estimate that k_2 for the $[Fe(CO)_3(PCy_3)_2{}^+]_{free}$ pathway is at most 4.5×10^{-4} M^{-1} s^{-1}. A k_2 of 1.5×10^5 M^{-1} s^{-1} for the rate of the direct reaction between $[Fe(CO)_3(PCy_3)_2{}^+]_{free}$ and $[Cl^-]_{free}$ is required on the basis of our present experimental data and the estimated K_d of 10^{-4}. This requires a nucleophilicity 10^8 greater for Cl$^-$ than for pyridine. Rather than attribute Cl$^-$ a tremendously enhanced nucleophilicity it seems more reasonable to attribute the difference to the special role ion pairing may play in enhancing the local concentration of Cl$^-$ for nucleophilic attack at the cationic metal center.

In the context of periodic trends for the reactivity of organometallic radicals, the data suggest a greatly reduced effect in comparison to analogous 18-electron complexes. For chloride as nucleophile the reactivity order at 25 °C Os (1) < Fe (2.9) < Ru (11.7) shows an enhanced rate for the second-row metal, but much reduced from the 10^7–10^8 increase in lability of Ru for the related 18-electron systems discussed in the Introduction. For bromide as nucleophile there is essentially no discrimination in reactivity between Fe, Ru, and Os. This cannot be simply attributed to the reactivity–selectivity principle, because the rates observed are not terribly fast. There are a few other examples in the literature, which suggest periodic trends are attenuated in 17-electron systems. The reasons behind this may be the importance of bond formation to the metal in the 19-electron intermediate or transition state postulated in such reactions. For 18-electron iron, ruthenium, and osmium carbonyls, a strong metal–carbonyl bond needs to be broken in the dissociative transition state. One postulate is the relative activation energies parallel relative bond strengths, which are weakest for second-row metals. In 17-electron systems, where the mechanism changes to an associative process, several factors should influence activation barriers (steric effects, entering and leaving group effects). An analysis of the activation parameters suggest that $\Delta H^{\ddagger}$ trends, related to stabilization of the 19-electron species by metal–nucleophile bonding, favor the third-row metals. Indeed, there are some parallels to the behavior of (mesitylene)W(CO)$_3{}^+$ and (mesitylene)Cr(CO)$_3{}^+$. The tungsten complex exhibits an enhanced reactivity in comparison to chromium.[28] This suggests that oxidation to a 17-electron complex is an excellent way to turn on the substitution reactivity of the sluggish third-row 18-electron metal complexes.

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Supplementary Material Available: Tables of pseudo-first-order rate constants (k_{obs}), first-order rate constants (k), and equilibrium constants for ion pair exchange (K) determined for Scheme III as a function of temperature for the reaction between $[M(CO)_3(PCy_3)_2]PF_6$ and $[Bu_4N]X$ (M = Fe, Ru, Os; X = Cl, Br) (8 pages). Ordering information is given on any current masthead page.

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The Deceptively Simple Thermolysis of Trivalent Permethyltitanocene Derivatives $(\eta^5\text{-}C_5Me_5)_2TiR$. Formation of a Tetramethylfulvene Titanium Compound $(\eta^6\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)Ti$ and RH, Catalyzed by Permethyltitanocene Hydride, $(\eta^5\text{-}C_5Me_5)_2TiH$

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Abstract: The complexes Cp*$_2$TiR (Cp* = η^5-C$_5$Me$_5$; R = Me, Et, *n*-Pr, C$_2$H$_3$, CH$_2$CMe$_3$, Ph) undergo thermolysis to yield the fulvene complex Cp*FvTi (Fv = η^6-C$_5$Me$_4$CH$_2$) and RH. Kinetic measurements and deuterium labeling studies show that the decomposition is catalyzed by Cp*$_2$TiH, which is formed either by β-hydrogen elimination from a titanium alkyl Cp*$_2$TiCH$_2$CH$_2$R at low temperature or by hydrogenolysis of Cp*$_2$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*$_2$TiCH$_2$CMe$_3$ is linear in [Cp*$_2$TiH]. For Cp*$_2$TiMe it is proportional to [Cp*$_2$TiH] and [Cp*$_2$TiMe] and inversely proportional to the starting concentration of Cp*$_2$TiMe. This is explained in a kinetic scheme, where H$_2$, eliminated from Cp*$_2$TiH to give Cp*FvTi, reacts with Cp*$_2$TiR to regenerate Cp*$_2$TiH and liberate RH. The model is supported by the reaction of (Cp*-d_{15})$_2$TiD and Cp*$_2$TiCH$_2$CMe$_3$ yielding Cp*$_2$TiD and (Cp*FvTi-d_{29}).

Introduction

The activation of C–H bonds of inert hydrocarbons has been a major topic in contemporary organometallic chemistry.[1] It is generally recognized that C–H bonds can be activated either by oxidative addition to an electron-rich metal center or by a nonoxidative pathway at a strongly electrophilic metal center.[2] The latter is typical for the strongly Lewis acidic d^0 transition metal and lanthanide compounds.[3] Intermediates may involve cu-

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mulenes, metalacycles, η^2-alkene, and aryne adducts.[4] Fulvenes are also well-known products and can be formed by H-abstraction from a methyl-substituted cyclopentadienyl ligand.[3d,4b–g] Several authors have discussed the thermodynamic and kinetic prerequisites for C–H activation reactions.[4] Elegant mechanistic studies have been published on a range of early transition metal and thorium compounds $Cp^*_2MR_2$ (M = Ti, R = Me;[4d] M = Zr, R = CH_2Ph;[4g] M = Hf, R = CH_2Ph;[5] M = Th, R = CH_2XMe_3, X = C, Si[6]). These compounds give metalated products Cp^*FvMR (Fv = η^6-$C_5Me_4CH_2$; M = Ti, Zr, Hf) or metalacyclic compounds $Cp^*_2Th(CH_2)_2XMe_2$ through intramolecular CH activation with a four-centered transition state (σ-bond metathesis)[4a] as the mechanistic key feature. Also in other cyclometalations, e.g. the decomposition of $Ta(OAr)_2Me_3$ (Ar = 2,6-di-*tert*-butylphenyl),[7] simple intramolecular processes proceeding by σ-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 identity of which is still mysterious, and until now only two complexes, the fulvalene bridged (μ-η^5:η^5-$C_{10}H_8$)-(μ-H)$_2$-(η^5-C_5H_5Ti)$_2$[9] and the cyclopentadienyl bridged (μ-η^1:η^5-C_5H_4)(η^5-C_5H_5)$_3$$Ti_2$,[10] have been reasonably well characterized. The reaction pathways leading to them are not clear. More detailed mechanistic information is available for permethyltitanocene derivatives, but the processes involved are complex and as yet not fully understood.[11]

We report here a study of thermally induced C–H activation in paramagnetic, trivalent titanium compounds Cp^*_2TiR (R = alkyl, aryl).[12] The thermolysis is a clean, stoichiometric process leading to a fulvene complex, Cp^*FvTi, with liberation of RH (eq 1). Exploratory studies of the thermolysis of simple alkyls with

$$Cp^*_2TiR \rightarrow Cp^*FvTi + RH \qquad (1)$$

$$(Fv = \eta^6\text{-}C_5Me_4CH_2)$$

R = Et, *n*-Pr showed first-order kinetics[13] and indicated intramolecular C–H abstraction, but deuterium labeling and crossover experiments suggested a more complicated mechanism. We therefore decided to carry out a detailed kinetic and mechanistic study of the thermolysis of Cp^*_2TiR for various carbyl ligands R.

Experimental Section

All operations were performed under inert atmosphere using Schlenk, vacuum-line, or glovebox techniques. Solvents were distilled from Na/K alloy prior to use. (Cp^*_2Ti)N_2[11] and Cp^*_2TiR (R = alkyl, hydride)[12] 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-d_8 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 Pye Unicam SP_{3-300} and Mattson-4020 Galaxy FT-IR spectrophotometers (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. (a) ^{1}H NMR Spectroscopy. Rates of thermolysis of Cp^*_2TiR were measured by ^{1}H NMR spectroscopy, by monitoring the increase in peak intensity of Cp^*FvTi at $\delta = -11.7$ ppm (vide infra). For the majority of the compounds there is no overlap with resonances of parent Cp^*_2TiR, and hence this resonance 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 homemade routine. Each spectrum consisted of 200 scans with a 0.24-s acquisition time. The reaction temperature was recorded and was found to be constant within 0.2 °C. The peak separation in ethylene glycol was used for temperature calibration.

(b) UV–Vis Spectroscopy. Thermal decomposition rates were measured by monitoring the absorbance at a fixed wavelength (545 nm). Cp^*_2TiR and Cp^*FvTi are colored compounds (UV–vis absorption data in THF are as follows: Cp^*_2TiMe—λ_{max} = 470 nm, ϵ = 109 L·mol^{-1}·cm^{-1} and λ_{max} = 605 nm, ϵ = 40 L·mol^{-1}·cm^{-1}; Cp^*_2TiEt—λ_{max} = 478 nm, ϵ = 130 L·mol^{-1}·cm^{-1} and λ_{max} = 625 nm, ϵ = 34 L·mol^{-1}·cm^{-1}; Cp^*_2Ti-*n*-Pr—λ_{max} = 465 nm, ϵ = 150 L·mol^{-1}·cm^{-1} and λ_{max} = 640 nm, ϵ = 32 L·mol^{-1}·cm^{-1}; $Cp^*_2TiCH_2CMe_3$—λ_{max} = 490 nm, ϵ = 192 L·mol^{-1}·cm^{-1} and λ_{max} = 655 nm, ϵ = 48 L·mol^{-1}·cm^{-1}; Cp^*_2TiPh—λ_{max} = 455 nm, ϵ = 105 L·mol^{-1}·cm^{-1} and λ_{max} = 585 nm, ϵ = 31 L·mol^{-1}·cm^{-1}; Cp^*FvTi—λ_{max} = 550 nm, ϵ = 220 L·mol^{-1}·cm^{-1}). The difference in optical density between Cp^*_2TiR and Cp^*FvTi is maximal at 545 nm and is sufficient to allow spectrophotometrical determination of reaction rates. UV–vis spectroscopy is convenient at relatively low concentrations of Cp^*_2TiR. The upper limit in concentration is set by the Lambert–Beer law at ca. 25 mmol·L^{-1}. At higher concentrations (>30 mmol·L^{-1}) ^{1}H 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 THF 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 PECSS program. Reactions were followed for at least 3 half-lives. Kinetic plots of Cp^*_2TiMe were fit by nonlinear 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 UV–vis measurements were prepared from stock solutions of Cp^*_2TiR in THF. For kinetic studies the various stock solutions were mixed and when necessary diluted. A typical solution consisted of 106.8 mg of $Cp^*_2TiCH_2CMe_3$ in 12.0 mL of THF ([$Cp^*_2TiCH_2CMe_3$] = 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 which was sealed with a Teflon stopper.

Labeling Experiments. Experiments with labeled compounds were carried out on an ca. 100 mg scale on a high-vacuum line. A typical experiment is described. Cp^*_2Ti(Me-d_3) (82 mg, 0.24 mmol) was dissolved in 2.0 mL of THF. After the solution was stirred for 80 h at 90 °C the gases were collected with a Toepler pump; 0.237 mmol, 0.97 equiv/Ti. Mass spectrum: *m/e* 17, CD_3H.

Thermolysis of Cp^*_2TiEt—Synthesis of Cp^*FvTi. Cp^*_2TiEt (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 was recrystallized from pentane. Yield: 3.60 g (11.4 mmol, 93%). Anal. Calcd for $C_{20}H_{29}Ti$: 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), 1020 (s), 845 (m), 800 (s), 750 (m), 610 (w), 515 (s), 430 (s). ^{1}H NMR (toluene-d_8, 20 °C, 300 MHz): δ 25.3 ppm (21 H, WHM 960 Hz), 12.7 (2 H, WHM 440 Hz), −11.7

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ppm (6 H, WHM 290 Hz). UV–vis (THF): λ_{max} = 550 nm (ϵ = 220 L·mol^{-1}·cm^{-1}). (WHM = width (Hz) at half maximum.)

Analysis of Evolved Gases. A typical experiment is described. Cp*$_2$TiEt (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 equiv/Ti) and analyzed by GC (ethane, 100%).

Competition Experiment. Cp*$_2$TiMe (51 mg, 0.158 mmol) and Cp*$_2$TiCH$_2$CMe$_3$ (54 mg, 0.138 mmol) were dissolved in 2 mL of THF under vacuum. At 0 °C dihydrogen was admitted (0.140 mmol). After the mixture was stirred 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 PbCl$_2$. The resulting red solution was characterized by ^{1}H NMR. Identified compounds: Cp*$_2$Ti(Me)Cl, δ = 1.73 ppm (Cp*, 30 H), 0.23 ppm (Me, 3 H); Cp*$_2$Ti(H)Cl, δ = 1.87 ppm (Cp*, 30 H), 4.45 ppm (H, 1 H). The compounds were identified on the basis of integrated signal ratios and comparison with authentic samples.[12,21b] Cp*FvTiCl was not present in the reaction mixture.

Results and Discussion

The compounds Cp*$_2$TiR (R = Me, Et, Pr, CH$_2$CMe$_3$, CH=CH$_2$, Ph) were studied. The thermal stability of Cp*$_2$TiR depends strongly on the nature of R. Cp*$_2$TiEt and especially higher alkyl derivatives readily decompose at room temperature, whereas the methyl, vinyl, and phenyl derivatives are thermally much more robust. For a convenient rate of thermolysis of the last three compounds, temperatures ranging from 90 to 150 °C are needed. The stoichiometry of the thermolysis in both solution and solid state is given by eq 1. The fulvene complex Cp*FvTi[14] is obtained as the sole organometallic product for R = Me, Et, Pr, and CH$_2$CMe$_3$ and RH is the only organic compound. Radical coupling products R–R or radical disproportionation products like olefins R(–H) were not found. The absence of olefins indicates further that β-hydrogen elimination, well-known for higher alkyl derivatives, is not a productive decomposition route. The vinyl compound, Cp*$_2$TiCH=CH$_2$, is thermally quite stable. It starts to decompose ($t_{1/2}$ ~ 40 h at 110 °C) at temperatures where Cp*FvTi itself loses hydrogen to form the previously described doubly metalated compound Cp*{C$_5$Me$_3$(CH$_2$)$_2$}Ti (eq 2).[15] This

$$\mathrm{Cp^*FvTi} \rightarrow \mathrm{Cp^*\{C_5Me_3(CH_2)_2\}Ti} + \tfrac{1}{2}\mathrm{H_2} \qquad (2)$$

reaction complicates the picture of the thermolysis of Cp*$_2$TiCH=CH$_2$ (and also of Cp*$_2$TiPh) somewhat. With Cp*$_2$TiCH=CH$_2$, mixtures of Cp*FvTi and Cp{C$_5$Me$_3$(CH$_2$)$_2$}Ti were obtained and initially formed ethene disappeared partly due to hydrogenation to ethane. The phenyl compound Cp*$_2$TiPh also needs elevated temperatures for a noticeable thermolysis rate and produces a mixture of Cp*FvTi, Cp*{C$_5$Me$_3$(CH$_2$)$_2$}Ti, and benzene.[16] Solvents do not participate in the thermolysis process. No deuterium incorporation was observed into the RH formed when Cp*$_2$TiMe, Cp*$_2$TiEt, or Cp*$_2$TiPr were thermolyzed in benzene-d_6 or THF-d_8 (GC-MS).

Exploratory Kinetic Studies. The thermally labile compounds Cp*$_2$TiR (R = Et, Pr), having relatively short half-live times (45 min and 1 h respectively at room temperature in THF), were studied first. Kinetic data were obtained by monitoring UV–vis spectra in THF solutions. In the first approximation the thermolysis is first order in Cp*$_2$TiR and independent of concentration (between 9 and 18 mmol·L^{-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 Cp*$_2$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, but the outcome of these showed that a much more complicated pathway is followed.

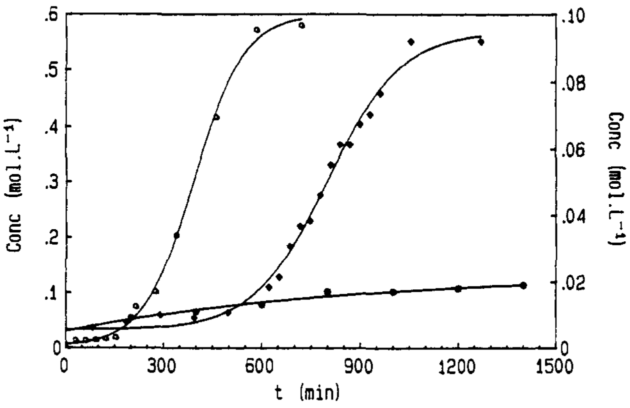

Figure 1. Thermal decomposition of Cp*$_2$TiMe in THF-d_8 at 363 K (increase of Cp*FvTi monitored by ^{1}H NMR): (○) [Cp*$_2$TiMe]$_0$ = 0.58 mol·L^{-1}, (◆) [Cp*$_2$TiMe]$_0$ = 0.092 mol·L^{-1}; (●) 1 equiv of ethene added, [Cp*$_2$TiMe]$_0$ = 0.58 mol·L^{-1}.

Labeling Experiments. The Cp* ligand is the exclusive source of hydrogen for methane formation in the thermolysis of Cp*$_2$TiMe. Cp*$_2$Ti(Me-d_3) in THF-d_8 produced only CD$_3$H compatible with simple intramolecular decomposition. As stated before, thermolysis of Cp*$_2$TiEt and Cp*$_2$TiPr in deuterated solvents showed no deuterium incorporation into the alkane formed, thus excluding solvent participation. However, thermolysis of Cp*$_2$Ti(Et-d_5) did not give exclusively C$_2$D$_5$H as anticipated from the results for Cp*$_2$TiMe. Instead substantial amounts of C$_2$D$_6$ were formed, together with partly deuterated ethanes C$_2$D$_{6-n}$H$_n$.[17] Similar observations were made for Cp*$_2$Ti(Pr-d_7) where a mixture of deuterated propanes was obtained with the highest mass corresponding to propane-d_8. Thermolysis of an equimolar mixture of Cp*$_2$TiMe and Cp*$_2$Ti(Et-d_5) or Cp*$_2$Ti(Pr-d_7) gave in addition to the thermolysis products of the compounds themselves also monodeuterated methane CH$_3$D. This shows that the decomposition proceeds via an intermolecular mechanism, for example by direct deuterium abstraction from an intact Ti–R (R = C$_2$D$_5$, n-C$_3$D$_7$) moiety,[18] or by indirect deuterium transfer through an intermediate titanium deuteride Ti–D. These results change the original picture completely. Thermolysis of compounds Cp*$_2$TiR is not a simple one-step process; it has at least an intermolecular component.

Thermal Decomposition of Cp*$_2$TiMe. Given the complex character of the thermal decomposition, we decided to concentrate on the simplest alkyl Cp*$_2$TiMe. For thermolysis at a convenient rate, experiments were carried out at 90 °C, while monitoring the mixture in THF-d_8 by ^{1}H NMR spectroscopy. As observed in exploratory experiments, the decomposition proceeded with exclusive formation of Cp*FvTi and CH$_4$. 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 Cp*$_2$TiMe. At higher concentrations the induction time was shorter.

S-shaped conversion plots are typical for second order autocatalytic reactions,[19] and they suggest that the thermal decomposition of Cp*$_2$TiMe is catalyzed. The possibility that Cp*FvTi is the catalyst can be excluded since a similar effect would be expected in the thermolysis of Cp*$_2$TiEt and Cp*$_2$TiPr which was not observed. Moreover, addition of Cp*FvTi to solutions of Cp*$_2$TiMe did not result in an immediate start of the thermolysis at high rate. Thus, if the active catalyst is formed from Cp*FvTi, this occurs only at elevated temperatures.

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(14) It appears to be identical with the decomposition product of permethyltitanocene as reported by Bercaw.[11] See also ref 15.

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(16) The evolved hydrogen gas reacts with Cp*$_2$TiPh or Cp*FvTi to give Cp*$_2$TiH, which is also present in trace amounts (^{1}H NMR: δ 23.0 ppm).

(17) Scrambling of deuterium label between ethane and methane is not catalyzed by the thermolysis mixture. Thermolysis of Cp*$_2$Ti(Et-d_5) (**2b**) in the presence of methane does not lead to incorporation of deuterium into methane (^{1}H NMR).

(18) De Vries, Hn. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 867.

(19) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley and Sons: New York, 1981; p 26. Also for Michaelis–Menten kinetics this type of plots can be found, but here no substrate–catalyst complex is formed.

Stabilization by Alkenes. A first indication for the identity of the catalyst was obtained from the fact that primary alkenes stabilize Cp^*_2TiR. This was observed during a study of the isomerization of 1-hexene with the *n*-hexyl compound $Cp^*_2TiC_6H_{13}$ as a catalyst. Decomposition of $Cp^*_2TiC_6H_{13}$ to Cp^*FvTi and *n*-hexane was found to be over one order of magnitude faster in cyclopentane ($t_{1/2} = 4.8$ h) than in 1-hexene ($t_{1/2} = 80$ h) at 20 °C. A comparable effect was observed for Cp^*_2TiPr in THF-d_8 in the presence of various amounts of propene. The half-life time at 35 °C changed from 1.6 to 3.4 h on addition of 2 equiv of propene. The stabilization was even more pronounced in the presence of 5 equiv of propene. Then Cp^*_2TiPr proved thermally stable at 35 °C: no measurable amounts of Cp^*FvTi were formed over a period of 7.5 h. Olefins also interfere with the thermal decomposition of Cp^*_2TiMe. Thermolysis of Cp^*_2TiMe (90 °C) in THF-d_8 in the presence of 1 equiv 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.[20] However, no spectroscopic evidence was found to support this. The IR spectrum of $Cp^*_2TiC_6H_{13}$ in 1-hexene and the ^1H NMR spectrum of Cp^*_2TiPr 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.

Catalytic Activity of the Hydride Cp^*_2TiH. The catalyst appears to be formed either directly from Cp^*_2TiR or from Cp^*FvTi and to react with olefins to lose catalytic activity. A likely candidate is the hydride Cp^*_2TiH,[21] which can be formed from the thermally instable alkyls (R = Et, Pr) by β-H elimination, or by hydrogenolysis of Cp^*_2TiR. The dihydrogen necessary for the latter process can be formed by thermal degradation of Cp^*FvTi at elevated temperatures.[15] It was decided to test the effect of Cp^*_2TiH on the thermolysis of various compounds Cp^*_2TiR. Addition of small amounts of Cp^*_2TiH to solutions of Cp^*_2TiR resulted in a dramatic increase of the rate of thermal decomposition. For example, the extremely stable phenyl compound Cp^*_2TiPh decomposed (60 °C, THF) smoothly to Cp^*FvTi and benzene after addition of 0.10 equiv of Cp^*_2TiH, while in its absence it could be refluxed for hours in toluene without noticeable decomposition.

Table I. Rate Constants for Thermolysis of $Cp^*_2TiCH_2CMe_3$ at 298 K at Various Concentrations of Cp^*_2TiH

$[TiH]^a$	$[TiCH_2CMe_3]^a$	$k_{obs}{}^b$	$k_{obs}/[TiH]^c$ (k_1)
1.9	23.0	0.78 (2)	4.0 (4)
3.9	23.0	1.4 (2)	3.5 (1)
9.9	23.0	3.5 (2)	3.5 (1)
16.3	23.0	5.5 (1)	3.4 (1)
19.8	23.0	6.3 (1)	3.2 (2)
50.1	23.0	14 (0.5)	2.8 (2)

[a] In mmol·L^{-1}. [b] In 10^{-2} L·mol^{-1}·s^{-1}. [c] In 10^{-4} s^{-1}.

Table II. Rate Constants *k* for Thermolysis of $Cp^*_2TiCH_2CMe_3$ at 298 K, Dependence on Concentration, and Effect of Added Cp^*FvTi^a

$[TiH]^b$	$[TiCH_2CMe_3]^b$	$[Fv]^b$	$k_{obs}{}^c$	$k_{obs}/[TiH]^d$
6.1	4.9		2.1 (2)	3.4 (5)
6.1	7.2		1.9 (2)	3.1 (5)
6.1	14.0		2.2 (2)	3.6 (3)
6.1	24.0		2.3 (2)	3.8 (5)
5.8	11.0	7.0	2.2 (2)	3.7 (5)
5.8	11.0	11.0	2.1 (2)	3.6 (5)

[a] Fv = Cp*FvTi. [b] In mmol·L^{-1}. [c] In 10^{-6} L·mol^{-1}·s^{-1}. [d] In 10^{-4} s^{-1}.

While catalytically active, Cp^*_2TiH appears to supply hydrogen atoms for the formation of RH, and the pentamethylcyclopentadienyl ligands of the thermolyzing molecule Cp^*_2TiR are not involved directly. This is concluded from an experiment in which Cp^*_2TiMe was thermolyzed in the presence of $(Cp^*\text{-}d_{15})_2TiD$.[15] Mass spectrometry showed that the methane produced in the initial phase of the reaction was predominantly CH_3D. It is evident that the hydride accelerates the thermal decomposition of Cp^*_2TiR by assisting in a rapid transfer of hydrogen from the cyclopentadienyl ligands to the leaving group R. The actual transfer mechanism and the presence (or formation) of the catalyst in solutions of pure Cp^*_2TiR are interesting problems which need further discussion. As noted earlier, Cp^*_2TiH can be formed from Cp^*_2TiR by hydrogen transfer from R. This process has been found to be kinetically quite facile at ambient temperatures for alkyl compounds with β-H on R,[22] and it explains their low thermal stability. β-Hydrogen-containing alkyl compounds Cp^*_2TiR easily form hydride–olefin complexes and are in equilibrium with Cp^*_2TiH and the corresponding olefin. The equilibrium, however, is almost completely on the side of the alkyl compound and olefins cannot easily be removed from solutions of Cp^*_2TiR, e.g. by applying a dynamic vacuum, which explains the absence of more than minute quantities of olefins as products in the thermolysis.[22] For the other compounds Cp^*_2TiR this low-energy hydrogen transfer is not accessible and therefore they are stable at ambient temperatures. Alternative mechanisms which may lead to formation of Cp^*_2TiH, like α-H transfer from the methyl group in Cp^*_2TiMe or from the neopentyl group in $Cp^*_2TiCH_2CMe_3$, are very unlikely to play a role. Experiments on the latter two compounds and on $Cp^*_2TiCH{=}CH_2$ and Cp^*_2TiPh show that thermolysis proceeds at temperatures (90–150 °C) where the fulvene Cp^*FvTi itself starts to decompose. We presume that thermolysis of Cp^*_2TiR starts with a concerted, intramolecular H-transfer from a pentamethylcyclopentadienyl ligand to R to yield Cp^*FvTi and RH. This slow, intramolecular mode of decomposition is not easy to study since at the temperatures where intramolecular thermolysis starts Cp^*FvTi is not stable and loses dihydrogen with concomitant formation of the doubly metalated compound $Cp^*\{C_5Me_3(CH_2)_2\}Ti$ (eq 2). The dihydrogen thus formed reacts with either Cp^*FvTi or Cp^*_2TiR to give decomposition catalyst Cp^*_2TiH (eq 3). Since the catalytic decom-

$$Cp^*FvTi + H_2 \rightarrow Cp^*_2TiH \tag{3a}$$

$$Cp^*_2TiR + H_2 \rightarrow Cp^*_2TiH + RH \tag{3b}$$

position is very effective, traces of Cp^*_2TiH are sufficient to cause a dramatic increase in decomposition rate of Cp^*_2TiMe at 90 °C leading to the observed S-shaped plots (Figure 1). At higher concentrations of Cp^*_2TiMe the concentration of Cp^*FvTi increases much faster, and consequently formation of Cp^*_2TiH too, leading to shorter induction times.

Trapping of the catalyst will lead to stabilization of compounds Cp^*_2TiR. This is very effectively achieved by addition of α-olefins. It has been observed for Cp^*_2TiMe in the presence of ethene (Figure 1), for Cp^*_2TiPr with propene added, and for the *n*-hexyl

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(20) For d^2 metal complexes alkyl–olefin adducts are reported: Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420.

(21) The exact nature of this compound is not clear yet. When exposed in solution to D_2, the Cp* ligands in Cp^*_2TiH are rapidly deuterated and HD is formed. Transfer of a hydrogen atom from the Cp* groups to the metal and extrusion of H_2 followed by the reverse reaction with D_2 appears to be facile, and this suggests that there is an equilibrium between Cp^*_2TiH and a fulvene–dihydride complex, Cp^*FvTiH_2, which under the right conditions loses H_2 and forms Cp^*FvTi. Spectroscopic data (^1H NMR, IR, EPR) and the general reactivity of Cp^*_2TiH are characteristic of a normal early transition metal hydride. With α-olefins it undergoes rapid insertion to give *n*-alkyl compounds Cp^*_2TiR. The best preparation of Cp^*_2TiH is by hydrogenolysis of Cp^*_2TiR. Oxidation with $PbCl_2$ yields $Cp^*_2Ti(H)Cl$, see ref 13 and Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1470.

(22) An attempt to prepare Cp^*_2TiEt with ^{13}C at the α position of the ethyl ligand by reaction of Cp^*_2TiCl and $CH_3{}^{13}CH_2MgBr$ resulted in a 50/50 distribution of the ^{13}C label over the α and β position of the ethyl group. Ethene and propene extrusion from Cp^*_2TiEt and Cp^*_2TiPr was observed when the compounds were exposed to reactive unsaturated substrates like CO_2, alkynes, and nitriles. These observations indicate facile formation of hydride–olefin intermediates in alkyl compounds with β-H. The olefin cannot easily be removed and even when applying a dynamic vacuum on solutions of Cp^*_2TiR (R = Et, Pr) only trace amounts of the olefins can be detected in the thermolysis products. See ref 12b and Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1987**, 849.

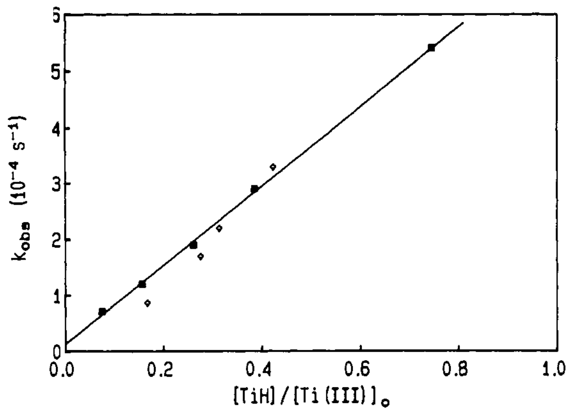


Figure 2. Observed first-order rate constant for the catalyzed decomposition of Cp^*_2TiMe at 308 K versus $[Cp^*_2TiH]/[Cp^*_2TiMe]_0$ + $[Cp^*FvTi]_0$) without (■) and with (◇) extra Cp^*FvTi (Table III).

Table III. Rate Constants k for the Catalytic Decomposition of Cp^*_2TiMe at 308 K, Dependence on Starting Concentration, and Added Cp^*FvTi[a]

[TiH][b]	[TiMe][b]	[Fv][b]	k_{obs}[c]	k_1[c]
4.7	6.3		5.4 (3)	7.2 (4)
4.7	12.0		2.9 (2)	7.4 (4)
4.7	18.0		1.9 (2)	7.3 (4)
4.7	30.0		1.2 (1)	7.6 (4)
4.7	63.0		0.61 (5)	8.1 (4)
4.7	11.0		3.3 (4)	7.7 (4)
4.7	11.0	4.0	2.2 (2)	7.0 (6)
4.7	11.0	6.0	1.7 (1)	6.1 (6)
4.7	11.0	17.0	0.87 (6)	5.2 (6)

[a] Fv = Cp^*FvTi. [b] In $mmol \cdot L^{-1}$. [c] In 10^{-4} s^{-1}.

compound $Cp^*_2TiC_6H_{13}$ in *n*-hexene (vide supra). The insertion of olefin into the Ti–H bond is fast and will lead to formation of an alkyl Cp^*_2TiR. The catalytic decomposition cannot start and thermolysis has to proceed in the slow intramolecular mode.

Kinetic Study of Decomposition of Cp^*_2TiR Catalyzed by Cp^*_2TiH. To get a better picture of the role of Cp^*_2TiH in the thermolysis of Cp^*_2TiR, a kinetic study was performed on mixtures of Cp^*_2TiR (R = Me, CH_2CMe_3, Ph) and Cp^*_2TiH in THF. The progress of thermolysis was followed by UV–vis (R = Me, CH_2CMe_3, Ph) and ^1H NMR (R = Me) spectroscopy. In all experiments the spectra obtained were superpositions of the components Cp^*_2TiR, Cp^*FvTi, and Cp^*_2TiH, 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 slow intramolecular thermolysis of Cp^*_2TiR.

Analysis of spectral data gave kinetic plots of variable complexity. For Cp^*_2TiPh a mathematical evaluation of the progression of the reaction proved not simple and a detailed analysis was not attempted.[23] However, for the neopentyl $Cp^*_2TiCH_2CMe_3$, the kinetics are quite simple. The overall rate is first order in Cp^*_2TiH and independent of $Cp^*_2TiCH_2CMe_3$ (eq 4, Table I). Addition of extra Cp^*FvTi has no effect on the rate (Table II).

$$-\frac{d[Cp^*_2TiCH_2CMe_3]}{dt} = k[Cp^*_2TiH] \qquad (4)$$

For Cp^*_2TiMe the kinetics are much more complicated. The decomposition shows a regular first-order progression for all

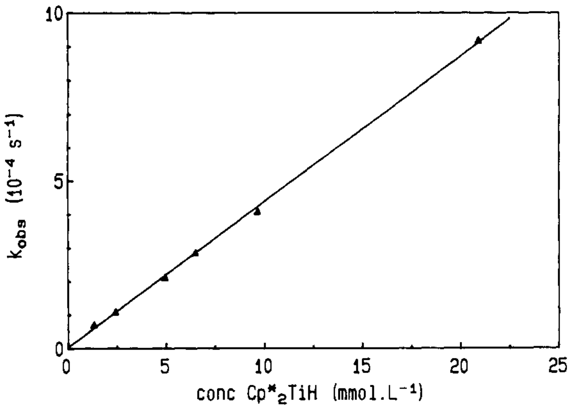


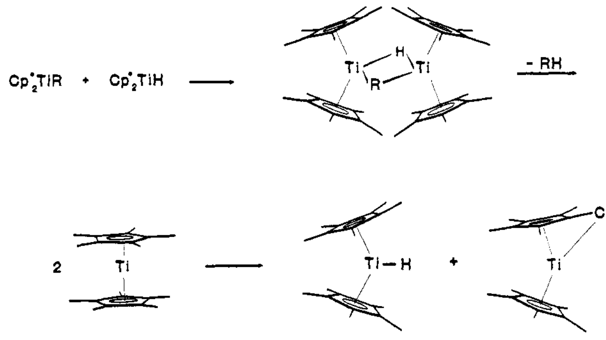
Figure 3. Observed first-order rate constant for the catalyzed decomposition of Cp^*_2TiMe at 308 K versus the concentration of Cp^*_2TiH. $[Cp^*_2TiMe]$ = 17.0 $mmol \cdot L^{-1}$ in THF (Table IV).

Table IV. Rate Constants k for the Thermolysis of Cp^*_2TiMe at 308 K at Various Concentrations of Cp^*_2TiH

[TiH][a]	[TiMe][a]	k_{obs}[b]	k_{obs}[c]/[TiH]
1.42	17.0	0.71 (5)	5.0 (5)
2.42	17.0	1.1 (4)	4.5 (2)
4.95	17.0	2.1 (4)	4.2 (2)
6.5	17.0	2.9 (4)	4.5 (2)
9.7	17.0	4.1 (4)	4.3 (2)
20.9	17.0	9.2 (4)	4.4 (1)

[a] In $mmol \cdot L^{-1}$. [b] In 10^{-4} s^{-1}. [c] In 10^{-2} $L \cdot mol^{-1} \cdot s^{-1}$.

Scheme I



concentrations studied (Table III), but k_{obs} depends, unlike a regular first-order process, on the starting concentration $[Cp^*_2TiMe]_0$. The observed rate constant has an apparent inverse proportionality to $[Cp_2TiMe]_0$ (Figure 2), which implies that decomposition is slower at higher starting concentrations of Cp^*_2TiMe. This is very puzzling since whereas the concentration of Cp^*_2TiMe during thermolysis and acceleration is expected to continuously decrease, this is not observed. Instead, the inhibition appears to be determined by the initial concentration of Cp^*_2TiR (which equals the sum of $[Cp^*_2TiMe]$ and $[Cp^*FvTi]$ during conversion). This suggests that the decomposition of Cp^*_2TiMe is also inhibited by Cp^*FvTi. Indeed addition of Cp^*FvTi leads to lower rates (Figure 2, Table III). Quantitatively, the inhibition by Cp^*_2TiMe and Cp^*FvTi appears to be identical within error limits. Since the sum of $[Cp^*_2TiMe]$ and $[Cp^*FvTi]$ 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 as appears to be the case for Cp^*_2TiPh. The decomposition of Cp^*_2TiMe shows the expected first-order relationship in Cp^*_2TiH (eq 5, Figure 3, Table IV).

$$-\frac{d[Cp^*_2TiMe]}{dt} = k\frac{[Cp^*_2TiH]}{[Cp^*_2TiMe]_0}[Cp^*_2TiMe] \qquad (5)$$

Mechanistic Aspects. The simplest mechanism for the hydride-catalyzed decomposition is a bimolecular reaction between

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(23) The decomposition of **6** has an initial period of exponential progression, followed in later stages by an almost linear conversion in time.

(24) From earlier studies on CO-induced disproportionation of Cp^*_2TiCl to $Cp^*_2TiCl_2$ and $Cp^*_2Ti(CO)_2$ it is known that there is no insuperable steric hinderance for two permethyltitanocene units to approach each other: Luinstra, G. A.; Teuben, J. H.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *375*, 183.

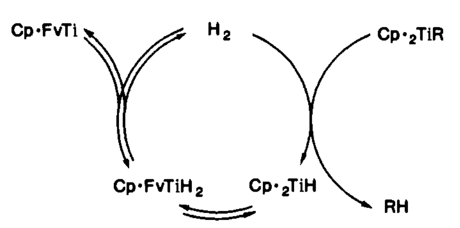

Figure 4. Proposed catalytic cycle for the thermolysis of Cp*$_2$TiR.

Cp*$_2$TiR and Cp*$_2$TiH to form a hydride–alkyl bridged dimer (Scheme I) and elimination of RH to give 2 equiv of permethyltitanocene which in a subsequent step undergoes disproportionation to Cp*FvTi and Cp*$_2$TiH, the catalyst. However, permethyltitanocene as an intermediate 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*$_2$Ti)$_2$N$_2$.[11,25] Moreover, addition of (Cp*$_2$Ti)$_2$N$_2$ did not result in a catalytic decomposition. In fact, the dinitrogen complex appeared to be perfectly stable under decomposition conditions for Cp*$_2$TiMe. Further evidence against Scheme I was obtained from the hydride-catalyzed decomposition of Cp*$_2$TiCH=CH$_2$. If the mechanism is as in Scheme I, ethene will be formed and trapped by permethyltitanocene to form Cp*$_2$Ti(η^2-C$_2$H$_4$),[4f] but this complex was not observed. In a separate experiment, Cp*$_2$Ti(η^2-C$_2$H$_4$) was mixed with Cp*$_2$TiH under conditions for rapid catalytic decomposition of Cp*$_2$TiCH=CH$_2$, but the ethene complex was found to be quite stable. It decomposed slowly by loss of ethene to form Cp*$_2$Ti (^{1}H NMR). The formed ethene rapidly reacted with Cp*$_2$TiH to give Cp*$_2$TiEt, which subsequently decomposed. Thus, the mechanism of the hydride-catalyzed decomposition of Cp*$_2$TiR cannot be as in Scheme I, and since it is not possible to rationalize the formation of RH by transfer of one hydrogen atom from Cp*$_2$TiH to a hydrocarbyl ligand without change of oxidation state, it cannot be the actual catalyst. The active species has to meet the following requirements: (a) it must supply hydrogen atoms for RH, (b) it must be formed from Cp*$_2$TiH with first-order kinetics, which excludes a bimolecular reaction between Cp*$_2$TiH and itself, and (c) there should be no change of formal oxidation state.

Taking this into consideration we propose a more realistic catalytic cycle in Figure 4. The role of Cp*$_2$TiH is facile generation of dihydrogen in an intramolecular process, presumably through intermediate formation of a fulvene–dihydride complex Cp*FvTiH$_2$. In this step the product Cp*FvTi is formed. Then hydrogenolysis of Cp*$_2$TiR takes place with formation of RH and Cp*$_2$TiH. In a competitive reaction, Cp*FvTi may react with H$_2$ and regenerate Cp*$_2$TiH. The cycle is not catalytic in a strict sense. Although the overall concentration of the catalyst does not change during catalysis, Cp*$_2$TiH is consumed during the reaction and not regenerated but replaced by a new molecule on closing the cycle. Labeling studies make clear that the hydride Cp*$_2$TiH acts as a dihydrogen source. Decomposition of Cp*$_2$TiCH$_2$CMe$_3$ in the presence of 2 equiv of (Cp*-d_{15})$_2$TiD gave in early stages of the reaction only Cp*$_2$TiD (^{1}H NMR) and Cp*FvTi-d_{29}.[26] Thus, Cp*FvTi is formed from the catalyst Cp*$_2$TiH, rather than from Cp*$_2$TiR. The latter is converted into a new molecule of catalyst. This hydrogenolysis cycle avoids elimination of RH by direct abstraction of hydrogen from a pentamethylcyclopentadienyl ligand, which evidently has a much higher activation barrier than elimination of H$_2$ from Cp*$_2$TiH (cf. slow mode of thermolysis of **1**).

The reaction sequence in Scheme II also accounts for the observed scrambling of deuterium in the alkyl group when partly deuterated compounds Cp*$_2$Ti(Et-d_5) and Cp*$_2$Ti(Pr-d_7) are thermolyzed. Transfer of β-D generates Cp*$_2$TiD, which forms the fulvene–hydride–deuteride Cp*FvTiHD. This may lose HD and form Cp*FvTi, or migrate either the hydride or the deuteride ligand to the fulvene group. Hydrogenolysis of Cp*$_2$TiC$_n$D$_{2n+1}$ with HD produces either completely deuterated alkane C$_n$D$_{2n+2}$ or C$_n$D$_{2n+1}$H. It also accounts for the formation of CH$_3$D from mixtures of Cp*$_2$Ti(Et-d_5) and Cp*$_2$TiMe.

Scheme II

Hydrogen formation:

$$\mathrm{Cp^*_2TiH} \xrightarrow{k_1} \mathrm{Cp^*FvTi} + \mathrm{H_2}$$

Productive reaction:

$$\mathrm{Cp^*_2TiR} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{Cp^*_2TiH} + \mathrm{RH}$$

Competitive reaction:

$$\mathrm{Cp^*FvTi} + \mathrm{H_2} \xrightarrow{k_{-1}} \mathrm{Cp^*_2TiH}$$

The overall reaction rate for the model in Scheme II 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 Cp*$_2$TiH, and between zero and first order in substrate Cp*$_2$TiR).

$$\frac{\mathrm{d[Cp^*_2TiR]}}{\mathrm{d}t} = k_1k_2\frac{\mathrm{[Cp^*_2TiH][Cp^*_2TiR]}}{k_2\mathrm{[Cp^*_2TiR]} + k_{-1}\mathrm{[Cp^*FvTi]}} \qquad (6)$$

For certain ratios of k_2:k_{-1} eq 6 will give the expressions for the kinetics of the hydride-catalyzed decomposition of Cp*$_2$TiMe and Cp*$_2$TiCH$_2$CMe$_3$. If k_2 is equal to k_{-1}, eq 6 will reduce to eq 5, the kinetics for Cp*$_2$TiMe. This can be interpreted as an equal affinity of Cp*$_2$TiMe and Cp*FvTi for dihydrogen. The retardation of the reaction at higher starting concentration of Cp*$_2$TiMe and Cp*FvTi is explained by a lower steady state concentration of dihydrogen k_1[Cp*$_2$TiH]k_2{[Cp*$_2$TiMe] + [Cp*FvTi]} = 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 Cp*$_2$TiCH$_2$CMe$_3$. This is the case when dihydrogen reacts much faster with Cp*$_2$TiCH$_2$CMe$_3$ than with Cp*FvTi. The elimination of dihydrogen from Cp*$_2$TiH then becomes rate determining. It also implies that overall rates should be much higher for Cp*$_2$TiCH$_2$CMe$_3$ than for Cp*$_2$TiMe and this has been observed experimentally. At all other ratios k_2:k_{-1} the progression of the reaction will be complex, the rate being dependent on starting concentration and conversions, as for example observed in the catalyzed thermolysis of Cp*$_2$TiPh.

Concluding Remarks. In contrast to intramolecular decomposition normally observed in the thermolysis of early transition metal hydrocarbyl complexes, the thermal decomposition of Cp*$_2$TiR is not a simple process. A low-energy catalytic pathway is opened as soon as Cp*$_2$TiH is present. The ability of Cp*$_2$TiR to generate the hydride catalyst determines the thermal stability of the compounds. For β-hydrogen-containing alkyl complexes catalyst formation is easily achieved at ambient temperatures by β-hydrogen transfer and olefin elimination. In this series Cp*$_2$TiEt is thermally the most robust compound. This might be caused by an agostic interaction of the ethyl ligand with the d^1, 15-electron titanium center in this complex, thus stabilizing the alkyl form relative to a hydride–olefin configuration.[12b] The decomposition can be retarded by adding olefins to solutions of Cp*$_2$TiR, which traps the hydride Cp*$_2$TiH by formation of an alkyl and decreases the catalyst concentration. Non-β-hydrogen-containing derivatives Cp*$_2$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 Cp*FvTi. At this temperature Cp*FvTi is not stable and loses dihydrogen. The dihydrogen reacts with Cp*$_2$TiR or with Cp*FvTi to give Cp*$_2$TiH. This will result in an autocatalytic decomposition of Cp*$_2$TiR, giving typical sigmoid conversion plots. The catalytic process has complicated kinetics, suggesting that elimination of dihydrogen from Cp*$_2$TiH is the key step. The catalytic thermolysis of Cp*$_2$TiR is essentially a hydrogenolysis of the Ti–C bond to give RH and Cp*$_2$TiH, followed by decomposition of

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(25) Dinitrogen adducts of permethyltitanocene are intensely colored ($\epsilon_{\mathrm{mol}} \gg 10.000$ M^{-1}·cm^{-1}) and even traces should lead to strong color changes, but this was not the case (observation of isobestic points in UV–vis).

(26) Later on Cp*FvTi was also observed.

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Cp*$_2$TiH to Cp*FvTi, and regenerating H_2.

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Registry No. Cp*$_2$TiH, 131954-87-5; Cp*$_2$Ti(H)Cl, 115912-71-5; Cp*$_2$TiMe, 99476-26-3; Cp*$_2$Ti(Me-d_3), 135973-60-3; Cp*$_2$Ti(Me)Cl, 107534-13-4; Cp*$_2$TiEt, 99476-27-4; Cp*$_2$TiCH=CH$_2$, 131954-86-4; Cp*$_2$TiPr, 99476-28-5; Cp*$_2$TiCH$_2$CMe$_3$, 103351-92-4; Cp*$_2$TiPh, 115564-94-8; Cp*FvTi, 53436-87-6.

Supplementary Material Available: Tables of rate constants for the thermolysis of Cp*$_2$TiR (R = Et, Pr) in THF, details on the synthesis of Cp*$_2$TiH and (Cp*-d_{30})$_2$TiD, and spectral data and plots of kinetic data for thermal decompositions of Cp*$_2$TiR (R = Me, Pr, CH$_2$CMe$_3$, Ph) catalyzed by Cp*$_2$TiH and the effect of propene on the thermolysis for R = Pr (6 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Re(VII) Alkylidene Alkylidyne Complexes of the Type Re(CR′)(CHR′)(OR)$_2$ and Related Species

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Abstract: A convenient one pot synthesis of Re(NAr)$_2$(py)Cl$_3$ consists of addition of excess trimethylchlorosilane, pyridine, and 2,6-dimethylaniline (ArNH$_2$) to Re$_2$O$_7$ or [NH$_4$][ReO$_4$] in dichloromethane. Re(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$(py)Cl$_3$ and Re(N-*t*-Bu)$_2$Cl$_3$ can be prepared similarly in high yield. Alkylation of these species with dineopentyl or dineophyl zinc or Grignard reagents affords complexes of the formula Re(NR)$_2$(CHR′)(CH$_2$R′) (R = 2,6-C$_6$H$_3$Me$_2$, 2,6-C$_6$H$_3$-*i*-Pr$_2$ or *tert*-butyl; R′ = CMe$_3$ or CMe$_2$Ph). Treatment of Re(NR)$_2$(CHR′)(CH$_2$R′) complexes with an appropriate HCl source yields dimers of the general formula [Re(CR′)(CHR′)(RNH$_2$)Cl$_2$]$_2$, which exist as a mixture of two isomers. An X-ray study of [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$ (a = 10.05 (1) Å, b = 21.65 (3) Å, c = 10.99 (1) Å, β = 98.28 (9)°, Z = 2, fw = 1031.08, ρ(calcd) = 1.446 g/cm^3, space group = $P2_1/n$) showed it to contain two bridging halides with mutually cis alkylidene and alkylidyne ligands trans to the bridging halides. Several monomeric derivatives having the general formula Re(C-*t*-Bu)(CH-*t*-Bu)L$_2$Cl$_2$ (L = *t*-BuNH$_2$, pyridine, $^1/_2$TMEDA, $^1/_2$phenylenediamine (pda)) were prepared, and related monoadducts, Re(C-*t*-Bu)(CH-*t*-Bu)(L)Cl$_2$, have been observed in solution. Treatment of Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl$_2$ with HCl(g) in dimethoxyethane affords air- and water-stable [Re(C-*t*-Bu)(CH-*t*-Bu)Cl$_2$]$_x$ ($x > 1$). An alternative route to [Re(C-*t*-Bu)(CH-*t*-Bu)Cl$_2$]$_x$ consists of treatment of Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) with HCl(g) in dimethoxyethane. Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) is prepared by the acid-catalyzed hydrolysis of Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) via intermediate Re(NAr)(O)(CH-*t*-Bu)(CH$_2$-*t*-Bu). Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) and Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) conproportionate in solution to give Re(NAr)(O)(CH-*t*-Bu)(CH$_2$-*t*-Bu). [Re(C-*t*-Bu)(CH-*t*-Bu)Cl$_2$]$_x$ is a versatile precursor to a variety of bisalkoxide complexes of the general formula Re(C-*t*-Bu)(CH-*t*-Bu)(OR)$_2$ (OR = O-*t*-Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, O-2,6-C$_6$H$_3$-*i*-Pr$_2$, OSi(*t*-Bu)$_3$). Syn and anti rotameric forms of the Re(C-*t*-Bu)(CH-*t*-Bu)(OR)$_2$ complexes interconvert thermally or photochemically. In syn rotamers usually J_{CH} = 120–135 Hz and in anti rotamers J_{CH} = 157–184 Hz. An X-ray study of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(THF) (a = 9.891 (1) Å, b = 17.543 (2) Å, c = 16.570 (2) Å, β = 95.90 (2)°, Z = 4, fw = 759.69, ρ = 1.764 g/cm^3, space group = $P2_1/n$) showed it to have a structure approximately halfway between a face-capped tetrahedron (THF trans to the neopentylidyne ligand) and a trigonal bipyramid.

Introduction

Rhenium is one of three metals (molybdenum and tungsten being the other two) that are active for the metathesis of olefins in classical metathesis systems.[1,2] Although both homogeneous and heterogeneous molybdenum and tungsten catalysts are known, rhenium catalysts of the classical type (e.g., Re$_2$O$_7$ on alumina) are heterogeneous. One of the potential advantages of rhenium catalysts is that they may tolerate functionalities (e.g., the ester in methyl oleate) more than tungsten or molybdenum catalysts.[3] Approximately ten years ago evidence began to accumulate in favor of the highest possible oxidation state for tungsten metathesis catalysts (d^0 if the alkylidene ligand is viewed as a dianion).[4-7] Therefore we felt that it should be possible to prepare well-characterized, soluble Re(VII) alkylidene complexes. At that time organometallic chemistry of Re(VII) was extremely rare.[8-10] We chose to attempt to synthesize complexes of Re(VII) containing imido ligands in the belief that imido complexes would not be reduced as readily as oxo complexes in alkylation reactions and that unwanted bimolecular reactions might be slowed down or prevented entirely if imido ligands are present instead of oxo ligands.

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