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# Synthesis and characterization of cyclopentadienyl/alkoxo titanium dichlorides: structural analysis of monocyclopentadienyl titanium dichlorides with ligands derived from menthol and borneol

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**Abstract**

A variety of monocyclopentadienyl alkoxo titanium dichloride and bisalkoxo titanium dichloride complexes have been prepared and characterized by spectroscopic techniques. The titanium derivatives containing both cyclopentadienyl and various alkoxo ligands $[Ti(\eta^5-C_5H_5)(OR)Cl_2]$ (**1**–**5**) have been synthesized from the reaction of $[Ti(\eta^5-C_5H_5)Cl_3]$ with 1 equivalent of the corresponding alcohol in THF in the presence of triethylamine (ROH = Adamantanol, 1*R*,2*S*,5*R*-(−)-menthol, 1*S*-endo-(−)-borneol, *cis*-1,3-(−)-benzylideneglycerol, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose). The bisalkoxo titanium dichloride derivatives $[TiCl_2(OR)_2]$ (**6**–**10**) have been prepared by a redistribution reaction between $Ti(OR)_4$ and $TiCl_4$ compounds **6**–**8** (OR = Adamantanoxy, (1*R*,2*S*,5*R*)-(−)menthoxy, (1*S*-endo)-(−)-borneoxy) and by reaction of $[Ti(OR)_2(OPr^i)_2]_2$ with $CH_3COCl$ compounds **9** and **10** (OR = 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoxy, and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoxy). The molecular structures of **2** and **3** have been determined by single crystal X-ray diffraction studies.

*Keywords:* Titanium; Cyclopentadienyl; Alkoxo; Chiral alcohols; Polymerization

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## 1. Introduction

Monocyclopentadienyl group 4 transition metal derivatives that are further ligated by a non-Cp group $[MCpLX_2]$ (Cp = cyclopentadienyl group, M = Ti, Zr, Hf; L = anionic ligand such as OR, OAr, $NR_2$, $NPR_3$; X = halogen, alkyl) [1,2] have attracted considerable attention as a type of olefin polymerization catalyst, because this type of complexes exhibits unique characteristics as olefin polymerization catalysts that are different from both ordinary metallocene type [3] and the so called "constrained geometry" systems [4–6], where the Cp and non Cp ligands are linked by some sort of bridging group. On the other hand, complexes of the general formula $[TiCl_2(OR)_2]$ serve as Lewis acid catalysts or mediators (in stoichoimetric amounts) in different reactions [7,8].

In the field of alkoxo and thiolate chemistry steric hindrance has commonly been introduced through 2,6-dialkyl substitution of aromatic alcohols and thiols and the use of bulky alkoxo ligands for supporting stoichiometric and catalytic chemistry of early transition metals continues to be an important area in organome-

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tallic chemistry [9]. These developments have led us to attempt the synthesis of some chiral analogues with the goal of studying the capacity of these derivatives for transferring their stereochemical information to transition metals and subsequently to their catalyzed reactions [10]. Sugars are natural chiral bulky alcohols and therefore sugar metal complexes should have pronounced three dimensional characteristics. There are only small number of titanium complexes with these type of ligands despite the synthesis of [Ti($\eta^5$-$C_5H_5$)(OR*)$_2$Cl] (OR* = 1,2:5,6-di-isopropylidene-α-D-glucofuranoso-3-*O*-yl) being first reported by Riediker and Duthaler [11].

## 2. Results and discussion

[Ti($\eta^5$-$C_5H_5$)(OR)$Cl_2$] {OR = adamantanoxy (OAdam (**1**)), (1*R*,2*S*,5*R*)-(−)menthoxy (OMent (**2**)), (1*S*-endo)-(−)-borneoxy (OBorn (**3**)), *cis*-1,3-*O*-benzylidenglyceroxy (OGly (**4**)), and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoxy (ODAGP (**5**))} were prepared in high yields from [Ti($\eta^5$-$C_5H_5$)$Cl_3$] by adding 1 equivalent of the corresponding higher boiling alcohol in THF at room temperature in the presence of triethylamine (Scheme 1) resulting in the desired product and triethylamine hydrochloride. Complex **2** has been previously synthesized by Whitby and coworkers [12].

Complexes [Ti(OR)$_2$Cl$_2$] {OR = adamantanoxy (OAdam (**6**)), (1*R*,2*S*,5*R*)-(−)menthoxy (OMent (**7**)), (1*S*-endo)-(−)-borneoxy (OBorn (**8**))} were synthesized by a redistribution reaction between the tetraalkoxo derivatives [Ti(OR)$_4$] previously prepared by our group [13] and titanium tetrachloride in toluene (Scheme 2). Complexes [Ti(OR)$_2$Cl$_2$] {OR = 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoxy (ODAGP (**9**)), and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoxy (ODAGF (**10**))} were synthesized by a more convenient method involving the treatment of [Ti(ODAGP)$_2$(OPr$^i$)$_2$]$_2$ or [Ti(ODAGF)$_2$(OPr$^i$)$_2$]$_2$ [13] with four equivalents of acetyl chloride $CH_3COCl$ in toluene, respectively [14].

Compounds [Ti($\eta^5$-$C_5H_5$)(OR)$Cl_2$] (**1**–**5**) were isolated by crystallization in good yields as yellow or beige solids. They are very soluble in aromatic solvents (benzene and toluene) and sparingly soluble in diethyl ether and aliphatic hydrocarbons. The replacement of the

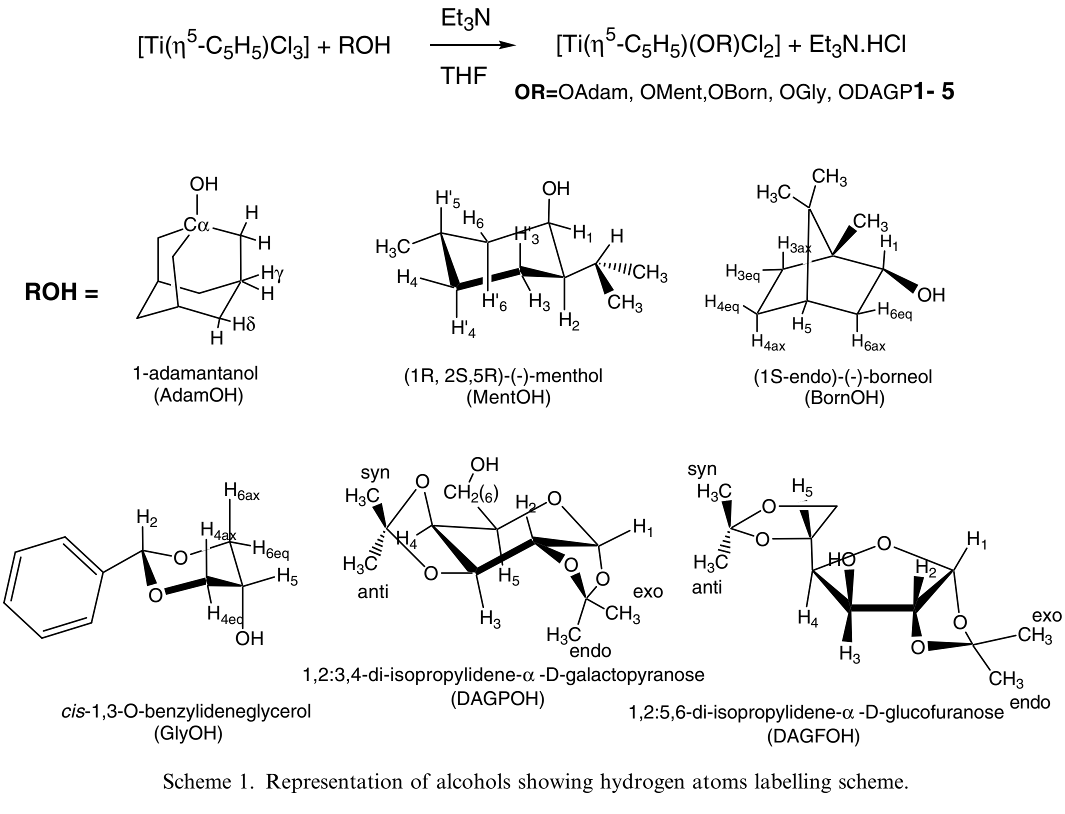
$$[TiCl_4] + [Ti(OR)_4] \xrightarrow{CH_2Cl_2} 2\,[Ti(OR)_2Cl_2]$$

**OR =** OAdam, OMent, OBorn **6-8**

$$[Ti(OR)_2(OPr^i)_2]_2 + 4\,CH_3COCl \xrightarrow{Toluene} 2\,[Ti(OR)_2Cl_2] + 4\,Pr^iOAc$$

**OR =** ODAGP, ODAGF. **9,10**

Scheme 2.



Scheme 1. Representation of alcohols showing hydrogen atoms labelling scheme.

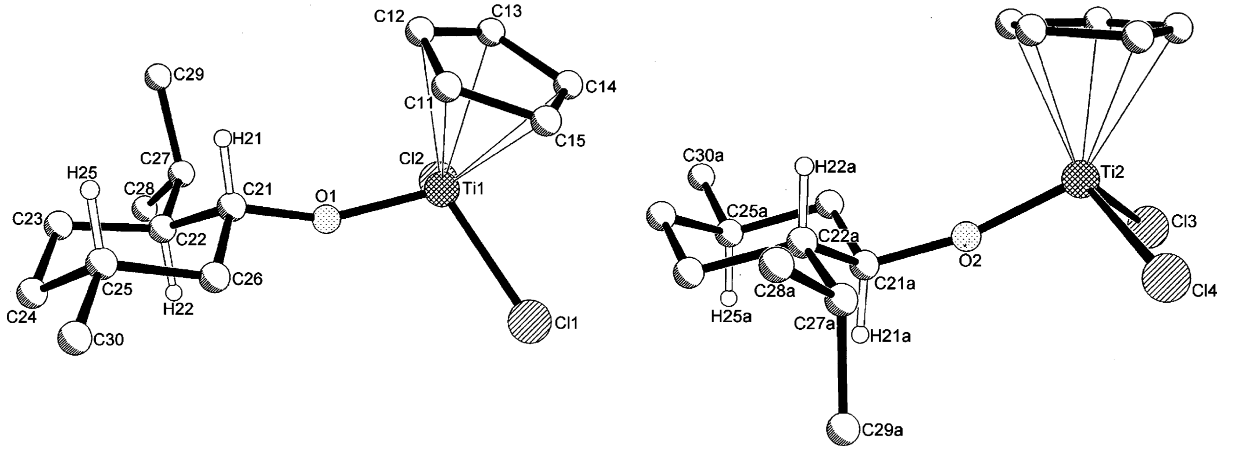


Fig. 1. Molecules 1 and 2 [Ti($\eta^5$-$C_5H_5$)(OMent)$Cl_2$] (**2**).

cyclopentadienyl ring by a second equivalent of bulky alkoxo ligand increases the solubility of the bisalkoxo derivatives, the dichlorides [Ti$(OR)_2Cl_2$] (**6**–**10**) were isolated as beige or red solids except compound **7** which is a colourless oil. The complexes **1**–**10** are thermally stable but very sensitive towards hydrolysis. Organometallic compounds **1**–**5** decompose slowly to the well known oxo complex [{Ti($\eta^5$-$C_5H_5$)$Cl_2$}($\mu$-O)] in the presence of trace amounts of water [15].

The $^1$H and $^{13}$C NMR spectra show very similar features for all the complexes. The solution NMR spectroscopic properties of compounds **1**–**5** appear, as expected, with single Cp signals and a single set of resonances for the corresponding bulky alkoxo ligand. The Cp protons resonate at 6.71 (**1**), 6.67 (**2**), 6.68 (**3**), 6.83 (**4**) and 6.79 (**5**), in the range typical for other monocyclopentadienyl alkoxo or aryloxo derivatives. The $^1$H and $^{13}$C NMR spectra of **6**–**10** show a single set of alkoxo signals in each case in accordance with a pseudo-tetrahedral environment around titanium and the presence of a $C_2$ axis leading to equivalent chloride and alkoxo ligands [16,17]. To further support our proposal of the monomeric structure of compounds **6**–**10**, a FAB mass spectroscopic study was carried out. Parent ions are not observed; the highest molecular weight ion is usually parent minus coordinated alkoxo and/or chloride unit (see Section 4). The IR spectra of the new alkoxo titanium complexes **1**–**10** contain bands due to the $\nu$(C–O) at ca. 1234–1263 cm$^{-1}$ and the $\nu$(Ti–O) at ca. 634–701 cm$^{-1}$.

Compounds **2** and **3** have been analyzed by X-ray crystallography. The yellow prismatic micro crystals were grown from concentrated toluene solutions at $-30$ °C. Drawings of the molecules based on the X-ray structural analyses and scheme used for labelling atoms for complexes **2** and **3** are shown in Figs. 1 and 2, respectively. Selected bond distances and bond angles are listed in Tables 1 and 2.

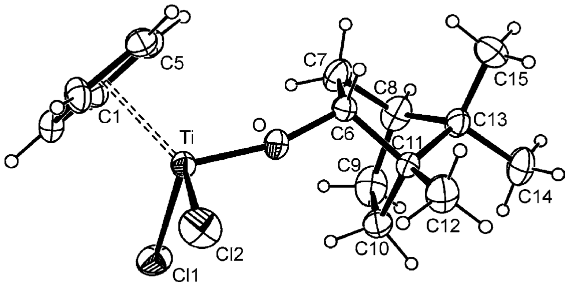


Fig. 2. ORTEP diagram of [Ti($\eta^5$-$C_5H_5$)(OBorn)$Cl_2$] (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for [Ti($\eta^5$-$C_5H_5$)(OMent)$Cl_2$] (**2**)

| | | | |
|---|---|---|---|
| Ti1–O1 | 1.72(1) | Ti3–O3 | 1.73(2) |
| Ti1–Cl1 | 2.23(1) | Ti3–Cl5 | 2.27(1) |
| Ti1–Cl2 | 2.27(1) | Ti3–Cl6 | 2.22(1) |
| O1–C21 | 1.42(2) | O3–C21b | 1.42(2) |
| Ti2–O2 | 1.72(2) | Ti4–O4 | 1.70(2) |
| Ti2–Cl3 | 2.25(1) | Ti4–Cl7 | 2.25(1) |
| Ti2–Cl4 | 2.25(1) | Ti4–Cl8 | 2.25(1) |
| O2–C21a | 1.45(3) | O4–C21c | 1.42(2) |
| Ti–C(Cp)[a] | 2.32(3) | | |
| | | | |
| O1–Ti1–Cl1 | 106.2(8) | O3–Ti3–Cl5 | 102.8(6) |
| O1–Ti1–Cl2 | 102.7(5) | O3–Ti3–Cl6 | 105.5(8) |
| Cl1–Ti1–Cl2 | 101.3(3) | Cl5–Ti3–Cl6 | 101.9(3) |
| C21–O1–Ti1 | 155(1) | C21b–O3–Ti3 | 165(1) |
| Cp–Ti1–O1 | 116.2 | Cp–Ti3–O3 | 115.4 |
| Cp–Ti1–Cl1 | 114.5 | Cp–Ti3–Cl5 | 114.2 |
| Cp–Ti1–Cl2 | 114.2 | Cp–Ti3–Cl6 | 115.3 |
| O2–Ti2–Cl3 | 103.1(8) | O4–Ti4–Cl7 | 103.1(7) |
| O2–Ti2–Cl4 | 101.3(5) | O4–Ti4–Cl8 | 100.6(6) |
| Cl3–Ti2–Cl4 | 102.7(3) | Cl7–Ti4–Cl8 | 102.6(3) |
| C21a–O2–Ti2 | 169(1) | C21c–O4–Ti4 | 166(1) |
| Cp–Ti2–O2 | 120.2 | Cp–Ti4–O4 | 121.1 |
| Cp–Ti2–Cl3 | 114.2 | Cp–Ti4–Cl7 | 113.3 |
| Cp–Ti2–Cl4 | 113.0 | Cp–Ti4–Cl8 | 113.8 |

[a] Cp is the centroid of C11–C15.

Table 2
Selected bond lengths (Å) and angles (°) for [Ti[($\eta^5$-$C_5H_5$)(OBorn)$Cl_2$] (**3**)

| | | | |
|---|---|---|---|
| Ti–O | 1.729(2) | C8–C13 | 1.533(5) |
| Ti–Cl1 | 2.262(1) | C9–C10 | 1.514(5) |
| Ti–Cl2 | 2.268(1) | C10–C11 | 1.536(4) |
| O–C6 | 1.423(3) | C11–C12 | 1.513(4) |
| C6–C7 | 1.540(4) | C11–C13 | 1.552(4) |
| C6–C11 | 1.538(4) | C13–C14 | 1.537(4) |
| C7–C8 | 1.541(5) | C13–C15 | 1.531(5) |
| C8–C9 | 1.512(6) | Ti–C(Cp)[a] | 2.360 |
| Cl1–Ti–Cl2 | 101.84(4) | C6–C11–C13 | 100.6(2) |
| O–Ti–Cl1 | 103.18(7) | C10–C11–C12 | 114.9(3) |
| O–Ti–Cl2 | 102.10(8) | C10–C11–C13 | 101.1(2) |
| C6–O–Ti | 165.0(2) | C12–C11–C13 | 119.1(3) |
| O–C6–C7 | 112.4(3) | C8–C13–C11 | 93.1(2) |
| O–C6–C11 | 110.5(2) | C8–C13–C14 | 114.1(3) |
| C6–C7–C8 | 102.1(3) | C8–C13–C15 | 115.4(3) |
| C7–C8–C9 | 107.0(3) | C11–C13–C14 | 114.2(3) |
| C7–C8–C13 | 102.6(3) | C11–C13–C15 | 114.0(3) |
| C9–C8–C13 | 103.4(3) | C14–C13–C15 | 106.1(3) |
| C8–C9–C10 | 103.1(3) | Cp–Ti–O | 118.9 |
| C9–C10–C11 | 104.4(3) | | |

[a] Cp is the centroid of C11–C15.

The structures of both complexes consist of discrete molecules separated by van der Waals distances. The complexes are chiral, and only one enantiomer is present in the asymmetric unit which indicates, as expected, a complete retention of configuration. There are four molecules per asymmetric unit in complex **2** corresponding to the same enantiomer, which shown basically 90° rotation around O1–C21 bonds with respect to each other (Fig. 1). Titanium atoms in both complexes have a piano stool structure, as expected, for these type of organotitatium compounds and are bonded to the cyclopentadienyl ring in an $\eta^5$ mode, to the alkoxo ligand through the oxygen atom and to two chlorine atoms in a pseudo-tetrahedral geometry about the metal centre. The menthoxy ligand in complex **2** shows a chair conformation in all molecules. Selected structural parameters along with those for other related derivatives (X)Ti(Y)$Cl_2$ (X,Y = ($\eta^5$-$C_5H_5$), OR or OAr) are collected in Table 3. All the Ti–Cp distances are identical within error limits.

Focusing on the effects of replacing Cp ligands by OAr or OR groups, some trends can be discerned. The Ti–Cl distances 2.25(1) and 2.265(1) Å in the complexes **2** and **3**, respectively, are significantly shorter with respect to the complex [Ti($\eta^5$-$C_5H_5$)$_2$$Cl_2$] [18], and similar to those reported for other complexes when Cp is replaced by OAr or OR (Table 3), which indicates an increase in the electrophilic nature of the metal centre. The angles Cl–Ti–Cl of 102.1(3) and 101.84(4)°, in complexes **2** and **3**, respectively, are similar to the angles found in the complexes Cp–Ti–OR and Cp–Ti–OAr [2,19,20].

The Ti–O distances in **2** and **3** of 1.72(2) and 1.729(2) Å, respectively, are comparable to those found in a variety of related compounds as [Ti($\eta^5$-$C_5H_5$)-(OPr$^i$)$Cl_2$] [21] and [Ti($\eta^5$-$C_5H_5$)($OC_6H_{11}$)$Cl_2$] [22] (Table 3). The angles Ti–O–C of 160.02(7) for complex **2** and 165.0(2)° for complex **3**, are similar to those found in related compounds sterically hindered, Cp–Ti–OAr, but certainly greater than those expected for a pyramidal oxygen atom, which supports the existence of $\pi(O \rightarrow Ti)$ donation into titanium, in addition to the regular $\sigma$-interaction.

According to the literature the angle of the M–O–C linkage along with the Ti–O bond length can be considered indicative of the alkoxo metal bond order. Thus as the M–O–C linkage approaches linearity a significant involvement of both p orbitals may be inferred. Likewise, a shortening of the M–O bond would reflect higher bond strength [23]. However, Rothwell has shown that there is little, if any, correlation between M–O–C bond angle and M–O distance [24]. Buchald et al. [20] reinforced this, studying [Ti($\eta^5$-$C_5R_5$)(OAr)$Cl_2$] (R = H, Me) systems, they found expanded Ti–O–C angles in moving from Cp to Cp* titanium complexes, whereas Ti–O distances either lengthened slightly or remains unchanged in basis of the sterically demanding size of the pentamethylcyclopentadienyl ligands.

With methylaluminoxane (MAO) (1000 molar equivalents) as co-catalyst compounds **1**–**5** are much less

Table 3
Selected structural data of some (X)Ti(Y)$Cl_2$ complexes

| Compound | X–Ti–Y | Cl–Ti–Cl | Ti–O–C | Ti–Cl | Ti–O | Reference |
|---|---|---|---|---|---|---|
| [Ti($\eta^5$-$C_5H_5$)$Cl_2$] | 131 | 94 | – | 2.367(2),2.361(1) | – | [18] |
| [Ti($\eta^5$-$C_5H_5$)($OC_6HNp_2$-2, 6-$Bu^t_2$-3, 5)$Cl_2$] | 119 | 102 | 164 | 2.230(2),2.244(2) | 1.774(3) | [19] |
| [Ti($\eta^5$-$C_5H_5$)($OC_6H_2$Ph-2-$Bu^t_2$-4, 6)$Cl_2$] | 118 | 99 | 160 | 2.226(8),2.269(8) | 1.785(2) | [19] |
| [Ti($\eta^5$-$C_5H_5$)($OC_6H_3(OCH_3)_2$-2,6)$Cl_2$] | 118 | 102 | 161 | 2.27(10),2.268(1) | 1. 778(18) | [20] |
| [Ti($\eta^5$-$C_5H_5$)($OC_6H_3Pr^i_2$-2, 6)$Cl_2$] | 117 | 104 | 163 | 2.262(1),2.262(1) | 1.76(4) | [2] |
| [Ti($\eta^5$-$C_5H_5$)(OPr$^i$)$Cl_2$] | 117 | 101 | 156.9(8) | 2.257(4),2.26(4) | 1. 709(9) | [21] |
| [Ti($\eta^5$-$C_5H_5$)($OC_6H_{11}$)$Cl_2$] | 111 | 103 | 156 | 2.268(1),2.265(1) | 1.723(1) | [22] |
| [Ti($\eta^5$-$C_5H_5$)(OMent)$Cl_2$] (**2**)[a] | 118.2(2) | 102.1(3) | 160.02(7) | 2.25(1) | 1.72(2) | This work |
| [Ti($\eta^5$-$C_5H_5$)(OBorn)$Cl_2$] (**3**) | 118.9[a] | 101.84(4) | 165.0(2) | 2.265(1)[a] | 1.729(2) | This work |

[a] Average distance.

Table 4
Crystal and structure refinement data for complexes **2** and **3**

| | **2** | **3** |
|---|---|---|
| Formula | $C_{15}H_{24}Cl_2OTi$ | $C_{15}H_{22}Cl_2OTi$ |
| $F_w$ | 339.14 | 337.13 |
| $T$ (K) | 293(2) | 293(2) |
| Crystal system | Triclinic | Orthorhombic |
| space group | $P1$ | $P2_12_12_1$ |
| $a$ (Å) | 6.667(1) | 6.7606(3) |
| $b$ (Å) | 10.143(2) | 11.4814(5) |
| $c$ (Å) | 26.497(5) | 21.5711(9) |
| $\alpha$ (°) | 95.10(3) | |
| $\beta$ (°) | 92.54(3) | |
| $\gamma$ (°) | 106.20(3) | |
| $V$ (Å$^3$) | 1709.4(5) | 1674.4(1) |
| $Z$ | 1 | 4 |
| $D_c$ (g/cm$^3$) | 1.318 | 1.337 |
| $\mu$ (mm$^{-1}$) | 0.804 | 0.821 |
| Crystal dimension (mm) | 0.4 × 0.2 × 0.2 | 0.25 × 0.30 × s0.35 |
| Reflections collected | 3855 | 22034 |
| Reflections observed | 2243 | 2901 |
| Goodness-of-fit on $F^2$ | 0.952 | 0.976 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1{}^a = 0.0788$ | $R_1{}^a = 0.0469$ |
| $wR_2{}^b = 0.1744$ | $wR_2{}^b = 0.1022$ | |
| Absolute structure parameter | −0.02(11) | 0.04(4) |
| Largest diff. peak (e Å$^{-3}$) | 0.744 and −0.303 | 0.296 and −0.296 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 5
Ethylene polymerization at 25 °C

| Catalyst | Millimoles of catalyst | Molar excess of MAO | Time (min) | Activity (kg mol cat$^{-1}$ h$^{-1}$) |
|---|---|---|---|---|
| $TiCp_2Cl_2$ | 0.025 | 1000 | 15 | 1371 |
| **1** | 0.025 | 1000 | 15 | 154 |
| **2** | 0.025 | 1000 | 15 | 141 |
| **3** | 0.025 | 1000 | 15 | 139 |
| **4** | 0.025 | 1000 | 15 | 142 |
| **5** | 0.025 | 1000 | 15 | 90 |

*1.5 atm $C_2H_4$ pressure.

effective catalyst precursors than [$TiCp_2Cl_2$] which was 10 times more active under identical conditions (Table 5). Other bulky monocyclopentadienyl-aryloxo derivatives such as [Ti($\eta^5$-$C_5R_5$)($OC_6H_3Pr^i_2$-2,6)$Cl_2$] (R = H, Me) have been shown to be active in ethylene polimerization [2].

## 3. Conclusions

Several mixed monocyclopentadienyl alkoxo and bisalkoxo titanium dichlorides have been prepared and spectroscopically characterized. With MAO as co-catalyst, monocyclopentadienyl alkoxo titanium(IV) dichlorides showed modest activities in ethylene polymerization. Complexes **2** and **3** with ligands derived from menthol and borneol have been also structurally characterized and their parameters compared to those of various alkoxo and aryloxo species.

## 4. Experimental

*General remarks.* All reactions were performed using standard Schlenk tube and dry box techniques under an atmosphere of dry nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before used. [Ti($\eta^5$-$C_5H_5$)(OMent)$Cl_2$], [Ti(OAdam)$_4$], [Ti(OMent)$_4$], [Ti(OBorn)$_4$], [Ti($OPr^i$)$_2$(ODAGP)$_2$]$_2$ and [Ti($OPr^i$)$_2$(ODAGF)$_2$]$_2$ were prepared as described earlier [12], [13]. 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, (1*R*,2*S*,5*R*)-(−)-menthol, (1*S*-endo)-(−)-borneol, adamantanol, *cis*-1,3-*O*-benzylidenglycerol, [Ti($\eta^5$-$C_5H_5$)-$Cl_3$] and $TiCl_4$ (1M toluene) were purchased from Aldrich and used as received. $NEt_3$ were purchased from Aldrich distilled and stored under an argon atmosphere prior to use.

IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer (4000–400 cm$^{-1}$) as nujol mulls between polyethylene pellets and KBr disks. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on Varian FT-300 and Varian FT-400 spectrometers and chemical shifts were measured relative to residual $^1$H and $^{13}$C resonances in the deuterated solvents. Elemental analyses were carried out with a Perkin–Elmer 2400 micro analyzer. Mass spectrometry analyses were performed on a Hewlett–Packard 5988 instrument.

### 4.1. Preparation of [Ti($\eta^5$-$C_5H_5$)(OAdam)$Cl_2$] (*1*)

To a solution of [Ti($\eta^5$-$C_5H_5$)$Cl_3$] (0.35 g, 1.6 mmol) and adamantanol (0.24 g, 1.6 mmol) in THF (30 ml) was added dropwise a solution of $NEt_3$ (0.22 ml, 1.6 mmol) in THF. The resulting suspension was stirred for 12 h at room temperature and the solvent removed under vacuum. The crude reaction mixture was extracted with diethyl ether (2 × 25 ml) to obtain a yellow solid (0.45 g, 85%). Recrystallization from toluene at −30°C gave **1** as yellow crystals.

$^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.62$ (ps t 6H, $H_\delta$, 1.98 (ps d 6H, $H_\beta$), 2.20 (m, 3H, $H_\gamma$), 6.71 (s, 5H, $C_5H_5$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.1$ ($C_\delta$), 35.7 ($C_\gamma$), 44.9 ($C_\beta$), 93.0 ($C_\alpha$), 118.4 ($C_5H_5$). IR (KBr disk, cm$^{-1}$): 468 (m), 668 (w), 757 (m), 821 (s), 931 (m), 1008 (s), 1072 (s), 1103 (s), 1261 (w), 1292 (m), 1346 (m), 1448 (m), 2846 (s), 2910 (s). MS (FAB) *m/z*: 334 [M$^+$ – 1, 33%], 300 [M$^+$ – Cl, 83%]. $TiC_{15}H_{20}OCl_2$ Calc.: C, 53.76; H, 6.02. Found: C, 53.49; H, 5.72%.

### 4.2. Preparation of $[Ti(\eta^5\text{-}C_5H_5)(OBorn)Cl_2]$ (**3**)

To a solution of $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ (1.13 g, 5.2 mmol) and (1*S*-endo)-(−)-borneol (0.80 g, 5.2 mmol) in THF (30 ml) was slowly added a solution of $NEt_3$ (0.72 ml, 5.2 mmol) in THF using an addition funnel. The resulting suspension was stirred for 12 h at room temperature and the solvent removed under vacuum. The crude reaction was extracted with diethyl ether (2 × 25 ml) to obtain a yellow solid (0.58 g, 83%). Recrystallization from toluene at −30 °C gave **3** as yellow needles suitable for X-ray studies.

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.85$ (s, 3H, C$H_3$), 0.86 (s, 3H, C$H_3$), 0.95 (s, 3H, C$H_3$), 1.22–1.38 (m, 3H, C(4)-*H*, C(6)-$H_{ax}$), 1.69 (m, 1H, C(3)-$H_{ax}$), 1.74 (m, 1H, C(3)-$H_{eq}$), 2.15 (m, 1H, C(5)-*H*), 2.39 (m, 1H, C(6)-$H_{eq}$), 5.08 (m, 1H, C(1)-*H*), 6.68 (s, 5H, $C_5H_5$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 13.9$ ($CH_3$), 14.0 ($C$ $H_3$), 20.0 ($CH_3$), 26.5 ($C_4$), 28.1 ($C_3$), 39.1 ($C_6$), 45.1 ($C_5$), 48.1 ($C$ $(CH_3)_2$), 53.0 ($C_2$), 102.38 ($C_1$), 118.8 ($C_5H_5$). IR (KBr disk, $cm^{-1}$): 701 (m), 819 (s), 846 (m), 1024 (m), 1035 (m), 1074 (s), 1083 (s), 1112 (s), 1139 (m), 1355 (w), 1369 (w), 1388 (w), 1452 (m), 2877 (s), 2917 (s), 2948 (s). $TiC_{15}H_{22}OCl_2$ Calc.; C, 53.44; H, 6.58; Found: C, 53.36; H, 6.19%.

### 4.3. Preparation of $[Ti(\eta^5\text{-}C_5H_5)(OGly)Cl_2]$ (**4**)

To a solution of $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ (0.40 g, 1.82 mmol) and *cis*-1,3-*O*-benzylidenglycerol (0.32 g, 1.82 mmol) in THF (30 ml) was slowly added a solution of $NEt_3$ (0.26 ml, 1.82 mmol) in THF using and addition funnel. The resulting suspension was stirred for 48 h at room temperature and the solvent removed under vacuum. The crude reaction was extracted with diethyl ether (2 × 25 ml) to obtain a brown solid (0.52 g, 80%). Recrystallization from toluene at −30 °C gave **4** as a beige crystalline solid.

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.65$ (m, 1H, C(5)-*H*), 4.15 (m, 2H, C(4)-$H_{ax}$, C(6)-$H_{ax}$), 4.21 (m, 2H, C(4)-$H_{eq}$, C(6)-$H_{eq}$), 5.64 (m, 1H, C(2)-*H*), 6.83 (s, 5H, $C_5H_5$), 7.36–7.59 (m, 5H $C_6H_5$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 66.0$ ($C_5$), 88.2 ($C_{4,6}$), 121.2 ($C_5H_5$), 120.54–129.30 ($C_6H_5$). IR (KBr disk, $cm^{-1}$): 701 (m), 819.60 (s), 846.60 (m), 1024.02 (m), 1035.59 (m), 1074.16 (s), 1083.80 (s), 1112.73 (s), 1139.73 (m), 1355.72 (w), 1369.22 (w), 1388.50 (w), 1452.14 (m), 2877.19 (s), 2917.78 (s), 2948.64 (s). $TiC_{15}H_{16}O_3Cl_2$ Calc.: C, 49.62; H 4.44. Found: C, 49.25; H 4.06%.

### 4.4. Preparation of $[Ti(\eta^5\text{-}C_5H_5)(ODAGP)Cl_2]$ (**5**)

To a solution of $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$ (1.13 g, 5.2 mmol) and 1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranose (0.80 g, 5.2 mmol) in THF (30 ml) was slowly added a solution of $NEt_3$ (0.72 ml, 5.2 mmol) in THF using an addition funnel. The resulting suspension was stirred for 12 h at room temperature and the solvent removed under vacuum. The crude reaction was extracted with diethyl ether (2 × 25 ml) to obtain a yellow solid (1.40 g, 80%). Recrystallization from toluene at −30 °C gave **5** as yellow crystals.

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.33$ (s, 3H, C$H_3$), 1.34 (s, 3H, C$H_3$), 1.48 (s, 3H, C$H_3$), 1.54 (s, 3H, C$H_3$), 3.85 (p td, 1H, $^3J_{H5,H4} = 1.46$ Hz, C(5)-*H*), 4.21 (m, 1H, C(4)-*H*), 4.31 (dd, 1H, $^3J_{H2,H3} = 2.56$ Hz, $^3J_{H2,H1} = 4.76$ Hz, C(2)-*H*), 4.60 (dd, 1H, $^3J_{H3,H4} = 4.4$ Hz C(3)-*H*), 4.68 (m, 2H, C(6)-*H*), 5.57 (d, 1H, $^3J_{H1,H2} = 4.76$ Hz, C(1)-*H*), 6.79 (s, 5H, $C_5H_5$). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 °C): = 24.4 ($CH_3$), 25.1 ($C$ $H_3$), 26.1 ($CH_3$), 26.2 ($C$ $H_3$), 68.9 ($C_6$), 70.4 ($C_5$), 70.6 ($C_3$), 70.8 ($C_4$), 83.0 ($C_2$), 96.2 ($C_1$), 108.9 ($-C(CH_3)_2$), 109.3 ($-C(CH_3)_2$), 120.2 ($C_5H_5$). I.R (KBr disk, $cm^{-1}$): 503 (m), 590 (w), 669 (m), 709 (m), 819 (s), 1002 (s), 1074 (s), 1106 (s), 1114 (s), 1170 (s), 1255 (s), 1380 (s), 1448 (m), 1554 (w), 1637 (w), 1772 (w), 2933 (s), 2989 (s), 3106 (m). MS (FAB) *m*/*z*: 440 [$M^+ - 2$, 40%], 407 [$M^+ - Cl$, 100%]. $TiC_{17}H_{24}O_6Cl_2$ Calc.: C, 46.08; H, 5.46. Found: C, 45.62; H, 5.15%.

### 4.5. Preparation of $[Ti(OAdam)_2Cl_2]$ (**6**)

A toluene (10 ml) solution of $[Ti(OAdam)_4]$ (1.20 g, 1.8 mmol) was slowly added to a stirred toluene (20 ml) solution of $TiCl_4$ (0.34 g, 1.8 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum to give a beige solid (1.24 g, 82%). Recrystallization from toluene at −30 °C gave **6** as beige needles.

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.61$ (ps t, 12H, $H_\delta$), 1.98 (ps d, 12H, $H_\beta$), 2.18 (m, 6H, $H_\gamma$). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.2$ ($C_\delta$), 35.8 ($C_\gamma$), 45.4 ($C_\beta$), 82.7 ($C_\alpha$). IR (KBr disk, $cm^{-1}$): 811 (m), 885 (br), 925 (s), 981 (m), 1089 (s), 1118 (s), 1224 (w), 1299 (w), 1355 (m), 1452 (m), 2846 (s), 2898 (s), 2913.93 (s). MS (FAB) *m*/*z*: 154 [$M^+ - Cl - Cl -$ AdamO, 100%]. $TiC_{20}H_{30}O_2Cl_2$ Calc.: C, 57.03; H, 7.18. Found: C, 56.86; H, 7.03%.

### 4.6. Preparation of $[Ti(OMent)_2Cl_2]$ (**7**)

A toluene (10 ml) solution of $[Ti(OMent)_4]$ (1.89 g, 2.8 mmol) was slowly added to a stirred toluene solution of $TiCl_4$ (0.53 g, 2.8 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum. The resulting product was a colourless oil spectroscopically pure (1.96 g, 82%).

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.81$ (d, 6H, $^3J_{H,H} = 6.9$ Hz, C$H_3$), 0.86 (d, 6H, $^3J_{H,H} = 3.4$ Hz, C$H_3$), 0.89 (d, 6H, $^3J_{H,H} = 2.9$ Hz, C$H_3$), 0.91–0.99 (m, 4H, C(4)-*H*), 1.15–1.29 (m, 2H, -C*H*), 1.35–1.45 (m, 4H, C(3)-*H*), 1.54–1.62 (m, 4H, C(6)-*H*), 2.2 (m, 2H, C(2)-*H*), 2.3 (m, 2H, C(5)-*H*), 4.5 (m, 2H, C(1)-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 15.9$ ($CH_3$), 21.1 ($CH_3$), 22.1 ($CH_3$), 22.8 ($C_3$), 25.5 (*C*H), 31.7 ($C_5$), 34.2 ($C_4$), 45.1 ($C_6$), 50.6 ($C_2$), 94.2 ($C_1$). IR (Nujol–polyethylene, $cm^{-1}$): 422 (m), 493 (m), 617 (m), 727 (s), 856 (s), 925 (m), 995 (s), 1039 (s), 1079 (s), 1099 (s), 1132 (s), 1321 (m), 1344 (s), 1367 (s), 1457 (s), 2657 (m), 2728 (m). $TiC_{20}H_{38}O_2Cl_2$ Calc.: C, 55.96; H, 8,92. Found: C, 55.64; H, 8.83%.

### 4.7. Preparation of [$Ti(OBorn)_2Cl_2$] (**8**)

A toluene (10 ml) solution of [$Ti(OBorn)_4$] (0.88 g, 1.3 mmol) was slowly added to a stirred toluene solution of $TiCl_4$ (0.25 g, 1.3 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum to give a white solid (1.01 g, 91%). The crude product was recrystallized from $Et_2O$ to obtain a white crystalline solid.

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.86$ (s, 6H, C*H*$_3$), 0.99 (s, 12H, C*H*$_3$), 1.29–1.34 (m, 6H, C(4)-*H*, C(6)-$H_{ax}$), 1.68 (m, 2H, C(3)-$H_{ax}$), 1.76 (m, 2H, C(3)-$H_{ec}$), 2.05 (m, 2H, C(5)-*H*), 2.41 (m, 2H, C(6)-$H_{ec}$), 5.18 (m, 2H, C(1)-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 13.8$ ($CH_3$), 18.8 ($CH_3$), 20.2 (*C* $H_3$), 26.9 ($C_4$), 28.2 ($C_3$), 39.5 ($C_6$), 45.0 ($C_5$), 48.0 (*C* $(CH_3)_2$), 52.3 ($C_2$), 101.6 ($C_1$). IR (KBr disk, $cm^{-1}$): 703 (w), 827 (s), 921 (s), 1022 (s), 1029 (s), 1056 (s), 1108 (m), 1137 (w), 1234 (w), 1307 (w), 1349 (m), 1367 (m), 1388 (m), 1452 (m), 1475 (m), 1621 (m), 2877 (s), 2952 (s), 2981 (s). $TiC_{20}H_{34}O_2Cl_2$ Calc.: C, 56.48; H, 8.06. Found: C, 56.16; H, 7.99%.

### 4.8. Preparation of [$Ti(ODAGP)_2Cl_2$] (**9**)

A toluene solution (20 ml) of [$Ti(OPr^i)_2(ODAGP)_2]_2$ (1.33 g, 0.95 mmol) was treated with $CH_3COCl$ (0.27 ml, 3.8 mmol). Upon addition the solution was stirred for 24 h. Hexane was added and a white solid precipitated $CH_3COOPr^i$ obtained. The solution was filtered off and the solvent was then removed under vacuum to give a beige solid (1.02 g, 85%).

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.31$ (s, 3H, C*H*$_3$), 1.32 (s, 3H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.50 (s, 3H, C*H*$_3$), 4.0 (m, 2H, C(5)-*H*), 4.16 (m, 2H, C(6)-*H*), 4.22 (dd, 2H, $^3J_{H4,H3} = 7.6$ Hz, $^3J_{H4,H5} = 1.9$ Hz, C(4)-*H*), 4.25 (m, 2H, C(6)-*H*), 4.30 (dd, 2H, $^3J_{H2,H3} = 2.56$ Hz, $^3J_{H2,H1} = 4.76$ Hz C(2)-*H*), 4.58 (dd, 2H, (3)-*H*), 5.5 (d, 2H, $^3J_{H1,H2} = 4.76$ Hz, C(1)-*H*). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 24.9$ ($CH_3$), 25.4 ($CH_3$), 26.3 ($CH_3$), 26.4 ($CH_3$), 63.9 ($C_6$), 66.2 ($C_5$), 70.7 ($C_4$), 70.9 ($C_3$), 71.4 ($C_2$), 96.5 ($C_1$), 108.9 (-*C*$(CH_3)_2$), 109.8 (-*C*$(CH_3)_2$). IR (KBr disk, $cm^{-1}$): 512 (m), 862 (m), 896 (m), 917 (m), 1008 (s), 1074 (s), 1168 (m), 1214 (s), 1253 (s), 1378 (s), 1452 (s), 1461 (s), 2665 (m), 2736 (m). MS (FAB) *m/z*: 341 [$M^+$ – Cl – DAGPO, 55%], 306 [$M^+$ – Cl – Cl – DAGPO, 100%]. $TiC_{24}O_{12}H_{38}Cl_2$ Calc.: C, 45.23; H, 6.01. Found: C, 45.62; H, 6.58%.

### 4.9. Preparation of [$Ti(ODAGF)_2Cl_2$] (**10**)

A toluene solution (20 ml) of [$Ti(OPr^i)_2(ODAGF)_2]_2$ (1.98 g, 1.4 mmol) was treated with $CH_3COCl$ (0.92 ml, 5.6 mmol). Upon addition the solution was stirred for 24 h. Hexane was added and a white solid precipitated $CH_3COOPr^i$ obtained. The solution was filtered off, concentrated under reduced pressure and cooled to −30 °C, to give a red crystalline solid (1.33 g, 75%).

$^1H$ NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.31$ (s, 6H, C*H*$_3$), 1.36 (s, 6H, C*H*$_3$), 1.44 (s, 6H, C*H*$_3$), 1.49 (s, 6H, C*H*$_3$), 3.97 (m, 2H, C(6)-*H*), 4.05 (dd, 2H, $^3J_{H4,H5} = 7.8$ Hz, $^3J_{H4,H3} = 2.7$ Hz, C(4)-*H*), 4.14 (m, 2H, C(6)-*H*), 4.29 (m, 2H, C(5)-*H*), 4.31 (d, 2H, $^3J_{H3,H4} = 2.7$ Hz, C(3)-*H*), 4.52 (d, 2H, C(2)-*H*), 5.92 (d, 2H, C(1)-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 25.2$ ($CH_3$), 26.3 ($CH_3$), 26.8 ($CH_3$), 26.9 ($CH_3$), 67.6 ($C_6$), 73.5 ($C_4$), 77.3 ($C_5$), 80.9 ($C_3$), 84.9 ($C_2$), 105.2 ($C_1$), 109.6 (-*C*$(CH_3)_2$), 111.7 (-*C*$(CH_3)_2$). IR (KBr disk, $cm^{-1}$): 634 (m), 759 (m), 809 (w), 856 (m), 952 (m), 1018 (s), 1072 (s), 1166 (s), 1220 (s), 1255 (m), 1378 (s), 1457 (m), 2933 (s), 2987 (s). $TiC_{24}O_{12}H_{38}Cl_2$ Calc.: C, 45.23; H 6.01. Found C, 45.18; H, 6.49%.

### 4.10. Ethylene polymerization studies

Toluene 200 ml was charged in a 1 L Schlenk flask under $N_2$ atmosphere, an excess of MAO (Al/Ti ratio = 1000/1) was added and the solution was stirred for several minutes. Next, a toluene solution of the catalyst precursor (0.025 mmol of Ti) was added and the mixture stirred for 15 min. The $N_2$ atmosphere was replaced with ethylene and the pressure adjusted to 1.5 atm. The polymerization was carried out for 15 min. Polymerizations were quenched with MeOH and HCl. The resulting suspension was vigorously stirred and polyethylene was filtered off, washed with HCl/MeOH and dried at 70 °C for 48 h.

### 4.11. Crystal structure determination and refinement of complex [$Ti(\eta^5\text{-}C_5H_5)(OMent)Cl_2$] (**2**)

Intensity data for complex **2** were collected on a NONIUS-MACH3 four-circle diffractometer equipped with a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using an $/2\theta$ scan technique. The final unit cell parameters were determined from 25 well-centered and refined by least-squares method. Two reflections were measured every 98 reflections as orientation and intensity control, an intensity decay of 55% was observed. The space group was determined from the systematic absences and this was vindicated by the success of the subsequent solutions and refinements. There are four molecules per asymmetric unit. The structures were solved by direct methods using SHELXS computer program [25] and refined on $F^2$ by full-matrix least-squares (SHELXL-97) [26]. Titanium, chlorine and oxygen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

### 4.12. Crystal structure determination and refinement of complex [Ti($\eta^5$-$C_5H_5$)(OBorn)$Cl_2$] (3)

The diffraction experiment for complex **3** was carried out at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo K radiation. Intensity data were measured over full diffraction spheres using 0.3° wide $\omega$ scans, crystal-to-detector distance 5.0 cm. Cell dimension and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different regions and eventually refined against all reflections. The software SMART was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by software SAINT [27] and an empirical absorption correction was applied with SADABS [28]. The structure was solved by direct methods (SIR 97) [29] and subsequent Fourier syntheses and refined by full matrix least-squares on $F^2$ (SHELXTL) [30] using anisotropic thermal parameters for all non hydrogens atoms. Furthermore in [Ti(g$^5$-$C_5H_5$)(OBorn)$Cl_2$] twofold orientational disorder of the cyclopentadienyl ligand around the metal-ring axis was detected and the site occupation factors were refined for this ligand yielding the values 0.62 and 0.38, respectively. The hydrogen atoms were included in calculated positions and allowed to ride on the carrier atoms with thermal parameters tied to those of the parent atom except the hydrogens bound to C(6) and C(8) in the borneol ligand of [Ti(g$^5$-$C_5H_5$)(OBorn)$Cl_2$] which were located in the Fourier map and refined isotropically. Crystallographic data and structure refinement details for [Ti(g$^5$-$C_5H_5$)(OBorn)$Cl_2$] are reported in Table 4.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 241565 for compound **2** and no. 242445 for compound **3.** Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk).

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