PREPARATION AND CRYSTAL STRUCTURE OF BIS(*tert*-BUTYLTETRAMETHYLCYCLOPENTADIENYL)-DICHLOROTITANIUM

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$[TiCl_2(\eta^5\text{-}C_5Me_4t\text{-}Bu)_2]$ (**1**) was prepared by the reaction of $[TiCl_3(thf)_3]$ with 2 equivalents of $Li(\eta^5\text{-}C_5Me_4t\text{-}Bu)$ (made by adding BuLi to a 1.33 molar excess of a mixture of *tert*-butyltetramethylcyclopentadiene isomers in THF) and subsequent oxidation of the Ti(III) intermediate to **1** by adding aqueous HCl. Neglecting the presence of cyclopentadiene isomers not forming the cyclopentadienide anion in the isomer mixture used for the synthesis of **1** resulted in the formation of hydrolytic product $[\{TiCl_2(\eta^5\text{-}C_5Me_4t\text{-}Bu)\}_2(\mu\text{-}O)]$ (**2**) and a considerable decrease of yield of **1**. The half sandwich complex $[TiCl_3(\eta^5\text{-}C_5Me_4t\text{-}Bu)]$ (**3**) was obtained by synproportionation of **1** and $TiCl_4$. Crystal structures of **1**, **2**, and **3** were determined. The electronic absorption spectra of **1** and **3** indicate a stronger electron-donor effect of *tert*-butyl group compared with methyl group.

Keywords: Titanium; Titanocene dichloride; *tert*-Butyltetramethylcyclopentadiene; Half-sandwich complexes; Metallocenes; Cyclopentadienes; *tert*-Butyl group; Electronic effect; Hydrolysis products; Crystal structures.

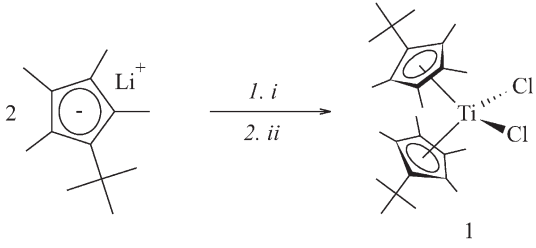
Physicochemical and catalytic properties of titanocene complexes can be tuned by substitution of cyclopentadienyl ligands both by electron-donating as well as by electron-attracting substituents[1]. The electron-donating effect of methyl groups[2] and electron-attracting effect of trifluoromethyl groups[3] in the substituted titanocene dichlorides have been most transparently revealed from the values of electrochemical first reduction potential[2] or $Ti(2p_{3/2})$ binding energy in ESCA (electron spectroscopy for chemical analysis)[3]. The electron-donating effect of Me group(s) was also demonstrated by electronic absorption spectra of cyclopentadienyltitanium

trichlorides $[TiCl_3(\eta^5\text{-}C_5H_{5-n}Me_n)]$ (n = 0–5) and the kinetics of their reduction with ethylaluminum chlorides[4], by monomer/dimer equilibria of titanocene monohalides or resistance to electron-donor coordination[5], or decay modes of titanocenes (Ti(II)) at the onset of their formation[6]. Spectroscopic investigations revealed smooth dependences on n of the ^{49}Ti and ^{47}Ti NMR chemical shifts of substituted trichlorocyclopentadienyltitaniums[7], valence electron energies obtained by UPS (ultraviolet photoelectron spectroscopy) in the series of $[TiCl_2(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (n = 0–5)[8] and $[TiCl(C_5H_{5-n}Me_n)_2$ (n = 0–5)[9] and differences in ESCA binding energies of $[TiX_2(\eta^5\text{-}C_5H_{5-n}Me_n)_2]$ (X = F, Cl, Br; n = 0, 5)[10]. In the $[TiCl_2(\eta^5\text{-}C_5H_{5-n}t\text{-}Bu_n)_2]$ (n = 0–2) compounds the electronic effect of *tert*-butyl group is always combined with its steric effect, and cannot be compared with the effect of methyl group(s). For example, the first reduction potential of $[TiCl_2(\eta^5\text{-}C_5H_4t\text{-}Bu)_2]$ was found to be less negative than that of $[TiCl_2(\eta^5\text{-}C_5H_4Me)_2]$ (ref.[11]). However, $[TiCl(\eta^5\text{-}C_5H_3Me_2\text{-}1,3)_2]$ is dimeric in nonpolar solvents and in the solid state[12] whereas $[TiCl(\eta^5\text{-}C_5H_3t\text{-}Bu_2\text{-}1,3)_2]$ does not dimerize[13]. This is apparently not due to saturation of the titanium atom with electron density but due to steric requirements of the rotating 1,3-di(*tert*-butyl)cyclopentadienyl ligands. Due to the bulkiness of *tert*-butyl group 1,2-bis(*tert*-butyl)cyclopentadienes can be prepared only by condensation of suitable precursors followed by dehydration[14], and alkylation of cyclopentadiene with *tert*-butyl group affords only 1,3- and 1,2,4-isomers[15]. Of the sterically congested titanocene dichlorides, dichloro(di-*tert*-butylcyclopentadienyl)(tri-*tert*-butylcyclopentadienyl)-titanium is known while the synthesis of dichlorobis(tri-*tert*-butylcyclopentadienyl)titanium failed[16].

From the point of view of the task to synthesize silicon free thermally stable titanocene[17] the 1-*tert*-butyl-2,3,4,5-tetramethylcyclopentadienyl ligand is the most promising since it combines the electron-donor effect of methyl groups with additional steric hindrance due to the *tert*-butyl group. This ligand has been known for nearly 10 years[18], however, the synthesis of titanocene monochloride $[TiCl(\eta^5\text{-}C_5Me_4t\text{-}Bu)_2]$ and titanocene $[Ti(\eta^5\text{-}C_5Me_4t\text{-}Bu)_2]$ was reported only recently[19]. The absence of any report on the synthesis of the titanocene dichloride $[TiCl_2(\eta^5\text{-}C_5Me_4t\text{-}Bu)_2]$ (**1**) can raise doubts about its stability, and therefore here we describe the syntheses and structures of **1**, $[\{TiCl_2(\eta^5\text{-}C_5Me_4t\text{-}Bu)\}_2(\mu\text{-}O)]$ (**2**) that can accompany **1**, and $[TiCl_3(\eta^5\text{-}C_5Me_4t\text{-}Bu)]$ (**3**), where no intramolecular steric hindrance can be considered.

RESULTS AND DISCUSSION

The synthesis of $[TiCl_2(\eta^5\text{-}C_5Me_4t\text{-}Bu)_2]$ (**1**) was carried out by the general procedure for preparation of highly substituted titanocene dichlorides consisting in the reaction of 2 equivalents of $Li(C_5Me_4t\text{-}Bu)$ with $[TiCl_3(thf)_3]$ followed by oxidation with aqueous HCl (Scheme 1). The cyclopentadienide salt was prepared by reacting a mixture of the cyclopentadiene isomers obtained according to ref.[18a] with equimolar amount of BuLi in THF. An acceptable yield of **1** was, however, obtained only after increasing the content of anion-forming isomers in a mixture containing also dihydrofulvene isomers incapable of forming the cyclopentadienyllithium salt and using the isomer mixture in an excess required by stoichiometry (see Experimental).



i $[TiCl_3(thf)_3]$, THF, boiling 30 h.

ii aqueous HCl, workup

SCHEME 1

Brown crystalline **1** was obtained in ca. 50% yield from hexane solution; its structure was determined by ^1H and ^{13}C NMR spectra, proving that its cyclopentadienyl ligands freely rotate at ambient temperature. The EI-MS spectrum shows a very small molecular peak (*m/z* 472). The most abundant fragment ions are $[M - Cl]^+$ (base peak), $[M - Cl - Cp']^+$, $[M - Cl - Cp' - MeH]^+$, and $[Cp']^+$, $[Cp' - Me]^+$, and $[Cp' - 2\ Me]^+$. This fragmentation is somewhat surprising because similar alkenyl-substituted titanocene dichlorides, $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$ (R = $CH_2CH_2CH{=}CH_2$, $CH(Me)CH{=}CH_2$ (ref.[20]) or $CH_2C(Me){=}CH_2$) (ref.[21])), showed the $[M - Cp']^+$ ions as base peaks and $[M - Cl]^+$ ions much less abundant. The electronic absorption spectrum of **1** displayed the longest-wavelength ligand-to-metal charge transfer (LMCT) transition[22] at 580 nm. A comparison with λ 560 nm for $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ (ref.[23]) indicates that the *tert*-butyl group is more electron-donating than Me group. This is in line with long Ti–CE and Ti–Cl distances found in the crystal structure of **1** (see below).

Compound [{$TiCl_2(\eta^5$-C_5Me_4t-Bu)}$_2$(μ-O)] (**2**) was obtained in early attempts to prepare **1** assuming that the reaction between 2,3,4,5-tetramethylcyclopent-2-en-1-one and *t*-BuLi following the protocol of ref.[18] afforded only the cyclopentadiene isomers capable of forming the anion upon reaction with BuLi. The insufficiency of the anion content in the reaction mixture according to Scheme 1 resulted in the formation of a THF solvate of Ti(III) compound [$TiCl_2(\eta^5$-C_5Me_4t-Bu)] and this then by adding aqueous HCl hydrolyzed to **2**. A mixture of **1** and **2** was obtained which could not be efficiently separated by fractional crystallization. Crystalline **2** in the amount sufficient for full characterization was separated mechanically. It gave the mass spectra characterized by the molecular ion and the loss of chlorine atoms, methyl groups, and the cyclopentadienyl ligand. The base peak was due to the cyclopentadienyl ligand ion subsequently losing 2 methyl groups. The ^{1}H and ^{13}C NMR spectra of **2** were only slightly shifted from resonances of **1**. Nevertheless, compound **2** is easily revealed in a mixture with compound **1** due to its extremely intense infrared absorption band at 731 cm^{-1} apparently belonging to Ti–O stretching vibration. Compound **2** seemed to be stable in air; however, it cannot be excluded that its hydrolysis slowly continues in humid air to give cyclic compounds of composition [{$TiCl(C_5Me_4t$-Bu)(μ-O)}$_n$] where n = 3 or 4. A trace of compound [{$TiCl(C_5Me_4t$-Bu)(μ-O)}$_3$] was detected by MS spectrometry after evaporation of compound **2**. Compounds of these types were previously isolated from reaction mixtures after addition of aqueous HCl and separation of titanocene dihalides[24].

Red crystalline [$TiCl_3(\eta^5$-C_5Me_4t-Bu)] (**3**) was obtained by synproportionation reaction of **1** with an equimolar amount of $TiCl_4$ at 140 °C. The compound was characterized by ^{1}H and ^{13}C NMR, IR, and EI-MS spectra, the latter showing the molecular ion and the fragment ions due to the loss of HCl and Me group. The base peak was again the cyclopentadienyl ion accompanied by fragments due to the loss of two methyl groups. This compound showed its longest-wavelength transition at 444 nm which is again at lower energy than the transition at 438 nm in [$TiCl_3(\eta^5$-C_5Me_5)] (ref.[4]). Since the crystal structure of **3** (see below) did not reveal any irregularity with respect to other compounds of this type, thus excluding steric hindrance of the cyclopentadienyl ligand due to chlorine atoms, one can conclude that the HOMO-LUMO gap is decreased as a result of a stronger electron-donating effect of the C_5Me_4t-Bu ligand compared with C_5Me_5.

*Crystal Structures of Compounds **1**, **2**, and **3***

All the compounds crystallize in monoclinic space groups, and molecules of **1** and **2** are symmetrical: **1** with respect to a two-fold axis bisecting the Cl–Ti–Cl angle, and **2** contains its oxygen atom in the center of symmetry. Therefore only one set of selected data for the cyclopentadienyl ligand of each compound is given in Table I. Compound **1** (Fig. 1) contains staggered cyclopentadienyl rings with their *tert*-butyl groups placed in side positions, closer to chlorine atoms. The mutual rotation of C(1) and C(1)′ carbon atoms bearing the *tert*-butyl groups, following from the C(1)–CE–CE′–C(1)′ torsion angle, is 162.17(10)°. The cyclopentadienyl ring is planar with maximum deviation of 0.0173(8) Å from its least-squares plane for C(5). The maximum deviation of methyl carbon atoms from the least-squares plane is 0.354(2) Å for C(6) and 0.347(2) Å for C(7), both of them occupying the hinge positions. The *tert*-butyl carbon atom C(10) is deviated by 0.3200(25) Å whereas C(9) lying close to Cl atom is not deviated at all (0.007(2) Å). The structure of the cyclopentadienyl ligand is slightly irregular due to the presence of a bulky *tert*-butyl substituent. The angle at the C(1) atom is smaller (106.70(12)°) than the other angles in the cyclopentadienyl ring. This de-

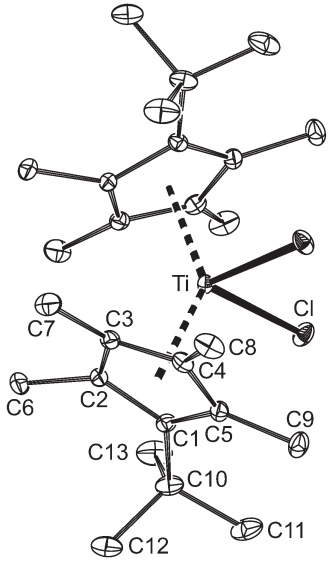


FIG. 1
PLATON drawing of compound **1** at the 30% probability level with atom labelling scheme. Hydrogens are omitted for clarity

formation is virtually the same as in $[TiCl_2(\eta^5\text{-}C_5Me_4SiMe_3)_2]$ (**4**) where it was attributed to a positive charge on Si atom (Si electronegativity 1.8 compared with 2.5 for C)[5b]. In the present case, the effect of a smaller angle is probably due to steric repulsion between the *tert*-butyl group and neighbouring methyl groups on the cyclopentadienyl ligand. This effect is not associated with the deviation of *tert*-butyl group from the least-squares plane because virtually the same values of this angle are found in compounds **2** and **3** (Table I, Figs 2–3), where such a deviation does not occur. It is of interest that the *tert*-butyl group is declined from the axis of the

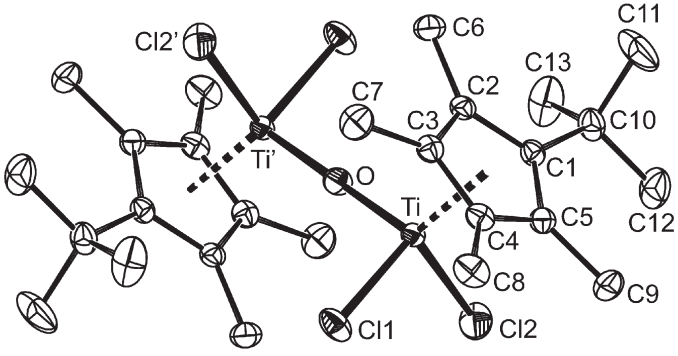


FIG. 2
PLATON drawing of compound **2** at the 30% probability level with atom labelling scheme. Hydrogens are omitted for clarity

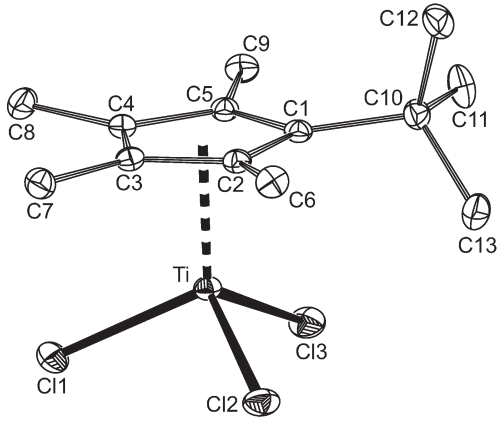


FIG. 3
PLATON drawing of compound **3** at the 30% probability level with atom labelling scheme. Hydrogens are omitted for clarity

TABLE I
Selected bond lengths (in Å) and angles (in °) for **1**[a], **2**[a], and **3**

Atoms	**1**	**2**	**3**
		Bond lengths	
Ti–C(1)	2.4929(13)	2.3836(3)	2.383(3)
Ti–C(2)	2.4575(13)	2.3418(19)	2.373(3)
Ti–C(3)	2.4303(13)	2.3283(19)	2.342(3)
Ti–C(4)	2.4543(13)	2.408(2)	2.346(3)
Ti–C(5)	2.4500(13)	2.422(2)	2.359(3)
Ti–Cg[b]	2.1378(6)	2.0459(10)	2.0242(17)
C(1)–C(2)	1.4296(18)	1.434(3)	1.446(4)
C(2)–C(3)	1.4262(19)	1.416(3)	1.419(4)
C(3)–C(4)	1.407(2)	1.418(3)	1.416(4)
C(4)–C(5)	1.417(2)	1.408(3)	1.420(4)
C(1)–C(5)	1.4409(19)	1.440(3)	1.442(4)
C(1)–C(10)	1.543(2)	1.535(3)	1.535(4)
Ti–Cl(1)	2.3666(4)	2.2667(7)	2.2511(9)
Ti–Cl(2)	–	2.2576(7)	2.2409(9)
Ti–Cl(3)	–	–	2.2465(9)
Ti–O	–	1.8170(4)	–
		Bond angles	
Cg–Ti–Cg[b]	138.04(3)	180	–
C(2)–C(1)–C(5)	106.70(12)	106.54(17)	106.3(2)
C(2)–C(1)–C(10)	123.79(13)	124.83(19)	124.4(3)
C(5)–C(1)–C(10)	128.17(12)	127.94(18)	128.8(3)
Cl(1)–Ti–Cl(2)	88.91(2)	100.06(3)	101.21(3)
Cl(1)–Ti–Cl(3)	–	102.52(2)	102.53(3)
Cl(2)–Ti–Cl(3)	–	104.86(2)	104.69(4)
ϕ[c]	42.63(4)	0	–

[a] Only one set of data for **1** and **2** stems from the symmetry of the molecules. Operators for generating equivalent atoms **1**: $-x + 1, y, -z + 1/2$; **2**: $-x, -y + 1, -z$. [b] Centroid of the C(1-5) cyclopentadienyl ring atoms. [c] Dihedral angle between least-squares planes of the cyclopentadienyl rings.

C(2)–C(1)–C(5) angle: C(2)–C(1)–C(10) 123.79(13)° versus C(5)–C(1)–C(10) 128.17(12)°, and a similar difference in the angles is observed also in compounds **2** and **3**. This is caused by the special position of *tert*-butyl group whose one methyl carbon atom (C(11)) lies close to the least-squares plane of the cyclopentadienyl ligand and is repelled by neighbouring methyl group (C(9)). A comparison of geometric parameters of **1** with those of **4** (ref.[5b]) and $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ (**5**) (ref.[25]) gives very similar figures. The Ti–Cg (Cg – centroid of gravity of cyclopentadienyl ring) distance is distinguishably longer (by 0.010 ± 5 Å) than in **4** and **5**, the Cg–Ti–Cg angle differs marginally but the angle ϕ (42.63(4)°) falls between the values for **4** (39.8°)[5b] and **5** (44.6°)[25a]. The Cl–Ti–Cl angle (88.91(2)°) is very close to the value for **4** (89.5(1)°) and both are smaller than the angle in **5** (92.9°)[25b]. The latter angle in **5** is surprisingly close to the Cl–Ti–Cl angle in $[TiCl_2(\eta^5\text{-}C_5H_4t\text{-}Bu)]$ (92.5°) whose overall structure with partly staggered cyclopentadienyl rings and *tert*-butyl groups on opposite sides of the molecule[26] is very similar to the structure of **1**. A comparison of the geometric data for **1** with those for **2** and **3** demonstrates the increase in bonding strength when an ancillary, soft π-bonded cyclopentadienyl ligand is replaced by chlorine anion: both Ti–C and Ti–Cl bonds are much shorter in the half-sandwich complexes (see Table I). On the other hand, the comparison of **3** with other half-sandwich complexes (Table II) indicates that the

TABLE II
Molecular parameters of trichloro(η^5-cyclopentadienyl)titanium(IV) complexes

Complex	Cyclopentadienyl ligand	$Ti–Cl_{av}$	$Ti–C_{av}$	Ref.[a]
I	C_5H_5	2.223	2.314	27
II	C_5H_4Me	2.224	2.323	28
III	$1,3\text{-}C_5H_3(SiMe_3)_2$	2.230	2.341	29
IV	$C_5H_4(t\text{-}C_4H_9)$	2.232	2.342	30
V	$C_5H_3(t\text{-}C_4H_9)_2$	2.243	2.355	31
VI	C_5HMe_4	2.243	2.350	32
VII	$C_5Me_4(CH_2CH_2Ph)$	2.235	2.346	33
VIII	$C_5Me_4[(CH_2)_3CH=CH_2]$	2.242	2.355	34
IX	C_5Me_4Et	2.243	2.352	35
X	$C_5Me_4(t\text{-}C_4H_9)$	2.462	2.361	this work
XI	$C_5Me_4(t\text{-}C_4H_9)$ in **2**	2.262	2.377	this work

[a] Structural data retrieved from Cambridge Crystallographic Data Centre.

induction of electron density at the titanium atom by a joint action of four Me groups and the *tert*-butyl group results in the unprecedented elongation of both Ti–Cl and Ti–C bonds. Assuming that the *tert*-butyl group does not hinder the chlorine atoms, the elongation should be accounted for by its electron-donating effect, which should be stronger than that exerted by CH_2CH_3 (complex IX) or CH_2CH_2R groups (complexes VII and VIII). The structure of compound **2** is peculiar due to the straight Ti–O–Ti angle. A comparison with structures of compounds $[\{TiCl_2(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}O)]$ and $[\{TiCl_2(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}O)]$ with Ti–O–Ti angles 154–159° (3 independent molecules in unit cell)[24] and 180° (ref.[36]), respectively, points to crystal packing effects rather than to intramolecular crowding. The observed shortening of Ti–Cl bonds and prolongation of Ti–C bonds in **2** relative to the structure of **3** can be due to the π-donor ability of oxygen bonded to titanium[37].

EXPERIMENTAL

General Comments and Methods

Synthesis of titanocene dichloride **1** was carried out under argon atmosphere. After addition of hydrogen chloride, the products **1** or **2** were worked up and handled in air. The reaction of **1** with $TiCl_4$ and the subsequent manipulations with **3** were performed on a vacuum line in all-sealed glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (10.0 and 1.0 mm, Hellma) was used for UV-VIS measurements. Crystals of **2** and **3** for EI-MS measurements and 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). ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in $CDCl_3$ solutions at 25 °C. Chemical shifts (δ, ppm) are given relative to solvent signals, coupling constants (*J*) are given in Hz. 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 340–2000 nm. IR spectra were recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm^{-1}. Samples of **3** in KBr pellets were prepared in a glovebox Labmaster 130 (mBraun). GC analysis was carried out on a GC 72F chromatograph (Labio, Prague, Czech Republic) using an RTX-1 capillary column (length 30 m, d = 0.32 mm). The GC-MS spectra were recorded on a Hewlett–Packard gas chromatograph (5890 series II) equipped with a mass spectrometric detector (5791 A) and a capillary column SPB-1 (Supelco). The EI-MS samples of **1**–**3** were completely evaporated without changing the fragmentation pattern; this proves the uniformity of the compounds. Furthermore, crystal structures of **1**, **2**, and **3** were determined by X-ray diffraction analysis.

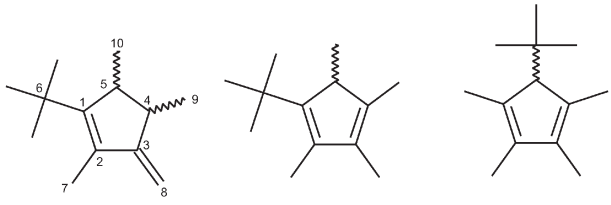
Chemicals

Solvents tetrahydrofuran (THF), hexane, and toluene were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$ (ref.[38]). 1.6 M Butyllithium (BuLi) in hexanes (Aldrich) and 1.7 M *tert*-butyllithium in pentane (Aldrich) were dosed with a syringe. 2,3,4,5-Tetramethylcyclopent-2-en-1-one (Aldrich) was distilled in vacuum before use. $[TiCl_3(thf)_3]$ was prepared by slow addition of 1.6 M BuLi 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, a 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%).

Synthesis of a Mixture of Isomers of *tert*-Butyltetramethylcyclopentadiene

1.7 M *tert*-Butyllithium in pentane (100 ml) was slowly added to a stirred solution of 2,3,4,5-tetramethylcyclopent-2-en-1-one (22.8 g, 165 mmol) in 500 ml of diethyl ether cooled to –78 °C in a dry ice/ethanol bath. The reaction mixture was stirred at –78 °C for 1 h, quenched by adding 2 ml of water, and allowed to warm up to room temperature with stirring. Then, concentrated sulfuric acid (2.0 ml) was added dropwise to a vigorously stirred solution. After 15 min, the solution was washed with aqueous solution of sodium hydrogencarbonate, and then twice with water. The solution was dried with anhydrous sodium sulfate, and the ether was distilled off using a 60 °C bath. The organic product was extracted from salts by hexane and purified by liquid column chromatography (silica gel, length 40 cm, eluent hexane). The first fractions were combined and analyzed by GC and GC-MS. The products gave two chromatographic peaks with retention times 4.1 min (fraction 1) and 6.0 min (fraction 2) of approximately equal intensity. The mass spectrometric detection revealed the molecular ion (*m/z* 178) for both the fractions. If components with the retention time higher than 10 min were present the above mentioned products should be separated from them by distillation at 1.33 kPa. The ^1H and ^{13}C NMR spectra of the total sample (fractions 1 + 2) and of distillation-enriched fraction 1 and fraction 2 were measured. Fraction 1 contained one major and one minor dihydrofulvenes. The major component was assigned to one of two diastereomers of 1-*tert*-butyl-2,4,5-trimethyl-3-methylidenecyclopent-1-ene (**I**). The presence of the exocyclic double bond in **I** is clearly evidenced by singlets at 4.60 and 4.74 ppm of two diastereotopic methylene protons in ^1H NMR for which carbon signal at 98.9 ppm was found by HSQC (Chart 1). The minor component signals at δ_H 4.65 and 4.83 ppm and at δ_C 102.1 ppm are attributable to either the second diastereomer of **I** or to any other *exo*-methylidene-containing tautomer. The fraction 2 contained major 1-*tert*-butyl-2,3,4,5-tetramethylcyclopenta-1,3-diene (**II**) and minor 5-*tert*-butyl-1,2,3,4-tetramethylcyclopenta-1,3-diene (**III**) (Chart 1). The identification of compounds was facilitated by precipitation of the lithium salt of **II** and **III** by adding BuLi in hexane to a total sample (fractions 1 + 2) in diethyl ether. The hydrolysis of the salt afforded tautomers **II** and **III** in equal amounts which allowed us to identify NMR spectra of **III**. The presence of the *exo*-methylidene compound **I** and and its minor tautomer in the mother liquor proved that they do not form the cyclopentadienyl anion. It has to be stressed that the composition and the yield of products varied in each experiment. Therefore the GC and NMR analysis of the products from each experiment is recommended. Previously, there was no necessity to determine the composition of the *tert*-butyltetramethylcyclopentadiene isomer mixture be-

cause the whole mixture was used in excess to be reacted with iron pentacarbonyl[18a] or sodium cyclopentadienide was first prepared thereof, isolated, and used in a stoichiometric ratio[18b]. The yields of sum of fractions 1 and 2 ranged between 50 and 70%. For the synthesis of **1** fraction 2 was enriched by fractional distillation at 1.33 kPa so that cyclopentadienes **II** and **III** formed 75% of the isomeric mixture. The yield of colorless liquid was 19.0 g (65%).



I II III

CHART 1

C_5HMe_4t-Bu (a mixture of isomers). B.p. 68 °C/1.33 kPa. IR (neat): 3079 (vw), 2957 (vs), 2912 (s), 2868 (s), 1625 (m), 1454 (s, b), 1393 (w), 1376 (m), 1362 (s), 1238 (w), 1210 (vw), 1195 (vw), 1123 (vw), 1089 (vw), 1034 (w), 986 (vw), 943 (w), 854 (m), 705 (vw), 669 (vw). GC-MS, *m/z* (%), fraction 1: 178 ($M^{\bullet+}$; 36), 163 ([M – Me]$^+$; 37), 135 (18), 122 ([M – C_4H_8]$^+$; 100), 121 (67), 107 (99), 105 (32), 93 (21), 91 (50); fraction 2: 178 ($M^{\bullet+}$; 50), 163 ([M – Me]$^+$; 39), 148 ([M – 2 Me]$^+$; 23), 133 (18), 122 ([M – C_4H_8]$^+$; 100), 121 (21), 107 (99), 105 (35), 91 (39).

Isomer **I**. ^{1}H NMR ($CDCl_3$): 1.00 (d, 3 H, ^3J = 7.2, $C^{10}\mathbf{H}_3$); 1.04 (d, ^3J = 6.9, 3 H, $C^9\mathbf{H}_3$); 1.21 (s, 9 H, *t*-Bu); 1.82 (d, 3 H, ^5J = 1.2, $C^7\mathbf{H}_3$); 2.14 (q, ^3J = 7.02, 1 H, $C^5\mathbf{H}$); 2.31 (q, ^3J = 6.9, 1 H, $C^4\mathbf{H}$); 4.60 (bs, 1 H, $C^8\mathbf{H}$); 4.74 (bs, 1 H, $C^8\mathbf{H}$). ^{13}C NMR ($CDCl_3$): 12.7 (C^7); 22.7 (C^9); 23.3 (C^{10}); 30.4 ($\mathbf{Me}_3C^6$); 33.6 (Me_3C^6); 45.8 (C^5); 48.6 (C^4); 98.9 (C^8); 129.8 (C^2); 157.6 (C^1); 163.2 (C^3) (for assignment see Chart 1).

Isomer **II**. ^{1}H NMR ($CDCl_3$): 1.14 (d, $^3J_{HH}$ = 7.2, 3 H, CH**Me**); 1.26 (s, 9 H, C$\mathbf{Me}_3$); 1.75 (br s, 3 H, =C**Me**); 1.79 (s, 3 H, =C**Me**); 1.94 (d, $^5J_{HH}$ = 1.5, 3 H, =C**Me**); 2.75 (m, 1 H, C**H**Me). ^{13}C{^{1}H} NMR ($CDCl_3$): 11.30, 11.72, 13.97 (=C**Me**); 16.93 (CH**Me**); 31.19 (C$\mathbf{Me}_3$); 34.30 (CMe_3); 50.84 (C**H**Me); 134.09, 134.47, 138.18, 150.29 (=C**M**e and =C**C**Me_3).

Isomer **III**. ^{1}H NMR ($CDCl_3$): 1.02 (s, 9 H, C$\mathbf{Me}_3$); 1.77 (s, 6 H, 2 × =C**Me**); 1.95 (s, 6 H, 2 × =C**Me**); 2.45 (br s, 1 H, C**H**CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 11.68, 16.42 (=C**Me**); 29.56 (C$\mathbf{Me}_3$); 33.59 (**C**Me_3); 67.58 (**C**HCMe_3); 135.54, 137.17 (=**C**Me).

Preparation of Titanocene Dichloride **1**

Titanocene dichloride [$TiCl_2(\eta^5$-C_5Me_4t-Bu)$_2$] (**1**) was prepared from a slurry of [$TiCl_3(thf)_3$] (9.2 g, 25.0 mmol) in 200 ml of THF and lithium cyclopentadienide obtained by reacting 1.6 M BuLi in hexanes (31.3 ml, 50.0 mmol) with the above mixture of cyclopentadiene isomers (11.87 g, 67.0 mmol) in THF (400 ml) at room temperature for 4 h under stirring. After mixing these components, the mixture was refluxed for 30 h, then cooled with ice to ca. 5 °C, and aqueous HCl (30 ml) was added against a stream of argon. Then, all volatiles were evaporated on a rotary evaporator at 60 °C, and the product was extracted with hexane in a Soxhlet extractor. Crystallization from a concentrated hexane solution afforded reddish brown crystals of **1**. Yield 6.14 g (52%).

Compound **1**. M.p. 174 °C. EI-MS (direct inlet, 70 eV, 120 °C), *m/z* (relative abundance): 472 ($M^{\bullet+}$; 0.2), 440 (15), 439 (46), 438 (37), 437 ([M – Cl]$^+$; 100), 436 (14), 402 ([M – 2 Cl]$^+$; 8), 325 (11), 323 ([M – Cl – 2 Bu]$^+$; 21), 281 (17), 279 (24), 260 ([M – Cl – Cp′]$^+$; 13), 257 (16), 255 ([M – Cl – 2 Bu – C_5H_8]$^+$; 31), 246 (31), 245 (20), 244 ([M – Cl – 2 Bu – C_6H_7]$^+$; 75), 243 (24), 242 (18), 241 (38), 227 (20), 177 ([Cp′]$^+$; 44), 162 ([Cp′ – Me]$^+$; 48), 147 ([Cp′ – 2 Me]$^+$; 37), 119 (17), 105 (14), 91 (14), 57 (17). ^{1}H NMR ($CDCl_3$): 1.37 (s, 9 H, C**Me**$_3$); 2.00, 2.26 (2 × s, **Me**Cp, 2 × 6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 13.1, 17.2 (**Me**Cp); 31.7 (C**Me**$_3$); 37.9 (**C**Me$_3$); 126.8, 129.8, 145.7 (Cp). IR (KBr): 3037 (vw), 3006 (m), 2993 (s), 2971 (m), 2954 (s), 2907 (vs), 1483 (s), 1470 (s), 1462 (vs), 1401 (m), 1386 (m), 1377 (vs), 1365 (m), 1230 (m), 1191 (w), 1122 (w), 1031 (m), 1023 (m), 1010 (m), 934 (vw), 670 (w), 590 (vw), 479 (w). UV-VIS (hexane, 22 °C): 472 > 580 (sh).

Preparation of [{$TiCl_2(\eta^5$-C_5Me_4t-Bu)}$_2$(μ-O)] (**2**)

Compound **2** was obtained from the unsuccessful synthesis of **1** when a mixture of cyclopentadienes was suggested to contain only the anion-forming isomers. The synthesis was carried out as described above for **1** except that only 8.9 g (50 mmol) of a mixture of the cyclopentadiene isomers was taken for the reaction with 50 mmol of BuLi. The work-up as above yielded a mixture of brown-red crystals of **1** and bright red, poorly crystallizing **2**. These products could not be efficiently separated by fractional crystallization from hexane or toluene. Crystals for X-ray analysis, EI-MS and melting point measurement were picked up from a mixture, crystalline samples of **2** for NMR and IR spectra were also mechanically separated from **1**. Very weak NMR resonances and IR absorption bands of **1** were easily recognized and subtracted. The presence of a very low content of cyclic trinuclear μ-oxo complex [{$TiCl(\eta^5$-C_5Me_4t-Bu)(μ-O)}$_3$] (**4**) was registered by EI-MS spectra after complete evaporation of complex **2**.

Compound **2**. M.p. 215 °C. EI-MS (direct inlet, 70 eV, 150 °C), *m/z* (relative abundance): 610 (13), 608 (21), 606 ($M^{\bullet+}$; 17), 557 (6), 555 ([M – HCl – Me]$^+$; 7), 433 (17), 432 (12), 431 (30), 430 (13), 429 ([M – Cp′]$^+$; 25), 281 (7), 279 (9), 178 (40), 177 ([Cp′]$^+$; 100), 162 ([Cp′ – Me]$^+$; 39), 135 (8). ^{1}H NMR ($CDCl_3$): 1.45 (s, 9 H, C**Me**$_3$); 2.26, 2.53 (2 × s, **Me**Cp, 2 × 6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 14.1, 17.6 (**Me**Cp); 31.8 (C**Me**$_3$); 39.0 (**C**Me$_3$); 133.6, 136.7, 146.9 (Cp). IR (KBr): 3009 (w), 2973 (m), 2952 (m), 2915 (w,b), 1475 (w), 1386 (w), 1367 (w), 1233 (w), 1195 (vw), 1040 (w), 1025 (w), 731 (vs), 669 (s), 625 (w), 503 (w), 450 (m), 417 (w).

Impurity [{$TiCl(C_5Me_4t$-Bu)(μ-O)}$_3$]. EI-MS (direct inlet, 70 eV, 250 °C), *m/z* (relative abundance): 832 (12), 831 (9), 830 (12), 828 ($M^{\bullet+}$; 9), 657 (13), 656 (22), 655 (49), 654 (53), 653 (100), 652 (65), 651 ([M – Cp′]$^+$; 95), 650 (35), 649 (27), 191 (14), 177 ([Cp′]$^+$; 53), 162 ([Cp′ – Me]$^+$; 20), 161 (12), 147 ([Cp′ – 2 Me]$^+$; 12), 57 (14).

Preparation of [$TiCl_3(\eta^5$-C_5Me_4t-Bu)] (**3**)

Compound **1** 0.472 g (1.00 mmol) was degassed, 0.1 M solution of $TiCl_4$ in toluene (10 ml) was added, and the mixture was sealed by flame in an ampule equipped with a magnetically breakable seal. This was heated to 140 °C for 5 h. After cooling to ambient temperature, all volatiles were evaporated in vacuum at 60 °C, and the residue was extracted with hexane. The concentrated extract afforded orange crystals of **3**. Yield 0.48 g (73%).

Compound **3**. M.p. 185 °C. EI-MS (direct inlet, 70 eV, 120 °C), *m/z* (relative abundance): 334 (7), 332 (17), 330 ($M^{\bullet+}$; 18), 317 (11), 315 ([M – Me]$^+$; 11), 297 (7), 296 (21), 295 (11), 294 ([M – HCl]$^+$; 27), 283 (13), 282 (12), 281 (53), 280 (21), 279 ([M – HCl – Me]$^+$; 84),

278 (9), 277 (9), 258 (17), 243 (9), 241 (16), 178 (16), 177 ([Cp′]$^+$; 99), 163 (14), 162 ([Cp′ – Me]$^+$; 100), 161 (17), 147 ([Cp′ – 2 Me]$^+$; 47), 135 (19), 119 (19), 105 (18), 91 (20). ^{1}H NMR (C_6D_6): 1.27 (s, 9 H, C**Me**$_3$); 1.86, 2.25 (2 × s, **Me**Cp, 2 × 6). ^{13}C{^{1}H} NMR (C_6D_6): 14.5, 17.8 (**Me**Cp); 31.3 (C**Me**$_3$); 37.5 (C**Me**$_3$); 135.6, 139.6, 150.3 (Cp). IR (KBr): 2996 (m), 2981 (m), 2964 (s), 2920 (m), 2872 (sh,w), 1480 (m), 1468 (m), 1402 (w), 1379 (s), 1230 (m), 1193 (vw), 1038 (w), 1020 (m), 737 (w), 673 (vw), 503 (w), 458 (s), 420 (s), 407 (vs). UV-VIS (hexane, 22 °C): 444.

Crystal Structure Analysis of **1**, **2**, and **3**

A brown prism of **1** or a red prism of **2** was mounted on a glass capillary with epoxy cement. A red elongated prism of **3** was inserted into a Lindemann glass capillary in a

TABLE III
Crystal and structure refinement data of compounds **1**, **2**, and **3**

Parameter	**1**	**2**	**3**
Formula	$C_{26}H_{42}Cl_2Ti$	$C_{26}H_{42}Cl_4Ti_2$	$C_{13}H_{21}Cl_3Ti$
Molecular weight	473.40	608.20	331.55
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c* (No. 15)	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)
a, Å	18.2930(5)	9.7430(11)	6.6020(2)
b, Å	8.1490(1)	10.6220(6)	24.230(1)
c, Å	16.5970(4)	15.7320(11)	10.9340(4)
β, °	95.9110(12)	117.085(8)	119.840(3)
V, Å^3; *Z*	2460.95(9); 4	1449.6(2); 2	1517.18(20); 4
D_{calc}, g cm^{-3}	1.278	1.393	1.452
μ, mm^{-1}	0.576	0.937	1.070
Color and habit	brown prism	red prism	red prism
Crystal size, mm^3	0.38 × 0.15 × 0.12	0.68 × 0.61 × 0.36	0.35 × 0.25 × 0.23
T, K	150(2)	293(2)	150(2)
F(000)	1016	636	688
θ_{min}; θ_{max}, °	3.16; 30.09	2.34; 24.92	3.22; 27.46
No. measured diffractions	25077	2611	10952
No. unique diffractions	3609	2460	3435
No. observed diffractions[a]	2905	2257	2671
No. of parameters	139	158	161
R; *wR*(F^2) obs. diffractions	0.0342; 0.0804	0.0316; 0.0865	0.0452; 0.1136
R(*F*); *wR*(F^2) all data	0.0489; 0.0879	0.0354; 0.0907	0.0648; 0.1253
GooF (F^2), all data	1.030	1.081	1.079
Δρ, e Å^{-3}	0.405; –0.436	0.541; –0.370	0.629; –0.589

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

glovebox. Diffraction data for **1** and **3** were collected on a Nonius KappaCCD diffractometer with CCD area detector at 150(2) K, and those for **2** on an Enraf–Nonius CAD-4 MACH III diffractometer using graphite-monochromatized MoKα radiation (λ 0.71069 Å) at room temperature. The structures were solved by direct methods (SIR-92)[39]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Refinement by full-matrix least-squares on F^2 was performed using the SHELXL97 program[40]. Crystallographic data, details of their collection and the structure refinement are given in Table III. CCDC 273645 (for **1**), 273644 and (for **2**) 273646 (for **3**) 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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