

Irregular cyclization reactions in titanocenes bearing pendant double bonds

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Abstract

Reduction of methyl-substituted titanocene dichlorides bearing pendant double bonds $[\text{TiCl}_2\{\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2\text{CMe}=\text{CH}_2)\}_2]$ (**1**) and $[\text{TiCl}_2\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)\}_2]$ (**2**) with magnesium yielded diamagnetic Ti(IV) compound $[\text{Ti}\{\eta^1:\eta^1:\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2)(\text{CH}_2\text{CH}(\text{Me})\text{CH}_2)\}\{\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2\text{C}(\text{Me})=\text{CH}_2)\}]$ (**4**) and paramagnetic Ti(III) compound $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CHMe})\}(\mu\text{-}\eta^3, \eta^1:\eta^5, \eta^1(\text{Ti:Mg})\{\text{C}_5\text{Me}_3(\text{CH}_2)(\text{SiMe}_2\text{CHCHCMe})\})\text{Mg}(\text{OC}_4\text{H}_8)_2]$ (**6**), respectively. The reluctance of titanocene intermediates to undergo intramolecular cyclization to cyclopentadienyl-ring-tethered titanacycles (as typically observed) can be explained by a shortness of the 2-methylallyl group and steric hindrance of its double bond in the former case and, in the latter case, by an attack of magnesium on the titanocene intermediate, faster than cyclization reactions. The crystal structures of **4** and **6** were determined by single-crystal X-ray diffraction.

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Keywords: Titanium; Magnesium; Titanocene; Pendant double bonds; C–H activation; Heterobinuclear complex; X-ray crystallography

1. Introduction

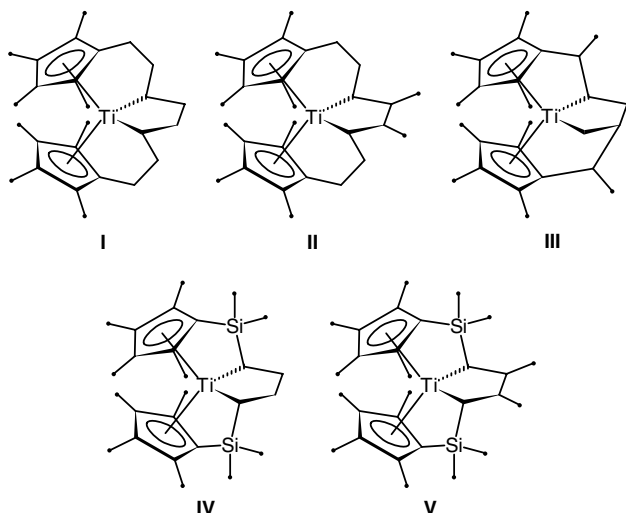
Pendant double bonds attached to cyclopentadienyl rings in early transition metal metallocenes can influence properties of olefin polymerization catalysts generated thereof. Albeit the first attempt to prepare a catalytic cationic complex from bis $\{\eta^5\text{-(3-buten-1-yl)tetramethylcyclopentadienyl}\}$ dimethyltitanium(IV) and $\text{B}(\text{C}_6\text{F}_5)_3$ failed [1], a number of well-defined boron-containing cationic catalysts based on pendant double bonds were obtained later on [2]. In catalytic systems with methylalumoxane (MAO), pendant double bonds showed no dramatic effect in polymerizations of ethene, propene [3] or styrene [4], likely due to an isomerization of the terminal double bonds into an internal position [5]. The pendant double bonds can be further utilized in anchoring of metallocene complexes onto inorganic or

polymeric matrices [6] or in binding Lewis acidic $\text{B}(\text{C}_6\text{F}_5)_2$ group in a proximity of a metal center via hydroboration with $\text{HB}(\text{C}_6\text{F}_5)_2$ [2a,2b].

The *synthetic* potential of bis $\{\eta^5\text{-(}\omega\text{-alkenyl)cyclopentadienyl}\}$ metallocenes lies mainly in the formation of cyclopentadienyl-ring-tethered metallacyclopentanes. The intramolecular cyclization involving both pendant double bonds and the metal atom occurs spontaneously when metallocene dichlorides are reduced to electron deficient metallocene intermediates [7]. The metallacyclopentane moiety is surprisingly stable and, if the length of the ω -alkenyl group is too long, a shift of double bond to internal position occurs before the cyclisation. Thus, in permethyltitanocene series the but-3-en-1-yl groups oxidatively add across the Ti(II) atom in a regular way giving mainly compound **I** while pent-4-en-1-yl groups undergo an isomerisation before the cyclization reaction yielding **II**. 1-Methylallyl groups react differently in order to minimize a steric strain providing compound **III**, which has only single carbon atom tethers (Scheme 1) [7b]. In the related

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Scheme 1.

bis{ η^5 -(ω -alkenyldimethylsilyl)tetramethylcyclopentadienyl}titanium compounds, the longer Si–C bonds enable vinylsilyl groups to form the regular titanacyclopentane compound **IV** though in an equilibrium with an opened structure having one double bond η^2 -coordinated to the titanium and the other one free. An analogue bearing allylsilyl groups undergoes the double bond shift to internal position to give stable compound **V** (Scheme 1). In both cases the tether consists of only one silicon atom [8]. Reduction of analogous bis(ω -alkenylcyclopentadienyl)zirconium dichlorides with butyllithium also provides zirconacyclopentane derivatives, however, with tethers consisting of 2 or 3 carbon atoms, the double bond shift occurring only with hex-5-en-1-yl groups [7c].

Here, we report about the products which are formed from bis{ η^5 -(2-methylallyl)tetramethylcyclopentadienyl}dichlorotitanium(IV) (**1**), whose double bonds are sterically hindered by methyl groups, and from bis{ η^5 -(but-3-en-1-yl)dimethylsilyl}tetramethylcyclopentadienyl} dichlorotitanium (**2**), the compound bearing so far the longest ω -alkenylsilyl group investigated by us, when reduced by magnesium in tetrahydrofuran.

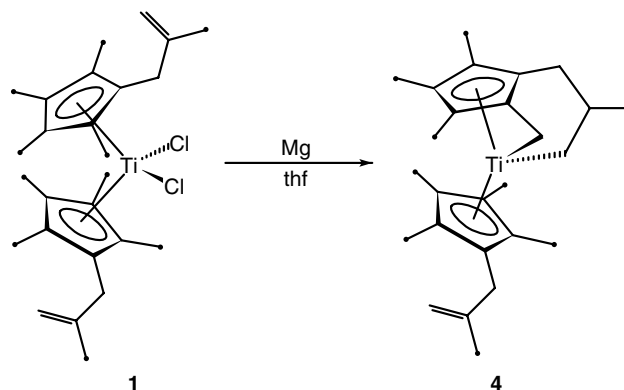
2. Results and discussion

The titanocene dichlorides **1** and **2** were obtained by reacting two molar equivalents of cyclopentadienide anions with $[\text{TiCl}_3(\text{THF})_3]$ in tetrahydrofuran (THF) followed by oxidation of the Ti(III) intermediate with stoichiometric amounts of PbCl_2 and AgCl , respectively [9]. The compounds were carefully purified by crystallization from hexane and then reduced with an excess of magnesium in thf. The reduction proceeded via an intermediate formation of titanocene monochlorides **3** and **5**, respectively, whose formation and decay in the reac-

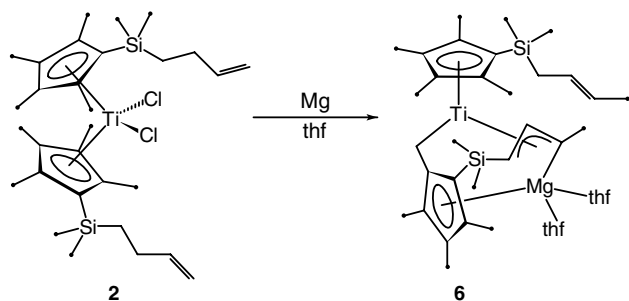
tion mixture was monitored by EPR spectroscopy. The monochloride **3** decayed rapidly to give the final diamagnetic compound **4** in high yield. On the other hand, the transient EPR signal of monochloride **5** was replaced by another EPR signal of a lower intensity and the transient blue coloration of the reaction mixture turned dark. A subsequent workup of the product mixture consisting of evaporation of all volatiles under vacuum followed by extraction with hexane and crystallization yielded **6** as the only product albeit in a low isolated yield of 12%. The paramagnetic monochlorides **3** and **5** were prepared in separate experiments by the reduction of dichlorides **1** and **2** with a half molar equivalent of magnesium in thf in order to determine their EPR spectral parameters (**3**: $g = 1.955$, $\Delta H = 18$ G; **5**: $g = 1.953$, $\Delta H = 15$ G), which were close to those found for highly methyl-substituted titanocene chlorides [10], and to prove by IR spectra that free terminal double bonds were preserved ($\nu_{\text{C}=\text{C}}$, $\nu_{\text{C}-\text{H}}$; **3**: 1651, 3074 cm^{-1} ; **5**: 1638, 3076 cm^{-1}).

The structures of products **4** and **6** were determined by X-ray crystallography and spectral methods as $[\text{Ti}\{\eta^1:\eta^1:\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2)(\text{CH}_2\text{CH}(\text{Me})\text{CH}_2)\}\{\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2\text{C}(\text{Me})=\text{CH}_2)\}]$ (**4**), a product with two new Ti–C bonds resulting from double C–H bond activation at one cyclopentadienyl ligand (Scheme 2), and $[\text{Ti}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CHMe})\}(\mu\text{-}\eta^3, \eta^1:\eta^5, \eta^1(\text{Ti:Mg})\text{-}\{\text{C}_5\text{Me}_3(\text{CH}_2)(\text{SiMe}_2\text{CHCHCMe})\})\text{Mg}(\text{OC}_4\text{H}_8)_2]$ (**6**) with an unusual, multiply bridging ligand between Ti^1 and Mg^2 : 1,2,3-trimethyl-4-methylene-1 κ^3 C-5-(dimethylsilyl)but-2-en-1-yl-1 κ^3 C(1–3):2 κ^3 C(3)-cyclopentadienyl-2 κ^5 C (Scheme 3).

^1H and ^{13}C NMR spectra of **4** clearly showed the presence of one tucked-in methylene group (δ_{C} 78.51) and one titanium-bonded methylene group of the 2-methylpropan-1,3-diyl bridge (δ_{C} 80.30) both resonances falling into the range observed for singly [11] and doubly tucked-in titanocene derivatives [12], and one unchanged 2-methylprop-2-en-1-yl group, proving thus that the solid state and solution structures do not differ.



Scheme 2.



Scheme 3.

The structure of **4** was further corroborated by IR spectra which showed lower intensities of $\nu_{C=C}$ and ν_{C-H} absorption bands due to the free 2-methylprop-2-en-1-yl group and an absorption band at 3053 cm^{-1} typical of the *exo*-methylene group bonded to titanium [11c,11g,12b–12e]. The EI-MS spectra of **4** displayed the molecular ion as the base peak and only a minimum fragmentation. The formation of **4** is likely initiated by reduction of **1** to the corresponding titanocene (for thermally stable titanocenes see [13]). A following transient π -coordination of one double bond to titanium does not result in a stable structure due to the shortness of the allyl chain but assists to hydrogen abstraction from a vicinal methyl group at the cyclopentadienyl ring by bringing it close to the titanium atom. The process can be formally described as an oxidative addition of the vicinal methyl C–H bond across the Ti(II) center followed by an insertion of the double bond into the Ti–H bond (or intramolecular hydrometallation) to give **4**.

The solid-state structure of **6** is very likely maintained in hydrocarbon solution since the solution EPR spectra of **6** consist of a single line $\Delta H = 6.0\text{ G}$ at $g = 1.976$, and in frozen organic glass, they display an axial g -tensor with $g_{\perp} > g_{\parallel}$ and $g_{av} = 1.977$. The EPR parameters resemble to some extent those found for powdery $[\text{Ti(III)}(\eta^5\text{-C}_5\text{H}_5)(\eta^8\text{-C}_8\text{H}_8)]$, where the unpaired d^1 electron is localized in a Ti d (z^2) orbital [14]. In the present case, the η^3 -allyl and η^1 -methylene bonds substitute the cyclooctatetraenide(2–) anion, which is reflected by a broadening of the EPR signal and its shift to a lower g -value. The actual loss of symmetry needs not be observed in the shape of the anisotropic spectrum because the titanium forms a top of a pyramid with an approximately square base of four binding carbon atoms (see the crystal structure) and, hence, the expected rhombic g -tensor may have two principal values close to each other, which need not be necessarily resolved in a frozen toluene solution (see discussion in [14]). The interaction of the unpaired d electron with two protons of the allyl group should be observable using ENDOR and TRIPLE resonance spectra [14b] or hyperfine sublevel correlation spectroscopy (HYSCORE) in pulse EPR experiments [15], which were not available, however. Of the other spectroscopic methods, IR spectra proved the

absence of terminal double bonds whereas not giving a clear evidence for the free internal double bond or the bridging allyl group. A weak absorption band at 3008 cm^{-1} can be tentatively assigned to ν_{C-H} vibration of the bridging allyl group or the ν_{C-H} vibration of the *exo*-methylene group. The latter vibration occurs at 3000 cm^{-1} in tucked-in titanocene complexes with strained structures (angle C–C–Ti at the methylene carbon atom ca. 65° ; see structure of **4**), however, in the non-strained arrangement of **6** (C(20)–C(24)–Ti $109.7(3)^\circ$ see below) the ν_{C-H} vibration of the *exo*-methylene group can well occur in the range of non-perturbed ν_{C-H} vibrations, close to or below 3000 cm^{-1} . The EI-MS spectra of **6** showed peaks due to thf (m/z 72 and 42) and two highly abundant fragments at m/z 510 and 452 (base peak), the former corresponding to the loss of $\text{Mg}(\text{thf})_2$ and one hydrogen atom from the crystallographic molecular structure. The latter has an elemental composition $\text{C}_{28}\text{H}_{40}\text{SiTi}$ and likely arises from the former one by a loss of SiMe_2 group. The other fragment ion exceeding 10% relative abundance is $[\text{HSiMe}_2]^+$ (m/z 59), which is commonly observable in EI-MS spectra of compounds containing SiMe_2 bridge [8,13c]. Since the chemical elemental analysis of **6** gave results allowing for an error of one mass unit, the construction of particularly the bridging allyl group had to rely on the structure obtained from the X-ray single-crystal analysis (vide infra) and the composition of the MS base peak.

2.1. Crystal structure of **4**

A view of molecular structure of **4** is shown in Fig. 1 and the selected geometric parameters are listed in Table 1. The cyclopentadienyl ring C(1–5) is doubly tethered to the titanium atom via vicinal methylene and 2-methylpropan-1,3-diyl groups. Consequently, the ring

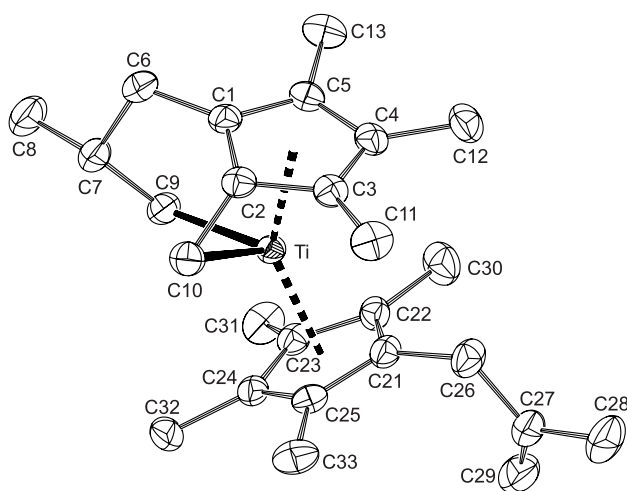


Fig. 1. The molecular structure of **4** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and bond angles (°) for **4**

Bond lengths			
Ti–Cg(1) ^a	2.013(1)	Ti–Cg(2) ^a	2.077(1)
Ti–C(1)	2.283(2)	Ti–C(2)	2.132(2)
Ti–C(3)	2.341(2)	Ti–C(4)	2.516(2)
Ti–C(5)	2.455(2)	Ti–C(9)	2.183(2)
Ti–C(10)	2.278(3)	C(2)–C(10)	1.435(4)
C(1)–C(6)	1.501(4)	C(6)–C(7)	1.527(4)
C(7)–C(8)	1.532(4)	C(7)–C(9)	1.524(4)
C(21)–C(26)	1.499(3)	C(26)–C(27)	1.499(4)
C(27)–C(28)	1.500(4)	C(27)–C(29)	1.323(5)
C _{ring} –C _{ring}	1.408(3)–1.441(3)	C _{ring} –C _{Me}	1.501(4)–1.513(4)
Bond angles			
Cg(1)–Ti–Cg(2) ^a	145.43(5)	Cg(1)–Ti–C(9)	103.56(9)
Cg(1)–Ti–C(10)	71.94(8)	Cg(2)–Ti–C(9)	107.21(9)
Cg(2)–Ti–C(10)	120.93(8)	C(2)–C(10)–Ti	65.6(1)
C(7)–C(9)–Ti	115.9(2)	C(9)–Ti–C(10)	93.2(1)
C(6)–C(7)–C(9)	107.5(2)	C(6)–C(7)–C(8)	112.2(2)
C(1)–C(6)–C(7)	111.0(2)	C(21)–C(26)–C(27)	115.9(2)
C(26)–C(27)–C(28)	114.1(3)	C(26)–C(27)–C(29)	124.1(3)
C(28)–C(27)–C(29)	121.6(3)	ϕ ^b	29.2(1)

^a Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(16–20) cyclopentadienyl rings, respectively.

^b Dihedral angle subtended by the cyclopentadienyl least-squares planes C(1–5) and C(21–25).

is inclined to the Ti atom by C(2) and the Ti–Cg(1) distance is shorter than that to the unchanged cyclopentadienyl ring C(21–25) (see Table 1). The latter ligand is nearly exactly perpendicular to the Ti–Cg(2) vector and its 2-methylprop-2-en-1-yl group is placed at the hinge position of the metallocene framework, directed outward the titanium atom. The open side of the sandwich titanocene structure is partly occupied by the 2-methylpropan-1,3-diyl bridge. The overall structure of **4** is very similar to the crystal structure of [Ti(η¹:η¹:η⁵-C₅Me₃(CH₂)(CH(Me)CH₂CH₂);(η⁵-C₅Me₅)] whose bridging system differs only by the position of the methyl group in the 1-methylpropan-1,3-diyl bridge [11g]. Hence, it is not surprising that the Cg(1)–Ti–Cg(2) angles and angles between the least-squares planes of the cyclopentadienyl rings are in both compounds identical within the precision of the measurements, being controlled by the geometry of *exo*-methylene tether as in simple tucked-in compound [Ti(η⁵:η¹-C₅Me₄CH₂)(η⁵-C₅Me₅)] [11d].

2.2. Crystal structure of **6**

X-ray diffraction analysis revealed that monoclinic crystals of Ti–Mg binuclear complex **6** contain two pairs of asymmetrical molecules in the unit cell (Fig. 2 and Table 2). The titanium atom is η⁵-coordinated to the tetramethylcyclopentadienyl ligand bearing (but-2-en-1-yl)dimethylsilyl group, η³-bonded to the C(25), C(26), and C(27) carbon atoms of butenyl group of the other cyclopentadienyl ligand, and σ-bonded to the methylene group in the vicinal position to the silyl substituent of the mentioned cyclopentadienyl ligand. The magnesium

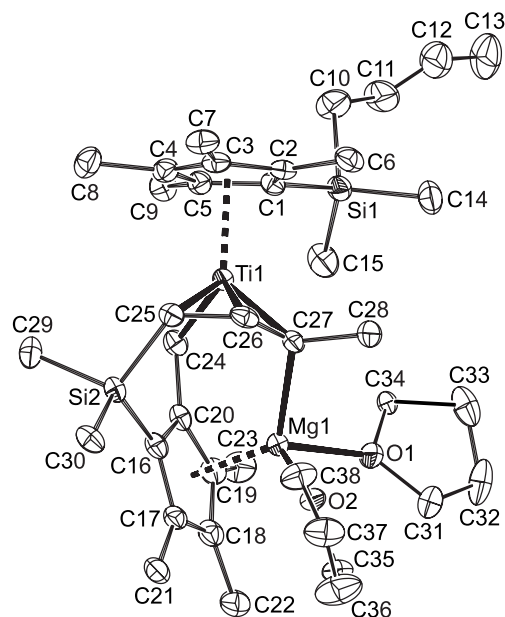


Fig. 2. The molecular structure of **6** (30% probability ellipsoids) with atom numbering scheme. Disordered positions in the ligands (C(31a), C(34a) and C(37a)) and the but-2-en-1-yl chain (C(11a), C(12a), C(13a)), and all hydrogen atoms are omitted for clarity.

atom is η⁵-coordinated to the latter cyclopentadienyl ligand and σ-bonded to C(27) atom of the bridging butenyl group. The metal–carbon σ-bond lengths Ti–C(24) and Mg–C(27) fit very well to the literature data for σ-Ti–C [1,7b,8,16] and σ-Mg–C bonds [16c,16g,17], and the angle C(20)–C(24)–Ti and angles at C(27) do not show any strain usually observed in the tucked-in complexes (cf. compound **4**). In addition, the bond lengths in the bridging allyl group and the Ti–C

Table 2
Selected bond distances (Å) and bond angles (°) for **6**

<i>Bond lengths</i>			
Ti–Cg(1) ^a	2.063(2)	Mg–Cg(2) ^a	2.103(3)
Ti–C(24)	2.162(5)	Ti–C(25)	2.203(5)
Ti–C(26)	2.272(5)	Ti–C(27)	2.185(5)
Mg–C(27)	2.231(5)	Ti–C _{Cp}	2.369(5)–2.422(4)
Mg–C(16)	2.342(5)	Mg–C(17)	2.433(5)
Mg–C(18)	2.502(5)	Mg–C(19)	2.473(5)
Mg–C(20)	2.386(5)	Si–C _{Me}	1.860(6)–1.882(5)
Si(1)–C(1)	1.869(5)	Si(1)–C(10)	1.892(6)
Si(2)–C(16)	1.848(5)	Si(2)–C(25)	1.861(5)
C(10)–C(11) _{av}	1.501(10)	C(11)–C(12) _{av}	1.302(14)
C(12)–C(13) _{av}	1.533(12)	C(20)–C(24)	1.492(7)
C(25)–C(26)	1.432(7)	C(26)–C(27)	1.387(7)
C(27)–C(28)	1.520(7)	Mg–O(1)	2.084(4)
Mg–O(2)	2.095(4)	Ti–Mg	3.361(2)
C _{ring} –C _{ring} (Cp)	1.401(7)–1.458(7)	C _{ring} –C _{Me} (Cp)	1.492(7)–1.515(7)
<i>Bond angles</i>			
Cg(1)–Ti–C(24)	117.8(2)	Cg(1)–Ti–C(25)	117.3(2)
Cg(1)–Ti–C(26)	116.9(2)	Cg(1)–Ti–C(27)	127.3(2)
C(25)–C(26)–Ti	68.7(3)	C(25)–Ti–C(26)	37.3(2)
C(25)–C(26)–C(27)	123.7(4)	C(20)–C(24)–Ti	109.7(3)
C(24)–Ti–C(25)	102.8(2)	C(24)–Ti–C(27)	110.2(2)
C(26)–C(27)–Ti	75.3(3)	C(26)–C(27)–C(28)	117.7(5)
C(26)–Ti–C(27)	36.2(2)	Ti–C(27)–C(28)	133.1(4)
Mg–C(27)–C(26)	119.9(3)	Ti–C(27)–Mg	99.1(2)
Cg(2)–Mg–C(27)	125.8(2)	Cg(2)–Mg–O(1)	117.1(1)
Cg(2)–Mg–O(2)	119.5(1)	O(1)–Mg–O(2)	93.6(2)
φ ^b	13.0(2)	ψ ^c	81.9(3)

^a Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(16–20) cyclopentadienyl rings, respectively.

^b Dihedral angle subtended by the cyclopentadienyl least-squares plane C(1–5) and the allyl group plane C(25–27).

^c Dihedral angle subtended by the cyclopentadienyl least-squares plane C(16–20) and the allyl group plane C(25–27).

distances to the carbon atoms of the allyl group fall into the ranges common to Ti–η³-allyl systems [18]. The plane of the allyl group and the least-squares plane of the cyclopentadienyl ring C(1–5) subtend an angle of 13.0(2)°. The angles Cg(1)–Ti–C(24–26) range 116.9(2)–117.7(2)° while the angle to magnesium-bonded C(27) is larger (127.2(2)°), proving the η³-bonding mode and the approximate square pyramidal coordination around the titanium atom. The coordination at the magnesium atom is further completed with two thf molecules, which are disordered in the structure at the carbon atoms attached to the oxygen. The but-2-en-1-yl group is disordered as well but the average bond lengths cleanly identify the position of the double bond between C(11) and C(12) atoms (1.30(1) Å). A similar disorder was recently observed in the but-2-en-2-yl attached to the cyclopentadienyl ligand in a CGC complex [5].

2.3. Conclusions

Reluctance of a transient titanocene, which is formed by reduction of titanocene dichloride **1** with magnesium in thf, to undergo an intramolecular cycloaddition reaction to afford a cyclopentadienyl-ring-tethered titanacyclopentane similarly to its isomer bearing

1-methylprop-2-en-1-yl substituent [7b] can be ascribed to steric effect of the methyl group residing on the inner side of the pendant double bond. As it was demonstrated by the formation of **III**, where one of the two double bonds was linked to titanium by the last carbon atom, the length of the allyl group is not sufficient to tether the regular titanacyclopentane moiety (see **I** in Scheme 1). Although compound **III** is thermally stable, some steric strain is to be anticipated because the angle between the least-squares cyclopentadienyl ring planes is considerably smaller than in compound **I** or **II** (30.6(5)° versus 40.7(5)° or 41.1(1)°) [7b]. A more rigid structure of **III** with only single-carbon tethers compared to double-carbon tethers in **I** and **II** would be even more strained in an analogue of **III** with methyl groups on C-2 of allyl substituents. On the other hand, the formation of **4** is not a great surprise since a titanocene intermediate containing only one 1-methylprop-2-en-1-yl group was stabilized via formation of the analogous intramolecular bridging system. A similar compound with by one carbon longer pendant but-3-en-1-yl group stabilized by the π-coordination of the double bond to Ti(II) ion, however [11g].

The reasons for formation of **6** are difficult to identify because the other products of the reduction of **2** could

not be isolated. It is very likely that a titanocene intermediate was formed, and caused the double bond isomerization from terminal to internal position. This process was clearly demonstrated in the formation of compounds **II** and **V** (Scheme 1). However, in the present case it did not lead to a stable product. Having in mind that a very stable cyclopentadienyl-ring-tethered titanacyclopentane **V** was obtained from bis{ η^5 -(allyldimethylsilyl)tetramethylcyclopentadienyl}titanocene after double bond shifts [8], the formation of the analogous stable product from **2** would require a two-fold double bond shift with the formation of ethyl groups. The shift of the double bond into vicinity of the silicon atom is slow compared with the shift from terminal position, and a reaction of the pendant arms with active magnesium present in the reaction mixture can well compete with the isomerization. Active magnesium is known to attack highly methyl-substituted cyclopentadienyl ligands, abstracting hydrogen from C–H bonds to form titanocene hydride-magnesium hydride complexes with Ti(III)(μ -H)₂Mg bridges [16c,16g,19]. In the case of reduction of dichloro-bis{ η^5 -(trimethylsilyl)tetramethylcyclopentadienyl}titanium, the magnesium even abstracts hydrogen from C–H bonds of the trimethylsilyl groups, forming Mg–C bonds [16c]. In view of this, it appears likely that the formation of **6** is initiated by an activation of one cyclopentadienyl ligand in a transient titanocene (Ti^{II}) to give a single tucked-in complex with the π -coordinated (but-2-en-1-yl)dimethylsilyl group, which is then the subject to magnesium attack. The hydrogen abstraction from the but-2-en-1-yl moiety by magnesium resulted in the formation of Ti– η^3 -allyl and Mg– σ -C bonds and a transfer of the cyclopentadienyl ring from titanium to magnesium. A smooth and quantitative transfer of the cyclopentadienyl ligand from titanium to magnesium is not unusual: the reduction of the [Ti(η^5 -C₅H_{5-n}Me_n)₂(η^2 -Me₃SiC≡CSiMe₃)] (*n* = 0–2) complexes by magnesium in the presence of free Me₃SiC≡CSiMe₃ in thf afforded Ti–Mg complexes containing CpTi and CpMg units bridged by two molecules of the alkyne [20]. The proposed scenario is only tentative, based on the knowledge of reactions proceeding in similar systems, and the fate of totally three hydrogen atoms removed from the forming complex **6** is unknown. Nevertheless, the formation of **4** from **1** and **6** from **2** shows that the reduction of permethyltitanocene dichlorides with pendant double bonds by excess magnesium needs not afford cyclopentadienyl-ring-tethered titanacyclopentanes in case that the pendant chain is short and the double bond is sterically hindered (2-methylallyl) or so long that the double bond shift over two carbon atoms is required ((but-3-en-1-yl)dimethylsilyl). Further investigations at reactivity of shorter and longer pendant double bonds under reduction conditions are currently performed.

3. Experimental

3.1. Methods

Syntheses of cyclopentadienyl ligands and titanocene dichlorides **1** and **2** were carried out under argon. All manipulations with Ti(III) compounds **3**, **5**, and **6** and Ti(IV) compound **4** were performed under vacuum on an all-glass high vacuum line using sealed glass devices equipped with breakable seals. ¹H (399.95 MHz) and ¹³C (100.58 MHz) NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer in C₆D₆ solutions at 25 °C. Chemical shifts (δ /ppm) are given relative to the solvent signal (δ_{H} 7.15, δ_{C} 128.0). EI MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. 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) in the X-band. *g*-Values were determined by using an Mn²⁺ standard at *g* = 1.9860 (*M*₁ = –1/2 line). A variable temperature unit STT-3 was used for measurements in the range from –140 to +25 °C. UV–Vis spectra were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma). IR spectra were measured in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{–1}. With the exception of air-stable titanocene dichlorides **1** and **2** all studied titanium compounds are extremely air- and moisture-sensitive and therefore their solid samples were handled in a glovebox Labmaster 130 (mBraun) under purified nitrogen. Crystalline samples for EI-MS measurements and determination of melting points were placed in glass capillaries and sealed out. KBr pellets were prepared and placed into an air-protecting cuvette in the glovebox. The purity and composition of air-sensitive compounds were determined by mass spectrometry.

3.2. Chemicals

The solvents THF, hexane, and toluene were dried by refluxing over LiAlH₄ and stored as solutions of dimeric titanocene [(μ - η^5 : η^5 -C₅H₄C₅H₄){(μ -H)(η^5 -C₅H₅)}₂] [21]. TiCl₄ (International Enzymes) was purified by refluxing over copper wire and distilled in vacuum. Butyllithium (2.5 M in hexanes), magnesium turnings (purum for Grignard reactions), 1,2,3,4-tetramethylcyclopentadiene (a mixture of isomers), 3-chloro-2-methylprop-1-ene, dichlorodimethylsilane and 4-chlorobut-1-ene (all Aldrich) were transferred via syringe under argon. A mixture of isomers of 5-(2-methyl-2-propenyl)-1,2,3,4-tetramethylcyclopentadienes was obtained by reacting 2,3,4,5-tetramethylcyclopent-2-enone with

Grignard reagent prepared from 3-chloro-2-methylprop-1-ene and by iodine-catalyzed dehydration of the formed alcohol as described elsewhere [7b]. But-3-enylchlorodimethylsilane was obtained by addition of a mixture of dichlorodimethylsilane and 4-chlorobut-1-ene (1.0:1.5 molar equivalents) to a twofold molar excess of magnesium turnings following the literature procedure [22].

3.3. Synthesis of 5-(2-methylprop-2-en-1-yl)-1,2,3,4-tetramethylcyclopentadiene

3-Chloro-2-methylprop-1-ene (27.0 g, 0.30 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-en-1-one (34.2 g; 0.248 mol) in diethyl ether (100 ml) was added to the solution of Grignard reagent during 60 min, the grey-green reaction mixture was refluxed for 2 h and then slowly poured onto a vigorously stirred 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-(2-methylprop-2-en-1-yl)-1,2,4,5-tetramethylcyclopent-2-ene, which was immediately dehydrated by addition of an iodine solution in diethyl ether (50 mg I₂ 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, two-times 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 boiling water bath. The GC analysis of the distillate showed the presence of ca. 2% of the unconverted alcohol, which was removed by addition of LiAlH₄ (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% on ketone). GC-MS: *m/z* (relative abundance) 176 (M⁺; 51), 161 (35), 135 (16), 134 (26), 133 (15), 121 (51), 120 ([M-C₄H₈]⁺; 100), 119 (44), 115 (9), 107 (9), 106 (12), 105 (83), 93 (28), 91 (34), 79 (24), 77 (22), 65 (10), 55 (15), 53 (10), 41 (18), 39 (15). IR (neat, cm⁻¹): 3074 (m), 2963 (vs), 2915 (vs), 2868 (s), 2855 (s), 2737 (w), 1780 (vw), 1652 (m), 1443 (s), 1374 (m), 1272 (w), 1224 (w), 1159 (w), 1105 (w), 973 (vw), 887 (s), 791 (vw), 685 (w), 563 (w), 510 (vw), 479 (w), 415 (w).

3.4. Preparation of [TiCl₂{(η⁵-C₅Me₄(CH₂C(Me)=CH₂)}₂] (1)

[TiCl₃(THF)₃] (generated in situ by adding LiBu in hexanes (22.5 ml of 1.6 M, 36.0 mmol) to TiCl₄ (4.0 ml, 36.0 mmol) in THF (50 ml) followed by a short reflux-

ing) was mixed with a suspension of lithium cyclopentadienide obtained by reacting LiBu (30 ml of 2.5 M in hexanes, 75.0 mmol) with HC₅Me₄(CH₂C(Me)=CH₂) (12.8 g, 73.0 mmol) in THF (500 ml) for 24 h at room temperature under stirring. After refluxing this mixture for 30 h and subsequent stirring with PbCl₂ [9] (5.0 g, 18.0 mmol) at 40 °C for 5 h, the reaction solution was poured away from precipitated lead, evaporated to dryness, and the residue was extracted into hexane. Compound **1** crystallized from hexane solution upon cooling. Yield of brown crystals of **1** was 7.1 g (42%).

EI-MS (100 °C): *m/z* (relative abundance) 468 (M⁺; 2), 433 ([M-Cl]⁺; 8), 297 (26), 296 (25), 295 (92), 294 (48), 293 ([M-Cp']⁺; 100), 292 (20), 291 (16), 260 (9), 259 (7), 258 ([M-Cp'-Cl]⁺; 24), 257 (10), 256 (10), 255 (24), 254 (10), 253 (23), 241 (15), 239 (7), 219 (8), 218 (13), 217 (19), 216 (10), 215 (10), 214 (6), 213 (18), 176 (18), 175 (90), 160 (18), 159 (16), 145 (39), 135 (20), 134 (20), 133 (42), 129 (19), 128 (16), 120 (14), 119 (85), 117 (17), 115 (17), 105 (44), 91 (47), 77 (26), 55 (30), 53 (20), 41 (40). ¹H NMR (C₆D₆): δ 1.55 (m, 3H, Me), 1.85, 1.98 (2 × s, 6H, Me₄C₅); 3.31 (m, 2H, CH₂), 4.27, 4.68 (2 × m, 1H, =CH₂). ¹³C{¹H} NMR (C₆D₆): δ 12.83, 13.32 (Me₄C₅); 23.17 (Me), 36.30 (CH₂), 110.54 (=CH₂), 127.51, 128.99, 130.69 (3 × C_{ipso}(Me₄C₅)); 143.93 (=C(Me)). IR (KBr, cm⁻¹): 3080 (m), 2989 (m), 2968 (s), 2904 (vs), 2721 (vw), 1650 (s), 1485 (m), 1444 (vs), 1390 (m), 1377 (vs), 1319 (w), 1222 (m), 1020 (s), 885 (vs), 816 (w), 582 (w), 474 (w), 418 (m). Anal. Calcd. for C₂₆H₃₈Cl₂Ti (M 469.37): C, 66.53; H, 8.16%. Found: C, 66.48; H, 8.12%.

3.5. Preparation of [TiCl{(η⁵-C₅Me₄(CH₂C(Me)=CH₂)}₂] (3)

Compound **1** (0.468 g, 1.0 mmol) and fine magnesium turnings (0.012 g, 0.5 mmol) were degassed and THF (20 ml) was added by condensation on a vacuum line. The ampoule with the reaction mixture was sealed off and was heated to 60 °C until all the magnesium metal disappeared and the initial reddish brown color of the solution turned dirty green. After evaporation of the solvent in vacuum, the residue was extracted by hexane, the solution concentrated, and a blue solid of **3** crystallized out by cooling to -18 °C. Compound **3** was identified by EI-MS, EPR, UV-Vis and IR spectra.

M.p. 55 °C. EI-MS (90 °C): *m/z* (relative abundance) 437 (10), 436 (15), 435 (30), 434 (18), 433 (M⁺; 35), 399 (7), 398 ([M-Cl]⁺; 12), 397 (7), 379 (7), 262 (12), 261 (16), 260 (76), 259 (37), 258 ([M-Cp']⁺; 100), 257 (19), 256 (18), 255 (11), 253 (9), 220 (10), 219 (10), 218 (31), 217 (16), 216 (11), 215 (8), 213 (13), 133 (10), 119 (10). EPR (toluene, 22 °C): *g* = 1.955, Δ*H* = 18.5 G. EPR (toluene, -140 °C): *g*₁ = 1.998, *g*₂ = 1.983, *g*₃ = 1.888, *g*_{av} = 1.956. UV-Vis (toluene, 22 °C): 360sh ≫ 555 > 650sh nm. IR (KBr, cm⁻¹): 3074 (m), 2982 (m), 2966 (s), 2907 (vs), 2723 (vw), 1651 (s), 1487 (m), 1444 (vs), 1430

(sh), 1377 (s), 1368 (sh), 1321 (vw), 1224 (w), 1025 (m), 884 (vs), 817 (vw), 669 (vw), 440 (s), 416 (m).

3.6. Preparation of $[Ti\{\eta^1:\eta^1:\eta^5-C_5Me_3(CH_2)(CH_2CH(Me)CH_2)\}(\eta^5-C_5Me_4(CH_2CH(Me)=CH_2))]$

Compound **1** (0.468 g, 1.0 mmol) and fine magnesium turnings (0.24 g, 10 mmol) were degassed and THF (20 ml) was added by condensation in vacuum. The sealed mixture was kept at 60 °C for 5 h whereupon the initial reddish brown solution of **1** turned bright green. Then the remaining magnesium was separated, the solution was evaporated under vacuum, and the residue was extracted with hexane (10 ml). The extract was concentrated to crystallization and then cooled in a freezer for several days. A turquoise crystalline material was separated from the mother liquor and dried in vacuum. Yield: 0.28 g (70%).

M.p. 78 °C. EI-MS (90 °C): m/z (relative abundance) 401 (6), 400 (23), 399 (35), 398 (M^{+} ; 100), 397 (15), 396 (15), 339 (5), 182 (6), 181 (7), 180 (6). 1H NMR (C_6D_6): δ -2.51 (dd, $^2J_{HH} = ^3J_{HH} = 12.0$ Hz, 1H, $TiCH_2CH$), 0.95 (filled-in d, 3H, $CHMe$), 1.33 (d, $^2J_{HH} = 4.1$ Hz, 1H, $TiCH_2Cp$), 1.44 (ddd, $^2J_{HH} = 12.0$, $^3J_{HH} = 1.8$, 4.1 Hz, 1H, $TiCH_2CH$; partly obscured by a $Me(Cp)$ resonance), 1.70 (br s, 3H, $CpCH_2C(Me)=CH_2$), 1.81 (dd, $^3J_{HH} = 1.8$, ca. 8 Hz, 1H, $TiCH_2CH$; obscured by a $Me(Cp)$ resonance), 2.01 (d, $^2J_{HH} = 4.1$ Hz, 1H, $TiCH_2Cp$), 2.48 (dd, $^2J_{HH} = 13.6$, $^3J_{HH} = 10.5$ Hz, 1H, $CpCH_2CH$), 2.80, 2.87 (2 \times d, $^2J_{HH} = 16.2$ Hz, 1H, AB system of $CpCH_2C(Me)=CH_2$), 3.05 (ddd, $^2J_{HH} = 13.6$, $^3J_{HH} = 1.7$, 8.6 Hz, 1H, $CpCH_2CH$), 4.78 (unresolved m, 1H, $=CH_2$), 4.86 (virtual octuplet, $J \approx 1.2$ Hz, 1H, $=CH_2$); 1.09, 1.46, 1.65, 1.72, 1.74, 1.75, 1.81 (7 \times s, 3H, Me_4C_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.87 ($CpCH_2C(Me)=CH_2$), 27.65 ($CpCH_2CH(Me)$), 35.19 ($CpC H_2C(Me)=CH_2$), 36.26 ($CpC H_2CH(Me)$), 44.53 ($CpCH_2CH(Me)$), 78.51 ($TiCH_2Cp$), 80.30 ($TiCH_2CH(Me)$), 110.76 ($=CH_2$), 144.67 ($CpCH_2C(Me)=CH_2$); 10.13, 10.79, 11.34, 11.59, 11.71, 11.79, 11.88 (7 \times Me_4C_5); 118.21, 118.58, 118.71, 118.90, 119.81, 121.11 (2 C), 123.28, 131.19, 140.35 (10 \times $C_{ipso}(Me_4C_5)$). IR (KBr, cm^{-1}): 3081 (w), 3053 (w), 2981 (m), 2962 (m), 2924 (vs), 2906 (vs), 2851 (s), 2802 (w), 1651 (m), 1448 (vs), 1376 (s), 1360 (m), 1281 (vw), 1221 (w), 1142 (vw), 1121 (w), 1084 (w), 1018 (m), 901 (s), 889 (m), 841 (w), 823 (m), 754 (w), 671 (w), 614 (w), 587 (vw), 512 (m), 488 (vw), 438 (w), 410 (m). UV-VIS (hexane, 23 °C): 615 nm.

3.7. Synthesis of 1,2,3,4-tetramethyl-5-((but-3-en-1-yl)dimethylsilyl)cyclopenta-1,3-diene

1,2,3,4-Tetramethyl-5-((but-3-en-1-yl)dimethylsilyl)cyclopenta-1,3-diene was obtained from 1,2,3,4-tetramethylcyclopentadiene (13.8 g, 0.113 mol) by the reaction of its lithium salt (generated from stoichiometric

amounts of 1,2,3,4-tetramethylcyclopentadiene and 2.5 M LiBu solution) with the equimolar amount of (but-3-en-1-yl)chlorodimethylsilane (16.7 g, 0.113 mol) in THF. The reaction mixture was stirred overnight (voluminous $Li[(C_5HMe_4)]$ salt disappeared) and the solution was reduced to volume of ca. 30 ml by distilling off THF. After evaporation of volatiles in vacuum the product was distilled from oil bath (150 °C) under vacuum of a rotary pump. Yield of yellow liquid: 23.0 g (87%).

1H NMR (C_6D_6): δ -0.04 (s, 6H, $SiMe_2$), 0.53–0.59 (m, 2H, $SiCH_2$), 1.80, 1.90 (2 \times s, 6H, Me_4C_5); 1.94–2.02 (m, 2H, $CH_2CH=$), 2.92 (br s, 1H, Me_4C_5H), 4.90–5.06 (m, 2H, $=CH_2$), 5.78–5.88 (m, 1H, $=CH$). $\{^{13}C\}^1H$ NMR (C_6D_6): δ -3.1 ($SiMe_2$), 11.3 (Me_4C_5), 13.9 ($SiCH_2$), 14.7 (Me_4C_5), 28.5 ($CH_2CH=$), 54.4 (Me_4C_5H , C H), 113.0 ($=CH_2$), 133.0, 135.6 (Me_4C_5H , CMe); 141.8 ($=CH$). IR (neat, cm^{-1}): 3076 (w), 2963 (s,b), 2915 (vs,b), 2859 (s), 1639 (s), 1444 (s), 1413 (m), 1379 (w), 1248 (vs), 1219 (m), 1171 (w,b), 1122 (w), 1110 (m), 1048 (m), 1023 (w), 990 (s), 952 (m), 905 (s), 834 (vs), 815 (vs), 775 (s), 726 (vw), 685 (vw), 639 (vw), 598 (w), 558 (vw), 484 (m).

3.8. Preparation of $[TiCl_2(\eta^5-C_5Me_4(SiMe_2(CH_2)_2CH=CH_2))_2]$ (**2**)

The synthesis of $[TiCl_2(\eta^5-C_5Me_4(SiMe_2(CH_2)_2CH=CH_2))_2]$ (**2**) was carried in exactly the same manner as for **1** except that $AgCl$ was used for the final oxidation of the Ti(III) intermediate instead of $PbCl_2$. Thus, $[TiCl_3(THF)_3]$ (generated in situ by adding LiBu in hexanes (22.5 ml of 1.6 M, 36.0 mmol) to $TiCl_4$ (4.0 ml, 36.0 mmol) in THF (50 ml) followed by a short refluxing) was mixed with a suspension of lithium cyclopentadienide obtained by reacting LiBu (30 ml of 2.5 M in hexanes, 75.0 mmol) with the above cyclopentadiene (17.1 g, 73.0 mmol) in THF (500 ml) for 24 h at room temperature under stirring. After refluxing this mixture for 30 h and subsequent stirring with $AgCl$ (5.16 g, 36.0 mmol) at 40 °C for 5 h [9], the reaction solution was poured away from precipitated silver, evaporated to dryness, and the residue was extracted into hexane. Brown crystals of **2** were obtained from hot concentrated hexane solution. Yield: 6.7 g (32%).

EI-MS (170 °C): m/z (relative abundance) 584 (M^{+} ; 0.1), 569 ($[M-Me]^{+}$; 0.4), 552 (8), 551 (18), 550 (16), 549 ($[M-Cl]^{+}$; 31), 494 ($[M-Cl-C_4H_7]^{+}$; 3), 353 (12), 352 (6), 351 ($[M-Cp]^{+}$; 17), 333 (7), 234 (14), 233 ($[Cp]^{+}$; 18), 180 (11), 179 (16), 178 ($[C_5Me_4SiMe_2]^{+}$; 19), 177 (12), 163 (12), 120 (7), 119 (13), 113 (41), 105 (10), 99 (13), 97 (20), 91 (8), 85 (35), 73 (17), 60 (9), 59 ($[SiMe_2H]^{+}$; 100), 43 (12), 41 (10). 1H NMR (C_6D_6): δ 0.54 (s, 6H, $SiMe_2$), 0.96–1.03 (m, 2H, $SiCH_2$), 1.63 (s, 6H, Me_4C_5), 2.01–2.08 (m, 2H, $SiCH_2CH_2$), 2.14 (s, 6H, Me_4C_5), 4.91 (ddt, $^3J_{HH} = 10.1$, $^2J_{HH} = 2.0$, $^4J_{HH} = 1.4$ Hz, 1H, $=CH_2$), 5.02 (ddt, $^3J_{HH} = 17.1$, $^2J_{HH} = 2.0$, $^4J_{HH} = 1.6$ Hz, 1H,

$=\text{CH}_2$), 5.86 (ddt, $^3J_{\text{HH}} = 17.1, 10.1, ^3J_{\text{HH}} = 6.2$ Hz, 1H, $=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 0.5 (SiMe_2), 12.1, 16.9 (Me_4C_5); 17.0 (SiCH_2), 28.8 (SiCH_2CH_2), 112.9 ($=\text{CH}_2$), 127.6, 135.6, 137.7 (Me_4C_5 , C_{ipso}); 141.9 ($=\text{CH}$). IR (KBr, cm^{-1}): 3079 (m), 3057 (w), 3000 (m), 2983 (s), 2956 (s), 2896 (vs,b), 1637 (s), 1481 (m), 1446 (m), 1427 (m), 1406 (m), 1375 (s), 1340 (m), 1244 (vs), 1180 (w), 1124 (w), 1087 (vw), 1023 (m), 994 (m), 899 (vs), 839 (vs), 810 (vs), 772 (s), 745 (w), 677 (w), 651 (w), 602 (vw), 580 (vw), 552 (w), 519 (vw), 429 (m). Anal. Calcd. for $\text{C}_{30}\text{H}_{50}\text{Cl}_2\text{Si}_2\text{Ti}$ (M 585.69): C, 61.52; H, 8.61%. Found: C, 61.42; H, 8.52%.

3.9. Preparation of $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2(\text{CH}_2)_2\text{-CH}=\text{CH}_2)_2)]$ (**5**)

Compound **2** (0.293 g, 0.5 mmol) and magnesium turnings (6.1 mg, 0.25 mmol) were evacuated, and THF (10 ml) was added by vacuum distillation. The mixture was stirred at temperature of 60 °C until all magnesium disappeared. A green solution was evaporated in vacuum, and the residue was extracted by hexane. A turquoise solution was concentrated and cooled. All attempts to get crystalline product, however, failed. The compound was characterized only by EI-MS spectra, EPR and UV-Vis spectra.

EI-MS (90 °C): m/z (relative abundance): 553 (15), 552 (27), 551 (60), 550 (56), 549 (M^+ ; 100), 548 (19), 547 (14), 534 (9), 533 (10), 497 (19), 496 (13), 495 (12), 494 ($[\text{M}-\text{C}_4\text{H}_7]^+$; 21), 400 (11), 399 (8), 381 (10), 353 (12), 351 (9), 318 (17), 316 ($[\text{M}-\text{Cp}]^+$; 15), 315 (11), 314 (9), 313 (16), 300 (11), 288 (15), 285 (8), 278 (11), 275 (9), 271 (14), 264 (10), 263 (9), 262 (19), 261 (14), 260 (18), 259 (12), 258 (9), 257 (12), 244 (8), 243 (11), 233 ($[\text{Cp}]^+$; 12), 213 (11), 189 (15), 168 (14), 133 (14), 119 (13), 113 (25), 85 (13), 73 (15), 59 ($[\text{Me}_2\text{SiH}]^+$; 42), 57 (15), 55 (11), 43 (12), 41 (11). IR (KBr, cm^{-1}): 3076 (w), 3058 (vw), 2976 (s), 2955 (s), 2913 (vs), 1639 (m), 1475 (m), 1445 (m), 1413 (m), 1379 (m), 1332 (s), 1249 (vs), 1178 (w), 1127 (w), 1087 (vw), 1050 (vw), 1023 (m), 993 (m), 899 (s), 837 (vs), 824 (vs), 773 (s), 684 (w), 646 (vw), EPR (toluene, 23 °C): $g = 1.953$, $\Delta H = 15$ G. EPR (toluene, -140 °C): $g_1 = 1.999$, $g_2 = 1.982$, $g_3 = 1.881$, $g_{\text{av}} = 1.954$. UV-Vis (hexane, 23 °C): 365 (sh) \gg 560 > 660 (sh) nm.

3.10. Preparation of compound **6**

Dichloride **2** (1.0 g, 1.71 mmol) was reduced by activated magnesium turnings (ca. 0.25 g, 10.3 mmol) in 20 ml of THF at 60 °C in a sealed ampule. After 4 h, a dirty blue solution was separated from unreacted Mg, and the THF solvent was distilled back on the magnesium. The residue was evaporated in vacuum and repeatedly extracted by hexane until the extract remained nearly colourless. A dirty turquoise solution was concentrated, and cooled to -5 °C in a refrigerator. After 2 days, a

crop of brown crystalline material was separated from a turquoise solution, washed with hexane and dried in vacuum. This was recrystallized from toluene to give a crop of paramagnetic brown crystals of **6**. Yield: 0.14 g (12%).

M.p. 151 °C (turns black at 140 °C). EI-MS (170 °C): m/z (relative abundance) 679 (M^+ ; not observed), 518 (10), 517 (19), 516 (23), 515 (19), 514 (37), 513 (56), 512 (89), 511 (91), 510 ($[\text{M}-\text{H}-\text{Mg}(\text{thf})_2]^+$; 97), 509 (38), 508 (21), 456 (12), 455 (26), 454 (59), 453 (68), 452 ($[\text{M}-\text{Me}_2\text{SiH}-\text{Mg}(\text{thf})_2]^+$; 100), 451 (22), 450 (17), 208 (12), 73 (14), 72 ($[\text{thf}]^+$; 37), 71 (31), 59 (36), 43 (21), 42 ($[\text{thf}-\text{CH}_2=\text{CHMe}]^+$; 96), 41 (50); analysis 452.2395, error -1.6×10^{-3} for $\text{C}_{28}\text{H}_{40}\text{SiTi}$. IR (KBr, cm^{-1}): 3008 (w), 2954 (s), 2914 (vs), 2856 (s), 2821 (m), 2794 (w), 1451 (m), 1418 (m), 1381 (w), 1328 (m), 1298 (w), 1245 (s), 1134 (m), 1088 (w), 1026 (s), 965 (w), 921 (vw), 878 (m), 827 (vs), 815 (s,sh), 781 (m), 750 (m), 678 (m), 631 (w), 592 (vw), 428 (s). EPR (toluene, 22 °C): $g = 1.977$; $\Delta H = 6.0$ G; (toluene, 140 °C): $g_{\perp} = 1.995$; $g_{\parallel} = 1.944$; $g_{\text{av}} = 1.978$. UV-Vis (toluene, 22 °C): absorption increasing from 650 nm, shoulder at 500 nm.

Table 3
Crystallographic data, data collection and structure refinement for **4** and **6**

Compound	4	6
Chemical formula	$\text{C}_{26}\text{C}_{38}\text{Ti}$	$\text{C}_{38}\text{H}_{63}\text{MgO}_2\text{Si}_2\text{Ti}$
Molecular weight	398.46	680.27
T (K)	293(2)	150(2)
Crystal description	Dark blue prism	Brown plate
Crystal size (mm)	$0.68 \times 0.45 \times 0.18$	$0.42 \times 0.25 \times 0.10$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2/c$ (No. 13)
a (Å)	10.2430(7)	18.8240(4)
b (Å)	10.9540(7)	12.2520(3)
c (Å)	11.5210(6)	17.6280(5)
α (°)	73.367(4)	90
β (°)	70.833(4)	106.785(1)
γ (°)	74.362(4)	90
V (Å ³)	1147.7(1)	3892.4(2)
Z	2	4
D_{calc} (g cm^{-3})	1.153	1.161
μ (Mo K α) (mm^{-1})	0.380	0.327
$F(000)$	432	1476
θ range (°)	3.04–27.47	3.25–25.07
Measured diffractions	15 958	43 095
Unique diffractions	5227	6869
Observed diffractions ^a	3745	5662
Parameters	253	437
R , wR^b observed diffractions	0.051, 0.126	0.079, 0.225
R , wR^b all data	0.080, 0.142	0.095, 0.235
$\Delta\rho$ (e Å^{-3})	0.29, -0.40	1.03, -0.47

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

^b $R(F) = \sum \|F_o\| - |F_c| / \sum |F_o|$, $wR(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$.

3.11. X-ray crystallography

A dark green prism of complex **4** and brown fragment of complex **6** were inserted into Lindemann glass capillaries in a glovebox and sealed by a wax. Diffraction data were collected on an Nonius KappaCCD diffractometer. The structures were solved by direct methods (SIR-92, [23]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [24]). Relevant crystallographic data are given in Table 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions except those in compound **6** residing at carbon atoms C(25) and C(26). These were identified on difference electron density maps and refined with isotropic thermal motion parameters.

4. Supplementary material

Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**4**: CCDC-215221, **6**: CCDC-226379). Copies of the data can be obtained free of charge upon application to CCDC (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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