

Generation of chiral bis(cyclopentadienyl)neodymium Schiff base complex bearing internal C–C bond formation and hydrogen transfer

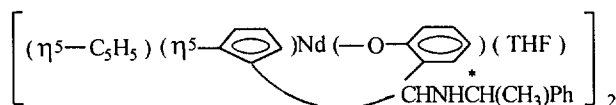
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Abstract

NdCl₃ reacts with excess CpNa (Cp=Cyclopentadienyl) in THF, followed by sequent treatment with (*S*)-(+)-*N*-(1-phenylethyl)salicylideneamine led to the formation of title compound,



. The X-ray structure determination shows that it is a dimer with internal C–C bond formation and hydrogen transfer between one of Cp ring and the C=N bond of Schiff base ligand. © 1997 Elsevier Science S.A.

Keywords: Organoneodymocene; Chirality; Schiff base complex; Crystal structure; C–C bond formation; Hydrogen transfer

1. Introduction

Trivalent organo-bis(cyclopentadienyl)lanthanide complexes especially organolanthanide alkoxides and phenoxides have been of interest for a few years [1,2]. Recently, Evans et al. revealed that bis(cyclopentadienyl)lanthanide alkyls could form organolanthanide enolate complexes [Cp₂Ln(μ-OCH=CH₂)₂] [3]. Others

found that [Cp₂LnPPh₂] could form [Cp₂Ln(μ-OCH₂CH₂CH₂CH₂PPh₂)₂] by cleaving of THF and [Cp₂Yb(μ-OCH₂CH=CH₂)₂] could dehydrogenize to form [Cp₂Yb(μ-OCH=C=CH₂)₂] [4,5]. Moreover, optically active lanthanocene complexes have been of great interesting in the very recent due to their excellent catalytic properties both in asymmetric syntheses and stereo-control polymerization. For example, chiral C₁-symmetric organolanthanide complexes have been utilized to catalyze enantio-selective hydrogenation of styrenic olefins, hydroamination–cyclization of amino-olefins, hydrosilylation of olefins as well as polymerization of methyl methacrylate [6–12], and chiral C₂-symmetric binaphthoxy linked ytterocene for α-olefin polymerization [13]. Furthermore, Stendel et al. reported a series of chiral lanthanocene alkoxides or thioxides [14]. Although a few lanthanide Schiff base complexes have been reported, those synthesized in non-aqueous condition are rare [15]. These results promoted us to investi-

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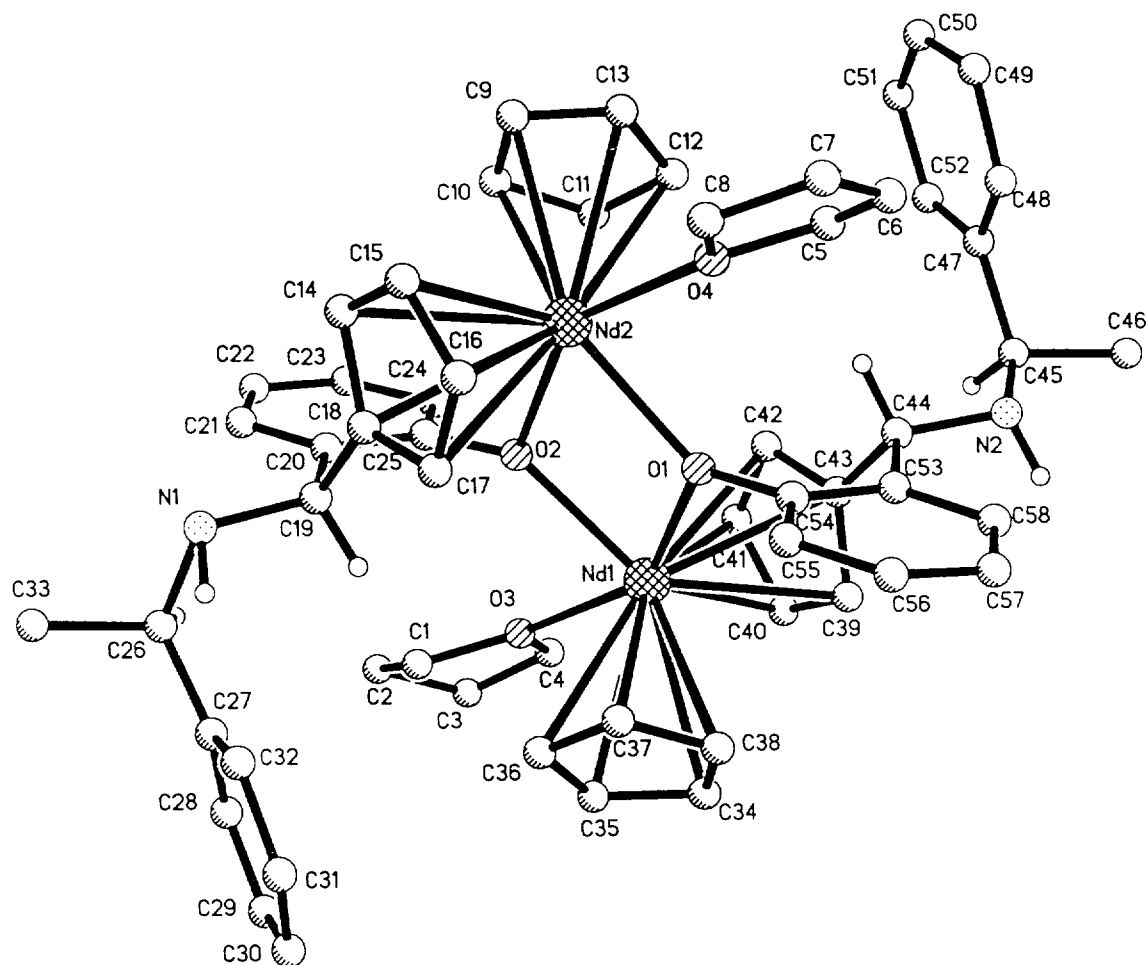


Fig. 1. Molecular structure of **1**, most hydrogen atoms have been omitted for clarity. The average Nd1–Cent1, Nd1–Cent2, Nd2–Cent3 and Nd2–Cent4 distances are 2.555 Å, 2.406 Å, 2.450 Å and 2.541 Å. The angles: Cent1–Nd1–Cent2 (124.1°), Cent1–Nd1–O1 (99.0°), Cent1–Nd1–O2 (118.1°), Cent1–Nd1–O3 (92.6°), Cent2–Nd1–O1 (95.7°), Cent2–Nd1–O2 (117.7°) and Cent2–Nd1–O3 (98.9°); Cent3–Nd2–Cent4 (125.7°), Cent3–Nd2–O1 (121.9°), Cent3–Nd2–O2 (100.5°), Cent3–Nd2–O4 (153.8°), Cent4–Nd2–O1 (112.0°), Cent4–Nd2–O2 (92.8°) and Cent4–Nd2–O4 (69.2°) [Cent1, Cent2, Cent3 and Cent4 are centroids of Cp1(C34–C38), Cp2(C39–C43), Cp3(C9–C13) and Cp4(C14–C18)].

gate the reactivity of chiral lanthanide metallocenes with optically active Schiff base as ligands.

2. Results and discussion

We wish to report the crystal structure of the title compound which is the only example of internal C–C formation and hydrogen transfer between one of the Cp rings and the C=N bond of Schiff base ligand up to now. Furthermore, this is also a very convenient route for substituted cyclopentadienyl complexes of lanthanides which can directly induce a substituent onto one Cp ring during the reaction process. **1** was synthesized by the reaction of NdCl₃ with 3.3 equivolar CpNa in THF, followed by sequent treatment with equivolar (*S*)-(+)-*N*-(1-phenylethyl) salicylideneamine

(**2**)³ at room temperature. Complex **1** has been fully characterized by elemental analysis (C, H, N and Nd), infrared spectroscopy. However, ¹H NMR of complex **1** in C₆D₆ or C₄D₈O were not obtained. Orange-red crystals were obtained in 61% yield several weeks later

³ Crystal data for **2**: C₁₅H₁₅NO, Mr = 225.28, monoclinic, *a* = 18.529(10) Å, *b* = 5.915(10) Å, *c* = 14.639(10) Å, β = 128.60(2)° (by least-squares analysis of 30 fine reflections), *V* = 1253.9(2) Å³, space group *C*₂ (No. 5) *Z* = 4, *D*_c = 1.193 g cm⁻³, *F*(000) = 480, *T* = 293(2) K, μ = 0.075 mm⁻¹. Crystal dimensions 0.42 × 0.38 × 0.32 mm³, 1645 reflections collected, 1449 independent and 1438 observed reflections and 214 refined parameters led to the final *R* = 0.0370. Synthesis of **2** was accomplished by the reaction of salicylaldehyde and (*S*)-(-)-phenylethylamine in toluene with azeotropic distillation of water, followed by crystallization in ethanol, [α]_D²⁰ = +185.2° (c 0.524, MeOH), see Ref. [16].

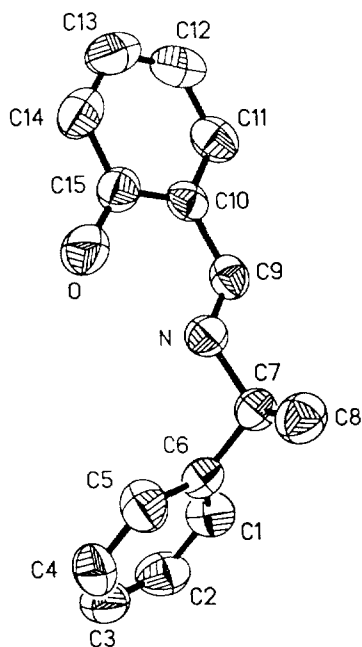


Fig. 2. Molecular structure of **2**, hydrogen atoms have been omitted for clarity. The bond distances of C7–N and C9=N are 1.264(4) Å and 1.480(4) Å, respectively.

at ambient temperature after workup. M.p. 212–214°C (dec.), $[\alpha]_D^{20} = -2418^\circ$ (c 0.0911, THF). $C_{58}H_{64}N_2Nd_2O_4$ requires: Nd, 25.27; C, 61.02; H, 5.65; N, 2.45%. Anal. Found: Nd, 25.10; C, 60.94; H, 5.71; N, 2.44%.⁴ The IR spectra doesn't give the characteristic peak of C=N double bond of Schiff base (1625 cm^{-1}).

In the crystal this dinuclear compound is close to C_2 -symmetry. The neodymium centers are each coordinated to two Cp rings and three oxygens to form a distorted trigonal bipyramidal geometry with two centroids of Cp ring and one of bridging oxygen from Schiff bases occupying the triangular plane, while the

oxygens from another Schiff base and THF in the apical sites. The average Nd1–C *a* (Cp1: C34–C38) and Nd1–C *b* (Cp2: C39–C43) distances are 2.826 Å and 2.736 Å, while those of Nd2–C *c* (Cp3: C9–C13) and Nd2–C *d* (Cp4: C14–C18) are 2.723 Å and 2.797 Å. The bond distances of Nd1–O1, Nd1–O2 and Nd1–O3 are 2.428(6) Å, 2.327(6) Å and 2.652(6) Å, and those of Nd2–O1, Nd2–O2 and Nd2–O4 are 2.389(6) Å, 2.499(6) Å and 2.552(6) Å, respectively. The plane (*P*1) through four atoms [Nd1, Nd2, O1, O2] is nearly coplanar [the sum of the angles in the tetragonal plane, 359.7°] with a maximum deviation of 0.043 Å. The dihedral angles of *P*1 with Cp1, Cp2, Cp3 and Cp4 are 31.15° , 27.29° , 30.91° and 26.42° , while those of Cp1 and Cp2, Cp3 and Cp4 are 58.17° and 57.24° . The C19–N1, C26–N1, C44–N2 and C45–N2 bond lengths are 1.476(11), 1.439(13), 1.475(10) and 1.463(12) Å, respectively, while the corresponding C=N(C9–N) and C–N(C7–N) in **2** are 1.264(4) Å and 1.480(4) Å, respectively. This is illustrated by Figs. 1 and 2, which show the molecular structures of **1** and **2**, respectively.

3. Conclusions

This study shows that substituted organolanthanocene Schiff base complex can be formed with internal C–C bond formation and hydrogen transfer. However, the mechanism of the formation of complex **1** remained unsettled, it seems that the reaction of excess of CpNa with the Schiff base through a formal insertion of C=N bond and the C–H bond of cyclopentadienyl group in the presence of lanthanide complex led to the formation of C–C bond and hydrogen transfer. Our further study is to find out more. Whether these C_2 -symmetric ligands can be used as chiral chelating ligands for synthesizing chiral C_2 -symmetric organolanthanocene complexes are now under investigation in this laboratory.

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⁴ Single-crystal studies of **1**. Crystal data for $C_{58}H_{64}N_2Nd_2O_4$, Mr = 1141.6, monoclinic, $a = 11.222(10)$ Å, $b = 20.304(3)$ Å, $c = 12.037(10)$ Å, $\beta = 110.74(10)^\circ$ (by least-squares analysis of 30 fine reflections), $V = 2564.9(5)$ Å³, space group $P2_1$ (No. 4), $Z = 2$, $D_c = 1.478\text{ g cm}^{-3}$, $F(000) = 1156$, $\mu = 2.049\text{ mm}^{-1}$, $T = 293(2)$ K. Crystal dimensions $0.42 \times 0.36 \times 0.24\text{ mm}^3$. Data were collected on a Siemens P4 four-circle diffractometer with monochromated graphite, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, 5890 reflections collected ($9.87^\circ \leq 2\theta \leq 24.98^\circ$), index ranges $-1 \leq h \leq 13$, $-1 \leq k \leq 24$, $-14 \leq l \leq 13$, producing 4918 unique data ($R_{\text{int}} = 0.0199$ after absorption correction). The structure was solved by heavy atoms methods and then subjected to full-matrix least-squares refinement based on F^2 . All the calculations were conducted on a Siemens PCD 4H computer by use of SHELXTL-Plus program ([17]). Final wR_2 and R_1 values are 0.0352 and 0.0858 respectively, for all data and 595 parameters ($\rho_{\text{max}}, \rho_{\text{min}} 0.379, -0.421\text{ e Å}^{-3}$). Corresponding wR_2 and R_1 values for 4918 data with $I > 2\sigma(I)$ are 0.0814 and 0.0294, respectively.

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