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Organometallic compounds of the lanthanides

LII *. Synthesis of a new soluble samarium(II) complex containing a ring bridged dicyclopentadiene. Crystal structure of $(C_5H_4CH_2CH_2CH_2C_5H_4)Yb(THF)_2$

S. Jagannatha Swamy **, Jörg Loebel and Herbert Schumann *

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, D-1000 Berlin 12 (B.R. Deutschland)

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Abstract

$(C_5H_4CH_2CH_2CH_2C_5H_4)Sm(THF)_2$ (**1**) has been obtained as purple crystals by treatment of $SmCl_2$ with $Na_2(C_5H_4CH_2CH_2CH_2C_5H_4)$ in tetrahydrofuran (THF). The corresponding ytterbium compound **2** results from the analogous reaction using $YbCl_2$ or from the reduction of $(C_5H_4CH_2CH_2CH_2C_5H_4)YbCl(THF)$ (**3**) with Na/Hg in THF. The structure of **2** has been determined by an X-ray diffraction study. The crystals are orthorhombic, space group *Fdd*2, with *a* 2938(3), *b* 3190(7), *c* 817.8(8) pm, $Z = 16$, $\rho_{calc.}$ 1.69 g/cm^3, $R = 0.0454$ for 1727 observed data ($F_o \geqslant 4\sigma(F_o)$).

Introduction

Recent attempts to synthesize organolanthanides containing Ln^{II} and to study their reactivity have increased understanding of the novel properties of such compounds [3–13]. The major breakthrough in the divalent organolanthanide chemistry in general and that of Sm^{II} in particular involved the use of pentamethylcyclopentadienyl, which confers stability, solubility and crystallinity on organometallic compounds [14]. Unlike the cyclopentadienyl [15] or methylcyclopentadienyl compounds [16], the bis- and mono-pentamethylcyclopentadienyl derivatives of Sm^{II} are soluble in aromatic and coordinating solvents [4,17].

The useful properties bestowed by pentamethylcyclopentadienyl may be attributed to its large size. Any such group may also be expected to offer similar

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* For part LI see ref. 1.

** Present address see ref. 2.

properties. The groups of Tsutsui [18,19] and Changtao Qian [20–22] have demonstrated that a ring bridged dicyclopentadienyl $[C_5H_4\text{-}(CH_2)_3\text{-}C_5H_4]^{2-}$ can be used to prepare stable dicyclopentadienyl halide or alkyl derivatives of early lanthanides, there being an analogy with the chemistry of pentamethylcyclopentadienyl derivatives of early lanthanides [23]. In recent years a good number of Ln^{III} derivatives containing similar ligands e.g. $[C_5H_4(CH_2)_5C_5H_4]^{2-}$ as well as $[C_5H_4(CH_2)_2O\text{-}(CH_2)_2C_5H_4]^{2-}$ [24,25] have been reported.

In the absence of any reports on the use of this ring bridged dicyclopentadienyl ligands in the preparation of divalent organolanthanides, we thought it of interest to investigate the reactions between $[C_5H_4(CH_2)_3C_5H_4]^{2-}$ and LnX_2. We now report the synthesis of $[C_5H_4(CH_2)_3C_5H_4]Sm(THF)_2$ (**1**) and $[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2$ (**2**) and the structural characterisation of the latter.

Results and discussion

The methods commonly used for the synthesis of organometallic compounds of the transition metals, such as metathesis, oxidative addition, and reductive elimination, do not work as well with organolanthanides [26]. The reaction between SmI_2 and the disodium salt of trimethylenedicyclopentadiene in THF gives a purple solution without any precipitate, and attempts to purify the product from dissolved NaI were unsuccessful. Thus $SmCl_2$, prepared by the reduction of $SmCl_3$ with lithium naphthalene [27], was used. Metathesis between red $SmCl_2$ and $Na_2(C_5H_4CH_2CH_2CH_2C_5H_4)$ gave a purple solution and a white NaCl precipitate, and compound **1** was purified by recrystallization from THF.

$$SmCl_2 + Na_2[C_5H_4(CH_2)_3C_5H_4] \xrightarrow{THF} \underset{(\mathbf{1})}{[C_5H_4(CH_2)_3C_5H_4]Sm(THF)_2} + 2NaCl$$

A similar reaction takes place between $YbCl_2$ and $Na_2(C_5H_4CH_2CH_2CH_2C_5H_4)$ in THF to give the ytterbium(II) analogue **2**. This compound can also be prepared by reduction of the Yb^{III} compound **3** [22] with Na/Hg in THF:

$$YbCl_2 + Na_2[C_5H_4(CH_2)_3C_5H_4] \xrightarrow{THF} \underset{(\mathbf{2})}{[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2} + 2NaCl$$

$$\underset{(\mathbf{3})}{[C_5H_4(CH_2)_3C_5H_4]YbCl(THF)} + Na/Hg \xrightarrow{THF}$$

$$\underset{(\mathbf{2})}{[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2} + NaCl$$

These reactions demonstrate that the solubility and stability of Sm^{II} compounds can be increased by increasing the size of the organic part of the anion, i.e. either by using permethylated cyclopentadienyl or ring-bridged dicyclopentadienyl groups.

Compounds **1** and **2** were found to be insoluble in aromatic and aliphatic solvents like benzene, toluene, pentane and hexane. Compound **2** loses its coordinated THF when it is repeatedly washed with or stored in toluene to give a green pyrophoric compound, and this gives a purple solution when be dissolved in THF. This indicates that Yb^{II} compounds readily lose coordinated solvent molecules, as reported by Deacon et al. [28].

Compounds, **1** and **2**, exhibit almost identical IR spectra; the THF-free Yb^{II} compound did not show the characteristic bands for coordinated THF at 862 and 1050 cm^{-1}.

The ^1H NMR spectrum of the diamagnetic Yb^{II} compound **2** exhibited two sharp singlets at 5.43 and 5.37 ppm. Such splitting of the ring protons was also observed for Lu^{III} and La^{III} [19], and Ti^{IV}, Zr^{IV} and Hf^{IV} compounds [29], and was attributed to the tilting of the rings in the case of bridged derivatives. Further, the $\Delta\delta$ value between two multiplets was found to depend on the solvent and on the ring–ring angle. Unfortunately, owing to the insolubility of this compound in solvents other than THF, such as C_6D_6 or $C_6D_5CD_3$, we are not able to determine the size of the ring–ring angle in order to compare it with the value obtained from structural studies. The resonance signals of the bridging methylene protons were observed in the range of 2.3 to 2.9 ppm as a multiplet. The α and β protons of the coordinated THF molecules were found to resonate at 1.75 and 3.62 ppm, respectively.

The ^1H NMR spectrum of the paramagnetic Sm^{II} complex **1** recorded in THF-d_8 exhibited a single sharp singlet corresponding to eight protons at 11.6 ppm, unlike that of the Yb^{II} analogue. The absence of splitting of the ring proton signals of bridged ring protons is not uncommon. The methylene proton resonance signals were observed at 2.8 and 5.3 ppm as multiplets. The coordinated THF proton resonance signals were found at 1.73 and 3.58 ppm.

Molecular structure of $[C_5H_4(CH_2)_3C_5H_4]Yb(THF)_2$

The crystal structure of **2** consists of discrete molecules without short contacts. The molecular structure shows an ytterbium atom pseudo-tetrahedrally coordinated by two cyclopentadienyl rings, linked together by three methylene groups, and the oxygen atoms of two tetrahydrofurans (Fig. 1). As a consequence of the connection of the two cyclopentadienyl rings, the angle centroid(1)–Yb–centroid(2) is with 127(1)° smaller than those in analogous dicyclopentadienylytterbium(II) derivatives

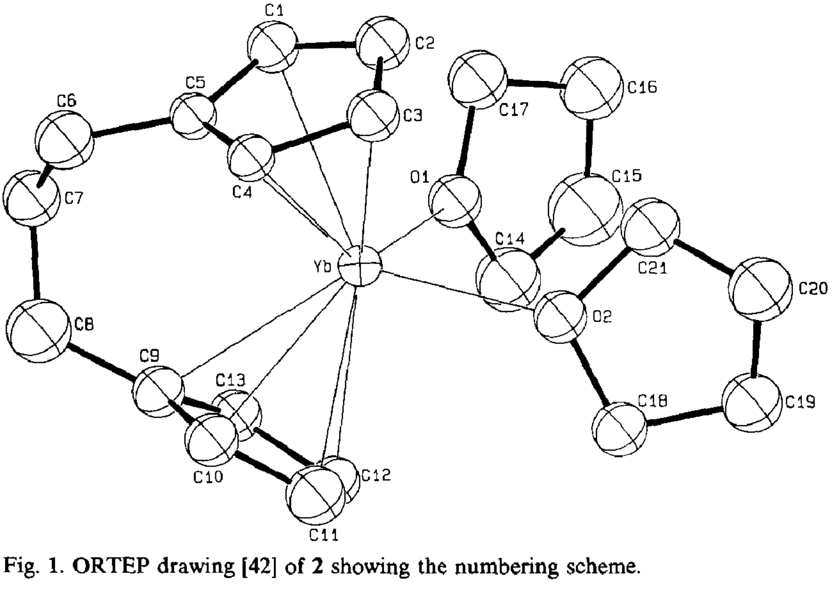

Fig. 1. ORTEP drawing [42] of **2** showing the numbering scheme.

such as $(C_5H_5)_2Yb(DME)_2$ (131° [28]), $(Me_3SiC_5H_4)_2Yb(THF)_2$ (133° [30]), $(C_5Me_5)_2Yb(NH_3)(THF)$ (135.1° [31]), $(C_5Me_5)_2Yb(py)_2$ (136.3° [32]), $(C_5Me_5)_2Yb(THF)$ (143.5° [26]) or in the solvent-free $(C_5Me_5)_2Yb$ (158° [33]). The angle O–Yb–O is with 82.4(5)° in the expected range and agrees well with the angles O–Yb–O in $(Me_3SiC_5H_4)_2Yb(THF)_2$ (85° [30]), O–Yb–N in $(C_5Me_5)_2Yb(NH_3)(THF)$ (87.5° [31]) and N–Yb–N in $(C_5Me_5)_2Yb(py)_2$ (82.5° [32]).

The bonds Yb–O1, 242(1) pm and Yb–O2, 241(1) pm have lengths in the same range as those in $(Me_3SiC_5H_4)_2Yb(THF)_2$ (241 [30]) and $(C_5Me_5)_2Yb(THF)$ (241 [26]), but are shorter than those in $(C_5Me_5)_2Yb(NH_3)(py)$ (246 [31]) and $(C_5H_5)_2Yb(DME)$ (250 [28]). The Yb–C(η^5) bond lengths range from 267(2) to 273(2) pm, which are comparable with those in the dicyclopentadienylytterbium(II) derivatives.

Experimental

The compounds described here are extremely air and moisture sensitive, and so the syntheses and subsequent manipulations were performed by use of Schlenk techniques under dried oxygen-free argon. Tetrahydrofuran and pentane were dried and freed from oxygen by distillations under argon from blue sodium benzophenone ketyl immediately before use. A small amount of diglyme was also added in the case of pentane. THF-d_8 was dried by refluxing over Na for several hours and distilled before use. Anhydrous $SmCl_3$ and $YbCl_3$ were prepared from the pure oxides (Auer–Remy, West Germany) by the reaction with NH_4Cl [34]. Anhydrous $YbCl_2$ was prepared by the reaction between stoichiometric amounts of ytterbium metal powder (Auer–Remy) and NH_4Cl in liquid NH_3 and subsequent removal of ammonia of crystallization under vacuum [35]. The red $SmCl_2$ was prepared by the reduction of $SmCl_3$ in THF with lithium naphthalene [27]. The disodium salt of the ring-bridged dicyclopentadiene was prepared as described previously [22]. Elemental analyses were carried out with a Perkin–Elmer CHN Analyzer 240C. Metal analyses involved complexometric titration using dithizone [36]. ^1H NMR spectra were recorded for samples in sealed 5 mm tubes on a Bruker WP 80 SI instrument. Infrared spectra were recorded as paraffin mulls between CsI plates on a Perkin–Elmer 560 B (200–4000 cm^{-1}) spectrometer.

$(C_5H_4CH_2CH_2CH_2C_5H_4)Sm(THF)_2$ (1). To a stirred suspension of 1.2 g (5.42 mmol) of red $SmCl_2$ in 50 ml of THF was slowly added a solution of 1.17 g (5.4 mmol) of $Na_2(C_5H_4CH_2CH_2CH_2C_5H_4)$ in 20 ml of THF. A purple color developed slowly as the red $SmCl_2$ disappeared, and a white NaCl precipitate appeared. The mixture was stirred for ca. 4 h after the addition, then concentrated to 30 ml by slow removal of THF under vacuum. The cold solution was filtered through a fine frit and the filtrate further concentrated to about 15 ml. Slow diffusion of pentane gave purple crystals of **1**. The solid was filtered and washed twice with pentane and dried, to give 2.0 g (80%) of **1**. Anal.: Found: C, 53.89; H, 6.45; Sm, 31.8. $C_{21}H_{30}O_2Sm$ calcd.: C, 54.26; H, 6.50; Sm, 32.35%. IR (Nujol/poly(chlorotrifluoroethylene) oil; cm^{-1}): 3055, 2925, 2870, 1440, 1050, 1030, 875, 770, 490, 365, 250, 220.

$(C_5H_4CH_2CH_2CH_2C_5H_4)Yb(THF)$ (2). (a) From $YbCl_2$: The method described above was used with 1.32 g (5.42 mmol) of $YbCl_2$ and 0.92 g (5.4 mmol, 20 ml of a 0.27 *M* THF solution) of the reagent, and gave 1.9 g (72%) of the compound **2**.

Anal.: Found: C, 51.10; H, 6.12, Yb, 34.8. $C_{21}H_{30}O_2Yb$ calcd.: C, 51.75; H, 6.20; Yb, 35.49%. IR (Nujol/poly(chlorotrifluoroethylene) oil, cm^{-1}): 3070, 2920, 2875, 1440, 1050, 1015, 862, 775, 465, 385, 255, 230. (b) From **3**: To a solution of 0.5 g (1.1 mmol) of **3** [22] in 10 ml of THF was added a slight excess of Na/Hg. The mixture was stirred for about 6 h during which the reddish color changed to violet with precipitation of NaCl. The solution was filtered the filtrate concentrated to 3 ml, and pentane slowly diffused into the flask. The purple solid was filtered off and dried (0.45 g, 82%). The analysis, IR, and NMR spectra were as shown above. Few crystals (0.2 g, 0.4 mmol) of compound **2** were suspended in 15 ml of toluene and left for one week, after which the purple crystals had turned green. The solid was filtered off and washed thoroughly with pentane to give 0.14 g (0.4 mmol) of the THF-free compound. Anal.: Found: C, 45.01; H, 3.98. $C_{13}H_{14}Yb$ calcd.: C, 45.48; H, 4.11%. IR: 3070, 2920, 2870, 1450, 1015, 770, 465, 390, 260, 235 cm^{-1}.

X-Ray crystal structure determination. Suitable crystals of **2** were obtained by recrystallization from THF, and were stored under tetrahydrofuran. A crystal with dimensions 0.60 × 0.25 × 0.25 mm was selected, attached with grease to a glass fiber, and placed in the nitrogen beam of the diffractometer. The intensities $0 \rightarrow h$, $0 \rightarrow k$, $-l \rightarrow l$ in the 2θ range $2° \leqslant 2\theta \leqslant 50°$ were measured for the C-centered monoclinic cell *a* 817.8(8), *b* 2938(3), *c* 1647.4(7) pm and β 104.47(6)° at 138(5) K, applying ω–2θ scans and Mo-K_α radiation (λ 71.069 pm). Three intensity check reflections were measured every 2 h. The crystal orientation was checked after each 200 intensity measurements by scanning three orientation check reflections. The raw data were corrected for Lorentz and polarization effects and converted into struc-

Table 1

Crystal and data collection parameters for $(C_5H_4CH_2CH_2CH_2C_5H_4)Yb(THF)_2$ (**2**) [a]

formula	$C_{21}H_{30}O_2Yb$
fw	487.51
space group	*Fdd*2
a	2938(3) pm
b	3190(7) pm
c	817.8(8) pm
V	7666×10^{-30} m^3
Z	16
$\rho_{calc.}$	1.69 g/cm^3
μ	46.66 cm^{-1}
F(000)	3872
diffractometer	Syntex $P2_1$
radiation, λ	Mo-K_α, 71.069 pm
temperature	138(5) K
scan technique	$\omega-2\theta$
data collected	$0 \rightarrow h, 0 \rightarrow k, -l \rightarrow l$
2θ limits	$2° \leq 2\theta \leq 50°$
no. of unique data	1909
no. of observed data, $F \geq 4\sigma(F_o)$	1727
$R = \Sigma[\Vert F_o \vert - \vert F_o \Vert]/\Sigma \vert F_o \vert =$	0.0454
no. of parameters	101
corrections	Lorentz, polarization, absorption

[a] Estimated standard deviations of the last significant digit are given in parentheses.

Table 2

Fractional atomic coordinates of $(C_5H_4CH_2CH_2CH_2C_5H_4)Yb(THF)_2$ with estimated standard deviations in parentheses and isotropic thermal parameters [Å^2]

Atom	x/a	y/b	z/c	U_{iso}
Yb	0.12213(2)	0.03339(2)	0.00000	
C1	0.0744(6)	0.0086(5)	−0.263(3)	0.036(4)
C2	0.1112(6)	−0.0193(5)	−0.254(3)	0.039(4)
C3	0.1519(6)	0.0036(6)	−0.288(2)	0.037(5)
C4	0.1371(6)	0.0463(5)	−0.326(2)	0.030(4)
C5	0.0911(6)	0.0483(5)	−0.309(2)	0.029(4)
C6	0.0634(7)	0.0873(6)	−0.338(3)	0.046(5)
C7	0.0341(6)	0.1044(6)	−0.204(2)	0.043(5)
C8	0.0593(8)	0.1323(7)	−0.087(3)	0.056(6)
C9	0.0945(6)	0.1144(5)	0.030(2)	0.037(4)
C10	0.1413(6)	0.1152(5)	0.015(3)	0.038(4)
C11	0.1625(8)	0.0986(6)	0.148(3)	0.047(5)
C12	0.1280(6)	0.0852(5)	0.256(4)	0.035(3)
C13	0.0849(7)	0.0953(6)	0.182(2)	0.037(4)
O1	0.0761(5)	−0.0144(4)	0.160(2)	0.039(4)
C14	0.0759(10)	−0.0144(8)	0.333(3)	0.056(7)
C15	0.0560(11)	−0.0542(9)	0.386(4)	0.075(9)
C16	0.0513(7)	−0.0812(6)	0.237(3)	0.054(5)
C17	0.0473(8)	−0.0496(7)	0.105(3)	0.047(6)
O2	0.1833(4)	−0.0070(4)	0.116(2)	0.038(3)
C18	0.2103(6)	0.0019(5)	0.261(3)	0.040(4)
C19	0.2286(7)	−0.0400(7)	0.321(3)	0.049(5)
C20	0.2304(8)	−0.0651(7)	0.166(3)	0.055(6)
C21	0.1894(7)	−0.0508(6)	0.076(3)	0.047(5)

ture factors. The data set was then transformed to the *F*-centered orthorhombic unit cell [37*]. After isotropic refinement of all nonhydrogen atoms with the merged data set, an absorption correction was made using DIFABS [38] (μ 46.66 cm^{-1}, min. correction 0.816, max. correction 1.235).

The positional parameters of the ytterbium atom were calculated from the Patterson map. A difference Fourier map based on the metal atom phases revealed the positions of all non-hydrogen atoms in the asymmetric unit. The positional parameters of these atoms were refined by full-matrix least squares with anisotropic thermal parameters for the ytterbium atom and isotropic ones for all C and O atoms. Hydrogen positions were calculated but not refined (d(C–H) 108 pm) and added to the structure model with constant temperature factors (U_{iso} 0.05 Å^2). A test for the correct absolute configuration (inversion of all positional parameters) was carried out. Maximum ratio of shift error in final cycle of refinement $(\Delta/\sigma) =$ 0.011 and maximum electron density in final difference Fourier map 1.98 e/Å^3 (55 pm from Yb position). All calculations were performed with the program SHELX 76 [39]. Atomic scattering factors for Yb were taken from the tabulations of Cromer and Weber [40], and anomalous dispersion terms from Cromer and Liberman [41]. Additional information on the crystal structure determination are summarized in

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* Reference number with asterisk indicates a note in the list of references.

Table 3

Selected interatomic distances (pm) and angles (deg) for $(C_5H_4CH_2CH_2CH_2C_5H_4)Yb(THF)_2$ (**2**) [a]. Cp denotes the centroids of the cyclopentadienyl groups.

Atoms	Distance	Atoms	Angle
Yb–C1	269(2)	O1–Yb–O2	82.4(5)
Yb–C2	269(3)	Cp1–Yb–Cp2	127(1)
Yb–C3	269(2)	C5–C6–C7	120(2)
Yb–C4	273(2)	C6–C7–C8	114(2)
Yb–C5	273(2)	C7–C8–C9	121(2)
Yb–Cp1	242(2)	plane Cp1–plane Cp2	50.2(8)
Yb–C9	272(2)		
Yb–C10	267(2)		
Yb–C11	268(3)		
Yb–C12	267(2)		
Yb–C13	270(2)		
Yb–Cp2	241(2)		
Yb–O1	242(1)		
Yb–O2	241(1)		

[a] Estimated standard deviations of the last significant digit are given in parentheses.

Table 1. Final positional parameters are listed in Table 2. The atomic numbering scheme followed in these listings is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 3. Further details of the structure determination are available on request from the Fachinformationszentrum Energie, Physik, Mathematik, D-5714 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54202, the names of the authors and the journal citation.

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