



Dinuclear titanium complexes with methylphenylsilylene bridge between cyclopentadienyl rings. Synthesis, characterization and reactivity towards ethylene

Michal Horáček^a, Róbert Gyepes^b, Jan Merna^c, Jiří Kubišta^a, Karel Mach^a, Jiří Pinkas^{a,*}

^aJ. Heyrovský Institute of Physical Chemistry of ASCR, v.v.i. Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

^bDepartment of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

^cDepartment of Polymers, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

ARTICLE INFO

Article history:

Received 30 November 2009

Received in revised form 26 January 2010

Accepted 31 January 2010

Available online 4 February 2010

Keywords:

Ansa-titanocene

Cyclopentadienyl

Dinuclear complexes

Ethylene polymerization

Crystal structure

ABSTRACT

The new *ansa*-titanocene dichloride $[(\eta^5\text{-C}_5\text{H}_4)_2\text{TiCl}_2]$ (**1**) was prepared by one pot reaction, whereas synthesis of its methylated analogue $[(\eta^5\text{-C}_5\text{Me}_4)_2\text{TiCl}_2]$ (**3**) was performed in two steps with isolation of corresponding silane intermediate $\text{SiMePh}(\text{HC}_5\text{Me}_4)_2$ (**2**). The reaction of **1** and **3** with TiCl_4 afforded the dinuclear complexes $[(\eta^5\text{-C}_5\text{R}_4)_2\text{TiCl}_3]_2$ ($\text{R} = \text{H}$ (**4**) and $\text{R} = \text{Me}$ (**5**)). The catalysts formed from **4** and **5** after their activation with excess MAO exhibited a modest activity in ethylene polymerization. The polymer products consisted of high molar mass linear polyethylenes with a broad molar mass distribution. The presence of three paramagnetic titanium species in the mixture **4**/MAO was revealed by EPR spectroscopy. All new prepared compounds **1–5** were characterized by multinuclear NMR, EI-MS, IR, and solid-state structures of **1**, **3** and **5** were determined by X-ray single crystal diffraction.

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1. Introduction

Monocyclopentadienyl titanium complexes in combination with strong Lewis acids (methylaluminoxane (MAO) or $\text{B}(\text{C}_6\text{F}_5)_3$) form active species for polymerization of a wide range of olefins. The most known applications are the polymerization of styrene to syndiotactic polystyrene (sPS) [1,2] and the polymerization of 1,3-butadiene to highly *cis*-1,4-polybutadiene [3]. Another interesting utilization was recently developed by Deckers et al. who introduced the catalytic system $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ar})\text{TiCl}_3]/\text{MAO}$ (where Ar = aryl) efficient with the selective ethylene trimerization to 1-hexene [4]. The arene pendant group was proposed to behave as a hemi-labile ligand, providing some stabilization for the reactive metal center while still maintaining its accessibility to the approaching ethylene molecule.

On the other hand, polymerization of ethylene catalyzed by monocyclopentadienyl complexes lies outside the mainstream due to their lower activity compared to group four metallocene dichlorides [5]. Treatment of $[(\text{C}_5\text{Me}_5)\text{TiMe}_3]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ offered the zwitterionic complex $[(\text{C}_5\text{Me}_5)\text{TiMe}_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$, which was able to polymerize ethylene to a polymer with high T_m [6]. Extending the catalytic system to compounds of general formula $[(\text{C}_5\text{Me}_5)\text{TiMe}_2\text{E}]$ ($\text{E} = \text{Me}, \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5, \text{Cl}$) activated by either

$\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ led to catalysts polymerizing ethylene with activities in the range $8\text{--}30 \text{ kg}_{\text{PE}} \text{ mol}_{\text{Ti}}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$, while the use of borate activator led to slightly higher activities in comparison to $\text{B}(\text{C}_6\text{F}_5)_3$ [7,8]. The authors declared that the produced polymers had high M_w ($>300,000 \text{ g mol}^{-1}$) and a linear microstructure. In contrast, Pellechia et al. obtained the low molecular weight butyl branched (up to 50 branches/1000 carbons) polyethylene of LLDPE type from a solely ethylene feed using the same catalytic system $[(\text{C}_5\text{Me}_5)\text{TiMe}_3]/\text{B}(\text{C}_6\text{F}_5)_3$ [9]. Moreover, the formation of high molar PE with isolated long chain branches (up to 25 branches/1000 carbons) was observed when the $[(\text{C}_5\text{Me}_5)\text{Ti}(\text{OBz})_3]/\text{mMAO}$ (m denotes modified) system was used [10].

To our best present knowledge there is no study on the preparation of polyethylene using dinuclear monocyclopentadienyltitanium/MAO catalyst.

Here, we present the preparation and characterization of new *ansa*-titanocene dichlorides bearing methylphenylsilylene bridge $[(\eta^5\text{-C}_5\text{R}_4)_2\text{TiCl}_2]$ (where $\text{R} = \text{H}$ (**1**) and $\text{R} = \text{Me}$ (**3**)) and the formation of dinuclear complexes $[(\eta^5\text{-C}_5\text{R}_4)_2\text{TiCl}_3]_2$ (where $\text{R} = \text{H}$ (**4**) and $\text{R} = \text{Me}$ (**5**)) thereof. The reactivity of catalysts formed from **4** and **5** and $[(\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_4)\text{TiCl}_3]_2$ (**6**) [11] by their activation with excess of MAO towards ethylene has been tested. The impact of two titanium centers constrained in close proximity along with the effect of a pendant phenyl group residing at the silicon bridge on the catalytic performance will be discussed.

* Corresponding author. Tel.: +420 2 8658 3735; fax: +420 2 8658 2307.

E-mail address: pinkas@jh-inst.cas.cz (J. Pinkas).

2. Results and discussion

2.1. Synthesis of dinuclear titanium complexes

The preparation of titanocene dichloride **1** was accomplished as depicted in Scheme 1. Although the preparation of the chelating (C₅Me₄)₂SiMePh ligand has already been published [12], our attempt to reproduce the procedure led only to a low yield of the desired ligand contaminated in addition by a variety of undefined compounds. Therefore the synthesis of **1** was performed by sequential addition of reagents in one-pot reaction arrangement. Thus two equivalents of cyclopentadienylsodium solution in THF were treated with dichloromethylphenylsilane in THF and the chelating ligand formed in situ was deprotonated by *n*-BuLi. The dilithium salt was further reacted with TiCl₄(THF)₂ for 40 h and after workup yielded complex **1** in a modest yield as air and moisture stable reddish-brown fine crystals.

The synthesis of the permethylated analogue of **1** was carried out in two steps with the isolation of the corresponding bis-cyclopentadienylsilane **2** (Scheme 2). Dichloromethylphenylsilane was reacted with two equivalents of tetramethylcyclopentadienyllithium in THF, and after a short reflux, the mixture was treated with one equivalent of hexamethylphosphoramide (HMPA). The use of HMPA in the synthesis was found to be crucial, as the sole mixing of dichloromethylphenylsilane with two equivalents of tetramethylcyclopentadienyllithium led to the substitution of only one chlorine atom on the silane even after a long reflux (6 days) in THF. The ¹H and ¹³C NMR spectra of the obtained chloromethylphenyl(2,3,4,5-tetramethylcyclopentadienyl)silane agreed with literature data [13].

The ligand **2** was obtained predominantly as 5,5'-isomer in a purity about 92% (by GC-MS), and was used without any further purification. Where it necessary, it could be purified by crystallizing from cold hexane (with a relatively low recoverability due to

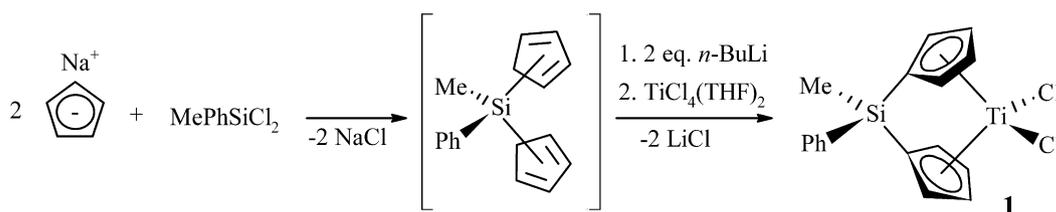
its high solubility). The resulting white solid is exclusively 5,5'-isomer as proved by NMR measurements of its CDCl₃ solution (see Section 4).

Ligand **2** was deprotonated with 2 equivalents of *n*-BuLi and the dilithium salt formed *in situ* was treated with TiCl₃(THF)₃. The oxidation of the intermediate *ansa*-titanocene monochloride was performed by aqueous HCl. Complex **3** was obtained in the form of air- and moisture-stable dark red crystals (directly suitable for single-crystal X-ray diffraction) after crystallization of the crude product from a CHCl₃/MeOH mixture.

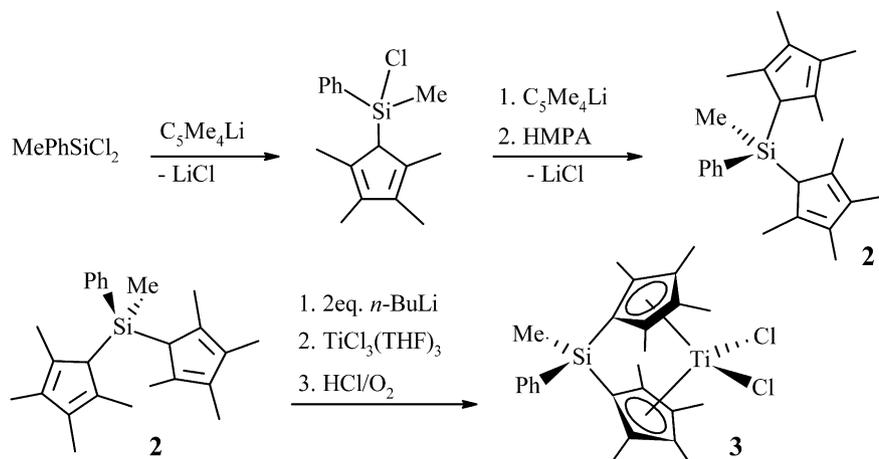
A general synthetic route to the dinuclear complexes **4** and **5** comprises of the respective synproportionation of **1** and **3** with TiCl₄ performed at elevated temperatures (Scheme 3). The reactions were successfully conducted both in toluene solutions or in neat TiCl₄.

It should be noted that an acidolytic route to the hexa(amido)dinuclear complex from the reaction of Ti(NMe₂)₄ and **2** was found to be unfeasible, as the reaction of ligand **2** with 2.1 molar equivalents of Ti(NMe₂)₄ failed to proceed even at 145 °C, apparently due to the low acidity of the ligand.

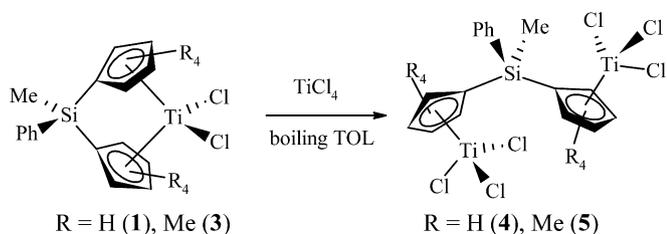
¹H and ¹³C NMR spectra of the *ansa*-titanocene dichlorides (**1** and **3**) and the dinuclear complexes (**4** and **5**) reflect an average C_s molecular symmetry in solution. The ¹H NMR spectra are consistent with the presence of two equivalent cyclopentadienyl rings, where each of them has four multiplet signals for the C₅H₄ protons in **1** (δ_H in ppm: 5.96–6.00; 6.07–6.11; 7.20–7.24; 7.25–7.28) and in **4** (δ_H in ppm: 6.18–6.22; 6.24–6.30; 6.48–6.53; 6.64–6.70). Similarly, four singlet signals were observed for the C₅Me₄ methyls in **3** (δ_H in ppm: 1.53; 1.92; 2.07; 2.17) and three signals (due to the overlap of two signals) in **5** (δ_H in ppm: 2.13; 2.31; 2.41). Both the cyclopentadienyl protons in **1** and the methyl protons in **3** located in vicinal positions to the bridging silicon atom showed strong through space contacts with both phenyl CH_{ortho} protons (δ_H in ppm: CH_{ortho}/CH(C₅H₄): 7.85–7.90/5.96–6.00 in **1**; CH_{ortho}/



Scheme 1.



Scheme 2.



Scheme 3.

$\text{CMe}(\text{C}_5\text{Me}_4)$: 7.88–7.94/1.53 in **3**) and the methyl group bonded to the bridging silicon atom (δ_{H} in ppm: $\text{SiMe}/\text{CH}(\text{C}_5\text{H}_4)$: 0.88/6.07–6.11 in **1**; $\text{SiMe}/\text{CMe}(\text{C}_5\text{Me}_4)$: 1.03/1.92 in **3**). The latter effect is however absent in the case of the dinuclear complexes **4** and **5** due to a free rotation around the Si–Cp bond.

The electron impact mass spectra of the *ansa*-titanocene dichlorides show quite different features. While the molecular peak m/z 366 of **1** is a base peak, the molecular peak m/z 478 of **3** possesses about half abundance of the base peak m/z 105. The molecular peak of the dinuclear complexes has a low intensity, e.g. m/z 668 for **5** or is absent for **4**.

The infrared spectra of all complexes display valence vibrations of the phenyl C–H groups in the region 3037–3131 cm^{-1} .

2.2. Crystal structure analyses and DFT studies

Compound **1** crystallized with an orthorhombic lattice (space group $Pnma$). The molecule (Fig. 1) exhibits an exact C_s point group symmetry as only one half of the formula unit is located in the asymmetric part of the unit cell. The remaining part of the molecule is generated by applying the mirror plane passing through the central titanium atom and the two chlorine ligands; this plane incorporates in addition the silicon atom together with the methyl carbon atom and the whole phenyl substituent.

The coordination environment of the titanium atom is a distorted tetrahedron consisting of two cyclopentadienyl rings and two chloride ligands. The effect of cyclopentadienyl bending caused by the presence of the SiPhMe bridging group is manifested by the decrease of the CE(1)–Ti–CE(1') angle (CE and CE' denote the two Cp centroids) to 129.17° as compared with the values 130.72(4)° and 130.70(3)° for the two independent molecules of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ [14]. Other structural features are within expected ranges; selected molecular parameters are listed in Table 1.

Compound **3** (Fig. 2) crystallized with a triclinic lattice (space group $P\bar{1}$). The cyclopentadienyl ring bending in this molecule caused by the SiPhMe bridge is more significant than in **1** due to

Table 1
Selected bond lengths [Å] and angles [°] for **1**.

Ti(1)–Cl(1)	2.3621(13)
Ti(1)–Cl(2)	2.3528(13)
Ti(1)–C(1)	2.376(3)
Ti(1)–C(2)	2.355(3)
Ti(1)–C(3)	2.430(3)
Ti(1)–C(4)	2.423(4)
Ti(1)–C(5)	2.363(3)
Si(1)–C(1)	1.866(4)
Si(1)–C(6)	1.868(5)
Si(1)–C(12)	1.860(5)
Cl(1)–Ti(1)–Cl(2)	96.95(5)
CE1–Ti(1)–CE(1)#1	129.17
C(1)–Si(1)–C(1)#1	90.2(2)
C(12)–Si(1)–C(6)	111.8(2)

Symmetry transformations used to generate equivalent atoms: #1x, $-y + 1/2, z$.

the presence of methyl substituents on the cyclopentadienyl rings. The CE1–Ti–CE2 angle for **3** is as low as 132.34(3)° as opposed to

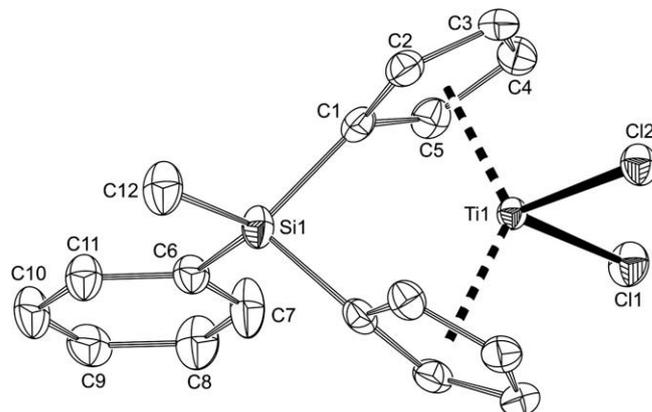


Fig. 1. Thermal ellipsoid plot (50% probability level) of **1**. Hydrogen atoms omitted for clarity.

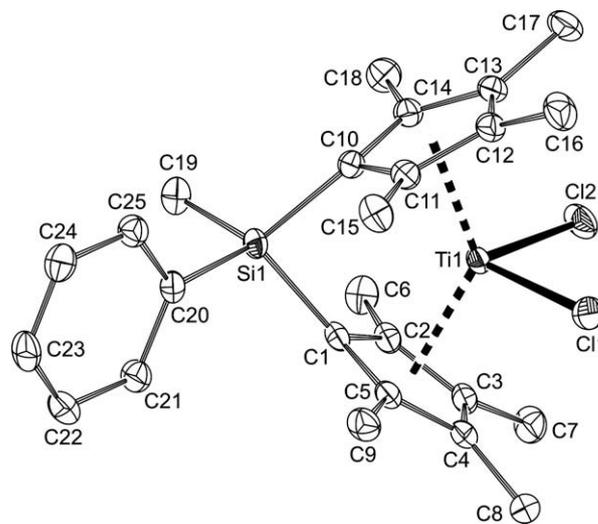


Fig. 2. Thermal ellipsoid plot (50% probability level) of **3**. Hydrogen atoms omitted for clarity.

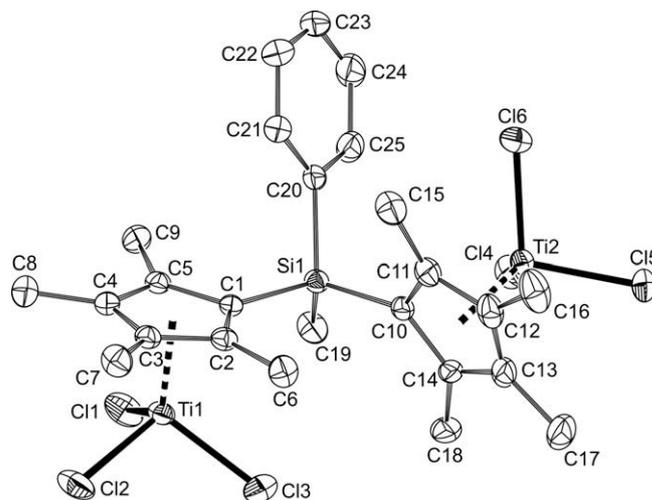


Fig. 3. Thermal ellipsoid plot (50% probability level) of **5**. Hydrogen atoms omitted for clarity.

Table 2
Selected bond lengths [Å] and angles [°] for **3**.

Ti(1)–Cl(1)	2.3191(5)
Ti(1)–Cl(2)	2.3385(5)
Ti(1)–C(1)	2.3660(17)
Ti(1)–C(2)	2.4260(17)
Ti(1)–C(3)	2.5495(18)
Ti(1)–C(4)	2.5422(17)
Ti(1)–C(5)	2.3842(17)
Ti(1)–C(10)	2.3767(17)
Ti(1)–C(11)	2.4178(18)
Ti(1)–C(12)	2.5277(18)
Ti(1)–C(13)	2.5082(18)
Ti(1)–C(14)	2.3869(18)
Si(1)–C(1)	1.8725 (18)
Si(1)–C(10)	1.8759(18)
Si(1)–C(19)	1.8636(19)
Si(1)–C(20)	1.8777(18)
CE(1)–Ti(1)–CE(2)	132.34(3)°
Cl(1)–Ti(1)–Cl(2)	96.89(2)
C(1)–Si(1)–C(10)	92.96(8)
C(19)–Si(1)–C(20)	102.41(8)

Table 3
Selected bond lengths [Å] and angles [°] for **5**.

Ti(1)–Cl(1)	2.2195(8)
Ti(1)–Cl(2)	2.2447(8)
Ti(1)–Cl(3)	2.2435(8)
Ti(1)–C(1)	2.328(2)
Ti(1)–C(2)	2.337(2)
Ti(1)–C(3)	2.375(2)
Ti(1)–C(4)	2.374(2)
Ti(1)–C(5)	2.360(2)
Ti(2)–Cl(4)	2.2202(8)
Ti(2)–Cl(5)	2.2496(8)
Ti(2)–Cl(6)	2.2310(8)
Ti(2)–C(10)	2.346(2)
Ti(2)–C(11)	2.352(2)
Ti(2)–C(12)	2.365(3)
Ti(2)–C(13)	2.373(3)
Ti(2)–C(14)	2.361(3)
Si(1)–C(1)	1.908(3)
Si(1)–C(10)	1.896(3)
Si(1)–C(19)	1.862(3)
Si(1)–C(20)	1.880(3)
Cl(1)–Ti(1)–Cl(2)	103.62(3)
Cl(1)–Ti(1)–Cl(3)	103.07(3)
Cl(2)–Ti(1)–Cl(3)	102.08(3)
C(1)–Si(1)–C(19)	110.56(11)
C(10)–Si(1)–C(20)	110.17(11)

137.45° for $\eta^5\text{-(C}_5\text{Me}_5\text{)}_2\text{TiCl}_2$ [15]. Selected molecular parameters are given in Table 2.

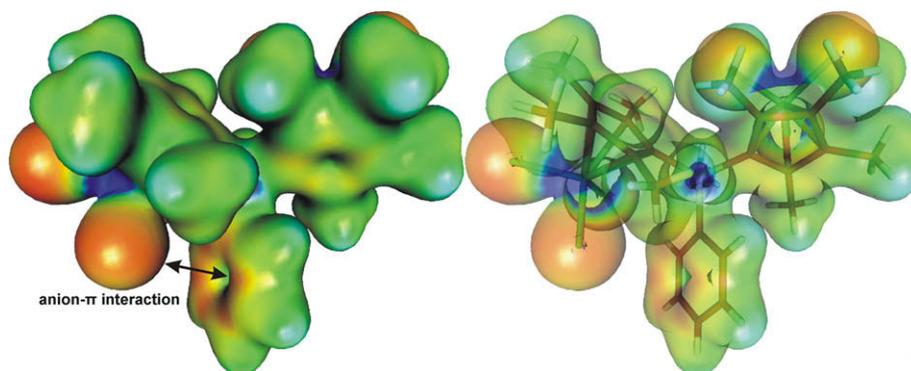


Fig. 4. Isodensity surface (2%) color coded with the electrostatic potential (left) and orientation of the molecule within the isodensity surface (right) color legend of the electrostatic potential: red <0.00, yellow = 0.05, green = 0.10, blue = 0.15, dark blue >0.20. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The dinuclear complex **5** consists of two ($\eta^5\text{-C}_5\text{Me}_4$)TiCl₃ moieties interconnected by a SiMePh bridge. Due to their steric demands, these two ($\eta^5\text{-C}_5\text{Me}_4$)TiCl₃ moieties are mutually rotated (Fig. 3). All molecular parameters (see Table 3) of **5** in solid-state are comparable with those of the previously published molecule [(SiMe₂)($\eta^5\text{-C}_5\text{Me}_4$)₂TiCl₂] [16].

A notable feature of the solid-state packing of **5** is the presence of the anion- π interaction between the phenyl substituent and one chloride ligand (Fig. 4) in solid-state, providing an explanation for the absence of any significant π - π interactions in the same structure. This anion- π interaction is only present in the solid-state – its nonexistence in solution is proved by NMR spectroscopy (*vide supra*) suggestive of an unhindered rotation of both cyclopentadienyl rings around the Si-C_{CP} bonds. Since solid-state anion- π interactions can be either of electrostatic nature or of a weak σ interaction [17–19], we have conducted some DFT studies on the target molecule.

According to these DFT results, the anion- π interaction is purely of electrostatic nature in the structure of **5** (Fig. 4). The Mayer bond orders [20] between the atoms involved were found to be negligible. Natural Bond Analysis [21] results performed on the Kohn–Sham orbitals suggested also the covalent contribution to be negligible, due to the lack of any significant chlorine lone pair delocalization into any phenyl C–C or C–H bonds.

2.3. Catalytic ethene conversion

Complexes **4**, **5** and [$\mu\text{-(SiMe}_2\text{)}\{(\eta^5\text{-C}_5\text{H}_4)\text{TiCl}_3\}_2$] (**6**) [11] were activated by excess of MAO and tested in ethene polymerization at different conditions (Table 4). All studied catalytic systems showed a rather low activity in the range 2–20 kg_{PE} mol_{Ti}⁻¹ with an increasing activity in order **5** < **4** < **6**. The order of activity reflects lower Lewis acidity of Ti centers in **5** compared to **4** and **6** due to a substantial electron-donating character of methyl groups bonded to cyclopentadienyl ring. The observed phenomenon is quite unexpected as about 10 times higher activity in polymerization was found for [($\eta^5\text{-C}_5\text{Me}_5$)TiCl₃]/MAO (215 kg_{PE} mol_{Ti}⁻¹ h⁻¹ bar⁻¹) in comparison to [($\eta^5\text{-C}_5\text{H}_5$)TiCl₃]/MAO (16–23 kg_{PE} mol_{Ti}⁻¹ h⁻¹ bar⁻¹) imputed to higher stability of the former system toward decomposition [5,22]. The activity lower by about a factor of two of **4** compared with **6** could possibly be assigned to the competition between the phenyl ring and the ethylene molecule during the coordination to the active titanium center in **4**.

Volatiles from all experiments were analyzed by GC–MS to detect the presence of low molar weight oligomers (mainly 1-hexene). Nevertheless, 1-hexene (ca 20 mg) was produced only in run 6 where the catalyst derived from **4** was used at a maximum ethylene pressure with the productivity ca 0.2 kg_{1-hexene}

Table 4Activity of **4**–**6**/MAO in ethylene polymerization and characterization of prepared polyethylene samples^a.

Run	Cat.	T_{polym} (°C)	p (bar)	m_{PE} (g)	A^b	$M_w^c \times 10^5$	M_w/M_n (MWD)	T_m^d (°C)	X_c^e
1	5	25	1	0.04	2			135.1	0.58
2	5	50	1	0.04	2			132.9	0.56
3	5	75	1	0.03	1			133.0	0.63
4	4	25	1	0.28	11	21.2	5.6	131.7	0.25
5	4	25	3	0.43	6	16.5	570.5	132.2	0.32
6	4	25	5	0.80	6	21.1	621.8	131.5	0.37
7	4	50	1	0.33	13	4.9	15.7	135.4	0.45
8	4	75	1	0.28	11			134.4	0.66
9	6	25	1	0.59	24			131.9	0.23
10	6	25	5	1.56	13			134.5	0.40

^a Polymerization conditions: $[\text{Ti}] = 5 \times 10^{-4}$ M, $\text{Ti}/\text{Al} = 1/1000$ (m/m), time 1 h, solvent toluene, total volume 50 ml, rpm 600.^b Activity $[\text{kg}_{\text{polymer}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}]$.^c Determined by GPC.^d Determined by DSC.^e Polymer crystallinity.

$\text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}$. The value obtained for the formation of 1-hexene is more close to the value obtained for $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]/\text{MAO}$ ($2 \text{ kg}_{1\text{-hexene}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}$) [23] and for $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_3)\text{TiCl}_3]/\text{MAO}$ ($13 \text{ kg}_{1\text{-hexene}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}$) [4] than to the value of the highly efficient 1-hexene producing catalyst $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3]/\text{MAO}$ ($535 \text{ kg}_{1\text{-hexene}} \text{mol}_{\text{Ti}}^{-1} \text{h}^{-1} \text{bar}^{-1}$) [24]. Therefore we supposed that the role of a pendant phenyl group for ethylene trimerization in **4** is negligible. This observation is in accord with the unfavourable Ti-arene coordination in the SiMe_2 -bridged species generated from $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{TiMe}_3]$ and $[\text{CPh}_3](\text{B}(\text{C}_6\text{F}_5)_4)$ [25].

The determination of microstructure of prepared PE matrices by NMR spectroscopy was hampered by low samples solubility in $\text{C}_2\text{D}_2\text{Cl}_4$ even at 120 °C. Nevertheless, ^1H NMR data indicate that samples were highly linear (single resonance at 1.34 ppm). The linearity of PE samples was further supported by ^{13}C NMR spectra, where only single signal at 30.00 ppm characteristic for methylene unit of the main chain was observed. Melting temperatures determined by DSC (see T_m value in Table 4) of all prepared PE samples are in the range 131.5–135.4 °C, typical for linear HDPE. Polymer samples were also poorly soluble in 1,2,4-trichlorobenzene and lack of solubility even at high temperatures precluded in some cases determination of molecular weights by GPC. Polymers obtained in runs 4–6 had high M_w in range $1.6\text{--}2.1 \times 10^6$ g/mol. At higher reaction temperature (compare run 4 and 7, Table 4) M_w was significantly lowered and molar weight distribution (MWD) increased, reflecting increased extent of transfer reactions. Furthermore, MWD was dramatically broadened with increase of ethylene pressure from 1 to 5 bar to extreme MWD values $MWD = 570$ at 3 bars (run 5) and $MWD = 620$ at 5 bars (run 6). Although MWD of polyethylenes prepared by monocyclopentadienyl titanium/MAO catalysts varies from relatively narrow with $MWD = 2.2$ for $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]/\text{MAO}$ [22], $MWD = 2.3\text{--}2.5$ for $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{OBz})_3]/\text{MAO}$ ($\text{Bz} = \text{benzyl}$) [10], to broad one with MWD ca. 40 for $[(\eta^5\text{-C}_5\text{H}_4(\text{cyclohex-1,1-diyl})\text{Ar})\text{TiCl}_3]/\text{MAO}$ [26], extra-high MWD values similar to those obtained from runs 5 and 6 are unexpected for HDPE polymer prepared by metallocene/MAO system.

Extremely broad MWD could be explained by the presence of more than one type of active species in the polymerization system. In addition to fully alkylated dicationic species of general formula $[\text{X}(\text{Cp}'\text{TiMe}_2)^+{}_2]$ also partly alkylated species $[\text{X}(\text{Cp}'\text{TiMeCl})^+{}_2]$ (where $\text{X} = \text{SiMePh}$ or SiMe_2 ; $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{Me}_5$) and their combination $[\{\text{Cp}'\text{TiMe}_2\}^+\text{X}\{\text{Cp}'\text{TiMeCl}\}^+]$ should be considered. The activity of mononuclear cationic monocyclopentadienyltitanium methylchloride species $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMeCl}]^+$ in polymerization of both ethylene or propylene was proved by Ewart et al. [7,8]. Likewise, other active species (e.g. monocationic dinuclear species) arising from a mutual interaction of both metals forced to a close

proximity by a short silicone bridge cannot be ruled out. Although Ti(IV) species are more beneficial for ethylene polymerization [10], the paramagnetic Ti(III) species formed (*vide infra*) could also contribute to the activity of studied systems. DFT calculations published recently showed that the polymerization of ethylene on $\text{CpTi}(\text{III})\text{Et}^+\text{A}^-$ (A^- denote counteranions $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ or $\text{B}(\text{C}_6\text{F}_5)_4^-$) is thermodynamically allowed although with a low polymerization degree only [27].

2.4. EPR study of the **4**/MAO system

Generally speaking, treating cyclopentadienyltitanium(IV) complexes with various organoaluminium compounds leads to the formation of paramagnetic species [28]. The formation of Ti(III) species from **4** after adding MAO as potential active species was therefore checked by EPR spectroscopy. The EPR spectrum of **4**/100 eq. MAO in toluene showed 3 singlet signals (Fig. 5) indicating the formation of paramagnetic species with g values $g = 1.9958$ ($\Delta H = 0.318$ mT), $g = 1.9871$ ($\Delta H = 0.79$ mT) and $g = 1.9741$ ($\Delta H = 1.381$ mT). The last value is close to the one characteristic for species of general formula $\text{CpTi}(\mu\text{-Cl}(\text{or Me}))_4\text{Al}_2(\text{Cl}(\text{or Me}))_4$ arising from the reduction of Ti(IV) by free AlMe_3 (see Section 4) known to be contained in MAO [29]. Surprisingly, the formation of Ti(III) hydrido species reported for the $\text{CpTiCl}_3/\text{MAO}$ mixture yielding doublets in the EPR spectrum at $g = 1.995$ and $g = 1.989$ [30] was not observed for the case of the **4**/MAO mixture.

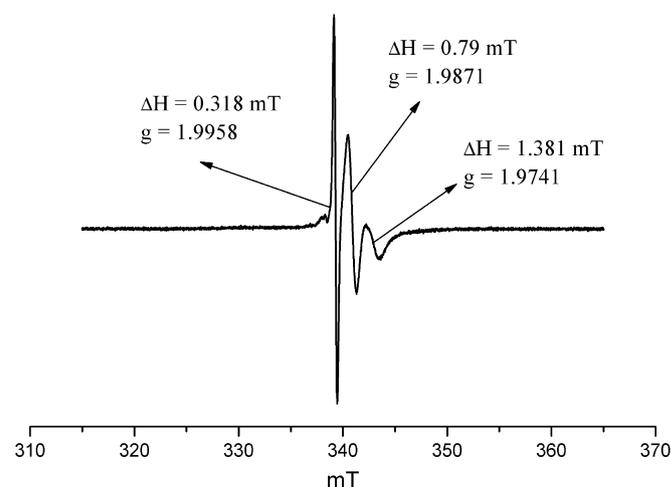


Fig. 5. EPR spectrum of the system **4**/MAO ($[\text{Ti}] = 4.49$ mM; $\text{Ti}/\text{Al} = 1/100$ (m/m)) in toluene.

3. Conclusions

The dinuclear complexes **4** and **5** were readily prepared from the corresponding *ansa*-titanocene dichlorides **1** and **3** via synproportionation with TiCl_4 . Complexes **4** and **5** activated by excess MAO exhibited a moderate to low activity in the polymerization of ethylene producing high molecular weight linear polyethylene with a broad MWD.

4. Experimental

All operations with air and moisture sensitive compounds were performed using standard Schlenk techniques under atmosphere of argon. THF, diethylether, hexane, and toluene were dried by distillation from sodium/benzophenone and stored over sodium mirror. Dichloromethane was dried by distillation from CaH_2 and stored over molecular sieves (4 Å).

n-BuLi (*n*-butyllithium) (1.6 M solution in hexane), dichloromethylphenylsilane and cyclopentadienylsodium (2 M in THF) were obtained from Sigma Aldrich and used as received. Methylaluminoxane (10 wt% in toluene) was obtained from Sigma Aldrich and the amount of free AlMe_3 (15%) was estimated on the basis of ^1H NMR measurements [31]. TiCl_4 was distilled from copper turnings prior to use. HMPA (hexamethylphosphoramide) was distilled from sodium and stored over 4A molecular sieves (WARNING! HMPA is a carcinogenic reagent). Tetramethylcyclopentadiene (a mixture of isomers) [32], $\text{TiCl}_3(\text{THF})_3$ [33] and $[\mu\text{-}(\text{SiMe}_2)\{\eta^5\text{-C}_5\text{H}_4\}\text{TiCl}_2]_2$ (**6**) [11] were prepared by published procedures. ^1H (300.0 MHz), ^{13}C (75.4 MHz) ^{29}Si (59.6 MHz) NMR spectra of ligands and organometallic species were recorded on a Varian Mercury 300 spectrometer in CDCl_3 solutions at 293 K. Chemical shifts (δ /ppm) are given relative tetramethylsilane as internal standard. ^1H and ^{13}C NMR spectra of PE samples were measured in CD_2Cl_4 at 105 °C on a Bruker Avance 500 MHz spectrometer and are referenced to residual solvent signal (5.99 ppm) for ^1H and to the signal of main PE chain at 30.00 ppm for ^{13}C . EPR spectra were measured on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-3 unit (Magnetech, Berlin, Germany) in the X-band. *g* values were determined using an Mn^{2+} standard at $g = 1.9860$ ($M_I = -1/2$ line). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. GC-MS measurements were performed on a Thermo Focus DSQ using the capillary column Thermo TR-5MS (15 m \times 0.25 mm ID \times 0.25 mm). IR spectra of air sensitive samples were taken in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{-1} . KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. Melting points were measured on a Koffler block (air sensitive compounds were measured in sealed capillaries) and were uncorrected. SEC data were measured on PL GPC 220 high-temperature chromatograph equipped with PL-220DRI and VISKOTEL 220R detectors. Separation was performed at 160 °C on set of three PL gel columns (10 μm MIXED-B, 300 \times 7.5 mm) in 1,2,4-trichlorobenzene stabilized by 0.025% of Santonox R at flow rate 1 ml min^{-1} . Polyethylene molecular weights and distributions were evaluated on the basis of PS calibration (23 standards 3 k–6 M) and corrected using universal calibration method (Viscotek TriSEC software). All the results are averages of two measurements. Thermal behaviour of PE was investigated by DSC (TA Instruments Q100) with both heating and cooling rate 10 °C min^{-1} under nitrogen (50 $\text{cm}^3 \text{min}^{-1}$). Melting temperatures and heats of fusion were obtained from second heating run. Degree of crystallinity (X_c) was calculated based on the value of heat of fusion 292 J g^{-1} for a 100% crystalline PE.

DFT studies have been carried out at the fermi cluster at the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, using Gaussian 03, Revision E.01 [34]. The calculations used the Becke exchange [35] and Perdew/Wang 91 correlational [36] functionals. The input geometry was the one obtained from X-ray single crystal diffraction. Calculations were done as single-point using the 6-31+G(d,p) basis set [37] employed for all atoms. After verifying the internal stability of the final wavefunction [38], Mayer Bond Order [20] studies have been carried out. Natural Bonding Analysis [21] was done by the NBO 5.0 program [39]. Visualization and examination of molecular orbitals and the distribution of the electrostatic potential was accomplished by Molden [40].

4.1. Preparation of $[\{\text{SiMePh}\}(\eta^5\text{-C}_5\text{H}_4)_2]\text{TiCl}_2$ (**1**)

Neat Cl_2SiMePh (5.9 g, 31 mmol) was added in several portions to a cold (−80 °C) solution of cyclopentadienylsodium (31 ml, 2 M, 62 mmol) in THF (80 ml). The reaction mixture was warmed to room temperature and then stirred for additional 5 h. The resulting red-brown mixture was cooled to 0 °C, and *n*-BuLi (24.8 ml, 2.5 M, 62 mmol) was dropped. The mixture was stirred for 2 h at room temperature and then transferred to a suspension of $\text{TiCl}_4(\text{THF})_2$ (prepared *in situ* by reaction of TiCl_4 (3.5 ml, 31 mmol) with 5 ml of THF) in 80 ml of toluene. The mixture was stirred for 40 h, evaporated almost to dryness and the crude product was precipitated by hexane (200 ml), washed several times with hexane and dried on air. The light brown solid was washed with boiling hexane for 8 h in Soxhlet extractor and then extracted with boiling dichloromethane for 30 h. The product crystallized from dichloromethane solution at −28 °C. The resulting red-brown microcrystals were separated, washed with dichloromethane/hexane (1/1, v/v) (20 ml), hexane (3 \times 30 ml) and dried on air. Yield 1.8 g (16%).

4.1.1. *M.p.* 230 °C (decomp.)

^1H NMR (300 MHz, CDCl_3): 0.88 (s, 3H, SiMe); 5.96–6.00 (m, 2H, C(5)H, C_5H_4); 6.07–6.11 (m, 2H, C(2)H, C_5H_4); 7.20–7.24 (m, 2H, C(3)H, C_5H_4); 7.25–7.28 (m, 2H, C(4)H, C_5H_4); 7.50–7.63 (m, 3H, CH_{meta} and CH_{para} , SiPh); 7.85–7.90 (m, 2H, CH_{ortho} , SiPh). ^{13}C $\{^1\text{H}\}(\text{CDCl}_3)$: −5.20 (SiMe); 105.17 (C(1), C_5H_4); 118.41, 121.29, 133.48, 137.88 (CH, C_5H_4); 129.03, 131.54, 134.63 (CH, Ph) 130.42 (C_{ipso} , Ph). ^{29}Si $\{^1\text{H}\}(\text{CDCl}_3)$: −17.98 (SiMePh). EI-MS, *m/z* (relative abundance): 369 (23), 368 (72), 367 (36), 366 (M^+ , 100), 365 (13), 364 (11), 333 (13), 332 (15), 331 ($[\text{M}-\text{Cl}]^+$, 29), 330 ($[\text{M}-\text{HCl}]^+$, 19), 329 (7), 295 (7), 294 ($[\text{M}-2\text{HCl}]^+$, 18), 178 (6), 177 (12), 176 ($[\text{C}_{10}\text{H}_8\text{Ti}]^+$, 58), 175 (8), 174 (9), 157 (13), 156 (6), 155 (39), 105 (18), 83 (13), 69 (14), 53 (13), 49 (13), 43 (9). IR (KBr; cm^{-1}): 3131 (m); 3101 (s); 3090 (s); 3071 (vs); 3016 (m); 2896 (m); 1663 (vw); 1587 (w); 1483 (vw); 1453 (vw); 1428 (m); 1401 (s); 1372 (w); 1363 (vw); 1323 (w); 1263 (m); 1207 (vw); 1171 (s); 1115 (vs); 1078 (w); 1060 (m); 1042 (m); 998 (vw); 900 (vw); 852 (w); 835 (vs); 802 (vs); 743 (vs); 702 (s); 688 (w); 667 (m); 623 (w); 492 (vs); 436 (m); 405 (m). EA Anal. Calc. for $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{SiTi}$ (367.18): C 55.61, H 4.39. Found C 55.47, H 4.35%.

4.2. Preparation of (methyl)(phenyl)bis(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane (**2**)

A hexane solution of *n*-BuLi (1.6 M, 75 ml, 120 mmol) was slowly dropped into a solution of tetramethylcyclopentadiene (14.5 g, 119 mmol) in THF (500 ml). The resulting white suspension was stirred for 15 h, Cl_2SiMePh (10.5 g, 55 mmol) was added in one portion, and the mixture was refluxed for 16 h. Then, the mixture was cooled to −78 °C and HMPA (9.9 g, 55 mmol) was drop-wise added. The mixture was heated to 60 °C and stirred

for 4 h, causing the transformation of suspension to a yellowish solution. The solution was cooled to room temperature and all volatiles were removed in vacuum. The oily residue was shaken with 150 ml of water and the product was extracted in diethyl ether (2 × 200 ml). Collected organic phases were washed by brine (2 × 50 ml), water (50 ml) and dried over Na₂SO₄. Diethyl ether was removed on a rotary evaporator and a yellow oily residue was heated to 60 °C in vacuum (0.1 mm Hg) for 10 h to remove unreacted tetramethylcyclopentadiene. The resulting yellow oily liquid has a satisfactory purity (>92% by GC–MS). Yield 17.1 g (85%). The storage of the product in a refrigerator at 5 °C led to its solidification. The analytically pure sample was obtained by recrystallization from hexane as a white solid.

4.2.1. M.p. 74 °C

¹H NMR (300 MHz, CDCl₃): 0.01 (s, 3H, SiMe); 1.69, 1.76, 1.88, 2.13 (4 × s, 4 × 6H, C₅Me₄H); 3.56 (br s, 2H, CH, C₅Me₄H); 7.16–7.48 (m, 5H, SiPh). ¹³C {¹H}(CDCl₃): –9.61 (SiMe); 11.11, 11.20, 15.14, 15.25 (C₅Me₄H); 52.41 (CH, C₅Me₄H); 126.10, 128.77, 133.90 (CH, SiPh); 132.55, 132.83, 137.20, 137.26 (C_q, C₅Me₄H); 133.60 (C_{ipso}, SiPh). ²⁹Si {¹H}(CDCl₃): –2.75 (SiMePh). GC–MS, *m/z* (relative abundance): 362 (M⁺; 4), 243 (6), 242 (26), 241 ([M–C₅Me₄H]⁺; 100), 240 (10), 163 (12), 135 (27), 122 (7), 121 ([C₅Me₄H]⁺; 52), 119 (10), 105 ([PhSi]⁺, 13), 91 (5), 59 (10). EA Anal. Calc. for C₂₅H₃₄Si (362.63): C 82.80, H 9.45. Found C 83.07, H 9.57%.

4.3. Preparation of [(SiMePh)(η⁵-C₅Me₄)₂TiCl₂] (3)

To a solution of the ligand **2** (4.03 g, 11.1 mmol) in THF (300 ml) previously precooled to –50 °C was dropped *n*-BuLi (13.9 ml, 1.6 M, 22.2 mmol). The obtained orange solution was allowed to warm to room temperature, stirred for 4 h and then TiCl₃(THF)₃ (4.12 g, 11.1 mmol) was gradually added. The resulting brown mixture was refluxed for 33 h. The volume of the solution was reduced to ca. 100 ml and then 200 ml of aqueous HCl was added at room temperature. The separated waxy solid was washed by methanol and crystallized from chloroform solution over layered by methanol. The formed intense red crystals (suitable for X-ray analysis) were isolated, washed with mixture chloroform/methanol (1:5, v/v), methanol and dried on air. The second crop of crystals was obtained from mother solution. Total yield 0.85 g (16%).

4.3.1. M.p. 260 °C

¹H NMR (300 MHz, CDCl₃): 1.03 (s, 3H, SiMe); 1.53 (s, 6H, C(5)Me, C₅Me₄); 1.92 (s, 6H, C(2)Me, C₅Me₄); 2.07 (s, 6H, C(4)Me, C₅Me₄); 2.17 (s, 6H, C(3)Me, C₅Me₄); 7.43–7.51 (m, 3H, CH_{meta} and CH_{para}, SiPh); 7.88–7.94 (m, 2H, CH_{ortho}, SiPh). ¹³C {¹H}(CDCl₃): 5.06 (SiMe); 13.73, 14.01, 16.26, 17.50 (C₅Me₄); 91.68 (C(1), C₅Me₄); 128.42, 130.14, 134.25 (CH, Ph); 129.36 (C(5)); 131.44 (C(2)); 137.85 (C_{ipso}, Ph); 142.86 (C(3)); 144.94 (C(4)). ²⁹Si {¹H}(CDCl₃): –16.37 (SiMePh). EI–MS, *m/z* (relative abundance): 481 (15), 480 (40), 479 (23), 478 (M⁺, 49), 445 (15), 444 (32), 443 ([M–Cl]⁺, 34), 442 ([M–HCl]⁺, 55), 441 (10), 428 (18), 428 (16), 427 ([M–HCl–Me]⁺, 35), 358 ([M–C₅Me₄]⁺, 10), 344 (13), 321 (16), 240 (18), 239 (68), 223 (19), 209 (18), 179 (17), 161 (18), 159 (26), 145 (27), 121 (58), 120 (37), 119 (42), 107 (15), 106 (13), 105 (100), 91 (43), 79 (17), 77 (23), 59 (29), 43 (31). IR (KBr; cm^{–1}): 3065 (w); 3054 (vw); 3014 (w); 3004 (vw); 2951 (w); 2909 (m); 2869 (vw); 1558 (vw); 1541 (vw); 1507 (w); 1489 (vw); 1458 (w); 1428 (m); 1405 (w); 1378 (s); 1353 (w); 1327 (m); 1258 (w); 1134 (w); 1107 (s); 1019 (w); 829 (w); 801 (s); 785 (m); 765 (w); 743 (w); 708 (vs); 684 (m); 669 (w); 655 (m); 560 (vw); 495 (m); 479 (w); 457 (vs); 419 (vw). EA Anal. Calc. for C₂₅H₃₂Cl₂SiTi (479.40): C 62.64, H 6.73. Found C 62.55, H 6.70%.

4.4. Preparation of [-(SiMePh){(η⁵-C₅H₄)TiCl₃]₂] (4)

An excess of TiCl₄ (1.00 ml, 9.00 mmol) was added to a suspension of **1** (0.88 g, 2.39 mmol) in toluene (30 ml). The mixture was heated to reflux for 17 h, causing gradual color change from red to yellow-brown. All volatiles were removed in vacuum, the residue was washed with hexane (10 ml), and repeatedly extracted with toluene. Concentration and cooling of the toluene solution gave **4** as yellow crystals. Yield 0.95 g (71%).

4.4.1. M.p. 150 °C

¹H NMR (300 MHz, C₆D₆): 1.00 (s, 3H, SiMe); 6.18–6.22, 6.24–6.30 (2 × m, 2 × 2H, C(3)H and C(4)H, C₅H₄); 6.48–6.53, 6.64–6.70 (2 × m, 2 × 2H, C(2)H and C(5)H, C₅H₄); 7.11–7.23 (m, 3H, CH_{meta} and CH_{para}, SiPh); 7.30–7.36 (m, 2H, CH_{ortho}, SiPh). ¹³C {¹H}(C₆D₆): –3.67 (SiMe); 126.72, 126.74, 130.06, 130.33 (CH, C₅H₄); 128.53, 131.08, 135.49 (CH, SiPh); 131.32 (C_{ipso}, SiPh); 134.33 (C_{ipso}, C₅H₄). ²⁹Si {¹H}(C₆D₆): –18.11 (SiMePh). EI–MS, *m/z* (relative abundance): 556 (M⁺, not observed), 543 (8), 541 (M–Me]⁺, 9), 504 (15), 502 (25), 500 (20), 486 ([M–2Cl]⁺, 16), 425 (7), 423 (6), 368 (71), 367 (36), 366 ([M–TiCl₄]⁺, 92), 365 (14), 333 (46), 332 (42), 331 ([M–TiCl₄–Cl]⁺, 100), 330 (28), 297 (25), 296 ([M–TiCl₄–2Cl]⁺, 85), 295 (20), 294 (33), 252 (18), 250 (11), 177 (14), 176 ([C₁₀H₈Ti]⁺, 62), 175 (12), 174 (15), 157 (27), 156 (15), 155 (71), 105 ([C₆H₅Si]⁺, 54), 85 (16), 83 ([TiCl]⁺, 40), 53 (24). IR (KBr; cm^{–1}): 3103 (m), 3068 (w), 3037 (w), 2963 (w), 2914 (w), 2843 (vw), 1589 (vw), 1484 (vw), 1429 (w), 1409 (m), 1369 (vw), 1312 (vw), 1259 (w), 1180 (w), 1112 (m), 1069 (w), 1048 (s), 919 (vw), 889 (vw), 842 (s), 796 (vs), 738 (m), 700 (w), 686 (vw), 633 (vw), 502 (w), 475 (m), 460 (m), 446 (w), 414 (vs). EA Anal. Calc. for C₁₇H₁₆Cl₆SiTi₂ (566.88): C 36.67, H 2.90. Found C 36.49, H 2.85%.

4.5. Preparation of [-(SiMePh){(η⁵-C₅Me₄)TiCl₃]₂] (5)

An excess of TiCl₄ (1.0 ml, 9.0 mmol) was added to solid titanocene dichloride **3** (0.12 g, 0.25 mmol). The mixture was heated to 135 °C with stirring for 21 h. After cooling to room temperature, all volatiles were removed in vacuum and the product was extracted with 10 ml of CH₂Cl₂. The volume of orange solution was concentrated to ca. 4 ml, and the solution was layered with hexane (ca. 10 ml). After four days the grey-yellow precipitate was formed, and was filtered off. The mother liquor was again concentrated and stored in a freezer (–28 °C) for several days. Formed orange microcrystals were isolated, washed with hexane (2 × 4 ml) and dried in vacuum. The combined hexane washings gave after several days a second crop of crystals. Overall yield 0.14 g (84%).

4.5.1. M.p. 210 °C

¹H NMR (300 MHz, C₆D₆): 1.46 (s, 3H, SiMe); 2.13 (s, 3H, C₅Me₄); 2.31 (s, 6H, C₅Me₄); 2.41 (s, 3H, C₅Me₄); 7.29–7.36 (m, 2H, SiPh); 7.38–7.45 (m, 3H, SiPh). ¹³C {¹H}(C₆D₆): 2.18 (SiMe); 14.49, 14.77, 18.01, 18.41 (C₅Me₄); 128.08, 130.55 (CH, Ph); 133.58 (C_{ipso}, C₅Me₄); 136.45 (CH, Ph); 136.91 (C_{ipso}, Ph); 143.00, 143.30, 144.05, 144.44 (C₅Me₄). ²⁹Si {¹H}(C₆D₆): –19.29 (SiMePh). EI–MS, *m/z* (relative abundance): 670 (20), 669 (13), 668 (M⁺, 22), 666 (12), 480 (43), 479 (34), 478 ([M–TiCl₄]⁺, 60), 477 (21), 464 (28), 462 (35), 444 (23), 443 ([M–TiCl₄–Cl]⁺, 30), 442 ([M–TiCl₄–HCl]⁺, 47), 441 (9), 428 (16), 427 ([M–2HCl–Me]⁺, 25), 360 (21), 358 (34), 240 (30), 239 (100), 223 (30), 209 (25), 169 (42), 159 (30), 145 (33), 121 (65), 120 (19), 59 (42). IR (KBr): 3063 (vw), 3042 (vw), 2971 (w), 2920 (m), 2843 (w), 1588 (vw), 1471 (w), 1428 (m), 1383 (m), 1324 (m), 1255 (w), 1127 (w), 1103 (w), 1022 (w), 999 (vw), 827 (w), 792 (s), 739 (m), 717 (w), 702 (w), 681 (vw), 559 (vw), 490 (m), 471 (s), 406 (vs). EA Anal. Calc. for C₂₅H₃₂Cl₆SiTi₂ (669.09): C 44.88, H 4.82. Found C 44.83, H 4.81%.

Table 5
Crystal data and structure refinement for **1**, **3** and **5**.

Formula	1 C ₁₇ H ₁₆ Cl ₂ SiTi	3 C ₂₅ H ₃₂ Cl ₂ SiTi	5 C ₂₅ H ₃₂ Cl ₆ SiTi ₂
Rel. Mol. Weight	367.19	479.40	669.10
Temperature (K)	200(1)	150(1)	150(1)
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>Pnma</i> (No. 62)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> ₂ / <i>c</i> (No. 14)
<i>a</i> (Å)	26.0143(13)	8.5266(2)	16.0334(5)
<i>b</i> (Å)	8.1182(4)	9.3937(2)	12.3749(4)
<i>c</i> (Å)	7.4846(3)	15.2355(4)	17.8280(4)
α (°)	90	99.1190(14)	90
β (°)	90	105.2732(15)	120.1791(18)
γ (°)	90	93.4474(16)	90
<i>V</i> (Å ³)	1580.67(13)	1155.66(5)	3057.83(15)
<i>Z</i>	4	2	4
<i>D</i> (g cm ⁻³)	1.543	1.378	1.453
μ (mm ⁻¹)	0.944	0.663	1.100
<i>F</i> (0 0 0)	752	504	1368
Crystal size (mm ³)	0.45 × 0.18 × 0.03	0.60 × 0.30 × 0.25	0.68 × 0.33 × 0.12
θ_{\min} ; θ_{\max} (°)	2.83; 27.50	1.41; 27.57	1.47; 27.49
<i>h</i> range	–33/33	–11/11	–20/20
<i>k</i> range	–10/10	–12/12	–16/12
<i>l</i> range	–9/9	–19/19	–23/23
Reflections collected/unique	6697/1896	18749/5284	21076/6995
Data/restraints/parameters	1896/2/117	5284/0/271	6995/0/316
Goodness-of-fit <i>F</i>	1.145	1.021	1.036
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>)) (%)	4.85	3.84	3.95
<i>wR</i> ₂ on all data (%)	12.00	10.15	9.52
$\Delta\rho$ (e Å ⁻³)	1.190; –0.51	0.358; –0.605	0.547; –0.353

4.6. Catalytic reactions of dinuclear complexes with ethene

The catalytic transformation of ethene was performed in a semi-bath mode (the ethene pressure was kept constant during process) in a 250 ml Büchi glass double jacketed autoclave equipped with a magnetic stirrer. The hot autoclave was evacuated and filled with argon three times, then toluene, 0.5 g of decane (as an internal standard) and the solution of methylaluminoxane (10 wt% in toluene; Ti/Al = 1/1000 (m/m)) were consequently injected. The autoclave was thermostated to desired temperature and the temperature was maintained by the external Pt100 sensor connected to Julabo F31-C bath.

The argon atmosphere was replaced with ethene by cyclic pressuring and venting. The polymerization was started by injecting of a desired amount of stock catalyst solution (final volume of polymerization solution was 50 ml and [Ti] = 5 × 10⁻⁴ M for all experiments), followed by pressuring autoclave to the desired pressure. After 1 h, the autoclave was vented, and a sample (ca 2 ml) was taken from a clear solution to analyze soluble components by GC-MS. The residual mixture in autoclave was quenched with 10% HCl in ethanol (80 ml). A precipitated polymer was stirred in acidified ethanol for 1 h, filtered, washed with ethanol, acetone and dried in vacuum to constant weight.

4.7. Reaction of **4** with MAO

A Schlenk flask directly connected to an EPR tube was filled with toluene solution of methylaluminoxane (10 wt% in toluene; 1.7 ml, 2.6 mmol) and a stock solution of **4** in toluene (4.49 mM, 2.8 ml, 13 μmol; Ti/Al = 1/100 (m/m)) was added. The resulting brown-violet mixture was transferred into the EPR tube and measured in EPR facility.

4.8. X-ray single crystal diffraction

Diffraction data of suitable single crystals of **1**, **3** and **5** were obtained on a Nonius Kappa CCD diffractometer. The phase problem

was solved by SIR-97 [41] and the structures were refined by the least-squares method using the SHELXL-97 [42] program. All heavy atoms were refined anisotropically; hydrogen atoms were put into their theoretical positions and refined isotropically.

Crystal data and structure refinement details for **1**, **3** and **5** are given in Table 5.

Acknowledgements

The financial support from the Grant Agency of the Academy of Sciences of the Czech Republic (project KJB400400602), Ministry of Industry and Trade of the Czech Republic (project No. FT-TA3/078) and Ministry of Education, Youth and Sports (research programmes MSM6046137302 and MSM0021620857) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 751822, 751823 and 751824 contain the supplementary crystallographic data for compounds **1**, **3** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.037.

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