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Reduction-induced double bond coordination and multiple C–H activation in fully-substituted titanocenes bearing a pendant double bond or an eight-membered hydrocarbyl *ansa*-chain

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Abstract

Reduction of isomeric, fully-substituted titanocene dichlorides having a pendant double bond, $[TiCl_2(\eta^5\text{-}C_5Me_4R)(\eta^5\text{-}C_5Me_5)]$ ($R = CH_2CH_2CH{=}CH_2$ (**1**); $R = CH(Me)CH{=}CH_2$, (**2**)), with magnesium in THF in the presence of bis(trimethylsilyl)ethyne (btmse) affords different products depending on the alkenyl chain length. Whereas the reduction of **1** yields a compound with intramolecularly η^2-coordinated double bond, $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^2{:}\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}]$ (**3**), compound **2** affords under identical conditions a product with two new Ti–C bonds, $[Ti\{(\eta^1{:}\eta^1{:}\eta^5\text{-}C_5Me_3(CH_2)(CH(Me)CH_2CH_2)\}(\eta^5\text{-}C_5Me_5)]$ (**4**). The formation of **3** can be rationalized as a simple intramolecular stabilization of a titanocene intermediate formed by reductive removal of the chloride ligands. The formation of **4** from the respective titanocene, however, requires formally an activation (oxidative addition) of one C–H bond at the methyl group adjacent to the unsaturated chain followed by a hydrogen shift (hydrometallation). Under similar conditions, the complex with asymmetric unsaturated *ansa*-bridge $[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4\}]$ (**5**) is reduced to a titanocene–η^2-alkene complex with the double bond shifted to the central position, *ansa*-$[Ti\{\eta^2{:}\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_3CH{=}CH(CH_2)_3C_5Me_4\}]$ (**7**). In the absence of btmse, analogous complex with saturated bridge *ansa*-$[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}]$ (**6**) undergoes a hydrogen abstraction to give **7** as well albeit in a lower yield. The reduction of **6** in the presence of btmse gives η^2-alkyne complex *ansa*-$[Ti\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**8**) which is converted upon thermolysis at 150 °C to a mixture of *asym*- and *sym*-isomers of the doubly tucked-in complex *ansa*-$[Ti\{(\eta^3{:}\eta^4\text{-}C_5Me_2(CH_2)_2)(CH_2)_8(\eta^5\text{-}C_5Me_4)\}]$ (**9**) in 2:1 ratio; no C–H activation involving methylene groups of the *ansa* tether was observed. The crystal structures of **4**, **7**, and **8** have been determined by X-ray crystallography.
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Keywords: Titanium; Titanocene; *ansa*-Titanocenes; Pendant double bonds; Alkene complexes; C–H activation; X-ray crystallography

1. Introduction

Electron-deficient titanocenes (14 valence electrons) resulting from a reduction of highly methylated titanocene dichlorides by magnesium or alkali metals, or from dealkylation of dialkyltitanocenes tend to rearrange by various ways in order to increase the valence electron count [1]. Rearrangements are usually initiated by hydrogen abstraction from the cyclopentadienyl ligand with the central atom affording, for instance, a singly tucked-in titanocene hydride $[TiH(\eta^5\text{-}C_5Me_5)\{\eta^1{:}\eta^5\text{-}C_5Me_4(CH_2)\}]$ from decamethyltitanocene $[Ti(\eta^5\text{-}C_5Me_5)_2]$ [2]. Upon heating, the hydride further eliminates dihydrogen to give Ti(III) complex $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^1{:}\eta^5\text{-}C_5Me_4(CH_2)\}]$ [2c,3]. The latter compound can be conveniently obtained by thermolysis of $[TiMe(\eta^5\text{-}C_5Me_5)_2]$ with liberation of methane [3,4] and also by other methods [5]. An elimination of two methane molecules from $[TiMe_2(\eta^5\text{-}C_5Me_5)_2]$ gives a doubly C–H activated compound $[Ti(\eta^5\text{-}C_5Me_5)\{\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2\}]$ [4].

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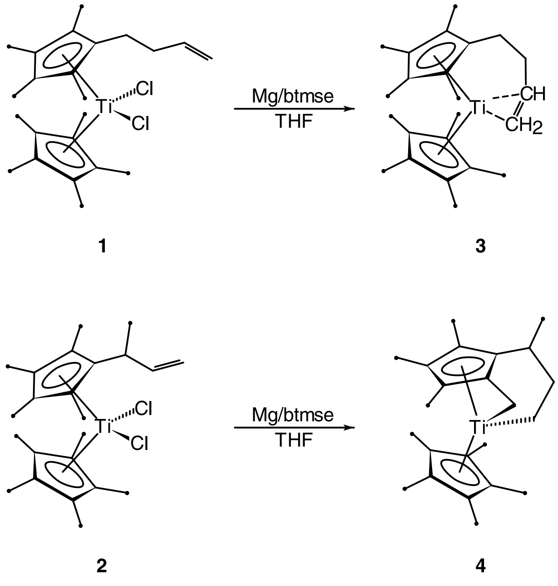
Fully substituted titanocenes can be stabilized by coordination of internal alkynes and alkenes [1]. A great attention has been paid to their complexes with bis(trimethylsilyl)ethyne (btmse), which represents a good leaving, bulky ligand capable of stabilizing highly reactive titanocenes by means of a strong back-bonding interaction. The η^2-btmse complexes thus represent an excellent source of the reactive titanocenes allowing to study interactions of the latter with various substrates [6,7]. Of the analogous η^2-alkene complexes, well-characterized are complexes of fully alkyl-substituted titanocenes with ethene [8,9]. The use of pendant four-alkenyl substituents, however, opens a wide range of applications in catalysis and synthesis. While the presence of pendant double bonds in cationic alkene polymerization catalysts [10] did not show any dramatic effect on the polymerization of ethene, propene [11] and styrene [12], the pendant double bonds were used to modify the catalyst indirectly. Among other, the pendant double bonds were utilized to anchor the catalysts onto inorganic or polymeric matrices [13] and to bind Lewis acid $B(C_6F_5)_2$ group in a proximity of the metal center via hydroboration with $HB(C_6F_5)_2$ [10b,10c]. In addition, bis(4-alkenylcyclopentadienyl) or *ansa*-bis{(4-alkenyl)indenyl}metallocene dichlorides undergo reductive cyclization affording cyclopentadienyl ring-tethered metallacyclopentanes [14] which can be conveniently converted to *ansa*-metallocene dichlorides bridged by long carbon chains [14a,15].

In this contribution, we report on the products formed during magnesium reduction from isomeric titanocene dichlorides bearing only one pendant double bond, $[TiCl_2(\eta^5\text{-}C_5Me_4R)(\eta^5\text{-}C_5Me_5)]$ ($R = CH_2CH_2CH{=}CH_2$ (**1**); $R = CH(Me)CH{=}CH_2$ (**2**)), and from *ansa*-titanocene dichlorides having eight-membered unsaturated, $[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4\}]$ (**5**) and saturated bridges, $[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}]$ (**6**). Different products of hydrogen abstraction arising from the reduction of **6** and from thermolysis of $[Ti\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**8**) are also described.

2. Results and discussion

2.1. Reactions of titanocenes containing pendant double bonds

The starting titanocene dichlorides $[TiCl_2\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}(\eta^5\text{-}C_5Me_5)]$ (**1**) and racemic $[TiCl_2\{\eta^5\text{-}C_5Me_4(C(Me)CH{=}CH_2)\}(\eta^5\text{-}C_5Me_5)]$ (**2**) were prepared in one pot by consecutive metathesis of $[TiCl_3(THF)_3]$ with $Li[C_5Me_5]$ (one equivalent) and the respective $Li[C_5Me_4R]$ (0.89 equivalent), followed by oxidation of the formed chloro-bis(cyclopentadienyl)titanium(III) intermediate with $PbCl_2$ (0.50 mol equivalent). A lower amount of lithium alkenylcyclopentadienides was used because, in our hands, the use of equimolar amounts resulted in mixtures containing all the possible isomers, $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$, $[TiCl_2(\eta^5\text{-}C_5Me_4R)(\eta^5\text{-}C_5Me_5)]$, and $[TiCl_2(\eta^5\text{-}C_5Me_4R)_2]$, whose separation by crystallization was ineffective. By using a substoichiometric amount of the alkenylcyclopentadienides, the formation of the bis(alkenylcyclopentadienyl) compounds was eliminated albeit the yields of titanium products were lower (for a review on the synthesis of mixed ligand titanocene dihalides see ref. [16]). The obtained mixtures of $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ with **1** or **2** (approximate molar ratios 21:79 and 27:73, respectively) could not be separated by fractional crystallization, however, the admixture of $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ did not hamper the reduction-induced reactions of **1** or **2**; after reducing the mixtures, products **3** and **4** were easily separated from the less soluble byproduct $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ by fractional crystallization from hexane. Thus, the reduction of **1**–$[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ mixture with magnesium in THF in the presence of btmse followed by removal of $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-btmse})]$ afforded yellow complex $[Ti(\eta^5\text{-}C_5Me_5)(\eta^2{:}\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)]$ (**3**) as the only isolated product (Scheme 1). Its structure was established from EIMS spectra showing $[M^{+\bullet}]$ at *m/z* 358 as the base peak and from ^{1}H- and ^{13}C-NMR spectra. The NMR spectra proved the presence of a double bond π-coordinated to Ti(II) center. Three proton resonances due to the $CH{=}CH_2$ group spanning the range δ_H 1.72–2.72 and, particularly, the carbon chemical shifts δ_C 102.5 ($={C}H_2$) and 128.7 ($-CH=$) are typical for π-coordinated double bonds. Similar characteristics were observed for $\eta^2\text{-}C_2H_4$ in $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}C_2H_4)]$ (δ_H 2.02, δ_C 105.1) [8] and $[Ti\{\eta^5\text{-}$



Scheme 1.

$C_5Me_4(SiMe_3)\}_2(\eta^2\text{-}C_2H_4)]$ (δ_H 2.34, δ_C 104.3) [9], for η^2-CH=CH$_2$ motif in [Ti(η^5-$C_5Me_4SiMe_2CH{=}CH_2$)(η^2:η^5-$C_5Me_4SiMe_2CH{=}CH_2$)] (δ_H 0.88, 1.37 and 3.25, δ_C 88.9 and 105.5) [17], and for an asymmetric η^2-CH=CH moiety in [Ti(II){η^5:η^2-$C_5Me_3(CH_2CH(t\text{-Bu})CH{=}CHCH(t\text{-Bu})CH_2)$}($\eta^5$-$C_5Me_5$)] δ_H (1.32 and 2.77, δ_C 119.4 and 122.5) [18]. The presence of π-coordinated double bond is also manifested by an absorption band at 970 nm in electronic absorption spectra which appears at virtually the same position for η^2-coordinated alkenes [9,17,18] and internal alkynes [9,19].

An analogous reduction and work-up in the case of the **2**–[TiCl$_2$(η^5-C_5Me_5)$_2$] mixture gave a different product which was characterized as [Ti{η^1:η^1:η^5-$C_5Me_3(CH_2)(CH(Me)CH_2CH_2)$}($\eta^5$-$C_5Me_5$)] (**4**) by X-ray diffraction analysis and NMR and MS spectroscopy (Scheme 1). The carbon resonance at δ_C 79.4 due to the tucked-in methylene carbon falls into the range observed for singly and doubly tucked-in titanocenes [2,4,19a,19c,19d] whilst that of titanium-bonded methylene group of the 1-methylprop-3-yl bridge (δ_C 69.3) is close to the upper limit for the values reported for σ-Ti–C bonds [2,4a,5,17,20]. Compound **4** is thermally stable, showing the molecular ion *m*/*z* 358 as the base peak in EIMS spectra.

2.2. The crystal structure of 4

A view of the molecular structure is shown in Fig. 1 and the selected geometric parameters are listed in Table 1. The cyclopentadienyl ring C(1–5) which is doubly tethered to the titanium atom via methylene and 1-methylprop-3-yl groups does not differ from the untouched cyclopentadienyl ring C(10–14) in the bond lengths and angles. However, the Ti–Cg(1) distance 2.014(2) Å is observably shorter than the Ti–Cg(2) distance of 2.065(2) Å [Cg(1) and Cg(2) are centroids of the C(1–5) and C(10–14) rings, respectively], and the C(1–5) ring is tilted from a position perpendicular to the Ti–Cg(1) vector so that the Ti–C(2) distance (2.129(2) Å) is the shortest and the Ti–C(4) distance the longest one (2.515(2) Å). This tilt apparently reflects a constraint imposed by the methylene–titanium bond (cf. Ti–C(6) 2.264(2) vs. Ti–C(22) 2.190(2) Å). As a consequence, the methylene C(6) atom is declined from the least-squares ring plane by as much as 0.900(3) Å. On the other hand, the bridge atom C(20) does not deviate from the ring plane and the bond lengths and angles in the 1-methylprop-1,3-diyl bridge do not depart from the values typical for sp^3 carbon atoms. The cyclopentadienyl rings are in a close-to-staggered conformation (Fig. 2) and the respective dihedral angle (ϕ) of 29.4(1)° corresponds well to that in the simple tucked-in compound [Ti(η^5:η^1-$C_5Me_4CH_2$)(η^5-C_5Me_5)] [5].

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

Bond lengths	
Ti–Cg(1) [a]	2.014(2)
Ti–C(1)	2.284(2)
Ti–C(3)	2.334(2)
Ti–C(5)	2.472(2)
Ti–C(11)	2.396(2)
Ti–C(13)	2.406(2)
Ti–C(6)	2.264(2)
C(1)–C(20)	1.519(2)
C(3)–C(4)	1.410(6)
C(20)–C(21)	1.533(3)
C_{ring}–C_{ring}	1.410(2)–1.450(2)
C_{ring}–C_{Me}	1.499(2)–1.511(2)
Ti–Cg(2) [a]	2.065(2)
Ti–C(2)	2.129(2)
Ti–C(4)	2.515(2)
Ti–C(10)	2.391(2)
Ti–C(12)	2.413(2)
Ti–C(14)	2.355(2)
Ti–C(22)	2.190(2)
C(2)–C(6)	1.440(2)
C(4)–C(5)	1.400(6)
C(21)–C(22)	1.526(3)
C(20)–C(23)	1.531(3)
Bond angles	
Cg(1)–Ti–Cg(2)	144.6(1)
C(2)–Ti–C(6)	38.11(7)
C(21)–C(22)–Ti	115.0(1)
C(1)–C(20)–C(21)	109.0(2)
C(6)–Ti–C(22)	92.67(8)
C(2)–C(6)–Ti	65.87(9)
C(20)–C(21)–C(22)	109.5(2)
ϕ [b]	29.4(1)

[a] Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(10–14) cyclopentadienyl rings, respectively.

[b] Dihedral angle subtended by the cyclopentadienyl least-squares planes.

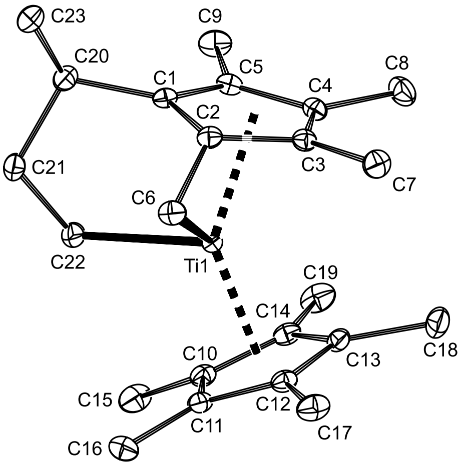


Fig. 1. The molecular structure of **4** (30% probability thermal motion ellipsoids) showing the atom labeling scheme. Hydrogen atoms were omitted for clarity.

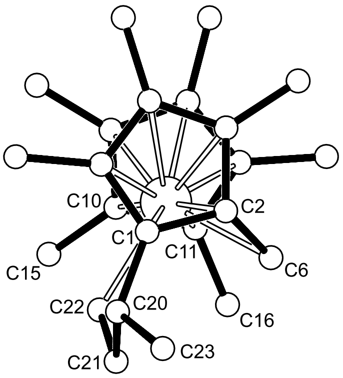
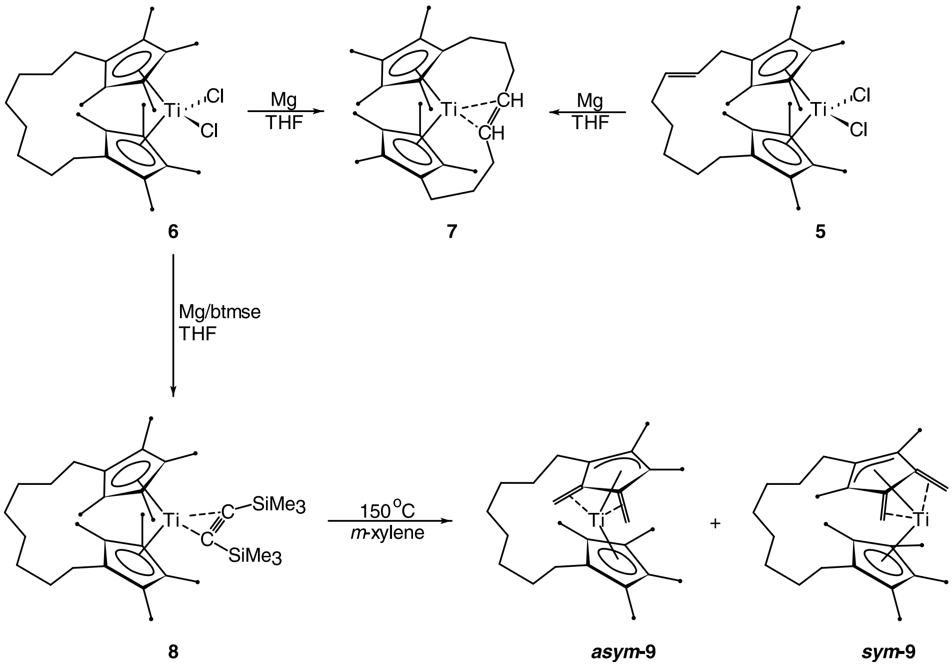


Fig. 2. A view of the molecular structure of **4** in the Cg(1)–Cg(2) direction.

2.3. Reactions of *ansa*-bridged titanocenes

Reduction of a mixture of *ansa*-bridged titanocene dichlorides *ansa*-[$TiCl_2\{\eta^5:\eta^5\text{-}C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4\}$] (**5**) and *ansa*-[$TiCl_2\{\eta^5:\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}$] (**6**) (**5**:**6** molar ratio ca. = 2:5) [14a] with magnesium in THF at 60 °C affords the *ansa*-titanocene complex with an η^2-coordinated double bond located in the center of the eight-membered bridge, *ansa*-[$Ti\{\eta^5:\eta^5\text{-}C_5Me_4(CH_2)_3CH{=}CH(CH_2)_3C_5Me_4\}$] (**7**), in 71% isolated yield (Scheme 2). A similar reduction reaction performed with enriched **6** (**6**:**5** ratio 95:5) yielded **7** in 54% yield whereas the reduction of enriched **5** (**5**:**6** ratio ca. 95:5) [15] gave the same product in 88% yield. Yellow crystalline complex **7** was analyzed by EIMS spectroscopy and its structure was further corroborated by single-crystal X-ray diffraction analysis. The presence of the π-coordinated double bond is manifested by the presence of the electronic absorption band at 1000 nm, which is typical for titanocenes coordinating internal alkynes and alkenes in the η^2-fashion [9,17–19]. The position of the absorption band in both titanocene–alkene and titanocene–alkyne complexes falls into the region 920–1050 nm (cf. compounds **7**: λ_{max} 940 nm, and **8**: λ_{max} 910 nm, see below) and fits to the concept of back-bonding interaction outlined by Lauher and Hoffmann [21]. The formation of **7** requires a reductive removal of both chloride ligands from **5** and **6** with magnesium, which was used in excess, followed by a double bond isomerization in the intermediate resulting from **5**, or an abstraction of two hydrogen atoms in an intermediate arising from **6**. Since no gas was evolved during the reduction reaction, the hydrogen abstraction by titanium(II) and their transfer to either THF or, more likely, to magnesium under formation of chloromagnesium hydrides should be considered. An evolution of hydrogen was observed when degassed water was added to the mother liquor remaining after crystallization of **7**, however, this cannot be considered an unequivocal evidence for magnesium hydride species to be involved in the hydrogen transfer because the decomposition of water with Ti(II) compounds is also well known [1]. In all cases, titanocene(Ti^{III}) hydride–magnesium hydride complexes of the Ti–Mg–Ti or Ti–Mg–Mg–Ti types which are easily recognized by ESR spectroscopy were not detected [22].

Another mode of stabilization of the plausible *ansa*-titanocene intermediate was encountered during the thermolysis of *ansa*-[$Ti\{\eta^5:\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}$-



Scheme 2.

(η^2-$Me_3SiC{\equiv}CSiMe_3$)] (**8**). The parent diamagnetic complex **8** was obtained quantitatively by reduction of **6** with excess magnesium in THF in the presence of btmse [6,19], and identified by ^{1}H- and ^{13}C-NMR, EIMS, IR and UV–near IR spectra as well as by single crystal X-ray diffraction analysis. The presence of the triple bond η^2-coordinated to Ti(II) is indicated by its ^{13}C-NMR signal occurring at δ_C 248.3 which is close to the values found for [Ti(η^5-C_5HMe_4)$_2$(η^2-btmse)] (δ_C 248.4) and [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] (δ_C 248.5) [19a]. Likewise, the IR absorption bands due to the coordinated triple bond in **8** at 1594 and 1558 cm^{-1} are found very close to the absorption bands of [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] (1595 and 1562 cm^{-1}) and the electronic absorption band at 910 nm is virtually identical with that of the latter complex (916 nm) [19a]. EIMS spectra of **8** do not show the molecular ion as the complex very likely dissociates into btmse and *ansa*-titanocene which subsequently looses hydrogen(s) even more easily than the corresponding titanocenes generated from the above mentioned methyl-substituted titanocene–btmse complexes [19a]. The crystal structure of **8** did not reveal any extraordinary structural features when compared with so far structurally characterized titanocene–btmse complexes (see below).

Thermolysis of **8** at 150 °C for 10 h in *m*-xylene in a sealed ampoule afforded a sky blue solid which was analyzed by ^{1}H- and ^{13}C-NMR spectra as a mixture of two isomeric doubly tucked-in compounds, *sym*- and *asym*-*ansa*-[Ti{(η^3:η^4-$C_5Me_2(CH_2)_2$)(CH_2)$_8$(η^5-C_5Me_4)}] (**9**) (Scheme 2). The third possible isomer in which the pivotal atom of the *ansa*-linking chain are a part of the η^4-diene system was not detected. All NMR resonances due to methyl groups of η^5-cyclopentadienyl and allyldiene ligands and their adjacent *ipso*-carbon atoms as well as the signals of the *exo*-methylene groups of both isomers present in the mixture are observed in ca. 1:1 ratio. This indicates that a mixture of *sym*-**9** and *asym*-**9** in ca. 1:2 molar ratio is obtained since a higher symmetry of the *sym* isomer renders only one half of the molecule symetrically independent. The products ratio thus corresponds to a ratio statistically predicted considering all the cyclopentadienyl methyl groups equivalent. The molecules of the both isomers are thermally very robust, ionizing upon electron impact without apparent fragmentation. The presence of the *exo*-methylene groups is further indicated by an IR absorption band at 3032 cm^{-1} and electronic absorption band at 585 nm which are both found in regions typical for doubly tucked-in titanocene complexes obtained from, e.g. [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] [4,19a], [Ti(η^5-C_5Me_4R)$_2$(η^2-btmse)] (R = benzyl, Ph, and 4-fluorophenyl) [19c], and [Ti{(η^5-$C_5Me_4SiMe_2$)$_2$O}(η^2-btmse)] [19d].

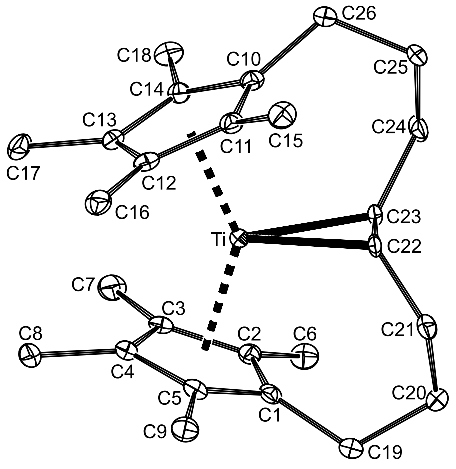


Fig. 3. The molecular structure of **7** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. Hydrogen atoms were omitted for clarity.

2.4. The crystal structure of 7

Compound **7** (Fig. 3 and Table 2) crystallizes in the monoclinic space group $P2_1/n$. The double bond between the central carbon atoms of the bridging chain is η^2-coordinated to the titanium center at the open side of the bent titanocene framework. The plane defined by the double bond carbon atoms C(22) and C(23), and titanium atom is approximately perpendicular to the plane formed by centroids of the cyclopentadienyl rings Cg(1) and Cg(2), and Ti, and very nearly bisects the Cg(1)–Ti–Cg(2) angle (Fig. 4). The cyclopentadienyl

Table 2
Selected bond lengths (Å) and bond angles (°) for **7** [a]

Bond lengths	
Ti–Cg(1)	2.101(2)
Ti–Cg(2)	2.099(2)
C(22)–C(23)	1.429(6)
Ti–C(22)	2.184(4)
C(1)–C(19)	1.510(6)
C(21)–C(22)	1.542(6)
C(CH_2)–C(CH_2)	1.505(6)–1.532(6)
Ti–C(Cp)	2.380(4)–2.447(4)
C(Cp)–C(Cp)	1.413(6)–1.438(6)
C(Cp)–Me	1.489(6)–1.518(6)
Ti–C(23)	2.192(4)
C(10)–C(26)	1.501(5)
C(23)–C(24)	1.534(5)
Bond angles	
Cg(1)–Ti–Cg(2)	140.4(1)
Ti–C(23)–C(22)	70.7(2)
C(21)–C(22)–C(23)	123.2(3)
ϕ [b]	40.2(2)
C(22)–Ti–C(23)	38.1(2)
Ti–C(22)–C(23)	71.2(2)
C(22)–C(23)–C(24)	123.1(3)

[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.

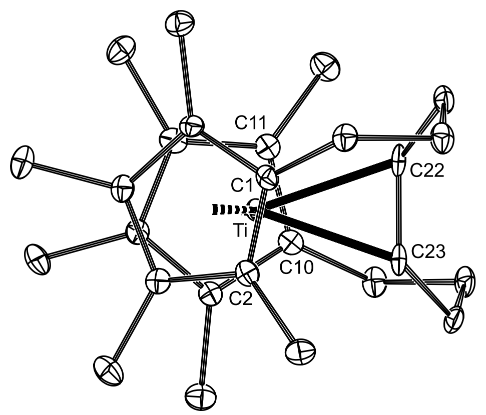


Fig. 4. A view of the molecular structure of **7** along the Cg(1)–Cg(2) line.

rings are in a close-to-staggered conformation with the dihedral angle (ϕ) subtended by their least-squares planes being 40.2(2)°. This value is close to the. values found in ethene complexes [Ti(η^5-C_5Me_5)$_2$(η^2-C_2H_4)] (ϕ 40.6(4)°) [8] and [Ti{η^5-$C_5Me_4(SiMe_3)$}$_2$(η^2-C_2H_4)] (ϕ 39.7(1)°) [9], and in another permethylated titanocene [Ti(η^5-C_5Me_5)(η^2:η^5-$C_{22}H_{35}$)] bearing an intramolecularly coordinated double bond within a cyclooctene annelated to one of the C_5Me_5 ligands [18a]. A smaller ϕ angle of 35.5(2)° was observed in the silyl modified analogue of **7**, *ansa*-[Ti(II){η^2:η^5:η^5-$C_5Me_4SiMe_2CH_2$-CH=CHCH$_2$SiMe$_2$C$_5$Me$_4$}] (**10**) [17], most likely due to a more rigid *ansa*-chain containing two SiMe$_2$ groups instead of four methylene groups in **7**. The length of the coordinated double bond 1.429(6) Å in **7** is slightly longer compared with that of **10** (1.411(6) Å) and, correspondingly, the Ti–C bond distances Ti–C(22) (2.184(4) Å) and Ti–C(23) (2.192(4) Å) are shorter compared with those of **10** (2.242(4) and 2.238(4) Å) [17]. These values indicate that the double bond in **7** is coordinated more strongly than that in **10**, apparently due to a better adjustment of the double bond at the bonding distance to the titanium center in the more flexible C_8 chain compared with the SiC$_4$Si bridge.

2.5. The crystal structure of 8

The molecule of **8** possesses no crystallographic symmetry (Fig. 5 and Table 3). The arrangement of the *ansa*-titanocene moiety is very similar to that in **6** [14a], adopting a near-to-staggered conformation of the cyclopentadienyl rings and having the octan-1,8-diyl chain attached to ring carbon atoms at the hinge positions. However, a remarkable difference is observed in the angle subtended by the least-squares planes of the cyclopentadienyl rings (ϕ). This angle is surprisingly smaller than in **6** (40.4(2) vs. 43.9(1)°) and, consequently, the methyl carbon atoms C(6) and C(13) are declined from the least-squares planes of the cyclopentadienyl rings by 0.294(4) and 0.170(4) Å, respectively. Some steric hindrance between the btmse ligand and methyl groups of the cyclopentadienyl ligands is indicated by declinations of the methyl carbon atoms from the least-squares planes of the cyclopentadienyl rings (cf. perpendicular distance from the least-squares planes: C(20), 0.246(3); C(21), 0.213(3); and C(25), 0.175(4) Å, the methyl group close to the hinge position C(23) being declined by as much as 0.362(3) Å due to its steric interactions with the C(6) carbon atom of the bridging chain. The planar geometry of the btmse ligand [C(27)–

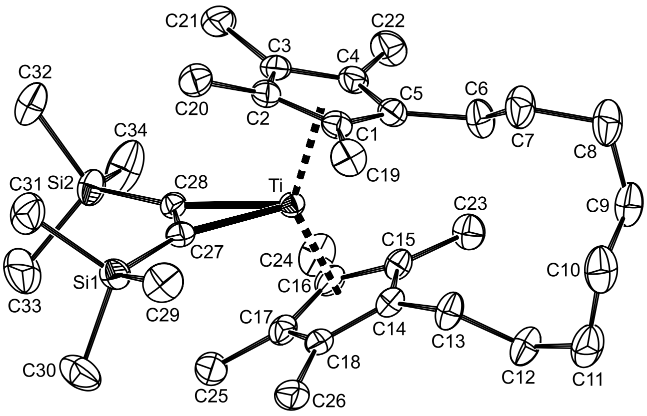


Fig. 5. The molecular structure of **8** (30% probability ellipsoids) with the atom numbering scheme. Hydrogen atoms were omitted for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) for **8** [a]

Bond lengths	
Ti–Cg(1)	2.129(1)
Ti–C(27)	2.120(3)
Ti–C(Cp)	2.400(3)–2.516(3)
C(Cp)–C(Me)	1.495(4)–1.510(4)
Si(1)–C(27)	1.873(3)
Si(1)–C(Me)	1.868(4)–1.873(4)
C(5)–C(6)	1.522(4)
C(CH$_2$)–C(CH$_2$)	1.501(5)–1.541(5)
Ti–Cg(2)	2.126(1)
Ti–C(28)	2.119(2)
C(Cp)–C(Cp)	1.400(4)–1.428(4)
C(27)–C(28)	1.298(4)
Si(2)–C(28)	1.872(3)
Si(2)–C(Me)	1.861(4)–1.885(4)
C(13)–C(14)	1.519(4)
Bond angles	
Cg(1)–Ti–Cg(2)	138.9(1)
C(28)–C(27)–Ti	72.1(2)
Si(1)–C(27)–C(28)	137.0(2)
ϕ [b]	40.4(2)
C(27)–Ti–C(28)	35.7(1)
C(27)–C(28)–Ti	72.2(2)
Si(2)–C(28)–C(27)	135.6(2)

[a] Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(14–18) cyclopentadienyl rings, respectively.

[b] Dihedral angle subtended by the cyclopentadienyl least-squares planes.

C(28) 1.298(4) Å, C–C–Si angles 137.0(2) and 135.6(2)°] does not virtually differ from the geometry observed in all other structurally characterized titanocene–btmse complexes: [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] [23], [Ti(η^5-C_5HMe_4)$_2$(η^2-btmse)] [19a], *ansa*-[Ti{η^5:η^5-(C_5Me_4)$_2$SiMe$_2$}(η^2-btmse) [24], [Ti{η^5-C_5Me_4(4-C_6H_4F)}$_2$(η^2-btmse)] [19c], [Ti(η^5-$C_5Me_4SiMe_3$)$_2$(η^2-btmse)] [9], and *ansa*-[Ti{(η^5-$C_5Me_4SiMe_2$)$_2$O}(η^2-btmse)] [19d].

2.6. Conclusions

Compound **3** is apparently formed by reductive removal of both chloride ligands followed by a subsequent intramolecular coordination of the pendant double bond. The back-bonding interaction of the double bond π-orbital and metal d^2 system makes compound **3** thermally robust (m.p. 111 °C) and reluctant to fragmentate upon ionization in EIMS. This is in accordance with the behaviour of an analogous bis{(but-3-enyl)tetramethylcyclopentadienyl)}titanium(II) intermediate where the alkenyl chain is long enough to allow the double bond to approach a low valent metal center in the first step of a formal [2+2+2] oxidative cycloaddition involving π-electrons of both double bonds and d^2 electrons of titanium(II) which results in the formation of symmetrical cyclopentadienyl ring-tethered titanacyclopentane compound [14a]. At variance, bis(1-methylallyl) titanocene intermediate with shorter alkenyl groups gave an asymmetrical ring-tethered titanacyclopentane [14a]. In the present case, it appears likely that during the unexpected formation of **4** the transiently formed titanocene cannot stabilize by forming a stable η^2-alkene complex from the same reason. A transient formation of an unstable intermediate with π-coordinated double bond should be, however, anticipated as it would assist hydrogen abstraction from the methyl group adjacent to the alkenyl substituent by bringing it into a proximity of the electron-poor metal center. Formally, the formation of **4** involves oxidative addition of one methyl C–H bond across the Ti(II) center and an insertion of the double bond into the Ti–H bond in the only sterically allowed way. The presence of bmtse during the reduction does not interfere with the formation of **3** and **4** because in a competition between btmse ligand and cyclopentadienyl ring-tethered double bond for the Ti(II) center, the intramolecular process is strongly preferred [14a,17]. Either of these π-donors, however, prevents the formation of paramagnetic multinuclear titanocene hydride–magnesium hydride complexes [22].

In view of the above results a smooth double bond isomerization occurring in the unsaturated eight-membered carbon chain of **5** during the reduction to a titanocene is well understandable. A feasible π-coordination of the symmetrically placed double bond in **7** is apparent from its molecular structure (Fig. 3) and the ability of low-valent titanium complexes to isomerize double bonds into their thermodynamically most convenient positions has been demonstrated many times [25]. Much more interesting, however, is the formation of **7** from bridge-saturated complex **6**. In this case, the reduction has to be carried in the absence of btmse because the otherwise resulting η^2-btmse complex **8** is resistant towards magnesium similarly to all titanocene–btmse complexes with highly methyl-substituted cyclopentadienyl ligands [19]. The yield of **7** from **6** is lower compared with that from **5** in accordance with a higher complexity of the transformation of **6** into **7** which requires an intermolecular hydrogen transfer from sp^3 carbon atoms. Such reactions catalyzed by low-valent titanium complexes were so far observed only for unsaturated hydrocarbons and at much higher temperatures [26]. The abstraction of hydrogen from the saturated methylene chain under mild conditions (Mg, 60 °C) is apparently facilitated by frequent encounters of titanium(II) with the flexible octane-1,8-diyl chain. An assistance of magnesium in this process can be considered because compound **7** was not formed when a titanocene intermediate was formed during the thermolysis of **8**. The thermally induced dissociation of btmse ligand from **8** as well as from [Ti(η^5-C_5Me_4R)$_2$(η^2-btmse)] (R = Me, H, [19a], Ph, and 4-fluorophenyl [19c]), and *ansa*-tetramethyldisiloxane [Ti{(η^5-C_5Me_4-$SiMe_2$)$_2$O}(η^2-btmse)] [19d] complexes is accompanied by hydrogen abstraction from two vicinal methyl groups on one of the two fully substituted cyclopentadienyl ligands to the leaving btmse. The *asym* isomer with the vicinal methylene groups neighboring the group R or the *ansa*-bridge is usually prevailing over the *sym* isomer with the vicinal methylene groups at positions distant from the substituent R or the *ansa*-bridge. Exceptional behavior was observed only for [Ti{η^5-C_5Me_4-(CH_2Ph)}$_2$(η^2-btmse)] complex where the isomer containing vicinal benzylidene and methylene groups dominated over the *asym* isomer with the benzyl group untouched [19c]. Here, we have shown that the eight-membered *ansa*-bridging chain does neither take part in the hydrogen abstraction reaction nor even influences the product distribution; the distribution of C–H activated allyldiene complexes is statistical, reflecting the number of the methyl groups on the cyclopentadienyl rings.

3. Experimental

3.1. General comments

Syntheses of titanocene dichlorides **1** and **2** were carried out under argon atmosphere and the products were worked up and handled in air. The reductions and all subsequent manipulations with solutions of the products were performed on a vacuum line in all-sealed-glass devices equipped with magnetically breakable seals. A combined device equipped with a pair of quartz cuvettes (10.0 and 1.0 mm, Hellma) and a quartz tube was used for UV–near IR and EPR measurements. Crystals for EIMS measurements and melting point determinations were placed into glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water lower than 2.0 ppm).

NMR spectra were recorded on a Varian UNITY INOVA 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58 MHz) at 298 K. Chemical shifts (δ ppm) are given relative to residual protio signal of the solvent (δ_H 7.15 in benzene-d_6) or to the solvent resonance (C_6D_6: δ_C 128.0). The assignment of NMR resonances is based on 2D COSY, DQF COSY, HMQC and HMBC experiments. NMR samples of Ti(II) compounds were prepared in evacuated all-glass devices from which the NMR tubes were sealed off by flame. UV–near IR measurements were performed on a Varian Cary 17 D spectrometer in the range 340–2000 nm. EIMS spectra were obtained on a VG-7070E double-focusing mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 6% and by important peaks of lower intensity. IR spectra were recorded in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range of 400–4000 cm^{-1}. Samples in KBr pellets were prepared in a glovebox Labmaster 130 (mBraun).

As low-valent titanium complexes are extremely sensitive to air and moisture, classical elemental analyses were not carried out. The EIMS samples of **3**, **4**, **7** and **9** were completely evaporated without changing the fragmentation pattern; this proves the uniformity of the compounds.

3.2. Chemicals

Solvents THF, hexane, and toluene were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$ [27]. Magnesium turnings (Aldrich, purum for Grignard reactions) were first used in large excess for the preparation of $[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ [19a]. Then, the unreacted activated magnesium was separated from the reaction mixture, washed thoroughly with THF and stored in ampoules equipped with breakable seals. Btmse (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and finally distributed into ampoules by distillation on a vacuum line. Mixtures of isomers of 5-(3-butenyl)-1,2,3,4-tetramethylcyclopentadienes and 5-(1-methyl-2-propenyl)-1,2,3,4-tetramethylcyclopentadienes were prepared as recently described [14a]. A mixture of compounds *ansa*-$[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4CH_2CH{=}CH(CH_2)_5C_5Me_4\}]$ (**5**) and *ansa*-$[TiCl_2\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}]$ (**6**) in molar ratio 2:5 as determined from NMR measurements was obtained from the reaction of ring-tethered titanacyclopentane $[Ti(IV)(\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_2CH(\mathit{Ti})\text{-}(CH_2)_2CH(\mathit{Ti})(CH_2)_2C_5Me_4]$ with HCl in hexane [14a]. Compounds **5** and **6** were separated from the above obtained mixture by fractional crystallization from toluene solution to give highly enriched compounds ($\geq$95 mol.% in both cases) [15].

3.3. Preparation of titanocene dichlorides *$[TiCl_2(\eta^5\text{-}C_5Me_5)\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CH_2)\}]$ (**1**) and $[TiCl_2(\eta^5\text{-}C_5Me_5)\{\eta^5\text{-}C_5Me_4CH(Me)CH{=}CH_2\}]$ (**2**)*

A slurry of $[TiCl_3(THF)_3]$ was prepared 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 reflux. In another flask, lithium cyclopentadienide $Li[C_5Me_5]$ was obtained by adding LiBu (14.5 ml of 2.5 M in hexanes, 36.25 mmol) to a solution of C_5Me_5H (4.90 g, 36.0 mmol) in THF (300 ml). After stirring for 8 h, a white suspension of the cyclopentadienide was mixed with the slurry of $[TiCl_3(THF)_3]$ and the mixture was refluxed for 1 h.

Meanwhile, lithium cyclopentadienide $[Li\{C_5Me_4\text{-}(CH_2CH_2CH{=}CH_2)\}]$ was prepared by adding LiBu (12.8 ml of 2.5 M in hexanes, 32.0 mmol) to the solution of a mixture of isomeric 5-(3-butenyl)-1,2,3,4-tetramethylcyclopentadienes (5.63 g, 32.0 mmol) in Et_2O (200 ml) followed by stirring for 8 h. The resulting white slurry was mixed with the above reaction mixture containing presumably $[TiCl_2(C_5Me_5)(THF)_n]$ [28]. Diethyl ether was distilled off, and the residual mixture was refluxed for 24 h. Then, the volume of the mixture reduced to ca. 100 ml, and dry, powdery $PbCl_2$ (5.0 g, 18.0 mmol) was added under argon [29]. A green reaction mixture turned to red after stirring for 2 h at 40 °C. The reaction mixture was opened to air, all volatiles were evaporated under vacuum, and the residue was extracted by hexane. Crystalline product was obtained by crystallization from a concentrated hexane solution. Yield of brown–red crystalline product was 4.8 g. According to ^{1}H- and ^{13}C-NMR spectra the product contained **1** and $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ in 79:21 molar ratio.

Analytical data for **1**: NMR (C_6D_6): δ_H 1.84 (s, 6H, Me_4C_5), 1.85 (s, 15H, Me_5C_5), 1.90 (s, 6H, Me_4C_5), 1.93–2.01 (m, 2H, $Me_4C_5CH_2C\mathit{H}_2$), 2.62–2.67 (m, 2H, $Me_4C_5C\mathit{H}_2$), 4.92 (ddt, $^3J_{HH} = 10.2$, $^2J_{HH} = 1.9$, $^4J_{HH} = 1.2$ Hz, 1H, $=C\mathit{H}_2$), 4.98 (ddt, $^3J_{HH} = 17.0$, $^2J_{HH} \approx {}^4J_{HH} \approx 1.7$ Hz, 1H, $=C\mathit{H}_2$), 5.70 (ddt, $^3J_{HH} = 17.0$, 10.1, $^3J_{HH} = 6.7$ Hz, 1 H, $=C\mathit{H}$); δ_C 12.9 (Me_4C_5), 13.0 (Me_5C_5), 13.1 (Me_4C_5), 27.8 ($Me_4C_5\mathit{C}H_2$), 34.0 ($Me_4C_5CH_2\mathit{C}H_2$), 115.0 ($=\mathit{C}H_2$), 127.1, 131.4 (Me_4C_5 and Me_5C_5, C_{ipso}; other resonances not found due to possible overlap with solvent signal), 138.3 (=*C*H). EIMS (170 °C, the spectrum was recorded after the more volatile complex [$TiCl_2(\eta^5$-$C_5Me_5)_2$] was evaporated, peaks at *m/z* 318 and 155 disappeared): *m/z* (relative abundance: 428 [$M^{\bullet +}$; 0.5], 393 ([M−Cl]$^+$; 9), 295 (7), 293 ([M−Cp*]$^+$; 14), 258 ([Cp′TiCl]$^+$; 12), 253 ([M−Cp′]$^+$; 9), 218 ([Cp*TiCl]$^+$; 28), 217 (23), 175 ([Cp′]$^+$; 25), 135 ([Cp*]$^+$; 100), 134 (32), 133 (18), 120 (16), 119 (56), 107 (12), 105 (32), 91 (30) [Cp*=C_5Me_5, Cp′=$C_5Me_4(CH_2CH_2CH{=}CH_2)$].

Complex **2** was prepared by exactly the same protocol using a mixture of 5-(1-methyl-2-propenyl)-1,2,3,4-tetramethylcyclopentadienes (5.63 g, 32.0 mmol). The yield of a brown–red crystalline product, which was shown by NMR spectroscopy to be a mixture of **2** and [$TiCl_2(C_5Me_5)_2$] in 73: 27 molar ratio, was 4.3 g.

Analytical data for **2**: NMR (C_6D_6): δ_C 1.21 (d, $^3J_{HH}=7.2$ Hz, 3H, CH*Me*), 1.69, 1.74 (2 × s, 3H, C_5Me_4); 1.87 (s, 15H, C_5Me_5), 2.04, 2.06 (2 × s, 3H, C_5Me_4); 3.86 (qddd, $^3J_{HH}$=7.2, 5.0, $^3J_{HH}$=1.9, 1.9 Hz, 1H, C*H*Me), 4.92 (ddd, $^3J_{HH}$=10.5, $^3J_{HH}\approx{}^2J_{HH}\approx 1.9$ Hz, 1H, =CH_2), 4.98 (ddd, $^3J_{HH}$=17.4, $^3J_{HH}\approx{}^2J_{HH}\approx$ 1.9 Hz, 1H, =CH_2), 6.09 (ddd, $^3J_{HH}$=17.4, 10.5, 5.0 Hz, 1H, =C*H*); δ_C 12.3, 12.8 (C_5Me_4); 13.1 (C_5Me_5), 13.6, 13.7 (C_5Me_4); 17.8 (CH*Me*), 36.8 (*C*HMe), 112.6 (=CH_2), 125.1, 126.9 (C_5Me_4, C_{ipso}); 128.4 (C_5Me_5), 129.1, 130.0, 135.4 (C_5Me_4, C_{ipso}); 142.5 (=*C*H). EIMS (170 °C, the spectrum was recorded as given above): *m/z* (relative abundance): 428 [$M^{\bullet +}$; 1], 393 ([M−Cl]$^+$; 11), 297 (13), 296 (13), 295 (55), 294 (21), 293 ([M−Cp*]$^+$; 78), 292 (9), 291 (7), 258 (9), 255 (12), 253 ([M−Cp′]$^+$; 16), 218 (8), 217 (8), 176 (11), 175 ([Cp′]$^+$; 74), 160 (9), 145 (15), 136 (12), 135 ([Cp*]$^+$; 100), 133 (16), 120 (9), 119 (29), 107 (8), 105 (22), 91 (12), 55 (11) [Cp*=C_5Me_5, Cp′=$C_5Me_4(CH(Me)CH{=}CH_2)$].

3.4. Preparation of [$Ti(\eta^5$-$C_5Me_5)\{\eta^2{:}\eta^5$-$C_5Me_4(CH_2CH_2CH{=}CH_2)\}$] (3)

Crude compound **1** (containing 31 mol.% of [$TiCl_2(\eta^5$-$C_5Me_5)_2$]; 1.50 g, ca. 2.6 mmol of **1**) was dissolved in THF (30 ml), btmse (0.9 ml, 4.0 mmol) was added and the solution was poured onto activated magnesium turnings (ca. 0.3 g, 12.5 mmol). The mixture was kept at 60 °C until the color of the solution turned greenish yellow (2 h). Then the remaining magnesium was separated, the solution was evaporated under vacuum and the residue was extracted repeatedly with hexane. The extract was concentrated to crystallization and then cooled in a refrigerator overnight whereupon yellow prisms of **5** separated (identified by IR and EIMS spectra, cf. [19a]). A further concentration of the mother liquor followed by cooling gave another crop of crystalline material, which still contained **5** as indicated by IR bands at 840 and 1240 cm^{-1}. Therefore, the solid was discarded and a repeated concentration of the mother liquor (to ca. 2.5 ml) followed by cooling in a freezer (−18 °C) gave a crop of crude **3** as somewhat waxy, yellow crystalline material. Finally, this solid was twice recrystallized by dissolution in hot hexane (60 °C) and cooling to −5 °C to give **3** as a yellow crystalline solid. Yield: 0.27 g (29%). The yield is not optimized as no attempt was made to recover more **3** from the mother liquors. M.p. 111 °C. EIMS (120 °C): *m/z* (relative abundance): 360 (12), 359 (32), 358 [$M^{+\bullet}$; 100], 357 (17), 356 (15), 355 (11), 354 (9), 353 (20), 218 (7), 181 (11), 180 (8), 179 (8), 178 (12), 177 (8). NMR (C_6D_6): δ_H 0.69, 0.96, 1.35 (3 × s, 3 H, C_5Me_4); ca. 1.55 (m, 1H, $C_5Me_4CH_2CH_2$), 1.63 (s, 15H, C_5Me_5), 1.72 (dd, 1H, $J_{HH}=5.2$, 11.3 Hz, =CH_2), 2.43 (dd, 1 H, $J_{HH}=4.6$, 9.8 Hz, =CH_2), 2.62 (s, 3H, C_5Me_4), 2.72 (t, 1H, $J_{HH}=9.9$ Hz, C*H*=), 3.05 (dd, 1H, $J_{HH}=7.5$, 12.9 Hz, $C_5Me_4CH_2CH_2$), 3.51 (dd, 1H, $J_{HH}=8.3$, 13.7 Hz, $C_5Me_4CH_2$), 4.34 (ddd, 1H, $J_{HH,1}\sim J_{HH,2}\sim 12.9$, $J_{HH,3}=7.6$ Hz, $C_5Me_4CH_2$); δ_C 9.6, 9.7, 11.0 (C_5Me_4); 11.6 (C_5Me_5), 15.1 (C_5Me_4), 25.2 ($C_5Me_4CH_2$), 44.5 ($C_5Me_4CH_2CH_2$), 102.5 (=CH_2), 115.1, 117.0, 118.1 (C_5Me_4); 119.7 (C_5Me_5), 121.9 (C_5Me_4), 128.7 (*C*H=), 141.5 (C_5Me_4). IR (KBr, cm^{-1}): 2955 (s), 2908 (vs), 2857 (s), 2811 (m), 1489 (m), 1442 (s, b), 1378 (vs), 1307 (w), 1094 (w), 1063 (w), 1022 (m), 792 (m), 747 (m), 722 (m), 630 (w), 613 (w), 586 (m), 436 (m). UV–NIR (hexane, 23 °C): 970 nm.

3.5. Preparation of [$Ti\{\eta^1{:}\eta^1{:}\eta^5$-$C_5Me_3(CH_2)(CH(Me)CH_2CH_2)\}(\eta^5$-$C_5Me_5)$] (4)

The reduction and work-up was carried out as described for **3** using **2**–[$TiCl_2(\eta^5$-$C_5Me_5)_2$] mixture (molar ratio 73:27, 1.50 g, ca. 2.6 mmol of **2**) to give green crystalline **4** (0.21 g, ca. 23%; not-optimized). M.p. 135 °C. EIMS (120 °C): *m/z* relative abundance 360 (12), 359 33), 358 [$M^{+\bullet}$; 100], 357 (16), 356 (22), 355 (23), 354 (56), 353 (17), 352 (15), 341 (11), 340 (8), 339 (11), 182 (8), 181 (8), 180 (9), 179 (6), 178 (13), 177 (13), 176 (9). NMR (C_6D_6): δ_H −2.50 (ddd, $^2J_{HH}=11.8$, $^3J_{HH}=13.4$, 7.0 Hz, 1 H, TiCH_2), 1.07 (s, 3 H, C_5Me_3), 1.30 (d, $^2J_{HH}=4.2$ Hz, 1 H, C_5Me_3–CH_2), 1.33 (dddd, $^2J_{HH}=13.2$, $^3J_{HH}=13.4$, 11.2, 4.2 Hz, 1H, TiCH$_2$CH_2), 1.44 (ddd, $^2J_{HH}=11.8$, $^3J_{HH}=4.2$, 1.9 Hz, 1H, TiCH_2), 1.45, 1.65 (2 × s, 3H, C_5Me_3), 1.65 (d, $^3J_{HH}=7.1$ Hz, 3H, CH*Me*), 1.72 (s, 15H, C_5Me_5), 1.94 (d, $^2J_{HH}=4.2$ Hz, 1H, C_5Me_3–CH_2), 2.50 (dddd, $^2J_{HH}=13.2$, $^3J_{HH}=$ 7.1, 7.0, 1.9 Hz, 1 H, TiCH$_2$CH_2), 3.27 (ddq, $^3J_{HH}=$ 11.2, 7.1, 7.1 Hz, 1H, C*H*Me); δ_C 10.0, 10.7, 11.3 (C_5Me_3); 11.6 (C_5Me_5), 21.3 (CH*Me*), 36.2 (*C*HMe), 47.1 (TiCH$_2$*C*H$_2$), 69.3 (Ti*C*H$_2$), 79.4 (C_5Me_3–CH_2), 118.1 (C_5Me_5), 120.5, 121.5, 122.3, 129.7, 148.1 (C_5Me_3). IR (KBr, cm^{-1}): 3058 (w), 2973 (m), 2961 (s), 2949 (s), 2922 (vs), 2902 (vs), 2862 (s), 2815 (vs), 1487 (m), 1460 (vs), 1429 (s), 1377 (vs), 1362 (s), 1209 (w), 1161 (vw), 1073 (w), 1023 (s), 960 (w), 825 (s), 771 (w), 671 (m), 612 (w), 464 (m), 431 (w), 410 (s). UV–vis (hexane, 23 °C): 610 nm.

3.6. *Preparation of ansa-*$[Ti\{\eta^2{:}\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_3CH{=}CH(CH_2)_3C_5Me_4\}]$ *(7)*

A mixture of **6** and **5** in molar ratio 5:2 [14a] (0.70 g, 1.48 mmol) and activated magnesium (0.3 g, 12.3 mmol) were evacuated in an ampoule and THF (30 ml) were distilled in on a vacuum line under cooling with liquid nitrogen. The ampoule was sealed off, warmed to 60 °C, and stirred until the color of the solution turned to dark yellow (5 h). The ampoule was opened on a vacuum line, THF was evaporated, and the residue extracted with hexane (30 ml). The solution was concentrated, and cooled to −18 °C overnight. Yellow crystals were separated from the mother liquor and recrystallized from hexane. Yield of yellow prisms was 0.44 g (74%).

Analytical data for **7**: M.p. 150 °C. EIMS (150 °C): *m*/*z* (relative abundance) 401 (14), 400 (39), 399 (44), 398 [M$^{\bullet +}$; 100], 397 (33), 396 (55), 395 (25), 394 (21), 393 (30), 392 (12), 391 (17), 390 (7), 389 (11), 192 (10), 191 (9), 190 (8), 182 (14), 181 (19), 180 (14), 179 (9), 178 (20), 177 (12), 176 (9), 133 (72), 122 (26), 121 (29), 120 (27), 119 (100), 117 (29), 119 (8), 41 (15). IR (KBr, cm^{-1}): 3008 (m), 2956 (sh), 2907 (vs, b), 2856 (s, b), 2810 (s), 1486 (m), 1438 (vs), 1376 (s), 1356 (w), 1324 (w), 1266 (w), 1179 (m), 1100 (w), 1084 (w), 1068 (w), 1022 (m), 982 (w), 930 (w), 876 (w), 860 (m), 817 (w), 789 (w), 714 (m), 615 (vw), 583 (m), 538 (w), 522 (vw), 502 (vw), 430 (m), 409 (s).

Compound **7** was analogously prepared from 0.40 g of **6** containing 5% of **5** [14a] in the yield of 0.18 g (54%), and from 0.20 g of **5** containing 5% of **6** [15] in yield of 0.15 g (88%).

3.7. *Preparation of ansa-*$[Ti\{\eta^5{:}\eta^5\text{-}C_5Me_4(CH_2)_8C_5Me_4\}(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ *(8)*

Compound **1** (1.4 g, 2.96 mmol) and activated magnesium (0.6 g, 24.6 mmol) were evacuated in an ampoule, and THF (50 ml) was distilled in on a vacuum line under cooling by liquid nitrogen. The ampoule was sealed off, and btmse (1.8 ml, 8.0 mmol) was added from an attached ampoule. The resulting mixture was heated to 60 °C with stirring until the colour of the mixture turned clear yellow (1 h). The ampoule was opened on a vacuum line, THF and excess btmse were evaporated, and the residue was extracted by hexane. The yellow solution was concentrated and the product crystallized from a solution at −18 °C. Yield of yellow crystals of **8**: 1.44 g (85%).

M.p. 140 °C. EIMS (150 °C): *m*/*z* (relative abundance) 401 (15), 400 ([M−btmse]$^+$, 40), 399 (20), 398 (60), 397 (22), 396 (30), 395 (19), 394 (17), 393 (28), 392 (11), 390 (7), 389 (12), 217 (8), 202 (9), 201 (13), 200 (8), 197 (9), 182 (10), 181 (16), 180 (11), 179 (8), 178 (13), 177 (9), 170 ([btmse]$^{+\cdot}$; 8), 157 (11), 156 (19), 155 ([btmse−Me]$^+$; 100), 135 (13), 133 (10), 119 (11), 91 (8), 73 (15). ^{1}H-NMR (C_6D_6): δ 0.02 (s, 9H, Si*Me*$_3$), 1.26–1.44 (br m, 6H, 3 × C*H*$_2$), 1.72 (s, 6H, C_5*Me*$_4$), 1.81–1.89 (m, 2H, C*H*$_2$), 2.08 (s, 6H, C_5*Me*$_4$). ^{13}C{^{1}H}-NMR (C_6D_6): δ 4.4 (Si*Me*$_3$), 13.4, 14.2 (C_5*Me*$_4$); 22.2, 23.9, 25.4, 27.2 (*C*H$_2$); 120.7 (2 C), 122.9 (1C), 125.2 (2 C) (*C*$_5$Me$_4$); 248.3 (η^2-C≡C). ^{29}Si-NMR (C_6D_6): δ −17.9 (*Si*Me$_3$). IR (KBr, cm^{-1}): 2938 (s), 2887 (vs), 2860 (sh), 2840 (sh), 1635 (w), 1594 (m), 1558 (s), 1450 (m, b), 1375 (m), 1348 (w), 1291 (w), 1241 (vs), 1070 (w, b), 1017 (m), 840 (vs, b), 750 (s), 679 (m), 655 (m), 618 (w), 564 (vw), 448 (s), 430 (m). UV–NIR (hexane, 22 °C): 395(sh) ≫ 910 nm.

3.8. *Thermolysis of* ***8*** *to give* ***9***

A solution of complex **8** (1.3 g, 2.3 mmol) in *m*-xylene (30 ml) in an evacuated ampoules was heated to 150 °C for 10 h. The conversion of **8** to **9** was indicated by a change of the solution colour from yellow to sky blue. *m*-Xylene and other volatiles were distilled off in vacuum, and the residue was extracted with hexane (5 ml). Compound **9** was crystallized from the concentrated hexane solution by cooling to give a blue finely polycrystalline material. Yield 0.80 g (87%).

M.p. 130 °C. ^{1}H-NMR signals due to the *ansa* chains are grouped between 0.45 and 2.35 ppm. Their extensive overlapping prevented any detailed analysis of the NMR spectra, thus only sharp signals of the *exo*-methylene and methyl groups that could be unequivocally identified are given here. ^{1}H-NMR (C_6D_6): δ 1.09, 1.31, 1.37, 1.41, 1.55, 1.59, 2.21, 2.21, 2.37 (9 × s, 3 H, *Me*$_4$C$_5$ and *Me*$_2$C$_5$); 0.78, 0.88 (2 × d, $^2J_{HH} = 4.2$ Hz, =C*H*$_2$ *A*); 0.85, 0.89 (2 × d, $^2J_{HH} = 4.6$ Hz, =C*H*$_2$ *B*); 0.87, 1.29 (2 × d, $^2J_{HH} = 4.9$ Hz, =C*H*$_2$ *C*). ^{13}C{^{1}H}-NMR (C_6D_6): δ 10.2, 11.0, 11.3, 11.4, 11.4, 11.8, 13.9, 14.0, 14.7 (*Me*$_4$C$_5$ and *Me*$_2$C$_5$); 24.3, 24.6, 26.3, 26.4, 26.5, 26.9, 28.5, 28.5 (*ansa*-(*C*H$_2$)$_8$ major); 24.0, 25.0, 25.1, 25.5, 25.7, 27.8, 28.3, 30.3 (*ansa*-(*C*H$_2$)$_8$ minor); 67.5 (=*C*H$_2$ *C*), 68.6 (=*C*H$_2$ *B*), 70.6 (=*C*H$_2$ *A*), 115.4, 118.8, 118.9, 121.0, 121.4, 121.6, 122.4, 122.5 (2 C), 125.8, 128.5, 134.3, 139.1, 144.1, 144.4, 144.9 (Me$_4$*C*$_5$ and Me$_2$*C*$_5$). EIMS (90 °C): *m*/*z* (relative abundance) 400 (16), 399 (44), 398 [M$^{+\bullet}$; 100], 397 (17), 396 (20), 395 (5), 394 (7), 393 (5), 192 (6), 182 (7), 181 (8), 180 (6), 178 (8), 177 (6), 91 (6). IR (KBr, cm^{-1}): 3032 (m), 2932 (s, b), 2903 (vs, vb), 2840 (s), 1626 (vw), 1480 (sh), 1465 (sh), 1440 (vs), 1377 (s), 1341 (m), 1301 (vw), 1287 (w), 1260 (w), 1076 (m, b), 1023 (s), 882 (vw), 867 (vw), 828 (s), 815 (sh), 805 (sh), 742 (w), 733 (m), 613 (vw), 605 (w), 579 (m), 561 (w), 464 (sh), 434 (m). UV–vis (hexane): 585 nm.

3.9. X-ray crystallography

A dark green prism of complex **4** and yellow prismatic crystals of **7** and **8** were inserted into Lindemann glass capillaries in a glove box and sealed by a wax. All diffraction data were collected on a Nonius KappaCCD diffractometer. The structures were solved by direct methods (SIR-92, [30]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [31]). Relevant crystallographic data are given in Table 4; particular details about the structure solution follow.

3.9.1. Compound 4

The non-hydrogen atoms were refined anisotropically. Hydrogen atoms residing on C(6), C(20), C(21), and C(22) were identified on difference electron density maps and refined with isotropic thermal motion parameters while methyl hydrogen atoms were included in calculated positions.

3.9.2. Compound 7

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the η^2-coordinated double bond (H(22) and H(23)) were found on a difference electron density maps and isotropically refined. All other hydrogen atoms were included in geometrically optimized positions. The crystals of complex **7** suffered from multiple twinning where diffraction contributions of the other (minor) parts could not be substracted from the major one. Although this results in rather high R-values and large residual electron density peaks in areas close to the heaviest atom in the structure, the chemical picture is unambiguous and the metric parameters are reliable.

3.9.3. Compound 8

The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the methyl groups were included in idealized position (riding model) while all other hydrogen atoms 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-192553, **7**: CCDC-189754, **8**: CCDC-189755). Copies of the data can be obtained free of charge upon application to The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 4
Crystallographic data, data collection and structure refinement data for **4**, **7** and **8**

Compound	**4**	**7**	**8**
Chemical formula	$C_{23}H_{34}Ti$	$C_{26}H_{38}Ti$	$C_{34}H_{58}Si_2Ti$
Molecular weight	358.40	398.46	570.88
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
T (K)	293	150	293
a (Å)	9.4100(2)	9.5550(3)	17.576(1)
b (Å)	16.9170(3)	14.1280(5)	9.6580(7)
c (Å)	12.4430(3)	15.6510(5)	21.042(2)
β (°)	96.1920(13)	91.488(2)	107.548(4)
V (Å^3)	1969.23(7)	2112.1(1)	3405.6(5)
Z	4	4	4
Crystal size (mm^3)	0.30 × 0.35 × 0.50	0.30 × 0.35 × 0.50	0.17 × 0.37 × 0.45
D_{calc} (g cm^{-3})	1.209	1.253	1.113
μ (Mo–K$_\alpha$) (mm^{-1})	0.436	0.413	0.341
F(000)	776	864	1248
θ Range (°)	3.1–27.5	3.0–26.0	3.2–25.1
Diffractions collected	13 209	12 429	12 332
Independent diffractions	4491	4152	5740
Diffraction observed [a]	3699	3179	4336
Number of parameters	254	260	412
R, wR (observed diffractions) [b]	0.0397, 0.0961	0.0893, 0.235	0.0484, 0.110
R, wR (all data) [b]	0.0537, 0.1035	0.112, 0.246	0.0727, 0.122
S [c]	1.02	1.69	1.05
ρ (e Å^{-3})	0.32, −0.293	2.73, −0.85	0.22, −0.23

[a] $I > 2\sigma(I)$.

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

[c] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

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References

[1] (a) N.J. Long, Metallocenes, Blackwell Science, Oxford, UK, 1998;
(b) R. Beckhaus, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, vol. 1 (Chapter 4), Wiley-VCH, Weinheim, Germany, 1998, p. 153.

[2] (a) J.E. Bercaw, H.H. Brintzinger, J. Am. Chem. Soc. 93 (1971) 2045;
(b) J.E. Bercaw, R.H. Marvich, L.G. Bell, H.H. Brintzinger, J. Am. Chem. Soc. 94 (1972) 1219;
(c) J.E. Bercaw, J. Am. Chem. Soc. 96 (1974) 5087.

[3] T. Vondrák, K. Mach, V. Varga, A. Terpstra, J. Organomet. Chem. 425 (1992) 27.

[4] (a) J.W. Pattiasina, C.E. Hissink, J.L. de Boer, A. Meetsma, J.H. Teuben, A.L. Spek, J. Am. Chem. Soc. 107 (1985) 7758;
(b) K. Mach, V. Varga, V. Hanuš, P. Sedmera, J. Organomet. Chem. 415 (1991) 87.

[5] J.M. Fischer, W.E. Piers, V.G. Young, Organometallics 15 (1996) 2410.

[6] (a) U. Rosenthal, V.V. Burlakov, in: I. Marek (Ed.), Titanium and Zirconium in Organic Synthesis (Chapter 10), Wiley-VCH, Weinheim, 2002, p. 355;
(b) U. Rosenthal, P.-M. Pellny, F.G. Kirchbauer, V.V. Burlakov, Acc. Chem. Res. 33 (2000) 119 (and references therein).

[7] (a) P.-M. Pellny, F.G. Kirchbauer, V.V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, J. Am. Chem. Soc. 121 (1999) 8313;
(b) P.-M. Pellny, F.G. Kirchbauer, V.V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, Chem. Eur. J. 6 (2001) 81 (and references cited therein).

[8] S.A. Cohen, P.R. Auburn, J.E. Bercaw, J. Am. Chem. Soc. 105 (1983) 1136.

[9] M. Horáček, V. Kupfer, U. Thewalt, P. Štěpnička, M. Polášek, K. Mach, Organometallics 18 (1999) 3572.

[10] (a) J. Okuda, K.E. du Plooy, P.J. Toscano, J. Organomet. Chem. 495 (1995) 195;
(b) R.E.V.H. Spence, W.E. Piers, Organometallics 14 (1995) 4617;
(c) W.E. Piers, Chem. Eur. J. 4 (1998) 13;
(d) B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, Angew. Chem. Int. Ed. Engl. 34 (1995) 1755;
(e) B. Temme, J. Karl, G. Erker, Chem. Eur. J. 2 (1996) 919;
(f) J. Karl, G. Erker, R. Fröhlich, J. Am. Chem. Soc. 119 (1997) 11165;
(g) A.H. Cowley, G.S. Hair, B.G. McBurnett, R.A. Jones, Chem. Commun. (1999) 437.

[11] (a) H. Schumann, D.F. Karasiak, S.H. Mühle, R.L. Haltermann, W. Kaminsky, U. Weingarten, J. Organomet. Chem. 579 (1999) 356;
(b) H. Schumann, D.F. Karasiak, S.H. Mühle, W. Kaminsky, U. Weingarten, J. Organomet. Chem. 636 (2001) 31.

[12] (a) T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 519 (1996) 21;
(b) T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 583 (1999) 11;
(c) J. Zemánek, L. Fröhlichová, P. Šindelář, P. Štěpnička, I. Císařová, V. Varga, M. Horáček, K. Mach, Collect. Czech. Chem. Commun. 66 (2001) 1359.

[13] (a) N. Suzuki, H. Asami, T. Nakamura, T. Huhn, A. Fukuoka, M. Ichikawa, M. Saburi, Y. Wakatsuki, Chem. Lett. (1999) 341;
(b) H. Zhu, G.-X. Jin, N. Hu, J. Organomet. Chem. 655 (2002) 167;
(c) H.G. Alt, J. Chem. Soc. Dalton Trans. (1999) 1703;
(d) H.G. Alt, M. Jung, J. Organomet. Chem. 580 (1999) 1;
(e) H.G. Alt, A. Reb, W. Milius, A. Weis, J. Organomet.Chem. 628 (2001) 169.

[14] (a) M. Horáček, P. Štěpnička, R. Gyepes, I. Císařová, I. Tišlerová, J. Zemánek, J. Kubišta, K. Mach, Chem. Eur. J. 6 (2000) 2397;
(b) T.H. Waren, G. Erker, R. Fröhlich, B. Wibbeling, Organometallics 19 (2000) 127.

[15] M. Horáček, P. Štěpnička, K. Fejfarová, R. Gyepes, I. Císařová, J. Kubišta, K. Mach, J. Organomet. Chem. 642 (2002) 148.

[16] M. Bochmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson, M.F. Lappert (Eds.), Comprehensive Organometallic Chemistry II, vol. 4 (Chapter 5), Elsevier, 1995, pp. 314–320.

[17] L. Lukešová, P. Štěpnička, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta, K. Mach, Organometallics 21 (2002) 2639.

[18] (a) P.-M. Pellny, V.V. Burlakov, W. Baumann, A. Spannenberg, M. Horáček, P. Štěpnička, K. Mach, U. Rosenthal, Organometallics 19 (2000) 2816;
(b) M. Horáček, P. Štěpnička, R. Gyepes, I. Císařová, M. Polášek, K. Mach, P.-M. Pellny, V.V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, J. Am. Chem. Soc. 121 (1999) 10638.

[19] (a) V. Varga, K. Mach, M. Polášek, P. Sedmera, J. Hiller, U. Thewalt, S.I. Troyanov, J. Organomet. Chem. 506 (1996) 241;
(b) P. Štěpnička, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta, K. Mach, Organometallics 18 (1999) 4869;
(c) V. Kupfer, U. Thewalt, I. Tišlerová, P. Štěpnička, R. Gyepes, J. Kubišta, M. Horáček, K. Mach, J. Organomet. Chem. 620 (2001) 39;
(d) M. Horáček, P. Štěpnička, J. Kubišta, R. Gyepes, I. Císařová, L. Petrusová, K. Mach, J. Organomet. Chem. 658 (2002) 235.

[20] G.A. Luinstra, J. Vogelzang, J.H. Teuben, Organometallics 11 (1992) 2273.

[21] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.

[22] (a) V. Varga, L. Petrusová, J. Čejka, K. Mach, J. Organomet. Chem. 532 (1997) 251;
(b) M. Horáček, J. Hiller, U. Thewalt, M. Polášek, K. Mach, Organometallics 16 (1997) 4185;
(c) R. Gyepes, K. Mach, I. Císařová, J. Loub, J. Hiller, P. Šindelář, J. Organomet. Chem. 497 (1995) 33;
(d) S.I. Troyanov, V. Varga, K. Mach, J. Organomet. Chem. 461 (1993) 85;
(e) S.I. Troyanov, V. Varga, K. Mach, J. Chem. Soc. Chem. Commun. (1993) 1174.

[23] V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Y.T. Struchkov, V.B. Shur, M.E. Vol'pin, U. Rosenthal, H. Görls, J. Organomet. Chem. 476 (1994) 197.

[24] V. Varga, J. Hiller, R. Gyepes, M. Polášek, P. Sedmera, U. Thewalt, K. Mach, J. Organomet. Chem. 538 (1997) 63.

[25] (a) M. Bochmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson, M.F. Lappert (Eds.), Comprehensive Organometallic Chemistry II, vol. 4 (Chapter 4), Elsevier, 1995, pp. 263–264;
(b) Y. Qian, G. Li, X. Zheng, Y.Z. Zhuang, J. Mol. Catal. 78 (1993) L31;
(c) K. Mach, F. Tureček, H. Antropiusová, L. Petrusová, V. Hanuš, Synthesis (1982) 53;
(d) K. Mach, H. Antropiusová, V. Hanuš, F. Turecek, J. Organomet. Chem. 269 (1984) 39.

[26] K. Mach, L. Petrusová, H. Antropiusová, V. Hanuš, F. Tureček, P. Sedmera, Collect. Czech. Chem. Commun. 48 (1983) 2924.

[27] H. Antropiusová, A. Dosedlová, V. Hanuš, K. Mach, Transition Met. Chem. (London) 6 (1981) 90.

[28] G. Schmid, U. Thewalt, P. Sedmera, V. Hanuš, K. Mach, Collect. Czech. Chem. Commun. 63 (1998) 636 (and references therein).

[29] G.A. Luinstra, J.H. Teuben, J. Chem. Soc. Chem. Commun. (1990) 1470.

[30] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, J. Appl. Crystallogr. 27 (1994) 435.

[31] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Göttingen, 1997.