Synthesis, characterization and reactivity of neutral trichloride and trialkyl \( \eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ar})\text{TiR}_3 \) compounds

2

2.1 Introduction

Monocyclopentadienyl (half-sandwich) titanium compounds are especially known as precursors for styrene polymerization catalysts\(^1\), although they are also of interest for the polymerization of other olefins\(^2\). For example, \( \text{Cp}^*\text{TiMe}_3 \) is an effective precatalyst for the (living) polymerization of propene\(^2b\) to give high molecular weight atactic polypropene with a narrow polydispersity, and can produce short-chain branched polyethylene from ethene homopolymerization\(^2c\). Despite the plethora of studies on half-sandwich titanium catalysts\(^3\) (predominantly related to syndiospecific styrene polymerization), several issues regarding these catalyst systems still need to be resolved: (a) the nature of the actual active species in styrene polymerization, e.g. whether Ti(IV) or Ti(III) species are involved, is subject of debate, and (b) the mechanism behind the formation of short-chain branched polyethylene via ethene homopolymerization is as yet unclear. In order to rationally improve these catalysts, a better understanding of the factors governing the catalytic properties (activity, selectivity, molecular weight) is essential.

We set out to investigate cationic monocyclopentadienyl dialkyl species, formed upon reaction of the corresponding neutral trialkyls with Lewis acidic activators, and their subsequent reactivity with olefin substrates, in order to address the issues described above. For this we decided to prepare cationic monocyclopentadienyl titanium species that are additionally stabilized via intramolecular interactions\(^4\). This stabilization by intramolecular coordination should ideally be reversible and relatively weak, as to not undo the reactive properties of the cationic titanium center completely, but allow us to observe and follow reactive intermediates. To this end we sought a cyclopentadienyl ligand with a tethered functionality, than can display hemilabile behavior\(^5\) on a cationic Ti(IV) center. Cyclopentadienyl-arene ligands, such as \([\text{C}_5\text{H}_4\text{CMe}_2\text{Ar}]\), can potentially suit our purpose\(^6\). Half-sandwich titanium dialkyl cations, \([\text{CpTiR}_2]^+\), have been reported to reversibly coordinate aromatic solvents, such as benzene and toluene\(^7\).

* Deckers, P.J.W., Hessen, B., manuscript in preparation
2.2 The $[\text{C}_5\text{H}_4\text{CMe}_2\text{Ar}]^-$ ligand

Cyclopentadienyl ligands with a -CMe$_2$Ar substituent are readily available from the reaction of 6,6-dimethylfulvene with the appropriate aryl lithium salt. The benzyl-cyclopentadienyl lithium salts can be optionally quenched with trimethylsilyl chloride (Me$_3$SiCl) to afford the corresponding trimethylsilyl reagents. The simplest $[\text{C}_5\text{H}_4\text{CMe}_2\text{Ar}]^-$ ligand, with Ar = Ph, was employed by Tainturier and coworkers in studies to determine the effect of different cyclopentadienyl substituents on the physical and chemical properties of group 4 metallocene complexes, Cp$^R_2$MR$^2$ or Cp$^R$(Cp)MR$^2$, and later by Coville and coworkers to study cyclopentadienyl substituent effects on olefin polymerization behavior. Erker and coworkers used the ligand to investigate the stability of (η$^2$-olefin)metallocene complexes. It had been reported that these species are kinetically stabilized by sterically demanding cyclopentadienyl ligand systems. Reaction of (η$^5$-C$_5$H$_4$CMe$_2$Ph)$_2$ZrCl$_2$ with Mg(butadiene), which was known to proceed through an η$^2$-diene intermediate for other metallocenes to give eventually η$^4$-butadiene complexes, was found to lead to intramolecular cyclometalation of the substituted ligand via ortho C-H bond activation by the highly reactive η$^2$-diene moiety (Scheme 1, top).

Thermolysis of the corresponding zirconocene diphenyl compound (η$^5$-C$_5$H$_4$CMe$_2$Ph)$_2$ZrPh$_2$ also led to cyclometalation of the ancillary ligand, presumably via a benzyne intermediate (Scheme 1, bottom). Similar ortho C-H bond activation processes have been observed for transition metal complexes with related phenyl-substituted cyclopentadienyl ligands.

During our studies on half-sandwich titanium compounds with $[\text{C}_5\text{H}_4\text{CMe}_2\text{Ar}]^-$ ligands, several reports on the use of this type of ancillary ligand in cationic group 4...
alkyl species appeared in the literature\textsuperscript{15}. Bochmann, Green and coworkers tried to establish the effect of the benzyl substituent on olefin polymerization behavior in metallocenes of the type Cp\textsubscript{Bz}\textsubscript{2}ZrMe\textsubscript{2} and CpCp\textsubscript{Bz}ZrMe\textsubscript{2}\textsuperscript{15a}, and to demonstrate potential Zr-arene interactions in the corresponding cationic species generated by activation with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} or [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{15b-d}. Related phenyl-substituted monocyclopentadienyl dialkyl titanium and zirconium cationic species, [(Cp\textsubscript{Ph})MR\textsubscript{2}]\textsuperscript{+}, were also reported\textsuperscript{15c,f}, and were found to polymerize propene with modest activity\textsuperscript{15e}. Recently, the catalyst system (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}Ph)TiCl\textsubscript{3} (1, \textit{vide infra})/MAO was found to show modest styrene and propene polymerization activity\textsuperscript{15g}.

In this chapter, we describe the preparation of monocyclopentadienyl titanium trichloride and trialkyl compounds with [C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}Ar]\textsuperscript{-} ligands (Ar = Ph, 3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}). In addition, the thermolysis of the trialkyl complexes (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}Ar)Ti(CH\textsubscript{2}R)\textsubscript{3} (R = Ph, CMe\textsubscript{3}, SiMe\textsubscript{3}), leading to \textit{ortho} cyclometalation of the ancillary ligand, is presented together with a kinetic study of this process.

2.3 General synthetic methodology for monocyclopentadienyl titanium trichloride compounds

![Scheme 2: Synthesis of (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}R)TiCl\textsubscript{3}](image-url)
The first half-sandwich titanium compound, CpTiCl₃, was prepared in the late 1950's by two independent routes: synproportionation of Cp₂TiCl₂ and TiCl₄, and chlorination of Cp₂TiCl₂ (Scheme 2). Other, more versatile routes to monocyclopentadienyl titanium trichlorides (Scheme 2), such as transmetalation of TiCl₄ with (C₅H₄R)M (M = Li, Na, K, MgX), were developed soon after. The same (C₅H₄R)M reagent can also be transmetalated with TiCl₃ and subsequently reacted with a mild oxidizing agent, such as AgCl or PbCl₂, to afford the desired half-sandwich Ti(IV) compound. An alternative for attaching cyclopentadienyl ligands directly to Ti(IV) is the reaction of TiCl₄ with the appropriately substituted trialkylsilyl (or trialkylstannyl) cyclopentadienes, (C₅H₄R)ER₃ (E = Si, Sn).

The transmetalation route of (C₅H₄R)M with TiCl₄ was historically the first widely applicable route to be developed. However, this strategy suffers from several drawbacks: (a) when the cyclopentadienyl ligand is not sterically demanding, substantial amounts of (C₅H₄R)₂TiCl₂ can be formed, (b) the separation of the half-sandwich titanium compound from the inorganic salts can be difficult in some cases, and (c) when the cyclopentadienyl ligand is sterically too congested the transmetalation method does not yield the desired complexes. Transmetalation of Ti(III) chloride with (C₅H₄R)M followed by oxidation proved to be a good alternative to circumvent the latter drawback, and obtain (sterically demanding) monocyclopentadienyl titanium(IV) trichlorides.

The best and most general methodology for the preparation of (C₅H₄R)TiCl₃ appears to be via trialkylsilyl (or trialkylstannyl) cyclopentadienes, (C₅H₄R)ER₃ (E = Si, Sn). This route is highly selective, producing exclusively the monocyclopentadienyl species, and has a high tolerance for a wide variety of ring substituents. Furthermore, the R₃ECI byproduct (preferably Me₃SiCl) is soluble and/or volatile and can be easily removed. It may be noted that (Diels-Alder) dimerization (or polymerization) of the ring-transfer agents can occur, especially for cyclopentadienes that are sterically not very demanding. Despite this potential drawback, the majority of new half-sandwich titanium compounds reported in recent years has been prepared via reaction of trimethylsilyl cyclopentadienes and TiCl₄.

### 2.4 Synthesis and characterization of (η⁵-C₅H₄CMe₂Ar)TiR₃ (R = Cl, Me, CH₂Ph)

The titanium trichlorides (η⁵-C₅H₄CMe₂Ar)TiCl₃ (Ar = Ph, 1, 3,5-Me₂C₆H₃, 2) are readily available via salt metathesis of the lithium salt with TiCl₄ in methylene chloride, or via Me₃SiCl elimination upon reaction of the corresponding trimethylsilyl reagent with TiCl₄ (Scheme 3). The titanium trichloride 1, together with the related compounds (η⁵-C₅H₄CH₂Ph₂)TiCl₃ and (η⁵-C₅H₄SiMe₂Ph)TiCl₃, was also independently prepared and characterized by Bochmann and coworkers. The titanium trichloride 2 was fully characterized by ¹H and ¹³C NMR spectroscopy, and elemental analysis. The ¹H NMR resonances of the ancillary ligand in 2 (Ar: δ 6.69,
Neutral \( (\eta^5-C_5H_4CMe_2Ph)TiR_3 \) Complexes; Synthesis and Reactivity

6.66; Cp: 6.37, 6.03; CMe_2: 1.63) are similar to those for 1 (Ar: \( \delta \) 7.0, 6.82; Cp: 6.25, 5.97; CMe_2: 1.53) and those for the related compound \( (\eta^5-C_5H_4CMe_2-4-MeC_6H_4)ZrCl_3(DME) \)\(^{15f}\).

\[ \text{Scheme 3: Preparation of } (\eta^5-C_5H_4CMe_2Ar)TiR_3 \]

Methylation of compounds 1 and 2 with 1.5 equiv of Me_2Mg(dioxane)\(_{n/2}\), as a solution in diethyl ether \((n = 0)\) or as a solid \((n = 1)\), in benzene or toluene solvent gives the trimethyl derivatives \( (\eta^5-C_5H_4CMe_2Ar)TiMe_3 \) (Ar = Ph, 3\(^{15e}\), 3,5-Me_2C_6H_3, 4) as thermally labile, air- and moisture-sensitive yellow crystals in 67-75% isolated yield (Scheme 3). The titanium trimethyl complexes 3 and 4 were fully characterized by NMR spectroscopy. The Ti-Me \(^1\)H NMR resonances are observed at \( \delta \) 1.33 and 1.31 ppm for 3 and 4, respectively, and resemble that observed for \( (\eta^5-C_5H_4CMe_2CH_2Ph)TiMe_3 \) \((\delta = 1.35 \text{ ppm})\)\(^{15e}\). The corresponding \(^{13}\)C NMR resonances are found at \( \delta \) 63.1 (3) and 63.0 ppm (4), and are similar to those observed for \( (\eta^5-C_5H_4CMe_2CH_2Ph)TiMe_3 \) \((\delta = 62.9 \text{ ppm})\)\(^{15e}\), \( (\eta^5-C_5H_4SiMe_2Ph)TiMe_3 \) \((\delta = 63.2 \text{ ppm})\)\(^{15e}\), and \( (\eta^5-C_5Me_4CH_2CH_2Ph)TiMe_3 \) \((\delta = 60.9 \text{ ppm})\)\(^{6a}\).

The corresponding titanium tribenzyl compounds \( (\eta^5-C_5H_4CMe_2Ar)Ti(CH_2Ph)_3 \) (Ar = Ph, 5, 3,5-Me_2C_6H_3, 6) are easily accessible by the reaction of the appropriate trichloride with 3 equiv of benzylmagnesium bromide in diethyl ether. Crystallization from pentane afforded 5 and 6 as air- and moisture-sensitive red crystals in 70-72% yield (Scheme 3). Compounds 5 and 6 were fully characterized by 1D and 2D NMR techniques, and elemental analysis. The methylene benzyl proton resonance appears as one singlet at \( \delta \) 2.97 and 2.99 ppm for 5 and 6, respectively. The corresponding methylene \(^{13}\)C NMR resonances are found at \( \delta \) 93.5 ppm for both 5 and 6 with respective \(^1J_{CH}\) coupling constants of 123 Hz and 124 Hz. These spectroscopic data are similar to those of the related species \( (\eta^5-C_5H_4PPh_2)Ti(CH_2Ph)_3 \)\(^{27}\) and \( (\eta^5-C_5H_4CHPh_2)Ti(CH_2Ph)_3 \)\(^{15e}\). The observed \(^1J_{CH}\) coupling constants are comparable to those displayed by the methylene carbon of...
CpTi(CH₂Ph)₃ (122 Hz)²⁸ and Cp*Ti(CH₂Ph)₃ (126 Hz)²⁹, which are both representative of η¹-coordinated benzyl ligands.

2.5 Thermolysis of the (η⁵-C₅H₄CMe₂Ar)Ti(CH₂Ph)₃ complexes

Warming benzene-d⁶ solutions of the titanium tribenzyl complexes (η⁵-C₅H₄CMe₂Ar)Ti(CH₂Ph)₃ (Ar = Ph, 5, 3,5-Me₂C₆H₃, 6) for 50 h at 50 °C, and monitoring the reaction by NMR spectroscopy, reveals gradual liberation of 1 equiv of toluene, and the formation of titanium dibenzyl species with an ortho cyclometalated pendant arene group, (η⁵,η¹-C₅H₄CMe₂C₆H₃)Ti(CH₂Ph)₂ (7) and (η⁵,η¹-C₅H₄CMe₂-3,5-Me₂C₆H₂)Ti(CH₂Ph)₂ (8) (Scheme 4). Cyclometalation at the aromatic ortho position has been reported previously for other systems with phenyl-substituted cyclopentadienyl ligands (see section 2.2)¹³,¹⁴, and Cp ligands with pendant 1-indene substituents³⁰.

![Scheme 4: Thermolysis of (η⁵-C₅H₄CMe₂Ar)Ti(CH₂Ph)₃](image)

The ¹³C NMR spectra show the Ar o-C ipso resonances of the cyclometalated arene group at δ 200.6 for 7 and δ 201.7 ppm for 8, which are comparable to the chemical shift found for the ipso carbon of the Ti-Ph group in the neutral metallocenes [Me₂Si(η⁵-C₅Me₄)₂]TiPh₂ (δ 199.6 ppm, CDCl₃, 25 °C) and (η⁵-C₅H₄CMe₃)₂TiPh₂ (δ 191.9 ppm, C₆D₆, 25 °C)³¹. The observed benzyl methylene 2JHH coupling constants (10 Hz for 7 and 9.5 Hz for 8), and the 1JCH coupling constants (122 Hz and 125 Hz, respectively) indicate η¹-coordination of the benzyl groups²⁸,²⁹,³².

Attempts to prepare compounds 7 and 8 on a preparative scale from hexane or benzene solutions (at 50 °C) reproducibly afforded viscous oils which could not be crystallized. It appears that isolation of the pure titanium dibenzyl species 7 and 8 is thwarted by further degradation to a secondary decomposition product in the course of the reaction. Prolonged thermolysis of benzene-d⁶ solutions of the (η⁵-C₅H₄CMe₂Ar)Ti(CH₂Ph)₃ compounds 5 and 6 (at least 12 h at 80 °C) leads to a secondary decomposition of the initially formed cyclometalated dibenzyl species 7 and 8. At the final stage of the decomposition (no changes of the ¹H NMR spectrum
could be observed for 1 day), 1.3 (± 0.1) equiv of toluene per titanium had been formed, as measured by comparison with an internal ferrocene standard. In addition, there is evidence for the formation of paramagnetic titanium species\textsuperscript{33}. Similar behavior has been reported by other researchers for the thermolysis of peralkyl complexes NbMe\textsubscript{5}, TaMe\textsubscript{5}, Ta(CH\textsubscript{2}Ph\textsubscript{5})\textsubscript{3} and WMe\textsubscript{6}, all of which lose more than 1 equiv of alkane upon decomposition\textsuperscript{34}. Oxidation of the low-valent titanium species, that is formed in the secondary decomposition process, with excess lead(II) chloride, a method used to cleanly oxidize Ti(III) to Ti(IV)\textsuperscript{19b,35}, did not afford a single characterizable compound. This suggests that the secondary decomposition process leads to a mixture of paramagnetic species.

2.6 Kinetic investigation of the thermolysis of (\(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph}\))Ti(CH\textsubscript{2}Ph\textsubscript{3})

Despite the occurrence of secondary decomposition reactions, the kinetics of the initial thermolysis process could be investigated by monitoring the disappearance of the titanium tribenzyl complex (\(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph}\))Ti(CH\textsubscript{2}Ph\textsubscript{3}) (5) in benzene-\(\text{d}_6\) relative to an internal ferrocene standard. The reaction follows simple first-order kinetics for over 3 half-lives in the temperature range 50.0-72.5 °C (Figure 1), and the rate constants \(k_1\) are independent of initial concentration (Table 1). The kinetic parameters were determined from an Eyring plot (of four \(k_1\)-determinations over the cited temperature range) as \(\Delta H^\ddagger = 24 \pm 2\) kcal mol\(^{-1}\) and \(\Delta S^\ddagger = -5 \pm 5\) cal mol\(^{-1}\) K\(^{-1}\) (Figure 2)\textsuperscript{36}.

**Table 1:** Rate constants of thermolysis of (\(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph}\))Ti(CH\textsubscript{2}Ph\textsubscript{3}) (5)

<table>
<thead>
<tr>
<th>T (in °C)</th>
<th>Solvent</th>
<th>Conc. (x 10(^{-2}) M)</th>
<th>(k_1) (x 10(^{-5}) s(^{-1}))</th>
<th>(k_2) (x 10(^{-6}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.5</td>
<td>C(_6)D(_6)</td>
<td>2.6</td>
<td>19.5</td>
<td>14.8</td>
</tr>
<tr>
<td>65.0</td>
<td>C(_6)D(_6)</td>
<td>2.6</td>
<td>7.6</td>
<td>8.0</td>
</tr>
<tr>
<td>57.5</td>
<td>C(_6)D(_6)</td>
<td>2.6</td>
<td>3.2</td>
<td>2.6</td>
</tr>
<tr>
<td>50.0</td>
<td>C(_6)D(_6)</td>
<td>2.6</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>65.0</td>
<td>C(_6)D(_6)</td>
<td>1.3</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td>65.0</td>
<td>C(<em>6)D(</em>{12})</td>
<td>2.7</td>
<td>7.2</td>
<td>7.0</td>
</tr>
<tr>
<td>65.0</td>
<td>THF-(\text{d}_8)</td>
<td>2.5</td>
<td>5.6</td>
<td>16.7</td>
</tr>
</tbody>
</table>
Figure 1: First-order kinetic plots of the thermolysis of 5 in C₆D₆ at different temperatures

Figure 2: Eyring plot of the thermolysis of 5 in C₆D₆ (with error bars)
The kinetics of the secondary degradation process were initially investigated in C_{6}D_{6} at 72.5 °C for starting compound 5 by monitoring the disappearance of the initial thermolysis product (η^5,η^1-C_{5}H_{4}CMe_{2}C_{6}H_{4})Ti(CH_{2}Ph)_{2} (7) relative to the internal ferrocene standard, after full conversion of 5. The secondary process also follows simple first-order kinetics in 7 with a rate constant k_{2} of 1.3 x 10^{-5} s^{-1}, an order of magnitude smaller than that found for the conversion of 5 to 7 at this temperature (Table 1). Assuming that the titanium tribenzyl 5 is cleanly converted to 7, followed by a secondary decomposition of 7, the overall disappearance of diamagnetic signal relative to the internal standard can be used to determine the rate constant of the secondary degradation process, since the organometallic species are completely soluble at the concentrations used and both decomposition processes are cleanly first-order, and thus independent on concentration. Indeed, monitoring the disappearance of diamagnetic titanium species in C_{6}D_{6} at 72.5 °C affords simple first-order kinetics with k_{2} = 1.5 x 10^{-5} s^{-1}, equal (within experimental error) to the rate constant determined for the decomposition of 7, thus indicating that there is no direct conversion of 5 to the secondary decomposition product. Similar analysis of the data from the experiments at other temperatures (Table 1) allowed the determination of the kinetic parameters for the secondary degradation process as ΔH^{‡} = 24 ± 2 kcal mol^{-1} and ΔS^{‡} = -11 ± 5 cal mol^{-1} K^{-1}.

Monitoring the thermolysis of 5 in cyclohexane-d_{12} and in THF-d_{8} at 65.0 °C shows that the decomposition processes follow first-order kinetics in these solvents also (Table 1). The rate constants in C_{6}D_{12} of k_{1} = 7.2 x 10^{-5} s^{-1} and k_{2} = 7.0 x 10^{-6} s^{-1} are close to those measured at 65 °C in benzene-d_{6} (k_{1} = 7.6 x 10^{-5} s^{-1}, k_{2} = 8.0 x 10^{-6} s^{-1}). The disappearance of 5 in THF-d_{8} proceeds at a slightly lower rate of k_{1} = 5.8 x 10^{-5} s^{-1}. In contrast, the secondary degradation process occurs significantly more rapidly in THF (k_{2} = 1.7 x 10^{-5} s^{-1}) than in benzene and cyclohexane. These observations suggest either participation of THF solvent in the secondary decomposition process, or significant differences in the polarity of the transition state for the two independent thermolysis processes, resulting in a lower rate constant in THF for the conversion of 5 to 7, but a higher rate constant for the degradation of 7.

The first-order kinetics observed in the course of ortho cyclometalation of the ancillary ligand in titanium tribenzyl 5 to 7 are consistent with an intramolecular pathway. The two most likely pathways are: (a) via formation of an electronically unsaturated benzylidene intermediate, which is likely to be too reactive to observe directly, followed by intramolecular addition of the aryl O-CH bond to the Ti=C bond (Scheme 5, top), or (b) via direct σ-bond metathesis (Scheme 5, bottom). For the cyclometalation of (η^5-C_{5}H_{4}CMe_{2}Ph)_{2}ZrPh_{2} in toluene solvent, Erker and coworkers proposed initial formation of an η^2-benzyne intermediate in the course of the reaction. In contrast, cyclometalation in the related half-sandwich niobium compound, (η^5-C_{5}H_{4}CMe_{2}Ph)Nb(=N[2,6-(i-Pr)_{2}C_{6}H_{3}](NMe_{2})_{2}, proceeds via direct σ-bond metathesis.
Scheme 5: Possible pathways for ligand ortho cyclometalation

The kinetic parameters as determined for thermolysis of 5 of $\Delta H^\ddagger = 24 \pm 2$ kcal mol$\text{⁻¹}$ and $\Delta S^\ddagger = -5 \pm 5$ cal mol$\text{⁻¹}$ K$\text{⁻¹}$ can be consistent with a pathway via a benzylidene intermediate. Bercaw and coworkers showed conclusively that a similar conversion of Cp*$_2$Hf(CH$_2$Ph)$_2$ to Cp*$_2$Hf(CH$_2$-$\sigma$-C$_6$H$_4$) proceeds through a benzylidene intermediate$^{37}$. The entropy of activation of 1 ± 3 cal mol$\text{⁻¹}$ K$\text{⁻¹}$ for this reaction is similar to that observed for the disappearance of 5. Other examples of processes involving alkylidene intermediates show similar small entropy of activation values$^{38}$, in contrast to most examples of direct $\sigma$-bond metathesis ($\Delta S^\ddagger = -10$ to -25 cal mol$\text{⁻¹}$ K$\text{⁻¹}$)$^{39}$. However, the kinetic parameters are no conclusive proof as such for a reaction sequence involving an alkylidene intermediate. Reactions proceeding via an alkylidene can in some cases exhibit large negative entropies of activation$^{40}$, and others, for which the involvement of an alkylidene species is highly unlikely show very small $\Delta S^\ddagger$ values$^{41}$. For example, Berg and coworkers recently found kinetic parameters similar to ours for the ortho cyclometalation of the pendant arene group in [(PhCHMe)N(CH$_2$CH$_2$C(O)Me)$_2$]$_2$Zr(CH$_2$Ph)$_2$. Although the entropy of activation suggests the possibility of a benzylidene intermediate, isotopic labeling experiments conclusively proved a direct $\sigma$-bond metathesis pathway$^{42}$.

2.7 Deuterium labeling studies

To establish the mechanism of the ligand cyclometalation in the decomposition of 5, isotopic labeling experiments were carried out. The partially labeled compound (η$^5$-C$_5$H$_4$CMe$_2$C$_6$D$_5$)Ti(CH$_2$Ph)$_3$ (9) was prepared via the same route as its non-deuterated analog 5, but using C$_6$D$_5$Li instead of PhLi. The $^1$H and $^{13}$C NMR data of 9 are identical to 5 except for the signals of the perdeutero-phenyl ring.
Thermolysis of 9 in $d_6$-benzene (14 h, 65 °C) was monitored by $^1$H and $^{13}$C NMR spectroscopy. This revealed the gradual formation of 1 equiv of toluene, identified as being exclusively C$_6$H$_5$CH$_3$, and the formation of the titanium dibenzyl ($\eta^5,\eta^1$-C$_5$H$_4$CMe$_2$C$_6$D$_4$)Ti(CH$_2$Ph)(CHDPh) (10). The methylene protons of the Ti-CH$_2$Ph group in 10 exhibit the same chemical shifts in the $^1$H NMR as those in 7. The corresponding methylene $^{13}$C NMR resonance splits up into two singlets of equal intensity at 90.6 and 90.5 ppm (90.5 ppm for 7), one for each of two diastereomers, most likely formed from the syn- and anticlinal alkylidene rotamers$^{43}$ (Scheme 6). The available data do not conclusively exclude other potential pathways.

Scheme 6: Formation of the syn- and anticlinal diastereomers of 10

The methylene $^1$H NMR resonances of the Ti-CHDPh ligand show a small upfield deuterium shift ($\Delta\delta = -0.06$ ppm), and are observed as two singlets (the H-D coupling is not resolved) of equal intensity, indicating that the two diastereomers are formed in a 1:1 ratio (vide infra). The methylene carbon is observed as a triplet at $\delta$ 89.6 ppm exhibiting an isotope shift of $\Delta\delta = -0.9$ ppm, and shows a $^1$J$_{CD}$ coupling constant of 19 Hz. Comparable isotope shifts and $^1$J$_{CD}$ coupling constants have been observed for the methylene group of the neopentyl ligand of Cp$_2$Ti(CHDCMe$_3$)(C$_6$D$_5$)$_2$.$^{40c}$

The observations conclusively rule out the presence of a direct $\sigma$-bond metathesis pathway, which would have led to the formation of ($\eta^5,\eta^1$-C$_5$H$_4$CMe$_2$C$_6$D$_4$)Ti(CH$_2$Ph)$_2$ and $\alpha$-d$_1$-toluene. The results confirm the involvement of a benzylidene intermediate (Scheme 5, top). Phosphines are known to be able to stabilize aryne and alkylidene (intermediate) species$^{44}$, but attempts to trap the reactive benzylidene intermediate with PMe$_3$ in our systems failed, resulting only in the formation of ill-defined paramagnetic titanium species.
There is only a very small deuterium isotope effect \( k_{\text{H}}/k_{\text{D}} = 1.23 \pm 0.05 \) at 65.0 °C observed for the thermolysis of 9, indicating that the aryl ortho C-H/D bond is not broken in the transition state of the rate-determining step. For direct \( \sigma \)-bond metathesis, kinetic isotope effects of 5.2-6.6 have been reported\(^{39a,b}\). The small kinetic isotope effect gives additional evidence for the proposed benzylidene pathway.

### 2.8 Thermolysis of other \((\eta^5-C_5H_4CMe_2Ph)Ti(CH_2R)_3\) complexes (\(R = \text{CMe}_3, \text{SiMe}_3\))

Having established the pathway for the thermolysis of \((\eta^5-C_5H_4CMe_2Ph)Ti(CH_2Ph)_3\) (5), we were interested in testing the generality of this reaction. Two examples of alkyl groups that have an established preference for \(\alpha\)-H abstraction processes in their early transition metal complexes are the neopentyl \((\text{CH}_2\text{CMe}_3)\)\(^{45}\) and the neosilyl \((\text{CH}_2\text{SiMe}_3)\)\(^{38c}\) ligands.

A reaction of \((\eta^5-C_5H_4CMe_2Ph)TiCl_3\) (1) with 3 equiv of \(\text{LiCH}_2\text{CMe}_3\) in \(\text{C}_6\text{D}_6\), performed in an NMR tube at ambient temperature, shows rapid release of 1 equiv of neopentane and formation of the ortho cyclometalated titanium dialkyl species \((\eta^5,\eta^1-C_5H_4CMe_2C_6H_4)\text{Ti(CH}_2\text{CMe}_3)_2\) (11). Diagnostic for the formation of the ortho cyclometalated pendant arene group is the resonance for the Ti-C ipso observed at \(\delta 195.5\) ppm in the \(^{13}\text{C}\) NMR. The resonances for the diastereotopic methylene protons of the neopentyl ligands show an AB system at \(\delta 2.72\) and 2.26 ppm with a \(\text{^3}J_{\text{HH}}\) coupling constant of 10.5 Hz. The NMR data closely resemble those found for 7, \((\eta^5,\eta^1-C_5H_4CMe_2C_6H_4)\text{Ti(CH}_2\text{Ph)}_2\). Repeated attempts to isolate 11 from reactions on preparative scale afforded viscous oils that could not be crystallized, probably due to secondary degradation processes similar to those observed for the benzyl species. In contrast with the tribenzyl complex 5, the corresponding trineopentyl compound, \((\eta^5-C_5H_4CMe_2Ph)\text{Ti(CH}_2\text{CMe}_3)_3\), could not be isolated, even at -78 °C.

Treatment of the titanium trichloride complex 1 with 3 equiv of \(\text{LiCH}_2\text{SiMe}_3\) in \(\text{C}_6\text{D}_6\) at ambient temperature affords the titanium trialkyl \((\eta^5-C_5H_4CMe_2Ph)\text{Ti(CH}_2\text{SiMe}_3)_3\) (12). The coordination chemical shifts of the ancillary ligand are comparable to those of 5, and the resonance of the methylene protons of the neosilyl ligands shows as a singlet at \(\delta 1.73\) ppm in the \(^1\text{H}\) NMR spectrum. Compound 12 can be obtained on preparative scale in good yield from \((\eta^5-C_5H_4CMe_2Ph)\text{TiCl}_3\) and 3 equiv of \(\text{ClMgCH}_2\text{SiMe}_3\) as a brown oil, which could not be crystallized. The purity of the compound thus obtained is >95%, as can be seen by \(^1\text{H}\) NMR.

Warming benzene-\(d_6\) solutions of 12 at 50 °C for 70 h leads to liberation of 1 equiv of tetramethyldisilane and the formation of a titanium dineosilyl species with an ortho cyclometalated arene group, \((\eta^5,\eta^1-C_5H_4CMe_2C_6H_4)\text{Ti(CH}_2\text{SiMe}_3)_2\) (13). The Ti-C ipso \(^{13}\text{C}\) NMR resonance is observed at \(\delta 198.6\) ppm, and the methylene protons of
the neosilyl ligands show two doublets at $\delta$ 2.27 and 2.05 ppm with a $^2J_{HH}$ coupling constant of 10.8 Hz.

The mechanistic aspects of the formation of the neopentyl and neosilyl ortho cyclometalated dialkyl titanium complexes 11 and 13 are similar to those previously outlined for the dibenzyl species 7. NMR-scale reaction of ($\eta^5$-C$_5$H$_4$CMe$_2$C$_6$D$_5$)TiCl$_3$ with 3 equiv LiCH$_2$CMe$_3$ gives release of 1 equiv of neopentane-$d_0$ and the formation of the titanium dialkyl species ($\eta^5$,$\eta^1$-C$_5$H$_4$CMe$_2$C$_6$D$_4$)Ti(CH$_2$CMe$_3$) (CHDCMe$_3$) (14, Scheme 7), similar to the conversion of the deuterated tribenzyl compound 9 to 10, indicating the presence of a neopentylidene intermediate. In contrast to the dibenzyl species 10, the two diastereomers of 14 are not formed in a 1:1 ratio. The methylene proton of the Ti-CHDCMe$_3$ group shows as two singlets at $\delta$ 2.65 and 2.18 ppm in a ratio 15:85.

Addition of the ortho C-D bond to the Ti=C bond is expected to proceed selectively in cis fashion$^{46}$ to generate the cyclometalated species 10 or 14 with two stereogenic centers, giving rise to diastereomers (Scheme 7). Apparently, the two possible isomers of the neopentylidene intermediate (syn and anti$^{43}$, Scheme 6) are not formed in equal quantities. Based on arguments formulated by Gibson for tetrahedral alkylidene complexes with one dominant $\pi$-donor ligand that possesses two orbitals of $\pi$-symmetry, such as Cp, the substituent on the alkylidene ligand in the electronically most favorable isomer is expected to point in the direction of that $\pi$-donor (synclinal rotamer)$^{47}$. For the monocyclopentadienyl group 4 alkylidene species [($\eta^5$,$\eta^1$-C$_5$H$_4$CH$_2$CH$_2$N($t$-Bu)]Ti(=CHR)(PMe$_3$)$^{48}$ and {$\eta^5$-C$_5$H$_3$-1,3- [SiMe$_2$CH$_2$P($i$-Pr)$_2$]$_2$}Zr(=CHR)Cl$^{49}$ (and Hf analog$^{50}$), NOESY NMR spectroscopy and X-ray analysis, respectively, indeed indicate the formation of the synclinal rotamer. The orientation is supplemented by agostic interaction of the $\alpha$-H with the metal center$^{51}$, and is generally retained in the solution structure. On the other hand, ready syn/anti isomerization has been reported for Mo(CHR)(NAr)(OR')$_2$ species ($\Delta G^\ddagger = 16$-$18$ kcal mol$^{-1}$)$^{52}$, even at temperatures as low as -70 $^\circ$C$^{53}$, and Re(CR)(CHR')(OR')$_2$ species ($\Delta G^\ddagger = 25$-$30$ kcal mol$^{-1}$)$^{54}$, and the molybdenum complexes were found to display a marked difference in reactivity between the anti and the syn isomer, e.g. in olefin metathesis$^{55}$. Nevertheless, it is likely that, in our titanium system, the tert-butyl group of the neopentylidene ligand in the transient alkylidene species will preferably adopt a synclinal orientation with respect to the cyclopentadienyl ligand (Scheme 7). Based on the data available we cannot establish whether, in the transformation of ($\eta^5$-C$_5$H$_4$CMe$_2$C$_6$D$_5$)Ti(CH$_2$Ph)$_3$ (9) to 10, the benzyldiene intermediate is immediately formed as a 1:1 syn/anti mixture, or if rapid rotation around the Ti=C bond equilibrates the initially formed syn rotamer to a syn/anti mixture$^{56}$. Given the highly reactive nature of the alkylidene species in our systems, rapid rotation around the Ti=C bond seems unlikely. It may be taken into account that the reactions of the benzyl and neopentyl species were conducted at different temperatures, 50 $^\circ$C and room temperature, respectively. As a consequence, the energy difference between the syn and anti benzyldiene species will presumably be (much) smaller than for the neopentylidene intermediates, which may explain the
1:1 syn/anti ratio in the former system. In summary, we cannot give an unambiguous explanation for the observed differences in syn/anti isomer preference for the two alkyl species.

Scheme 7: Formation of (η⁵,η¹-C₅H₄CMe₂C₆D₄)Ti(CH₂R)(CHDR)

The instantaneous ortho cyclometalation of the trineopentyl system (η⁵-C₅H₄CMe₂Ph)Ti(CH₂CMe₃)₃ precludes a kinetic study of this system. An analysis of the reaction kinetics for the thermolysis of the neosilyl complex 12 was conducted by ¹H NMR, for reactions at 50.0, 57.5, 65.0 and 72.5 °C, relative to an internal ferrocene standard. In all instances, the primary thermolysis of 12 follows first-order kinetics (Table 2) and an overall disappearance of diamagnetic signal by a secondary process can be observed, similar to the decomposition pattern observed for the benzyl derivative 5. The corresponding Eyring plot is shown in Figure 3, from which the activation parameters ΔH‡ = 21 ± 2 kcal mol⁻¹ and ΔS‡ = -18 ± 4 cal mol⁻¹ K⁻¹ are obtained.

Table 2: Rate constants of the thermolysis of (η⁵-C₅H₄CMe₂Ph)Ti(CH₂SiMe₃)₃ (12) in C₆D₆

<table>
<thead>
<tr>
<th>T (in °C)</th>
<th>Conc. (x 10⁻² M)</th>
<th>k₁ (x 10⁻⁵ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.5</td>
<td>2.6</td>
<td>6.0</td>
</tr>
<tr>
<td>65.0</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td>57.5</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>50.0</td>
<td>2.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>
The trend reported in the literature for the relative rates of alkylidene formation from metal dialkyl complexes follows the order neopentyl > neosilyl > benzyl, which reflects faster rate-determining α-H abstraction for complexes with alkyl ligands that provide greater steric congestion at the metal center. For example, for the first-order decomposition of Ta(CH₂R)₅ (R = Ph, SiMe₃, or CMe₃), the rate constants follow the order Ph (k = 4.3 x 10⁻⁵ s⁻¹, at 313 K)⁵⁷ < SiMe₃ (k = 3.5 x 10⁻⁴ s⁻¹, 311 K)³⁸c < CMe₃ (too fast to monitor)³⁸c. Our results indicate a deviation from this trend for the complexes studied here. Whereas the neopentyl species *ortho* cyclometalates instantaneously, even at low temperatures, comparison of the first-order rate constants in Table 1 and Table 2 for the other trialkyl species reveals a slower rate of α-H abstraction (expressed in the rate constant k₁) of neosilyl 12 versus benzyl 5 over the temperature range studied. Similar behavior has been observed by Fryzuk and coworkers for the [(η⁵-C₅H₃-1,3-(SiMe₂CH₂P(i-Pr)₂)₂]Zr(CH₂R)₂Cl (R = Ph, SiMe₃, or CMe₃) system, in which a reversal of the trend in rates is observed (Ph > SiMe₃ > CMe₃)⁴⁹b. In these compounds coordination of the two sterically demand phosphine groups, attached to side-arms on the Cp-ligand, is necessary in the transition state for alkylidene formation. This becomes less favorable with increasing bulk of the alkyl ligands, and helps to explain the otherwise anomalous observation that the more sterically demanding alkyl ligands are thermally less reactive.

While the enthalpies of activation, associated with the rate-determining α-abstraction step, are similar for the benzyl and neosilyl complexes (24 kcal mol⁻¹ for 5, and 21 kcal mol⁻¹ for 12), a large difference in the entropy of activation is observed between 5 and 12. As mentioned above, the ΔS‡ of -5 cal mol⁻¹ K⁻¹ for the

**Figure 3:** Eyring plot of the thermolysis of 12 in C₆D₆ (with error bars)
initial decomposition of the tribenzyl complex 5 is in accord with the small negative values of -1 to -10 cal mol\(^{-1}\) K\(^{-1}\) typically observed for the majority of C-H bond abstraction processes studied\(^{38}\). The result for the trineosilyl compound 12 (\(\Delta S^\ddagger = -18\) cal mol\(^{-1}\) K\(^{-1}\)) shows considerable departure from these values, but compares well with the activation parameters found for the related compound \([\eta^5-C_5H_7-1,3-(SiMe_2CH_2P(i-Pr)_2)]Zr(CH_2Ph)_2\)Cl (\(\Delta H^\ddagger = 19\) kcal mol\(^{-1}\), \(\Delta S^\ddagger = -22\) cal mol\(^{-1}\) K\(^{-1}\))\(^{49b}\). The more negative entropy of activation for 12 suggests a more ordered transition state for alkylidene formation with respect to that of 5. Applying Fryzuk’s arguments (\textit{vide supra})\(^{49b}\) for our systems, the pendant arene group may perform a similar function as the pendant phosphine arms in their systems in the alkylidene formation. Interaction with the arene moiety would facilitate \(\alpha\)-H elimination, and give a more negative entropy of activation due to the more ordered transition state with respect to the starting dialkyl. It may be noted that in the related \(\text{Cp}(O-PR_2)\)TiNp\(_2\) systems, the pendant phosphine group is not coordinated in the starting dineopentyl compound, but does coordinate to the titanium center in the neopentylidene complex \(\text{Cp}(O-PR_2)\)Ti(\(-CHCMe_3\))\(^{58}\). Similarly, multihapto coordination, e.g. \(\eta^2\)-coordination, of the benzyl ligands in the tribenzyl species 5 can help to induce \(\alpha\)-H elimination, and the availability of three benzyl groups, and thus three ligands that can potentially facilitate alkylidene formation, will presumably afford a less negative entropy value. In the transformation of \(\text{Cp}^*\text{W(NO)}(CH_2\text{CMe}_3)(CH_2R)\) (\(R = \text{CMe}_3\) or \(\text{Ph}\)) in benzene-\(d_6\) solvent, to give free neopentane and \(\text{Cp}^*\text{W(NO)}(CHDR)(C_6D_5)\) via rate-limiting alkylidene formation and 1,2-\(\text{cis}\) addition of benzene-\(d_6\), the first-order rate constant is higher for the mixed benzyl/neopentyl species than for the sterically more demanding dineopentyl species\(^{56}\). It is well possible that multihapto coordination of the benzyl ligand increases the propensity for \(\alpha\)-H elimination. In our systems, a subtle balance between aromatic interactions in the transition state for alkylidene formation, and the intrinsic steric congestion of the alkyl ligands as such, may explain the rapid cyclometalation observed for the neopentyl species.

2.9 Conclusions

Trichloride and trialkyl titanium complexes with the benzyl-substituted cyclopentadienyl ligand \([C_5H_4\text{CMe}_2\text{Ar}]^-\) (\(\text{Ar} = \text{Ph}, 3,5-\text{Me}_2\text{C}_6\text{H}_3\)) can be conveniently prepared in good yields. The pendant arene group in \((\eta^5-C_5H_4\text{CMe}_2\text{Ar})\)Ti(CH_2Ph)_3 complexes can be cyclometalated via C-H addition to a benzylidene moiety initially generated by \(\alpha\)-elimination from one of the benzyl ligands. The process is relatively slow (\(k \approx 10^{-5}\) s\(^{-1}\) at 333 K), the rate-determining step being the formation of the benzylidene intermediate. Kinetic investigations show that the initial decomposition of these compounds follows first-order kinetics, despite the occurrence of a secondary degradation process. The deuterium labeling experiments and the activation parameters obtained from the initial thermolysis reaction are consistent with an intramolecular \(\alpha\)-H abstraction process. Analysis of
other trialkyl (η⁵-C₅H₄CMe₂Ph)Ti-complexes with -CH₂R ligands (R = SiMe₃, CMe₃) reveals that the reaction rates for the different alkyl ligands follow the order neopentyl > benzyl > neosilyl. This trend is different from that observed in the literature, presumably as a consequence of a subtle balance between aromatic interactions, via the pendant arene group or the benzyl ligands, in the alkylidene formation transition state, and the intrinsic steric bulk of the alkyl ligands.

2.10 Experimental Section

General considerations - All experiments were performed under a nitrogen atmosphere using standard Schlenk and glove-box techniques. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use. Diethyl ether and pentane (Aldrich) were distilled from Na/K alloy prior to use. Methylene chloride (Aldrich) was dried on molecular sieves (4Å, Aldrich) before use. - NMR spectra were recorded on Varian Gemini 200/300 and Unity 500 spectrometers. The ¹H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ = 7.15 ppm for C₆D₆, δ = 7.24 ppm for CDCl₃), and the ¹³C NMR spectra to resonances of the carbon atoms in the deuterated solvents (δ = 128 ppm for C₆D₆). Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive). Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Given values are the average of at least two independent determinations. For compounds 5, 6 and 9 the found C content is low whereas the Ti and H values are as expected. This may be due to the formation of inert Ti-carbides upon combustion. - TiCl₄, Me₃SiCl, Mg and PhCH₂Br (Aldrich) were used as received. Li[C₅H₄CMe₂Ar]⁹, Me₂Mg(dioxane)₅⁹, LiCH₂CMe₃⁶¹ and LiCH₂SiMe₃⁶¹ were prepared according to published procedures. C₅H₄(SiMe₃)CMe₂Ar was prepared from Li[C₅H₄CMe₂Ar] and Me₃SiCl, and PhCH₂MgBr from Mg and PhCH₂Br.

Preparation of (η⁵-C₅H₄CMe₂Ph)TiCl₃ (1) - To a stirred solution of TiCl₄ (0.78 g, 4.1 mmol) in 20 ml of methylene chloride, cooled at -40 °C, 0.80 g (3.7 mmol) of solid Li[C₅H₄CMe₂Ph] was added. The red-brown suspension was warmed to room temperature, after which it was stirred for another 16 hours. The solvent was removed in vacuo and the residue was stirred with 10 ml of pentane, which was subsequently pumped off. The resulting red-brown oil was extracted with toluene. Cooling the extract to -40 °C yielded 1 as brown crystals in a 50% yield (0.67 g; 1.83 mmol). Compound 1 was also obtained from the reaction of TiCl₄ with C₅H₄(SiMe₃)CMe₂Ph in CH₂Cl₂ in 65% yield. - ¹H NMR (300 MHz, C₆D₆): δ 7.0 (m, 3H, Ph p- and m-H), 6.82 (m, 2H, Ph o-H), 6.25 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 5.97 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 1.53 (s, 6H, CMe₂) - ¹³C NMR (75.4 MHz, C₆D₆): δ 154.4 (Ph C ipso), 148.1 (Cp C ipso), 128.7 (Ph m-CH), 126.8 (Ph p-CH), 126.2 (Ph o-CH), 123.5, 121.8 (Cp CH), 41.0 (CMe₂ C ipso), 28.8 (CMe₂)

Preparation of (η⁵-C₅H₄CMe₂-3,5-Me₂C₆H₃)TiCl₃ (2) - To a stirred solution of TiCl₄ (1.0 g, 5.3 mmol) in 20 ml of dichloromethane, cooled at -40 °C, 1.16 g (5.3 mmol) of solid Li[C₅H₄CMe₂-3,5-Me₂C₆H₃] was added. The red suspension was warmed to room temperature and stirred for 16 h. The salts were separated by centrifugation and subsequent
decanting. The solvent was removed in vacuo from the supernatant, and the resulting red-brown oil was extracted with pentane. Cooling the extract to -40 °C yielded orange crystals of the title compound. Yield: 1.28 g (3.50 mmol, 66%). Compound 2 was also obtained from the reaction between TiCl₄ and C₅H₄(SiMe₃)CMe₂-3,5-Me₂C₆H₃ in methylene chloride in 70% yield. 

- ¹H NMR (300 MHz, C₆D₆): δ 6.69 (s, 2H, Ar o-H), 6.66 (s, 1H, Ar p-H), 6.37 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 6.03 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 2.10 (s, 6H, ArMe), 1.63 (s, 6H, CMe₂) - ¹³C NMR (75.4 MHz, CD₂Cl₂): δ 158.0 (Ar C ipso), 149.8 (Cp C ipso), 140.2 (Ar m-C ipso), 130.3 (Ar p-CH), 126.5 (Cp CH), 127.4 (Ar o-CH), 124.5 (Cp CH), 43.1 (CMe₂ C ipso), 30.8 (CMe₂), 23.4 (ArMe) - Anal. Calcd. for C₁₆H₁₉TiCl₃: C, 52.57; H, 5.24; Ti, 13.10; Cl, 29.09. Found: C, 52.42; H, 5.32; Ti, 12.85; Cl, 28.91.

Preparation of (η⁵-C₅H₄CMe₂Ph)TiMe₃ (3) - To a solution of 1 (360 mg, 1.07 mmol) in 30 ml of toluene, cooled at -50 °C, 1.63 mmol of dimethyl magnesium (as a 1.3M solution in diethyl ether) was added. The suspension was allowed to warm to room temperature and stirred for another 2 hours. The solvent was removed in vacuo and the residue extracted with pentane. Pumping off the pentane yielded 3 as a brown oil that solidified upon standing at -40 °C. Yield: 67% (200 mg, 0.72 mmol). - ¹H NMR (200 MHz, C₆D₆): δ 7.1-7.2 (m, 4H, Ph o- and m-H), 7.04 (m, 1H, Ph p-H), 5.89 (ps. t, 3JHH = 2.8 Hz, 2H, Cp), 5.80 (ps. t, 3JHH = 2.8 Hz, 2H, Cp), 1.39 (s, 6H, CMe₂), 1.31 (s, 9H, TiMe) - ¹³C NMR (75.4 MHz, C₆D₆): δ 150.4 (Ph C ipso), 144.3 (Cp C ipso), Ph m-CH overlapped by solvent, 126.7 (Ph o-CH), 126.2 (Ph p-CH), 114.1 (Cp CH), 109.6 (Cp CH), 63.1 (TiMe), 34.4 (CMe₂ C ipso), 29.5 (CMe₂)

Preparation of (η⁵-C₅H₄CMe₂-3,5-Me₂C₆H₃)TiMe₃ (4) - To a solution of 2 (0.95 g, 2.6 mmol) in 15 ml of benzene, 1.86 g (4.0 mmol) of Me₂Mg(dioxane)₀.₅ was added. The suspension was stirred at ambient temperature for 2 hours while the color changed gradually from red to yellow. The mixture was centrifuged and the salts were separated by decantation. The solvent was removed in vacuo, and the residue extracted with pentane. Evaporation of the solvent yielded 4 as a yellow oil that solidified on standing (0.59 g, 2.0 mmol, 75%). The compound is very soluble in pentane, but may be crystallized from this solvent at low temperature to yield analytically pure material. - ¹H NMR (300 MHz, C₆D₆): δ 6.94 (s, 2H, Ar o-H), 6.69 (s, 1H, Ar p-H), 5.95 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 5.80 (ps. t, 3JHH = 2.7 Hz, 2H, Cp), 1.39 (s, 6H, ArMe), 1.31 (s, 9H, TiMe) - ¹³C NMR (75.4 MHz, C₆D₆): δ 150.3 (s, Ar C ipso), 144.7 (s, Cp C ipso), Ph m-CH overlapped by solvent, 127.6 (Ph o-CH), 126.7 (Ph p-CH), 114.1 (Cp CH), 109.6 (Cp CH), 63.1 (TiMe), 34.4 (CMe₂ C ipso), 29.5 (CMe₂)

Preparation of (η⁵-C₅H₄CMe₂Ph)Ti(CH₂Ph)₃ (5) - To a stirred solution of 1 (1.54 mmol) in 30 ml of diethyl ether, cooled at -40 °C, a solution of benzyl magnesium bromide (4.62 mmol) in diethyl ether (1.26M) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 3 hours. The solvent was removed in vacuo after which the red solid was extracted with pentane. Cooling to -40 °C yielded red crystals of 5 (0.56 g, 1.11 mmol, 72%). - ¹H NMR (500 MHz, C₆D₆): δ 7.17-7.11 (m, 10H, Ph m- and o-H and Bz m-H), 7.02 (m, 1H, Ph p-H), 6.90 (t, 3JHH = 7.5 Hz, 3H, Bz p-H),
Neutral (η^5-C₅H₄CMe₂Ph)TiR₃ Complexes: Synthesis and Reactivity

6.81 (d, ^3JHH = 7.5 Hz, 6H, Bz o-H), 5.74 (ps. t, ^3JHH = 2.8 Hz, 2H, Cp), 5.50 (ps. t, ^3JHH = 2.8 Hz, 2H, Cp), 2.97 (s, 6H, Ti-CH₂), 1.38 (s, 6H, CMe₂) - ^13C NMR (125.7 MHz, C₆D₆): δ 149.6 (s, Ph C ipso), 149.1 (s, Bz ipso), 146.7 (s, Cp ipso), 128.8 (dm, ^1JCH = 158 Hz, Bz m-CH, overlap with solvent), 128.5 (d, ^1JCH = 151 Hz, Ph m-CH, overlap with solvent), 127.0 (dm, ^1JCH = 161 Hz, Bz o-CH), 126.5 (dm, ^1JCH = 156 Hz, Ph o-CH), 126.4 (dm, ^1JCH = 156 Hz, Ph p-CH), 123.0 (dm, ^1JCH = 160 Hz, Bz p-CH), 118.4 (dm, ^1JCH = 168 Hz, Cp CH), 113.5 (dm, ^1JCH = 172 Hz, Cp CH), 93.5 (t, ^1JCH = 123 Hz, Ti-CH₂), 40.5 (s, CMe₂ C ipso), 30.2 (q, ^1JCH = 122 Hz, CMe₂) - Anal. Calcd. for C₃5H₃₆Ti: C, 83.32; H, 7.19; Ti, 9.49. Found: C, 82.63; H, 7.32; Ti, 9.35.

Preparation of (η^5-C₅H₄CMe₂-3,5-Me₂C₆H₃)Ti(CH₂Ph)₃ (6) - To a stirred solution of 0.48 g (1.31 mmol) of 2 in diethyl ether (-40 °C), 3.94 mmol PhCH₂MgBr was added dropwise as a solution in diethyl ether (1.26M). The reaction mixture was allowed to warm to room temperature and was subsequently stirred for 3 hours. The volatiles were removed in vacuo and the residue was stirred with 10 ml of pentane, which was subsequently pumped off. The red solid was extracted with pentane and concentration and cooling to -40 °C gave dark red crystals of 6 in a 70% yield (0.49 g, 0.92 mmol). - ^1H NMR (500 MHz, C₆D₆): δ 7.15 (t, ^3JHH = 7.5 Hz, 6H, Bz m-H), 6.95 (s, 2H, Ar o-H), 6.90 (t, ^2JHH = 7.5 Hz, 2H, Bz o-H), 6.70 (s, 1H, Ar p-H), 5.80 (ps. t, ^2JHH = 2.8 Hz, 2H, Cp), 5.51 (ps. t, ^2JHH = 2.8 Hz, 2H, Cp), 2.99 (s, 6H, Ti-CH₂), 2.16 (s, 6H, ArMe), 1.45 (s, 6H, CMe₂) - ^13C NMR (125.7 MHz, C₆D₆): δ 149.4 (s, Ar C ipso), 149.2 (s, Bz ipso), 147.3 (s, Cp ipso), 137.7 (s, Ar m-C ipso), 128.8 (dm, ^1JCH = 156 Hz, Bz m-CH, overlap with solvent), 128.3 (dm, ^1JCH = 131 Hz, Ar p-CH, overlap with solvent), 127.0 (dm, ^1JCH = 153 Hz, Bz o-CH), 124.5 (d, ^1JCH = 155 Hz, Ar o-CH), 123.0 (d, ^1JCH = 160 Hz, Bz p-CH), 118.4 (dm, ^1JCH = 171 Hz, Cp CH), 113.5 (dm, ^1JCH = 172 Hz, Cp CH), 93.5 (t, ^1JCH = 124 Hz, Ti-CH₂), 40.4 (s, CMe₂ C ipso), 30.3 (q, ^1JCH = 126 Hz, CMe₂) - Anal. Calcd. for C₃₇H₄₀Ti: C, 83.44; H, 7.57; Ti, 8.99. Found: C, 82.54; H, 7.62; Ti, 8.76.

In situ preparation of (η^5,η^1-C₅H₄CMe₂C₆H₄)Ti(CH₂Ph)₂ (7) - A solution of 5 in C₆D₆ (5 x 10⁻² M) was kept at 50 °C for 50 hours. Upon thermolysis the color of the solution changed from red to dark red. NMR spectroscopy indicates the formation of toluene and compound 7. - ^1H NMR (500 MHz, C₆D₆): δ 8.00 (d, ^3JHH = 7.5 Hz, 1H, Ph m-H, next to o-C ipso), 7.12 (t, ^3JHH = 7.5 Hz, 4H, Bz m-H), 7.02 (m, Ph m-H, overlap with toluene), 6.94 (t, ^3JHH = 6.8 Hz, 1H, Ph p-H), 6.86 (t, ^3JHH = 7.5 Hz, 2H, Bz p-H), 6.77 (d, ^3JHH = 7.5 Hz, 1H, Ph o-H), 6.71 (d, ^3JHH = 7.5 Hz, 4H, Bz o-H), 5.84 (ps. t, ^3JHH = 2.8 Hz, 2H, Cp), 5.74 (ps. t, ^3JHH = 2.8 Hz, 2H, Cp), 3.11 (d, ^2JHH = 10 Hz, 2H, Ti-CH₂), 2.77 (d, ^2JHH = 10 Hz, 2H, Ti-CH₂), 1.32 (s, 6H, CMe₂) - ^13C NMR (125.7 MHz, C₆D₆): δ 200.6 (Ph o-C ipso), 170.5 (Cp C ipso), 148.8 (Ph C ipso), 146.6 (Bz C ipso), 129.7 (Ph m-CH²), next to o-C ipso), 129.7 (Ph m-CH), 128.8 (Bz m-CH), 127.2 (Bz o-CH), 123.8 (Ph p-CH), 123.7 (Ph o-CH), 122.9 (Bz p-CH), 119.3 (Cp CH), 114.5 (Cp CH), 90.5 (^1JCH = 125 Hz, Ti-CH₂), 43.9 (CMe₂ C ipso), 29.3 (CMe₂).

In situ preparation of (η^5,η^1-C₅H₄CMe₂-3,5-Me₂C₆H₂)Ti(CH₂Ph)₂ (8) - A solution of 6 in C₆D₆ (4.5 x 10⁻² M) was kept at 50 °C for 50 hours. Upon thermolysis the color of the solution changed from red to dark red. NMR spectroscopy indicates the formation of
Chapter 2

toluene and compound 8. - 1H NMR (500 MHz, C6D6): δ 7.12 (t, \(3J_{HH} = 7.5\) Hz, 4H, Bz m-H), 6.83 (t, \(3J_{HH} = 7.5\) Hz, 2H, Bz p-H), 6.69 (s, 1H, Ar p-H), 6.65 (d, \(3J_{HH} = 7.5\) Hz, 4H, Bz o-H), 6.58 (s, 1H, Ar o-H), 5.84 (ps. t, \(3J_{HH} = 2.5\) Hz, 2H, Cp), 5.71 (ps. t, \(3J_{HH} = 2.5\) Hz, 2H, Cp), 3.27 (s, 3H, ArMe, adjacent to Ti-C ipso), 3.14 (d, \(2J_{HH} = 9.5\) Hz, 2H, Ti-CH2), 3.03 (d, \(2J_{HH} = 9.5\) Hz, 2H, Ti-CH2), 2.10 (s, 3H, ArMe, overlap with toluene), 1.37 (s, 6H, CMe2) - 13C NMR (125.7 MHz, C6D6): δ 201.7 (Ar o-C ipso), 171.8 (Cp C ipso), 148.4 (Bz C ipso), 148.0 (Ar C ipso), 139.4 (Ar m-C ipso, adjacent to Ti-C ipso), 137.3 (Ar m-C ipso), 128.6 (Bz m-CH), 127.6 (Ar p-CH), 125.3 (Bz o-CH), 122.5 (Bz p-CH), 121.7 (Ar o-CH), 119.5 (Cp CH), 116.7 (Cp CH), 94.1 (\(1J_{CH} = 122\) Hz, Ti-CH2), 43.3 (CMe2 C ipso), 29.8 (CMe2), 26.1 (ArMe), 21.8 (ArMe, adjacent to Ti-C ipso)

Preparation of C5H4(SiMe3)CMe2C6D5 - To a solution of 3.20 g (19.8 mmol) bromobenzene-d5 in 50 ml of diethyl ether 7.8 ml of a 2.5M solution (19.7 mmol) of n-BuLi in hexanes was added dropwise. The mixture was stirred for 3 hours. The mixture was cooled to -30 °C and 2.4 ml (2.1 g, 19.8 mmol) of 6,6-dimethylfulvene was added. The yellowish suspension was allowed to warm to room temperature and was stirred for an additional 3 hours. The reaction mixture was cooled with an ice bath and 1.2 equivalents of trimethylsilyl chloride were added. The ice bath was removed and the yellow-white suspension was stirred overnight. The reaction mixture was poured into 100 ml of ice water. The organic and water layers were separated and the water layer was extracted twice with 50 ml of light petroleum. The combined organic layers were dried over magnesium sulfate and the low-boiling volatiles were removed using a rotary evaporator. The residue was distilled using a Kugelrohr apparatus. The product distilled at 130 °C at 0.4 Torr. Yield: 3.30 g (12.5 mmol, 64%) - 1H NMR (300 MHz, CDCl3): δ 6.35, 6.28, 6.13 (br, 1H, Cp), 3.22 (s, 1H, Cp), 1.53 (s, 6H, CMe2), -0.06 (s, 9H, SiMe3)

Preparation of (η^5-C5H4CMe2C6D5)TiCl3 (1a) - The same procedure was followed as described for the preparation of the non-isotope labeled analog 1, using C5H4(SiMe3)CMe2C6D5 (3.20 g, 12.1 mmol) and TiCl4 (1.3 ml, 2.3 g, 12 mmol). Yield: 2.67 g (7.8 mmol, 65%). - 1H NMR (300 MHz, C6D6): δ 6.27 (ps. t, \(3J_{HH} = 2.8\) Hz, 2H, Cp), 5.99 (ps. t, \(3J_{HH} = 2.8\) Hz, 2H, Cp), 1.53 (CMe2) - 13C NMR (75.4 MHz, C6D6): δ 154.2 (Cp C ipso), 123.3, 121.7 (Cp CH), 40.8 (CMe2 C ipso), 28.7 (CMe2) - Anal. Calcd for C14H10D5Cl3Ti62: C, 49.09; H+D, 5.88; Ti, 13.98. Found: C, 49.13; H+D, 5.91; Ti, 13.87.

Preparation of (η^5-C5H4CMe2C6D5)Ti(CH2Ph)3 (9) - The same procedure was followed as described for the preparation of 5, using (η^5-C5H4CMe2C6D5)TiCl3 (1.11 g, 3.2 mmol) to afford the title compound in 75% yield (1.23 g, 2.4 mmol). - 1H NMR (300 MHz, C6D6): δ 7.15 (t, \(3J_{HH} = 7.7\) Hz, 6H, Bz m-H), 6.91 (t, \(3J_{HH} = 7.3\) Hz, 3H, Bz p-H), 6.82 (d, \(3J_{HH} = 7.3\) Hz, 6H, Bz o-H), 5.75 (ps. t, \(3J_{HH} = 2.7\) Hz, 2H, Cp), 5.50 (ps. t, \(3J_{HH} = 2.7\) Hz, 2H, Cp), 2.97 (s, 6H, Ti-CH2), 1.38 (s, 6H, CMe2) - 13C NMR (75.4 MHz, C6D6): δ 149.1 (Bz C ipso), 146.7 (Cp C ipso), 128.8, 127.0, 123.0 (Bz CH), 118.4, 113.4 (Cp CH), 93.5 (Ti-CH2), 40.4 (CMe2 C ipso), 30.1 (CMe2) - Anal. Calcd for C35H31D5Ti62: C, 82.49; H+D, 8.11. Found: C, 82.00; H+D, 8.12.

In situ preparation of [η^5,η^1-C5H4CMe2C6D4]Ti(CH2Ph)(CHDPH) (10) - A solution of 26.5 mg (52 µmol) of 9 in 0.6 ml of benzene in an NMR tube with Teflon valve was
warmed at 50 °C for 50 hours. The color of the solution changed from red to dark red. - \( ^1H \) NMR (300 MHz, \( CD_6D_6 \)): \( \delta \) 7.12 (t, \( J_{HH} = 7.7 \) Hz, 4H, Bz \( m \)-H), 6.86 (t, \( J_{HH} = 7.3 \) Hz, 2H, Bz \( p \)-H), 6.71 (d, \( J_{HH} = 7.3 \) Hz, 4H, Bz \( o \)-H), 5.85 (ps, t, \( J_{HH} = 2.6 \) Hz, 2H, Cp), 5.74 (ps, t, \( J_{HH} = 2.6 \) Hz, 2H, Cp), 3.11 (d, \( J_{HH} = 9.9 \) Hz, 1H, Ti-CH\(_2\)), 3.05 (s, 0.5H, Ti-CDH, anti), 2.75 (d, \( J_{HH} = 9.9 \) Hz, 1H, Ti-CH\(_2\)), 2.71 (s, 0.5H, Ti-CDH, syn), 1.32 (s, 6H, CMe\(_2\)) - \( ^13C \) NMR (75.4 MHz, \( CD_6D_6 \)): \( \delta \) 200.6 (Ph \( o \)-C\(_{ipso}\)), 170.2, 148.9 (Cp and Ph C\(_{ipso}\)), 146.6, 146.5 (Bz C\(_{ipso}\)), 128.8 (Bz \( m \)-CH), 127.2 (Bz \( o \)-CH), 122.9 (Bz \( p \)-CH), 119.3, 114.5 (Cp CH), 90.6, 90.5 (Ti-CH\(_2\)), 89.6 (t, \( J_{CD} = 19 \) Hz, Ti-CDH), 43.9 (CMe\(_2\) C\(_{ipso}\)), 29.3 (CMe\(_2\)).

In situ preparation of \( (\eta^5-C_5H_4CMe_2Ph)Ti(CH_2CMe_3)_2 \) (11) - A solution of 20.7 mg (61.3 \( \mu \)mol) of 1 in 0.5 ml benzene-\( d_6 \) was added to 14.4 mg (184 \( \mu \)mol) neopentyl lithium to form the title compound, one equivalent of neopentane, and three equivalents of lithium chloride. To remove the LiCl, the benzene solution was filtered over a small piece of paper (pre-dried at 75 °C) wedged in a Pasteur pipette. - \( ^1H \) NMR (300 MHz, \( CD_6D_6 \)): \( \delta \) 8.38 (d, \( J_{HH} = 7.1 \) Hz, 1H, Ph \( m \)-H next to \( o \)-C\(_{ipso}\)), 7.01-6.82 (m, 3H, Ph \( o \)-, \( m \)-, \( p \)-H), 6.56 (ps. t, \( J_{HH} = 2.6 \) Hz, 2H, Cp), 6.22 (ps. t, \( J_{HH} = 2.6 \) Hz, 2H, Cp), 2.72 (d, \( J_{HH} = 10.6 \) Hz, 2H, Ti-CH\(_2\)), 2.26 (d, \( J_{HH} = 10.3 \) Hz, 2H, Ti-CH\(_2\)), 1.50 (s, 6H, CMe\(_2\)), 0.94 (s, 18H, CMe\(_3\)), 0.90 (s, 12H, CMe\(_4\)) - \( ^13C \) NMR (75.4 MHz, \( CD_6D_6 \)): \( \delta \) 195.5 (Ph \( o \)-C\(_{ipso}\)), 170.5, 145.7 (Ph and Cp C\(_{ipso}\)), 132.4, 128.8, 124.1, 123.5 (Ph CH), 117.0, 109.0 (Cp CH), 112.8 (Ti-CH\(_2\)), 38.6 (CMe\(_2\) C\(_{ipso}\)), 34.1 (CMe\(_3\) C\(_{ipso}\)), 33.9 (CMe\(_3\)), 31.6 (CMe\(_2\)), 29.8 (CMe\(_4\)), 29.5 (CMe\(_4\) C\(_{ipso}\)).

Preparation of \( (\eta^5-C_5H_4CMe_2Ph)Ti(CH_2SiMe_3)_3 \) (12) - To a solution of 1.03 g (3.05 mmol) of 1 in 70 ml of diethyl ether cooled at -70 °C, 9.2 mmol of ClMgCH\(_2\)SiMe\(_3\) was added dropwise as a 1.62M solution in diethyl ether. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. The volatiles were removed in vacuo and the residue was extracted with pentane. The pentane was pumped off to afford 0.93 g (1.88 mmol, 62%) of the title compound as a brown oil. The purity of 12 is >95%, as seen by \( ^1H \) NMR. - \( ^1H \) NMR (300 MHz, \( CD_6D_6 \)): \( \delta \) 7.2-6.9 (m, 5H, Ph), 6.05 (m, 2H, Cp), 6.01 (m, 2H, Cp), 1.73 (s, 6H, Ti-CH\(_2\)), 1.46 (s, 6H, CMe\(_2\)), 0.14 (s, 27H, SiMe\(_3\)) - \( ^13C \) NMR (75.4 MHz, \( CD_6D_6 \)): \( \delta \) 149.8, 144.4 (Ph and Cp C\(_{ipso}\)), 128.4, 126.5, 126.3 (Ph CH), 111.9, 109.87 (Cp CH), 85.8 (Ti-CH\(_2\)), 40.1 (CMe\(_2\) C\(_{ipso}\)), 34.1 (CMe\(_3\) C\(_{ipso}\)), 33.9 (CMe\(_3\)), 31.6 (CMe\(_2\)), 29.8 (CMe\(_4\)), 29.5 (CMe\(_4\) C\(_{ipso}\)).

In situ preparation of \( (\eta^5-C_5H_4CMe_2C_6H_4)Ti(CH_2SiMe_3)_2 \) (13) - An NMR tube with a solution of 12 in \( CD_6D_6 \) (6 x 10\(^{-2}\) M) was heated at 50 °C for 70 h. NMR spectroscopy reveals the formation of tetramethylsilane and 13. - \( ^1H \) NMR (300 MHz, \( CD_6D_6 \)): \( \delta \) 8.26 (d, \( J_{HH} = 7.0 \) Hz, 1H, Ph \( m \)-H next to o-C\(_{ipso}\)), 7.05-6.9 (m, 5H, Ph), 6.05 (m, 2H, Cp), 6.01 (m, 2H, Cp), 1.73 (s, 6H, Ti-CH\(_2\)), 1.46 (s, 6H, CMe\(_2\)), 0.14 (s, 27H, SiMe\(_3\)) - \( ^13C \) NMR (75.4 MHz, \( CD_6D_6 \)): \( \delta \) 195.5 (Ph o-C\(_{ipso}\)), 170.5, 145.7 (Ph and Cp C\(_{ipso}\)), 132.4, 128.8, 124.1, 123.5 (Ph CH), 117.0, 109.0 (Cp CH), 112.8 (Ti-CH\(_2\)), 38.6 (CMe\(_2\) C\(_{ipso}\)), 34.1 (CMe\(_3\) C\(_{ipso}\)), 33.9 (CMe\(_3\)), 31.6 (CMe\(_2\)), 29.8 (CMe\(_4\)), 29.5 (CMe\(_4\) C\(_{ipso}\)).

In situ preparation of \( (\eta^5-C_5H_4CMe_2C_6D_4)Ti(CH_2CMe_3)(CHDCMe_3) \) (14) - A solution of 15.5 mg (46 \( \mu \)mol) of 1a in 0.5 ml benzene-\( d_6 \) was added to 10.8 mg (138 \( \mu \)mol) neopentyl lithium to form the title compound, one equivalent of neopentane, and three

61
equivalents of lithium chloride. To remove the LiCl, the benzene solution was filtered over a small piece of paper (pre-dried at 75 °C) wedged in a Pasteur pipette. - \( ^1 \)H NMR (500 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta \) 6.56 (s, 2H, Cp), 6.22 (s, 2H, Cp), 2.73 (d, \( J_{HH} = 10.3 \) Hz, 1H, Ti-CH\(_2\)), 2.65 (s, 0.15H, Ti-CDH, anti), 2.26 (d, \( J_{HH} = 10.3 \) Hz, 1H, Ti-CH\(_2\)), 2.18 (s, 0.85H, Ti-CDH, syn), 1.50 (s, 6H, CMe\(_2\)), 0.94 (s, 18H, CMe\(_3\)), 0.90 (s, 12H, CMe\(_4\)) - \( ^{13} \)C NMR (125.7 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta \) 195.4 (Ph \( \text{o-Cipso} \)), 170.4, 145.7 (Ph and Cp C \( \text{ipso} \)), 117.0, 109.0 (Cp CH), 113.2, 113.0, 112.8 (Ti-CH\(_2\)), 111.6 (t, \( J_{CD} = 17 \) Hz, Ti-CDH), 111.6 (t, \( J_{CD} = 17 \) Hz, Ti-CDH), 38.6 (CMe\(_2\) C \( \text{ipso} \)), 34.1 (CMe\(_3\) C \( \text{ipso} \)), 33.9 (CMe\(_3\)), 31.6 (CMe\(_2\)), 29.8 (CMe\(_4\)), 29.5 (CMe\(_4\) C \( \text{ipso} \))

**Kinetic experiments** - In a typical experiment, the compound of interest (A, 0.0188 mmol) was dissolved in 0.7 ml of benzene-\( \text{d}_6 \) (2.6 x 10\(^{-2} \) M) at ambient temperature, together with ferrocene (1.0 mg) used as internal standard. The solution was transferred to an NMR tube with Teflon valve, which was then directly inserted into the (pre-heated) probe of the NMR spectrometer. The sample was given 20 min to equilibrate to the specified temperature. \( ^1 \)H NMR spectra were recorded at regular intervals (1 hour). The progress of thermolysis was monitored by integration of the Cp peak(s) in the \( ^1 \)H NMR relative to the internal ferrocene standard. The rate constants were calculated via nonlinear-least-squares analysis of the plot of \( \ln([A]/[A_0]) \) versus time using Microcal\textsuperscript{TM} Origin\textsuperscript{TM} 5.0 software (Version 5.0; Microcal Software, Inc., 1991-1997). The maximum relative error found (2.1%) was used as the standard error for all determined \( k_1 \) rate constants. The temperature of the NMR probe was measured using a methanol temperature standard. At a NMR probe setting of 65 °C (for different experiments), the temperature was found to fluctuate between 65 ± 1 °C. The established error in the temperature of 1K at this temperature was used for the whole temperature range.

### 2.11 References and notes


(8) The \([\text{C}_5\text{H}_4\text{CMe}_2\text{Ph}]\) ligand was for the first time prepared by: Nesmeyanov, A.N., Materikova, R.B., Brainina, E.M., Kochetkova, N.S., Bull. Acad. Sci. USSR Div. Chem. Sci. 1969, 1220


(16) Gorsich, R.D., J. Am. Chem. Soc. 1958, 80, 4744

(17) Gorsich, R.D., J. Am. Chem. Soc. 1960, 82, 4211


(22) Powell, J., Shaw, B.L., J. Chem. Soc. A 1968, 597

(23) Okuda, J., Chem. Ber. 1990, 123, 87


(25) Lund, E.C., Livinghouse, T., Organometallics 1990, 9, 2426


The $^1$H NMR spectrum obtained after complete thermolysis (24 h, 80 °C) only showed the toluene resonances. No precipitation was observed.

The errors in the kinetic parameters were calculated from the error propagation formulas derived from the Eyring equation (by: Morse, P.M., Spencer, M.D., Wilson, S.R., Girolami, G.S., Organometallics 1994, 13, 1646).

The synclinal and anticlinal diastereomers of the cyclometalated species are defined with respect to the orientation of the alkylidene substituents in the two possible alkylidene rotamers they are formed from (synclinal: alkylidene substituent pointing towards the Cp ligand; anticlinal: pointing away).

Organometallics 2001, 20, 2533

Neutral ($\eta^5$-C$_5$H$_4$CMe$_2$Ph)TiR$_3$ Complexes; Synthesis and Reactivity


The synclinal and anticlinal diastereomers of the cyclometalated species are defined with respect to the orientation of the alkylidene substituents in the two possible alkylidene rotamers they are formed from (synclinal: alkylidene substituent pointing towards the Cp ligand; anticlinal: pointing away)

Organometallics 1999, 13, 1646).


Schrock, R.R., Acc. Chem. Res. 1979, 12, 98
Van der Heijden, H., Hessen, B., manuscript in preparation


Since the detection method used in the elemental analysis cannot distinguish between D$_2$O and H$_2$O, the sample H+D content was calculated by multiplying the experimentally found H+D content with $(2n+m)/(n+m)$ for a sample containing $n$ D and $m$ H atoms.