

Synthesis of Derivatives of Lanthanocene Complexes for the Isomerization of 1,5-Hexadiene

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The title complexes were prepared by the reaction of *tris*(cyclopentadienyl)lanthanides [Ln = Sm, Dy or Er] and *tris*(cyclopentadienyl)yttrium with tridentate Schiff base, N-(2-methoxyphenyl)salicylidineamine in THF under argon at ambient temperature and were characterized by elemental analysis and spectroscopic techniques (MS and IR). These lanthanide complexes were applied for the isomerization of 1,5-hexadiene. The isomerization resulted into a mixture of 1,4-hexadiene and methylenecyclopentane as intermediate and 2,4-hexadiene and methylcyclopentene as end products. The ratio of the linear to the cyclic product in the reaction is dependent upon amount of catalyst used.

Key Words: Tridentate Schiff base, Cyclopentadiene, Lanthanocene, 1,5-Hexadiene, Isomerization.

INTRODUCTION

The study on the lanthanide alkoxide complexes was intensified^{1,2} by the discovery of high temperature superconducting ceramics based on YBa₂Cu₂O. Likewise the co-ordination compounds formed by Schiff bases and *d*-transition elements have been extensively studied³. However, very limited efforts have been made to study the interaction between Schiff base ligands and lanthanide elements. It was revealed⁴ that *bis*(cyclopentadienyl) lanthanide alkyls could form organolanthanide enolate complexes {Cp₂Ln(μ-OC₂H₃)}₂. It was also found that the development of lanthanocene complexes with σ-bonded ligands was only possible when the *bis*(cyclopentadienyl)-lanthanide halides become available. Literature survey explains that Schiff base ligands are widely used to prepare Schiff base derivatives of lanthanocene complexes. These complexes have exhibited their importance in the chemical and biological fields^{5,6}. Recent research in organolanthanoid chemistry has been focused on complexes stabilized with Schiff base ligand system. Further interest in exploring the metal ion complexes with Schiff base ligands has continuously increased, since it has been recognized that many of the Schiff base derivatives of lanthanocene complexes may serve biologically as, naturally occurring ionophores.

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On the other hand, metal hydride complexes has proved a fundamental components in a wide range of stoichiometric and catalytic organometallic reactions⁷. However, the hydrides of lanthanoid metals have been previously described only for interstitial metallic compounds. The simple binary hydrides, LnH_x, have been known for many years⁸.

The research concerning lanthanoid complexes with Schiff bases have been devoted to their synthesis, structural studies and biological application of enzymes or protein bondings. In this regard, a large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as their ability to reversibly bound oxygen⁵, catalytic activity in hydrogenation of olefins⁹, transfer of amino group¹⁰, photochromic properties¹¹, complexing ability towards certain metals¹², catalytic synthesis of polyMMA¹³ and so on.

In this study, we are interested to prepare novel monomeric lanthanocene complexes {Cp₂Ln(C₁₄H₁₃NO₂)} Ln = Sm, Dy, Y, Er (**1-4**) by using tridentate Schiff base, N-(2-methoxyphenyl)salicylideneamine, ligand that has an electronic equivalency with cyclopentadienyl and then to study their catalytic effect on the isomerization of 1,5-hexadiene.

EXPERIMENTAL

All the complexes were synthesized by using the literature procedures¹⁴⁻¹⁶ and were characterized.

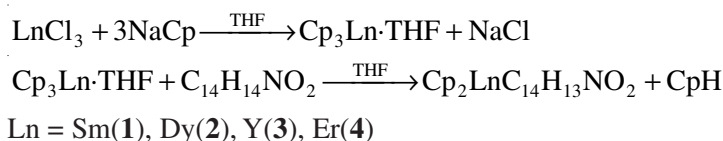
Synthesis of (η⁵-C₅H₅)₂Sm(C₁₄H₁₃NO₂) (1**):** Equimolar solutions of tridentate Schiff base and N-(2-methoxyphenyl) salicylideneamine in THF were added to a THF solution of Cp₃Sm (8.8 mmol/40 mL), stirred for 16 h at room temperature, concentrated under reduced pressure and kept aside for several days to afford orange yellow crystals of compound **1**. yield 55 %. Anal. calcd. (C₂₄H₂₂NO₂Sm): C 56.69, H 4.33, N 2.76 %; found: C 55.72, H 4.25, N 2.87 %. MS (EI): 443 (M⁺-Cp-schiffbase 100 %), 362 (M⁺-Schiff base 59.9 %), 283 (M⁺-2Cp 2.9 %), 217 (M⁺-Cp 1.5 %), 66 (Cp 18.3 %).

Synthesis of (η⁵-C₅H₅)₂Dy(C₁₄H₁₃NO₂) (2**):** The compound **2** was synthesized by reacting Cp₃Dy(THF) (5.46 mmol) and N-(2-methoxyphenyl) salicylideneamine (5.46 mmol) in THF to afford yellow crystals of compound **2** yield 55 %. Anal. calcd. (C₂₄H₂₂NO₂Dy): C 55.38 H 4.23, N 2.69 %; found: C 54.96, H 4.26, N 2.89 %. MS(EI): 455 (M⁺-Cp-Schiff base 100 %), 374 (M⁺-Schiff base 5.1 %), 294 (M⁺-2Cp 0.5 %), 229 (M⁺-Cp 0.4 %), 66 (Cp 11.6 %).

Synthesis of (η⁵-C₅H₅)₂Y(C₁₄H₁₃NO₂) (3**):** The compound **3** was synthesized by reaction of equimolar Cp₃Y(THF) (7.51 mmol) and N-(2-methoxyphenyl) salicylideneamine (7.51 mmol) in THF to afford yellow crystals of compound (**3**) yield 46 %. Anal. calcd. (C₂₄H₂₂NO₂Y): C 64.72, H 4.94, N 3.15 %; found: C 64.49, H 4.95, N 3.48 %. MS (EI): 379 (M⁺-Cp-Schiff base 100 %), 299 (M⁺-Schiff base 43.9 %), 219 (M⁺-2Cp 0.4 %), 154 (M⁺-Cp 0.2 %), 66 (Cp 11.6 %).

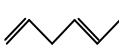
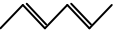


Synthesis of $(C_5H_5)_2Er(OC_{14}H_{13}NO)$ (4): The compound **4** was synthesized by reaction of equimolar $Cp_3Er(THF)$ (2.82 mmol) and N-(2-methoxyphenyl) salicylideneamine in (2.82 mmol) THF to afford bright yellow crystals. yield 45 %. Anal. calcd. ($C_{24}H_{22}NO_2Er$): C 55.17, H 4.21, N 2.68 %; found: C 55.11, H 4.22, N 2.73 %. MS (EI): 457 (M^+ -Cp-Schiff base 100 %), 376 (M^+ -Schiff base 66.4 %), 297 (M^+ -2Cp 0.0.9 %), 232 (M^+ -Cp 1.4 %), 65 (Cp 10.6 %).

The synthetic scheme for the title complexes is illustrated below:



The newly synthesized lanthanocene complexes along with NaH were attempted for the isomerization of 1,5-hexadiene. Sodium hydride was washed with THF and dried under vacuum. 1,5-Hexadiene was dried by treating with CaH_2 and distilled under argon. Following general procedure was adopted for the isomerization (for example, entry 1 in Table-1): A 25 mL schlenk flask equipped with a Teflon stopcock was charged under argon with 0.052 g (0.10 mmol) of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ and 0.12 g of NaH. Then, 3 mL THF was poured along with stirring, cooled to $-78^\circ C$ and then 0.164 g (0.24 mL) of 1,5-hexadiene was introduced by a syringe. The reaction mixture was allowed to warm upto $60^\circ C$ and was continued at this temperature for 24 h. The reaction was quenched with 1 mL of methanol. Then reaction mixture was distilled under reduced pressure and the distillate was collected in the Schlenk flask at $-78^\circ C$. The distillate thus obtained was injected into the GC and the products were identified by comparing with standard compounds.

TABLE-1
EFFECT OF CATALYST ON ISOMERIZATION OF 1,5-HEXADIENE

Cat.	Conv. (%)	Selectivity (%)				Linear/cyclic
						
$(C_5H_5)_2Sm(OC_{14}H_{13}NO)$	28.7	80.6	2.4	12.4	4.6	83.0/17.0
$(C_5H_5)_2Dy(OC_{14}H_{13}NO)$	25.8	81.3	2.7	11.0	4.2	84.0/16.0
$(C_5H_5)_2Y(OC_{14}H_{13}NO)$	25.7	75.0	7.1	13.1	4.8	82.1/17.9
$(C_5H_5)_2Er(OC_{14}H_{13}NO)$	20.6	55.8	9.1	25.2	9.9	64.9/35.1
$(C_5H_5)_2ErCl(OC_{14}H_{13}NO) \cdot THF$	2.0	62.1	7.0	23.3	7.6	69.1/30.9
$ErCl_3$	1.1	100.0	trace	trace	trace	–

Reaction condition: time: 24 h, temperature: $60^\circ C$, solvent: THF.

RESULTS AND DISCUSSION

Since the percentage conversion of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ is more than any other attempted complexes (Table-1), therefore for convenience this complex was used as a representative of all others in order to study the effect of catalyst,

temperature, catalyst/substrate ratio and time on the isomerization of 1,5-hexadiene (HD). In addition to these, $(C_5H_5)_2ErCl(OC_{14}H_{13}NO) \cdot THF$ complex and $ErCl_3$ were used as standards.

At 60 °C (Table-1), the $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ favours the conversion of 1,5-hexadiene into linear products, especially 1,4-hexadiene (80.6 %) while $(C_5H_5)_2Er(OC_{14}H_{13}NO)$ converts 1,5-hexadiene into cyclic ones, preferably methylenecyclopentane (25.2 %). No significant difference is observed between the conversion efficiency of $(C_5H_5)_2Er(OC_{14}H_{13}NO)$ and $(C_5H_5)_2ErCl(OC_{14}H_{13}NO) \cdot THF$. This suggests that both complexes may offer same kind of hydride system. Generally, the catalytic efficiency of $(C_5H_5)_2Sm(OC_{14}H_{13}NO)$ is better (28.7 %) than any other used complexes which may be because of the ionic radius of samarium is larger than any other used metals. Further no catalytic activity was found with $ErCl_3/NaH$ system.

Effect of temperature (Fig. 1) shows that at high temperature 1,4-hexadiene is the prominent product while at lower temperature methylene cyclopentane is the major one (Table-2). Conclusively 60 °C is the favourable temperature for the isomerization of 1,5-hexadiene by such type of the lanthanoid complexes.

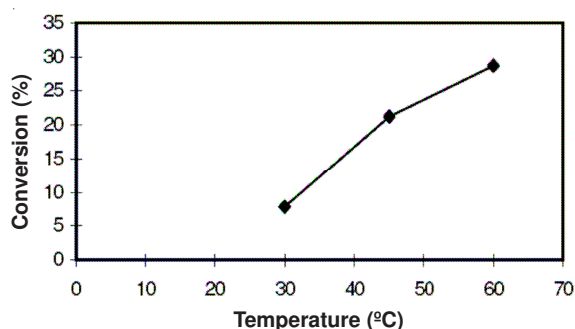

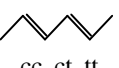




Fig. 1. Effect of temperature on the conversion of 1,5-hexadiene

TABLE-2
EFFECT OF TEMPERATURE ON ISOMERIZATION OF 1,5-HEXADIENE

Temp. (°C)	Conv. (%)	Selectivity (%)				Linear/cyclic
						
30	7.9	28.8	5.2	49.0	17.0	36.7/63.3
45	21.3	75.3	3.5	15.6	5.6	78.8/21.2
60	28.7	80.6	2.4	12.4	4.6	83.0/17.0

Reaction condition: $(C_5H_5)_2Sm(OC_{14}H_{13}NO)/NaH$: 1:50; time = 24 h; solvent: THF.

The results of catalyst/substrate ratio explain (Fig. 2) that at 1:10-1:20 molar ratios, there was no significant difference in the conversion of 1,5-hexadiene into either linear (87 and 83 %) products or cyclic (13 and 17 %) ones. However, at 1:40 molar ratio, the difference was remarkable. The linear products were smaller but

cyclic were higher at this molar ratio (Table-3). This indicates that the quantity of linear products increases with increase in the amount catalyst, which is in accordance with results reported earlier¹⁷.

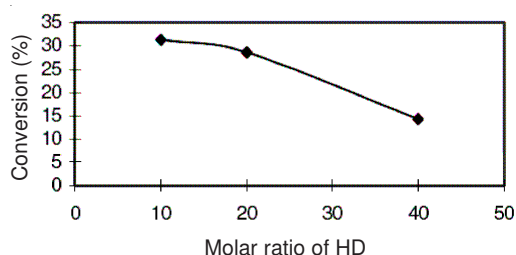
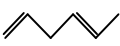
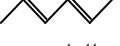




Fig. 2. Effect of catalyst/1,5-hexadiene molar ratio on isomerization of 1,5-hexadiene

TABLE-3
EFFECT OF MOLAR RATIO ON ISOMERIZATION OF 1,5-HEXADIENE

Mole ratio cat./HD	Conv. (%)	Selectivity (%)				Linear/ cyclic
			 cc, ct, tt			
1:10	31.3	84.0	3.0	9.5	3.5	87.0/13.0
1:20	28.7	8.6	2.4	12.4	4.6	83.0/17.0
1:40	14.4	46.1	10.9	32.4	10.5	51.0/43.0

Reaction conditions: $(C_5H_5)_2Sm(OC_{14}H_{13}NO)/NaH$; 1:50, time = 24 h; temp. = 60 °C; solvent: THF.

The effect of time on the isomerization of 1,5-hexadiene explains (Fig. 3) that up till 10 h, the efficiency of the catalyst is very rapid (25.6 %). During further 10 h, it is comparatively slower (27.4 %) and after this there was no significant increase (28.7 %) in the conversion of 1,5-hexadiene (Table-4). It is concluded that isomerization of 1,5-hexadiene can be completed during 20 h by using such type of catalytic system.

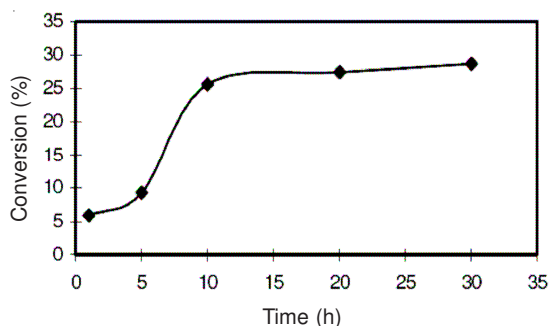






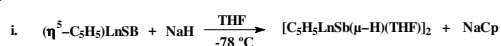
Fig. 3. Effect of time on isomerization of 1,5-hexadiene

TABLE-4
EFFECT OF TIME ON ISOMERIZATION OF 1,5-HEXADIENE

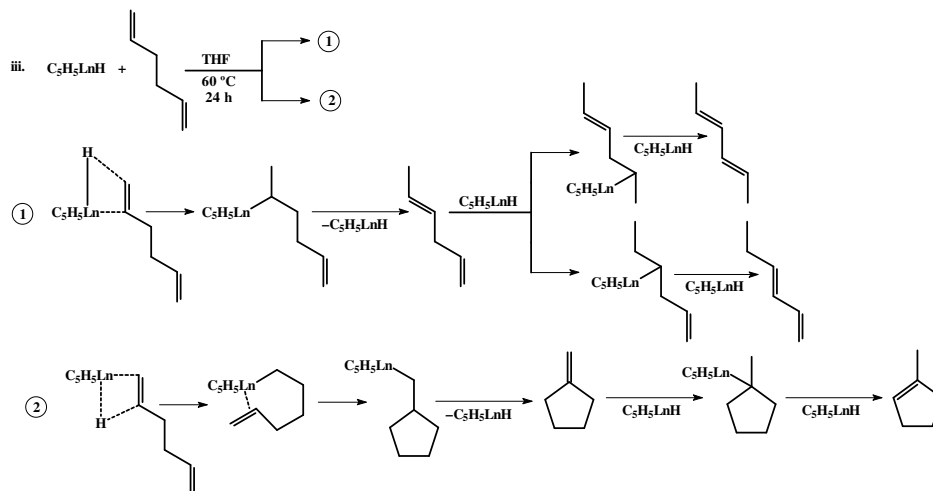
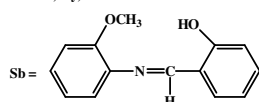
Time (h)	Conv. (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
1	5.9	8.2	18.4	53.7	19.7	26.6/73.4
5	9.3	5.5	33.2	41.9	19.4	38.7/61.3
10	25.6	81.7	3.2	11.2	9.0	84.8/15.2
20	27.4	82.4	2.3	11.1	4.2	84.7/15.3
30	28.7	80.6	2.4	12.4	4.6	83.0/17.0

Reaction conditions: $(C_5H_5)_2Sm(OC_{14}H_{13}NO)/NaH = 1:50$, temp.: 60 °C, solvent: THF.

The proposed mechanistic pathway for the isomerization of 1,5-hexadiene is illustrated by the following **Scheme-I**.



Ln = Sm, Dy, Y and Er



Scheme-I

Conclusion

Isomerization of 1,5-hexadiene by organolanthanoid/NaH system, results in a mixture of 1,4-hexadiene, 1,3-hexadiene, 2,4-hexadiene, methylene-cyclopentane and methylcyclopentene, respectively. Further study is to improve the catalytic efficiency of such type of complexes.

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