



# Synthesis and structure of dinuclear dimethylene- or 1,4-phenylene-linked bis(decamethyltitanoceneoxide) (Ti<sup>III</sup>) complexes

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## ABSTRACT

The singly tucked-in titanocene [Ti(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>:η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)] (**1**) reacts smoothly with ethylene glycol or hydroquinone to give bis(titanoceneoxide) (Ti<sup>III</sup>) complexes [CH<sub>2</sub>OTi(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (**2**) and [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiOC<sub>6</sub>H<sub>4</sub>OTi(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (**3**) containing dimethylene and 1,4-phenylene link, respectively. EPR spectra of **2** in 2-methyltetrahydrofuran glass and **3** in toluene glass revealed that the unpaired d<sup>1</sup> electrons are in interaction to form triplet state molecules. The Ti–Ti distance derived from the zero-field splittings *D* for the two conformations of **2** (7.42 Å and 7.66 Å) are in good agreement with the Ti–Ti distance of 7.2430(7) Å from the X-ray diffraction single-crystal analysis. For **3**, however, the Ti–Ti distance derived from *D* (7.65 Å) is by 1.47 Å shorter than the crystallographic distance of 9.1230(8) Å that indicates an enhancement of the through-space dipole–dipole interaction due to the presence of a conjugated quinonide link.

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## 1. Introduction

Dinuclear titanocene Ti(III)–Ti(III) complexes attract attention because they form electronic triplet states that are easily evidenced by zero-field splitting EPR spectra in diluted frozen organic solutions forming the glassy state. Plethora of complexes falling into this type of compounds involve some coordinatively associated dimers or σ-bonded complexes. The former are represented by the alkoxides [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(μ-OR)]<sub>2</sub> [(R = Me, Et)] and chlorides [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>-<sub>*n*</sub>Me<sub>*n*</sub>)<sub>2</sub>Ti(μ-Cl)]<sub>2</sub> (*n* = 0) [1], (*n* = 2) [2], or the chlorides, alkoxides or hydrides associated via coordination to an appropriate metal derivative, e.g., [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(μ-X)]<sub>2</sub>Zn (X = Cl, Br) [3,4], [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>-<sub>*n*</sub>Me<sub>*n*</sub>)<sub>2</sub>Ti(μ-OMe)]<sub>2</sub>Mg] (*n* = 4 and 5) [5], [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>-<sub>*n*</sub>Me<sub>*n*</sub>)<sub>2</sub>Ti(μ-H)]<sub>2</sub>Mg] (*n* = 3–5) [6]. It is of interest that the dimers using coordination of N, P, or S in [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(μ-NMe<sub>2</sub>)]<sub>2</sub> [7a], [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(μ-PR<sub>2</sub>)]<sub>2</sub>, (R = Et, Bu) [7b], and [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(μ-SPh)]<sub>2</sub> [7c] are reported to be diamagnetic. The σ-bonded sterically rigid dinuclear titanocene complexes contained the titanocene moieties linked to the uracilato dianion via the Ti–O bond and Ti–N coordination [8a], to biimidazole, bibenzimidazole or

pyrazole with the two anions forming two bridging Ti–N..N–Ti bonds [8b], or to carboxylate groups of dicarboxylic acids of cyclic aliphatic hydrocarbons [8c], or to 1,2-, 1,3- and 1,4-benzenedicarboxylates or fumarate [8d]. The aliphatic dicarboxylate dititanium(III) complexes with the linking methylene chain (CH<sub>2</sub>)<sub>*n*</sub> (*n* = 1–4, 6, 8, 10) form less defined systems due to the chain motion. The zero-field splitting (*D*) was decreasing with increasing number of methylene units, not being observable for *n* = 10 only. The magnetic susceptibility measurements revealed that the magnitude of antiferromagnetic exchange interaction is correspondingly decreasing with increasing *n*, however, not observable for *n* ≥ 4 [9]. The nonbonding Ti–Ti distance as estimated from the magnitude of *D* agreed reasonably with the dicarboxylate models considering various conformations of the methylene carbon chain differing from the most stretched one. No X-ray single crystal structure could be determined to get the Ti–Ti distance for a particular chain conformation [9]. All these carbon-linked dititanocene complexes were obtained by reacting [Cp<sub>2</sub>Ti(CO)<sub>2</sub>] with the O–H or N–H bonds of the above ligand precursors [8,9].

We have recently prepared a number of Ti(III) siloxy and alkoxy permethyltitanocenes [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(OR)] (R = Si(OtBu)<sub>3</sub>, SiPh<sub>3</sub>, Si<sup>*i*</sup>Pr<sub>3</sub>, <sup>*t*</sup>Bu) [10] using a straightforward protonolysis of the Ti–C bond in the singly tucked-in permethyltitanocene [Ti(III)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>:η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)] (**1**) [11] with silanols or alcohols. Here, we extend our previous investigations by reacting **1** with two

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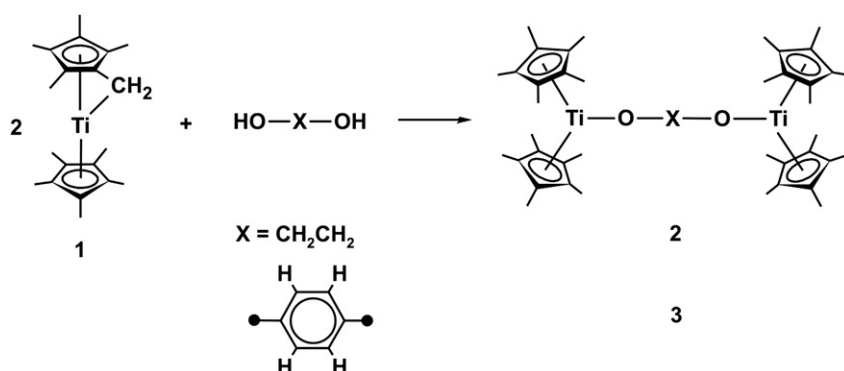
different diols, ethylene glycol and hydroquinone, respectively, with the aim to study crystal structures of the obtained dinuclear titanocene(TiIII) complexes and electron spin–spin coupling therein as observed by EPR spectroscopy.

## 2. Results and discussion

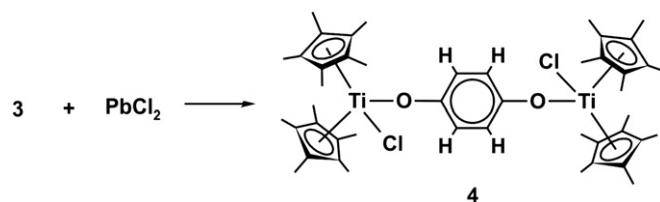
Compound **1** was reacted with ethylene glycol and hydroquinone in toluene to give compounds **2** and **3**, respectively, according to Scheme 1. A slight (5–10%) excess of **1** over the 2:1 molar ratio was actually used to ascertain that the reaction will go to completion, and no mononuclear complexes  $\text{Cp}^*_2\text{TiOXOH}$  will be present in the products. Since compound **2** was practically insoluble and compound **3** low-soluble in toluene the excessive **1** was easily removed from solid products with the mother liquor and repeated washings.

Compound **2** precipitated from the reaction mixture as a pale purple finely crystalline powder not melting till 360 °C. The infrared spectrum of **2** in KBr pellet showed the bands appropriate to permethyltitanocene moiety and the very strong band at 1127  $\text{cm}^{-1}$  of the C–O valence vibration. As concerns the Ti–O valence vibration which was assigned to the band at 528  $\text{cm}^{-1}$  for  $[(\text{Cp}^*_2\text{Ti}(\text{O}t\text{-Bu}))]$  [10] and 571  $\text{cm}^{-1}$  for  $[\text{Cp}^*_2\text{TiOH}]$  [11f] there is no absorption band at least of weak intensity in the range 500–1000  $\text{cm}^{-1}$ , hence the medium-to-strong intensity band at 496  $\text{cm}^{-1}$  should be attributed to this vibration. Compound **2** was only very slightly soluble in tetrahydrofuran (THF) or 2-methyltetrahydrofuran (MTHF), however, using 1.0 cm cuvette its UV–vis spectrum could be identified showing similar features as the spectrum of **3** and similar permethyltitanocene alcoholates or silanolates [10]. The low concentration of **2** did not allow to observe the expected  $1a_1 \rightarrow b_2$  transition of very low intensity in near-infrared region [12], however. The composition of **2** was corroborated by H and C elemental analysis, and was visualized by X-ray diffraction analysis of single crystals grown from its THF solution (see below).

Compound **3** was crystallized from a warm toluene solution as ocher-green plates tending to agglomerate. The crystals did not melt till 360 °C, however, they afforded a sufficient vapor tension at 320 °C in a direct inlet of mass spectrometer to give the EI-MS spectrum. The spectrum displayed the molecular ion  $m/z$  744 in a 57% abundance and among the titanium-containing fragment ions the low abundant  $[\text{M}-\text{Cp}^*\text{TiC}_5\text{Me}_4\text{CH}_2]^+$  ion and the base peak of  $[\text{Cp}^*_2\text{Ti}]^+$ . The IR spectrum of **3** in KBr pellet indicated the presence of the 1,4-phenylene bridging ligand showing absorption bands of  $\nu(\text{C}-\text{H})$  at 3062  $\text{cm}^{-1}$  and  $\nu(\text{C}=\text{C})$  at 1597  $\text{cm}^{-1}$  both of very weak intensity in comparison with the very strong absorption band of the C–O valence vibration at 1256  $\text{cm}^{-1}$ .



Scheme 1.



Scheme 2.

Compared to other absorption bands of the hydroquinone moiety at 1486  $\text{cm}^{-1}$  (vs), 866  $\text{cm}^{-1}$  (s), and 822  $\text{cm}^{-1}$  (m) the most intense absorption band of the  $\text{Cp}^*_2\text{Ti}$  moiety at 1378  $\text{cm}^{-1}$  is classified to be of weak intensity. The Ti–O valence vibration can be attributed only a weak absorption band at 522  $\text{cm}^{-1}$ , the only absorption band observed in the 800–450  $\text{cm}^{-1}$  range. The UV–near IR spectrum of **3** displayed in addition to an absorption band at 450 nm and a shoulder at 640 nm a well-discernible absorption band at 1500 nm of very low intensity which can be assigned to the  $1a_1 \rightarrow b_2$  transition well-known from electronic absorption spectra of  $\text{Cp}^*_2\text{TiOR}$  compounds [10,12]. This transition which reflects the extent of oxygen  $\pi$ -donation to the Ti–O bond is quite close to the analogous transition for  $\text{Cp}^*_2\text{TiOPh}$  found at 1528 nm [12]. The structure and composition of **3** was further corroborated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the diamagnetic product of its oxidative chlorination using  $\text{PbCl}_2$  agent [11e,13] (Scheme 2).

Proton single resonances for the  $\eta^5\text{-C}_5\text{Me}_5$  ligands and 1,4-phenylene were in proper 60:4 integral ratio, and their proximity within one molecule was proved by 1D NOESY experiment. Compound **4** was also obtained by reacting  $[\text{Cp}^*_2\text{TiCl}]$  with benzoquinone in toluene, and characterized by X-ray single crystal diffraction and  $^1\text{H}$  NMR spectrum [14] agreeing with our data. Another titanocene compound of this type,  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{Cl})\text{TiOC}_6\text{H}_4\text{OTi}(\text{Cl})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  displayed only slightly shifted resonances for the  $\text{C}_6\text{H}_4$  moiety  $\delta_{\text{H}}$  6.54 ppm and  $\delta_{\text{C}}$  116.5 ppm [15] compared to  $\delta_{\text{H}}$  6.78 ppm and  $\delta_{\text{C}}$  117.09 ppm for **4**.

### 2.1. Molecular structures of **2** and **3**

Single-crystal X-ray diffraction analysis of **2** and **3** confirmed the expected composition of dinuclear decamethyltitanoceneoxyl complexes containing the dimethylene and 1,4-phenylene link, respectively. The crystal structures of **2** and **3** with atom labeling scheme are shown in Figs. 1 and 2, respectively, and some common molecular parameters are listed in Table 1.

Compound **2** possesses an inversion center in the middle of the C–C bond so the geometric parameters for only one half of the

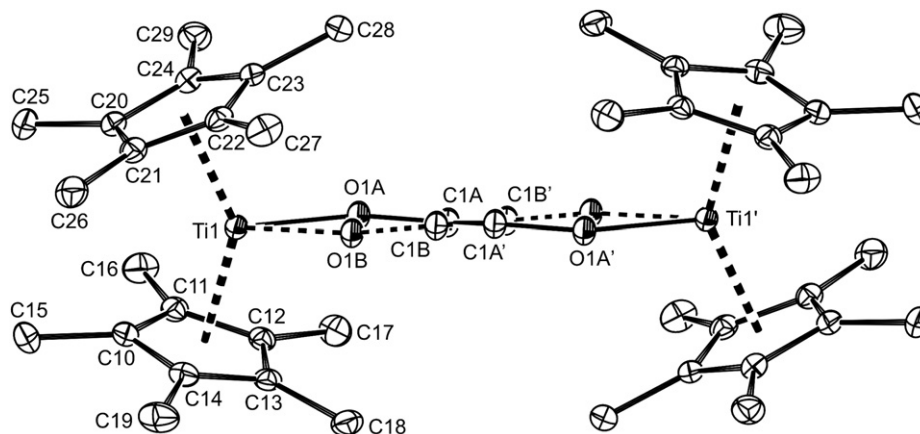


Fig. 1. PLATON drawing of **2** at the 30% probability level with atom labeling scheme. Hydrogen atoms are omitted for clarity.

molecule are given. Unfortunately, the glycol moiety is strongly disordered in two equally populated positions (denoted A, B) subtending the angle O(1A)–Ti(1)–O(1B) of  $17.08(18)^\circ$  that is perpendicular to the Cg(1), Ti(1), and (Cg(2) plane (see Fig. 3a). The “trans” conformation at the glycol C–C bond was taken as more realistic on the basis of DFT structure optimization (see below). The molecule of **3** is unsymmetrical, and in distinction from **2** the titanoceneoxyl moieties are linked to the 1,4-phenylene ring from one side of its plane (“cis”-like conformation) while the planes defined by Cg(1), Ti(1), Cg(2) and Cg(3), Ti(2), Cg(4) are nearly coplanar (see Fig. 3b).

The permethyltitanoceneoxyl moieties in **2** and **3** do not differ from those found in mononuclear alcoholates or silanolates since short contacts (repulsion interactions) between the cyclopentadienyl methyl groups close to hinge position and between the oxygen atom and the closest cyclopentadienyl ring carbon atoms are common to both mono- and dinuclear compounds. The bulky alcoholate or silanolate substituents, however, resulted in Ti–O–C or Ti–O–Si angles close to  $174^\circ (\pm 2^\circ)$  [10] whereas a smaller steric hindrance between the links and the C<sub>5</sub>Me<sub>5</sub> ligands in **2** and **3** allowed for the Ti–O–C angle close to  $167^\circ$  (see Table 1). The sp<sup>3</sup> dimethylene carbon atoms in **2** form longer bonds to the oxygen atoms than sp<sup>2</sup> carbon atoms of **3** (see Table 1) that is in agreement with the lower frequency of infrared  $\nu$  (C–O) vibration ( $1127\text{ cm}^{-1}$  versus  $1256\text{ cm}^{-1}$ ). The dimethylene C–C bond length of  $1.520(10)\text{ \AA}$  and the bond lengths in the phenylene ring of **3** spanning  $1.383(4)$ – $1.396(4)\text{ \AA}$  range are not unusual. Oxygen atoms in **3** are declined from the phenylene least-squares plane to one side, (O(1) by  $0.0911(39)\text{ \AA}$  and O(4) by  $0.0955(40)\text{ \AA}$ ). The nonbonding distance Ti–Ti is  $7.2430(7)\text{ \AA}$  for **2**,

and  $9.1230(8)\text{ \AA}$  for **3**. It is of interest that chlorine-containing compound **4** crystallized as a centrosymmetric molecule in *Pbca* space group giving virtually equal Ti–O and O–C bond lengths as compound **3**. In spite of the “trans” conformation of the 1,4-phenylene link the Ti–Ti distance of  $9.041\text{ \AA}$  in **4** is slightly shorter than that of **3** due to a smaller Ti–O–C angle of  $155.1(2)^\circ$  resulting from a pseudotetrahedral coordination at the titanium atom [14].

## 2.2. DFT optimization of **2**

The disorder in the solid state structure of **2** raised some ambiguities concerning the assignment of the oxygen atoms to the two disordered dimethylene bridges. Since the two disordered moieties were found to be present in a nearly 1:1 ratio, the disambiguation of assigning the disordered oxygen atom to the correct CH<sub>2</sub>–CH<sub>2</sub> moiety could not be done on the basis of the oxygen peak heights. A possible wrong assignment would not show up during the structure refinement, however it would lead to incorrect structural parameters (namely the Ti–O and O–C distances, and the Ti–O–C angle). The DFT optimization done on the arrangement chosen *per analogiam* with other structures featuring similar oxygen bridges did not lead to any significant change of molecular parameters, confirming the correctness of model chosen for the refinement of the solid state structure.

## 2.3. EPR spectra of **2** and **3**

The purple powder of **2** was completely insoluble in toluene, and only very slightly soluble in THF or MTHF. The solid powder

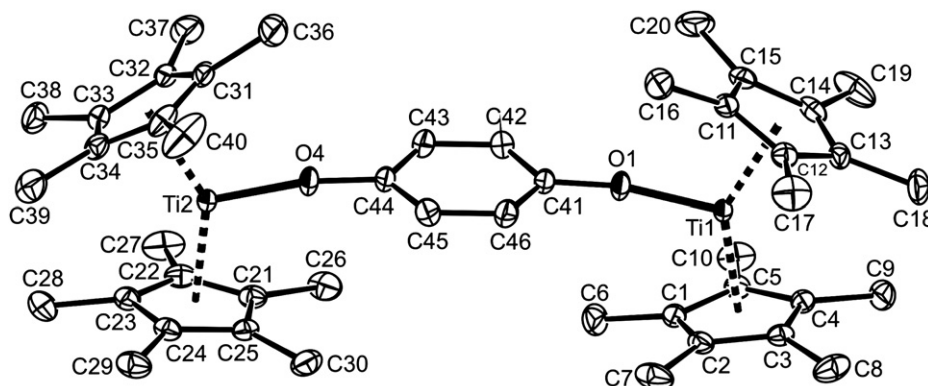


Fig. 2. PLATON drawing of compound **3** at the 30% probability level with atom labeling scheme. Hydrogen atoms are omitted for clarity.

**Table 1**  
Selected bond lengths (Å) and angles (°) for **2** and **3**.

Compound	<b>2</b> <sup>a</sup>	<b>3</b>
<i>Bond lengths</i>		
Ti(1)–O(1)	1.868(5)	1.8646(18)
Ti(2)–O(4)	–	1.8670(19)
Ti(1)–Cg(1) <sup>b</sup>	2.0789(11)	2.0709(13)
Ti(1)–Cg(2) <sup>b</sup>	2.0840(12)	2.0660(13)
Ti(2)–Cg(3) <sup>b</sup>	–	2.0699(13)
Ti(2)–Cg(4) <sup>b</sup>	–	2.0734(14)
O–C <sup>c</sup>	1.374(7)	1.349(3)
O(4)–C(44)	–	1.348(3)
<i>Angles</i>		
Cg(1)–Ti–Cg(2) <sup>b</sup>	141.88(5)	142.12(6)
Cg(1)–Ti–O	109.78(16)	110.56(7)
Cg(2)–Ti–O	108.01(16)	107.32(7)
Cg(3)–Ti–Cg(4) <sup>b</sup>	–	142.16(6)
Cg(3)–Ti–O	–	110.10(8)
Cg(4)–Ti–O	–	107.74(7)
Ti(1)–O–C <sup>c</sup>	167.2(4)	169.59(19)
Ti(2)–O(4)–C(44)	–	165.2(2)

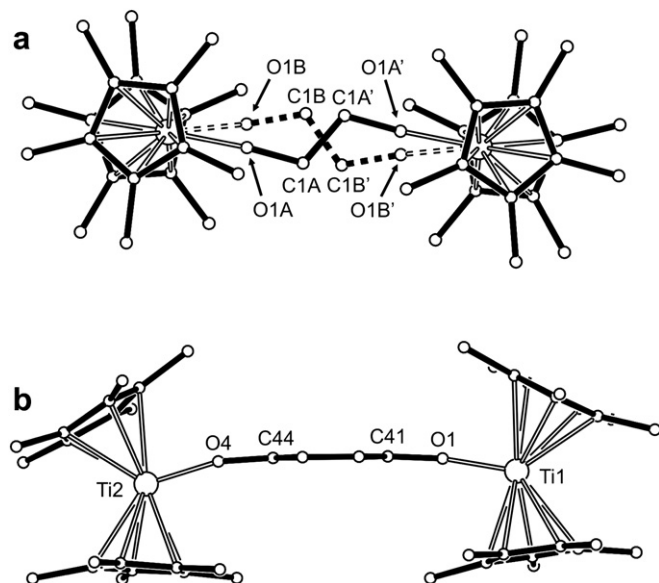
<sup>a</sup> Molecule of **2** contains the center of inversion; therefore the data for one half of the molecule are given. Operator for generating equivalent (prime denoted) atoms:  $-x+1, -y, -z$ .

<sup>b</sup> Cg(1)–Cg(4) denote the centroids of the cyclopentadienyl rings according to the increasing label numbers of the ring carbon atoms.

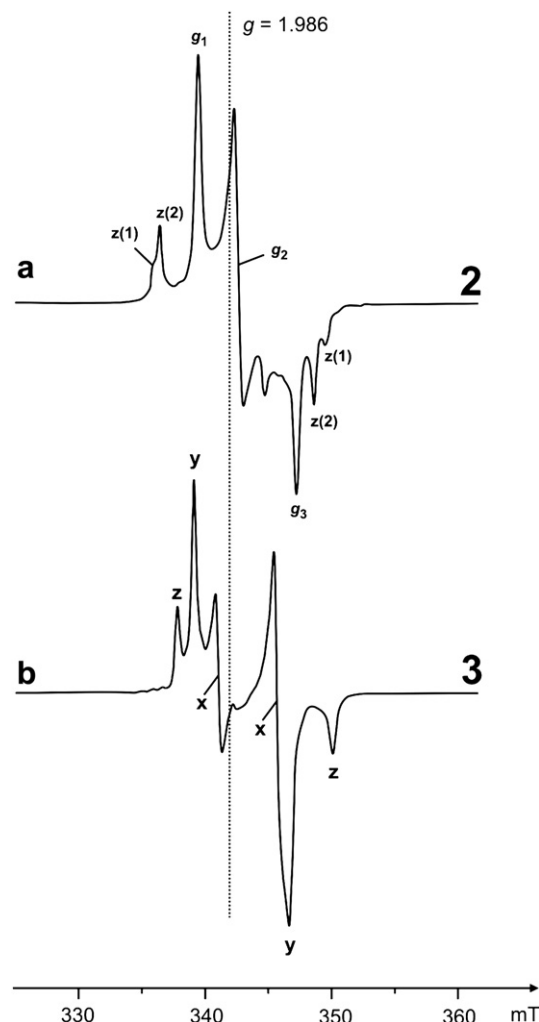
<sup>c</sup> For **2**: O(1A)–C(1A); for **3**: O(1)–C(41).

yielded an EPR spectrum with  $g$ -tensor of axial symmetry at  $-196\text{ }^\circ\text{C}$  ( $g_{\parallel} = 1.999$ ,  $g_{\perp} = 1.972$ ,  $g_{\text{av}} = 1.981$ ) and a very weak and broad  $\Delta M_s = 2$  transition ( $\Delta H \sim 110\text{ G}$ ) indicating the presence of an electronic triplet state species. The solution spectra in MTHF displayed signals of two species: a sharp signal ( $\Delta H = 3.0\text{ G}$ ) at  $g = 1.978$  and a broad signal ( $\Delta H \sim 10\text{ G}$ ) at  $g = 1.977$ . The intensity ratio of these signals remained roughly constant after repeated extraction of the solid with MTHF distilled back from the previously measured solution. The EPR spectra of the MTHF solution at  $-150\text{ }^\circ\text{C}$  also revealed the presence of two species (Fig. 4a).

The mononuclear one with the rhombic  $g$ -tensor ( $g_1 = 2.000$ ,  $g_2 = 1.982$ ,  $g_3 = 1.956$ ,  $g_{\text{av}} = 1.979$ ) which is typical of  $\text{Cp}^*_2\text{TiOR}$  compounds [10,12], and dinuclear one showing features of triplet state spectra. The evidence for its presence is given by outer



**Fig. 3.** A view of molecule **2** in the Cg(1), Ti(1), Cg(2) plane (a), and a view of molecule **3** perpendicular to such a plane (b).



**Fig. 4.** EPR spectra of **2** in MTHF glass (a), and **3** in toluene glass (b).

resonances (denoted  $z, z$ ) whose separation ( $\Delta H_{zz}$ ) determines a two-fold value of zero-field splitting ( $D$ ) [16]. The inner features of the triplet spectra are overlaid with the spectrum of the mononuclear species and cannot be recognized, however, the centrosymmetric crystal structure of **2** with disordered dimethylene link (vide supra) indicates that the  $g$  and  $D$  tensors will be close to axial symmetry. A closer inspection of the outer features of the triplet spectra revealed the presence of two very similar species characterized by  $g_z(1) = 1.9817(\pm 5)$ ,  $\Delta H_{zz}(1) = 135\text{ G}$ , and  $D(1) = 0.0062\text{ cm}^{-1}$  and  $g_z(2) = 1.9826(\pm 5)$ ,  $\Delta H_{zz}(2) = 122\text{ G}$ , and  $D(2) = 0.0057\text{ cm}^{-1}$ . Using the formula (1) relating through-space dipole–dipole zero-field splitting  $D_{dd}$  to the Ti–Ti distance  $R$  in axially symmetric complex [17]

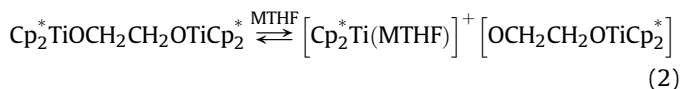
$$R = \left(0.650g_{\parallel}^2/D_{dd}\right)^{1/3} \quad (1)$$

$R(1)$  would be  $7.42\text{ \AA}$ , and  $R(2)$   $7.66\text{ \AA}$ . These data are discernibly longer compared to the crystallographic Ti–Ti distance of  $7.2430(7)\text{ \AA}$ , however, they look reasonable when considering that the molecules of **2** are entrapped in a polar matrix of MTHF glass. The two, rather mutually close  $D$  (and  $R$ ) values should correspond to two conformations of the dimethylene link. Moreover, the inherent presence of the mononuclear species in a very diluted MTHF solution and glass points to dissociation of **2**, e.g.



**Table 2**  
Crystal and structure refinement data for compounds **2** and **3**.

Parameter	<b>2</b>	<b>3</b>
Empirical formula	C <sub>42</sub> H <sub>64</sub> O <sub>2</sub> Ti <sub>2</sub>	C <sub>46</sub> H <sub>64</sub> O <sub>2</sub> Ti <sub>2</sub>
Formula weight	696.73	744.77
Crystal system	Monoclinic	Triclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P1</i>
<i>a</i> , Å	8.4485(3)	8.5494(3)
<i>b</i> , Å	10.9045(5)	16.0375(8)
<i>c</i> , Å	21.3292(10)	16.0953(8)
$\alpha$ , °	90	106.760(2)
$\beta$ , °	100.004(3)	98.416(3)
$\gamma$ , °	90	95.430(3)
<i>V</i> , Å <sup>3</sup>	1935.11(14)	2068.42(16)
<i>Z</i>	2	2
Calculated density, g cm <sup>-3</sup>	1.196	1.196
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	0.445	0.421
<i>F</i> (000), e	752	800
Crystal size, mm <sup>3</sup>	0.43 × 0.37 × 0.30	0.4 × 0.17 × 0.1
$\theta_{\min}$ , $\theta_{\max}$ , °	1.94, 27.47	1.58, 26.36
Range of <i>hkl</i>	-10 → 10, -14 → 10, -27 → 27	-10 → 10, -20 → 20, -20 → 20
Reflections collected	15364	33533
Independent reflections	4402	8411
Data/restraints/parameters	4402/0/227	8411/0/471
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.064	1.009
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0809, 0.1288	0.0880, 0.1176
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0495, 0.1177	0.0465, 0.1025
Max. and min. residual density, e Å <sup>-3</sup>	0.340, -0.275	0.253, -0.234



On the other hand, the EPR spectra of **3** in toluene glass at -140 °C (Fig. 4b) give a clean evidence of electronic triplet state of rhombic symmetry. The *g*-tensor components  $g_z = 1.975$ ,  $g_y = 1.980$ ,  $g_x = 1.977$  give  $g_{av} = 1.977$  in good agreement with  $g_{iso} = 1.976$  observed in solution. The zero-field splitting  $D = 0.00567 \text{ cm}^{-1}$  and  $E = 0.00043 \text{ cm}^{-1}$  were calculated from separations  $\Delta H_{zz}$ ,  $\Delta H_{yy}$ , and  $\Delta H_{xx}$  [16]. The  $\Delta M_s = 2$  was observed at  $g = 3.954$  as a weak signal ( $\Delta H \sim 22 \text{ G}$ ). Calculation of the Ti–Ti distance *R* according to Equation (1) afforded the value of 7.65 Å. This is a considerably shorter distance than the crystallographic 9.1230(8) Å. Shortening of the latter distance in toluene glass is highly improbable since a larger bending of the molecule at the 1,4-phenylene link than that observed in the crystal structure cannot be expected due to the retained *sp*<sup>2</sup> hybridization at the ipso-carbon atoms of the aromatic ring and the steric hindrance between the C<sub>5</sub>Me<sub>5</sub> ligands and the phenylene link. It is more likely that the crystallographic “*cis*” conformation, apparently induced by crystal packing demands, will turn to the symmetric “*trans*” in toluene glass possessing an even longer Ti–Ti distance. Since the *g*-tensor deviations from axial symmetry in the triplet EPR spectrum of **3** are low and since the dipole–dipole zero-field splitting  $D_{dd}$  is far the main component of **D**, the calculation of *R* according to Equation (1) for an axially symmetric *g*-tensor cannot be responsible for its extremely low value (see discussion in Ref. [1]). No such effects of extraordinary large *D* values were reported for bis(titanocene) aromatic dicarboxylates [8d].

#### 2.4. Conclusions

Both complexes **2** and **3** possess crystallographic molecular structures with their SOMO *d*<sup>1</sup> orbitals in parallel orientation, and their EPR spectra in MTHF and toluene glass, respectively, prove that these unpaired electrons form a triplet state. The use of polar MTHF matrix for **2** which was necessary due to its extremely low

solubility in toluene resulted in its partial dissociation to give mononuclear titanocene alcoholate species. The triplet state EPR spectra for **2** revealed the presence of two species differing slightly in *g* and *D* parameters. The corresponding Ti–Ti distances calculated from Equation (1) were slightly longer than the crystallographic one that can be accounted for the presence of two conformations of the dimethylene link in the polar MTHF matrix. Surprisingly enough, compound **3** displayed nearly the same zero-field splitting *D* as compound **2** whereas its crystallographic Ti–Ti distance was by 1.47 Å longer. Such a large discrepancy between the crystallographic distance and that determined from zero-field splitting is reported for the first time. Since a good agreement has been achieved independently of mutual orientation of titanocene moieties (and hence SOMO *d*<sup>1</sup> orbitals) (for perpendicular see Refs. [3–6], for parallel Refs. [1,2]) an enhancing contribution to the through-space dipole–dipole interaction is to be sought in the effect of conjugation in the 1,4-dioxophenylene quinonide link. A more detailed investigation into this effect is behind the scope of this work.

### 3. Experimental

#### 3.1. Methods

The singly tucked-in titanocene [Ti( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^5$ : $\eta^1$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)] (**1**) and titanium(III) products were extremely air- and moisture-sensitive, therefore all reactions, isolation, and handling were done under vacuum using an all-glass high-vacuum line operated with metal valves and all-sealed glass devices equipped with breakable seals. 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 (Magnetech, Berlin, Germany) in the X-band. *g*-Values were determined by using an Mn<sup>2+</sup> standard at  $g = 1.9860$  ( $M_I = -1/2$  line). A variable temperature unit STT-3 was used for measurements in the range -150 to +25 °C. UV–near IR spectra in the range of 300–1800 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma). Crystalline samples for melting point and EI-MS spectra and KBr pellets for IR spectra were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen. IR spectra were taken in an air-protecting cuvette on a Nicolet Avatar FTIR spectrometer in the range 400–4000 cm<sup>-1</sup>. <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 and 75.4 MHz, respectively, in C<sub>6</sub>D<sub>6</sub> solutions at 25 °C. Chemical shifts ( $\delta$ /ppm) are given relative to solvent signals ( $\delta_H$  7.15,  $\delta_C$  128.0).

#### 3.2. Chemicals

The solvents hexane, toluene, tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) were dried by refluxing over LiAlH<sub>4</sub> and stored as solutions of dimeric titanocene [( $\mu$ - $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>)Ti( $\mu$ -H)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] [18]. Crystalline **1** was obtained by thermolysis of [TiMe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] in toluene [11e], and purified by crystallization from hexane. Ethylene glycol and hydroquinone (both Aldrich) were used as received. They were weighed on air, and degassed in high vacuum.

#### 3.3. Synthesis of [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiOCH<sub>2</sub>CH<sub>2</sub>OTi( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (**2**)

Ethylene glycol (0.050 g, 0.80 mmol) was degassed on a vacuum line, and a solution of **1** in toluene (2.0 mmol/10 ml) was added

from an attached ampule. This mixture was heated under stirring to 60 °C for 1 h changing the initial purple color of **1** to brown. After standing overnight a finely crystalline pale purple solid sedimented from a brown solution. The solution was decanted, the toluene distilled back to wash the sediment until the decanted solution was colorless. The pale purple solid of **3** was dried in vacuum and then, 10 ml of THF was distilled over it on a vacuum line. A brownish solution was decanted away, and THF was distilled back onto the solid. After standing for 3 days a light pink solution was separated from the pale purple solid. This was dried in vacuum, and weighed. The solution was used for EPR and UV–near IR measurements, and for crystallization by a slow evaporation of the solvent from one to another arm of a crystallization ampule. IR spectra of crystalline aggregates were identical with those of the pale purple solid. Several needle-like single crystals were used for X-ray diffraction analysis.

### 3.3.1. Compound **2**

Yield 0.46 g (84%). M.p. > 360 °C. IR (KBr, cm<sup>-1</sup>): 2970 (m,sh), 2906 (vs), 2860 (s), 2832 (m), 2720 (vw), 2655 (vw), 1494 (w), 1442 (m), 1377 (s), 1309 (vw), 1204 (vw), 1168 (m), 1127 (vs), 1064 (w), 1024 (m), 496 (s), 415 (s). UV–vis (THF): 365(sh) >> 495 > 620(sh) nm. EPR (purple powder, -196 °C):  $g_{\parallel} = 1.999$ ,  $g_{\perp} = 1.972$ ,  $g_{av} = 1.981$ ,  $\Delta Ms = 2$ ,  $\Delta H \sim 110$  G; (MTHF, 22 °C): two species,  $g = 1.978$ ,  $\Delta H = 3.0$  G, and  $g \sim 1.977$ ,  $\Delta H \sim 10.0$  G; (MTHF, -150 °C):  $S = 1/2$ :  $g_1 = 2.000$ ,  $g_2 = 1.982$ ,  $g_3 = 1.956$ ,  $g_{av} = 1.979$ ;  $S = 1$ : only outer features detected at  $g_z(1) = 1.9817(\pm 5)$ ,  $\Delta H_{zz}(1) = 135$  G,  $D = 0.0062$  cm<sup>-1</sup>;  $g_z(2) = 1.9826(\pm 5)$ ,  $\Delta H_{zz}(2) = 122$  G,  $D = 0.0057$  cm<sup>-1</sup>. Calcd. for C<sub>42</sub>H<sub>64</sub>O<sub>2</sub>Ti<sub>2</sub>: C, 72.40; H, 9.26. Found: C, 72.46; H, 9.31.

### 3.4. Synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiOC}_6\text{H}_4\text{OTi}(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**3**)

Hydroquinone (0.083 g, 0.75 mmol) was degassed on a high-vacuum line and a solution of **1** in toluene (2.0 mmol/10 ml) was added from an attached ampule. This mixture was heated to 60 °C for 10 h with stirring while changing the initial purple color of **1** to brown. After cooling to -5 °C overnight a reddish brown mother liquor containing some unreacted **1** was separated from greenish brown crystalline solid. This was washed with 3 ml of toluene and dried in vacuum to give pale green crystalline solid.

### 3.4.1. Compound **3**

Yield 0.42 g (76%). M.p. > 360 °C. EI-MS (320 °C):  $m/z$  (relative abundance) 746 (20), 745 (36), 744 (M<sup>+</sup>; 57), 743 (20), 742 (15), 596 (6), 595 (10), 573 (7), 428 (7), 427 ([M-Cp\*TiC<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>]<sup>+</sup>; 15), 337 (9), 320 (13), 319 (30), 318 ([Cp\*<sub>2</sub>Ti]<sup>+</sup>; 100), 317 (34), 316 (21), 315 (10), 136 (10), 135 (15), 119 (21), 105 (17), 91 (23), 57 (19), 55 (15), 43 (26), 41 (25). IR (KBr, cm<sup>-1</sup>): 3062 (vw), 3018(w), 2980(m), 2956(m, sh), 2906 (s), 2858 (m), 2722 (vw), 1597 (vw), 1486 (vs), 1451 (m), 1432 (m), 1378 (m), 1256 (vs), 1165 (w), 1081 (w), 1061 (vw), 1023 (w), 866 (s), 822 (m), 801 (vw), 522 (vw), 422 (m). UV–near IR (toluene): 345 >> 450 > 630 (sh) > 1500–1510 nm. EPR (toluene, 22 °C):  $g = 1.9757$ ,  $\Delta H = 2.7$  G;  $a_{Ti} = 3.9$  G; (toluene, -140 °C): electronic triplet state  $S = 1$ ,  $g_z = 1.975$ ,  $\Delta H_{zz} = 123$  G,  $g_y = 1.980$ ,  $\Delta H_{yy} = 75$  G,  $g_x \sim 1.977$ ,  $\Delta H_{xx} = 47$  G,  $g_{av} = 1.977$ ,  $D = 0.00567$  cm<sup>-1</sup>,  $E = 0.00043$  cm<sup>-1</sup>.  $\Delta Ms = 2$  transition observed at  $g \sim 3.954$ ,  $\Delta H \sim 22$  G. Calcd. for C<sub>46</sub>H<sub>64</sub>O<sub>2</sub>Ti<sub>2</sub>: C, 74.18; H, 8.66. Found: C, 74.24; H, 8.70.

### 3.5. Oxidation of **3** with PbCl<sub>2</sub> to give $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiCl}(\text{OC}_6\text{H}_4\text{O})\text{TiCl}(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**4**)

Compound **3** (0.08 g, 0.1 mmol) was dissolved in 20 ml of THF, and the pale brown solution was poured onto degassed PbCl<sub>2</sub> (0.033 g, 0.12 mmol), and stirred at 40 °C. Within 1 h, the solution

turned through yellow-green to yellow color while a black powder of precipitated lead was formed. After evaporating the solvent, the residue was extracted with toluene to give a low-soluble amorphous yellow solid. Its saturated solution in C<sub>6</sub>D<sub>6</sub> contained **4** in at least 85%.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.87 (s, 60H, C<sub>5</sub>Me<sub>5</sub>); 6.78 (s, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C {<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>): 12.6 (C<sub>5</sub>Me<sub>5</sub>); 117.1 (CH, C<sub>6</sub>H<sub>4</sub>); 125.9 (C<sub>5</sub>Me<sub>5</sub>); 161.0 (C<sub>ipso</sub>, C<sub>6</sub>H<sub>4</sub>). 1D NOESY (C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H<sub>irr</sub>/<sup>1</sup>H<sub>res</sub> 1.87/6.78 (C<sub>5</sub>Me<sub>5</sub>/C<sub>6</sub>H<sub>4</sub>). The  $\delta H$  values agree with those of Ref. [14].

### 3.6. X-ray crystallography

Single crystals of compounds **2** and **3** were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen, and sealed by wax. Diffraction data were collected on a Nonius KappaCCD diffractometer and processed by the HKL program package [19]. The phase problem was solved by direct methods (SIR-92) [20], followed by consecutive Fourier syntheses and refined by full-matrix least-squares on  $F^2$  (SHELXL-97 [21]). Relevant crystallographic data are given in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions. Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**2**: CCDC-773126, **3**: CCDC-772675). Copies of the data can be obtained free of charge upon application to CCDC (e-mail: deposit@ccdc.cam.ac.uk).

### 3.7. Computational details

DFT studies have been carried out at the Fermi cluster at the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, v.v.i., using Gaussian 03, Revision E.01 [22]. The calculations used the Becke three parameter hybrid exchange functional [23] and the Perdew 86 correlational functionals [24]. The geometry of **2** was optimized using the 6-31G(d) basis set employed for all atoms.

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