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Reduction-Induced Cyclization and Redox Reactions of Fully Methylated Titanocene Dichlorides Bearing Pendant Alkenyldimethylsilyl Groups, $[\mathrm{TiCl_2}\{\eta^5\text{-}\mathrm{C_5Me_4(SiMe_2R)}\}_2]$ (R = Vinyl and Allyl)

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Reduction of titanocene dichlorides bearing (ω-alkenyl)dimethylsilyl substituents $[\mathrm{TiCl_2}\{\eta^5\text{-}\mathrm{C_5Me_5(SiMe_2R)}\}_2]$, where R = $\mathrm{CH{=}CH_2}$ (**3**) and $\mathrm{CH_2CH{=}CH_2}$ (**4**), affords highly reactive Ti(II) intermediates, which immediately undergo intramolecular reactions with the pendant double bonds in a way dependent on the length of the alkenyl chain. The reduction of **4** with magnesium at 60 °C affords cleanly the cyclopentadienyl-ring-tethered titanacyclopentane, $[\mathrm{Ti}(\eta^1{:}\eta^1{:}\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH}(\mathit{Ti})\mathrm{CH(Me)CH(Me)CH}(\mathit{Ti})\mathrm{SiMe_2C_5Me_4}]$ (**5**), which can be opened by HCl to an *ansa*-titanocene dichloride with a six-membered saturated bridging chain, $[\mathrm{TiCl_2}\text{-}\{\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH_2CH(Me)CH(Me)CH_2SiMe_2C_5Me_4)_2}\}]$ (**6**). An analogous reaction of **3** can be accomplished at low temperatures and only to some extent, providing a mixture of titanacyclopentane complex $[\mathrm{Ti}(\eta^1{:}\eta^1{:}\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH}(\mathit{Ti})\mathrm{CH_2CH_2CH}(\mathit{Ti})\mathrm{SiMe_2C_5Me_4}]$ (**10**) and the fluxional η^2-alkene complex $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH{=}CH_2})(\eta^2{:}\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH{=}CH_2})]$ (**9**). At 60 °C, the reduction of **3** yields a mixture of *ansa*-η^2-alkene complex $[\mathrm{Ti}\{\eta^2{:}\eta^5{:}\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH_2CH{=}CHCH_2SiMe_2C_5Me_4}\}]$ (**7**) and the product of a hydrogen loss, the doubly tethered, paramagnetic η^3-allyl Ti(III) complex $[\mathrm{Ti}\{\eta^3{:}\eta^5{:}\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CHCH{=}CHCH_2SiMe_2C_5Me_4}\}]$ (**8**). When the reduction of **3** with magnesium is carried out in the presence of bis(trimethylsilyl)ethyne as the proton acceptor, **8** is obtained as the sole isolated product. Complex **8** reacts with protic reagents such as HCl and methanol under protonation/decomplexation of the allyl system to give the d^1 paramagnetic complexes $[\mathrm{TiX}\{\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4\text{-}SiMe_2CH_2CH{=}CHCH_2SiMe_2C_5Me_4}\}]$ (X = Cl, **12**; OMe, **13**). Oxidation of **8** with $\mathrm{PbCl_2}$ yields η^1-alkenyl complex $[\mathrm{TiCl}\{\eta^1{:}\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH}(\mathit{Ti})\mathrm{CH{=}CHCH_2SiMe_2C_5Me_4}\}]$ (**11**). A similar oxidation of **12** to *ansa*-titanocene dichloride $[\mathrm{TiCl_2}\{\eta{:}^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CHCH{=}CHCH_2\text{-}SiMe_2C_5Me_4}\}]$ (**14**) containing a symmetrical unsaturated bridging chain requires a stronger oxidizing agent, AgCl. Compounds **5**, **7**, **8**, and **10**−**14** have been characterized by X-ray crystallography.

Introduction

Pendant alkenyl groups attached to cyclopentadienyl ligands of group 4 metallocene-based alkene polymerization catalysts may influence the catalyst properties in a number of ways. Among others, the double bond(s) may competitively coordinate the catalytic center and thus influence the polymerization rate, molecular weight, and stereoregularity of the resulting polymers.[1] Although the ability of the η^5-(3-butenyl)tetramethylcyclopentadienyl ligand to interact with transition metals via both the carbon−carbon double bond and the cyclopentadienyl π-system was clearly demonstrated,[2] and the competition of the η^2-coordinated pendant double bond in $[\mathrm{Co}\{\eta^2{:}\eta^5\text{-}\mathrm{C_5Me_4(CH_2CH_2CH{=}CH_2)}\}(\eta^2\text{-}\mathrm{C_2H_4})]$ with excess ethene was established,[2j] the results so far obtained for half-sandwich group 4 complexes in the polymerization of styrene[3] as well as for bent metal-

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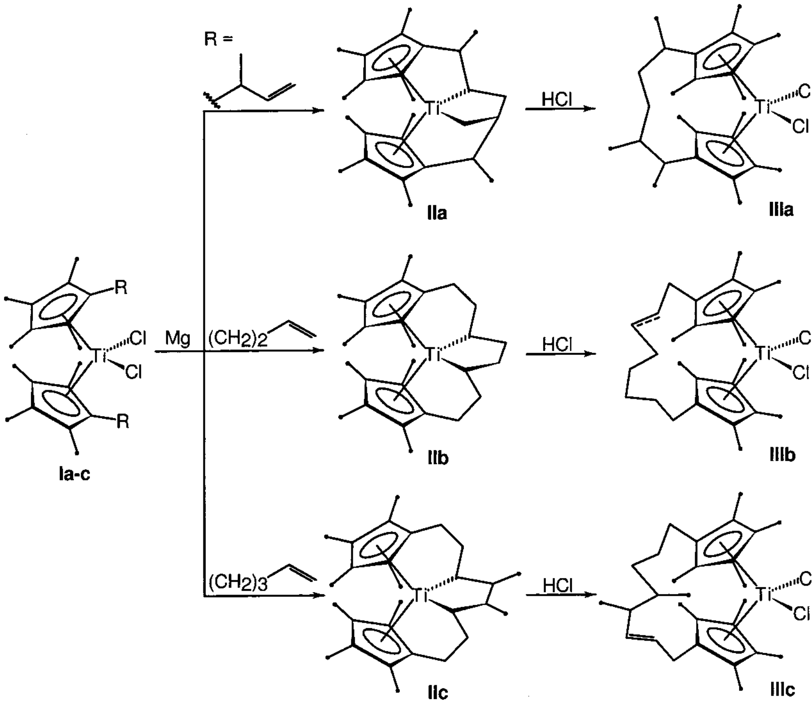
Scheme 1. Cyclization of Titanocene Dichlorides with ω-Alkenyl Substituents



locene catalysts in the polymerization of ethene and propene[4] did not show any dramatic change in polymerization kinetics and polymer properties, as it had been expected. Up-to-date knowledge of the effect of the substituents attached to the cyclopentadienyl ligands in alkene polymerization catalysts indicates that highly methyl-substituted metallocenes can hardly form the catalytically active cationic center because of their low Lewis acidity and steric hindrance.[5] Surprisingly, fully methylated *ansa*-metallocene catalysts are able to polymerize higher 1-alkenes at elevated pressure, affording polyalkenes with exceedingly high molecular weights.[6]

Pendant double bonds have also been used as reactive functionalities for modification of the parent bent metallocene structures. Thus, a photoinduced [2+2] cycloaddition reaction of the terminal C−C double bonds in bis{η^5-(1-alkylethenyl)cyclopentadienyl}zirconium(IV) dichlorides produces cyclobutane-bridged *ansa*-zirconocene complexes,[7] while a Mannich-type coupling affords 1-(dialkylamino)-1,3-butadien-1,3-diyl *ansa*-bridged group 4 metallocenes from bis{1-(dialkylamino)ethenyl}metallocene dichlorides.[8] More importantly for catalysis, the pendant double bonds are cleanly hydroborated with $HB(C_6F_5)_2$ to firmly anchor the Lewis acidic group $B(C_6F_5)_2$ in proximity of the titanium center.[1b,c] They are also capable of binding counterions based on either $[MeAlO]_x$ (MAO) or $B(C_6F_5)_3$ cocatalysts.[9] Another approach relevant to catalysis relies on immobilization of such metallocene complexes via grafting onto silica supports[10a] or onto a polymer by copolymerization with a suitable monomer.[10b,c]

In titanocene chemistry, a number of titanium derivatives including $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}_2]$ were 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. An attempt to isolate a cationic complex from the latter compound by reacting it with $B(C_6F_5)_3$ was, however, unsuccessful.[1a] Recently, it has been reported that reduction of *ansa*-zirconocene and -hafnocene dichlorides containing silyl-bridged bis(1-indenyl) ligands with pendant 4-pentenyl groups by sodium amalgam affords ring-tethered metallacyclopentanes.[11]Independently, we have shown that bis(ω-alkenyl)titanocene dichlorides $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$ (R = 1-methyl-2-propenyl, $CH(Me)CH{=}CH_2$; 3-butenyl, $(CH_2)_2CH{=}CH_2$; and 4-pentenyl $(CH_2)_3CH{=}CH_2$) are cleanly reduced with magnesium to give ring-tethered titanacyclopentane complexes, whose acidolysis with HCl affords *ansa*-titanocene dichlorides with five- and eight-membered aliphatic bridging chains in high yields (Scheme 1).[12]

In this work we report the reactions initiated by the magnesium reduction of silicon-modified titanocene

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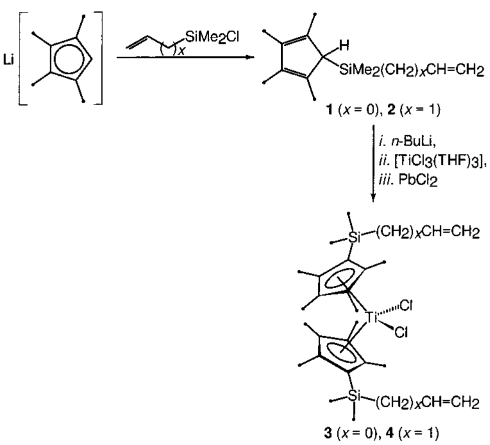
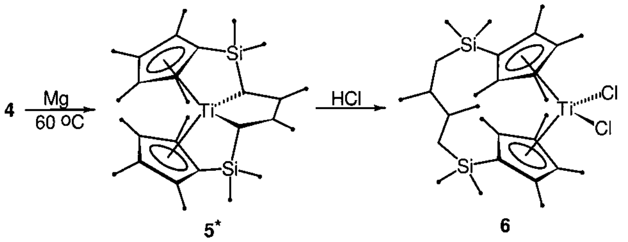
Scheme 2



Scheme 3. Reactions with Allyldimethylsilyl Complex 3[a]



[a] Asterisk indicates that the crystal structure has been determined.

dichlorides [$TiCl_2(\eta^5\text{-}C_5Me_4SiMe_2R)_2$], where R = vinyl (**3**) and allyl (**4**), showing some peculiar features in subsequent oxidative addition reactions due to the presence of the silylene groups and different lengths of the silylalkenyl groups.

Results

Synthesis of Ring-Silylated Titanocene Dichlorides 3 and 4. Cyclopentadienes $C_5HMe_4\{SiMe_2(CH_2)_x\text{-}CH{=}CH_2\}$ ($x = 0$, **1**; $x = 1$, **2**) were obtained in good yields from metathesis of lithium tetramethylcyclopentadienide with commercially available chlorosilanes $CH_2{=}CH(CH_2)_xSiMe_2Cl$ (Scheme 2). This route provides the silylated cyclopentadienes **1** and **2** as only one double-bond isomer. The synthesis of titanocene dichlorides thereof followed the procedure outlined for preparation of analogous alkenyl-substituted titanocene dichlorides:[12] in situ generated [$TiCl_3(THF)_3$] and the corresponding lithium cyclopentadienide were reacted to give Ti(III) intermediates, which were without isolation oxidized with $PbCl_2$ to titanocene dichlorides **3** and **4**, respectively, in ca. 50% isolated yields.

Reactions with Allyl-Substituted Complex 4. Reduction of titanocene dichloride **4** with excess magnesium in THF at 60 °C affords ring-tethered titanacyclopentane **5** in 87% yield (Scheme 3). The removal of chloride ligands proceeds in a stepwise manner, producing first a paramagnetic titanocene monochloride intermediate, whose presence was corroborated by EPR spectra of the reaction mixture. This intermediate is further reduced to a 14 valence electron titanocene, which immediately undergoes intramolecular oxidative cycloaddition of the pendant double bonds combined with concurrent double bond isomerization to yield complex **5** as the final stable product. Compound **5** is thermally robust, melting at 171 °C; upon electron impact MS (70 eV) it shows the molecular ion as the base peak. Its NMR spectra are in accordance with the results of X-ray crystallography, showing signals due to the titanium-bonded methine group (Ti*CH* δ_H ca. 0.4, δ_C 60.2) within the region typical for the analogous derivatives with silicon-free tether.[12]

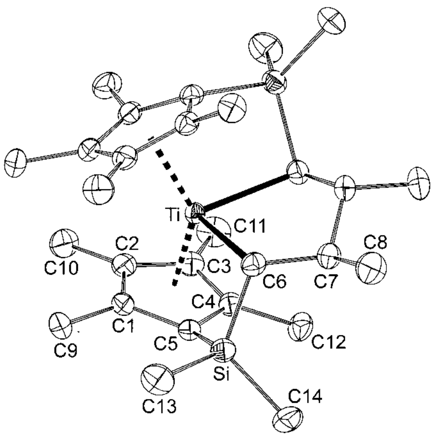


Figure 1. Molecular structure of **5**.

Acidolysis of the titanium−carbon bonds in metallacycle **5** with gaseous HCl provides titanocene dichloride with a six-membered saturated *ansa*-chain, **6**, in 63% isolated yield. The yield of **6** is only moderate because a Si−C bond cleavage under the action of HCl occurs inherently as the side reaction, producing a mixture of trichloro(η^5-cyclopentadienyl)titanium(IV) complexes as minor, more soluble byproducts, whose amount and distribution depend on the reaction conditions. Among the byproducts, [$TiCl_3(\eta^5\text{-}C_5Me_4H)$] and [$TiCl_3(\eta^5\text{-}C_5Me_4\text{-}SiMe_2Cl)$] were isolated and identified by MS and NMR spectra (see Experimental Section for details).

Crystal Structure of 5. Complex **5** crystallizes with $P2_1/c$ space group symmetry, so that the molecule is symmetrical with respect to a 2-fold axis which passes through the titanium atom and the midpoint of the C7−C7^i bond (Figure 1, Table 1). Hence, only half of the molecule is crystallographically independent, the other half being generated by the symmetry operation ($-x$, y, $1/2 - z$). Molecule **5** is chiral but related to its centrosymmetric counterpart in a racemic crystal. Compounds of this structural type have been recently obtained similarly from alkenyl-substituted titanocene dichlorides (Scheme 1).[12] Actually, compound **5** differs from **IIc** by mainly having a dimethylsilylene instead of ethane-1,2-diyl tether. This difference induces only minor changes in the overall molecular geometry. The angle subtended by the least-squares cyclopentadienyl planes (ϕ) is smaller in **5** than in **IIc** (38.74(7)° vs 41.1-(1)°), the Ti−C bond in **5** is longer (2.253(2) Å) than in **IIc** (2.215(4) Å), and the angle C(6)−Ti−C6^i (81.9(1)°) is smaller than that in **IIc** (84.9(2)°). The presence of a silicon atom within the tether in **5** results in a different mutual twist of the cyclopentadienyl rings as expressed by the torsion angle C5−Cg−Cg^i−C5^i (ω, 111.2(2)° and 101.9(4)° for **5** and **IIc**, respectively). The Si−C bonds

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Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for 5[a,b]

Distances			
Ti−Cg(1)[a]	2.124(2)	C(Cp)−C(Cp)	1.409(3)−1.436(3)
Ti−C(Cp)	2.373(2)−2.512(2)	C(Cp)−Me	1.497(3)−1.509(3)
Ti−C(6)	2.253(2)	C(6)−C(7)	1.545(3)
C(7)−C(8)	1.539(3)	C(7)−C(7′)	1.529(5)
Si−C(5)	1.880(2)	Si−C(13)	1.870(3)
Si−C(6)	1.853(2)	Si−C(14)	1.883(3)
Angles			
Cg(1)−Ti−Cg(1′)	137.0(1)	Cg(1)−Ti−C(6)	102.4(1)
C(6)−Ti−C(6′)	81.9(1)	Cg(1)−Ti−C(6′)	109.8(1)
Ti−C(6)−C(7)	107.9(1)	Ti−C(6)−Si	97.7(1)
C(5)−Si−C(6)	93.8(1)	Si−C(6)−C(7)	112.5(2)
C(6)−C(7)−C(8)	110.4(2)	C(6)−C(7)−C(7′)	112.4(2)
ϕ[c]	38.74(7)	ω[d]	111.2(2)
τ[e]	48.8(2)	C(8)−C(7)−C(7′)−C(8′)	61.2(2)

[a] Prime labeled equivalent positions are generated by the symmetry operation ($-x$, y, $1/2 - z$). [b] Cg(1) denotes centroid of the C(1−5) cyclopentadienyl ring. [c] Dihedral angle between the least-squares cyclopentadienyl planes. [d] Torsion angle C(5)−Cg−Cg′−C(5′). [e] Torsion angle C(6)−C(7)−C(7′)−C(6′).

(Si−C5 1.880(2)°, Si−C6 1.853(2)°) are longer than sp^3 C−C bonds in the tether of **IIc** (av 1.52(1) Å), and this is likely the reason for the double bond shift from terminal to internal position occurring upon cyclization. Whereas the complex with a two-carbon link, **IIb**, is formed without a double bond isomerization, the geometry of the Si−C tether would apparently lead to a structure more strained than **5**. The presence of steric strain in **5** is indicated by a large deviation of the silicon atom from the least-squares cyclopentadienyl ring plane toward the titanium atom (0.760(3) Å) and an outward deviation of the methyl carbon atoms at the hinge position (C10 by 0.354(4) Å) and in proximity of the titanacyclopentane ring (C12 by 0.283(4) Å).

Reactions of the Vinyl-Substituted Complex 3. The processes following the reductive removal of the chloride ligands from titanocene dichloride **3** are much more complicated than the reactions occurring with the homologous complex **4** (Scheme 4). When the magnesium reduction was carried out as for **3** (at 60 °C in THF), a mixture of η^2-alkene complex **7** (major) and paramagnetic η^3-allyl complex **8** resulted in 83% combined yield. Compounds **7** and **8** could not be isolated by fractional crystallization due to their similar solubilities in hexane and toluene, but brown crystals of **7** were manually separated from purple crystals of **8** in a glovebox and the X-ray crystal structure of **7** was determined (see below). The solution prepared from the selected crystals still contained traces of paramagnetic **8**, whose presence precluded an analysis of NMR spectra. Nevertheless, the coordination of the double bond to the titanium center in **7** was proved by electronic absorption spectra showing an absorption band at 980 nm typical for a π-coordinated double or triple bond to Ti(II) in titanocene species.[13] Compound **8** obviously arises from **7** by hydrogen transfer to an unknown proton acceptor since upon prolonged heating of the reaction mixture the proportion of **8** increases, however, with concurrent formation of unidentified inseparable byproducts. To avoid the byproduct formation, the reduction of **3** was carried out as above but with added bis(trimethylsilyl)ethyne (btmse), which had been shown to act as a hydrogen acceptor in some reactions of highly substituted titanocene complexes.[13a,14] Accordingly, complex **8** resulted in 77% isolated yield, while btmse was hydrogenated to a mixture of (*Z*)- and (*E*)-1,2-bis(trimethylsilyl)ethene. Compound **8** contains the η^3-bonded allyl group formed in the *ansa*-chain, as indicated by the ESR signal at g_{iso}= 1.9905 ($\Delta H = 5.0$ G) and electronic absorption band at 550 nm, which both are typical of d^1 (η^3-allyl)titanocene derivatives.[15] The structure of **8** has been determined by X-ray crystallography (see below).

Upon lowering the reaction temperature, the course of reactions following the removal of chloride ligands changes dramatically. Reduction of **3** with excess magnesium metal at −5 °C and in the absence of btmse yields a mixture of complexes **9** and **10** (Scheme 4) in ca. 2.3:1 ratio according to NMR analysis. Crystallization of the mixture from hexane affords pure **10**, which, however, gives a **9**/**10** mixture after redissolving in C_6D_6. NMR spectra of **10** are analogous to spectra of metallacycle **5**. Complex **9** exhibits haptotropic fluxionality (Scheme 5). The exchange of the free and titanium-coordinated double bonds is rather slow at room temperature. A variable-temperature NMR study in the range 0−60 °C and in benzene-d_6 solution has shown that while heating to 60 °C is not sufficient for a full coalescence to occur, resulting only in an extensive broadening of the signals due to **9**, cooling to 0 °C significantly lowers the exchange rate. At a temperature of +5 °C, the mean line widths at half-maximum for the methyl signals (SiMe_2 and η^5-C_5Me_4) are 4.8 Hz (**9**) and 1.0 (**10**). The resonances due to **10** as well as the **9**:**10** ratio remain unchanged over the temperature range studied. Furthermore, neither standing at room temperature for several days nor heating to 90 °C for 6 h changes the product distribution.

In the solid state, complex **10** has been characterized by X-ray crystallography and IR spectroscopy. The melting point of **10** is low compared with that of **5** (117 vs 171 °C), and it is therefore possible that the melting point indicates the temperature of conversion of **10** to probably low-melting **9** or **7**. Also, the EI-MS spectrum of **10** (evaporated at 90 °C) may be contributed to by **9** or **7**, the spectra of the latter and **10** displaying the molecular ions $M^{\bullet+}$ as the base peaks. Evaporation of the **9**/**10** mixture leaves a brown solid, whose IR spectrum shows in addition to less intense bands of **10** the bands cleanly attributable to an uncoordinated vinyl group of **9** (see Experimental Section). Oxidation of the **9**/**10** mixture with solid $PbCl_2$ quantitatively recovers the parent titanocene dichloride **3** similarly to oxidation

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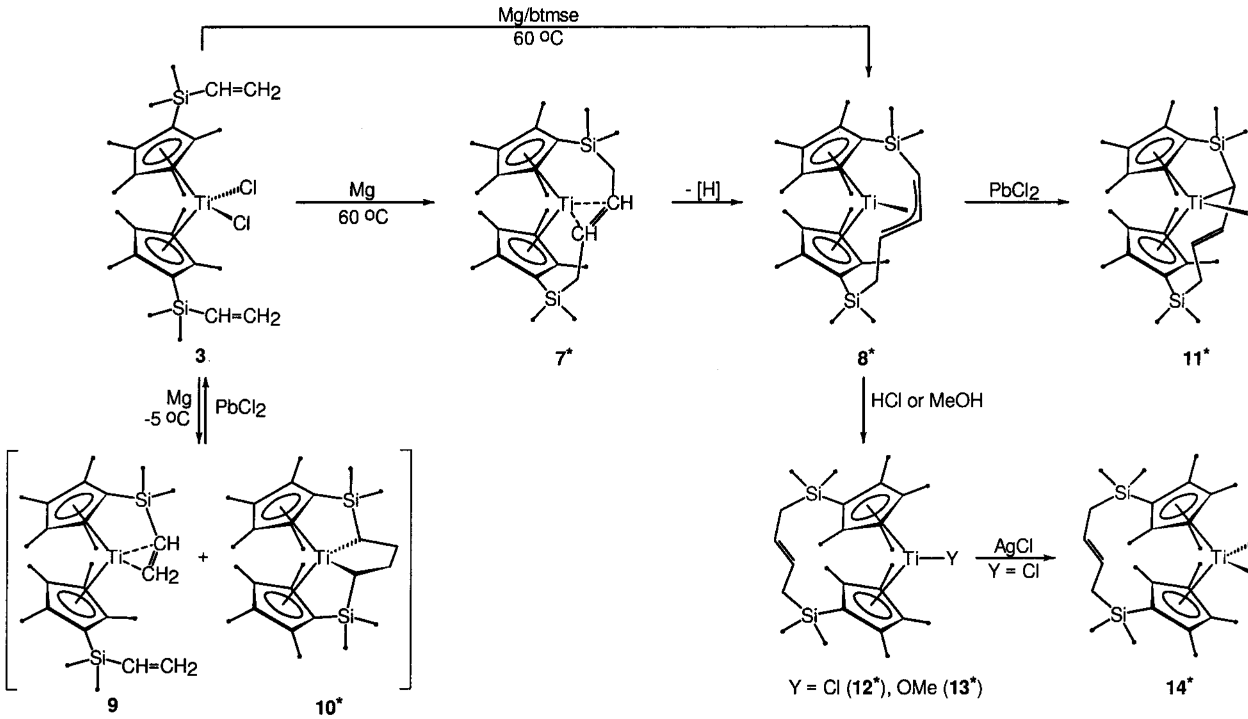
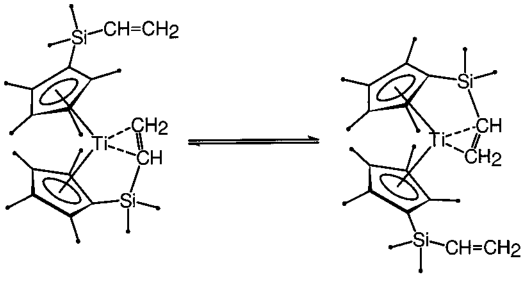
Scheme 4. Reactions Involving the Vinyldimethylsilyl Titanocene Dichloride 4[a]



[a] The asterisk indicates that the crystal structure has been determined.

Scheme 5



of titanacyclopentane compounds derived from pendant alkenyl permethyltitanocene precursors (**IIa**−**c**, Scheme 1).[12]

Compound **8** represents an excellent precursor for a number of *ansa*-titanocene d^0 and d^1 complexes. An oxidation of **8** by $PbCl_2$ should preserve the Ti−C bond, as it has been expected from well-known reactions of this reagent with Ti(III) titanocene η^1-hydrocarbyl compounds.[17] In the present case, the oxidation is accompanied by $\eta^3 \rightarrow \eta^1$ rearrangement of the allyl group, leaving intact the Ti−C σ-bond to the sp^3 carbon atom neighboring the silicon atom. The obtained cyclopentadienyl ring-tethered chloro(η^1-organyl) titanocene complex **11** (Scheme 4) contains the uncoordinated double bond in the center of the *ansa*-chain, but the chain is surprisingly linked to the titanium atom in the most asymmetric way, which induces different steric strain at the cyclopentadienyl ligands (see discussion of the crystal structure below). Compound **11** is the main product (76%); a poorly soluble minor byproduct has not been identified.

Alternatively, the titanium−allyl bond in **8** is cleaved by protic reagents such as HCl or methanol to yield paramagnetic d^1 *ansa*-titanocene monochloride **12** and methoxide **13** complexes, which have the uncoordinated double bond in the center of the *ansa*-chain. The reaction of **8** with HCl proceeds with concomitant formation of byproducts resulting from cleavage of Si−C bonds similarly to the opening of titanacyclopentane **5** (see Experimental Section). Solid-state structures of **12** and **13** were determined by X-ray diffraction (see below) and further corroborated by ESR and electronic absorption spectra. The turquoise compound **12** shows in toluene solution a lower g_{iso} and, in a frozen solution, more anisotropic ESR spectra than $[TiCl(\eta^5\text{-}C_5Me_5)_2]$.[18] In UV−vis spectra, the d−d transitions ($1a_1 \rightarrow 2a_1$ 590 nm and $1a_1 \rightarrow b_1$ 690 nm) are shifted to longer wavelengths by ca. 50 nm compared to the same reference compound.[18a] Following the MO model described by Andersen et al.[18a] these data are compatible with a decreased destabilization of the LUMO b_2 orbital attributable to a lower π-donation effect of the chloride ligand in **12**. The extent of the destabilization can be influenced by the magnitude of angle between the cyclopentadienyl ring planes (ϕ) and by placement of the electron donor substituent away from the plane of the trigonally coordinated titanium atom. Since the angle ϕ is virtually equal for **12** (36.6(1)°; see below) and $[TiCl(\eta^5\text{-}C_5Me_5)_2]$ (36.4(2)°)[18c,d] in the solid state, we have to assume that a lower destabilization effect of chlorine is

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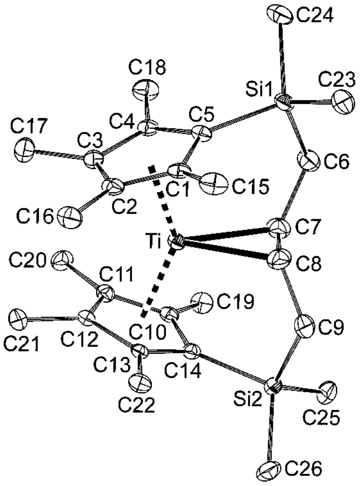

Figure 2. Molecular structure of **7**.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for 7[a,b]

Distances			
Ti−Cg(1)[a]	2.086(4)	Ti−C(Cp)	2.371(3)−2.450(3)
Ti−Cg(2)[a]	2.086(4)	C(Cp)−C(Cp)	1.402(5)−1.439(5)
C(7)−C(8)	1.411(6)	C(Cp)−Me	1.504(5)−1.515(5)
Ti−C(7)	2.242(4)	Ti−C(8)	2.238(4)
C(6)−C(7)	1.528(5)	C(8)−C(9)	1.494(5)
Si(1)−C(5)	1.873(3)	Si(1)−C(6)	1.869(4)
Si(2)−C(9)	1.857(4)	Si(2)−C(14)	1.870(3)

Angles			
Cg(1)−Ti−Cg(2)	140.6(3)	C(7)−Ti−C(8)	36.7(2)
Ti−C(7)−C(6)	122.4(3)	Ti−C(8)−C(9)	121.9(3)
C(5)−Si(1)−C(6)	101.3(2)	C(9)−Si(2)−C(14)	101.2(2)
Si(1)−C(6)−C(7)	109.2(3)	Si(2)−C(9)−C(8)	111.0(3)
C(6)−C(7)−C(8)	124.4(4)	C(7)−C(8)−C(9)	125.1(4)
ϕ[b]	35.5(2)	ω[c]	35.6(4)
τ[d]	53.8(5)		

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(10−14) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares cyclopentadienyl planes. [c] Torsion angle C(5)−Cg(1)−Cg(2)−C(14). [d] Torsion angle C(6)−C(7)−C(8)−C(9).

due to the placement of the Cl atom 1.69(1) Å away from the Cg1TiCg2 plane. A slightly more anisotropic ESR spectrum of **13** in frozen solution and a red shift of the $1a_1 \rightarrow b_2$ absorption band compared with data for $[Ti(OMe)(\eta^5\text{-}C_5Me_5)_2]$[18a] (1420 vs 1282 nm) also indicate a lower destabilization effect of the methoxy group in this compound. The placement of the oxygen atom 1.358(9) Å away from the Cg1TiCg2 plane can also be accounted for.

Compound **12** offers an easy access to *ansa*-titanocene dichloride, a simple, unsaturated homologue of **6**. Surprisingly, the oxidative addition of chlorine did not proceed with commonly used $PbCl_2$, as **12** in THF remained resistant even at a temperature of 100 °C (in a sealed ampule). Nevertheless, the oxidation reaction was effected by using a slight molar excess of AgCl (at 80 °C for 1 h)[17a] to afford compound **14** in 80% isolated yield.

Crystal Structure of 7. Compound **7** crystallizes in orthorhombic space group $P2_12_12_1$ (No. 19), however, with no imposed *crystallographic* symmetry (Figure 2, Table 2). The geometry of molecule indicates some steric strain induced by the requirements of the η^2-coordinated double bond which resides in the center of the six membered *ansa*-chain. As a result, the angle between the least-squares planes of the cyclopentadienyl rings is rather small ($\phi = 35.5(2)°$), the cyclopentadienyl rings are mutually rotated at the twist angle C5−Cg1−Cg2−C14 of 35.6(4)°, and the three-membered metallacycle TiC7C8 is very nearly perpendicular to the Cg1TiCg2 plane. The torsion angle at the coordinated double bond C6−C7−C8−C9, 53.8(5)°, indicates a contribution of sp^3 hybridization, which is compatible with the elongation of the coordinated double bond (C7−C8 1.411(6) Å). Slightly longer values for η^2-coordinated double bond were found in $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}C_2H_4)]$ (1.438(5) Å),[16] $[Ti(\eta^5\text{-}C_5Me_4SiMe_3)_2(\eta^2\text{-}C_2H_4)]$ (1.442(9) Å),[13b] and $[Ti(\eta^5\text{-}C_5Me_5)(\eta^2{:}\eta^5\text{-}C_{22}H_{35})]$ (1.462(4) Å) with the coordinated double bond of the cyclooctene ring annelated to one of the two C_5Me_5 ligands.[13c] Accordingly, the values of Ti−C bond lengths to the coordinated double bond Ti−C7, 2.242(4) Å, and Ti−C8, 2.238(4) Å, are somewhat longer than in the above-mentioned complexes, thus pointing to a weaker π-coordination, apparently due to the steric strain.

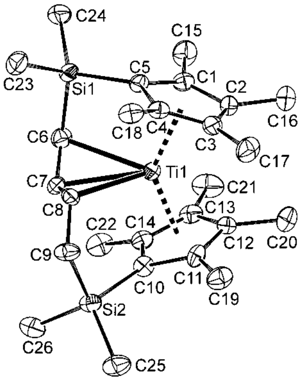

Figure 3. Molecular structure of **8**.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Molecule 1 of Complex 8

Distances			
Ti(1)−Cg(1)[a]	2.120(9)	Ti−C(Cp)	2.327(9)−2.551(9)
Ti(1)−Cg(2)	2.109(9)	C(Cp)−C(Cp)	1.396(12)−1.439(12)
Si−Me	1.87(1)−1.89(1)	C(Cp)−Me	1.474(13)−1.519(12)
Ti(1)−C(6)	2.509(9)	C(6)−C(7)	1.381(12)
Ti(1)−C(7)	2.392(8)	C(7)−C(8)	1.383(12)
Ti(1)−C(8)	2.435(8)	C(8)−C(9)	1.496(12)
Si(1)−C(5)	1.855(8)	Si(2)−C(9)	1.883(9)
Si(1)−C(6)	1.864(9)	Si(2)−C(10)	1.890(9)

Angles			
Cg(1)−Ti(1)−Cg(2)	138.0(4)	C(6)−Ti(1)−C(8)	60.4(3)
C(6)−Ti(1)−C(7)	32.6(3)	C(7)−Ti(1)−C(8)	33.3(3)
C(6)−C(7)−C(8)	128.5(8)	C(7)−C(8)−C(9)	122.2(8)
C(5)−Si(1)−C(6)	96.9(4)	C(9)−Si(2)−C(10)	103.4(4)
Si(1)−C(6)−C(7)	121.9(7)	Si(2)−C(9)−C(8)	111.0(6)
ϕ[b]	36.7(5)	ψ[c]	108.2(9)
ω[d]	58.3(7)	τ[e]	6.0(8)

[a] Cg(1) and Cg(2) are the centroids of the C(1−5) and C(10−14) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares cyclopentadienyl planes. [c] Dihedral angle subtended by the Ti(1)C(6)C(8) and C(6)C(7)C(8) planes. [d] Torsion angle C(5)−Cg(1)−Cg(2)−C(10). [e] Torsion angle C(6)−C(7)−C(8)−C(9).

Crystal Structure of 8. Crystals of **8** contain two pairs of different molecules within triclinic unit cell. The structure of molecule **1** is shown in Figure 3, and the relevant geometrical parameters are listed in Table 3. Despite a rather low accuracy of the crystallographic data, the location of the allyl group in the six-membered *ansa*-chain can be unequivocally recognized. The allyl

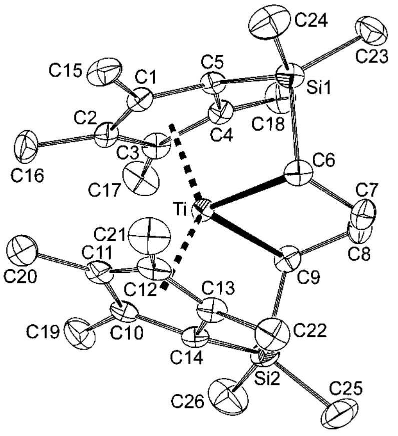

Figure 4. Molecular structure of **10**.

group is bonded to titanium in a η^3-mode and the *ansa*-carbon chain is nearly planar, as demonstrated by the torsion angle C6−C7−C8−C9, which amounts to only 6.0(8)°. The Ti−C bond lengths (Ti−C6 2.509(9) Å, Ti−C7 2.392(8) Å, Ti−C8 2.435(8) Å) are longer than those in $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}1,2\text{-dimethylallyl})]$,[19a] $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}1,3\text{-dimethylallyl})]$,[19b] $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}2\text{-methylallyl})]$,[19b] and $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)(\eta^3\text{-allyl})]$.[19b] The dihedral angle between the C6Ti1C8 and C6C7C8 planes (108.2(9)°) is smaller than the corresponding angle in the 1,3-dimethylallyl compound (av 112.8°), which is the smallest value found among the above-mentioned compounds.[19a,b] The difference in bond lengths between the titanium center and outer carbon atoms of the allyl group likely arises from a steric strain and does not indicate a contribution of a η^1-coordination mode because the bond length to the central carbon atom is far the shortest one. A strong contribution of the η^1-allyl mode has been recently found in bis(allyl)titanium(III) derivatives $[\mathrm{TiCl}(\mathrm{Et_2PCH_2CH_2PEt_2})(\eta^3\text{-}C_3H_5)_2]$,[19c] and $[\{\eta^3\text{-}(^t\mathrm{BuMe_2SiCH})_2\mathrm{CH}\}_2\mathrm{Ti}(\mu\text{-Cl})_2\mathrm{Li}(\mathrm{Me_2NCH_2CH_2NMe_2})]$,[19d] where the Ti−C distances increase in the order $C_1 < C_2 < C_3$ along the allyl group. The rigidity of the *ansa*-chain apparently forces the cyclopentadienyl rings to twist by as much as 58.3(7)° and to decline the attached silicon atoms from the least-squares cyclopentadienyl planes by 0.50(1) Å (Si1) and 0.12(1) Å (Si2) toward the titanium atom. The methyl groups on the cyclopentadienyl rings opposite to the dimethylsilylene substituents (C16 and C20) decline from the least-squares planes of the cyclopentadienyl rings in an outward direction by 0.42(2) and 0.39(2) Å, respectively, despite approximately staggered configuration of the cyclopentadienyl rings.

Crystal Structure of 10. The monoclinic crystal of **10** contains two pairs of chiral molecules in a racemic crystal (Figure 4 and Table 4). The titanacyclopentane moiety features Ti−C bonds marginally shorter than Ti−C bonds in **5**, while the C6−Ti−C9 angle is equal to that in **5** within the precision of measurement. However, the cyclopentadienyl rings are less twisted than in **5** (ω 98.2(5)° vs 111.2(2)°), and this results in a larger strain which is further demonstrated in the titanocene framework: the silicon atoms decline from the least-squares planes of the cyclopentadienyl rings by 0.784(8) Å (Si1) and 0.767(8) Å (Si2) toward the titanium center, and a relatively large tilt angle ϕ of 39.2(2)° forces the carbon atoms at hinge position C16 and C20 to decline by as much as 0.353(9) and 0.358(9) Å in an outward direction. Comparison of these structure features with those of **5** indicates a slightly larger strain in **10**, which is in accordance with the observed lower stability.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for 10[a,b]

	Distances		
Ti−Cg(1)[a]	2.114(5)	Ti−C(Cp)	2.359(4)−2.510(5)
Ti−Cg(2)[a]	2.124(5)	C−C(Cp)	1.385(8)−1.461(6)
Si−Me	1.841(7)−1.880(6)	C(Cp)−Me	1.491(7)−1.514(6)
Ti−C(6)	2.270(5)	Ti−C(9)	2.266(4)
C(6)−C(7)	1.528(6)	C(7)−C(8)	1.499(8)
Si(1)−C(5)	1.880(5)	Si(2)−C(9)	1.829(5)
Si(1)−C(6)	1.829(5)	Si(2)−C(14)	1.883(5)
C(8)−C(9)	1.524(7)		
	Angles		
Cg(1)−Ti−Cg(2)	137.6(3)	C(6)−Ti−C(9)	82.4(2)
Ti−C(6)−Si(1)	96.9(2)	Ti−C(9)−Si(2)	97.1(2)
Ti−C(6)−C(7)	106.1(3)	Ti−C(9)−C(8)	106.2(3)
C(5)−Si(1)−C(6)	97.1(2)	C(9)−Si(2)−C(14)	96.7(2)
Si(1)−C(6)−C(7)	120.4(4)	Si(2)−C(9)−C(8)	120.5(4)
C(6)−C(7)−C(8)	114.1(4)	C(7)−C(8)−C(9)	114.7(4)
ϕ[b]	39.2(3)	ω[c]	98.2(5)
τ[d]	48.7(6)		

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(10−14) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares cyclopentadienyl planes. [c] Torsion angle C(5)−Cg(1)−Cg(2)−C(14). [d] Torsion angle C(6)−C(7)−C(8)−C(9).

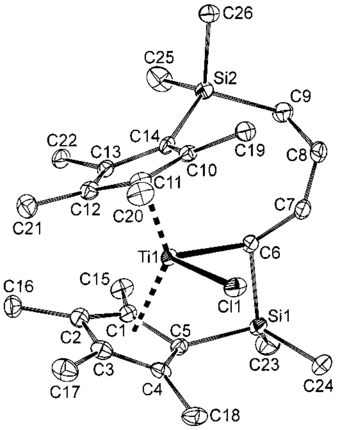

Figure 5. Molecular structure of **11**.

Crystal Structure of 11. Compound **11** crystalizes in a monoclinic unit containing two asymmetrical molecules (Figure 5 and Table 5). Oxidation of **8** lowers the hapticity of the allyl system in the *ansa*-chain but leaves the C6 atom σ-bonded to titanium at a distance of 2.312(3) Å. The noncoordinated double bond C7−C8 (1.323(5) Å) in *cis* configuration displays a torsion angle C6−C7−C8−C9 of only 1.8(6)°. Strongly asymmetric anchoring of the *ansa*-chain to the pseudotetrahedrally coordinated titanium atom results in different deformations at the cyclopentadienyl ligands. The Si1 atom declines from the cyclopentadienyl ring least-squares plane toward the titanium atom by 0.714(6) Å, whereas the Si2 atom declines by 0.492(5) Å in an outward

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Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for 11[a,b]

	Distances		
Ti−Cg(1)[a]	2.137(4)	Ti−C(Cp)	2.365(3)−2.531(4)
Ti−Cg(2)[a]	2.133(3)	C−C(Cp)	1.402(5)−1.451(5)
Si−Me	1.866(4)−1.882(4)	C(Cp)−Me	1.490(5)−1.509(5)
Ti−Cl(1)	2.3350(8)	Ti−C(6)	2.312(3)
Si(1)−C(5)	1.873(4)	Si(2)−C(9)	1.886(4)
Si(1)−C(6)	1.863(3)	Si(2)−C(14)	1.892(4)
C(6)−C(7)	1.461(5)	C(8)−C(9)	1.497(6)
C(7)−C(8)	1.323(5)		
	Angles		
Cg(1)−Ti−Cg(2)	137.1(3)	Cl(1)−Ti−C(6)	90.70(9)
Ti−C(6)−C(7)	115.7(2)	Ti−C(6)−Si(1)	96.0(2)
C(5)−Si(1)−C(6)	93.6(2)	Si(1)−C(6)−C(7)	119.9(2)
C(6)−C(7)−C(8)	126.0(3)	C(7)−C(8)−C(9)	123.2(4)
Si(2)−C(9)−C(8)	115.3(3)	C(9)−Si(2)−C(14)	116.1(2)
ϕ[b]	41.6(2)	ω[c]	37.0(4)
τ[d]	1.8(6)		

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(10−14) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares cyclopentadienyl planes. [c] Torsion angle: C(5)−Cg(1)−Cg(2)−C(14). [d] Torsion angle C(6)−C(7)−C(8)−C(9).

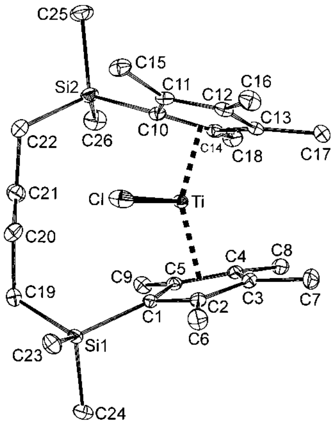

Figure 6. Molecular structure of **12**.

direction. The methyl carbon atoms bonded to cyclopentadienyl rings at hinge positions are declined from the ring least-squares planes in an outward direction (C16 by 0.430(6) Å, C21 by 0.294(6) Å). The cyclopentadienyl rings are twisted by only 37.0(4)°, which is compatible with the large angle subtended by the least-squares planes of the cyclopentadienyl rings (41.6(2)°). Surprisingly, the Cl−Ti−C6 plane is nearly perpendicular with respect to the Cg1−Ti−Cg2 plane (87.1(2)°) and subtend dihedral angles with the least-squares cyclopentadienyl ring planes of 17.5(2)° (C(1−5)) and 25.2(2)° (C(10−14)). The Ti−Cl bond length of 2.3350(8) Å in **11** is shorter than the Ti−Cl bonds in pseudotrigonally coordinated complexes, cf. Ti−Cl bond lengths in [TiCl(η^5-C_5Me_5)$_2$][18c] (2.363(1) Å) or **12** (see below).

Crystal Structures of 12 and 13. Solid-state structures of **12** ans **13** are both unsymmetric, showing similar overall geometry (Figures 6 and 7, Table 6). The *trans* double bond C20−C21 is located in the center of the *ansa*-chain and displays a torsion angle of 4.6(2)° in **12** and 4.4(2)° in **13**. The least-squares cyclopentadienyl-ring planes adopt an identical dihedral angle of 36.6(1)° and show similar twist (C1−Cg1−Cg2−C10 43.6(1)° and 44.2(1)°). The steric strain is releaved by placing the *ansa*-chain in a side position with respect to the Cg1−Ti−Cg2 plane, which is directed toward the electronegative substituents (Cl, OMe). As a result of a low steric strain, the Si atoms are only moderately declined from the cyclopentadienyl ring planes in outward positions (max. 0.408(3) Å for Si1 in **13**), and the geometry of the titanocene skeleton of **12** differs only negligibly from that of [TiCl(η^5-C_5Me_5)$_2$].[18c,d] The trigonally coordinated Ti(III) atoms tend to dimerize through the electronegative substituents but only for derivatives having up to two methyl groups per one cyclopentadienyl ring;[20] highly methylated titanocene monohalides,[18c,21a−c] monoalkoxides,[18a,c,21d] and permethylated $SiMe_2$-bridged *ansa*-titanocene monochloride remain monomeric.[18d] The side placement of the *ansa*-chain has been observed in permethyl-substituted titanocene monochlorides with bridging 1,2,5-trimethylpentane-1,5-diyl and 4,5-dimethyloct-2-ene-1,8-diyl *ansa*-chains.[21e] In **13**, the bending of the methoxytitanium bond at the carbon atom is smaller (Ti−O−C27 165.0(2)°) than in [Ti($OCMe_3$)(η^5-C_5HMe_4)$_2$] (162.2(1)°).[21d]

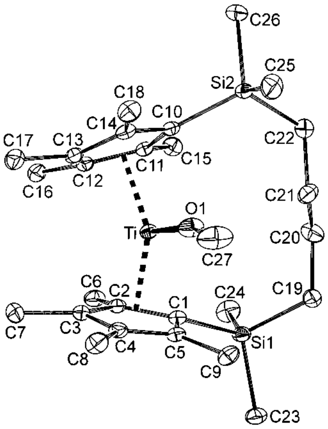

Figure 7. Molecular structure of **13**.

Crystal Structure of 14. The monoclinic unit cell contains two pairs of asymmetric molecules (Figure 8 and Table 7). The arrangement of the titanocene unit with the *ansa*-chain in the side position does not differ from that of **12** except that the presence of two chloride ligands at pseudotetrahedrally coordinated Ti(IV) enlarges the dihedral angle of the least-squares cyclopentadienyl planes to 42.2(1)°. The twist angle is somewhat smaller (39.0(4)°) than in **12** (43.6(1)°). An increased strain in **14** is displayed by a larger torsion angle at the double bond in the *ansa*-chain (11.0(5)°) and by a larger outward declination of the Si atoms (Si1 0.565(5) Å, Si2 0.612(5) Å) and methyl groups at the hinge position (C8 0.316(5) Å, C15 0.422(5) Å) from the parent ring planes. The Ti−Cg distances (2.139(4) and 2.142(4) Å) and Ti−Cl bond lengths (2.340(1) and 2.383(1) Å) are marginally longer while Cl1−Ti−Cl2 angle is slightly more acute than that in [$TiCl_2$(η^5-C_5Me_5)$_2$] (cf.

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Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 12, 13, and 14

A. Complexes **12** and **13**

	12	**13**		**12**	**13**
Distances					
Ti−Cl	2.3537(5)		Ti−O		1.843(2)
Ti−Cg(1)[a]	2.074(2)	2.101(2)	Ti−Cg(2)[a]	2.077(2)	2.119(2)
Ti−C(Cp)	2.375(2)−2.437(2)	2.408(2)−2.495(2)	C(Cp)−C(Cp)	1.409(2)−1.436(2)	1.403(3)−1.443(3)
Si−Me av	1.865(2)−1.874(2)	1.869(3)−1.882(2)	C(Cp)−Me	1.501(3)−1.505(3)	1.495(3)−1.508(3)
Si(1)−C(1)	1.882(2)	1.869(2)	Si(1)−C(19)	1.888(2)	1.880(2)
Si(2)−C(10)	1.878(2)	1.872(2)	Si(2)−C(22)	1.886(2)	1.883(2)
C(19)−C(20)	1.505(3)	1.498(3)	C(20)−C(21)	1.321(3)	1.323(3)
C(21)−C(22)	1.494(3)	1.492(3)	O−C(27)		1.387(3)
Angles					
Cg(1)−Ti−Cg(2)[a]	141.8(1)	140.5(1)	C(1)−Si(1)−C(19)	113.36(8)	113.9(1)
C(10)−Si(2)−C(22)	112.84(8)	113.3(1)	Si(1)−C(19)−C(20)	114.2(1)	113.8(2)
Si(2)−C(22)−C(21)	113.6(1)	114.7(2)	C(20)−C(21)−C(22)	125.8(2)	124.8(2)
C(19)−C(20−C(21)	125.1(2)	125.7(2)	Ti−O−C(27)		165.0(2)
Cl−Ti−Cg(1)	109.0(1)		Cl−Ti−Cg(2)	108.2(1)	
O−Ti−Cg(1)		109.7(1)	O−Ti−Cg(2)		108.9(1)
ϕ[b]	36.6(1)	36.6(1)	ω[c]	43.6(1)	44.2(1)
τ[d]	4.6(2)	4.4(2)			

B. Complex **14**

Distances			
Ti−Cg(1)[a]	2.139(4)	Ti−Cg(2)[a]	2.142(4)
Ti−C(Cp)	1.424(3)−1.489(3)	C(Cp)−C(Cp)	1.399(4)−1.439(4)
Si−Me	1.865(3)−1.876(3)	C(Cp)−Me	1.500(4)−1.509(4)
Ti−Cl(1)	2.340(1)	Ti−Cl(2)	2.383(1)
C(1)−Si(1)	1.895(3)	C(10)−Si(2)	1.891(3)
Si(1)−C(19)	1.872(4)	Si(2)−C(22)	1.889(3)
C(19)−C(20)	1.490(5)	C(22)−C(21)	1.518(5)
C(20)−C(21)	1.310(5)		
Angles			
Cg(1)−Ti−Cg(2)	138.0(1)	Cl(1)−Ti−Cl2	90.46(3)
C(1)−Si(1)−C(19)	116.37(14)	C(10)−Si(2)−C(22)	114.50(15)
Si(1)−C(19)−C(20)	113.8(3)	Si(2)−C(22)−C(21)	108.6(2)
C(19)−C(20)−C(21)	124.9(4)	C(22)−C(21)−C(20)	126.8(3)
ϕ[b]	42.2(1)	ω[c]	39.0(4)
τ[d]	11.0(5)		

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(10−14) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares cyclopentadienyl planes. [c] Dihedral angle: C(1)−Cg(1)−Cg(2)−C(10). [d] Torsion angle C(19)−C(20)−C(21)−C(22).

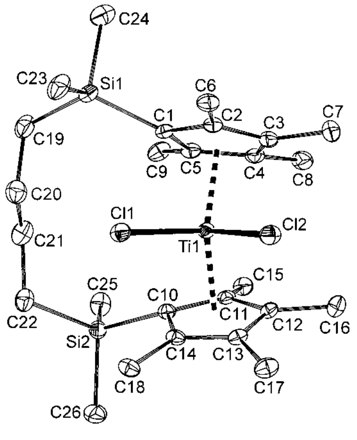

Figure 8. Molecular structure of **14**.

90.46(3)° vs 92.9°).[22] Comparison with structures of analogous permethyltitanocene dichlorides containing a saturated octane-1,8-diyl chain which is attached at hinge positions[12] and an unsaturated oct-2-ene-1,8-diyl chain which is attached at side positions[21e] shows that steric strain can be relieved either by a conformational change of the *ansa*-chain or by twisting of the cyclopentadienyl ligands.

Discussion

The reduction-induced reactions of **3** and **4** parallel in many regards the behavior of analogous nonsilylated complexes shown in Scheme 1.[12] The parent titanocene dichlorides are first reduced in a stepwise manner (with paramagnetic titanocene monochlorides as the intermediates) and, second, the product of the complete removal of the chloride ligands, coordinatively unsaturated 14 valence electron titanocene complexes, immediately interact with the pendant double bonds to increase their valence electron count. The general reaction scheme differs significantly not only between the parent complexes **3** and **4** but also with respect to nonsilylated complexes having the same number of atoms in the pendant chain.[12] The difference between hydrocarbyl chain and its dimethylsila analogue can be accounted for by changed steric properties, namely, increased chain lengths upon replacement of the pivotal carbon atom with a SiMe$_2$ group. This is best reflected in the behavior of the silylallyl-substituted titanocene dichloride **4**, which reacts analogously to $[\mathrm{TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2)_3CH{=}CH_2\}_2}]$ (**Ic**). In both cases, the oxidative cycloaddition of the double bonds across the titanium(II) atom in the titanocene intermediate is accompanied by C−C double bond shift to provide dimethyl-substi-

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Table 7. Crystallographic Data, Data Collection, and Structure Refinement for Compounds 5, 7, 8, 10, 11, 12, 13, and 14[a]

	5	**7**	**8**	**10**
chemical formula	$C_{28}H_{46}Si_2Ti$	$C_{26}H_{42}Si_2Ti$	$C_{26}H_{41}Si_2Ti$	$C_{26}H_{42}Si_2Ti$
molecular weight	486.73	458.68	457.67	458.68
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	18.0110(4)	9.6340(3)	12.1010(8)	14.207(3)
b (Å)	11.4660(6)	10.7540(4)	12.7240(8)	11.713(2)
c (Å)	14.4660(7)	24.3360(8)	16.528(1)	15.210(2)
α (deg)	90	90	84.570(4)	90
β (deg)	114.198(3)	90	83.716(4)	92.91(1)
γ (deg)	90	90	85.603(4)	90
V (Å^{-3})	2724.9(2)	2521.3(2)	2512.6(3)	2527.7(8)
T (K)	293	293	293	293
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.186	1.208	1.210	1.205
μ (mm^{-1})	0.416	0.445	0.446	0.444
cryst color	greenish-brown	brown	purple-blue	brown
cryst size (mm^3)	0.3× 0.3× 0.25	0.4× 0.3× 0.2	0.3× 0.2× 0.2	0.6× 0.5× 0.5
θ_{max} (deg)	26.0	25.0	25.2	25.0
hkl range	−22/22;−14/14;−17/16	0/11;0/12;−28/28	0/14;−14/−15;−19/19	0/16;−13/13;−11/18
no. of diffrns collected	10 671	4265	8835	5672
no. of unique diffrns	2672	4265	8835	2786
F(000)	1056	992	988	992
no. of params	156	388	547	388
$R(F)$; $wR(F^2)$ all data (%)	5.4; 11.5	5.12; 11.82	16.97; 26.97	9.15; 12.1
GooF (F^2) all data	1.101	1.174	1.191	1.032
$R(F)$ [$I > 2\sigma(I)$]	4.24	4.40	11.9	4.47
$\Delta\rho$ (e Å^{-3})	0.27; −0.26	0.363; −0.601	0.966; −0.762	0.313; −0.301

	11	**12**	**13**	**14**
chemical formula	$C_{26}H_{41}ClSi_2Ti$	$C_{26}H_{42}ClSi_2Ti$	$C_{27}H_{45}OSi_2Ti$	$C_{26}H_{42}Cl_2Si_2Ti$
molecular weight	493.12	494.13	489.71	529.58
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	8.6141(3)	8.5100(2)	28.401(1)	8.1660(2)
b (Å)	16.0382(8)	10.1080(3)	15.4320(7)	32.0790(7)
c (Å)	9.9644(3)	16.8920(4)	14.4340(5)	10.7310(2)
α (deg)	90	72.868(2)	90	90
β (deg)	109.099(2)	86.070(2)	119.653(2)	103.524(1)
γ (deg)	90	74.859(2)	90	90
V (Å^3)	1300.85(9)	1340.30(6)	5497.7(4)	2733.1(1)
T (K)	150	150	150	150
Z	2	2	8	4
D_{calc} (g cm^{-3})	1.259	1.224	1.183	1.287
μ (mm^{-1})	0.535	0.520	0.415	0.609
cryst color	greenish-brown	blue	dark red	brown-red
cryst size (mm^3)	0.3× 0.3× 0.2	0.5× 0.3× 0.2	0.6× 0.45× 0.4	0.75× 0.2× 0.1
θ_{max} (deg)	27.5	27.5	27.5	25.0
hkl range	−11/11;−20/20;−12/12	−11/11;−12/13;−21/21	−36/36;−20/20;−18/16	−9/9;−38/38, −12/12
no. of diffrns collected	23 210	19 285	26 869	25 642
no. of unique diffrns	5515	5959	6225	4810
F(000)	528	530	2120	1128
no. of params	270	439	317	316
$R(F)$; $wR(F^2)$ all data (%)	5.10; 11.83	4.28; 8.36	6.57; 11.5	6.31; 11.6
GooF (F^2) all data	1.066	1.066	1.026	1.056
$R(F)$ [$I > 2\sigma(I)$]	4.49	3.40	4.31	4.52
$\Delta\rho$ (e Å^{-3})	0.456; −0.485	0.86; −0.27	0.32; −0.35	0.70;−0.38

[a] Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$, GooF $= [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

tuted titanacyclopentane, possessing the optimum ring size (compare **7** and structure **IIc** in Scheme 1).[11,12]

Extending this analogy to a pair of lower homologues, complex **3** should yield a simple titanacyclopentane similarly to [$TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2)_2CH{=}CH_2\}_2$] (**Ib**).[12] However, this occurs only partly at low temperature, where the expected titanacycle **10** is obtained as a minor product together with prevailing fluxional titanacyclopropane **9** resulting from coordination of only one double bond. The π-coordination of one of the two double bonds to the Ti(II) atom to give **9** is a common stabilization step with only low activation energy.[13b,16] Oxidative cycloaddition of both double bonds is apparently reversible. Compound **10** has limited stability due to probably unfavorable length of the dimethylsilylene tether.

At elevated temperatures, the primary oxidative addition is succeeded by a ring-opening rearrangement (2H-shift) which yields the less strained *ansa*-η^2-alkene complex **7**. Complex **7** then undergoes a hydrogen elimination or, formally, an activation of the C−H bond adjacent to the η^2-coordinated double bond followed by a loss of hydrogen, to give a Ti(III) η^3-allyl complex **8**. Since all this proceeds in the presence of active magnesium, an involvement of a titanocene-magnesium species in conversions **10** → **7** and **7** → **8** should be taken into consideration. The presence of btmse as a suitable hydrogen acceptor makes the **7** → **8** conversion highly effective.

In conclusion, the intramolecular oxidative cycloaddition of pendant double bonds to titanocene intermediates proceeds equally for silylalkenyl and alkenyl compounds, giving similar titanacyclopentane products where the $\mathrm{SiMe_2}$ tether formally replaces two methylene groups (ethane-1,2-diyl). The length of an extended C−Si−C unit (2 × 1.86(2) Å) is shorter than that of a linear C−C−C−C chain (3 × 1.52(2) Å), and its flexibility is lower. Therefore the steric strain in **5** and **10** is higher than in the nonsilylated compounds.[12] This makes particularly compound **10** remarkably unstable: it partially dissociates to give **9** by only dissolving in hydrocarbon solvents at ambient temperature, and in the presence of magnesium at moderate temperature it undergoes opening of the titanacycle to yield an *ansa*-titanocene complex stabilized by a π-coordinated double bond. These reactions do not occur with **5**, which is stabilized by methyl groups at the central carbon atoms of the titanacyclopentane moiety, which make the opening of the titanacyclopentane ring and the hydrogen shifts more difficult.

Compound **5** can cleanly be opened with HCl and thus represents a convenient source of *ansa*-bridged titanocene dichloride **6** with a six-membered saturated *ansa*-chain, which would be otherwise accessible only with difficulty.[23] This result is at variance with that for the pentenyl-derived analogue, whose opening by HCl affords the unsaturated eight-membered *ansa*-chain due to β-hydrogen elimination accompanying the scission of one of the two Ti−C bonds.[12] A similar acidolysis of compound **10** was not attempted because a product mixture would be obtained from a mixture of **9** and **10** present in solution. Instead of **10**, the η^3-allyl compound **8** may serve as an excellent starting material for the synthesis of *ansa*-titanocene derivatives, as it has been demonstrated by reaction of **8** with $\mathrm{PbCl_2}$ and protonic acids.

Experimental Section

General Considerations. Syntheses of silylated cyclopentadienes and titanocene dichlorides were carried out under argon atmosphere. All manipulations with Ti(III) and Ti(II) complexes were performed under vacuum on a vacuum line in sealed all-glass devices equipped with breakable seals. NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58 MHz) in $\mathrm{C_6D_6}$ solutions at 25 °C unless noted otherwise. Chemical shifts (δ/ppm) are referenced to residual proton solvent signal (δ_{H} 7.15) and solvent resonance (δ_{C} 128.0). EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into a direct inlet probe under argon. GC−MS analyses were performed on a Hewlett-Packard gas chromatograph (5890 series II) equipped with a capillary column SPB-1 (length 30 m; Supelco) and a mass spectrometric detector (5971 Å). IR spectra were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400−4000 cm^{-1}. KBr pellets were prepared in a Labmaster 130 (mBraun) glovebox under purified nitrogen. X-Band EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany). *g*-values were determined by using an $\mathrm{Mn^{2+}}$ standard at $g = 1.9860$ ($M_{\mathrm{I}} = -1/2$ line). A STT-3 variable-temperature unit was used for measurements in the range −196 to +25 °C. UV−near-IR spectra in the range 280−2000 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma).

Chemicals. The solvents THF, hexane, and toluene were dried by refluxing over $\mathrm{LiAlH_4}$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_5H_4C_5H_4})(\mu\text{-H})_2\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})\}_2]$.[24] $\mathrm{TiCl_4}$ (International Enzymes) was purified by refluxing over copper wire and distilled under vacuum. Butyllithium in hexanes, 1,2,3,4-tetramethylcyclopentadiene, allylchlorodimethylsilane, and chlorodimethylvinylsilane (Aldrich) were transferred by syringe under argon. Magnesium turnings (Aldrich, purum for Grignard reactions) were first used in large excess for the preparation of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})_2(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})]$,[13a] and the unreacted, activated magnesium was separated from the reaction mixture, washed thoroughly with THF, and stored in ampules equipped with breakable seals. Anhydrous HCl was prepared by mixing 98% $\mathrm{H_2SO_4}$ with dry NaCl on a vacuum line. Bis(trimethylsilyl)ethyne (btmse, Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and distilled into ampules on a vacuum line.

Preparation of Cyclopentadienes $[\mathrm{C_5Me_4H(SiMe_2R)}]$ [R = $\mathrm{CH{=}CH_2}$ (1) and $\mathrm{CH_2CH{=}CH_2}$ (2)]. LiBu (2.5 M in hexanes, 46.0 mL, 0.115 mol) was slowly added to a stirred solution of 1,2,3,4-tetramethylcyclopentadiene (13.84 g, 0.113 mol) in dry THF (500 mL) at room temperature. The resulting suspension of lithium cyclopentadienide $\mathrm{Li[C_5HMe_4]}$ was stirred for 3 h, slowly treated with, respectively, neat chlorodimethylvinylsilane (13.8 g, 0.115 mol) and allylchlorodimethylsilane (15.4 g, 0.115 mol), and stirred at ambient temperature for another 10 h. THF was removed under reduced pressure, and the slurry of LiCl and the product was extracted with hexane. The extract was evaporated under reduced pressure and the residue distilled from a water bath under oil pump vacuum.

$[\mathrm{C_5Me_4(SiMe_2CH{=}CH_2)H}]$ (1). Yield: 19.1 g (82%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.00 (s, 6 H, $\mathrm{Si}Me_2$), 1.81, 1.91 (2× s, 6 H, $\mathrm{C_5}Me_4\mathrm{H}$); 2.76 (s, 1 H, $\mathrm{C_5Me_4}H$), 5.61 (dd, $^3J_{\mathrm{HH}} = 20.3$, $^2J_{\mathrm{HH}} = 3.7$ Hz, 1 H, $=\mathrm{C}H_2$), 5.89 (dd, $^3J_{\mathrm{HH}} = 14.6$, $^2J_{\mathrm{HH}} = 3.7$ Hz, 1 H, $=\mathrm{C}H_2$), 6.15 (dd, $^3J_{\mathrm{HH}} = 20.3$, 14.6 Hz, 1 H, $=\mathrm{C}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −4.0 ($\mathrm{Si}Me_2$), 11.3, 14.7 ($\mathrm{C_5}Me_4\mathrm{H}$); 54.6 ($\mathrm{C_5Me_4H}$, $\mathrm{C}H$), 131.2 ($=C\mathrm{H_2}$), 132.8, 135.7 ($\mathrm{C_5Me_4H}$, C-Me); 139.2 (CH=). GC−MS: *m*/*z* (relative abundance, %) 206 ($\mathrm{M^{\bullet+}}$; 26), 191 (7), 121 (10), 120 (24), 105 (34), 91 (22), 85 (100), 79 (10), 77 (12), 73 (24), 59 (56), 43 (12). IR (neat, cm^{-1}): 3048 (m), 3007 (w), 2964 (s), 2914 (vs), 2858 (s), 1634 (m), 1592 (m), 1444 (s), 1404 (s), 1379 (m), 1302 (w), 1247 (vs), 1219 (m), 1123 (m), 1110 (m), 1047 (m), 1009 (s), 980 (m), 950 (s), 820 (vs, b), 795 (m), 775 (s), 729 (w), 695 (m), 612 (m), 559 (w), 525 (m), 497 (w), 483 (w).

$[\mathrm{C_5Me_4(SiMe_2CH_2CH{=}CH_2)H}]$ (2). Yield: 21.1 g (85%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ −0.03 (s, 6 H, $\mathrm{Si}Me_2$), 1.45 (dt, $^3J_{\mathrm{HH}} = 8.1$, $^4J_{\mathrm{HH}} = 1.1$ Hz, 2 H, $\mathrm{SiC}H_2$), 1.79, 1.89 (2× s, 6 H, $Me_4\mathrm{C_5}$); 2.73 (br s, 1 H, $\mathrm{Me_4C_5}H$), 4.85−4.93 (m, 2 H, $=\mathrm{C}H_2$), 5.72 (ddt, $^3J_{\mathrm{HH}} = 16.8$, 10.4, 8.1 Hz, 1 H, $=\mathrm{C}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −3.6 ($\mathrm{Si}Me_2$), 11.3, 14.7 ($Me_4\mathrm{C_5}$); 54.1 ($\mathrm{Me_4C_5H}$, $C\mathrm{H}$), 113.4 ($=C\mathrm{H_2}$), 132.8 ($\mathrm{Me_4C_5H}$, $C\mathrm{Me}$), 135.3 ($C\mathrm{H}{=}$), 135.8 ($\mathrm{Me_4C_5H}$, $C\mathrm{Me}$). GC−MS: *m*/*z* (relative abundance, %) 220 ($\mathrm{M^{\bullet+}}$; 24), 205 (4), 180 (18), 179 (100), 119 (13), 105 (14), 99 (28), 91 (15), 73 (24),

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(23) Synthesis of group 4 *ansa*-metallocene dichlorides with six-membered and longer *ansa* chains: (a) Burk, M. J.; Colletti, S. L.; Halterman, R. L. *Organometallics* **1991**, *10*, 2998−3000. (b) Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812−2816. (c) Jödicke, T.; Menges, F.; Kehr, G.; Erker, G.; Höweler, U.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2001**, 2097−2106. (d) Erker, G.; Mollenkopf, C.; Grehl, M.; Fröhlich, R.; Krüger, C.; Noe, R.; Riedel, M. *Organometallics* **1994**, *13*, 1950−1955.

(24) Antropiusová, H.; Dosedlová, A.; Hanuš, V.; Mach, K. *Transition Met. Chem.* (*London*) **1981**, *6*, 90−93.

59 (42). IR (neat, cm^{-1}): 3073 (m), 3054 (w), 2964 (s), 2913 (vs), 2858 (s), 1631 (s), 1445 (s), 1420 (m), 1391 (m), 1380 (m), 1304 (w), 1258 (sh), 1251 (vs), 1222 (m), 1193 (w), 1157 (s), 1124 (m), 1111 (m), 1048 (m,b), 987 (s), 954 (m), 932 (m), 897 (s), 837 (vs, b), 701 (w), 753 (vw), 725 (vw), 687 (vw), 650 (m), 575 (s), 487 (m).

Preparation of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2CH{=}CH_2)\}_2]$ (3). $TiCl_4$ (4.0 mL, 36 mmol) was co-condensed with THF (100 mL) at the liquid nitrogen temperature in a 0.5 L three-necked bulb on a vacuum line. The vacuum was replaced by an argon atmosphere, and the mixture was allowed to warm to room temperature and brought to gentle reflux to wash the adduct from the walls of the reaction vessel. (*Warning:* very often an exothermic reaction of the components occurs which may cause the contamination of the vacuum line by the formed yellow adduct $[TiCl_4(THF)_2]$.) After cooling to room temperature, LiBu in hexane (22.5 mL, 1.6 M, 36 mmol) was added under vigorous stirring, and the mixture was refluxed for 30 min and, finally, allowed to cool to room temperature, whereupon a crystalline, pale blue complex $[TiCl_3(THF)_3]$ separated.

In another three-necked bulb, LiBu in hexane (30 mL of 2.5 M, 75 mmol) was added to a solution of cyclopentadiene **1** (15.0 g, 73 mmol) in THF (500 mL) under stirring, and the resulting yellowish solution was stirred for another 5 h at room temperature. Then, a slurry of $[TiCl_3(THF)_3]$ was poured under an argon blanket into the lithium cyclopentadienide solution, and the mixture was refluxed for 40 h. The volume of the reaction mixture was reduced to ca. 50 mL, anhydrous powdered $PbCl_2$ (5.0 g, 18 mmol) was added, and stirring continued for another 3 h with warming to 40 °C. The initially dark brown-green mixture turned dark red due to the formation of **3**. Solvents were removed under vacuum, the oily residue was dissolved in heptane (70 mL), and the solution was filtered from solid lead and LiCl and cooled in a freezer (−18 °C) overnight. While cold, the formed crystalline slurry was filtered, and the residue was washed with ethanol (20 mL) and dried. The obtained brown crystalline solid was recrystallized from hot heptane. Yield of **3**: 9.9 g (52%). ^1H NMR (C_6D_6): δ 0.59 (s, 6 H, Si*Me*$_2$), 1.64, 2.18 (2× s, 6 H, *Me*$_4$C$_5$); 5.69 (dd, $^3J_{HH} = 20.4$, $^2J_{HH} = 3.7$ Hz, 1 H, =C*H*$_2$), 5.92 (dd, $^3J_{HH} = 14.5$, $^2J_{HH} = 3.7$ Hz, 1 H, =C*H*$_2$), 6.61 (dd, $^3J_{HH} = 20.4$, 14.5 Hz, 1 H, =C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.5 (Si*Me*$_2$), 12.3, 16.8 (*Me*$_4$C$_5$); 128.3 (*C*$_5$Me$_4$), 130.8 (=*C*H$_2$), 134.2, 137.5 (*C*$_5$-Me$_4$); 141.6 (=*C*H). EI MS (130 °C): *m*/*z* (relative abundance, %) 528 ($M^{\bullet+}$, <1), 496 (11), 495 (32), 494 (28), 493 ($[M - Cl]^+$; 63), 492 (21), 490 (8), 489 (13), 408 ($[M - Cl - Me_2SiCH{=}CH_2]^+$; 10), 345 (16), 343 (17), 333 (9), 331 (9), 327 (20), 326 (20), 325 (74), 324 (33), 323 ($[Cp'TiCl_2]^+$; 100), 322 (13), 321 (12), 290 (12), 289 (12), 288 ($[Cp'TiCl]^+$, 29), 287 (16), 286 (15), 285 (33), 262 (8), 230 (11), 229 (17), 228 (8), 227 (27), 206 (20), 205 ($[Cp']^+$; 34), 204 (14), 190 (12), 189 (33), 178 (7), 177 (20), 175 (12), 163 (14), 161 (9), 145 (12), 133 (12), 120 (14), 119 (14), 105 (17), 97 (7), 91 (10), 86 (8), 85 (70), 83 (9), 73 (22), 71 (10), 59 (79), 43 (11). IR (KBr, cm^{-1}): 3046 (m), 3009 (m), 2960 (s), 2944 (m), 2897 (vs,b), 1901 (w), 1589 (w), 1478 (s), 1439 (m), 1408 (s), 1377 (s), 1340 (m), 1265 (w), 1246 (vs), 1125 (w), 1025 (s), 1007 (s), 949 (s), 841 (s), 826 (vs), 810 (vs), 773 (s), 701 (m), 620 (m), 557 (w), 523 (m), 436 (s). Anal. Calcd for $C_{26}H_{42}Cl_2Si_2Ti$ (529.58): C, 58.97; H, 8.00. Found: C, 59.06; H, 7.96.

Preparation of $[TiCl_2\{\eta^5\text{-}C_5Me_4(SiMe_2CH_2CH{=}CH_2)\}_2]$ (4). The synthesis was carried out as above starting from $TiCl_4$ (4.0 mL, 36 mmol) and **2** (16.0 g, 73 mmol). Yield of finely crystalline brown **4** was 8.8 g (44%). ^1H NMR (C_6D_6): δ 0.57 (s, 6 H, Si*Me*$_2$), 1.63 (s, 6 H, C$_5$*Me*$_4$), 1.92 (dt, 2 H, $^3J_{HH} = 8.1$, 1.1 Hz, SiC*H*$_2$), 2.13 (s, 6 H, C$_5$*Me*$_4$), 4.89−4.93 (m, 2 H, =C*H*$_2$), 5.87 (ddt, 1 H, $^3J_{HH} = 16.7$, 10.3, 8.1 Hz, C*H*=). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.1 (Si*Me*$_2$), 12.1, 16.9 (C$_5$*Me*$_4$); 25.7 (Si*C*H$_2$), 113.3 (=*C*H$_2$), 127.5, 135.2, 137.9 (*C*$_5$Me$_4$); 135.8 (*C*H=). EI MS (130 °C): *m*/*z* (relative abundance, %) 556 ($M^{\bullet+}$, <1), 525 (9), 524 (21), 523 (53), 522 (50), 521 ($[M - Cl]^+$, 100), 520 (15), 519 (11), 484 (7), 483 (15), 482 (35), 481 (33), 480 ($[M - Cl - C_3H_5]^+$, 68), 479 (10), 478 (7), 381 (10), 346 (7), 339 (7), 337 (10), 335 (18), 334 (12), 333 (45), 332 (15), 331 (44), 304 (23), 303 (18), 302 (54), 301 (27), 300 (22), 299 (49), 298 (19), 297 (18), 296 (20), 295 (11), 285 (9), 263 (7), 262 (25), 261 (15), 260 (44), 259 (16), 258 (14), 257 (15), 256 (7), 245 (12), 244 (12), 243 (23), 242 (7), 229 (9), 220 (7), 219 (18), 204 (8), 191 (15), 179 (20), 178 (36), 177 (34), 163 (21), 161 (8), 159 (8), 149 (7), 133 (8), 119 (24), 105 (13), 99 (35), 97 (15), 93 (8), 91 (10), 85 (8), 83 (13), 73 (28), 71 (8), 69 (8), 59 (95), 45 (11), 43 (24), 41 (15). IR (KBr, cm^{-1}): 3066 (m), 2983 (m), 2959 (s), 2900 (s,b), 1625 (s), 1476 (m), 1447 (s), 1414 (m), 1373 (s), 1346 (m), 1334 (w), 1293 (vw), 1251 (vs), 1241 (vs), 1185 (w), 1141 (s), 1118 (w), 1081 (vw), 1034 (m), 1018 (s), 981 (m), 943 (vw), 927 (w), 883 (vs), 824 (vs,b), 759 (m), 732 (vw), 711 (vw), 690 (w), 656 (w), 643 (m), 579 (m), 560 (w), 415 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{46}Cl_2Si_2Ti$ (557.63): C, 60.31; H, 8.31. Found: C, 60.06; H, 8.26.

Preparation of $[Ti(IV)(\eta^1{:}\eta^1{:}\eta{:}^5\eta^5\text{-}C_5Me_4SiMe_2CHCH(Me)CH(Me)CHSiMe_2C_5Me_4]$ (5). Complex **4** (0.56 g, 1.0 mmol) and magnesium (0.24 g, 10 mmol) were placed into an ampule and carefully evacuated on a vacuum line, and THF (30 mL) was distilled onto the solid mixture at the liquid nitrogen temperature. The ampule was sealed off and, after warming to room temperature, heated in a water bath kept at 60 °C. After an induction period of various length (usually less than 1 h) the red color of the solution turned to turquoise, 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 (Note: no induction period is observed when the recovered activated magnesium is reused). The solid residue was extracted with hexane (30 mL), the solution was concentrated, and the product was crystallized in a refrigerator (−5 °C). The crystals formed were separated from the mother liquor, washed by a cold solvent, dried in a vacuum, and sealed off in one arm of the ampule. Yield of orange-brown crystals was 0.42 g (87%). Mp: 171 °C. ^1H NMR (C_6D_6): δ −0.17 (s, 3 H, Si*Me*$_2$), 0.36−0.41 (m, 1 H, TiC*H*), 0.70 (s, 3 H, Si*Me*$_2$), 0.72 (d, 3 H, $^3J_{HH} = 5.8$ Hz, TiCHCH*Me*), 1.40, 1.47, 1.54 (3× s, 3 H, C$_5$*Me*$_4$); 2.02−2.14 (m, 1 H, TiCHC*H*Me), 3.06 (s, 3 H, C$_5$*Me*$_4$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.5, 2.1 (Si*Me*$_2$); 11.5, 11.8, 14.0, 19.1 (C$_5$*Me*$_4$); 26.8 (TiCHCH*Me*), 46.3 (TiCH*CH*Me), 60.2 (Ti*CH*), 109.6, 123.7, 127.0, 134.3, 134.9 (*C*$_5$Me$_4$). EI-MS (110 °C): *m*/*z* (relative abundance, %) 489 (10), 488 (28), 487 (48), 486 ($M^{\bullet+}$, 100), 485 (59), 484 (76), 483 (76), 482 (40), 480 (19), 479 (23), 478 (8), 477 (10), 470 (12), 469 (11), 468 (8), 467 (7), 385 (9), 374 (7), 383 (12), 381 (7), 208 (8), 207 (8), 73 (10), 59 (23). IR (KBr, cm^{-1}): 2960 (sh), 2900 (vs, vb), 2847 (s), 1475 (sh), 1447 (s), 1376 (s), 1346 (m), 1336 (m), 1247 (vs), 1187 (vw), 1140 (m),1120 (vw), 1088 (w), 1027 (s, b), 947 (w), 903 (s), 833 (vs, b), 807 (s), 766 (m), 754 (m), 715 (m), 674 (m), 657 (s), 573 (w), 554 (m), 472 (s). Anal. Calcd for $C_{28}H_{46}Si_2Ti$ (486.73): C, 69.10; H, 9.53. Found: C, 68.88; H, 9.49.

Preparation of *ansa*-$[TiCl_2\{\eta{:}^5\eta^5\text{-}C_5Me_4SiMe_2CH_2CH(Me)CH(Me)CH_2SiMe_2C_5Me_4)_2\}]$ (6). Gaseous HCl (100 mL, 350 Torr) was condensed into a solution of compound **5** (0.49 g, 1.0 mmol) in hexane (50 mL) by cooling with liquid nitrogen. The mixture was slowly warmed to room temperature under vigorous stirring, warmed to 60 °C, and, finally, cooled to −5 °C overnight to complete crystallization. Complex **6**, which separated as fine brown needles from a yellow solution, was washed with hexane and recrystallized from toluene. Yield: 0.35 g (63%). Mp: 196 °C. ^1H NMR (C_6D_6): δ 0.04 (s, 3 H, Si*Me*$_2$), 0.54 (dd, $^3J_{HH} = 6.2$, $^2J_{HH} = 14.6$ Hz, 1 H, C*H*$_2$ *A*), 0.58 (s, 3 H, Si*Me*$_2$), 0.95 (s, $^3J_{HH} = 6.2$ Hz, 3 H, CH*Me*), 1.14 (dd, $^3J_{HH} = 6.0$, $^2J_{HH} = 14.6$ Hz, 1 H, C*H*$_2$ *B*), 1.51 (m (ddq), 1 H, C*H*Me), 1.72, 1.86, 2.29, 2.31 (4× s, 3 H, *Me*$_4$C$_5$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.6, 2.7 (Si*Me*$_2$); 13.3 (δ_H 1.86), 13.8 (δ_H 1.72), 16.2 (δ_H 2.31), 17.1 (δ_H 2.29) (*Me*$_4$C$_5$); 20.5 (CH*Me*), 27.6 (*C*H$_2$), 37.7

(CHMe), 128.8, 133.9, 134.7, 135.4, 136.9 ($C_5\mathrm{Me}_4$). EI-MS (150 °C): *m*/*z* (relative abundance, %) 558 ($\mathrm{M}^{\bullet+}$; 0.4), 526 (14), 525 (36), 524 (35), 523 ($[\mathrm{M}-\mathrm{Cl}]^+$; 70), 522 (11), 521 (9), 381 (8), 347 (7), 346 (21), 345 (25), 344 (40), 343 (24), 342 (8), 335 (8), 333 (19), 331 (18), 300 (8), 299 (10), 298 (27), 297 (15), 296 (39), 295 (9), 262 (10), 260 (8), 259 (7), 257 (9), 243 (11), 213 (7), 180 (10), 179 (48), 178 (32), 177 (26), 168 (7), 163 (19), 141 (8), 125 (9), 120 (7), 119 (31), 105 (10), 99 (17), 97 (13), 93 (9), 85 (13), 83 (9), 73 (41), 60 (7), 59 (100), 43 (12). IR (KBr, cm^{-1}): 2986 (sh), 2952 (vs), 2932 (s), 2888 (vs), 2869 (s), 1477 (s), 1449 (s), 1442 (sh), 1407 (m), 1385 (sh), 1373 (vs), 1344 (m), 1317 (m), 1250 (vs), 1244 (vs), 1227 (w), 1121 (w), 1059 (m), 1020 (s), 900 (w), 834 (vs, b), 788 (m), 777 (s), 765 (s), 740 (w), 694 (w), 679 (w), 638 (m), 627 (sh), 610 (vw), 465 (w), 431 (s), 419 (s). Anal. Calcd for $\mathrm{C_{28}H_{48}Cl_2Si_2Ti}$ (559.63): C, 60.01; H, 8.64. Found: C, 59.88; H, 8.61.

Preparation of *ansa*-$[\mathrm{Ti(II)}\{\eta^2{:}\eta^5{:}\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH_2CH{=}CHCH_2SiMe_2C_5Me_4}\}]$ (7). Degassed complex **3** (0.53 g, 1.0 mmol) was dissolved in THF (30 mL), the solution added onto activated magnesium (ca. 0.20 g, 8.3 mmol), and the mixture stirred at 60 °C for 4 h. During this period the originally red-brown supernatant turned brown-yellow. The solution was separated from unreacted magnesium, THF distilled off under vacuum, and the solid residue repeatedly extracted with hexane (50 mL) until the extract was only slightly yellow. The hexane extract was concentrated and cooled to −5 °C to afford brown microcrystalline **7** as a mixture with purple crystals of **8** (**7** prevailing). Crystals of **7** were manually selected for X-ray diffraction analysis, EI-MS, and IR spectra. Compounds **7** and **8** could not be separated by fractional crystallization; the presence of paramagnetic **8** precluded an NMR analysis of **7**. Combined yield of **7** and **8**: 0.39 g (86%).

Analytical Data for 7. EI-MS (90 °C): *m*/*z* (relative abundance, %) 462 (22), 461 (48), 460 (82), 459 (47), 458 ($\mathrm{M}^{\bullet+}$; 100), 457 (43), 456 (59), 455 (17), 454 (15), 371 (13), 369 (8), 367 (7), 59 (15). IR (KBr, cm^{-1}): 2965 (s), 2947 (s), 2909 (vs, b), 2864 (s), 2817 (m), 1479 (m), 1450 (m, b), 1405 (m), 1378 (s), 1346 (s), 1244 (vs), 1128 (m), 1107 (m), 1022 (s), 953 (w), 838 (vs, b), 814 (s), 779 (s), 745 (m), 699 (m), 683 (m), 664 (w), 648 (m), 576 (w), 508 (w), 474 (w), 450 (m), 426 (m). UV−vis (toluene, 22 °C): 980 nm.

Preparation of *ansa*-$[\mathrm{Ti(III)}\{\eta^3{:}\eta^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CHCHCHCH_2SiMe_2C_5Me_4}\}]$ (8). Complex **3** (0.53 g, 1.0 mmol) was carefully evacuated in an ampule on a vacuum line, and THF (30 mL) was distilled in at the liquid nitrogen temperature. Reused magnesium (0.20 g, 8.4 mmol) and btmse (1.0 mL, 4.5 mmol) were added from attached ampules, and the mixture was kept at 60 °C for 4 h with ocassional shaking. The THF solution was separated from nonconsumed magnesium, all volatiles were distilled into a cooled trap under vacuum, and the residue was repeatedly extracted with hexane (50 mL). The reddish-blue extract was concentrated and cooled to −5 °C to yield **8** as fine crystalline aggregates. Another crop of **8** was obtained from the mother liquor after concentrating and cooling. Total yield: 0.35 g (77%). Mp: 165 °C. EPR (toluene, 22 °C): $g = 1.9905$, $\Delta H = 0.5$ mT. EPR (toluene, −140 °C): $g_{\|} = 2.002$, $g_{\perp} = 1.988$, $g_{\mathrm{av}} = 1.992$. EI-MS (130 °C): *m*/*z* (relative abundance, %) 462 (8), 461 (20), 460 (30), 459 (65), 458 (75), 457 ($\mathrm{M}^{\bullet+}$; 100), 456 (40), 455 (18), 454 (12). IR (KBr, cm^{-1}): 3070 (vw), 3038 (w), 2994 (m), 2974 (s), 2947 (s), 2902 (vs,b), 2863 (s), 2847 (s), 1509 (m), 1483 (m), 1440 (m,b), 1406 (w), 1376 (s), 1343 (m), 1324 (s), 1247 (vs,b), 1166 (m), 1125 (w), 1116 (w), 1084 (vw), 1021 (s), 991 (vw), 953 (vw), 839 (vs,b), 814 (s), 791 (m), 773 (m), 741 (m), 708 (m), 695 (w), 663 (m), 649 (w), 479 (m), 445 (w), 430 (w), 411 (w). UV−vis (toluene, 22 °C): 555 nm. Anal. Calcd for $\mathrm{C_{26}H_{41}Si_2Ti}$ (457,66): C, 68.23; H, 9.03. Found: C, 67.99; H, 8.99.

The GC−MS analysis of a higher boiling fraction of the collected volatiles revealed the presence of (*Z*)- and (*E*)-1,2-bis(trimethylsilyl)ethene in addition to excessive btmse.[13a]

Reduction of 3 with Magnesium at −5 °C. Synthesis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH{=}CH_2})(\eta^2{:}\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH{=}CH_2})]$ (9) and $[\mathrm{Ti}(\eta^1{:}\eta^1{:}\eta^5\eta^5\text{-}\mathrm{C_5Me_4SiMe_2CH}(\mathit{Ti})\mathrm{CH_2CH_2CH}(\mathit{Ti})\text{-}\mathrm{SiMe_2C_5Me_4})]$ (10). Compound **3** (1.0 g, 1.9 mmol) was dissolved in THF (30 mL), the solution was added to activated magnesium (ca. 0.21 g, 9.0 mmol), and the mixture was put into a refrigerator (−5 °C) and occasionally shaken. After 10 h, the solution was separated from unreacted magnesium, THF was removed under vacuum, and the residue was repeatedly extracted with hexane (30 mL). The extracts were concentrated to crystallization and cooled to −5 °C to yield brown crystals (0.26 g, 30%), which were identified by X-ray diffraction as **10** (see also MS and IR spectra below). The crystals of **10** when dissolved in $\mathrm{C_6D_6}$ displayed the NMR spectra showing the presence of complexes **9** and **10** in approximately 2.3:1.0 ratio. Resonances of compounds **9** and **10** were easily distinguished because those of **9** were broader and their line width was thermally dependent as a result of exchange of the coordinated and uncoordinated double bonds (see NMR data below). The presence of **9** in toluene or THF solution of the crude reaction product as well as in the solutions made from crystals of **10** was clearly demonstrated by the electronic absorption band at 1060 nm, which is due to the η^2-coordinated double bond.[13b,c] The mother liquor after separation of **10** was evaporated under vacuum, and the residue gave the infrared spectrum indicative of an uncoordinated vinylsilyl group (italicized). **9**: IR (KBr, cm^{-1}): *3050* (w), *3010* (sh), 2951 (s), 2905 (vs), *1901* (w), *1590* (w), 1478 (m), 1450 (m), 1405 (m), 1378 (s), 1348 (m), 1331 (s), 1247 (vs), 1126 (m), 1086 (vw), 1023 (s), *950* (m), 827 (vs, b), 769 (s), 692 (m), *619* (m), 560 (w), 520 (w), 465 (w), 425 (s). ^{1}H NMR ($\mathrm{C_6D_6}$, 5 °C): δ −0.48, −0.17, −0.07, 0.46 (4× s, 3 H, $\mathrm{Si}Me_2$); 0.88 (m, 1 H, η^2-$\mathrm{C}H{=}\mathrm{CH_2}$; obscured by a methyl resonance at δ_{H} 0.89); 0.89, 0.97, 0.98, 1.08, 1.14 (5× s, 3 H, $\mathrm{Si}Me_2$); 1.37 (m, 1 H, η^2−$\mathrm{CH{=}C}H_2$; obscured by a sharp singlet due to **10** at δ_{H} 1.37), 1.47, 3.00, 3.23 (3× s, 3 H, $\mathrm{Si}Me_2$); 3.25 (dd, $J_{\mathrm{HH}} = 12.3$, 4.1 Hz, 1 H, η^2-$\mathrm{CH{=}C}H_2$), 5.46 (dd, $^2J_{\mathrm{HH}} = 4.0$, $^3J_{\mathrm{HH}} = 20.1$ Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 5.61 (dd, $^3J_{\mathrm{HH}} = 20.1$, 14.2 Hz, 1 H, $\mathrm{C}H{=}\mathrm{CH_2}$), 5.72 (dd, $^2J_{\mathrm{HH}} = 4.0$, $^3J_{\mathrm{HH}} = 14.2$ Hz, 1 H, $\mathrm{C}H{=}\mathrm{C}H_2$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 5 °C): δ −0.5, −0.4, −0.1, 6.0 ($\mathrm{Si}Me_2$); 10.6, 10.8, 11.2, 11.9, 12.5, 12.7, 16.5, 18.7 ($\mathrm{C_5}Me_4$); 88.9 (η^2-$C\mathrm{H{=}CH_2}$), 105.5 (η^2-$\mathrm{CH{=}}C\mathrm{H_2}$), 119.6, 122.5, 123.7, 123.8, 124.8, 126.9, 127.1, 127.6 (the latter is uncertain due to an overalp with the solvent signal) ($C_5\mathrm{Me}_4$); 131.0 ($\mathrm{CH{=}}C\mathrm{H_2}$), 131.5, 135.3 ($C_5\mathrm{Me}_4$); 140.3 ($C\mathrm{H{=}CH_2}$).

Analytical Data for Complex 10. Mp: 117 °C. ^{1}H NMR ($\mathrm{C_6D_6}$, 5 °C): δ −1.34 (ddd, $J_{\mathrm{HH}} = 7.8$, 2.5, 2.5 Hz, 1 H, $\mathrm{TiC}H$), −0.01, 0.80 (2× s, 3 H, $\mathrm{Si}Me_2$), 1.26 (s, 3 H, $\mathrm{C_5}Me_4$), 1.37, 1.51 (2× s, 3 H, $\mathrm{C_5}Me_4$); 1.62 (ddd, $J_{\mathrm{HH}} = 7.8$, 2.5, 2.5 Hz, 1 H, $\mathrm{TiCHC}H_2$), 2.96 (s, 3 H, $\mathrm{C_5}Me_4$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 5 °C): δ 1.4, 3.6 ($\mathrm{Si}Me_2$); 11.3, 12.2, 12.7, 16.9 ($\mathrm{C_5}Me_4$); 31.5 ($\mathrm{TiCH}C\mathrm{H_2}$), 39.9 ($\mathrm{Ti}C\mathrm{H_2}$), 122.4 127.7 (obscured by the solvent signal), 136.8 (C_5Me_4). EI-MS (90 °C): *m*/*z* (relative abundance, %) 461 (11), 460 (33), 459 (46), 458 ($\mathrm{M}^{\bullet+}$; 100), 457 (19), 456 (21), 371 (13), 369 (8), 313 (7), 85 (7), 59 (17). IR (KBr, cm^{-1}): 2964 (s), 2939 (vs), 2896 (vs), *2813* (s), *2798* (s), 1480 (m), 1441 (s), 1405 (m), 1378 (s), 1349 (m), 1321 (s), 1243 (vs), *1145* (m), 1124 (m), 1078 (w), 1019 (s), 986 (m), *886* (vs), 825 (vs, b), 758 (vs), 729 (w), 688 (s), 652 (s), 626 (m), 556 (w), *465* (s), *454* (m), 417 (s). Diagnostic bands typical for **10**, not occurring in the spectrum of complex **9**, are given in italics. Anal. Calcd for $\mathrm{C_{26}H_{42}Si_2Ti}$ (458.67): C, 68.08; H, 9.23. Found: C, 67.97; H, 9.21.

Reaction of the Mixture of Complexes 9 and 10 with $\mathrm{PbCl_2}$. The content of the NMR tube (**9**:**10** ratio ca. 2.3:1.0) was transferred to a vacuum line, the solvent ($\mathrm{C_6D_6}$) was replaced by THF (7 mL), and the solution was poured onto vacuum-dried $\mathrm{PbCl_2}$ (0.08 g, 0.38 mmol). After stirring at 60 °C for 3 h, the solvent was distilled off, the residue redissolved in $\mathrm{C_6D_6}$ (ca.. 1.5 mL), and the solution transferred to an NMR tube. The only product detected by ^{1}H NMR spectroscopy was titanocene dichloride **3**.

Preparation of [TiCl{η^1:η:$^5\eta^5$-$C_5Me_4SiMe_2\mathit{C}HCH{=}CH\text{-}CH_2SiMe_2C_5Me_4$}] (11). Compound **8** (0.40 g, 0.87 mmol) was dissolved in THF (20 mL), and the solution was poured onto vacuum-dried, solid $PbCl_2$ (0.25 g, 0.90 mmol). The mixture was stirred at 60 °C for 4 h. The initial purple color turned to khaki-green, but $PbCl_2$ was only partly reduced. Thus, the solution was separated from a gray solid mixture of $PbCl_2$ and Pb, THF was removed under vacuum, and the residue was extracted with hexane (20 mL). A khaki-green solution was separated from a small amount of a turquoise powder and concentrated to crystallization. Cooling to −18 °C overnight afforded **11** as a turquoise crystalline precipitate. Yield: 0.32 g (76%). Mp: 181 °C. ^{1}H NMR (C_6D_6): δ −1.00 (d, $^3J_{HH} = 11.2$ Hz, 1 H, TiC*H*), 0.25, 0.38, 0.46, 0.66 (4× s, 3 H, Si*Me*$_2$); 1.35, 1.48 (2× s, 3 H, $C_5\mathit{Me}_4$); 1.54 (dd, $^3J_{HH} = 8.1$, $^2J_{HH} = 14.0$ Hz, 1 H, CH_2), 1.62, 1.66, 1.67, 1.75 (4× s, 3 H, $C_5\mathit{Me}_4$); 1.86 (ddd, $^3J_{HH} = 2.2$, 6.3, $^2J_{HH} = 14.0$ Hz, 1 H, CH_2), 2.50, 2.64 (2× s, 3 H, $C_5\mathit{Me}_4$); 5.11−5.25 (m, 2 H, C*H*=C*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ −2.1, 1.7, 2.8, 5.2 (Si*Me*$_2$); 10.3, 11.5, 12.7, 13.5, 14.4, 14.9 ($C_5\mathit{Me}_4$); 16.9 (*C*H_2), 18.1, 18.6 ($C_5\mathit{Me}_4$); 58.0 (Ti*C*H), 111.0 (*C*$_5$Me$_4$), 114.8 (*C*H=), 121.1, 123.6, 123.8, 124.6, 124.7, 130.0, 132.7, 139.0, 143.4 (*C*$_5$Me$_4$); 143.6 (*C*H=). EI-MS (140 °C): *m*/*z* (relative abundance, %) 496 (11), 495 (28), 494 (59), 493 (72), 492 ($M^{\bullet+}$; 100), 491 (23), 490 (13), 458 (9), 457 (19), 456 (21), 455 (35), 454 (18), 453 (28), 452 (7), 451 (9), 383 (7), 381 (11), 179 (8), 177 (7), 119 (10), 111 (9), 83 (7), 73 (16), 71 (11), 69 (9), 59 (31, 57 (19), 55 (11), 43 (15), 41 (9). IR (KBr, cm^{-1}): 3002 (m), 2974 (w), 2949 (s), 2906 (vs), 2860 (s), 1586 (vw), 1478 (m), 1450 (m), 1405 (m), 1378 (s), 1336 (w), 1319 (w), 1244 (vs), 1198 (w), 1161 (w), 1132 (m), 1072 (w), 1072 (m), 964 (vw), 855 (s), 837 (vs), 802 (s), 776 (m), 755 (w), 739 (s), 702 (w), 671 (s), 651 (m), 640 (w), 626 (vw), 612 (vw), 548 (w), 497 (vw), 465 (m), 421 (s). Anal. Calcd for $C_{26}H_{41}Si_2ClTi$ (493.11): C, 63.33; H, 8.38. Found: C, 63.11; H, 8.34.

Preparation of *ansa*-[TiCl{η:$^5\eta^5$-$C_5Me_4SiMe_2CH_2CH{=}CHCH_2SiMe_2C_5Me_4$}] (12). Compound **8** (0.46 g, 1.0 mmol) was dissolved in hexane (50 mL), the solution was cooled with liquid nitrogen, and HCl (100 mL at 170 Torr, ca. 1.0 mmol) was condensed into the ampule. The ampule was sealed off and slowly warmed with vigorous shaking, whereupon the blue color due to **8** turned turquoise. After warming to 60 °C, all volatiles were distilled off, and the residue was extracted with hot hexane (20 mL). The extract was concentrated while warm and allowed to crystallize at −5 °C overnight. Turquoise crystals of **12**, which separated from a yellow-green mother liquor that contained products of acidolysis of Si−C bonds (see below), were washed with cold hexane and dried under vacuum. Yield: 0.42 g (85%). Mp: 179 °C. EI-MS (170 °C): *m*/*z* (relative abundance, %) 497 (16), 496 (27), 495 (65), 494 (49), 493 ($M^{\bullet+}$; 100), 492 (23), 491 (31), 490 (9), 489 (14), 478 (7), 455 (7), 279 (9), 262 (9), 261 (11), 260 (7), 259 (13), 258 (7), 257 (16), 243 (10), 180 (10), 177 (9), 163 (12), 119 (16), 97 (9), 73 (23), 59 (48). IR (KBr, cm^{-1}): 3012 (w), 3000 (sh), 2976 (m), 2952 (s), 2905 (vs), 2856 (s), 1479 (m), 1452 (m), 1409 (m), 1379 (s), 1333 (s), 1248 (vs), 1154 (s), 1127 (m), 1060 (w), 1022 (s), 1002 (w), 956 (m), 834 (vs), 803 (m), 790 (m), 774 (w), 756 (m), 706 (m), 668 (w), 653 (vw), 622 (vw), 435 (s). EPR (toluene, 22 °C): $g = 1.948$, $\Delta H = 1.6$ mT. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.984$, $g_3 = 1.875$, $g_{av} = 1.952$. UV−vis (toluene, 22 °C): 365(sh) ≫ 590 > 690(sh) nm. Anal. Calcd for $C_{26}H_{42}Si_2ClTi$ (494.12): C, 63.20; H, 8.57. Found: C, 63.08; H, 8.54.

Preparation of *ansa*-[Ti(OMe){η:$^5\eta^5$-$C_5Me_4SiMe_2CH_2\text{-}CH{=}CHCH_2SiMe_2C_5Me_4$}] (13). Dry, degassed methanol (3.0 mL, 75 mmol) was added to a solution of complex **8** (0.46 g, 1.0 mmol) in hexane (50 mL). Upon warming the mixture to 60 °C for 20 min, a clean purple-red solution resulted, which was evaporated under vacuum, and the residue was dissolved in hexane (10 mL). Partial solvent removal and crystallization at −70 °C afforded dark purple crystalline **13**, which was separated and dried in a vacuum. Yield: 0.38 g (78%). Mp: 150 °C. EI-MS (90 °C): *m*/*z* (relative abundance, %) 493 (8), 492 (16), 491 (42), 490 (48), 489 ($M^{\bullet+}$; 100), 488 (19), 487 (23), 486 (9), 485 (16), 483 (7), 474 ($[M - Me]^+$; 6), 460 (8), 459 (12), 458 (26), 457 (30), 456 (35), 455 (71), 454 (28), 453 (50), 452 (12), 451 14), 386 (6), 385 (6), 353 (7), 311 (6), 309 (6), 281 (14), 271 (11), 257 (10), 255 (12), 253 (8), 251 (7), 243 (10), 242 (33), 241 (24), 240 (9), 239 (7), 237 (8), 227 (16), 226 (7), 225 (13), 224 (7), 223 (10), 221 (7), 180 (9), 179 (50), 119 (12), 73 (19), 59 (43). IR (KBr, cm^{-1}): 3012 (w,sh), 3000 (sh), 2975 (sh), 2951 (s), 2904 (vs,b), 2862 (s), 2793 (m), 1485 (w), 1451 (m,b), 1404 (m), 1377 (m), 1333 (s), 1245 (vs), 1139 (vs), 1062 (w), 1021 (s), 958 (w), 835 (vs), 788 (m), 756 (m), 707 (w), 570 (m), 496 (w), 421 (s). EPR (toluene, 22 °C): $g = 1.9768$. EPR (toluene, −140 °C): $g_1 = 1.9965$, $g_2 = 1.9777$, $g_3 = 1.9552$, $g_{av} = 1.9765$. UV−vis (toluene, 22 °C): 525 > 655 ∼ 1420 nm. Anal. Calcd for $C_{27}H_{45}Si_2OTi$ (489.71): C, 66.22; H, 9.26. Found: C, 65.97; H, 9.22.

Preparation of [$TiCl_2$(η:$^5\eta^5$-$C_5Me_4SiMe_2CH_2CH{=}CH\text{-}CH_2SiMe_2C_5Me_4$)] (14). Compound **11** (0.42 g, 0.85 mmol) was dissolved in THF (15 mL) and the solution poured onto vacuum-dried powdery AgCl (0.14 g, 1.0 mmol). The mixture was stirred at 80 °C for 1 h, whereupon the color changed from turquoise to brown. THF was evaporated under vacuum, and the residue was washed out with hexane (5 mL) and then extracted into toluene (10 mL). The brown solution was concentrated to crystallization and cooled to −18 °C overnight. Brown crystalline **14** was separated and dried in a vacuum. Yield: 0.36 g (80%). Mp: 195 °C. ^{1}H NMR (C_6D_6): δ 0.27 (s, 6 H, Si*Me*$_2$), 1.65−1.68 (m, 2 H, SiC*H*$_2$), 1.80, 2.31 (2× s, 6 H, $C_5\mathit{Me}_4$); 5.56 (tt, $^3J_{HH} = 4.3$, $^4J_{HH} = 1.8$ Hz, 1 H, C*H*=). ^{13}C{^{1}H} NMR (C_6D_6): δ 1.5 (Si*Me*$_2$), 13.7, 16.6 ($C_5\mathit{Me}_4$); 24.6 (Si*C*H_2), 125.3 (*C*H=), 136.0 (*C*$_5$Me$_4$, the other two signals were not found). EI MS (180 °C): *m*/*z* (relative abundance, %) 497 (13), 496 (24), 495 (59), 494 (49), 493 ($[M - Cl]^+$; 100), 492 (21), 491 (25), 490 (6), 489 (10), 478 ($[M - Me]^+$; 6), 333 (10), 331 (10), 298 (19), 297 (9), 296 (25), 259 (7), 257 (10), 243 (7), 180 (8), 179 ($[C_5Me_4SiMe_2H]^+$; 46), 178 (12), 177 (11), 163 (11), 119 (14), 97 (8), 73 (18), 59 (40). IR (KBr, cm^{-1}): 3027 (vw), 2991 (w), 2947 (m), 2898 (s), 2863 (w), 2848 (m), 1480 (m), 1439 (m), 1376 (s), 1343 (m), 1323 (m), 1261 (m), 1243 (vs), 1147 (s), 1123 (w), 1093 (w), 1064 (w), 1013 (s), 961 (m), 835 (vs), 806 (m), 790 (w), 778 (w), 757 (w), 712 (w), 687 (w), 670 (w), 621 (w), 427 (m). Anal. Calcd for $C_{26}H_{42}Si_2Cl_2Ti$ (529.58): C, 58.97; H, 7.99. Found: C, 58.89; H, 7.96.

Identification of Byproducts Resulting from Acidolysis of 5 and 8 with HCl. Reaction of hexane solutions of **5** and **8** with anhydrous HCl yielding poorly soluble **6** and moderately soluble **12**, respectively (see above), also gave yellow-to-red byproducts highly soluble in hexane. Their amount and composition varied depending on the molar excess of HCl and conduction of the reaction (rapid or slow addition of HCl, stirring, time elapsed between HCl addition, and separation of excess HCl). Of all the byproducts, only [$TiCl_3$(η^5-C_5Me_4H)] and [$TiCl_3$(η^5-$C_5Me_4SiMe_2Cl$)] could be separated in pure form by crystallization and identified by EI-MS, NMR, and IR spectra. The other compounds precipitated from concentrated solutions as yellow powders. These complexes represent the common components of the byproduct mixtures obtained from **5** and **8**. The other components differed for **5** and **8**, probably being [$TiCl_3${$C_5Me_4SiMe_2CH(Me)CH{=}CHCH\text{-}(Me)SiMe_2Cl$}] and [$TiCl_3${$C_5Me_4SiMe_2CH_2CH{=}CHCH_2SiMe_2\text{-}Cl$}], respectively.

Analytical Data for [$TiCl_3$(η^5-C_5Me_4H)]. ^{1}H NMR (C_6D_6): δ 1.80, 1.90 (2× s, 6 H, $C_5\mathit{Me}_4$H); 5.89 (s, 1 H, C_5Me_4*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 13.5, 15.9 ($C_5\mathit{Me}_4$H); 124.1 (C_5Me_4H, *C*H), 137.3, 138.4 (C_5Me_4H, *C*Me).

Analytical Data for [$TiCl_3${η^5-$C_5Me_4(SiMe_2Cl)$}]. EI-MS (110 °C): *m*/*z* (relative abundance, %) 337 (7), 336 (9), 335 (39), 334 (26), 333 (100), 332 (32), 331 $[M - Cl]^+$; 98), 330 (11), 329 (10), 298 (7), 297 (7), 296 (10), 295 (8), 179 (16), 178 (30), 177 (13), 163 (15), 119 (16), 105 (7), 97 (10), 95 (12), 93 (31), 83

(6), 73 (14), 69 (11), 59 (33), 43 (9), 41 (7). Abundances in the isotope cluster due to the $[M - Cl]^+$ ion fit well to calculated intensities.

Analytical Data for $[TiCl_3\{\eta^5\text{-}C_5Me_4(SiMe_2CH_2CH{=}CHCH_2SiMe_2Cl)\}]$. ^{1}H NMR ($C_6D_6$): δ 0.17, 0.44 (2× s, 6 H, Si*Me*$_2$); 1.50−1.52 (m, 2 H, C*H*$_2$), 1.72−1.75 (m, 2 H, C*H*$_2$), 1.89, 2.25 (2× s, 6 H, C_5*Me*$_4$H); 5.15−5.19 (m, 2 H, C*H*=C*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.7, 1.1 (Si*Me*$_2$); 13.8, 17.5 (C_5*Me*$_4$); 23.1, 24.8 (*C*H$_2$); 123.4, 129.9 (*C*H=*C*H); 141.7, 144.2 (*C*$_5$Me$_4$; one C_{ipso} signal not found).

X-ray Crystallography. The diffraction data for complexes **5**, **7**, **8**, **12**, **13**, and **14** were collected on a Nonius KappaCCD image plate diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) and analyzed by the HKL program package.[25] In all cases, the structures were solved by direct methods (SIR97),[26] followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97).[27]

The data for **10** were collected on an Enraf-Nonius CAD 4-MACH III diffractometer using graphite-monochromated Mo Kα radiation and $\theta-2\theta$ scans. The cell parameters were determined by least-squares fitting of 25 automatically centered diffractions with $12° \le \theta \le 13.5°$. The structure was solved and expanded as described above.

In all cases, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were treated as follows. For **7**, **10**, and **12**: all hydrogen atoms were located on difference electron density maps and refined isotropically. For **5**, **13**, **14**: the methyl hydrogen atoms were included in calculated positions with fixed C−H bond lengths (0.97 Å) and assigned $U_{iso}(H) = 1.5U_{eq}(C)$, where C is the adjacent carbon atom. The remaining hydrogen atoms were identified on a difference Fourier map and refined with isotropic thermal motion parameters. For **8**: all hydrogen atoms were placed into calculated positions with fixed C−H bond lengths (methyl 0.96, methine 0.93 Å) and assigned $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl and $1.2U_{eq}(C)$ for methine hydrogens.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, intramolecular distances and angles, dihedral angles of least-squares planes, and packing diagrams for **5**, **7**, **8**, and **10**−**14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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