

# Titanium Dichloro, Bis(carbyl), Aryne, and Alkylidene Complexes Stabilized by Linked Cyclopentadienyl–Amido Auxiliary Ligands

Piet-Jan Sinnema,<sup>†</sup> Loes van der Veen,<sup>†</sup> Anthony L. Spek,<sup>‡</sup> Nora Veldman,<sup>‡</sup> and Jan H. Teuben<sup>\*,†</sup>

Center for Catalytic Olefin Polymerization, Department of Chemistry, Groningen University, Nijenborgh 4, 9747 AG Groningen, The Netherlands, and Bijvoet Center for Biomolecular Research, Padualaan 8, 3585 CH Utrecht, The Netherlands

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**Summary:** Thermal decomposition of the carbyl compounds  $\{C_5H_4(CH_2)_2NR\}TiR_2$  proceeds through  $\alpha$ - and  $\beta$ -H elimination to give stable aryne, alkylidene, and olefin complexes in the presence of  $PMe_3$ . Reaction of the dibenzyl compound  $\{C_5H_4(CH_2)_2N-t-Bu\}Ti(CH_2Ph)_2$  with  $B(C_6F_5)_3$  gives the cationic  $[C_5H_4(CH_2)_2N-t-Bu\}TiCH_2Ph]^+$ , which is an active catalyst for the polymerization of ethene and propene.

The replacement of the classical bis(cyclopentadienyl) ligand set in group 4 metal chemistry by bidentate ligands in which a cyclopentadienyl ligand is linked to another cyclopentadienyl type ligand (*ansa*-metallocenes)<sup>1</sup> or to a different anionic functionality (amide or alkoxide)<sup>2</sup> has created a range of new olefin polymerization catalysts with a remarkable variation in catalytic properties. Catalysts based on *ansa*-metallocenes have excellent selectivity for stereoregular polymerization of  $\alpha$ -olefins such as propene. The open coordination space of the Cp–alkoxy and Cp–amido systems allows efficient  $\alpha$ -olefin comonomer incorporation into a growing polyethylene chain.<sup>3</sup>

In contrast with the extensively investigated (*ansa*)-metallocene compounds of Group 4 metals the organometallic chemistry of cyclopentadienyl–alkoxy- and the cyclopentadienyl–amido-stabilized group 4 derivatives has yet to be explored and systematic reactivity studies have not been reported so far. An efficient and general synthetic methodology for these

types of compounds is lacking, despite the obvious scientific and economic importance.

One of the reasons for this relative paucity of study in field may be that design and implementation of new ligand systems on metal centers is not straightforward. Hughes *et al.* have described a high-yield route for introduction of linked cyclopentadienyl–amido ligands through the reaction of Ti, Zr, and Hf tetraamido precursors,  $M(NR_2)_4$ , with the neutral form of the ligands.<sup>4</sup> This route has been used since for the introduction of other ligand systems as well.<sup>5</sup>

In this communication we report a simple and efficient route to new titanium dichloride complexes stabilized by  $C_2$ - or  $C_3$ -linked cyclopentadienyl–amido ligands,  $\{\eta^5\text{-}\eta^1\text{-}C_5H_4(CH_2)_nNR\}TiCl_2$ , further derivatization of the dichloride to new bis(alkyl) and bis(aryl) derivatives  $\{\eta^5\text{-}\eta^1\text{-}C_5H_4(CH_2)_nNR\}TiR_2$ , and some exploratory reactivity studies of the latter.

The basic synthesis step is introduction of the linked dianionic ligands  $[C_5H_4(CH_2)_nNR]^{2-}$  ( $n = 2$ ,  $R = Me$ , *i*-Pr, *t*-Bu;  $n = 3$ ,  $R = Me$ , *i*-Pr) through reaction of the neutral form of the ligand,  $C_5H_5(CH_2)_nN(R)H$ , with metal halides  $MX_n$  in the presence of a base ( $Et_3N$ ) to trap generated  $HX$ . This method has been applied before for the introduction of cyclopentadienyl<sup>6</sup> and alkoxide<sup>7</sup> ligands.

We have been able to prepare a range of complexes  $\{\eta^5\text{-}\eta^1\text{-}C_5H_4(CH_2)_nNR\}TiCl_2$  ( $n = 2$ ,  $R = Me$  (**1**), *i*-Pr (**2**), *t*-Bu (**3**);  $n = 3$ ,  $R = Me$  (**4**), *i*-Pr (**5**)) by reaction of  $C_5H_5(CH_2)_nN(R)H$  with  $TiCl_4$  in the presence of  $Et_3N$  (Scheme 1).<sup>9</sup>

In order to assess the structural consequences of a  $C_2$  or a  $C_3$  backbone, molecular structures of **2** and **5**

\* To whom correspondence should be addressed. E-mail: teuben@chem.rug.nl.

<sup>†</sup> Groningen University.

<sup>‡</sup> Bijvoet Center for Biomolecular Research.

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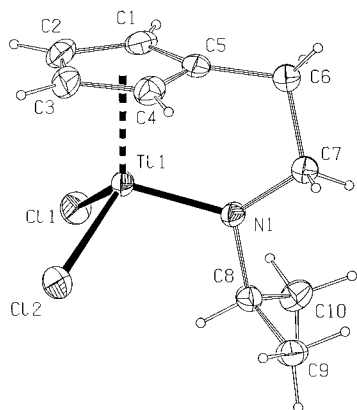
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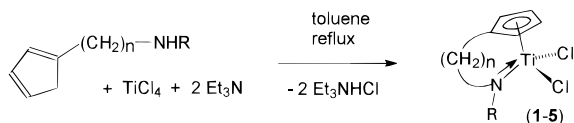
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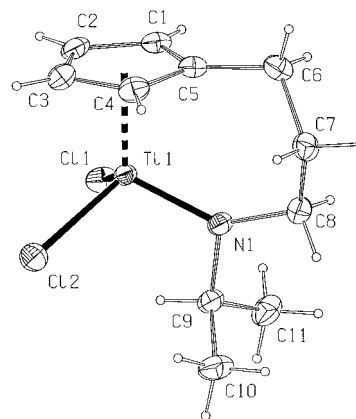


**Figure 1.** Molecular structure of  $\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(i\text{-Pr})\}\text{TiCl}_2$  (**2**) (atoms represented as 50% probability ellipsoids) with adopted numbering scheme. Relevant geometrical data: Ti1–Cl1, 2.2752(11) Å; Ti1–Cl2, 2.2996(12) Å; Ti1–N1, 1.864(2) Å; Ti1–Cg, 2.008(4) Å; N1–Ti1–Cg, 104.4(1)°; Cl1–Ti1–Cl2, 103.01(4)°; Ti1–N1–C7, 129.2(2)°; Ti1–N1–C8, 114.23(19)°; C7–N1–C8, 116(4)(3)°.

### Scheme 1



(Figures 1 and 2) were determined by X-ray diffraction methods.<sup>10</sup> Both compounds are monomeric with a distorted-tetrahedral coordination geometry of the metal centers. The Cp ligands are  $\eta^5$ -bonded in the regular way and have normal bond distances (C–H, C–C, and Ti–C) in both complexes. There is almost no difference between the Ti–Cl, Ti–N, and Ti–Cg (Cg = center of gravity of the Cp ring) distances and Cl–Ti–Cl angles of the two compounds. Clearly these parameters are hardly affected by variation of the length of the backbone. The short Ti–N distances (**2**, 1.864(2) Å; **5**, 1.8668(15) Å) and the planar geometry of the nitrogen atoms in both complexes indicate  $\text{sp}^2$  hybridization of the N atom with the out-of-plane lone pair giving an



**Figure 2.** Molecular structure of  $\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{N}(i\text{-Pr})\}\text{TiCl}_2$  (**5**) (atoms represented as 50% probability ellipsoids) with adopted numbering scheme and relevant geometrical data: Ti1–Cl1, 2.2849(5) Å; Ti1–Cl2, 2.3025(6) Å; Ti1–N1, 1.8668(15) Å; Ti1–Cg, 2.027(2) Å; Ti1–H9, 2.38(2) Å; N1–Ti1–Cg, 112.6(1)°; Cl1–Ti1–Cl2, 103.40(3)°; Ti1–N1–C8, 142.08(13)°; Ti1–N1–C9, 104.47(10)°; C8–N1–C9, 112.98(14)°.

$\text{N}(\text{p}_\pi) \rightarrow \text{M}(\text{d}_\pi)$  interaction. Therefore, the complexes can be considered to be 14-electron complexes.

The main structural effect of the variation of the length of spacer with one methylene unit is a substantial difference in bond angles of the linked bidentate ligand and titanium. In **5**, the Cg–Ti–N (112.6(1)°) and Ti–N–CH<sub>2</sub> angles (142.08(13)°) are clearly larger, while the Ti–N–C<sub>i-Pr</sub> angle (104.47(10)°) is considerably smaller, compared to those in **2** (104.4(2), 129.2(2), and 114.23(19)°, respectively).

It is clear that the shorter (C<sub>2</sub>) spacer leaves a much more open metal center, whereas the C<sub>3</sub> bridge shifts the amido function further toward the two chloro ligands and thus narrows the reaction space. The amido function seems to move in the plane bisecting the Cl–Ti–Cl angle, and the most notable difference between the two structures is that in the C<sub>3</sub>-linked compound the isopropylamido ligand is pushed forward toward the chloro ligands, resulting in a much smaller Ti–N–C angle (114.23(19)° in **2** vs 104.47(10)°). The relative orientation of the cyclopentadienyl and the two chloro ligands does not seem to be affected to a great extent.

The conformation of the isopropyl groups of the amido functions is remarkable. In both complexes steric interactions force these substituents into a conformation in which the methine protons point toward the metal centers. This appears to be the cause of substantial downfield shifts of the methine protons in the <sup>1</sup>H NMR spectrum (**2**, 5.92 ppm; **5**, 6.57 ppm).<sup>11</sup>

The amido-functionalized cyclopentadienyltitanium dichlorides could readily be converted to the bis(alkyl) or bis(aryl) compounds  $\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}\}\text{TiR}_2$  by salt metathesis using Grignard or organolithium reagents. In this way  $\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}\}\text{TiR}_2$  species (R = Me (**6**), CH<sub>2</sub>Ph (**7**), Ph (**8**), CH<sub>2</sub>CMe<sub>3</sub> (**9**), and

(8) The ligands were prepared analogous to  $\text{C}_5\text{H}_5(\text{CH}_2)_3\text{N}(\text{H})\text{Me}$ .<sup>4</sup>

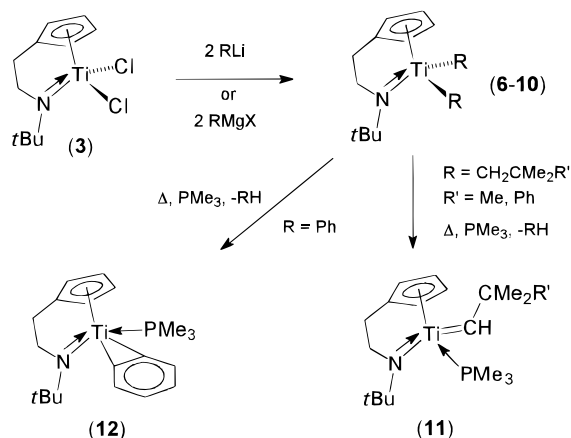
(9) Compounds **1–5** were made by refluxing  $\text{TiCl}_4$  and  $\text{C}_5\text{H}_5(\text{CH}_2)_n\text{N}(\text{R})\text{H}$  and 2 equiv of  $\text{Et}_3\text{N}$  in toluene. Recrystallization or sublimation afforded the complexes in ca. 60% yield. The compounds are soluble in aromatic solvents and THF but virtually insoluble in pentane. As a typical example the synthesis of  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{N-}t\text{-Bu}]\text{TiCl}_2$  (**3**) is given here. To a heated (75–80 °C) solution of 32.3 g (0.195 mol) of  $\text{C}_5\text{H}_5(\text{CH}_2)_2\text{N}(\text{H})\text{-}t\text{-Bu}$  and 55 mL (0.40 mol) of  $\text{Et}_3\text{N}$  in toluene (450 mL) was added a solution of 22 mL (0.20 mol) of  $\text{TiCl}_4$  in toluene (250 mL) over 20 min with vigorous stirring. Subsequently the mixture was refluxed for 3 h to give a deep red solution and a dark precipitate. The solution was filtered, and the solvent was removed under vacuum to give a red product. The crude product was continuously extracted with ether. The ether was removed under vacuum. The product was washed two times with 100 mL of pentane and dried under vacuum. Yield: 33.65 g (119 mmol, 60%) of red, microcrystalline **3**. <sup>1</sup>H NMR (200 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.19 (t, <sup>3</sup> $J_{\text{HH}}$  = 2.56 Hz, 2H,  $\text{C}_5\text{H}_4$ ); 5.90 (t, <sup>3</sup> $J_{\text{HH}}$  = 2.56 Hz, 2H,  $\text{C}_5\text{H}_4$ ); 3.66 (t, <sup>3</sup> $J_{\text{HH}}$  = 6.87 Hz, 2H,  $\text{CH}_2\text{N}$ ); 2.37 (t, <sup>3</sup> $J_{\text{HH}}$  = 6.87 Hz, 2H,  $\text{C}_5\text{H}_4\text{CH}_2$ ); 1.42 (s, 9H,  $t\text{-Bu}$ ). <sup>13</sup>C NMR (50 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  144.10 (s,  $\text{C}_5\text{H}_4\text{-ipso}$ ); 118.12 (d, <sup>1</sup> $J_{\text{CH}}$  = 171.9 Hz,  $\text{C}_5\text{H}_4$ ); 118.04 (d, <sup>1</sup> $J_{\text{CH}}$  = 178.7 Hz,  $\text{C}_5\text{H}_4$ ); 69.96 (t, <sup>1</sup> $J_{\text{CH}}$  = 137.4 Hz,  $\text{CH}_2\text{N}$ ); 64.59 (s,  $\text{CMe}_3$ ); 29.72 (t, <sup>1</sup> $J_{\text{CH}}$  = 130.2 Hz,  $\text{C}_5\text{H}_4\text{CH}_2$ ); 28.82 (q, <sup>1</sup> $J_{\text{CH}}$  = 126.2 Hz,  $\text{CMe}_3$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_{17}\text{Cl}_2\text{NTi}$ : C, 46.84; H, 6.08; Ti, 16.98. Found: C, 46.88; H, 6.09; Ti, 16.90.

(10) Crystal data for **2**:  $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{NTi}$ , space group  $P\bar{1}$ , with  $a = 7.6327(11)$  Å,  $b = 7.810(2)$  Å,  $c = 10.716(2)$  Å,  $\alpha = 102.821(10)^\circ$ ,  $\beta = 102.618(10)^\circ$ ,  $\gamma = 101.211(10)^\circ$ ,  $V = 587.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150$  K,  $R = 0.0441$  for 2016 reflections with  $I > 2\sigma(I)$ . Crystal data for **5**:  $\text{C}_{11}\text{H}_{17}\text{Cl}_2\text{NTi}$ , space group  $P2_1/c$ , with  $a = 8.5385(5)$  Å,  $b = 12.9690(7)$  Å,  $c = 11.9157(6)$  Å,  $\beta = 108.722(4)^\circ$ ,  $V = 1249.08(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150$  K,  $R = 0.0314$  for 2552 reflections with  $I > 2\sigma(I)$ .

(11) Recently the structure of  $[\text{C}_5\text{H}_4\text{SiMe}_2\text{N-}i\text{-Pr}]\text{TiCl}_2$  has been published, in which the methine proton is directed to the metal center (<sup>1</sup>H NMR:  $\delta = 5.69$ ): Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber./Recl.* **1997**, 130, 209.

(12) The bis(alkyl) and bis(aryl) complexes were made by addition of Grignard or organolithium reagents to a cooled (–80 to –60 °C) suspension of the dichloride complex in ether and subsequent workup from pentane in 67–81% yield. Complexes **6** and **7** were isolated as oils but could be properly identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

Scheme 2



$\text{CH}_2\text{CMe}_2\text{Ph}$  (**10**) have been synthesized from **3**.<sup>12</sup> In comparison to the analogous  $\text{Cp}_2\text{TiR}_2$  compounds<sup>13</sup> the dialkyl complexes are thermally considerably more stable. In contrast, the diphenyl compound  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{N-}t\text{-Bu}\}\text{TiPh}_2$  (**8**) is less stable (75 °C, 0.5 h) than  $\text{Cp}_2\text{TiPh}_2$  (110 °C, 5 h).<sup>13b</sup> Thermal decomposition (75–120 °C) of all alkyl and aryl derivatives  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{N-}t\text{-Bu}\}\text{TiR}_2$  proceeds with formation of RH.

Thermolysis of the diphenyl complex **8** in the presence of  $\text{PMe}_3$  (75 °C, 30 min) produced the 16-electron benzyne complex  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{Ti(C}_6\text{H}_4)_2\text{PMe}_3$  (**11**) and benzene (Scheme 2).

The bis(neopentyl) complex **9** was thermolyzed in the presence of  $\text{PMe}_3$  (75 °C, 1.5 h), with formation of neopentane and the neopentylidene complex  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{Ti=C(H)CMe}_3\text{PMe}_3$  (**12**) (Scheme 2).<sup>14</sup> The bis(neophyl) compound **10** gave phenyltrimethylmethane and the corresponding neophylidene complex  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{Ti=C(H)CMe}_2\text{Ph.PMe}_3$  (**13**); this formation is much slower (75 °C, 8.5 h). The clean  $\alpha\text{-H}$  abstraction in titanium bis(neopentyl) and bis(neophyl) derivatives stabilized by linked cyclopentadienyl–amido ligands is in marked contrast with e.g. the  $\text{CpVR}_2\text{PMe}_3$  ( $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{CMe}_2\text{Ph}$ ) compounds, where the bis(neopentyl) species undergoes  $\alpha\text{-H}$

abstraction and the bis(neophyl) derivative cyclometallates through  $\delta\text{-H}$  activation instead.<sup>15</sup>

The alkylidene complexes **12** and **13** have been tested for catalytic ROMP activity (norbornene), but they proved to be inactive, even at elevated temperatures (50–100 °C). The neopentylidene complex **12** reacted with ethene via cycloaddition and subsequent  $\beta\text{-hydrogen}$  elimination rather than metathesis to give the ethylene complex  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{Ti(C}_2\text{H}_4)_2\text{PMe}_3$  (**14**).<sup>16</sup>

The dibenzyl complex  $\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{Ti(CH}_2\text{-Ph)}_2$  (**7**) has been reacted with strong Lewis acids  $\text{B(C}_6\text{F}_5)_3$  to give the cationic complex  $[\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_2\text{N-}t\text{-Bu}\}\text{TiCH}_2\text{Ph}]^+$ , charge-balanced by the complex anion  $[\text{PhCH}_2\text{B(C}_6\text{F}_5)_3]^-$ . The cationic complex has interesting activity as a catalyst for olefin (ethene, propene) polymerization. An important preliminary observation is that the molecular weight of polyethene formed appears to depend on the nature of the complex anion and more specifically its coordinative properties.<sup>17</sup>

In conclusion, we have developed a facile route for the preparation of the complexes  $[\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{(CH}_2)_n\text{NR}]\text{-TiCl}_2$ , which appears to be quite tolerant to variation of chain length and alkylamido group. The dichloro complexes can be easily converted into their carbyl derivatives which, upon thermolysis in the presence of a Lewis base, show selective C–H activation processes resulting in stable benzyne, alkylidene, and olefin complexes. The dichlorides and carbyl complexes are of particular interest as catalyst precursors, and their behavior in the catalytic polymerization of olefins is currently under investigation.

**Acknowledgment.** We wish to thank the SON and NWO for the X-ray facilities and Dr. Bart Hessen (University of Groningen) for helpful discussions.

**Supporting Information Available:** Text giving full experimental details of the synthesis and characterization of the compounds described and structure determination summaries and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for **2** and **5** (44 pages). Ordering information is given on any current masthead page.

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(14) The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances of the  $\text{Ti=CHR}$  moiety in **12** are found at  $\delta$  6.39 (d,  $J_{\text{PH}} = 1.7$  Hz) and  $\delta$  251.4 (dd,  $J_{\text{CH}} = 83.1$  Hz,  $J_{\text{PC}} = 13.1$  Hz), respectively. Pure **12** and **13** were obtained in 66–68% yield. The  $^1\text{H}$  NMR resonance is found significantly more upfield than in a recently reported, related Cp(phosphinoalkoxide)Ti–alkylidene complex, viz.  $\delta$  12.27; Van Doorn, J. A.; Van der Heijden, H.; Orpen, A. G. *Organometallics* **1995**, *14*, 1278.

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(16) Compound **14** has also been prepared by reaction of **3** with 2 equiv of  $\text{EtMgBr}$  in the presence of  $\text{PMe}_3$ .

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