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Synthesis and crystal structures of μ-1,3-bis(η^5-tetramethylcyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)[η^2-bis(trimethylsilyl)ethyne]titanium(II) and a doubly tucked-in product of its thermolysis

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Abstract

Reduction of dichloro-{1,3-bis(η^5-tetramethylcyclopentadienyl)-1,1,3,3-tetramethyldisiloxane}titanium(IV), $[TiCl_2\{\eta^5:\eta^5\text{-}(C_5Me_4SiMe_2)_2O\}]$ (**1**), with magnesium in the presence of bis(trimethylsilyl)ethyne affords the *ansa*-$[Ti\{\eta^5:\eta^5\text{-}(C_5Me_4SiMe_2)_2O\}(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**2**) complex in high yield. Compound **2** is thermally robust, decomposing at 170 °C in high vacuum with liberation of 1,2-bis(trimethylsilyl)ethene to give predominantly an asymmetric, allydiene complex *ansa*-$[Ti\{(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2\{\eta^3:\eta^4\text{-}C_5Me_2(CH_2)_2\}]$ (**3**) as a result of twofold C–H bond activation. Crystal structures of **2** and **3** were determined by X-ray diffraction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; *ansa*-Titanocene complexes; Siloxane bridge; Bis(trimethylsilyl)ethyne complex; C–H activation; Thermolysis; Allyldiene ligand; Crystal structures

1. Introduction

Early transition metal metallocenes having the cyclopentadienyl ligands bridged with short *ansa*-chains of up to three carbon or silicon atoms usually exert a higher thermal stability and lower reactivity than their non-bridged analoga [1a,1b]. An advantage of the *ansa*-metallocenes is to be sought in well defined steric properties of the metallocene unit, namely in conformational rigidity, which a property has been particularly appreciated in designing new alkene polymerization catalysts [1c,1d]. Among titanocene complexes with short hydrocarbyl *ansa*-bridges $[TiCl_2\{\eta^5:\eta^5\text{-}(C_5H_4)_2E\}]$, where $E = CH_2$ [2a], CMe_2 [2b], $(CH_2)_2$ [2a], and $(CH_2)_3$ [2c], a fundamental study on the reactivity towards reduction agents has been carried out by Smith and Brintzinger for *ansa*-$[TiCl_2\{\eta^5:\eta^5\text{-}(C_5H_4)_2CMe_2\}]$ [3]. A number of products arising from reduction of sila-analogue of the latter complex, *ansa*-$[TiCl_2\{\eta^5:\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$, was reported by Royo et al. [4]. We have reported on similar, fully methylated compounds *ansa*-$[TiCl_2\{\eta^5:\eta^5\text{-}C_5Me_4)_2SiMe_2\}]$, *ansa*-$[TiCl\{\eta^5:\eta^5\text{-}C_5Me_4)_2SiMe_2\}]$, and *ansa*-$[Ti\{\eta^5:\eta^5\text{-}(C_5Me_4)_2SiMe_2)\}(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$, compared their properties with the non-bridged compounds, and investigated the catalytic activity of the titanium–alkyne complex in linear dimerization of terminal alkynes [5].

A three-membered Si–O–Si bridge, usually 1,1,3,3-tetramethyldisiloxane-1,3-diyl, has also been used for construction of *ansa*-metallocene compounds. The classical synthetic route to *ansa*-$[TiCl_2\{\eta^5:\eta^5\text{-}(C_5H_4SiMe_2)_2O\}]$ is based on the reaction of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane with cyclopentadienide salts, double deprotonation of the resulting bis(cyclopentadienyl)disiloxane and, finally, metathesis of the dianion with $TiCl_4$ [6]. An alternative approach consists

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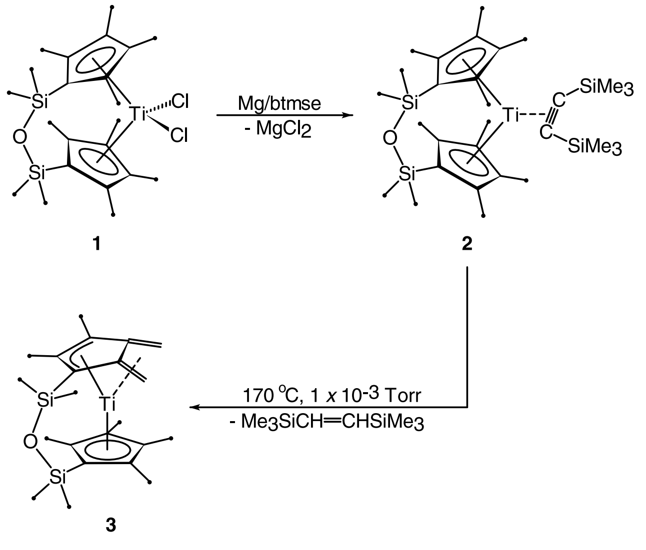
of the hydrolysis of titanocene dichlorides [$TiCl_2(\eta^5$-$C_5H_4SiMe_2Cl)_2$] [7]. We have recently obtained analogous, fully ring-methylated complex *ansa*-[$TiCl_2\{\eta^5:\eta^5$-$(C_5Me_4SiMe_2)_2O\}$] (**1**) in high yield by hydrolysis of the Si–N bonds in dichloro-bis{η^5-(dimethylaminodimethylsilyl)tetramethylcyclopentadienyl]titanium(IV), [$TiCl_2\{\eta^5$-$C_5Me_4(SiMe_2NMe_2)\}_2$] [8].

Here we report the synthesis and crystal structure of alkyne complex *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5Me_4SiMe_2)_2O\}(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$] (**2**), its thermal stability under vacuum, and the structure of the doubly tucked-in product of its thermolysis.

2. Results and discussion

The key compound, {1,3-bis(η^5-tetramethylcyclopentadienyl) - 1,1,3,3 - tetramethyldisiloxane}{η^2 - bis(trimethylsilyl)ethyne}titanium(II), *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5Me_4SiMe_2)_2O\}(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$] (**2**), was prepared by the reduction of [$TiCl_2\{\eta^5:\eta^5$-$(C_5Me_4SiMe_2)_2O\}$] (**1**) with magnesium in THF in the presence of bis(trimethylsilyl)ethyne (btmse) [9] in nearly quantitative yield (Scheme 1). Both magnesium and btmse were used in excess because compound **2** does not react further with excess of the reagents as it has been observed for titanocene dichlorides bearing up to two methyl groups on the cyclopentadienyl rings [10]. Yellow crystalline **2** is only moderately soluble in hexane and thermally very robust. In vacuum of 10^{-4} Torr, it sublimes at temperatures 160–170 °C with only partial decomposition. At a slightly higher pressure of 10^{-3} Torr, it decomposes at 170 °C with liberation of a mixture of (*E*)- and (*Z*)-1,2-bis(trimethylsilyl)ethene and a product of double C–H bond activation, 1-(η^5-tetramethylcyclopentadienyl)-3-($\eta^3:\eta^4$-1,2-dimethylene-3,4-dimethylcyclopenten-5-yl)-1,1,3,3-tetramethyldisiloxanetitanium(II), *asym*-[$Ti\{(\eta^5$-$C_5Me_4)SiMe_2$-$OSiMe_2(\eta^3:\eta^4$-$C_5Me_2(CH_2)_2)\}$] (**3**) as the major titanium-containing product, which was isolated in 79% yield after crystallization from hexane.



Scheme 1. Preparation and thermolysis of **2**.

Structures of compounds **2** and **3** were determined by NMR spectra and X-ray single crystal diffraction. The $\delta_C(C{\equiv}C)$ value observed for **2** (δ_C 247.7) is higher than that for *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5H_4SiMe_2)_2O\}$ (η^2-$Me_3SiC{\equiv}CSiMe_3)$] (δ_C 242.0) [11], reflecting thus an electron donating effect of methyl substituents at cyclopentadienyl ligands that enhances the strength of back-bonding between titanium and btmse. The value for **2** falls on the scale of $\delta_C(C{\equiv}C)$ chemical shifts in the series [$Ti(\eta^5$-$C_5H_{5-n}Me_n)_2(\eta^2$-btmse)] ($n = 0$–5; δ_C 244.8–248.5) [9a] in between the values for complexes with $n = 3$ and 4. This would imply that the $O(SiMe_2)_2$ bridge acts as a stronger electron withdrawing group than hydrogen. However, the increments in $\delta_C(C{\equiv}C)$ *per* one methyl group in the above series are far from equidistant and hence, the δ_C (C≡C) value is not a reliable parameter to determine electronic effects of substituents on the cyclopentadienyl ligands. Moreover, as illustrated by δ_C values for *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5H_4)_2$-$SiMe_2)\}(\eta^2$-btmse)] (δ_C 248.9) [5,12], and *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5Me_4)_2SiMe_2)\}(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$] (**4**) ($\delta_C$ 254.9) [5], the chemical shift depends strongly also on other factors, e.g. on the dihedral angle subtended by the cyclopentadienyl ring planes. Thus, it turns out that electronic effects seem to be better reflected in $\nu(C{\equiv}C)$ values which decrease with increasing contribution of π-back donation resulting from increased electron density at the titanium atom. The IR spectrum of **2** in the region of the η^2-coordinated triple bond [1640(sh), 1598(s), 1562(m)] is very similar to that of [$Ti(\eta^5$-$C_5Me_5)_2(\eta^2$-btmse) (**5**) [9a] whilst the absorption bands of compound **4** are shifted to lower energies [1622(sh), 1580(m)] [5]. A similar difference in $\nu(C{\equiv}C)$ has also been observed for non-methylated analogues *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5H_4$-$SiMe_2)_2O\}(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$] (1687 cm^{-1}) [11] and *ansa*-[$Ti\{\eta^5:\eta^5$-$(C_5H_4)_2SiMe_2)\}(\eta^2$-btmse)] (1683 cm^{-1}) [5,12]. This difference can result from either an electron attracting effect of the oxygen atom within the *ansa*-bridge in **2** or from a larger angle between the cyclopentadienyl ring planes in **4** (53.5° compared to 41.1° in **5** and 44.0° in **2**). The electronic absorption band of **2** at 920 nm is very close to the band of **5** (916 nm) and **4** (970 nm). In spite of a high thermal stability, **2** exhibits in its EI-MS spectrum only very poorly abundant molecular ion. This indicates that the dissociation of **2** to btmse and a titanocene species occurs after electron ionisation but not by thermal degradation.

Compound **3** was identified as a derivative of the asymmetric compound [$Ti(\eta^5$-$C_5Me_5)\{\eta^3:\eta^4$-C_5Me_2-$(CH_2)_2\}$] (**6**) which was discovered by Teuben and coworkers [13]. It displays typical ^1H- and ^{13}C-NMR spectra showing anisochronic *exo*-methylene and methyl groups on the allyldiene ligand. The chemical shifts for *exo*-methylene carbon atoms are found in the range observed for **6** [13] and similar compounds obtained from thermolysis of benzyltetramethyl and phenyltetramethyl substituted titanocene–btmse complexes [14] or analogues of **6** having the cyclopentadienyl ligand annelated with a cyclooctene ring [15]. In its IR spectrum, complex **3** shows an absorption band due to *exo*-methylene ν(C–H) vibration at 3037 cm^{-1} similarly to **6** (3035 cm^{-1}). Likewise, an electronic absorption band occuring at 540 nm for **3** was observed for all the mentioned allydiene compounds. The EI-MS spectrum of **3** displays only a molecular isotope cluster (m/z 418, 100%) and only low abundant fragment ions arising from a loss of one methyl group (m/z 403, 5%). This poor fragmentation is also in keeping with behaviour of all the mentioned doubly tucked-in allyldiene compounds.

2.1. Crystal structure of 2

The molecule of **2** possesses no crystallographic symmetry (Fig. 1 and Table 1). The *ansa*-titanocene moiety is very similar to that in **1** adopting a close-to-staggered position of the cyclopentadienyl rings. However, a remarkable difference is observed in the angle between least-squares planes of the cyclopentadienyl rings (ϕ). This angle is surprisingly larger in **1** [48.2(1)°] than in **2** [44.0(1)°] and, correspondingly, the declination of the silicon atoms from the cyclopentadienyl ring least-squares planes away from titanium atom is on average larger in **1** [av. 0.615(4)°] than in 2 [av. 0.558(3)°]. It indicates that the chloride ligands in **1** induce a larger steric congestion on the open side of the bent titanocene unit than does coordinated btmse. The planar geometry of the coordinated btmse [C(23)–C(24) 1.307(3) Å, C–C–Si angles 137.9(2) and 137.3(2)°] does not virtually differ from its geometry in all known titanocene–btmse complexes: [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] [9b], [Ti(η^5-C_5HMe_4)$_2$(η^2-btmse)] [9a], [Ti{η^5:η^5-(C_5Me_4)$_2$$SiMe_2$}-($\eta^2$-btmse) [5], [Ti{$\eta^5$-$C_5Me_4$(4-$C_6H_4F$)}$_2$($\eta^2$-btmse)] [14], and [Ti($\eta^5$-$C_5Me_4SiMe_3$)$_2$($\eta^2$-btmse)] [16].

Table 1
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Ti–Cg(1) [a]	2.117(2)	Ti–Cg(2) [a]	2.120(2)
Ti–C(23)	2.134(2)	Ti–C(24)	2.130(2)
Ti–C(Cp)	2.379(2)–2.492(2)	C(Cp)–C(Cp)	1.404(3)–1.37(3)
C(Cp)–C(Me)	1.495(3)–1.502(3)	Si–C(5)	1.869(2)
Si–C(10)	1.870(2)	Si(1)–O	1.635(2)
Si(2)–O	1.630(2)	C(23)–C(24)	1.307(3)
Si(3)–C(23)	1.863(2)	Si(4)–C(24)	1.863(2)
Si–C(Me)	1.853–1.875(4)		
Bond angles			
Cg(1)–Ti–Cg(2) [b]	139.6(2)	C(23)–Ti–C(24)	35.7(1)
C(23)–C(24)–Ti	72.3(1)	C(24)–C(23)–Ti	72.0(1)
Si(3)–C(23)–C(24	137.9(2)	Si(4)–C(24)–C(23)	137.3(2)
Si(1)–O–Si(2)	140.2(1)	O–Si(1)–C(5)	110.6(1)
O–Si(2)–C(10)	109.9(1)	ϕ [b]	44.0(1)

[a] Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(6–10) cyclopentadienyl rings, respectively.

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

2.2. Crystal structure of 3

Compound **3** crystallizes in the monoclinic $P2_1/c$ space group with four molecules in the unit cell. The molecular structure is shown in Fig. 2 and important geometric parameters are listed in Table 2. The five-membered ring bearing two vicinal *exo*-methylene groups adjacent to the pivotal carbon atom has its least-squares plane with larger deviations of the plane defining carbon atoms (maximum deviation 0.020(2) Å) than the non-disturbed cyclopentadienyl ring (maximum deviation 0.009(2) Å). The angle subtended by these two

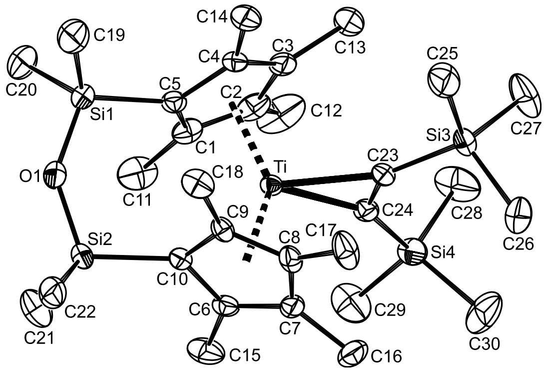


Fig. 1. Molecular structure of **2** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. For clarity, the hydrogen atoms are omitted.

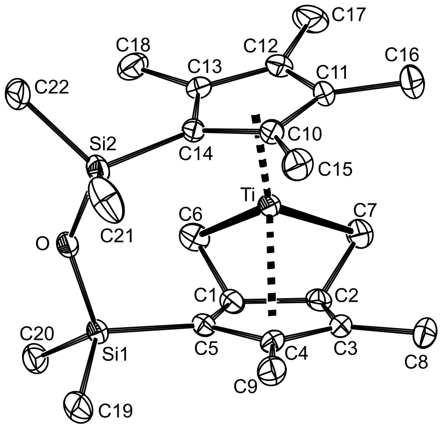


Fig. 2. Molecular structure of **3** (30% probability ellipsoids) with the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Ti–Cg(1) [a]	1.922(3)	Ti–Cg(2) [a]	2.017(3)
Ti–C(1)	2.075(3)	Ti–C(2)	2.090(3)
Ti–C(3)	2.381(3)	Ti–C(4)	2.505(3)
Ti–C(5)	2.312(3)	Ti–C(6)	2.239(4)
Ti–C(7)	2.283(4)	Ti–C(10–14)	2.322(3)–2.379(3)
C(1)–C(2)	1.469(4)	C(2)–C(3)	1.434(5)
C(3)–C(4)	1.396(5)	C(4)–C(5)	1.434(4)
C(1)–C(5)	1.464(4)	C(1)–C(6)	1.416(5)
C(2)–C(7)	1.438(5)	C(3)–C(8)	1.508(5)
C(4)–C(9)	1.502(5)	C(Cp)–C(Cp)	1.414(5)–1.446(5)
C(Cp)–C(Me)	1.495(5)–1.517(5)	Si(1)–C(5)	1.867(3)
Si(2)–C(14)	1.871(3)	Si–C(Me)	1.860(5)–1.864(4)
O–Si(1)	1.653(2)	O–Si(2)	1.633(3)
Bond angles			
Cg(1)–Ti–Cg(2) [b]	155.6(2)	C(6)–Ti–C(7)	76.4(2)
C(1)–C(6)–Ti	64.7(2)	C(2)–C(7)–Ti	63.7(2)
C(2)–C(1)–C(5)	106.7(3)	C(1)–C(5)–C(4)	107.0(3)
C(2)–C(3)–C(4)	109.2(3)	C(3)–C(4)–C(5)	109.8(3)
Si(1)–O–Si(2)	141.4(2)	O–Si(1)–C(5)	109.5(1)
O–Si(2)–C(14)	110.7(1)	C(1)–C(2)–C(3)	107.2(3)
ϕ [b]	14.1(2)	ω [c]	43.2(2)

[a] Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(1–140) cyclopentadienyl rings, respectively.

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

[c] The angle subtended by the least-squares planes defined by atoms C(1–5) and by atoms C(1), C(2), C(6) and C(7).

planes (ϕ) is opened on the side of *exo*-methylene groups and amounts to 14.1(2)°. The angle (ω) between the least-squares plane of the *exo*-methylene carbons atoms {C(1)C(2)C(6)C(7)} and the plane of the formally η^3-coordinated cyclopentadiendienyl ring is 43.2(2)°. Magnitudes of these angles are rather typical for doubly tucked-in titanocene complexes; cf. complexes derived from bis(benzyltetramethylcyclopentadienyl)titanium [ϕ 44.0(4), ω 12.4(4)°] and bis(phenyltetramethylcyclopentadienyl)titanium [ϕ 43.0(3), ω 8.3(3)°] [14], and the complexes derived from bis(pentamethylcyclopentadienyl)titanium and bis(tetramethylcyclopentadienyl)titanium both containing the other ring fused with a cyclooctene ring [ϕ 42.5(2)/43.9(2) and ω 10.7(2)/12.9(2)°] [15a].

The tetramethyldisiloxane bridge is placed in a side position with respect to the Cg(1)TiCg(2) plane and the silicon atoms are only slightly deviated from the least-squares planes of the cyclopentadienyl rings: the Si(1) atom is declined towards the titanium centre by 0.083(5)° while the Si(2) atom by 0.014(6)° away from it. The Si(1)–O–Si(2) angle [141.4(2)°] is only slightly larger than in the parent titanocene dichloride **1** [139(1)°] [8] and **2** [140.2(1)°]. Also, in agreement with geometric parameters of all the structures mentioned above, the Ti–C(1) and Ti–(C2) distances are the shortest ones [2.075(3) and 2.090(3) Å] followed by longer Ti–C(6) and Ti–C(7) [2.239(4) and 2.283(4) Å] and Ti–C(5) and Ti–C(3) distances [2.312(3) and 2.381(3) Å], and the longest distance Ti–C(4) of 2.505(3) Å. The Ti–C distances for the unperturbed cyclopentadienyl ring span the range of 2.322(3)–2.379(3) Å.

2.3. *Thermolytic behaviour of **2** and similar compounds*

The thermal stability of **2** is remarkably higher than that of **5** which affords cleanly **6** by heating its *m*-xylene solution to 150 °C for 4 h. Under these conditions, the solution of **2** remained bright yellow even after heating for 10 h. On the other hand, compound **2** is less stable than **4**, which remains unaffected by heating to 200 °C in *m*-xylene solution and sublimed in vacuum without decomposition [5]. The particularly high stability of **4** can be accounted for a rigid structure of its highly bent molecule (ϕ 53.5°) [5] which does not probably allow for effective encounters of the coordinated btmse with methyl groups on the cyclopentadienyl rings. The electronic effect of the bridging silicon atom in **4** can also aid to the high thermal stability: the only thermally stable titanocenes so far reported are fully methylated ones bearing one trimethylsilyl substituent on each cyclopentadienyl ligand [16]. In compound **2**, the Si–O–Si bridge allows for tilting the cyclopentadienyl rings towards btmse in solution but may lower the frequency of encounters of the cyclopentadienyl methyl groups and η^2-btmse compared to **5**. Furthermore, the electronegative oxygen atom likely decreases the mentioned stabilizing effect of the silicon atoms and a certain through space electron donation from oxygen to metal has been supposed to explain behaviour of disiloxane-bridged bis(η^5-indenyl)titanium and zirconium catalysts in alkene polymerization [17].

3. Experimental

3.1. *Materials and methods*

All the reactions and handling of products in solutions were performed under vacuum conditions using all-glass devices equipped with magnetically breakable seals. Solid compounds were handled in a glovebox (mBraun, nitrogen atmosphere, O_2 and H_2O concentrations below 2.0 ppm). Solvents THF and C_6H_{14} were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$ [18]. C_6D_6 for NMR spectroscopy was degassed and stored as a solution of dimeric titanocene on a vacuum line. Bis(trimethylsilyl)ethyne (Fluka) was degassed, stored as a solution of dimeric titanocene for 4 h, and finally distilled into ampoules on a vacuum line. Magnesium turnings (Fluka, purum for Grignard reactions) were initially used in large excess for the preparation of [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] [9] and the unreacted, highly active Mg was washed with THF, separated in vacuum and used in subsequent reductions. Compound **1** was obtained as recently reported [8].

NMR samples of **2** and **3** were prepared in evacuated all-glass devices from which the NMR tubes were sealed off by flame. The adjustment of single crystals of **2** and **3** into Lindemann glass capillaries for X-ray analyses as well as the preparation of samples for IR and MS measurements were made in the glovebox. Infrared spectra of samples in KBr pellets were recorded on a Nicolet Avatar FTIR spectrometer under nitrogen in an air-protecting cuvette. ^1H (399.95 MHz)- and ^{13}C (100.58 MHz)-NMR spectra were measured on a Varian UNITY Inova 400 spectrometer in C_6D_6 solutions at 298 K. Chemical shifts (δ/ppm) are given relative to the solvent signal (δ_H 7.15, δ_C 128.0). Mass spectra were measured on a VG 7070E spectrometer at 70 eV using a direct inlet probe (samples in sealed capillaries were opened and inserted into the probe in an Ar flow). GC analyses were performed on a CHROM 5 gas chromatograph (Laboratory Instruments, Prague, Czech Republic) equipped by 10% SE-30 on a Chromaton N-AW-DMCS column. GC–MS analyses were carried out on a Hewlett-Packard gas chromatograph (5890 series II; capillary column SPB-1 (Supelco)) interfaced to a mass spectrometric detector (5791 Å). Melting points were determined for samples in sealed capillaries under nitrogen on a Kofler apparatus and are uncorrected.

*3.2. Preparation of ansa-[Ti{η^5:η^5-$C_5Me_4SiMe_2$)O}(η^2-btmse)] (**2**)*

Compound **1** (0.98 g, 2.0 mmol) was dissolved in THF (30 ml), btmse (0.9 ml, 4.0 mmol) was added and the solution was poured onto activated Mg turnings (ca. 0.3 g, 12.5 mmol). The mixture was kept at 60 °C until the colour of the solution turned cleanly yellow (2 h). Then the remaining Mg was separated, the solution was evaporated in vacuum and the residue was extracted repeatedly with C_6H_{14}. Finely crystalline yellow product was obtained by slow cooling of the warm solution (80 °C) in a sealed ampoule to room temperature. Yield: 1.0 g (84%). After cooling in refrigerator, the mother liquor afforded larger crystals suitable for X-ray analysis (ca. 0.05 g).

M.p. 217 °C (dec.). EI-MS (210 °C): *m/z* (relative abundance) 590 ([$M^{+\bullet}$; <1], 422 (11), 421 (24), 420 ([M$-$btmse]$^{+\bullet}$; 62), 419 (40), 418 (48), 417 (9), 405 (8), 170 (btmse$^{+\bullet}$; 7), 156 (16), 155 ([btmse$-$Me]$^+$; 100), 73 (15), 70 (9). ^1H-NMR (C_6D_6): δ -0.02 (s, 9H, SiMe_3), 0.29 (s, 6H, SiMe_2), 1.43, 2.33 ($2\times$s, 6H, Me_4C_5). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 4.1 (SiMe_2), 4.2 (SiMe_3), 14.9, 15.0 (Me_4C_5); 112.8, 132.1 (C_5Me_4; the third C_{ipso} signal was not observed), 247.7 (η^2-$C{\equiv}C$). IR (KBr, cm^{-1}): $\bar{\nu}$ 2940 (vs,b), 2887 (vs,b), 2860 (sh), 1640 (sh), 1598 (s), 1562 (m), 1540 (sh), 1480 (w), 1449 (m), 1380 (m), 1553 (w), 1336 (s), 1247 (vs), 1133 (w), 1020 (vs,b), 832 (vs,b), 773 (s), 747 (s), 698 (w), 680 (m), 667 (w), 653 (w), 640 (w), 620 (w), 587 (m), 567 (w), 447 (s). UV–NIR (C_6H_{14}, 22 °C): 920 nm.

*3.3. Thermolytic preparation of asym-ansa-[Ti(η^3:η^4:η^5-$C_5Me_4SiMe_2OSiMe_2C_5Me_2(CH_2)_2$)] (**3**)*

Compound **2** (0.52 g, 0.88 mmol) in a breakable seal was opened into vacuum on a vacuum line and heated by an oven gradually to 170 °C under a dynamic vacuum of a preevacuated charcoal cooled by liquid nitrogen (about 1×10^{-4} Torr). A mixture of (*E*)- and (*Z*)-1,2-bis(trimethylsilyl)ethene and btmse (as determined by GC–MS [9a]) was collected in a trap cooled by liquid nitrogen and a blue solid with some yellow spots condensed on cold walls of the glass tube outside the oven. All the sublimed product was washed with C_6H_{14} into an ampoule. NMR analysis of the crude product revealed the presence of **2** and **3** in a ratio ca. 0.6:1, and trace amount of impurities which should contain the symmetric isomer of **3**.

The content of NMR sample was combined with the major part of the crude product, the solution was evaporated in vacuum and the residue was again sublimed under a dynamic vacuum of oil rotary pump (about 1×10^{-3} Torr). A blue material sublimed at 170 °C while the volatiles collected in a trap at 77 K consisted of a mixture of (*E*)- and (*Z*)-1,2-bis(trimethylsilyl)ethene. The blue product was dissolved in C_6H_{14} and crystallized from a concentrated solution by cooling. Sky-blue crystals of **3** were used for all the characterization including X-ray single crystal diffraction. Yield: 0.29 g (79%).

M.p. 160 °C. EI-MS (150 °C): *m/z* (relative abundance) 421 (8), 420 (27), 419 (53), 418 ([$M^{+\bullet}$; 100]), 417 (19), 416 (16), 403 (5). ^1H-NMR: δ 0.25, 0.28, 0.34, 0.35 ($4\times$s, 3 H, SiMe_2), 0.89 (d, $^2J_{HH}=4.1$ Hz, 1H, $=CH_2$ *A*), 1.07 (s, 3H, *Me*), 1.09 (d, $^2J_{HH}=4.7$ Hz, 1H, $=CH_2$ *B*), 1.16 (d, $^2J_{HH}=4.1$ Hz, 1H, $=CH_2$ *A*), 1.32 (d, $^2J_{HH}=4.7$ Hz, 1H, $=CH_2$ *B*), 1.49, 1.56, 1.63, 2.30, 2.33 ($5\times$s, 3 H, *Me*). $^{13}C\{^1H\}$-NMR: δ 2.02, 3.21, 3.72, 3.99 (SiMe_2); 10.5 (δ_H 1.07), 11.6 (δ_H 1.49), 13.8 (2 C, δ_H 1.56 and 2.30), 14.2 (δ_H 1.63), 17.3 (δ_H 2.33) (*Me*); 75.3 ($=CH_2$ *A*), 66.7 ($=CH_2$ *B*), 116.0, 121.6, 123.6, 125.5, 125.8, 129.1, 129.3, 142.0, 149.4, 151.6 (allydiene and cyclopentadienyl C_{ipso}). IR (KBr, cm^{-1}): $\bar{\nu}$ 3037 (w), 2960 (s), 2901 (vs), 2860 (sh), 1480 (w), 1447 (m), 1434 (s), 1400 (w), 1381 (m), 1336 (s,b), 1306 (w), 1242 (s), 1163 (vw), 1137 (m), 1090 (w), 1024 (vs,b), 893 (w), 834 (vs,b), 784 (s,b), 747 (w), 722 (vw), 694 (m), 667 (m), 623 (w), 583 (m), 559 (w), 448 (m). UV–vis (C_6H_{14}, 22 °C): 540 nm.

3.4. X-ray crystallography

A yellow prism of complex **2** and a fragment of a blue prism of **3** were inserted into Lindemann glass capillaries in a glove box. All diffraction data were collected on an image plate Nonius Kappa CCD diffractometer. The structures were solved by direct methods (SIR-92, [19]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [20]). Relevant crystallographic data are given in Table 3; particular details about the structure solution are as follows:

Complex **2**: all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were identified on difference electron density maps and isotropically refined;

Complex **3**: the crystal of **3** suffered from pseudo-merohedral twinning mimicking an orthorhombic symmetry of the diffraction pattern. The diffractions were corrected for a contribution of the second part during refinement, using the twin operation:

$$\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

applied on (*hkl*). The refinement yielded fractional contribution of the two components 0.476:0.524. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of methyl groups were included into idealized position and allowed to ride during the refinement on the respective pivotal carbon atom with the thermal motion parameter assigned 1.5 U_{eq}(C). The hydrogens of CH_2 moieties were found on difference electron density maps and refined with isotropic thermal motion parameters.

Table 3
Crystallographic data, data collection and structure refinement data for compounds **2** and **3** [a]

Compound	**2**	**3**
Chemical formula	$C_{30}H_{54}OSi_4Ti$	$C_{22}H_{34}OSi_2Ti$
Molecular weight	590.99	418.57
Temperature (K)	293	150
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	9.0680(2)	18.3920(4)
b (Å)	12.2310(4)	13.0220(5)
c (Å)	17.0720(6)	9.3590(7)
α (°)	93.319(2)	90
β (°)	105.161(2)	90.020(2)
γ (°)	108.3620(19)	90
V (Å^3)	1714.05(9)	2241.5(2)
Z	2	4
D_{calc} (g cm^{-3})	1.145	1.240
μ(Mo K$_\alpha$) (mm^{-1})	0.410	0.497
F(000)	640	896
Crystal size (mm)	0.85 × 0.48 × 0.33	0.4 × 0.3 × 0.3
θ Range (°)	3.84–27.52	1.56–26.02
Index ranges	$0 \leq h \leq 11$, $-15 \leq k \leq 15$, $-22 \leq l \leq 20$	$-21 \leq h \leq 22$, $-16 \leq k \leq 16$, $-8 \leq l \leq 11$
Diffractions collected	7657	4313
Parameters	541	262
R, wR [$I > 2\sigma(I)$]	0.0419, 0.0976	0.0453, 0.1100
R, wR (all data)	0.0510, 0.1057	0.0508,0.1149
S	1.113	1.040
$\Delta\rho_{max,\ min}$ (e Å^{-3})	0.239, −0.384	0.738, −0.522

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

4. Supplementary material

Crystallographic data, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 183174, 183173 for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge from 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).

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