text{NpCl-}d_1$  (10.7 g, 0.1 mol) and the reaction mixture was refluxed for 3 days. The solution was filtered, the solvent was removed under vacuum, and the crude gray product was purified by sublimation ( $130^\circ\text{C}$ ,  $10^{-3}$  Torr, 24 h) to afford the product as a white crystalline solid. Yield: 3.37 g (43%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.13 (s,  $\text{CMe}_3$ ),  $-0.73$  (s, CHD). The  $\text{CMe}_3\text{:CH}$  peak intensity ratio was 9:1. Hydrolysis gave 99.1% neopentane- $d_1$  and 0.9% neopentane- $d_0$  as established by mass spectroscopy.

**Neopentyltitanium- $d_2$ ,  $\text{Li}(\text{CD}_2\text{CMe}_3)_5$ .**<sup>56</sup>  $\text{LiNp-}d_2$  was prepared by the same method from  $\text{NpCl-}d_2$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  1.13 (s,  $\text{CMe}_3$ ). Hydrolysis gave 98.6% neopentane- $d_2$  and 1.4% neopentane- $d_1$  as established by mass spectroscopy.

**Solution Thermolysis Experiments.** Samples of  $\text{TiNp-}d_0$ ,  $-d_4$ , and  $-d_8$  (0.10 to 4 mmol) in 0.5 to 1.0 mL of solvent were thermolyzed under vacuum in flame-sealed 5-mm NMR tubes at  $80^\circ\text{C}$  (ca. 24 h for  $\text{TiNp-}d_0$  and  $-d_4$  and ca. 50 h for  $\text{TiNp-}d_8$ ). A sealed capillary containing a solution of hexamethylbenzene in  $\text{C}_6\text{D}_6$  was inserted into the NMR tubes for use as an integration standard. The samples were kept at constant temperature in an oil bath, and every 30 min the samples were cooled to room temperature and analyzed by  $^1\text{H}$  NMR spectroscopy. Each spectrum consisted of 32 scans and the post-acquisition delay was normally 1 s, but was set to 120 s (five times the longest  $T_1$ ) when relative peak integrals were of interest. The samples were then returned to the oil bath for further heating. Kinetic plots and Eyring plots were fit by unweighted nonlinear least-squares methods by using the software package Passage by Passage Software, Inc. Errors in the derived activation parameters were calculated from error propagation formulas that explicitly take into account the range of temperatures studied;<sup>90</sup> the estimated temperature error was 1 K, and the estimated error in the rate constants from the nonlinear least-squares fits was estimated to be 20%.

For NMR experiments to determine the amount of neopentane eliminated per mole of  $\text{TiNp}_4$  thermolyzed, a correction must be made for the presence of neopentane in the "head space" above the solution level in the NMR tube. Neopentane and benzene form mixtures that show a positive deviation from Raoult's law,<sup>91</sup> but unfortunately the composition of the vapor above such mixtures has never been measured. We can, however, use vapor composition data for similar mixtures such as *n*-pentane/benzene<sup>92</sup> to estimate that, at low concentrations of neopentane in benzene, the partial pressure of neopentane above the mixture is approximately 2 times higher than that predicted by Raoult's law. From this estimate, we can calculate the fraction of neopentane in the head space from the volume of benzene (1 mL), the total internal volume of our sealed 5-mm NMR tubes (7 mL), and the vapor pressure of neopentane at  $25^\circ\text{C}$  (171 kPa).<sup>93</sup> We find that about 7% of the total amount of neopentane present is in the head space.

After the  $\text{TiNp}_4$  samples had thermolyzed completely, the sealed tubes were broken in a closed vessel and the volatile organic by-

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products were analyzed by GC/MS. Neopentane was the only organic byproduct generated upon thermolysis of  $\text{TiNp}_4$  at 80 °C regardless of the solvent.

**Thermolysis of  $\text{TiNp}_4$  in the Presence of 1,2-Bis(dimethylphosphino)ethane (dmpe).**  $\text{TiNp}_4$  (0.12 g, 3.6 mmol) and dmpe (0.08 mL, 4.7 mmol) were dissolved in  $\text{C}_6\text{D}_6$  (0.8 mL) in an NMR tube. After the NMR tube had been flame-sealed, the reaction mixture was heated at 80 °C and the progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. The decomposition of  $\text{TiNp}_4$  followed first-order kinetics with a rate constant,  $10.1 \times 10^{-5} \text{ s}^{-1}$ , that was quite similar to that observed for the thermolysis of  $\text{TiNp}_4$  alone (Table 1). No peaks due to new organotitanium species were observed at any time.

**Thermolysis of  $\text{TiNp}_4$  in the Presence of Bis(trimethylsilyl)acetylene (BTMSA).**  $\text{TiNp}_4$  (0.33 g, 1.0 mmol) and BTMSA (0.17 g, 1.0 mmol) were dissolved in  $\text{C}_6\text{D}_6$  (0.8 mL) in an NMR tube. After the NMR tube had been flame sealed, the reaction mixture was heated to ca. 55 °C and the progress of the reaction was monitored periodically by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. After 6 h at 55 °C, new peaks at  $\delta$  0.33, 0.37, 0.97, 1.08, 1.41, and 5.26 with relative intensities of 9:9:9:9:1 were present in the  $^1\text{H}$  NMR spectrum. These peaks are relatively small compared to those due to  $\text{TiNp}_4$  and BTMSA. Tentative  $^1\text{H}$  NMR peak assignments:  $\delta$  0.33 ( $\alpha\text{-SiMe}_3$ ), 0.37 ( $\beta\text{-SiMe}_3$ ), 0.97 ( $\text{CH}_2\text{CMe}_3$ ), 1.08 ( $\text{CH}_2\text{CMe}_3$ ), 1.41 ( $\text{CHCMe}_3$ ),  $\delta$  5.26 ( $\text{CHCMe}_3$ ). The  $^{13}\text{C}$  NMR spectrum at this point exhibits the following new peaks: 1.7 ( $\text{SiMe}_3$ ), 2.4 ( $\text{SiMe}_3$ ), 33.0 ( $\text{CH}_2\text{CMe}_3$ ), 33.6 ( $\text{CH}_2\text{CMe}_3$ ), 34.9 ( $\text{CHCMe}_3$ ), 101.4 ( $\text{CSiMe}_3$ ), 104.3 ( $\text{CSiMe}_3$ ), 111.9 ( $\text{CHCMe}_3$ ). After 30 h at 55 °C, no peaks due to  $\text{TiNp}_4$  or the titanacyclobutene complex remained.

**Analysis of Deuterated Neopentanes by Mass Spectroscopy.** The determination of the isotopic composition of samples of neopentane is not straightforward because neopentane does not give a parent peak in its 80-eV electron-impact mass spectrum. Instead, ionization of neopentane- $d_0$  gives large amounts of the *tert*-butyl cation ( $\text{C}_4\text{H}_9^+$ ), which appears as a major peak at mass 57 (along with a minor peak at mass 58 due to the natural-abundance  $^{13}\text{C}$  isotopolog). In comparison, the mass spectrum of monodeuterated neopentane contains two main peaks (ignoring for the moment the  $^{13}\text{C}$  isotopologs): one at mass 57 and one at mass 58 whose relative intensities are approximately 1:3. The relative intensities of these peaks reflect the relative probability of neopentane- $d_1$  losing a  $\text{CH}_3$  group or a  $\text{CH}_2\text{D}$  group upon ionization. Similarly, the mass spectrum of neopentane- $d_2$  with both deuterium atoms on the same methyl group will consist of peaks at 57 and 59, while neopentane- $d_3$  will give peaks at 57 and 60; in both these cases the peak at mass 57 is approximately  $1/3$  the intensity of the other. Thus, the mass spectrum of a mixture of deuterated neopentanes will give peaks at mass 57, 58, 59, and 60 whose relative intensities are not directly proportional to the amounts of neopentane- $d_0$ , - $d_1$ , - $d_2$ , and - $d_3$ . There are two reasons for this: all the isotopologs give reasonably strong peaks at mass 57, and the intensities of the mass 58 to 60 peaks are complicated by the presence of  $^{13}\text{C}$  isotopologs. The isotopic composition of a sample of deuterated neopentanes was deduced from its mass spectrum by solving the set of linear equations  $C_{ij}X_i = Y_j$ , where  $C_{ij}$  is the normalized intensity of the peak at mass  $57 + j$  of a

**Table 6.** Mass Spectra of the *tert*-Butyl Cations Generated upon Ionization of Various Neopentane Isotopologs

isotopolog	intensity of peak at $m/e$					ref
	57	58	59	60	61	
$d_0$	100	4.3	0	0	0	this work <sup>a</sup>
$d_1$	33.8	100	4.0	0	0	this work <sup>b</sup>
$d_2$	32.9	2.8	100	4.5	0	this work <sup>c</sup>
$d_3$	30.0	4.5	0	100	4.4	this work <sup>d</sup>
$d_0$	100	4.4	0	0	0	20, 96
$d_1$	32.4	100	4.3	0	0	calcd <sup>e</sup>
$d_2$	33	1.45	100	4.4	0	calcd <sup>e</sup>
$d_3$	33	1.45	0	100	4.4	calcd <sup>e</sup>

<sup>a</sup> Prepared by hydrolysis of  $\text{LiNp-}d_0$  with  $\text{H}_2\text{O}$ . <sup>b</sup> Prepared by hydrolysis of  $\text{LiNp-}d_1$  with  $\text{H}_2\text{O}$ . <sup>c</sup> Prepared by hydrolysis of  $\text{LiNp-}d_1$  with  $\text{D}_2\text{O}$ . <sup>d</sup> Prepared by hydrolysis of  $\text{LiNp-}d_2$  with  $\text{D}_2\text{O}$ . <sup>e</sup> The calculated mass spectra were derived by assuming that the neopentane isotopologs fragment *randomly* to give the observed *tert*-butyl cations, i.e., that loss of a methyl group upon ionization occurs with equal probability whether or not that methyl group is deuterated. Corrections are made for natural abundance  $^{13}\text{C}$  isotopologs, and all the peaks are normalized so that the strongest peak has an intensity of 100.

pure sample of neopentane with  $i$  deuterium atoms,  $X_i$  is the mole fraction (in a sample of mixed neopentane isotopologs) of neopentane molecules with  $i$  deuterium atoms, and  $Y_j$  is the observed normalized intensity of the peak at mass  $57 + j$  in a sample of mixed neopentane isotopologs.<sup>94,95</sup> The Gauss–Jordan elimination method was used to invert the coefficient matrix, and by multiplying both sides of the equation by  $C_{ij}^{-1}$ , the distribution of deuterated neopentanes,  $X_i$ , can be obtained:  $X_i = C_{ij}^{-1}C_{ij} X_i = C_{ij}^{-1}Y_j$ .

The  $C_{ij}$  coefficients were determined experimentally from the mass spectra of authentic samples of neopentane- $d_0$ , - $d_1$ , - $d_2$ , and - $d_3$ . The complete set of  $C_{ij}$  values is given in Table 6.<sup>96</sup> In a few cases where neopentane- $d_4$  was present, a  $5 \times 5$  matrix equation was solved to obtain the isotopolog distribution.

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