

Organolanthanides with 3-(2-pyridylmethyl) indenyl ligands: synthesis, crystal structures and catalytic activities of divalent complexes for ϵ -caprolactone polymerization

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Abstract

Reaction of 3-(2-pyridylmethyl)indenyl lithium (**1**) with $\text{LnI}_2(\text{THF})_2$ ($\text{Ln} = \text{Sm}, \text{Yb}$) in THF produced the divalent organolanthanides $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}(\text{THF})$ ($\text{Ln} = \text{Sm}$ (**2**), Yb (**3**)) in high yield. **1** reacts with LnCl_3 ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Yb}$) in THF to give bis(3-(2-pyridylmethyl)indenyl) lanthanide chlorides $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{III}}\text{Cl}$ ($\text{Ln} = \text{Nd}$ (**4**), Sm (**5**)) and the unexpected divalent lanthanides **3** ($\text{Ln} = \text{Yb}$). Complexes **2–5** show more stable in air than the non-functionalized analogues. X-ray structural analyses of **2–4** were performed. **2** and **3** belong to the high symmetrical space group (C_{2h}) with the same structures, they are THF-solvated 9-coordinate monomeric in the solid state, while **4** is an unsolvated 9-coordinate monomer with a *trans* arrangement of both the side-arms and indenyl rings in the solid state. Additionally, **2** and **3** show moderate polymerization activities for ϵ -caprolactone (CL).
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Keywords: 3-(2-Pyridylmethyl) indenyl; Divalent lanthanides; Crystal structure; ϵ -Caprolactone

1. Introduction

Recently, considerable efforts have been devoted to exploring the organometallic chemistry of metallocenes with donor-functionalized side chains [1], because the donor-functionalized side chains can increase the stability of highly reactive organolanthanide complexes by forming intramolecular chelating coordination with the central metal. Most of the ligands used are those with ether- or amino-substituted cyclopentadienyl groups. Although divalent lanthanides with η^5 -bonded aromatic carbocyclic ligands are regarded as the prospective catalysts for the polymerization of both polar and non-polar

monomers [2], investigations on divalent indenyllanthanides are still limited. So far, only few amino-substituted indenyl ligands of divalent lanthanocenes were reported, such as $[\text{Me}_2\text{Si}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_5)(t\text{-BuNH})]_2\text{Yb}$ [3], $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Yb}$ [3], $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Yb}$ [3,4] and $(\text{C}_4\text{H}_8\text{NMe}_2\text{SiCH}_2\text{C}_9\text{H}_5\text{Me})_2\text{Eu}$ [5], but no samarium(II) complexes were X-ray characterized. Since no pyridyl-functionalized indenyl ligands have been used in lanthanides, we prepared 3-(2-pyridylmethyl) indenyl ligand in order to study its coordination behavior in divalent lanthanides and trivalent lanthanide chlorides. Here, we report the synthesis and crystal structures of bis(3-(2-pyridylmethyl)indenyl) divalent lanthanide complexes $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}(\text{THF})$ ($\text{Ln} = \text{Sm}$ (**2**), Yb (**3**)), and bis(3-(2-pyridylmethyl)indenyl) trivalent lanthanide chlorides $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{III}}\text{Cl}$ ($\text{Ln} = \text{Nd}$ (**4**), Sm (**5**)). The polymerization activities of **2** and **3** for ϵ -caprolactone were investigated.

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2. Results and discussion

2.1. Synthesis

The reaction of 3-(2-pyridylmethyl) indenyl lithium (**1**) with $\text{LnI}_2 (\text{THF})_2$ ($\text{Ln} = \text{Sm}, \text{Yb}$) in THF generates the divalent organolanthanides $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Sm}^{\text{II}}(\text{THF})$ (**2**) and $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Yb}^{\text{II}}(\text{THF})$ (**3**) in high yields (Scheme 1). The complexes are dissolved in a donor solvent such as THF and diglyme, only soluble on heating in aromatic solvents such as toluene, and insoluble in hexane. Complexes **2** and **3** in solution are air and moisture sensitive, but their crystals can be kept in air for several minutes without decomposition.

Complex **3** was obtained as an unexpected product in the attempted synthesis of $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Yb}^{\text{III}}\text{Cl}$ by the reaction of YbCl_3 with 3-(2-pyridylmethyl) indenyl lithium (**1**) (Scheme 2). It is possible that the alkyl-lithium of the ligand acts as a reductant. Other alkali salts [6] were reported to reduce the Yb(III) to Yb(II) complexes, such as KC_7H_{11} , $\text{Na}_2[(\text{C}_9\text{H}_6)_2\text{C}(\text{CH}_3)_2]$ and $n\text{-BuLi}$.

The reaction between anhydrous lanthanide chlorides ($\text{Ln} = \text{Nd}, \text{Sm}$) and two equivalents of 3-(2-pyridylmethyl) indenyl lithium (**1**) in THF afforded $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Nd}^{\text{III}}\text{Cl}$ (**4**) and $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Sm}^{\text{III}}\text{Cl}$ (**5**). These complexes are soluble in THF and dissolved in toluene only on heating. All complexes in solution

are air and moisture sensitive, but their crystals can be kept for long time (about 1 h) in air.

All the complexes were characterized by spectroscopic and elemental analyses. IR spectroscopic analyses showed obvious characteristic absorption of pyridyl group at about 1591 cm^{-1} , and indenyl group at about $3060, 3030, 1475, 1435$ and 770 cm^{-1} . In EI-mass spectrum, the fragments of the ligand, such as $[\text{C}_5\text{H}_4\text{N}]^+$ and $[\text{C}_5\text{H}_4\text{CH}_2\text{C}_9\text{H}_6]^+$, show high intensity, while the intensities of other fragments, such as $[\text{M}]^+$ and $[\text{M-L}]^+$ are weak.

3. Molecular structures of **2** and **3**

Crystals of complexes **2** and **3** suitable for X-ray diffraction were obtained by recrystallization from THF and diglyme, respectively. Details of crystal data collections and the structure refinements are listed in Table 1, and selected bond lengths and angles are given in Table 2.

Complexes **2** and **3** belong to the same crystal system (orthorhombic) and space group ($Cmcm$) with similar crystal data. So, they are isostructural and the molecular structure of **3** is presented in Fig. 1. In complex **3**, the whole molecule shows one C_2 symmetry about the Yb–O(1) axis and two symmetrical planes, perpendicular each other. It means that five atoms of THF and Yb are on the same plane. This is almost certainly an artifact of crystallographic disorder. Therefore, complexes **2** and **3** show very high symmetry, which is most unusual in low valent organolanthanide complexes. This molecule can also be described as the overlapping of two enantiomorphous molecules (part a and part b, as shown in Fig. 2) in the same position in the unit cell, and their space occupation ratio is 50:50. While most of the coordination number of divalent lanthanocenes is 8, only several complexes are 9-coordinate, such as $(\text{C}_9\text{H}_7)_2\text{Sm}^{\text{II}}(\text{THF})_3$ [7] and $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_5)_2\text{Yb}^{\text{II}}(\text{THF})$ [8]. As shown in Fig. 2, complex **3** is

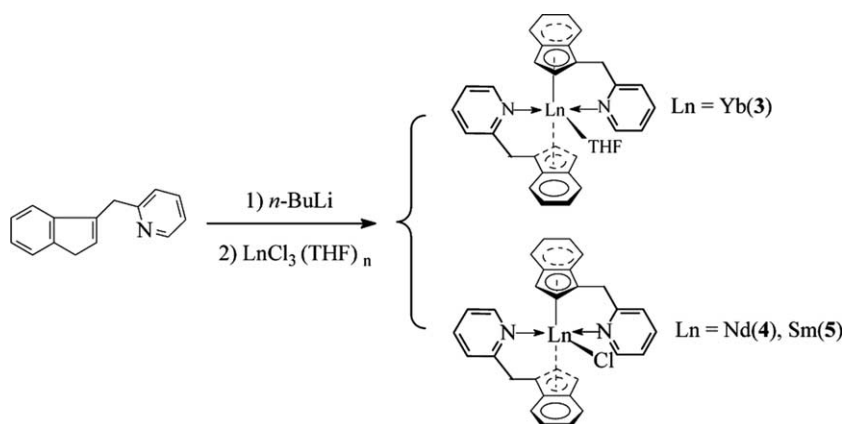
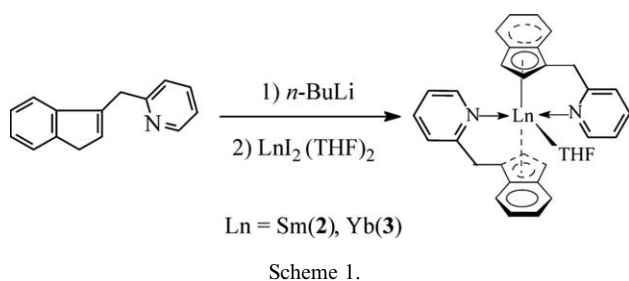


Table 1
Crystal data and structure refinements for collection parameters for **2–4**

	2	3	4
Empirical formula	C ₃₄ H ₃₂ N ₂ O ₅ Sm	C ₃₄ H ₃₂ N ₂ O ₅ Yb	C ₃₀ H ₂₄ ClN ₂ Nd
Formula weight	634.97	657.66	592.20
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Cmcm</i>	<i>Cmcm</i>	<i>P2₁2₁2₁</i>
<i>a</i> (Å)	11.3616(4)	11.400(2)	10.4993(2)
<i>b</i> (Å)	14.5789(7)	14.401(3)	14.8582(4)
<i>c</i> (Å)	16.9142(5)	16.725(3)	15.6449(5)
<i>V</i> (Å ³)	2801.66(19)	2745.7(10)	2440.62(11)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g/cm ³)	1.505	1.591	1.612
μ (Mo K α) (mm ^{−1})	2.125	3.436	2.258
<i>F</i> (000)	1280	1312	1180
Crystal size (mm ^{−3})	0.42×0.35×0.27	0.69×0.52×0.42	0.30×0.16×0.134
θ_{\min} , θ_{\max} (°)	2.27, 27.44	2.28, 27.48	1.89, 27.43
Number of reflections collected	1732	1703	3131
Number of unique reflections	1732	1703	3131
Number of parameters	162	162	298
Goodness-of-fit on <i>F</i> ²	1.054	1.057	1.057
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0285, <i>wR</i> ₂ = 0.0695	<i>R</i> ₁ = 0.0339, <i>wR</i> ₂ = 0.0877	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0594
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0315, <i>wR</i> ₂ = 0.0702	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0894	<i>R</i> ₁ = 0.0340, <i>wR</i> ₂ = 0.0803
$\Delta\rho_{\max/\min}$ (e Å ^{−3})	0.565/−0.493	1.201/−1.117	0.695/−0.618

Table 2
Selected bond lengths (Å) and angles (°) for complexes **2** and **3**

	2	3
<i>Bond lengths</i>		
Ln–O(1)	2.584(4)	2.449(5)
Ln–N(1)	2.691(5)	2.587(7)
Ln–C(1)	2.809(4)	2.710(5)
Ln–C(2)	2.866(4)	2.831(5)
Ln–C(7)	2.911(5)	2.903(5)
Ln–C(8)	2.853(6)	2.766(6)
Ln–C(9)	2.815(6)	2.699(8)
Ln–Cent ^a	2.580	2.496
Ln–C(av)	2.851	2.782
<i>Bond angles</i>		
O(1)–Ln–Cent	118.8	117.3
O(1)–Ln–N(1)	81.6	79.9
N(1)–Ln–Cent	86.9	89.3
Cent–Ln–Cent'	122.5	125.3
<i>Dihedral angles</i>		
P(1)···P(2) ^b	76.1	76.2
P(1)···P(3)	63.8	66.9
P(1)···P(4)	14.7	11.6
P(2)···P(4)	87.1	84.6

^a Cent define the centroid of C(1), C(2), C(7)–C(9).

^b P(1) define the indenyl plane of C(1)–C(9); P(2) define the pyridyl plane of C(10)–C(14) and N(1); P(3) define the indenyl plane of C(1A), C(2B)–C(9B); P(4) define the pyridyl plane of C(10B)–C(14B) and N(1B).

THF-solvated 9-coordinate monomeric in the solid state. The central ytterbium atom is coordinated by two indenyls, two nitrogen atoms of pyridyls and one oxygen atom of THF to form a distorted trigonal bipy-

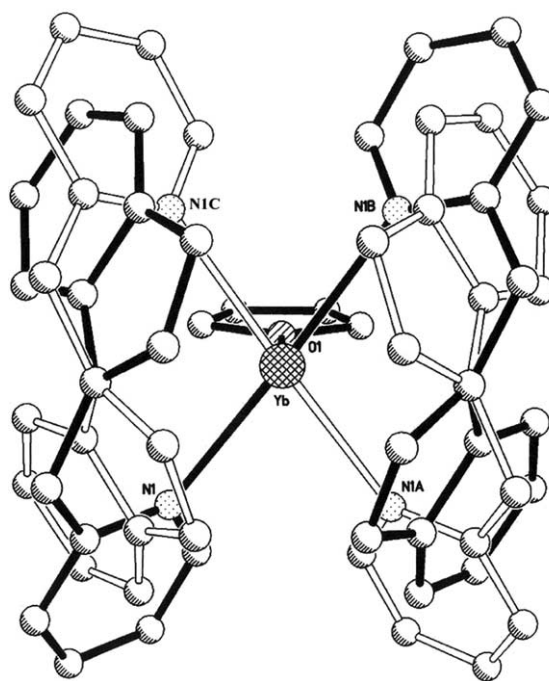


Fig. 1. Molecular structure of (C₅H₄NCH₂C₉H₆)₂Yb^{II}(THF) (**3**) (carbon atoms are not marked for clarity).

amid. The two nitrogen atoms lie at both apices, and the oxygen atom, the central metal atom and the two centroids of cyclopentadienyl rings of indenenes form the equatorial plane.

The general structural features of complex **2** are similar to those already discussed for complex **3**. The

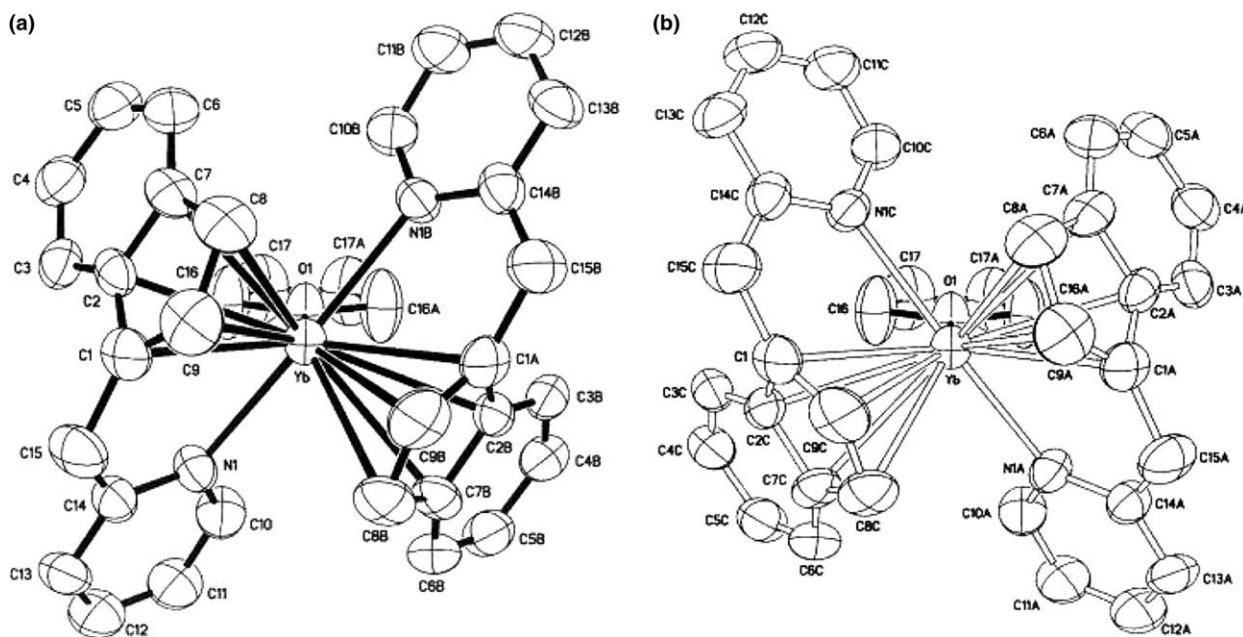


Fig. 2. ORTEP drawing of two enantiomorphous molecules (part a and part b) with 40% thermal ellipsoids in $(C_5H_4NCH_2C_9H_6)_2Yb^{II}(THF)$ (**3**).

samarium center is bound to the indenyl ring in an η^5 -manner; the samarium–carbon bond lengths range from 2.809(4) to 2.911(5) Å with an average 2.851 Å as compared to a range of 2.81(1)–2.91(1) Å and an average of 2.86(3) Å in $(C_5Me_5)_2Sm^{II}(THF)_2$ [9]. The Sm–C distance of 2.580 Å is also comparable to a related value of 2.631 Å reported for $(C_{13}H_9)_2Sm^{II}(THF)_2$ [7], 2.583 Å for $[C_5Me_4SiMe_2(iPr-tacn)]Sm^{II}$ [10] and 2.534 Å for $[(C_5Me_5)Sm^{II}(\mu-I)(THF)_2]_2$ [9]. The samarium–nitrogen bond length is 2.691(5) Å, which is typical for distances between samarium and bulky amine donors, and is similar to the bond lengths observed in (1,4,7-triazacyclononane-1,4,7-tris(2-(ethylimino)-propionato))samarium (2.669(4)–2.690(4) Å) [11]. The samarium–oxygen bond length of 2.584(4) Å is longer than the corresponding bonds observed in $(C_{13}H_9)_2Sm^{II}(THF)_2$ (2.560(6)–2.540(6) Å) [7], but shorter than that reported for $(C_5Me_5)_2Sm^{II}(THF)_2$ (2.62(1)–2.66(1) Å) [9].

In complex **2**, the Cent–Sm–Cent' angle of 122.5° is significantly smaller than the 136.8° in $(C_5Me_5)_2$

$Sm^{II}(THF)_2$ [9]. From the dihedral angles of four planes, it is concluded that two pyridyl rings are almost perpendicular ($P(2) \cdots P(4) = 87.1^\circ$), while one indenyl ring is nearly parallel to the pyridyl ring connected with the another indenyl ring ($P(1) \cdots P(4) = 14.7^\circ$).

The smaller ionic radius of ytterbium versus samarium results in smaller Ln–O (2.449(5) vs 2.584(4) Å), Ln–N (2.691(5) vs 2.587(7) Å), and Ln–C (2.782(av) vs 2.851(av) Å) bond lengths in complex **3**.

A comparison of selected geometric parameters in some ytterbium(II) complexes bearing pendent N-donors is listed in Table 3. It should be noted that the geometry of other Yb(II) complexes is a distorted tetrahedron, different from **3**. It is found that the N–Yb–N angle (159°) in **3** is the largest in all these Yb(II) complexes. The average value of the Yb–C distance 2.782(8) Å in **3** is shorter than the corresponding value of 2.806(12) Å in $[Me_2Si(Me_2NCH_2CH_2C_9H_5)-(t-BuNH)_2]_2Yb$ [3], but is longer than the related values in other Yb(II) complexes. The average Yb–N distance 2.587(7) Å in **3** is shorter than the value of 2.673(11) Å in

Table 3
Comparison of the selected geometric parameters in Yb(II) complexes

Complex	(Yb–C)av (Å)	(Yb–N)av (Å)	N–Yb–N (°)	Reference
3	2.782(8)	2.587(7)	159.8	This work
$[Me_2Si(Me_2NCH_2CH_2C_9H_5)-(t-BuNH)_2]_2Yb$	2.806(12)	2.673(11)	95.1(1)	[3]
$(Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb$	2.778(14)	2.650(12)	92.8(5)	[3]
$(Me_2NCH_2CH_2C_9H_6)_2Yb$	2.722(10)	2.588(7)	103.7(2)	[3,4]
$[Me_2NCH(Me)CH_2C_5H_4]_2Yb$	2.683(5)	2.603(4)	103.1(2)	[12]
$Yb(Cp^{py})_2$	2.68(1)	2.48(1)	100.8(2)	[13]
$Yb(Cp^{py(s)})_2$	2.68(2)	2.48(1)	84.04(4)	[13]

$[\text{Me}_2\text{Si}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_5)(t\text{-BuNH})_2]\text{Yb}$ [3] and 2.650 (12) Å in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Yb}$ [3], similar to the value of 2.588(7) Å in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Yb}$ [3,4] and 2.603(4) Å in $[\text{Me}_2\text{NCH}(\text{Me})\text{CH}_2\text{C}_5\text{H}_4]_2\text{Yb}$ [12], but significantly larger than 2.48(1) Å in $\text{Yb}(\text{Cp}^{\text{py}})_2$ [13] and $\text{Yb}(\text{Cp}^{\text{py(s)}})_2$ [13]. All these results depend on the steric effects and geometry.

It is interesting to note that the bond lengths of $\text{Yb}-\text{C}(2)$ and $\text{Yb}-\text{C}(7)$ in **3** are significantly longer than those of $\text{Ln}-\text{C}(1)$, $\text{Ln}-\text{C}(8)$ and $\text{Ln}-\text{C}(9)$, indicating that the coordination mode of the metal atom with indenyl ligands is beginning to partially slipped toward η^3 - from η^5 -mode.

4. Molecular structures of **4**

Crystals of complex **4** suitable for X-ray diffraction were grown by cooling the concentrated solution to -30°C . The molecular structure of **4** is presented in Fig. 3, and selected bond lengths and angles are listed in Table 4. Although complex **4** crystallizes from the THF solutions, it remains to be unsolvated 9-coordinate monomeric in solid state. The central Nd atom is coordinated by two indenyls, two nitrogen atoms of pyridyls and one chlorine atom to form a distorted trigonal bipyramid. The two nitrogen atoms lie at both apices, and the chlorine atom, the central metal atom and the two centroids of cyclopentadienyl rings of indenenes form the equatorial plane.

The Nd center is bound to the indenyl ring in a η^5 -manner. The Nd–C bond lengths range from 2.707(7) to 2.836(8) Å with an average 2.766 Å, resulting in a Nd–Cent(av) distance of 2.491 Å. This compares with a related value of 2.513 Å reported for $(\text{C}_4\text{H}_7\text{O}-\text{CH}_2\text{C}_9\text{H}_6)_2\text{NdCl}$ [14]. The Nd–Cl bond length of 2.682(2) Å is longer than the corresponding value of 2.678(3) Å in $(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6)_2\text{NdCl}$ [13], 2.672(2) Å

Table 4

Selected bond lengths (Å) and angles ($^\circ$) for complex **4**

Bond lengths			
Nd–Cl	2.682(2)		
Nd–N(1)	2.652(6)	Nd–N(2)	2.642(6)
Nd–C(1)	2.707(7)	Nd–C(16)	2.745(8)
Nd–C(2)	2.723(6)	Nd–C(17)	2.727(7)
Nd–C(3)	2.751(7)	Nd–C(18)	2.763(7)
Nd–C(4)	2.808(7)	Nd–C(19)	2.827(7)
Nd–C(9)	2.776(7)	Nd–C(24)	2.836(8)
Nd–Cent(1) ^a	2.472	Nd–Cent(2)	2.510
Bond angles			
N(2)–Nd–N(1)	161.9(2)	Cent(1)–Nd–N(2)	101.0
N(2)–Nd–Cl	80.18(16)	Cent(2)–Nd–N(1)	99.6
N(1)–Nd–Cl	81.79(14)	Cent(2)–Nd–N(2)	87.3
Cent(1)–Nd–Cl	120.1	Cent(1)–Nd–Cent(2)	125.8
Cent(2)–Nd–Cl	114.0	RA	157.9
Cent(1)–Nd–N(1)	88.7		
Dihedral angles			
P(1)···P(2) ^b	74.2	P(1)···P(3)	51.9
P(2)···P(3)	23.8	P(1)···P(4)	9.7
P(2)···P(4)	82.6	P(3)···P(4)	60.9

^a Cent(1) define the centroid of C(1)–C(4) and C(9), Cent(2) define the centroid of C(16)–C(19) and C(24).

^b P(1) define the indenyl plane of C(1)–C(9); P(2) define the pyridyl plane of C(11)–C(15) and N(1); P(3) define the indenyl plane of C(16)–C(24); P(4) define the pyridyl plane of C(26)–C(30) and N(2).

in $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{NdCl}$ [15] and 2.668(2) Å in $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_9\text{H}_6)_2]\text{NdCl}$ [16], but shorter than 2.6989(7) Å in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{NdCl}$. The Nd–N bond lengths of (2.652(6), 2.642(6) Å) is shorter than those observed in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)_3\text{Nd}$ (2.73(1), 2.70(1) Å) [17] and $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{NdCl}$ (2.804(2), 2.772(2) Å) [18].

The N(1)–Nd–N(2) angle of 164.48° is similar to the corresponding value of $161.9(2)^\circ$ in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{NdCl}$. The RA angle of 157.9° , which means the conformation of two indenyl rings is staggering, is similar to 157.7° in $(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6)_2\text{NdCl}$ [14]. From the dihedral angles of four planes, it is concluded that two pyridyl rings are almost perpendicular ($\text{P}(2)\cdots\text{P}(4)=82.6^\circ$), while one indenyl ring is nearly parallel to the pyridyl ring connected with the other indenyl ring ($\text{P}(2)\cdots\text{P}(3)=23.8^\circ$, $\text{P}(1)\cdots\text{P}(4)=9.7^\circ$).

5. Polymerization of ϵ -caprolactone

The activities of complexes **2** and **3** as single-component catalysts in ϵ -caprolactone polymerization were investigated. The results are summarized in Table 5. It was found that **2** shows higher activity than **3**, consist with their different electrode potentials (E^0) between the trivalent and divalent oxidation states. With the increase in molar ratio of $[\text{CL}]/[\text{Cat}]$, the molecular weight of the polymers increases, while PDI begins to broaden, which

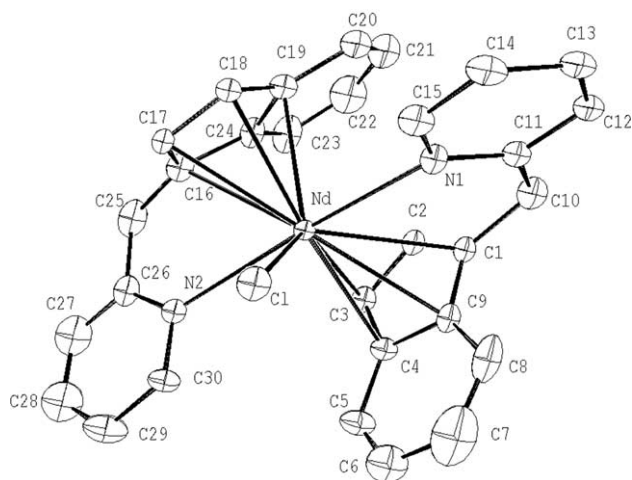


Fig. 3. ORTEP drawing of $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Nd}^{\text{III}}\text{Cl}$ (**4**) with 40% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 5
Data for the polymerization of CL

Cat.	[CL]/[Cat] (mol/mol)	Conv. (%)	M_n ($\times 10^4$)	M_w ($\times 10^4$)	PDI
2	200	94.1	2.7	7.3	1.68
	300	98	5.8	10.6	1.82
	500	99	6.3	12.3	1.94
3	200	76.5	2.4	3.7	1.56
	300	85.2	3.5	6.3	1.79
	500	87.6	6.5	11.0	1.70

Conditions: solvent, toluene; temperature, 0 °C; [Cat] = 6×10^{-3} mol/l; time, 1 h.

can be explained by partial chain termination caused by deactivation of the catalysts by a trace amount of impurities or living chain transfer in the reaction. Compared with other high active catalysts for CL, such as $(C_{13}H_9)_2Sm(THF)_2$ [19], $Sm(ArO)_2(THF)_3$ [20], and $[(C_5Me_5)Sm(\mu-OAr)]_2$ [20], which were reported that polymers with millions of molecular weights can be got in several minutes with high conversion, **2** and **3** show low activities. These can be explained by the fact that the introduction of intramolecular coordination can increase the stability of the complexes and decrease their catalyst activities at the same time. The existence of coordinated THF in the molecule can be the other reason.

The catalytic activities of complexes **2** and **3** for the polymerization for other monomers, such as MMA, lactide, are disappointed, only lower molecular weights of polymers were got.

6. Conclusion

We have synthesized a series of complexes of divalent and trivalent lanthanides with pyridyl-functionalized indenyl ligand by metathesis reaction of Ln(II) iodides or Ln(III) chlorides with the alkyllithium of the ligand. The intramolecular coordination of the pyridyl groups with the central atom was confirmed by X-ray structure determination for complexes **2–4**. Molecular structures of **2** and **3** show high symmetry, significantly different from previous reports on divalent bis-indenyl lanthanides. **4** is unsolvated 9-coordinate monomeric complex with a *trans* arrangement of both the pyridyl and indenyl rings in the solid state.

7. Experimental

7.1. Materials and methods

All manipulations involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. After drying over 4A molecular sieves, tetrahydrofuran (THF), diglyme ([Me-

$OCH_2CH_2)_2O$), toluene, and hexane were distilled under argon from sodium/potassium alloy with benzophenone ketyl prior to use. $C_5H_4NCH_2C_9H_7$ [21], $NdCl_3$ [22], $YbCl_3$ [22], $SmCl_3$ [22], $SmI_2(THF)_2$ [23], $YbI_2(THF)_2$ [23] were prepared according to published procedures; *n*-butyllithium and ϵ -caprolactone (CL) were purchased from Aldrich, the latter being distilled over CaH_2 before use. Analyses of rare earth metals and chlorine were accomplished using direct complexometric titration with disodium EDTA and the Volhard method, respectively. Carbon and hydrogen analysis were carried out by combustion method. IR spectra were recorded on Bio-Rad FTS135 spectrometer in the form of KBr pellets. Mass spectra were recorded on a LGQ spectrometer. Gel permeation chromatography (GPC) analysis of polymer samples were carried at 35 °C using THF as eluent on Water410 instrument and calibrated using monodispersed polystyrene standards at a flow rate of $1.0 \text{ ml} \cdot \text{min}^{-1}$.

7.2. Preparation of 3-(2-pyridylmethyl) indenyl lithium (1) [24]

To a solution of *n*-butyllithium (1.6 M in hexane, 30 ml) in 30 ml hexane was added dropwise $C_5H_4NCH_2C_9H_7$ (9.3 g, 0.045 mol in 50 ml hexane) with rigorous stirring at 0 °C, the resultant mixture was stirred for 1 h, then warmed to r.t. and stirred overnight. After centrifugation, the pale yellow precipitation was washed with hexane ($2 \times 30 \text{ ml}$), then 80 ml THF was added, and a clear orange yellow solution was obtained. Pale yellow crystals were obtained upon standing the solution at 0 °C for several days (10.77 g, 67%).

7.3. Preparation of $(C_5H_4NCH_2C_9H_7)_2Sm^{II}(THF)$ (2)

A THF solution of 3-(2-pyridylmethyl) indenyl lithium (1) (0.0072 mol, excess) was added to a solution of $SmI_2(THF)_2$ (0.0035 mol) in THF (50 ml) at 0 °C. The reaction mixture was allowed to warm up to r.t. and stirred for 24 h. After centrifugation, the resulting dark solution was slowly concentrated in vacuum at r.t. until

crystallization started. The concentrate was then cooled to $-10\text{ }^{\circ}\text{C}$ and kept for several days. The mother liquor was decanted from the black crystals of **2**, which were washed with cold THF and dried in vacuum (2.11 g, 95% yield). X-ray-quality crystals were grown from THF at $0\text{ }^{\circ}\text{C}$ for several weeks. Anal. Calc. (%) for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{OSm}$: Sm, 23.78; C, 64.25; H, 5.04; N, 4.41. Found (%): Sm, 24.12; C, 65.05; H, 5.84; N, 5.01. EI-MS m/z (relative intensity (%)): 206(100), 152(5), 128(22), 115(48), 79(78), 43(28). IR (cm^{-1}): 3062(m), 3012(m), 2920(w), 1703(w), 1591(s), 1568(s), 1521(m), 1474(s), 1462(m), 1434(s), 1395(m), 1150(w), 1090(w), 1051(w), 994(w), 972(w), 916(w), 771(s), 755(s), 719(m), 622(w), 570(w), 402(w).

7.4. Preparation of $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Yb}^{\text{II}}(\text{THF})$ (**3**)

(a) From $\text{YbI}_2(\text{THF})_2$. The procedure followed was similar to that for complex **2**. This ytterbium complex was prepared from the reaction of **1** (0.0072 mol) with $\text{YbI}_2(\text{THF})_2$ (0.0035 mol) in THF as a dark red solid (2.07 g, 90% yield). X-ray-quality ruby-red crystals were obtained when recrystallizing **3** in diglyme at $0\text{ }^{\circ}\text{C}$. Anal. Calc. (%) for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{OYb}$: Yb, 26.18; C, 62.10; H, 4.87; N, 4.26. Found (%): Yb, 27.23; C, 63.55; H, 5.02; N, 5.32. EI-MS m/z (relative intensity (%)): 206(100), 172(5), 128(28), 115(52), 79(80), 42(23). IR (cm^{-1}): 3064(m), 3012(m), 2920(w), 2897(w), 1591(s), 1569(m), 1474(s), 1461(m), 1434(s), 1396(m), 1148(w), 1091(w), 1050(w), 995(m), 972(m), 917(w), 772(s), 756(s), 719(m), 622(w), 570(m), 403(m).

(b) From YbCl_3 . A THF solution of **1** (0.006 mmol) was added slowly to a suspension of YbCl_3 (0.8386 g, 0.003 mol in 20 ml THF) at low temperature (-60 to $-78\text{ }^{\circ}\text{C}$). The reaction mixture was allowed to warm up to r.t. and stirred for 24 h. After centrifugation the solvent was evaporated in vacuo. The compound was extracted with 30 ml toluene/THF (10:1) and kept at $-30\text{ }^{\circ}\text{C}$. Dark red crystals were obtained in 35% yield [25].

7.5. Preparation of $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Nd}^{\text{III}}\text{Cl}$ (**4**)

A THF solution of **1** (0.006 mol) was added dropwise to a stirred suspension of NdCl_3 (0.7522 g, 0.003 mol in 20 ml THF) at low temperature (-60 to $-78\text{ }^{\circ}\text{C}$). The mixture was allowed to warm up to r.t. and stirred to give a green solution. After centrifugation, the resulting solution was concentrated to about 10 ml. The complex $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Nd}^{\text{III}}\text{Cl}$ was isolated as green crystals (0.85 g, 48% yield) by cooling the solution to $-30\text{ }^{\circ}\text{C}$ for several days. Anal. Calc. (%) for $\text{C}_{30}\text{H}_{24}\text{ClN}_2\text{Nd}$: Nd, 24.36; Cl, 6.00; C, 60.79; H, 4.05. Found (%): Nd, 25.31; Cl, 6.32; C, 61.12; H, 4.61. EI-MS m/z (relative intensity (%)): 206(100), 177(6), 142(2), 129(4), 115(18), 79(42),

42(38). IR (cm^{-1}): 3065(m), 3035(m), 3015(m), 2775(w), 1710(w), 1635(m), 1598(s), 1568(m), 1557(m), 1474(s), 1460(s), 1435(s), 1394(m), 1291(w), 1149(m), 1050(m), 1020(w), 770(s), 756(m), 718(m), 570(w), 402(w).

7.6. Preparation of $(\text{C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)_2\text{Sm}^{\text{III}}\text{Cl}$ (**5**)

The samarium derivative **5** was prepared in a similar procedure as complex **4** from the reaction of **1** (0.006 mol) with SmCl_3 (0.7702 g, 0.003 mol) in THF as orange red crystals (1.34 g, 75% yield). Anal. Calc. (%) for $\text{C}_{30}\text{H}_{24}\text{ClN}_2\text{Sm}$: Sm, 25.21; Cl, 5.92; C, 60.10; H, 4.01. Found (%): Sm, 25.82; Cl, 6.35; C, 61.22; H, 4.61. EI-MS m/z (relative intensity (%)): 206(100), 186(5), 151(2), 129(8), 115(20), 79(50), 42(42). IR (cm^{-1}): 3065(e), 3035(e), 3015(m), 2775(m), 1712(m), 1635(m), 1596(s), 1568(m), 1557(m), 1475(s), 1460(s), 1440(s), 1394(m), 1291(w), 1150(m), 1052(m), 1024(w), 770(s), 758(m), 718(m), 570(w), 404(m).

8. X-ray data collection and structure determination for **2–4**

A suitable crystal of the title complexes was mounted in a sealed capillary for X-ray diffraction study. Data was collected on a Rigaku Rapid Diffractometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.071073\text{ }\text{\AA}$) radiation using the ω - 2θ technique at 293 K. The crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods, expanded using Fourier techniques [26]. All the non-hydrogen atoms were refined anisotropically. In complex **4**, all the hydrogen atoms were added according to theoretical models with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. The hydrogen atoms were not added in complexes **2** and **3** because of their special structures. All calculations were performed using the SHELXS-97 crystallographic software package [27].

9. Polymerization of ϵ -caprolactone

All polymerization reactions were carried out under argon. In a typical procedure, ϵ -caprolactone was added to the solution of the initiator at the desired temperature. After a certain time, the polymerization was quenched with acidified methanol, and the polymer was precipitated. The resulting polymer was washed with methanol and dried in a vacuum at $35\text{ }^{\circ}\text{C}$ to a constant weight.

10. Supplementary material

Crystallographic data for the structures reported in this paper (1–4) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 235620–235623. Copies of this information may be obtained free of charge from the The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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- [24] Pale yellow crystals of $(C_5H_4NCH_2C_9H_6)Li(THF)_2$ (1) were grown from THF in space group $P\bar{1}$ with $a=7.994(2)$ Å, $b=10.6530(15)$ Å, $c=12.384(3)$ Å, $\alpha=94.562(8)^\circ$, $\beta=100.008(10)^\circ$, $\gamma=92.323(10)^\circ$, $V=1033.7(4)$ Å³, $Z=2$, and $D_{calc}=1.148$ Mg/m³. Because of decomposition of the crystal during X-ray experiment, the value of R_1 and wR_2 are high. See supplementary material for details.
- [25] Dark red crystals were confirmed to be 3 by IR, X-ray. The crystal data are listed: crystal system (orthorhombic), space group ($Cmcm$), $a=11.466(9)$ Å, $b=14.400(9)$ Å, $c=16.832(11)$ Å, $V=2799.28(33)$ Å³, $Z=4$, similar to data in Table 1.
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