

A NEW CONVENIENT SYNTHESIS OF CYCLOOCTATETRAENYLLANTHANIDE
COMPLEXES: X-RAY CRYSTAL STRUCTURE OF CeI(C₈H₈)(THF)₃

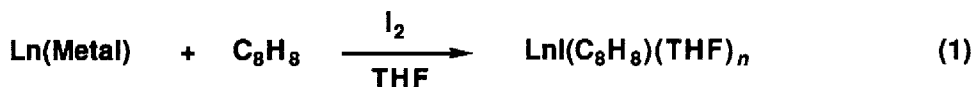
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Abstract: Lanthanide metals react with cyclooctatetraene in the presence of iodine to give cyclooctatetraenyliodolanthanide complexes LnI(C₈H₈)(THF)_n (Ln = La, Ce, Pr, Nd, or Sm; n = 1, 2, or 3). The monomeric nature of CeI(C₈H₈)(THF)₃ (**1b**) is established by a single crystal X-ray analysis. The mechanism of the formation of SmI(C₈H₈)(THF) (**1e**) is discussed.

Although the chemistry of cyclopentadienyl complexes of lanthanide elements has been extensively studied,¹ a relatively small number of cyclooctatetraene (C₈H₈) derivatives has been reported.²⁻⁴ Cyclooctatetraenyllanthanide(III) complexes have mostly been prepared by the reaction of anhydrous halides of lanthanide elements with cyclooctatetraenyl dianion followed by Soxhlet extraction.^{3a,4a} However, removal of by-products such as K[Ln(C₈H₈)₂] formed in these procedures is often troublesome. We communicate here a convenient one-pot synthesis of cyclooctatetraenyliodolanthanide complexes.

As shown in equation 1, various complexes of Ln(III) having the general formula LnI(C₈H₈)(THF)_n (**1**) (n = 1, 2, or 3) were synthesized in THF by the direct reaction of lanthanide metals with C₈H₈ in the presence of a stoichiometric amount of iodine. For example, a mixture of powdery cerium metal, C₈H₈, and iodine in THF was stirred at 50 °C for a period of 48 h under argon atmosphere and then the reaction mixture was filtered through a pad of Celite 545. The filtrate was concentrated to afford **1b** as bright yellow plates in 85% yield. Corresponding complexes of La, Pr, Nd, and Sm were similarly obtained in high yields.



1a; Ln = La, n = 3, 90%

1b; Ln = Ce, n = 3, 85%

1c; Ln = Pr, n = 3, 92%

1d; Ln = Nd, n = 2, 83%

1e; Ln = Sm, n = 1, 81%

Elemental analyses of the complexes established the stoichiometry of ligands and metals.⁵ The structure of the diamagnetic complex **1a** is determined based on elemental analysis and ¹H and ¹³C{¹H} n.m.r. spectra.⁵

The monomeric piano stool structure of **1b** was established by an X-ray crystal structure determination.⁶ In contrast to the known dimeric complex $[\text{CeCl}(\text{C}_8\text{H}_8)(\text{THF})_2]_2$ (**2**),^{4a} **1b** is monomeric and has no unusually short intermolecular nonbonded interactions. An ORTEP view of **1b** is shown in Figure 1. The cyclooctatetraene ligand is planar and is π -bonded to the cerium atom. All the Ce—C and C—C bond lengths in cyclooctatetraenyl ligand are comparable to those of complex **2**. The cerium atom is coordinated by three THF molecules and can be regarded as having formally a coordination number of 9 (C_8H_8 dianion has five π -electron pairs available for coordination). The cerium—iodine bond length of 3.300(1) Å is a little longer than those found in $\text{CeI}_2(\text{C}_5\text{Me}_5)(\text{THF})_3$ (3.273 and 3.227 Å).⁷

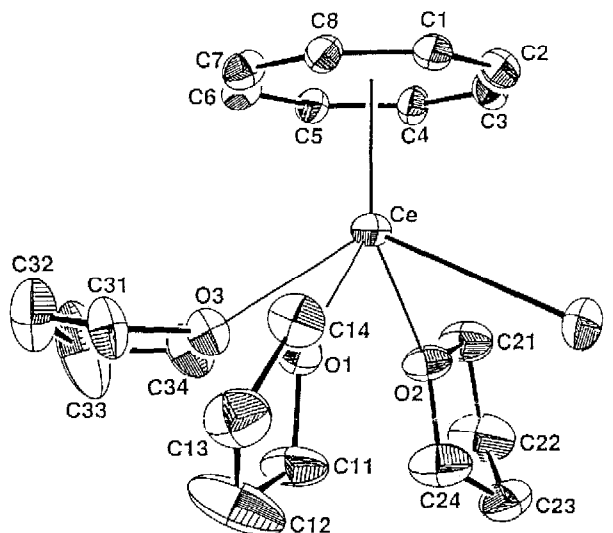
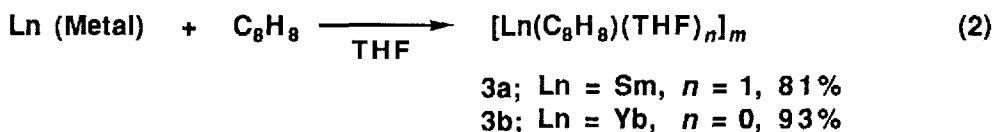
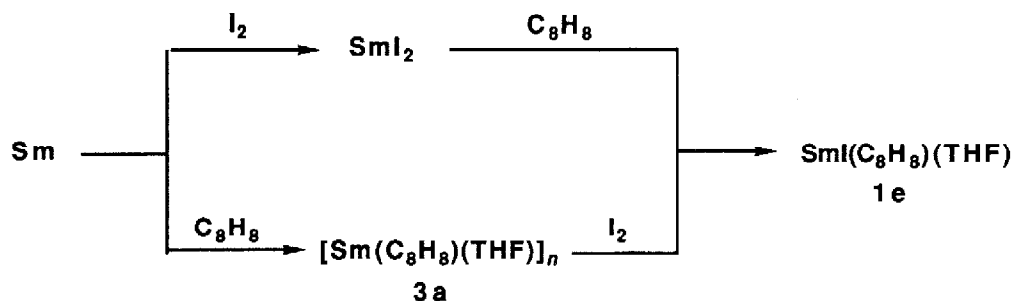


Figure 1. An ORTEP drawing of complex **1b** with numbering scheme. All hydrogen atoms and carbons of disordered cyclooctatetraene are omitted for simplicity. Selected bond distances and angles: Ce—I 3.299(1) Å; Ce—O1 2.583(7) Å; Ce—O2 2.555(7) Å; Ce—O3 2.640(7) Å; Ce— C_8H_8 2.010 Å; I—Ce— C_8H_8 116.0°; O1—Ce— C_8H_8 134.2°; O2—Ce— C_8H_8 127.1°; O3—Ce— C_8H_8 116.9°; I—Ce—O1 73.5(2)°; I—Ce—O2 78.8(2)°; I—Ce—O3 127.0(2)°; O1—Ce—O2 98.4(2)°; O1—Ce—O3 67.9(2)°; O2—Ce—O3 72.6(2)°, where C_8H_8 is the centroid of cyclooctatetraenyl ligand.

Samarium metal also reacted easily with C_8H_8 in THF in the presence of catalytic amount of iodine at 50 °C to afford polymeric $[\text{Sm}(\text{C}_8\text{H}_8)(\text{THF})]_n$ (**3a**) as brown solid in high yield,^{8,9} which does not dissolve in common organic solvents. Similar reaction of ytterbium with C_8H_8 in THF gave **3b** as pink solid.¹⁰

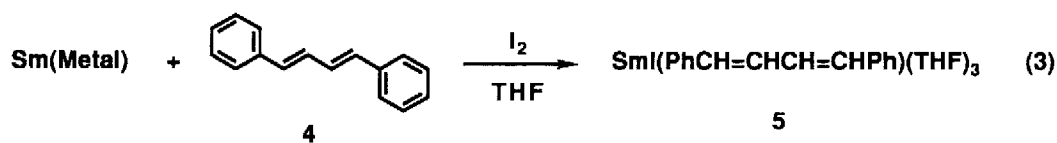


Although details on the mechanism of the formation of **1** are to be further investigated, control experiments showed that there are at least two possible routes to complex **1e**, as shown in Scheme 1. Samarium metal reacts easily with iodine in THF to afford SmI_2 ,¹¹ which could then react with cyclooctatetraene to give **1e**. During the present reaction some yellow SmI_3 precipitated, but in the course of the reaction this species disappeared probably because of further reaction with metallic Sm to give SmI_2 .¹¹ On the other hand, samarium reacted directly with C_8H_8 as shown in equation 2 to give polymeric **3a**. Addition of a stoichiometric amount of iodine to a suspension of **3a** in THF rapidly gave rise to a purple solution, from which complex **1e** was obtained.



Scheme 1

The present method allows preparation of other iodolanthanide-olefin complexes. Reaction of samarium with (E,E)-1,4-diphenyl-1,3-butadiene (**4**) in the presence of a stoichiometric amount of iodine afforded $\text{SmI}(\text{1,4-diphenyl-1,3-butadiene})(\text{THF})_3$ (**5**) in 66% yield as deep red crystalline solid.^{8,12}



Chemical properties of these complexes and preparation of organolanthanide complexes from these compounds are subjects of our present interest.

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References and Notes

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- 5) **1a**: pale yellow plate; ^1H n.m.r. in THF- d_8 δ 6.29 (s, C_8H_8); ^{13}C n.m.r. in THF- d_8 δ 98.4 ppm ($J_{\text{C-H}} = 156$ Hz); m.p. 95–103 °C and >400 °C (dec); Anal. Calcd. C, 40.97; H, 5.50. Found. C, 40.75; H, 5.28. **1b**: bright yellow plate; m.p. 70–75 °C (dec); Anal. Calcd. C, 40.89; H, 5.49. Found. C, 40.61; H, 5.61. **1c**: greenish yellow plate; m.p. 77–85 °C and >380 °C (dec); Anal. Calcd. C, 40.83; H, 5.48. Found. C, 40.60; H, 5.61. **1d**: green plate; m.p. >320 °C (dec); Anal. Calcd. C, 36.99; H, 4.66. Found. C, 36.77; H, 4.76. **1e**: purple needle; m.p. 210–220 °C (dec); Anal. Calcd. C, 32.94; H, 3.69. Found. C, 32.87; H, 4.07.
- 6) Crystal Data for 1b: Orthorhombic space group P_{cab} with cell parameters; $a = 22.342(2)$ Å, $b = 15.276(1)$ Å, $c = 13.146(2)$ Å, and $U = 4486.7(8)$ Å³; $Z = 8$; $D_{\text{calcd}} = 1.740$; F.W. = 587.50. No systematic damage on three reflections measured after every 50 reflections was observed. A total 3272 reflections with $|F_o| > 3\sigma(F_o)$ were corrected for polarization and Lorentz factors, and absorption ($\mu = 35.83$ cm⁻¹ for $\text{MoK}\alpha$). The position of the Ce atom was located from the Patterson synthesis, and the remaining atoms were found on subsequent Fourier maps, hydrogen atoms being located at calculated positions. Carbons of cyclooctatetraene occupy the disordered position with 0.5 probability. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically to reach R and R_w values of 0.059 and 0.062, respectively. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.
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- 8) Formation of $\text{Ln}(\text{olefin})(\text{THF})_n$ has been proposed in the reaction of metallic Sm and Yb with olefins such as cyclooctatetraene and 1,3-dienes in ethereal solvent in the presence of 1,2-diiodoethane: L. Saussine, H. Olivier, D. Commereuc, and Y. Chauvin, New J. Chem., 1988, **12**, 13.
- 9) **3a**: deep brown powder; >400 °C (dec); Anal. Calcd. C, 44.13; H, 4.94. Found. C, 44.20; H, 5.03.
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- 12) **5**: Calcd. C; 48.05, H; 5.47. Found. C; 47.98, H; 5.36. Hydrolysis of **5** gave a mixture of 1,4-diphenyl-1-butene (25%) and 1,4-diphenyl-2-butene (75%) in quantitative yield.

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