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Synthesis and crystal structure of bis(2-dimethylaminoethylindenyl) divalent organolanthanides (Ln = Sm, Yb)

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Abstract

First examples of racemic bis(2-dimethylaminoethylindenyl) divalent unsolvated organolanthanide complexes $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Sm}$ (**1**) and $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Yb}$ (**2**) have been synthesized by the reaction of $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)\text{K}$ with LnI_2 (Ln = Sm, Yb). The two compounds have been characterized by elemental analysis and ^1H -NMR spectrometry. The X-ray crystal structure of **2** has been determined by diffraction study. The crystals are prismatic, space group $P2_1/a$ ($\neq 14$), with $a = 17.342(6)$ Å, $b = 8.542(7)$ Å, $c = 17.353(2)$ Å, $\beta = 118.70^\circ$, $V = 2254(1)$ Å³, $Z = 4$, $D = 1.607$ g cm⁻³. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2-Dimethylaminoethylindenyl; Organolanthanide; NMR

1. Introduction

Over the past several years, cyclopentadienyl ligands bearing a donor-functionalized side chain have attracted much attention in lanthanide [1] and alkaline-earth [2] chemistry, because the donating ability of the terminal functional group in the side chain can stabilize π -complexes by additional intramolecular coordination and sidearm participation may play an important role in catalytic processes. Consequently, the ether- or amine-substituted cyclopentadienyl ligands have been used to stabilize bis(cyclopentadienyl) lanthanide complexes [3,4]. A series of lanthanide complexes containing ether- or amine-substituted cyclopentadienyl ligands has been prepared by Qian et al. In order to seek better catalysts for the organic reactions and olefin polymerization, we designed the dimethylaminoethyl indene as a ligand and found it very useful for coordination to lanthanide ions; we hope to reveal possible application of these complexes in stereospecific catalytic reactions.

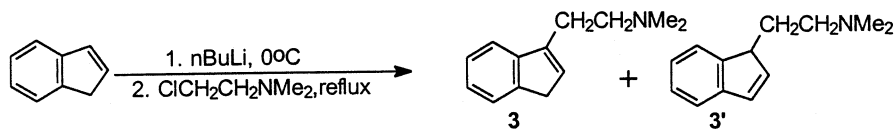
We started to prepare chiral samarium(II), and ytterbium(II) complexes involving a new donor-functionalized indenyl ligand and present X-ray structure determinations of representative complexes. Herein, we report the synthesis of bis(2-Dimethylaminoethylindenyl) divalent lanthanide complexes $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Ln}$ (Ln = Sm(**1**), Yb(**2**)) and the X-ray structure of $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Yb}$.

2. Results and discussion

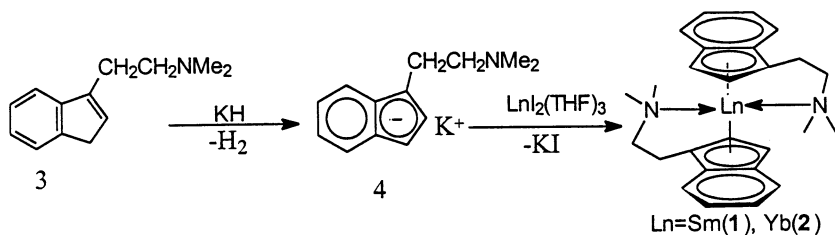
2.1. Synthesis of metallocenes **1** and **2**

(2-Dimethylaminoethyl)indene was synthesized by the reaction of indenyl lithium and 2-dimethylaminoethylchloride, as shown in Scheme 1. In the substitution, it may produce two isomers **3** and **3'**, but no isomer **3'** was detected by ^1H -NMR spectrometry. Compound (2-dimethylaminoethyl)indene (**3**) was deprotonated with potassium hydride to afford the indenyl anions (**4**). Reaction of the indenyl potassium salts with samarium(II) and ytterbium(II) diiodide in THF at room temperature (r.t.), cleanly gave the sol-

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Scheme 1.



Scheme 2.

vent-free metallocenes **1** and **2**, as shown in Scheme 2. Crystallization from toluene afforded the complexes in 20–21% isolated yields. The red Sm and Yb compounds are air- and moisture-sensitive and soluble in polar solvents like THF, and aromatic solvents such as toluene. The complexes were characterized by elemental analyses and mass spectrometry. From the thermodynamics, complexes **1**, **2** have the most favorable configuration, as shown in Fig. 1. By X-ray crystallography, we found they are *rac*-isomer in solid state.

2.2. Molecular structure of $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Yb}$ (**2**)

A crystal suitable for X-ray diffraction analysis was obtained by recrystallization from toluene. The structure of one of the four identical well-separated molecules in the unit cell of complex **2** is shown in Fig. 2. The crystallographic data are given in Table 1, and selected structural data are given in Table 2. Nitrogen atoms of both dimethylaminoethyl group are intramolecularly coordinated to the Yb atom to form an intramolecular coordination bond. Only one possible diastereomeric conformation with *trans* arrangement of both indenyl rings and coordinated sidearms (Fig. 2) is present. The compound is unsolvated 8-coordinate monomeric complex in solid state. Overall, the structure of **2** closely resembles the distorted-tetrahedral coordination geometry of $[\text{Yb}\{\eta^5\text{:}\eta^1\text{-(Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\}]$ with $\text{N-Yb-N}' = 103.6^\circ$. Two indenyl groups are bonded to central metal in η^5 fashion. The dihedral angle of the two indenyl rings is 47.73° . The Yb-N distances, at 2.58 and 2.608 Å, are very close to those reported for $[\text{Yb}\{(\text{s})\text{-}\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}(\text{Me})\text{NMe}_2\}_2]$ [4].

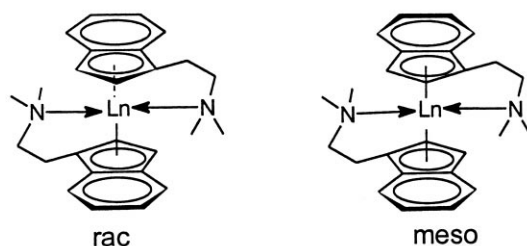


Fig. 1.

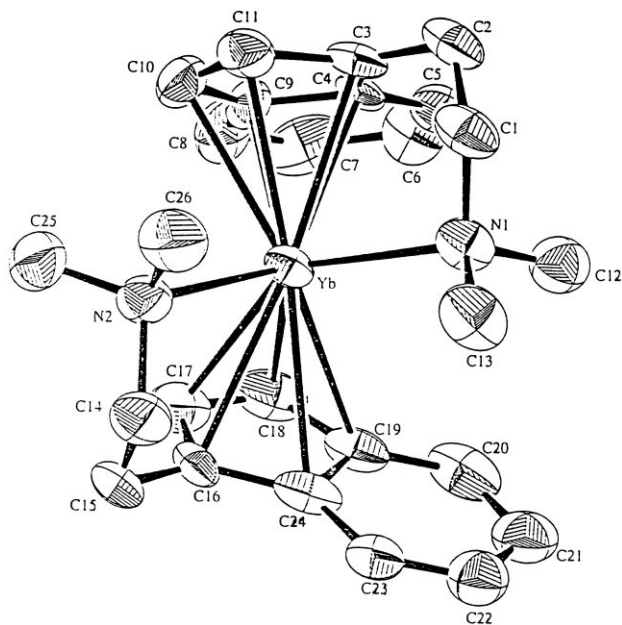
Fig. 2. ORTEP plot of the molecular structure and numbering scheme of **2**.

Table 1
Crystal data and structure refinement for **2**

Compound	(Me ₂ NCH ₂ CH ₂ C ₉ H ₆) ₂ Yb
Empirical formula	C ₂₆ H ₃₂ N ₂ Yb
Formula weight	545.59
Crystal color	Red
Crystal dimensions (mm)	0.20 × 0.20 × 0.30
<i>a</i> (Å)	17.342(6)
<i>b</i> (Å)	8.452(7)
<i>c</i> (Å)	17.353(2)
β (°)	118.70(3)
<i>Z</i> value	4
<i>V</i> (Å ³)	2254(1)
<i>D_c</i> (g cm ⁻³)	1.607
<i>F</i> (000)	1088.00
μ (Mo–K α) (cm ⁻¹)	41.61
Reflections collected	3610
Independent reflections	3461
Observed data	2243
Parameters	262
Goodness-of-fit	1.94
<i>R</i> , <i>wR</i>	0.046, 0.051

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **2**^a

Yb–N(1)	2.58(1)	N(1)–Yb–N(2)	103.6(3)
Yb–N(2)	2.608(10)	N(1)–Yb–C(4)	85.0(3)
Yb–C(3)	2.69(1)	N(1)–Yb–C(10)	117.4(4)
Yb–C(9)	2.77(1)	N(1)–Yb–C(11)	89.8(4)
Yb–C(11)	2.70(1)	N(1)–Yb–C(3)	69.5(4)
Yb–C(17)	2.61(1)	N(1)–Yb–C(9)	114.3(3)
Yb–C(19)	2.78(1)	N(2)–Yb–C(16)	67.8(4)
Yb–C(4)	2.745(9)	N(2)–Yb–C(18)	115.2(4)
Yb–C(10)	2.76(1)	N(2)–Yb–C(17)	85.0(5)
Yb–C(24)	2.79(1)	N(2)–Yb–C(24)	87.5(4)
Yb–C(16)	2.70(1)	N(2)–Yb–C(19)	116.2(4)
Yb–C(18)	2.66(1)	C(3)–Yb–C(9)	48.9(4)

^a Dihedral angle of indene planes: 47.73°.

3. Conclusions

We have prepared two novel chiral metallocenes of divalent lanthanides samarium(II) and ytterbium(II) involving a new donor functionalized indenyl ligands. The intramolecular coordination of the donor arm with *trans* orientation of both indene rings and sidearms has been confirmed by X-ray structural analyses carried out for complex **2**. We shall continue to examine these complexes with respect to their potential use in catalytic reactions. Supplementary information is available from the authors.

4. Experimental

4.1. General procedures

All operations involving organometallics were carried

out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry, oxygen-free solvents. All solvents were distilled under argon from sodium-benzophenone prior to use. LnI₂ [5] (Ln = Sm, Yb), and Me₂NCH₂CH₂Cl [6] were prepared according to published procedures. *n*-Butyllithium and indene were purchased from Aldrich. All chemical shifts are reported in ppm relative to the residues of the deuterated solvents. Mass spectra were recorded on a HP 5989A spectrometer (50–400°C, 1.3 kV) and ¹H-NMR spectra were obtained on Am-300 (300 MHz) spectrometers. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

4.2. Preparation of (2-dimethylaminoethyl)indene

To a solution of indene (18 ml), THF (150 ml) ^{*n*}BuLi (1.0 M in hexane, 18 ml) was added dropwise with rigorous stirring at 0°C, the mixture was stirred for 3 h at r.t. until no gas was given off, then added slowly to Me₂NCH₂CH₂Cl (22 ml) at 0°C. The resulting yellow mixture was stirred overnight, allowed to warm to r.t., then quenched with water. The organic phase was separated and the aqueous phase extracted with diethyl ether (2 × 100 ml). The combined organic solution was dried over anhydrous MgSO₄ overnight. The solvent was removed in vacuo and the residue was fractionally distilled under reduced pressure to provide 13.13 g (39%) of **3** as a light yellow liquid. B.p. 75–80°C/20 Pa. ¹H-NMR (CDCl₃, 300 MHz): 7.45–7.21 (m, 4H), 6.27 (s, 1H), 3.29 (s, 2H), 2.74 (m, 2H), 2.56 (m, 2H), 2.24 (s, 6H). EI mass spectrum (70 eV), *m/z*: 187 (2.28 M⁺) 141 (5.53) 58 (100.00).

4.3. Preparation of (Me₂NCH₂CH₂C₉H₆)K

A solution of compound **3** (6.372 g, 0.036 mol in 30 ml THF) was added dropwise to a stirred suspension of potassium hydride (1.455 g, 0.036 mol) in 70 ml THF at 0°C. The resulting mixture was stirred overnight and warmed to r.t. After centrifugation, a clear red solution was obtained. The solvent was removed under vacuum and the residue washed with hexane (2 × 30 ml). After drying under vacuum, the compound **4** was obtained as yellow solids. Yields: 47%. ¹H-NMR (THF-*d*₈, 300 MHz): 7.21–7.17 (m, 2H); 6.37–6.34 (m, 2H); 6.25 (m, 1H); 5.73 (m, 1H); 2.92 (m, 2H); 2.51 (m, 2H); 2.05 (s, 6H).

4.4. Preparation of (Me₂NCH₂CH₂C₉H₆)₂Sm (**1**)

To a solution of (Me₂NCH₂CH₂C₉H₆)K (1.493 g, 6.6 mmol) in THF (40 ml) was added dropwise SmI₂ (0.1 M THF solution, 30 ml) with rigorous stirring, then warmed to r.t., and stirred for 48 h. The precipitate was separated and the clear solution concentrated until a solid appeared. The product was washed with cool THF (10 ml) and dried

in vacuo at r.t. affording 0.7 g of a red solid, yield: 20%. Anal. Found: C, 59.51; H, 6.04; N, 5.37; Sm, 26.68%. $C_{26}H_{32}N_2Sm$; Calc.: C, 59.71; H, 6.17; N, 5.36; Sm, 28.76%. MS, m/z : 268 (4.74) 141 (29.53) 129 (100.00) 115 (79.98) 44 (94.34).

4.5. Preparation of $(Me_2NCH_2CH_2C_9H_6)_2Yb$ (**2**)

A procedure similar to that for compound $(Me_2NCH_2CH_2C_9H_6)_2Sm$ was adopted using YbI_2 (0.06 M THF solution, 48 ml) and afforded 0.7 g of a red solid, yield: 21%. Anal. Found: C, 56.99; H, 5.82; N, 5.01; Yb, 32.05%. $C_{26}H_{32}N_2Yb$; Calc.: C, 57.23; H, 5.91; N, 5.14; Yb, 31.72%. MS, m/z : 253 (3.38) 141 (10.64) 91 (15.09) 58 (100.00) 44 (63.61). 1H -NMR (THF- d_8 , 300 MHz): 7.41–7.32 (m, 4H); 6.82 (m, 4H); 6.12 (m, 2H); 5.38 (m, 2H); 2.92 (m, 4H); 2.71 (m, 4H); 2.10 (s, 12H).

4.6. Crystallography

A suitable crystal with $0.20 \times 0.20 \times 0.30$ mm³ dimensions was sealed in thin-walled glass capillaries under argon. Crystal data and details of data collection and structure refinement are given in Tables 1 and 2, respectively. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo- K_α radiation $\lambda = 0.71069$ Å using the ω - 2θ technique at 20°C. A total of 3461 unique reflection was collected. The data were corrected for Lorentz polarization effects; The structure were solved by direct methods and expanded using Fourier techniques [7]. The non-hydrogen

atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in calculated position. All calculations were performed using the TEXSAN crystallographic software package. Final R and wR values were 0.046 and 0.051 for 3610 observed reflections.

Acknowledgements

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