

# Titanium(IV) compounds with cyano ligands: crystal structures of $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$ and $[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$ <sup>1</sup>

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## Abstract

The reaction of  $\text{Cp}_2\text{TiCl}_2$  with KCN in methanol, that contains some water, gives the dinuclear oxo-bridged cyano complex  $[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$  (**2**). The structure of **2**, as well as the structure of the known mononuclear complex  $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$  (**1**), was determined by X-ray crystallography. **1** crystallizes in the monoclinic space group  $P2_1/n$  with  $Z=4$  and unit cell dimensions  $a = 7.879(2)$ ,  $b = 12.235(3)$ ,  $c = 12.078(3)$  Å,  $\beta = 107.58(3)^\circ$  and **2** crystallizes in the monoclinic space group  $C2/c$  with  $Z=4$  and cell dimensions  $a = 13.354(11)$ ,  $b = 8.112(5)$ ,  $c = 18.017(19)$  Å,  $\beta = 92.52(10)^\circ$ .

**Keywords:** Titanium; Cyanide; Crystal structure; Cyclopentadienyl; Oxo-bridge; Metallocenes

## 1. Introduction

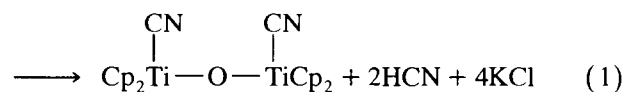
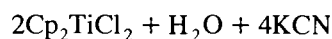
Whereas the pseudohalogenide complexes  $\text{Cp}_2\text{TiX}_2$  with  $\text{X}^- = \text{SCN}^-$ ,  $\text{OCN}^-$  or  $\text{N}_3^-$  can easily be prepared [1], the corresponding dicyano derivative  $\text{Cp}_2\text{Ti}(\text{CN})_2$  has not previously been prepared. The lack of electron density at the  $d^0$   $\text{Ti}^{\text{IV}}$  center precludes any possible stabilisation of the Ti–CN bonds via back-donation. The earliest attempt to prepare  $\text{Cp}_2\text{Ti}(\text{CN})_2$  was that of Pink in 1958 [2] who reacted  $\text{Cp}_2\text{TiCl}_2$  and KCN in chloroform/methanol. He observed that only one  $\text{Cl}^-$  could be replaced by  $\text{CN}^-$ . Since then, several reports of the synthesis of  $\text{Cp}_2\text{Ti}(\text{CN})\text{X}$ -type compounds have appeared. Some data for  $\text{Cp}_2\text{Ti}(\text{CN})\text{Cl}$  are given in a patent [3]. Recently, Moran and Fernandez [4,5] reported the preparation of  $\text{Cp}_2\text{Ti}(\text{CN})\text{X}$  with  $\text{X}^- = \text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ , and  $\text{NCSe}^-$ . These complexes were obtained by oxidative additions of the pseudohalogens  $\text{XCN}$  to  $\text{Cp}_2\text{Ti}(\text{CO})_2$ . Nesmeyanov et al. [6] found that the methanolate  $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$  forms in the reaction of  $\text{Cp}_2\text{TiCl}_2$  with KCN in methanol.

Evidently, a  $\pi$ -donor ligand X in  $\text{Cp}_2\text{Ti}(\text{CN})\text{X}$  induces a stabilisation of the Ti–CN bond through enhancement of the electron density at titanium. We report

here the preparation of the dinuclear oxo-bridged complex  $[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$  (**2**), its structure, and the X-ray structure of the known  $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$  (**1**).

## 2. Results and discussion

The reaction of  $\text{Cp}_2\text{TiCl}_2$  and KCN in a methanol/chloroform mixture proceeds with the formation of a yellow solutions of  $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$  (**1**) within less than 1 h at room temperature [2]. This compound can also be prepared in boiling methanol [6]. Attempts to prepare an ethoxy or phenoxy analog of **1** in solutions of ethanol/chloroform or phenol/chloroform were unsuccessful. When this reaction is repeated in the presence of small amounts of water, the corresponding oxo-bridged complex  $[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$  (**2**) is obtained (Eq. (1)). Depending on the relative amount of water, only crystals of **2** or mixtures of yellow crystals of **1** and orange crystals of **2** can be isolated.



It is well known that oxo-bridged dinuclear complexes are formed in the reaction of  $\text{Cp}_2\text{TiCl}_2$  with alkali-metal salts  $\text{MX}$  ( $\text{M} = \text{Na}, \text{K}$ ;  $\text{X}^- = \text{I}^-, \text{Br}^-, \text{NO}_3^-$ ,

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<sup>1</sup> Dedicated to Professor M.D. Rausch on the occasion of his sixty-fifth birthday.

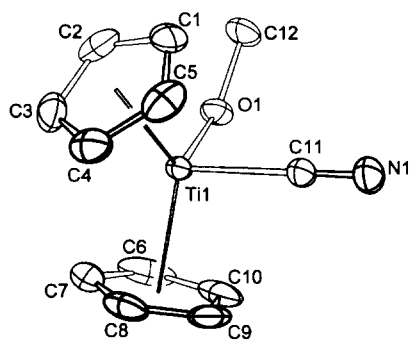
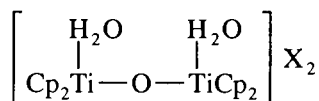


Fig. 1. Molecular structure and atom numbering scheme of  $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$  (**1**).

$0.5\text{S}_2\text{O}_6^{2-}$ ) in aqueous solutions [7,8]. **2** cannot be prepared by this method, because first the high pH of an aqueous KCN solution leads to a cleavage of the Ti–Cp bonds [9] and second, even if an oxo-bridged species is formed, it would probably be of the following type with  $\text{H}_2\text{O}$  instead of  $\text{CN}^-$  ligands at the Ti atoms [8]:



The IR spectrum of **2** shows a very strong absorption band at  $741 \text{ cm}^{-1}$ . This band is characteristic for titanium(IV) compounds with a  $\text{Cp}_2\text{Ti}-\text{O}-\text{TiCp}_2$  unit [7]. It should be mentioned here that **2** has been proposed by Coutts and Wailes [10] to be the yellow product that forms during the decomposition of the  $\text{Ti}^{\text{III}}$  complex  $[\text{Cp}_2\text{Ti}(\text{CN})]_n$  by air. Their conclusion was based upon the observation of “a strong band in the infrared around  $720 \text{ cm}^{-1}$ ”.

The molecular structures of **1** and **2** are shown in Figs. 1 and 2. Crystallographic data are listed in Table 1. Distances and angles are listed in Table 2. The geometry of **2** is constrained by crystallographic  $\text{C}_2$  symmetry. In Table 3 the essential structural parameters of both compounds are tabulated, together with those of related complexes. Comparison of the data indicates that the structures of the  $\text{Cp}_2\text{Ti}^{\text{IV}}$  unit in complexes with and without CN ligands are comparable. The Ti–CN

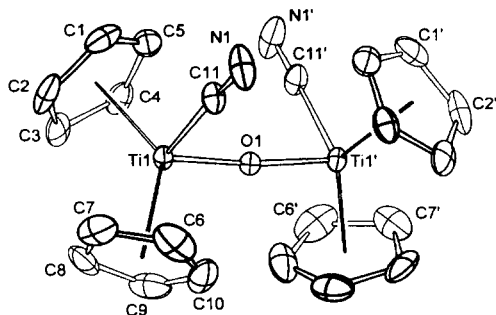


Fig. 2. Molecular structure and atom numbering scheme of  $[\text{Cp}_2\text{Ti}(\text{CN})_2]_2\text{O}$  (**2**).

Table 1  
Crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{12}\text{H}_{13}\text{NOTi}$	$\text{C}_{22}\text{H}_{20}\text{N}_2\text{OTi}_2$
<i>F</i> <sub>w</sub>	235.12	424.17
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
<i>a</i> (Å)	7.879(2)	13.354(11)
<i>b</i> (Å)	12.235(3)	8.112(5)
<i>c</i> (Å)	12.078(3)	18.017(19)
$\beta$ (°)	107.58(3)	92.52(10)
<i>Z</i>	4	4
<i>D</i> <sub>obsd</sub> (g cm <sup>-3</sup> )	1.41	1.45
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.407	1.445
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	6.8	7.7
Crystal dimensions (mm)	0.4, 0.5, 0.8	0.5, 0.5, 0.5
Data collection and refinement		
<i>hkl</i> range	–9/+9, 0/+15,	–14/+14, 0/+8,
	0/+14	0/+19
$2\theta_{\text{max}}$ (°)	50	45
Unique reflections	2166	1438
Observed reflections ( $F_o \geq 2\sigma(F_o)$ )	1992	1302
Parameters refined	138	127
<i>R</i>	0.040	0.043
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.048	0.053
Residual density (e Å <sup>-3</sup> )	0.39	0.53

bonds of 2.164(3) and 2.162(3) Å in **1** and **2** respectively are slightly longer than those in the titanium(III) complex  $[\text{Cp}_2\text{Ti}(\text{CN})]_4$  (2.13 Å), which contains bridging CN groups [15], and slightly shorter than the Ti–C  $\sigma$  bonds in  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$  (2.170(2) and 2.181(2) Å) [16]. The Ti–C–N bond angles of **1** and **2** are almost linear (176.3(2)° and 177.9(3)° respectively) and the C–N bond lengths of 1.150(4) and 1.144(5) Å are typical for a CN triple bond. As in other dinuclear oxo-bridged titanium compounds, the Ti–O–Ti fragment in **2** is nearly linear. This indicates additional

Table 2  
Selected distances (Å) and angles (°) for **1** and **2**<sup>a</sup>

Atoms	<b>1</b>	<b>2</b>
Ti–C(Cp)	2.356(3)–2.414(4)	2.356(4)–2.423(4)
Ti–C(11)	2.164(3)	2.162(3)
Ti–O(1)	1.835(2)	1.840(2)
Ti–Cp(1)	2.07	2.07
Ti–Cp(2)	2.09	2.08
N(1)–C(11)	1.150(4)	1.144(5)
O(1)–C(12)	1.407(4)	–
O(1)–Ti(1)–C(11)	91.5(1)	93.7(2)
Cp(1)–Ti(1)–Cp(2)	132.0	133.0
Ti(1)–C(11)–N(1)	176.3(2)	177.9(3)
Ti(1)–O(1)–C(12)	140.1(2)	–
Ti(1)–O(1)–Ti(1')	–	174.3(2)

<sup>a</sup> Cp(1) and Cp(2): centroids of the Cp rings containing C(1)–C(5) and C(6)–C(10) respectively.

$\pi$ -bonding of the oxygen atom to the two titanium centers [14,17]. As Fig. 2 shows, the two  $\text{Cp}_2\text{Ti}(\text{CN})\text{O}$  units of a  $[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$  molecule are rotated against each other around their Ti–O vectors. The rotation (measured by the C11–Ti–Ti'–C11' dihedral angle) is  $106.6(2)^\circ$ .

The importance of Ti–O  $\pi$ -bonding in organotitanium(IV) alkoxides has been emphasized by Caulton and coworkers [12]. They proposed that the alkoxy ligand in  $\text{Cp}_2\text{Ti}(\text{OEt})\text{Cl}$  donates three electrons ( $\text{Ti} \leftarrow \text{OR}$ ) resulting in an effective 18-electron configuration for the titanium atom. A comparison of the structural parameters of  $\text{Cp}_2\text{Ti}(\text{OEt})\text{Cl}$  with those of related compounds such as  $\text{Cp}_2\text{TiCl}_2$  indicates that alkoxide exceeds chloride in  $\pi$ -donor ability. The structure determination of **1** provides an opportunity to evaluate the extent to which the Ti–O and Ti–Cp distances in  $\text{Cp}_2\text{Ti}(\text{OR})\text{X}$ -type compounds are influenced by the presence of a  $\pi$ -acceptor ( $\text{CN}^-$ ) and  $\pi$ -donor ( $\text{Cl}^-$ ) ligand respectively. As Table 3 shows, the Ti–Cp distances are the same for **1** and  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ . The Ti–O distances are different, however. For **1** the Ti–O distance is  $0.020 \text{ \AA}$  shorter than for  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ . Therefore, we conclude that the degree of  $\pi$ -donation of the alkoxy ligand in **1** is higher than in  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ . The corresponding relatively high electron density at the metal atom of **1** is suggested to be available for back-donation to the cyanide ligand and thus to be responsible for the existence and high stability of **1**.

### 3. Experimental details

Methanol was distilled from magnesium turnings.  $\text{CHCl}_3$  was dried by refluxing over phosphorus(V) ox-

ide.  $\text{Cp}_2\text{TiCl}_2$  and KCN were stored over  $\text{CaCl}_2$ . Mass spectra were recorded on a Varian MAT 711 spectrometer. IR spectra were performed on a Mattson Galaxy 2020 FTIR instrument, and UV-visible spectra on a Hitachi V-2000 spectrometer.

#### 3.1. Preparation of $\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$ (**1**)

The method is essentially that of Pink [2] with the exception that an inert gas atmosphere was used. To a stirred solution of 2.50 g  $\text{Cp}_2\text{TiCl}_2$  (10 mmol) in dry  $\text{CHCl}_3$  at room temperature, 100 ml of absolute methanol and 2.50 g KCN (19 mmol) were added. Within 1 h the color changed from red to yellow. The solvents were removed by distillation under reduced pressure. The solid residue was treated with  $\text{CHCl}_3$  and the filtered solution was layered with *n*-pentane. Clear yellow crystals of **1** grew after some days in a refrigerator. The yield was 0.72 g (31%). Anal. Found: C, 61.22; H, 5.51; N, 5.81%.  $\text{C}_{12}\text{H}_{13}\text{NOTi}$ . Calc.: C, 61.30; H, 5.57; N, 5.96.

The crystals are stable for several days in air, soluble in  $\text{CHCl}_3$ , THF and methanol, and almost insoluble in *n*-pentane. Heating causes decomposition above  $160^\circ\text{C}$  without melting (m.p. according to Ref. [6]:  $164.5\text{--}166^\circ\text{C}$ ).

MS  $m/z$  (%): 235 (47.0)  $\text{M}^+$ , 220 (5.6), 204 (6.0)  $[\text{Cp}_2\text{TiCN}]^+$ , 178 (9.6)  $[\text{Cp}_2\text{Ti}]^+$ , 170 (17.0), 144 (100.0)  $[\text{CpTiOMe}]^+$ , 129 (36.0), 113 (84.8)  $[\text{CpTi}]^+$ , 86 (11.0), 74 (10.0), 65 (10.6), 64 (25.5), 48 (4.0), 39 (19.3), 31 (2.6).

IR (KBr-pellet,  $\text{cm}^{-1}$ ): 3100(m), 3095(m), 2936(w), 2911(m), 2868(m), 2124(m), 1455(m), 1439(m), 1422(m), 1366(m), 1088(s), 1065(s), 1030(m), 855(m), 822(s), 544(s), 428(s).

UV-vis ( $\text{CHCl}_3$ , nm): maxima at 256 and 388.

Table 3  
Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in **1**, **2**, and related  $\text{Cp}_2\text{TiXY}$  compounds

Compound	Ti–CN	Ti–Cp	Ti–OR or Ti–OTi	Cp–Ti–Cp'	X–Ti–Y	Ti–O–C or Ti–O–Ti	Ref.
<i>Mononuclear compounds</i>							
$\text{Cp}_2\text{Ti}(\text{CN})(\text{OCH}_3)$ <b>1</b>	2.164(2)	2.07 2.09	1.835(2)	132.0	91.5(2)	140.1(2)	
$\text{Cp}_2\text{TiCl}_2$	–	2.06	–	130.9	94.5	–	[11]
$\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$	–	2.08 2.09	1.855(2)	130.5	93.1(1)	133.2(2)	[12]
<i>Oxo-bridged compounds</i>							
$[\text{Cp}_2\text{Ti}(\text{CN})]_2\text{O}$ <b>2</b>	2.162(3)	2.07 2.08	1.840(2)	133.0	93.7(1)	174.3(1)	
$[\text{Cp}_2\text{Ti}(\text{NO}_3)]_2\text{O}$	–	2.07 2.08	1.841(5) 1.829(5)	131.4 131.8	87.9 88.9	171.8(3)	[13]
$[\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_5)]_2\text{O}$	–	2.11 2.12	1.840(3) 1.838(3)	127.3 129.3	91.2(2) 91.2(2)	173.7(2)	[14]

Cp, Cp' centroids of cyclopentadienyl rings.

Table 4  
Atomic parameters for **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ti(1)	0.30504(5)	0.22312(3)	0.47491(3)	0.030(1)
C(1)	0.0078(4)	0.2708(2)	0.4688(4)	0.066(2)
C(2)	0.1234(5)	0.3226(3)	0.5644(3)	0.066(2)
C(3)	0.2241(4)	0.3971(2)	0.5257(3)	0.063(2)
C(4)	0.1676(4)	0.3949(2)	0.4046(3)	0.065(2)
C(5)	0.0362(4)	0.3160(3)	0.3683(3)	0.068(2)
C(6)	0.6212(4)	0.2058(4)	0.5570(3)	0.081(2)
C(7)	0.5842(4)	0.3121(3)	0.5191(3)	0.068(2)
C(8)	0.5213(4)	0.3107(3)	0.4004(3)	0.061(2)
C(9)	0.5126(4)	0.2026(3)	0.3646(3)	0.070(2)
C(10)	0.5741(4)	0.1391(2)	0.4642(4)	0.079(2)
C(11)	0.1761(3)	0.1095(2)	0.3381(2)	0.041(1)
C(12)	0.1953(3)	0.0705(2)	0.6411(2)	0.054(1)
N(1)	0.1118(3)	0.0446(2)	0.2693(2)	0.058(1)
O(1)	0.3100(2)	0.1208(1)	0.5870(1)	0.041(1)

### 3.2. Preparation of [Cp<sub>2</sub>Ti(CN)]<sub>2</sub>O (**2**)

The reaction steps of Section 3.1 were repeated. The reaction was carried out in methanol containing 2% water, however, and the reaction was conducted in air. Orange crystals of **2** were obtained after layering the CHCl<sub>3</sub> filtrate with *n*-pentane. Yield 0.96 g (46%). Anal. Found: C, 61.94; H, 4.72; N, 6.52%. C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Ti<sub>2</sub>. Calc.: C, 62.30; H, 4.75; N, 6.60. The crystals are stable for days in air, slightly soluble in CHCl<sub>3</sub>, THF and methanol, and almost insoluble in *n*-pentane. Heating causes decomposition above 170 °C without melting.

MS *m/z* (%): 612 (5.8), 408 (7.8), 382 (9.6), 359 (44.0), 333 (2.4), 294 (8.7), 268 (3.5), 204 (17.4), 178 (100) [Cp<sub>2</sub>Ti]<sup>+</sup>, 139 (7.1), 113 (17.6), 66 (21.6), 65 (24.2), 39 (25.5), 27 (37.1).

IR (KBr-pellet, cm<sup>-1</sup>): 3096(s), 2124(m), 1439(s), 1364(m), 1022(s), 872(s), 839(s), 816(s), 741(vs), 600(m), 434(s).

UV-vis (CHCl<sub>3</sub>, nm): maxima at 391 and 434.

Table 5  
Atomic parameters for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ti(1)	0.55320(3)	0.32271(6)	0.15763(2)	0.027(1)
C(1)	0.6350(3)	0.5804(4)	0.1293(2)	0.059(2)
C(2)	0.6922(4)	0.4493(9)	0.1014(3)	0.067(3)
C(3)	0.7291(2)	0.3562(5)	0.1629(2)	0.053(2)
C(4)	0.6941(2)	0.4295(4)	0.2264(2)	0.048(2)
C(5)	0.6360(3)	0.5650(4)	0.2057(2)	0.053(2)
C(6)	0.4487(3)	0.1543(6)	0.0759(3)	0.079(3)
C(7)	0.5432(4)	0.1688(4)	0.0446(2)	0.077(3)
C(8)	0.6095(3)	0.0860(5)	0.0944(3)	0.075(3)
C(9)	0.5550(4)	0.0324(5)	0.1523(2)	0.071(3)
C(10)	0.4606(4)	0.0719(6)	0.1403(3)	0.077(3)
C(11)	0.4356(2)	0.4818(4)	0.1128(2)	0.044(2)
N(1)	0.3714(2)	0.5638(4)	0.0905(2)	0.068(2)
O(1)	0.5	0.3115(3)	0.25	0.030(2)

### 3.3. X-ray analyses of **1** and **2**

Crystals were mounted on glass fibers. The X-ray measurements were carried out at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The structures were solved by the Patterson method and refined via standard least-squares and Fourier techniques [18]. Crystal data, data collection parameters and refinement details are listed in Table 1. Hydrogen atoms were included for the *F*<sub>c</sub> calculations at their calculated positions. Atomic coordinates are given in Tables 4 and 5 [19].

### Acknowledgements

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