

Note

# Synthesis and molecular structure of hexanuclear organotitanium ion complex: $[\text{Cp}'_6\text{Ti}_6(\mu_3\text{-O})_8][\text{C}_2\text{B}_{10}\text{H}_{10}(\mu\text{-S}_2)_2\text{C}_2\text{B}_9\text{H}_{10}]_2$

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## Abstract

The reaction of bis[(2-methoxyethyl)cyclopentadienyl] titanium dichloride with dilithium dithiolato carborane in THF give a novel hexanuclear organotitanium ion complex  $[\text{Cp}'_6\text{Ti}_6(\mu_3\text{-O})_8][\text{C}_2\text{B}_{10}\text{H}_{10}(\mu\text{-S}_2)_2\text{C}_2\text{B}_9\text{H}_{10}]_2$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3$ ) ( $[\mathbf{1}][\mathbf{2}]_2$ ) as yellow crystal blocks. The cation  $[\mathbf{1}]^{2+}$  has an octahedral metallic skeleton of six titanium atoms with the tricoordinated oxygen ( $\mu_3\text{-O}$ ) and the anion  $[\mathbf{2}]^-$  consists of two  $\text{S}_2$  bridged 7,8-dicarbaundecaborate cluster and 1,2-dicarba-*closo*-dodecaborate cluster.

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**Keywords:** Hexanuclear complex; Cluster; Carborane; Titanium; Structure

## 1. Introduction

Since Corradini and Allegra [1] reported the first structure of the complex  $[\text{CpTiCl}_2]_2(\mu\text{-O})$  which contains an unusual, linear Ti–O–Ti arrangement, such kind of organotitanium oxides have been received great attentions, due to their remarkable structures and their unexpected reactivities and applications [2]. So far, many organotitanium oxides with open-chain and cyclic structures have been reported, such as  $(\text{Cp}_2\text{Ti})_2(\mu\text{-O})$  [3],  $[\text{Cp}_2\text{TiCl}]_2(\mu\text{-O})$  [4],  $[\text{CpTiCl}_2]_2(\mu\text{-O})$  [5],  $(\text{Cp}_2\text{TiCl})(\mu\text{-O})(\text{CpTiCl})(\mu\text{-O})(\text{Cp}_2\text{TiCl})$  [6],  $[\text{Cp}^*\text{TiCl}(\mu\text{-O})]_3$  [7],  $[\text{Cp}^*\text{Ti}(\mu\text{-O})]_3(\mu_3\text{-CR})$  ( $\text{R} = \text{H}, \text{Me}$ ) [8],  $[\text{CpTiCl}(\mu\text{-O})]_4$  [9],  $(\text{Cp}^*\text{Ti})_4\text{X}_2(\mu\text{-O})_5$  ( $\text{X} = \text{Cl}, \text{Me}$ ) [10]. As we know, organometallic oxides with the tricoordinated oxygen  $\mu_3\text{-O}$  allow the formation of polyhedral cages [2a]. Capping of the eight faces of an octahedron with the oxygen atoms results as  $\text{M}_6(\mu_3\text{-O})_8$  cage structure. The first hexanuclear organotitanium oxide  $(\text{CpTi})_6(\mu_3\text{-O})_8$  with  $\mu_3\text{-O}$  bridging was reported in 1977 [11]. However, the analogues of such hexanuclear organotitanium oxide are really rare except a few examples of replacing some oxygen atoms with chlorine atoms [12] or sulfur atoms [13]. A significant aspect of this chemistry is the electronic configuration of such organometallic aggregate. The neutral cluster  $(\text{CpTi})_6(\mu_3\text{-O})_8$  has two electrons in excess of those required by the inert gas formalism, so an integral metal oxidation state cannot be identified. However, with high symmetry and diamagnetism, those compounds exclude a localized  $\text{Ti}_4^{\text{IV}}\text{Ti}_2^{\text{III}}$  description. Fortunately, MO calculations explain the diamagnetism by placing the two excess electrons in the lowest  $a_{1g}$  orbital [14,15]. And the two electrons may be considered as located at the center of the octahedron. For comparison with this organotitanium oxide, a similar organozirconium oxide  $(\text{C}_5\text{Me}_4\text{Et})_6\text{Zr}_6(\mu_6\text{-O})(\mu_3\text{-O})_8$ , encapsulating a central  $\mu_6\text{-O}^{2-}$  ion within the cage, was described by Roesky and co-workers [16]. All of the zirconium atoms have the same valence +4 and no excess electrons occupy the 12 cluster orbitals. To the best of our knowledge so far, all of the reported hexanuclear organotitanium or organozirconium oxides are neutral clusters.

On the other hand, during the past decade considerable attention has been devote to half-sandwich transition metal complexes with dichalcogenolato-*ortho*-carboranyl ligands,

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to take the advantage of their unique molecular structures and their wide-ranging potential applications [17]. Up to date intensive studies on half-sandwich transition metal complexes of Co, Rh and Ir containing the dichalcogenolato-*ortho*-carboranyl ligands have illustrated that these complexes serve as excellent precursors to study the addition reaction of low valent organometallic complexes [18] and substitution of the carborane cage in the position B(3)/B(6) [19]. However, the group IV transition metal complexes with dichalcogenolato-*ortho*-carboranyl ligands are really rare and the further studies on these complexes are not reported so far [20]. These prompted us to investigate the reactions of metallocene complexes with dilithium dichalcogenolato-*ortho*-carborane.

As a further study to these fields, we report the synthesis, characterization and X-ray structure of novel hexanuclear organotitanium ion complex  $[\text{Cp}'_6\text{Ti}_6(\mu_3\text{-O})_8][\text{C}_2\text{B}_{10}\text{H}_{10}(\mu\text{-S}_2)_2\text{C}_2\text{B}_9\text{H}_{10}]_2$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3$ ) (**[1][2]**<sub>2</sub>).

## 2. Results and discussion

We previously reported that the reactions of  $\text{Cp}_2\text{TiCl}_2$  with dilithium dichalcogenolato carboranes  $\text{Li}_2\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$  ( $\text{E} = \text{S}, \text{Se}$ ) afforded mononuclear ionic half-sandwich titanium complexes  $[\text{Li}(\text{THF})_4]\{\text{CpTi}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]_2\}$  ( $\text{E} = \text{S}, \text{Se}$ ) in which one cyclopentadienyl ring was omitted [17a]. As an extension of this work, we used bis[(2-methoxyethyl)cyclopentadienyl] titanium dichloride as the starting material to react with dilithium dithiolato carborane in THF. After recrystallization of product from THF/hexane in the air at  $-15^\circ\text{C}$ , an unexpected product **[1][2]**<sub>2</sub> was isolated in moderate yield (Scheme 1). Complex **[1][2]**<sub>2</sub> is a yellow crystalline solid with unusual thermal stability. The melting point of the compound exceeds  $300^\circ\text{C}$ . Complex **[1][2]**<sub>2</sub> is very stable to air. No reaction was observed on exposing the solid of the compound to air. This thermally stable compound is readily soluble in THF, and is less soluble in hexane, benzene, toluene and diethyl ether.

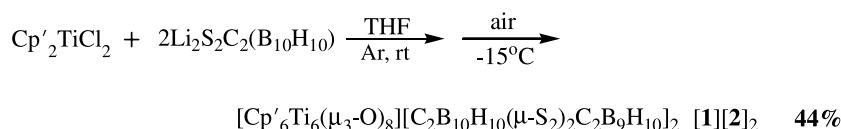
During our research, as the existence of detected anion  $[\text{C}_2\text{B}_{10}\text{H}_{10}(\mu\text{-S}_2)_2\text{C}_2\text{B}_9\text{H}_{10}]^-$  (**[2]**<sup>-</sup>), the cationic cluster  $[\text{Cp}'_6\text{Ti}_6(\mu_3\text{-O})_8]_{2+}$  (**[1]**<sup>2+</sup>) is identified as a +2 cation. Furthermore, the six titanium atoms should have the same valence +4. As the confirmation of the electronic arrangement, the diamagnetic phenomenon of the complex could be easily proved. This is, to our best knowledge, the first reported divalent cationic hexanuclear organotitanium oxide.

Because we have confirmed the existence of mononuclear ionic half-sandwich titanium complexes  $[\text{Li}(\text{THF})_4]\{\text{CpTi}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]_2\}$  ( $\text{E} = \text{S}, \text{Se}$ ), we presume that the first step

of the reaction should bring the intermediate  $[\text{Li}(\text{THF})_4]\{\text{Cp}'\text{Ti}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]_2\}$ , and then this mononuclear complex react with  $\text{O}_2$  (or  $\text{H}_2\text{O}$ ) during the crystallization at  $-15^\circ\text{C}$  to generate the cationic hexanuclear organotitanium oxide **[1][2]**<sub>2</sub>, which should be more thermally stable.

The IR spectrum of the product contains a strong IR band assigned to  $\nu(\text{BH})$  at  $2543\text{ cm}^{-1}$ , showing the presence of the boron cage. We also found two infrared absorptions ( $729$  and  $613\text{ cm}^{-1}$ ), which could be assigned to the two allowed ( $\text{T}_{1\mu}$ ) Ti–O vibrations of the  $\text{Ti}_6\text{O}_8$  core [11]. In the  $^1\text{H}$  NMR spectrum of **[1][2]**<sub>2</sub> in  $\text{THF-}d_8$ , the signals of cyclopentadienyl protons were observed at 6.93, 6.91 ppm, and the signals of the ether chain ( $\text{CH}_2$ ,  $\text{OCH}_2$  and  $\text{OCH}_3$ ) appeared at 3.15, 3.70 and 3.42 ppm, respectively. In the  $^{13}\text{C}$  NMR spectrum, six peaks (141.9, 123.1, 122.6, 71.8, 58.1, 31.0 ppm) were observed for the monosubstituted cyclopentadienyl carbons [21], and in particular, the signals for the carbon atoms of **[2]**<sup>-</sup> were found at 86.7 and 85.4 ppm. In the  $^{11}\text{B}$  NMR spectrum, there were three peaks ( $-33.84$ ,  $-34.86$ ,  $-35.85$  ppm), which should be assigned to B(9), B(11), B(10) in the open cage of *nido*-carborane [22]. All these data were consistent with the structure established by X-ray diffraction. And the structures of the cation **[1]**<sup>2+</sup> and its counter ion **[2]**<sup>-</sup>, which crystallise in the monoclinic space group  $P2(1)/c$ , are shown in Fig. 1, along with selected metrical data and crystal data and refinement details are given in Table 1.

The main cluster feature of this cation **[1]**<sup>2+</sup> is an octahedral metallic skeleton of six titanium atoms. Bridging oxygen atoms occupy the eight triangular faces of the hexanuclear octahedral centrosymmetrically. Each titanium atom connects a Cp ring with an oxygen-functionalized side chain (the average distance between Ti and Cp'(cent) is 2.018 Å). Generally observed, the coordination environment of each titanium atom is a square pyramid bearing the basal plane of oxygen atoms and the apex with Cp' (Fig. 2). The average distance (1.969 Å) between Ti and O is similar to that in neutral cluster  $(\text{CpTi})_6(\mu_3\text{-O})_8$  (1.973 Å), which indicates a symmetrical  $\mu_3\text{-O}$  functionality. The average Ti–O–Ti angles are  $100.36^\circ$ . There are two kinds of O–Ti–O angles, the average one is  $78.00^\circ$ , and another is  $125.74^\circ$ . And a significant elongation of the metallic octahedral cage was detected, as revealed by the increase in the average Ti···Ti distance from 2.891 Å in the neutral cluster  $(\text{CpTi})_6(\mu_3\text{-O})_8$  [11] to 3.020 Å in **[1]**<sup>2+</sup>. The average angles between adjacent titanium atoms (Ti···Ti···Ti angles) are either  $60.04^\circ$  or  $90.00^\circ$ . We estimated these separations are highly affected by the changing elec-



Scheme 1. Synthesis of complex **[1][2]**<sub>2</sub>.

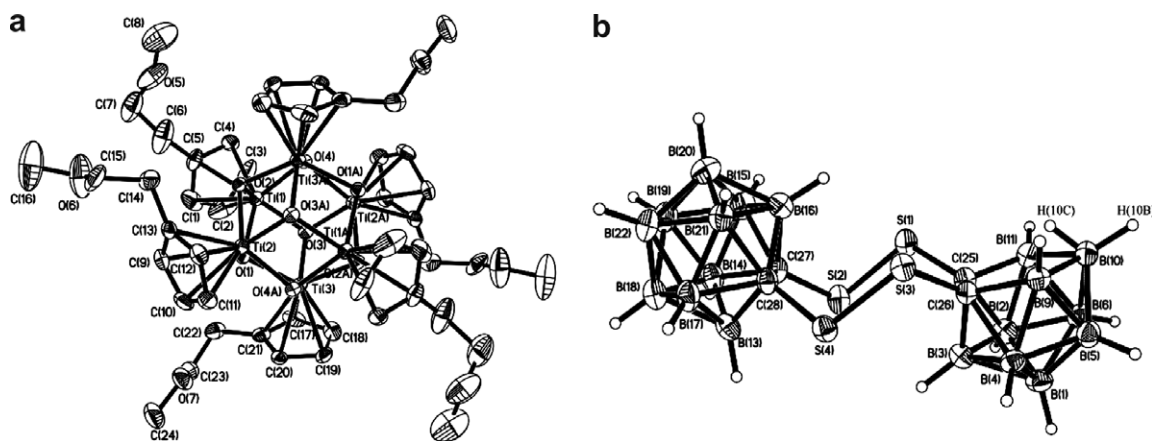


Fig. 1. (a) Structure of the cation  $[1]^{2+}$ , hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ( $^{\circ}$ ): Ti(1)–O(1) 1.960(3), Ti(1)–O(2) 1.975(3), Ti(1)–O(3) 1.977(3), Ti(1)–O(4) 1.958(3), Ti(1)–Ti(2) 3.013(2), Ti(1)–Ti(3) 3.027(2); O(1)–Ti(1)–O(2) 78.33(12), O(4)–Ti(1)–O(1) 125.46(12), Ti(2)–Ti(1)–Ti(3) 60.16(3), Ti(3A)–Ti(1)–Ti(3) 90.15(4), Ti(2)–O(1)–Ti(3) 100.33(13), Ti(1)–Cp'(1) 2.019(7), Cp'(1) refers to the centroid of the ring C1...C5. (b) Structure of the anion  $[2]^{-}$ . Selected bond lengths (Å) and angles ( $^{\circ}$ ): S(1)–C(25) 1.788(5), S(1)–S(2) 2.029(2), S(2)–C(27) 1.779(5), S(3)–C(26) 1.783(4), S(3)–S(4) 2.029(2), S(4)–C(28) 1.784(5), B(11)–B(10) 1.843(8), B(9)–B(10) 1.836(8); C(25)–S(1)–S(2) 108.98(18), C(26)–C(25)–S(1) 123.9(3).

Table 1  
Crystallographic data for  $[1][2]_2$

Empirical formula	$C_{56}H_{106}B_{38}O_{14}S_8Ti_6$
Fw	1958.07
Crystal system	Monoclinic
Space group	$P2(1)/c$
$a$ (Å)	16.766(13)
$b$ (Å)	19.443(15)
$c$ (Å)	14.330(11)
$\alpha$ ( $^{\circ}$ )	90
$\beta$ ( $^{\circ}$ )	91.875(12)
$\gamma$ ( $^{\circ}$ )	90
$V$ (Å $^3$ )	4669(6)
$Z$	2
$F(000)$	2008
Crystal size (mm)	0.10 × 0.08 × 0.05
$\theta$ Range ( $^{\circ}$ )	1.22–25.01
$\sigma_{calc}$ (Mg m $^{-3}$ )	1.393
$\mu$ (mm $^{-1}$ )	0.721
Number of reflections collected	46336
Number of index reflections	8200
$R_{int}$	0.0601
Number of data/restraints/parameters	8200/0/580
Goodness-of-fit on $F^2$	0.912
$R$ indices ( $I > 2\sigma I$ ) <sup>a</sup>	$R_1 = 0.0541$ $wR_2 = 0.1234$
$R$ indices (all data)	$R_1 = 0.1012$ $wR_2 = 0.1404$
Largest peak and hole (e Å $^{-3}$ )	0.964/−0.502

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}.$$

tronic configuration. The bond length of Ti(1)–C(5) is the longest among the ones of titanium and the five carbon atoms in the cyclopentadienyl group. This indicates that there is a slight repulsion between the side-chain and the bridging oxygen atoms. These data indicate that the cation  $[1]^{2+}$  has the same molecule skeleton with neutral cluster  $(CpTi)_6(\mu_3-O)_8$ , but different electronic configuration.

The crystal structure of the anion  $[2]^{-}$  also attracts our attentions. The uncentrosymmetrical anion  $[2]^{-}$  consists

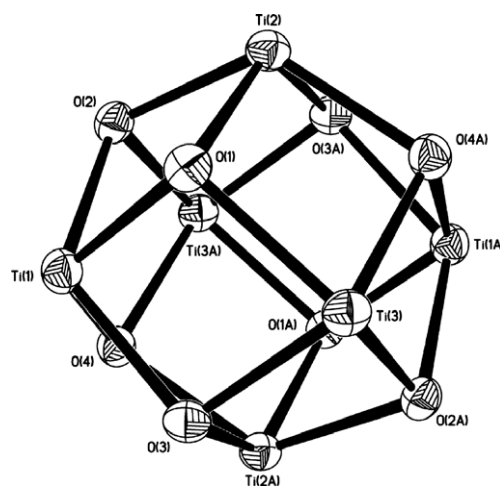


Fig. 2. The core of the cation  $[1]^{2+}$ .

of a 7,8-dicarbaundecaborate cluster, a 1,2-dicarba-*closo*-dodecaborate cluster and two  $S_2$  bridges. As we observed, the two cluster components are relatively placed in an anti fashion. Some selected distances are indicated in Fig. 1. The S–S distance is 2.029(2) Å, which is a little shorter than that of the anion  $[C_2B_9H_{10}(\mu-S_2)_2C_2B_9H_{10}]^{2-}$  [22]. And the average bond length of S–C is 1.784 Å. The bond length B(9)–B(10) [1.836(8) Å] and B(10)–B(11) [1.843(8) Å] suggest a *endo* terminal hydrogen atom H(10C) [23]. This anion was first speculated from FBAMS spectrum in McKinney's research in 1996 [24]. However, no crystal structure was obtained then. Our crystal study confirms the existence of the negative ion.

In summary, we found a novel divalent cationic hexanuclear organotitanium ion complex  $[1][2]_2$ . The electronic structures of the cation  $[1]^{2+}$  and  $(CpTi)_6(\mu_3-O)_8$  should provide fundamental information on their properties and ultimately on their chemical behavior. The excess orbitals

mainly derived from the d metal orbitals may behave as a metallic band with potential for electronic storage and corresponding electron release processes [15]. Although  $[1]^{2+}$  and  $(\text{CpTi})_6(\mu_3\text{-O})_8$  have different electronic configuration, the molecule skeletons are almost same. Owing to these features, a compound of the type  $(\text{CpTi})_6(\mu_3\text{-O})_8$  may be used as molecular batteries. On the other hand, the structure of the anion 7,8-dicarbaundecaborate derivative  $[2]^-$  is first reported, which give a strong proof to this field. However, the formative process of this compound should contain hydrolyzation and oxidation, which should be very complex. Further studies are in progress.

### 3. Experimental

All syntheses were conducted using standard Schlenk techniques under an inert atmosphere of nitrogen. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use.  $\text{Cp}'_2\text{TiCl}_2$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3$ ) [21] and  $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})_2]_2$  [25] were synthesized according to the procedures described in the literature. The element analyses were performed on a Rapid CHN-O 240C Analyzer. Infrared spectra were recorded on Nicolet- FT-IR-50X spectrophotometer, only characteristic frequencies were listed.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{11}\text{B}$  NMR spectra were obtained using Bruker DMX-500 and DMX-300 spectrophotometer in  $\text{CDCl}_3$ , respectively. Chemical shifts (downfield from TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ), and  $\text{BF}_3 \cdot \text{OEt}_2$  ( $^{11}\text{B}$ )) and coupling constants are reported in ppm and in Hz, respectively.

**Synthesis of  $[1][2]_2$ :** A solution of  $\text{Cp}'_2\text{TiCl}_2$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_3$ ) (73 mg, 0.2 mmol) in THF (20 ml) was cooled to  $-78^\circ\text{C}$  and a solution of  $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  in  $\text{Et}_2\text{O}$  (10 ml, 0.4 mmol) was added dropwise over a period of 10 min. The resulting mixture was warmed to room temperature and stirred overnight. Afterwards, the solvent was removed in vacuo and replaced with an equal volume of toluene. The clear solution was separated from the insoluble material by centrifugal purification. Hexane (5 mL) was slowly layered onto a THF solution (5 mL) of the product in a test tube in the air. Storage of the solution at  $-15^\circ\text{C}$  for a week afforded yellow crystal of  $[1][2]_2$  (29 mg, 44%). Elemental Anal. Calc. for  $\text{C}_{56}\text{H}_{106}\text{B}_{38}\text{O}_{14}\text{S}_8\text{Ti}_6$ : C, 34.35; H, 5.46. Found: C, 34.28; H, 5.38%.  $^1\text{H}$  NMR (500 MHz,  $\text{THF}-d_8$ , 293 K): 6.93 (d, 12H, Cp,  $J_{\text{H-H}} = 2.34$  Hz), 6.91 (d, 12H, Cp,  $J_{\text{H-H}} = 2.40$  Hz), 3.70 (t, 12H,  $\text{CH}_2\text{O}$ ,  $J_{\text{H-H}} = 11.52$  Hz), 3.15 (t, 12H,  $\text{CH}_2\text{Cp}$ ,  $J_{\text{H-H}} = 11.43$  Hz), 3.42 (s, 18H,  $\text{CH}_3\text{O}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{THF}-d_8$ , 293 K): 141.9, 123.1, 122.6 (s, Cp), 71.8 (s,  $\text{OCH}_2$ ), 58.1 (s,  $\text{OCH}_3$ ), 31.0 (s,  $\text{CpCH}_2$ ), 86.7, 85.4 (s,  $\text{C}_2$ -carborane).  $^{11}\text{B}$  NMR (160 MHz,  $\text{THF}-d_8$ , 293 K):  $-2.66$ ,  $-3.59$ ,  $-4.48$ ,  $-5.51$ ,  $-6.50$ ,  $-7.97$ ,  $-8.84$ ,  $-10.67$ ,  $-11.62$ ,  $-12.97$ ,  $-13.81$ ,  $-14.50$ ,  $-15.26$ ,  $-16.00$ ,  $-18.00$ ,  $-18.99$ ,  $-33.84$ ,  $-34.86$ ,  $-35.85$ . IR (KBr):  $1111\text{ cm}^{-1}$  ( $\nu_{\text{C-O-C}}$ , as),  $2543\text{ cm}^{-1}$  ( $\nu_{\text{B-H}}$ ),  $729\text{ cm}^{-1}$ ,  $613\text{ cm}^{-1}$  ( $\nu_{\text{Ti-O}}$ ).

**Crystal structure determination:** Yellow single crystals of  $[1][2]_2$  suitable for X-ray diffraction studies were grown by

slow diffusion of hexane into THF solution at  $-15^\circ\text{C}$ . Crystal data were measured at 298 K on a Bruker SMART APEX CCD diffractometer [ $\lambda(\text{Mo-K}\alpha) = 0.71073\text{ \AA}$ ], graphite monochromator, the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELXTL program [26]. All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Crystal data, data collection parameters, and the results of the analyses of complex  $[1][2]_2$  are listed in Table 1.

### 4. Supplementary material

CCDC 616925 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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