Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2LuCl]_2$: A Precursor for the Production of Lu_2O_3 Films

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The single crystal X-ray diffraction study of $[(\eta^5\text{-}C_5H_4SiMe_3)_2LuCl]_2$, prepared from $LuCl_3$ and $Na[C_5H_4SiMe_3]$, shows the compound to be a centrosymmetric dimer with two η^5-bonded cyclopentadienyl rings and two symmetrically bridging chlorine atoms coordinated to each of the two metal centers. The coordination geometry around the lutetium atoms is that of a distorted pseudo tetrahedron. The Lu-C(Cp) distances lie within the narrow range of 2.571 – 2.608 Å. The Lu-Cl bond lengths are 2.639(1) and 2.653(1) Å. The crystal structure shows no significant intermolecular contacts.

Key words: Lutetium, Cyclopentadienyl Complex, X-Ray Structure

Introduction

Within the last two decades many efforts were made to prepare organlanthanide compounds potentially useful in organic synthesis and catalysis [1]. Besides this dominating topic more recently the research on lanthanide compounds applicable in material science also expanded in the last few years [1a]. One of the conventional techniques in material science is the *Metalorganic Chemical Vapor Deposition* (MOCVD). Organic derivatives of the lanthanides show several of the properties generally demanded for substances suitable for MOCVD procedures, including a sufficient volatility at low pressure. One of the most challenging tasks in this field is the preparation of materials with a high dielectric constant, which are able to substitute SiO_2 in its function as an insulating layer in metal oxide semiconductor (CMOS) devices [2]. The results of investigations conducted quite recently [3] suggest that rare earth metal oxides might be good candidates for this purpose. Until now, the manufacture of lanthanide oxide films by MOCVD methods, using rare earth metal alkoxides as starting materials, has been the subject of only one paper and two patents [4]. Lutetium oxide, Lu_2O_3, is of particular interest for CMOS devices because of its predicted thermodynamic stability on silicon surfaces [5] and its large conduction band as compared to silicon [6]. Just recently, it was possible to grow a Lu_2O_3 film by the *Atomic Layer Deposition* (ALD) technique using $[(C_5H_4SiMe_3)_2LuCl]_2$ [7] as an oxygen-free precursor and H_2O as an oxygen source [6]. This prompted us to study more intensively a family of cyclopentadienyl lutetium complexes to find out the best precursor for ALD uses.

As part of this work, we report on the crystal and molecular structure as well as the mass spectra of $[(C_5H_4SiMe_3)_2LuCl]_2$.

Results and Discussion

Synthesis

Dimeric $[(C_5H_4SiMe_3)_2LuCl]_2$ was prepared in a way similar to that previously reported [7], but using trimethylsilylcyclopentadienyl sodium (instead of potassium). The reaction of $LuCl_3$ with two equiv. of $Na[C_5H_4SiMe_3]$ proceeds smoothly in THF and affords colorless crystalline $[(C_5H_4SiMe_3)_2LuCl]_2$ with yields up to 60% after crystallization of the crude product either from diethyl ether or hexane. The NMR and MS spectroscopic data agree with those already published [7].

$$2\,LuCl_3 + 4\,Na[C_5H_4SiMe_3] \xrightarrow{THF} [(C_5H_4SiMe_3)_2LuCl]_2 + 4\,NaCl$$

In order to obtain a more volatile monomeric silylcyclopentadienyllutetium derivative, we also tried to synthesize tris(trimethylsilylcyclopentadienyl)lutetium. However, even the use of four equiv. of $Na[C_5H_4SiMe_3]$ in the reaction with $LuCl_3$ led only to the formation of $[(C_5H_4SiMe_3)_2LuCl]_2$. This observation agrees well with the results reported by Lappert *et al.* concerning the synthesis of tris(cyclopentadienyl)lanthanide complexes with monosilyl substituted Cp-ligands. These authors succeeded in synthesizing the monomeric complexes of the type $(C_5H_4SiMe_2Bu^t)_3Ln$ of all elements of the lanthanide series, but they failed also with the lutetium derivative [8]. This fact clearly indicates, that in spite of the very small differences in the radii of the trivalent ions of the neighboring elements Yb and Lu (0.868 and 0.861 Å for coordination number 6; 1.042 and 1.032 Å for coordination number 10) [9], the structural chemistry of these two elements appears to be significantly different, with lutetium being closer to the behavior of hafnium than to that of ytterbium.

Crystal and molecular structure of $[(C_5H_4SiMe_3)_2LuCl]_2$

Independent of whether the compound was crystallized from diethyl ether or hexane the crystals formed were isomorphous. The complex crystallizes in the triclinic space group $P\overline{1}$ with one centrosymmetric, chlorine bridged dimer in the unit cell (Fig. 1).

Each lutetium atom is coordinated by two cyclopentadienyl rings in an η^5-manner [Lu-C(Cp1) 2.584 – 2.608; Lu-C(Cp2) 2.571 – 2.597 Å]. The two chlorine atoms and the centroids of the two cyclopentadienyl rings form a flattened tetrahedron around each metal atom with an Cl-Lu-Cl angle of 81.67(3)° and an Cp'$_{centroid}$-Lu-Cp'$_{centroid}$ angle of 130.10(1)°. The main bond lengths and angles in $[(C_5H_4SiMe_3)_2LuCl]_2$ compared well with those of the chlorine bridged biscyclopentadienyl lanthanide complexes $[\{C_5H_3(SiMe_3)_2\}_2LuCl]_2$ [11a], $[(C_5H_4SiMe_3)_2YbCl]_2$ [11b], and $[(C_5H_4SiEt_3)_2LuCl]_2$ [11c]. The lengths of the Lu–Cl bonds in $[(C_5H_4SiMe_3)_2LuCl]_2$ [2.639(1) and 2.653(1) Å] are fully consistent with those in $[(C_5H_4SiMe_3)_2YbCl]_2$ [2.643(2) and 2.659(2) Å] [11b], but are somewhat elongated compared to those in $[(C_5H_4SiEt_3)_2LuCl]_2$ [2.617(3) and 2.619(3) Å] [11c]. On the other hand, the

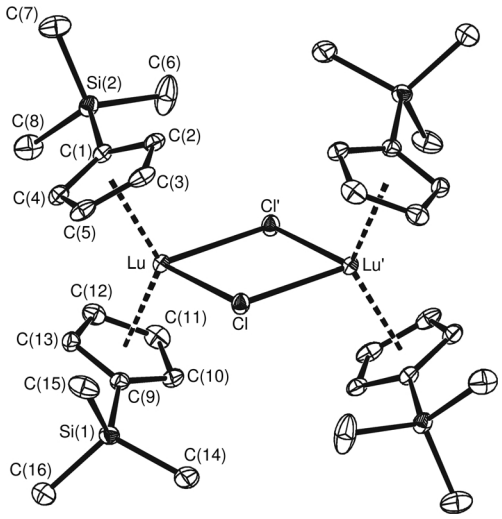

Fig. 1. ORTEP [10] presentation of the molecular structure of $[(C_5H_4SiMe_3)_2LuCl]_2$. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°]: C(1)-Lu(1) 2.608(4), C(2)-Lu(1) 2.597(4), C(3)-Lu(1) 2.584(4), C(4)-Lu(1) 2.560(4), C(5)-Lu(1) 2.584(4), C(1)-Si(2) 1.870(4), C(6)-Si(2) 1.863(6), C(9)-Lu(1) 2.597(4), C(10)-Lu(1) 2.594(4), C(11)-Lu(1) 2.593(4), C(12)-Lu(1) 2.576(4), C(13)-Lu(1) 2.571(4), C(9)-C(10) 1.423(6), C(10)-C(11) 1.419(6), C(11)-C(12) 1.408(7), C(12)-C(13) 1.417(6), C(9)-C(13) 1.423(5), C(7)-Si(2) 1.857(5), C(8)-Si(2) 1.874(5), Cl(1)-Lu(1) 2.639(1), Cl(1a)-Lu(1) 2.653(1); Lu(1)-Cl(1)-Lu(1a) 98.33(3), Cl(1)-Lu(1)-Cl(1a) 81.67(3).

Lu-Cp(centroid) distances in $[(C_5H_4SiMe_3)_2LuCl]_2$ (2.288(1) Å) and $[(C_5H_4SiEt_3)_2LuCl]_2$ (2.287 Å) [11c] are fairly identical and the average Lu-C(Cp) distances in $[(C_5H_4SiMe_3)_2LuCl]_2$ (2.586 Å) and $[\{C_5H_3(SiMe_3)_2\}_2LuCl]_2$ (2.598 Å) [11a] are very close.

Mass spectra of $[(C_5H_4SiMe_3)_2LuCl]_2$

In order to investigate the thermal stability of $[(C_5H_4SiMe_3)_2LuCl]_2$ and the way of its thermal decomposition, EI (70 eV) mass spectra were recorded. The ion concentration of the complex in the gase phase reaches a maximum at temperatures between 180 and 190 °C. Actually, this is the same temperature range in which the compound starts to sublime under vacuum. Table 1 summarizes the MS data at 160 °C [7] and at 181 °C. In spite of the small difference in temperature, the spectra differ considerably apart from the fact, that in both spectra the molecular ion peak $[(C_5H_4SiMe_3)_2LuCl]_2^+$ appears with comparable intensity (5 and 11%, respectively).

Table 1. MS data for $[(C_5H_4SiMe_3)_2LuCl]_2$ (EI, 70 eV).

Ions (m/z)	Relative intensities [%]	
	160 °C[a]	181 °C[b]
$[M]_2^+$ (968)	5	11
$[M]_2^+ - (C_5H_4SiMe_3)$ (831)	46	100
$[M]^+$ (484)	2	0.7
$[M]^+ - CH_3$ (469)	–[c]	13
$[M]^+ - Cl$ (449)	100	68
$[M]^+ - Cl - SiMe_3 - CH_3$ (361)	–[c]	13

[a] Ref. [7]; [b] this work; [c] not given in ref. [7].

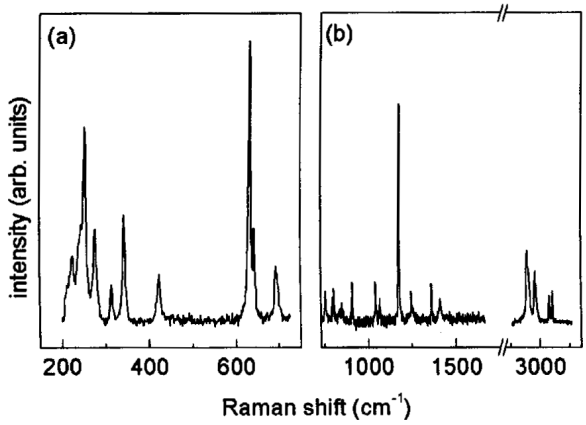

Fig. 2. Raman spectrum of $[(C_5H_4SiMe_3)_2LuCl]_2$; (a) spectral region including bands characteristical of Lu-ligand vibrations; (b) spectral region with vibrations arising from the $C_5H_4SiMe_3$ group.

At 160 °C, the peak of highest intensity corresponds to the dechlorinated monomer $[(C_5H_4SiMe_3)_2Lu]^+$ (m/z 449, 100%), wheras at 181 °C, the dimer having lost one of its four silylsubstituted Cp ligands, $[(C_5H_4SiMe_3)_3Lu_2Cl_2]^+$ (m/z 831, 100%), is the dominating fragment. These data allow the conclusion that the way of decomposition of the precursor, either via splitting off one of the silylsubstituted Cp-ligands or *via* cleavage of the Lu-Cl bonds, strongly depends on the temperature conditions.

Raman spectrum of $[(C_5H_4SiMe_3)_2LuCl]_2$

The Raman spectrum of $[(C_5H_4SiMe_3)_2LuCl]_2$ (Fig. 2) can be subdivided in three sections. By comparison with Raman data of other rare earth cyclopentadienyl compounds [12] the bands in the section ranging from 100 to 300 cm^{-1} must be assigned to Lu-ligand stretching vibrations. The second section, ranging from 300 to 700 cm^{-1}, is characterized by medium energy bands tentatively ascribed to normal modes involving the Cl or the Si atoms, and the third section, ranging from 700 to 3200 cm^{-1}, is dominated by bands which are caused by vibrations of the cyclopentadienyl ring systems and the methyl groups.

Experimental Section

All operations were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques, and in dry, oxygen-free solvents. $[(C_5H_4SiMe_3)_2LuCl]_2$ has been prepared according to [7] in several batches up to 20 g amounts each. The mass spectra (EI, 70 eV) were obtained using a Varian MAT 311A instrument. The Raman spectrum was acquired with a Renishaw 2000 system equipped with a 10 mW 633 nm HeNe excitation laser with an exposure of 60 s per point. The Rayleigh-rejection notch-filter employed on the spectrometer cuts the spectrum below 100 cm^{-1}. The spectrum was then baseline-corrected in order to remove a small photoluminescence background. The spectral region not shown in Fig. 2 is flat.

Crystal structure determination. The data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å) with area-detector by use of ω scans at 173 K. The structure was solved by direct methods using SHELXS-97 [12] and was refined on F^2 using all reflections with SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and were assigned to an isotropic displacement parameter of 0.08 $Å^2$. SADABS [14] was used to perform area-detector scaling and absorption corrections (max/min transmission 0.727 and 0.455). The geometrical aspects of the structure were analyzed using PLATON [15]. Data collection: crystal dimensions $0.38 \times 0.22 \times 0.16$ mm^3, triclinic, $P\bar{1}$, $a = 8.7016(2)$, $b = 9.6940(2)$, $c = 12.3895(3)$ Å, $\alpha = 70.639(1)°$, $\beta = 76.995(1)°$, $\gamma = 88.743(1)°$, $V = 959.13(4)$ $Å^3$, $Z = 1$, $\rho_{calcd.} = 1.679 \cdot 10^3$ $kg\,m^{-3}$, $\mu = 5.400$ mm^{-1}, $F(000) = 476$, $1.79 \leq \theta \leq 29.00°$, $-11 \leq h \leq 10$, $-11 \leq k \leq 12$, $-16 \leq l \leq 14$, 7482 data collected, 4404 unique data ($R_{int} = 0.0462$), 187 refined parameters, GOF(F^2) = 0.966, final R-indices ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$), $R_1 = 0.0310$, $wR_2 = 0.0681$, max./min. residual electron density $1.667/-1.711$ e·$Å^{-3}$. CCDC-237831 contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk.

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