

# Syntheses of indenyl lanthanide derivatives and the molecular structures of $[(C_9H_7)_2PrCl(THF)]_2$ and $[(C_9H_7)_3La(THF)]$

Qi Shen <sup>a,\*</sup>, Minhua Qi <sup>b</sup>, Sheping Song <sup>b</sup>, Lili Zhang <sup>a</sup>, Yonghua Lin <sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China

<sup>b</sup> Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, China

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## Abstract

The reaction of anhydrous  $PrCl_3$  with  $Na(C_9H_7)$  in 1:2 mole ratio in THF gives  $[(C_9H_7)_2PrCl(THF)]_2$  **1**. **1** crystallized in monoclinic system, space group  $P2_1/c$  with  $a = 7.808(2)$ ,  $b = 17.796(6)$ ,  $c = 14.070(4)$  Å,  $\beta = 93.97(2)^\circ$ ,  $V = 1950.3(9)$  Å<sup>3</sup>,  $D_{calc} = 1.63$  g/cm<sup>3</sup> and  $Z = 2$ . Each Pr ion is surrounded by two indenyl, two Cl and one THF in a roughly trigonal bipyramid arrangement with average Pr–C(ring) and Pr–Cl distances of 2.81 and 2.84 Å. The reaction of  $LaCl_3$  with  $Na(C_9H_7)$  in 1:3 mole ratio gives  $(C_9H_7)_3La(THF)$  **2**, which crystallizes in the monoclinic space group  $P2_1/a$  with unit cell constants  $a = 21.871(8)$ ,  $b = 10.585(3)$ ,  $c = 23.652(7)$  Å,  $\beta = 114.62(2)^\circ$ ,  $V = 4977.9$  Å<sup>3</sup> and  $Z = 8$ . © 1997 Elsevier Science S.A.

**Keywords:** Lanthanum; Praseodymium; Indenyl; X-ray diffraction; Synthesis

## 1. Introduction

Indene is a versatile auxiliary ligand used in synthesis of organometallic compounds. The first triindenyl lanthanides  $(C_9H_7)_3Ln(THF)$  ( $Ln = La, Sm, Gd, Tb, Dy, Yb$ ; [1,2]) were reported to be synthesized from the reaction of  $LnCl_3$  with  $Na(C_9H_7)$  in 1:3 mole ratio in 1969. However, no corresponding crystal structure was obtained whereas an ion-pair complex  $[Na(THF)_6][Ln(\eta^5-C_9H_7)_3(\mu-Cl)Ln(\eta^5-C_9H_7)_3]$  was isolated and structurally characterized from this reaction [3,4]. By the reaction of  $LnCl_3$  with stoichiometric amounts of  $Mg(C_9H_7)_2$  [5] or  $K(C_9H_7)$  [6], an unsolvated  $(C_9H_7)_3Ln$  was prepared and the molecular structure of Sm complex was determined. Later, the crystal structures of  $(C_9H_7)_3Ln(THF)$  ( $Ln = Nd, Gd$ ), which were synthesized from the reaction of  $LnCl_3$ ,  $K(C_9H_7)$  and  $K_2(C_8H_8)$  as byproducts, were published [7].

Compared with triindenyllanthanide complexes, indenyllanthanide chlorides are poorly characterized until now, although indenyllanthanide chlorides are the useful precursors for further transformation. With bulky substituted indenyl, heptamethylindenyl, as a ligand,

heptamethylindenyl complexes of lanthanids,  $(C_9Me_7)_nLnCl_{3-n}$  ( $Ln = La, Er, Nd$ ;  $n = 1-3$ ), were conveniently synthesized [8]. However, for unsubstituted indenyl complex there is only  $(C_9H_7)GdCl_2(THF)_2$  reported in the literature [9]. We

Table 1  
Crystallographic data of complexes **1** and **2**

	<b>1</b>	<b>2</b>
Formula	$C_{44}H_{44}Cl_2Pr_2O_2$	$C_{11}H_{29}O_1La$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/a$
Cell constants		
$a$ , Å	7.808(2)	21.871(3)
$b$ , Å	17.796(6)	10.585(3)
$c$ , Å	14.070(4)	23.652(7)
$\beta$ , °	93.97(2)	114.62(2)
$V$ , Å <sup>3</sup>	1950.3(9)	4977.94
$Z$	2	8
$D_c$ , g/cm <sup>-3</sup>	1.63	1.48
scan range, $2\theta$	3–40	3–50
$\mu$ , cm <sup>-1</sup>	26.31	17.59
$F(000)$	952	2240
Reflections	2092	7885
Reflections for $I \geq 3\sigma(I)$	1069	6460
$R$	0.045	0.053
$R_w$	0.039	0.056

\* Corresponding author.

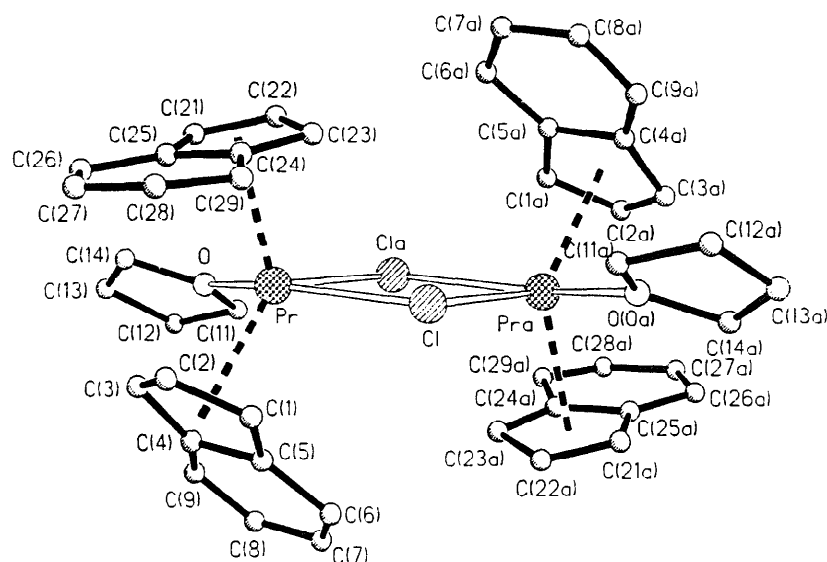


Fig. 1. The molecule structure of complex 1.

have recently synthesized THF-solvated diindenyl praseodymium chloride  $[(C_9H_7)_2PrCl(THF)]_2$  **1** and determined its molecular structure. To our knowledge, this is the first structure for this kind of complex. In this paper we also like to report the synthesis and molecular structure of  $(C_9H_7)_3La$  THF **2**.

## 2. Experimental

All manipulations were conducted under Ar using standard Schlenk techniques. THF was distilled from solutions of sodium benzophenone ketyl. Indene (Fluka)

was dried over 4A molecular sieves and was distilled before use.  $Na(C_9H_7)$  was prepared from Na and indene in THF. Anhydrous  $LnCl_3$  ( $Ln = Pr, La$ ) was prepared by published method [10].  $C_6D_6$  was dried over Na and was vacuum-distilled.  $^1H$  NMR spectra were obtained on Varian 400-MHz NMR spectrometer. IR were recorded on a ALPHA Fourier infrared spectrometer as KBr pellet.

### 2.1. Preparation of complex 1

Into the reaction flask containing  $PrCl_3$  (1.94 g, 7.6 mmol) and 40 ml THF was added 8.90 ml (1.74 M) of

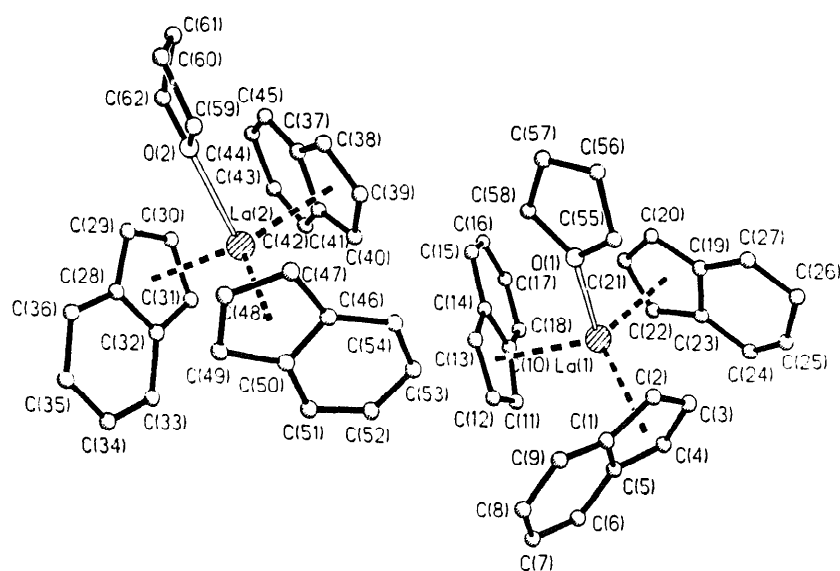


Fig. 2. The molecular structure of complex 2.

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent temperature factors ( $\times 10^3 \text{ \AA}^2$ ) for non-hydrogen atoms of complex 1

Atom	X	Y	Z	$U_{eq}$
Pr	749(2)	5924(1)	6087(1)	33(1)
Cl	1662(6)	5216(3)	4359(3)	50(2)
C(1)	4291(21)	5758(10)	6179(14)	57(8)
C(2)	4024(21)	6431(11)	6737(16)	53(8)
C(3)	3173(25)	6287(10)	7547(13)	62(8)
C(4)	3083(19)	5475(10)	7667(11)	49(7)
C(5)	3762(22)	5144(11)	6813(13)	49(8)
C(6)	3946(24)	4331(10)	6643(14)	61(9)
C(7)	3335(25)	3889(11)	7357(16)	87(10)
C(8)	2697(23)	4215(12)	8181(16)	89(10)
C(9)	2551(22)	4991(12)	8297(13)	70(8)
O	-981(13)	5884(7)	7548(7)	56(4)
C(11)	-1887(23)	5239(11)	7873(11)	61(8)
C(12)	-2243(26)	5372(11)	8957(14)	72(9)
C(13)	-1683(39)	6157(12)	9062(17)	131(15)
C(14)	-1158(34)	6543(12)	8215(16)	106(12)
C(21)	-1185(32)	7259(11)	6051(14)	65(9)
C(22)	-1812(23)	6854(10)	5264(15)	62(8)
C(23)	-455(25)	6795(9)	4601(13)	61(8)
C(24)	851(21)	7250(10)	5007(12)	49(7)
C(25)	379(24)	7529(10)	5933(14)	54(8)
C(26)	1569(37)	8066(12)	6450(17)	100(12)
C(27)	3110(33)	8241(13)	6006(25)	154(17)
C(28)	3492(29)	7932(13)	5087(18)	134(13)
C(29)	2517(29)	7396(12)	4602(17)	122(12)

$\text{Na}(\text{C}_9\text{H}_7)$ . The mixture was stirred for 3 days at about  $70^\circ\text{C}$ . After centrifugation to remove NaCl precipitate, the solution was concentrated to 10 ml and crystallized at room temperature. The yellow-green crystals of **1** were obtained (2.50 g, 68.8%). Elemental analysis: Found: Pr, 29.40; C, 54.24; H, 4.60; Cl, 7.57%. Calcd. for  $\text{C}_{44}\text{H}_{44}\text{Cl}_2\text{Pr}_2\text{O}_2$ , Pr, 29.45; C, 55.18; H, 4.60; Cl, 7.42. IR( $\text{cm}^{-1}$ ): 3060(m), 3030(m), 2965(s), 2862(s), 1675(s), 1602(s), 1450(s), 1390(m), 1358(m), 1060(s), 1038(m), 1010(m), 940(m), 910(w), 855(w), 760(s), 710(s), 690(w).

## 2.2. Preparation of complex 2

$\text{LaCl}_3$  (1.2 g, 4.89 mmol) was placed in a Schlenk flask. THF solution of  $\text{Na}(\text{C}_9\text{H}_7)$  (19 ml, 14.67 mmol) was added. After stirring for 24 h at room temperature, the mixture was centrifuged to remove NaCl and the solution was concentrated until to slightly turbid, then placed for crystallization at  $-10^\circ\text{C}$ . Very pale crystals were isolated (1.95 g, 71.7%) m.p.  $185\text{--}190^\circ\text{C}$ . Elemental analysis, Found: C, 66.28; H, 5.15; La, 24.54%. Calcd. for  $\text{C}_{31}\text{H}_{29}\text{OLa}$  C, 66.91; H, 5.25; La, 24.98%. IR( $\text{cm}^{-1}$ ): 3061(m), 2886(m), 1677(m), 1602(m), 1457(m), 1392(m), 1292(m), 1069(m), 1016(m), 914(m), 861(m), 766(s), 718(m), 694(m), 550(m).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )ppm: 3.18(t,1), 5.91(d,2), 7.15(d,2), 7.35(d,2)(indenyl); 1.29, 3.29 (THF).

## 3. Determination of crystal structure

### 3.1. Complex 1

A yellow green crystal with dimensions of  $0.28 \times 0.34 \times 0.41$  mm was sealed in a thin walled lithium glass capillary. The intensity data were collected on a Nicolet R3M/E four circle diffractometer using graphite monochromated  $\text{MoK}\alpha$  radiation in the W-2  $\theta$  scan mode with  $3^\circ \leq 2\theta \leq 40^\circ$ , 2092 reflections were collected, 1069 reflections with  $I \geq 3\sigma(I)$  were considered observed. The intensities were corrected for LP and absorption factors. A summary of data collection parameters is given in Table 1.

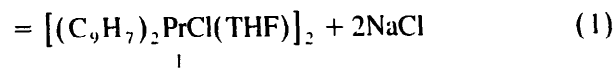
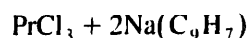
All calculations were carried out on an Eclipse S/140 micro computer with the SHELXTL computer program system. The position of the heavy atom was found from patterson methods. All the non-hydrogen atoms were revealed by successive Fourier and difference Fourier syntheses. The coordinates of hydrogen atoms were determined according to theoretical modes. Further refinement led to final convergence of  $R = 0.045$  and  $R_w = 0.039$ .

### 3.2. Complex 2

A very pale crystal with dimensions of  $0.26 \times 0.36 \times 0.34$  mm was sealed in a thin-walled lithium glass capillary. 7885 reflections with  $3^\circ \leq 2\theta \leq 52^\circ$  in the W-2  $\theta$  scan mode were collected, 6460 reflections with  $I \geq 3\sigma(I)$  were considered observed. The intensity data collection and structure resolution are as same as mentioned above. A summary of data collection parameters is given in Table 1. Further refinement led to final convergence at  $R = 0.053$ ,  $R_w = 0.056$ .

## 4. Results and discussion

$\text{PrCl}_3$  reacted with  $\text{Na}(\text{C}_9\text{H}_7)$  in 1:2 mole ratio giving complex **1** in good yields. Attempt to prepare the analogous complexes with Nd, La, and Ce failed.



$\text{LaCl}_3$  reacted with 3 equivalents of  $\text{Na}(\text{C}_9\text{H}_7)$  to form complex **2** as very pale crystals in good yields, although ion-pair complexes formulated as  $[\text{Na}(\text{THF})_6][\text{Ln}(\text{C}_9\text{H}_7)_3\text{ClLn}(\text{C}_9\text{H}_7)_3]$  are often isolated by the same reaction [3,4].

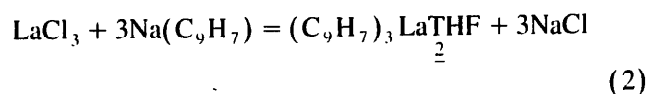


Table 3  
Atomic coordinates ( $\times 10^4$ ) and equivalent temperature factors ( $\times 10^3 \text{Å}^2$ ) for non-hydrogen atoms of complex **2**

Atom	X	Y	Z	$U_{\text{awake}}^a$
La(1)	3825(1)	7001(1)	6410(1)	33(1)
La(2)	2489(1)	1665(1)	8520(1)	38(1)
O(1)	3812(3)	4557(4)	6382(2)	56(2)
O(2)	2617(3)	−738(5)	8698(3)	71(3)
C(1)	2349(3)	7064(6)	5512(3)	39(3)
C(2)	2764(6)	6604(6)	5230(3)	43(3)
C(3)	3138(3)	7598(7)	5169(3)	42(3)
C(4)	3036(3)	8670(7)	5462(3)	44(3)
C(5)	2520(3)	8356(6)	5659(3)	41(3)
C(6)	2134(4)	9087(9)	5891(4)	68(4)
C(7)	1595(4)	8517(11)	5964(4)	78(4)
C(8)	1457(4)	7225(10)	5830(4)	72(4)
C(9)	1820(4)	6499(8)	5608(3)	57(3)
C(10)	4221(5)	8041(7)	7685(4)	59(4)
C(11)	3557(4)	8462(8)	7274(4)	60(4)
C(12)	3125(4)	7441(9)	7139(4)	68(4)
C(13)	3500(5)	6365(9)	7421(4)	64(4)
C(14)	4180(5)	6731(8)	7774(4)	58(4)
C(15)	4766(5)	6053(9)	8183(4)	75(4)
C(16)	5335(5)	6756(10)	8485(4)	85(5)
C(17)	5378(6)	8035(10)	8412(4)	90(5)
C(18)	4834(5)	8689(9)	8015(4)	74(4)
C(19)	4846(4)	6841(7)	5886(4)	54(4)
C(20)	5093(4)	6279(8)	6475(4)	55(3)
C(21)	5209(4)	7224(10)	6916(4)	70(4)
C(22)	4991(4)	8389(9)	6598(4)	66(4)
C(23)	4778(4)	8172(7)	5950(4)	54(3)
C(24)	4598(4)	8963(9)	5427(4)	66(4)
C(25)	4489(4)	8445(9)	4976(4)	73(4)
C(26)	4525(4)	7137(10)	4798(4)	75(4)
C(27)	4677(4)	6320(9)	5291(4)	70(4)
C(28)	1901(4)	1815(7)	9464(4)	50(3)
C(29)	2583(4)	1364(7)	9752(3)	54(3)
C(30)	3006(4)	2370(7)	9770(3)	52(3)
C(31)	2613(4)	3408(7)	9464(4)	54(4)
C(32)	1934(4)	3087(7)	9295(4)	52(3)
C(33)	1329(5)	3804(9)	9049(5)	77(5)
C(34)	740(5)	3245(10)	8980(5)	96(6)
C(35)	717(5)	1990(11)	9145(5)	91(6)
C(36)	1294(5)	1248(9)	9368(4)	72(4)
C(37)	4003(4)	1683(7)	8964(4)	49(3)
C(38)	3693(4)	1006(8)	8389(4)	62(4)
C(39)	3350(5)	1824(9)	7920(4)	76(5)
C(40)	3369(5)	3034(8)	8175(4)	73(5)
C(41)	3799(4)	2978(7)	8823(4)	50(3)
C(42)	4078(4)	3906(8)	9299(5)	75(5)
C(43)	4500(4)	3501(9)	9860(5)	77(5)
C(44)	4691(4)	2214(11)	10010(4)	83(5)
C(45)	4441(4)	1368(9)	9553(4)	71(4)
C(46)	1662(4)	2096(9)	7177(3)	70(4)
C(47)	1608(6)	785(10)	7280(4)	94(5)
C(48)	1258(5)	741(11)	7659(4)	98(5)
C(49)	1102(5)	1942(10)	7819(4)	80(4)
C(50)	1370(4)	2792(9)	7501(4)	71(4)
C(51)	1361(6)	4106(11)	7486(5)	100(6)
C(52)	1627(7)	4692(12)	7129(5)	123(7)
C(53)	1894(6)	4024(12)	6774(5)	113(6)
C(54)	1919(6)	2770(12)	6799(4)	97(5)
C(55)	3660(8)	3811(11)	5841(5)	116(7)
C(56)	4018(11)	2578(12)	6078(7)	211(13)
C(57)	4230(12)	2521(11)	6706(7)	169(12)
C(58)	4153(7)	3795(10)	6951(5)	103(6)

Table 3 (continued)

Atom	X	Y	Z	$U_{\text{awake}}^a$
C(59)	2293(7)	−1748(12)	8234(8)	159(10)
C(60)	2628(9)	−2905(10)	8581(7)	158(12)
C(61)	3274(8)	−2491(14)	9001(7)	136(9)
C(62)	3087(10)	−1279(12)	9214(7)	156(10)

$^a U_{\text{awake}}$ : Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

The two complexes are very sensitive to air and moisture. They are soluble in THF but not in aromatic solvents. The proton NMR spectrum of complex **2** in  $C_6D_6$  exhibits the two resonances, each of relative intensity 2, at 7.15, 7.35(ppm) assigned to the protons of the six-membered ring and two other resonances at 5.91 (relative intensity of 2) and at 3.18(ppm) (relative intensity of 1) for the protons of the five membered ring [1] and at 3.29 and at 1.29(ppm) for the protons of THF.

According to no crystal structures for the above two complexes published, we have undertaken a single X-ray structure determination. The molecular structures of complex **1** and complex **2** are shown in Figs. 1 and 2, respectively. The atomic coordinates, selected bond angles and bond distances are listed in Tables 2–5, respectively.

Complex **1** is a dimer connected by two asymmetric chlorine bridges. The central metal Pr is coordinated by two indenyl groups, two bridged chlorines and one THF to form a trigonal bipyramidal geometry. The coordination number of Pr is nine. Obviously, the coordination of THF to metal ion reflects the demand of the bigger lanthanide ion Pr to adopt higher coordination numbers.

Table 4  
Selected bond lengths (Å) and bond angles ( $^\circ$ ) of complex **1**

Pr–Cl	2.872(5)	Pr–Cl <sub>a</sub>	2.808(5)
Pr–C(1)	2.775(16)	Pr–C(21)	2.814(22)
Pr–C(2)	2.8056(17)	Pr–C(22)	2.786(18)
Pr–C(3)	2.772(18)	Pr–C(23)	2.719(17)
Pr–C(4)	2.888(15)	Pr–C(24)	2.811(18)
Pr–C(5)	2.858(18)	Pr–C(25)	2.878(18)
Pr–O	2.538(10)	Pr–O	2.808(5)
C(1)–C(2)	1.454(27)	C(21)–C(22)	1.382(28)
C(1)–C(5)	1.486(27)	C(21)–C(25)	1.334(31)
C(2)–C(3)	1.384(29)	C(22)–C(23)	1.463(28)
C(3)–C(4)	1.457(26)	C(23)–C(24)	1.392(25)
C(4)–C(5)	1.469(25)	C(24)–C(25)	1.466(26)
Pr–C(ring 1)ave.	2.810	Pr–C(ring 2)ave.	2.802
Pr–Cent(1)	2.534(2)	Pr–Cent(2)	2.533(2)
Cl–Pr–Cl <sub>a</sub>	72.3(2)	Cl–Pr–O	148.3(3)
Cl <sub>a</sub> –Pr–O	77.0(3)	Cent(1)–Pr–Cent(2)	123.6(2)
Cent(1)–Pr–Cl	97.2(2)	Cent(1)–Pr–Cl <sub>a</sub>	128.7(3)
Cent(2)–Pr–Cl	96.2(4)	Cent(1)–Pr–O	95.9(2)
Cent(2)–Pr–Cl <sub>a</sub>	107.2(2)	Cent(2)–Pr–O	98.3(3)
Pr–Cl–Pr <sub>a</sub>	107.7(2)		

Cent(1), (2) indicates the centrals of the cyclopentadienyl ring(1) formed by C(1), C(2), C(3), C(4), C(5) and ring(2) by C(21), C(22), C(23), C(24), C(25), respectively.

Table 5  
Selected bond lengths and bond angles of complex 2

La(1)–C(1)	3.036(6)	La(1)–C(2)	2.820(6)
La(1)–C(3)	2.756(6)	La(1)–C(4)	2.812(6)
La(1)–C(5)	3.021(6)	La(1)–C(10)	2.980(8)
La(1)–C(11)	2.812(10)	La(1)–C(17)	2.782(11)
La(1)–C(13)	2.845(11)	La(1)–C(14)	3.000(8)
La(1)–C(19)	2.975(10)	La(1)–C(20)	2.820(8)
La(1)–C(21)	2.763(8)	La(1)–C(22)	2.815(9)
La(1)–C(23)	2.993(10)	La(2)–C(28)	3.010(10)
La(2)–C(29)	2.854(9)	La(2)–C(30)	2.792(7)
La(2)–C(31)	2.822(8)	La(2)–C(32)	2.995(10)
La(2)–C(37)	3.028(8)	La(2)–C(38)	2.862(10)
La(2)–C(39)	2.794(13)	La(2)–C(40)	2.788(12)
La(2)–C(41)	2.990(8)	La(2)–C(46)	2.964(7)
La(2)–C(47)	2.910(8)	La(2)–C(48)	2.789(9)
La(2)–C(49)	2.801(9)	La(2)–C(50)	2.882(8)
La(1)–O(1)	2.587(5)	La(2)–O(2)	2.574(5)
La–C(average)	2.889	Cent(1-1)–La(1)	2.632
Cent(1-2)–La(1)	2.624	Cent(1-3)–La(1)	2.611
Cent(2-1)–La(2)	2.634	Cent(2-2)–La(2)	2.634
Cent(2-3)–La(2)	2.606	Cent(1-1)–La(1)–Cent(1-2)	114.53
Cent(1-1)–La(1)–Cent(1-3)	115.50	Cent(1-2)–La(1)–Cent(1-3)	118.99
Cent(2-1)–La(2)–Cent(2-2)	115.92	Cent(2-1)–La(2)–Cent(2-3)	118.56
Cent(2-2)–La(2)–Cent(2-3)	117.92		

Cent(1-1), (1-2), (1-3) and Cent(2-1), (2-2), (2-3) represents the centrals of ring 1 [C(1)–C(5); C(28)–C(31)], 2 [C(10)–C(14); C(37)–C(41)], 3 [C(19)–C(23); C(46)–C(50)] in molecule *a* and in molecule *b* respectively.

The tendency is also found in the structures of biscyclopentadienyl lanthanide chlorides [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl(THF)]<sub>2</sub> [11] and [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ErCl(THF)]<sub>2</sub> [12]. The solid state structure of **1** strongly resembles those of the two above complexes.

This is the first structure of diindenyl lanthanide chloride, therefore, the bond parameters can only be compared with those of triindenyl complexes or of the biscyclopentadienyl lanthanide chloride resemble in solid state structure. Pr–C bond distances are in the range of 2.719(17) to 2.878(18) Å and the average bond length is 2.81 Å, comparable with 2.75 Å in nine-coordinated complex (C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>Sm [5], if the difference in ionic radius between Pr and Sm is taken account [13]. The value is somewhat longer than 2.75 Å in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl(THF)]<sub>2</sub> [11]. This might be caused by the difference in bulkness between indenyl and cyclopentadienyl. Pr–Cl distances are 2.872(5) and 2.808(5) Å which are comparable with 2.787(4) and 2.861(4) Å in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl(THF)]<sub>2</sub> when the ionic radius difference is considered. The bond angles of

Pr–Cl–Pr(a) 107.7(2) and Cl–Pr–Cl(a) 72.3(2)° are very close to 106.3(1) and 73.7(1)° respectively in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl(THF)]<sub>2</sub>. The angle Cent(1)–Pr–Cent(2) 123.6(2)° is much bigger than 57.4° in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>NdCl(THF)]<sub>2</sub>. This is reasonable due to the steric congestion by two indenyl groups.

Single crystal X-ray diffraction analysis showed that **2** has a distorted tetrahedron geometry. Three indenyl groups (in an η<sup>5</sup>-fashion) and one THF coordinated to the central metal La whose coordination number is 10. The analogous coordinated geometry has been found in the structures of the related complexes (C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>UCl [14], (C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>CePy [15] and (C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>LnTHF (Ln = Nd, Gd) [7]. In the crystal packing there are two independent molecules of **2** (*a* and *b*, see Fig. 2) which have similar structure. La–C distance ranges from 2.756(6) to 3.036(6) Å, the average La–C distance is 2.889 Å. In order to compare with other triindenyl complexes, Table 6 listed Ln–Cave. values of all the triindenyl complexes of lanthanide published. It is obvious that the bond length of Ln–C decreases regularly according to La > Ce > Nd > Sm > Gd sequence which agrees well with the result expected by lanthanide contraction.

Table 6  
Ln–Cave. length of triindenyl lanthanide complexes

Complex	Ln–Cave A	Reference
(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> LaTHF	2.889	this work
(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> CePy	2.851	[13]
(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> NdTHF	2.812	[7]
(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> GdTHF	2.795	[7]
[Na(THF) <sub>6</sub> ] <sub>2</sub> [(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> Sm] <sub>2</sub> Cl	2.795	[3]

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