

# Effects of substituents in cyclopentadienyltitanium trichlorides on electronic absorption and $^{47,49}\text{Ti}$ NMR spectra and styrene polymerization activated by methylalumoxane

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Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday.

## Abstract

In the series of the methylated compounds  $(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$  ( $n=0\text{--}5$ ) **1–6**, linear correlations of  $\lambda_{\text{max}}$  of the absorption band and  $\delta$   $^{49,47}\text{Ti}$  chemical shift with the number of Me groups were found. It is due to the dependence of both the magnitudes on the HOMO–LUMO energy gap which is influenced by electron donating methyl substituents. The catalysts made by combining **1–6** with MAO (molar ratio Al/Ti 500) showed only a gross dependence of decreasing activity with the number of methyl groups. For compounds  $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TiCl}_3$  **7–14** and  $(\eta^5\text{-C}_5\text{H}(1,2,3\text{-})\text{Me}_3\text{R})\text{TiCl}_3$  **15–20** where R = alkyl, silyl or phenyl no correlation between  $\lambda_{\text{max}}$  and  $\delta$  was found. Limited DFT calculations were performed to assign HOMO/LUMO orbitals involved. Crystal structures of **16** and **20** were determined and some other inspected to prove the absence of steric hindrance. The poor correlation of the spectroscopic properties with the catalytic activity is not surprising because steric effects of cyclopentadienyl ligands at cationic polymerization centers are generally anticipated.

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## 1. Introduction

Bent sandwich titanocene dichlorides, constrained geometry titanium complexes (CGC), or half-sandwich titanium trichlorides combined with aluminium alkyls or methylalumoxane (MAO) are frequently used homogeneous catalysts for  $\alpha$ -olefin polymerization or copolymerization. Due to the outstanding steric and electronic versatility of the cyclopentadienyl-based ligands, such catalysts can produce polyolefins with a broad range of molecular weights and their distributions, compositions and microstructures. The catalyst properties can be finely tuned by electron donating/withdrawing and steric effects of the

substituents attached to the cyclopentadienyl ligands [1]. Particularly, the effect of methyl group(s), which increases electron density at the metal center, has been investigated by various spectroscopic, physico-chemical and chemical methods with the aim to effectively design new catalyst systems based on sandwich titanocene compounds. ESCA (electron spectroscopy for chemical analysis) measurements revealed that replacement of cyclopentadienyl by permethylcyclopentadienyl ligands in the metallocene dihalide series  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{MX}_2$  ( $n=0,5$ ) ( $\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$ ) ( $\text{X}=\text{F}, \text{Cl}, \text{Br}$ ) results in the decrease of binding energies of the inner shell metal ( $2p_{3/2}$ ) electrons by ca. 0.8 eV [2]. Similar dependences for valence electron energies were obtained by UPS (ultraviolet photoelectron spectroscopy) in the series of  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}_2$  [3] and  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}$  [4] ( $n=0\text{--}5$ ) compounds. Chemical shifts in the  $^{49}\text{Ti}$  and  $^{47}\text{Ti}$

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NMR also closely correlate with the electron density at the metal nucleus [5,6]. Moreover, the linewidth of signals brings information on the ligand field symmetry around the metal atom which applies in structure/reactivity studies [7]. Similar studies on the  $^{91}\text{Zr}$  NMR spectra/structure correlations are also numerous [8]. The standard first reduction potentials ( $E_1^0$ ) for the  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}_2$  ( $n=0-5$ ) series showed a negative increment of 0.093 V per methyl group for  $n=0-3$ , a decline to a lower value for  $n=4$ , and a positive shift for  $n=5$  and for bulkier fifth substituents. This was accounted for by an increase in the Cg–Ti–Cg (Cg, centroid of the cyclopentadienyl ring) angle due to a steric hindrance, diminishing the HOMO–LUMO energy gap [9]. Also, the chemical behavior as expressed in the affinity to coordinate THF in the series of  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}$  [10a] and  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)_2\text{Zr}(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$  ( $n=0-5$ ) compounds [10b] decreasing with increasing  $n$  and becoming negligible for the permethylated compounds can be due to combination of electronic and steric effects. In the half-sandwich series of  $(\text{C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$  ( $n=0-5$ ) compounds the electronic absorption spectra showed a shift of the visible absorption band to longer wavelength by ca. 11 nm per methyl group band. Accordingly, the compounds showed a decrease of their reducibility by an excess of  $\text{Et}_2\text{AlCl}$  expressed by a decrease in the reduction rate constant ( $1.1 \times 10^{-3}$  to  $6.1 \times 10^{-5} \text{ s}^{-1}$ ) [11]. The  $^{49}\text{Ti}$  and  $^{47}\text{Ti}$  NMR spectra of a number of  $\text{Cp}'\text{TiCl}_3$  compounds proved that methyl and trimethylsilyl substituents move chemical shifts down-field, however, the latter in a much lower extent. Similar bathochromic trends were also observed for the electronic absorption band, the shifts per  $\text{SiMe}_3$  group being again smaller than for a Me group [12].

The cyclopentadienyl substituent effects in polymerizations were widely explored in metallocene or *ansa*-metallocene catalysts [1]. Among CGC catalysts, replacement of one methyl group in  $\alpha$ -position to the dimethylsilylene bridge in the parent CGC complex by other substituents exerted large impacts on copolymerization of styrene with ethene in optimum affording an alternating copolymer [13], however, no syndiotactic enrichment of atactic polypropene was detected with the same catalysts [14]. The half-sandwich catalysts turned out to be high-performance catalysts for the polymerization of styrene to syndiotactic polystyrene (s-PS) when activated with excess methylalumoxane (MAO). The auxiliary cyclopentadienyl ligand in initially used  $\text{CpTiCl}_3$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) [15] was modified both by electron releasing as well as electron withdrawing substituents, or replaced by annelated cyclopentadienyl ligands ( $\eta^5$ -indenyl,  $\eta^5$ -fluorenyl, and their derivatives) whereas the leaving chloride ligands are advantageously replaced by fluorides or various alkyl- or aryloxides [16]. In addition, the performance of the catalysts is dependent on the molar Al/Ti ratio, the quality of MAO (namely content of free trimethylaluminum), temperature of polymerization, nature of solvents, and procedure of the catalyst preparation. Although the above conditions are apparently controlled, different laboratories report varying data about catalyst activity and molecular weight of s-PS. This can lead to a misleading generalization for the fundamental catalysts like  $\text{CpTiCl}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  quoting increasing polymerization activity for the cyclopentadienyl ligands

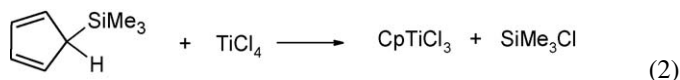
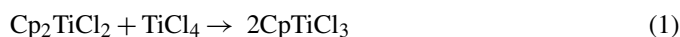
$\text{Cp} < \text{C}_5\text{H}_4\text{Me} = \text{C}_5\text{H}_2\text{Me}_3 < \text{Cp}^*$  in Ref. [16d]. Indeed, a higher activity for  $\text{Cp}^* > \text{Cp}$  was reported for polymerizations at  $90^\circ\text{C}$  and Al/Ti = 1000 [17] contrary to ca. five times higher activity for  $\text{Cp} > \text{Cp}^*$  at  $50^\circ\text{C}$  and Al/Ti = 300 [18], and even ca. 70 times higher activity for  $\text{Cp} > \text{Cp}^*$  at  $50^\circ\text{C}$  and Al/Ti = 300 [19]. Surprisingly, partly methyl-substituted  $\text{Cp}'\text{TiCl}_3$  compounds were tested in catalytic systems with MAO only scarcely [16a].

In this paper we report the electronic absorption spectra and  $^{49}\text{Ti}$  and  $^{47}\text{Ti}$  NMR data for a series of the  $(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$  ( $n=0-5$ ) compounds and highly methyl-substituted compounds  $\text{Cp}'\text{TiCl}_3$  where  $\text{Cp}'$  is  $(\eta^5\text{-C}_5\text{Me}_4\text{R})$  or  $(\eta^5\text{-C}_5\text{H}(1,2,3\text{-})\text{Me}_3\text{R})$  with R being an alkyl, phenyl or silyl substituent. The nature of the electronic absorption band is elucidated and the NMR shifts are correlated with DFT calculations for representative complexes. The spectroscopic data are compared with results of styrene polymerization using the  $\text{Cp}'\text{TiCl}_3/\text{MAO}$  catalysts with  $\text{Cp}' = \text{C}_5\text{H}_{5-n}\text{Me}_n$  ( $n=0-5$ ),  $\text{C}_5\text{Me}_4\text{R}$  (R = but-3-en-1-yl, Bu, Ph,  $\text{SiMe}_3$ ), and  $\text{C}_5\text{H}(1,2,3\text{-})\text{Me}_3(4\text{-})\text{R}$  (R = Ph,  $\text{SiMe}_3$ ) with the aim to evaluate applicability of spectroscopic data for tuning the catalysts performance.

## 2. Results and discussion

### 2.1. Synthesis of half-sandwich complexes and their electronic absorption spectra

The investigated half-sandwich complexes consist of three series of compounds, methyl-substituted cyclopentadienylium titanium trichlorides of general formula  $(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$  ( $n=0-5$ ) **1-6**, pentasubstituted compounds containing one other substituent in addition to four Me groups  $(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{TiCl}_3$  **7-14**, and tetrasubstituted compounds containing one other substituent in addition to three vicinal Me groups  $(\eta^5\text{-C}_5\text{H}(1,2,3\text{-})\text{Me}_3\text{R})\text{TiCl}_3$  **15-20**. The compounds are listed in Table 1 together with the reference to their origin, the longest wavelength absorption band  $\lambda_{\text{max}}$ , and chemical shifts of  $^{49}\text{Ti}$  and  $^{47}\text{Ti}$  resonances and their line widths. Compounds **1-14** were prepared by synproportionation reaction between titanocene dichloride and  $\text{TiCl}_4$  (Eq. (1)) in nearly quantitative yields [22]. Compounds **15-20** were obtained by transmetallation reaction (Eq. (2)) in rather moderate yields [23]. All compounds were characterized by EI-MS, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and melting points in sealed capillaries under nitrogen. Structures of compounds **16** and **20**, representatives of the new, tetrasubstituted compounds series, were proved by X-ray diffraction single crystal analysis.



The electronic absorption bands for all the measured complexes (Table 1) consist of a broad, mostly asymmetrical band whose  $\lambda_{\text{max}}$  occurs in the range 384–450 nm and its approximate halfwidth is 70–100 nm. The largest changes in  $\lambda_{\text{max}}$  were observed in the series of the  $(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)\text{TiCl}_3$  ( $n=0-5$ ) compounds in agreement with previous measurements [11], the

Table 1  
Electronic absorption band and  $^{49,47}\text{Ti}$  chemical shifts of  $(\eta^5\text{-Cp}')\text{TiCl}_3$  compounds

Cpd	Cp'	$\lambda$	$\delta(^{49}\text{Ti})$	$w_{1/2}$	$\delta(^{47}\text{Ti})$	$w_{1/2}$	Synthesis
1	C <sub>5</sub> H <sub>5</sub>	384	-387.0	26	-653.2	84	[9]
2	C <sub>5</sub> H <sub>4</sub> Me	393	-334.7	23	-601.0	81	[9]
3	C <sub>5</sub> H <sub>3</sub> (1,3-)Me <sub>2</sub>	405	-280.3	16	-546.3	53	[9]
4	C <sub>5</sub> H <sub>2</sub> (1,2,4-)Me <sub>3</sub>	417	-229.4	20	-495.5	62	[9]
5	C <sub>5</sub> HMe <sub>4</sub>	428	-164.7	9	-431.1	28	[9]
6	C <sub>5</sub> Me <sub>5</sub>	439	-98.2	3	-364.5	8	[9]
7	C <sub>5</sub> Me <sub>4</sub> Et	439	-112.4	3	-378.7	9	[9]
8	C <sub>5</sub> Me <sub>4</sub> Bu	439	-114.0	3	-380.3	9	[10]
9	C <sub>5</sub> Me <sub>4</sub> (CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )	440	-115.5	3	-381.8	8	[10]
10	C <sub>5</sub> Me <sub>4</sub> (CHMeCH=CH <sub>2</sub> )	441	-113.0	7	-379.2	22	[10]
11	C <sub>5</sub> Me <sub>4</sub> Ph	445	-113.8	19	-379.9	56	[10]
12	C <sub>5</sub> Me <sub>4</sub> <sup>t</sup> Bu	444	-106.7	15	-372.9	53	[12]
13	C <sub>5</sub> Me <sub>4</sub> (SiMe <sub>3</sub> )	432	-132.1	21	-399.0	66	This work
14	C <sub>5</sub> Me <sub>4</sub> (SiMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub> )	430	-142.8	42	n.d. <sup>a</sup>	-	This work
15	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> Ph	450	-159.0	35	-426.3	176	This work
16	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> (SiMe <sub>3</sub> )	425	-197.8	27	-464.7	141	This work
17	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> ( <sup>i</sup> Pr)	430	-174.5	15	-441.0	48	This work
18	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> ( <sup>c</sup> Bu)	430	-172.2 <sup>b</sup> ; -169.4 <sup>b</sup>	18; 23	-438.5 <sup>b</sup> ; -435.6 <sup>b</sup>	n.d. <sup>a</sup> ; -	This work
19	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> ( <sup>t</sup> Bu)	435	-171.5	16	-440.0	73	This work
20	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> (cyclohexyl)	432	-173.4	20	-440	73	This work

<sup>a</sup> Not determined.

<sup>b</sup> Two diastereomers due to chiral center in *sec*-butyl group.

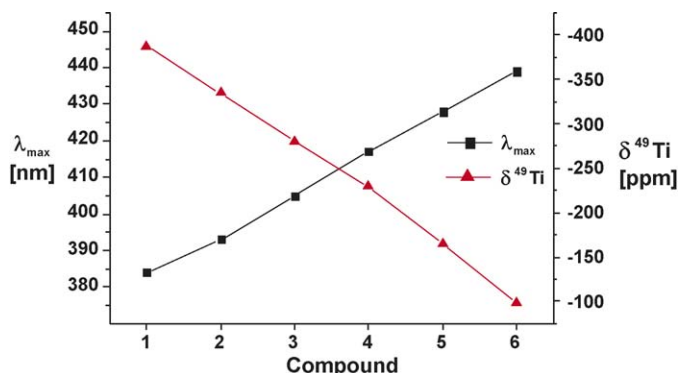


Fig. 1. The dependence of  $\lambda_{\max}$  and  $\delta^{49}\text{Ti}$  on the number of methyl groups in compounds 1–6.

parent complex **1** showing the highest energy of the transition ( $\lambda_{\max}$  384 nm) and the smallest band half-width ca. 70 nm. The band wavelength was increasing with increasing number of Me substituents by ca. 11 nm per Me group to give 439 nm for **6** in practical linear dependence (Fig. 1). This value was not changing further for compounds with the fifth substituent being Et (**7**), Bu (**8**) or pendant alkenyl groups (**9**, **10**). A distinct red shift to 445 nm was observed for the bulky <sup>t</sup>Bu group in compound **12**. On the other hand, the bulky silyl groups SiMe<sub>3</sub> and SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> in compounds **13** and **14** induced remarkable blue shifts (see Fig. 2).

Analogously, replacement of one methyl group vicinal to the proton in tetramethylated compound **5** ( $\lambda_{\max}$  428 nm) by alkyl groups resulted in small red shifts, the largest shift for the <sup>t</sup>Bu group in compound **19** to 435 nm. In this series of compounds the SiMe<sub>3</sub> group in **16** shifted  $\lambda_{\max}$  slightly to shorter wavelengths (425 nm) (Fig. 3). These blue shifts for compounds with one methyl group being substituted by SiMe<sub>3</sub>

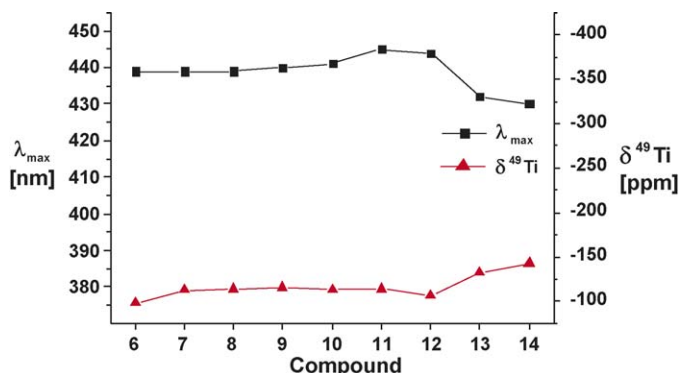


Fig. 2. The dependence of  $\lambda_{\max}$  and  $\delta^{49}\text{Ti}$  on the nature of group R in compounds 6–14.

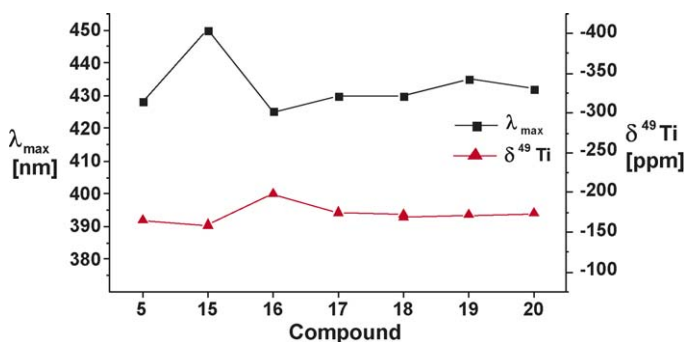


Fig. 3. The dependence of  $\lambda_{\max}$  and  $\delta^{49}\text{Ti}$  on the nature of group R in compounds 5 and 15–20.

group show that the electron releasing effect of the SiMe<sub>3</sub> group is weaker than the effect of Me group. This is in line with the electronic absorption spectra of  $(\eta^5\text{-C}_5\text{H}_5\text{-}_n(\text{SiMe}_3)_n)\text{TiCl}_3$  ( $n=1\text{--}3$ ) which displayed smaller red shifts than the methyl-substituted compounds [12a]. On the other hand, the red shifts

induced by the <sup>t</sup>Bu group in compounds **12** or **19** show that this group is more electron releasing than all other applied alkyl substituents. Surprisingly large red shifts for the phenyl group in compounds **11** and **15** are not compatible with the generally known electron-withdrawing effect of this group. The observed red shifts are tentatively ascribed to conjugation of phenyl and cyclopentadienyl aromatic systems apparently diminishing the HOMO–LUMO energy differences.

The nature of the observed absorption band which is broad and whose shape is more or less asymmetrical was semiquantitatively elucidated by DFT calculations (see below). It was confirmed that the band consists of several charge transfer transitions from cyclopentadienyl ligand based HOMO orbitals to LUMO Ti d-orbitals. The precision of the performed calculations does not allow the successful simulation of the band position and its shape, however, the orbital assignment is correct as proved by an assignment for UPS spectrum of **1** [24] (see below).

## 2.2. <sup>49</sup>Ti and <sup>47</sup>Ti NMR spectra of Cp'TiCl<sub>3</sub> compounds

A series of Cp'TiCl<sub>3</sub> compounds were measured in C<sub>6</sub>D<sub>6</sub> solutions under comparable conditions, and their <sup>49</sup>Ti and <sup>47</sup>Ti chemical shifts (relative to TiCl<sub>4</sub>) and resonance half-widths are given in Table 1. The two <sup>49</sup>Ti (*I* = 7/2) and <sup>47</sup>Ti (*I* = 5/2) nuclei have almost identical magnetogyric ratios, and hence, the resonances of both are readily apparent in the NMR spectra of most compounds with separation of ca. 266 ppm. The <sup>49</sup>Ti nucleus, although of lower natural abundance (5.51% against 7.75% for <sup>47</sup>Ti), is easier observable because of smaller quadrupolar broadening of its resonance line [25]. Therefore, the further discussion will confine largely to <sup>49</sup>Ti data. The <sup>49</sup>Ti chemical shifts for compounds **1** and **6** are in reasonable agreement with literature data which were obtained in CDCl<sub>3</sub> solvent: **1**, δ –390 ppm, *w*<sub>1/2</sub> 60 Hz [12a], δ –396 ppm, *w*<sub>1/2</sub> 49 Hz [12b]; **6**, δ –85 ppm, *w*<sub>1/2</sub> 10 Hz [12a], δ –94.7 ppm, *w*<sub>1/2</sub> 23 Hz [12b]. Larger *w*<sub>1/2</sub> values compared with the data in Table 1 can be due to outer sphere coordination of the CDCl<sub>3</sub> solvent. The chemical shifts for compounds **1–6** are moving downfield with an increment of ca. 60 ppm per Me group. The plot of <sup>49</sup>Ti chemical shifts against the number of Me groups in the (η<sup>5</sup>-C<sub>5</sub>H<sub>5–*n*</sub>Me<sub>*n*</sub>)TiCl<sub>3</sub> (*n* = 0–5) compounds is shown in Fig. 1 together with the λ<sub>max</sub> plot. Both the dependencies are close to linear, and this implies that the shielding effect of methyl groups mimics their electron-donating effect in electronic absorption spectra. This is in line with the suggestion that the chemical shifts of transition metal nuclei are dominated by the paramagnetic shielding which correlates with the energy difference between the ground state and low-lying electronic excited states [25b]. Indeed, the very good correlation between δ <sup>49</sup>Ti and λ<sub>max</sub> determines an increase of 5.254 ppm/nm. A similar relationship was found in incomplete series of Cp'TiCl<sub>3</sub> compounds [12] and in substituted (η<sup>5</sup>-indenyl)TiCl<sub>3</sub> compounds [26]. This is, however, not valid for compounds of the (η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>R)TiCl<sub>3</sub> or (η<sup>5</sup>-C<sub>5</sub>H(1,2,3-)*n*Me<sub>3</sub>R)TiCl<sub>3</sub> types. The groups bulkier than methyl in compounds **7–11** move δ upfield to –112 to –115 ppm whereas their λ<sub>max</sub> values indicate the same electronic effect as

in **6** (Table 1). A slight downfield shift from these values to δ –106.7 ppm was observed for the bulkiest <sup>t</sup>Bu group in compound **12**, however, another very bulky SiMe<sub>3</sub> group in **13** moved δ to –132.1 ppm and the SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> group in **14** to –142.8 ppm (Fig. 2). These observations are in accord with previous reports that the SiMe<sub>3</sub> group exerts only a small downfield shift with respect to proton [12]. A similar situation was found also for the (η<sup>5</sup>-C<sub>5</sub>H(1,2,3-)*n*Me<sub>3</sub>R)TiCl<sub>3</sub> compounds **17–20**. Their chemical shifts were observed upfield from δ –164.7 ppm for **5** spanning –170 to –175 ppm region. Also here, the SiMe<sub>3</sub> group in **16** caused a larger upfield shift. On the other hand, the phenyl group in **15** exerted a large shielding effect shifting δ below the value for **5** (Fig. 3).

Over the whole series of investigated compounds, it is difficult to correlate the resonance halfwidth *w*<sub>1/2</sub> with the compound structure. It was generally accepted [26] and confronted in a number of papers [5–8], that increasing *w*<sub>1/2</sub> follows an increase in molecular asymmetry. In the present data it is, however, difficult to explain large values of *w*<sub>1/2</sub> for compounds **1–3**, a sudden drop for compound **5** and a minimum value of 3 Hz for **6** as well as for asymmetrical alkyl-substituted compounds **7–10**. It seems that a large increase in *w*<sub>1/2</sub> among compounds **7–20** occurs only when the linking atom of the substituent differs remarkably from *sp*<sup>3</sup> carbon atom bearing 1–3 protons, i.e. in Ph, <sup>t</sup>Bu or silyl groups.

The DFT GIAO calculation of <sup>49</sup>Ti NMR chemical shifts showed the downfield shift of ca. 300 ppm when going from **1** to **6**, however, virtually no difference in δ between **6**, **12** and **13**.

## 2.3. DFT calculations

DFT calculations were performed using the B3LYP functional. The Gaussian 98, Revision A.7 program [27] was used in all cases. DFT studies were carried out for the Cp'TiCl<sub>3</sub> compounds **1**, **6**, **12**, and **13**. All model structures were generated by application of a mirror plane containing the Ti atom, one of the chlorine atoms and bisecting the cyclopentadienyl ligand. The structures were optimized using the 3-21G basis set; all molecular properties were obtained employing the 6-311G(d) basis set for the optimized structures. Of the calculated MO orbitals listed in Table 2 only two HOMO frontier orbitals involving the cyclopentadienyl ligand orbitals (Nos. 10 and 11) and three LUMO frontier orbitals Nos. 12–14, which are predominantly Ti d-orbitals, are involved in the generation of the observed absorption band. Obeying transition rules, only three symmetrically allowed transitions 6a' → 7a', 6a' → 8a', and 5a'' → 6a'' should be present, however, the other three were also observed (albeit with smaller oscillator strengths) since the symmetry exclusion rule is broken due to the presence of the metal. The calculation of totally six transitions which constitute the absorption band for compounds **1**, **6**, **12**, and **13** followed the trend of λ<sub>max</sub> values, however, all calculated values were systematically shifted by ca. 20 nm to shorter wavelengths. This discrepancy is probably the consequence of using a rather limited basis set for all atoms and/or the insufficient treatment of relativistic effects caused by the presence of the metallic atom. Larger basis sets and effective core potentials were not used in order to avoid excessive

Table 2  
Calculated frontier orbitals, their energies and OVGf energies for **1**

No.	Orbital notation	Orbital energy (a.u.)	OVGF energy (eV)
1	1a'	-0.37932	12.12
2	1a''	-0.37861	11.78
3	2a'	-0.37399	11.73
4	3a'	-0.36298	11.64
5	2a''	-0.35948	11.57
6	4a'	-0.35400	11.51
7	5a'	-0.34536	11.21
8	3a''	-0.34219	11.18
9	4a''	-0.31388	10.50
10	6a'	-0.29675	9.54
11	5a'' (HOMO)	-0.29205	9.32
12	7a' (LUMO)	-0.12520	
13	6a''	-0.12418	
14	8a'	-0.11532	
15	9a'	-0.07384	

Orbitals are classified according to  $C_s$  symmetry.

calculational time. The same is true for not using more elaborate methods for treating the near-degeneracies present in these types of molecules (the original degeneracy of the two HOMO and three LUMO orbitals must be removed, since the  $C_s$  point group does not allow degenerate representations). The essential correctness of assignment of the HOMO orbital energies was proved by calculation of photoelectron spectrum (UPS) for **1** by means of Outer Valence Green's Function (OVGF) and using a larger basis set (6-311 + G(2d)) which reasonably fitted to the experimental spectrum published by Terpstra et al. [24]. It became apparent that a broad valence band at vertical ionization energy of 9.79 eV is due to electron ionization from the two cyclopentadienyl-based 5a'' and 6a' orbitals (calc. values 9.32 and 9.54 eV). A sharp valence band at 10.77 eV is due to the electron ionization from the 4a'' orbital (calc. 10.50 eV) and the next peak at 11.64 eV at the edge of a very broad unresolved valence band takes origin from the 3a'' orbital (calc. value 11.18 eV). The valence bands extending over 12–15 eV are due to electron ionization from MO orbitals 1a'–5a', 1a'', and 2a'' (Table 2). The reason for lower values of calculated ionization potentials may be caused by relativistic effects. This is also the reason that GIAO shifts of  $^{49}\text{Ti}$  NMR spectra do reflect a change between compounds **1** and **6** but they do not distinguish substituents R in compounds **12** or **13** from the methyl group.

#### 2.4. Crystal structures of $Cp^*\text{TiCl}_3$ compounds

Of the investigated compounds X-ray diffraction crystal structures are known for **1** [28], **5** [29], **7** [30], and **12** [21], and the crystal structures for **16** and **20** were determined in this work. The crystal structures of **16** and **20** are drawn in Figs. 4 and 5, respectively, and the important geometric parameters are listed in Table 3. The structures are in no respect exceptional having the least-squares plane of the cyclopentadienyl ring virtually parallel with the plane of chlorine atoms (angle  $\varphi$ ). In **20**, having  $\varphi$  1.15(11)° the cyclopentadienyl ring is slightly inclined

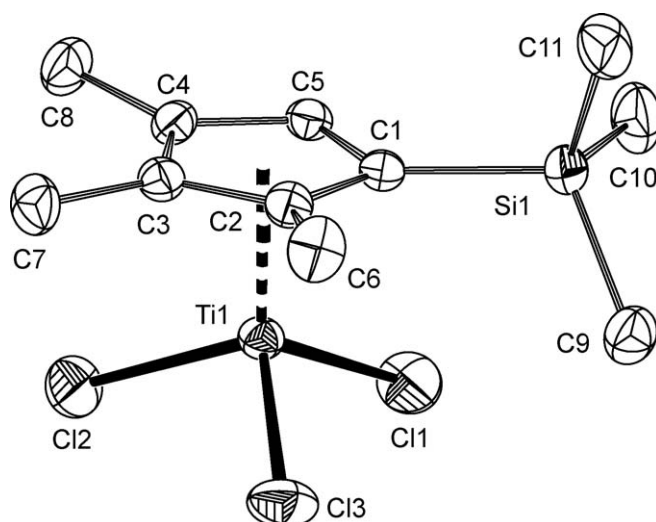


Fig. 4. PLATON drawing of compound **16** at the 30% probability level and atom labeling scheme. Hydrogen atoms are omitted for clarity.

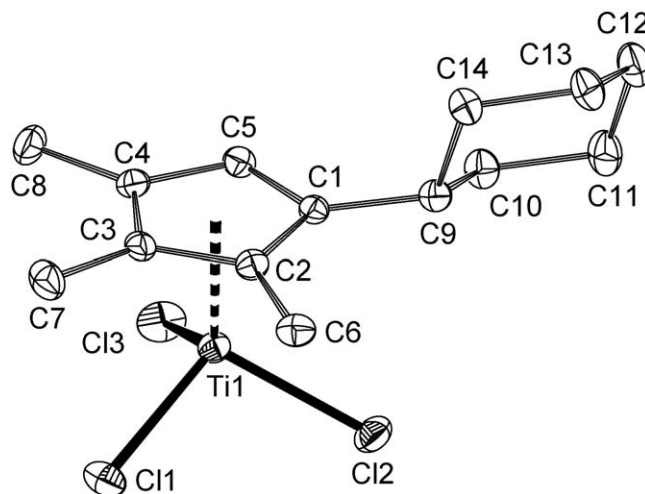


Fig. 5. PLATON drawing of compound **20** at the 30% probability level and atom labeling scheme. Hydrogen atoms are omitted for clarity.

toward the titanium atom by the carbon atom C(5) bearing the hydrogen atom. This is probably caused by the vicinity of very bulky cyclohexyl group and its crystal packing effect in the unit cell. The cyclohexyl group adopts the chair structure, and the dihedral angle  $\tau$  of the least-squares plane of its  $\beta$  and  $\gamma$  carbon atoms and the cyclopentadienyl ring plane is 52.73(14)°. The Si atom in **16** and the C(9) atom of the cyclohexyl group in **20** are declined from the least-squares plane of the Cp ring by 0.159(6) and 0.171(6) Å farther away from the Ti atom. Such values are common for the methyl substituents and do not indicate any steric hindrance of the bulky groups with the Ti–Cl bonds. The comparison of the main structure parameters for compounds involved is shown in Table 4. The average Ti–Cl and Ti–C bond lengths demonstrate that the main elongation of both the bonds occurs between the non-methylated and tetramethylated compound whereas the introduction of  $^t\text{Bu}$  group has only marginal elongation effect. In none of the crystal structures of Table 4

Table 3  
Selected bond lengths (Å) and angles (°) for **16** and **20**

	Compound	
	<b>16</b>	<b>20</b>
Bond lengths		
Ti–Cg <sup>a</sup>	2.0149(17)	2.0087(15)
Ti–C(1–5) <sub>av</sub>	2.349(3)	2.342(3)
Ti–Cl(1)	2.2358(13)	2.2378(10)
TiCl(2)	2.2301(12)	2.2438(10)
Ti–Cl(3)	2.2292(13)	2.2425(10)
Si–C(1)	1.889(3)	–
C(1)–C(9)	–	1.506(4)
C–C(Cp ring)	1.413–1.425(5)	1.403–1.425
Angles		
Cl(1)–Ti–Cl(2)	102.28(6)	102.15(4)
Cl(2)–Ti–Cl(3)	102.28(6)	103.33(4)
Cl(1)–Ti–Cl(3)	103.57(6)	104.04(4)
φ <sup>b</sup>	0.11(11)	1.15(11)
τ <sup>c</sup>	–	52.73(14)

<sup>a</sup> Cg denotes the centroid of the C(1–5) cyclopentadienyl ring.

<sup>b</sup> Dihedral angle between the least-squares plane of the C(1–5) cyclopentadienyl ring and the Cl(1–3) plane.

<sup>c</sup> Dihedral angle between the least-squares plane of the C(1–5) cyclopentadienyl ring and the least-squares plane of C(10), C(11), C(13), and C(14) atoms of the cyclohexyl substituent.

Table 4  
Molecular parameters of Cp<sup>′</sup>TiCl<sub>3</sub> complexes

Complex	Cyclopentadienyl ligand	Ti–Cl <sub>av</sub>	Ti–C <sub>av</sub>	References <sup>a</sup>
<b>1</b>	C <sub>5</sub> H <sub>5</sub>	2.223	2.314	[28]
<b>5</b>	C <sub>5</sub> HMe <sub>4</sub>	2.243	2.350	[29]
<b>7</b>	C <sub>5</sub> Me <sub>4</sub> Et	2.243	2.352	[30]
<b>12</b>	C <sub>5</sub> Me <sub>4</sub> ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> )	2.246	2.361	[21]
<b>16</b>	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> (SiMe <sub>3</sub> )	2.232	2.349	This work
<b>20</b>	C <sub>5</sub> H(1,2,3-)Me <sub>3</sub> (cyclohexyl)	2.241	2.342	This work

<sup>a</sup> Structural data retrieved from Cambridge Crystallographic Data Centre.

Table 5  
Styrene polymerization catalyzed by the [Cp<sup>′</sup>TiCl<sub>3</sub>]/MAO systems<sup>a</sup>

Cpd	Cp <sup>′</sup>	A <sup>b</sup> × 10 <sup>−2</sup>	M <sub>w</sub> × 10 <sup>−3</sup>	D M <sub>w</sub> /M <sub>n</sub>	T <sub>m</sub> <sup>c</sup> (°C)
<b>1</b>	C <sub>5</sub> H <sub>5</sub>	81.46	72.65	1.9	255.6
<b>2</b>	C <sub>5</sub> H <sub>4</sub> Me	12.34	102.84	2.1	265.4
<b>3</b>	C <sub>5</sub> H <sub>3</sub> Me <sub>2</sub>	10.20	144.92	1.9	268.5
<b>4</b>	C <sub>5</sub> H <sub>2</sub> Me <sub>3</sub>	9.71	184.41	2.1	267.7
<b>5</b>	C <sub>5</sub> HMe <sub>4</sub>	11.43 (61.30)	168.01	1.6	269.6 (268.9)
<b>6</b>	C <sub>5</sub> Me <sub>5</sub>	3.95 (31.09)	254.73	1.9	271.1 (268.7)
<b>8</b>	C <sub>5</sub> Me <sub>4</sub> (butyl)	32.43	193.10	1.9	255.6
<b>9</b>	C <sub>5</sub> Me <sub>4</sub> (3-butenyl)	23.33	181.80	2.1	265.4
<b>11</b>	C <sub>5</sub> Me <sub>4</sub> Ph	34.42	304.90	1.9	268.5
<b>13</b>	C <sub>5</sub> Me <sub>4</sub> (SiMe <sub>3</sub> )	(35.21)	–	–	(269.3)
<b>15</b>	C <sub>5</sub> HMe <sub>3</sub> Ph	(41.44)	–	–	(271.9)
<b>16</b>	C <sub>5</sub> HMe <sub>3</sub> (SiMe <sub>3</sub> )	(35.57)	–	–	(266.2)

<sup>a</sup> Polymerization conditions: [Ti] = 5.8 μM, [styrene] = 4.36 × 10<sup>−2</sup> M in toluene, Al/Ti = 500, temperature 50 °C, reaction time 1 h; in parentheses: [Ti] = 10.0 μM, [styrene] = 4.54 × 10<sup>−2</sup> M in toluene, Al/Ti = 1500, temperature 50 °C, reaction time 1 h.

<sup>b</sup> Activity: kg of polymer/[mol(Ti) × mol(styrene) × h].

<sup>c</sup> Melting point of polystyrene.

any steric hindrance between the cyclopentadienyl ligand and chlorine atoms was noticed.

## 2.5. Polymerization of styrene

A series of variously substituted cyclopentadienyltitanium trichlorides (η<sup>5</sup>-C<sub>5</sub>H<sub>5−*n*</sub>Me<sub>*n*</sub>)TiCl<sub>3</sub> (*n* = 0–5; **1**–**6**) were combined with MAO at molar ratio Al/Ti = 500 and used to catalyze the polymerization of styrene in toluene at 50 °C under standard conditions. The polymerization results given in Table 5 show a sharp decrease of catalytic activity for **2**/MAO followed by a moderate decrease for **3**/MAO and **4**/MAO. The **5**/MAO system was, however, more active, showing the activity between those for **2**/MAO and **3**/MAO. The lowest activity, ca. 20 times lower than for **1**/MAO, was found for **6**/MAO. The molecular weight (*M<sub>w</sub>*) of essentially s-PS polymer was increasing with decreasing catalyst activity, reaching maximum *M<sub>w</sub>* 254 730 for **6**/MAO. The s-PS *M<sub>w</sub>* for **5**/MAO was, however, higher than for the less active **3**/MAO catalyst. It was previously shown that replacement of one methyl group in **6** by an alkyl or aryl group increased the activity while the s-PS molecular weight remained high [20]. Therefore, we have carried out polymerizations with **8**/MAO, **9**/MAO, and **11**/MAO catalysts and have found a good reproducibility of activities and s-PS molecular weights with previous data (Table 5). In contrast to Ref. [19] all these catalysts gave a higher activity than the **6**/MAO system. This was previously [20] accounted for the most difficult reduction of **6** among the studied Cp<sup>′</sup>TiCl<sub>3</sub> compounds to give a Ti(III) cationic species which is thought to be the active catalytic center for the styrene polymerization to s-PS [31]. As a consequence, it was proposed that the activity of **6**/MAO catalyst will grow faster with increasing Al/Ti molar ratio than for the other persubstituted compounds **7**–**10** [20]. Indeed, a series of experiments performed at the molar ratio Al/Ti = 1500 showed that the activity of **6** approached activities of variously penta- and tetra-substituted compounds (Table 5, activity in parentheses). Polydispersity of all the s-PS polymers was close to 2, indicat-

ing their single site catalyst formation, syndiotacticity ranged 85–93%. Melting points of polymers (typically 265–271 °C) reflected the polymer crystallinity rather than their molecular weight. The catalysts based on **8**, **9**, **11**, **13**, **15**, and **16** did not show a dramatical increase in their performance, and since these and other Cp'TiCl<sub>3</sub> compounds were not useful for correlation with their spectroscopic properties they were not used for polymerization tests.

## 2.6. Conclusions

The ( $\eta^5$ -C<sub>5</sub>H<sub>5-n</sub>Me<sub>n</sub>)TiCl<sub>3</sub> ( $n=0-5$ ) compounds **1–6** display red shifts of their lowest lengths absorption band ( $\lambda_{\max}$ ) and downfield shifts of their <sup>49,47</sup>Ti NMR chemical shift ( $\delta$ ) proportionally to the number of methyl groups  $n$ . The both magnitudes linearly correlate (constant of proportionality 5.254 ppm/nm) since both are determined by the energy gap between HOMO and LUMO orbitals. The DFT calculations proved that the absorption band is due to transitions from nearly degenerate HOMO orbitals largely located on cyclopentadienyl ligand to predominantly titanium d-orbitals. The above  $\delta/\lambda_{\max}$  correlation, however, does not apply for compounds ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)TiCl<sub>3</sub> **7–14**, and ( $\eta^5$ -C<sub>5</sub>H(1,2,3-)Me<sub>3</sub>R)TiCl<sub>3</sub> **15–20**. The alkyl groups R induce a slight upfield shift of  $\delta$  relative to the methyl derivatives **6** and **5** whereas  $\lambda_{\max}$  is moved slightly to longer wavelengths. This discrepancy can be caused by a pronounced asymmetry of the absorption band extending toward a short wavelengths side. This moves the center of gravity of the absorption band to blue side (correlating with  $\delta$ ) while  $\lambda_{\max}$  moves very slightly to red side. The silyl groups induce the blue shift of  $\lambda_{\max}$  as well as the upfield shift of  $\delta$  which indicates that they are weaker electron donors than methyl group. The  $\delta$  upfield shifts for phenyl group in **11** and **15** correspond qualitatively with its electron withdrawing property, however, the red shifts of  $\lambda_{\max}$  indicate the conjugation of aromatic phenyl and cyclopentadienyl systems. This will be treated experimentally as well as by more precise DFT calculations in our next work.

The styrene polymerizations catalyzed by (**1–6**)/MAO systems showed a general decreasing trend of activities with increasing number of Me groups, the difference between **1**/MAO and **6**/MAO being ca. 20-fold. In contrast to linear dependences of spectroscopic magnitudes, a large drop of activity was found for **2**/MAO whereas the **5**/MAO system was more active than **3**/MAO and **4**/MAO systems. Thus the correlation of spectroscopic data with the catalytic activity is gross only. A limited correlation between the catalytic activity and the pure electronic effect (HOMO–LUMO energy gap) in the catalyst precursor is not surprising when considering that the catalytic center differs from the precursor. The catalytic cationic centers in these systems are usually not accessible to structural investigations, however, it is generally accepted that steric effects of the auxiliary cyclopentadienyl ligand participate in the control of polymer chain growth, chain transfer, and termination reactions [31]. A similar, not clear correlation between  $\delta$  <sup>49</sup>Ti and polymerization activity in substituted ( $\eta^5$ -indenyl)TiCl<sub>3</sub>/MAO catalysts was reported [26]. The activities are further sensitive to changes in the Al/Ti molar ratio, particularly the activity of

the **6**/MAO system dramatically increased at the three times higher Al/Ti molar ratio. The non-methyl substituents R in the ( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>R)TiCl<sub>3</sub> series increased the activity with respect to **6**/MAO, however, the opposite effect was observed for the ( $\eta^5$ -C<sub>5</sub>H(1,2,3-)Me<sub>3</sub>R)TiCl<sub>3</sub> representatives with respect to **5**/MAO. These systems were not investigated in more detail because the reproducibility of polymerization experiments should not meet the precision in determination of e.g.  $\delta$  shifts.

## 3. Experimental

### 3.1. General procedures

All reactions with moisture and air-sensitive compounds were carried out under argon atmosphere using standard Schlenk techniques, or in vacuum using all-sealed glass devices equipped with breakable seals. Samples of solid products for melting point and EI MS measurements were sealed into capillaries and KBr pellets were pressed in a glovebox Labmaster 130 (mBraun) under purified nitrogen. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in CDCl<sub>3</sub> solutions at 25 °C. Chemical shifts ( $\delta$ /ppm) are given relative to the solvent signal ( $\delta_{\text{H}}$  7.15,  $\delta_{\text{C}}$  128.00). <sup>49,47</sup>Ti NMR spectra at 20.32 MHz were measured on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe at 300 K. The samples were dissolved in C<sub>6</sub>D<sub>6</sub> and sealed in 5 mm NMR tubes. The chemical shifts were referred to the <sup>49</sup>Ti NMR signal of external neat TiCl<sub>4</sub> ( $\delta(^{49}\text{Ti})=0.0$ ) in a co-axial capillary placed into 5 mm NMR tube containing C<sub>6</sub>D<sub>6</sub> using absolute resonance frequency. Negative values of titanium chemical shifts denote shifts to lower frequencies. Line broadening of 2–100 Hz (depending on the signal half-widths) were applied prior Fourier transformation. This broadening was subtracted when line half-widths were determined. EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. UV–vis measurements were performed on a Varian Cary 17 D spectrometer in the range 340–800 nm. Solutions in hexane or toluene were measured in a pair of quartz cells (0.1 and 1.0 cm) in the absence of air. Infrared spectra of KBr pellets were recorded in an air-protective cuvette on a Nicolet Avatar FT-IR spectrometer in the range 400–4000 cm<sup>-1</sup>. Melting points were determined in nitrogen-filled sealed capillaries on a Kofler apparatus and are uncorrected. Syndiotacticity of polystyrene was determined by the polymer extraction in boiling ethylmethylketone for 8 h and drying in vacuum to constant weight.

### 3.2. Chemicals

Solvents hexane, toluene, and *m*-xylene were refluxed with LiAlH<sub>4</sub>, degassed, and stored as solutions of green dimeric titanocene, [( $\mu$ - $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)( $\mu$ -H)<sub>2</sub>{Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>}]<sub>2</sub> [32] on a vacuum line. Diethyl ether or tetrahydrofuran (THF) were dried by potassium benzophenone or Na–K alloy, and freshly distilled prior to use. Phenylbromide, polyphosphoric acid (PPA), *n*-butyllithium, dichlorodimethylsilane, and chlorotrimethyl-

silane were obtained from Aldrich and used as received. Methylalumoxane (10% in toluene (w/v)) was purchased from Crompton (Germany).  $\text{TiCl}_4$  (Aldrich) was degassed, refluxed with copper wire in a sealed ampoule, and distributed by distillation on a vacuum line. Its 0.1 M solution in toluene and 0.2 M solution in *m*-xylene were made by mixing known volumes in evacuated all-sealed glass distributing devices. Cyclopentadienyltitanium trichlorides containing  $\text{Cp}'=\text{C}_5\text{H}_5$  (**1**),  $\text{C}_5\text{H}_4\text{Me}$  (**2**),  $\text{C}_5\text{H}_3\text{Me}_2(1,3-)$ ,  $\text{C}_5\text{H}_2\text{Me}_3(1,2,4-)$  (**4**),  $\text{C}_5\text{HMe}_4$  (**5**),  $\text{C}_5\text{Me}_5$  (**6**), and  $\text{C}_5\text{Me}_4\text{Et}$  (**7**) [9],  $\text{C}_5\text{Me}_4\text{Bu}$  (**8**),  $\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$  (**9**),  $\text{C}_5\text{Me}_4(\text{CHMeCH}=\text{CH}_2)$  (**10**),  $\text{C}_5\text{Me}_4\text{Ph}$  (**11**), [20], and  $\text{C}_5\text{Me}_4\text{tert-Bu}$  (**12**) [21] were prepared by synproportionation of the appropriate  $\text{Cp}'_2\text{TiCl}_2$  compounds with  $\text{TiCl}_4$ . This method was also convenient for obtaining of the  $(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{R}))\text{TiCl}_3$  compounds where  $\text{R}=\text{Me}$  (**13**) or 3,3,3-trifluoropropyl (**14**). The corresponding titanocene dichlorides were prepared previously:  $[\text{TiCl}_2\{\text{C}_5\text{Me}_4(\text{SiMe}_3)\}_2]$  [33] and  $[\text{TiCl}_2\{\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CF}_3)\}_2]$  [34]. Precursors of  $\text{Cp}'\text{TiCl}_3$  compounds containing  $\text{Cp}'=1\text{-alkyl-}2,3,4\text{-trimethylcyclopentadienyl}$  (**17–20**), mixtures of (isopropyltrimethylcyclopentadienyl)trimethylsilanes, (*sec*-butyltrimethylcyclopentadienyl)chlorodimethylsilanes, (*tert*-butyltrimethylcyclopentadienyl)trimethylsilanes, and chloro(cyclohexyltrimethylcyclopentadienyl)dimethylsilanes were identical with those recently reported [35].

### 3.3. Preparation of compounds **13** and **14**

A typical synthesis is described for  $[\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_3)\}\text{TiCl}_3]$  (**13**). Compound  $[\text{TiCl}_2\{\text{C}_5\text{Me}_4(\text{SiMe}_3)\}_2]$  [33] (1.08 g, 2.0 mmol) was degassed, and 10 ml of *m*-xylene (distilled from  $\text{LiAlH}_4$  on a vacuum line) was added. Then, a solution of  $\text{TiCl}_4$  in *m*-xylene (0.2 M, 10 ml, 2.0 mmol) was added, and the reaction ampule was heated to 130 °C for 2 h. After cooling to ambient temperature, all volatiles were evaporated in vacuum at 100 °C and discarded. The residue was extracted repeatedly by 20 ml of hexane in a closed system until the extract was yellow. The extracted solid was then dissolved in the hexane at 100 °C and the product crystallized by slow cooling. Orange-yellow crystals were washed with hexane and dried in vacuum.

**13**: Yield 1.22 g (88%). m.p. 164 °C. EI-MS (direct inlet, 110 °C;  $m/z$  (%)): 348 (6), 346 ( $M^{•+}$ ; 6), 336 (9), 335 (40), 334 (26), 333 (98), 332 (33), 331 ( $[\text{M}-\text{Me}]^+$ ; 100), 330 (11), 329 (10), 315 (6), 312 (5), 310 ( $[\text{M}-\text{HCl}]^+$ ; 6), 298 (7), 297 (7), 296 ( $[\text{M}-\text{Me}-\text{Cl}]^+$ ; 9), 295 ( $[\text{M}-\text{Me}-\text{HCl}]^+$ ; 8), 194 (7), 193 ( $[\text{Cp}'^+]$ ; 33), 178 (16), 177 (15), 163 (14), 133 (26), 119 (15), 105 (10), 73 (45), 59 (38). IR (KBr,  $\text{cm}^{-1}$ ): 2963 (m), 2919 (w), 2854 (vw), 1477 (m), 1445 (w), 1409 (w), 1379 (m), 1335 (m), 1250 (s), 1128 (w), 1091 (w), 1021 (m), 845 (vs), 758 (w), 696 (vw), 636 (vw), 466 (s), 409 (vs).

Compound (**14**) was made analogously from  $[\text{TiCl}_2\{\text{C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CF}_3)\}_2]$  [34] (1.34 g, 2.0 mmol).

**14**: Yield 1.34 g (78%). m.p. 102 °C. EI-MS (direct inlet, 90 °C;  $m/z$  (%)): 430 (4), 428 ( $M^{•+}$ ; 4), 395 (5), 393 ( $[\text{M}-\text{Cl}]^+$ ; 5), 379 (6), 377 ( $[\text{M}-\text{HCl}-\text{Me}]^+$ ; 7), 359 (4), 357 ( $[\text{M}-\text{Cl}-\text{HCl}]^+$ ; 4), 336 (13), 335 (15), 334 (62), 333 (40), 332 (100), 331 ( $[\text{M}-\text{CH}_2\text{CH}_2\text{CF}_3]^+$ ; 100), 330 (17),

329 (15), 296 (10), 294 ( $[\text{M}-\text{Cl}-\text{CH}_2\text{CH}_2\text{CF}_3]^+$ ; 13), 275 ( $[\text{Cp}'^+]$ ; 7), 197 (11), 178 ( $[\text{Cp}'-\text{CH}_2\text{CH}_2\text{CF}_3]^+$ ; 19), 177 (19), 164 (21), 135 (29), 133 (30), 120 (16), 119 (61), 105 (38), 91 (29), 81 (22), 77 (79), 59 ( $[\text{SiMe}_2\text{H}]^+$ ; 49).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): 0.22 (s, 6H,  $\text{SiMe}_2$ ); 0.76–0.90 (m, 2H,  $\text{SiCH}_2$ ); 1.58–1.76 (m, 2H,  $\text{CH}_2\text{CF}_3$ ); 1.82 (s, 6H,  $\beta\text{-Me}$ ,  $\text{C}_5\text{Me}_4$ ); 2.11 (s, 6H,  $\alpha\text{-Me}$ ,  $\text{C}_5\text{Me}_4$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): –0.97 ( $\text{SiMe}_2$ ); 8.57 (q,  $^3J_{\text{FC}}=2\text{ Hz}$ ,  $\text{SiCH}_2$ ); 13.71, 17.24 ( $\text{C}_5\text{Me}_4$ ); 28.82 (q,  $^2J_{\text{FC}}=30\text{ Hz}$ ,  $\text{CH}_2\text{CF}_3$ ); 128.09 (q,  $^1J_{\text{FC}}=277\text{ Hz}$ ,  $\text{CF}_3$ ); 136.41, 141.76, 143.96 ( $\text{C}_q$ ,  $\text{C}_{\text{ipso}}$  and  $\text{C-Me}$ ).  $^{19}\text{F}$  ( $\text{C}_6\text{D}_6$ ): –68.60 (t,  $^3J_{\text{FH}}=10.9\text{ Hz}$ ,  $\text{CF}_3$ ).  $^{28}\text{Si}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): –2.86 ( $\text{SiMe}_2\text{CH}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 2964 (m), 2950–2907 (w,b), 1476 (w), 1445 (m), 1383 (m), 1367 (m), 1334 (w), 1322 (w), 1261 (vs), 1206 (s), 1127 (s), 1068 (s), 1022 (m), 901 (m), 846 (m), 814 (m), 781 (w), 737 (w), 623 (vw), 549 (vw), 467 (s), 410 (vs).

### 3.4. Preparation of $(\eta^5\text{-}1,2,3\text{-trimethylphenyl-cyclopentadienyl})\text{trichlorotitanium}$ (**15**)

A hexane solution of *n*-butyllithium (7.9 ml, 1.6 M, 12.7 mmol) was drop wise added at 0 °C to a solution of mixture trimethylphenylcyclopentadienes [36] (2.12 g, 11.5 mmol) in diethyl ether (60 ml). The reaction mixture was warmed to room temperature and stirred overnight. The resulting white precipitate was filtered, washed three times with 20 ml of diethyl ether and dried in vacuum to obtain 1.98 g of lithium salt as white powder. The cyclopentadienyl lithium salt was dissolved in THF (20 ml) and the resulting yellow THF solution was slowly added to a mixture of excess chlorotrimethylsilane in THF (15 ml) previously cooled to –78 °C. The reaction mixture was warmed to room temperature and then stirred for an additional 14 h. The volatiles were removed in vacuum, the yellow-orange oily residue was dissolved in pentane (30 ml) and filtered to remove LiCl. The pentane was removed in vacuum to leave a slightly yellow liquid of (3,4,5-trimethyl-2-phenylcyclopenta-2,4-dienyl)trimethylsilane.

Yield 2.57 g (87%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): –0.25 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ); 1.82–1.86 (m, 3H,  $\text{C}(3)\text{CH}_3$ ); 1.97 (s, 3H,  $\text{C}(5)\text{CH}_3$ ); 1.99 (d,  $^5J_{\text{HH}}=1.8\text{ Hz}$ , 3H,  $\text{C}(4)\text{CH}_3$ ); 3.39 (br s, 1H,  $\text{CH}$ ); 7.05–7.10 (m, 1H,  $\text{Ph}$ ); 7.18–7.22 (m, 4H,  $\text{Ph}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): –2.00 ( $\text{Si}(\text{CH}_3)_3$ ); 11.27, 12.65, 14.89 ( $3\times\text{CH}_3$ ); 54.16 ( $\text{CH}$ ); 125.87, 128.30, 129.45 ( $\text{CH}$ ,  $\text{Ph}$ ); 136.12, 136.39, 136.87, 138.44, 139.32 ( $\text{C}_q$ ;  $\text{C-CH}_3$ ,  $\text{C-Ph}$  and  $\text{Ph}$ ). GC-MS ( $m/z$  (%)): 257 (23), 256 ( $M^{•+}$ ; 100), 241 ( $[\text{M}-\text{Me}]^+$ ; 10), 183 (21), 182 ( $[\text{M}-\text{SiMe}_3\text{H}]^+$ ; 86), 167 ( $[\text{M}-\text{SiMe}_3\text{H}-\text{Me}]^+$ ; 26), 165 (17), 152 (9), 141 (5), 135 (4), 128 (4), 115 (6), 91 (3), 73 ( $[\text{SiMe}_3]^+$ ; 85).

The silane (2.56 g, 10.0 mmol) in 30 ml  $\text{CH}_2\text{Cl}_2$  was cooled to 0 °C and  $\text{TiCl}_4$  solution (10.0 ml, 1 M, 10.0 mmol) in  $\text{CH}_2\text{Cl}_2$  was added in one portion. The mixture was allowed to warm to room temperature and then stirred for 14 h. The resulting dark red mixture was transferred into a sublimator, volatiles were removed and the solid residue was sublimed in vacuum. Pure product sublimed at 120–125 °C/ $4\times 10^{-5}$  mbar as a red solid.

Yield 1.79 g (53%). m.p. 70 °C. EI-MS (direct inlet, 80 °C;  $m/z$  (%)): 338 (18), 336 ( $M^{•+}$ ; 19), 301 ( $[\text{M}-\text{Cl}]^+$ ; 3), 184 (17), 183 ( $[\text{C}_5\text{HMe}_3\text{Ph}]^+$ ; 100), 168 (11), 167 (14), 165 (16),



153 (10), 152 (11).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 1.83, 1.96, 2.16 (3 s, 3 3H, 3  $\text{CCH}_3$ ); 6.50 (s, 1H, CpH); 7.04 (tt,  $^3J_{\text{HH}} = 7.2$  Hz,  $^4J_{\text{HH}} = 1.5$  Hz, 1H, Ph). 7.09–7.16 (m, 2H, Ph); 7.40–7.45 (m, 2H, Ph).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 13.62, 15.20, 16.04 (3  $\text{CH}_3$ ); 122.06 (CH, Cp); 128.74, 128.99, 129.10 (CH, Ph); 134.33, 134.86, 138.33, 139.05, 141.11 ( $\text{C}_q$ ; C- $\text{CH}_3$ , C-Ph and Ph). IR (KBr,  $\text{cm}^{-1}$ ): 3106 (w), 3053 (vw), 2986 (vw), 2963 (vw), 2919 (w), 2852 (vw), 1957 (vw), 1890 (vw), 1815 (vw), 1752 (vw), 1600 (vw), 1576 (w), 1484 (s), 1451 (m), 1381 (s), 1205 (vw), 1183 (w), 1159 (w), 1127 (w), 1076 (w), 1021 (m), 1003 (w), 923 (vw), 877 (m), 772 (s), 764 (s), 699 (s), 659 (w), 643 (m), 617 (vw), 560 (w), 544 (vw), 503 (vw), 458 (vs), 412 (vs).

### 3.5. Preparation of ( $\eta^5$ -1,2,3-trimethyl(trimethylsilyl)-cyclopentadienyl)trichlorotitanium (**16**)

A mixture of 1,2,3-trimethylcyclopentadiene isomers [19] (6.0 g, 55.5 mmol) in diethyl ether (100 ml) was mixed with BuLi (1.6 M in hexane, 35 ml) and stirred overnight. Then, a solution of chlorotrimethylsilane (6.2 g, 57 mmol) in 50 ml of diethyl ether was added, and the mixture was refluxed for 2 h. At room temperature, BuLi (1.6 M in hexane, 37 ml) was added and the mixture stirred for 8 h. Then, a solution of chlorotrimethylsilane (7.0 g, 65 mmol) in 50 ml of diethyl ether was added, the mixture was refluxed for 4 h, and then, the solvents were distilled from a water bath (90 °C). The fraction distilling at 5 Torr and a lower pressure was collected. Yield of 1,2,3-trimethyl-5,5-bis(trimethylsilyl)cyclopenta-1,3-diene was 9.1 g (65%).

GC-MS ( $m/z$ , %): 252 ( $M^{\bullet+}$ ; 57), 237 ( $[M - \text{Me}]^+$ ; 40), 179 (4), 178 ( $[M - \text{Me} - \text{HSiMe}_2]^+$ ; 10), 165 (16), 164 ( $[\text{HC}_5\text{Me}_3\text{SiMe}_2]^+$ ; 100), 149 (22), 105 (5), 73 ( $[\text{SiMe}_3]^+$ ; 70), 59 ( $[\text{HSiMe}_2]^+$ ; 13), 45 (17).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.00 (s, 18 H,  $\text{SiMe}_3$ ); 1.81 (bs, 3 H), 1.94 (d,  $J = 1.3$  Hz, 3 H), 1.97 (s, 3 H) ( $\text{C}_5\text{Me}_3$ ); 5.83 (s, 1 H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.7 ( $\text{SiMe}_3$ ), 10.7, 14.0, 14.8 ( $\text{C}_5\text{Me}_3$ ); 53.6 ( $\text{C}(\text{SiMe}_3)_2$ ), 135.7, 138.9, 141.5 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ). IR (neat): 3047 (w), 2947 (s), 2900 (s), 2853 (s), 1440 (m), 1400 (w), 1377 (m), 1243 (vs), 1230 (m), 1117 (m), 1089 (m), 1047 (m), 980 (w), 957 (s), 927 (m), 870 (vs), 833 (vs), 777 (s), 753 (s), 680 (s), 667 (m), 640 (w), 627 (m), 615 (m), 537 (w), 498 (m).

$\text{TiCl}_4$  (1.3 ml 14.5 mmol) was distilled in vacuum onto a frozen solution of  $\text{C}_5\text{Me}_3(\text{SiMe}_3)_2\text{H}$  (3.78 g, 15.0 mmol) in 40 ml of toluene cooled by liquid nitrogen. The mixture was then slowly warmed up with vigorous shaking. After subsequent warming to 80 °C all volatiles were evaporated in vacuum and the residue was extracted by 60 ml of hexane. The orange-yellow solution was concentrated, and cooled in a refrigerator. Orange crystals obtained overnight were separated, washed with hexane, and dried in vacuum.

**16**: Yield 3.0 g (63%). m.p. 98 °C. EI-MS (direct inlet, 70 °C;  $m/z$  (%)): 332 ( $M^{\bullet+}$ ; 0.7), 323 (7), 322 (8), 321 (39), 320 (24), 319 (98), 317 ( $[M - \text{Me}]^+$ ; 100), 316 (10), 315 (10), 302 (6), 284 (7), 283 (9), 282 ( $[M - \text{Me} - \text{Cl}]^+$ ; 11), 281 ( $[M - \text{Me} - \text{HCl}]^+$ ; 11), 179 ( $[\text{C}_5\text{HMe}_3\text{SiMe}_3]^+$ ; 15), 164 ( $[\text{C}_5\text{HMe}_3\text{SiMe}_2]^+$ ; 12), 163 (9), 149 (11), 119 (12), 105 (10), 97 (6), 93 (6), 91 (7), 83 (8), 73 ( $[\text{SiMe}_3]^+$ ; 35), 59 ( $[\text{SiHMe}_2]^+$ ; 40), 58 (6), 45 (11), 43

(16).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.25 (s, 9 H,  $\text{SiMe}_3$ ), 1.75, 1.99, 2.18 (3  $\times$  s, 3  $\times$  3H,  $\text{C}_5\text{Me}_3$ ); 6.53 (s, 1 H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ): -0.5 ( $\text{SiMe}_3$ ), 12.8, 15.9, 17.0 ( $\text{C}_5\text{Me}_3$ ); 129.5 (CH,  $\text{C}_5\text{Me}_3\text{H}$ ), 141.6, 142.3, 142.5, 144.6 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3080 (vw), 2959 (m), 2918 (w), 2851 (vw), 1477 (w), 1445 (w), 1404 (w), 1381 (m), 1348 (w), 1287 (vw), 1267 (w), 1252 (vs), 1150 (m), 1139 (m), 1026 (m), 931 (vw), 872 (m), 842 (vs), 753 (m), 697 (vw), 629 (w), 498 (vw), 464 (s), 410 (vs).

### 3.6. Preparation of ( $\eta^5$ -1-isopropyl-2,3,4-trimethylcyclopentadienyl)titanium trichloride (**17**)

A mixture of (1-isopropyl-2,3,4-trimethylcyclopentadienyl)trimethylsilanes [35] (0.75 g, 3.38 mmol) was degassed on a vacuum line, and a solution of  $\text{TiCl}_4$  in toluene (0.1 M, 35 ml) was added under stirring. The mixture was heated to 90 °C for 30 min, cooled to room temperature, and all volatiles including unreacted  $\text{TiCl}_4$  were distilled off in vacuum. The residue was extracted repeatedly by 30 ml of hexane in a sealed system. The extracted solid was dissolved in the mother liquor by warming to 100 °C and crystallized by slow cooling. Yield of orange crystals was 0.76 g (74%).

**17**: m.p. 111 °C. EI-MS (direct inlet, 70 °C;  $m/z$  (%)): 304 (14), 302 ( $M^{\bullet+}$ ; 15), 269 (17), 268 (53), 267 (28), 266 ( $[M - \text{HCl}]^+$ ; 70), 265 (11), 232 (39), 231 (24), 230 ( $[M - 2\text{HCl}]^+$ ; 97), 150 (17), 149 ( $[\text{C}_5\text{HMe}_3(\text{i}Pr)]^+$ ; 100), 135 (14), 134 (65), 133 (55), 119 (51), 115 (12), 105 (25), 91 (36), 79 (13), 77 (19), 41 (28).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.74, 1.17 (2  $\times$  d, 2  $\times$   $^3J_{\text{HH}} = 7.0$  Hz, 2  $\times$  3H,  $\text{CHMe}_2$ ); 1.89 (s, 6H,  $\text{C}_5\text{Me}_3$ ); 1.92 (s, 3H,  $\text{C}_5\text{Me}_3$ ); 3.07 (septuplet,  $^3J_{\text{HH}} = 7.0$  Hz, 1H,  $\text{CHMe}_2$ ); 6.28 (s, 1H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 13.49, 13.80, 15.80 ( $\text{C}_5\text{Me}_3$ ); 20.33, 23.88 ( $\text{CHMe}_2$ ); 29.66 ( $\text{CHMe}_2$ ); 119.26 (CH,  $\text{C}_5\text{Me}_3$ ); 136.39, 137.01, 139.47, 149.68 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3096 (vw), 2967 (s), 2925 (m), 2873 (w), 1498 (m), 1470 (m), 1447 (m), 1416 (w), 1383 (m), 1364 (m), 1349 (w), 1311 (vw), 1186 (w), 1144 (vw), 1098 (vw), 1070 (vw), 1047 (vw), 1021 (w), 880 (vw), 862 (m), 762 (m,b), 673 (vw), 617 (vw), 496 (w), 457 (s), 411 (vs).

### 3.7. Preparation of (1-sec-butyl-2,3,4-trimethylcyclopentadienyl)titanium trichloride (**18**)

Analogously to the synthesis of **16**, a mixture of (1-sec-butyl-2,3,4-trimethylcyclopentadienyl)chlorodimethylsilanes [35] (0.85 g, 3.3 mmol) was reacted with the toluene solution of  $\text{TiCl}_4$  (0.1 M, 35 ml). Orange crystalline material consisted of two diastereomers (I and II) due to a chiral center in the sec-butyl substituent and a planar chirality of the cyclopentadienyl ring as indicated by two sets of resonances in  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{49,47}\text{Ti}$  NMR spectra. Yield 0.81 g (78%).

**18**: m.p. 92 °C. EI-MS (direct inlet, 80 °C;  $m/z$  (%)): 318 (9), 316 ( $M^{\bullet+}$ ; 10), 283 (10), 282 (29), 281 (17), 280 ( $[M - \text{HCl}]^+$ ; 41), 246 (36), 245 (21), 244 ( $[M - 2\text{HCl}]^+$ ; 85), 243 (13), 165 (18), 164 (10), 163 ( $[\text{C}_5\text{HMe}_3(\text{s}Bu)]^+$ ; 48), 135 (100), 134 (30), 133 (29), 121 (21), 119 (65), 107 (23), 105 (32), 91 (42), 43 (16), 41 (28). IR (KBr,  $\text{cm}^{-1}$ ): 3091 (vw), 2965 (s), 2924 (m),

2876 (w), 1494 (w), 1455 (m), 1414 (vw), 1381 (m), 1349 (vw), 1260 (vw), 1182 (vw), 1019 (m), 877 (m), 764 (w,b), 673 (vw), 617 (vw), 497 (w), 458 (s), 414 (vs).

### 3.7.1. I (56%)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.56 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 3H,  $\text{CH}_2\text{Me}$ ); 0.96–1.28 (m, 2H,  $\text{CH}_2\text{Me}$ ); 1.18 (d,  $^3J_{\text{HH}} = 6.5$  Hz, 3H,  $\text{CHMe}$ ); 1.88, 1.90, 1.93 ( $3 \times$  s,  $3 \times$  3H,  $\text{C}_5\text{Me}_3$ ); 2.90–3.02 (m, 1H,  $\text{CHMe}$ ); 6.30 (s, 1H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 11.01 ( $\text{CH}_2\text{Me}$ ); 13.70, 13.87, 15.74 ( $\text{C}_5\text{Me}_3$ ); 17.30 ( $\text{CHMe}$ ); 31.23 ( $\text{CH}_2\text{Me}$ ); 35.62 ( $\text{CHMe}$ ); 119.65 ( $\text{CH}$ ,  $\text{C}_5\text{Me}_3$ ); 136.45, 136.72, 139.45, 149.04 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ).

### 3.7.2. II (44%)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.77 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 3H,  $\text{CHMe}$ ); 0.87 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 3H,  $\text{CH}_2\text{Me}$ ); 0.96–1.28 (m, 2H,  $\text{CH}_2\text{Me}$ ); 1.88, 1.89, 1.92 ( $3 \times$  s,  $3 \times$  3H,  $\text{C}_5\text{Me}_3$ ); 2.79–2.91 (m, 1H,  $\text{CHMe}$ ); 6.27 (s, 1H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 12.13 ( $\text{CH}_2\text{Me}$ ); 13.56, 13.80, 15.79 ( $\text{C}_5\text{Me}_3$ ); 20.14 ( $\text{CHMe}$ ); 27.61 ( $\text{CH}_2\text{Me}$ ); 36.49 ( $\text{CHMe}$ ); 119.98 ( $\text{CH}$ ,  $\text{C}_5\text{Me}_3$ ); 136.26, 136.82, 139.49, 149.83 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ).

## 3.8. Preparation of (1-tert-butyl-2,3,4-trimethylcyclopentadienyl)titanium trichloride (**19**)

Compound **19** was obtained from a mixture of isomers of (1-tert-butyl-2,3,4-trimethylcyclopentadienyl)trimethylsilane [35] (0.78 g, 3.3 mmol) reacted with the toluene solution of  $\text{TiCl}_4$  (0.1 M, 35 ml). Orange crystalline product was obtained from hexane. Yield 0.72 g (69%).

**19**: m.p. 98 °C. EI-MS (direct inlet, 80 °C;  $m/z$  (%)): 320 (12), 318 (31), 316 ( $M^{++}$ ; 32), 305 (14), 303 (34), 302 (10), 301 ( $[\text{M} - \text{Me}]^+$ ; 37), 283 (10), 282 (22), 281 (14), 280 ( $[\text{M} - \text{HCl}]^+$ ; 30), 269 (16), 268 (15), 267 (76), 266 (25), 265 ( $[\text{M} - \text{Me} - \text{HCl}]^+$ ; 100), 246 (7), 244 ( $[\text{M} - 2 \text{HCl}]^+$ ; 15), 230 (12), 229 (8), 227 (13), 164 (9), 163 ( $[\text{C}_5\text{HMe}_3(\text{tBu})]^+$ ; 69), 149 (7), 148 ( $[\text{C}_5\text{HMe}_2(\text{tBu})]^+$ ; 41), 147 (15), 133 (23), 91 (11), 41 (10).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 1.17 (s, 9H,  $\text{CMe}_3$ ); 1.74, 1.99, 2.18 ( $3 \times$  s,  $3 \times$  3H,  $\text{C}_5\text{Me}_3$ ); 6.34 (s, 1H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 13.49, 16.38, 16.44 ( $\text{CpMe}_3$ ); 30.11 ( $\text{CMe}_3$ ); 35.17 ( $\text{CMe}_3$ ); 121.24 ( $\text{CH}$ ,  $\text{C}_5\text{Me}_3\text{H}$ ); 134.58, 138.13, 140.26, 153.78 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3113 (vw), 2970 (s), 2918 (m), 2873 (w), 1496 (w), 1479 (m), 1463 (m), 1370 (m), 1231 (m), 1018 (m), 869 (m), 756 (w,b), 674 (vw), 610 (vw), 495 (w), 456 (s), 407 (vs).

## 3.9. Preparation of (1-cyclohexyl-2,3,4-trimethylcyclopentadienyl)titanium trichloride (**20**)

Following the previous receipts, a mixture of chloro(1-cyclohexyl-2,3,4-trimethylcyclopentadienyl)dimethylsilanes [35] (0.93 g, 3.3 mmol) was reacted with 35 ml of 0.1 M toluene solution of  $\text{TiCl}_4$ . Orange finely crystalline product was obtained after workup and crystallization from hexane. Yield 0.82 g (73%).

**20**: m.p. 108 °C. EI-MS (direct inlet, 80 °C;  $m/z$  (%)): 344 (9), 342 ( $M^{++}$ ; 9), 308 (35), 307 (19), 306 ( $[\text{M} - \text{HCl}]^+$ ; 47), 273

(12), 272 (54), 271 (35), 270 ( $[\text{M} - 2\text{HCl}]^+$ ; 100), 269 (18), 189 ( $[\text{C}_5\text{HMe}_3(\text{cyclohexyl})]^+$ ; 33), 134 (11), 133 (73), 121 (22), 119 (17), 117 (14), 115 (11), 109 (10), 107 (21), 105 (24), 91 (35), 81 (24), 79 (13), 77 (15), 55 (15), 53 (11), 41 (38).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.60–0.80 (m, 1H, cyclohexyl); 0.94–1.32 (m, 4H, cyclohexyl); 1.42–1.72 (m, 4H, cyclohexyl); 1.90, 1.92, 1.93 ( $3 \times$  s,  $3 \times$  3H,  $\text{C}_5\text{Me}_3$ ); 2.02–2.22 (m, 1H, cyclohexyl); 2.76–2.92 (m, 1H,  $\text{C}_5\text{Me}_3\text{CH}$ , cyclohexyl); 6.31 (s, 1H,  $\text{C}_5\text{Me}_3\text{H}$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ ): 13.48, 13.83, 15.80 ( $\text{C}_5\text{Me}_3$ ); 26.15, 26.75, 30.64, 35.06 ( $\text{CH}_2$ , cyclohexyl); 39.69 ( $\text{CH}$ , cyclohexyl); 119.66 ( $\text{CH}$ ,  $\text{C}_5\text{Me}_3$ ); 136.39, 136.78, 139.62, 148.84 ( $\text{C}_q$ ; C-Me and  $\text{C}_{\text{ipso}}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3093 (w), 2981 (vw), 2926 (vs), 2851 (s), 1496 (m), 1475 (w), 1447 (s), 1382 (m), 1375 (m), 1270 (vw), 1176 (vw), 1135 (vw), 1021 (m), 1000 (w), 891 (w), 762 (vw), 680 (vw), 617 (vw), 532 (vw), 490 (m), 457 (s), 409 (vs).

## 3.10. Styrene polymerization

The polymerizations were carried out at 50 °C in a 70 ml glass reactor. The reactor was equipped with a magnetic stirring bar and connected to a nitrogen/high vacuum line. After evacuation for 2 h, the reactor was filled with purified nitrogen and charged by syringes in nitrogen stream subsequently with purified toluene (30 ml), styrene (5.2 ml), the MAO solution in toluene and a toluene solution of a titanium complex. The mixture was then heated to 50 °C and the temperature was kept constant during the polymerization (60 min). The polymerization was quenched by addition of a mixture of aqueous HCl (5 ml of 35% HCl) and methanol (50 ml). The precipitated polymer was filtered off, washed with methanol and dried in vacuum at 80 °C to constant weight. Syndiotacticity was determined by polymer extraction in boiling 2-butanone for 8 h followed by drying of the residue till constant weight.

## 3.11. X-ray crystal structure of compounds **16** and **20**

Crystal fragments of **16** and **20** were inserted into a Lindemann glass capillary under nitrogen atmosphere in a glovebox and the capillary was sealed with wax. Diffraction data were collected on an Enraf-Nonius CAD 4-MACH III diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **16** and on a Nonius KappaCCD diffractometer with CCD area detector for **20**, both at ambient temperature. The structures were solved by direct methods (SIR-92) [37] and refined by full-matrix least squares on  $F^2$  (SHELXL-97) [38]. Crystallographic data, details on data collection and the structure refinement are given in Table 6.

## 4. Supplementary material

Relevant crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 296372 for compound **16** and CCDC 296371 for **20**. Copies of the data can be obtained free of charge on application to CCDC, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

Table 6  
Crystallographic data, data collection and structure refinement data for compounds **16** and **20**

	Compound	
	<b>16</b>	<b>20</b>
Chemical formula	C <sub>11</sub> H <sub>19</sub> Cl <sub>3</sub> SiTi	C <sub>14</sub> H <sub>21</sub> Cl <sub>3</sub> Ti
Molecular weight	333.60	343.56
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>a</i> (Å)	6.8139(9)	6.9420(5)
<i>b</i> (Å)	24.054(3)	11.5560(6)
<i>c</i> (Å)	9.7860(16)	20.1620(16)
$\alpha$ (°)	90	90
$\beta$ (°)	97.921(13)	94.214(3)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	1588.7(4), 4	1613.06(19), 4
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.395	1.415
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.093	1.009
<i>F</i> (000)	688	712
Crystal size (mm <sup>3</sup> )	0.5 × 0.25 × 0.2	0.25 × 0.18 × 0.15
<i>T</i> (K)	293(2)	293(2)
$\theta$ range (°)	2.27–24.95	3.43–27.47
<i>hkl</i> range	0/8; 0/28; –11/11	–8/8; –11/14; –26/26
Diffractions collected	2769	5802
Unique diffractions	1967	3641
Parameters	151	166
<i>R</i> , <i>wR</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0389, 0.0952	0.0494, 0.0933
<i>R</i> , <i>wR</i> (all data)	0.0795, 0.1126	0.1049, 0.1126
<i>S</i>	1.028	1.037
$\Delta\rho_{\max,\min}$ (eÅ <sup>-3</sup> )	0.634, –0.266	0.353, –0.378

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