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Note

Synthesis and molecular structure of hexanuclear organotitanium ion complex: $[Cp'_6Ti_6(\mu_3\text{-}O)_8][C_2B_{10}H_{10}(\mu\text{-}S_2)_2C_2B_9H_{10}]_2$

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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 $[Cp'_6Ti_6(\mu_3\text{-}O)_8][C_2B_{10}H_{10}(\mu\text{-}S_2)_2C_2B_9H_{10}]_2$ ($Cp' = C_5H_4CH_2CH_2OCH_3$) ([**1**][**2**]$_2$) as yellow crystal blocks. The cation $[\mathbf{1}]^{2+}$ has an octahedral metallic skeleton of six titanium atoms with the tricoordinated oxygen (μ_3-O) and the anion $[\mathbf{2}]^-$ consists of two S_2 bridged 7,8-dicarbaundecaborate cluster and 1,2-dicarba-*closo*-dodecaborate cluster.

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

1. Introduction

Since Corradini and Allegra [1] reported the first structure of the complex $[CpTiCl_2]_2(\mu\text{-}O)$ 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 $(Cp_2Ti)_2(\mu\text{-}O)$ [3], $[Cp_2TiCl]_2(\mu\text{-}O)$ [4], $[CpTiCl_2]_2(\mu\text{-}O)$ [5], $(Cp_2TiCl)(\mu\text{-}O)(CpTiCl)(\mu\text{-}O)(Cp_2TiCl)$ [6], $[Cp^*TiCl(\mu\text{-}O)]_3$ [7], $[Cp^*Ti(\mu\text{-}O)]_3(\mu_3\text{-}CR)$ (R = H, Me) [8], $[CpTiCl(\mu\text{-}O)]_4$ [9], $(Cp^*Ti)_4X_2(\mu\text{-}O)_5$ (X = Cl, Me) [10]. As we know, organometallic oxides with the tricoordinated oxygen μ_3-O allow the formation of polyhedral cages [2a]. Capping of the eight faces of an octahedron with the oxygen atoms results as $M_6(\mu_3\text{-}O)_8$ cage structure. The first hexanuclear organotitanium oxide $(CpTi)_6(\mu_3\text{-}O)_8$ with μ_3-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 $(CpTi)_6(\mu_3\text{-}O)_8$ 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 $Ti_4^{IV}Ti_2^{III}$ 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 $(C_5Me_4Et)_6Zr_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8$, encapsulating a central μ_6-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 elections 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 $[Cp'_6Ti_6(\mu_3\text{-}O)_8][C_2B_{10}H_{10}(\mu\text{-}S_2)_2C_2B_9H_{10}]_2$ ($Cp' = \eta^5\text{-}C_5H_4CH_2CH_2OCH_3$) ([**1**][**2**]$_2$).

2. Results and discussion

We previously reported that the reactions of Cp_2TiCl_2 with dilithium dichalcogenolato carboranes $Li_2E_2C_2(B_{10}H_{10})$ (E = S, Se) afforded mononuclear ionic half-sandwich titanium complexes $[Li(THF)_4]\{CpTi[E_2C_2(B_{10}H_{10})]_2\}$ (E = S, 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°C, an unexpected product [**1**][**2**]$_2$ was isolated in moderate yield (Scheme 1). Complex [**1**][**2**]$_2$ is an yellow crystalline solid with unusual thermal stability. The melting point of the compound exceeds 300 °C. Complex [**1**][**2**]$_2$ 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 $[C_2B_{10}H_{10}(\mu\text{-}S_2)_2C_2B_9H_{10}]^-$ ([**2**]$^-$), the cationic cluster $[Cp'_6Ti_6(\mu_3\text{-}O)_8]_{2+}$ ([**1**]$^{2+}$) is identified as a +2 cation. Further more, 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 $[Li(THF)_4]\{CpTi[E_2C_2(B_{10}H_{10})]_2\}$ (E = S, Se), we presume that the first step of the reaction should bring the intermediate $[Li(THF)_4]\{Cp'Ti[S_2C_2(B_{10}H_{10})]_2\}$, and then this mononuclear complex react with O_2 (or H_2O) during the crystallization at −15°C to generate the cationic hexanuclear organotitanium oxide [**1**][**2**]$_2$, which should be more thermally stable.

The IR spectrum of the product contains a strong IR band assigned to ν(BH) at 2543 cm^{-1}, showing the presence of the boron cage. We also found two infrared absorptions (729 and 613 cm^{-1}), which could be assigned to the two allowed ($T_{1\mu}$) Ti–O vibrations of the Ti_6O_8 core [11]. In the ^1H NMR spectrum of [**1**][**2**]$_2$ in THF-d_8, the signals of cyclopentadienyl protons were observed at 6.93, 6.91 ppm, and the signals of the ether chain (CH_2, OCH_2 and OCH_3) appeared at 3.15, 3.70 and 3.42 ppm, respectively. In the ^{13}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**]$^-$ were found at 86.7 and 85.4 ppm. In the ^{11}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**]$^{2+}$ and its counter ion [**2**]$^-$, which crystallise in the monoclinic space group *P*2(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**]$^{2+}$ 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 $(CpTi)_6(\mu_3\text{-}O)_8$ (1.973 Å), which indicates a symmetrical μ_3-O functionality. The average Ti–O–Ti angles are 100.36 Å. There are two kinds of O–Ti–O angles, the average one is 78.00°, and another is 125.74°. 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 $(CpTi)_6(\mu_3\text{-}O)_8$ [11] to 3.020 Å in [**1**]$^{2+}$. The average angles between adjacent titanium atoms (Ti···Ti···Ti angles) are either 60.04° or 90.00°. We estimated these separations are highly affected by the changing elec-

$$Cp'_2TiCl_2 + 2Li_2S_2C_2(B_{10}H_{10}) \xrightarrow[\text{Ar, rt}]{\text{THF}} \xrightarrow[\text{-15°C}]{\text{air}}$$

$$[Cp'_6Ti_6(\mu_3\text{-}O)_8][C_2B_{10}H_{10}(\mu\text{-}S_2)_2C_2B_9H_{10}]_2 \quad [\mathbf{1}][\mathbf{2}]_2 \qquad \mathbf{44\%}$$

Scheme 1. Synthesis of complex [**1**][**2**]$_2$.