Reduction of Bis[η^5-(ω-alkenyl)tetramethylcyclopentadienyl]titanium Dichlorides: An Efficient Synthesis of Long-Chain *ansa*-Bridged Titanocene Dichlorides by Acidolysis of Cyclopentadienyl-Ring-Tethered Titanacyclopentanes

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Dedicated to Professor Karl-Heinz Thiele on the occassion of his 70th birthday

Abstract: The reduction of symmetric, fully-substituted titanocene dichlorides bearing two pendant ω-alkenyl groups, $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$, R = CH(Me)CH=$CH_2$ (**1a**), $(CH_2)_2CH{=}CH_2$ (**1b**) and $(CH_2)_3CH{=}CH_2$ (**1c**), by magnesium in tetrahydrofuran affords bis(cyclopentadienyl)titanacyclopentanes $[Ti^{IV}\{\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}C_5Me_4CH(Me)CH(Ti)CH_2CH(CH_2\text{-}(Ti))CH(Me)C_5Me_4\}]$ (**2a**), $[Ti^{IV}\{\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_2CH(Ti)(CH_2)_2CH(Ti)\text{-}(CH_2)_2C_5Me_4\}]$ (**2b**) and $[Ti^{IV}\{\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_2CH(Ti)CH(Me)CH(Me)\text{-}CH(Ti)(CH_2)_2C_5Me_4\}]$ (**2c**), respectively, as the products of oxidative coupling of the double bonds across a titanocene intermediate. For the case of complex **1c**, a product of a double bond isomerisation is obtained owing to a preferred formation of five-membered titanacycles. The reaction of the titanacyclopentanes with $PbCl_2$ recovers starting materials **1a** from **2a** and **1b** from **2b**, but complex **2c** affords, under the same conditions, an isomer of **1c** with a shifted carbon–carbon double bond, $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CHMe)\}_2]$ (**1c′**). The titanacycles **2a–c** can be opened by HCl to give *ansa*-titanocene dichlorides *ansa*-$[\{\eta^5{:}\eta^5\text{-}C_5Me_4CH(Me)\text{-}CH_2CH_2CH(Me)CH(Me)C_5Me_4\}TiCl_2]$ (**3a**), *ansa*-$[\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}\text{-}TiCl_2]$ (**3b**), along with a minor product *ansa*-$[\{\eta^5{:}\eta^5\text{-}C_5Me_4CH_2CH{=}CH(CH_2)_5\text{-}C_5Me_4\}TiCl_2]$ (**3b′**), and *ansa*-$[\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_3CH(Me)CH(Me)CH{=}CH\text{-}CH_2C_5Me_4\}TiCl_2]$ (**3c**), respectively, with the bridging aliphatic chain consisting of five (**3a**) and eight (**3b**, **3b′** and **3c**) carbon atoms. The course of the acidolysis changes with the nature of the pendant group; while the cyclopentadienyl ring-linking carbon chains in **3a** and **3b** are fully saturated, compounds **3c** and **3b′** contain one asymetrically placed carbon–carbon double bond, which evidently arises from the β-hydrogen elimination that follows the HCl addition.

Keywords: metallacycles · NMR spectroscopy · pendant alkenyls · structure elucidation · titanium

Introduction

Pendant alkenyl groups attached to cyclopentadienyl ligands of bent metallocene polymerisation catalysts have a great potential in modifiyng their catalytic properties. The alkenyl groups can anchor counter anions based on either $[MeAlO]_x$ (MAO) or $B(C_6F_5)_3$ co-catalysts[1] or undergo a clean hydroboration with $HB(C_6F_5)_2$.[2] They may compete for free coordination sites at the cationic polymerisation centre[3] and can also be used for immobilisation of the catalyst by copolymerisation with the formed polymer or by grafting onto a suitable polymer.[4] With respect to the knowledge accumulated on the structure of the efficient polymerisation catalysts,[5] the alkenylcyclopentadienyl complexes so far studied from the point of view of a potential catalytic application in polymerisation of ethene possessed low-substituted cyclopentadienyl ligands. However, fully substituted (3-butenyl)-tetramethylcyclopentadienyl ligands, although decreasing the Lewis acidity of the metal atom due to electron-donating effect of its hydrocarbyl groups, showed an ability to interact with transition metals by both carbon–carbon double bonds and cyclopentadienyl ligands.[6] Bis[(1-alkylethenyl)cyclopentadienyl]zirconium dichlorides were also used for the syn-

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thesis of cyclobutane-bridged *ansa*-metallocene complexes by a photo-induced [2+2] cycloaddition.[7] Very recently, 1-(dialkylamino)-1,3-butadien-1,3-diyl *ansa*-bridged Group 4 metallocenes were obtained by a Mannich type coupling from bis{1-(dialkylamino)ethenyl}metallocene dichlorides and were also tested for catalytic activity towards alkene polymerization.[8] In titanocene chemistry, a number of titanium derivatives including $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}_2]$ have been prepared and the crystal structure of the dimethyl derivative $[TiMe_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}_2]$ was determined.[9] However, interaction of the pendant double bond(s) with the titanium atom in all the Ti^{IV} complexes synthesized has not yet been reported.

Herein we report about the behaviour of pendant double bonds in a homologous series of bis(ω-alkenyl) titanocene dichlorides $[TiCl_2(\eta^5\text{-}Cp''R)_2]$ ($Cp'' = C_5Me_4$; R = 1-methyl-2-propenyl, CH(Me)CH=CH_2 (**1a**), 3-butenyl, $(CH_2)_2CH{=}CH_2$ (**1b**) and 4-pentenyl $(CH_2)_3CH{=}CH_2$ (**1c**)) during their reduction by magnesium and the use of the products obtained in the synthesis of *ansa*-titanocene dichlorides with five- and eight-membered aliphatic bridging chains.

Results and Discussion

Bis[(ω-alkenyl)tetramethylcyclopentadienyl]titanium dichlorides $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH(Me)CH{=}CH_2)\}_2]$ (**1a**), $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}_2]$ (**1b**) and $[TiCl_2\{\eta^5\text{-}C_5Me_4\text{-}(CH_2CH_2CH_2CH{=}CH_2)\}_2]$ (**1c**) were synthesised using the protocol reported by Okuda, du Plooy and Toscano[9] for **1b**, except that the reaction of the corresponding alkenylcyclopentadienyl lithium with $[TiCl_3(THF)_3]$ was carried out in THF and not in 1,2-dimethoxyethane. The use of THF may account for noticeably lower isolated yields of **1a** (39%) and **1b** (45% vs. reported yield of 60%[9]). Yet the lower yield of **1c** (21%) was also brought about by a very high solubility of the complex in the attempted solvents (hexane, ethanol). The dark red compounds **1a**–**c** are stable in air in the solid state for at least one year. Their solution NMR spectra are, in accordance with NMR data for **1b**,[9] indicative of C_2 or mirror symmetry of the molecules with all resonances observed in the expected region. There is also no sign of any interaction of the alkenyl groups with the metal atom in the NMR spectra. The presence of two independent chiral centres in **1a** leads to the duplication of ^1H and ^{13}C NMR signals due to the formation of diastereoisomers (*R,S*), (*S,R*) and (*R,R*), (*S,S*); the resonances of the methyl groups on the cyclopentadienyl rings are diastereotopic and significantly anisochronic in both ^1H and ^{13}C NMR spectra owing to their proximity to the *C*-chiral centre in the side chain of the cyclopentadienyl ligand. Unfortunately, the ^1H NMR resonances of **1a** are not separated enough to classify the signals into two groups due to the diastereoisomers. In the EI-MS spectra, titanocene dichlorides **1a**–**c** exhibit only poorly abundant molecular ions, the fragmentation patterns being dominated by $[M - Cl]^+$, $[M - Cp''R]^+$ and $[Cp''R]^+$ ions. Their infrared spectra show intense absorption bands of non-coordinated terminal double bond at about 1635 and 3065 cm^{-1}.

The solid-state structure of **1a** (Figure 1, Table 1) resembles in all respects the structures of other related titanocene dichlorides. Both bond lengths and angles within the titanocene part of the molecule are unexceptional when compared with, for example, $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$,[10a] $[TiCl_2(\eta^5\text{-}C_5Me_4Ph)_2]$[10b] or $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$.[10c] As the titanium atom resides in a special position, the molecule has C_2 symmetry due to the crystallographically imposed symmetry. The dihedral angle of the least-squares cyclopentadienyl planes of 41.6(1)° is similar to that of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$ (39.8°) but lower than that in $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ (44.6°) and $[TiCl_2(\eta^5\text{-}C_5Me_4Ph)_2]$ (45.6°). The conformation of the cyclopentadienyl rings is about half-way between eclipsed and staggered. The methylpropenyl group adopts an almost perfectly planar arrangement as indicated by the dihedral angle C(9)-C(6)-C(7)-C(8) of 1.7(7)° and its geometry corresponds well to the average values reported for "purely" organic compounds.[11] The least-squares planes of cyclopentadienyl and methylpropenyl moieties are mutualy rotated at an angle of 84.5(4)°, and the methylpropenyl plane is bent outwards the open side of the bent metallocene moiety. The crystal structure of **1a** also confirms the absence of any bonding between the double bonds and the titanium atom of their own or a neighbouring molecule.

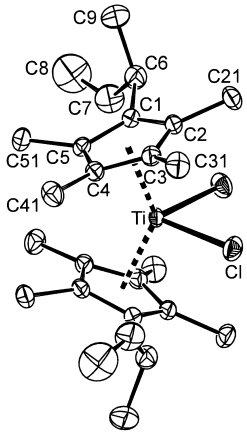

Figure 1. Molecular structure of **1a** with 30% probability thermal ellipsoids and the atom numbering scheme. For clarity all hydrogen atoms are omitted. The non-labelled atoms are generated by the symmetry operation $(-x, y, 1/2 - z)$.

Table 1. Selected bond lengths [Å], bond angles, torsion angles and dihedral angles of least-squares planes [°] for **1a**.[a]

Ti–Cl	2.356(1)	Cl-Ti-Cl^i	89.44(6)
C1–C6	1.523(5)	C1-C6-C7	115.0(3)
C6–C7	1.497(5)	C1-C6)-C9	108.5(3)
C6–C9	1.559(5)	C7-C6-C9	115.4(3)
C7–C8	1.288(6)	C6-C7-C8	127.6(5)
C1-C6-C7-C8	125.8(5)	C9-C6-C7-C8	1.7(7)
C1-CE-CE^i-C1^i	161.3(3)		
Titanocene moiety			
Ti–C(ring)	2.420(3) – 2.474(3); av. 2.445(3)		
Ti–CE	2.129(3)	CE–CE	3.971(3)
C–C(ring)	av. 1.413(4)	∢ ring,ring	41.6(1)
C(ring)–Me	av. 1.503(4)	∢ ring,Ti-Cl-Cl^i	20.8(1)
C-C-C(ring)	av. 1.08.0(3)	CE-Ti-CE	137.6(1)

[a] Symmetry transformation used to generate equivalent positions *i*: $-x, y, 1/2 - z$.

Cyclopentadienyl-ring-tethered titanacyclopentanes: The reduction of **1a**–**c** by magnesium metal in THF afforded complexes **2a**–**c**, respectively, which all were found to possess titanacyclopentane rings linking the tetramethylcyclopentadienyl ligands (see Scheme 1). The titanacycles are thermally

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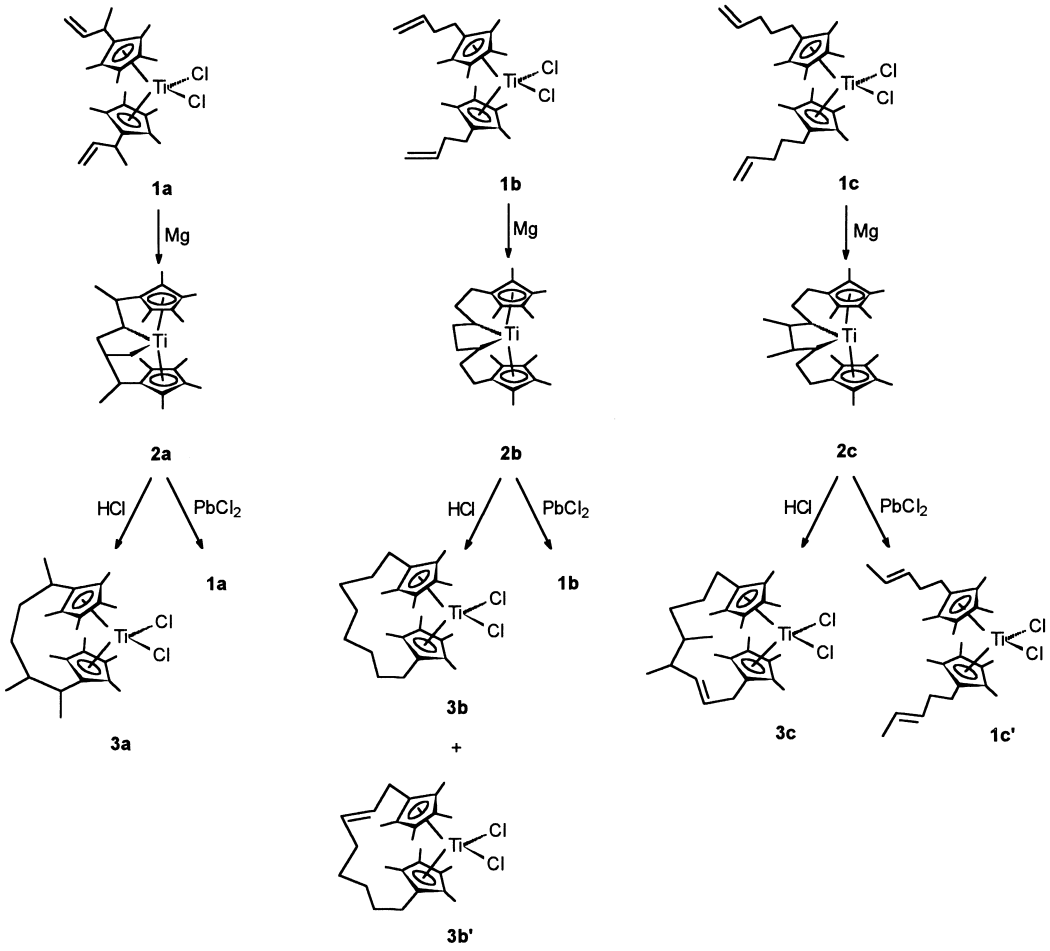

Scheme 1. Reductions of bis[η^5-(ω-alkenyl)tetramethylcyclopentadienyl]titanium dichlorides **1a–c** to titanacyclopentanes **2a–c** and their reactions with HCl and $PbCl_2$.

robust; compounds **2c** and **2b** melt without an apparent decomposition at 74 and 127 °C, respectively, whilst **2a** does not melt up to 260 °C. Upon electron ionisation (70 eV) in a mass spectrometer, they do not fragment, showing only molecular ions. Although the signals in the ^{1}H NMR spectrum of the simplest compound **2b** are observed in the expected region, the spectrum is less informative due to ill-resolved or overlapped (or both) multiplets. In ^{13}C NMR spectra, however, the δ_C values of 30.1 (TiCH*C*H_2) and 78.4 (Ti*C*HCH_2) for **2b** compare well with those reported for analogous compounds *cyclo*-[{(η^5-C_5Me_5)$_2$Ti}$(CH_2)_4$][12] and bis(aryloxide), *cyclo*-[{$(ArO)_2$Ti}$(CH_2)_4$][13]—mainly when one considers the influence of the 1,2-ethanediyl bridges on the δ_C value of C_α carbon atoms. The NMR data of **2b** are also in keeping with the results of X-ray analysis, indicating a C_2 (or mirror) symmetrical structure. According to the NMR spectra, the structure of **2c** differs from that of **2b** only by the presence of methyl group on each of the two C_β carbon atoms of the titanacyclopentane moiety. This is the result of a double bond isomerisation that takes place during the reduction of **1c**, thus giving rise to a thermodynamically stable species with five-membered titanacycle. The NMR spectra of **2a** are relatively complicated due to the presence of two diastereoisomers in a statistical 1:1 ratio. Nonetheless, the two sets of ^{1}H and ^{13}C NMR signals were separated from each other by means of two-dimensional NMR techniques.

It is worth noting that although the reductive cyclisation of **1a** to **2a** creates a new chirality centre, that is, the titanium atom itself, the NMR spectra of **2a** exhibit only two sets of signals. This reflects very likely a flexibility of the titanocene moiety that precludes the formation of further diastereoisomers, thus rendering the metal-based chirality simplex virtually optically inactive. The assignment of the signals indicates a $C_\alpha C_\beta$ disubstitution on the TiC_4 ring, that is, a head-to-tail linkage of the double bonds, different from a $C_\alpha C_\alpha$ disubstitution in **2b** and **2c**. Although the ^{13}C NMR resonances of methine and methylene groups directly σ-bonded to the titanium in **2a** are found within the expected region, their signals in ^{1}H NMR spectra are remarkably up-field shifted relative to **2b** and **2c**. This shift should rather be attributed to an anisotropy of NMR shielding of the titanocene framework than to an agostic interaction between titanium and Ti*C*H or Ti*C*H_2, since both Ti–H distances of about 2.7 Å are longer (by around 0.4 Å) than those in an α-agostic complex [$TiMeCl_3(Me_2PCH_2CH_2PMe_2)$] and a β-agostic complex [$TiEtCl_3(Me_2PCH_2CH_2PMe_2)$].[14]

The structure proposed for **2a** was corroborated by the X-ray diffraction analysis, which, although with relatively

poor data, allowed us to prove unequivocally the assigned structure (Figure 2). The structure suffers from a statistical disorder since the four stereoisomers, which differ only in the configuration on the carbon atom adjacent to the cyclopentadienyl ring, are packed in a racemic crystal as one

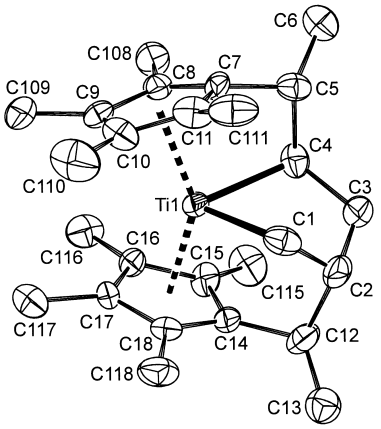

Figure 2. Crystal structure of **2a** drawn at the 30% probability level. Only one position of the disordered C(13) is shown. Selected geometric parameters: Ti(1)-C(1) 2.19(1), Ti(1)-C(4) 2.18(1), C(1)-C(2) 1.55(2), C(2)-C(3) 1.50(2), C(3)-C(4) 1.52(2) Å; C(1)-Ti-C(4) 73.8(5), Ti-C(1)-C(2) 102.1(8), Ti-C(4)-C(3) 111.0(8), C(1)-C(2)-C(3) 107(1), C(2)-C(3)-C(4) 111(1)°; C(1)-C(2)-C(3)-C(4) −33(1)°; ∢Cp1, Cp2 30.6(5)°, ∢Cp1, TiC(1)C(4) 18.3(6)°, ∢Cp2, TiC(1)C(4) 19.8(7)°; Cp1: C(7)−C(11), Cp2: C(14)−C(18).

species. Although the chemical picture is unequivocal, the disorder of the methylpropenyl methyl groups (see Experimental Section) lowers the overall precision of the structure determination and the structural parameters will not be discussed here in detail.

Crystal structure of 2b: According to a search in the Cambridge Structural Database (1999 release),[15] the structure of **2b** (Figure 3, Table 2) represents the first example of structurally characterized simple bis(η^5-cyclopentadienyl)titanacyclopentane with no further ring systems (either spiro cyclic[16] or *ortho* annelated[17]) or without any reactive

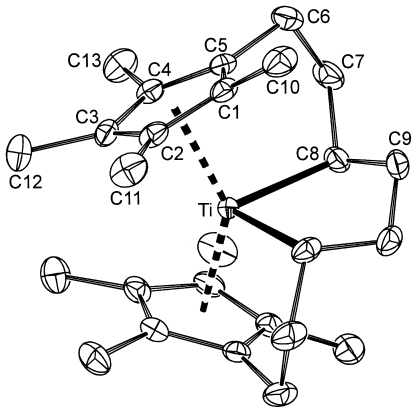

Figure 3. Molecular structure of **2b** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level; all hydrogen atoms are omitted for clarity. The non-labelled atoms are generated by the symmetry operation $(-x, y, 1/2-z)$.

Table 2. Selected bond lengths [Å], bond angles, torsion angles and dihedral angles of least-squares planes [°] for **2b**.[a]

Ti−C8	2.208(2)	C8-Ti-C8^i	86.4(1)
C8−C9	1.526(4)	C9-C8-C7	113.7(2)
C8−C7	1.533(3)	Ti-C8-C9	102.8(2)
C9−C9^i	1.533(6)	Ti-C8-C7	115.1(2)
C7−C6	1.527(4)	C8-C9-C9^i	112.7(2)
C6−C5	1.499(3)	C6-C7-C8	110.3(2)
		C5-C6-C7	109.0(2)
Ti-C8-C9-C9^i	39.0(3)	C8^i-Ti-C8-C9	−13.2(2)
C8-C9-C9^i-C8^i	−56.8(3)	C8-C7-C6-C5	−-84.4(3)
C5-CE-CE^i-C5^i	102.4(2)		
Titanocene moiety			
Ti−C(ring)	2.396(2)-2.482(2); av. 2.44(5)		
Ti−CE	2.120(1)	CE−CE	3.991(1)
C−C(ring)	av. 1.414(6)	∢ ring,ring	40.7(5)
C(ring)−Me	av. 1.503(4)	∢ ring,Ti-C8-C8^i	21.3(7)
C-C-C(ring)	av. 108.0(3)	CE-Ti-CE	140.3(1)

[a] Symmetry transformation used to generate equivalent positions i: $-x, y, 1/2-z$.

functionality attached to the titanacycle (e.g., imino group[18]). Bis(2,6-diphenylphenoxy-κO)titanacyclopentane[13] appears to be the most closely related compound whose solid-state structure is known. Complex **2b** crystallises with the symmetry of the *C*2/*c* space group, so that the crystallographic twofold axis passes through the titanium atom and the midpoint of the C(2)-C(2^i) bond (i position: $x, -y, 1/2-z$). This makes only one half of the molecule crystallographically independent. Molecule of **2b** is chiral but related to its centrosymmetric counterpart in a racemic crystal. The bond lengths within the titanacycle fall into the range reported for four analogous compounds:[13, 16–18] Ti−C_α 2.06–2.19, C_α−C_β 1.49–1.54 and C_β−C_β 1.51–1.65 Å, respectively, thus confirming the assumed titanacylopentane-like structure. The C(1)-Ti-C(1^i) angle of 86.4(1)° also compares well with the value of 85.6° reported for the mentioned bis(phenoxide) complex[13] (cf. range 81–89° for all the four examples). As for the titanocene moiety, the mutual conformation of the cyclopentadienyl rings is dictated by the molecular symmetry and by conformational flexibility of the CH_2CH_2 linking groups: looking along the centroid–centroid line, the rings appear half-way between the eclipsed and staggered conformations. The dihedral angle of the least-squares cyclopentadienyl planes of 40.7(5)° is very similar to that reported for the decamethyltitanocene-alkyne complex [Ti(η^5-C_5Me_5)$_2$(η^2-$Me_3SiC{\equiv}CSiMe_3$)], 41.1°;[19] this shows that no unexceptional steric strain arises from the linkage of the titanacycle to the tetramethylcyclopentadienyls in the structure of **2b**. To reduce steric hindrance, the methyl groups are bent outwards from the metal centre with their perpendicular distance to the cyclopentadienyl least-squares plane ranging from 0.05(2) to 0.37(2) Å.

The crystal structure of **2c** resembles very closely that of **2b**, exhibiting a crystallographically inherent C_2 symmetry (Table 3, Figure 4). As the result of double-bond shift, the titanacycle has a methyl group attached to each of the two equatorial C_β atoms. The titanacyclopentane unit is tethered to the cyclopentadienyl ligands in such a way that the cyclopentadienyl carbon atoms bearing the linking chains are rotated at an angle of 101.6(6)° in **2c** and 102.4(2)° in **2b**

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Table 3. Selected bond lengths [Å], bond angles, torsion angles and dihedral angles of least-squares planes [°] for **2c**.[a]

Ti–C8	2.215(4)	C8–C9	1.537(5)
C9–C10	1.534(5)	C9–C9^{i}	1.550(8)
C7–C8	1.533(5)	C6–C7	1.538(6)
C1–C6	1.497(5)		
Ti-C8-C9	104.8(2)	Ti-C8-C7	113.7(3)
C8-C9-C9^{i}	111.5(3)	C7-C8-C9	113.7(3)
C6-C7-C8	110.1(4)	C8-C9-C10	110.9(3)
C1-C6-C7	109.6(4)	C8-Ti-C8^{i}	84.9(2)
Ti-C8-C9-C10	162.9(3)	C6-C7-C8-C9	71.4(4)
C8-C9-C9^{i}-C8^{i}	55.4(4)	C1-CE-CE^{i}-C1^{i}	101.9(4)
Titanocene moiety			
Ti–C(ring)	2.376(5)-2.485(5); av. 2.437(5)		
Ti–CE	2.121(4)	CE–CE	3.988(5)
C–C(ring)	av. 1.407(8)	⩝ ring,ring	41.1(1)
C(ring)–Me	av. 1.507(8)	⩝ ring,Ti-C8-C8^{i}	21.5(3)
C-C-C(ring)	av. 108.0(5)	CE-Ti-CE	140.2(2)

[a] Symmetry transformation used to generate equivalent positions *i*: $-x, y, 1/2-z$.

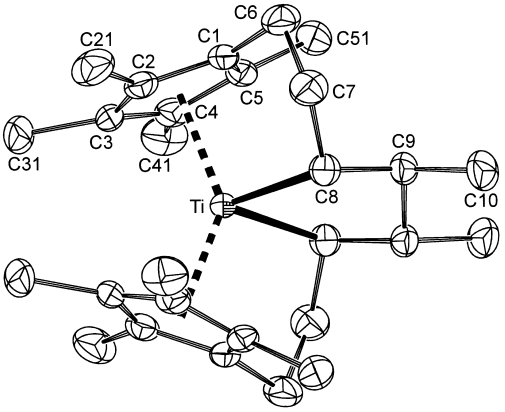

Figure 4. Molecular structure of **2c** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level; all hydrogen atoms are omitted for clarity. The non-labelled atoms are generated by the symmetry operation $(1/2-x, -y, z)$.

(torsion angle C-CE-CE^{i}-C^{i} is given; CE = centroid of the cylopentadiene ring). The angle between the least-squares planes of the cyclopentadienyl rings is 41.1(1)° in **2c** and 40.7(5)° in **2b**, but only 30.6(5)° in **2a**. An unusually low value of this angle points to the reason why the titanium atom in **2a** binds to one terminal and one internal atom of the double bonds; binding to both internal carbon atoms, as it is in **2b**, would lead to a close to parallel orientation of the cyclopentadienyl rings which is apparently energetically less favourable. It is also worth noting that all the titanacycles **2a–c** adopt an almost perfect or even ideal half-chair conformation due to crystallographically imposed symmetry (**2b**, **2c**) as follows from an inspection of ring-puckering coordinates:[20] **2a**, $Q_2 = 0.71(1)$ Å and $\varphi_2 = 204(1)°$ (for ring defined as Ti-C(1)-C(2)-C(3)-C(4); $\varphi_2 = 198°$ for an ideal half-chair conformation); **2b**, $Q_2 = 0.438(3)$ Å and $\varphi_2 = 90.0(3)°$ (ring defined as Ti-C(8)-C(9)-C(9^{i})-C(8^{i}); φ_2 is identical with the ideal value of 90° for symmetry reasons); **2c**, $Q_2 = 0.442(4)$ Å and $\varphi_2 = 270.0(5)°$ (ring defined as Ti-C(8)-C(9)-C(9^{i})-C(8^{i}); φ_2 does not differ from the ideal value 270° because of the imposed symmetry).

With regard to the high thermal stability of **2a–c**, it is somewhat surprising that a reverse process of the titanacycle formation is also feasible. Chlorination of **2a** and **2b** by $PbCl_2$[21] in THF recovered tinanocene dichlorides **1a** and **1b**, while the opening of **2c** affords the thermodynamically more stable isomer $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CHMe)\}_2]$ (**1c′**) with the double bond shifted from the terminal position and in an *E* configuration. All these products were isolated in a crystalline form and identified by means of spectroscopic methods. Moreover, the structure of **1c′** was determined by single-crystal X-ray crystallography. The molecule of **1c′** (Figure 5, Table 4) shows a titanocene skeleton practically

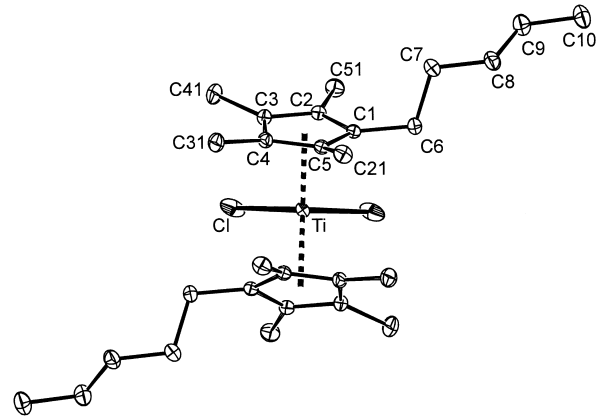

Figure 5. Molecular structure of **1c′** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level; all hydrogen atoms are omitted for clarity. The non-labelled atoms are generated by the symmetry operation $(1-x, y, 3/2-z)$.

Table 4. Selected bond lengths [Å], bond angles, torsion angles and dihedral angles of least-squares planes [°] for **1c′**.[a]

Ti–Cl	2.3458(6)	Cl-Ti-Cl^{ii}	93.52(4)
C1–C6	1.500(2)	C1-C6-C7	111.0(2)
C6–C7	1.538(3)	C6-C7-C8	113.2(2)
C7–C8	1.490(3)	C7-C8-C9	126.2(2)
C8–C9	1.313(3)	C8-C9-C10	125.2(2)
C9–C10	1.487(3)		
C1-C6-C7-C8	177.5(2)	C7-C8-C9-C10	176.6(2)
C6-C7-C8-C9	123.6(2)	C1-CE-CE^{ii}-C1^{ii}	175.1(2)
Titanocene moiety			
Ti–C(ring)	2.418(2)-2.479(2); av. 2.444(2)		
Ti–CE	2.126(2)	CE–CE	3.965(2)
C–C(ring)	av. 1.416(2)	⩝ ring,ring	44.01(6)
C(ring)–Me	av. 1.501(2)	⩝ ring,Ti-Cl-Cl^{ii}	22.02(6)
C-C-C(ring)	av. 108.0(2)	CE-Ti-CE	137.6(1)

[a] Symmetry transformation used to generate equivalent positions *ii*: $1-x, y, 3/2-z$.

identical to that of **1a**. A difference is observed in the Cl-Ti-Cl^{ii} angles (ii position: $1-x, y, 3/2-z$) and in the angles between the least-squares planes of the cyclopentadienyl rings, which are both larger by approximately 3° than in **1c′**. This is apparently a consequence of the crystal packing effects that cause the pendant alkenyl substituents to divert more than in **1a** (dihedral angle at the centroid–centroid line is

175.1(2)° in **1c′** and 161.3(3)° in **1a**). And again, the CE-Ti-CE angles amount equally to 137.6(1)° in both **1c′** and **1a**.

As heating to 60 °C for 8 h is necessary to complete the chlorination, it can be concluded that the withdrawal of "formerly d^2 electrons" from the titanacycle by oxidation with $PbCl_2$ requires a higher activation energy than analogous oxidation of titanocene Ti^{III} or Ti^{II} derivatives, which proceeds rapidly at room temperature.[21] This is in agreement with the fact that the reductive cleavage is apparently favoured by compounds with a relatively high electron density at the titanium atom, for example, complexes with carbyl-substituted cyclopentadienyl ligands. For instance, the carbonylation of *cyclo*-[Ti(η^5-$C_5Me_5)_2(CH_2)_4$] cleanly affords [Ti(η^5-$C_5Me_5)_2(CO)_2$] and ethene[12], whereas the non-methylated analogue *cyclo*-[Ti(η^5-$C_5H_5)_2(CH_2)_4$] undergoes an insertion of CO to yield cyclopentanone and [Ti(η^5-$C_5H_5)_2(CO)_2$].[22]

***ansa*-Bridged titanocene dichlorides**: Addition of excess hydrogen chloride to **2a–c** affords *ansa*-bridged titanocene dichlorides. The products and, hence, the mechanism of this acidolysis depend on the nature of the parent titanacycle. Addition of two molecules of HCl to **2a** gives cleanly *ansa*-[{η^5:η^5-$C_5Me_4CH(Me)CH_2CH_2CH(Me)CH(Me)C_5Me_4$}$TiCl_2$] (**3a**), which contains a saturated five-membered bridge as the expected product of the scission of two Ti–C bonds. Similarly to **2a**, the symmetry of the molecule of **3a** is very low owing to the presence of independent chirality centres.

In the case of **2b**, the same titanacycle-opening reaction gave a mixture of two new complexes in approximately a 5:2 ratio. The major component (**3b**) was obtained in a pure form by crystallisation from a toluene solution of the crude product while the minor, more soluble product (**3b′**) was not isolated. Compound **3b** was identified to be *ansa*-[{η^5:η^5-C_5Me_4-$(CH_2)_8C_5Me_4$}$TiCl_2$] on the basis of its NMR spectra, which displayed only one half of the principal signals as the consequence of flexibility of the 1,8-octanediyl linking group, resulting in an overall C_2 or σ symmetry of the molecule in solution. The structure of **3b** in the solid state was also confirmed by the X-ray diffraction analysis (see below). The minor component **3b′** was characterised directly in the reaction mixture by NMR spectroscopy and identified as an unsaturated analogue of the major component, that is, *ansa*-[{η^5:η^5-$C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4$}$TiCl_2$]. The ^{1}H NMR spectra of **3b′** are less informative due to an extensive overlap of the CH_2 multiplets with those of **3b**; however, a comparison of ^{13}C and ^{1}H NMR data allowed us to identify the position of the double bond in the cyclopentadienyl-linking aliphatic chain. The reaction pathway leading to **3b′** became the only one in the case of **2c**, whereby an analogous titanacycle opening by HCl afforded exclusively an asymmetrical bridge-unsaturated complex, *ansa*-[{η^5:η^5-$C_5Me_4(CH_2)_3CH(Me)CH(Me)CH{=}CHCH_2C_5Me_4$}$TiCl_2$] (**3c**) as follows from spectral and analytical data. In both the systems which afforded unsaturated *ansa*-complexes **3b′** and **3c**, gaseous hydrogen was liberated. This indicates that unlike formation of **3a** and **3b**, in which the Ti–C bonds are cleanly cleaved by HCl, compounds **3b′** and **3c** are formed by the above acidolysis combined with a β-hydrogen elimination reaction. However, it is amazing that **2b** and **2c**, which have the same skeleton of the titanacycle, differ so much by the abundance of the β-hydrogen elimination pathway. It appears evident that the presence of methyl group on the fourth carbon atom of the *ansa*-chain has a promoting effect on the formation of the double bond in the allylic position with respect to the cyclopentadienyl ligand.

Crystal structure of 3b: In contrast to more symmetrical complexes mentioned above, a poor packing of a voluminous and partially mobile eight-membered *ansa*-carbon chain renders the whole molecule of complex **3b** crystallographically independent. Nevertheless, the geometry of titanocene dichloride framework (Figure 6, Table 5) does not differ from

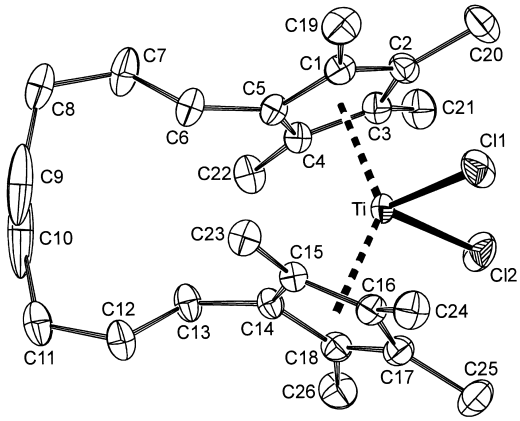

Figure 6. Perspective view of the molecular structure of **3b** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level. For clarity, all hydrogen atoms are omitted.

Table 5. Selected bond lengths [Å], bond angles, torsion angles and dihedral angles of least-squares planes [°] for **3b**.[a]

Ti–Cl1	2.3493(8)	Cl1-Ti-Cl2	93.81(4)
Ti–Cl2	2.3483(9)	C5-C6-C7	116.4(2)
C5-C6	1.507(4)	C6-C7-C8	113.0(3)
C6-C7	1.520(4)	C7-C8-C9	115.7(3)
C7-C8	1.527(5)	C8-C9-C10	107.2(5)
C8-C9	1.741(8)	C9-C10-C11	106.2(5)
C9-C10	1.336(8)	C10-C11-C12	116.3(3)
C10-C11	1.66(1)	C11-C12-C13	112.9(3)
C11-C12	1.512(5)	C12-C13-C14	115.6(2)
C12-C13	1.523(4)		
C13-C14	1.509(4)		
C5-C6-C7-C8	168.2(3)	C9-C10-C11-C12	68.2(6)
C6-C7-C8-C9	47.3(4)	C10-C11-C12-C13	44.1(5)
C7-C8-C9-C10	67.2(5)	C11-C12-C13-C14	169.2(3)
C8-C9-C10-C11	157.9(4)	C5-CE1-CE2-C14	42.1(3)
Titanocene moiety			
Ti–C(ring)	2.432(3)-2.490(3); av. 2.457(3)	∢ ring1,ring2	43.9(1)
Ti–CE(1,2)	2.140(3), 2.140(3)	CE1–CE2	3.994(3)
C–C(ring)	av. 1.419(4)	∢ ring1,Ti-Cl1-Cl2	21.8(1)
C(ring)–Me	av. 1.502(4)	∢ ring2,Ti-Cl1-Cl2	22.15(4)
C-C-C(ring)	av. 108.0(2)	CE1-Ti-CE2	137.9(1)

[a] Ring1: C(1)-C(5), ring2: C(14)-C(18).

those of **1a** or **1c′**, giving virtually identical values of the CE-Ti-CE and Cl-Ti-Cl angles as well as of the angles between least-squares cyclopentadienyl planes. The *ansa*-chain is attached close to the hinge position of the titanocene cyclo-

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pentadienyls so that the corresponding carbon atoms of the cyclopentadienyl rings are mutually rotated by only 42.1(3)° with respect to the centroid–centroid interconnection. It indicates that a sufficiently long carbon chain does not impose a steric hindrance on the cyclopentadienyl ligands larger than that of the methyl groups. Two central carbon atoms of the *ansa*-chain are partly disordered, reflecting that the flexibility of the *ansa*-bridge observed in solution is partially retained even in the solid state.

All the compounds **3a–c** are unique, since no similar *ansa*-bridged bent metallocene dichlorides with aliphatic bridge of comparable length are known except for *ansa*-bis(indenyl)-zirconium dichloride with 1,12-dodecanediyl bridging chain.[23] However, despite high dilution, both *rac*- and *meso*-forms of this compound were obtained in only 15% and 11% yields by the metathesis of 1,12-bis(lithioindenyl)-dodecane with $ZrCl_4$ in THF and toluene, respectively. Among other *ansa*-metallocenes prepared by the methatetical approach, *ansa*-titanocene dichlorides with a trimethylene bridge were obtained in a maximum 11% yield[24] and those with the $SiMe_2CH_2CH_2SiMe_2$ chain in 23% yield.[25] The effect of mobility of the *ansa*-linking chain on the yield of mononuclear metallocene complexes is even more pronounced in the series of ferrocenophanes with three, four and five bridging methylene groups that were synthesized in 2.5, 0.053 and 0.025% yields by metathesis of bis(sodiocyclopentadienyl) derivative with $FeCl_2$.[26] The only *ansa*-titanocene dichlorides with relatively long C_4 and C_6 bridges obtained in good yields contain a semi-rigid spacer derived from, for example, biphenyl,[27] 9,10-ethanoanthracene[28] or binaphthyl,[29] which directs the corresponding dimetallated bis(cyclopentadienyl) ligands into a position suitable for the subsequent reaction with one molecule of metal halide.

Conclusion

The magnesium-mediated reductive coupling of the pendant double bonds in bis(ω-alkenyltetramethylcyclopentadienyl)-titanium dichlorides **1a–c** affords cleanly titanacyclopentane derivatives **2a–c**. This reaction proceeds very likely via a titanocene intermediate that originates from reductive removal of the chloro ligands. Such an assumption is justified by a good thermal stability of highly carbyl-substituted titanocenes, $[Ti(\eta^5\text{-}C_5Me_5)_2]$,[30] $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_2t\text{-}Bu)\}_2]$[31] and $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2]$[32] and their tendency to react with unsaturated hydrocarbons: the complexes $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}C_2H_4)]$[12] and $[Ti\{\eta^5\text{-}C_5Me_4(SiMe_3)\}_2(\eta^2\text{-}C_2H_4)]$[32] were obtained in a crystalline form and the former was shown to react with excess ethene to give an unstable titanacyclopentane *cyclo*-$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}(CH_2)_4]$.[12]

The titanocene intermediate immediately undergoes an intramolecular oxidative coupling of the pendant double bonds[33] to give thermally robust titanacyclopentanes **2a–c** with the titanacycle linked to the tetramethylcyclopentadienyl ligands. This intramolecular oxidative addition proceeds very cleanly and with high isolated yields. It is evident, that the stability of the titanacycle depends strongly on the number of members within the TiC_n cycle. The exclusive formation of titanacyclopentane compounds from C_3–C_5 alkenyl groups indicates that five-membered cycle is the most stable (at least when linked to the titanocene cyclopentadienyls). To achieve this "magic size" of the titanacycle in **2c**, both double bonds are shifted to the internal position. In the case of **2a**, the double bonds are attached in a mutually opposite way in order to keep the dihedral angle between the least-squares planes of the cyclopentadienyl rings (30.6(5)°) as close as possible to the usual value in bent titanocene compounds (note that this angle varies between 40.7(5)° and 44.0(1)° for all the compounds reported here).

The reaction of titanacycles **2a–c** with $PbCl_2$ recovers **1a** and **1b**, while the position of the shifted double bond is retained in **1c′**. Simple acidolysis of the Ti–C bonds in the titanacycles **2a–2c** affords titanocene dichlorides with five- (from **2a**) and eight-membered (from **2b** and **2c**) *ansa*-bridges. The ring opening of **2a** and **2c** proceeds cleanly to afford bridge-saturated and bridge-unsaturated *ansa*-complexes (**3a** and **3c**, respectively) as the sole products, but a mixture of both products (**3b** and **3b′**) in a 5:2 ratio was obtained from titanacycle **2b**. Such a formation of both aliphatic and olefinic bridging chains from structurally similar precursors still remains rather puzzling although the formation of the latters seems to be satisfactorily explained by a β-hydrogen elimination reaction. Despite the fact that accounting for all factors that control the mechanisms of reactions of **2a–c** with HCl is still impossible, this method complements the synthetic routes leading to *ansa*-bridged Group 4 metallocene derivatives through modification of functional groups on preformed metallocene complexes. More importantly, the synthetic approach presented here allows one to synthesize selectively long-chain *ansa*-metallocenes that are accessible by the traditional metathesis of organic-chain-spaced bis-(cyclopentadienyl) salts with an appropriate source of a transition metal only with difficulties.

Note: After submission of this paper, it was reported that the reduction of *ansa*-zirconocene and -hafnocene dichlorides with silyl-bridged bis(1-indenyl) ligands bearing pendant 4-pentenyl groups by sodium amalgam also affords ring-tethered metallacyclopentanes.[34]

Experimental Section

General comments: Syntheses of the starting bis{(ω-alkenyl)tetramethylcyclopentadienyl}titanium(IV) dichlorides **1a–c** were carried out in an argon atmosphere. All other experiments were performed under high-vacuum conditions on a vacuum line with exclusion of greased joints, and with all-glass devices equipped with breakable seals. Samples for NMR and UV/Vis spectra were prepared on a vacuum line and sealed off. Crystals for X-ray analyses were mounted into Lindemann glass capillaries under purified nitrogen in glovebox (mBraun Labmaster 130, O_2 and H_2O concentrations lower than 2.0 ppm). Crystals for mass spectral measurements and melting point determination were placed into capillaries in the glovebox and sealed by flame. KBr pellets for infrared spectra were prepared in the glovebox and measured under nitrogen in an air-proof cell on a Specord IR-75 spectrometer. NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^1H, 399.95 MHz; ^{13}C, 100.58 MHz) in C_6D_6 solutions at 298 K. Chemical shifts (δ/ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.00). The assignment of the NMR signals is based on ^1H, $^{13}C\{^1H\}$, ^{13}C APT/DEPT, COSY-90/DQF (double quantum

filtered) COSY and ^{13}C HMQC spectra. Mass spectra were measured on a VG 7070E instrument (EI, 70 eV; only important mass peaks are reported). UV/Vis spectra were recorded on a Varian Cary instrument in the range of 280 – 2000 nm using all-sealed quartz cells (Hellma, 0.1 and 1.0 cm). The melting points were determined in sealed glass capillaries under nitrogen, and are uncorrected.

Chemicals: Hexane, toluene, tetrahydrofuran (THF) and C_6D_6 were refluxed with $LiAlH_4$ and stored as solutions of dimeric titanocene [(μ-η^5:η^5-$C_{10}H_8$)(μ-H)$_2${Ti(η^5-C_5H_5)}$_2$][35] on a vacuum line. The (ω-alkenyl)-tetramethylcyclopentadiene ligands C_5HMe_4R, where R = CH(Me)CH=CH_2, $(CH_2)_2CH{=}CH_2$ and $(CH_2)_3CH{=}CH_2$) were obtained as a mixture of regioisomers by addition of 2,3,4,5-tetramethylcyclopent-2-enone to the appropriate alkenyl Grignard reagent[9] and dehydration of the resulting 1-hydroxy-1-(alkenyl)-2,3,4,5-tetramethylcyclopent-2-enes induced by a catalytic amount of iodine. The procedure is described in detail for C_5HMe_4(CHMeCH=CH_2).

Preparation of 5-(1-methyl-2-propenyl)-1,2,3,4-tetramethylcyclopentadiene: 3-Chloro-1-butene (22.50 g, 0.248 mol) in diethyl ether (100 mL) was added dropwise to magnesium turnings (10.0 g, 0.41 mol) in diethyl ether (250 mL) over a period of 60 min and the mixture was refluxed for 30 min. Then, a solution of 2,3,4,5-tetramethylcyclopent-2-enone (34.2 g, 0.248 mol) in diethyl ether (100 mL) was added to the solution of Grignard reagent over 60 min, the grey-green reaction mixture was refluxed for 2 h and then slowly poured onto a vigorously stirrred slurry of ice (200 g) in water (300 mL). The organic layer was separated and aqueous phase was extracted with diethyl ether (3 × 50 mL). Organic phases were combined, and diethyl ether was removed on a rotary evaporator, leaving 3-hydroxy-3-(1-methyl-2-propenyl)-1,2,4,5-tetramethylcyclopent-2-ene, which was immediately dehydrated by addition of an iodine solution in diethyl ether (50 mg I_2 in 20 mL). A water layer which separated after standing overnight was removed, the organic layer was shaken with a saturated aqueous solution of sodium thiosulfate and twice with water, and dried by anhydrous sodium sulfate. Ether was evaporated and the crude product was distilled under dynamic vacuum of a rotary pump at the temperature of a boiling water bath. The GC analysis of the distillate showed the presence of about 2 % of the unconverted alcohol, which was removed by addition of $LiAlH_4$ (ca. 0.05 g) and stirring for 1 h. Repeated vacuum distillation gave a mixture of isomeric cyclopentadienes as a colourless liquid. Yield: 34.9 g (80.0 %); IR (neat): $\tilde{\nu}$ = 3070 (m), 2955 (s), 2915 (s), 2850 (s), 2730 (w), 1815 (w), 1650 (m), 1630 (s), 1440 (s), 1410 (s), 1370 (s), 1330 (w), 1235 (w), 1150 (w), 990 (s), 850 (m), 730 (m), 695 (m), 560 (w), 520 cm^{-1} (w); EI-MS (GC-MS, 70 eV): *m*/*z* (%): 176 (5) $[M]^+$, 161 (6), 133 (6), 122 (10), 121 (23), 120 (11), 119 (17), 115 (7), 107 (11), 106 (8), 105 (40), 103 (8), 93 (24), 91 (47), 79 (32), 78 (11), 77 (39), 65 (21), 63 (10), 55 (41), 53 (33), 41 (64), 40 (11), 39 (100).

Preparation of 5-(3-butenyl)-1,2,3,4-tetramethylcyclopentadiene: A similar reaction with 4-bromo-1-butene (10.0 g, 74 mmol) afforded a mixture of isomeric 5-(3-butenyl)-1,2,3,4-tetrametylcyclopentadienes as a colourless liquid. Yield: 10.3 g (76.2 %); IR (neat): $\tilde{\nu}$ = 3070 (m), 2960 (s), 2900 (s), 2860 (s), 2725 (w), 1815 (w), 1650 (m), 1635 (s), 1445 (vs), 1375 (s), 1305 (w), 1075 (m), 990 (s), 905 (s), 635 (m), 555 (w), 475 cm^{-1} (w); EI-MS (GC-MS, 70 eV): *m*/*z* (%): 176 (45) $[M]^+$, 136 (10), 135 (100), 133 (11), 122 (13), 120 (23), 119 (39), 117 (11), 115 (12), 107 (48), 105 (58), 103 (10), 93 (23), 91 (49), 79 (20), 77 (26), 65 (10), 55 (8), 41 (27), 39 (25).

Preparation of 5-(ω-pentenyl)-1,2,3,4-tetramethylcyclopentadiene: Starting from 5-bromo-1-pentene (23.75 g, 0.16 mol), the above procedure afforded a mixture of 5-(ω-pentenyl)-1,2,3,4-tetrametylcyclopentadienes as a colourless liquid. Yield: 21.3 g (70.5 %); IR (neat): $\tilde{\nu}$ = 3050 (w), 2960 (s), 2930 (s), 2860 (s), 1815 (w), 1650 (m), 1635 (s), 1440 (vs), 1375 (s), 990 (s), 905 (s), 850 (w), 630 (w), 555 cm^{-1} (w); EI-MS (GC-MS, 70 eV): *m*/*z* (%): 190 (48) $[M]^+$, 175 (38), 149 (100), 147 (16), 135 (32), 133 (29), 120 (66), 119 (36), 117 (10), 115 (9), 107 (40), 105 (37), 93 (16), 91 (36), 79 (15), 77 (18), 55 (9), 41 (17), 39 (12).

Synthesis of bis{(ω-alkenyl)tetramethylcyclopentadienyl}titanium dichlorides: The procedure used follows the general principles for the synthesis of highly ring-substituted titanocene dichlorides.[36] Only the procedure for obtaining the methylpropenyl derivative is described here in detail, since all other compounds were prepared in a similar manner.

Preparation of [$TiCl_2${η^5-C_5Me_4(CH(Me)CH=CH_2)}$_2$] (1a): $TiCl_4$ (4.0 mL, 36 mmol) was co-condensed with THF (100 mL) at liquid nitrogen temperature in a 0.5 L three-necked flask on a vacuum line. The vacuum was replaced by an argon atmosphere and the mixture was allowed to warm up slowly to room temperature and THF was brought to a gentle reflux to wash the adduct from walls (*Warning:* very often an exothermic reaction of the components takes place which may cause the contamination of the vacuum line by the formed yellow adduct [$TiCl_4(THF)_2$]). After cooling to room temperature, *n*BuLi (Aldrich) in hexane (22.5 mL 1.6 M, 36 mmol) was added from a syringe under vigorous stirring. The mixture was refluxed for 30 min and then allowed to cool to room temperature, whereupon a crystalline slurry of the pale blue [$TiCl_3(THF)_3$] separated at the bottom of the reaction vessel. In another one-liter three-necked flask, the mixture of 5-(1-methyl-2-propenyl)-1,2,3,4-tetramethylcyclopentadienes (19.14 g, 86 mmol) was dissolved in diethyl ether (500 mL) and *n*BuLi in hexane (59 mL 1.6 M, 90 mmol) was added by a syringe through a septum under stirring, and the resulting white voluminous precipitate suspended in a yellow solution was stirred for 3 h at room temperature. The slurry of [$TiCl_3(THF)_3$] was then poured under argon into the suspension of cyclopentadienyllithium, diethyl ether was distilled off and a largely THF solution was refluxed for 24 h. The volume of the solution was reduced to about 50 mL, anhydrous powdered $PbCl_2$ (10.0 g, 36 mmol) was added and the mixture was stirred for another 2 h during which the originally dark brown-green mixture turned dark red due to the formation of complex **1a**. Solvents were evaporated under vacuum, the oily residue was dissolved in heptane (20 mL) and the solution was cooled in a refrigerator overnight. Still cold, the crystalline slurry was filtered, the residue was washed with ethanol (20 mL) and extracted with heptane in a Soxhlet apparatus. Concentration and cooling of the heptane solution afforded crude complex **1a** which was washed by ethanol (20 mL) and, after drying, recrystallised from heptane. Yield: 6.6 g (39 %); brown crystalline powder; ^1H NMR (C_6D_6): δ = 1.23, 1.24 (2 d, ^3J(H,H) = 7.1 Hz, 3 H; CH*Me*), 1.69, 1.71, 1.74, 1.77, 2.04, 2.05, 2.07, 2.08 (8 s, 3 H; Me_4C_5), 3.98 (m, 2 H; C*H*Me), 4.90 – 5.02 (m, 4 H; =CH_2), 6.13 (m, 1 H; −*CH*=); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 12.17, 12.40, 12.69, 12.96, 13.59, 13.68, 13.73 (2 C; Me_4C_5), 17.57, 17.73 (CH*Me*), 37.20, 37.26 (*C*HMe), 112.61, 122.63 (=*C*H$_2$), 124.61, 125.39, 126.52, 128.77, 129.20, 129.45, 130.17 (Me_4C_5, *C*-Me), 137.23, 137.31 (Me_4C_5, *C*-CH), 142.52, 142.63 (−*C*H=), signal of the second *C*(Me_4C_5)-Me carbon atom was not observed; EI-MS (direct inlet, 70 eV, 120 °C): *m*/*z* (%): 468 (1) $[M]^+$, 435 (8), 433 (19) $[M - Cl]^+$, 297 (15), 296 (15), 295 (70), 294 (28), 293 (100) $[M - Cp'']^+$, 292 (12), 291 (10), 260 (10), 258 (27) [Cp″TiCl]$^+$, 241 (12), 227 (9), 176 (8), 175 (48) [Cp″]$^+$, 160 (11), 145 (21), 133 (12), 119 (10), 105 (10), 91 (10), 55 (11), 41 (12); IR (KBr): $\tilde{\nu}$ = 3072 (m), 2980 (s), 2956 (vs), 2897 (vs), 1815 (w), 1630 (s), 1489 (s), 1437 (s), 1420 (s), 1387 (m), 1371 (vs), 1302 (w), 1136 (w), 1087 (w), 1047 (w), 1016 (vs), 1000 (s), 965 (w), 907 (vs), 775 (m), 702 (m), 664 (w), 593 (w), 560 (w), 492 (w), 458 cm^{-1} (m); elemental analysis calcd (%) for $C_{26}H_{38}Cl_2Ti$ (469.37): C 66.53, H 8.16; found C 66.50, H 8.14.

Data for [$TiCl_2${η^5-C_5Me_4($CH_2CH_2CH{=}CH_2$)}$_2$] (1b): Brown-red crystals; yield: 7.6 g (45 %); ^1H NMR (C_6D_6): δ = 1.86, 1.91 (2 s, 6 H; Me_4C_5), 1.97 (m, 2 H; Cp″CH_2CH_2), 2.66 (m, 2 H; Cp″CH_2), 4.85 – 5.02 (m, 2 H; =CH_2), 5.70 (m, 1 H; −*CH*=); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.1, 13.2 (Me_4C_5), 27.9 (Cp″*C*H$_2$), 34.0 (Cp″CH_2*C*H$_2$), 115.1 (=*C*H$_2$), 127.3, 128.4 (Me_4C_5, *C*-Me), 131.5 (Me_4C_5, *C*-CH$_2$), 138.2 (−CH=); EI-MS (direct inlet, 70 eV, 120 °C): *m*/*z* (%): 468 (2) $[M]^+$, 435 (16), 434 (14), 433 (34) $[M - Cl]^+$, 297 (20), 296 (19), 295 (88), 294 (34), 293 (100) $[M - Cp'']^+$, 292 (14), 291 (13), 260 (15), 259 (10), 258 (39) [Cp″TiCl]$^+$, 218 (8), 217 (18), 216 (10), 215 (9), 213 (15), 176 (11), 175 (67) [Cp″]$^+$, 135 (17), 134 (74), 133 (36), 119 (63), 105 (12), 91 (21), 77 (10), 69 (10), 57 (11), 55 (14), 43 (8), 41 (26), 39 (11); IR (KBr): $\tilde{\nu}$ = 3060 (m), 2977 (br m), 2965 (s), 2937 (s), 2894 (vs), 2855 (s), 1812 (w), 1635 (s), 1489 (m), 1479 (m), 1448 (s), 1427 (vs), 1393 (m), 1371 (vs), 1360 (sh), 1297 (w), 1259 (w), 1063 (w), 1010 (s), 994 (m), 949 (w), 898 (vs), 793 (w), 754 (w), 662 (w), 649 (m), 615 (w), 574 (w), 458 (m), 400 cm^{-1} (m); elemental analysis calcd (%) for $C_{26}H_{38}Cl_2Ti$ (469.37): C 66.53, H 8.16; found C 66.51, H 8.15.

Data for [$TiCl_2${η^5-C_5Me_4($CH_2CH_2CH_2CH{=}CH_2$)}$_2$] (1c): Brown-red powder; the product is very soluble in hexane; yield 3.8 g (21 %); ^1H NMR (C_6D_6): δ = 1.32 (m, 2 H; Cp″CH_2CH_2), 1.88, 1.95 (2 s, 6 H; Me_4C_5), 1.96 (m, 2 H; Cp″$CH_2CH_2CH_2$), 2.57 (m, 2 H; Cp″*C*H$_2$), 4.94 – 5.03 (m, 2 H; =CH_2), 5.73 (m, 1 H; -*CH*=); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.1, 13.2 (Me_4C_5), 27.9 (Cp″*C*H$_2$), 29.2 (Cp″CH_2*C*H$_2$), 34.3 (Cp″CH_2CH_2*C*H$_2$), 115.1 (=*C*H$_2$), 127.2, 128.4 (Me_4C_5, *C*-Me), 132.2 (Me_4C_5, *C*-CH$_2$), 138.5 (-*C*H=); EI-MS (direct inlet, 70 eV, 140 °C): *m*/*z* (%): 496 (4) $[M]^+$, 463 (18), 462 (17), 461

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(41) $[M-Cl]^+$, 311 (9), 310 (9), 309 (41), 308 (17), 307 (57), 272 (14), 227 (10), 219 (8), 218 (14), 217 (18), 216 (9), 213 (10), 190 (16), 189 (100), 161 (10), 148 (9), 147 (49), 135 (11), 134 (27), 133 (45), 121 (7), 120 (8), 119 (49), 105 (12), 91 (15), 55 (22), 41 (16); IR (KBr): $\tilde{\nu}$ = 3066 (m), 2970 (br s), 2900 (br vs), 2847 (s), 1638 (s), 1488 (s), 1460 (m), 1438 (vs), 1420 (sh), 1387 (s), 1377 (vs), 1348 (w), 1209 (w), 1067 (w), 1020 (s), 993 (s), 963 (m), 927 (vs), 916 (vs), 811 (m), 752 (m), 636 (m), 613 (w), 440 cm^{-1} (m); elemental analysis calcd (%) for $C_{28}H_{42}Cl_2Ti$ (497.43): C 67.61, H 8.51; found C 67.64, H 8.53.

Reduction of 1a–1c by magnesium: Complexes **1a**–**1c** (**1a** 0.47 g, **1b** 0.47 g, **1c** 0.50 g; 1.0 mmol) and magnesium (0.24 g, 10 mmol) were placed into an ampoule, which was carefully evacuated on a vacuum line. THF (30 mL) was distilled onto the solid mixture at liquid nitrogen temperature. The ampoule was sealed off, and after warming to room temperature, it was immersed into a water bath kept at 60 °C. After an induction period of varying length (usually few hours) the red colour of the solution turned to yellow-brown, indicating the formation of a titanocene monochloride (evidenced by EPR spectra). After further heating to 60 °C for 5 h, the solution was decanted from the remaining magnesium, unreacted magnesium was washed by THF and finally all THF was distilled off (the induction period is markedly reduced when the recovered activated magnesium is reused). The solid residue was extracted by hexane (30 mL), the solution was concentrated and the product crystallised in refrigerator (−5 °C) or a freezer (−18 °C). The crystals formed were separated from the mother liquor, washed by a cold solvent, dried in vacuum and sealed off in one arm of the ampoule.

Data for [Ti^{IV}(η^1:η^1:η^5:η^5-$C_5Me_4CH(Me)CH(Ti)CH_2CH\{CH_2(Ti)\}CH(Me)C_5Me_4$] (2a): Khaki green crystals; yield: 0.33 g (83 %); m.p. > 260 °C; ^{1}H NMR (C_6D_6): δ = 1.10, 1.12, 1.29, 1.29, 1.30, 1.31, 1.41, 1.42, 1.51, 1.53, 1.67, 1.79, 2.01, 2.10 2.35, and 2.36 (16 s, 3H; Me_4C_5); enantiomeric pair A: −3.09 (t, ^3J(H,H) = 7.1 Hz, 1H; TiC*H*), −0.04 (dt, J(H,H) = 11.3, 3.3 Hz, 1H; TiCH_2), 0.99 (dd, J(H,H) = 11.4, 2.5 Hz, 1H; TiCH_2), 1.51–1.59 (m, 1H; TiCHCH_2), 1.62 (d, ^3J(H,H) = 7.3 Hz, 3H; TiCHCH*Me*), 1.82 (d, ^3J(H,H) = 7.5 Hz, 3H; $TiCH_2CHCH$*Me*), 2.05 (apparent qi, 1H; $TiCH_2CH$), 2.48 (ddd, J(H,H) = 13.9, 8.0, 2.8 Hz, 1H; TiCHCH_2), 3.02 (qi, J(H,H) = 7.4 Hz, 1H; TiCHC*H*), 3.84 (q, J(H,H) = 7.5 Hz, 1H; $TiCH_2CHCH$); enantiomeric pair B: −3.00 (t, ^3J(H,H) = 7.6 Hz, 1H; TiC*H*), −0.34 (dt, J(H,H) = 11.2, 3.0 Hz, 1H; TiCH_2), 1.23–1.28 (m, 2H; TiCH_2, TiCHCH_2), 1.63 (d, ^3J(H,H) = 7.3 Hz, 3H; TiCHCH*Me*), 1.90 (d, ^3J(H,H) = 7.4 Hz, 3H; $TiCH_2CHCH$*Me*), 2.14–2.19 (m, 1H; $TiCH_2CH$), 2.89 (ddd, J(H,H) = 14.5, 8.0, 2.8 Hz, 1H; TiCHCH_2), 3.05 (qi, J = 7.4 Hz, TiCHC*H*), 4.01 (dq, J(H,H) = 7.4, 4.6 Hz, 1H; $TiCH_2CHCH$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.44, 9.48, 9.61, 10.06, 10.26, 10.37, 10.54, 10.62, 12.53, 12.56, 13.14, 14.04, 14.92, 15.16, 15.20 and 15.92 (16 Me of Me_4C_5), 110.46, 110.81, 113.92, 115.44, 115.75, 115.85, 116.83, 117.58, 117.87, 118.04, 121.39, 121.83, 121.88, 122.99 (2 C), 123.11, 123.30, 123.75, 132.00, and 134.03 (20 C_{ipso} of Me_4C_5); enantiomeric pair A: 22.15 ($TiCH_2CHCH$*Me*), 23.36 (TiCHCH*Me*), 42.53 ($TiCH_2CHCH$), 43.61 or 43.48 (TiCH*C*H), 48.20 (TiCH*C*H_2), 52.80 ($TiCH_2CH$), 63.48 (Ti*C*H), 72.70 (Ti*C*H_2); enantiomeric pair B: 15.64 ($TiCH_2CHCH$*Me*), 23.36 (TiCHCH*Me*), 38.07 ($TiCH_2CHCH$), 38.25 (TiCH*C*H_2), 43.48 or 43.61 (TiCH*C*H), 51.37 ($TiCH_2CH$), 64.99 (Ti*C*H), 76.56 (Ti*C*H_2); EI-MS (direct inlet, 70 eV, 160 °C): *m*/*z* (%): 401 (6), 400 (21), 399 (37), 398 (100) $[M]^+$, 397 (22), 396 (27), 395 (11), 394 (11), 381 (14), 380 (7), 379 (6), 342 (10), 192 (13), 191 (8), 190 (7), 41 (7); IR (KBr): $\tilde{\nu}$ = 2942 (br s), 2887 (br vs), 2857 (sh), 2808 (s), 1479 (s), 1439 (br vs), 1410 (s), 1373 (vs), 1220 (w), 1094 (m), 1073 (w), 1016 (s), 1098 (m), 1057 (w), 1038 (w), 803 (br m), 737 (m), 696 (m), 662 (m), 642 (w), 575 (w), 517 (w), 480 (vs), 468 (s), 440 cm^{-1} (m); UV/Vis (hexane): λ_{max} = 380 > 560 nm; elemental analysis calcd (%) for $C_{26}H_{38}Ti$ (398.47): C 78.37, H 9.61; found C 78.35, H 9.61.

Data for [Ti^{IV}(η^1:η^1:η^5:η^5-$C_5Me_4(CH_2)_2CH(Ti)(CH_2)_2CH(Ti)(CH_2)_2C_5Me_4$] (2b): Dark red crystals; yield 0.34 g (86 %); m.p. 127 °C; ^{1}H NMR (C_6D_6): δ = 1.38 (s, 3H; Me_4C_5), 1.38–1.49 (m, 2H; TiCHCH_2, Cp″CH_2CH_2), 1.43, 1.57 (2 s, 3H; Me_4C_5), 1.78–1.85 (m, 1H; TiCHCH_2), 1.98–2.03 (br m, 1H; TiC*H*CH_2), 2.09–2.18 (m, 1H; Cp″CH_2CH_2), 2.48 (dd, J(H,H) = 13.4, 8.1 Hz, 1H; Cp″CH_2CH_2), 2.66 (s, 3H; Me_4C_5), 3.17 (ddd, J_1(H,H) ≈ J_2(H,H) ≈ 13, J_3(H,H) = 6.8 Hz, 1H; Cp″CH_2CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 10.0, 10.5, 11.8, 15.3 (Me_4C_5; δ_H 1.38, 1.43, 1.57, 2.66, respectively), 24.4 (Cp″CH_2CH_2), 30.1 (TiCHCH_2), 46.3 (Cp″CH_2CH_2), 78.4 (TiCHCH$_2$), 113.8, 114.4, 117.0, 126.9 (Me_4C_5, *C*-Me), 140.4 (Me_4C_5, *C*-CH_2); EI-MS (direct inlet, 70 eV, 170 °C) *m*/*z* (%): 400 (14), 399 (36), 398 (100) $[M]^+$, 397 (18), 396 (17), 395 (9), 394 (7), 393 (10), 355 (7), 354 (7), 353 (18), 181 (10), 180 (6), 178 (8), 177 (6), 41 (6). IR (KBr): $\tilde{\nu}$ = 2990 (w), 2938 (s), 2907 (br s), 2853 (s), 2812 (s), 2782 (vs), 1488 (s), 1433 (br vs), 1373 (vs), 1332 (w), 1303 (s), 1279 (w), 1231 (m), 1185 (w), 1171 (w), 1066 (m), 1018 (s), 934 (w), 896 (m), 860 (w), 797 (m), 781 (w), 677 (m), 598 (w), 548 (w), 525 (m), 505 (s), 443 (sh), 413 cm^{-1} (s); UV/Vis (hexane): λ_{max} = 400 (sh) ≫ 640 nm (sh); elemental analysis calcd (%) for $C_{26}H_{38}Ti$ (398.47): C 78.37, H 9.61; found C 78.34, H 9.60.

Data for [Ti^{IV}(η^1:η^1:η^5:η^5-$C_5Me_4(CH_2)_2CH(Ti)\{CH(Me)\}_2CH(Ti)(CH_2)_2C_5Me_4$)] (2c): Ochre crystals; yield: 0.36 g (84 %); m.p. 74 °C; ^{1}H NMR (C_6D_6): δ = 0.85 (filled-in d, 3H; TiCHCH*Me*), 1.10 (dddd, J_1(H,H) ≈ J_2(H,H) ≈ 13.5, J_3(H,H) = 7.8, J_4(H,H) = 4.9 Hz, 1H; Cp″CH_2CH_2), 1.39, 1.40 (2 s, 3H; Me_4C_5), 1.45–1.52 (m, 1H; TiCHC*H*Me), 1.55–1.61 (m, 1H; TiC*H*CHMe), 1.59 (s, 3H; Me_4C_5), 2.29 (ddd, J(H,H) = 13.7, 6.1, 1.8 Hz, 1H; Cp″CH_2CH_2), 2.41 (dd, 1H; J(H,H) = 13.4, 7.7 Hz, Cp″CH_2CH_2), 2.60 (s, 3H; Me_4C_5), 3.06 (ddd, J_1(H,H) ≈ J_2(H,H) ≈ 13.3, J_3 = 6.4 Hz, 1H; Cp″CH_2CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 10.0, 10.4, 11.8, 15.4 (Me_4C_5), 19.8 (TiCHCH*Me*), 24.1 (Cp″CH_2CH_2), 41.1 (TiCH*C*HMe), 42.6 Cp″CH_2CH_2), 86.2 (Ti*C*HCHMe), 113.7, 114.4, 117.7, 127.2 (Me_4C_5, *C*-Me), 139.8 Me_4C_5, *C*-CH_2); EI-MS (direct inlet, 70 eV, 170 °C): *m*/*z* (%): 428 (14), 427 (37), 426 (100) $[M]^+$, 425 (15), 424 (15), 370 (11), 367 (5), 182 (9), 181 (11), 180 (8), 179 (5), 178 (9), 177 (5), 55 (6), 41 (7); IR (KBr): $\tilde{\nu}$ = 2935 (vs), 2904 (vs), 2849 (vs), 2811 (s), 2795 (s), 1490 (m), 1445 (br vs), 1374 (s), 1352 (m), 1335 (w), 1308 (m), 1256 (m), 1203 (w), 1190 (w), 1137 (w), 1017 (s), 977 (m), 953 (m), 932 (w), 880 (w), 817 (w), 790 (br m), 672 (m), 600 (m), 558 (w), 472 (w), 445 (w), 427 (m), 407 cm^{-1} (s); UV/Vis (hexane): λ_{max} = 460 > 540 nm (sh); elemental analysis calcd (%) for $C_{28}H_{42}Ti$ (426.52): C 78.85, H 9.93; found C 78.82, H 9.92.

Reaction of complexes 2a–c with $PbCl_2$: Compounds **2a** and **2b** (0.40 g each, 1.0 mmol) and **2c** (0.43 g, 1.0 mmol) were reacted with dry, degassed $PbCl_2$ powder (Fluka; 0.278 g, 1.0 mmol) in THF (20 mL) at 60 °C with stirring for 8 h. All volatiles were evaporated in vacuum, and the residue was extracted by hexane. The extracts were concentrated and the residue was crystallised by cooling. The products were identified by MS, and IR, ^{1}H and ^{13}C NMR spectroscopy. Compounds **2a** and **2b** afforded **1a** (0.44 g, 94 %) and **1b** (0.40 g, 85 %), respectively.

[$TiCl_2$(η^5-$C_5Me_4(CH_2CH_2CH{=}CHMe)$)$_2$] (1c′). Complex **2c** was converted to **1c′**. Yield: 0.45 g (91 %); m.p. 138 °C; ^{1}H NMR (C_6D_6): δ = 1.54 (dt, 3H; J(H,H) = 4.6, 1.2 Hz, =CH*Me*), 1.89 (s, 6H; $\eta^5-Me_4C_5H$), 1.96 (m, 2H; Cp″CH_2CH_2), 1.94 (s, 6H; Me_4C_5H), 2.66 (m, Cp″CH_2), 5.31–5.36 (m, 2H C*H*=C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.1 (δ_H 1.89), 13.2 (δ_H 1.94) (Me_4C_5H), 18.0 (=CH*Me*), 28.6 (Cp″CH_2), 33.0 (Cp″CH_2CH_2), 125.5 (*C*H=CH), 127.1, 128.7 (Me_4C_5H; *C*-Me, *C*-CH_2), 131.0 (*C*H=CH), 131.7 (Me_4C_5H; *C*-Me and *C*-CH_2); IR (KBr): $\tilde{\nu}$ = 3020 (m), 2980 (m), 2950 (s), 2906 (vs), 2854 (s), 2814 (m), 1493 (m), 1484 (m), 1452 (s), 1434 (s), 1375 (vs), 1307 (w), 1260 (m), 1070 (m), 1020 (s), 973 (vs), 798 (s), 606 (w), 440 cm^{-1} (m); EI-MS (direct inlet, 70 eV, 120 °C): *m*/*z* (%): 496 (0.5) $[M]^+$, 463 (11), 462 (9), 461 (23) $[M-Cl]^+$, 428 (14), 427 (39), 426 (100) $[M-2Cl]^+$, 425 (15), 423 (15), 370 (14), 309 (30), 308 (11), 307 (40), 274 (10), 272 (21), 217 (12), 189 (19), 181 (11), 135 (24), 134 (31), 133 (21), 119 (25), 83 (11), 81 (8), 69 (15), 57 (18), 55 (27); elemental analysis calcd (%) for $C_{28}H_{42}Cl_2Ti$ (497.43): C 67.61, H 8.51; found C 67.62, H 8.52.

Reaction of titanacycles 2a–c with hydrogen chloride: Compounds **2a**, **2b** (0.40 g each, 1.0 mmol) and **2c** (0.43 g, 1.0 mmol) were dissolved in hexane (40 mL) and a solution of hydrogen chloride (3 mmol, generated from 5 mL of degassed 98 % H_2SO_4 and NaCl, 0.174 g, 3.0 mmol) in hexane (50 mL) was added. In all cases, a voluminous dark red crystalline precipitate formed immediately. The mixture was briefly warmed to 60 °C and then slowly cooled, finally in a refrigerator. The products crystallised out in nearly quantitative yields. They were isolated by decantation and dried in vacuo.

Data for *ansa*-[{η^5:η^5-$C_5Me_4CH(Me)CH_2CH_2CH(Me)CH(Me)C_5Me_4$}-$TiCl_2$] (3a): Yellow brown tiny needles; yield: 0.45 g (96 %); m.p. 237 °C; ^{1}H NMR (C_6D_6): δ = 0.74 (d, ^3J(H,H) = 6.6 Hz, 3H; *Me*CH), 0.81 (d, ^3J(H,H) = 6.6 Hz, 3H; *Me*CH), 0.87 (d, J(H,H) = 7.7 Hz, 3H; *Me*CH), 0.98–1.02, 1.13–1.22 (2 m, 1H; CH_2), 1.51–1.57 (m, 2H; CH_2), 1.64, 1.66, 1.81, 1.85 (4 s, 3H; Me_4C_5), 1.85–1.94 (m, 1H; C*H*Me), 2.14, 2.15, 2.35, 2.37 (4 s, 3H; Me_4C_5), 2.50 (dq, J_1(H,H) ≈ J_2(H,H) ≈ 6.6 Hz, 1H; C*H*Me), 2.70–2.81 (m, 1H; C*H*Me); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.19, 13.23, 13.30, 13.56, 15.20 (2C), 16.60, 16.86 (Me_4C_5), 18.04, 20.93, 23.71 (*Me*CH), 28.46, 28.79

(CH_2), 33.34, 34.77, 39.89 ($CHMe$), 121.31, 121.63, 125.69, 129.12, 131.75, 131.85, 133.77, 135.91, 137.10, 137.52 (C-CH_2, C-Me, Me_4C_5); EI-MS (direct inlet, 70 eV, 150 °C): m/z (%): 472 (11), 470 (15) $[M]^+$, 437 (14), 435 (32) $[M-Cl]^+$, 434 (9), 398 (9), 395 (10), 288 (14), 287 (10), 286 (36), 266 (9), 232 (21), 231 (14), 230 (31), 229 (16), 228 (11), 227 (33), 213 (12), 176 (8), 150 (11), 149 (90), 148 (100), 147 (25), 134 (11), 133 (44), 121 (14), 119 (18), 117 (10), 105 (19), 91 (19), 79 (8), 69 (14), 57 (9), 55 (23), 43 (12), 41 (27); IR (KBr): $\tilde{\nu}$ = 2962 (vs), 2951 (s), 2914 (br vs), 2870 (sh), 1487 (s), 1447 (vs), 1425 (m), 1375 (vs), 1361 (m), 1259 (w), 1180 (vw), 1140 (vw), 1068 (w), 1045 (vw), 1018 (vs), 967 (w), 793 (m), 743 (w), 652 (w), 617 (vw), 580 (vw), 467 (vw), 423 cm^{-1} (m); elemental analysis calcd (%) for $C_{26}H_{40}Cl_2Ti$ (471.39): C 66.25, H 8.55; found C 66.23, H 8.54.

Data for *ansa*-[{η^5:η^5-$C_5Me_4(CH_2)_8C_5Me_4$}$TiCl_2$] (3b): Purple needlelike crystals; yield: 0.40 g (85%); m.p. 142 °C; ^{1}H NMR (C_6D_6): δ = 1.20–1.48 (m, 4H; γ,δ-CH_2), 1.54–1.65 (m, 2H; β-CH_2), 1.96, 2.04 (2s, 6H; Me_4C_5), 2.39–2.46 (m, 2H; α-CH_2); ^{13}C{^{1}H} NMR (C_6D_6): δ = 14.0, 14.1 (Me_4C_5), 22.1 (γ or δ-CH_2), 23.7 (β-CH_2), 25.7 (α-CH_2), 26.9 (γ or δ-CH_2), 125.7, 126.8 (C-Me, Me_4C_5), 132.9 (C-CH_2, Me_4C_5); EI-MS (direct inlet, 70 eV, 190 °C): m/z (%): 474 (8), 473 (10), 472 (30), 471 (17), 470 (41) $[M]^+$, 438 (13), 437 (42), 436 (42), 435 (100) $[M-Cl]^+$, 434 (32), 433 (17), 398 (13), 227 (12), 219 (11), 218 (19), 217 (23), 216 (10), 215 (9), 213 (15), 135 (35), 134 (10), 133 (18), 121 (7), 119 (24), 105 (9), 91 (10), 55 (9), 41 (14); IR (KBr): $\tilde{\nu}$ = 1490 (s), 1465 (vs), 1444 (s), 1422 (s), 1375 (vs), 1366 (sh), 1321 (m), 1262 (w), 1213 (w), 1162 (w), 1100 (sh), 1080 (w), 1067 (m), 1048 (w), 1013 (vs), 955 (m), 844 (w), 820 (w), 788 (m), 728 (m), 702 (s), 642 (m), 621 (w), 433 cm^{-1} (s); elemental analysis calcd (%) for $C_{26}H_{40}Cl_2Ti$ (471.39): C 66.25, H 8.55; found C 66.21, H 8.52. The NMR spectra of the crude product revealed the presence of a minor isomer (minor:major = 2:5). The minor component was not isolated but identified by means of NMR spectroscopy directly in the mixture as **3b′**.

Data for *ansa*-[{η^5:η^5-$C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4$}$TiCl_2$] (3b′): ^{1}H NMR ($C_6D_6$): δ = 1.20–1.28 (m, 2H; CH_2), 1.38–1.45 (m, 4H; $2CH_2$), 1.84 (s, 12H; Me_4C_5), 2.00–2.15 (m, 4H; $2CH_2$), 2.06, 2.10 (2s, 6H; Me_4C_5), 3.44 (br d, ^3J(H,H) = 6.2 Hz, 2H; $CH_2CH{=}$), 5.52–5.66 (m, 2H; $CH{=}CH$); ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.2, 13.3, 13.5, 14.0 (Me_4C_5), 27.8 (CH_2, δ_H 1.38–1.45), 28.1 (CH_2, δ_H 2.00–2.15), 29.3 (CH_2, δ_H 1.38–1.45), 31.5 (CH_2, δ_H 1.20–1.28), 33.5 ($CH_2CH{=}$), 34.7 (CH_2, δ_H 2.00–2.15), 126.5 (C-CH_2, C-Me, Me_4C_5), 126.8 ($CH{=}$), 128.8, 129.1, 130.7, 133.3 (C-CH_2, C-Me, Me_4C_5), 135.5 ($=CH$).

Data for *ansa*-[{η^5:η^5-$C_5Me_4(CH_2)_3CH(Me)CH(Me)CH{=}CHCH_2C_5Me_4$}-$TiCl_2$] (3c): Purple needles; yield: 0.51 g (97%); m.p. 127 °C; ^{1}H NMR (C_6D_6): δ = 0.91 (d, ^3J(H,H) = 6.4 Hz, 3H; $CHMe$), 0.98 (d, J(H,H) = 6.6 Hz, 3H; $CHMe$), 0.98–1.12 (m, 2H; Cp″$CH_2CH_2CH_2$, CH_2CHMe), 1.23 (br ddd, J_1(H,H) = 4.5, J_2(H,H) ≈ J_3(H,H) ≈ 12.5 Hz, 1H; Cp″CH_2-CH_2CH_2), 1.34–1.57 (m, 2H; Cp″CH_2CH_2), 1.62 (s, 3H; Me_4C_5), 1.64–1.71 (m, 1H; $MeCHCH{=}$), 1.76, 1.88 (2s, 3H; Me_4C_5), 1.90–1.98 (m, 2H; Cp″CH_2CH_2), 1.92, 1.99, 2.11, 2.15, 2.20 (5s, 3H; Me_4C_5), 3.12–3.19, 4.01–4.10 (2m, 1H; $CH_2CH{=}$), 5.50–5.60 (m, 2H; $CH{=}CH$); ^{13}C{^{1}H} NMR (C_6D_6) = δ 12.0, 12.5, 12.9 (2 C), 13.1, 14.3, 14.8, 15.2 (Me_4C_5), 20.2, 21.4 ($MeCH$), 27.0 (Cp″CH_2CH_2), 29.1 (Cp″CH_2CH_2), 34.8 (Cp″$CH_2CH{=}$), 39.6 (CH_2CHMe), 40.1 (Cp″$CH_2CH_2CH_2$), 46.5 ($MeCHCH{=}$), 121.3, 123.2 (2 C), 126.7 (2 C), 134.1, 134.2, 136.9, 137.3 (2 C; C-CH_2, C-Me, Me_4C_5), 122.7 ($CH_2CH{=}$), 141.1 ($=CHCH$); EI-MS (direct inlet, 70 eV, 120 °C): m/z (%): 496 (1) $[M]^+$, 463 (10), 462 7), 461 (16) $[M-Cl]^+$, 311 (17), 310 (14), 309 (54), 308 (20), 307 (100) $[M-Cp''-H]^+$, 306 (11), 305 6), 274 (9), 273 (6), 272 (24), 254 5), 252 (6), 220 (6), 219 (11), 218 (16), 217 (19), 216 (13), 215 (10), 213 (15), 190 (8), 189 (43), 174 (7), 147 (17), 135 (39), 134 (93), 133 (46), 121 (5), 120 (8), 119 (67), 117 (7), 115 (5), 105 (12), 93 (5), 91 (20), 79 (8), 77 (8), 69 (10), 57 (6), 55 (34), 53 (6), 43 (6), 41 (20); IR (KBr): $\tilde{\nu}$ = 3012 (w), 2981 (m), 2945 (s), 2897 (vs), 2864 (s), 1492 (m), 1480 (s), 1448 (s), 1430 (vs), 1387 (w), 1373 (vs), 1334 (vw), 1305 (w), 1258 (w), 1113 (vw), 1068 (w), 1015 (s), 989 (m), 970 (vs), 905 (vw), 798 (w), 666 (vw), 604 (w), 542 (vw), 509 (vw), 438 cm^{-1} (m); elemental analysis calcd (%) for $C_{28}H_{42}Cl_2Ti$ (497.43): C 67.61, H 8.51; found C 67.58, H 8.49.

X-ray crystallography: Crystals of **1a**, **1c′**, **2a**, **2b**, **2c** and **3b** suitable for single-crystal X-ray analysis were obtained by slow evaporation from hexane (**1a**, **1c′**, **2a** and **2b**) or toluene (**2c** and **3b**). The selected specimens were inserted into Lindemann-glass capillaries and sealed by wax under nitrogen in a glovebox. The diffraction measurement was carried out on a CAD4-MACHIII four-circle diffractometer using graphite monochromatic $Mo_{K\alpha}$ radiation and θ–2θ scan. For all cases, the lattice parameters were determined by least-squares refinement from 25 automatically centered diffractions with 2θ range given in Table 6. Three standard diffractions were monitored every hour. The intensities were corrected for Lorentz polarization effects and linear decay;[37] absorption was neglected. The structures were solved by direct methods (SIR92)[38] or (SIR97),[39] affording the positions of all non-hydrogen atoms, and refined by full-matrix least-squares on F_o^2 (SHELXL97).[40] Relevant crystallographic data and details about data collection and structure refinement are given in Table 6. Further comments for each particular case are given below.

Compound ***1a***: The molecule of **1a** has perfect C_2 symmetry with the titanium atom residing on a crystallographic two-fold axis (Ti: x = 0, z = 0.250; occupancy 0.50). Hence, only one half of the molecule is symetrically independent. All non-hydrogen atoms were refined anisotropically. Methylene and all methyl hydrogens were included in calculated positions (C–H 0.93 and 0.96 Å, respectively) and assigned U_{iso}(H) 1.2 and 1.5 times of U_{eq}(C), respectively. The methine hydrogen was found on an difference electron-density map and refined with U_{iso}(H) = 1.2 U_{eq}(C).

Compound ***1c′***: Similarly to **1a**, only a half of the molecule of complex **1c′** is crystallographically independent (Ti: x = 0, z = 0.75; occupancy 0.50), the two halves being related by a $(1-x, y, 3/2-z)$ symmetry transformation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were identified on diferrence electron density maps and isotropically refined.

Compound ***2a***: Because all the repeatedly selected crystals diffracted poorly and gave relatively broad diffractions whose intensity decreased rapidly with increasing θ angle, indicating a disordered structure, the data collection had to be stopped at 2θ = 40°. The structure solution revealed a statistical disorder of the methyl groups in the "methylpropenyl" part of the molecule. As the relative position of the methyl groups is the only difference between both diastereomeric pairs in the crystal lattice, the disorder reflects very likely only marginal difference in shape of the diastereomeric molecules that leads to their packing in the racemic crystal as of one species. The structure was refined with the methyl group of the methylpropenyl chain (C(13) and C(13′)) located over two positions with occupancies 0.50:0.50. The disorder is partly transferred even onto adjacent atoms, but a refinement of those atoms over two positions with identical occupancies proved unstable. The non-hydrogen atoms were refined anisotropically; hydrogen atoms of the titanacyclopentane ring were identified on difference electron-density maps and isotropically refined. All the remaining methyl and methine groups were refined with hydrogen atoms in calculated positions with C–H 0.96 and 0.98 Å, respectively, and U_{iso}(H) = 1.2 U_{eq}(C).

Compound ***2b***: The titanium atom resides on the crystallographic two-fold axis (x = 0, z = 0.25; occupancy 0.50) and only one half of the molecule is crystallographically independent. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the CH and CH_2 groups were found on the difference electron-density maps and isotropically refined, whereas those of methyl groups were fixed in calculated positions, assuming C–H 0.96 Å and U_{iso}(H) = 1.2 U_{eq}(C).

Compound ***2c***: Similarly to **2b**, the molecule is placed in a special position (Ti: x = 0.25, y = 0; occupancy 0.50) so that only its half is symmetrically independent. Non-hydrogen atoms were refined anisotropically. All hydrogens except the methine H(9) were refined in their theoretical positions with U_{iso}(H) = 1.2 U_{eq}(C) for the methylene groups and U_{iso}(H) = 1.5 U_{eq}(C) for the methine and methyl hydrogen atoms. The H(9) atom was isotropically refined in a position identified on difference electron-density map. Note: another crystal modification of **2c** crystallized out from hexane and its crystal structure was determined as well. The structure resembles closely the structure of **2b**, but it does not possess any crystallographically imposed symmetry. Both polymorphs show only marginall differences in overall molecular geometry and the structure of the less symmetric polymorph will not be discussed here in detail. Structural data have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC-134862.

Compound ***3b***: All non-hydrogen atoms were refined anisotropically. However, two inner atoms of the eight membered cyclopentadienyl-linking side chain, C(9) and C(10) are partly disordered. A model describing this disorder by two partially occupied positions for each atom failed, resulting in unrealistic atom distances (the refinement in non-centrosymetric space group also proved unsuccessful due to large correlation of parametres of

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Table 6. Crystallographic data, data collection and structure refinement for **1a**, **1c′**, **2a**, **2b**, **2c** and **3b**.

	1a	**1c′**	**2a**	**2b**	**2c**	**3b**
formula	$C_{26}H_{38}Cl_2Ti$	$C_{28}H_{42}Cl_2Ti$	$C_{26}H_{38}Ti$	$C_{26}H_{38}Ti$	$C_{28}H_{42}Ti$	$C_{26}H_{40}Cl_2Ti$
M_w	469.36	497.42	398.47	398.46	426.52	471.38
crystal size [mm^3]	$0.2\times0.2\times0.3$	$0.3\times0.8\times0.5$	$0.2\times0.3\times0.3$	$0.1\times0.3\times0.5$	$0.3\times0.3\times0.4$	$0.5\times0.6\times0.6$
crystal description	red prism	red prism	red bar	ruby red prism	red prism	red prism
T [K]	293(2)	150(2)	293(2)	296(1)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$Pbca$	$P\bar{1}$
2θ range [°]	26–28	26–28	22–24	26–28	24–26	26–28
λ [Å]	0.71069	0.71069	0.71069	0.71073	0.71069	0.71069
a [Å]	21.374(8)	12.986(2)	13.694(3)	11.417(1)	9.865(1)	8.7563(8)
b [Å]	8.166(2)	12.103(1)	15.463(2)	14.806(2)	15.789(1)	8.8929(8)
c [Å]	16.656(7)	16.693(2)	20.829(5)	12.741(2)	30.155(5)	16.583(2)
α [°]	90	90	90	90	90	99.064(8)
β [°]	121.44(2)	91.15(1)	92.06(2)	91.12(1)	90	103.723(8)
γ [°]	90	90	90	90	90	101.188(7)
V [Å^3]	2481(1)	2623.1(7)	4407(2)	2153.3(5)	4697(2)	1202.2(2)
Z	4	4	8	4	8	2
$F(000)$	1000	1064	1728	864	1856	504
ρ_{calcd} [g mL^{-1}]	1.26	1.26	1.20	1.23	1.21	1.30
μ [mm^{-1}]	0.571	0.544	0.396	0.405	0.376	0.589
$2\theta_{max}$ [°]	48.0	50.0	40.0	50.0	46.0	50.0
hkl range	−24/23, 0/9, −18/19	0/15, 0/14, −19/19	0/13, 0/14, −19/20	0/14, −14/17, −15/15	0/10, 0/17, 0/33	−10/10, 0/10, −19/19
measured reflections	1945	2432	2150	3211	3254	4220
unique reflections	1945	2313	2047	1892	3254	4220
observed reflections [$I>2\sigma(I)$]	1379	2111	1541	1573	1808	3601
parameters	140	225	278	151	369	262
GOF[a] all data	1.02	1.06	1.21	1.07	1.02	1.01
$R(F)/wR(F^2)$[a] all data (%)	7.10/10.1	3.74/9.21	10.4/23.1	5.14/10.2	5.4/6.9	5.45/2.5
$R(F)/wR(F^2)$[a] obs reflns (%)	3.61/8.91	3.26/8.95	7.62/21.3	3.70/9.59	5.60/3.6	4.42/1.8
w_1/w_2[b]	0.0518/1.9076	0.0576/2.3697	0.0738/51.958	0.0545/2.1460	0.0885/3.1946	0.0639/1.195
$\Delta\rho$ [e Å^{-3}]	0.40/−0.24	0.35/−0.32	0.72/−0.31	0.25/−0.31	0.86/−0.36	0.82/−0.67

[a] Definitions: $R(F)=\Sigma||F_o|-F_c||/\Sigma|F_o|$, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$, $GOF=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{reflns}-N_{params})]^{1/2}$. [b] Weighting scheme: $w=[\sigma^2(F_o^2)+(w_1P)^2+w_2P]^{-1}$; $P=[\max(F_o^2)+2F_c^2]/3$.

other atoms). All hydrogen atoms were included in calculated positions (C–H bond lengths 0.96 and 0.97 Å for methyl and methylene groups, respectively) and assigned $U_{iso}(H)=1.5\,U_{eq}(C)$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134863 (**1a**), CCDC-134861 (**1c′**), CCDC-134858 (**2a**), CCDC-134859 (**2b**), CCDC-135122 (**2c**), and CCDC-134860 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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