3 Cyclopentadienyl Amido Titanium Bis-alkyl and Bis-aryl Complexes \([C_5H_4(CH_2)_nNR]TiR'_2\). A Study of C-H Activation Processes. Stable Alkylidene and Olefin Complexes.

3.1 Introduction.

In the previous chapter a facile route has been described for a wide range of cyclopentadienyl amido titanium dichloro complexes \([C_5H_4(CH_2)_nNR]TiCl_2\). These dichlorides provide a good opportunity to prepare and investigate the Cp-amido titanium carbyl compounds \([C_5H_4(CH_2)_nNR]Ti(Cl)R'\) and \([C_5H_4(CH_2)_nNR]TiR'_2\).

Bis-cyclopentadienyl and bis-pentamethylcyclopentadienyl group 4 metal bis-carbyl complexes, \(Cp'_2MR_2\), are well-known and have been studied extensively but the information on the synthesis and properties of analogues with linked amido (or alkoxy/aryloxy) cyclopentadienyl spectator ligands is scarce. These carbyl complexes can be of scientific and industrial importance since they form sources for cationic species \({[C_5H_4(CH_2)_nNR]TiR'}^+\), the active species in catalytic olefin polymerization. Furthermore, bis-carbyl complexes \(Cp'_2MR_2\) are known to undergo C-H activation (e.g. yielding alkylidene, aryne/alkyne and olefin complexes), Cp ligand activation and C-X activation and have a very rich and interesting insertion chemistry with unsaturated substrates which gives valuable synthons for organic synthesis. It would be interesting to explore possibilities to make new alkylidene, aryne/alkyne and olefin complexes starting from Cp-amido titanium complexes \([C_5H_4(CH_2)_nNR]TiR'_2\). In addition, the intrinsic reactivity of the Cp-amido ligands is hardly investigated and we want to know whether these Cp-amido ligands can be regarded as truely inert spectator ligands or whether they may bring additional reactivity to the compounds.

Here we report the synthesis and characterization of Cp-amido titanium alkyl and aryl species \([C_5H_4(CH_2)_nNR]TiR'_2\). In the second part of this chapter the thermolyses of a representative selection of bis carbyl compounds \([C_5H_4(CH_2)_nNR]TiR'_2\) will be described and discussed.
3.2 Synthesis of Cp-Amido Titanium Bis(carbyl) Complexes $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{TiR'}_2$. 

The amido functionalized cyclopentadienyl titanium dichlorides $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{TiCl}_2$ (Chapter 2) are excellent precursors for the preparation of alkyl and aryl compounds $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{TiR'}_2$ of which a wide range could be obtained in moderate to high yields (Scheme 1, Table 1). The general procedure is the classical but efficient salt metathesis route. The complexes were obtained by adding the appropriate organolithium or Grignard reagents to cooled (-80°C) ether solutions of the dichlorides, $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{TiCl}_2$, followed by work up and crystallization from pentane. Some of the products are oils, but they could be identified satisfactorily by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy.

![Scheme 1. Routes to Cp-amido titanium carbyl complexes.](image-url)
Table 1. Cp-amido titanium carbyl complexes \([\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{TiR}'\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield(%)</th>
<th>Color</th>
<th>Cryst./Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiMe}_2) (15)</td>
<td>61</td>
<td>yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{i-Pr}]\text{TiMe}_2) (16)</td>
<td>83</td>
<td>yellow</td>
<td>cryst.</td>
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<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiMe}_2) (17)</td>
<td>76</td>
<td>yellow</td>
<td>oil</td>
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<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiMe}_2) (18)</td>
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<td>yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{N}-\text{i-Pr}]\text{TiMe}_2) (19)</td>
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<td>yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{Ti}(\text{CH}_2\text{Ph})_2) (20)</td>
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<td>red</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{i-Pr}]\text{Ti}(\text{CH}_2\text{Ph})_2) (21)</td>
<td>84</td>
<td>red</td>
<td>oil</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{Ph})_2) (22)</td>
<td>69</td>
<td>red</td>
<td>oil</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{Ti}(\text{CH}_2\text{Ph})_2) (23)</td>
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<td>red</td>
<td>oil</td>
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<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{N}-\text{i-Pr}]\text{Ti}(\text{CH}_2\text{Ph})_2) (24)</td>
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<td>red</td>
<td>oil</td>
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<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiPh}_2) (25)</td>
<td>26</td>
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<td>cryst.</td>
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<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiPh}_2) (26)</td>
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<td>orange-yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{TiPh}_2) (27)</td>
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<td>green-yellow</td>
<td>cryst.</td>
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<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{Ti}(\text{CH}_2\text{CMe}_3)_2) (28)</td>
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<td>oil</td>
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<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_3)_2) (29)</td>
<td>68</td>
<td>orange-yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2) (30)</td>
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<td>oil</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2) (31)</td>
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<td>yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2) (32)</td>
<td>67</td>
<td>yellow</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}) (33)</td>
<td>69</td>
<td>red</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{Me})\text{Cl}) (34)</td>
<td>64</td>
<td>brown</td>
<td>cryst.</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{i-Pr}]\text{Ti}(\text{Me})\text{Cl}) (35)</td>
<td>74</td>
<td>red</td>
<td>oil</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{C}_3\text{H}_5)\text{Cl}) (37)</td>
<td>32</td>
<td>red-brown</td>
<td>cryst./oil</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{C}_3\text{H}_5)_2) (38)</td>
<td>75</td>
<td>red</td>
<td>oil</td>
</tr>
</tbody>
</table>

### 3.3 Synthesis of Cp-amido titanium chloro alkyl complexes \([\text{C}_5\text{H}_4(\text{CH}_2)_n\text{NR}]\text{Ti(Cl)}\text{R}'\).

Reaction of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\) with 1 eq. \text{PhCH}_2\text{MgCl} in ether afforded the mono benzyl chloro complex \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}\) (33) in 69% yield as red crystals. Performing a similar reaction with 1 eq. of \text{MeLi} resulted in a mixture of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\), \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiMe}_2\) and the methyl-chloro complex \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{Me})\text{Cl}\) (34). Heating the reaction mixture at 50 °C (benzene) for 24 h resulted in the
desired product $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(\text{Me})\text{Cl}$ (34). Complexes 33 and 34 could also be synthesized by synproportionation of the bis(alkyl) and dichloro compounds. When an equimolar mixture of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$ (4) and $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiMe}_2$ (17) in C$_6$D$_6$ was monitored by $^1$H NMR spectroscopy virtually no reaction occurred at room temperature but at 50 °C the methyl-chloro complex 34 started to form slowly and after 24 h the conversion was complete (Scheme 2).$^6$

![Scheme 2](image)

**Scheme 2.** Synproportionation of 4 and 17 to 34.

Under similar conditions, the reaction of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$ and $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(\text{CH}_2\text{Ph})_2$ appeared to be considerably slower. After 98 h at 50 °C the conversion was completed. Attempts to prepare the analogous chloro phenyl, chloro neopentyl and chloro dimethyl-phenyl-methyl (neophyl) complexes failed. Under these conditions, the thermolysis of the bis(carbyl) compounds (vide infra) competes with the synproportionation.

### 3.4 Stable Titanium(IV) Allyl and iso-Propyl Complexes.

Interestingly, the reaction of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$ with 1 eq. of $i\text{-PrMgCl}$ did not result in the formation of a trivalent titanium species like the formation of Cp$_2$TiCl by treatment of Cp$_2$TiCl$_2$ with $i\text{-PrMgCl}$.$^{11a}$ Instead a red-brown oil was obtained and a $^1$H NMR spectrum indicated exclusive formation of the titanium(IV) species $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(i\text{-Pr})\text{Cl}$ (35) (Scheme 3).
Treatment of [C₅H₄(CH₂)₂N-t-Bu]TiCl₂ under similar conditions with 2 eq of i-PrMgCl gave a dark red solution as expected for [C₅H₄(CH₂)₂N-t-Bu]Ti(i-Pr)$_2$ (36) but on workup it decomposed and a black tarry product was isolated which could not be identified. However, the location and the narrow line widths of the $^1$H NMR resonances of the mixture showed that no paramagnetic species had been formed and presumably no reduction had occurred. Although the iso-propyl group is known to give β-H transfer, the iso-propyl chloro compound (35) is thermally stable and can be heated at 70 °C for hours without decomposition. A similar lack for β-H transfer has been reported for the tert-butyl complex (2,6,-i-Pr₂-C₆H₃O)$_3$TiCMe₃. Similarly, the reaction of C₅H₄(CH₂)₂N-t-Bu]TiCl₂ with 1 or 2 eq. of the allyl Grignard did not proceed by reduction of the titanium complex. Diamagnetic dark red oils were obtained which were identified on the basis of their $^1$H and $^{13}$C NMR spectra as the allyl complexes complexes [C₅H₄(CH₂)₂N-t-Bu]Ti(η$^3$-C₃H₅)Cl (37) and [C₅H₄(CH₂)₂N-t-Bu]Ti(η$^3$-C₃H₅)$_2$ (38) (Scheme 4).
Scheme 4.

The reactions of the dichloride 4 with iso-propyl and allyl Grignard reagents proceed clearly different from Cp₂TiCl₂. Instead of reduction of the metal center, simple salt metathesis occurred and Ti(IV)-species are obtained. The reactions observed clearly demonstrate the higher resistance of the Cp-amido titanium dichlorides against reduction than their Cp₂Ti congeners and are in accordance with the higher reduction potentials observed for the Cp-amido titanium dichlorides.

Titanium(IV) alkyls Cp₂TiR₂ and Cp⁺₂TiR₂ are borderline cases with respect to their oxidation/reduction stabilities. They tend to disproportionate to Ti(III) or even Ti(II) species. Photochemical reduction of Cp₂TiMe₂ has been observed¹⁰ whereas the reduction of other titanocene (Cp⁺₂Ti(Cl)R)¹⁰b alkyls are thermally induced. Reduction also is often observed when early transition metal halides react with Grignard reagentia and aluminum alkyls.¹¹,¹²

As shown, the cyclopentadienyl amido stabilized titanium alkyls [C₅H₅(CH₂)ₙNR]TiR’₂ and [C₅H₅(CH₂)ₙNR]TiR'Cl are substantially more stable against reduction than the bis(pentamethyl)cyclopentadienyl analogues.
3.5 Spectroscopic Characterization.

The $^1$H and $^{13}$C NMR spectra of the carbyl complexes 15-37 show for the Cp-amido ligand the same general features as observed for the dichloro compounds. For example, the methine proton of the N-iso-propyl groups of $[C_5H_4(CH_2)_2N-i-Pr]TiMe_2$ (16), $[C_5H_4(CH_2)_2N-i-Pr]TiMe_2$ (19), $[C_5H_4(CH_2)_2N-i-Pr]Ti(\text{CH}_2\text{Ph})_2$ (21) and $[C_5H_4(CH_2)_2N-i-Pr]Ti(\text{CH}_2\text{Ph})_2$ (24) are strongly shifted down-field and an extra CH$_2$ unit in the backbone results in a larger $\Delta\delta$ of the C$_5$H$_4$-A$_2$B$_2$ resonances as well as an upfield shift of the NCH$_2$ resonance (Table 2).

For the dimethyl complexes 15-19 the $^1$H NMR resonances of the two methyl groups bonded to titanium were found at 0.49, 0.42, 0.47, 0.40 and 0.30 ppm respectively, at higher field compared to the 12 electron complex CpTiMe$_3$ (1.16 ppm)$^{13}$ but at lower field than for the 16 electron complex Cp$_2$TiMe$_2$ (-0.17 ppm). However, care should be taken suggesting a direct relation between electronic structure and chemical shifts in $^1$H and $^{13}$C NMR since the methyl resonance for the 14 electron complex Cp[Ph(NSiMe$_3$)$_2$]TiMe$_2$ is found at 1.20 ppm and for the 12 electron complex [CPh(NSiMe$_3$)$_2$]TiMe$_2$ at 1.94 ppm. For all benzyl (20-24), neopentyl (28 and 29) and 2-phenyl-2-methyl propyl (neophyl; 30, 31 and 32) compounds the protons of the $\alpha$-carbon of the alkyl groups are diastereotopic (figure 1) giving an AB spin system with $^2J_{HH}$ of 9-11.5 Hz.

![Figure 1](image-url)

Figure 1. Illustration of the diastereotopic $\alpha$-protons in 20-24 and 28-32.
Table 2. Selected $^1$H and $^{13}$C NMR data of the bis-benzyl compounds 20-24.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C$_5$H$_4$</th>
<th>C$_5$H$_4$CH$_2$</th>
<th>NCH$_2$</th>
<th>NCCH$_2$</th>
<th>NR</th>
<th>$R_2$</th>
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<tbody>
<tr>
<td>20</td>
<td>5.93, 5.15</td>
<td>2.23</td>
<td>3.34</td>
<td>3.40</td>
<td>7.19, 6.90$^a$, 6.80$^a$, 2.40, 2.19</td>
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<td>136.79$^a$, 117.30, 113.63</td>
<td>28.51</td>
<td>73.70</td>
<td>44.39</td>
<td>75.90 (122.3)</td>
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<tr>
<td>21</td>
<td>5.83, 5.25</td>
<td>2.26</td>
<td>3.41</td>
<td>5.73, 1.03</td>
<td>7.19, 6.89$^a$, 6.83$^b$, 2.38, 2.17</td>
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<tr>
<td></td>
<td>136.59$^a$, 116.85, 115.04</td>
<td>29.06</td>
<td>61.78</td>
<td>51.23, 20.45</td>
<td>74.40 (120.9)</td>
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<tr>
<td>22</td>
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<td>2.10</td>
<td>3.29</td>
<td>1.50</td>
<td>7.22$^m$, 6.90$^a$, 6.82$^b$, 2.73, 2.27</td>
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<tr>
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<td>135.67$^a$, 118.04, 117.42</td>
<td>30.61</td>
<td>62.61</td>
<td>60.96, 30.11</td>
<td>78.04 (120.5)</td>
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<tr>
<td>23</td>
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<td>1.96</td>
<td>2.43</td>
<td>1.36</td>
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<td>124.84$^a$, 117.59, 114.20</td>
<td>30.87</td>
<td>60.11</td>
<td>26.47</td>
<td>42.55</td>
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<tr>
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<td>2.03</td>
<td>2.58</td>
<td>1.40</td>
<td>6.57, 1.22</td>
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<td></td>
<td>125.10$^a$, 118.84, 114.13</td>
<td>32.79</td>
<td>47.37</td>
<td>26.87</td>
<td>46.91, 20.59</td>
<td>72.88 (120.9)</td>
</tr>
</tbody>
</table>

$^a$) ipso-C$_5$H$_4$
To relieve their electronic unsaturation, early transition metal complexes tend to bind benzyl ligands in a $\eta^2$ or $\eta^3$ fashion. $^{1a,16}$ $\eta^2$-Benzyl complexes show some characteristic features in the $^1$H and $^{13}$C NMR spectra: (a) high-field shifts of the ortho $^1$H ($\delta < 6.8$ ppm, i.e. Ti(CH$_2$Ph)$_4$: 6.42 ppm$^{16a}$) and CH$_2$ $^{13}$C ($\delta < 75$ ppm) resonances and (b) large $^1$J$_{CH}$ coupling constants for the CH$_2$ group ($^1$J$_{CH} > 130$ Hz). $^{17}$ For the bis-benzyl complexes 20-24 (Table 3) the $^1$H resonances of the ortho protons (6.77-6.83 ppm) are shifted only slightly up-field indicating a regular $\eta^1$-bonded benzyl. Additionally, the $^{13}$C NMR spectra of 20-24 showed the benzylic resonances between 72 and 78 ppm and the normal values of the coupling constants ($^1$J$_{CH} = 120-122$ Hz) exclude significant $\eta^2$-bonding of the benzyl ligands. Whether this is due to the fact that these titanium complexes are not very electrophilic or that the $\eta^2$-bonding of the benzyl ligands is sterically prohibited in these species is not clear yet.

3.6 Stability of Cp-Amido Titanium Carbyl Complexes; Ligand Activation.

In Cp$_2$M and Cp$_2$ZrR$^+$ complexes of the early transition metals, many examples are known in which the ligands interfere in processes like $\alpha$, $\beta$, $\gamma$ and $\delta$ C-H activation$^{18}$. Some well defined systems have been used to study these C-H activations of the ligands. These systems can be roughly divided in two classes: (a) complexes with ligands containing $\beta$-hydrogen atoms like ethyl or phenyl groups, known to give olefin$^{19}$ or aryne species$^{20}$, (b) complexes lacking $\beta$-hydrogen but with $\alpha$, $\gamma$ and $\delta$-hydrogens like methyl, neopentyl or neophyl groups which are sources for alkylidenes$^{21}$ and metallacycles$^{22}$.

Another point is that the cyclopentadienyl and pentamethylcyclopentadienyl$^{23}$ ligands seldom are strictly inert spectator ligands and interfere in reactions between ligands and substrates of choice at the metal center. $^{24}$ This can have dramatic consequences for the reactivity and catalytic activity of the complexes. For example, for the cationic Cp$_2$ZrR$^+$, chain transfer by activation of a Cp$^*$ ligand is found to interfere with insertion of olefin$^{25}$. Also other substituted Cp ligands like tert-butyl cyclopentadienyl show similar ligand activation$^{26}$ and other alkyl/aryl substituted cyclopentadienyls may be prone to ligand activation as well. When designing a catalyst, it should be kept in mind that the auxiliary ligand system used may interfere in the catalytic cycle. Therefore, if a stable catalytic process is to be designed it is important to have full information about the intrinsic reactivity of the spectator ligand used.
3.6.1 Thermal Stability: All carbyl complexes 15-38 can be handled at room temperature although the (bis)allyl and bis(phenyl) species have to be stored at -30 °C. Cyclohexane-$d_{12}$ solutions of the bis(phenyl) compounds 25-27 show thermal decomposition with benzene formation at room temperature. For all alkyl and aryl derivatives formation of RH was observed at elevated temperatures (75-120 °C). A comparison of the thermal stability of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiR}_2\) versus \(\text{Cp}_2\text{TiR}_2\) is given in Table 3. Compared to the \(\text{Cp}_2\text{Ti}\)-analogues the bis-methyl 17, the bis-benzyl 22, bis-neopentyl 29 and bis-neophyl 31 complexes are thermally considerably more stable. In contrast the bis-phenyl compound 26 is considerably less stable than their \(\text{Cp}_2\text{Ti}\)-analogue.

Table 3. Half life-times \((t_{1/2})\) of a selection of \(\text{Cp}\)-amido titanium bis(carbyl) complexes \([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NR}]\text{TiR}_2\) compared with bis(carbyl) titanocenes \(\text{Cp}_2\text{TiR}\). Samples were prepared as \(\approx 0.4\) M solutions

<table>
<thead>
<tr>
<th>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiMe}_2) (15)</th>
<th>temp. ((^\circ\text{C})), (t_{1/2}), solv.</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100, 4 h, (\text{C}<em>7\text{D}</em>{14})</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{i-Pr}]\text{TiMe}_2) (16)</td>
<td>100, 4.5 h, (\text{C}<em>7\text{D}</em>{14})</td>
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</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiMe}_2) (17)</td>
<td>100, 4.5 h, (\text{C}<em>7\text{D}</em>{14})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{TiMe}_2) (18)</td>
<td>80, 1.3 h, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{N}-\text{i-Pr}]\text{TiMe}_2) (19)</td>
<td>80, 14 min, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{i-Pr}]\text{Ti}(\text{CH}_2\text{Ph})_2) (21)</td>
<td>120, 4.5 h, (\text{C}<em>7\text{D}</em>{14})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{Ph})_2) (22)</td>
<td>120, 1.7 h, (\text{C}<em>7\text{D}</em>{14})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}]\text{Ti}(\text{CH}_2\text{Ph})_2) (23)</td>
<td>100, 2 h, (\text{C}<em>7\text{D}</em>{14})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_3\text{N}-\text{i-Pr}]\text{Ti}(\text{CH}_2\text{Ph})_2) (24)</td>
<td>80, 1.5 h, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiPh}_2) (26)</td>
<td>75, 7 min, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_3)_2) (29)</td>
<td>75, 11 min, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
<tr>
<td>([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2) (31)</td>
<td>75, 60 min, (\text{C}<em>6\text{D}</em>{12})</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\(\text{Cp}_2\text{TiMe}_2\) | 76, 70 min, \(\text{C}_6\text{D}_6\) | 27a |
| \(\text{Cp}_2\text{Ti}(\text{CH}_2\text{Ph})_2\) | 80, 7 h, \(\text{C}_6\text{H}_6\) | 27b |
| \(\text{Cp}_2\text{TiPh}_2\) | 74, 2.5 h, \(\text{C}_6\text{H}_{12}\) | 27c |
| \(\text{Cp}_2\text{Ti}(\text{CH}_2\text{CMe}_3)_2\) | 20, 56 min, \(\text{C}_6\text{H}_{12}\) | 21g |

In relation to the different \(\text{Cp}\)-amido ligands in bis(methyl) and bis(benzyl) compounds some interesting trends in the order of thermal stability can be observed. The amido
substituent R in the C$_2$-bridged compounds hardly affects the thermal stability. The C$_3$-bridged complexes are thermally less stable than the C$_2$-bridged analogues and for the C$_3$-bridged carbyl complexes the group R of the amide function also affects the thermal stability. The [C$_5$H$_4$(CH$_2$)$_3$N-i-Pr]TiR$_2$ compounds are significantly less stable than [C$_5$H$_4$(CH$_2$)$_3$NMe]TiR$_2$ (R = Me, CH$_2$Ph) and are the least stable of the series tested.

3.6.2 Light Sensitivity: A number of group 4 metal carbyls have been reported to be light sensitive e.g. Cp$_2$TiMe$_2$, Cp$_2$TiPh$_2$. Of the complexes discussed here, [C$_5$H$_4$(CH$_2$)$_2$NMe]TiMe$_2$ (15) is sensitive to light and has to be stored in the dark. Sterically more demanding Cp-amido ligands seem to influence the light sensitivity of these complexes. [C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]TiMe$_2$ (16), [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiMe$_2$ (17), [C$_5$H$_4$(CH$_2$)$_2$NMe]TiMe$_2$ (18) and [C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]TiMe$_2$ (19) are considerably less light sensitive than 15. The character of the carbyl is also important: benzyl, neopentyl and neophyl complexes 20-32 are light stable.

3.7 Synthesis of Cp-Amido Titanium Olefin, Benzyne and Alkylidene Complexes.

Since bis(carbyl) complexes are frequently used as sources for olefin, aryne, alkylidene and metallacycle complexes, it was decided to see whether it is possible to prepare these types of compounds starting from the Cp-amido titanium bis(carbyl) species. Because the rather open structure of the Cp-amido complexes, it was expected that the olefin, aryne and alkylidene compounds need to be stabilized with a Lewis-base like PMe$_3$. Therefore a selection of [C$_5$H$_4$(CH$_2$)$_n$NR]TiR$_2$ compounds was thermolyzed in the presence of PMe$_3$. An exploratory preliminary investigation revealed that [C$_5$H$_4$(CH$_2$)$_n$N-t-Bu]TiR$_2$ gave the most consistent results.

![Scheme 5](image-url)
3.7.1 Generation of Olefin Complexes: Complexes with two linear alkyl groups often show β-hydrogen transfer followed by reductive elimination of RH and formation of the olefin complex\textsuperscript{19} (Scheme 5), an important reaction for the synthesis of metallacycles and dimerization of alkenes\textsuperscript{32}.

Scheme 6.
An in situ prepared solution of \([C_5H_4(CH_2)2N-t-Bu]TiEt_2\) \((38)\) (-40 °C) in ether was warmed to room temperature in the presence of PMe_3. The solution became dark purple and evolution of ethane (GC-MS, 1.02-1.03 mol gas/mol Ti) was observed. Workup gave a dark purple oil of which the \(^1\)H NMR spectrum was consistent with the formation of the PMe_3 stabilized ethene complex \([C_5H_4(CH_2)2N-t-Bu]Ti(C_2H_4)(PMe_3)\) \((39)\) by \(\beta\)-hydrogen elimination in the initially formed diethyl complex \((38)\) (Scheme 6). The same reaction without phosphine also gave ethane but the organometallic product(s) (a black oil) could not be identified. A \(^1\)H NMR spectrum showed broad resonances in region of 7-0 ppm which could not be assigned to an ethene complex.

The \(^1\)H NMR spectrum \((C_6D_6)\) of \(39\) shows besides a doublet at 0.86 ppm \((9H, PMe_3)\) and a singlet at 0.82 ppm \((9H, t-Bu)\), 12 resonances which integrate each for 1H. A Cosy NMR experiment reveals that these 12 resonances originate from 3 independent ABCD spin systems. Two spin systems at low field \((6.6-4.2\) and \(3.6-2.4\) ppm, resp. \(C_5H_4\) and \(CH_2CH_2\)) are assigned to the \(C_5H_4(CH_2)2N\) moiety. The remaining ABCD spin system with resonances at resp 2.18, 1.64, 1.39 and 0.35 ppm is assigned to an ethene coordinated to titanium. In the \(^{13}\)C NMR spectrum the resonances for the ethene are found at 49.14 \((^2J_{CP} = 10.0\ Hz, ^1J_{CH} = 145.8\ Hz)\) and 44.45 ppm \((^1J_{CH} = 147.5\ Hz)\).

The bonding of the ethene ligand in \(39\) can be considered either as a coordinated ethene to a divalent titanium or as a metallacyclop propane with two sp\(^3\) carbons (Figure 3). NMR data provides indication of which bonding type prevails. The chemical shifts of the ethene protons \((2.2-0.3\ ppm)\) are comparable with, for example, those of the methyl ligands in \([C_5H_4(CH_2)2N-t-Bu]TiMe_2\) \((0.47\ ppm)\) and the benzylic protons in \([C_5H_4(CH_2)2N-t-Bu]Ti(CH_2Ph)_2\) \((2.73, 2.27\ ppm)\). Also the \(^{13}\)C resonances for the complexed ethene \((49.14\ and 44.45\ ppm)\) compare well with the one found for the methyl ligand in \([C_5H_4(CH_2)2N-t-Bu]TiMe_2\) \((47.14\ ppm)\) but are dramatically shifted upfield compared with \(Cp^*\)\(^2\)Ti\((C_2H_4)\)
(105.1 ppm) and free ethene (123 ppm). Hence the conclusion seems justified that 39 can be best represented as a titanacyclopropane species with oxidation state IV rather than an ethene titanium II complex. An example of separate Ti(II) and Ti(IV) isomers has been observed for the constrained-geometry titanium diene complexes $[\text{C}_5\text{Me}_3\text{SiMe}_2\text{NR}]\text{Ti}((\text{R}')\text{CH}=\text{CH}(\text{CHR}')).$ Changing the amido substituent R from t-Bu into Ph, the diene fragment changes from predominantly $\pi$-bound to partly $\pi$-bound and $\sigma$-bound.

Attempts to substitute the ethene in 39 by propene or to insert propene failed. When a large excess of propene was added 39 remained unchanged. In the $^1\text{H}$ NMR spectrum no resonance of free ethene was observed. The propene complex $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(\text{C}_3\text{H}_6)(\text{PMe}_3)$ (40) was prepared independently from $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$ with 2 eq. of $n$-PrMgCl in the presence of PMe$_3$. $^1\text{H}$, $^{13}\text{C}$ and $^{31}\text{P}$ NMR data showed that all 4 possible isomers had been formed. The fact that treatment of 40 with 1 eq. of ethene leads to complete conversion to 39 illustrates the far better affinity of ethene compared to propene. Furthermore, the facile olefin exchange indicates that 39 behaves, at least partly, as a $\eta^2$-olefin Ti(II) species, even though NMR spectroscopy suggests otherwise.
Scheme 7. Equilibrium between $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{C}_2\text{H}_2)(\text{PMe}_3)$ (39) and $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{CH}_2)_4$ (41) and PMe$_3$ in the presence of ethene.

Reaction of 39 with an excess of ethene resulted immediately in a color change from dark purple to brown. $^1$H NMR spectroscopy showed the mixture to be an equilibrium between 39, ethene, the metallacyclopentane complex $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{CH}_2)_4$ (41) and free PMe$_3$ (Scheme 7). Titanacyclopentane complexes have been reported for Cp$_2$Ti$^{35}$ and Cp$^*_2$Ti compounds$^{33}$ but were never isolated and no structural data are available. Cp$_2$Ti(CH$_2$)$_4$ decomposes already at -30 °C and Cp$^*_2$Ti(CH$_2$)$_4$ is in equilibrium with Cp$^*_2$Ti(η$^2$-C$_2$H$_4$) and ethene. When $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{TiCl}_2$ (4) was treated at low temperature (-80 °C) with ClMg(CH$_2$)$_4$MgCl a yellow solution was obtained on warming to -40 °C. Further raising of the temperature resulted in a black solution. The yellow color observed probably can be attributed to the titanacyclopentane complex 41. At higher temperatures this complex looses ethene and generates the unstable Lewis-base free ethene compound $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{C}_2\text{H}_4)$ (42). A black solid was obtained which could not be characterized.$^{36}$ Performing the reaction of 4 with ClMg(CH$_2$)$_4$MgCl in the presence of PMe$_3$ gave 39 and ethene (Scheme 6).$^{37}$

3.7.2 Generation of Benzyne Complexes: Heating (75 °C, 30 min.) of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{TiPh}_2$ in C$_6$D$_{12}$ in the presence of PMe$_3$ resulted in the formation of the benzyne complex $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{C}_6\text{H}_4)(\text{PMe}_3)$ (43) (Scheme 8) and 1 eq. of benzene ($^1$H NMR). A preparative synthesis yielded 53% of pure material. The complex was fully characterized with $^1$H NMR, $^{13}$C NMR, IR spectroscopy and elemental analysis. The structure was elucidated by single crystal X-ray diffraction. A full discussion concerning the synthesis, structure and reactivity towards unsaturated substrates like alkenes, alkynes, nitriles and ketones will be given in the next chapter.

![Scheme 8](image-url)
In the absence of a Lewis-base, thermolysis of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiPh}_2\) (26) in cyclohexane (55-60 °C, 5 h) gave an orange precipitate. $^1$H and $^{13}$C NMR spectra (C$_6$D$_{12}$) reveal the formation of a highly symmetric complex. Resonances are found at 7.92, 7.00, 6.19, 4.87, 4.05, 2.85 and 0.73 ppm which integrate in 2 : 2 : 2 : 2 : 2 : 2 : 9 ratio. This suggests the formation of a Lewis-base free benzyne complex and this observation is supported by the $^{13}$C NMR spectrum which show resonances in the aromatic part at 188.71 (s), 139.60 (d) and 133.48 (d) ppm indicative for a benzyne or $\sigma$-phenylene ligand.

![Figure 4. Two possible structures for \([[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti(C}_6\text{H}_4)\]_2\) (44).](image)

From the low solubility of the orange compound in organic solvents, the complex was tentatively formulated as a dimer \([[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti(C}_6\text{H}_4)\]_2\) (44) with two $\sigma$-phenylene moieties bridging between the metal centers, but higher associations cannot be excluded. Adopting a dinuclear species for 44, two structures are possible (Figure 4). Thermolysis of 26 first generates the monomeric \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti(C}_6\text{H}_4)\) (45) which dimerizes to 44. That 44 must have at least a dimeric structure is indicated by its slow reaction with PMe$_3$ (10 h, 75 °C) to 43 in contrast to the fast formation of 43 by thermolysis of 26 in the presence of PMe$_3$, under the same conditions.

**Table 4.** Selected $^1$H and $^{13}$C NMR data for some $\sigma$-phenylene compounds compared with complexes 26, 43 and 44.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$_3$, H$_5$</th>
<th>H$_4$, H$_5$</th>
<th>C$_1$, C$_2$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(C$_6$H$_4$)$_2$] (44)</td>
<td>7.93</td>
<td>7.00</td>
<td>188.71</td>
<td></td>
</tr>
<tr>
<td>[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(C$_6$H$_4$)(PMe$_3$) (43)</td>
<td>7.82, 7.64</td>
<td>7.16</td>
<td>190.73, 184.53</td>
<td></td>
</tr>
<tr>
<td>[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiPh$_2$ (26)</td>
<td></td>
<td></td>
<td>C$_{ipso}$: 192.50</td>
<td></td>
</tr>
</tbody>
</table>
The quarternary carbons of the ortho-phenylene moiety of 44 show shifts similar as found for 43 (190.73, 184.53 ppm) and 26 (192.50 ppm). Several polynuclear ortho-phenylene compounds have been reported for magnesium,38 mercury39 and zinc.40 The NMR data of 44 resemble those of the tetrameric ortho-phenylene magnesium compound [Mg₄(C₆H₄)₄](THF)₄ (Table 4). The formation of Lewis base free ortho-phenylene titanium 44 is unprecedented and has not been reported for Cp₂Ti and Cp*₂Ti systems.

The thermolysis of [C₅H₅(CH₂)₂N-t-Bu]TiPh₂ (26) was studied in detail in C₆D₆ and C₆D₁₂ at 55 °C. In C₆D₆ 44 and benzene were formed. First, a rather rapid decrease of 26 and a simultaneous increase of 44 and benzene was observed but after 10 hours the ratio of 26 and 44 did not change further and the system appeared to reach an equilibrium. Further heating resulted in slow decomposition of 26 and 44 (products not identified). In C₆D₁₂, at similar concentrations, a rapid and complete conversion of 26 within 6 h was observed together with the formation of 44 (55 %), benzene and unidentified decomposition products. Further heating resulted in further decomposition of 44.
Scheme 9. Reversible decomposition of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiPh}_2 \ (26)$ and trapping of $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{Ti}(\text{C}_6\text{H}_4)$ with PMe$_3$. 
The difference in behavior of 26 in C₆D₆ and C₆D₁₂ can be rationalized by assuming that 44 is in equilibrium with [C₅H₅(CH₂)₂N-t-Bu]Ti(C₆H₄) (45) which reacts with C₆D₆ to give the partially phenyl deuterated 26 (Scheme 9). In addition, the integral of the phenyl and o-phenylene resonances decreased with respect to those of the [C₅H₅(CH₂)₂N-t-Bu] ligand and benzene. This indicates that complex 44 is involved in σ-bond metathesis with C₆D₆ giving deuterated [C₅H₅(CH₂)₂N-t-Bu]Ti(Ph-d₅n)₂. The formation of a mixture of 26 and 44 after heating of 44 in C₆D₆ (75 °C) is a strong evidence for an equilibrium between 26 and 44 in benzene. In C₆D₁₂ 26 is converted into 44 and other decomposition products which presumably are formed by another reaction path from 26 and/or the hypothetical monomeric species [C₅H₅(CH₂)₂N-t-Bu]Ti(C₆H₄) (45).

3.7.3 Generation of Alkylidenes: When a yellow solution of [C₅H₅(CH₂)₂N-t-Bu]Ti(CH₂CMe₃)₂ (29) was heated at 75 °C in C₆D₁₂ in the presence of 2 equivalents of PMe₃ it turned red-brown. After 1.5 h, ¹H NMR spectroscopy showed the exclusive formation of one organometallic product and neopentane. In the Cp range (6.8-4.8 ppm) 5 resonances were present integrating for 1H each. One resonance (d, 6.28 ppm) displayed a small coupling of 1.37 Hz, which is attributed to a Jₚₕ coupling. This proton was tentatively assigned to the α-proton of the alkylidene species [C₅H₅(CH₂)₂N-t-Bu]Ti=C(H)CMe₂(PMe₃) (46). This alkylidene is proposed to be formed by α-H abstraction from one of the neopentyl groups of the bis(neopentyl) complex 29 (Scheme 10).

Thermolysis of [C₅H₅(CH₂)₂N-t-Bu]Ti(CH₂CMe₂Ph)₂ (31) proceeded much slower reaching completion only after 8.5 hours (NMR). The ¹H NMR spectrum showed the same general features as 46 and it is reasonable to identify this as the neophylidene complex [C₅H₅(CH₂)₂N-t-Bu]Ti=C(H)CMe₂Ph(PMe₃) (47).

![Scheme 10](image-url)
The thermolysis of 29 proceeds similar to that of Cp₂Ti(CH₂CMe₃)₂ and CpV(CH₂CMe₅)₂(PMe₃) giving the alkylidene complex 46. In contrast to CpV(CH₂CMe₅Ph)₂(PMe₃) which shows δ-H activation of a phenyl group on the alkyl ligand, producing a metallacycle, 31 undergoes exclusively α-hydrogen abstraction affording the neophyldiene complex 47.

The alkylidene complexes 46 and 47 are easily prepared on multigram scale as red-brown crystalline solids in resp 68 and 66% yield. In C₆D₆, the $^1$H NMR spectrum show the =C(=H)CMe₂R (R = Me, Ph) resonances (6.39 and 6.44 ppm resp.) as phosphorus coupled doublets ($^3J_{PH} = 1.70, 1.28$ Hz resp). The Cp-amido ligand resonances in the $^1$H NMR spectra of 46 and 47 have roughly the same appearance as those of the ethene (39) and the benzyne (43) complexes showing four resonances for the Cp protons and a ABCD spin system for the C₂-bridge. $^{13}$C and $^1$H-coupled $^{13}$C NMR spectra show the carbene resonances at resp 251.39 ppm ($^1J_{CH} = 83.1$ and $^2J_{CP} = 13.1$ Hz) and 245.96 ppm ($^1J_{CH} = 88.0$ and $^2J_{CP} = 12.8$ Hz).

Analogous to a C-C double bond, the double bond of metal alkylidenes is fixed and has a high barrier for rotation around metal-carbon axis. For Cp₂ metal alkylidenes, the p-orbital of the alkylidene is generally believed to be perpendicular to the plane through the metal and the cyclopentadienyl centroids. This fixed orientation of the alkylidene ligand causes, in the case of 46 and 47, two possible orientations (Figure 4). $^1$H, $^{13}$C and $^{31}$P NMR spectra show for each compound that one rotamer is present and NOESY NMR experiments suggest structure A as the most likely.
Figure 4. Possible rotamers for 46 and 47.

Both 46 and 47 show small $^1J_{CH}$ coupling constants (83.1 and 88.0 Hz resp.) for the $\alpha$-carbon of the alkylidene which indicate an agostic interaction between this $\alpha$-proton and titanium. Such interactions have also been reported for $[\eta^5-C_5H_3-1,3-(SiMe_2CH_2P(i-Pr_2))_2]Zr=C(H)Ph(Cl),^{44}$ CpTi(OC(Me_2C_6H_4CMe_2)CH_2PMe_2C(H)CMe_3,^{45}$ and CpV=C(H)CMe_3(DMPE).^{22}

Table 5. Selected NMR data of group IV alkylidene complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>δ M=CH</th>
<th>δ M=CH</th>
<th>$^1J_{CH}$</th>
<th>$^2J_{CP}$</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3(PMe_3) (46)</td>
<td>6.39</td>
<td>251.39</td>
<td>83.1</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td>[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3Ph(PMe_3) (47)</td>
<td>6.44</td>
<td>245.96</td>
<td>88.0</td>
<td>12.8</td>
<td>-</td>
</tr>
<tr>
<td>Cp_2Ti=CH_2(PMe_3)</td>
<td>12.1</td>
<td>286</td>
<td>127</td>
<td>31.7</td>
<td>21f</td>
</tr>
<tr>
<td>Cp_2Ti=C(H)CMe_3(PMe_3)</td>
<td>12.32</td>
<td>312.9</td>
<td>110</td>
<td>27</td>
<td>21g</td>
</tr>
<tr>
<td>Cp_2Ti=C(H)CMe_3C(H)=CH_2</td>
<td>12.06</td>
<td>306.9</td>
<td>111</td>
<td>26.6</td>
<td>46</td>
</tr>
<tr>
<td>CpTi(OC(Me_2C_6H_4CMe_2)CH_2PMe_2)=C(H)CMe_3</td>
<td>11.92</td>
<td>278.1</td>
<td>95</td>
<td>12.2</td>
<td>45</td>
</tr>
<tr>
<td>Cp_2Zr=CH_2(PPh_3)</td>
<td>11.0</td>
<td>248</td>
<td>121</td>
<td>14.6</td>
<td>47</td>
</tr>
<tr>
<td>$[\eta^5-C_5H_3-1,3-(SiMe_2CH_2P(i-Pr_2))_2]Zr=C(H)Ph(Cl)</td>
<td>8.08</td>
<td>229.4</td>
<td>86.8</td>
<td>8.0</td>
<td>44</td>
</tr>
</tbody>
</table>

Compared to the NMR data with other group 4 metal alkylidene complexes, the resonance of the $\alpha$-proton of 46 and 47 shows a large upfield shift (Table 5). The electronic unsaturation of the 16 electron complexes can not be the main reason for the upfield shift. In the related 16 electron complex CpTi(OC(Me_2C_6H_4CMe_2)CH_2PMe_2)=C(H)CMe_3, the $\alpha$-H resonance is observed at 11.92 ppm.^{45} Possibly this strong upfield shift is due to anisotropic effects but without further structural data available no definite conclusions are possible.

3.7.3.1 Insertion of Olefins: To check if the complexes 46 and 47 are active in ROMP catalysis they were reacted with an excess of norbornene but no catalytic activity was observed (25 to 80 °C). In an additional experiment the neopentylidene complex 46 was reacted with 2 eq. of ethene (50 °C) but showed no metathesis. Instead formation of the ethene complex [C_5H_4(C_2H_3)_2N-t-Bu]Ti(C_2H_4)(PMe_3) was observed.^{48} Apparently, the insertion product 48 undergoes fast $\beta$-hydrogen transfer followed by reductive elimination and coordination of 4,4-dimethyl-1-pentene or 4,4-dimethyl-2-pentene yielding the phosphine
olefin adducts 50a-b. A second ethene molecule replaces the 4,4-dimethyl-1-pentenes giving the ethene complex 39 (Scheme 11).

A similar preference for β-hydrogen transfer has been observed for the related complex CpTi(OC(CMe₂C₆H₄CMe₂)CH₂PMe₂)=C(H)CMe₃ although this process is much slower and the metallacyclobutane species could be isolated and fully characterized. The two systems mentioned here differ remarkably from the well known Tebbe reagent which is an excellent precursor for a catalytically active species in olefin metathesis, ROMP catalysis and the living polymerization of norbornene.

Scheme 11. Reaction of [C₅H₄(CH₂)₂N- t-Bu]Ti=C(H)CMe₃(PMe₃) (46) with ethene resulting in the formation of [C₅H₄(CH₂)₂N- t-Bu]Ti(C₂H₄)(PMe₃) (39), 4,4-dimethyl-1-pentene and 4,4-dimethyl-2-pentene.

3.8 Activation of the Cp-Amido Ligands:
Thermolysis of the complexes \([C_5H_4(CH_2)_2N-t-Bu]TiMe_2\) (17) (100 °C) and \([C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2Ph)_2\) (22) (120 °C) in the presence of PMe_3 did not proceed by \(\alpha\)-hydrogen abstraction of the carbyl ligands. When monitored by \(^1\)H NMR spectroscopy, formation of methane (toluene) and, in both cases, iso-butene (\(^1\)H NMR, GC-MS) was observed. No information about the identity of the organometallic product(s) could be obtained as the \(^1\)H NMR spectra showed broad resonances in the region of 7-4 and 3-1 ppm. Similar observations were made during the thermolysis of \([C_5H_4(CH_2)_2N-i-Pr]Ti(CH_2Ph)_2\) (21) (120 °C). In this case toluene and propene were liberated. However, in the case of \([C_5H_4(CH_2)_2N-i-Pr]TiMe_2\) (100 °C) only methane was found and \(^1\)H NMR showed further the usual broad resonances at 7-4 and 3-1 ppm. As already mentioned before, the C\(_3\)-bridged iso-propyl amido titanium dimethyl and dibenzyl complexes 19 and 24 are far less stable than the C\(_2\)-bridged complexes.

Scheme 12. Two possible mechanism for C-H activation of the amido alkyl group in \([C_5H_4(CH_2)_2N-t-Bu]TiR_2\) complexes (\(R = Me, CH_2Ph\)).

The elimination of propene and iso-butene indicates activation of the amido substituent, most probably by \(\gamma\)-H transfer generating imido-like species. Two routes are possible (Scheme 12), one with a six membered transition state in which RH, iso-butene and the imido species are formed in one step (A) or a two-step process with a metalla-aza-cyclobutane compound as intermediate (B). The imido species may decompose or form
dimers or higher aggregates. In fact, activation of the amido substituents is not so surprising since especially the t-Bu group can point a methyl towards the metal center, so that C-H activation becomes feasible. This may be also the case for i-Pr substituents and gives a reasonable explanation for the decreased stability of the C₃-bridged carbyl complexes, since the amido group is pushed closer to the metal than in the C₂-bridged analogues (cf. Chapter 2).

The possibility that [C₅H₄(CH₂)₂N-t-Bu]Ti(C₆H₄)(PMe₃) (43) is generated via the metalla-aza cyclobutane intermediate can be excluded. Only a minor amount of C₆D₅H was obtained (<5%, ¹H NMR) by thermolysis of deca-deutero [C₅H₄(CH₂)₂N-t-Bu]Ti(Ph-d₅)₂ (26-d₁₀)⁵¹ in the presence of excess PMe₃ (C₆D₁₂, 65 °C)⁵². Considering the reaction conditions, it is very likely that also the alkylidenes 46 and 47 are generated directly from the corresponding bis alkyl complexes without the metalla-aza cyclobutane intermediate.

The participation of the iso-propyl and tert-butyl group of the [C₅H₄(CH₂)₂(3)N-i-Pr] and [C₅H₄(CH₂)₂N-t-Bu] ligands respectively in the thermolyses of [C₅H₄(CH₂)₂N-t-Bu]TiMe₂ and [C₅H₄(CH₂)₂NR]Ti(CH₂Ph)₂ (R = i-Pr, t-Bu) is a clear indication that the Cp-amido ligands are chemically not inert. This may have important consequences for the use of these Cp-amido complexes as catalysts, especially at higher temperatures. From the thermolyses of the [C₅H₄(CH₂)₂N-t-Bu]TiR₂ complexes (R = Me, Et, CH₂Ph, Ph, CH₂CMe₃, CH₂CMe₂Ph), a fair estimate can be made about the thermal stability limit for [C₅H₄(CH₂)₂NR] ligands. Below 100 °C the [C₅H₄(CH₂)₂NR] ligands do not interfere in C-H activation processes but this becomes increasingly important at higher temperatures. The temperature limit for C₃-bridged Cp-amido ligands is according to Table 3 considerably lower than 100 °C.

3.9 Concluding Remarks.

The amido functionalized cyclopentadienyl titanium dichlorides [C₅H₄(CH₂)nNR]TiCl₂ are good precursors for the preparation of mono and bis(carbyl) complexes [C₅H₄(CH₂)nNR]TiR₂. The successful isolation of stable Ti(IV) iso-propyl and allyl compounds from the reaction with the corresponding Grignard reagents clearly demonstrates the better resistance against reduction of the dichlorides.

The bis-alkyl complexes [C₅H₄(CH₂)₂N-t-Bu]TiR₂ are thermally more stable than the C₅₂Ti analogues. In contrast, the bis-aryl complexes are less stable. In general, the thermal stability of the bis carbyl compounds strongly depends on the nature of the Cp-amido
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ligands. The C₄-bridged complexes are considerably more stable than the C₃-bridged analogues.

Like the Cp₂TiR₂ and Cp*₂TiR₂ systems, the [C₅H₅(CH₂)₂N-t-Bu]TiR₂ complexes undergo C-H activation processes. Phosphine stabilized olefin, arylene and alkylidene complexes can be isolated and studied. It was possible to isolate a Lewis base free benzyne species \{[C₅H₄(CH₂)₂N-t-Bu]Ti(C₆H₄)}₂ but stable Lewis base free olefin [C₅H₄(CH₂)₂N-t-Bu]Ti(C₆H₄R) and alkylidene complexes [C₅H₄(CH₂)₂N-t-Bu]Ti=C(H)R could not be isolated. The alkylidene complexes [C₅H₄(CH₂)₂N-t-Bu]Ti=C(H)R(PMe₃) (46, R = t-Bu; 47, R = CMe₂Ph) are not active in ROMP catalysis. Instead of olefin metathesis, the metallacyclobutane complex undergo fast β-hydrogen elimination giving olefin coordinated organometallic species.

From the decomposition studies on the [C₅H₄(CH₂)₂NR]TiR₂ complexes it is evident that the Cp-amido ligands do not behave as inert spectator ligands but can be involved in C-H activation processes. From the thermolyses of the [C₅H₄(CH₂)₂NR]TiR₂ compounds a lower limit of about 100 °C is estimated for Cp-amido ligand activation. The resulting organometallic complexes, however, could not be identified and the precise reaction pathway remains to be elucidated.

3.10 Experimental.

For general considerations see Chapter 2.

**General procedure for syntheses of [C₅H₄(CH₂)₂NR]TiR₂ complexes:** All syntheses were performed in diethylether. Reagents were taken from stock solutions in ether or THF (MeLi, EtMgBr, n-PrMgCl, i-PrMgCl, C₆H₅MgCl, PhCH₂Cl, PhMgBr) or pentane (Me₃CCH₂Li, PhMe₂CCH₂Li) and added by means of a syringe or dropping funnel to a cooled (-80 to -40 °C) suspension of the titanium dichloride [C₅H₄(CH₂)₂NR]TiCl₂. The mixtures were then slowly warmed to room temperature and kept at this temperature for 0.5 h. The volatiles were removed in vacuum and the residue was stripped several times with 5-10 mL of pentane. The residue was extracted with pentane and crystallized by concentrating and subsequent cooling of the solutions. When the products were oils, the pentane was removed in vacuum. Unless mentioned otherwise, the workup was performed at room temperature.

\([C₅H₄(CH₂)₂NMe]TiMe₂\) (15): [C₅H₄(CH₂)₂NMe]TiCl₂ (1.39 g, 5.8 mmol), MeLi (11.6 mmol) (-80 °C, 40 mL, 1.5 h, workup at 0 °C). Yield: 0.71 g (3.6 mmol, 61%, yellow crystals). ¹H NMR (200 MHz, C₆D₆): δ 6.21 (m, J_HH = 2.58 Hz, 2H, C₅H₄); 5.60 (m, J_HH = 2.58 Hz, 2H, C₅H₄); 3.67 (s, 3H, NMe); 3.49 (t, J_HH = 5.55 Hz, 2H, NCH₂); 2.39 (t, J_HH = 5.4 Hz, 2H, C₅H₄CH₂); 0.49 (s, 6H, Me). ¹³C NMR
(50 MHz, C₆D₆): δ 134.64 (s, C₅H₅-1); 115.33 (d, 1JCH = 170.0 Hz, C₅H₅); 110.17 (d, 1JCH = 173.1 Hz, C₅H₅); 73.41 (t, 1JCH = 134.4 Hz, NCH₂); 45.71 (q, 1JCH = 118.1 Hz, Me); 42.58 (q, 1JCH = 134.1 Hz, NMe); 28.40 (t, 1JCH = 127.3 Hz, C₅H₅CH₂). IR (cm⁻¹): 3082 (w), 2782 (m), 2752 (m), 2674 (m), 2178 (w), 1763 (m), 1674 (m), 1615 (m), 1449 (m), 1447 (sh, Nujol), 1435 (sh), 1412 (m), 1389 (m), 1346 (w), 1314 (m), 1256 (w), 1233 (s), 1194 (m), 1167 (m), 1103 (s), 1067 (w), 1051 (s), 1042 (s), 1011 (s), 964 (s), 920 (m), 866 (s), 835 (w), 810 (vs), 724 (w), 696 (s), 646 (s), 590 (s), 544 (s), 498 (m), 422 (m). Anal. Calcd: C, 60.31; H, 8.60; Ti, 24.05. Found: C, 60.23; H, 8.68; Ti, 23.93.

[C₆H₄(CH₂)₂N-i-Pr]TiMe₂ (16): [C₆H₄(CH₂)₂N-i-Pr]TiCl₂ (1.44 g, 5.37 mmol), MeLi (10.8 mmol) (-50 °C, 60 mL, 2 h). Yield: 1.02 g (4.49 mmol, 83%, yellow crystals). ¹H NMR (300 MHz, C₆D₆): δ 6.25 (m, JHH = 2.56 Hz, 2H, C₅H₅); 6.07 (hept, 3JHH = 6.41 Hz, 1H, CHMe₂); 5.57 (m, JHH = 2.56 Hz, 2H, C₅H₅); 3.50 (d, 3JHH = 6.77 Hz, 2H, NCH₂); 2.38 (d, 3JHH = 6.77 Hz, 2H, C₅H₅CH₂); 1.11 (d, 3JHH = 6.59 Hz, 6H, CHMe₂); 0.42 (s, 6H, Me). ¹³C NMR (75.4 MHz, C₆D₆): δ 134.47 (s, C₅H₅-1); 115.04 (d, 1JCH = 173.4 Hz, C₅H₅); 61.26 (t, 1JCH = 138.6 Hz, NCH₂); 50.01 (d, 1JCH = 131.9 Hz, CHMe₂); 43.44 (q, 1JCH = 118 Hz, Me). 29.89 (t, 1JCH = 128.8 Hz, C₅H₅CH₂); 20.49 (q, 1JCH = 125.7 Hz, CHMe₂). IR (cm⁻¹):

[C₆H₄(CH₂)₂N-t-Bu]TiMe₂ (17): [C₆H₄(CH₂)₂N-t-Bu]TiCl₂ (0.85 g, 3.0 mmol), MeLi (6.0 mmol) (-80 °C, 30 mL, 1 h). Yield: 0.55 g (2.3 mmol, 76%, yellow oil). ¹H NMR (200 MHz, C₆D₆): δ 6.30 (t, 3JHH = 2.56 Hz, 2H, C₅H₅); 5.64 (t, 3JHH = 2.56 Hz, 2H, C₅H₅); 3.41 (t, 3JHH = 6.41 Hz, 2H, NCH₂); 2.27 (t, 3JHH = 6.41 Hz, 2H, C₅H₅CH₂); 1.54 (s, 9H, t-Bu); 0.47 (s, 6H, 2 Me). ¹³C NMR (50 MHz, C₆D₆): δ 133.24 (s, C₅H₅-1); 114.60 (d, 1JCH = 171.6 Hz, C₅H₅); 113.62 (d, 1JCH = 178.7 Hz, C₅H₅); 62.34 (t, 1JCH = 134.9 Hz, NCH₂); 59.50 (s, CMe₂); 47.14 (q, 1JCH = 118.9 Hz, Me); 29.88 (q, 1JCH = 125.3 Hz, CMe₂); 29.46 (t, 1JCH = 128.5 Hz, C₅H₅CH₂). IR (cm⁻¹, neat): 3088 (w), 2968 (vs), 2933 (vs), 2864 (s), 2835 (s), 2789 (w), 2764 (w), 2673 (w), 1811 (w), 1774 (w), 1720 (w), 1678 (w), 1628 (w), 1494 (w), 1471 (m), 1442 (m), 1388 (m), 1357 (s), 1342 (m), 1321 (w), 1244 (s), 1224 (m), 1194 (vs), 1105 (w), 1074 (s), 1043 (m), 1026 (w), 983 (s), 947 (s), 904 (vw), 868 (s), 844 (m), 815 (vs), 769 (m), 680 (m), 646 (m), 567 (s), 534 (w), 497 (s).

[C₆H₄(CH₂)₃NMe]TiMe₂ (18): [C₆H₄(CH₂)₃NMe]TiCl₂ (2.23 g, 8.8 mmol), MeLi (17.5 mmol) (-80 °C, 50 mL, 2 h, workup at 0 °C). Yield: 1.55 g (7.3 mmol, 82%, yellow crystals). ¹H NMR (200 MHz, C₆D₆): δ (6.19 t, 3JHH = 2.42 Hz, 2H, C₅H₅); 5.33 (t, 3JHH = 2.56 Hz, 2H, C₅H₅); 4.07 (s, 3H, NMe); 2.62 (m, 2H, NCH₂); 2.14 (m, 2H, C₅H₅CH₂); 1.54 (m, 2H, CH₂CH₂N); 0.40 (s, 6H, Me). ¹³C NMR (50 MHz, C₆D₆): δ 122.34 (s, C₅H₅-1); 113.79 (d, 1JCH = 172.3 Hz, C₅H₅); 111.42 (d, 1JCH = 172.8 Hz, C₅H₅); 59.40 (t, 1JCH = 130.0 Hz, NCH₂); 44.36 (q, 1JCH = 119.0 Hz, Me); 40.56 (q, 1JCH = 134.4 Hz, NMe); 30.86 (t, 1JCH = 126.1 Hz, C₅H₅CH₂); 26.62 (t, 1JCH = 127.3 Hz, CH₂CH₂N). IR (cm⁻¹): 3111 (w), 3097 (w), 2823 (sh, Nujol), 2789 (m), 2715 (w), 2700 (m), 1805 (w), 1763 (w), 1713 (w), 1668 (m), 1616 (m), 1494 (m), 1440 (s), 1411 (m), 1394 (m), 1367 (m), 1334 (m), 1273 (m), 1253 (s), 1186 (s), 1163 (m), 1109 (s), 1084 (w), 1072 (m), 1051 (m), 1031 (s), 987 (s), 931 (s), 906 (s), 880 (w), 860 (s), 845
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([C₅H₄(CH₂)₂N-i-Pr]TiMe₂) (19): [C₅H₄(CH₂)₂N-i-Pr]TiCl₂ (1.45 g, 5.14 mmol), MeLi (10.3 mmol) (-50 °C, 60 mL, 2 h). Yield: 0.96 g (3.98 mmol, 77%, yellow crystals). ¹H NMR (300 MHz, C₆D₆): δ 7.00 (hept, 3JHH = 6.13 Hz, 1H, CHMe₂); 6.53 (m, 3JHH = 2.38 Hz, 2H, C₅H₄); 5.29 (m, 3JHH = 2.38 Hz, 2H, C₅H₄); 2.61 (m, 2H, NCH₂); 2.17 (m, 2H, C₅H₄CH₂); 1.28 (d, 3JHH = 6.23 Hz, 6H, CMe₂); 0.30 (s, 6H, Me). ¹³C NMR (75.4 MHz, C₆D₆): δ 122.51 (s, C₅H₄); 111.30 (d, 3JHH = 169.7 Hz, C₅H₄); 46.57 (t, 1JCH = 131.3 Hz, NCH₂); 45.43 (d, 1JCH = 125.7 Hz, CHMe₂); 41.94 (q, 1JCH = 118.8 Hz, Me); 32.44 (t, 1JCH = 126.4 Hz, CH₂CH₂N); 26.95 (t, 1JCH = 126.4 Hz, C₅H₄CH₂); 20.54 (q, 1JCH = 126.1 Hz, CHMe₂).

([C₅H₄(CH₂)₂NMe]Ti(CH₂Ph)₂) (20): [C₅H₄(CH₂)₂NMe]TiCl₂ (1.02 g, 4.25 mmol), PhCH₂MgCl (8.5 mmol), (-80 °C, 30 mL, 3 h). Yield: 0.99 g (2.82 mmol, 66%, red crystals). ¹H NMR (200 MHz, C₆D₆): δ 7.19 (m, 4H, 2 x m-Ph); 6.90 (m, 2H, 2 x p-Ph); 6.80 (m, 4H, 2 x o-Ph); 5.93 (t, 3JHH = 2.78 Hz, 2H, C₅H₄); 5.15 (t, 3JHH = 2.78 Hz, 2H, C₅H₄); 3.40 (s, 3H, NMe); 3.34 (t, 2JHH = 6.84 Hz, 2H, CH₂Ph); 2.40 (d, 2JHH = 9.83 Hz, 2H, 2 x PhCH₂); 2.23 (t, 3JHH = 6.84 Hz, 2H, C₅H₄CH₂); 2.19 (d, 2JHH = 9.83 Hz, 2H, 2 x PhCH₂). ¹³C NMR (50 MHz, C₆D₆): δ 149.08 (s, Ph-ipso); 136.79 (s, C₅H₄-ipso); 128.50 (d, 1JCH = 168.2 Hz, m-Ph); 125.68 (d, 1JCH = 153.5 Hz, o-Ph); 121.55 (d, 1JCH = 156.3 Hz, p-Ph); 117.30 (d, 1JCH = 172.3 Hz, C₅H₄); 113.63 (d, 1JCH = 165.9 Hz, C₅H₄); 75.90 (t, 1JCH = 122.3 Hz, CH₂Ph); 73.70 (t, 1JCH = 135.4 Hz, NCH₂); 44.39 (q, 1JCH = 134.6 Hz, NMe); 28.51 (t, 1JCH = 128.8 Hz, C₅H₄CH₂). IR (cm⁻¹): 3059 (m), 3014 (m), 2775 (w), 1938 (w), 1851 (w), 1793 (w), 1776 (w), 1722 (w), 1691 (w), 1591 (s), 1479 (m), 1446 (w), 1406 (w), 1311 (sh, Nujol), 1288 (w), 1243 (w), 1211 (s), 1178 (m), 1149 (w), 1089 (m), 1064 (w), 1049 (m), 1037 (vvs), 1026 (m), 1008 (s), 983 (m), 962 (s), 873 (s), 839 (w), 815 (vs), 796 (w), 744 (vs), 696 (vs), 646 (m), 584 (m), 561 (m), 540 (m), 528 (w), 515 (w), 457 (m), 423 (vs). Anal. Calcd.: C, 75.21; H, 7.17; Ti, 13.63.

([C₅H₄(CH₂)₂N-i-Pr]Ti(CH₂Ph)₂) (21): [C₅H₄(CH₂)₂N-i-Pr]TiCl₂ (1.08 g, 4.03 mmol), PhCH₂MgCl (8.4 mmol), (0 °C, 30 mL, 3 h). Yield: 1.31 g (3.45 mmol, 84%, red oil). ¹H NMR (300 MHz, C₆D₆): δ 7.19 (t, 3JHH = 7.51 Hz, 4H, m-Ph); 6.89 (t, 3JHH = 7.33 Hz, 2H, p-Ph); 6.83 (d, 3JHH = 7.32 Hz, 4H, o-Ph); 5.83 (m, 3JHH = 2.56 Hz, 2H, C₅H₄); 5.73 (sept, 3JHH = 6.50 Hz, 1H, CHMe₂); 5.25 (m, 3JHH = 2.56 Hz, 2H, C₅H₄); 3.41 (t, 3JHH = 6.78 Hz, 2H, NCH₂); 2.38 (d, 3JHH = 9.52 Hz, 2H, CH₂Ph); 2.26 (t, 3JHH = 6.78 Hz, 2H, C₅H₄CH₂); 2.17 (d, 2JHH = 9.52 Hz, 2H, CH₂Ph); 1.03 (d, 3JHH = 6.50 Hz, 6H, CHMe₂). ¹³C NMR (75.4 MHz, C₆D₆): δ 149.99 (s, ipso-Ph); 136.59 (s, ipso-C₅H₄); 128.52 (d, 1JCH = 153.8 Hz, o-Ph); 125.72 (d, 1JCH = 153.8 Hz, m-Ph); 121.38 (d, 1JCH = 156.3 Hz, p-Ph); 116.85 (d, 1JCH = 172.1 Hz, C₅H₄); 115.04 (d, 1JCH = 173.4 Hz, C₅H₄); 74.40 (t, 1JCH = 120.9 Hz, PhCH₂); 61.78 (t, 1JCH = 135.5 Hz, NCH₂); 51.23 (d, 1JCH = 130.6 Hz, CHMe₂); 29.06 (t, 1JCH = 129.4 Hz, C₅H₄CH₂); 20.45 (q, 1JCH = 126.1 Hz, CHMe₂). IR (cm⁻¹): 3069 (m), 3055 (m), 3015 (s), 2965 (s), 2926 (s), 2853 (s), 2770 (vs), 2750 (vs).
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1933 (w), 1846 (w), 1790 (w), 1717 (w), 1593 (s), 1487 (s), 1449 (m), 1385 (m), 1358 (m), 1339 (m), 1300 (m), 1209 (s), 1177 (m), 1154 (m), 1107 (w), 1055 (m), 1040 (m), 1028 (m), 990 (s), 876 (w), 855 (w), 818 (s), 745 (s), 698 (s), 646 (m), 619 (w), 561 (w), 521 (w), 449 (m), 424 (m), 409 (m).

$[\text{C}_6\text{H}_4(\text{CH}_2)_2\text{N-i-Bu}]{\text{Ti(Ch}_2\text{P)})_2}$ (22): $[\text{C}_6\text{H}_4(\text{CH}_2)_2\text{N}-t\text{-Bu}]{\text{TiCl}_2}$ 1.21 g (4.3 mmol, PhCH$_2$MeCl (8.6 mmol), (0 °C, 30 mL, 2h). Yield: 1.15 g (3.0 mol%, 69%, red oil). $^1$H NMR (200 MHz, C$_6$D$_6$): δ 7.22 (m, 4H, 2 × m-Ph); 6.90 (m, 2H, 2 × p-Ph); 6.82 (m, 4H, 2 × o-Ph); 9.22 (t, $^3$J$_{HH}$ = 2.56 Hz, 2H, C$_6$H$_4$); 5.27 (t, $^3$J$_{HH}$ = 2.56 Hz, 2H, C$_6$H$_4$); 3.29 (t, $^3$J$_{HH}$ = 6.63 Hz, 2H, NCH$_2$): 2.73 (d, $^2$J$_{HH}$ = 9.40 Hz, 2H, PhCH$_2$): 2.27 (d, $^2$J$_{HH}$ = 9.40 Hz, 2H, PhCH$_2$): 2.10 (t, $^3$J$_{HH}$ = 6.63 Hz, 2H, C$_6$H$_4$CH$_2$): 1.50 (s, 9H, t-Bu). $^{13}$C NMR (75.4 MHz, C$_6$D$_6$): δ 150.70 (s, Ph-ipsos); 135.67 (s, C$_5$H$_4$-ipsos); 128.45 (d, $^1$J$_{CH}$ = 154.0 Hz, o-Ph); 125.73 (d, $^1$J$_{CH}$ = 153.1 Hz, m-Ph); 121.59 (d, $^1$J$_{CH}$ = 156.3 Hz, p-Ph); 118.04 (d, $^1$J$_{CH}$ = 173.7 Hz, C$_6$H$_4$); 117.42 (d, $^1$J$_{CH}$ = 171.4 Hz, C$_6$H$_4$); 78.04 (t, $^1$J$_{CH}$ = 120.5 Hz, CH$_2$Ph); 62.61 (d, $^1$J$_{CH}$ = 135.4 Hz, CH$_2$N); 60.96 (s, CMe$_3$): 30.16 (t, $^1$J$_{CH}$ = 129.0 Hz, C$_6$H$_4$CH$_2$): 30.11 (d, $^1$J$_{CH}$ = 125.3 Hz, CMe$_3$). IR (cm$^{-1}$, neat): 3084 (m), 3061 (m), 2926 (s), 2837 (m), 2702 (w), 1946 (w), 1863 (d, 1.86 g, 7.35 mmol), PhCH$_2$MeCl (14.7 mmol), (-80 °C, 30 mL, 3 h). Yield: 1.83 g (5.0 mol%, 68%, red oil). $^1$H NMR (200 MHz, C$_6$D$_6$): δ 7.17 (m, 4H, 2 × m-Ph); 6.88 (m, 2H, 2 × p-Ph); 6.77 (m, 4H, 2 × o-Ph); 6.21 (t, $^3$J$_{HH}$ = 2.56 Hz, 2H, C$_6$H$_4$): 4.89 (t, $^2$J$_{HH}$ = 2.56 Hz, 2H, C$_6$H$_4$): 3.87 (s, 3H, NMe): 2.43 (m, 2H, NCH$_2$): 2.45 (d, $^2$J$_{HH}$ = 9.83 Hz, 2H, PhCH$_2$): 2.20 (d, $^2$J$_{HH}$ = 9.83 Hz, PhCH$_2$): 1.96 (m, 2H, C$_6$H$_4$CH$_2$): 1.36 (m, 2H, CH$_2$CH$_2$). $^{13}$C NMR (50 MHz, C$_6$D$_6$): δ 150.05 (s, Ph-ipsos); 128.38 (d, $^1$J$_{CH}$ = 154.1 Hz, m-Ph); 125.59 (d, $^1$J$_{CH}$ = 153.6 Hz, o-Ph): 124.84 (s, C$_5$H$_4$-ipsos); 121.46 (d, $^1$J$_{CH}$ = 155.6 Hz, p-Ph): 117.59 (d, $^1$J$_{CH}$ = 174.2 Hz, C$_6$H$_4$); 114.20 (d, $^1$J$_{CH}$ = 171.2 Hz, C$_6$H$_4$): 74.53 (t, $^1$J$_{CH}$ = 122.4 Hz, PhCH$_2$): 60.11 (t, $^1$J$_{CH}$ = 135.0 Hz, NCH$_2$): 42.55 (m, $^1$J$_{CH}$ = 134.5 Hz, NMe): 30.87 (t, $^1$J$_{CH}$ = 126.7 Hz, C$_6$H$_4$CH$_2$): 26.47 (t, $^1$J$_{CH}$ = 127.7 Hz, NCH$_2$CH$_2$).

$[\text{C}_6\text{H}_4(\text{CH}_2)_3\text{N-i-Pr}]{\text{Ti(Ch}_2\text{P)})_2}$ (24): $[\text{C}_6\text{H}_4(\text{CH}_2)_3\text{N-i-Pr}]{\text{TiCl}_2}$ (of 1.22 g, 4.33 mmol), PhCH$_2$MeCl (8.9 mmol), (0 °C, 30 mL, 3 h). Yield: 1.57 g (3.99 mmol, 92%, red oil). $^1$H NMR (300 MHz, C$_6$D$_6$): δ 7.19 (t, $^3$J$_{HH}$ = 7.69 Hz, 4H, m-Ph); 6.89 (t, $^3$J$_{HH}$ = 7.32 Hz, 2H, p-Ph); 6.81 (d, $^3$J$_{HH}$ = 7.69 Hz, 4H, o-Ph); 6.57 (sept, $^3$J$_{HH}$ = 6.11 Hz, CHMe$_3$): 6.10 (m, $^4$J$_{HH}$ = 2.57 Hz, 2H, C$_6$H$_4$): 4.96 (m, $^5$J$_{HH}$ = 2.57 Hz, 2H, C$_6$H$_4$): 2.58 (m, 2H, NCH$_2$): 2.34 (d, $^2$J$_{HH}$ = 9.88 Hz, 2H, CH$_2$Ph): 2.15 (d, $^2$J$_{HH}$ = 9.88 Hz, 2H, CH$_2$Ph): 2.03 (m, 2H, C$_6$H$_4$CH$_2$): 1.40 (m, 2H, NCH$_2$CH$_2$): 1.22 (d, $^3$J$_{HH}$ = 6.11 Hz, 6H, CH$_3$Me$_3$). $^{13}$C NMR (75.4 MHz, C$_6$D$_6$): δ 151.39 (s, Ph-ipsos); 128.44 (d, $^1$J$_{CH}$ = 153.8 Hz, o-Ph); 125.91 (d, $^1$J$_{CH}$ = 153.8 Hz, m-Ph): 125.10 (s, C$_5$H$_4$-ipsos); 121.43 (d, $^1$J$_{CH}$ = 156.3 Hz, p-Ph): 118.84 (d, $^1$J$_{CH}$ = 173.4 Hz, C$_6$H$_4$); 114.13 (d, $^1$J$_{CH}$ = 172.1 Hz, C$_6$H$_4$): 72.88 (t, $^1$J$_{CH}$ = 120.9 Hz, CH$_2$Ph): 47.37 (t, $^1$J$_{CH}$ = 133.1 Hz, NCH$_2$): 46.91 (d, $^1$J$_{CH}$ = 124.5 Hz, CHMe$_3$): 32.79 (t, $^1$J$_{CH}$ = 127.0 Hz, C$_6$H$_4$CH$_2$): 26.87 (t, $^1$J$_{CH}$ = 127.6 Hz, NCH$_2$CH$_2$).
Cyclopentadienyl Amido Titanium Carbonyl Complexes

\([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiPh}_2\) (25): [C_5H_4(CH_2)_2NMe]TiCl_2 (of 1.43 g, 5.96 mmol), PhLi (1.04 g, 12.4 mmol), (-80 °C, 30 mL, 2h, workup at -15 °C). Yield: 0.51 g (1.58 mmol, 26%, yellow-brown crystals). \(^1\)H NMR (300 MHz, CD_2Cl_2): δ 7.30 (m, 4H, 2 x m-Ph); 6.94 (m, 6H, 2 x o-Ph + 2 x p-Ph); 6.30 (t, \(^3\)J_HH = 2.56 Hz, 2H, C_2H_4); 5.99 (t, \(^3\)J_HH = 2.56 Hz, 2H, C_2H_4); 3.93 (t, \(^3\)J_HH = 6.60 Hz, 2H, NCH_2); 3.62 (s, 3H, NMe); 2.86 (t, \(^3\)J_HH = 6.60 Hz, 2H, C_3H_6CH_2). \(^13\)C NMR (75.4 MHz, CD_2Cl_2): δ 191.50 (s, Ph-ipsos); 136.67 (s, C_5H_5-ipsos); 133.93 (d, \(^1\)J_CCH = 156.4 Hz, m-Ph); 127.91 (d, \(^1\)J_CCH = 157.6 Hz, p-Ph); 127.10 (d, \(^1\)J_CCH = 154.1 Hz, o-Ph); 117.50 (d, \(^1\)J_CCH = 170.7 Hz, C_2H_4); 112.98 (d, \(^1\)J_CCH = 172.2 Hz, C_2H_4); 74.57 (t, \(^1\)J_CCH = 134.0 Hz, NCH_2); 43.74 (q, \(^1\)J_CCH = 134.8 Hz, NMe); 29.43 (t, \(^1\)J_CCH = 128.7 Hz, C_3H_6CH_2). IR (cm\(^{-1}\)): 3105 (w), 3080 (w), 3045 (s), 2787 (m), 2733 (vw), 2681 (w), 1954 (w), 1876 (w), 1817 (w), 1768 (w), 1722 (w), 1687 (w), 1631 (w), 1589 (vw), 1564 (m), 1527 (m), 1487 (w), 1429 (w), 1413 (s), 1348 (m), 1325 (w), 1309 (w), 1288 (w), 1259 (w), 1232 (m), 1190 (m), 1165 (w), 1153 (vw), 1095 (m), 1057 (s), 1039 (w), 1008 (s), 989 (m), 962 (s), 920 (w), 906 (w), 868 (m), 812 (vs), 777 (m), 721 (vs), 700 (vs), 646 (m), 563 (s), 520 (m), 449 (s), 420 (m).

\([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiPh}_2\) (26): [C_5H_4(CH_2)_2N-t-Bu]TiCl_2 (1.13 g, 4.0 mmol), PhMgBr (8.1 mmol), (-80 °C, 30 mL, 2h, workup at 0 °C). Yield: 0.64 g (1.75 mmol, 44%, orange-yellow crystals). \(^1\)H NMR (300 MHz, CD_2Cl_2): δ 7.31 (m, 4H, 2 x m-Ph); 6.99 (m, 6H, 2 x p-Ph + 2 x o-Ph); 6.21 (t, \(^3\)J_HH = 2.56 Hz, 2H, C_2H_4); 6.04 (t, \(^3\)J_HH = 2.56 Hz, 2H, C_2H_4); 4.01 (t, \(^3\)J_HH = 6.47 Hz, 2H, NCH_2); 2.83 (t, \(^1\)J_CCH = 6.47 Hz, 2H, C_3H_6CH_2); 1.41 (s, 9H, t-Bu). \(^13\)C NMR (75.4 MHz, CD_2Cl_2): δ 192.50 (s, Ph-ipsos); 136.49 (s, C_5H_5-ipsos); 134.25 (d, \(^1\)J_CCH = 154.1 Hz, m-Ph); 127.19 (d, \(^1\)J_CCH = 155.1 Hz, o-Ph); 126.93 (d, \(^1\)J_CCH = 157.6 Hz, p-Ph); 117.84 (d, \(^1\)J_CCH = 175.3 Hz, C_2H_4); 115.18 (d, \(^1\)J_CCH = 174.8 Hz, C_2H_4); 64.07 (t, \(^1\)J_CCH = 134.5 Hz, NCH_2); 61.87 (s, CMe_3); 30.89 (s, \(^1\)J_CCH = 128.4 Hz, C_3H_6CH_2); 28.96 (q, \(^1\)J_CCH = 125.4 Hz, CMe_3). IR (cm\(^{-1}\)): 3113 (w), 3090 (w), 3043 (m), 1952 (w), 1874 (w), 1726 (w), 1631 (w), 1562 (w), 1552 (w), 1493 (m), 1460 (sh, Nujol), 1411 (m), 1357 (m), 1344 (w), 1325 (w), 1298 (w), 1240 (m), 1207 (sh), 1190 (s), 1074 (s), 1055 (s), 1016 (w), 985 (s), 941 (m), 906 (w), 869 (m), 844 (m), 820 (vs), 775 (m), 727 (vs), 702 (vs), 565 (m), 526 (m), 480 (w), 453 (m). Anal Calcd: C, 75.61; H, 7.45; Ti, 13.11. Found: C, 75.17; H, 7.35; Ti, 12.97.

\([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}]\text{TiPh}_2\) (27): [C_5H_4(CH_2)_2NMe]TiCl_2 (1.23 g, 4.84 mmol), PhLi (0.79 g, 9.40 mmol), (-80 °C, 25 mL, 4 h, workup at 0 °C). Yield: 0.36 g (1.07 mmol, 22%, green-yellow crystals). \(^1\)H NMR (300 MHz, CD_2Cl_2): δ 7.32 (m, 4H, 2 x o-Ph); 7.12 (m, 6H, 2 x m-Ph + 2 x p-Ph); 6.41 (t, \(^3\)J_HH = 2.57 Hz, C_2H_4); 5.53 (t, \(^3\)J_HH = 2.57 Hz, C_2H_4); 3.78 (s, 3H, NMe); 2.61 (m, 2H, NCH_2); 2.24 (m, 2H, C_3H_6CH_2); 1.68 (m, 2H, NCH_2CH_2). \(^13\)C NMR (75.4 MHz, CD_2Cl_2): δ 191.06 (s, Ph-ipsos); 134.00 (d, \(^1\)J_CCH = 155.6 Hz, CMe_3).
Chapter 3

1H NMR (200 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta \) 6.69 (t, \( J_{HH} = 2.35 \) Hz, 2H, C\textsubscript{5}H\textsubscript{4}); 5.90 (t, \( J_{HH} = 2.56 \) Hz, 2H, C\textsubscript{5}H\textsubscript{4}); 3.41 (t, \( J_{HH} = 6.63 \) Hz, 2H, NCH\textsubscript{3}); 2.25 (t, \( J_{HH} = 6.63 \) Hz, 2H, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 2.05 (d, \( J_{HH} = 11.11 \) Hz, 2H, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 1.58 (s, 9H, N-t-Bu); 1.00 (s, 18H, 2 x CH\textsubscript{3}CH\textsubscript{3}Cl); 0.97 (d, \( J_{HH} = 11.11 \) Hz, 2H, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}).

13C NMR (50 MHz, C\textsubscript{6}D\textsubscript{6}): \( \delta \) 131.73 (s, C\textsubscript{5}H\textsubscript{4}-ipso); 115.41 (d, \( J_{CH} = 170.2 \) Hz, C\textsubscript{5}H\textsubscript{4}); 110.67 (d, \( J_{CH} = 173.2 \) Hz, C\textsubscript{5}H\textsubscript{4}); 93.94 (t, \( J_{CH} = 109.0 \) Hz, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 63.04 (t, \( J_{CH} = 134.5 \) Hz, NCH\textsubscript{3}); 60.77 (s, NCHMe\textsubscript{3}); 38.31 (s, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 34.64 (q, \( J_{CH} = 123.9 \) Hz, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 30.61 (t, \( J_{CH} = 128.4 \) Hz, C\textsubscript{5}H\textsubscript{4}CH\textsubscript{3}); 30.56 (q, \( J_{CH} = 125.4 \) Hz, NCHMe\textsubscript{3}).

Found: C, 71.31; H, 11.11; Ti, 13.43.
73.51 (t, $^1J_{CH} = 134.5$ Hz, NCH$_2$); 46.38 (q, $^1J_{CH} = 134.0$ Hz, NMe); 43.98 (s, CH$_2$CMe$_2$Ph); 35.29 (q, $^1J_{CH} = 125.4$ Hz, CH$_2$CMe$_2$Ph); 32.53 (q, $^1J_{CH} = 123.4$ Hz, CH$_2$CMe$_2$Ph); 28.53 (t, $^1J_{CH} = 128.4$ Hz, C$_6$H$_4$CH$_3$). IR (cm$^{-1}$): 3101 (w), 3082 (m), 3059 (m), 3018 (w), 2816 (w), 2793 (w), 2783 (w), 2737 (w), 2721 (w), 2679 (w), 1936 (w), 1866 (w), 1797 (w), 1599 (m), 1493 (s), 1444 (m), 1408 (m), 1357 (s), 1311 (w), 1275 (m), 1259 (w), 1234 (m), 1188 (s), 1168 (m), 1099 (m), 1082 (w), 1053 (m), 1039 (w), 1028 (m), 1010 (s), 964 (m), 920 (w), 904 (w), 871 (m), 854 (w), 839 (m), 810 (vs), 765 (s), 742 (vw), 700 (vs), 648 (m), 596 (s), 574 (m), 555 (m), 520 (m), 491 (m), 464 (m), 424 (m).

$[\text{C}_3\text{H}_4(\text{CH}_2)_2\text{N-t-Bu}]\text{Ti}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (31): [C$_3$H$_4$(CH$_2$)$_2$N-t-Bu]TiCl$_2$ (1.37 g, 4.85 mmol), LiCH$_2$CMe$_2$Ph (1.32 g, 9.42 mmol), (-70 °C, 50 mL, 2 h). Yield: 1.56 g (3.27 mmol, 67%). $^1$H NMR (200 MHz, C$_6$D$_6$): δ 7.41-7.15 (m, 10H, 2 x CH$_2$CMe$_2$Ph); 5.71 (t, $^3J_{HH} = 2.35$ Hz, 2H, C$_3$H$_4$); 5.49 (t, $^3J_{HH} = 2.35$ Hz, 2H, C$_3$H$_4$); 3.48 (t, $^3J_{HH} = 6.41$ Hz, 2H, NCH$_2$); 2.28 (d, $^2J_{HH} = 10.69$ Hz, 2H, 2 x CH$_2$CMe$_2$Ph); 2.23 (t, $^3J_{HH} = 6.41$ Hz, 2H, C$_6$H$_4$CH$_3$); 1.65 (s, 9H, t-Bu); 1.45 (d, $^2J_{HH} = 10.69$ Hz, 2H, 2 x CH$_2$CMe$_2$Ph); 1.37 (s, 6H, 2 x CH$_2$CMe$_2$Ph); 1.32 (s, 6H, 2 x CH$_2$CMe$_2$Ph). $^13$C NMR (75.4 MHz, C$_6$D$_6$): δ 152.82 (s, CH$_2$CMe$_2$Ph); 131.80 (s, C$_6$H$_4$-ipso); 128.18 (d, $^1J_{CH} = 158.6$ Hz, CH$_2$CMe$_2$-ipso); 125.81 (d, $^1J_{CH} = 155.1$ Hz, CH$_2$CMe$_2$-m-Ph); 125.49 (d, $^1J_{CH} = 160.1$ Hz, CH$_2$CMe$_2$-p-Ph); 116.43 (d, $^1J_{CH} = 171.2$ Hz, C$_3$H$_4$); 111.02 (d, $^1J_{CH} = 174.25$ Hz, C$_3$H$_4$); 92.59 (d, $^1J_{CH} = 109.8$ Hz, CH$_2$CMe$_2$Ph); 92.53 (t, $^1J_{CH} = 109.8$ Hz, CH$_2$CMe$_2$Ph); 62.88 (t, $^1J_{CH} = 134.7$ Hz, NCH$_2$); 50 mL, 2 h). Yield: 1.56 g (3.27 mmol, 67%). $^1$H NMR (300 MHz, C$_6$D$_6$): δ 7.31-7.08 (m, 10H, 2 x CH$_2$CMe$_2$Ph); 6.03 (t, $^3J_{HH} = 2.56$ Hz, 2H, C$_3$H$_4$); 4.99 (t, $^3J_{HH} = 2.56$ Hz, 2H, C$_3$H$_4$); 3.94 (s, 3H, NMe); 2.59 (m, 2H, NCH$_2$); 2.03 (m, 2H, C$_6$H$_4$CH$_3$); 1.84 (d, $^2J_{HH} = 11.11$ Hz, 2H, 2 x CH$_2$CMe$_2$Ph); 1.51 (m, 2H, NCH$_2$CH$_3$); 1.45 (d, $^2J_{HH} = 11.11$ Hz, 2H, 2 x CH$_2$CMe$_2$Ph); 1.27 (s, 6H, 2 x CH$_2$CMe$_2$Ph); 1.16 (s, 6H, CH$_2$CMe$_2$Ph). $^13$C NMR (75.4 MHz, C$_6$D$_6$): δ 152.94 (s, CH$_2$CMe$_2$Ph-ipsos); 128.00 (d, $^1J_{CH} = 158.1$ Hz, CH$_2$CMe$_2$-o-Ph); 125.70 (d, $^1J_{CH} = 154.6$ Hz, CH$_2$CMe$_2$-m-Ph); 125.32 (d, $^1J_{CH} = 159.1$ Hz, CH$_2$CMe$_2$-p-Ph); 120.84 (s, C$_6$H$_4$-ipso); 113.57 (d, $^1J_{CH} = 170.7$ Hz, C$_3$H$_4$); 112.17 (d, $^1J_{CH} = 173.7$ Hz, C$_3$H$_4$); 87.95 (s, $^1J_{CH} = 111.0$ Hz, CH$_2$CMe$_2$Ph); 60.38 (t, $^1J_{CH} = 134.7$ Hz, NCH$_2$); 46.05 (q, $^1J_{CH} = 133.8$ Hz, NMe); 44.32 (s, CH$_2$CMe$_2$Ph); 35.45 (q, $^1J_{CH} = 125.1$ Hz, CH$_2$CMe$_2$Ph); 32.14 (q, $^1J_{CH} = 128.9$ Hz, CH$_2$CMe$_2$Ph); 31.01 (t, $^1J_{CH} = 126.4$ Hz, C$_6$H$_4$CH$_3$); 26.70 (t, $^1J_{CH} = 126.7$ Hz, NCH$_2$CH$_3$). IR (cm$^{-1}$): 3101 (m), 3082 (m), 3055 (m), 3028 (w), 3016 (w), 2814 (m), 2793 (sh), 2742 (w), 2727 (w), 1942 (w), 1875 (w), 1800 (w), 1670 (w), 1624 (w), 1599 (s), 1579 (w), 1552 (w), 1522 (m), 1493 (s), 1444 (m), 1408 (m), 1357 (s), 1311 (w), 1275 (m), 1259 (w), 1234 (m), 1188 (s), 1168 (m), 1099 (m), 1082 (w), 1053 (m), 1039 (w), 1028 (m), 1010 (s), 964 (m), 920 (w), 904 (w), 871 (m), 854 (w), 839 (m), 810 (vs), 765 (s), 742 (vw), 700 (vs), 648 (m), 596 (s), 574 (m), 555 (m), 520 (m), 491 (m), 464 (m), 424 (m).
[C5H4(CH2)2N-t-Bu]Ti(C2H5)Cl (33): [C5H4(CH2)2N-t-Bu]TiCl2 (4.05 g, 14.36 mmol), PhCH2MgCl (28.6 mmol), (-40 °C, 50 mL, 5 h). Yield: 3.34 g (9.89 mmol, 69%, red crystals). 1H NMR (300 MHz, CD6): δ 7.19 (t, 3JCH = 7.69 Hz, 2H, m-Ph); 6.96 (d, 3JCH = 7.81 Hz, 2H, o-Ph); 6.89 (t, 3JCH = 7.33 Hz, 1H, p-Ph); 6.15 (m, 1H, C6H4); 5.61 (m, 2H, C6H4); 5.41 (m, 2H, C6H4); 3.50 (m, 2H, NCH2); 2.97 (d, 2JCH = 9.28 Hz, 1H, PhCH3); 2.80 (d, 2JCH = 9.28 Hz, 1H, PhCH3); 2.23 (m, 2H, C5H4CH2); 1.47 (s, 9H, CMe3). 13C NMR (75.4 MHz, CD6): δ 153.37 (s, ipso); 138.88 (s, C5H4-ipso); 128.49 (d, 1JCH = 157.2 Hz, o-Ph); 126.73 (d, 1JCH = 157.8 Hz, m-Ph); 122.18 (d, 1JCH = 156.7 Hz, p-Ph); 118.96 (d, 1JCH = 169.5 Hz, C5H4); 117.43 (d, 1JCH = 176.0 Hz, C5H4); 111.86 (d, 1JCH = 176.0 Hz, C5H4); 114.95 (d, 1JCH = 173.7 Hz, C5H4); 76.06 (t, 1JCH = 124.4 Hz, PhCCH2); 65.30 (t, 1JCH = 136.3 Hz, NCH2); 62.22 (s, CMe3); 30.99 (q, 1JCH = 125.9 Hz, CMe3); 29.85 (t, 1JCH = 129.7 Hz, C5H4CH2). IR (cm⁻¹): 3111 (vw), 3073 (w), 3045 (vw), 3017 (w), 2946 (vw), 1928 (w), 1863 (vw), 1845 (w), 1800 (vw), 1720 (w), 1657 (w), 1595 (s), 1481 (s, CMe); 1458 (s, CMe); 1415 (s, CMe); 1388 (s, CMe); 1367 (s, CMe); 1359 (s, CMe); 1340 (s, CMe); 1330 (s, CMe); 1303 (vw), 1277 (m), 1249 (m), 1182 (s), 1165 (w), 1078 (m), 1053 (m), 1030 (s), 993 (m), 962 (vw), 939 (m), 908 (m), 875 (w), 858 (m), 835 (w), 814 (vs), 767 (vs), 700 (vs), 667 (w), 607 (m), 570 (s), 553 (w), 468 (m), 430 (m).

NMR tube reaction of [C5H4(CH2)2N-t-Bu]TiCl2 with [C5H4(CH2)2N-t-Bu]TiMe2. A solution of 80.0 mg (0.28 mmol) of [C5H4(CH2)2N-t-Bu]TiCl2 in 0.6 mL of CD6 was added to 68.5 mg (0.28 mmol) of [C5H4(CH2)2N-t-Bu]TiMe2. The mixture was transferred to an NMR tube. After 10 min a 1H NMR spectrum was recorded. At this stage no reaction had occurred. The NMR tube was heated at 50 °C and the reaction was monitored at regular intervals with 1H NMR spectroscopy. The reaction was complete after 24 h. One single complex was formed which was identical with [C5H4(CH2)2N-t-Bu]Ti(PhMe)Cl (34).

NMR tube reaction of [C5H4(CH2)2N-t-Bu]TiCl2 with [C5H4(CH2)2N-t-Bu]Ti(CH2Ph)2. A solution of 78.0 mg (0.28 mmol) of [C5H4(CH2)2N-t-Bu]TiCl2 in 0.6 mL of CD6 was added to 111 mg (0.28 mmol) of [C5H4(CH2)2N-t-Bu]Ti(CH2Ph)2 and transferred to an NMR tube. The NMR tube was heated at 50 °C and the reaction was monitored by 1H NMR spectroscopy. After 98 h 99% conversion to [C5H4(CH2)2N-t-Bu]Ti(CH2Ph)Cl had been reached.

Synthesis of [C5H4(CH2)2N-t-Bu]Ti(PhMe)Cl (34). To a cooled (0 °C) suspension of 1.02 g (3.62 mmol) of [C5H4(CH2)2N-t-Bu]TiCl2 in 50 mL of ether, 4.6 mL 0.88 M (4.0 mmol) of MeLi in ether was added dropwise. The mixture was stirred for 1 h at room temperature. The solvent was removed and the residue was stripped with 30 mL of pentane. The residue was extracted three times with 40 mL of
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toluene and the combined solutions were concentrated to 8 mL. The solution was heated at 60-70 °C for 16 h giving a brown solution. Removal of the toluene in vacuum yielded an oil which solidified which turned solid after stripping twice with 30 mL of pentane. The brown solid was dissolved in 50 mL of pentane and filtered. The solution was concentrated at reflux to 5 mL. Slowly cooling to 0 °C resulted in the formation of red-brown crystals. The crystals were washed with cold (-20 °C) pentane and dried in vacuum. Yield: 0.61 g (2.33 mmol, 64%) of [C₆H₄(CH₂)₃N-t-Bu]Ti(Me)Cl. A ¹H NMR spectrum revealed the presence of a small amount (ca. 2.5%) of the dichloride complex [C₆H₄(CH₂)₂N-t-Bu]TiCl₂. ¹H NMR (300 MHz, C₆D₆): δ 6.19 (m, 1H, C₆H₄); 6.17 (m, 1H, C₆H₄); 5.73 (m, 1H, C₆H₄); 5.70 (m, 1H, C₆H₄); 3.50 (m, 2H, NCH₂); 2.27 (m, 2H, C₅H₄CH₂); 1.47 (s, 9H, CMe₃); 0.84 (s, 3H, Me). ¹³C NMR (75.4 MHz, C₆D₆): δ 138.04 (s, C₅H₄-ipso); 116.48 (d, ¹JC₆H₄ = 172.1 Hz, C₆H₄); 115.52 (d, ¹JC₆H₄ = 177.0 Hz, C₆H₄); 114.47 (d, ¹JC₆H₄ = 175.8 Hz, C₆H₄); 114.29 (d, ¹JC₆H₄ = 169.9 Hz, C₆H₄); 65.42 (t, ¹JC₆H₄ = 136.1 Hz, NCH₂); 61.39 (s, CMe₃); 48.38 (q, ¹JC₆H₄ = 122.9 Hz, Me); 29.75 (t, ¹JC₆H₄ = 129.4 Hz, C₅H₄CH₂); 29.60 (q, ¹JC₆H₄ = 125.7 Hz, CMe₃). IR (cm⁻¹): 3100 (w), 2983 (w), 2776 (w), 1840 (w), 1796 (w), 1694 (w), 1657 (w), 1368 (m), 1358 (s), 1344 (m), 1323 (m), 1244 (m), 1225 (m), 1190 (s), 1107 (w), 1076 (s), 1044 (m), 1026 (w), 984 (s), 941 (s), 922 (w), 876 (s), 825 (vs), 768 (m), 683 (m), 642 (m), 571 (m), 538 (m), 494 (s). Anal. calcd: C, 55.10; H, 7.71; Ti, 18.31. Found: C, 54.96; H, 7.67; Ti, 18.22.

[C₆H₄(CH₂)₂N-t-Bu]Ti(1-PrCl) (35): [C₆H₄(CH₂)₂N-t-Bu]TiCl₂ (2.53 g, 8.97 mmol), i-PrMgCl (8.9 mmol), (-40 °C, 40 mL, 2 h). Yield: 1.92 g (6.63 mmol, 74%, orange-red oil). ¹H NMR (300 MHz, C₆D₆): δ 6.20 (m, 1H, C₆H₄); 6.12 (m, 1H, C₆H₄); 5.68 (m, 1H, C₆H₄); 5.64 (m, 1H, C₆H₄); 3.47 (m, 2H, NCH₂); 2.26 (m, 2H, C₅H₄CH₂); 2.19 (hept, ³J_HCH = 6.04 Hz, 1H, CHMe₂); 1.46 (s, 9H, CMe₃); 1.31 (d, ³J_HCH = 5.49 Hz, 3H, CHMe₂); 1.25 (d, ³J_HCH = 5.86 Hz, 3H, CHMe₂); ¹³C NMR (75.4 MHz, C₆D₆): δ 135.85 (s, C₅H₄-ipso); 117.21 (d, ¹JC₆H₄ = 179.5 Hz, C₆H₄); 114.73 (d, ¹JC₆H₄ = 174.6 Hz, C₆H₄); 114.18 (d, ¹JC₆H₄ = 165.8 Hz, C₆H₄); 114.10 (d, ¹JC₆H₄ = 174.6 Hz, C₆H₄); 86.05 (d, ¹JC₆H₄ = 112.3 Hz, CHMe₂); 63.25 (t, ¹JC₆H₄ = 135.5 Hz, NCH₂); 61.55 (s, CMe₃); 30.41 (q, ¹JC₆H₄ = 125.7 H, CMe₃); 29.64 (t, ¹JC₆H₄ = 127.6 Hz, C₅H₄CH₂); 29.07 (q, ¹JC₆H₄ = 124.5 Hz, CHMe₂); 25.88 07 (q, ¹JC₆H₄ = 124.5 Hz, CHMe₂). IR (cm⁻¹, neat): 3109 (w), 3090 (w), 2947 (s), 2920 (s), 2868 (s), 2837 (s), 2697 (w), 1821 (w), 1778 (w), 1724 (w), 1692 (w), 1628 (w), 1493 (m), 1456 (s), 1393 (m), 1370 (s), 1360 (s), 1344 (m), 1323 (w), 1244 (s), 1223 (m), 1190 (s), 1163 (w), 1143 (s), 1072 (s), 1044 (m), 1026 (w), 984 (s), 937 (m), 912 (w), 885 (m), 845 (m), 814 (s), 770 (m), 679 (m), 646 (m), 608 (w), 561 (m), 534 (m), 486 (m), 442 (s), 424 (w).

[C₆H₄(CH₂)₂N-t-Bu]Ti(C₅H₄)Cl (37): [C₆H₄(CH₂)₂N-t-Bu]TiCl₂ (0.98 g, 3.47 mmol), C₅H₅MgCl (3.5 mmol), (-35 °C, 30 mL, 2 h, workup at 0 °C). Yield: 0.32 g (1.11 mmol, 32%, dark red crystals/oil). ¹H NMR (300 MHz, C₆D₆): δ 6.19 (m, 1H, C₆H₄); 6.16 (m, 1H, C₆H₄); 6.09 (quint, ³J_HCH = 10.98 Hz, 1H, CH₃CHCH₃); 5.67 (m, 2, C₆H₄); 3.54 (d, ³J_HCH = 10.98 Hz, 4H, CH₃CHCH₃); 3.42 (m, 1H, NCH₂), the other resonance of NCH₂ is overlapped with the resonance at 3.54 ppm); 2.25 (m, 2H, C₅H₄CH₂); 1.41 (s, 9H, CMe₃); ¹³C NMR (75.4 MHz, C₆D₆): δ 144.09 (d, ¹JC₆H₄ = 146.5 Hz, CH₃CHCH₂); 138.49 (s, C₅H₄-ipso); 119.86, 117.41, 114.99 (C₆H₄); 90.05 (t, ¹JC₆H₄ = 141.6 Hz, CH₂CHCH₂); 65.13 (t, ¹JC₆H₄ =
138.6 Hz, NCH₂); 62.05 (s, CMe₃); 29.90 (q, J_CH = 126.6 Hz, CMe₃); 29.85 (t, J_CH = 129.4 Hz, C₆H₄CH₃). IR (cm⁻¹): 3075 (w), 2726 (w), 2674 (w), 1603 (s), 1497 (w), 1362 (m), 1343 (w), 1323 (w), 1244 (m), 1225 (w), 1188 (s), 1072 (m), 1044 (m), 1017 (m), 982 (m), 937 (m), 862 (m), 845 (w), 826 (s), 770 (m), 739 (w), 723 (w), 681 (w), 646 (m), 593 (w), 534 (w), 484 (m), 459 (w), 428 (m).

\[\text{[C₆H₆(CH₂)₃N-t-Bu]Ti(C₆H₅)₂} \text{ (38): [C₆H₆(CH₂)₃N-t-Bu]TiCl₂ (1.16 g, 4.11 mmol), C₆H₆MgCl (8.1 mmol), (-50 °C, 30 mL, 2 h, workup at 0 °C). Yield: : 0.91 g (3.10 mmol, 75%, dark red oil).} \]

1H NMR (300 MHz, C₆D₆): δ 5.77 (m, 2H, C₆H₄); 5.74 (quint, 3J_HH = 5.61 Hz, 2H, CH₂CH₂C₆H₄); 4.94 (m, 2H, C₆H₄); 3.55 (t, 3J_HH = 5.13 Hz, 2H, NCH₂); 3.44 (d, 3J_HH = 11.47 Hz, 8H, CH₂CH₂C₆H₄); 2.45 (t, 3J_HH = 5.13 Hz, 2H, C₆H₄CH₃); 0.94 (s, 9H, CMe₃). 13C NMR 75.4 MHz, C₆D₆): δ 139.85 (d, J_CH = 146.6 Hz, CH₂CH₂C₆H₄); 133.60 (s, C₆H₄-ipso); 112.67 (d, J_CH = 176.8 Hz, C₆H₄); 111.32 (d, J_CH = 174.8 Hz, C₆H₄); 80.01 (t, J_CH = 145.8 Hz, CH₂CH₂C₆H₄); 61.94 (t, J_CH = 134.4 Hz, NCH₂); 59.76 (s, CMe₃); 30.78 (t, J_CH = 129.9 Hz, C₆H₄CH₃); 28.94 (q, J_CH = 124.4 Hz, CMe₃). IR (cm⁻¹, neat): 3065 (s), 2970 (s), 2860 (s), 2765 (w), 1639 (w), 1597 (s), 1525 (s), 1496 (m), 1473 (s), 1458 (m), 1388 (m), 1357 (s), 1342 (d), 1323 (w), 1288 (w), 1244 (s), 1224 (m), 1188 (s), 1066 (s), 1024 (s), 981 (s), 941 (s), 912 (m), 871 (sh, 830 cm⁻¹), 830 (s), 765 (m), 731 (m), 694 (w), 670 (m), 646 (m), 623 (w), 557 (w), 536 (m), 486 (w), 443 (m).

**Synthesis of [C₆H₆(CH₂)₃N-t-Bu]Ti(C₆H₅)(PMe₃) (39):** To a cooled (-60 °C) solution of 1.82 g (6.45 mmol) of [C₆H₆(CH₂)₃N-t-Bu]TiCl₂ and 1.5 mL (14 mmol) of PMe₃ in 40 mL of ether, 7.8 mL of 1.65 M (13 mmol) of EtMgBr in ether was added quickly. On warming up the reaction mixture to -40 °C, the solution turned yellow. Further warming to room temperature resulted in darkening of the solution and after 16 h stirring a deep purple solution and an off-white precipitate was obtained. The solvent was removed in vacuum resulting in a dark tarry residue. The residue was stripped with 20 mL of pentane and then extracted with 40 mL of pentane. The solution was concentrated to 5 mL and cooled to -50 °C. Crystallisation of a dark purple compound was observed but on warming to room temperature the crystals melted and the remaining pentane was removed in vacuum. Yield: 1.73 g (5.49 mmol, 85%) of 39. 1H NMR (300 MHz, C₆D₆): δ 6.59 (m, 1H, C₆H₄); 5.78 (m, 1H, C₆H₄); 4.97 (m, 1H, C₆H₄); 4.27 (m, 1H, C₆H₄); 3.54 (m, 1H, NCH₂); 3.09 (m, 1H, NCH₂); 2.57 (m, 1H, C₆H₄CH₃); 2.47 (m, 1H, C₆H₄CH₃); 2.18 (m, 1H, C₆H₄); 1.64 (m, 1H, C₆H₄); 1.39 (m, 1H, C₆H₄); 0.90 (d, Jₚ = 5.38 Hz, 9H, PMe₃); 0.87 (s, 9H, N-t-Bu); 0.35 (m, 1H, C₆H₄). 13C NMR (50 MHz, C₆D₆): δ 130.38 (s, C₆H₄-ipso); 110.58 (d, J_CH = 170.6 Hz, C₆H₄); 105.43 (d, J_CH = 172.0 Hz, C₆H₄); 102.80 (d, J_CH = 167.8 Hz, C₆H₄); 100.21 (d, J_CH = 167.6 Hz, C₆H₄); 57.62 (t, J_CH = 132.9 Hz, NCH₂); 56.51 (s, NCMes); 49.14 (dt, J_CH = 145.8 Hz, J_Cp = 10.0 Hz, C₆H₄); 44.45 (t, J_CH = 147.5 Hz, C₂H₄); 31.21 (t, J_CH = 127.2 Hz, C₂H₄CH₃); 29.54 (q, J_CH = 124.5 Hz, NCMe₃); 16.74 (dq, J_CH = 128.1 Hz, J_Cp = 13.6 Hz, PMe₃). 31P NMR (80.96 MHz, C₆D₆): δ 6.86 (PMe₃).

**Töpler-pump experiment of [C₆H₆(CH₂)₃N-t-Bu]TiCl₂ with 2 eq EtMgBr and 1 eq PMe₃:** A double legged Schlenk vessel (volume 180 mL) was filled with a solution of 571 mg (2.03 mmol) of
Synthesis of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\) (40). A cooled (-50 °C) suspension of 1.77 g (6.27 mmol) of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\) in 35 mL of ether and 2.0 mL (19 mmol) of \(\text{PMe}_3\) was reacted with 6.2 mL 2.02 M (12.5 mmol) of \(\text{n-PrMgBr}\) in ether. The mixture turned yellow. When the temperature was raised to -20 °C the color changed into dark green. The mixture was stirred overnight at room temperature. The ether was removed in vacuum and the oily residue was stripped with 50 mL of pentane followed by extraction with pentane (2x 50 mL). Complete removal of the solvent yielded a dark oil: 1.80 g (5.46 mmol, 87%) of \(\text{[C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\), 2.6 mL 1.46 M (3.80 mmol) of \(\text{EtMgBr}\) and 200 µL (1.93 mmol) of \(\text{PMe}_3\), gave 1.02 mole gas/mole Ti. GC Anal.: Ethane, 100%. A second Töpler pump experiment carried out with 528.2 mg (1.873 mmol) of \(\text{[C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiCl}_2\), 2.6 mL 1.46 M (3.80 mmol) of \(\text{EtMgBr}\) and 200 µL (1.93 mmol) of \(\text{PMe}_3\), gave 1.02 mole gas/mole Ti. GC Anal.: Ethane, 100%

Thermalysis of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiPH}_2\) (26) in the presence of 2 eq. \(\text{PMe}_3\). In an NMR tube 45.4 mg (0.124 mmol) of 26 was dissolved in 0.4 mL of \(\text{C}_6\text{D}_6\) and 2 eq. of \(\text{PMe}_3\) was added. The NMR tube was sealed and heated to 75 °C. After 30 min 26 had been converted in to 43. Thermalysis of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiPH}_2\) (26) in \(\text{C}_6\text{D}_6\). In an NMR tube a solution of 50.6 mg (0.138 mmol) of 26 in 0.5 mL of \(\text{C}_6\text{D}_6\) (0.276 M) was prepared and the tube was sealed under nitrogen. The tube was heated at 55.0 °C and \(^1\text{H}\) NMR spectra were recorded using the following time intervals: first eight spectra with an interval of 15 min, then 8 spectra with an interval of 30 min and at last 18 spectra with an interval of 60 min.

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Thermolysis of $[C_5H_4(CH_2)_2N-t-Bu]TiPh_2$ (26) in $C_6D_{12}$. A similar NMR tube experiment as described above was performed using 35.5 mg (0.097 mmol) of 26 in 0.35 mL of $C_6D_{12}$ (0.277 M). Within 6 h 26 was completely converted into 44 (55%), benzene and decomposition products which could not be identified.

Synthesis of $([C_5H_4(CH_2)_2N-t-Bu]Ti(C_6H_5)]_2$ (44). A solution of 0.95 g (2.60 mmol) of 26 in 40 mL of hexane was heated at 57 °C. The dark-yellow solution became dark and after 30 min. an orange powder started to precipitate. After 5 h the reaction mixture was cooled to room temperature, filtered and the orange residue was washed 3 times with 10 mL of pentane. Yield: 0.26 g (0.91 mmol, 35%) of 44. $^1H$ NMR (200 MHz, $C_6D_{12}$): δ 7.92 (dd, $J_{1H1} = 5.56$ Hz, $J_{1H2} = 2.99$ Hz, 2H, $C_6H_4$); 7.00 (dd, $J_{1H1} = 5.56$ Hz, $J_{1H2} = 2.99$ Hz, 2H, $C_6H_4$); 6.19 (t, $J_{1H1} = 2.56$ Hz, 2H, $C_6H_4$); 4.87 (t, $J_{1H1} = 2.56$ Hz, 2H, $C_6H_4$); 4.05 (t, $J_{1H1} = 6.41$ Hz, 2H, NCH$_2$); 2.85 (t, $J_{1H1} = 6.41$ Hz, 2H, $C_6H_4CH_2$); 0.73 (s, N-t-Bu) $^{13}C$ NMR (75.4 MHz, $C_6D_{12}$): δ 188.71 (s, $C_6C_6H_4$); 139.60 (s, $C_6C_6H_4$); 133.48 (d, $J_{1CH} = 157.4$ Hz, $C_6H_4$); 126.44 (d, $J_{1CH} = 156.0$ Hz, $C_6H_4$); 113.22 (d, $J_{1CH} = 173.2$ Hz, $C_6H_4$); 110.65 (d, $J_{1CH} = 171.84$ Hz, $C_6H_4$); 64.82 (t, $J_{1CH} = 133.3$ Hz, NCH$_2$); 62.35 (s, N$_2$Me$_2$); 32.00 (t, $J_{1CH} = 127.8$ Hz, $C_6H_4CH_2$); 29.11 (q, $J_{1CH} = 125.1$ Hz, NCMe$_2$). IR (cm$^{-1}$): 3057 (w), 3030 (w), 3003 (sh, nujol), 1520 (w), 1500 (w), 1491 (w), 1471 (s), 1411 (s), 1381 (s), 1334 (w), 1294 (w), 1284 (w), 1249 (s), 1235 (s), 1220 (w), 1194 (s), 1116 (w), 1088 (m), 1041 (w), 1013 (w), 973 (m), 940 (w), 864 (m), 844 (m), 819 (s), 792 (w), 767 (m), 733 (s), 677 (m), 644 (w), 605 (m), 542 (m). Anal. calcd for $C_{24}H_{31}$NTi: C, 71.08; H, 7.37. Found: C, 68.36; H, 7.33.

Thermolysis of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2CMe_3)_2$ (29) in $C_6D_{12}$ in the presence of 2 eq. of PMe$_3$. In an NMR tube, a solution of 42.7 mg (0.120 mmol) of 29 and 25 µL (0.242 mmol) of PMe$_3$ in 0.4 mL of $C_6D_{12}$ was prepared and the tube was sealed. The tube was heated at 75 °C and a $^1H$ NMR spectrum was recorded every 30 min. After 90 min 29 was been completely converted into 46.

Thermolysis of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2CMe_3Ph)_2$ (31) in $C_6D_6$ in the presence of excess PMe$_3$. A solution of 70.2 mg (0.147 mmol) of 31 and 20 mL of PMe$_3$ in 0.4 mL of $C_6D_6$ was sealed in a NMR tube and heated at 75 °C. A $^1H$ NMR spectrum was recorded after resp. 50, 140, 210, 360, 510 min. After 8.5 h the starting material had been completely converted into $[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3Ph)PMe_3$ (47) and t-butylbenzene.

Synthesis of $[C_5H_4(CH_2)_2N-t-Bu]Ti=C(H)CMe_3(PMe_3)$ (46). A solution of 2.50 g (7.07 mmol) of $[C_5H_4(CH_2)_2N-t-Bu]Ti(CH_2CMe_3)_2$ and 1.5 mL (14 mmol) of PMe$_3$ in 35 mL of cyclohexane was heated at 75-80 °C during 3 h. The yellow-brown solution turned red-brown. The solvent was removed in vacuum and the red-brown residue was stripped with 20 mL of pentane. The residue was extracted with 20 mL of pentane and the solution was concentrated to 5 mL while refluxing. Standing overnight at room temperature, dark purple crystals were formed resulting in 0.45 g (1.26 mmol) of product. Concentration of the mother liquor and cooling to -30 °C gave a second crop 1.26 g (3.52 mmol) of
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Synthesis of [C₅H₅(CH₂)₂N-t-Bu]Ti=C(H)CMes₂Ph(PMe₃) (47). A solution of 3.07 g (6.46 mmol) of [C₅H₅(CH₂)₂N-t-Bu]Ti(CH₂CMes₂Ph)₂ and 1.6 mL (15 mmol) of PMe₃ in 40 mL of cyclohexane was heated at 80 °C for 8 h. The dark yellow solution became red-brown. The solvent was removed in vacuum and the red-brown residue was stripped three times with 30 mL of pentane and dried in vacuum (10⁻¹ torr) for 1 h. The residue was extracted with 50 mL of pentane and the solution was concentrated while refluxing until the complex started to crystallize. Pentane (3 mL) was added. On refluxing all crystals dissolved and the solution was cooled overnight to -30 °C. In a first crop 1.36 g (3.24 mmol) of dark red crystals were obtained. Concentration and slowly cooling of the mother liquor gave a second crop, 0.43 g (1.03 mmol) of product. Yield: 1.71 g (4.78 mmol, 68%) of 46. ¹H NMR (300 MHz, C₅D₅): δ 7.01 (m, 1H, C₅H₅); 6.39 (d, ²Jₚₙ = 1.70 Hz, 1H, =C(H)CMes₃); 6.10 (m, 1H, C₅H₅); 5.39 (m, 1H, C₅H₅); 4.98 (m, 1H, C₅H₅); 3.46 (m, 1H, NCH₂); 3.07 (m, 1H, NCH₂); 2.44 (m, 1H, C₅H₅CH₂); 2.07 (m, 1H, C₅H₅CH₂); 1.37 (s, 9H, N-t-Bu); 1.16 (s, 9H, =C(H)CMes₃); 0.91 (d, ²Jₚₙ = 6.1 Hz, 9H, PMe₃). ¹³C NMR (75.4 MHz, C₅D₅): δ 251.39 (dd, Jₐ = 3.2 Hz, =C(H)CMe₄); 171.70 (sh, Nujol), 1420 (m), 1350 (s), 1302 (m), 1279 (s), (C₅H₅CH₂); 124.6 Hz, C₅H₅; 103.24 (d, JCH = 172.2 Hz, C₅H₅); 101.97 (d, JCH = 167.19 Hz, C₅H₅); 100.79 (d, JCH = 166.2 Hz, C₅H₅); 57.94 (t, JCH = 132.5 Hz, NCH₂); 56.70 (s, NCMes); 45.48 (s, =C(H)CMes₃); 33.63 (dq, JCH = 124.6 Hz, HCP₃ = 3.0 Hz, =C(H)CMes₃); 32.79 (q, JCH = 124.6 Hz, NCMes); 31.87 (t, JCH = 126.9 Hz, C₅H₅CH₂); 17.70 (dq, JCH = 128.9 Hz, HCP₃ = 17.1 Hz, PMe₃). ³¹P NMR (80.96 MHz, C₅D₅): δ -6.01 (PMe₃). IR (cm⁻¹): 3117 (vw), 3094 (w), 2814 (w), 2714 (vw), 2675 (m), 1572 (w), 1458 (sh, Nujol), 1420 (m), 1350 (s), 1302 (m), 1279 (s), 1244 (s), 1227 (m), 1190 (s), 1146 (m), 1059 (m), 1045 (m), 1030 s), 984 (w), 972 (w), 951 (vs), 856 (m), 839 (m), 828 (w, 787 (vs), 762 (m), 729 (m), 687 (m), 673 (m), 554 (m), 542(m). Anal. Calcd. for C₁₉H₉₈NPTiC: 63.86; H: 10.15; Ti: 13.40. Found: C: 64.13; H: 9.89; Ti: 13.55.
(vs), 1157 (w), 1120 (m), 1091 (m), 1068 (m), 1043 (s), 1028 (s), 1006 (w), 970 (w), 954 (vs), 910 (m), 873 (m), 839 (s), 823 (s), 787 (vs), 765 (s), 727 (m), 700 (s), 682 (m), 578 (s), 559 (w), 540 (m), 489 (w), 468 (m), 445 (vw). Anal. Calcd. for C$_{24}$H$_{38}$NPTi: C, 68.72; H, 9.13; Ti, 11.42. Found: C, 68.40; H, 9.13; Ti, 11.58.

### 3.11 References and Notes


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(6) The formation of \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{TiMe}_2\) may be also due to fact that when the MeLi is added the dichloride is only partially dissolved. The initially formed \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti(Me)}\text{Cl}\) can react with another equivalent MeLi. Probably \([\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti(CH}_2\text{Ph})\text{Cl}\) is under these conditions much less reactive towards PhCH\(_2\text{MgCl}\).

(7) When the same reaction was carried out in the presence of excess PMe\(_3\) a tarry brown oil was obtained. \(^1\text{H} \text{NMR spectroscopy revealed the same resonances as observed for the propene complex [C}_5\text{H}_4(\text{CH}_2)_2\text{N}-\text{t-Bu}]\text{Ti(C}_3\text{H}_6).\text{PMe}_3\).

(8) A nice example is the reaction of \(\text{Cp}^*\text{Zr(C}_8\text{H}_8)\text{Cl with i-PrMgCl resulting in the hydride Cp}^*\text{Zr(C}_8\text{H}_8)\text{H by extrusion of propene. Highcock, W.J.; Mills, R.M.; Spencer, J.L.; Woodward, P. J. Chem. Soc., Dalton Trans. 1986, 821.}


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(29) The photochemically induced decompositions as they are reported are not fully understood. Probably these processes can better be considered as photochemically catalyzed thermal decompositions.

(30) Phosphines are commonly used to stabilize olefin, aryne and alkylidene complexes, see ref. 19, 20 and 21.

(31) Thermolyses of the [C₅H₅(CH₂)ₙNMe]TiR₂ (n = 2, 3; R = Et, Ph, CH₂CMe₃ and CH₂CMe₂Ph) in the presence of PMe₃ did not result in the formation of olefin, aryne and alkylidene complexes. The aryne complex [C₅H₅(CH₂)₂N-t-Pr]Ti(C₆H₄)(PMe₃) was obtained on thermolysis of the diphenyl compound in the presence of PMe₃. From this it can be assumed that bulky amido substituents are required to get the desired olefin, aryne and alkylidene complexes.


(36) A ¹H NMR spectrum showed resonances characteristic for a [C₅H₅(CH₂)₂N-t-Bu]Ti moiety together with some broad resonances but the identity of the complexes formed could not be elucidated.

(37) A Töpler experiment revealed the formation of 0.91 mol C₂H₄/mol Ti.


(41) At this stage the NMR tube still contains 44 as a solid, therefore no proper conversion degree of 44 could be estimated.

(42) NOESY experiments revealed that the resonances for 46 (6.28 ppm) and 47 (6.45 ppm) showed no coupling with the other resonances in that region.


(48) At the beginning, the formed [C₅H₄(CH₂)₅N-t-Bu]Ti(C₂H₄)(PMe₃) (39) reacts further with the present ethene resulting in the formation of some [C₅H₄(CH₂)₅N-t-Bu]Ti(CH₂)₄ (41).


(51) 26-d₁₀ was prepared analogous to 26 in 66% yield using C₆D₅MgBr.

(52) The thermolyses of 26 and 26-d₁₀ (66 °C, C₆D₁₂, 3 equiv. PMe₃) obey first order kinetics with 
k_H = 4.77 ± 0.14 x 10⁻⁴ s⁻¹, k_D = 1.08 ± 0.06 x 10⁻⁴ s⁻¹, k_H/k_D = 4.4 at 339 K.