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Syntheses and properties of some *exo*,*exo*-bis(isodicyclopentadienyl)titanium low-valent complexes

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Abstract

The paramagnetic compounds *exo*,*exo*-bis(η^5-isodicyclopentadienyl)chlorotitanium(III) (**3**) and its analogue with trimethylsilyl-substituted isodicyclopentadienide (isodiCp) ligand (**4**), and the similar pair of diamagnetic *exo*,*exo*-bis(isodicyclopentadienyl)[η^2-bis(trimethylsilyl)ethyne]titanium(II) complexes **5** and **6** were obtained by common reduction procedures from *exo*,*exo*-bis(isodicyclopentadienyl)titanium(IV) dichloride (**1**) and *exo*,*exo*-bis[η^5-2-(trimethylsilyl)isodicyclopentadienyl]titanium(IV) dichloride (**2**), respectively. As indicated by ESR spectroscopy compound **3** is a dimer in the solid state and in frozen toluene glass but monomeric in toluene solution. Compound **4** is monomeric in solution as well as in the solid state. As judged from the red shift of the ν(C≡C) vibration, compound **6** binds bis(trimethylsilyl)ethyne more strongly than compound **5**. A comparison of their wavenumbers with those of the $[Ti(C_5H_{5-n}Me_n)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ ($n = 2$–5) complexes shows that Lewis acidity of the central titanium atom decreases in the order of ligands 1,3-dimethylcyclopentadienyl > isodiCp ~ 1,2,3-trimethylcyclopentadienyl > (trimethylsilyl)isodiCp ~ tetramethylcyclopentadienyl. The crystal structure of the most bulky complex **6** shows a bis-lateral (anti) conformation of the isodiCp ligands with the π-coordinated five-membered rings nearly eclipsed. © 2002 Published by Elsevier Science B.V.

Keywords: Titanium; Isodicyclopentadienyl ligand; Trimethylsilylisodicyclopentadienyl ligand; Bis(trimethylsilyl)ethyne complexes; ESR spectra; NMR spectra; Crystal structures

1. Introduction

The chemistry of titanocene dichloride and cyclopentadienyltitanium trichloride complexes has become extremely voluminous as a result of modifying the very basic cyclopentadienyl ligand by introduction of various substituents including some annelated saturated and aromatic carbocycles in an effort to control electronic and steric properties of the complexes which are applied as precursors of alkene polymerization catalysts [1]. The use of the isodicyclopentadienide ligand (isodiCp; 4,5,6,7-tetrahydro-4,7-methano-2*H*-indenyl) represents an effective way to change steric demands of the cyclopentadienyl ligand. The latter can further be tuned by a modification of the isodiCp skeleton or, more importantly, by coordinating the isodiCp ligand to $\{TiCl_3\}$ or $\{Cp'TiCl_2\}$ ($Cp' = \eta^5$-alkylcyclopentadienyl) fragments by either its *exo* or *endo* faces. An *endo*-faced coordination has been generally observed at low temperature whereas *exo*-faced coordination mode operates at ambient temperature [2]. Thus, *exo*,*exo*-dichloro-bis(η^5-isodiCp)titanium(IV) (**1**) was obtained by reaction of lithium isodicyclopentadienide, [Li(isodiCp)], with $TiCl_3 \cdot 3THF$ in THF at room temperature and *endo*,*endo*-dichloro-bis(η^5-isodiCp)titanium(IV) was obtained with 91% selectivity when the same reaction was carried out at −64 °C [2a]. The *endo*,*exo*-isomer

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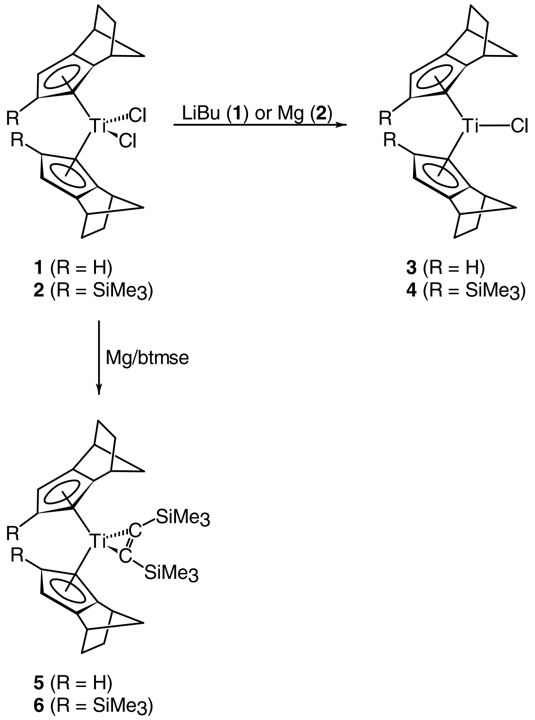
was prepared by reacting Li(isodiCp) with *exo*-[$TiCl_3$(η^5-isodiCp)] at a low temperature [2b], the precursor being stereoselectively obtained from *endo*-(trimethylsilyl)isodicyclopentadiene and $TiCl_4$ [3]. The *endo*-faced coordination of the isodiCp anion occurs likely due to the dimeric form of Li(isodiCp) prevailing at low temperatures. At room temperature, the monomeric Li(isodiCp) with *exo*-faced π-bonded lithium cation is believed to be responsible for the selective formation of *exo*-faced titanium derivatives [4]. In the redox reaction of isodiCpH with the titanium(II) complex [(η^6-C_6H_6)Ti{(μ-Cl)$_2$$AlCl_2$}$_2$] the *exo*-faced titanium(III) complex *exo*-[(η^5-isodiCp)Ti{(μ-Cl)$_2$$AlCl_2$}$_2$] exclusively formed at room temperature [5]. *exo*,*exo*-Dichloro-bis(η^5-isodiCp)titanium(IV) and -zirconium(IV) derivatives were recently examined in combination with methylalumoxane as catalysts for propene polymerization [6].

Here we describe the preparation of titanocene monochlorides and titanocene-bis(trimethylsilyl)ethyne complexes derived from *exo*,*exo*-[$TiCl_2$(η^5-isodiCp)$_2$] and its 2-trimethylsilyl derivative, 4,5,6,7-tetrahydro-4,7-methano-2-(trimethylsilyl)-indenyl anion (TMSisodiCp) [7]. This investigation is aimed at estimating the electronic and steric properties of the isodicyclopentadienyl ligands in comparison with methyl-substituted cyclopentadienyl ligands.

2. Results and discussion

Isodicyclopentadienyl titanium(III) complexes *exo*,*exo*-[{Ti(μ-Cl)(η^5-isodiCp)$_2$}$_2$] (**3**) and *exo*,*exo*-[TiCl(η^5-TMSisodiCp)$_2$] (**4**) were obtained by common alkylation/β-hydrogen elimination and magnesium reduction, respectively (Scheme 1) from the corresponding titanocene dichloride complexes. An analogous series of titanium(II)-alkyne complexes *exo*,*exo*-[Ti(η^5-isodiCp)$_2$(η^2-btmse)] (**5**) and *exo*,*exo*-[Ti(η^5-TMSisodiCp)$_2$(η^2-btmse)] (**6**) was obtained by magnesium reduction in the presence of excess bis(trimethylsilyl)ethyne (btmse).

Compounds **3** and **4** are paramagnetic; their ESR spectra were compared with spectra of methyl-substituted titanocene monochlorides: chloro-bis(η^5-1,3-dimethylcyclopentadienyl)titanium(III) (**7**), chloro-bis(η^5-1,2,3-trimethylcyclopentadienyl)titanium(III), and chloro-bis(η^5-tetramethylcyclopentadienyl)titanium(III), whose Lewis acidities are reflected in the formation of dimers and THF coordination onto monomeric species [8,9]. Compounds **5** and **6** were compared to the series of methyl-substituted complexes [Ti($C_5H_{5-n}Me_n$)$_2$(η^2-btmse)] ($n = 0$–5), where the red shift of the ν(C≡C) band serves as a measure of the strength of alkyne coordination [10].



Scheme 1.

Compound **3** forms a brown crystalline material whose mass spectrum shows only the monomer ions and their fragments, however, at a temperature much higher than expected for evaporation of monomeric **3**. Similarly, only the monomer spectrum was obtained for a crystal of **7** although the dimeric structure of the complex was unequivocally corroborated by X-ray diffraction analysis [8]. In toluene solution, the ESR spectrum of **3** showed the presence of three different species at ambient temperature (Fig. 1a) and two species in frozen toluene glass (Fig. 1b). One of the species giving a sharp signal at $g_{iso} = 1.980$ ($\Delta H = 6.0$ G) in the solution and a slightly anisotropic spectrum in toluene glass ($g_1 = 2.001$, $g_2 = 1.986$, $g_3 = 1.956$; $g_{av} = 1.981$) is attributed to a yet unidentified minor impurity, likely an alkoxytitanocene compound. A very broad asymmetric signal at about $g = 1.986$ ($\Delta H = 135$ G) occurring in solution belongs to a chloride-bridged dimer which in toluene glass displays a broad spectrum due to electronic triplet state with approximate axial symmetry ($g_{av} = 1.986$, $D = 0.0359$ cm^{-1}, $E = 0$). Such a spectrum was first described by Samuel et al. for [{Ti(μ-Cl)(η^5-C_5H_5)$_2$}$_2$] and [{Ti(μ-Cl)(η^5-C_5H_4Me)$_2$}$_2$] [11]. Later, a very similar spectrum was also reported for [{Ti(μ-Cl)(η^5-1,3-Me–$C_5H_3Me_2$)$_2$}$_2$] **7** [8]. At variance with the results for **7**, the ESR spectrum of **3** in toluene solution shows an additional broad signal at a low g-value ($g = 1.964$, $\Delta H = 13$ G) which undoubtedly belongs to a monomeric titanium(III) species, accomodating the unpaired electron in $1a_1$ orbital (cf. [9,12]). This assumption is supported by temperature dependence of

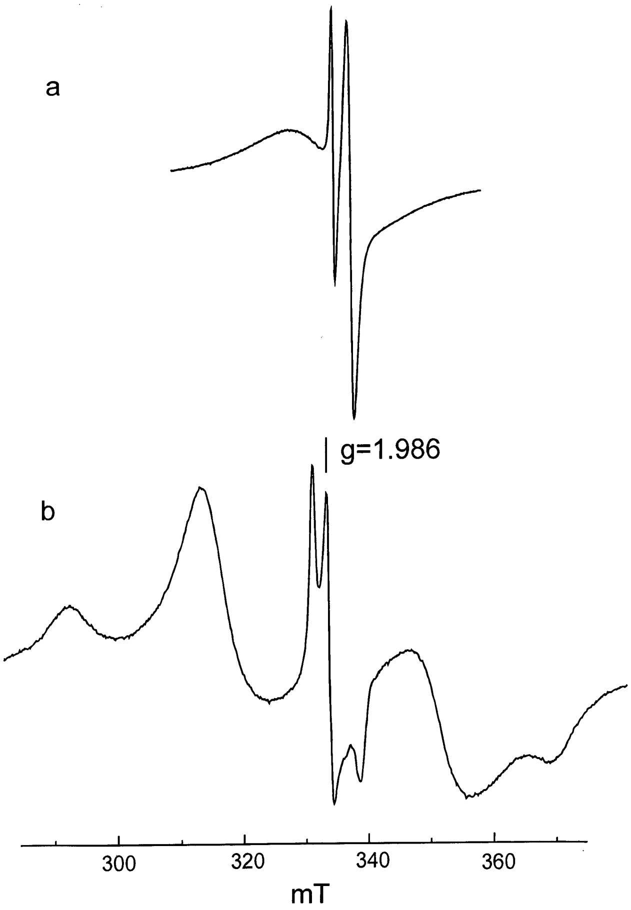
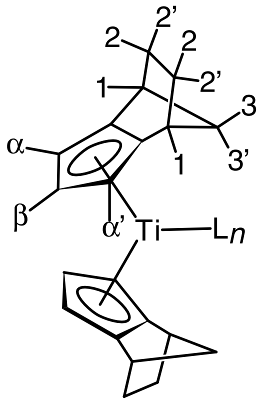


Fig. 1. ESR spectrum of **3** in toluene solution at room temperature (a) and in toluene glass at −140 °C (b).

this signal: it grows upon heating and diminishes on cooling. In toluene glass, no ESR spectrum of monomeric **3** is observed (highly anisotropic spectra of similar monomeric compounds are well known [9,12], see also ESR of **4**). The presence of a monomer in toluene solution implies that the titanium atom in **3** is more reluctant to associate into a dimer than that in **7** and hence, it is a weaker Lewis acid. A weaker Lewis acidity of **3** with respect to **7** is also manifested by a smaller zero field splitting value D (**3**, 0.0359 cm^{-1}; **7**, 0.0365 cm^{-1} [8]). As the distance between the unpaired electrons forming the electronic triplet state is inversely proportional to D [11], the distance R between the titanium atoms in **3** should be longer than in **7**. Though the agreement between R calculated from ESR spectra and crystallographic distance is only approximate because D depends also on further factors [11] and, in both cases, the D values were determined from the outermost features of the spectrum which were very difuse (Fig. 1b), for the iso-structural compounds **3** and **7** we can estimate that R(**3**) will be longer by about 0.02–0.03 Å than R(**7**). Since the crystallographic Ti–Ti distance for **7** was found to be 3.9155(8) Å, the Ti–Ti distance in **3** should amount to 3.93–3.95 Å. In 2-methyltetrahydrofuran (MTHF), compound **3** exhibits only a single ESR spectrum in both the solution ($g = 1.981$, $\Delta H = 4.0$ G, $a_{\mathrm{Ti}} = 12.1$ G) and MTHF glass ($g_1 = 2.000$, $g_2 = 1.985$, $g_3 = 1.961$; $g_{\mathrm{av}} = 1.982$), which is fully consistent with the presence of a monomer coordinating one solvent molecule [8,13].

A brick-red compound **4** forms an amorphous powder which dissolves in hexane, toluene or MTHF to give sky blue solutions showing an absorption band at 555 nm and a shoulder at 620 nm which are typical for monomeric, unsolvated titanocene monochlorides [12,14]. The solutions also display practically the same ESR spectra which are attributable to a monomeric species ($g = 1.962$, $\Delta H = 9.0$ G). Likewise, virtually the same ESR spectra indicative of a monomeric structure were observed in toluene and MTHF glasses ($g_1 = 2.000$, $g_2 = 1.986$, $g_3 = 1.899$; $g_{\mathrm{av}} = 1.962$) [8,12]. The anisotropy of the solid state spectra results from g_3 component of the g-tensor moving to low g-values with increasing electron density at the titanium atom [9]. According to the anisotropy, the η^5-TMSisodiCp ligand should induce electron density at the titanium centre higher than η^5-C_5HMe_4 ($g_3 = 1.910$) and lower than η^5-C_5Me_5 ($g_3 = 1.889$) [9] or η^5-$C_5Me_4(SiMe_3)$ ($g_3 = 1.893$) [14b] ligands. The reluctance of **4** to coordinate MTHF even at low temperature resembles the behaviour of $[TiCl(\eta^5\text{-}C_5Me_5)_2]$; a solution of $[TiCl(\eta^5\text{-}C_5Me_4H)_2]$ in MTHF glass contains an equilibrium (low) concentration of the adduct $[TiCl(\eta^5\text{-}C_5HMe_4)_2(MTHF)]$ [9]. The MS spectrum of **4** exhibits only the monomeric molecular ion at m/z 489 as the base peak which eliminates $SiMe_3$ group (40% abundance). In contrast to the temperature required for evaporation of **3** (210–220 °C) which also shows only a monomeric species in the gas phase, compound **4** evaporates at only 90 °C that is an expected evaporation temperature for monomeric titanocene monochlorides [14].

Diamagnetic compound **5** was obtained as a yellow crystalline material not suitable for single crystal X-ray investigation. The molecular peak in the EIMS spectrum at m/z 480 was found with only a very low intensity because such alkyne complexes tend to dissociate at elevated temperature, likely even prior to electron impact, giving titanocene and btmse. The IR spectrum and ^{1}H-, ^{13}C-, ^{29}Si- and ^{1}H-, ^{1}H-COSY NMR spectra are fully consistent with the expected C_2-symmetric titanocene structure with η^2-coordinated ligated btmse. The above NMR data are not sufficient to decide among various coordination modes of the isodiCp units to the metal centre (*exo–exo*, *endo–endo* and *exo–endo*) although the chemical shift values might be considered indicative of one of the alternatives. The stereochemistry has been assigned with the aid of NOESY spectra. The presence of NOESY cross peaks due to Hα–H3′, Hα–H2,2′ and H1–Me_3Si correlations which are not observed in COSY spectra on one hand and the absence of



Scheme 2.

a peak due to an H3′–H2 through space interaction on the other hand points to *exo* coordination of both isodiCp ligands as shown in Scheme 2. Whereas the δ_{C} and δ_{Si} values are unexceptional when compared to the data reported for **1** [2a] and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_{5-n}Me_n})_2(\eta^2\text{-btmse})]$ complexes ($n = 0$–5) [10], the δ_{H} values differ markedly in comparison with the parent dichloro complex **1**. Except for C*H*α and C*H*β, the signals of the aliphatic protons show a marked upfield shift of up to 3.4 ppm for H-3′ (δ_{H} −2.07) upon replacement of the two chloride ligands with η^2-btmse. Such a high shift is most likely caused by proximity of the respective hydrogen atoms to the anisotropically shielding coordinated alkyne or the metal centre.

Spectroscopic properties of compound **5** do not differ much from those found in the series of the $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_{5-n}Me_n})_2(\eta^2\text{-btmse})]$ complexes [10]. The electronic band at 980 nm falls into the range where these bands occur in the above series of compounds (without any apparent dependence on the number of the methyl groups). The δ_{C} chemical shift of the triple bond carbon atoms (247.2) is in between that for $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_2Me_3})_2(\eta^2\text{-btmse})]$ and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5HMe_4})_2(\eta^2\text{-btmse})]$ compounds, which hardly respects the electron donation ability of the particular cyclopentadienyl ligands. In the series of complexes $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_{5-n}Me_n})_2(\eta^2\text{-btmse})]$ ($n = 0$–5), the $\delta_{C}(\mathrm{C{\equiv}C})$ values increase with increasing n (244.8–248.5), however, the increments per one methyl group differ widely [10]. Thus, the strength of btmse coordination is most reliably reflected in the wavenumber of $\nu(\mathrm{C{\equiv}C})$ bond, moving in the above series of the $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_{5-n}Me_n})_2(\eta^2\text{-btmse})]$ compounds from 1662 $\mathrm{cm^{-1}}$ for $n = 0$ to 1598 $\mathrm{cm^{-1}}$ for $n = 5$ [10]. The value of 1628 $\mathrm{cm^{-1}}$ for **5** is practically identical with the value observed for $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_2Me_3})_2(\eta^2\text{-btmse})]$ and this is accordance with **3** possesing titanium centre of a lower Lewis acidity than **7**.

Compound **6** was obtained as yellow crystals highly soluble in hexane. Unlike **5**, ^{1}H-NMR spectrum of **6** shows no unusual chemical shifts for the protons of the bicyclic fragment: signals due to the methylene bridge are observed as characteristic multiplets at δ_{H} 0.25 and 1.18 whilst a multiplet due to ethano bridge appears at around δ_{H} 2.0. ^{13}C-NMR spectrum exhibits the resonance of the triple bond at 238.9. This is in keeping with the observed upfield shift induced by $\mathrm{SiMe_3}$ [15] or *ansa*-$\mathrm{SiMe_2}$ ring-substituents [16]. Hence, the $\nu(\mathrm{C{\equiv}C})$ wavenumber [**6**: 1610 $\mathrm{cm^{-1}}$] represents the only reliable probe into the nature of alkyne coordination. Thus, based on the $\nu(\mathrm{C{\equiv}C})$ vibration wavenumbers, the strength of btmse coordination increases in the series of compounds (wavenumber in parentheses): $[\mathrm{Ti}(\eta^5\text{-}1,3\text{-}\mathrm{C_5H_3Me_2})_2(\eta^2\text{-btmse})]$ (1657) < $[\mathrm{Ti}(\eta^5\text{-}1,2,3\text{-}\mathrm{Me{-}C_5H_2Me_3})_2(\eta^2\text{-btmse})]$ (1627) ≈ **5** (1628) < **6** (1610) ≈ $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5HMe_4})_2(\eta^2\text{-btmse})]$ (1609) < $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})_2(\eta^2\text{-btmse})]$ (1598) ≈ $[\mathrm{Ti}\{\eta^5\text{-}\mathrm{C_5Me_4(SiMe_3)}\}_2(\eta^2\text{-btmse})]$ (1595) [15] < *ansa*-$[\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})_2\mathrm{Ti}(\eta^2\text{-btmse})]$ (1585) [16].

2.1. Solid state structure of 6

Compound **6** crystallizes in tetragonal space group ($I4_1$/a) with eight molecules in the unit cell. Molecule of **6** is symmetrical with respect to a twofold axis passing the titanium atom and bisecting the coordinated triple bond (Fig. 2, see Table 1). The titanocene moiety has slightly staggered cyclopentadienyl rings with the bicyclic substituents oriented away from each other in such a way that they are close to open side whilst the trimethylsilyl groups are located close to the hinge position of the bent titanocene framework. The Cg–Ti–Cg′ (Cg, Cg′-centres of gravity of cyclopentadienyl rings of TMSisodiCp ligands) angle of 137.1(2)° and the

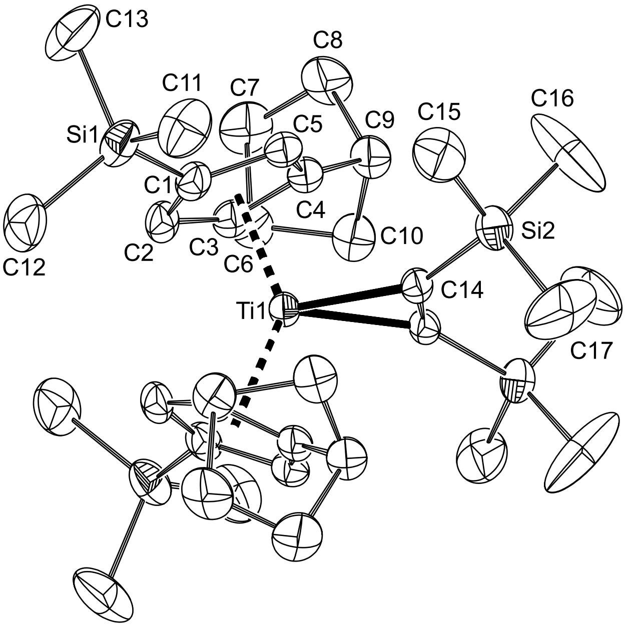


Fig. 2. The molecular structure of **6** with atom numbering scheme drawn at 30% probability level.

Table 1
Selected bond distances (Å) and bond angles (°) for **6**

Bond lengths			
Ti–Cg	2.089(5)	Ti–C(14)	2.138(4)
Ti–C(1)	2.360(5)	Ti–C(2)	2.430(4)
Ti–C(3)	2.465(4)	Ti–C(4)	2.419(4)
Ti–C(5)	2.384(5)	Si(1)–C_{Me} (av.)	1.862(7)
Si(1)–C(1)	1.867(5)	Si(2)–C_{Me} (av.)	2.391(2)
Si(2)–C(14)	1.858(4)	C(1)–C(2)	1.425(7)
C(1)–C(5)	1.446(6)	C(2)–C(3)	1.408(6)
C(3)–C(4)	1.410(6)	C(4)–C(5)	1.400(6)
C(3)–C(6)	1.500(7)	C(4)–C(9)	1.497(6)
C(6)–C(7)	1.553(7)	C(6)–C(10)	1.542(7)
C(7)–C(8)	1.544(8)	C(8)–C(9)	1.556(7)
C(9)–C(10)	1.532(7)	C(14)–C(14′) [a]	1.286(8)
Bond angles			
Cg–Ti–Cg′ [a]	137.1(2)	C(14)–Ti–C(14′) [a]	35.0(2)
Si(2)–C(14)–C(14′) [a]	135.8(2)	ϕ [b]	42.5(2)

[a] Symmetry transformation used to generate equivalent positions:$(1-x,\ 1/2-y,\ z)$.
[b] Dihedral angle subtended by the least-squares planes of the cyclopentadienyl rings.

angle subtended by the cyclopentadienyl least-squares planes, $\phi = 42.5(2)°$, indicate a steric congestion between the isodiCp ligands and between them and coordinated btmse. The angle values fall between those reported for [Ti(η^5-C_5Me_5)$_2$(η^2-btmse)] (**8**) (138.6 and 41.1°, [17]) and [Ti{C_5Me_4(4-C_6H_4F)}$_2$(η^2-btmse)] (**9**) (138.9(1) and 41.5(1)°, [18]) on one side and [Ti(η^5-C_5Me_4H)$_2$(η^2-btmse)] (**10**) (134.9 and 50.0°, [10]) on the other side. The Ti–Cg distance of 2.089(4) Å in **6** is, however, shorter than that of **8** (2.114(4) Å) and **9** (2.139(2) Å) and nearly identical with that of **10** (2.092(4) Å). The structure of the btmse ligand does not differ from that in other known titanocene complexes being planar with the angle Si(2)–C(14)–C(14′) of 135.8(2)°. The C(14)–C(14′) bonding distance of 1.286(8) Å is shorter than in **8**–**10** (1.303–1.309(5) Å) and, correspondingly, the bonding distance Ti–C(14) of 2.138(4) Å is slightly longer than in **8** (2.122(3) and 2.126(3) Å), **9** (2.114(2) and 2.121(2) Å) and **10** (2.106(3) Å). According to these distances compound **6** binds btmse less strongly than **8** although the angle ϕ in **8** is smaller than in **6** (41.1 vs. 42.5(2)°). The substituents on the cyclopentadienyl ligand, the $SiMe_3$ group and norbornane fragment, are declined from its least-squares plane in an outward direction: the Si(1) atom lies 0.414(5) Å away and the least-squares plane defined by C(3), C(4), C(6) and C(9) atoms subtends the angle of 169.2(4)°. This is very close to the values found in **1** (168.1 and 169.3°) [2c] and *exo*-[(η^5-isodiCp)Ti{(μ-Cl)$_2$AlCl_2}$_2$] (171.9°) [5].

3. Conclusions

Comparison of chemical and spectroscopic properties of the isodiCp compounds **3** and **5** with the analogous methylcyclopentadienyl derivatives indicates that the isodiCp ligand has a stronger electron donating effect

Table 2
Crystallographic data, data collection and structure refinement for **6**

Empirical formula	$C_{34}H_{56}Si_4Ti$
M (g mol^{-1})	625.1
Temperature (K)	293
Crystal system	Tetragonal
Crystal description	Orange fragment
Space group	$I4_1/a$ (No. 88)
a, b (Å)	13.069(5)
c (Å)	44.842(5)
V (Å^3)	7659(4)
Z	8
D_{calc} (g cm^{-3})	1.084
μ(Mo–K_α) (mm^{-1})	0.368
F(000)	2704
Crystal size (mm)	0.30 × 0.30 × 0.60
θ Range (°)	3.7–25.0
Data completeness (%)	95.0
Index ranges	$0 \le h \le 15$, $-10 \le k \le 10$, $0 \le l \le 53$
Measured diffractions	41,787
Unique diffractions	3255
Observed diffractions [a]	2217
Parameters	183
Final [Δ/σ]	< 0.001
w_1, w_2 [b]	0.0381, 15.8481
R, wR for observed diffractions (%) [c]	7.12, 14.0
R for all data (%) [c]	12.0
Goodness-of-fit for all data [d]	1.14
Residual electron density (e Å^{-3})	0.21, −0.27

[a] Diffractions with $I_o > 2\sigma(I_o)$.
[b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1 P)^2 + w_2 P]^{-1}$, where $P = 1/3[\max(F_o^2) + 2F_c^2]$.
[c] $R(F) = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|$, $wR(F^2) = [\Sigma\ (w(F_o^2 - F_c^2)^2)/(\Sigma\ w(F_o^2)^2)]^{1/2}$.
[d] Goodness-of-fit $= [\Sigma\ (w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

that the 1,3-dimethylcyclopentadienyl ligand. The comparisons in pairs of compounds **3**–**4** and **5**–**6** show that trimethylsilyl substituent remarkably increases electron density at the titanium atom, the extent of the effect depending on the property followed. For instance, the reactivity of **4** towards MTHF is comparable with that of [TiCl(η^5-C_5Me_5)$_2$] whereas the ν(C≡C) vibration of **6** is virtually equal to that of [Ti(η^5-C_5HMe_4)$_2$(η^2-btmse)]. Bulkiness of TMSisodiCp ligand does not hinder the coordination of btmse. However, steric demands of the trimethylsilyl group at the isodiCp ligand in cooperation with its net electron donating effect render the titanium centre in **4** less prone to associate into dimer and to coordinate donor solvents such as MTHF.

4. Experimental

4.1. General comments and methods

The reductions of **1** and **2** as well as the purification, handling and spectroscopic measurements of the products obtained thereof were performed in vacuo using all-sealed glass devices equipped with breakable seals, an EPR sample tube and a pair of quartz cuvettes ($d = 1.0$ and 10 mm; Hellma) for measurement of ESR and UV–vis spectra. The adjustment of single crystals into Lindemann glass capillaries for X-ray analysis, preparation of capillaries for MS analysis and preparation of KBr pellets for IR measurements were performed in a glovebox (mBraun) under purified nitrogen. Mass spectra were measured on a VG 7070E spectrometer at 70 eV. Samples in capillaries were introduced into the direct inlet under Ar. NMR spectra of **5** and **6** were recorded in C_6D_6 solutions on a Varian UNITY Inova 400 instrument (^{1}H, 399.95; ^{13}C, 100.58; ^{29}Si, 79.5 MHz) at 298 K. Chemical shifts (δ, ppm) were given relative to solvent signal (δ_H 7.15, δ_C 128.0) and relative to external tetramethylsilane standard (δ_{Si} 0). X-Band ESR spectra were registered on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) equipped with a magnet controlling and data acquisition CU1 unit (Magnettech, Berlin, Germany). g-Values were determined using an Mn^{2+} ($M_I = -1/2$ line) standard at $g = 1.9860$. Concentrations of paramagnetic compounds were estimated from integrated first-derivative spectra. An STT-3 variable temperature unit was used for the measurement in the range −130–+20 °C. UV–vis spectra were measured in the range 270–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). Infrared spectra in KBr pellets were recorded in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer.

4.2. Chemicals

Tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), C_6H_{14} and $C_6H_5CH_3$ were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene [(μ-η^5:η^5-$C_5H_4C_5H_4$){Ti(μ-H)(η^5-C_5H_5)}$_2$] [19]. Butyllithium (BuLi) in C_6H_{14} (1.6 M, Aldrich) was degassed, diluted with C_6H_{14} to 0.1 M concentration and distributed into ampoules under vacuum. Bis(trimethylsilyl)ethyne (btmse; Aldrich) was degassed and distributed into ampoules on a vacuum line. Complexes **1** [2a] and **2** [6] were obtained as described elsewhere.

4.3. Preparation of chloro-exo,exo-bis(η^5-isodicyclopentadienyl)titanium(III) (3)

Compound **1** (0.19 g, 0.5 mmol) was dissolved in THF (30 ml) and mixed with BuLi solution in C_6H_{14} (5 ml 0.1 M, 0.5 mmol) under vigorous stirring. After warming to 80 °C for 20 min, all solvents were evaporated under vacuum and the residue was washed out with a small amount of C_6H_{14} to remove some impurities. The remaining solid was extracted with $C_6H_5CH_3$ to give a brown solution, which yielded upon partial solvent removal and cooling complex **3** as brown crystals. Yield: 0.14 g (80%). M.p. 255 °C. EIMS (210–220 °C): m/z (relative abundance): 347 (41), 345 ([M/2]$^{+\bullet}$; 100), 307 (26), 305 (26), 281 (52), 279 (24), 253 (21), 213 (18), 211 (21), 198 (30), 187 (17), 185 (40), 176 (13), 163 (20), 150 (45), 91 (15), 83 (15). ESR ($C_6H_5CH_3$, 22 °C): three signals A–C; (A) $g = 1.980$, $\Delta H = 0.6$ mT; (B) very broad asymmetrical signal $g \approx 1.986$, $\Delta H \approx 13.4$ mT; (C) $g = 1.964$, $\Delta H = 1.3$ mT. ESR ($C_6H_5CH_3$, −140 °C): two overlapping spectra A and B; (A) $g_1 = 2.001$, $g_2 = 1.986$, $g_3 = 1.956$, $g_{av} = 1.981$; (B) triplet state spectrum, $g_\parallel = 2.000$, $g_\perp = 1.979$, $g_{av} = 1.986$, $D = 0.0359$ cm^{-1}, $E = 0$. ESR (MTHF, 22 °C): $g = 1.981$, $H = 0.37$ mT, $a_{Ti} = 1.21$ mT. ESR (MTHF, −140 °C): $g_1 = 2.000$, $g_2 = 1.985$, $g_3 = 1.961$, $g_{av} = 1.982$. UV–vis ($C_6H_5CH_3$): 480 ≫ 670 > 820sh > 1080sh nm. UV–vis (MTHF): 478 ≫ 680 (extending to longer wavelengths region) nm.

4.4. Preparation of chloro-exo,exo-bis(η^5-trimethylsilylisodicyclopentadienyl)titanium(III) (4)

Complex **2** (58 mg, 0.11 mmol) was reduced with Mg metal (3.0 mg, 1.25 mmol) in THF (5 ml) at 60 °C until the brown colour turned blue. Then the solution was rapidly evaporated under vacuum and the residue extracted with C_6H_{14}. Evaporation of the blue extract afforded **4** as a non-crystallizing pink–red powder. The same colour change is observed when the product is dissolved in $C_6H_5CH_3$ and evaporated. Yield of pink–red powder 43 mg (80%). EIMS (90 °C): m/z (relative abundance): 493 (9), 492 (21), 491 (53), 490 (48), 489

[M$^{+\bullet}$; 100], 488 (14), 487 (10), 474 ([M−Me]$^{+}$; 5), 257 (8), 73 (41), 59 (8). HR MS analysis: 489.16801, error < 1×10^{-3} for $C_{26}H_{38}ClSi_2Ti$. UV–vis (C_6H_{14}): 280 > 345 ≫ 555 > 620 (sh) nm. ESR ($C_6H_5CH_3$, 20 °C): $g = 1.9618(3)$, $\Delta H = 9.0$ G (impurity: $g = 1.9804$, $\Delta H = 2.4$ G). ESR ($C_6H_5CH_3$, −140 °C): $g_1 = 2.0004$, $g_2 = 1.9860$, $g_3 = 1.8986$, $g_{av} = 1.962$.

4.5. Preparation of η^2-bis(trimethylsilyl)ethyne-exo,exo-bis(η^5-isodicyclopentadienyl)titanium(II) (**5**)

A mixture of **1** (0.19 g, 0.5 mmol), Mg (12 mg, 0.5 mmol), btmse (0.2 ml, 0.9 mmol) and THF (15 ml) was sealed in an evacuated ampoule and heated to 60 °C until the red colour turned to yellow and all the Mg disappeared (ca. 16 h). All volatiles were evaporated under vacuum and the yellow residue was extracted with C_6H_{14}. The solution was concentrated and slowly evaporated over 2 days to afford a crop of well developped yellow crystals. Yield: 0.21 g (87%). M.p. 135 °C. EIMS (130 °C): *m*/*z* (relative abundance): 480 [M$^{+\bullet}$, ca. 0.1]; signals due to 'titanocene': 310 ([M−btmse]$^{+\bullet}$, 40), 295, 293, 281, 279, 278; ions due to btmse 170, 155 (100), 97, 73, 70, 45 (intensity varies during evaporation). ^{1}H-NMR: δ −2.07 (d of qi, 1H, $^2J_{HH} = 8.8$ Hz ($J_{33'}$), H-3′), −0.16 (s, 9 H, Me_3Si), 0.57 (dt, 1 H, $^2J_{HH} = 8.8$ Hz ($J_{33'}$), H-3), 1.67–1.77 (m, 4H, H-2,2′), 6.29 (d, 2H, $^3J_{HH} = 2.9$ Hz, Hα), 6.88 (d, 1H, $^3J_{HH} = 2.9$ Hz, Hβ). ^{13}C-NMR ($^2J_{CH}$ not read): δ 1.8 (q, $^1J_{CH} = 118$ Hz, Me_3Si), 30.3 (t, $^1J_{CH} = 133$ Hz, C-2), 41.8 (dd, $^1J_{CH} = 147$ Hz, C-1), 46.9 (tt, $^1J_{CH} = 133$ Hz, C-3), 111.6 (dt, $^1J_{CH} = 172$ Hz, *C*Hα), 116.2 (dt, $^1J_{CH} = 118$ Hz, *C*Hβ), 138.2 (s, C_{ipso}), 247.2 (s, η^2-$C{\equiv}C$). ^{29}Si DEPT: δ −15.9 (s, Me$_3$*Si*). IR (KBr, cm^{-1}): 3090 (w), 2963 (sh), 2945 (vs), 2923 (sh), 2892 (sh), 2861 (s), 1717 (sh), 1666 (sh), 1628 (s), 1444 (m), 1434 (m), 1392 (w), 1373 (w), 1285 (m), 1273 (w), 1240 (s), 1200 (vw), 1161 (vw), 1135 (m), 1114 (m), 1073 (w), 1020 (m), 975 (w), 947 (m), 913 (w), 855 (vs), 833 (vs), 780 (vs), 750 (s), 685 (m), 649 (m), 616 (w), 609 (m), 531 (m), 469 (sh), 462 (m). UV–vis (C_6H_{14}): 355 > 430 (sh) > 990 nm.

4.6. Preparation of η^2-bis(trimethylsilyl)ethyne-exo,exo-bis(η^5-trimethylsilylisodicyclopentadienyl)titanium(II) (**6**)

A mixture of **2** (0.26 g, 0.5 mmol), Mg (12 mg, 0.5 mmol), btmse (0.2 ml, 0.9 mmol) and THF (15 ml) was sealed in an ampoule and heated to 60 °C until the originally red colour of the mixture turned to yellow and all the Mg disappeared (ca. 6 h). Then, all volatiles were evaporated under vacuum and the yellow residue was extracted with C_6H_{14}. The solution was concentrated and cooled in refrigerator for 2 days to give a crop of yellow crystals. Yield: 0.24 g (78%). The crystals contain some uncoordinated btmse which is observed by IR band at 2134 cm^{-1}; upon m.p. measurement a liquid separated at 110 °C and the residue melted at 140 °C with decomposition. EIMS (130 °C): *m*/*z* (relative abundance) 456 (16), 455 (35), 454 ([M−btmse]$^{+\bullet}$; 57), 453 (13), 452 (11), 451 (7), 170 ([btmse]$^{+\bullet}$; 9), 157 (11), 156 (23), 155 ([btmse−Me]$^{+}$; 100), 73 (8). The ions of btmse were observed already at low temperature, before ions [M−btmse]$^{+\bullet}$ at *m*/*z* 454 occurred. ^{1}H-NMR (C_6D_6): δ −0.13, 0.03 (2 × s, 9H, SiMe_3); 0.25 (d of quintets, $^2J_{HH} = 8.3$, $^3J_{HH} = 1.8$ Hz, 1H, CH_2 bridge), 1.18 (dt, $^2J_{HH} = 8.3$, $^3J_{HH} = 1.7$ Hz, 1 H, CH_2 bridge), 1.94–2.05 (m, 4H, CH_2CH_2 bridge), 3.11 (s, 1H, C*H* bridgehead), 6.75 (s, 2H, η^5-C$_5$$H_2$). ^{13}C{^{1}H}-NMR ($C_6D_6$): δ 0.6, 3.2 (SiMe_3); 30.2 (*C*H$_2$*C*H$_2$ bridge), 42.1 (*C*H bridgehead), 49.7 (*C*H$_2$ bridge), 112.9 (η^5-C$_5$H$_2$, *C*H), 130.6, 146.8 (η^5-C$_5$H$_2$, C_{ipso}); 238.9 (η^2-$C{\equiv}C$). ^{29}Si-NMR (DEPT): δ −13.2 (η^2-btmse), −8.5 (C$_5$H$_2$*Si*Me$_3$). IR (KBr, cm^{-1}): 3091 (vw), 2981 (sh), 2952 (vs), 2921 (s), 2896 (s), 2867 (s), 1642 (sh), 1610 (s), 1576 (sh), 1471 (m), 1439 (s), 1398 (m), 1319 (m), 1285 (s), 1243 (vs), 1173 (vw), 1128 (w), 1115 (m), 1074 (s), 1021 (w), 947 (m), 937 (s), 902 (m), 843 (vs,b), 752 (vs), 686 (s), 656 (m), 632 (m), 622 (m), 536 (w), 449 (m), 409 (s).

4.7. X-ray crystallography

A fragment of a yellow platelet of **6** was mounted into Lindemann glass capillary in a glovebox under purified nitrogen. Diffraction data were collected on a Nonius KappaCCD image plate diffractometer at 293 K using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). One hundred and fifty frames were measured (0.5° ω oscillation and 30 s counting time each, 7158 integrated diffractions) and analysed with HKL program package [20]. The cell parameters were determined by least-squares fitting from 31 205 diffractions with $1.0 \le \theta \le 25.0°$.

The structure was solved by direct methods (SIR-97) [21] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic thermal motion parameters; the hydrogen atoms were included in calculated positions. Crystallographic data, details on data collection, and the structure refinement are given in Table 2.

5. Supplementary material

Relevant crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178473 for compound **6**. Copies of the information may be obtained free of charge from The Director, CCDC, 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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