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Journal of Organometallic Chemistry 493 (1995) 149–151

Dicyclopentadienyl complexes of ytterbium(III). The crystal structure of $[Yb(\eta^5\text{-}C_5H_4SiMe_3)_2(\mu\text{-}Cl)]_2$

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Received 10 October 1994

Abstract

The title complex was prepared by reaction of $YbCl_3$ with Li $(C_5H_4SiMe_3)$ in tetrahydrofuran. A single crystal X-ray diffraction study has revealed that the complex is dimeric with bridging chlorine atoms. A flattened tetrahedron around each ytterbium atom is formed by the centroids of two cyclopentadienyl rings and the two bridging chlorine atoms. Comparison of bond distances and angles with those reported for similar dicyclopentadienylytterbium complexes shows that substitution on the cyclopentadienyl ligands by bulky trimethylsilyl groups does not affect the stereochemistry about the lanthanide atom.

Keywords: Ytterbium; Crystal structure; Lanthanide; X-ray diffraction

1. Introduction

Variously substituted cyclopentadienyl ligands have been widely used and studied in d and f organometallic chemistry. Among dicyclopentadienyl complexes of Ln(III), several compounds have been identified as dimeric species and, for ytterbium(III), the following dimeric complexes have been fully characterized by X-ray diffraction: $[Yb(\eta\text{-}C_5h_5)_2(\mu\text{-}Me]_2$ [1], $[Yb(\eta\text{-}C_5H^3(SiMe_3)_2)(\mu\text{-}Cl]_2$ [2], $[Yb(\eta\text{-}C_5H_5)_2(\mu\text{-}Cl]_2$ [3], $[Yb(\eta\text{-}C_5H_4)_2SiMe_2(\mu\text{-}Cl]_2$ [4] and $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(\mu\text{-}OH]_2$ [5]. The title compound is the chlorine-bridged derivative corresponding to the last of these compounds. Its characterization and determination of its crystal structure completes the informations on the bonding and coordination geometry in this group of complexes.

2. Experimental details

2.1. Preparation

$[Yb(C_5H_4SiMe_3)_2Cl]_2$ was made from YbCl3 and $Li(C_5H_4SiMe_3)$ in tetrahydrofuran followed by precipitation with $n\text{-}C_6H_{14}$. Extraction, followed by recrystallisation from $n\text{-}C_6H_{14}$, gave orange prismatic single crystals suitable for X-ray analysis. A selected specimen (0.35 × 0.30 × 0.25 mm.) was sealed in a thin-walled glass capillary. The complex is extremely air and moisture sensitive. Therefore both the synthesis and subsequent manipulations of the compound were conducted under nitrogen, with strict exclusion of air and water, by the use of Schlenk techniques.

2.2. Structural studies

The X-ray diffraction data were obtained with a Siemens R3m/V four circle computer-controlled X-ray diffractometer (using graphite-monochromated Mo Kα radiation: $\lambda = 0.71073$ Å) at room temperature. The unit cell parameters and standard deviations were calculated for the setting angles of 25 reflections with $7° < 2\theta < 45°$. The space group $P\bar{1}$ was indicated during the structure resolution by the observation of a centre of symmetry in the dimeric molecule.

Crystal data: $Yb_2Si_4Cl_2C_{32}$, $M = 913.7$, $a = 8.790(2)$ Å, $b = 9.754(4)$ Å, $c = 12.495(2)$ Å, $\alpha = 70.750(1)$, $\beta = 77.650(1)$, $\gamma = 88.660(1)°$, $V = 986.7(6)$ Å^3, $Z = 1$, $D_{calc} = 1.538$ Mg m^{-3}, $\mu(\text{Mo K}\alpha) = 4.98$ mm^{-1}, $F(000) = 422$. The intensities of 5558 independent reflections were measured by the ω scan technique in the range $7° < 2\theta < 45°$ ($h0 \rightarrow 12$, $k\text{-}12 \rightarrow 12$, $l\text{-}17$

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SSDI 0022-328X(94)05330-8

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
Yb	4744(1)	777(1)	3357(1)	34(1)
Cl	3070(2)	−671(2)	5444(2)	45(1)
Si(1)	2050(3)	−1635(3)	2313(2)	47(1)
Si(2)	7215(3)	4550(2)	2199(2)	47(1)
C(1)	4024(9)	−1045(8)	2365(6)	39(2)
C(2)	5055(10)	72(9)	1495(7)	45(3)
C(3)	6544(10)	−15(10)	1770(8)	54(3)
C(4)	6454(10)	−1196(10)	2817(9)	56(4)
C(5)	4919(10)	−1822(8)	3197(7)	45(3)
C(6)	3000(11)	2711(10)	2315(9)	57(3)
C(7)	4525(10)	3223(8)	1776(7)	45(3)
C(8)	5256(9)	3589(7)	2584(6)	37(2)
C(9)	2699(11)	2709(10)	3505(10)	62(4)
C(10)	4109(10)	3274(9)	3647(7)	49(3)
C(11)	2312(15)	−3137(12)	1654(14)	91(7)
C(12)	1165(13)	−113(11)	1303(10)	70(4)
C(13)	748(15)	−2256(21)	3774(11)	115(8)
C(14)	7589(16)	4810(12)	3543(10)	78(5)
C(15)	8771(13)	3505(11)	1611(12)	81(5)
C(16)	7179(13)	6355(9)	1061(8)	60(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

→ 17). Three standard reflections monitored every 97 reflections showed no decrease in intensity. Data were corrected for Lorentz-polarization and absorption effects, the latter by a semi-empirical method. The transmission factors range from 0.42 to 1.00. The structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics was used: $w = 1/[\sigma(F_o)]^2 + 0.0010F_o^2$. Refinement was carried out for 4536 reflections with $F > 4\sigma(F)$. The non-hydrogen atoms were treated anisotropically. Riding H atoms, with C–H bond lengths of 0.95 Å and fixed isotropic U's of 0.08 $Å^2$ were included in refinement. The final conventional agreement factors were $R = 0.048$, $wR = 0.062$, $s = 1.13$. The data-to-parameter ratio was 25.1 : 1. The maximum shift/e.s.d. in final cycle was less than 0.001. The highest peak in the final difference Fourier map, 1.91 $eÅ^{-3}$, was located near the Yb atom. Atomic scattering factors and anomalous-dispersion terms were taken from International tables for X-ray crystallography [6]. Calculations were performed with Siemens SHELXTL PLUS package programs.

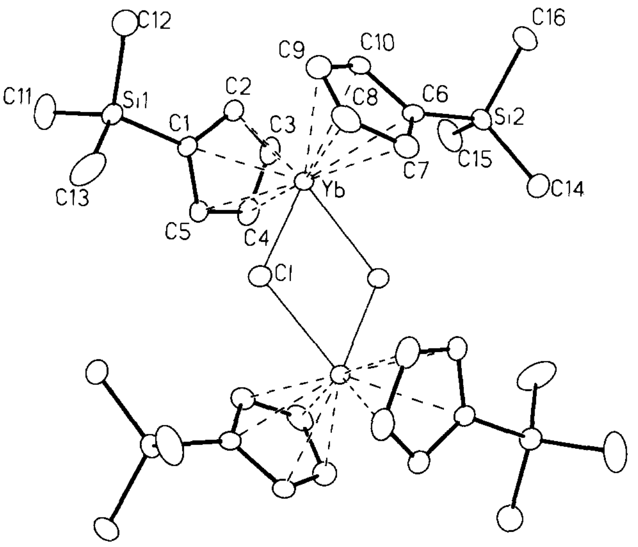

Fig. 1. The molecular structures showing the atom labelling. Thermal ellipsoids are at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) in $[Yb(\eta^5\text{-}C_5H_4SiMe_3)_2(\mu\text{-}Cl)]_2$. Standard deviations are given in parentheses

Bond lengths			
Yb–Cl	2.643(2)	C1–C2	1.426(9)
Tb–Cl [a]	2.659(2)	C1–C5	1.441(11)
		C2–C3	1.417(13)
Yb–C1	2.634(9)	C3–C4	1.418(12)
Yb–C2	2.596(9)	C4–C5	1.412(12)
Yb–C3	2.578(10)	C6–C7	1.387(12)
Yb–C4	2.589(10)	C6–C9	1.453(17)
Yb–C5	2.606(8)	C7–C8	1.443(13)
Yb–C6	2.590(10)	C8–C(10)	1.431(10)
Yb–C7	2.582(7)	C9–C10	1.435(15)
Yb–C8	2.605(7)		
Yb–C9	2.597(9)	Si1–C1	1.861(8)
Yb–C10	2.609(9)	Si1–C11	1.891(17)
		Si1–C12	1.880(11)
Yb–Yb [a]	4.001(2)	Si1–C13	1.849(12)
		Si2–C8	1.871(8)
		Si2–C14	1.876(14)
		Si2–C15	1.857(12)
		Si2–C16	1.868(8)
Bond angles			
Cl–Yb–Cl [a]	82.0(1)	C1–Si1–C12	110.3(4)
Yb–Cl–Yb [a]	98.0(1)	C11–Si1–C12	110.3(4)
		C1–Si1–C13	111.5(6)
Cl–Yb–C1	95.1(1)	C11–Si1–C13	111.3(8)
Cl–Yb–C2	126.8(2)	C12–Si1–C13	110.1(6)
Cl–Yb–C3	133.3(2)		
Cl–Yb–C4	52.6(3)	C8–Si2–C14	107.9(5)
Cl–Yb–C5	81.9(2)	C8–Si2–C15	111.4(5)
Cl–Yb–C6	107.3(2)	C14–Si2–C15	110.6(7)
Cl–Yb–C7	135.0(2)	C8–Si2–C16	108.5(4)
Cl–Yb–C8	131.7(2)	C14–Si2–C16	109.9(5)
Cl–Yb–C9	82.2(2)	C15–Si2–C16	108.4(5)
Cl–Yb–C10	92.0(2)		
C2–C1–C5	106.2(7)		
C1–C2–C3	109.3(7)		
C2–C3–C4	107.4(7)		
C3–C4–C5	108.6(8)		
C1–C5–C4	108.4(6)		
C7–C6–C9	108.8(9)		
C6–C7–C8	109.3(8)		
C7–C8–C10	106.6(7)		
C6–C9–C10	106.3(8)		
C8–C10–C9	108.9(9)		

[a] Refers to atoms at $(-x+1, -y, -z+1)$ with respect to the coordinates listed in Table 1.

The atomic coordinates and isotropic thermal parameters are listed in Table 1. A full list of bond lengths and angles, and tables of anisotropic thermal coefficients and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The molecular structure with the numbering scheme is shown in Fig. 1. Corresponding bond lengths and angles are listed in Table 2. The structural unit is a dimer in which the two ytterbium atoms are related by a centre of symmetry. There is a pseudo-tetrahedral arrangement around each Yb atom, coordinated by two clorine atoms and, in a pentahapto fashion, by two cyclopentadienyl rings mono-substituted by a trimethylsilyl ligand. The Yb–Cl bond lengths, 2.643(2) Å and 2.659(2) Å are in agreement with the values observed in the other dicyclopentadienyl chlorine complexes [2–4]. The ytterbium–carbon distances range from 2.570(9)–2.634(8) Å, corresponding to normal pentahapto Yb–C (cyclopentadienyl) bond distances. In the Yb–Cl–Yb–Cl planar unit, the angles at Yb are smaller than at Cl (Table 2). They are consistent with the corresponding angles, respectively of 82.0(1)° and 98.0(1)°, observed in $[Yb(C_5H_5)_2(\mu\text{-}Cl)]_2$ [3], but they differ significantly from the corresponding angles of 77.9(7)° and 102(1)° in $[Yb(\eta\text{-}C_5H_4SiMe_3)_2(\mu\text{-}OH)]_2$ [5] and those of 93.4(4)° and 86.6(3)° in $[Yb(\eta\text{-}C_5H_5)_2(\mu\text{-}Me]_2$ [1]. All the other bonding parameters (Table 2) agree closely with those reported for $[Yb(C_5H_5)_2(\mu\text{-}Cl)]_2$ [3] and differ only weakly from those observed in $[Yb\{C_5H_3(SiMe)_2\}_2(\mu\text{-}Cl)]_2$ [2]. From these comparisons it appears that the presence of an Me_3Si substituents on the cyclopentadienyl ligand has no effect on the bonding parameters at the metal atom. Bonding parameters are affected when a trimethylsilyl group acts as a bridging unit between two cyclopentadienyls, as in the complex $[Yb(\eta\text{-}C_5H_4)_2SiMe_2(\mu\text{-}Cl]_2$ [4]. There are no significant intermolecular contacts.

Acknowledgments

We are grateful to the Inter-University Institute for Nuclear Sciences and to the National Fund for Scientific Research (Brussels) for financial support to the Laboratory of Analytical Chemistry and Radiochemistry of the University of Liège.

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