

Synthesis of Substituted Indenyl Lanthanide Chloride and Molecular Structure of $[(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2]$

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Reaction of anhydrous ytterbium trichlorides with 2 equiv. of cyclopentylindenyl lithium in THF solution, followed by removal of the solvent and crystallization of the product from diethyl ether, affords a crystal complex of the composition $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$. Crystallographic analysis shows that the ytterbium coordinated by two cyclopentylindenyl rings and lithium surrounded by two ether molecules are bridged by the two chlorine atoms and Yb, Li and two chlorine atoms form a plane.

Keywords indenyl, structure, synthesis, lanthanide complex

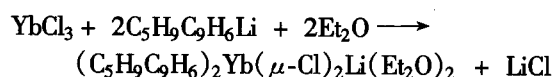
Introduction

Lanthanocene halides are useful precursor for the synthesis of lanthanide complexes with σ -bonded ligands which are active for many organic reactions especially polymerization and co-polymerization of polar and non-polar monomers.¹⁻⁴ To date many bis(cyclopentadienyl)lanthanide halides and bis(substituted cyclopentadienyl)lanthanide halides have been synthesized and characterized.⁵ Reports on synthesis of bis(indenyl)lanthanide halides, however, are scarce. The first synthesis and characterization of THF-solvated diindenyl praseodymium chloride $[(C_9H_7)_2PrCl(THF)]_2$ were reported by Shen *et al.* in 1997.⁶ Recently, bis(2-methoxyethylindenyl)lanthanocene chlorides $(CH_3OCH_2CH_2C_9H_6)_2LnCl$ ($Ln = Y, La, Nd, Gd$) and chelating ether-functionalized indenyl ligated lanthanide chlorides $O(CH_2CH_2C_9H_6)_2LnCl$ ($Ln = Nd, Gd, Ho$) were reported by Qian *et al.*^{7,8} The oxygen atoms in the later complexes exert great effect on stabilizing molecule by intramolecular coordination to the central metals. An attempt to obtain ethylenebis(η^5 -indenyl)ytterbium chloride without intramolecular coordination failed.⁹ However, the oxygen atoms also lower the activity of the consequent complexes with σ -bonded ligands due to lowering the acidity of the central metal atoms and their competing for the coordination site with the other reactants. In this article, we report the synthesis and crystallographic characterization of

$(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$, which is the first reported bis(substituted indenyl)lanthanide lithium chloride with ether adduct.

Results and discussion

$YbCl_3$ reacted with $C_5H_9C_9H_6Li$ (molar ratio: 1:2) in THF; the complex, however, was not apt to crystallize in THF. After removal of THF solvent, the residue was extracted with ether and single crystals of complex $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$ (**1**) were isolated in yield up to 89.7% (based on $YbCl_3$) even at room temperature! The reaction is shown in the following equation:



Due to containing the paramagnetic ytterbium, the ¹H NMR spectrum of the complex is complicated. However, its ¹³C NMR spectrum shows that chemical shifts appear at about δ 1.5 downfield compared to those of cyclopentylindenyl ligand.

The molecular structure and the selected bond lengths and angles of complex $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$ are presented in Fig. 1 and Table 1, respectively. The molecule of the complex comprises a ytterbium atom residing in the center of a distorted tetrahedron formed by the centroids of the five-membered rings and the two asymmetric μ_2 -chlorine atoms and the lithium atom sitting in the center of another distorted tetrahedron made up of chlorine atoms and oxygen atoms of diethyl ether molecules. Ytterbium, chlorine atoms and lithium are planar. The four angles Cl(1)-Li-Cl(2), Cl(1)-Yb-Cl(2), Li-Cl(1)-Yb and Li-Cl(2)-Yb are 94.6°, 86.97°, 89.6° and 88.5°, respectively, which are close to 90°. This is different from the dilanthanide complexes $Cp_2Ln(\mu-Cl)_2LnCp_2$ ($Cp = C_5H_4$), in which the two large Cp_2Ln

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units are bridged, requiring a larger Ln-Ln separation which results in larger Ln-Cl-Ln and smaller Cl-Ln-Cl angles. The angle Cl(1)-Yb-Cl(2), 86.97(6)°, is much smaller than the 107.7° in $[(C_9H_7)_2PrCl(THF)]_2$.⁶ The angle Cent(1)-Yb-Cent(2), 130.1°, is comparable to 131.4°, 132.3° and 132.6° (Nd, Gd and Ho, respectively) in the racemic five-atom-bridged bis(indenyl)lanthanocenes⁷ and larger than 123.6° for angle Cent(1)-Pr-Cent(2) in complex $[(C_9H_7)_2PrCl(THF)]_2$ ⁶ and 122.0° for Cent-Yb-Cent in meso $[CH_2CH_2(C_9H_6)_2]Yb(TMS)$ ⁹, respectively. The Yb-(μ -Cl) distances, 0.2562 and 0.2573 nm, are very close to the terminal Y-Cl bond distances 0.2575 nm in complex $(C_5Me_5)_2YCl(\mu-Cl)[Li(THF)_3]$ ¹⁰ and 0.2579 nm in complex $[(C_5Me_5)_2Y(\mu-Cl)YCl(C_5Me_5)_2]$ ¹¹, but shorter than Yb-(μ -Cl) bond distances in $(C_5Me_5)_2YbCl_2[Li(Et_2O)]$ (0.2596, 0.2594 nm)¹² and in ytterbium complex with a Yb(μ -Cl)₂Yb unit (0.2628, 0.2647 nm).¹³ However the bond lengths Yb-C(ring) of the complex, within the range from 0.2553(7) to 0.2723(6) nm averaging 0.2651 nm (for ring 1) and 0.2633 nm (for ring 2), are even larger than the average Yb-C(ring), 0.2611(4) nm in the complex $(C_5Me_5)_2YbCl_2[Li(Et_2O)]$. Thus, the structure of complex 1 is quite different from those of the corresponding bis(cyclopentadienyl)lanthanide chlorides which are usually dimer,^{14,15} tetramer,¹⁶ infinite double chains¹⁷ or monomer with one or two THF molecules adduct depending on its cen-

tral metal ionic radius.¹⁸ Clearly, the structure of 1 is similar to the bulky bis(pentamethylcyclopentadienyl)lanthanide chlorides complexes, $Cp'_2LnCl_2ML_2$ (M = Li, Na, K; L = Et₂O, THF, DME) and are found only for the bulky ligand $Cp' = (C_5Me_5)$ up till now. This suggests that the easily made substituted indenyl ligand may have similar steric effect

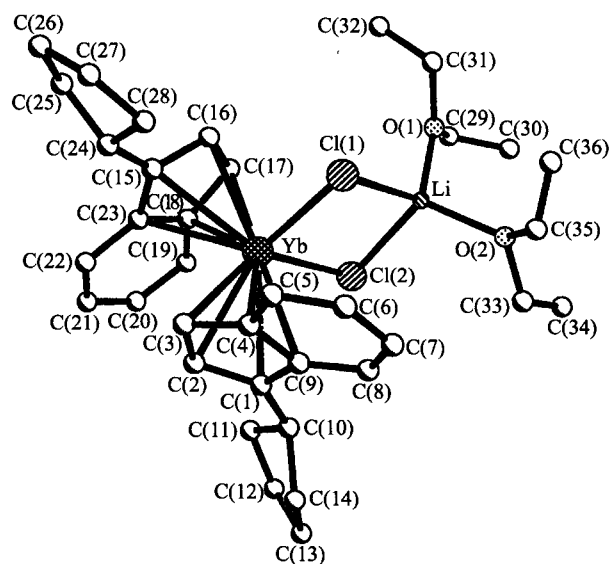


Fig. 1 Molecular structure of complex $[(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2]$.

Table 1 Selected bond lengths (nm) and angles (°) of complex $[(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2]$

Yb—C(1)	0.2682(6)	Yb—C(15)	0.2674(6)
Yb—C(2)	0.2585(6)	Yb—C(16)	0.2605(7)
Yb—C(3)	0.2553(7)	Yb—C(17)	0.2572(7)
Yb—C(4)	0.2664(7)	Yb—C(18)	0.2622(7)
Yb—C(9)	0.2723(6)	Yb—C(23)	0.2690(7)
Yb—C(ring1) ave.	0.2651	Yb—C(ring2) ave.	0.2633
C(1)—C(2)	0.1384(9)	C(15)—C(16)	0.1407(10)
C(1)—C(9)	0.1439(9)	C(15)—C(23)	0.1411(9)
C(2)—C(3)	0.1424(9)	C(16)—C(17)	0.1401(10)
C(3)—C(4)	0.1410(10)	C(17)—C(18)	0.1415(10)
C(4)—C(9)	0.1438(9)	C(18)—C(23)	0.1452(10)
C(4)—C(5)	0.1426(10)	C(18)—C(19)	0.1418(10)
C(5)—C(6)	0.1366(11)	C(19)—C(20)	0.1375(12)
C(6)—C(7)	0.1379(11)	C(20)—C(21)	0.1376(13)
C(7)—C(8)	0.1366(11)	C(21)—C(22)	0.1382(10)
C(8)—C(9)	0.1377(10)	C(22)—C(23)	0.1416(10)
Yb—Cl(1)	0.2561(2)	Yb—Cl(2)	0.2573(2)
Li—Cl(1)	0.2384(12)	Li—Cl(2)	0.2423(12)
Li—O(1)	0.1937(14)	Li—O(2)	0.191(2)
Yb—Cent(1)	0.2350	Yb—Cent(2)	0.2341
Cl(1)-Yb-Cl(2)	86.97(6)	Cl(1)-Li-Cl(2)	94.6(4)
Li-Cl(2)-Yb	88.5(3)	Li-Cl(1)-Yb	89.6(3)
Cent(1)-Yb-Cent(2)	130.1	Cent(1)-Yb-Cl(1)	109.7
Cent(2)-Yb-Cl(1)	106.1	Cent(1)-Yb-Cl(2)	106.8
Cent(2)-Yb-Cl(2)	108.8		

as that of famous C_5Me_5 and the corresponding complexes may show the same chemical activity.

It can be seen from Fig. 2 that the indene rings are staggered. This can be proved by the rotation angle (RA).¹⁹ An RA of 0° would indicate a completely eclipsed geometry, whereas an RA of 180° corresponds to the fully staggered arrangement of the two rings. Thus, an RA of 145.1° for complex **1** indicates that the two indenyl rings are staggered. However, the substituted indenyl rings, though staggered, are still distorted due to their extremely steric crowding, and they are not planar as none of HAs and FAs of the two indenyl rings is 0°. HA, the hinge angle, as the angle between the planes [C(1), C(2), C(3)] and [C(1), C(3), C(4), C(9)], is 1.9° and the fold angle, FA, as the angle between the planes [C(1), C(2), C(3)] and [C(4), C(5), C(6), C(7), C(8), C(9)], is 4.0° for ring(1). HA and FA are 1.9° and 5.6° for ring(2), respectively. The slip parameter Δ_{M-C} [the difference between the average bond lengths of the metal to the ring junction carbons C(4), C(9) and the metal to the adjacent carbon atoms of the five-membered ring, C(1), C(3)], has been developed to quantify the distortion: $\eta^5-\eta^3$ slippage within indenyl metal complexes.¹⁹ Δ_{M-C} are 0.0033 nm and 0.0076 nm for the two indenyl rings in complex **1**, respectively, fall within the established range for a fundamentally-ionic η^5 -bonding between the metals and indenyl ligands.

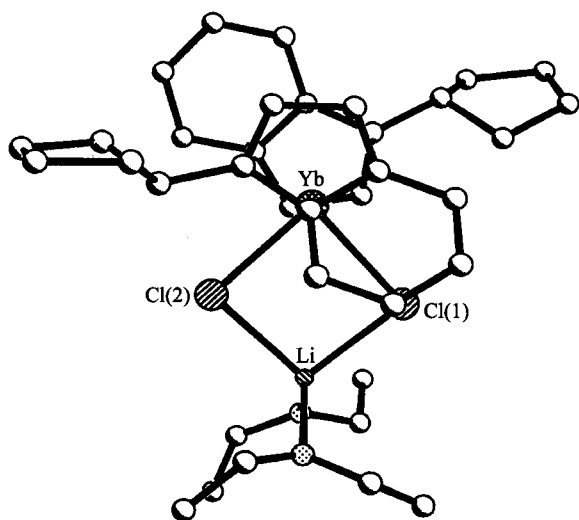


Fig. 2 View of the molecule depicting the staggered $C_5H_9C_9H_7$ rings.

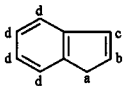
Experimental

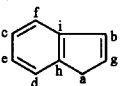
The manipulations were performed under high purity argon with rigorous exclusion of air and moisture using the Schlenk techniques. Solvents, indene and cyclopentyl bromide were dried over 4 Å molecular sieves for several weeks and refluxed and distilled over sodium-benzophenone under argon before use. Analysis of Sm was accomplished using direct complexometric titration with disodium EDTA. Analysis of Cl was carried out using the Volhard method. Carbon and

hydrogen were determined on a TQ-2 elementary analyzer. IR spectra were recorded on a FTS135 spectrometer with KBr pellet. ¹H NMR (¹³C NMR) spectra were obtained on a Unity-400 (Unity-100) spectrometer in C_7D_8 solution referenced to internal Me_4Si .

Synthesis of $C_5H_9C_9H_7$

Freshly distilled indene (20 mL, 170 mmol) reacted with slightly overweighed sodium sands (4.5 g, 195 mmol) in 60 mL THF at 50 °C for 24 h. The mixture was filtered to remove excess sodium and then 18 mL of freshly distilled cyclopentyl bromide was added to it at 0 °C. The resulting solution was kept stirred for 3 h and washed with an aqueous solution of ammonium chloride, and the organic layer was collected. This procedure was repeated until the organic phase showed neutrality. Later, the organic compound solution was dried over $MgSO_4$ for 10 h, distilled, and the yellow distillate of 95–100 °C/263 Pa was collected. Yield 39%, n_D^{20} 1.566; ¹H NMR δ : 1.680–1.772 (m, CH_2 , C_5H_9),

2.065 (br, CH_2 , C_5H_9);  3.053 (br, —^aCH, cyclopentadienyl ring), 6.193 (s, = ^bCH, cyclopentadienyl ring), 7.171–7.208 (t, = ^dCH, benzene ring), 7.255–7.307 (q, ^dCH, benzene ring), 7.407–7.461 (q, 2 (= ^dCH), benzene ring);²⁰ ¹³C NMR δ : 25.251 (CH_2 , C_5H_9), 31.669 (CH_2 , C_5H_9), 37.495

(—CH, C_5H_9);^{21a}  21b: 38.572 (—^aCH), 119.611 (= ^bCH), 123.678 (= ^cCH), 124.330 (= ^dCH), 125.347 (= ^eCH), 125.832 (= ^fCH), 144.768 (= ^eCH), 145.496 (= ^bC=), 148.607 (= ⁱC=); IR ν : (C_9H_7) 3065 (w), 3017 (w), (C_5H_9) 2952 (m), 2867 (m), (C_9H_7) 1635 (w), 1458 (m), (C_9H_7) 1021 (s) cm^{-1} .

Synthesis of $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$

A solution of $C_5H_9C_9H_6Li$ in THF (31.6 mL, 17.9 mmol) (0 °C, $C_5H_9C_9H_7$ reacted with 1 equiv. hexane solution of *n*-butyllithium for 12 h) was added at –78 °C to a 35 mL THF suspension of anhydrous $YbCl_3$ (2.5 g, 8.9 mmol). The mixture was kept stirring over night and centrifuged to remove the precipitates. THF was evacuated from the solution and the residue was extracted with ether (45 mL). The green ether solution was cooled at 0 °C to give single crystals of complex **1**, in yield 89.7%. ¹³C NMR δ : 15.458 (CH_3 , ether), 26.018 (CH_2 , C_5H_9), 31.95 (CH_2 , C_5H_9), 39.385 (^aCH), 65.390 (OCH_2 , ether), 120.45 (= ^bCH), 123.348 (= ^cCH), 124.425 (= ^dCH), 126.670 (= ^eCH), 127.232 (= ^fC);^{21b} IR (KBr) ν : 3050 (w), 3030 (w), 2953 (m), 2868 (m), 1636 (w), 1600 (m), 1021 (s), 969 (Et_2O) cm^{-1} . Anal. calcd for $C_{36}H_{50}Cl_2LiO_2Yb$: C 56.47, H 6.53, Cl 9.26, Yb 22.60;

found C 56.00, H 7.01, Cl 9.51, Yb 22.11.

X-Ray data collection and structures determination

Crystal data and details of structure refinement for $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$ are listed in Table 2. The intensity data were collected on a Siemens P4 four-circle diffractometer at room temperature using graphite monochromated Mo K α radiation ($\lambda = 0.071073$ nm) in the ω scan mode. All the intensities were corrected for Lorentz, polarization and absorption effects. The positions of the heavy atoms were found from Patterson methods. Successive Fourier and difference Fourier syntheses revealed non-hydrogen atoms. The coordinates of hydrogen atoms were determined according to theoretical modes. All calculations were carried out on an Eclipse S/140 microcomputer with the SHELXTL program.

Table 2 Crystallographic data and structure refinement for complex $(C_5H_9C_9H_6)_2Yb(\mu-Cl)_2Li(Et_2O)_2$

Formula	$C_{36}H_{30}Cl_2LiO_2Yb$
F. W. ($g \cdot mol^{-1}$)	765.64
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (nm)	1.1002(2)
<i>b</i> (nm)	1.1398(3)
<i>c</i> (nm)	1.5253(5)
α ($^\circ$)	84.11(2)
β ($^\circ$)	71.09(2)
γ ($^\circ$)	88.11(2)
<i>V</i> (nm^3), <i>Z</i>	1.799(8), 2
<i>D</i> (calcd) ($g \cdot cm^{-3}$)	1.413
<i>F</i> (000)	778
Crystal size (mm)	0.50 × 0.32 × 0.16
2 θ limit for data ($^\circ$)	1.80 to 25.04
Reflection collected	7660
No. of indep reflns	6336 ($R_{int} = 0.0232$)
Goodness-of-fit on F^2	0.981
Final <i>R</i> , <i>wR</i>	$R = 0.0425$, $wR = 0.1002$
Largest diff. peak and hole ($e \cdot nm^{-3}$)	1526 and -1520

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