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## Synthesis and structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb} \cdot \text{DME}$ \*

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### Abstract

$(\eta^5\text{-C}_5\text{H}_5)_2\text{YbCl} \cdot \text{THF}$  reacts with an equivalent molecular quantity of  $\text{K}(2,4\text{-C}_7\text{H}_{11})$  (2,4-dimethyl pentadienyl potassium), and treatment of the product with DME yields  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb} \cdot \text{DME}$ . The crystal of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb} \cdot \text{DME}$  belongs to the orthorhombic space group *Fdd2* with  $a = 13.678(4)$  Å,  $b = 23.255(6)$  Å,  $c = 9.192(2)$  Å and  $Z = 8$ . The crystal parameters are found to differ from previously reported data.

### Introduction

To date, many preparative methods for substituted cyclopentadienyl ytterbium(II) compounds have been reported, along with proposed crystal structures [1]. We describe a new method for synthesis of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$ , extending that previously reported [2], by the reaction of  $\text{K}(2,4\text{-C}_7\text{H}_{11})$  [3] with  $\text{Cp}_2\text{YbCl} \cdot \text{THF}$  [4] followed by the addition of DME, and report that its structure has crystallographic parameters differing slightly from the reported data [2].

### Experimental

The complex is extremely air- and moisture-sensitive. Therefore, both the synthesis and subsequent manipulation of the compound were conducted under nitrogen with strict exclusion of air and water by the use of Schlenk techniques. Non-aqueous solvents were thoroughly dried and deoxygenated in an appropriate manner and were distilled under nitrogen immediately prior to use.

Metal analysis was carried out by complexometric titration. Infrared spectra were recorded on a Digilab FTS-20E spectrometer as KBr pellets.

#### *Preparation of $\text{Cp}_2\text{Yb} \cdot \text{DME}$*

To a magnetically stirred slurry of 0.7 g (2.50 mmol) of anhydrous ytterbium trichloride in 20 ml THF under nitrogen at  $-78^\circ\text{C}$  was added dropwise a solution of  $\text{CpNa}$  (9 ml, 4.96 mmol) in THF. Then the mixture was allowed to warm to room temperature. After the reaction solution was stirred for 10 h, a solution of  $\text{K}(2,4$

$C_7H_{11}$ ) (4.4 ml, 2.46 mmol) in THF was added to the mixture and stirred at room temperature to give a purple solution. The solution was stirred for a further 10 h and was filtered to remove the remaining metal chlorides; the solvent was evaporated *in vacuo*. The compound was isolated by recrystallization from a DME solution on cooling to  $-20^\circ\text{C}$ , leading to a deep green crystalline product, 0.45 g (45.8%). dec.  $140^\circ\text{C}$ . Anal. Found: Yb, 44.1.  $\text{YbC}_{14}\text{H}_{20}\text{O}_2$  calcd.: Yb, 44.0%. IR (KBr): 3080m, 2980m, 2920s, 2880s, 2820m, 1710w, 1660w, 1620w, 1580m, 1510m, 1450m, 1360m, 1290w, 1240w, 1190m, 1100s, 1075sh, 1010s, 975w, 885w, 845m, 770s, 665m.

#### Determination of crystal structure

The crystal parameters of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$  are listed in Table 1. The intensity data were collected on a Nicolet R3m/E four-circle diffractometer at room temperature, by use of graphite monochromatized Mo- $K_\alpha$  radiation, with scan speed of  $5.86^\circ/\text{min}$  and scan range of  $1.2^\circ$ . One check reflection was measured after every 70 reflections. A total of 1840 reflections were collected within the range  $3 < 2\theta < 65^\circ$ , of which 908 reflections with  $I > 3\sigma(I)$  were considered observed. No significant change was observed in the intensity of the check reflection. The intensities were corrected for Lorentz and polarization factors and an empirical absorption correction was applied, based on  $\psi$  scan data and crystal dimensions.

Patterson synthesis revealed the position of the Yb atom, and the remaining non-hydrogen atoms were located using different Fourier maps. Hydrogen atoms were added according to theoretical models. Isotropic thermal parameters were assigned to all non-hydrogen atoms and the refinement of least-squares parameters converged to  $R = 0.030$ ,  $R_w = 0.028$  and a maximum shift/error ratio of 0.036. The function minimised in the refinement was  $\sum W(|F_o| - |F_c|)^2$  where  $W = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$ . A difference Fourier calculation after the final cycle of least-squares refinement had a maximum electron density of ca.  $0.57 \text{ e}/\text{\AA}^3$  approximately  $0.007 \text{ \AA}$  from ytterbium.

Table 1

Crystal parameters of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$

	Current study	Previous study [2]
Crystal system	Orthorhombic	Monoclinic
Space group <sup>a</sup>	<i>Fdd2</i>	<i>Cc</i>
<i>a</i> , \AA	13.678(4)	9.25(2)
<i>b</i> , \AA	23.255(6)	23.49(5)
<i>c</i> , \AA	9.192(2)	8.23(2)
$\beta$ , deg		123.59(4)
<i>V</i> , \AA <sup>3</sup>	2924(1)	1489.4
<i>Z</i>	8	4
<i>D<sub>c</sub></i> , g/cm <sup>3</sup>	1.79	1.754
$\mu$ , cm <sup>-1</sup>	67.1	33.70
<i>F</i> (000)	1520	760

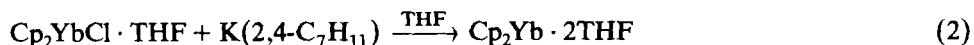
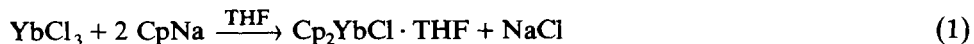
<sup>a</sup> The space group of the crystal can be transformed from *Cc* to *Fdd2* by the transformation matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & -2 \end{pmatrix}$$

All calculations were performed on an Eclipse S/140 computer by a SHELXTL program.

## Results and discussion

The reaction of anhydrous ytterbium trichloride with 2 equivalents of CpNa (eq. 1) leads to the formation of a red compound  $\text{Cp}_2\text{YbCl} \cdot \text{THF}$ , which reacts with one equivalent of  $\text{K}(2,4\text{-C}_7\text{H}_{11})$  (eq. 2) to give  $\text{Cp}_2\text{Yb} \cdot 2\text{THF}$  instead of  $\text{Cp}_2\text{Yb}(2,4\text{-C}_7\text{H}_{11})$ . This is due to the strong reducing ability of  $\text{K}(2,4\text{-C}_7\text{H}_{11})$ . However,  $\text{Cp}_2\text{SmCl} \cdot 2\text{THF}$  could not be reduced by the action of  $\text{K}(2,4\text{-C}_7\text{H}_{11})$ .



The THF in complex  $\text{Cp}_2\text{Yb} \cdot 2\text{THF}$  is displaced by DME to yield  $\text{Cp}_2\text{Yb} \cdot \text{DME}$  in DME solution.

The molecular structure of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$  consists of discrete monomer units. A perspective drawing of the complex is shown in Fig. 1. Atomic coordinates and thermal parameters are given in Table 2. The tetrahedron around the ytterbium ion is formed with the centroids of the cyclopentadienyl rings and the two oxygens of DME at the apices of the tetrahedron. Selected bond lengths and angles are given in Table 3.

The angles around the ytterbium atom are displaced from a perfect tetrahedron in keeping with the steric requirements of the cyclopentadienyl ligands. The centroid–Yb–centroid angle is  $133.9^\circ$  while the centroid–Yb–oxygen angles are  $108.6^\circ$ ,  $109.1^\circ$  and  $109.1^\circ$ , respectively. The angle O–Yb–O(A) is considerably smaller,  $69.3(4)^\circ$ , and is comparable with the corresponding angle,  $60.8(2)^\circ$ , reported for  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Eu}(\text{DME})_2$  [5].

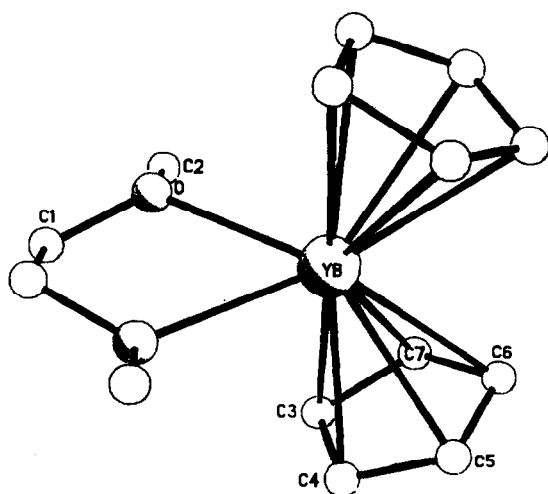


Fig. 1. Perspective diagram of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$  molecule.

Table 2

Atom coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

Atom	x	y	z	$U_{\text{eq}}^a$
Yb	0	0	3250	45(1)
O	401(7)	555(4)	1042(9)	84(3)
C(1)	407(12)	236(9)	-235(16)	113(8)
C(2)	1141(10)	984(5)	1098(24)	108(7)
C(3)	1911(8)	-245(12)	3190(21)	115(9)
C(4)	1485(16)	-733(9)	3468(31)	150(12)
C(5)	1075(13)	-711(9)	4802(30)	163(13)
C(6)	1229(12)	-224(11)	5445(15)	111(8)
C(7)	1761(11)	72(6)	4456(22)	111(8)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

Table 3

Selected bond lengths ( $\text{\AA}$ ) and angles (deg)

Cyclopentadienyl		1,2-Dimethoxyethane	
Yb–C(3)	2.673(13)	Yb–O	2.466(9)
Yb–C(4)	2.654(21)		
Yb–C(5)	2.629(22)	O–C(1)	1.388(19)
Yb–C(6)	2.678(15)		
Yb–C(7)	2.655(16)	O–C(2)	1.419(16)
Av.	2.658		
Yb–cent. <sup>a</sup>	2.402		
<i>Pseudo-tetrahedral angles around ytterbium</i>			
Cent(1)–Yb–Cent(A)	133.9	Cent(1)–Yb–O	108.6
Cent(1)–Yb–O(A)	109.1	Cent(A)–Yb–O	109.1
Cent(A)–Yb–O(A)	108.6	O–Yb–O(A)	69.3(4)
<i>Angle between planes</i>			
Cp(1)–Cp(A)	46.1		

<sup>a</sup> Cent. denotes the centre of the rings described by the carbon atoms C(3)  $\rightarrow$  C(7), C(3A)  $\rightarrow$  C(7A).

The ytterbium–carbon distances ranged from 2.629(22) to 2.678(15)  $\text{\AA}$  and average 2.658  $\text{\AA}$ , which is smaller than that (2.72  $\text{\AA}$ ) of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$ , reported by Deacon et al. [2]. Subtracting the ionic radius of eight-coordinate  $\text{Yb}^{2+}$  (1.14  $\text{\AA}$ ) [6] from the average ytterbium–carbon bond distance of  $\text{Cp}_2\text{Yb} \cdot \text{DME}$  (2.66  $\text{\AA}$ ) gives 1.52  $\text{\AA}$  as the effective ionic radius of the cyclopentadienyl ligand. Values of 1.60  $\text{\AA}$  and 1.58  $\text{\AA}$  have been reported for  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{pyridine})_2$  [7] and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb} \cdot (\text{THF})$  [8], respectively, and a value of 1.61  $\text{\AA}$  is calculated for  $(\eta^5\text{-Me}_3\text{SiC}_5\text{H}_4)_2\text{Yb}(\text{THF})_2$  [9]. These indicate that the volume of  $\text{C}_5\text{H}_5$  is smaller than that of  $\text{C}_5\text{Me}_5$  or  $\text{Me}_3\text{SiC}_5\text{H}_4$ .

## Acknowledgement

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