SYNTHESIS AND CRYSTAL STRUCTURES OF DINUCLEAR TRICHLORO(TETRAMETHYLCYCLOPENTADIENYL)TITANIUM COMPLEXES

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Dinuclear half-sandwich complexes $[\{TiCl_3(\eta^5\text{-}C_5Me_4)\}_2SiMe_2]$ (**2**) and $[\{TiCl_3(\eta^5\text{-}C_5Me_4SiMe_2CH_2)\}_2]$ (**4**) were prepared by synproportionation of *ansa*-titanocene dichlorides $[TiCl_2\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}]$ (**1**) and $[TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2CH_2)_2]$ (**3**), respectively, with $TiCl_4$. Compound **3** was synthesized from 1,2-bis(chlorodimethylsilyl)ethane, 1,2,3,4-tetramethylcyclopentadienyllithium, and $[TiCl_3(thf)_3]$ by a common procedure. Crystal structures of **2**, **3**, and **4** were determined by X-ray diffraction analysis.

Keywords: Titanium; Dinuclear complexes; Half-sandwich titanocene; Silicon bridge; *ansa*-Titanocene; Crystal structure; Metallocenes; X-ray diffraction.

Catalytic properties of single-site metallocene polymerization catalysts are modified, in addition to other means[1], by coupling two equivalent or different metallocenes into one dinuclear complex. Dinuclear early transition metal (Ti, Zr, Hf) precursors of the catalytic species can be classified according to the nature of the mononuclear complexes and the linking mode into three types. Metallocene dichlorides and half-sandwich complexes which are linked through their ancillary ligands (η^5-cyclopentadienyl (Cp), η^5-indenyl (Ind) or η^5-fluorenyl (Flu)) constitute type **A** and *ansa*-metallocene complexes linked through their bridging element (largely the SiMe group) represent type **B**. The type **C** of dinuclear catalytic precursors

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are constrained-geometry catalysts (CGC) containing links between the methylsilanediyl groups (**Ca**) or between the ancillary ligands (**Cb**) (Chart 1). The known homo- and heteronuclear early transition metal complexes of type **A** are listed in Table I. Some of them were used in combination with methylalumoxane (MAO) as the catalysts for polymerization of ethene[4,7,9,11,13,14], propene[4,10], styrene[8] or copolymerization of ethene/hex-1-ene[12]. Several Ti or Zr complexes with doubly linked cyclopentadienyl ligands were also synthesized[5,15,16] and used for polymerization of ethene[16]. The **B**-type *ansa*-zirconocene complexes had the silanediyl bridging atoms linked through methylene chains[17–19] or biphenyl-4,4′-diyl group[20], all of them used for polymerization of ethene. The dinuclear **C**-type (η^5-indenyl)titanium complexes were linked by $(CH_2)_n$ (n = 6, 9 or 12) chains in positions 3 of indenyls; they were used for polymerization of ethene[21]. Marks' group synthesized analogous $(CH_2)_2$-linked (η^5-indenyl)-dimethylmetal complexes containing two titanium[22], two zirconium[23] or titanium and zirconium centers[24] which, after activation with modified $Ph_3C^+[B(C_6F_5)_4]^-$ complexes were used to polymerize ethene and to co-

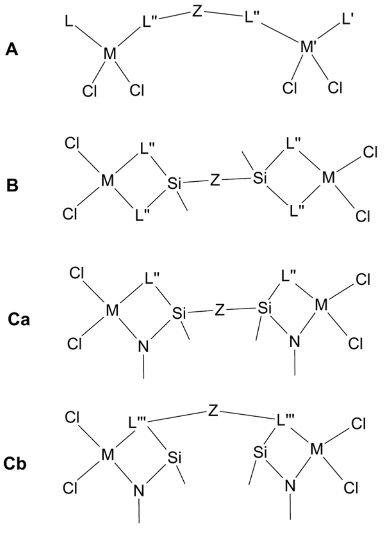


CHART 1
Main types of dinuclear early transition metal complexes (M,M′ = Ti, Zr, Hf; Z = CR_2, $SiMe_2$, C- or Si-containing chains; L,L′ = η^5-cyclopentadienyl (Cp), η^5-indenyl (Ind), η^5-fluorenyl (Flu), or Cl; L″ = η^5-cyclopentadienyl-η^1-yl, C_5H_4 (Cp′), η^5-indenyl-η^1-yl, C_9H_6 (Ind′); L‴ = η^5-indenyl-η^1-diyl, C_9H_5

polymerize it with α-olefins. Combinations of **B**- and **C**-type complexes were also obtained using hexamethylene chain to bind the bridging silicon atom in *ansa*-zirconocene and the silicon atom or 2-indenyl carbon atom in CGC indenylzirconocene dichlorides[25]. No general conclusion can be drawn from comparison of catalytic properties of dinuclear with respect to mononuclear complexes, however, in most cases at least some catalytic properties were changed. Very often the length of the linking chain was a very important factor influencing the catalyst performance[13,14,17–19,21,25]. In

TABLE I
A survey of **A**-type complexes (see Chart 1)

Complex	Cl_2ML	L″	Z	L″	$Cl_2M'L'$	Ref.
1	Cl_2TiCp	Cp′	$SiMe_2$	Cp′	Cl_2TiCp	3
2	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_2ZrCp	4
3	Cl_2HfCp	Cp′	$SiMe_2$	Cp′	Cl_2HfCp	4
4	Cl_2ZrCp^*	Cp′	$SiMe_2$	Cp′	Cl_2ZrCp^*	2
5	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_2TiCp	4,5
6	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_2HfCp	4
7	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_2TiCp^*	4
8	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_3Ti	4
9	Cl_2ZrCp	Cp′	$SiMe_2$	Ind′	Cl_2ZrCp	4
10	Cl_3Ti	Cp′	$SiMe_2$	Cp′	Cl_3Ti	6
11	Cl_2ZrCp	Cp′	$SiMe_2$	Cp′	Cl_2TiCpR^a	7
12	Cl_2ZrCp	Cp′	$SiMe_2CH_2CH_2SiMe_2$	Cp′	Cl_2ZrCp	4
13	Cl_3Ti	Ind′	CH_2CH_2	Ind′	Cl_3Ti	8
14	Cl_2ZrCp	Ind′	$C(CH_2)_5$	Cp′	Cl_2ZrCp	9
15	Cl_2HfCp	Ind′	$C(CH_2)_5$	Cp′	Cl_2ZrCp	9
16	Cl_2ZrCp	Cp′	$p\text{-}C_6H_4$	Cp′	Cl_2ZrCp	10
17	Cl_2TiCp^b	C_5H_3Me	$CH_2(p\text{-}C_6H_4)CH_2$	C_5H_3Me	Cl_2TiCp^c	11
18	Cl_2ZrInd	Cp′	$C(CH_2)_5$	Cp′	Cl_2ZrInd	12
19	Cl_2ZrInd	Cp′	$C(CH_2)_n$ $n = 3,5,7,9$	Cp′	Cl_2ZrInd	13
20	Cl_2MCp^c	Cp'^c	$C(CH_2)_n$ $n = 0–10$	Cp'^d	Cl_2MCp^c	14

[a] R = Ph or allyl. [b] Cp is C_5H_4Me. [c] Series of complexes containing combinations of M = Ti, Zr, Hf and combinations of Cp, Ind, Flu, Cp′, Ind′.

the polymerization of styrene to syndiotactic polystyrene, which we have recently studied using highly methyl-substituted cyclopentadienyltitanium trichloride–methylalumoxane systems[26], the dinuclear 1,2-bis(η^5-indenyl-1-yl)trichlorotitanium)ethane (Table I, complex 13)/MAO system displayed a lower activity compared with the $IndTiCl_3$/MAO system[8]. On the other hand, the 1,2-bis(η^5-indenyl-1-yl)dimethyltitanium)ethane CGC complex activated with a borane cocatalyst showed a much higher activity in polymerization of styrene to a atactic polymer than the monomeric indenyl CGC standard[22].

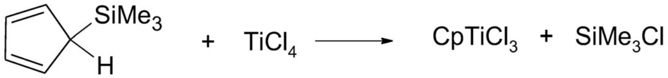
Here we report the synthesis and crystal structures of dinuclear dimethylsilanediyl- and 1,2-bis(dimethylsilanediyl)ethane-linked (tetramethylcyclopentadienyl)titanium trichlorides, where the different link length can influence the catalyst performance in syndiotactic styrene polymerization.

RESULTS AND DISCUSSION

*Synthesis of Dinuclear Half-Sandwich Complexes **2** and **4***

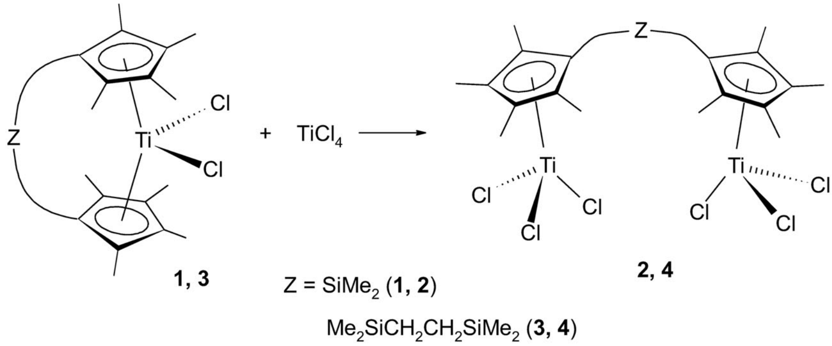
Half-sandwich complexes of the $CpTiCl_3$ type have been usually prepared by the synproportionation reaction between titanocene dichlorides and $TiCl_4$ (Eq. (*1*)) in high yield[27] or by the reaction of a 5-(trimethylsilyl)cyclopentadiene derivative with $TiCl_4$ (Scheme 1) in somewhat lower yields[28].

$$Cp_2TiCl_2 + TiCl_4 \longrightarrow 2\ CpTiCl_3 \qquad (1)$$



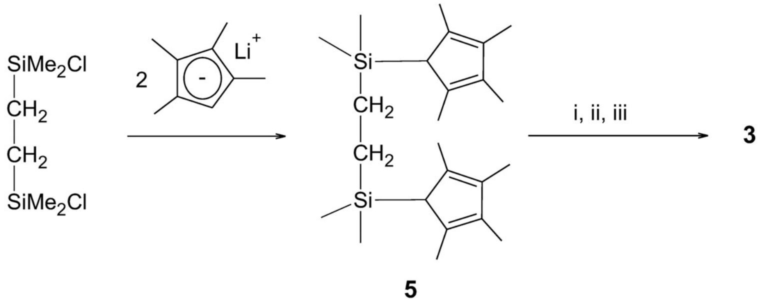
SCHEME 1

The former method was used in the synthesis of dinuclear half-sandwich complexes containing cyclopentadienyl ligands linked by CMe_2 or $SiMe_2$ bridges by Nifantev et al.[6] using *ansa*-titanocene dichlorides in combination with $TiCl_4$. We have used the known *ansa*-titanocene dichloride $[TiCl_2\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}]$ (**1**) (ref.[29]) and new *ansa*-titanocene dichloride bearing $Me_2SiCH_2CH_2SiMe_2$ bridge $[TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2CH_2)_2]$ (**3**) to prepare dinuclear half-sandwich complexes $[\{TiCl_3(\eta^5\text{-}C_5Me_4)\}_2SiMe_2]$ (**2**) and $[\{TiCl_3(\eta^5\text{-}C_5Me_4SiMe_2CH_2)\}_2]$ (**4**), respectively (Scheme 2).



SCHEME 2

Compound **3** was prepared in moderate yield by a sequence of steps depicted in Scheme 3. A dark red crystalline product was fully characterized, including the X-ray diffraction analysis. Extraordinary was its EI-MS spectrum showing a low-abundant molecular ion easily eliminating ethene from the *ansa*-bridge. Elimination of the chlorine atom was much less abundant. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3** corroborate its composition and crystal structure as determined by X-ray diffraction analysis (vide infra).



(i) BuLi (2 equiv.), workup; (ii) [TiCl$_3$(thf)$_3$], THF, reflux 34 h; (iii) PbCl$_2$ (0.5 equiv.), workup

SCHEME 3

Compounds **1** or **3** were heated with a slightly higher than equimolar amount of TiCl$_4$ in *m*-xylene to 150 °C for 5 h in sealed ampules. An excess of TiCl$_4$ was used in order to complete the conversion of *ansa*-titanocene dichloride in a conveniently short time. After removal of the solvent and unreacted TiCl$_4$ in vacuum the residue was extracted with toluene. Bright red crystalline products **2** and **4** were obtained by cooling their saturated solutions, and used for spectroscopic characterization and X-ray diffraction analysis (see below). Upon electron impact the compounds fragmentate in different ways. Compound **2** is successively eliminating one Me group and all chlorine atoms and one Ti atom to give a base peak (*m/z* 331) corresponding to an *ansa*-titanocene without one methyl $[Ti(C_5Me_4)_2SiMe]^+$. On the other hand, compound **4** loses ethene and dissociates to give the $[TiCl_3(C_5Me_4)SiMe_2]^+$ (*m/z* 331) base peak. This then loses either chlorine or the whole $TiCl_3$ group. The ease of elimination of ethene from the bridge can be enhanced by the presence of silicon atoms in “allylic” positions[30]. The ^1H, ^{13}C, and ^{29}Si NMR spectra are in agreement with the composition and structure of **2** and **4**. The ^1H NMR spectra of the cyclopentadienyl moieties display the AA′BB′ spin system. The 1D NOESY experiment showed that the signals of methyls in the proximity of the silicon atoms are shifted downfield (AA′: 2.03 ppm for **2** and 2.25 ppm for **4**) with respect to the other methyls (BB′: 1.82 ppm for **2** and 1.90 ppm for **4**). The difference in the ^{29}Si chemical shifts (–12.26 ppm for **2**, –0.95 ppm for **4**) reflects the number of vicinal cyclopentadienyl ligands. The electronic absorption spectra showed the HOMO-LUMO transfer at 412 nm for **2** and at 432 nm for **4**. Compared with the position of this absorption band in a series of $[TiCl_3(\eta^5\text{-}C_5H_{5-n}Me_n)]$ ($n = 0$–5) compounds spanning the 384–438 nm range[31] the red shift due to the $SiMe_2CH_2$- group in **4** is only slightly smaller than the effect of the fifth Me group in $[TiCl_3(\eta^5\text{-}C_5Me_5)]$. Sharing of the dimethylsilanediyl group by two half-sandwich moieties in **2** results in a distinctly smaller red shift of the transition. Both the compounds decomposed when exposed in solution to sunlight, as previously observed for $[\{TiCl_3(\eta^5\text{-}C_5H_4)_2\}SiMe_2]$ (ref.[6]), especially in dilute hexane solutions.

*Crystal Structures of Compounds **2**–**4***

All the compounds crystallize in monoclinic space group, however, only **4** displays the molecular symmetry due to the centre of inversion in the middle of C–C bond of the bridge. Important geometric parameters of **2**, **3**, and **4** are listed in Table II, and PLATON drawings of the molecules with labeling schemes are given in Figs 1, 2, and 3, respectively. A comparable precision of measurements allows to compare molecular parameters for all the compounds. Negligible differences between Ti–Cg (Cg – centroid of the cyclopentadienyl ring) and Ti–Pl (Pl – least-squares plane of the cyclopentadienyl ring) indicate that the Ti–Cg vectors are virtually perpendicular to ring planes. Shorter Ti–Cg and Ti–Cl distances in compounds **2** and **4** compared with the same parameters in **3** show that the titanium

TABLE II
Selected bond lengths (in Å) and angles (in °) for **2**, **3**, and **4**[a]

Atoms	**2**	**3**	**4**
		Bond length	
Ti(1)–Cg(1)[b]	2.0179(13)	2.1259(15)	2.0155(14)
Ti(1)–Pl(1)[c]	2.073(14)	2.1228(5)	2.0146(5)
Ti(2)–Cg(2)[b]	2.0213(14)	2.1351(15)	–
Ti(2)–Pl(2)[c]	2.0199(5)	2.1335(5)	–
Ti(1)–Cl(1)	2.2290(8)	2.3376(10)	2.2336(12)
Ti(1)–Cl(2)	2.2243(9)	2.3366(9)	2.2391(11)
Ti(1)–Cl(3)	2.2383(8)	–	2.2414(10)
Ti(2)–Cl(4)	2.2252(9)	–	–
Ti(2)–Cl(5)	2.2357(10)	–	–
Ti(2)–Cl(6)	2.2302(9)	–	–
Si(1)–C(1)	1.895(2)	1.892(3)[d]	1.897(3)
Si(1)–C(10)	1.899(2)	1.869(3)[e]	1.863(3)
Si–C_{Me}(av.)	1.860(3)	1.870(4)	1.860(4)
C(10)–C(30)[f]	–	1.539(5)	1.525(6)
		Bond angle	
Cg(1)–Ti–Cg(2)[b]	–	139.51(6)	–
C(1)–Si(1)–C(10)	101.45(9)	115.92(14)	106.80(13)
C(21)–Si(2)–C(30)	–	117.49(14)	–
Si(1)–C(10)–C(30)	–	118.1(2)	114.0(3)
Si(2)–C(30)–C(10)	–	121.1(2)	–
C_{Me}–Si–C_{Me}	106.67(16)	106.77(17)[g]	107.6(2)
Cl–Ti–Cl(min.)	102.76(4)	92.11(5)	102.56(5)
Cl–Ti–Cl(max.)	103.24(5)	–	103.66(5)

[a] Only one set of data for **4** stems from the symmetry of the molecule. Operator for generating equivalent (prime denoted) atoms: –*x*, –*y* + 1, –*z*. [b] Cg(1) denotes centroid of the C(1–5) cyclopentadienyl ring atoms; Cg(2) denotes centroid of the C(21–25) cyclopentadienyl ring. [c] Pl(1) denotes the least-squares plane of the C(1–5) atoms; Pl(2) denotes least-squares plane of the C(21–25) atoms. [d] Average value of Si(1)–C(1) and Si(2)–C(21). [e] Average value of Si(1)–C(10) and Si(2)–C(30). [f] For compound **4**, read C(10)–C(10′). [g] Average value for Si(1) and Si(2) dimethylsilanediyl groups. [h] Dihedral angle between least-squares planes of the cyclopentadienyl rings.

bonding capacity is better exploited in polar than in covalent bonds. This is a general trend found always where a comparison of Cp'_2TiCl_2 and $Cp'TiCl_3$ parameters is available, e.g. in ref.[32]. As far as the bridge parameters are concerned, the silicon–cyclopentadienyl carbon bond length does not differ for **2** and **4**. In the latter compound, this bond (Si(1)–C(1) 1.897(3) Å)) is longer

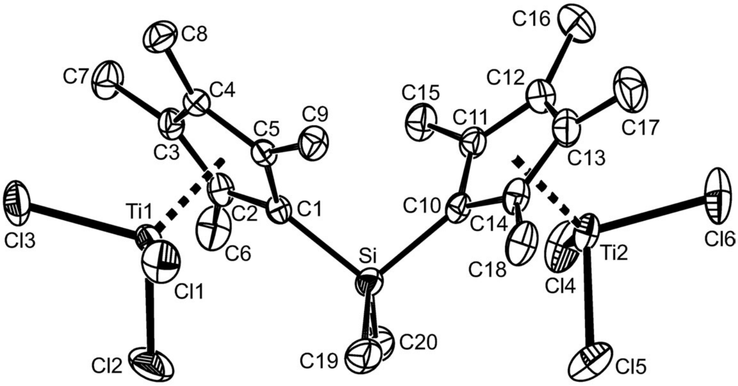


FIG. 1
PLATON drawing of compound **2** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

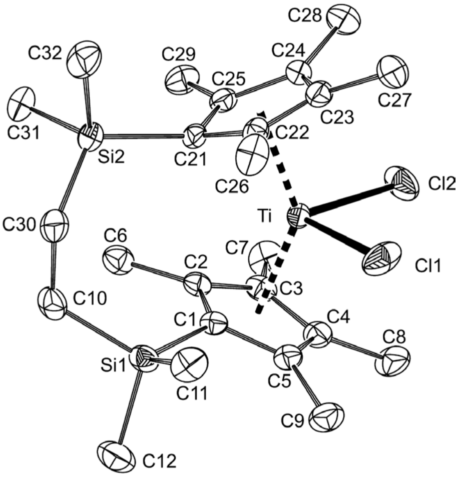


FIG. 2
PLATON drawing of compound **3** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

than the bond to methylene carbon atom (Si(1)–C(10) 1.863(3) Å). Similar values are found for **3**. The angles at the silicon atom to the bridging carbon atoms differ for all the compounds (Table I), being controlled by inter- and intramolecular forces; however, this has no effect on the C_{Me}–Si–C_{Me} angle which is virtually constant. There is also no variation in the structure of $TiCl_3$ fragments as it is common for highly substituted $CpTiCl_3$ complexes[26,32].

It is of interest to compare the structure of **3** with that of compound **1** (ref.[29b]), the precursor of **2**. The bonding distances at the titanium and silicon atoms are virtually equal in both compounds, although compound **1** is strained, with the bridging angle at the silicon atom of 91.8(2)° and the Cg–Ti–Cg angle of 132.2(2)° or angle ϕ = 59.3(2)° (the angle between the least-squares planes of the cyclopentadienyl rings). As a consequence, the Cl–Ti–Cl angle is more open than in **3** (95.9(1)° versus 92.11(5)°). Whereas in **1** the bridging silicon atom is declined from the least-squares planes of the cyclopentadienyl rings closer to the metal, the silicon atoms in **3** are deviated from the Pl(1) and Pl(2) planes of the cyclopentadienyl rings by 0.436(5) Å (Si(1)) and 0.852(5) Å (Si(2)) farther away from the metal. In **3**, the cyclopentadienyl rings are staggered, with C(2), C(21), and C(25) carbon atoms placed in hinge positions (Fig. 2). The steric hindrance between Si(2) and C(6) results in deviation of the latter by as much as 0.417(5) Å from Pl(1). The bridging chain is situated on one side of the Cg(1),Ti,Cg(2) plane. This is not unusual – in *ansa*-titanocene chlorides containing the C_5 or C_8 bridging chain, these chains were placed in side positions with respect to the Cg(1),Ti,Cg(2) plane[33]. In a similar compound, *ansa*-

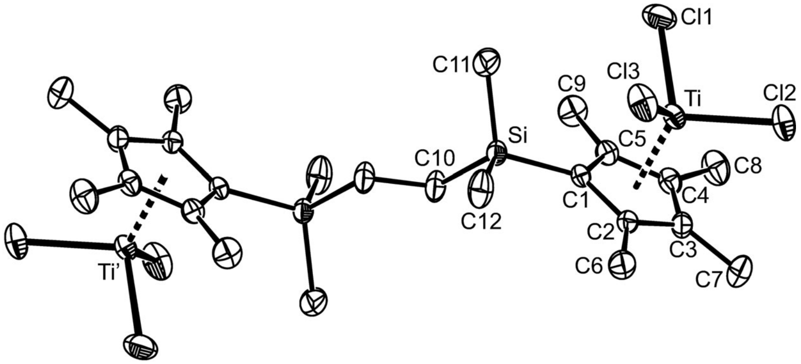


FIG. 3
PLATON drawing of compound **4** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

[$TiCl_2\{\eta^5:\eta^5-C_5Me_4SiMe_2CH_2CH=CHCH_2SiMe_2C_5Me_4\}$], differing from **3** only by the presence of double bond in the bridge, the silicon atoms were declined from the planes by 0.565(5) and 0.612(5) Å and the bridging chain was situated opposite to hinge position, spanning the chlorine atoms[34].

Conclusion

An easy and relatively clean synproportionation of permethylated *ansa*-titanocene dichlorides **1** and **3** with titanium tetrachloride opened the access to dinuclear half-sandwich complexes **2** and **4**.

Compared with the known dimethylsilanediyl-bridged unsubstituted complex **2** of Table I, the above compounds have, due to the methyl substitution of cyclopentadienyl rings, a better chance to form – in combination with MAO – catalysts producing a high-molecular-weight syndiotactic polystyrene[26]. The compounds are suitable for studying the effect of active center separation on the catalyst polymerization performance.

EXPERIMENTAL

General

Syntheses of 1,2-bis(dimethyl(1,2,3,4-tetramethylcyclopenta-1,3-dien-5-yl)silyl)ethane and titanocene dichloride **2** prepared thereof were carried out under argon atmosphere. All manipulations with $TiCl_4$ and its reaction with titanocene dichlorides were performed under vacuum in sealed all-glass devices equipped with breakable seals. ^1H (300 MHz), ^{13}C (75 MHz) and ^{29}Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C_6D_6 or $CDCl_3$ solutions at 25 °C. Chemical shifts (δ, ppm) are given relative to solvent signals or tetramethylsilane. The NOESY 1D experiment was performed using a mixing time of 500 ms. 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. The spectra are represented by the peaks of relative abundance higher than 6% and by important peaks of lower intensity. UV-VIS measurements were performed on a Varian Cary 17 D spectrometer in the range 300–800 nm using a device equipped with a pair of quartz cuvettes (10.0 mm and 1.0 mm, Hellma). Crystals of **2** and **4** for EI-MS measurements and **2**, **3**, and **4** for melting point determinations were placed in glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). Samples of **2** and **4** in KBr pellets were prepared in a glovebox Labmaster 130 (mBraun), and their IR spectra in the range 400–4000 cm^{-1} were recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer. The EI-MS samples of **2**–**4** were completely evaporated without changing the fragmentation pattern; this proves the uniformity of the compounds. Furthermore, crystal structures of **2**, **3**, and **4** were determined by X-ray diffraction analysis.

Chemicals

The solvents THF, toluene, and *m*-xylene were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$ (ref.[35]). $TiCl_4$ (International Enzymes) was purified by refluxing over copper wire and distilled under vacuum into ampules with breakable seals. Butyllithium in hexanes, 1,2,3,4-tetramethylcyclopentadiene (a mixture of isomers), and 1,2-bis(chlorodimethylsilyl)ethane (Aldrich) were transferred by syringe under argon. $[TiCl_3(thf)_3]$ was prepared by slow addition of BuLi (1.6 M in hexanes, 22.5 ml, 36.0 mmol) to a stirred slurry of $[TiCl_4(thf)_2]$ made by dissolving $TiCl_4$ (4.0 ml, 36.0 mmol) in THF (50 ml) (*attention* – exothermic reaction). After a short reflux, the dark solution was decanted from solid, the solvents distilled back to extract dark byproducts, and this was repeated until the extract from the blue crystalline $[TiCl_3(thf)_3]$ remained pale-blue. Yield of dry $[TiCl_3(thf)_3]$ was 10.0 g (76%). Compound *ansa*-$[TiCl_2\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}]$ (**1**) was identical with that reported in ref.[30b].

Preparation of $[\{TiCl_3(\eta^5\text{-}C_5Me_4)\}_2SiMe_2]$ (**2**)

Crystalline **1** (1.50 g, 3.60 mmol) and *m*-xylene (30 ml) were degassed on a vacuum line in an ampule with a breakable seal containing degassed $TiCl_4$ and a spare breakable seal. After sealing off and cooling the content with liquid nitrogen, $TiCl_4$ (0.5 ml, 4.55 mmol) was added by distillation. The used broken seal was sealed off, and the ampule after warming to room temperature was heated to 150 °C in a thermostatted oven with occasional shaking. After 5 h, when a red solution was obtained, the ampule was cooled to ambient temperature, attached through a breakable seal to another ampule which was then evacuated on a vacuum line. This device was sealed off, the solution transferred to the empty ampule, and the solvent repeatedly distilled back to extract all the crystallized product. Then, all volatiles were distilled to the reaction ampule cooled with liquid nitrogen, and this was sealed off. The $TiCl_4$ contained in volatiles was decomposed by adding ethanol. The solid red product was crystallized from hot toluene solution in similar all-sealed devices. The red product forming largely crystalline aggregates was dried in vacuum to give 2.00 g (92% based on **1**).

2: M.p. 305 °C, decomp. EI-MS (190 °C), *m/z* (rel.%): 610 (8), 608 (14), 607 (9), 606 (16), 605 (7), 604 ($M^{\bullet+}$; 10), 595 (15), 594 (13), 593 (28), 592 (17), 591 (34), 590 (13), 589 ($[M - Me]^+$; 19), 571 (6), 569 ($[M - Cl]^+$; 6), 536 (7), 534 ($[M - 2\,Cl]^+$; 7), 501 (4), 499 ($[M - 3\,Cl]^+$; 5), 417 (18), 416 (18), 415 ($[M - Ti - 3\,Cl - HCl]^+$; 24), 414 (17), 383 (11), 382 (19), 381 (29), 380 ($[M - Ti - 4\,Cl - HCl]^+$; 30), 379 (15), 367 (12), 366 (13), 365 ($[M - Me - Ti - 4\,Cl - HCl]^+$; 27), 364 (12), 336 (15), 335 (20), 334 (78), 333 (51), 332 (98), 331 ($[M - Me - Ti - 6\,Cl]^+$; 100), 330 (28), 329 (20), 297 (15), 296 (14), 295 ($[M - Ti - 3\,Cl - HCl - C_5Me_4]^+$; 23), 294 (16), 281 (14), 178 (40), 177 ($[C_5Me_4SiMe_2 - H]^+$; 96), 163 (30), 161 (23), 159 (15), 119 ($[C_5Me_4 - H]^+$; 50), 105 ($[C_5HMe_3]^+$; 60), 97 (33), 91 (29), 83 (25), 77 (25), 73 (25), 59 ($[SiMe_2H]^+$; 95). ^1H NMR (C_6D_6): 0.96 (s, 6 H, $SiMe_2$); 1.82 (s, 6 H, β-Me); 2.03 (s, 6 H, α-Me). ^{13}C $\{^1H\}$(C_6D_6): 2.92 ($SiMe_2$); 13.90, 17.74 ($C_5\mathbf{Me}_4$); 140.92, 141.72, 143.16 (C_q; C_{ipso} and C-Me). ^{29}Si $\{^1H\}$(C_6D_6): –12.26. IR (KBr): 2991 (w), 2964 (m), 2919 (m), 2854 (vw, sh), 1477 (m), 1449 (m), 1415 (w), 1382 (m), 1377 (m), 1329 (m), 1262 (m), 1256 (m), 1128 (w), 1092 (vw), 1023 (m), 847 (m), 830 (s), 815 (vs), 783 (m), 746 (w), 698 (vw), 676 (w), 465 (s), 409 (vs). UV-VIS (toluene, 22 °C): 412 nm.

Preparation of 1,2-Bis{dimethyl(1,2,3,4-tetramethylcyclopenta-1,3-dien-5-yl)silyl}ethane (**5**)

BuLi (2.5 M in hexanes, 40.0 ml, 0.100 mol) was slowly added to a stirred solution of 1,2,3,4-tetramethylcyclopentadienes (12.2 g, 0.100 mol) in dry THF (500 ml) at room temperature. The resulting suspension of lithium tetramethylcyclopentadienide was stirred for 3 h, treated with neat 1,2-bis(chlorodimethylsilyl)ethane (10.8 g, 50 mmol) and refluxed for 8 h. Solvents were removed under reduced pressure, and the product was extracted from a slurry of LiCl with hexane. The extract was evaporated under reduced pressure and the residue distilled at rotary oil pump vacuum at 160 °C as a yellow oil. Yield 16.5 g (85%).

5: ^{1}H NMR (C_6D_6): 0.00 (s, 12 H, $SiMe_2$); 0.41 (s, 4 H, CH_2); 1.81, 1.92 (2 × s, 12 H, $C_5\mathbf{Me}_4H$); 2.78 (s, 1 H, $C_5Me_4\mathbf{H}$). $^{13}C\{^1H\}$ NMR (C_6D_6): –3.7 ($SiMe_2$); 11.4, 14.8 ($C_5\mathbf{Me}_4H$); 54.3 (C_5Me_4H, CH); 133.1, 135.5 (C_5Me_4H, C-Me). IR (neat): 2960 (s), 2915 (vs), 2858 (s), 2737 (vw), 1632 (m), 1444 (s), 1404 (m), 1379 (m), 1304 (w), 1247 (vs), 1219 (s), 1178 (w), 1134 (s), 1110 (m), 1056 (s), 1021 (m), 982 (s), 951 (s), 920 (w), 830 (vs), 815 (vs), 774 (s), 723 (m), 706 (m), 624 (m), 559 (vw), 484 (m).

Preparation of *ansa*-$[TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2CH_2)_2]$ (**3**)

Lithium cyclopentadienide was obtained by reacting BuLi (1.6 M in hexanes, 31.3 ml, 50.0 mmol) with **5** (9.65 g, 25.0 mmol) in THF (400 ml) at room temperature for 5 h under stirring. Then, a slurry of $[TiCl_3(thf)_3]$ (9.20 g, 25.0 mmol) in 200 ml of THF was added under argon, and the mixture was refluxed for 34 h. The volume of the reaction mixture was reduced to ca. 50 ml, powdered anhydrous $PbCl_2$ (3.5 g, 12.5 mmol) was added and stirring continued for another 3 h while heating to 40 °C. The initially dark brown-green mixture turned dark red due to the formation of **3**. The reaction solution was decanted from precipitated lead, evaporated to dryness and the residue was extracted with hexane. The solution was concentrated and slowly cooled to –18 °C. After standing overnight, the formed crystalline material was filtered off, washed with ethanol (20 ml) and dried in vacuum. The obtained reddish-brown crystalline solid was recrystallized from hot hexane. Yield 4.64 g (37%).

3: M.p. 234 °C. EI-MS (150 °C), *m/z* (rel.%): 504 (6), 502 ($M^{\bullet+}$; 8), 478 (17), 477 (24), 476 (57), 475 (34), 474 ($[M - C_2H_4]^+$; 71), 473 (10), 472 (8), 469 (12), 468 (12), 467 ($[M - Cl]^+$; 23), 466 (7), 298 (10), 296 ($[M - C_2H_4 - SiMe_2C_5Me_4]^+$; 15), 289 ($[M - Cl - SiMe_2C_5Me_4]^+$; 10), 263 (12), 262 (10), 261 ($[M - Cl - C_2H_4 - SiMe_2C_5Me_4]^+$; 28), 260 (7), 259 (11), 257 (10), 243 (8), 180 (11), 179 (41), 178 ($[SiMe_2C_5Me_4]^+$; 100), 177 (10), 163 (31), 119 (24), 97 (10), 73 (17), 59 ($[SiMe_2H]^+$; 44). ^{1}H NMR (C_6D_6): 0.15 (s, 6 H, $SiMe_2$); 1.01 (s, 2 H, $SiCH_2$); 1.99 (s, 6 H, β-Me); 2.11 (s, 6 H, α-Me). $^{13}C\ \{^1H\}(C_6D_6)$: 1.38 ($SiMe_2$); 12.65 ($SiCH_2$); 13.92, 17.11 (Me_4Cp); 116.85, 135.89, 138.49 (C_q; C_{ipso} and C-Me). $^{29}Si\ \{^1H\}(C_6D_6)$: –3.98. IR (KBr): 2956 (m), 2927 (m), 2899 (s), 2863 (m), 1493 (w), 1452 (w), 1415 (w), 1382 (w), 1371 (m), 1345 (w), 1328 (m), 1257 (s), 1247 (s), 1129 (w), 1068 (vw), 1020 (m), 834 (vs), 799 (m), 770 (s), 701 (s), 681 (w), 595 (m), 570 (vw), 448 (w), 428 (vw), 405 (w).

Preparation of $[\{TiCl_3(\eta^5\text{-}C_5Me_4SiMe_2CH_2)\}_2]$ (**4**)

The synproportionation reaction of **3** (1.25 g, 2.49 mmol) and $TiCl_4$ (0.30 ml, 2.73 mmol) in *m*-xylene (15 ml) was carried out under the same conditions as for the synthesis of **2**. The crude product was crystallized from toluene to give, after drying in vacuum, red crystalline **4**. Yield 1.48 g (86%).

TABLE III
Crystal and structure refinement data for **2**, **3**, and **4**

Parameter	**2**	**3**	**4**
Formula	$C_{20}H_{30}Cl_6SiTi$	$C_{24}H_{40}Cl_6Si_2Ti$	$C_{24}H_{40}Cl_6Si_2Ti_2$
Molecular weight	607.03	503.54	693.24
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	16.0426(4)	9.8221(3)	8.7580(3)
b, Å	12.6620(4)	35.0484(14)	15.4440(9)
c, Å	14.9997(4)	8.4205(4)	13.3750(5)
β, °	115.2671(13)	114.6881(15)	114.010(3)
V, Å^3; Z	2755.40(13); 4	2633.79(18); 4	1652.55(13); 2
D_{calcd}, g cm^{-3}	1.463	1.270	1.393
μ, mm^{-1}	1.212	0.628	1.054
Color and habit	orange prism	dark red needle	orange prism
Crystal size, mm	0.78 × 0.43 × 0.25	0.50 × 0.12 × 0.05	0.58 × 0.15 × 0.10
T, K	293(2)	293(2)	293(2)
F(000)	1240	1072	716
θ_{min}; θ_{max}, °	1.00; 27.48	2.91; 27.48	1.00; 27.48
No. of measured diffractions	21261	18991	11778
No. of unique diffractions	6276	5887	3753
No. of observed diffractions	5059	3322	2533
No. of parameters	272	274	160
R; $wR^2(F^2)$ obsd. diffractions	0.0389; 0.0977	0.0533; 0.1147	0.0471; 0.1080
$R(F)$; $wR^2(F^2)$ all data	0.0523; 0.1089	0.1242; 0.1408	0.0808; 0.1261
GOOF (F^2), all data	1.038	1.030	1.024
$\Delta\rho$, e Å^{-3}	0.454; –0.522	0.448; –0.478	0.272; –0.465

[a] Diffractions with $I_o > 2\sigma(I_o)$.

4: M.p. 190 °C. EI-MS (170 °C), *m/z* (rel.%): 690 ($M^{\bullet +}$, not observed), 668 (6), 667 (6), 666 (11), 665 (7), 664 (12), 663 (5), 662 ($[M - C_2H_4]^+$; 7), 336 (20), 335 (26), 334 (87), 333 (71), 332 (99), 331 ($[\{M - C_2H_4\}/2]^+$; 100), 330 (29), 329 (28), 318 (9), 317 (6), 316 ($[\{M - C_2H_4\}/2 - Me]^+$; 9), 300 (18), 299 (21), 298 (70), 297 (43), 296 $[\{M - C_2H_4\}/2 - Cl]^+$; 86), 295 (31), 294 (13), 179 (14), 178 ($[C_5Me_4SiMe_2]^+$; 45), 177 (28), 163 (44), 161 (12), 135 (10), 133 (12), 119 (36), 105 (15), 97 (15), 73 (18), 59 ($[SiMe_2H]^+$; 55). ^{1}H NMR (C_6D_6): 0.40 (s, 6 H, $SiMe_2$); 0.70 (s, 2 H, $SiCH_2$); 1.90 (s, 6 H, β-Me), 2.25 (s, 6 H, α-Me). ^{13}C {^{1}H}(C_6D_6): –1.14 ($SiMe_2$); 9.54 ($SiCH_2$); 13.81, 17.52 ($C_5\mathbf{Me}_4$); 139.10, 142.10, 144.23 (C_q; C_{ipso} and C-Me). ^{29}Si {^{1}H}(C_6D_6): –0.95. IR (KBr): 2966 (m), 2917 (m), 1475 (m), 1450 (w), 1404 (w), 1377 (m), 1332 (m), 1251 (s), 1142 (m), 1063 (w), 1022 (m), 836 (s), 825 (s), 815 (vs), 777 (m), 743 (w), 712 (w), 635 (w), 470 (s), 412 (vs). UV-VIS (toluene, 22 °C): 432 nm.

X-Ray Crystal Structure Determination

Red fragments of **2** and **4** were inserted into Lindenmann glass capillaries under purified nitrogen in a glovebox (mBraun) and the capillaries were sealed by flame. A dark red prism of **3** was mounted on a glass capillary with epoxy cement. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed using the HKL program package[36]. The structures were solved by direct methods (SIR97 [37]), followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97 [38]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. Relevant crystallographic data for all the compounds are given in Table III. CCDC 283691 (for **2**), 283690 (for **3**) and 283689 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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