Thermolysis of titanocene methyl compounds bearing *t*-butyl- and benzyltetramethylcyclopentadienyl ligands

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ABSTRACT

Elimination of methane during thermolysis of title compounds results in the formation of σ-Ti–C bond to *t*-butyl or benzyl group. The *t*-butyl-containing titanocene methyl compound [Ti(III)Me(η^5-C_5Me_4*t*-Bu)$_2$] (**5**) eliminates methane at 110 °C to give cleanly [Ti(III)(η^5:η^1-$C_5Me_4CMe_2CH_2$)(η^5-C_5Me_4*t*-Bu)] (**6**). The methyl derivative of analogous benzyl-containing titanocene [Ti(III)Me(η^5-$C_5Me_4CH_2Ph$)$_2$] was not isolated because it eliminated methane at ambient temperature to give [Ti(III)(η^5:η^1-$C_5Me_4CH_2$-*o*-C_6H_4)(η^5-$C_5Me_4CH_2Ph$)] (**7**) with one phenyl ring linked to titanium atom in *ortho*-position. The corresponding titanocene dimethyl compound [TiMe$_2${η^5-C_5Me_4*t*-Bu)}$_2$] (**9**) eliminates two methane molecules at 110 °C to give the singly tucked-in 1,1-dimethylethane-1,2-diyl-tethered titanocene [Ti{η^5:η^1:η^1-$C_5Me_3(CH_2)(CMe_2CH_2)$}(η^5-C_5Me_4*t*-Bu)] (**11**). In distinction, the analogous benzyl derivative [TiMe$_2$(η^5-$C_5Me_4CH_2Ph$)$_2$] (**10**) eliminates at 110 °C only one methane molecule to afford [TiMe(η^5:η^1-$C_5Me_4CH_2$-*o*-C_6H_4)(η^5-$C_5Me_4CH_2Ph$)] (**12**) containing one phenyl group attached to titanium in *o*-position and one methyl group persisting on the titanium atom. This compound is stable at 150 °C for at least 3 h. The crystal structures of **5**, **6**, **7**, and **10** were determined.

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1. Introduction

Decamethyltitanocene chemistry was thoroughly investigated very early by Brintzinger and Bercaw [1], and later succeeded by Teuben and co-workers [2]. Thermal treatment of the dimethyl compound [TiMe$_2$(η^5-C_5Me_5)$_2$] afforded subsequently the singly tucked-in methyl derivative [TiMe{η^5:η^1-$C_5Me_4(CH_2)$}(η^5-C_5 Me$_5$)] (**1a**) [1a,b,d], and at higher temperature the doubly tucked-in permethyltitanocene [Ti{η^4:η^3-$C_5Me_3(CH_2)_2$}(η^5-C_5Me_5)] (**1b**) [2a]. The monomethyl compound [Ti(III)Me(η^5-C_5Me_5)$_2$] gave cleanly the singly tucked-in paramagnetic [Ti(III){η^5:η^1-$C_5Me_4(CH_2)$}-(η^5-C_5Me_5)] compound (**1c**) [1a,b,2c,3], another precursor for **1b** [2a] (Scheme 1).

A minimum change in substituents of the cyclopentadienyl ring, e.g., replacement of one methyl group with hydrogen, trimethyl-silyl or phenyl group led to mostly surprising thermolytic results. Thermolysis of [TiMe$_2$(η^5-C_5HMe_4)$_2$] afforded cleanly the singly tucked-in methyl derivative [TiMe{η^5:η^1-$C_5HMe_3(CH_2)$}(η^5-C_5 HMe$_4$)] (**2a**), however, its further thermolysis did not give an isolable yield of doubly tucked-in compound [Ti{η^4:η^3-C_5HMe_2 $(CH_2)_2$}(η^5-C_5HMe_4)] (**2b**). Compound **2b** was obtained from

boiling of the [TiCl$_2$(η^5-C_5HMe_4)$_2$]/LiAlH$_4$ mixture [4a] or by thermolysis of [Ti(η^2-Me$_3$SiC≡CSiMe$_3$)(η^5-C_5HMe_4)$_2$] albeit in low yields [4b]. The monomethyl compound [TiMe(η^5-C_5HMe_4)$_2$] eliminated methane under the exclusive formation of para-magnetic dimer (**2c**) (Scheme 2) [4c].

Compound [TiMe$_2$(η^5-$C_5Me_4SiMe_3$)$_2$] easily eliminated two molecules of methane at only 90 °C to give singly tucked-in and silylmethylene-tethered compound **3a** whereas [Ti(III)Me(η^5-$C_5Me_4SiMe_3$)$_2$] gave at the same temperature the silylmethylene-tethered product **3b** (Scheme 3) [5].

The phenyl-modified dimethyltitanocene [TiMe$_2$(η^5-C_5Me_4 Ph)$_2$] afforded a mixture of stereoisomers [TiMe(η^5-C_5Me_4Ph){η^5: η^1-$C_5Me_3Ph(CH_2)$}] (**4a**) which at higher temperature gave a mixture of singly tucked-in [Ti(η^5-C_5Me_4Ph){η^5:η^1-$C_5Me_3Ph(CH_2)$}] (**4c**) and among other minor products the doubly tucked-in titanocene [Ti(η^5-C_5Me_4Ph){η^4:η^3-$C_5Me_2Ph(CH_2)_2$}] (**4b**) (Scheme 4) [6].

In contrast to the above mentioned substituents, the phenyl group did not participate in hydrogen abstraction reactions due to its orientation close to the cyclopentadienyl ring plane, which precludes the phenyl group to approach the thermally excited Ti–Me bonds.

Here we investigate the thermolytic behavior of permethyltit-anocene mono- and dimethyl derivatives modified by replacing one methyl group on each cyclopentadienyl ring with *t*-butyl or

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Scheme 1.

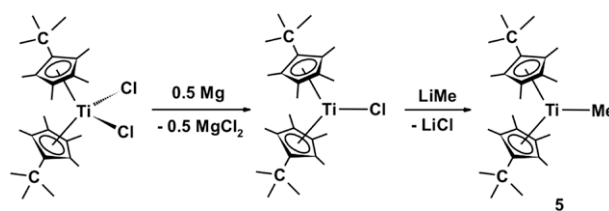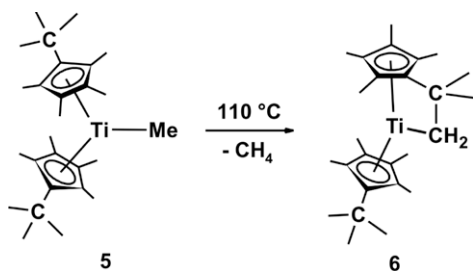**Scheme 2.**

Scheme 3.

Scheme 4.
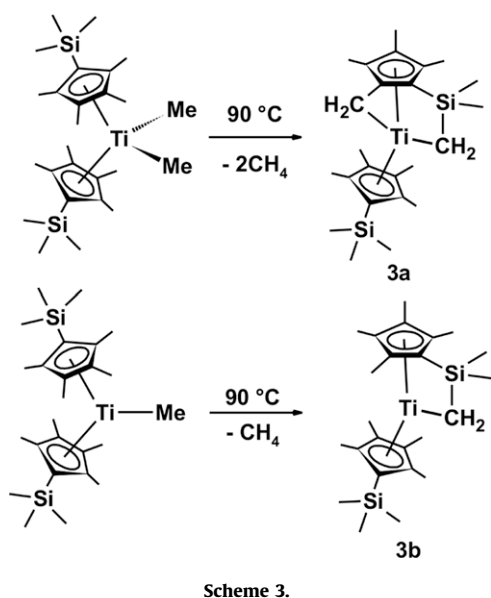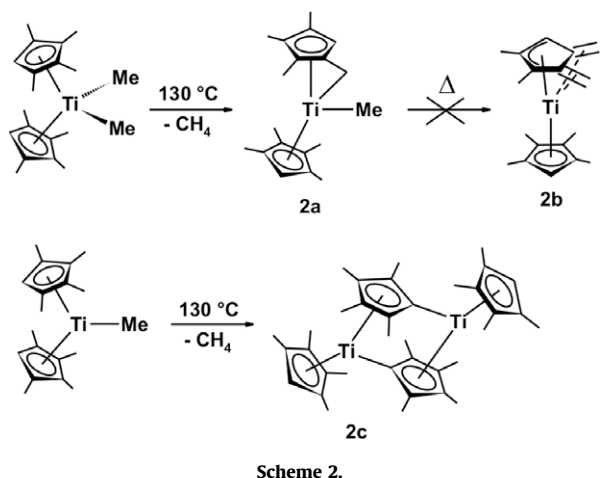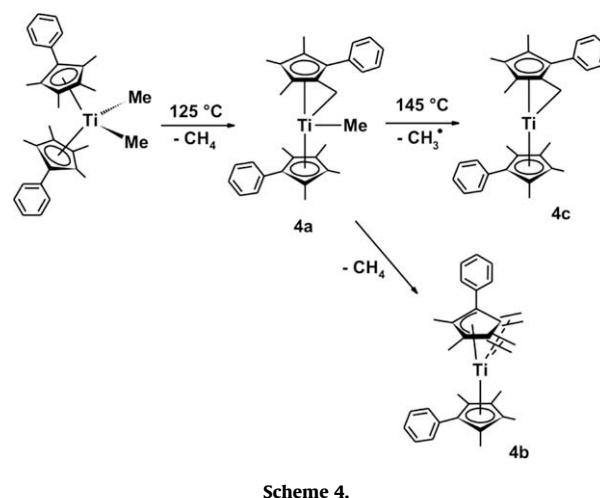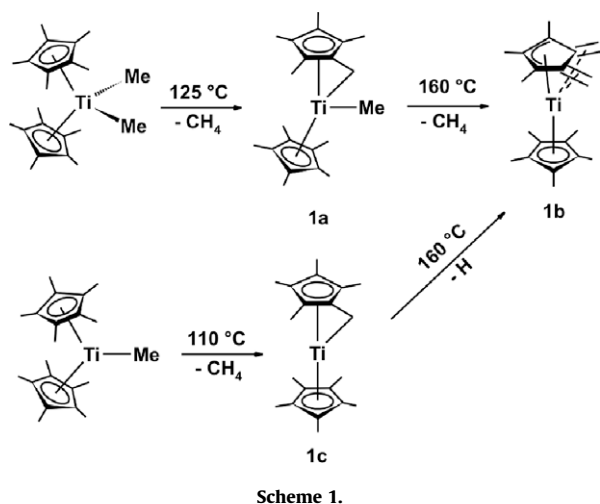
benzyl substituent with the aim to see their reactivity toward thermally excited titanium-methyl moieties.

2. Results and discussion

The *t*-butyl-containing titanocene monomethyl compound [Ti(III)Me(η^5-C_5Me_4t-Bu)$_2$] (**5**) was prepared from the dichloride [7] via its reduction with a half molar equivalent of magnesium followed by salt metathesis of the monochloride [Ti(III)Cl(η^5-C_5Me_4 t-Bu)$_2$] with methyl lithium (LiMe) (Scheme 5).

The metathesis reaction was carried out using solid LiMe in hexane, where LiMe was nearly insoluble. Because of heterogeneity of the reaction system a large molar excess of solid LiMe was used and the mixture was magnetically stirred and hand shaken until the blue color of the chloride turned to the dark green color of **5**. Compound **5** is paramagnetic, giving a broad signal ($\Delta H = 14$ G) at $g = 1.955$ similar to the signals of [Ti(III)Me(η^5-C_5Me_5)$_2$] [2b,8], [Ti(III)Me(η^5-$C_5Me_4SiMe_3$)$_2$] [4], [Ti(III)Me(η^5-C_5HMe_4)$_2$] [**4c**] or [Ti(III)CH_2CMe_3(η^5-C_5Me_5)$_2$] [2b]. Its electronic absorption spectrum was characterized by two absorption bands in visible region close to the band positions for the above mentioned alkyl titanocenes [2c,5,8]. The molecular structure of **5** was determined by single crystal X-ray diffraction analysis (see below). Heating a toluene solution of **5** to 110 °C resulted in only a slight color change and evolution of a gas. A greenish brown crystalline product **6** was isolated from hexane in nearly quantitative yield. The EPR and electronic absorption spectra of **6** were similar to those of **5**, however, the EI-MS spectra for **6** were different from those for **5** showing the base peak m/z 401 to be the molecular ion whereas the base peak for **5** was the fragment ion $[M–Me]^+$ m/z 402. The X-ray diffraction analysis revealed that **6** is [Ti(III)(η^5:η^1-C_5Me_4C-Me_2CH_2)(η^5-C_5Me_4t-Bu)] with one cyclopentadienyl ring linked to the titanium atom via the 1,1-dimethylethane-1,2-diyl tether (see Scheme 6). Compound **6** can be considered to be thermally extremely stable as it was recovered unchanged after heating to 160 °C.
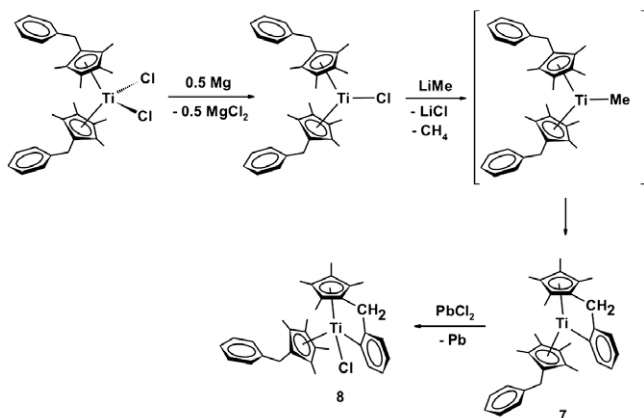

Scheme 5.

Scheme 6.

Following the procedure for synthesis of **5** an attempt was made to prepare the analogous benzyl-containing derivative [Ti(III)-Me(η^5-$C_5Me_4CH_2Ph)_2$]. The monochloride [Ti(III)Cl(η^5-C_5Me_4 $CH_2Ph)_2$] was obtained by stoichiometric reduction of the dichloride [TiCl$_2$(η^5-$C_5Me_4CH_2Ph)_2$] [9] with a half molar equivalent of magnesium as a non-crystallizing waxy solid, and therefore was characterized only by spectroscopic methods. Its salt metathesis with solid LiMe afforded a brown single product **7** crystallizing as aggregates of thin leaves. A considerable amount of gas evolved during the reaction and the base peak m/z 469 of the EI-MS spectrum of **7**, however, indicates that the salt metathesis reaction is accompanied by methane elimination. Whereas EPR and UV–Vis spectra could not safely distinguish between [Ti(III)Me(η^5-$C_5Me_4CH_2Ph)_2$] and the product of its demethanation the X-ray crystal structure of **7** (see below) revealed that it is the latter, [Ti(III)(η^5:η^1-$C_5Me_4CH_2$-o-C_6H_4)(η^5-$C_5Me_4CH_2Ph$)] (**7**), containing one benzyl substituent linked to the titanium atom by $ortho$-carbon of its phenyl ring. This indicates that [Ti(III)Me(η^5-$C_5Me_4CH_2Ph)_2$] was unstable at ambient temperature, and the leaving methyl group abstracted selectively one hydrogen atom from $ortho$-position of one phenyl ring. Compound **7** was similarly to **6** thermally stable to 170 °C in m-xylene solution. The structure of **7** was in agreement with ^{1}H and ^{13}C NMR spectra of the bright orange product of its chlorination with PbCl$_2$, [Ti(IV)Cl(η^5:η^1-$C_5Me_4CH_2$-o-C_6H_4)(η^5-$C_5Me_4CH_2Ph$)] (**8**) (Scheme 7).

Compound **8** possesses C_1 molecule symmetry, where one cyclopentadienyl unit is tethered to the titanium atom via a CH$_2$-o-C_6H_4 three-carbon atom spacer. The ^{13}C NMR signal of the phenylene carbon atom linked to titanium appears at 199.00 ppm, close to the resonances for similar compounds. For example, the σ-Ti–C_{ipso}(phenyl) resonates typically in the δ_C 190–194 ppm region [10], and in the cationic complex [Ti(η^5:η^1-$C_5H_4CMe_2$-o-C_6H_4)(η^5-C_5H_5)]$^+$ at 208.0 ppm [11]. Binding of the phenyl group in $ortho$-position follows from DFT calculations on the latter complex [11] as well as from the crystal structure of **7**. The presence of

stereogenic titanium centre in **8** gives rise to eight signals for the C_5Me_4 groups in ^{1}H and ^{13}C NMR spectra, and diastereotopic protons of both methylene units generate a system of two pairs of doublets. A close proximity of the stereogenic centre to the tethered CH_2-o-C_6H_4 methylene induced a considerably larger separation of resonances compared to those of methylene signals of the untethered benzyl group (CH_2-o-C_6H_4: δ_H ($^2J_{HH}$) 3.71, 3.85 ppm (16.2 Hz); CH_2Ph: δ_H ($^2J_{HH}$) 3.35, 3.40 (16.5 Hz)).

The respective titanocene dimethyl compounds [TiMe$_2$(η^5-C_5Me_4t-Bu)$_2$] (**9**) and [TiMe$_2$(η^5-$C_5Me_4CH_2Ph)_2$] (**10**) were also obtained by the salt metathesis of the dichlorides [TiCl$_2$(η^5-C_5 Me_4t-Bu)$_2$] [7] and [TiCl$_2$(η^5-$C_5Me_4CH_2Ph)_2$] [9] with the solid LiMe. In this case, a complete exchange of chlorine ligands for methyl groups has to be ensured. To accomplish this, a mixture of the dimethyl and methylchloro derivatives obtained after the first salt metathesis reaction was treated once more with fresh solid LiMe.

Compound **9** in toluene was heated to 110 °C for 5 h to give a dark green solution from which a waxy solid extremely well soluble in hexane was obtained. This circumstance prevented its purification by crystallization, and thus all the bulk product was investigated by NMR methods. The C$_6$D$_6$ solution of the product displayed a rather complicated signal pattern in both ^{1}H and ^{13}C spectra. Nevertheless, the presence of two characteristic doublets at −3.28 and −1.06 ppm ($^2J_{HH}$ = 9.9 Hz) and combination of NMR techniques (APT, gCOSY, gHMBC) allowed us to identify the most abundant compound. The above mentioned strongly upfield signals were typical for the methylene group TiCH$_2$CMe$_2$ of a metallacycle formed by the hydrogen atom abstraction from one t-Bu group residing on cyclopentadienyl ring. The corresponding ^{13}C signal of the methylene was found at 55.14 ppm. The similar features are known from ^{1}H and ^{13}C NMR spectra of complexes [TiPh(η^5:η^1-$C_5H_4CMe_2CH_2$)(η^5-C_5H_4t-Bu)] (TiCH$_2$: δ_H ($^2J_{HH}$)/δ_C: −1.94, −0.08 ppm (10.5 Hz)/57.6 ppm) [10] and [Ti(CH$_2$CMe$_3$)(η^5: η^1-$C_5H_4CMe_2CH_2$)(η^5-C_5H_4t-Bu)] (TiCH$_2$: δ_H ($^2J_{HH}$)/δ_C: −2.60, −0.02 ppm (9.3 Hz)/46.8 ppm) [12]. The CMe$_2$ group gave rise to two sets of signals for diastereotopic methyl groups in both ^{1}H and ^{13}C NMR spectra (CMe$_2$ δ_H/δ_C: 1.30, 1.42 ppm/29.28, 32.05 ppm) and a signal at δ_C 36.38 ppm for its quaternal carbon. The other t-Bu group remained unactivated as evidenced by only one signal for its methyl groups in both ^{1}H and ^{13}C NMR spectra (CMe_3 δ_H/δ_C: 1.16 ppm/32.65 ppm; CMe_3 δ_C: 35.59 ppm). In addition, the presence of ring exo-methylene TiCH$_2$ group was established on the basis of gCOSY and APT spectra. The data for TiCH$_2$ δ_H/δ_C: 0.89, 1.21 ppm/77.00 ppm are close to those for tucked-in **1a**, **2a**, **3a**, and **4a** complexes (see Schemes 1–4) and a number of other singly and doubly tucked-in titanocene complexes [13]. It follows from the above arguments that the main product of the thermolysis of **9** is the single tucked-in, 1,1-dimethylethane-1, 2-diyl-tethered titanocene [Ti{η^5:η^1:η^1-$C_5Me_3(CH_2)(CMe_2CH_2)$} (η^5-C_5Me_4t-Bu)] (**11**) (Scheme 8), a carbon analogue of the known complex **3a** whose crystal structure was determined by X-ray diffraction analysis [5].
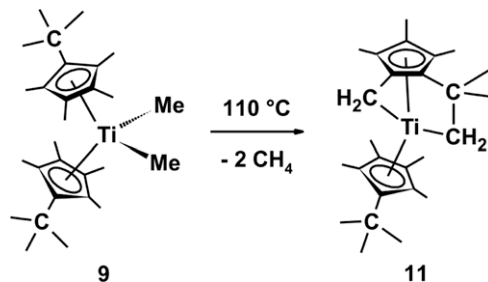
Scheme 7.
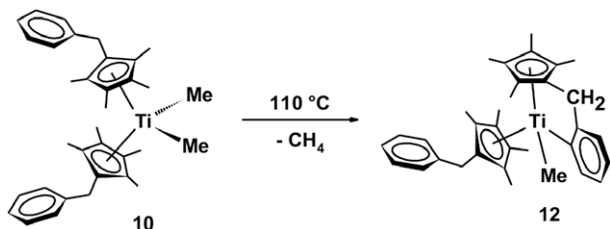
Scheme 8.

Scheme 9.

Heating of **10** in toluene to 110 °C for 12 h did not result in an observable change of its yellow color, however, replacement of toluene with hexane followed by attempted crystallization afforded a yellow non-crystallizing solid apparently different from **10**. Its ^{1}H and ^{13}C NMR spectra revealed that **10** was completely converted to the new compound [TiMe(η^5:η^1-C$_5$Me$_4$CH$_2$-o-C$_6$H$_4$)(η^5-C$_5$Me$_4$CH$_2$Ph)] (**12**) containing one phenyl group attached to titanium in ortho-position and one methyl group preserved on the titanium atom (Scheme 9).

The presence of TiMe group (δ_H/δ_C: 0.10 ppm/54.63 ppm) was unambiguously confirmed by gHSQC, and a highly downfield shifted signal at 196.33 ppm was assigned to C$_{ipso}$ of the TiCH$_2$-o-C$_6$H$_4$ fragment, close to the analogous resonance for compound **8**. Interaction of the Ti–C$_{ipso}$(phenyl) with the tether methylene group (δ_H/δ_C: 3.53, 3.64 ppm/33.37 ppm) was corroborated by gHMBC. The methylene group bearing an unattended phenyl ring appeared as a singlet (δ_H/δ_C: 3.46 ppm/ 34.22 ppm) contrary to the pair of doublets in **8**, presumably due to a lower anisotropic effect of the Ti–Me moiety with respect to the Ti–Cl effect in **8**. Nevertheless, ^{1}H and ^{13}C NMR spectra of **12** are very similar to those of **8** except for the Ti–Me resonances. The composition of **12** was further corroborated by its EI-MS spectra showing an easy elimination of methyl group to give the very stable ion [**7**]$^+$ which further fragmenated similarly as in the EI-MS spectra of **7**. Surprisingly, compound **12** is thermally very robust being recovered unchanged after heating in m-xylene to 150 °C for 3 h.
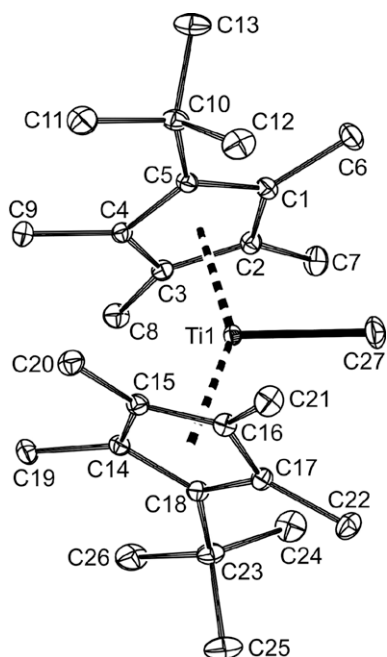
2.1. Molecular structures of 5 and 6

Compounds **5** and **6** are paramagnetic Ti(III) titanocene carbyl complexes where the methyl and 1,1-dimethylethane-1,2-diyl, respectively, are σ-bonded to titanium (see Figs. 1 and 2, respectively).

The selected geometric data for **5** and **6** (Table 1) demonstrate differences in the pseudotrigonal coordination of the titanium atom. Molecule of **5** shows a non-crystallographic symmetry with respect to the Ti–C(27) bond and the absence of slippage or tilting of the cyclopentadienyl rings as it follows from virtually equivalent Ti–Cg and Ti–Pl distances (Cg – centroid of and Pl – least-square plane of the cyclopentadienyl ring). The t-butyl groups occupying opposite side carbon atoms of the cyclopentadienyl rings in bent titanocene skeleton do not impose additional steric hindrance. The Ti–Cg distance of 2.0961(6) Å is longer than that for [Ti(III)-Me(η^5-C$_5$Me$_4$SiMe$_3$)$_2$] (av. 2.080(1) Å) [5] and other simple [Ti(III)-X(η^5-C$_5$Me$_5$)$_2$] derivatives (X = more electronegative element than carbon) [14], and close to that of [Ti(III)CH$_2$CMe$_3$(η^5-C$_5$Me$_5$)$_2$] (av. 2.099(6) Å) [2b]. The Ti–C(27) bond length of 2.1731(15) Å is slightly shorter than the analogous bond in [Ti(III)Me(η^5-C$_5$-Me$_4$SiMe$_3$)$_2$] (2.213(2) Å) [5] and [Ti(III)CH$_2$CMe$_3$(η^5-C$_5$Me$_5$)$_2$] (2.231(5) Å [2b]. The Cg(1)–Ti–Cg(2) angle of 146.63(3)° is one of the largest angles known for permethyltitanocene(Ti(III))

Fig. 2. PLATON drawing of **6** with 30% probability ellipsoids and atom numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for **5** and **6**.

Compound	5	6
Bond lengths		
Ti–Cg(1)[a]	2.0961(6)	2.0225(12)
Ti–Cg(2)[a]	2.0962(6)	2.0354(13)
Ti–Pl(1)[b]	2.0959(2)	2.0158((5)
Ti–Pl(2)[b]	2.0962(6)	2.0352(4)
Ti–C(X)[c]	2.1731(15)	2.210(4)
Angles		
Cg(1)–Ti–Cg(2)[a]	146.63(3)	152.17(5)
Cg(1)–Ti–C(X)[c]	106.60(5)	93.94(10)
Cg(2)–Ti–C(X)[c]	106.77(5)	112.49(10)
φ[d]	34.35(5)	23.46(9)

[a] Cg(1) denotes the centroid of the C(1–5) cyclopentadienyl ring, and Cg(2) is the centroid of the C(14–18) cyclopentadienyl ring.
[b] Pl(1) denotes the least-squares plane of the C(1–5) cyclopentadienyl ring, and Pl(2) is the least-squares plane of the C(14–18) cyclopentadienyl ring.
[c] C(X) is C(27) for **5**, and C(11) for **6**.
[d] Dihedral angle between Pl(1) and Pl(2).

Fig. 1. PLATON drawing of **5** with 30% probability ellipsoids and atom numbering scheme.

compounds, comparable to that of [Ti(III)Me{η^5-C$_5$Me$_4$(SiMe$_3$)}$_2$] (145.94(2)°) [5] and smaller only compared to 152.3° and 152.0° for the two molecules of [Ti(III)H(η^5-C$_5$Me$_5$)$_2$] [15]. Accordingly, the pairs of cyclopentadienyl methyl groups residing at hinge position of the bent titanocene C(8)/C(9) and C(19)/C(20) and the methyl groups C(6) and C(22) being close to the methyl C(27) were deviated from the least-squares planes of the cyclopentadienyl rings by only 0.221–0.294(2) Å away from titanium. Such values indicate a very low steric hindrance for bent permethyltitanocene compounds.

Conversion of one *t*-Bu group into a tether with the methylene carbon atom C(11) σ-bonded to titanium in **6** causes shortening of Ti–Cg distances and a slight elongation of the Ti–C(11) bond compared to the Ti–C(27) bond in **5**. The tethered cyclopentadienyl ring is slightly tilted with respect to normal to the Ti–Cg(1) vector, and this causes yet larger opening of the Cg(1)–Ti–Cg(2) angle (see Table 1). A relief of steric hindrance between the hinge methyl groups results in a decrease of their deviations from the least-squares planes to a maximum of 0.182(5) Å for C(7). On the other hand, the strain in the tether is revealed by deviation of the quaternary carbon atom C(10) from the least-squares plane of the cyclopentadienyl ring toward titanium by as much as 0.467(5) Å, and by valence angles C(5)–C(10)–C(11) 96.1(3)° and C(10)–C(11)–Ti 100.2(2)°, markedly low for sp^3 carbon atoms. In this respect, the unusually long C(10)–C(11) bond length of 1.596(5) Å is apparently also caused by the tether strain. The isopropylidene methyl carbon atoms C(12) and C(13) sterically hinder with their neighbours on the ring C(6) and C(9) inducing large valence angles C(5)–C(1)–C(6) and C(5)–C(4)–C(9) equally 129.2(3)°. A similar effect of the *t*-butyl group minimizing its steric hindrance by putting one carbon atom close to the least-squares plane of the cyclopentadienyl ring is observed for the untethered cyclopentadienyl ligand (C(18)–C(17)–C(22) 130.1(3)°) of **5** and for all the so far known titanocene compounds with this ligand [7].

2.2. Molecular structures of **7** and **10**

The PLATON drawing of molecule 1 of the two independent molecules in the unit cell of **7** is shown in Fig. 3.

The main geometric parameters for molecules 1 and 2 (Table 2) show that differences between them arise from crystal packing demands, and can be neglected in the structure discussion, referring
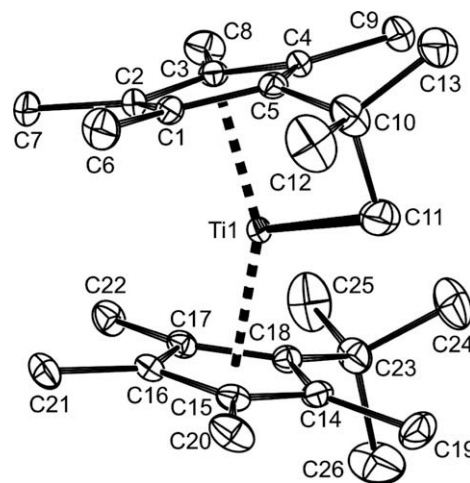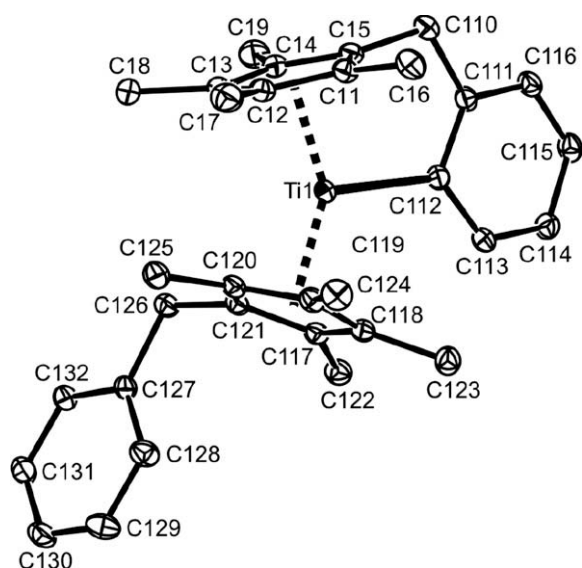

Fig. 3. PLATON drawing of molecule 1 of **7** with 30% probability ellipsoids and atom numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for two independent molecules of **7**.

	Molecule 1	Molecule 2
Bond lengths		
Ti–Cg(1)[a]	2.0577(16)	2.0494(16)
Ti–Cg(2)[a]	2.0828(15)	2.0704(16)
Ti–Pl(1)[b]	2.0514(15)	2.0429(14)
Ti–Pl(2)[b]	2.0818(14)	2.0701(15)
Ti–C(X)[c]	2.263(3)	2.257(3)
Angles		
Cg(1)–Ti–Cg(2)[a]	141.40(6)	141.50(7)
Cg(1)–Ti–C(X)[c]	104.09(10)	104.48(10)
Cg(2)–Ti–C(X)[c]	114.49(10)	113.78(10)
φ[d]	35.96(14)	35.08(12)
ψ[e]	87.87(10)	88.94(10)

[a] Cg(1) denotes the centroid of the C(11–15) cyclopentadienyl ring for molecule 1, and C(21–25) for molecule 2; Cg(2) is the centroid of the C(117–121) cyclopentadienyl ring for molecule 1 and C(217–221) for molecule 2.
[b] Pl(1) denotes the least-squares plane of the C(11–15) cyclopentadienyl ring for molecule 1, and C(21–25) for molecule 2; Pl(2) is the least-squares plane of the C(117–121) cyclopentadienyl ring for molecule 1 and C(217–221) for molecule 2.
[c] C(X) is C(112) for molecule 1, and C(212) for molecule 2.
[d] Dihedral angle between Pl(1) and Pl(2).
[e] Dihedral angle between the least-squares plane of the phenyl C(111–116) and Pl(1) for molecule 1, and the least-squares plane of the phenyl ring C(211–216) and Pl(1) for molecule 2.

to molecule 1 only. The tether phenyl ring, situated nearly perpendicular to the cyclopentadienyl ring planes, brings about a larger steric congestion to the bent titanocene moiety than the methyl group in **5**. It results in a smaller Cg(1)–Ti–Cg(2) angle and a larger deviation of methyl groups in hinge position from the least-squares planes of the cyclopentadienyl rings (max. 0.363(5) Å for C(125)) Å. Compared with the two-carbon atoms tether of **6** the three-carbon atom tether of **7** causes a less discernible steric strain. The benzyl carbon atom C(110) lies almost exactly in the least-squares plane of the tethered cyclopentadienyl ring, and the angle C(15)–C(110)–C(111) of 110.8(3)° is close to the theoretical value for sp^3 carbon atom. The valence angles at the *ipso*-carbon atom C(110)–C(111)–C(116) and C(110)–C(111)–C(112) as well as the C(111)–C(112)–Ti(1) angle are virtually equal (118.5–118.7(3)°) and the Ti(1)–C(112) bond length of 2.263(3) Å falls into the range of Ti–C≡ distances in permethyltitanocenes with one cyclopentadienyl ring tethered to titanium with a 3-membered C≡C–C chain [16]. The presence of some strain in the phenyl ring is indicated by a large Ti(1)–C(112)–C(113) angle of 127.3(2)° and a small C(111)–C(112)–C(113) angle of 113.8(3)°.

The PLATON drawing for **10** is shown in Fig. 4 and important molecular parameters are given in Table 3.

The pseudotetrahedral coordination at the titanium atom further decreased the Cg(1)–Ti–Cg(2) angle (138.50(4)°) and the steric strain at the hinge position of the cyclopentadienyl ligands led to a yet larger deviation of methyl carbon atoms from the least-squares planes of the cyclopentadienyl rings (max. 0.412(4) Å for C(8)). The dimethyltitanium plane C(33)–Ti–C(34) is close to bisect the Cg(1)–Ti–Cg(2) angle, and is almost perpendicular to it. Whereas the Cg–Ti distances are slightly elongated with respect to those in **5** the Ti–methyl carbon bond lengths are comparable. The C(33)–Ti–C(34) angle of 88.20(10)° is very close to the Cl–Ti–Cl in e.g., [TiCl$_2$(η^5-C$_5$Me$_4$*t*-Bu)$_2$] (88.9(1)°), where also the Cg(1)–Ti–Cg(2) angle 138.04(3)° is approaching the value found for **10** [7].

2.3. Conclusions

Whereas the decamethyltitanocene mono- and dimethyl compounds upon thermolysis eliminate methane under formation of tucked-in titanocene derivatives (Scheme 1) the hydrogen- or tri-
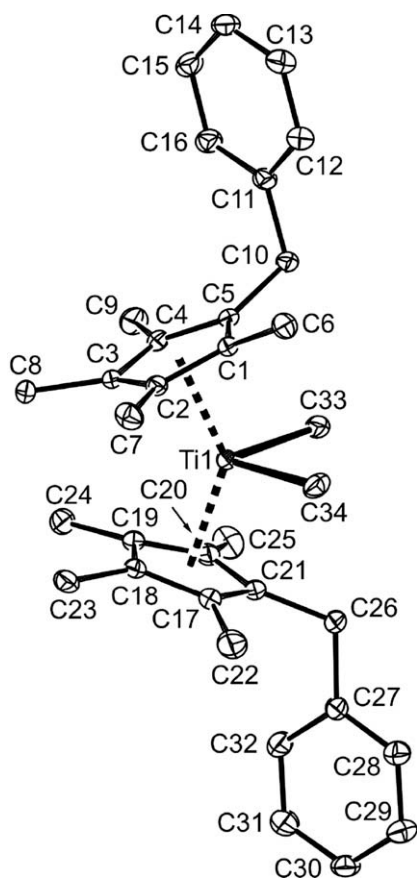
Fig. 4. PLATON drawing of **10** with 30% probability ellipsoids and atom numbering scheme.

Scheme 10.

methylsilyl-containing analogs showed various thermolytic reactions with activation of both, the cyclopentadienyl methyl groups and the above mentioned H or SiMe$_3$ moieties (Schemes 2 and 3). In distinction, the phenyl substituent was not activated because of its remoteness from the leaving methyl groups (Scheme 4). Concerning the reactivity of t-Bu group, it has been previously established that leaving phenyl ligand in [TiPh$_2$(η^5-C$_5$H$_4$t-Bu)$_2$] abstracts hydrogen from t-Bu group on otherwise non-substituted cyclopentadienyl ligand to give [TiPh(η^5-C$_5$H$_4$-t-Bu)(η^5:η^1-C$_5$H$_4$-CMe$_2$CH$_2$)] [10], and analogous titanocene dineopentyl complex at the onset of its formation eliminates neopentane yielding the

Table 3
Selected bond lengths (Å) and angles (°) for **10**.

| Bond lengths			
Ti–Cg(1)[a]	2.1296(10)	Ti–Cg(2)[a]	2.1402(10)
Ti–Pl(1)[b]	2.1295(4)	Ti–Pl(2)[b]	2.1402(4)
Ti–C(33)	2.164(2)	Ti–C(34)	2.185(2)
Angles			
Cg(1)–Ti–Cg(2)[a]	138.50(4)	C(33)–Ti–C(34)	88.20(10)
Cg(1)–Ti–C(33)	105.65(8)	Cg(1)–Ti–C(34)	104.34(7)
Cg(2)–Ti–C(33)	104.46(7)	Cg(2)–Ti–C(34)	104.50(8)
φ[c]	41.80(7)	ω(1)[d]	21.38(10)
ω(2)[e]	20.42(8)		

[a] Cg(1) denotes the centroid of the C(1–5) cyclopentadienyl ring, and Cg(2) is the centroid of the C(17–21) cyclopentadienyl ring.

[b] Pl(1) denotes the least-squares plane of the C(1–5) cyclopentadienyl ring, and Pl(2) is the least-squares plane of the C(17–21) cyclopentadienyl ring.

[c] Dihedral angle between Pl(1) and Pl(2).

[d] Dihedral angle between the plane C(33)–Ti–C(34) and Pl(1).

[e] Dihedral angle between the plane C(33)–Ti–C(34) and Pl(2).
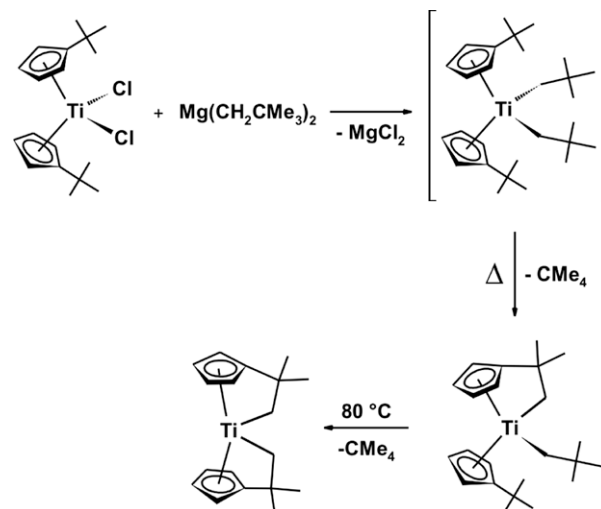
monotethered [TiCH$_2$CMe$_3$(η^5:η^1-C$_5$H$_4$CMe$_2$CH$_2$)(η^5-C$_5$H$_4$t-Bu)] and even the ditethered product [Ti(η^5:η^1-C$_5$H$_4$CMe$_2$CH$_2$)$_2$] (Scheme 10) [12].

On the other hand, in a recent study on bis(di-t-butylcyclopentadienyl)titanium derivatives the titanocene monomethyl compound [TiMe(η^5-C$_5$H$_3$t-Bu$_2$)$_2$] has been found thermally stable upon sublimation at 60–70 °C in vacuum [17]. No activation of t-butyl group was also noticed during synthesis of the most sterically crowded attainable t-butyl titanocene derivatives of [Ti(η^5-C$_5$H$_3$t-Bu$_2$) (η^5-C$_5$H$_2$t-Bu$_3$)] [18].

In this study, the thermolysis of **5** and **9** revealed the overwhelming propensity of the t-butyl group to react with thermally excited Ti-methyl bond, yielding **6** and **11**, respectively. In **11**, one of the two leaving methyl groups abstracted hydrogen from the cyclopentadienyl methyl in vicinal position to the tether, leaving the other t-butyl group intact. Since the methane elimination from both **5** and **9** occurred at the same temperature of 110 °C (Schemes 6 and 8) it is probable that the t-butyl group in **9** was the first reacting with the thermally excited Ti–Me bond. The primary abstraction of hydrogen from the cyclopentadienyl methyl group is improbable because the formation of **1a** from [TiMe$_2$(η^5-C$_5$Me$_5$)$_2$] requires a higher temperature (Scheme 1) [1d]. The structures of **6** and **11** are analogous to products **3b** and **3a** which arise from thermolysis of [TiMe(η^5-C$_5$Me$_4$SiMe$_3$)$_2$] and [TiMe$_2$(η^5-C$_5$Me$_4$SiMe$_3$)$_2$], respectively, at even lower temperature (Scheme 3) [5]. The similar behavior of the t-butyl and trimethylsilyl complexes could be expected in view of a surprisingly high thermal stability of monomeric titanocenes [Ti(II)(η^5-C$_5$Me$_4$t-Bu)$_2$] [19a] and [Ti(II)(η^5-C$_5$Me$_4$SiMe$_3$)$_2$] [19b], in which a large bulkiness of the CMe$_3$ and SiMe$_3$ groups was apparently the decisive factor. In this respect, a larger size of SiMe$_3$ compared to t-Bu (Si–C ~ 1.86 Å versus C–C ~ 1.53 Å) can rationalize the observed lower temperature of the formation of **3b** and **3a** (90 °C) against 110 °C for **6** and **11**.

Of the benzyl-containing complexes, an unprecedented easy elimination of methane from the transiently formed [TiMe(η^5-C$_5$Me$_4$CH$_2$Ph)$_2$] at ambient temperature to give cleanly **7** (Scheme 7) indicates that rotating benzyl substituent on a rotating cyclopentadienyl ligand can approach the methyl group residing on titanium with its phenyl proton in ortho-position causing that the elimination of methane (or the ortho-phenyl metallation) proceeds with a low thermal activation. On the other hand, the same reaction of dimethyltitanocene **10** requires the thermal activation of 110 °C. This can be accounted for by steric congestion at a

tetrahedrally coordinated titanium resulting in a larger angle of the cyclopentadienyl ring planes (φ) compared to a trigonal monomethyltitanocene (cf. **10**: φ = 41.87(7)° and e.g., **5**: φ = 34.35(5)°) which implies a larger distance of the rotating benzyl group from either of the two Ti–Me bond. In distinction to **3a** and **11** compound **12** does not explore the remaining Ti–Me group for the formation of a tucked-in moiety from the cyclopentadienyl methyl; surprisingly, the Ti–Me bond in **12** was found to persist 150 °C. This can be accounted for the rigid and comfortably long three-carbon tether, as established in **7**, which precludes the thermally excited Ti–Me bond to interact with the vicinal-to-tether cyclopentadienyl methyl substituent.

The high thermal stability of **12** is also of interest from a view that thermolysis of [Ti(η^2-Me$_3$SiC≡CSiMe$_3$){η^5-C$_5$Me$_4$(CH$_2$Ph)}$_2$] at 150 °C afforded a mixture of doubly tucked-in titanocenes [Ti(η^5-C$_5$Me$_4$CH$_2$Ph)(η^4:η^3-C$_5$Me$_3$(CH$_2$)CHPh)] (major) and [Ti(η^5-C$_5$Me$_4$CH$_2$Ph){η^4:η^3-C$_5$Me$_2$(CH$_2$)$_2$CH$_2$Ph}] (minor) in virtually quantitative yield [13a]. Such a high selectivity for the formation of doubly tucked-in titanocenes was also found for thermolysis of the [Ti(η^2-Me$_3$SiC≡CSiMe$_3$)(η^5-C$_5$Me$_4$R)$_2$] complexes for R = Me [4b] or SiMe$_3$ [5]. In all cases two hydrogen atoms were transferred from two vicinal sp^3 carbon atoms to the leaving acetylene ligand. A high selectivity of these thermolyses features this process as a concerted one whereas thermolyses of titanocene dimethyls are distinctly stepwise reactions although the particular intermediates could not be detected in the formation of **3a** and **11**.

3. Experimental

3.1. Methods

Syntheses of 5-*t*-butyl-1,2,3,4-tetramethylcyclopenta-1,3-diene [7] and 5-benzyl-1,2,3,4-tetramethylcyclopenta-1,3-diene [9] and titanocene dichlorides thereof were carried out under argon. All titanium(III) compounds were extremely air- and moisture-sensitive, therefore they were handled under vacuum using an all-glass high vacuum line operated with metal valves and all-sealed glass devices equipped with breakable seals. Thermolytic reactions with toluene or *m*-xylene solutions were carried out in glass ampules equipped with breakable seals in a thermostatted oven. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300.0 and 75.4 MHz, respectively, in C$_6$D$_6$ solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to solvent signals (δ_H 7.15, δ_C 128.0). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. *g*-Values were determined by using an Mn^{2+} standard at *g* = 1.9860 (M_I = −1/2 line). A variable temperature unit STT-3 was used for measurements in the range −140 to +25 °C. UV–Vis spectra in the range of 300–800 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma). IR spectra were taken in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm^{-1}. KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen.

3.2. Chemicals

The solvents tetrahydrofuran (thf), hexane, and toluene were dried by refluxing over LiAlH$_4$ and stored as solutions of dimeric titanocene [(μ-η^5:η^5-C$_5$H$_4$C$_5$H$_4$){Ti(μ-H)(η^5-C$_5$H$_5$)}$_2$] [20]. Methyllithium (LiMe) (1.6 M in diethyl ether), PbCl$_2$, and magnesium

turnings were purchased from Aldrich. Titanocene dichlorides [TiCl$_2$(η^5-C$_5$Me$_4$*t*-Bu)$_2$] [7] and [TiCl$_2${η^5-C$_5$Me$_4$(CH$_2$Ph)}$_2$] [9] were prepared as reported.

3.3. Synthesis of [Ti(III)Me(η^5-C$_5$Me$_4$t-Bu)$_2$] (**5**)

Titanocene dichloride [TiCl$_2$(η^5-C$_5$Me$_4$*t*-Bu)] (0.944 g, 2.00 mmol) and magnesium (0.0243 g, 1.00 mmol) were weighed into an ampule and thf (30 ml) was distilled in on a vacuum line with cooling to liquid nitrogen temperature. The ampule was sealed off and the content stirred at 60 °C until all magnesium was consumed. Tetrahydrofuran was distilled off in vacuum, and the residue extracted with hexane (50 ml). Crystallization from saturated hexane solution upon cooling to −28 °C followed by drying of separated crystalline solid in vacuum afforded 0.84 g (1.92 mmol) of blue crystals of [TiCl(η^5-C$_5$Me$_4$*t*-Bu)$_2$]. These were dissolved in 50 ml of hexane, and the solution poured onto solid LiMe which was prepared by evaporation of 5 ml of 1.6 M solution in vacuum, finally at 80 °C. The mixture was shaken until the blue solution turned brownish green (ca. 30 min). Then, the solution was separated from a yellow slurry which was extracted with hexane. The combined volume of the solution and extracts was reduced to ca. 20 ml, and this was cooled to −28 °C overnight. A clear green solution was decanted from white sediment on ampule walls, and concentrated to a saturated solution for crystallization at −28 °C. A green crystalline material was separated from the mother liquor and dried in vacuum.

5: Yield 0.52 g (84%); m.p. decomposes at 115 °C with gas evolution. EI-MS (90 °C): *m/z* (relative abundance) 417 (*M*$^{+•}$; 4), 404 (16), 403 (43), 402 ([*M*−Me]$^+$; 100), 401 (26), 400 (16), 399 (7), 361 (6), 360 ([*M*−Me−Bu]$^+$; 16), 339 (8), 327 (9), 303 ([*M*−Me−2 Bu]$^+$; 6), 206 (11), 202 (7), 201 (8), 57 ([Bu]$^+$; 17). IR (KBr, cm^{-1}): 2988 (s,sh), 2953 (vs), 2905 (vs), 2866 (s,sh), 1480 (m), 1470 (m), 1462 (m), 1451 (m), 1380 (s), 1359 (s), 1234 (m), 1198 (w), 1123 (vw), 1033 (m), 1021 (m), 927 (vw), 836 (vw), 784 (vw), 744 (vw), 672 (vw), 620 (w), 572 (m), 481 (w), 423 (s). EPR (toluene, 22 °C): *g* = 1.955(3), Δ*H* = 14.0 G; (toluene, −140 °C): g_1 = 1.999, g_2 = 1.981, g_3 = 1.889, g_{av} = 1.956. UV–Vis (toluene, nm): 475 > 620. Anal. Calc. for C$_{27}$H$_{45}$Ti: C, 77.67; H, 10.86. Found: C, 77.74; H, 10.91%.

3.4. Thermolysis of **5** to [Ti(III)(η^5-C$_5$Me$_4$t-Bu)(η^5:η^1-C$_5$Me$_4$CMe$_2$CH$_2$)] (**6**)

A solution of **5** (0.42 g, 1.01 mmol) in 10 ml of toluene was heated to 110 °C for 3 h. After opening the ampule to a vacuum line a sample of gas evolved was collected by condensing into liquid nitrogen-cooled ampule and the toluene was replaced with hexane. Cooling of the saturated solution yielded greenish brown plate crystals.

6: Yield 0.34 g (85%); m.p. 113 °C. EI-MS (110 °C): *m/z* (relative abundance) 403 (15), 402 (37), 401 (*M*$^{+•}$; 100), 400 (43), 399 ([*M*−2H]$^+$; 78), 398 (40), 397 ([*M*−4H]$^+$; 74), 396 (34), 395 (39), 394 (18), 393 (43), 392 (13), 391 (18), 390 (18), 389 (16), 381 (19), 345 (12), 344 ([*M*−Bu]$^+$; 33), 342 (11), 341 (10), 340 (10), 339 (14), 328 (11), 327 ([*M*−BuH−MeH]$^+$; 25), 326 (10), 325 (16), 206 (19), 205 (13), 204 (12), 203 (11), 202 (24), 201 (30), 200 (18), 191 (14), 187 (14), 167 (14), 57 ([Bu]$^+$; 30). IR (KBr, cm^{-1}): 2955 (vs), 2909 (vs), 2869 (s,sh), 1480 (m), 1462 (m), 1452 (m), 1381 (s), 1359 (s), 1235 (m), 1198 (w), 1124 (vw), 1034 (m), 1023 (m), 930 (vw), 866 (vw), 784 (vw), 744 (vw), 711 (w), 672 (vw), 664 (vw), 620 (w), 572 (m), 488 (w), 423 (s). EPR (toluene, 22 °C): *g* = 1.960, Δ*H* = 24.4 G; (toluene, −140 °C): g_1 = 2.000, g_2 = 1.983, g_3 = 1.898, g_{av} = 1.960. UV–Vis (toluene, nm): 315 (sh) > 370 (sh) ≫ 570 (broad). Anal. Calc. for C$_{26}$H$_{41}$Ti: C, 77.78; H, 10.29. Found: C, 77.76; H, 10.28%.

3.5. Synthesis of [Ti(III)(η^5-C$_5$Me$_4$CH$_2$Ph)(η^5:η^1-C$_5$Me$_4$CH$_2$-o-C$_6$H$_4$)] (7)

The monochloride [Ti(III)Cl(η^5-C$_5$Me$_4$CH$_2$Ph)$_2$] was obtained from [TiCl$_2$(η^5-C$_5$Me$_4$CH$_2$Ph)$_2$] (1.080 g, 2.00 mmol) and magnesium 0.0243 g, 1.00 mmol) in 20 ml of thf. The mixture was stirred and heated to 60 °C until the red solution turned blue. The thf was evaporated in vacuum, and the residue was extracted with hexane (50 ml). The monochloride did not crystallize forming a blue waxy solid characterized as follows: EI-MS (140 °C): m/z (relative abundance) 508 (12), 507 (32), 506 (31), 505 ($M^{+\cdot}$; 68), 297 (10), 296 (40), 295 (33), 294 ([M−C$_5$Me$_4$CH$_2$Ph]$^+$; 100), 293 (24), 292 (13), 212 (13), 211 ([C$_5$Me$_4$CH$_2$Ph]$^+$; 13), 135 ([C$_5$Me$_5$]$^+$; 11), 121 ([C$_5$HMe$_4$]$^+$; 12), 119 ([C$_5$Me$_3$CH$_2$]$^+$; 13), 92 ([CH$_3$Ph]$^+$; 52), 91 ([CH$_2$Ph]$^+$; 91), 65 (15). EPR (toluene, 22 °C): g = 1.956(7), ΔH = 25.0 G; (toluene, −140 °C): g_1 = 1.999(8), g_2 = 1.983(8), g_3 = 1.889(3), g_{av} = 1.957. UV−Vis (toluene, nm): 358 (sh) ≫ 558 > 660 (sh). The monochloride solution was poured onto solid LiMe which was prepared by evaporation of 5 ml of 1.6 M solution in vacuum, finally at 80 °C. The mixture was shaken at 60 °C until the blue solution turned brown (ca. 4 h). Then the solution was separated from a yellow slurry, and this was repeatedly extracted with hexane. The extract was reduced to ca. 20 ml, and this was cooled to −28 °C overnight. A clear brown solution was decanted from a white sediment on ampule walls, and concentrated to a saturated solution for crystallization at −28 °C. Brown needle aggregates were separated from the mother liquor and dried in vacuum.

7: Yield 0.82 g (87%); m.p. 122 °C. EI-MS (120 °C): m/z (relative abundance) 471 (16), 470 (42), 469 ($M^{+\cdot}$; 100), 468 (19), 467 (15), 453 ([M−CH$_4$]$^+$; 7), 363 ([M−Me−CH$_2$Ph]$^+$; 13), 278 (11), 260 (19), 259 ([M−C$_5$Me$_4$CH$_2$C$_6$H$_4$]$^+$; 73), 258 (15), 257 (18), 255 (12), 254 (12), 253 (39), 252 (13), 251 (14), 250 (11), 181 (23), 180 (10), 179 (13), 178 (13), 91 ([CH$_2$Ph]$^+$; 18). IR (KBr, cm^{-1}): 3104 (w), 3081 (w), 3058 (w), 3026m), 2970 (s), 2908 (vs), 2861 (s), 2724 (vw), 1601 (m), 1582 (w), 1493 (vs), 1450 (s), 1427 (s), 1379 (m), 1322 (vw), 1285 (vw), 1233 (w), 1181 (vw), 1155 (vw), 1098 (w), 1074 (w), 1029 (m), 1002 (w), 932 (vw), 825 (vw), 812 (w), 794 (w), 734 (s), 724 (s), 698 (s), 573 (w), 562 (w), 443 (s). EPR (toluene, 22 °C): g = 1.946, ΔH = 27.4 G. UV–Vis (toluene, nm): 475 (sh) > 620 (sh). Anal. Calc. for C$_{32}$H$_{37}$Ti: C, 81.86; H, 7.94. Found: C, 81.90; H, 7.98%.

Compound **7** appeared to be thermally very stable. Heating of its toluene solution to 150 °C and, after replacement of toluene with m-xylene, to 170 °C for 4 h did not result in evolution of a gas, and EI-MS, IR and EPR spectra of such treated **7** remained the same.

3.6. Chlorination of 7 with PbCl$_2$ to give [Ti(IV)Cl(η^5-C$_5$Me$_4$CH$_2$Ph)(η^5:η^1-C$_5$Me$_4$CH$_2$-o-C$_6$H$_4$)] (8)

A solution of **7** (0.30 g, 0.64 mmol) in thf (7.0 ml) was poured on a degassed powdery PbCl$_2$ (0.10 g, 0.36 mmol), and the mixture was vigorously stirred for 20 min. A dark orange solution was separated from black lead sediment, and thf was replaced with hexane (20 ml). The volume of the solution was reduced to ca. 3 ml of a brown solution which were separated from a precipitated orange powder, and discarded. The orange product was crystallized from hexane to give a microcrystalline orange solid.

8: Yield 0.29 g, (91%); m.p. 171 °C. ^{1}H NMR (C$_6$D$_6$): 1.62, 1.63, 1.64, 1.76, 1.80, 1.84, 1.94, 2.01 (8 × s, 8 × 3H, C$_5$Me$_4$); 3.35, 3.40 (2 × d, 2 × $^2J_{HH}$ = 16.5 Hz, 2 × 1H,, CH$_2$Ph); 3.71, 3.85 (2 × d, 2 × $^2J_{HH}$ = 16.2 Hz, 2 × 1H, CH$_2$C$_6$H$_4$); 6.88–7.12 (m, 8H, Ph and C$_6$H$_4$); 7.21–7.26 (m, 1H, C$_6$H$_4$). ^{13}C {^{1}H}(C$_6$D$_6$): 10.76, 12.12, 12.46, 12.66, 12.96, 13.32, 14.04, 14.37 (C$_5$Me$_4$); 33.73, 33.85 (CH$_2$C$_6$H$_4$ and CH$_2$Ph); 114.34, 123.53, 123.72, (C$_q$, C$_5$Me$_4$); 123.80, 124.26, 124.83 (CH, C$_6$H$_4$); 125.26, 125.68 (C$_q$, C$_5$Me$_4$);

126.07 (CH, Ph); 126.47 (C$_q$, C$_5$Me$_4$); 128.41 (CH, Ph); 128.60 (C$_q$, C$_5$Me$_4$); 128.63 (CH, Ph); 134.95, 135.08 (C$_q$, C$_5$Me$_4$); 137.02 (CH, C$_6$H$_4$); 141.13 (C$_{ipso}$, Ph); 155.05 (CH$_2$C, C$_6$H$_4$); 199.00 (TiC, C$_6$H$_4$). IR (KBr, cm^{-1}): 3100 (vw), 3084 (vw), 3065 (vw), 3040 (s), 3028 (m), 2977 (m), 2952 (m), 2904 (vs), 2883 (s), 2720 (vw), 1602 (m), 1580 (w), 1495 (s), 1483 (w), 1454 (m), 1442 (m), 1429 (m), 1254 (w), 1237 (w), 1099 (vw), 1079 (vw), 1036 (w), 1019 (m), 795 (vw), 742 (s), 728 (m), 697 (w), 461 (w), 438 (m). Anal. Calc. for C$_{32}$H$_{37}$ClTi: C, 76.11; H, 7.39. Found: C, 76.14; H, 7.41%.

3.7. Synthesis of [TiMe$_2$(η^5-C$_5$Me$_4$t-Bu)$_2$] (9)

A slurry of [TiCl$_2$(η^5-C$_5$Me$_4$t-Bu)$_2$] (0.944 g, 2.00 mmol) in 50 ml of hexane was poured onto solid LiMe which was prepared by evaporation of 10 ml of 1.6 M solution in vacuum, finally at 80 °C. The mixture was shaken until all solid titanocene dichloride dissolved and the red solution turned orange-yellow (ca. 3 h). Then the solution was separated from a yellowish slurry, and this was extracted with hexane. The combined extract was poured over the same amount of fresh solid LiMe and treated as above in order to convert the titanocene chloromethyl byproduct (see below for NMR data) to **9**. The solution was separated from a white sediment, and concentrated to a saturated solution for crystallization at −28 °C. A lemon yellow crystalline material was separated from the mother liquor and dried in vacuum (Warning: During the methylation, crystallization, and storing of the solid and the solution avoid their exposure to sun light as well as strong artificial light).

9: Yield 0.72 g (83%). ^{1}H NMR (C$_6$D$_6$): −0.24 (s, 6H, TiMe$_2$); 1.28 (s, 18H, CMe$_3$); 1.63, 2.20 (2 × s, 2 × 12H, C$_5$Me$_4$). ^{13}C {^{1}H}(C$_6$D$_6$): 12.20, 16.05 (C$_5$Me$_4$); 32.16 (CMe$_3$); 35.91 (CMe$_3$); 49.98 (TiMe$_2$); 119.88, 120.89 (C$_5$Me$_4$); 136.79 (C$_{ipso}$). EI-MS (90 °C): m/z (relative abundance) 432 ($M^{+\cdot}$; not found), 417 ([M−Me]$^+$; 9), 416 ([M−CH$_4$]$^+$; 7), 404 (14), 403 (37), 402 ([M−2 Me]$^+$; 100), 401 (45), 400 (27), 399 (20), 361 (11), 360 ([M−Me−Bu]$^+$; 27), 359 (12), 357 (13), 327 (13), 303 ([M−Me−2 Bu]$^+$; 10), 206 (17), 202 (11), 201 (13). IR (KBr, cm^{-1}): 2983 (s), 2959 (vs), 2907 (vs), 1481 (w), 1464 (m), 1450 (w), 1381 (s), 1359 (m), 1233 (w), 1196 (vw), 1123 (vw), 1022 (w), 786 (vw), 667 (vw), 571 (vw), 422 (m). Anal. Calc. for C$_{28}$H$_{48}$Ti: C, 77.75; H, 11.19. Found: C, 77.76; H, 11.17%.

NMR data for [TiClMe(η^5-C$_5$Me$_4$CMe$_3$)$_2$]: ^{1}H NMR (C$_6$D$_6$): 0.55 (s, 3H, TiMe); 1.45 (s, 18H, CMe$_3$); 1.56, 1.59, 2.16, 2.23 (4 × s, 4 × 6H, C$_5$Me$_4$). ^{13}C {^{1}H}(C$_6$D$_6$): 12.19, 12.39, 16.30, 16.51 (C$_5$Me$_4$); 31.90 (CMe$_3$); 37.41 (CMe$_3$); 54.60 (TiMe); 121.49, 121.66, 123.27, 125.16 (C$_5$Me$_4$); 139.38 (C$_{ipso}$).

3.8. Thermolysis of 9 to [Ti{η^5:η^1:η^1-C$_5$Me$_3$(CH$_2$)(CMe$_2$CH$_2$)}(η^5-C$_5$Me$_4$t-Bu)] (11)

Heating of **4** (0.17 g, 0.4 mmol) in toluene (10 ml) to 110 °C for 5 h followed by workup with hexane afforded a dark green solution which in no way afforded crystalline products but viscous oil only. This circumstance precluded the product purification or identification by X-ray diffraction. The structure of the main product **11** was identified by ^{1}H and ^{13}C NMR spectroscopy using additional gCOSY, gHMBC experiments.

^{1}H NMR (C$_6$D$_6$, 300 Hz): −3.29, −1.06 (2 × d, 2 × $^2J_{HH}$ = 9.9 Hz, 2 × 1H, TiCH$_2$CMe$_2$); 0.89 (m, 1H, TiCH$_2$); 1.07 (s, 3H, C$_5$Me$_3$); 1.16 (s, 9H, CMe$_3$); 1.21 (m, 1H, TiCH$_2$); 1.26 (s, 3H, C$_5$Me$_4$); 1.30, 1.42 (2 × s, 2 × 3H, CMe$_2$); 1.54 (s, 3H, C$_5$Me$_3$); 1.70, 1.83 (2 × s, 2 × 3H, C$_5$Me$_4$); 1.91 (s, 3H, C$_5$Me$_3$); 2.15 (s, 3H, C$_5$Me$_4$). ^{13}C {^{1}H}(C$_6$D$_6$): 11.44, 11.91, 12.31, 12.70, 14.43, 15.09, 15.04 (C$_5$Me$_3$ and C$_5$Me$_4$); 29.28, 32.05 (CMe$_2$); 32.65 (CMe$_3$); 35.59 (CMe$_3$); 36.38 (CMe$_2$); 55.14 (TiCH$_2$CMe$_2$); 77.00 (TiCH$_2$); 117.49, 118.36, 118.67, 120.62, 120.69, 123.80 (C$_q$, C$_5$Me$_4$ and C$_5$Me$_3$); 125.95 (CCMe$_2$, C$_5$Me$_3$); 129.99 (C$_q$); 130.65 (CCMe$_3$, C$_5$Me$_4$); 132.52 (C$_q$).

3.9. Synthesis of [TiMe₂(η⁵-C₅Me₄CH₂Ph)₂] (10)

A suspension of [TiCl₂(η⁵-C₅Me₄CH₂Ph)₂] (1.080 g, 2.0 mmol) in hexane (50 ml) was poured onto solid LiMe made by evaporation of 5 ml of 1.6 M solution in vacuum, finally at 80 °C. The mixture was shaken at 60 °C until all red titanocene dichloride was consumed (ca. 4 h). The solution was separated from a yellowish slurry, and this was repeatedly extracted with hexane. The extract was reduced to ca. 20 ml, and this was cooled to −28 °C overnight. A clear orange solution was decanted from a white sediment on ampule walls, and concentrated to a saturated solution for crystallization at −28 °C. A sample of orange crystals was separated, dissolved in C₆D₆ and investigated by ¹H and ¹³C NMR spectroscopy. The spectra revealed the presence of chloromethyl derivative (30%) (NMR data see below) in addition to 10. The hexane solution of this product was treated again with the same portion of solid LiMe for 2 h, and the solution removed and purified as above. Orange crystalline solid was obtained from saturated hexane solution after cooling to −5 °C.

10: Yield 0.81 g (81%); m.p. at 85 °C with gas evolution. ¹H NMR (C₆D₆): −0.38 (s, 6H, TiMe₂); 1.82 (s, 12H, β-Me, C₅Me₄); 1.87 (s, 12H, α-Me, C₅Me₄); 3.73 (CH₂); 7.11–7.28 (m, 10H, Ph). ¹³C {¹H}(C₆D₆): 11.96, 12.31 (C₅Me₄); 33.01 (CH₂); 49.93 (TiMe₂); 119.95, 120.10 (C₅Me₄); 122.30 (C_ipso, C₅Me₄); 125.96, 128.38, 128.58 (CH, Ph); 141.55 (C_ipso, Ph). EI-MS (130 °C): m/z (relative abundance) 500 (M⁺˙; not observed), 486 (7), 485 (19), 484 ([M−CH₄]⁺; 44), 483 (18), 482 (11), 471 (16), 470 (42), 469 ([M−CH₄−Me]⁺; 100), 468 (19), 467 (15), 453 ([M−2 CH₄−Me]⁺; 7), 363 ([M−CH₄−2 Me−CH₂Ph]⁺; 13), 274 ([M−CH₄−C₅Me₄ CHPh]⁺; 13), 260 (13), 259 ([M−C₅Me₄CHPh−CH₄−Me]⁺; 45), 258 (19), 257 (15), 255 (10), 254 (12), 253 (36), 252 (14), 251 (13), 250 (10), 181 (21), 179 (11), 178 (12), 91 ([CH₂Ph]⁺; 14). IR (KBr, cm⁻¹): 3104 (vw), 3084 (w), 3060 (w), 3027 (m), 2974 (s), 2954 (vs), 2905 (s), 2892 (s), 2725 (vw), 1601 (m), 1583 (w), 1494 (vs), 1452 (s), 1440 (sh), 1379 (m), 1288 (vw), 1074 (w), 1030 (m), 801 (w), 752 (m), 733 (m), 704 (s), 675 (w), 607 (w), 579 (w), 555 (w), 460 (m). UV–Vis (hexane, nm): 430 (sh). Anal. Calc. for C₃₄H₄₄Ti: C, 81.58; H, 8.86. Found: C, 81.60; H, 8.89%.

NMR data for [TiClMe(η⁵-C₅Me₄CH₂Ph)₂]: ¹H NMR (C₆D₆): 0.44 (s, 3H, TiMe); 1.83, 1.85, 1.94, 1.95 (4 × s, 4 × 6H, C₅Me₄); 3.91 (CH₂); 7.11–7.28 (m, 10H, Ph). ¹³C {¹H}(C₆D₆): 12.28, 12.33, 12.82, 12.86 (C₅Me₄); 33.55 (CH₂); 54.97 (TiMe); 123.08, 123.13, 123.43, 124.02 (C₅Me₄); 126.02 (CH, Ph); 126.14 (C_ipso, C₅Me₄); 128.35, 128.58 (CH, Ph); 141.10 (C_ipso, Ph).

3.10. Thermolysis of 10 to [TiMe(η⁵:η¹-C₅Me₄CH₂-o-C₆H₄) (η⁵-C₅Me₄CH₂Ph)] (12)

A solution of 10 (0.50 g, 1.0 mmol) in toluene (20 ml) was heated to 110 °C for 12 h without observable change in its dark yellow color. The ampule was opened at ambient temperature on a vacuum line showing that a volatile gas was evolved. All volatiles were evaporated under vacuum, and the residue was dissolved in hexane (8 ml). A clear yellow solution was concentrated by slow distillation of hexane to an attached ampule in refrigerator leaving a brownish-yellow solid on ampule walls. The yellow microcrystalline solid was collected, and assigned to 12 on the basis of ¹H, ¹³C NMR methods (APT, 1DNOESY, gCOSY, gHSQC, gHMBC).

12: Yield 0.46 g (95%). m.p. 124–126 °C. ¹H NMR (C₆D₆): 0.10 (s, 3H, TiMe); 1.47, 1.59, 1.64, 1.69, 1.71, 1.78, 1.85, 1.97 (8 × s, 8 × 3H, C₅Me₄); 3.46 (s, 2H, CH₂Ph); 3.53, 3.64 (2 × d, 2 × ²J_HH = 16.2 Hz, 2 × 1H, CH₂C₆H₄); 6.98–6.73 (m, 1H, C₆H₄); 6.87–6.92 (m, 2H, C₆H₄); 6.98–7.02 (partially overlapped, m, 1H, C₆H₄); 7.01–7.06 (m, 3H, Ph); 7.08–7.13 (m, 2H, Ph). ¹³C {¹H}(C₆D₆): 10.78, 11.77, 12.22, 12.33, 12.35, 12.52, 12.85, 14.02 (C₅Me₄); 33.37 (CH₂C₆H₄); 34.22 (CH₂Ph); 54.63 (TiMe); 113.13, 120.73, 120.99, 121.77, 121.92, 122.10 (C_q, C₅Me₄); 123.39, 123.92 (CH, C₆H₄); 124.06 (C_q, C₅Me₄); 124.55 (CH, C₆H₄); 126.01 (CH, Ph); 126.07, 126.90 (C_q, C₅Me₄); 128.46, 128.62 (CH, Ph); 133.48 (C_q, C₅Me₄); 135.16 (CH, C₆H₄); 141.54 (C_ipso, Ph); 155.57 CH₂C, C₆H₄); 196.33 (TiC, C₆H₄). EI-MS (130 °C): m/z (relative abundance) 486 (6), 485 (17), 484 (M⁺; 40), 483 (15), 482 (9), 471 (15), 470 (40), 469 ([M−Me]⁺; 100), 468 (19), 467 (15), 453 ([M−CH₄−Me]⁺; 6), 378 ([M−Me−CH₂Ph]⁺; 4), 363 ([M−2 Me−CH₂Ph]⁺; 12), 274 ([M−C₅Me₄CHPh]⁺; 13), 260 (12), 259 ([M−C₅Me₄CHPh−Me]⁺; 44), 258 (18), 257 (14), 255 (8), 254

Table 4
Crystallographic data, data collection and structure refinement for **5**, **6**, **7** and **10**.

	5	6	7	10
Chemical formula	C₂₇H₄₅Ti	C₂₆H₄₁Ti	C₃₂H₃₇Ti	C₃₄H₄₄Ti
Molecular weight	417.53	−401.49	469.52	500.59
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic
Space group	P$\bar{1}$ (No. 2)	Pbcn (No. 60)	P$\bar{1}$ (No. 2)	P$\bar{1}$ (No. 2)
a (Å)	8.4272(2)	32.0322 (1)	8.5452 (2)	9.3007(2)
b (Å)	8.7685(2)	8.6546 (3)	16.5668 (5)	11.5286 (2)
c (Å)	18.1869 (3)	16.5204 (7)	18.9231 (5)	13.8560 (3)
α (°)	95.1510 (12)	90.0	104.0030 (12)	90.1856 (10)
β (°)	91.6517 (11)	90.0	91.2402 (16)	104.2855 (11)
γ (°)	115.8135 (11)	90.0	103.1375 (15)	107.7355 (11)
V (Å³)	1201.45 (4)	4579.9 (3)	2522.90 (12)	1366.37 (5)
Z	2	8	4	2
D_calc (g cm⁻³)	1.154	1.165	1.236	1.217
μ (mm⁻¹)	0.366	0.382	0.357	0.334
Crystal description	Dark green prism	Brown prism	Brown prism	Orange prism
Crystal size (mm³)	0.5 × 0.45 × 0.35	0.6 × 0.3 × 0.1	0.4 × 0.3 × 0.1	0.5 × 0.4 × 0.22
θ range (°)	2.71–27.48	2.44–26.03	1.92–25.04	1.52–27.61
hkl range	−10/10; −11/7; −23/23	−39/39; −10/10; −20/20	−9/10; −19/19; −22/22	−12/12; −14/14; −18/18
Diffractions collected	22 185	42 506	43 043	41 920
Unique diffractions	5475	4508	8879	6296
F(000)	458	1752	1004	540
Number of parameters	268	257	611	326
R(F); wR(F²) (%)	3.89; 9.08	7.55; 15.30	8.16; 16.11	6.07; 14.09
GOF (F²) all data	1.069	1.050	1.092	1.023
R(F); wR(F²) [I > 2σ(I)]	3.44; 8.73	5.66; 14.10	5.67; 14.11	5.32; 13.56
Δρ (e Å⁻³)	0.314; −0.390	0.994; −0.340	0.621; −0.596	1.545; −0.811

(10), 253 (35), 252 (13), 251 (12), 250 (9), 181 (19), 179 (10), 178 (11), 91 ([CH$_2$Ph]$^+$; 14). IR (KBr, cm^{-1}): 3100 (vw), 3084 (vw), 3059 (vw), 3036 (s), 2986 (s), 2971 (m), 2956 (s), 2908 (vs), 2888 (s), 2720 (vw), 1601 (w), 1583 (vw), 1494 (s), 1451 (s), 1442 (m), 1426 (m), 1377 (m), 1236 (vw), 1097 (vw), 1075 (vw), 1028 (w), 1017 (w), 787 (m), 735 (vs), 701 (s), 580 (vw), 465 (w), 433 (m), 406 (m). Anal. Calc. for C$_{33}$H$_{40}$Ti: C, 81.80; H, 8.32. Found: C, 81.78; H, 8.30%.

3.11. X-ray crystallography

Single crystals or crystal fragments of compounds **5**, **6**, **7**, and **10** were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen, and sealed by a wax. Diffraction data were collected on a Nonius KappaCCD diffractometer and processed by a HKL program package [21].The phase problem was solved by direct methods (SIR-92) [22], followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXL-97 [23]). Relevant crystallographic data are given in Table 4. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions. The final difference Fourier map for **10** displayed a high positive maximum in close vicinity of Ti atom (Ti-1 0.82 Å), probably resulting from the imperfection of the measured crystal.

4. Supplementary material

CCDC 702259, 702260, 702261 and 702262 contains the supplementary crystallographic data for **5**, **6**, **7** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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