CHAPTER 4

THERMOLYSIS OF Tervalent Permethyltitanocene Derivatives, (η⁵-C₅Me₅)₂TiR, TO (η⁶-C₅Me₅CH₂)(η⁵-C₅Me₅)Ti AND RH CATALYZED BY Permethyltitanocene Hydride, (η⁵-C₅Me₅)₂TiH

Summary
The complexes Cp*:TiR (Cp*: η⁵-C₅Me₅; R = Me, Et, Pr, C₂H₅, CH₂CMe₃, Ph) undergo thermolysis to yield the ring–metalated complex Cp*FvTi (Fv: η⁶-C₅Me₅CH₂) and RH. Kinetic measurements and deuterium labeling studies show that the decomposition is catalyzed by Cp*:TiH, which is formed either by β–hydrogen elimination from a titanium alkyl Cp*:TiCH₂CH₂R at low temperature, or by hydrogenolysis of Cp*:TiR or Cp*FvTi, using dihydrogen eliminated from Cp*FvTi at elevated temperatures. Permethyltitanocene is not an intermediate. The rate of the catalyzed decomposition of Cp*:TiCH₂CMe₃ is linear in [Cp*:TiH]. The rate for Cp*:TiMe is proportional to [Cp*:TiH] and [Cp*:TiMe] and inversely proportional to the starting concentration of Cp*:TiMe. This is explained in a kinetic scheme, where H₂, eliminated from Cp*:TiH to give Cp*FvTi, reacts with Cp*:TiR to regenerate Cp*:TiH and liberate RH. The model is supported by the reaction of (Cp*-d₁₅)₂TiD and Cp*:TiCH₂CMe₃ yielding Cp*:TiD and (Cp*FvTi-d₂₉). The activation parameters for thermolysis of Cp*:TiH are calculated from the overall kinetics of the catalyzed decomposition of Cp*:TiMe and Cp*:TiCH₂CMe₃ (ΔH° = 77.1 (2) kJ.mol⁻¹ and ΔS° = −54 (4) J.mol⁻¹.K⁻¹).

Introduction
The activation of C-H bonds of inert hydrocarbons has been a major topic in contemporary organometallic chemistry. Alkanes are chemically inert because they have high bond energies and ionization potentials, low acidities and negative electron affinities. One strategy to functionaize selectively these molecules is to allow them to react with coordinatively unsaturated
organometallic complexes. It is generally recognized that C-H bonds can be activated either by oxidative addition to an electron–rich metal center, or by a non–oxidative pathway at a strongly electrophilic metal center. The latter is typical for the strongly Lewis acidic sites common for d0 transition and lanthanide metal compounds. C-H activation between carbonyl fragments at the metal and external, neutral substrates (like coordinating solvents, alkenes) with sp, sp2 or even sp3 CH bonds are well known.3 Best documented, however, are intramolecular CH activations, where C-H bonds of ancillary ligands function as hydrogen donor for the formation of RH. The entropic advantage of intramolecular over intermolecular C-H activation is obvious. The ancillary ligands are metalated first and then may undergo further rearrangement to more stable configurations depending on the metal and C-H bonds involved. Intermediates may involve species like cumulenes, metalacycles, η2-alkene and aryne adducts.4 Fulvenes are also well–known products and can be formed by H–abstraction from a methyl substituted cyclopentadienyl ligand. Several authors have discussed the thermodynamic and kinetic prerequisites for C-H activation reactions.4 Especially, the study of intramolecular C-H activations has rendered new, fundamental knowledge of mechanisms and thermodynamics in early transition metal chemistry. An elegant example has been worked out by Marks et al. in Cp*2Th2 chemistry (Cp*: η2-C5Me5; R = CH2XMe3, X = C, Si).5 The extensive use of the pentamethylcyclopentadienyl ligand (Cp*) in early transition metal chemistry, coupled with the current interest in CH activation has led to several reports on reactive ring–metalated (fulvene) species. These processes are frequently observed during thermolysis of metal hydrocarbyls. In a number of cases extensive kinetic and mechanistic studies have been carried out. Thermal decomposition of Cp*2TiMe24d, Cp*2ZrPh24g and Cp*2HfBz26 to Cp*FvMR species (Fv: η6-C5Me4CH2) follow first order kinetics, and labeling studies indicate intramolecular pathways, which are now reasonably well understood. These early transition metal compounds lack accessible higher oxidation states and oxidative additions are not possible. Moreover, they have high dissociation energies which exclude homolytic pathways. The reactions appear to proceed in a concerted fashion via a highly polar four–centered transition state, usually referred to as a–bond metathesis.4a Also in other cyclometalations, e.g. the decomposition of Ta(OAr)2Me3 (Ar = 2,6-di–t–butylphenyl)7, simple intramolecular processes proceeding by o–bond metathesis were observed. C-H activation is also a prominent feature of low–valent titanium metallocene derivatives. This has led to reports of several “titanocenes”.8 The relationship between these is still mysterious, and until now only two
complexes have been reasonably well characterized. These are the fulvalene bridged \((\mu-\eta^5:\eta^5-C_{10}H_{14})-(\mu-H)_2-(\eta^5-C_5H_5Ti)_2\) and the bridging \((\mu-\eta^1:\eta^5-C_5H_4)(\eta^5-C_5H_5)_3Ti_2\). The reaction pathways leading to them are not clear. Also for low valent permethyltitanocenes C-H activation of the methyl groups of the Cp* ligand is the dominant chemistry. The mechanistic aspects of these reactions have been studied in some more detail, but the processes involved are complex and as yet not fully understood. We report here a study of thermally induced C-H activation in paramagnetic, tervalent titanium compounds \(\text{Cp}^*\text{TiR} (R = \text{alkyl, aryl})\). The thermolysis is a clean, stoichiometric process leading to the fulvene complex \(\text{Cp}^*\text{FvTi} \) with the liberation of \(\text{RH} \) (eq 1).

\[
\text{Cp}^*_2\text{TiR} \rightarrow \text{Cp}^*\text{FvTi} + \text{RH} \\
(\text{Fv} = \eta^5-C_5\text{Me}_4\text{CH}_2)
\]

Exploratory studies of the thermolysis of simple \textit{alkyls} with \(R = \text{Et, n–Pr}\) showed first order kinetics and indicated intramolecular C-H abstraction, but deuterium labeling and cross-over experiments suggested a more complicated mechanism. We therefore decided to carry out a detailed kinetic and mechanistic study of the thermolysis of \(\text{Cp}^*\_2\text{TiR} \) for various carbyl ligands \(R\).

**Experimental section**

All operations were performed using Schlenk, vacuum–line or glove box techniques under nitrogen. Solvents were distilled from Na/K alloy prior to use. \((\text{Cp}^*\text{Ti})\text{N}_2\) and \(\text{Cp}^*_2\text{TiR} (R = \text{alkyl, hydride})\) and partly deuterated analogues were synthesized by published procedures. NMR spectra were recorded on Bruker WH–90 and Varian VXR–300 spectrometers. Chemical shifts are reported in ppm and referenced to residual protons in the deuterated solvents (THF–d8 δ 3.57 ppm, upfield from TMS). Gas chromatography was performed on a HP–5890A apparatus using a Porasil B packed column. Quantitative gas analyses were done using a Toepler pump. Isotopic distributions of deuterated alkanes were determined with an AEI Metrovac VC9 mass spectrometer, operated at 15 kV. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer and IR spectra on a Perkin Elmer EPS–3T spectrophotometer (as Nujol mulls between KBr disks). Elemental analyses were performed at the Micro–Analytical Center of our Department. Given values are the average of at least two independent determinations.

**Kinetic Measurements.** \(^1\text{H} \) NMR spectroscopy. Rates of thermolysis of \(\text{Cp}^*_2\text{TiR} \) were measured by \(^1\text{H} \) NMR monitoring the increase in peak intensity of \(\text{Cp}^*\text{FvTi} \)
at $\delta = -11.7$ ppm (vide infra). For the majority of the compounds there is no overlap with resonances of parent $\text{Cp}^*\text{TiR}$, and hence the resonance at $\delta = -11.7$ ppm can be used conveniently as a kinetic probe. Thermolysis was carried out in the temperature-controlled probe of a NMR spectrometer, in THF-$d_8$ solutions in sealed 5 mm NMR tubes. FT-NMR spectra were recorded automatically at preset intervals using a home-made routine. Each spectrum consisted of 200 scans with 0.24 s acquisition time. The reaction temperature was recorded and was found constant within 0.2 °C. The peak separation in ethylene glycol was used for temperature calibration.

**UV−Vis** spectroscopy. Thermal decomposition rates were measured by monitoring the absorbance at fixed wavelength (545 nm). $\text{Cp}^*\text{TiMe}$ and $\text{Cp}^*\text{FvTi}$ are colored compounds (W-Vis absorption data in THF' are as follows: $\text{Cp}^*\text{TiMe}$: $\lambda_{max} = 470$ nm, $\varepsilon = 103$ dm$^3$.mol$^{-1}$.cm$^{-1}$ and $\varepsilon = 605$ nm, $\varepsilon = 40$ dm$^3$.mol$^{-1}$.cm$^{-1}$; $\text{Cp}^*\text{TiEt}$: $\lambda_{max} = 478$ nm, $\varepsilon = 130$ dm$^3$.mol$^{-1}$.cm$^{-1}$ and $\lambda_{max} = 625$ nm, $\varepsilon = 34$ dm$^3$.mol$^{-1}$.cm$^{-1}$; $\text{Cp}^*\text{Ti-n-Pr}$: $\lambda_{max} = 465$ nm, $\varepsilon = 150$ dm$^3$.mol$^{-1}$.cm$^{-1}$ and $\lambda_{max} = 640$ nm, $\varepsilon = 32$ dm$^3$.mol$^{-1}$.cm$^{-1}$; $\text{Cp}^*\text{TiCH}_2\text{CMe}_3$: $\lambda_{max} = 490$ nm, $\varepsilon = 192$ dm$^3$.mol$^{-1}$.cm$^{-1}$ and $\lambda_{max} = 655$ nm, $\varepsilon = 48$ dm$^3$.mol$^{-1}$.cm$^{-1}$; $\text{Cp}^*\text{TiPh}$: $\lambda_{max} = 485$ nm, $\varepsilon = 105$ dm$^3$.mol$^{-1}$.cm$^{-1}$ and $\lambda_{max} = 585$ nm, $\varepsilon = 31$ dm$^3$.mol$^{-1}$.cm$^{-1}$; $\text{Cp}^*\text{FvTi}$: $\lambda_{max} = 550$ nm, $\varepsilon = 220$ dm$^3$.mol$^{-1}$.cm$^{-1}$). The difference in optical density between $\text{Cp}^*\text{TiMe}$ and $\text{Cp}^*\text{FvTi}$ is maximal at 545 nm and is sufficient to allow spectrophotometrical determination of reaction rates. UV−Vis spectroscopy is conveniently applied at relatively low concentrations of $\text{Cp}^*\text{TiR}$. The upper limit in concentration is set by the Lambert–Beer law at appr. 25 mmol.L$^{-1}$ (using 2 mm cuvets). At higher concentrations (> 30 mmol.L$^{-1}$) THF NMR spectroscopy is better, although some price has to be paid in terms of accuracy. Thermolyses were carried out in a thermostated cuvet holder (+ 0.01 °C) of the spectrophotometer as the solutions in 2 mm glass cuvets. Data were collected automatically at preset intervals by computer controlled operation of the spectrometer, using a local version of the PECS program. Reactions were followed for at least 3 half-lives. Kinetic plots of $\text{Cp}^*\text{TiMe}$ (1) were fit by non-linear regression as an associated exponential, or by linear regression after linearization by $\ln(A_t-A_\infty)/(A_0-A_\infty)$. Other plots were fitted by linear regression, if necessary after proper linearization of the data.

**Preparation of Samples.** Samples for W−Vis measurements were prepared from stock solutions of $\text{Cp}^*\text{TiR}$ in THF. For kinetic studies the various stock solutions were mixed and when necessary diluted. A typical solution consisted of 106.8 mg $\text{Cp}^*\text{TiCH}_2\text{CMe}_3$ in 12.0 mL THF ($[\text{Cp}^*\text{TiCH}_2\text{CMe}_3] = 23.0$ mmol.L$^{-1}$). The quality of these solutions did not change when stored at −35 °C. The solutions were transferred to a 2 mm glass cuvet and sealed with a teflon...
Labeling Experiments. Experiments with labeled compounds were carried out on appr. 100 mg scale on a high vacuum line. A typical experiment is described. \( \text{Cp}^*\text{Ti}(\text{Me}-d_3) \) (82 mg, 0.24 mmol) was dissolved in 2.0 mL of THF. After stirring the solution for 80 h at 90 °C the gases were collected with a Toepler pump: 0.237 mmol, 0.97 eq/Ti. Mass spectrum: m/e = 17, CD₃H.

Thermolysis of \( \text{Cp}^*\text{TiEt} \) (2); Synthesis of \( \text{Cp}^*\text{FvTi} \) (7). \( \text{Cp}^*\text{TiEt} \) (2) (4.23 g, 12.2 mmol) was dissolved in 20 mL of THF. The solution was subsequently heated for 3 days at 50 °C during which time the color changed to purple. The solvent was removed in vacuum, and the purple residue recrystallized from pentane. Yield: 3.60 g (11.4 mmol, 93%). Anal. Calcd for \( \text{C}_{20}\text{H}_{25}\text{Ti} \): C, 75.96; H, 9.31; Ti, 15.09. Found: C, 75.31; H, 9.17; Ti, 14.97. IR (cm⁻¹): 3020 (w), 2720 (w), 1480 (m), 1375(s), 1335 (w), 1160 (w), 1140 (w), 1070 (w), 1070 (w), 1020 (s), 845 (m), 800 (s), 750 (m), 610 (w), 515 (s), 430 (s). ¹H NMR (toluene-\( d_6 \), 20°C, 300 MHz): 6 25.3 ppm (21H, WHM 960 Hz), 12.7 (2H, WHM 440 Hz), −11.7 ppm (6H, WHM 290 Hz). W – Vis (THF): \( \text{\lambda}_{\text{max}} \) = 550 nm (ε = 220 dm³.mol⁻¹.cm⁻¹). (WHM = width (Hz) at half maximum).

Analysis of Evolved Gases. A typical experiment is described below. \( \text{Cp}^*\text{TiEt} \) (2) (92 mg, 0.18 mmol) was dissolved in 2 mL of toluene. The solution was heated for 6 h at 60 °C during which the color changed to purple. The gas evolved was collected with a Toepler pump (0.17 mmol, 0.94 eq/Ti) and analyzed by GC (ethane, 100%).

Competition Experiment. \( \text{Cp}^*\text{TiMe} \) (51 mg, 0.158 mmol) and \( \text{Cp}^*\text{TiCH₃OMe₃} \) (54 mg, 0.138 mmol) were dissolved in 2 mL of THF under vacuum. At 0 °C dihydrogen was admitted (0.140 mmol). After stirring for 0.5 h at 0 °C, the volatiles were removed in vacuum. The residue was then dissolved in benzene-\( d_6 \) and oxidized with PbCl₂. The resulting red solution was characterized by H NMR. Identified compounds : \( \text{Cp}^*\text{Ti}(\text{Me})\text{Cl} \) 6 = 1.73 ppm (Cp*, 30H), 0.23 ppm (Me, 3H); \( \text{Cp}^*\text{Ti}(\text{H})\text{Cl} \) δ = 1.87 ppm (Cp*, 30H), 4.45 ppm (H, 1H). The compounds were identified on the basis of integrated signal ratios and comparison with authentic samples.¹²,²¹b \( \text{Cp}^*\text{FvTiCl} \) was not present in the reaction mixture.
Results and Discussion

The compounds \( \text{Cp}^*\text{TiR} \) (\( \text{R} = \text{Me} \) (1), \( \text{Et} \) (2), \( \text{Pr} \) (3), \( \text{CH}_2\text{CMe}_3 \) (4), \( \text{C}_2\text{H}_3 \) (5), \( \text{Ph} \) (6)) were studied. Except for the propyl derivative 3, which has to be handled below \( 0 \, ^\circ\text{C} \), the compounds are thermally sufficiently stable to allow manipulation at ambient temperature. The thermal stability of \( \text{Cp}^*\text{TiR} \) depends strongly on the nature of \( \text{R} \). \( \text{Cp}^*\text{TiEt} \) (2) and especially higher alkyl derivatives readily decompose at room temperature, whereas the methyl (1), vinyl (5) and phenyl (6) derivatives are thermally much more robust. For a convenient rate of thermolysis of the last three compounds, temperatures ranging from 90 to 150 \( ^\circ\text{C} \) are needed.\(^{13}\) The stoichiometry of the thermolysis in both solution and solid state is given by eq 1. The fulvene complex \( \text{Cp}^*\text{FvTi} \) (7) is obtained as the sole organometallic product from 1–4\(^{14}\) and \( \text{RH} \) is the only organic compound. Radical coupling products \( \text{R}–\text{R} \) or radical disproportionation products like olefins \( \text{R}–(\text{H}) \) were not found. The absence of olefins indicates further that \( \beta \)-hydrogen elimination, well known for higher alkyl derivatives, is not a productive decomposition route. The vinyl compound 5 is thermally quite stable. It starts to decompose (t\(_{1/2} \approx 40 \) h at 110 \( ^\circ\text{C} \)) at temperatures where 7 itself loses hydrogen to form the previously described doubly metalated compound \( \text{Cp}^*\{\text{C}_5\text{Me}_3(\text{CH}_2)_2\}\text{Ti} \) (8) (eq 2).\(^{15}\)

\[
\text{Cp}^*\text{FvTi} \rightarrow \text{Cp}^*\{\text{C}_5\text{Me}_3(\text{CH}_2)_2\}\text{Ti} + \text{H}_2
\]  

This reaction complicates the picture of the thermolysis of 5 (and 6) somewhat. Mixtures of 7 and 8 were obtained and initially formed ethene disappeared partly due to hydrogenation to ethane. The phenyl compound 6 also needs elevated temperatures for a noticeable thermolysis rate and produces a mixture of 7, 8 and benzene.\(^{16}\) Solvents do not participate in the thermolysis process. No deuterium incorporation was observed into the \( \text{RH} \) formed when 1, 2 or 3 were thermolyzed in benzene–\( \text{d}_6 \) or \( \text{THF–d}_8 \) (GC–MS).

Exploratory kinetic studies. The thermally labile alkyls 2 and 3, having relatively short half–life times (45 resp. 1 h at room temperature in THF) were studied first. Kinetic data were obtained by monitoring UV–Vis spectra in THF solutions. In first approximation the thermolysis is first order in \( \text{Cp}^*\text{TiR} \), and independent of concentration (between 9 and 18 mmol L\(^{-1} \), Table 1). Isobestic points were observed during the decomposition indicating that no measurable amounts of intermediates are formed. This suggests that, analogous to other ring metalations, thermolysis of \( \text{Cp}^*\text{TiR} \) is a simple intramolecular C–H activation, without intermediates, showing first order kinetics and no
participation of the solvent. To confirm this simple mechanism isotope labeling studies were carried out, the outcome of which showed that a much more complicated pathway is operative.

Table 1. Rate constants for the thermolysis of \( \text{Cp}^*\text{TiEt} \) (2) and \( \text{Cp}^*\text{Ti-n-Pr} \) (3) in THF monitored by W–Vis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>([\text{TiR}]) (mmol.L(^{-1}))</th>
<th>(k_{\text{obs}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>313</td>
<td>10.0</td>
<td>1.5 (2) 10(^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>313</td>
<td>15.0</td>
<td>1.7 (2) 10(^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>313</td>
<td>18.0</td>
<td>1.9 (2) 10(^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>302</td>
<td>6.0</td>
<td>2.1 (2) 10(^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>302</td>
<td>8.0</td>
<td>2.3 (2) 10(^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>302</td>
<td>9.5</td>
<td>2.3 (2) 10(^{-4})</td>
</tr>
</tbody>
</table>

Labeling experiments. The \( \text{Cp}^* \) ligand is the exclusive source of hydrogen for methane formation in the thermolysis of 1. \( \text{Cp}^*\text{Ti(Me-d\(_3\))} \) (lb) in THF–d\(_8\) produced only \( \text{CD}_3\text{H}_4 \) compatible with simple intramolecular decomposition. As stated before, thermolysis of 2 and 3 in deuterated solvents showed no deuterium incorporation into the alkane formed, thus excluding solvent participation. However, thermolysis of \( \text{Cp}^*\text{Ti(Et-d\(_5\))} \) (2b) did not give exclusively \( \text{C}_2\text{D}_5\text{H} \) as anticipated on the results for 1. Instead substantial amounts of \( \text{C}_2\text{D}_6 \) were formed, together with partly deuterated ethanes \( \text{C}_2\text{D}_6\text{n-H}_n \).\(^{17}\) Similar observations were made for \( \text{Cp}^*\text{Ti(Pr-d\(_7\))} \) (3b) where a mixture of deuterated propanes was obtained with the highest mass corresponding to \( \text{propane-d}_8 \). Thermolysis of an equimolar mixture of 1 and 2b (or 3b) gave in addition to the thermolysis products of the compounds themselves, monodeuterated methane \( \text{CH}_3\text{D} \). This shows that the decomposition proceeds via an intermolecular mechanism, for example by direct deuterium abstraction from an intact \( \text{Ti-R} \) \((R = \text{C}_2\text{D}_5, \text{n-C}_3\text{D}_7)\) moiety\(^1\), or by indirect deuterium transfer through an intermediate titanium deuteride \( \text{Ti-D} \). These results change the original picture completely. Thermolysis of \( \text{Cp}^*\text{TiR} \) compounds is not a simple one step process; it has at least an intermolecular component.

Thermal decomposition of \( \text{Cp}^*\text{TiMe} \) (1). Given the complex character of the thermal decomposition, we decided to concentrate on the simplest alkyl \( \text{Cp}^*\text{TiMe} \) (1). For thermolysis at a convenient rate, experiments were carried
out at 90 °C, while monitoring the mixture in THF–d₈ by H NMR. As observed before in exploratory experiments the decomposition proceeded without the formation of other species than 1, 7 and CH₄. The thermolysis took a very pronounced course. A slow start was followed by a sudden rate increase by orders of magnitude to give S-shaped conversion curves (Figure 1). The initial period of slow conversion was dependent on the concentration of 1. At higher concentrations the induction time is shorter.

S-shaped conversion plots are typical for second order autocatalytic reactions¹⁰, and they suggest that the thermal decomposition of 1 is catalyzed. The possibility that 7 is the catalyst can be excluded since a similar effect would be expected in the thermolysis of 2 and 3 which was not observed. Moreover, addition of 7 to solutions of 1 did not result in an immediate start of the thermolysis at high rate. Thus, if the active catalyst is formed from 7, it occurs only at elevated temperatures.

Stabilization by alkenes. An indication for the identity of the catalyst is obtained from the observation that primary alkenes stabilize Cp*₂TiR. This was first observed during a study of 1-hexene isomerization with the n-hexyl compound Cp*₂TiC₆H₁₃ as a catalyst. Decomposition of Cp*₂TiC₆H₁₃ to 7 and n-hexane was found to be over one order of magnitude faster in cyclopentane (t₁/₂ = 4.8 h) than in 1-hexene (t₁/₂ = 80 h) at 20 °C. A comparable effect was
observed for 3 in THF–d₈ in the presence of various amounts of propene (Figure 2). The half-life time of 3 at 35 °C changed from 1.6 to 3.4 h on addition of 2 equivalents of propene. The stabilization was even more pronounced in the presence of 5 equivalents of propene. Then 3 is thermally virtually stable at 35 °C; no measurable amounts of 7 were formed over a period of 7.5 h.

Olefins also interfere with the thermal decomposition of 1. Thermolysis of 1 (90 °C) in THF–d₈ in the presence of one equivalent of ethene apparently followed a normal, first order rate law (Figure 1). The autocatalytic rate increase was not observed. A plausible explanation for the stabilization by alkenes could be formation of an olefin adduct in which a coordination site necessary for decomposition is blocked. However, no spectroscopic evidence was found to support this. The IR spectrum of Cp*₂TiC₆H₁₃ in 1-hexene and the ¹H NMR spectrum of 3 in the presence of propene are superpositions of the individual components. A more realistic reason for the enhanced stabilities of Cp*₂TiR in the presence of olefins is the inhibited formation or trapping of the catalysts for decomposition.

Figure 2. Thermal decomposition of Cp*₂Ti–n–Pr (3) in THF–d₈ at 308 K, increase of Cp*FVTi (7) monitored by ¹H NMR ([3]₀ = 0.20 mol.L⁻¹) with added propene at 35°C: (o) no propene present, (o) 2 equivalents of propene added, (*) 5 equivalents of propene added.

Decomposition catalyst. The catalyst is either formed directly from Cp*₂TiR (1–6) or from 7 and reacts with olefins to lose catalytic activity. A likely candidate is the titanium hydride Cp*₂TiH (9), which may be formed by β–H elimination from alkyls like 2 or 3 at ambient temperatures, or by reaction of Cp*₂TiR with dihydrogen, the latter formed by thermal degradation of 7 at
elevated temperatures. Indeed a vast increase of the decomposition rate was observed when 9 was added to solutions of \( \text{Cp}^*\text{TiR} \). For example, the extremely stable phenyl derivative \( \text{Cp}^*\text{TiPh} \) (6) was found to decompose smoothly to 7 and benzene at 60 °C after addition of 0.10 equivalents of 9. Under normal conditions this compound can be refluxed for hours in toluene without noticeable decomposition.

\( \text{Cp}^*\text{TiH} \) (9) directly intervenes with the thermal decomposition of \( \text{Cp}^*\text{TiR} \). It thereby acts as a hydrogen source. Thermolysis of 1 in the presence of (\( \text{Cp}^*-\text{d}15 \))\( \text{TiD} \) (\( \Theta b \)) resulted in the formation of monodeuterated methane, \( \text{CH}_3\text{D} \). It is evident that 9 accelerates the decomposition of \( \text{Cp}^*\text{TiR} \). At ambient temperatures the only source for 9 is \( \beta\)-H elimination from \( \beta\)-hydrogen containing alkyl complexes. This explains the low thermal stability of 2, 3 and higher alkyls. \( \beta\)-Hydrogen containing alkyl derivatives are in equilibrium with 9 and the corresponding olefin. Although the equilibrium lies almost fully on the side of the alkyl, which explains the absence of olefins in the thermal decomposition \( ^{22} \), \( \beta\)-hydrogen elimination has a very low kinetic barrier. Addition of \( \alpha\)-olefins to solutions of these compounds will decrease the concentration of 9 and consequently effect stabilization of \( \text{Cp}^*\text{TiR} \). Generation of \( \text{Cp}^*\text{TiD} \) (9c) during thermolysis of 2b accounts for the observed scrambling of isotope labels in the ethane produced. A consecutive reaction between 9c and 2b will lead to the observed perdeuteroethane (Scheme 1). Reinsertion of \( \text{C}_2\text{D}_4 \) into a Ti–H bond, followed by hydrogen transfer from a \( \text{Cp}^* \) ligand or another molecule of 9 will give \( \text{C}_2\text{D}_4\text{H}_2 \). Similar reactions could lead to compounds with even less deuterium in the alkyl ligand and explain the observed generation of partly deuterated alkanes from fully deuterated alkyl ligands. Formation of 9c also explains the incorporation of deuterium into the methane formed when 1 is thermolyzed in the presence of 2b (Scheme 1).

\[
\begin{align*}
\text{Cp}^*\text{TiEt-d}_5 & \rightleftharpoons \text{Cp}^*\text{TiD} + \text{C}_2\text{D}_4 \\
\text{Cp}^*\text{TiD} + \text{Cp}^*\text{TiEt-d}_5 & \rightarrow \text{Cp}^*\text{TiH} + \text{Cp}^*\text{FvTi} + \text{C}_2\text{D}_6 \\
\text{Cp}^*\text{TiH} + \text{C}_2\text{D}_4 & \rightarrow \text{Cp}^*\text{TiEt-d}_4 \\
\text{Cp}^*\text{TiD} + \text{Cp}^*\text{TiMe} & \rightarrow \text{Cp}^*\text{TiH} + \text{Cp}^*\text{FvTi} + \text{CH}_3\text{D}
\end{align*}
\]

SCHEME 1
When $\beta$-hydrogen is absent on $R$ in $\text{Cp}^*\text{TiR}$, formation of 9 is not so straightforward. At ambient temperatures these complexes are therefore stable. For thermolysis at an observable rate, elevated temperatures (90 – 150 °C) are necessary. We presume that thermolysis starts with H-transfer from a Cp* ligand to R to yield 7 and RH (Scheme 2). This slow, intramolecular mode of decomposition is not easy to study since at elevated temperatures the thermolysis product $\text{Cp}^*\text{FvTi}$ (7) is not stable and loses dihydrogen with concomitant formation of the doubly metalated compound 8 (eq 2). The formed dihydrogen will react with either 1 or 7 to form the decomposition catalyst 9 (eq 3). Since the catalytic decomposition is very effective, traces of 9 are sufficient to cause a dramatic increase in decomposition rate of 1 at 90 °C leading to the observed S-shaped plots (Figure 1). At higher concentrations of 1 the concentration of 7 increases much faster, and consequently formation of 9 too, leading to shorter induction times. When 1 is thermolyzed in the presence of ethene the build-up of 9 will be blocked. Since insertion of ethene into the Ti–H bond is fast any 9 formed will be trapped to give the ethyl complex 2. This means that the catalytic decomposition will not start and thermolysis continues in the slow intramolecular mode (Figure 1).

$$\text{Cp}^*\text{FvTi} + \text{H}_2 \rightarrow \text{Cp}^*\text{TiH}$$ (3a)
$$\text{7}$$
$$\text{Cp}^*\text{TiR} + \text{H}_2 \rightarrow \text{Cp}^*\text{TiH} + \text{RH}$$ (3b)
$$\text{8}$$

Kinetic Study of Decomposition of $\text{Cp}^*\text{TiR}$ Catalyzed by $\text{Cp}^*\text{TiH}$. To get a better picture of the effect of $\text{Cp}^*\text{TiH}$ on the thermolysis of $\text{Cp}^*\text{TiR}$ a kinetic study was performed on mixtures of $\text{Cp}^*\text{TiR}$ ($R = \text{Me}$ (1), $\text{CH}_2\text{CMes}$ (4), Ph (6)) and $\text{Cp}^*\text{TiH}$ (9) in THF. The progress of thermolysis was followed by W–Vis (1, 4, 6) and $^1\text{H}$ NMR (1) spectroscopy (Figure 3). A number of kinetic runs were carried out on mixtures of 1 (or 4) and 9. In all experiments the spectra obtained were genuine superpositions of the components $\text{Cp}^*\text{TiR}$, 7 and 9, so there is again no indication for complex formation between the various components. The temperatures (293 – 318 K) at which the experiments were performed are sufficiently low to exclude participation of the slow intramolecular thermolysis of $\text{Cp}^*\text{TiR}$.

Analysis of spectral data gave kinetic plots of variable complexity. For the phenyl compound 6 a mathematical evaluation of the progression of the reaction proved not simple and a detailed analysis was not attempted. However, for the neopentyl derivative 4 the kinetics are quite simple. The overall rate for 4 is first order in hydride 9 and independent of 4 (eq 4, Table 2). Addition of
extra 7 has no effect on the rate (Table 3).

$$- \frac{d[4]}{dt} = k [9]$$

(4)

Figure 3. A: W–Vis spectra of the $\text{Cp}^*\text{TM}_2$ (9) catalyzed decomposition of $\text{Cp}^*\text{TiMe}_2$ (1) monitored at 20 min intervals. $[1]_0 = 30.0 \text{ mmol.L}^{-1}$, $[Q] = 5 \text{ mmol.L}^{-1}$ in THF at 308 K.

B: $^1\text{H}$ NMR spectra of the $\text{Cp}^*\text{TM}_2$ (9) catalyzed decomposition of $\text{Cp}^*\text{TiMe}_2$ (1) at 30 min intervals. $[1]_0 = 60.0 \text{ mmol.L}^{-1}$, $[9] = 7 \text{ mmol.L}^{-1}$ in THF–$d_8$ at 308 K. (Cp$^*$_TM$_2$ (Q), $\delta$ 23 ppm; Cp$^*$_TM$_2$Me (1), $\delta$ 19 ppm, -23 ppm; Cp$_*$_FvTi (7), $\delta$ 26 ppm, 13 ppm, -11 ppm)
C: UV–vis spectra of the Cp*₂TiH (9) catalyzed decomposition of Cp*₂TiCH₂CMe₃ (4) monitored at 8 min intervals. [4] = 23.0 mmol.L⁻¹, [9] = 9.9 mmol.L⁻¹ in THF at 293 K.

Table 2. Rate constants for thermolysis of Cp*₂TiCH₂CMe₃ (4) at 298 K at various concentrations of Cp*₂TiH (9).

<table>
<thead>
<tr>
<th>[TiH]ₐ</th>
<th>[TiCH₂CMe₃]ᵇ</th>
<th>kₐᵇ</th>
<th>kₐᵇ/[TiH]ᶜ (k₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>23.0</td>
<td>0.78 (2)</td>
<td>4.0 (4)</td>
</tr>
<tr>
<td>3.9</td>
<td>&quot;</td>
<td>1.4 (2)</td>
<td>3.5 (1)</td>
</tr>
<tr>
<td>9.9</td>
<td>&quot;</td>
<td>3.5 (2)</td>
<td>3.5 (1)</td>
</tr>
<tr>
<td>16.3</td>
<td>&quot;</td>
<td>5.5 (1)</td>
<td>3.4 (1)</td>
</tr>
<tr>
<td>19.8</td>
<td>&quot;</td>
<td>6.3 (1)</td>
<td>3.2 (2)</td>
</tr>
<tr>
<td>50.1</td>
<td>&quot;</td>
<td>14 (0.5)</td>
<td>2.8 (2)</td>
</tr>
</tbody>
</table>

ᵃ in mmol.L⁻¹, ᵇ in 10⁻² L.mol⁻¹.s⁻¹, ᶜ in 10⁻⁴ s⁻¹.
Table 3. Rate constants k for thermolysis of $\text{Cp}^*\text{TiCH}_2\text{CMe}_3$ (4) at 298 K, dependence on concentration and effect of added $\text{Cp}^*\text{FvTi}$ (7).

<table>
<thead>
<tr>
<th>[TiH]$^a$</th>
<th>[TiCH$_2$CMe$_3$]$^a$</th>
<th>[Fv]$^b$</th>
<th>$k_{obs}$$^b$</th>
<th>$k_{obs}/[TiH]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>4.9</td>
<td>-</td>
<td>2.1 (2)</td>
<td>3.4 (5)</td>
</tr>
<tr>
<td>6.1</td>
<td>7.2</td>
<td>-</td>
<td>1.9 (2)</td>
<td>3.1 (5)</td>
</tr>
<tr>
<td>6.1</td>
<td>14.0</td>
<td>-</td>
<td>2.2 (2)</td>
<td>3.6 (3)</td>
</tr>
<tr>
<td>6.1</td>
<td>24.0</td>
<td>-</td>
<td>2.3 (2)</td>
<td>3.8 (5)</td>
</tr>
<tr>
<td>5.8</td>
<td>11.0</td>
<td>7.0</td>
<td>2.2 (2)</td>
<td>3.7 (5)</td>
</tr>
<tr>
<td>5.8</td>
<td>11.0</td>
<td>11.0</td>
<td>2.1 (2)</td>
<td>3.6 (5)</td>
</tr>
</tbody>
</table>

$^a$ in mmol.L$^{-1}$, $^b$ in $10^{-6}$ L.mol$^{-1}$.s$^{-1}$, $^c$ in $10^{-4}$ s$^{-1}$ (Fv: $\text{Cp}^*\text{FvTi}$).

For the methyl derivative 1 the kinetics are much more complicated. The decomposition shows a regular first order progression for all concentrations studied (Figure 4, Table 4), but $k_{obs}$ depends, unlike a regular first–order process, on the starting concentration $[1]_0$. The observed rate constant has an apparent inverse proportionality to $[1]_0$ (Figure 5), so that the decomposition is slower at higher starting concentrations of 1. This is very puzzling since whereas the concentration of 1 continuously decreases during thermolysis and acceleration is expected, this is not observed. Instead the inhibition appears to be determined by the initial concentration of $\text{Cp}^*_2\text{TiR}$ (which equals the sum of $[1]$ and $[7]$ during conversion). This suggests that the decomposition of 1 is also inhibited by 7. Indeed addition of the thermolysis product 7 leads to lower rates (Figure 5, Table 4). Quantitatively, the inhibition by 1 and 7 appears to be identical within error limits. Since the sum of 1 and 7 is constant there is a constant inhibition leading to a net first–order progression with time. When both inhibition effects are very dissimilar it would lead to considerable deviation from first order kinetics and this maybe the case for the phenyl compound 6. The decomposition of 1 shows the expected first order relationship in 9 (eq 5, Figure 6, Table 5).

$$- \frac{d[1]}{dt} = k \frac{[9]}{[1]_0}[1]$$  \hspace{1cm} (5)
Figure 4. First order dependence of the Cp*₂TiH (9) catalyzed decomposition of Cp*₂TiMe (1) at 308 K: (*) [1] = 6.3 mmol.L⁻¹, (α) [1] = 30 mmol.L⁻¹; ([θ] = 4.7 mmol.L⁻¹).

Figure 5. Observed first order rate constant for the catalyzed decomposition of Cp*₂TiMe (1) at 308 K versus [Cp*₂TiH]/([Cp*₂TiMe]₀ + [Cp*FvTi]₀) without (■) and with (◇) extra Cp*FvTi (Table 4).
Figure 6. Observed first order rate constant for the catalyzed decomposition of Cp*₂TiMe (1) at 308 K versus the concentration of Cp*₂TiH (9). [1] = 17.0 mmol.L⁻¹ in THF. (Table 5).

![Graph showing the relationship between the concentration of Cp*₂TiH and the observed rate constant.]

Table 4. Rate constants k for the catalytic decomposition of Cp*₂TiMe (1) at 308 K, dependence on starting concentration and added Cp*FvTi (7).

<table>
<thead>
<tr>
<th>[TiH]ᵃ</th>
<th>[TiMe]ᵃ</th>
<th>[Fv]ᵃ</th>
<th>kᵦᵇ</th>
<th>k₁ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>6.3</td>
<td></td>
<td>5.4  (3)</td>
<td>7.2  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>12.0</td>
<td></td>
<td>2.9  (2)</td>
<td>7.4  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>18.0</td>
<td></td>
<td>1.9  (2)</td>
<td>7.3  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>30.0</td>
<td></td>
<td>1.2  (1)</td>
<td>7.6  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>63.0</td>
<td></td>
<td>0.61 (5)</td>
<td>8.1  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>11.0</td>
<td></td>
<td>3.3  (4)</td>
<td>7.7  (4)</td>
</tr>
<tr>
<td>4.7</td>
<td>11.0</td>
<td>4.0</td>
<td>2.2  (2)</td>
<td>7.0  (6)</td>
</tr>
<tr>
<td>4.7</td>
<td>11.0</td>
<td>6.0</td>
<td>1.7  (1)</td>
<td>6.1  (6)</td>
</tr>
<tr>
<td>4.7</td>
<td>11.0</td>
<td>17.0</td>
<td>0.87 (6)</td>
<td>5.2  (6)</td>
</tr>
</tbody>
</table>

ᵃ in mmol.L⁻¹, ᵇ in 10⁻⁴ s⁻¹. (Fv: Cp*FvTi)
Table 5. Rate constants $k$ for the thermolysis of $\text{Cp}^*\text{TiMe} \,(1)$ at 308 K at various concentrations of $\text{Cp}^*\text{TiH} \,(9)$.

<table>
<thead>
<tr>
<th>$[\text{TiH}]^a$</th>
<th>$[\text{TiMe}]^a$</th>
<th>$k_{obs}^b$</th>
<th>$k_{obs}/[\text{TiH}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.42</td>
<td>17.0</td>
<td>0.71 (5)</td>
<td>5.0 (5)</td>
</tr>
<tr>
<td>2.42</td>
<td>,,</td>
<td>1.1 (4)</td>
<td>4.5 (2)</td>
</tr>
<tr>
<td>4.95</td>
<td>,,</td>
<td>2.1 (4)</td>
<td>4.2 (2)</td>
</tr>
<tr>
<td>6.5</td>
<td>,,</td>
<td>2.9 (4)</td>
<td>4.5 (2)</td>
</tr>
<tr>
<td>9.7</td>
<td>,,</td>
<td>4.1 (4)</td>
<td>4.3 (2)</td>
</tr>
<tr>
<td>20.9</td>
<td>,,</td>
<td>9.2 (4)</td>
<td>4.4 (1)</td>
</tr>
</tbody>
</table>

$^a$ in mmol.L$^{-1}$, $^b$ in $10^{-4}$ s$^{-1}$, $^c$ in $10^{-2}$ L.mol$^{-1}$.s$^{-1}$

The hydride–catalyzed decomposition of 1 has a complex rate expression, indicative for a multi step mechanism. The rate expressions for 1 and 4 have close resemblance, indicating that the same mechanism is operative in both cases. They become identical when the inhibition by 7 is negligible compared with that of $\text{Cp}^*\text{TiR}$.

Mechanistic aspects. A discussion of the mechanism of the decomposition of $\text{Cp}^*\text{TiR}$ can be separated into a part on the intrinsic thermolysis and another on the catalyzed decomposition. The uncatalyzed thermolysis is very likely an intramolecular hydrogen transfer from a methyl group of a pentamethylcyclopentadienyl ligand to the leaving carbyl R. A plausible mechanism for this reaction is the familiar, concerted, a–bond metathesis as shown in Scheme 2.$^{4a}$

The simplest mechanism for the hydride catalyzed decomposition is a bimolecular reaction between $\text{Cp}^*\text{TiR}$ and 9 to form a hydride–alkyl bridged dimer (Scheme 3). In a subsequent step, RH is reductively eliminated to yield
two equivalents of permethyltitanocene with simultaneous reduction of the metal from Ti(III) to Ti(II). In the final step two molecules of permethyltitanocene undergo disproportionation to form 7 and the regenerated catalyst 9. In this step the metal is re-oxidized to formally Ti(II). From earlier studies on CO-induced disproportionation of Cp*TiCl to Cp*TiCl₂ and Cp*Ti(CO)₂ it is known that there is no insuperable steric hindrance for two permethyltitanocene units to approach each other.²⁴

However, the intermediacy of permethyltitanocene can be excluded for two reasons. First, all experiments were carried out under nitrogen. Under such conditions titanocene should be trapped to form the stable dinitrogen complex (Cp*₂Ti)₂N₂.¹¹ Dinitrogen adducts of permethyltitanocene are intensely colored ($ε_{mol} \gg 10.000 \: M^{-1}.cm^{-1}$), hence even traces should lead to strong color changes, but this was not the case (observation of isobestic points in UV–Vis). Moreover, addition of (Cp*₂Ti)₂N₂ to 1 in THF did not result in a catalytic decomposition. In fact, the dinitrogen complex appeared to be perfectly stable under decomposition conditions of 1, and thus permethyltitanocene cannot be an intermediate. Further evidence against Scheme 3 was obtained from the hydride catalyzed decomposition of Cp*₂TiC₂H₃ (5). If the mechanism is as in Scheme 3, ethene will be formed during decomposition of 5 in close vicinity of permethyltitanocene. Ethene is known to react with permethyltitanocene to form Cp*₂Ti(η²-C₂H₄) (10). However, this complex was not observed during thermolysis of 5. In a separate experiment, 10 was mixed with 9 to test its possible intermediacy. Under the conditions for catalytic decomposition of 5, the ethene adduct 10 was found to be quite stable. It
decomposed slowly by loss of ethene to form \(\text{Cp}*\text{Ti}(\text{H NMR})\). The formed ethene rapidly reacted with 9 to give \(\text{Cp}*\text{TiEt}\) (2), which subsequently decomposed. Thus, the mechanism of the hydride catalyzed decomposition of \(\text{Cp}*\text{TiR}\) cannot be as in Scheme 3. The reductive elimination of RH from a hydride carbyl bridged dimer is very unlikely and divalent titanium compounds like permethyltitanocene are not involved.

It is unlikely that the hydride \(\text{Cp}*\text{TiH}\) (9) is the catalytically active species. This follows from the aforementioned absence of divalent intermediates in the catalyzed decomposition of \(\text{Cp}*\text{TiR}\). Since it is not possible to rationalize the formation of RH by transfer of one hydrogen atom from 9 to a hydrocarbyl ligand without change of oxidation state, 9 cannot be the actual catalyst. Further indication comes from the overall kinetics of the catalyzed decomposition of 1 and 4. For 1, decomposition is retarded by 7 (and 1), whereas for 4 this effect is not observed. Since there is no experimental evidence for a complex between \(\text{Cp}*\text{TiH}\) and \(\text{Cp}*\text{TiR}\), which could explain the differences in overall kinetics, and since 7 is the decomposition product in all cases, it should inhibit thermal decomposition independent of R in \(\text{Cp}*\text{TiR}\). This is in clear contrast with experimental facts.

The actual catalytically active species has to meet the following requirements: (a) it must be a hydrogen donor; (b) it must be formed from 9 with first order kinetics, which excludes a bimolecular reaction between 9 and itself; (c) there should be no change of formal oxidation state during catalysis, as only \(\text{Ti(III)}\) is present, excluding the involvement of permethyltitanocene. Taking this into consideration, a more realistic pathway is suggested in Scheme 4. In the first step dihydrogen is eliminated from 9 to give product 7. Then hydrogenolysis of \(\text{Cp}*\text{TiR}\) takes place leading to the regeneration of 9 and formation of RH. In a competitive reaction dihydrogen can react with 7 to regenerate 9. From labeling experiments it is clear that \(\text{Cp}*\text{TiH}\) reacts as a dihydride donor.

**Hydrogen formation:**

\[
\text{Cp}*\text{TiH} \xrightarrow{k_1} \text{Cp*FvTi} + \text{H}_2
\]

**Productive reaction:**

\[
\text{Cp}*\text{TiR} + \text{H}_2 \xrightarrow{k_2} \text{Cp}*\text{TiH} + \text{RH}
\]

**Competitive reaction:**

\[
\text{Cp*FvTi} + \text{H}_2 \xrightarrow{k_{-1}} \text{Cp}*\text{TiH}
\]

**Scheme 4**
Decomposition of \( \text{Cp}^*\text{TiCH}_2\text{CMe}_3 \) (4) in the presence of 2 equivalents of \((\text{Cp}^*-\text{d}_{15})\text{TiD}\) gave in early stages of the reaction only \( \text{Cp}^*\text{TiD} \) \(^{25}\text{H NMR}\) and \( \text{Cp}^*\text{FvTi-d}_{15}\). Thus, 7 indeed originates from the catalyst precursor \( \text{Cp}^*\text{TiR} \), rather than from \( \text{Cp}^*\text{TiR} \). Catalytic decomposition of \( \text{Cp}^*\text{TiR} \) therefore proceeds in two steps, first hydrogenolysis to \( \text{Cp}^*\text{TiH} \) and RH, followed by thermolysis of \( \text{Cp}^*\text{TiH} \) to \( \text{Cp}^*\text{FvTi} \) and dihydrogen. This reaction pathway avoids elimination of \( \text{RH} \) from \( \text{Cp}^*\text{TiR} \), which evidently has a higher activation energy than elimination of \( \text{H}_2 \) from \( \text{Cp}^*\text{TiH} \) (cf. slow mode thermolysis of 1). The overall reaction rate for the model in Scheme 4 has been calculated for a steady state in dihydrogen. The overall rate expression (eq 6) is complex, predicting a rate law between first and second order (first order in catalyst precursor 9, and between zero and first order in substrate \( \text{Cp}^*\text{TiR} \)).

\[
\frac{\text{d}[\text{Cp}^*\text{TiR}]}{\text{dt}} = k_1k_2 \cdot \frac{[9]}{k_2[\text{Cp}^*\text{TiR}]} + \frac{k_{-1}[7]}{k_2[\text{Cp}^*\text{TiR}]} \quad \text{(6)}
\]

For certain ratios of \( k_2/k_{-1} \), eq 6 will give the expressions for the kinetics of the hydride catalyzed decomposition of 1 and 4. If \( k_2 \) is equal to \( k_{-1} \), eq 6 will reduce to eq 5, the kinetics for 1. This can be interpreted as an equal affinity of 1 and 7 for dihydrogen. The retardation of the reaction at higher starting concentration of 1 and 7 is explained by a lower steady state concentration of dihydrogen \( k_1[9]/k_2([1] + [7]) \) \((= k_{obs}/k_2)\). If \( k_{-1} \) is much smaller than \( k_2 \), eq 6 will simplify to the overall kinetics for the catalyzed decomposition of 4, and consequently lose its dependence on the concentration of 4. This is the case when dihydrogen reacts much faster with 4 than with 7. The elimination of dihydrogen from 9 then becomes rate determining. It also implies that overall rates are much higher for 4 than for 1 as is observed experimentally. The relative rate of hydrogenolysis of 1 and 4 was determined in a competition experiment. Equimolar amounts of 1, 4 and dihydrogen were mixed at 0 °C. After oxidation of the reaction mixture with PbCl₂ the only products present were \( \text{Cp}^*\text{Ti}(\text{Me})\text{Cl} \) and \( \text{Cp}^*\text{Ti}(\text{H})\text{Cl} \). This illustrates that 4 indeed reacts much faster with \( \text{H}_2 \) than 1. At all other ratios \( k_2/k_{-1} \) the progression of the reaction is complex, the rate being dependent on starting concentration and conversions, as for example observed in the catalyzed thermolysis of 6. Thus the model proposed explains the experimental facts correctly.

The rate constant \( k_1 \) for thermolysis of \( \text{Cp}^*\text{TiH} \) can be calculated from the overall rate constants of the catalyzed decomposition of 1 and 4. Values obtained from the resp. kinetics are equal within error limits (Table 6). The temperature dependence of the rate constant \( k_1 \) (Table 6) gives a linear Eyring plot with \( \Delta H^\ddagger = 77.1 \) \(2\text{ kJ.mol}^{-1}\) and \( \Delta S^\ddagger = - 54 \) \(4\text{ J.mol}^{-1}.\text{K}^{-1}\), well below
Ti–C bond dissociation energies\textsuperscript{26}, and typical for a−bond metathesis.\textsuperscript{4d,5,7}

Table 6. Temperature dependence of rate constants $k_1$ for thermolysis of $\text{Cp}^*\text{TiMe} (1)$ and $\text{Cp}^*\text{TiCH}_2\text{CMe}_3 (4)$ in the presence of $\text{Cp}^*\text{TiH} (9)$.

<table>
<thead>
<tr>
<th>$T$ (in K)</th>
<th>$k_1^a$ (1)</th>
<th>$k_1^b$ (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.7 (1)</td>
<td>1.8 (2)</td>
</tr>
<tr>
<td>298</td>
<td>3.0 (2)</td>
<td>3.2 (2)</td>
</tr>
<tr>
<td>303</td>
<td>4.6 (3)</td>
<td>4.9 (2)</td>
</tr>
<tr>
<td>308</td>
<td>7.4 (4)</td>
<td>7.5 (5)</td>
</tr>
<tr>
<td>313</td>
<td>14 (1)</td>
<td>12 (1)</td>
</tr>
<tr>
<td>318</td>
<td>22 (2)</td>
<td>19 (2)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: in $10^{-4} \text{ s}^{-1}$, $[\text{Cp}^*\text{TiMe}] = 17.0 \text{ mmol.L}^{-1}$, $[\text{Cp}^*\text{TiH}] = 8.8 \text{ mmol.L}^{-1}$

\textsuperscript{b}: in $10^{-4} \text{ s}^{-1}$, $[\text{Cp}^*\text{TiCH}_2\text{CMe}_3] = 23.0 \text{ mol.L}^{-1}$, $[\text{Cp}^*\text{TiH}] = 9.9 \text{ mmol.L}^{-1}$.

Concluding remarks. In contrast to intramolecular decomposition normally observed in the thermolysis of early transition metal hydrocarbyl complexes, the thermal decomposition of $\text{Cp}^*\text{TiR}$ is not a simple process. A low−energy catalytic pathway is opened as soon as $\text{Cp}^*\text{TiH}$ is present. The ability of $\text{Cp}^*\text{TiR}$ to generate the hydride catalyst determines the thermal stability of the compounds. For $\beta$−hydrogen containing alkyl complexes catalyst formation is easily achieved at ambient temperatures by olefin elimination. In this series $\text{Cp}^*\text{TiEt}$ is thermally the most robust compound. This might be caused by the agostic interaction of the ethyl ligand with the titanium center in this complex, stabilising the alkyl form relative to a hydride olefin configuration.\textsuperscript{12b} The decomposition can be retarded by adding olefins to solutions of $\text{Cp}^*\text{TiR}$, thus trapping the hydride $\text{Cp}^*\text{TiH}$ by formation of an alkyl and decreasing the catalyst concentration. Non $\beta$−hydrogen containing derivatives $\text{Cp}^*\text{TiR}$ are thermally much more stable. At relatively high temperatures (> 90 °C) RH is liberated first in probably an intramolecular process with the concomitant formation of $\text{Cp}^*\text{FvTi}$. At this temperature $\text{Cp}^*\text{FvTi}$ is not stable and loses dihydrogen. The dihydrogen reacts with $\text{Cp}^*\text{TiR}$ or with $\text{Cp}^*\text{FvTi}$ to give $\text{Cp}^*\text{TiH}$. This will result in an autocatalytic decomposition of $\text{Cp}^*\text{TiR}$, giving typical sigmoid conversion plots. The catalytic process has complicated kinetics, suggesting that elimination of dihydrogen from 9 is the key step. The catalytic thermolysis of $\text{Cp}^*\text{TiR}$ is essentially a hydrogenolysis of the Ti–C bond to give RH and $\text{Cp}^*\text{TiH}$, followed by decomposition of $\text{Cp}^*\text{TiH}$ to $\text{Cp}^*\text{FvTi}$, and regenerating $\text{H}_2$. 
References and Notes.


14. It appears to be identical to the decomposition product of permethyltinocene as reported by Bercaw. See also ref. 15.
16. The evolved hydrogen gas reacts with 6 or 7 to give Cp*₂TiH, which is also present in trace amounts. (¹H NMR: δ 23.0 ppm).
17. Scrambling of deuterium label between ethane and methane is not catalyzed by the thermolysis mixture. Thermolysis of Cp*₂Ti(Et-d₅) (2b) in the presence of methane does not lead to building-in of deuterium into methane (H NMR).
22. In early stages of the thermolysis of 3 traces of propene (<2%) were found in the thermolysis gas (applying a dynamic vacuum); Also in some NMR samples of 3 traces of propene and 9 could be detected. Propene and ethene extrusion, induced by CO₂ has been observed. Luinstra, G.A.; Teuben, J.H. J. Chem. Soc., Chem. Commun. 1987, 849.
23. The decomposition of 6 has an initial period of exponential progression, followed in later stages by an almost linear conversion in time.
25. Later on Cp*FvTi also was observed.