

Chiral lanthanocene complexes with an ether-functionalized indene ligand: synthesis and structure of bis{1-(2-methoxyethyl)indenyl}lanthanocene chlorides

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Abstract

Chiral lanthanocene chlorides $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{LnCl}$ ($\text{Ln} = \text{Y}$ **1**, La **2**, Nd **3**, Gd **4**, Ho **5** and Lu **6**) with an ether-functionalized indenyl ligand were synthesized by the reaction of 1-(2-methoxyethylindenyl) potassium (in situ) with corresponding anhydrous lanthanide chlorides in THF. The X-ray crystal structures of four such complexes were determined and these indicated that they were unsolvated monomeric complexes with a *trans* arrangement of both the sidearms and indenyl rings in the solid state. This configuration also predominated in THF solution, as evidenced by NMR spectra of the diamagnetic complexes **1**, **2** and **6**, although some minor species of **1** and **2** did form upon dissolution. © 1998 Elsevier Science S.A. All rights reserved.

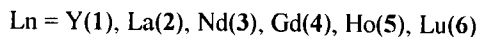
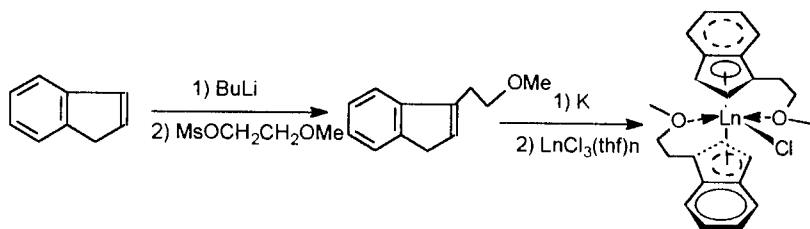
Keywords: Chiral lanthanocene; Indenyl ligand; Synthesis; Crystal structure; Lanthanide chlorides; Yttrium

1. Introduction

The chemistry of chiral lanthanocenes [1–4] has been very limited, especially when compared with that of the neighboring Group IV metallocenes [5–7], probably due to difficulties encountered in preparation and purification of them by routine physical or chemical methods. However, rationally designed ligands should facilitate the exploration of the synthesis, structure and reactivity of chiral lanthanocene complexes. We have focused on the chemistry of lanthanocenes with ether-functionalized cyclopentadienyl (Cp) ligands and established that these type of ether-containing Cp derivatives were broadly applicable to organolanthanide complexes [8–11]. More recently, we have turned to organolanthanide complexes with a well-defined coordination environment, using 2-methoxyethylcyclopentadienyl as the ligand which enabled the isolation of the most

important precursor of all organolanthanide complexes i.e. the metallocene chloride [12,13]. Although the intramolecular coordinated sidearms showed certain flexibility responding to the change of coordination environment, for instance, to satisfy the more saturated coordination requirement some complexes formed dimers [14] or even at the cost of breaking the intramolecular coordination bond [15,16], the joint effect of the coordination geometry of central metals and steric factors led to the *trans* arrangement of the sidearms in the majority of cases. We envisioned that a properly-enhanced, sterically-demanding ligand could further suppress the flexibility to afford complexes with a defined structure, which in turn would facilitate the formation and isolation, stereoselectively or even exclusively, of some diastereoisomers of chiral lanthanocene complexes. In this article, we wish to report the synthesis and structure of several representative chiral bis{1-(2-methoxyethyl)indenyl}lanthanide chlorides. The selection of this sterically-demanding and chelating

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Scheme 1.

ether-functionalized indenyl ligand was premised on a number of considerations: the easy preparation of the ligand, larger but planar shape of the indenyl ring, which was expected to serve with a dual purpose—satisfying the requirement of steric saturation of the central metals and yet leaving the easily accessible central metals relative to some bulky substituted Cp, such as trimethylsilyl or *tert*-butyl substituents, etc.—the oxophilic nature of lanthanide ions, the well-documented geometry (bend metallocene) of lanthanocenes and even η^3 - η^5 slippage of indenyl moieties in indenyl complexes of transition metals [17]. During the course of this work, Molander et. al. [18] reported the divalent Sm, Yb complexes with similar but optically-pure Cp derivatives, which also adopt a *trans* arrangement of ligands in the solid state.

2. Results and discussion

2.1. Synthesis

The indene derivative $\text{MeOCH}_2\text{CH}_2\text{C}_9\text{H}_7$ could be prepared directly from the reaction of methanesulfonate with indenyllithium at -50°C with a 89% yield. Deprotonation of the indene derivative with excess potassium metal suspended in THF provided a clear, slightly-yellow solution. Reaction of the solution with a stoichiometric amount of anhydrous lanthanide chlorides ($\text{Ln} = \text{Y}, \text{La}, \text{Nd}, \text{Gd}, \text{Ho}$ and Lu) in THF, followed by separation of the precipitate KCl , concentration of the resulted solution and allowing it to stand for several days, provided corresponding complexes as crystals in moderate yields (Scheme 1). These complexes are readily dissolved in THF, but are just sparingly soluble in toluene at room temperature (r.t.). All complexes remain air and moisture sensitive, whether in solid or solution phase.

2.2. Spectroscopic properties

In the cases of diamagnetic complexes **1**, **2** and **6**, the ^1H - and ^{13}C -NMR spectra were recorded in THF-d_8 .

The ^1H -NMR spectra indicated that when dissolved in THF some isomerizations occurred varying with the radial size of the central metal ions. For complex **1**, one species predominates the ^1H -NMR spectrum with an approximate ratio of 25:1 for the major and minor isomers, determined from integration of the corresponding resonances of protons on the five-membered portion of the indenyl rings. Examining the possible structural forms **I–IV** (Fig. 1), one finds that forms **II** and **III** are geometrically and sterically prohibited since the two coordinated sidearms are in a *cis* arrangement, and the most favorable form is **I** with a *trans* orientation of both the indene rings and sidearms. It is clear from the NMR spectra that the major isomer assumes a symmetrical structure in THF solution. The assignments were made on the basis of chemical shifts, splitting patterns and NOE's (Fig. 2). Typically, arising from restricted rotation, the methylene resonances show splitting patterns due to the diastereotopic protons. The downfield shift of protons of OCH_3 was attributed to the coordination of the ether fragments to the metal. The protons H^2 appear as a broad singlet at 5.35 ppm, instead of a doublet or d-d multiplet, presumably due to the twinkling effect of the five-membered segments of the ligand [19]. The crosspeaks of H^3 - OCH_3 , H^3 - H^x , H^4 - OCH_3 , H^3 - H^7 (on different rings) in NOESY spectrum implied that the major species adopted form **I**, i.e. the *rac* isomer with a *trans* ring and sidearm orientation. Unfortunately, we could not identify the structure of the minor species with these experiments. However, we tentatively assigned it as form **IV** in view of the coordination geometry and steric factors in this molecule.

For complex **6**, the ^1H - and ^{13}C -NMR spectra showed one set of signals which were similar to that of the major species of **1** within the experimental error (ca. 2%) implying the higher stereoselectivity.

^1H -NMR of complex **2** was markedly different from those of **1** and **6**, with four sets of clearly resolved resonances appearing between 6.60 and 4.55 ppm, with an approximate integral intensity ratio of 5:2:1:1, which were assigned to the five-membered ring protons of the indene moieties. Among them, the dominant one (55%)

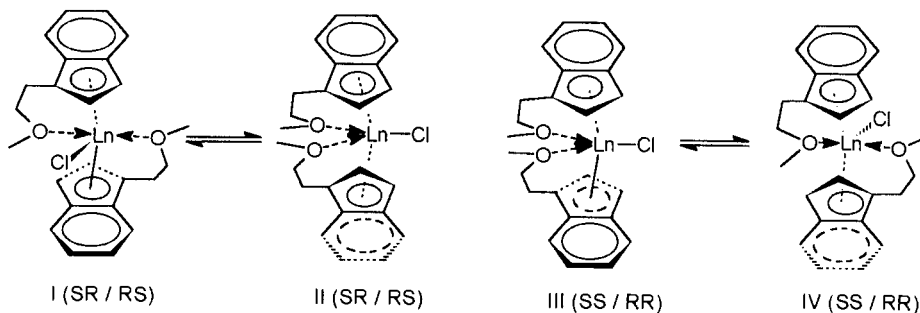


Fig. 1. Possible structure forms of the bis{1-(2-methoxyethyl)indenyl}lanthanide chlorides.

showed a pattern similar to those of **6** and the major species of **1**, except with more severe peak broadening (*vide supra*), so we proposed that they had similar structures. We could not assign the others present ambiguously. Because of the larger radius size of lanthanum(III) ion other structural forms could not be excluded. Although the ^{13}C -NMR spectrum of **2** was rather complicated due to the isomers, at least three groups of four resonances clearly found at 80–72, 64–58, and 38–28 ppm (see Section 4) indicated that four isomers were probably present in the THF solution, which differed greatly from the corresponding heavy lanthanide complexes **1** and **6**.

2.3. Molecular structure

X-ray quality crystals were grown from THF solution at ca. 0°C . All complexes are *rac*-isomers and have very similar structures in solid state. Complex **1** crystallizes in a triclinic system with a $P\bar{1}$ space group and with two similar but independent molecules in the unit cell, while **2**, **3** and **4** all crystallize in an orthorhombic system with $Pna2_1$ (for **2**) and $Pbca$ (**3** and **4**) space groups and with a discrete molecule in the unit cell. Since the four crystal structures are essentially identical, the representative ORTEP drawing of **1** is shown in Fig. 3. The coordination geometry is best described as distorted trigonal bipyramidal if an indenyl ring is regarded as occupying a single polyhedral vertex where the basal plane is defined by O(1), O(2) and Cl. All compounds are unsolvated 9-coordinate monomeric

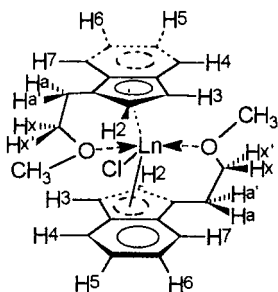


Fig. 2. The numbering scheme for NMR.

complexes in solid state, although they crystallize from the strongly coordinating solvent THF. It is worth noting that **2** has the monomeric structure considering its Cp analogue is a dimer in solid state [5,19]. The approximate planar indene rings are η^5 -bonded to the central metals and both the indene rings and sidearms adopt a *trans* configuration as expected, presumably governed by the coordination geometry of the central metals together with steric factors, implying enhanced regularity relative to the Cp analogue. The bond lengths between the metal ions and ligands within these complexes are unexceptional. A comparison of the bond distances within these series complexes showed the bond distances M–C, M–Cl, and M–O (Table 2), on going from **1** (Y) to **2** (La), followed a trend, this trend being consistent with that of ionic radii, indicating the difference of bonding nature between these complexes, although almost negligible, attributed to the lack of participation of their f orbitals. The slip parameter $\Delta_{\text{M-C}}$ [20,21], which has been developed to quantify the η^5 - η^3 slippage within indenyl metal complexes, ranging from 0.151 (0.130) Å for the indene rings of **1** (Y) to 0.05 (0.05) Å for **2** (La), fell within the established range for a fundamentally-ionic η^5 -bonding between metals and indenyl ligands. However, the slip distortion gradually increases as the radial size of the metals also increases. Although triindenyllanthanide complexes were first synthesized about 30 years ago [22], the structurally-characterized indenyl complexes were relatively limited [23–25]. Gross comparison of the slip parameter $\Delta_{\text{M-C}}$ for unsymmetric *ansa* complexes of $\text{O}(\text{CH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{LnCl}(\text{THF})$ ($\text{Ln} = \text{Nd}$ 0.103 (0.043), Gd 0.126 (0.038), Ho 0.147 (0.050) Å) [25], triindenyllanthanide complexes $(\text{C}_9\text{H}_7)_3\text{Ln}(\text{base})$ ($\text{Ln} = \text{Ce}$ 0.169, Nd 0.219, Gd 0.269 Å, base = pyrroline, THF) [26,27] and $[(\text{Na}(\text{THF})_6)(\eta^5\text{-C}_9\text{H}_7)_3\text{Ln}(\mu\text{-Cl})\text{Ln}(\eta^5\text{-C}_9\text{H}_7)_3]$ ($\text{Ln} = \text{Pr}$ 0.139, Nd 0.157, Sm 0.159 Å) [28–30] displayed the same trend: the more crowded the coordination environment, the more distorted the η^5 -indenyl rings. Besides the slip parameter $\Delta_{\text{M-C}}$, the intramolecular Ln–O bonding is also sensitive to the steric crowding of the coordination environment of the central metal ions. For this particular type of ether-

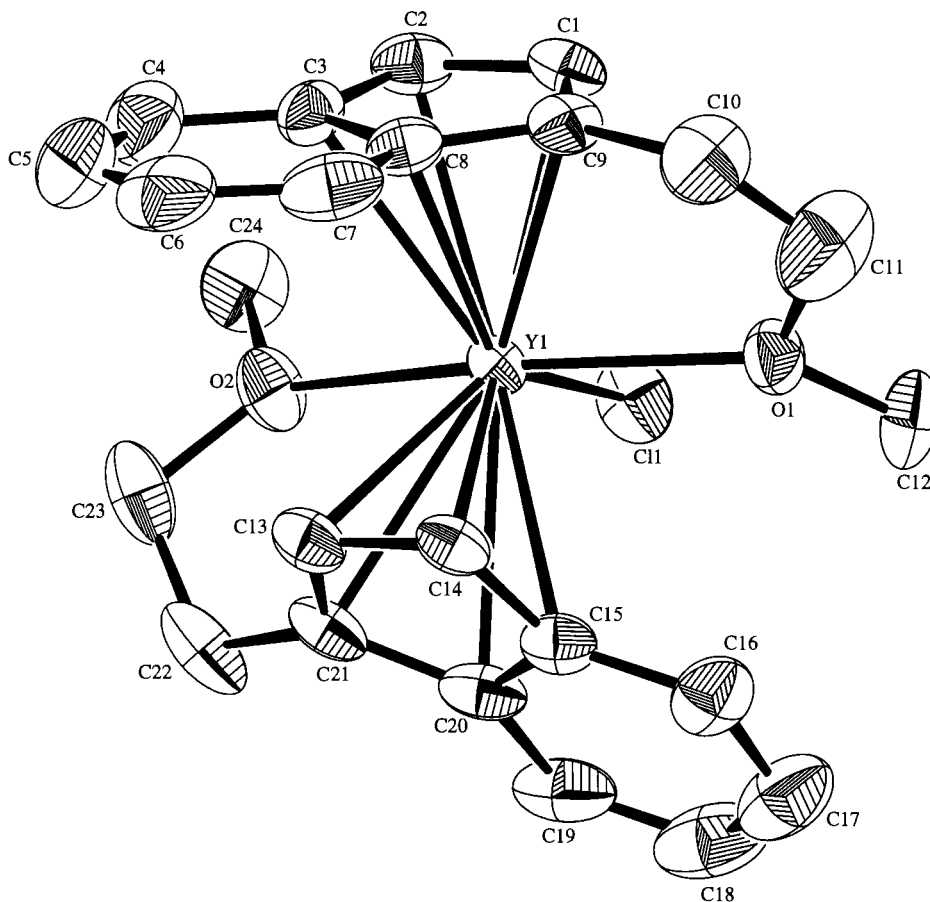


Fig. 3. An ORTEP drawing of 1 showing the numbering scheme employed (one of two independent molecules in the unit cell).

functionalized indenyl lanthanide complex, among the structure parameters, the O–Ln–O angles are informative with values increasing gradually in the following order Y (159.0) < Gd (160.3) < Nd (162.1) < La (167.1°) [31].

IR spectra of all complexes showed similar pattern (see Section 4) with characteristic bands of lanthanide complexes appearing at ca. 3060, 1435, 1290 and 1015 cm^{-1} (for η^5 -indenyl moieties), 3030, 1600 and 750 cm^{-1} (for aromatic groups) and 250 cm^{-1} for the Ln–C bond and, hence, no detailed discussion was given [32–35]. Although these complexes are less thermally stable relative to their Cp analogues, the EI-MS of these complexes, somewhat surprisingly, displayed $[\text{M}]^+$, $[\text{M}-\text{Cl}]^+$, and $[\text{M}-\text{L}]^+$ fragments, with a high intensity in some cases.

3. Conclusion

Due to the so-called lanthanide contraction effect and overwhelming ionic nature of lanthanide ions, few ligands could afford organolanthanide chlorides with a unit structure through the group elements except for pentamethylcyclopentadiene. In this paper, we reported

the synthesis and characterization of several representative chiral organolanthanide chlorides, including the lanthanum and lutetium complexes as favorable *rac*-isomers using an ether-functionalized indenyl ligand. The remaining chloro ligand in these complexes promises a wide range of derivatives, such as those containing Ln–H, Ln–N and Ln–C, etc. It is hoped that the structural feature could be maintained in derivatives to facilitate a systematical comparison but further investigations are needed.

4. Experimental section

4.1. General procedures

All operations involving organometallics were carried out under an inert atmosphere of argon using standard Schlenk techniques. THF was distilled under argon from sodium benzophenone ketyl prior to use. Methoxyethylmethanesulfonate [36] and anhydrous lanthanide chlorides [37] were prepared according to the procedures in literature and the reactants *n*-butyllithium and indene were purchased from Aldrich, the latter being distilled prior to use. THF- d_8 was degassed

Table 1
Details of the crystal data and refinements for complexes 1–4

Complex	1	2	3	4
Formula	(C ₂₄ H ₂₆ O ₂ ClY) ₂	C ₂₄ H ₂₆ O ₂ ClLa	C ₂₄ H ₂₆ O ₂ ClNd	C ₂₄ H ₂₆ O ₂ ClGd
FW	941.65	520.83	526.16	539.17
Crystal dimensions (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.30 × 0.40	0.20 × 0.30 × 0.30
Color	Colorless	Colorless	Green	Yellow
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (no.)	<i>P</i> $\bar{1}$ (2)	<i>Pna</i> 2 ₁ (33)	<i>Pbca</i> (61)	<i>Pbca</i> (61)
<i>a</i> (Å)	10.531(4)	16.209(4)	18.236(8)	18.224(3)
<i>b</i> (Å)	20.150(6)	11.768(6)	16.582(7)	16.471(3)
<i>c</i> (Å)	10.285(2)	11.534(5)	14.466(4)	14.416(3)
α (°)	97.82(2)	90	90	90
β (°)	94.94(3)	90	90	90
γ (°)	91.57(3)	90	90	90
<i>V</i> (Å ³)	2152(1)	2199(2)	4374(4)	4326(2)
<i>Z</i>	2	4	8	8
<i>D</i> _{calc.} (g cm ⁻³)	1.453	1.572	1.598	1.655
<i>F</i> (000)	968.00	1040.00	2104.00	2136.00
μ (Mo–K α) (cm ⁻¹)	28.53	20.71	25.10	32.13
2 θ _{max} (°)	45.0	50.0	50.0	50.0
Reflections collected	4983	3759	3570	3711
Independent reflections	4619	1953		
Observed data	3609	1558	2492	2476
Parameters	506	253	254	253
GOF	1.71	1.69	1.87	1.58
<i>R</i> , <i>R</i> _w ^a	0.037, 0.048	0.028, 0.036	0.033, 0.046	0.024, 0.036
$\Delta\rho$ _{max/min}	0.54/–0.55	0.35/–0.37	0.77 / –1.24	0.48/–0.47

$$^a R = \sum \|F_o\| - |F_c| / \sum \|F_o\|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{0.5}.$$

and dried over a Na/K alloy and all chemical shifts were reported in ppm relative to the residues of the deuterated solvent. IR spectra were recorded using a Perkin-Elmer 983, with Nujol and Fluorolube mulls prepared in an argon-filled glove-box between disc-shaped CsI crystals from 180 to 4000 cm⁻¹. Mass spectra were recorded on a HP5989A spectrometer (*T* = 50–400°C, 1.3 kV). ¹H- and ¹³C-NMR were recorded on FX-90Q (90 MHz) or Am-300 (300 MHz) spectrometers. Elemental analyses were performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry.

4.2. Preparation of 1-(2-methoxyethyl)indene

To a solution of *n*-butyllithium (2.5 M in hexane, 60 ml) in 200 ml THF was added dropwise freshly distilled indene (17.4 g, 150 mmol) in 50 ml THF with rigorous stirring at 0–10°C. The mixture was stirred for another 2 h at r.t. until no gas was given off, then cooled to –50°C and 2-methoxyethylmethanesulfonate (22.0 g, 143 mmol) in 30 ml THF was added slowly while maintaining the low temperature (–50 to –30°C). The resultant pink mixture was stirred for 1 h, then was allowed to naturally warm to r.t. and stirred for a further 3 h. The reaction was then quenched with water. The organic phase was separated and the aqueous was extracted with ethylether (2 × 30 ml). The

combined organic solution was dried overnight over anhydrous MgSO₄. Removal of the solvent, followed by distillation under reduced pressure, provided a colorless liquid (yield: 22.1 g, 89%) with a b.p. in the range 69–71°C, 0.05 mmHg. ¹H-NMR (90 MHz, CDCl₃, 25°C): δ 7.35 (m, 4H, aromatic), 6.30 (br s, 1H, H²), 3.70 (t, 2H, CH₂O), 3.40 (s, 3H, CH₃O), 3.30 (br s, 2H, H³), 2.85 (t, 2H, CH₂) ppm.

4.3. Synthesis of bis{1-(2-methoxyethyl)indenyl}yttrium chloride (1)

A solution of CH₃OCH₂CH₂C₉H₇ (3.2 g, 18 mmol in 30 ml THF) was added dropwise to a stirred suspension of potassium metal in THF (1.7 g, excess) at 0°C, the resultant mixture was stirred for 5 h, then warmed to r.t. and stirred overnight. After centrifugation, a clear yellow solution was obtained and this was added to a suspension of YCl₃ (1.74 g, 8.9 mmol in 20 ml THF) by syringe and stirred for 2 days. The precipitate was separated and the resultant clear solution was carefully concentrated to a slightly supersaturated solution and allowed to stand for 4 days at ambient temperature. Colorless, crystalline thin plates were obtained from this solution and these were dried under vacuum at r.t. (1.4 g, 33%) and some more (1.5 g, 36%) were recovered from the mother liquor by repeating the process several times (total yield: 2.9 g, 69%). Anal. Found (Calc. for

$C_{24}H_{26}O_2ClY$): C 60.88 (61.21), H 5.69 (5.53%). 1H -NMR (300 MHz, THF- d_8 , 25°C): (major species) δ 7.60 (d, $J = 8.2$ Hz, 2H, H⁷), 7.50 (d, $J = 8.1$ Hz, 2H, H⁴), 7.05 (m, 4H, H⁵, H⁶), 5.82 (d, $J = 3$ Hz, 2H, H³), 5.35 (br s, 2H, H²), 4.40 (m, 2H, H^X), 4.05 (m, 2H, H^X), 3.55 (s, 6H, OCH₃), 3.13 (m, 2H, H^a), 2.80 (m, 2H, H^a) ppm. ^{13}C -NMR: δ 128.5, 126.5, 123.5, 122, 121.5, 121 (aromatic carbons), 120.5 (C²), 111.5 (C¹), 97.5 (C³), 78.5 (CH₂O), 64.5 (OCH₃), 27.5 (CH₂) ppm. EI-MS (70 eV) m/z (%): 470 (15.03) [M]⁺, 435 (4.36) [M-Cl]⁺, 297 (61.57) [M-L]⁺, 141 (100.00). IR (cm⁻¹): 3054(m), 3030(m), 3006(sh), 2941(s), 2894(s), 2844(m), 1685(w), 1603(w), 1577(w), 1550(w), 1482(m), 1459(m), 1436(m), 1398(w), 1384(w), 1342(s), 1290(w), 1262(w), 1236(m), 1212(m), 1197(m), 1152(m), 1126(s), 1083(s), 1056(vs), 1016(s), 1002(s), 984(s), 961(s), 778(vs), 755(s), 722(m), 694(w), 441(s), 269(s), 248(m).

4.4. Synthesis of bis{1-(2-methoxyethyl)indenyl}lanthanum chloride (**2**)

A procedure similar to that for **1** was adopted for LaCl₃ (1.21 g, 4.9 mmol), affording **2** as a rather pale yellow, macrocrystalline product (yield: 1.37 g, 54%).

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1–4**

Complex	1	2	3	4
Bond length (Å)				
Ln–C1	2.581(2)	2.713(3)	2.672(2)	2.617(2)
Ln–O(1)	2.472(4)	2.588(7)	2.570(4)	2.520(4)
Ln–O(2)	2.476(4)	2.618(6)	2.560(4)	2.520(4)
Ln–C(1)	2.601(5)	2.802(9)	2.735(6)	2.663(5)
Ln–C(2)	2.664(6)	2.835(9)	2.752(6)	2.706(6)
Ln–C(3)	2.760(6)	2.860(8)	2.832(6)	2.797(5)
Ln–C(8)	2.760(6)	2.875(9)	2.839(6)	2.811(5)
Ln–C(9)	2.625(5)	2.83(1)	2.741(6)	2.694(5)
Δ_{M-C} (ring 1) ^a	0.130	0.05	0.093	0.116
Ln–C(13)	2.613(6)	2.80(1)	2.716(6)	2.641(5)
Ln–C(14)	2.694(6)	2.824(8)	2.731(6)	2.680(5)
Ln–C(15)	2.837(5)	2.875(9)	2.826(6)	2.775(5)
Ln–C(20)	2.773(6)	2.870(9)	2.808(6)	2.787(5)
Ln–C(21)	2.656(5)	2.83(1)	2.753(6)	2.693(5)
Δ_{M-C} (ring 2) ^a	0.151	0.05	0.084	0.110
Bond angle (°)				
O(1)–Ln–C1	81.6(1)	83.2(2)	82.8(1)	81.5(1)
O(2)–Ln–C1	77.4(1)	84.0(2)	79.3(1)	78.82(10)
O(1)–Ln–O(2)	159.0(1)	167.1(3)	162.1(1)	160.3(1)
C(1)–Ln–C(13)	129.7(2)	131.2(4)	125.9(2)	126.5(2)
C(3)–Ln–C(13)	86.5(2)	87.7(3)	83.5(2)	83.6(2)
C(3)–Ln–C(20)	135.9(2)	132.1(3)	129.3(2)	129.8(2)
C(8)–Ln–C(14)	77.2(2)	85.2(3)	79.9(2)	79.4(2)
C(8)–Ln–C(15)	104.3(2)	111.6(3)	108.2(2)	108.7(2)
Dihedral angle of indene planes	51.80	50.48	53.78	53.68

^a Δ_{M-C} was calculated by subtracting the average values of the Ln–C bond length of the bridging-carbon atoms from those of the remaining three carbon bonds in the indene ring.

Anal. Found (Calc. for $C_{24}H_{26}O_2ClLa$): C 55.02 (55.32), H 5.10 (5.00%), 1H -NMR (300 MHz, THF- d_8 , 25°C): δ 7.70–7.60 (m), 7.55–7.45 (m, overlap), 7.28, 7.18 (m, small peaks), 7.10–6.90 (m, overlap), 6.62 (d, $J = 3$ Hz), 6.40, 6.30 (br s, small peaks), 6.12 (d, $J = 3$ Hz), 5.88 (br s), 5.50 (br s), 5.39 (d, $J = 3.2$ Hz), 5.31 (d, $J = 2.6$ Hz), 4.60 (br s), 4.55 (br s), 4.50–4.35 (m, overlap), 4.25–4.10 (m, overlap), 3.95 (m), 3.85 (s), 3.80 (m, overlap), 3.65, 3.60 (s, overlap), 3.45 (s), 3.20–3.10 (m), 3.05–2.80 (m, overlap), 2.75 (m) ppm. ^{13}C -NMR: δ 132–114, 100, 99.5 (multiplets), 79.5, 78, 77, 72 (CH₂O), 64, 63, 61, 58.5 (OCH₃), 38, 29.5, 29, 28 (CH₂) ppm. EI-MS (70 eV) m/z (%): 520 (29.16) [M]⁺, 485 (32.36) [M-Cl]⁺, 347 (100.00) [M-L]⁺. IR (cm⁻¹): 3060(sh), 3026(m), 2934(m), 2888(m), 2839(m), 1684(vw), 1603(vw), 1540(vw), 1500(vw), 1459(w), 1439(w), 1382(w), 1339(m), 1290(w), 1273(w), 1261(w), 1236(m), 1213(w), 1190(m), 1156(w), 1126(w), 1082(m), 1051(s), 1014(m), 987(m), 956(m), 877(vw), 862(vw), 817(m), 772(s), 751(s), 723(w), 443(m), 382(w), 242(m).

4.5. Synthesis of bis{1-(2-methoxyethyl)indenyl}neodymium chloride (**3**)

Analogous to **1**, 1.35 g NdCl₃ (5.4 mmol) afforded **3** as green macrocrystals (yield: 1.63 g, 58%). Anal. Found (Calc. for $C_{24}H_{26}O_2ClNd$): C 54.65 (54.80), H 5.10 (4.95%). EI-MS (70 eV, based on ^{142}Nd) m/z (%): 523 [M]⁺, 350 (2.06) [M-L]⁺, 141 (100.00). IR (cm⁻¹): 3060(sh), 3025(m), 2930(s), 2885(s), 2838(s), 1683(w), 1609(w), 1580(w), 1541 (w), 1459(m), 1434(m), 1397(w), 1339(s), 1290(w), 1273(w), 1261(w), 1236(m), 1190(m), 1156(m), 1124(s), 1082(s), 1052(s), 1015(m), 987(m), 957(m), 877(w), 862(w), 817(m), 772(vs), 752(s), 722(m), 690(w), 443(m), 410(w), 238(m).

4.6. Synthesis of bis{1-(2-methoxyethyl)indenyl}gadolinium chloride (**4**)

Analogously, 1.04 g (3.9 mmol) GdCl₃ provided **4** as yellow, crystalline plates (yield: 1.30 g, 62%). Anal. Found (Calc. for $C_{24}H_{26}O_2ClGd$): C 53.32 (53.48), H 4.92 (4.82%). EI-MS (70 eV, based on ^{158}Gd) m/z (%): 539 (1.65) [M]⁺, 366 (9.32) [M-L]⁺, 141 (100.00). IR (cm⁻¹): 3060(w), 3029(m), 2926(s), 2875(m), 2837(m), 1684(w), 1609(w), 1562(w), 1453(m), 1434(m), 1387(w), 1340(s), 1291(w), 1267(w), 1237(w), 1215(w), 1198(w), 1182(w), 1159(w), 1127(m), 1082(m), 1065(s), 1052(s), 1019(m), 1003(m), 979(m), 959(m), 876(w), 818(m), 769(s), 755(s), 722(sh), 441(m), 238(m).

4.7. Synthesis of bis{1-(2-methoxyethyl)indenyl}holmium chloride (**5**)

Analogously, 1.30 g (4.8 mmol) HoCl₃ provided **5** as tiny yellow crystals (yield: 1.63 g, 62%). Anal. Found

(Calc. for $C_{24}H_{26}O_2ClHo$): C 52.55 (52.70), H 4.83 (4.76%). EI-MS (70 eV, based on ^{165}Ho) m/z (%): 546 (1.52) $[M]^+$, 373 (9.95) $[M-L]^+$, 128 (100.00). IR (cm^{-1}): 3055(m), 3030(sh), 3006(w), 2940(s), 2892(s), 2844(m), 1656(vw), 1604(vw), 1559(vw), 1541 (vw), 1482(m), 1459(m), 1435(m), 1384(m), 1342(s), 1290(w), 1262(m), 1236(m), 1215(m), 1197(m), 1153(w), 1125(s), 1083(s), 1062(s), 1016(s), 984(s), 961(m), 874(w), 851(w), 820(s), 780(vs), 755(s), 739(s), 722(m), 442(s), 250(s), 230(s).

4.8. Synthesis of bis{1-(2-methoxyethyl)indenyl}lutetium chloride (**6**)

Analogously, 1.55 g (5.5 mmol) $LuCl_3$ afforded **6** as colorless tablets (yield: 1.54 g, 50%). Anal. Found (Calcd. for $C_{24}H_{26}O_2ClLu$): C 52.27 (51.75), H 4.62 (4.67%). 1H -NMR (300 MHz, THF- d_8 , 25°C): δ 7.60 (d, $J=8.1$ Hz, 2H, H^7), 7.50 (d, $J=8.1$ Hz, 2H, H^4), 7.05 (m, 4H, H^5, H^6), 5.80 (d, $J=3$ Hz, 2H, H^3), 5.35 (s, 2H, H^2), 4.40 (m, 2H, H^X), 4.10 (m, 2H, H^X), 3.50 (s, 6H, OCH_3), 3.10 (m, 2H, H^a), 2.75 (m, 2H, H^a) ppm. ^{13}C -NMR: δ 129.5, 127, 125, 123, 122.5, 122 (aromatic carbons), 121 (C^2), 111 (C^1), 98 (C^3), 80 (CH_2O), 66 (CH_3O), 28.5 (CH_2) ppm. EI-MS (70 eV) m/z (%): 556 (43.15) $[M]^+$, 521 (98.23) $[M-Cl]^+$, 383 (100.00) $[M-L]^+$. IR (cm^{-1}): 3062(m), 3024(m), 2929(s), 2875(m), 2837(m), 1684(w), 1609(w), 1577(w), 1523(w), 1476(m), 1458(m), 1434(m), 1391(m), 1339(s), 1290(w), 1270(w), 1262(w), 1236(m), 1216(m), 1197(m), 1157(w), 1124(s), 1082(m), 1063(s), 1018(m), 984(m), 963(m), 894(w), 873(w), 862(sh), 821(m), 774(s), 755(s), 739(s), 722(s), 635(w), 441(m), 411(m), 262(m), 226(m).

4.9. X-ray structural determination

Single crystals were sealed in thin-walled glass capillaries under an atmosphere of argon. Crystal data and experimental details are given in Table 1, while selected bond lengths and bond angles for complexes **1–4** are listed in Table 2. Data was collected on a Rigaku AFC7R diffractometer with graphite-monochromated $Mo-K_{\alpha}$ radiation ($\lambda = 0.71069$ Å) using the $\omega-2\theta$ technique at 20°C and corrected for Lorentz-polarization effects. An empirical absorption correction was applied using the program DIFABS [38] for **2** and **4** or based on azimuthal scans of several reflections for **1** and **3**. The structures were solved by direct methods [39] for **1**, **3** and **4** or heavy-atom Patterson methods [40] for **2**, and expanded using Fourier techniques [41]. All non-H atoms were refined anisotropically by the full-matrix least-squares technique. Hydrogen atoms were included but not refined. All H atoms were introduced in calculated positions. Scatter factors were taken from the International Tables for X-ray Crystallography [42]. All calculations

were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [43].

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