

The crystal and molecular structure of $[\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Yb}(\text{THF})$ ¹

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Abstract

$[\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2]_2\text{Yb}(\text{THF})$ has been structurally characterized. The compound crystallizes in the orthorhombic space group *Pbcn* with $a = 11.345(4)$, $b = 13.552(4)$, $c = 21.185(6)$ Å, and $D_{\text{calc}} = 1.354$ mg m⁻³ for $Z = 4$. The Yb and O atoms reside on a crystallographic two-fold axis. The formally seven-coordinate Yb(II) ion is symmetrically coordinated to the Cp'' ligands with an average Yb–C bond length of 2.67(2) Å. The Yb–O bond length and centroid–Yb–centroid angle are 2.34(1) Å and 136°, respectively. The calculated effective ionic radius of the Cp'' ligand, 1.59 Å, is at the low end of those calculated for 18 Cp'' lanthanide, lanthanum, or scandium compounds.

Keywords: Ytterbium; Cyclopentadienyl

1. Introduction

On the occasion of Professor Marvin Rausch's 65th birthday, it is appropriate to publish a crystal structure of an organolanthanide compound. My interest in the structural chemistry of lanthanides dates back to my days in graduate school under the supervision of Jerry Atwood. One of my first collaborative efforts was working on the structures of $\text{Cp}_3\text{La}(\text{THF})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5^-$) and $\text{Cp}_3\text{Y}(\text{THF})$ [1] prepared in Professor Rausch's labs. This developed into a collaboration which is still active today, but it also led to my own research effort aimed toward finding ways to control the f-element coordination sphere. In this report the structure of $\text{Cp}_2''\text{Yb}(\text{THF})$ ($\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2^-$) is examined and compared with other Cp-like Yb(II) compounds, as well as 17 other Cp'' compounds of the lanthanides, lanthanum, and scandium.

2. Experimental

2.1. X-Ray data collection, structure determination, and refinement for $\text{Cp}_2''\text{Yb}(\text{THF})$

Crystals of the title compound were obtained from Andrea L. Wayda, then of AT&T Bell Laboratories in Murray Hill, New Jersey. A fragment of a much larger crystal was sealed in a glass capillary under Ar and transferred to the goniometer. The space group was determined to be the centric *Pbcn* from the systematic absences. The fragments available for data collection all came from one very large crystal. Each suffered from a higher than desired mosaic spread and as a result, fewer than anticipated observed data were noted. Very little data was found beyond $\theta = 18^\circ$ and data collection was carried out only to $\theta = 21^\circ$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.080$. The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2 \times U_{\text{eq}}$ (C). The methyl hydrogen atoms were included as a rigid group with rotational freedom at the

¹ Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.

Table 1
Crystal data and structure refinement

Compound	Cp ^{''} ₂ Yb·THF
Color/shape	dark brown/fragment
Empirical formula	C ₂₆ H ₅₀ OSi ₄ Yb
Formula weight	664.06
Temperature	123(2) K
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	$a = 11.345(4) \text{ \AA}$, $\alpha = 90^\circ$
(25 reflections $15 < \theta < 25$)	$b = 13.552(4) \text{ \AA}$, $\beta = 90^\circ$
	$c = 21.185(6) \text{ \AA}$, $\gamma = 90^\circ$
Volume	$3257(2) \text{ \AA}^3$
Z	4
Density (calculated)	$1.354 \text{ (Mg m}^{-3}\text{)}$
Absorption coefficient	3.034 mm^{-1}
Diffractometer/scan	Enraf-Nonius CAD4
	/omega-2theta
Radiation/wavelength	Mo-K α (graphite monochrom.)
	/0.71073 \AA
<i>F</i> (000)	1360
Crystal size	$0.40 \times 0.35 \times 0.35 \text{ mm}$
θ range for data collection	$1.92^\circ\text{--}20.99^\circ$
Index ranges	$0 \leq h \leq 11, 0 \leq k \leq 13, 0 \leq l \leq 21$
Reflections collected	1755
Independent/observed refls.	1755 ($R_{\text{int}} = 0.0000$)
	/1489 [$I > 2\sigma(I)$]
Absorption correction	Semi-empirical from psi-scans
Range of relat. transm. factors	1.00 and 0.64
Refinement method	Full-matrix least-squares on F^2
Computing	SHELXS-86 ¹ , SHELXL-93 ²
Data/restraints/parameters	1742/0/138
Goodness-of-fit on F^2	1.079
SHELXL-93 weight parameters	0.0686, 125.6334
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0664$, $wR2 = 0.1646$
<i>R</i> indices (all data)	$R1 = 0.0772$, $wR2 = 0.1784$
Extinction coefficient	0.0000(3)
Largest diff. peak and hole	4.342 and -1.683 e\AA^{-3}

bonded carbon atom ($B = 1.2 \times U_{\text{eq}}(\text{C})$). Refinement of the nonhydrogen atoms (except for C1, C4, and C13) was carried out with anisotropic temperature factors. The final values of the positional parameters are given in Table 2.

3. Results and discussion

The structure and atom labeling scheme for the title compound are presented in Fig. 1. Yb and O(1) reside on a crystallographic two-fold axis, resulting in staggered Cp^{''} rings. The unique five membered ring is planar to within 0.01 \AA , with each Si atom an average 0.14 \AA out of this plane directed away from Yb.

The two ring centroids and the oxygen atom give Yb an approximate trigonal planar geometry. Distortions occur as a result of steric repulsion between the Cp^{''} rings. The centroid–Yb–centroid angle is expanded to 136° with centroid–Yb–O(1) angles of 112° (Table 3).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{ \AA}^2 \times 10^3$) for Cp^{''}₂Yb(THF)

Atom	<i>x</i> / <i>a</i>	<i>y</i> / <i>b</i>	<i>z</i> / <i>c</i>	U_{eq}^a
Yb	0	−752(1)	7500	16(1)
Si(1)	−1830(3)	−1333(3)	9073(2)	24(1)
Si(2)	−2880(3)	−323(3)	6453(2)	20(1)
O(1)	0	974(8)	7500	18(3)
C(1)	−1843(12)	−1367(10)	8202(6)	18(3) ^b
C(2)	−2292(12)	−643(11)	7781(7)	24(4)
C(3)	−2268(12)	−971(11)	7151(6)	22(4)
C(4)	−1772(12)	−1937(10)	7182(6)	16(3) ^b
C(5)	−1521(12)	−2161(11)	7791(7)	25(4)
C(6)	−563(17)	−2043(15)	9387(8)	53(5)
C(7)	−3225(15)	−1863(14)	9378(7)	42(5)
C(8)	−1744(17)	−29(13)	9346(7)	49(5)
C(9)	−3122(14)	−1237(12)	5807(7)	32(4)
C(10)	−1860(14)	648(11)	6175(7)	33(4)
C(11)	−4301(14)	294(13)	6656(8)	40(4)
C(12)	757(14)	1631(10)	7122(7)	27(4)
C(13)	289(14)	2680(11)	7164(7)	29(4) ^b

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b Isotropic refinement.

The Yb–C separations are equivalent at the 3σ level and average $2.67(2) \text{ \AA}$ with Yb–centroid = 2.39 \AA .

By utilizing Shannon's effective ionic radii [15], it is possible to compare this structure to other lanthanide compounds containing cyclopentadienyl-like ligands. The effective ionic radius of Yb(II) with a formal coordination number of seven is 1.08 \AA , resulting in a value of 1.59 \AA for the effective ionic radius of the Cp^{''} ligand. A comparison of the bonding parameters in cyclopentadienyl-like Yb(II) compounds is presented in

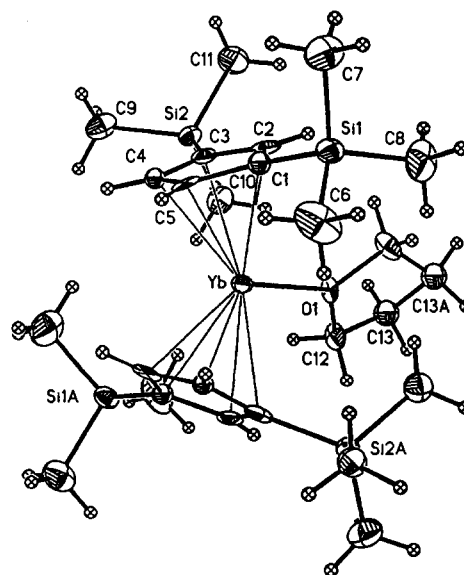


Fig. 1. ORTEP representation of Cp^{''}₂Yb(THF) with the atoms represented by their 50% probability thermal ellipsoids. (The hydrogen atoms have been given arbitrarily reduced radii.)

Table 3
Comparison of bonding parameters in cyclopentadienyl ytterbium(II) compounds

Compound	CN	IR (Å)	M–Cp (Å)			EIR–Cp (Å) ^b	M–Cent (Å)	Cent– M– Cent (°)	M–O (THF) (Å)	Ref.
			Range	Δ	Avg.					
Cp ₂ [*] Yb(THF)	7	1.08	2.65(1)–2.70(1)	0.05	2.67(2)	1.59	2.39	136	2.34(1)	This study
[Cp ₂ [*] Yb] _∞	7	1.08	2.642(6)–2.684(6)	0.042	2.66(1)	1.58	2.374	138		[2]
Cp ₂ [*] Yb(THF) ₂	8	1.14	2.64(4)–2.84(4)	0.20	2.75	1.61		133	2.40(2)	[3]
(Cp [†] Bu) ₂ Yb(THF) ₂	8	1.14	2.64(2)–2.81(2)	0.17	2.72(5)	1.58	2.442	134	2.431(8)	[4]
Cp ₂ [*] Yb(THF) · 1/2toluene	7	1.08	2.643(7)–2.694(8)	0.051	2.66(1)	1.58	2.37	144	2.412(5)	[5]
Cp ₂ [*] Yb(pyridine) ₂	8	1.14	2.692(7)–2.770(8)	0.078	2.74(4)	1.60	2.46	136		[6]
Cp ₂ [*] Yb(NH ₃)(THF)	8	1.14	2.70(4)–2.84(4)	0.14	2.78(4)	1.64	2.505	137	2.46(3)	[7]
Cp ₂ [*] Yb	8	1.14			2.665(4)	1.53		145		[2]
(Cp ₂ (CH ₂) ₃)Yb(THF) ₂	8	1.14	2.67(2)–2.73(2)	0.06	2.70(2)	1.56	2.42	127	2.42(1)	[8]
(MeOCH ₂ CH ₂ Cp) ₂ - Yb(THF)	9	—	2.707(4)–2.759(4)	0.052	2.73(2)	—	2.440(4)	128	2.496(4)	[9]
(CpMe) ₂ Yb(DME)	8	1.14	2.57(3)–2.78(4)	0.21	2.68(6)	1.54	2.41	130		[10]
(CpMe) ₂ Yb(THF)	10	—	2.75(3)–2.77(3) ^c	0.02	2.762(7)	—			2.53(2)	[11]
Cp ₂ Yb(DME)	8	1.14	2.60(3)–2.91(5)	0.31	2.72(8)	1.58	2.46	129		[12]
Cp ₂ Yb(DME)	8	1.14	2.63(2)–2.68(2)	0.05	2.66(2)	1.52	2.402	134		[13]
[(CpPPPh) ₂ Ni(CO) ₂]- Yb(THF) ₂	8	1.14	2.678(5)–2.740(7)	0.062	2.71(2)	1.57	2.42	130	2.426(2)	[14]

^a Effective ionic radius for Yb²⁺ in coordination number shown from Ref. [15].

^b Effective ionic radius calculated for the cyclopentadienyl ligand.

^c Terminal η⁵-Cp ligand only.

Table 3. The effective ionic radii of the Cp-like ligands range from 1.52 Å for Cp in Cp₂Yb(DME) [13] to 1.64 Å for Cp* (η⁵-C₅Me₅⁻) in Cp₂^{*}Yb(NH₃)(THF) [7]. Within the accuracy of the crystallographic determinations, there does not appear to be a consistent trend in the effective ionic radii of the Cp-like ligands.

In the closely related structure, Cp₂^{*}Yb(THF) · (1/2)-toluene [5], the Yb–C average separation is almost

identical (2.66(1) Å) to that in the title compound giving an effective ionic radius of 1.58 Å for the Cp* anion. An interesting comparison of the Yb–THF interaction can be made since both of these compounds contain substituted cyclopentadienyl ligands of different electronic environment in identical geometries with almost identical M–C separations. The Yb–O distance in the electron-rich Cp* compound is 2.412(5) Å, while

Table 4
Comparison of effective ionic radius of Cp'' in lanthanide compounds

Compound	CN	Oxidation state	IR (Å) ^a	M–Cp'', Avg. (Å)	EIR–Cp'' ^b	Ref.
[Cp ₂ ^{''} ScCl] ₂	8	+3	0.870	2.51	1.64	[16]
Cp ₂ ^{''} Sc(BH ₄)	8	+3	0.870	2.47(1)	1.60	[17]
[Cp ₂ ^{''} La(NCMe)(DME)][BPh ₄] · DME	9	+3	1.216	2.83(3)	1.61	[18]
[Cp ₂ ^{''} Ce((OC)W(CO) ₂ Cp)] ₂	8	+3	1.143	2.76(3)	1.62	[19]
Cp ₃ ^{''} Ce	9	+3	1.196	2.83(4)	1.63	[20]
Cp ₃ ^{''} Ce(CN [†] Bu)	10	+3	1.25	2.87(3)	1.62	[20]
[Cp ₂ ^{''} PrCl] ₂	8	+3	1.126	2.76(2)	1.63	[16]
Cp ₂ ^{''} NdCl ₂ Li(THF) ₂	8	+3	1.109	2.76(2)	1.65	[21]
[AsPh ₄][Cp ₂ ^{''} NdCl ₂]	8	+3	1.109	2.78(2)	1.67	[22]
Cp ^{'''} Cp ^{''} Sm(THF) · 1/2toluene ^c	7	+2	1.22	2.83(1) ^d	1.61	[23]
Cp ₃ ^{''} Sm	9	+3	1.132	2.76(4)	1.63	[24]
[Cp ₂ ^{''} Sm(OH)] ₂	8	+3	1.079	2.72(3)	1.64	[25]
[Cp ₂ ^{''} Eu] _∞	8	+2	1.25	2.828	1.58	[2]
[Cp ₂ ^{''} YbCl] ₂	8	+3	0.985	2.62	1.64	[16]
Cp ₂ ^{''} Yb(THF)	7	+2	1.08	2.67(2)	1.59	This study
[Cp ₂ ^{''} Yb] _∞	7	+2	1.08	2.66(1)	1.58	[2]
[Cp ₂ ^{''} LuCl] ₂	8	+3	0.977	2.60(2)	1.62	[26]
[Cp ₂ ^{''} Lu(OH)] ₂	8	+3	0.977	2.63(2)	1.65	[26]

^a Effective ionic radius for Mⁿ⁺ in coordination number and oxidation state shown from Ref. [15].

^b Calculated effective ionic radius of the Cp'' ligand.

^c Cp^{'''} = η⁵-C₅H₂(SiMe₃)₃⁻.

^d Cp'' ligand only.

for the title compound this same value is only 2.34(1) Å.

While the bond distances do not seem to bear out different steric demands of the Cp-like ligands, the range of compounds does. In the synthesis of substituted cyclopentadienyl-like compounds of Yb(II), the bulkier Cp* and Cp'' ligands have resulted in the formally seven-coordinate structures mentioned above. The use of sterically less demanding ligands, like CpMe ($\eta^5\text{-C}_5\text{H}_4\text{Me}^-$) and Cp' ($\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)^-$), however, have resulted in the formally ten-coordinate and polymeric (CpMe)₂Yb(THF) [11] and the eight-coordinate bis-THF adduct Cp'₂Yb(THF)₂ [3]. Eight-coordination predominates with a single example each of nine- and ten-coordination.

Table 4 compares the effective ionic radius of the Cp'' ligand in 18 reported Cp'' compounds of the lanthanides, lanthanum, and scandium. These values range from 1.58 Å in [Cp''₂Yb]_z [2] to 1.67 Å in the anionic [AsPh₄][Cp''₂NdCl₂] [22]. The title compound is at the low end of this range. Despite the range in metal ion size, coordination number, and oxidation state, there is less than a 0.1 Å difference in the entire range of Cp'' effective ionic radii.

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