

INTRAMOLECULAR ALKOXIDE-TETHERED PERMETHYLTTANOCENE(III) COMPLEXES – SYNTHESIS AND CRYSTAL STRUCTURE

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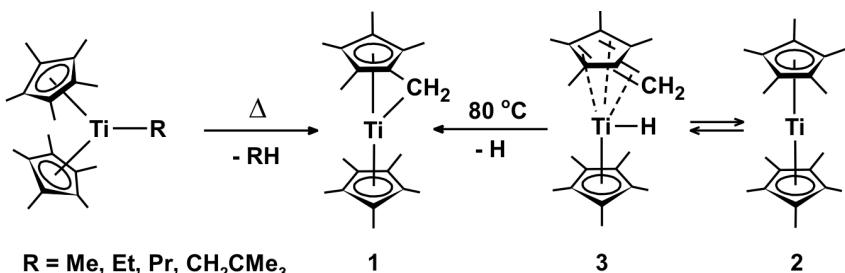
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Singly tucked-in titanocene $[\text{Ti(III)}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)]$ (**1**) reacted readily with di-*tert*-butyl ketone and 2,4,6-trimethylacetophenone to give permethyltitanocene derivatives $[\text{Ti(III)}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}(t\text{-Bu})_2\text{O}\text{-}\kappa\text{O}\}]$ (**2**) and $[\text{Ti(III)}(\eta^5\text{-C}_5\text{Me}_5)\text{-}\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CMe(C}_6\text{H}_2\text{Me}_3\text{)}\text{O}\text{-}\kappa\text{O}\}]$ (**3**) with the tetramethylcyclopentadienyl ring tethered to the titanium atom by ethoxy group disubstituted at C_α . Crystal structures of **2** and **3** showed that the Ti-O bond is only slightly inclined to the tethered cyclopentadienyl ligand, and the bulky mesityl or *tert*-butyl substituents did not impose an observable steric hindrance into molecules of **2** and **3**. Whereas the Ti-O bond lengths in **2** and **3** do not significantly differ, a higher wavenumber of the $1\text{a}_1 \rightarrow \text{b}_2$ electronic transition for **2** (7326 cm^{-1}) compared with that for **3** (6666 cm^{-1}) indicates a more efficient oxygen-to-titanium π -electron back donation in **2**. This is induced by two electron-donating *tert*-butyl groups on C_α compared with a combined effect of electron-donating methyl and electron-attracting mesityl substituents in **3**.

Keywords: Titanium; Permethyltitanocene; Ketones; Di-*tert*-butyl ketone; 2,4,6-Trimethylacetophenone; Crystal structures; Electronic absorption spectra; Metallocenes; Titanocenes; Sandwich complexes.

The singly tucked-in titanocene $[\text{Ti(III)}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)]$ (**1**) has been one of key compounds for understanding the decamethyltitanocene $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$ chemistry^{1,2}. It was first obtained by vacuum sublimation of an equilibrium mixture of decamethyltitanocene $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**2**) with its singly tucked-in (aka η^6 -fulvene) hydride $[\text{TiH}\{\eta^6\text{-C}_5\text{Me}_4(\text{CH}_2)\}(\eta^5\text{-C}_5\text{Me}_5)]$

(3)^{1c}. Later on, the thermolysis of decamethyltitanocene monoalkyl compounds $[\text{Ti(III)}\text{R}(\eta^5\text{-C}_5\text{Me}_5)_2]$ ($\text{R} = \text{Me, Et, Pr, CH}_2\text{CMe}_3$) appeared to be another clean, convenient method for obtaining **1** (Scheme 1)².



SCHEME 1

The structure of **1** is known from single-crystal X-ray diffraction measurement only tentatively because of an extensive disorder³. Although some properties of **1** can be interpreted as arising from $\eta^4\text{:}\eta^2$ -bonded tucked-in ligand the compound is unequivocally a paramagnetic d¹ complex⁴ and, therefore, the $\eta^5\text{:}\eta^1$ -bonding mode of the ligand compatible with Ti(III) is used for its representation in this paper (Chart 1).

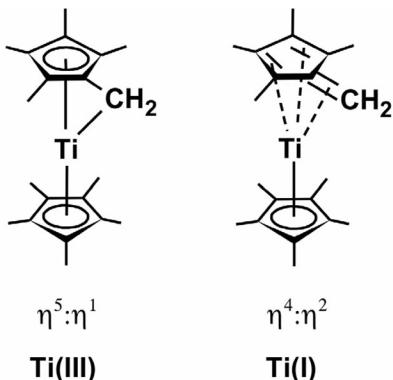
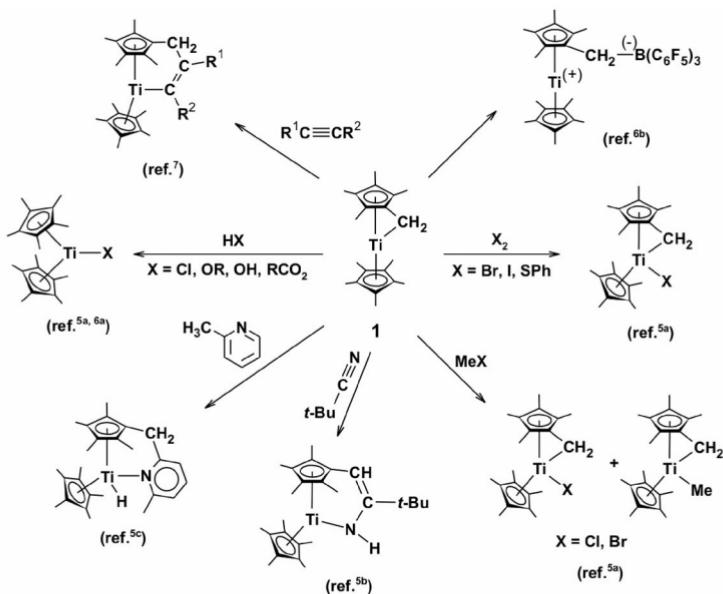


CHART 1

Compound **1** is a highly reactive reagent of choice for obtaining a variety of permethyltitanocene(III) compounds. Its reactions with weak protonic acids, hydrogen, halogens, methyl halides, nitriles, isonitriles and 2-methylpyridine were studied by Pattiasina in his Ph.D. Thesis and partly published in journals⁵. The protonic acids HX like hydrogen halides, carboxylic acids, alcohols or pyrrole cleave the Ti-methylene bond to give Ti(III) decamethyltitanocene derivatives $[\text{Ti(III)}\text{X}(\eta^5\text{-C}_5\text{Me}_5)_2]$. Oxidation with halo-

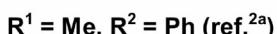
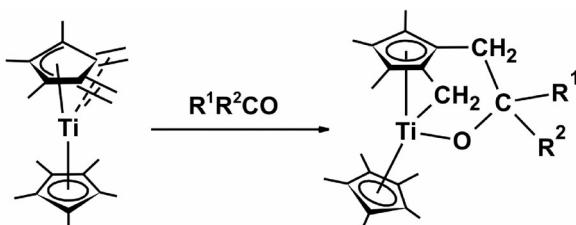
gens, organic disulfides or methyl halides gave rise to Ti(IV) products with the preserved Ti-methylene bond $[\text{TiX}\{\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)\}(\eta^5\text{-C}_5\text{Me}_5)]$ ($\text{X}' = \text{Br, I, SPh, Me}$). *tert*-Butylcyanide underwent an insertion of its $\text{C}\equiv\text{N}$ bond into the Ti-methylene bond of **1** followed by a proton transfer from the methylene group to the nitrogen atom giving an unsaturated titanium amide, $[\text{Ti(III)}\{\eta^5\text{-C}_5\text{Me}_4\text{CH}=\text{C}(t\text{-Bu})\text{NH-}\kappa\text{N}\}(\eta^5\text{-C}_5\text{Me}_5)]$ (refs^{5a,5b}). The most interesting reaction of **1** was observed for 2-methylpyridine whose C-H bond in position 2 reacted in an opposite way with respect to protonic acids. The hydrogen atom was transferred to Ti, the carbon atom linked to the methylene carbon and the nitrogen atom coordinated to the metal thus affording the Ti(III) titanocene hydride stabilized by intramolecular nitrogen coordination^{5c}. Recently, compound **1** was shown to react with water to give titanocene hydroxide $[\text{Ti(III)}\text{OH}(\eta^5\text{-C}_5\text{Me}_5)_2]$ (ref.^{6a}), with the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ to give the paramagnetic zwitterionic complex $[\text{Ti(III)}^{(+)}\text{-}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{B}^{(-)}(\text{C}_6\text{F}_5)_3\}]$ (ref.^{6b}), and with internal alkynes or ethene to afford the products of their insertion into the Ti-methylene bond⁷ (Scheme 2).



SCHEME 2

In spite of the above mentioned interest in reactivity of **1** this compound has not been so far reacted with ketones. Insertion reaction of acetophenone and alkynyl methyl ketones $\text{C}=\text{O}$ bonds into one of the two

Ti-methylene bonds of doubly tucked-in permethyltitanocene is well known (Scheme 3)^{2a,8}, and a similar reaction is expected to occur with **1**. Here, compound **1** is reacted with di-*tert*-butyl ketone and 2,4,6-trimethylacetophenone with the aim to see whether the presence of bulky alkyl or aryl substituents influences their insertion reaction, the structure of products, and the $1a_1 \rightarrow b_2$ transition⁹ in their electronic absorption spectra.

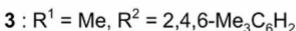
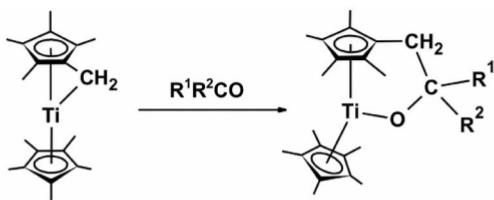


SCHEME 3

RESULTS AND DISCUSSION

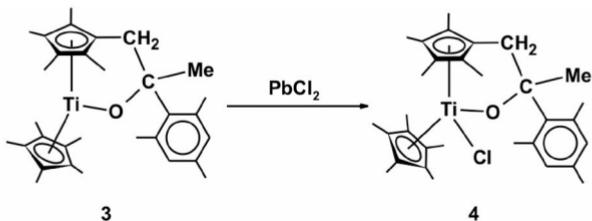
Purple paramagnetic compound **1** in hexane solution reacted immediately with a slight excess of both bulky ketones, di-*tert*-butyl ketone and 2,4,6-trimethylacetophenone to give brown solutions of products **2** and **3**, respectively, from which a mass of brown, low-soluble finely crystalline products separated. The mother liquor containing excess ketones was removed, and the solids were recrystallized from toluene. Their EI-MS spectra showed low-abundant molecular ions which eliminated the ketone (L) to give m/z 317 of $[1]^+$ as the base peak. Infrared spectra were dominated by the most intense band of the C-O valence vibration at 999 cm^{-1} for **2** and at 955 cm^{-1} for **3**, however, the Ti-O valence vibration is to be observed in the range of $400\text{--}600\text{ cm}^{-1}$, and both these vibrations should couple with other vibrations¹⁰. The EPR and UV-near-IR spectra of the toluene solutions afforded features similar to those known for permethyltitanocene alkoxides. Narrow EPR signals at $g = 1.980$, $\Delta H = 2.5\text{ G}$ for **2** and at $g = 1.978$, $\Delta H = 3.3\text{ G}$ for **3** with well discernible superhyperfine coupling to ^{47}Ti and ^{49}Ti nuclei (natural abundance 7.75 and 5.51% and spin $I_N = 5/2$ and $7/2$, respectively) with $a_{\text{Ti}} = 8.4\text{ G}$ for **2** and 9.2 G for **3** resemble those for $[\text{Ti}(\text{O}-t\text{-Bu})(\eta^5\text{-C}_5\text{Me}_5)_2]$ (ref.^{11a}), $[\text{Ti}(\text{O}-t\text{-Bu})(\eta^5\text{-C}_5\text{HMe}_4)_2]$ (ref.^{11b}) and

$[\text{Ti}(\text{OMe})(\eta^5\text{-C}_5\text{Me}_5)_2]$ (ref. ⁹). The electronic absorption spectra of **2** and **3** in the range of 300–2000 nm are also similar to the spectra of the above alkoxides^{9,11} (see below), and thus both methods indicate that the C=O bond is regiospecifically inserted into the Ti-CH₂ bond of **1**. The molecular structures of the products were determined by X-ray diffraction analysis to be $[\text{Ti}(\text{III})(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{C}(t\text{-Bu})_2\text{O}-\kappa\text{O}\}]$ (**2**) and $[\text{Ti}(\text{III})(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CMe}(\text{C}_6\text{H}_2\text{Me}_3)\text{O}-\kappa\text{O}\}]$ (**3**), both with one tetramethylcyclopentadienyl ring tethered to the titanium atom by the -CH₂-CR¹R²O- group (Scheme 4).



SCHEME 4

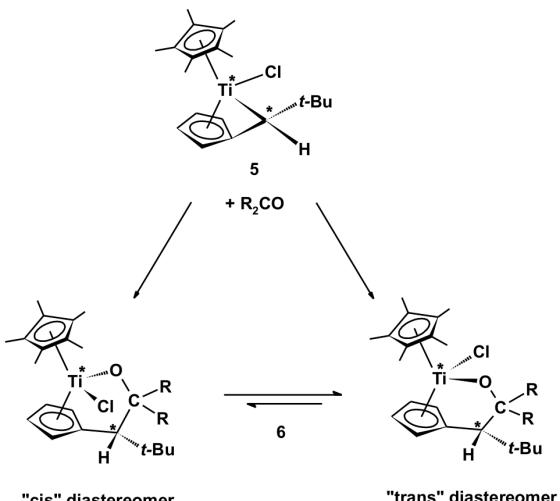
Compound **3** was further chlorinated with PbCl₂ in tetrahydrofuran to diamagnetic $[\text{Ti}(\text{IV})\text{Cl}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CMe}(\text{C}_6\text{H}_2\text{Me}_3)\text{O}-\kappa\text{O}\}]$ (**4**) (Scheme 5) in an attempt to correlate its crystallographic structure with ¹H and ¹³C NMR data.



SCHEME 5

Unfortunately, compound **4** did not afford single crystals suitable for X-ray diffraction analysis, and thus it was described by combination of EI-MS and ¹H and ¹³C NMR methods, and by elemental analysis. The molecular ion **4**⁺ was very low abundant in EI-MS spectra; it easily eliminated the C₅Me₅ ligand. The fragment ion *m/z* 379 [M - C₅Me₅]⁺ was a base peak, and *m/z* 218 ([C₅Me₅TiCl]⁺), formed by elimination of the whole tethered ligand, was the next most abundant fragment ion. Although compound **4**

contains two stereogenic centres, one at the titanium atom and the other at the quaternary carbon atom of the ketone moiety, ^1H and ^{13}C NMR spectra revealed the presence of only one diastereomer. Non-equivalent methyl groups in the C_5Me_4 ring gave rise to four signals (δ_{H} 1.65, 1.69, 1.86 and 1.91 ppm; δ_{C} 11.51, 12.24, 12.45 and 13.75 ppm) and diastereotopic protons of CH_2 split into pair of doublets centered at 2.90 and 3.59 ppm with the geminal coupling constant $^2J_{\text{HH}} = 13.2$ Hz. Rotation of the bulky 2,4,6-trimethylphenyl substituent is hindered at room temperature (298 K) as evidenced by two broad resonances (ca. 30 Hz) for methyl groups in *ortho*-positions at 2.37 and 2.72 ppm. Similar compounds possessing the tether of the same length as in **4** were prepared by Beckhaus et al from diastereomerically pure singly tucked-in titanocene chloride [$\text{Ti(IV)Cl}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{CH}(t\text{-Bu})\}$] (**5**) and various aromatic ketones, acetone, or *R*-(+)-camphor (Scheme 6)¹².



SCHEME 6

Crystal Structures of **2** and **3**

The PLATON drawing of molecule **1** of the two independent molecules in the unit cell of **2** is shown in Fig. 1 and that of single molecule of **3** in Fig. 2.

The common geometric parameters for molecule **1** of **2** and **3** are given in Table I. The molecule **2** of **2** possesses both *tert*-butyl groups and the non-tethered cyclopentadienyl ligand strongly disordered. Therefore the bond lengths for the latter are not presented and discussed. The data in Table I

show that Ti–Cg (Cg is the centroid of gravity of the cyclopentadienyl ring) distances and the titanocene bending as measured by the Cg(1)–Ti–Cg(2) angle and the dihedral angle between the least-squares planes of the cyclopentadienyl rings (ϕ) do not differ from analogous parameters for simple $[\text{Ti(III)}\text{X}(\eta^5\text{-C}_5\text{Me}_5)_2]$ compounds with $\text{X} = \text{Cl}$ (ref.¹¹), OH (ref.^{6a}), NH_2 (ref.¹³).

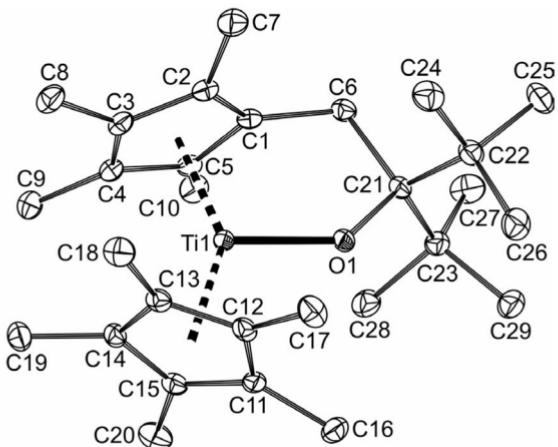


FIG. 1

PLATON drawing of molecule 1 of compound 2 at the 30% probability level with atom labeling scheme. Hydrogen atoms are omitted for clarity

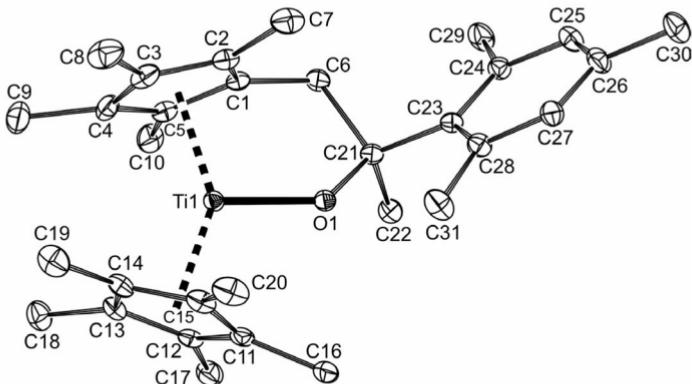


FIG. 2

PLATON drawing of compound 3 at the 30% probability level with atom labeling scheme. Hydrogen atoms are omitted for clarity

TABLE I

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

	2	3
Bond lengths		
Ti–O	1.8879(13)	1.892(3)
Ti–Cg(1) ^a	2.0665(9)	2.046(2)
Ti–Cg(2) ^a	2.0766(9)	2.075(2)
Ti–C(Cp)	2.3095(18)–2.4523(19)	2.305(5)–2.433(5)
C–C(Cp)	1.410(3)–1.439(3)	1.402(7)–1.425(7)
C(Cp)–C(Me)	1.501(3)–1.508(3)	1.496(7)–1.511(7)
O–C(21)	1.422(2)	1.414(5)
C(6)–C(21)	1.599(3)	1.594(6)
C(1)–C(6)	1.508(3)	1.495(6)
C(21)–C(22)	1.600(3)	1.534(7)
C(21)–C(23)	1.606(3)	1.559(7)
Bond and dihedral angles		
Cg(1)–Ti–Cg(2) ^a	143.14(4)	143.44(10)
Cg(1)–Ti–O	107.69(5)	104.09(12)
Cg(2)–Ti–O	109.17(5)	112.09(12)
Ti–O–C(21)	132.95(11)	132.9(3)
O–C(21)–C(6)	106.60(15)	107.0(4)
O–C(21)–C(22)	106.54(15)	104.9(4)
O–C(21)–C(23)	108.01(14)	113.7(4)
C(6)–C(21)–C(22)	110.26(15)	110.9(4)
C(6)–C(21)–C(23)	110.16(15)	110.1(4)
C(22)–C(21)–C(23)	114.86(16)	110.0(4)
ϕ^b	32.54(7)	31.65(24)
ψ^c	89.51(6)	81.61(17)
τ^d	89.63(6)	82.05(19)

^a Cg(1) and Cg(2) denote the centroids of the C(1–5) and C(11–15) cyclopentadienyl rings, respectively. ^b Dihedral angle subtended by the cyclopentadienyl least-squares planes. ^c Dihedral angle subtended by the C(1–5) cyclopentadienyl least-squares plane and the least-squares plane defined by atoms Ti, O, C(1), C(6) and C(21). ^d Dihedral angle subtended by the least-squares plane defined by atoms Ti, O, C(1), C(6) and C(21), and the plane defined by C(21), C(22) and C(23) atoms.

However, the actual steric effect of the alkoxy tether on achieving these parameters becomes apparent from comparison of parameters for **2** and **3** with those of $[\text{Ti(III)}(\text{O}-t\text{-Bu})(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**7**) which is their closest non-tethered analogue¹⁴. The Ti-Cg, Ti-O and C-O bond lengths are very similar for **2** and **3** (see Table I), however, they differ from those of **7**. The Ti-Cg distances are discernibly shorter and Ti-O bond lengths longer compared with those of **7** whereas the C-O bond lengths differ negligibly (**7**: Ti-Cg av. 2.1158(7) Å, Ti-O 1.8658(9) Å and C-O 1.4137(15) Å)¹⁴. A comparison of angles for **7** Cg(1)-Ti-Cg(2) 136.04(3)° and ϕ 41.24(5)° with those for **2** and **3** (Table I) shows that the tether considerably decreases the steric hindrance at the hinge position of the cyclopentadienyl ligands. The tether whose least-squares plane (defined by Ti, O, C(1), C(6) and C(21) atoms) is nearly perpendicular to the planes of cyclopentadienyl rings (ψ) requires the Ti-O-C(21) angle to be close to 133° in both **2** and **3** (Table I). This is in contrast to the Ti-O-C angle of 174.34(9)° for non-tethered **7** (ref.¹⁴), however, it is close to the angles observed in the $[\text{Ti(IV)}\text{Cl}(\text{OR})(\eta^5\text{-C}_5\text{H}_5)_2]$ (R = aryl) complexes^{15a}, $[\text{Ti(IV)}\text{Cl}(\text{OR})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ (R = CH_2 -ferrocenyl or aryl) complexes^{15b}, and virtually the same angle as in sterically non-hindered $[\text{Ti(IV)}\text{Cl}(\text{OEt})(\eta^5\text{-C}_5\text{H}_5)_2]$ (ref.^{15c}). For **2**, the Cg(1)-Ti-O angle is only negligibly smaller than Cg(2)-Ti-O, and the sum of these angles and Cg(1)-Ti-Cg(2) makes exactly 360°. For **3**, the Cg(1)-Ti-O angle is by 8.00(12)° smaller than the Cg(2)-Ti-O one, the least-squares plane of the tether shows large atom deviations (O -0.1011(26) Å, Ti 0.0913(18) Å and C(1) -0.0994(28) Å), and the plane is discernibly declined from perpendicular position with respect to the planes of cyclopentadienyl rings (ψ = 81.61(17)°). However, the sum of angles around the trigonally coordinated titanium fits to 360° within esd's. The bond lengths in tether chains for both **2** and **3** are nearly identical, remarkable only because of unusually long C(6)-C(21) bonds, close to 1.60 Å. Bond lengths slightly over 1.60 Å were also found in compounds **6** derived from the reaction of **5** with benzophenone or *R*(+)-camphor. On the other hand, the corresponding bond for the reaction product of **5** with acetone was of rather usual length (1.569(3) Å)¹². In **2**, unusually long, close to 1.60 Å, are also the bonds from the carbonyl carbon atom to *tert*-butyl groups (C(21)-C(22) and C(21)-C(23)). This can be hardly related to the vicinity of the C-O bond since analogous bonds to methyl and phenyl in **3** are rather short (1.534(7) Å) and normal, respectively (see Table I). The plane of ketone core atoms C(22), C(21) and C(23) is nearly perpendicular to the tether plane for **2** whereas for **3** it is more deviated from perpendicular position due to

different substituents. The mesityl ring is in a common position containing the dihedral angle of $69.51(36)^\circ$ with the ketone core carbon atom plane.

Electronic Absorption Spectra of **2** and **3**

The electronic absorption spectra of **2** and **3** are of interest because the lowest energy transition in the $[\text{Ti(III)}\text{X}(\eta^5\text{-C}_5\text{Me}_5)_2]\text{ d}^1$ complexes can indicate the presence and extent of π -donation ability of X to the Ti-X bond. According to qualitative MO diagram developed by Andersen et al.⁹ the transition from the SOMO orbital, which is essentially d_{z^2} (perpendicular to the Cg-Ti-Cg plane), to the vacant orbital $\text{d}_{x,z}$ becomes observable when the latter is sufficiently destabilized by interaction with the electron pair in p_z orbital of X (Fig. 3). The $1\text{a}_1 \rightarrow \text{b}_2$ transition has been observed at $\lambda <$

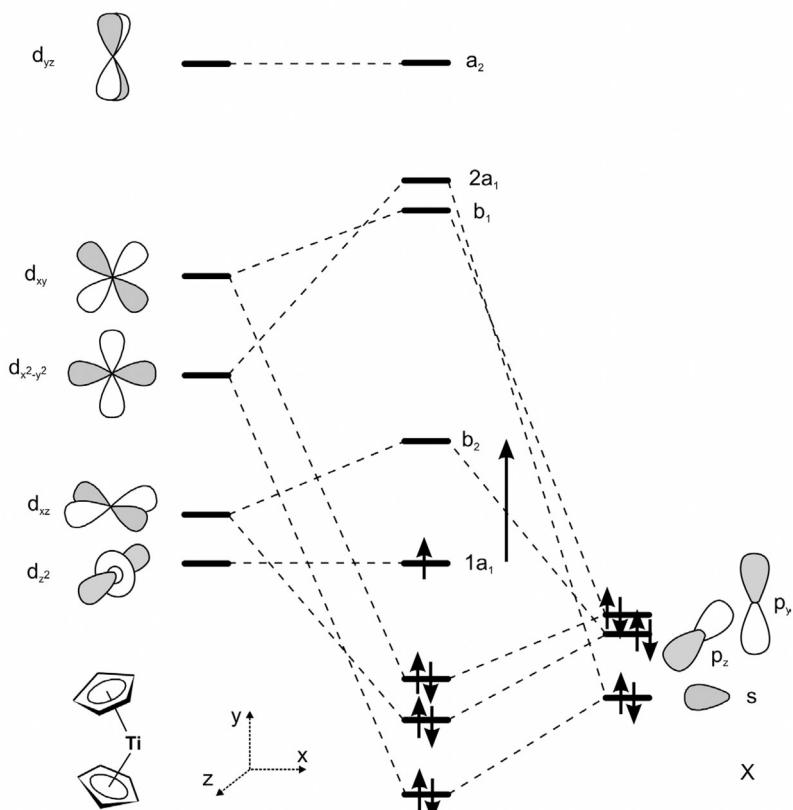


FIG. 3
Qualitative MO diagram showing the origin of $1\text{a}_1 \rightarrow \text{b}_2$ transition (adapted after ref.⁹)

2000 nm for $X = F, NH_2, NHMe, OMe$ and OPh^9 , and in $[Ti(III)(O-t-Bu)(\eta^5-C_5Me_5)_2]$ (ref.¹⁴) and $[Ti(III)(O-t-Bu)(\eta^5-C_5HMe_4)_2]$ (ref.^{11b}). Compounds **2** and **3** undergo the $1a_1 \rightarrow b_2$ transition at 1365 and 1500 nm, respectively, indicating a stronger π -electron donation effect for **2**. This is in accord with the presence of electron-donating *tert*-butyl substituent in **2** and an electron-attracting mesityl group in **3**.

A comparison of the known $1a_1 \rightarrow b_2$ transition wavenumbers (cm^{-1}) for $[Ti(III)OR(\eta^5-C_5Me_5)_2]$ compounds, $R = Me$ 7800 cm^{-1} , Ph 6545 cm^{-1} (ref.⁹) and $t-Bu$ 7692 cm^{-1} (ref. ¹⁴) with those of the tethered compounds (**2** 7326 cm^{-1} and **3** 6666 cm^{-1}) allows to conclude that the latter are sensitive to substituents on C_α of the tether surprisingly strongly and with a similar trend as for the substituents on the oxygen atom. Very similar energies of the $1a_1 \rightarrow b_2$ transition for the $[Ti(III)OR(\eta^5-C_5Me_5)_2]$ compounds with the $Ti-O-C$ angle close to 180° and for compounds **2** and **3** show that a large bending of this angle in the latter compounds does not result in a decrease in the π -electron donation effect^{12,15a,15c}. This is because the plane of the $Ti-O-C$ angle is nearly perpendicular to the equatorial (x,z) plane and hence, the oxygen p_z orbital remains in the optimum overlap position to the $d_{x,z}$ orbital of titanium. Evaluation of the effect of strain in the tether bond (a long $C(6)-C(21)$ bond), the above mentioned declination of oxygen from the equatorial (x,z) plane, and electronic as well as steric effects of bulky substituents on C_α are beyond the scope of this work.

Conclusions

The smooth formation of **2** and **3** from **1** and corresponding ketones indicates that the whole class of $Ti(III)$ permethyltitanocenes with one cyclopentadienyl ring tethered to titanium by a $-CH_2- CR^1(R^2)-O-$ chain can be prepared in high yields even for bulky substituents R^1 and R^2 . The X-ray crystal structures of **2** and **3** revealed that the $Ti-O$ bond declines from the equatorial plane negligibly for **2** and by 4° for **3**, and that the tether equally decreases the bending of titanocene skeleton in both the compounds. The $Ti-O$ bond lengths were equal within the precision of measurement for both **2** and **3**, however, the effect of substituents R^1 and R^2 on the oxygen π -donation was deduced from the energy of $1a_1 \rightarrow b_2$ transition in near-infrared region of electronic absorption spectra. The presence of two electron-donating *tert*-butyl groups in **2** induced a larger π -donation effect of oxygen in the $Ti-O$ bond than one electron-donating methyl and one electron-attracting aryl substituent in **3**.

EXPERIMENTAL

General

All manipulations with **1** and its reaction with the ketones were performed under vacuum in sealed all-glass devices equipped with breakable seals as recently described for reactions of **1** with internal alkynes and ethene⁷. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C₆D₆ solutions at 25 °C. Chemical shifts (δ , ppm) are given relative to solvent signals or tetramethylsilane, coupling constants (J) are given in Hz. The NOESY 1D experiment was performed using a mixing time of 500 ms. EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Sealed capillaries with crystalline samples were opened and the samples were inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 7% and by important peaks of lower intensity (the ketone molecule is denoted L). Crystals of **2** and **3** for EI-MS measurements and melting point determinations were placed in glass capillaries, and KBr pellets for IR measurements were pressed in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). Infrared spectra of KBr pellets in an air-protecting cuvette were recorded on a Nicolet Avatar FT-IR spectrometer in the range 400–4000 cm⁻¹. UV-near-IR measurements were performed on a Varian Cary 17 D spectrometer in the range 300–2000 nm using a device equipped with a pair of quartz cuvettes (10.0 mm and 1.0 mm, Hellma). ESR spectra were registered on an ESR-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 (Magnetech, Berlin, Germany) in the X-band. *g*-Values were determined using an Mn²⁺ ($M_I = -1/2$ line) standard at $g = 1.9860$. An STT-3 variable temperature unit was used for the measurement in the range from -140 to +22 °C. Single crystals of **2** and **3** were mounted into Lindemann glass capillaries under purified nitrogen in the glovebox.

Chemicals

The solvents toluene, hexane and tetrahydrofuran were dried by refluxing over LiAlH₄, and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{-}\text{C}_5\text{H}_4\text{C}_5\text{H}_4)(\mu\text{-H})_2\{\text{Ti}(\eta^5\text{-}\text{C}_5\text{H}_5)\}_2]$ (ref.¹⁶). Di-*tert*-butyl ketone and 2,4,6-trimethylacetophenone (Aldrich) were degassed on a vacuum line and distilled in vacuum. Purple crystalline **1** (ref.⁷) was weighed in the glovebox, distributed into ampules, and sealed off with flame.

Preparation of $[\text{Ti}(\eta^5\text{-}\text{C}_5\text{Me}_5)\{\eta^5\text{-}\text{C}_5\text{Me}_4\text{CH}_2\text{C}(t\text{-}\text{Bu})_2\text{O}\text{-}\kappa\text{O}\}]$ (**2**)

Compound **1** (0.50 g, 1.57 mmol) was dissolved in hexane (20 ml), and the solution mixed with 2,2,4,4-tetramethylpentan-3-one (0.35 ml, 2.0 mmol) in hexane (5.0 ml). A brown solution was obtained immediately. Its volume was reduced to 7.0 ml by distillation, and the solution was stored at -5 °C overnight. A mass of needle-like crystals was separated from the mother liquor containing an excess of the ketone, and washed with condensing hexane vapor. The product was recrystallized from toluene (10 ml) at -28 °C. Pale brown needle-like crystals were separated and dried in vacuum. Yield 0.62 g (86%). M.p. 145–150 °C. EI-MS (direct inlet, 70 eV, 140 °C), *m/z* (rel. abundance, %): 460 (14), 459 (M⁺; 36), 404 (3), 403 (84), 402 ([M - Bu]⁺; 100), 401 (41), 400 (30), 387 ([M - Bu - Me]⁺; 16), 319 (43), 318 (82).

317 ($[M - L]^+$; 97), 316 (63), 315 (62), 314 (12), 313 (25), 312 (8), 311 (14), 253 (17), 201 (23), 200 (22), 199 (37), 198 (22), 197 (16), 196 (10), 195 (26), 182 (25), 181 (42), 180 (22), 179 (16), 178 (23), 177 (16), 158 (15), 134 (27), 133 (14), 119 (42), 105 (11), 91 (15), 57 ($[Bu]^+$; 81). IR: 2984 (s), 2949 (s), 2909 (vs), 2869 (m), 2719 (vw), 1483 (w), 1445 (m), 1378 (m, b), 1398 (w), 1378 (m), 1366 (w), 1281 (vw), 1192 (vw), 1063 (s), 1042 (m), 1023 (m), 999 (vs), 945 (vw), 818 (vw), 758 (w), 656 (w), 619 (w), 608 (vw), 469 (w), 447 (m), 428 (m). EPR (toluene, 23 °C): $g = 1.9796$, $\Delta H = 2.5$ G, $a_{Ti} = 8.43$ G; (toluene, -140 °C): $g_1 = 2.0005$, $g_2 = 1.9826$, $g_3 = 1.9570$, $g_{av} = 1.980$. UV-near-IR (toluene): 475 (sh) > ~640 (sh) > 1365.

Preparation of $[Ti(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CMe}(\text{C}_6\text{H}_2\text{Me}_3)\text{O}-\kappa O\}]$ (3)

Compound **1** (0.50 g, 1.57 mmol) was reacted with 2,4,6-trimethylacetophenone (0.33 ml, 2.0 mmol) as described for **2**. A brown crystalline solid precipitated from hexane in a refrigerator. This was separated from the mother liquor, washed out with hexane, and recrystallized from 20 ml of hot hexane. Pale brown needle-like crystals were separated and dried in vacuum. Yield 0.62 g (82%). M.p. 240–250 °C. EI-MS (direct inlet, 70 eV, 220 °C), m/z (rel. abundance): 480 (7), 479 (M^{+} ; 18), 319 (17), 318 (44), 317 ($[M - L]^+$; 100), 316 (24), 315 (24), 313 (10), 181 (12), 147 (8), 119 (10). IR: 3032 (sh, w), 2988 (sh, m), 2960 (s), 2907 (vs), 2856 (s), 2723 (vw), 1610 (w), 1564 (vw), 1491 (m), 1437 (s, b), 1378 (s), 1356 (m), 1287 (m), 1242 (w), 1198 (vw), 1161 (m), 1143 (m), 1106 (m), 1097 (s), 1078 (s), 1023 (s), 995 (m), 956 (s), 930 (w), 851 (m), 823 (m), 798 (w), 772 (vw), 750 (w), 738 (w), 660 (w), 633 (m), 619 (s), 585 (w), 543 (w), 524 (vw), 491 (m), 440 (s). EPR (toluene, 23 °C): $g = 1.9775$, $\Delta H = 3.3$ G, $a_{Ti} = 9.2$ G; (toluene, -140 °C): $g_1 = 2.0005$, $g_2 = 1.9830$, $g_3 = 1.9508$, $g_{av} = 1.978$. UV-near-IR (toluene): 460 > ~600 (sh) > 1500.

Preparation of $[TiCl(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CMe}(\text{C}_6\text{H}_2\text{Me}_3)\text{O}-\kappa O\}]$ (4)

Compound **3** (0.39 g, 0.81 mmol) was dissolved in tetrahydrofuran (10 ml), and the solution was poured on degassed powdery PbCl_2 (0.14 g, 0.5 mmol). The mixture was vigorously stirred for 20 min, and then the yellow solution was separated from black lead precipitate. The solvent was evaporated in vacuum, and the residue extracted repeatedly with 30 ml of hexane. Slow cooling of a warm solution afforded a finely crystalline yellow solid. Yield 0.32 g (78%). M.p. 290 °C. EI-MS (direct inlet, 70 eV, 260 °C), m/z (rel. abundance): 514 (M^{+} ; 8), 384 (13), 383 (15), 382 (40), 381 (61), 380 (91), 379 ($[M - \text{C}_5\text{Me}_5]^+$; 100), 378 (23), 377 (15), 361 (15), 354 (10), 353 (12), 352 ($[M - L]^+$; 13), 344 (12), 343 (22), 318 (10), 317 ($[M - L - \text{Cl}]^+$; 20), 235 (16), 220 (27), 219 (23), 218 ($[M - L - \text{C}_5\text{Me}_4\text{CH}_2]^+$; 64), 217 (31), 216 (26), 215 (18), 214 (13), 213 (25), 203 ($[M - L - \text{C}_5\text{Me}_4\text{CH}_2 - \text{Me}]^+$; 13), 201 (11), 199 (13), 181 (13), 147 (13), 145 (26), 135 (47), 119 (50), 105 (25), 91 (28). ^1H NMR (C_6D_6): 1.65, 1.69 (2 \times s, 2 \times 3 H, C_5Me_4); 1.72 (s, 3 H, OCMe); 1.86 (s, 3 H, C_5Me_4); 1.87 (s, 15 H, C_5Me_5); 1.91 (s, 3 H, C_5Me_4); 2.13 (s, 3 H, $p\text{-Me}$, $\text{C}_6\text{Me}_3\text{H}_2$); 2.37, 2.72 (2 \times br s, 2 \times 3 H, $o\text{-Me}$, $\text{C}_6\text{Me}_3\text{H}_2$); 2.90, 3.59 (2 \times d, 2 \times $^2J_{\text{HH}} = 13.2$, 2 \times 1 H, CH_2); 6.81 (s, 2 H, CH, $\text{C}_6\text{Me}_3\text{H}_2$). ^{13}C { ^1H } (C_6D_6): 11.51, 12.24, 12.45 (C_5Me_4); 12.73 (C_5Me_5); 13.75 (C_5Me_4); 20.43 ($p\text{-Me}$, $\text{C}_6\text{Me}_3\text{H}_2$); 24.61 ($o\text{-Me}$, $\text{C}_6\text{Me}_3\text{H}_2$); 36.22 (OCMe); 44.82 (CH₂); 113.89 (C_5Me_4); 115.00 (OCMe); 118.58 (C_5Me_4); 123.61 (C_5Me_5); 128.88 (C_5Me_4); 131.4, 132.1 (both broad, CH, $\text{C}_6\text{Me}_3\text{H}_2$); 134.46 ($\text{C}_q\text{-p-Me}$, $\text{C}_6\text{Me}_3\text{H}_2$); 139.86 (C_5Me_4); 146.71 (C_{ipso} , $\text{C}_6\text{Me}_3\text{H}_2$); $\text{C}_q\text{-p-Me}$ ($\text{C}_6\text{Me}_3\text{H}_2$) was not detected. IR: 3026 (sh, w), 2977 (s), 2910 (vs, b), 2858 (m), 1610 (w), 1495 (w), 1461 (m), 1438 (s), 1379 (s), 1356 (w), 1294 (m), 1248 (s), 1162 (w), 1142 (w), 1117 (m), 1095 (s), 1078 (vs), 1057 (vs), 1019 (s), 998 (w), 948 (s), 929 (m).

848 (m), 833 (w), 803 (w), 747 (vw), 659 (vw), 639 (w), 627 (w), 618 (m), 587 (vw), 542 (vw), 525 (vw), 506 (vw), 482 (w), 416 (m). For $C_{31}H_{43}ClOTi$ (515.0) calculated: 72.30% C, 8.42% H; found: 72.24% C, 8.38% H.

X-ray Crystal Structure Determination

Pale brown needle-like crystals of **2** and **3** were mounted into Lindemann glass capillaries under purified nitrogen in a Labmaster 130 glovebox (mBraun) under purified nitrogen, and sealed with flame. Diffraction data were collected on a Nonius KappaCCD diffractometer

TABLE II
Crystal and structure refinement data for compounds **2** and **3**

Parameter	2	3
Empirical formula	$C_{29}H_{47}OTi$	$C_{31}H_{43}OTi$
Formula weight	459.57	479.55
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> , Å	24.1995(3)	8.5143(2)
<i>b</i> , Å	8.5287(1)	10.9394(3)
<i>c</i> , Å	25.0050(3)	28.8184(7)
β , °	91.0356(6)	93.8304(15)
<i>V</i> , Å ³	5159.95(11)	2678.19(12)
<i>Z</i>	8	4
Calculated density, g cm ⁻³	1.183	1.189
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.350	0.340
<i>F</i> (000), e	2008	1036
Crystal size, mm ³	0.5 × 0.27 × 0.15	0.27 × 0.25 × 0.10
θ_{\min} , θ_{\max} , °	1.16, 27.10	1.42, 25.09
Range of <i>hkl</i>	-30→31, -10→10, -32→32	-10→10, -13→13, -34→34
Reflections collected	76857	34044
Independent reflections	11347	4707
Data/restraints/parameters	11347/0/621	4707/0/312
Goodness-of-fit on <i>F</i> ²	1.024	1.172
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0642, 0.1133	0.0853, 0.1754
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0450, 0.1031	0.0721, 0.1680
Maximal and minimal residual density, e Å ⁻³	0.540, -0.481	0.566, -0.410

and processed by the HKL program package¹⁷. The phase problem was solved by direct methods (SIR97)¹⁸, followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97)¹⁹. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions and refined isotropically using the riding model. Refinements of both structures were complicated by the real structure of measured crystals. In the crystal of **2** one of the two symmetrically independent molecules appears to be vastly disordered and majority of its atoms should be split into two positions. The geometric parameters of the disordered molecule were excluded from further discussion. The correction for reticular pseudomerohedric twinning was applied during refinement of **3**, resulting in the ratio of twinned parts 0.88:0.22. Relevant crystallographic data for both the compounds are given in Table II. CCDC 710855 (for **2**) and 710854 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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