

## Schiff Base Derivative of Cyclooctatetraenyl Lanthanoid/NaH Catalytic Systems for the Isomerization of 1,5-Hexadiene

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The different types of the tridentate Schiff base {N-(2-methoxyphenyl)-salicylideneamine} derivative of lanthanoid cyclooctatetraenyl complexes [COTLn Schiff base·2THF (Ln = Sm, Eu, Gd and Er)] along with NaH are proved to be a versatile tool for the isomerization of 1,5-hexadiene. The isomerization resulted a mixture of products such as 1,4-hexadiene, 1,3-hexadiene, 2,4-hexadiene, methylenecyclopentane and methylcyclopentene. Among these 1,4-hexadiene and methylenecyclopentane were the end products while 1,3-hexadiene, 2,4-hexadiene and methylcyclopentene were the intermediates. From the results it is assumed that radius of the metal is an important factor in determining the catalytic efficiency of the complexes.

**Key Words:** Tridentate Schiff base, Cyclooctatetraene, Lanthanocene, 1,5-hexadiene, Isomerization.

### INTRODUCTION

Schiff base ligands are considered "Privileged ligands" because they are easily prepared by the condensation between aldehydes and imines. The stereogenic centres or other elements of chirality can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for the large variety of useful catalytic transformations<sup>1</sup>. The development in organolanthanoid chemistry has primarily focused on complexes stabilized by Schiff base ligand system. Moreover interest in exploring the metal ion complexes with Schiff base ligands has continually increased, since it has been recognized that many of such complexes may serve as biologically important as well as naturally occurring ionophores.

The literature verifies that metal hydride complexes are fundamental components in a wide range of stoichiometric and catalytic organometallic reactions<sup>2</sup>. It is also clear that hydride complexes of lanthanoid metals are important factors for the rapid advancement of the developing organolanthanoid chemistry.

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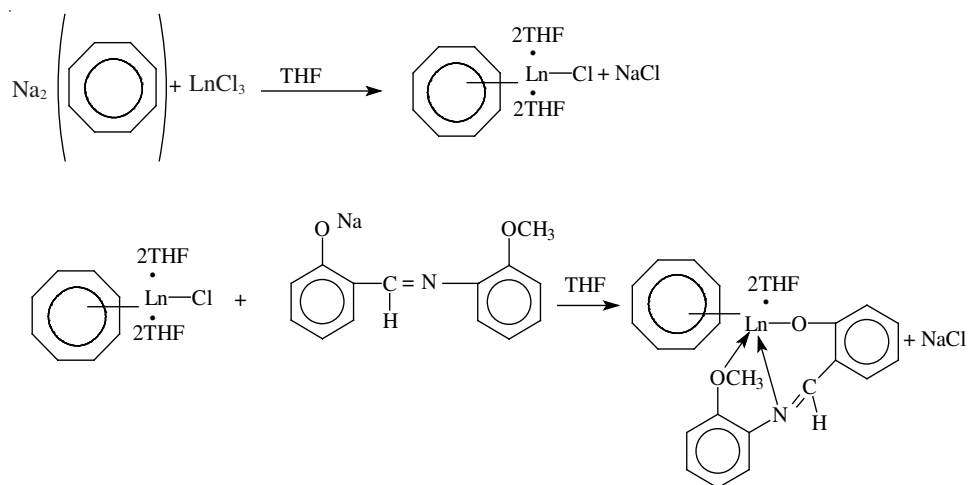
In past, a large number of Schiff bases and their metal-complexes have been studied for their interesting properties such as their ability to reversibly bind oxygen<sup>3</sup>, catalytic activity in the hydrogenation of olefins<sup>4</sup>, transfer of amino group<sup>5</sup>, photochromic properties<sup>6</sup>, complexing ability towards toxic metals<sup>7</sup>, catalytic synthesis of polymethylmethacrylate<sup>8</sup> and isomerization of 1,5-hexadiene<sup>9</sup>, *etc.*

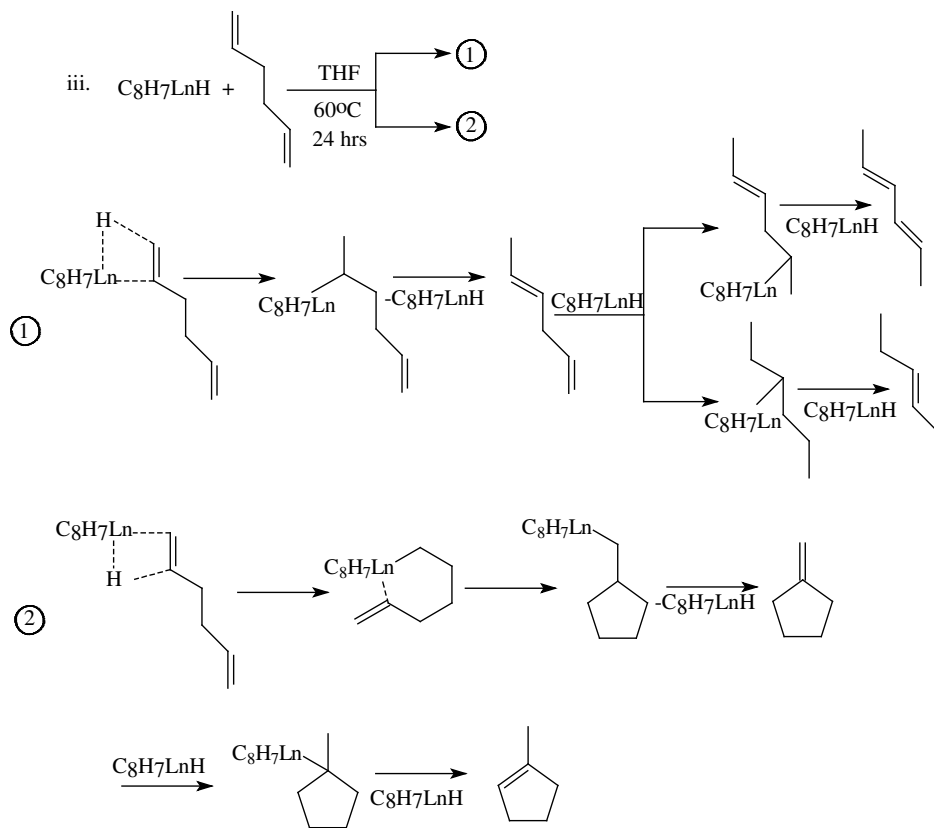
In another study, a high molecular weight poly( $\beta$ -pinene) along with high productivity was prepared by using Schiff base nickel complexes belended with methylaluminumoxane.

It was also found that ligand structure had a substantial effect on the polymerization in terms of the productivity and the molecular weight<sup>10</sup>. Later on it was also observed that ruthenium complexes of Schiff base exhibit a high activity and chemoselectivity in a variety of catalytic processes such as ring closing metathesis, alkyne dimerization, enol ester synthesis and ring opening metathesis polymerization<sup>11</sup>. Keeping in mind the importance of Schiff base ligands, the present study was carried out to check the effect of catalyst, temperature, catalyst/hexadiene molar ratio and time on the isomerization 1,5-hexadiene by using the titled lanthanoid complexes.

### EXPERIMENTAL

The tridentate Schiff base {N-(2-methoxyphenyl)salicylideneamine} was synthesized by the condensation of equimolar quantities of prepurified salicylaldehyde and anisidine in toluene at room temperature. The resulting tridentate Schiff base was purified by recrystallization in petroleum ether, dried well under vacuum and was used for complexation. The tridentate Schiff base derivative of lanthanoid cyclooctatetraenyl complexes, used for this study, were synthesized by using the literature procedure<sup>8,12</sup> and were characterized with the help of elemental analysis and mass spectrometric technique (**Scheme-I**).





Scheme-I

**$C_{30}H_{35}NO_4Sm$  (1):**  $m/z$  (%): 425 ( $M^+$ -COT-THF 5.7), 448 ( $M^+$ -Schiff base-THF 2.5), 203 (COT 100), 226 (Schiff base 5.5) 72 (THF 1.5). Anal.  $C_{30}H_{35}NO_4Sm$ . Calcd: C, 57.78; H, 5.62; N, 2.25. Found: C, 57.74; H, 5.60; N, 2.21.

**$C_{30}H_{35}NO_4Eu$  (2):**  $m/z$  (%): 427 ( $M^+$ -COT-THF 6.2), 450 ( $M^+$ -Schiff base-THF 55.8), 203 (COT 100), 226 (Schiff base 2.1), 72 (THF 1.9) Anal.  $C_{30}H_{35}NO_4Eu$ . Calcd: C, 57.60; H, 5.60; N, 2.24. Found: C, 57.63; H, 5.57; N, 2.21.

**$C_{30}H_{35}NO_4Gd$  (3):**  $m/z$  (%): 432 ( $M^+$ -COT-THF 5.6), 455 ( $M^+$ -Schiff base-THF 56.1), 203 (COT 100), 226 (THF 1.5). Anal.  $C_{30}H_{35}NO_4Gd$ . Calcd: C, 57.14; H, 5.55; N, 2.22. Found: C, 57.16; H, 5.57; N, 2.21.

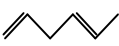
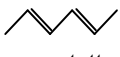


**$C_{30}H_{35}NO_4Er$  (4):**  $m/z$  (%): 442 ( $M^+$ -COT-Schiff base 5.5), 465 ( $M^+$ -Schiff base-THF 55.9), 203 (COT 100), 226 (THF 1.8). Anal.  $C_{30}H_{35}NO_4Er$ . Calcd: C, 56.25; H, 5.47; N, 2.19. Found: C, 56.22; H, 5.50; N, 2.21.

These complexes along with a cocatalyst (NaH) were used for the isomerization of 1,5-hexadiene<sup>13</sup>. The resulting isomerized products were identified with the help GLC technique by comparing the chromatograms of the unknown with that of known ones.

## RESULTS AND DISCUSSION

Since the catalytic efficiency and per cent yield of complex **1** ( $C_{30}H_{35}NO_4Sm$ ) was observed better than other attempted (**2-4**) complexes (Table-1), therefore for simplification the complex **1** was used as a representative of all the tested catalysts in order to study the effect of catalyst, temperature, catalyst/substrate molar ratio and time on the isomerization of 1,5-hexadiene.

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

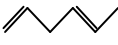
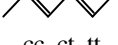


Cat.	Conv. (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
<b>1</b> $C_{30}H_{35}NO_4Sm$	29.6	84.6	2.6	13.5	5.6	87.2/19.1
<b>2</b> $C_{30}H_{35}NO_4Eu$	26.8	80.3	2.9	11.8	4.9	83.2/16.7
<b>3</b> $C_{30}H_{35}NO_4Gd$	25.7	74.0	8.4	14.1	4.6	82.4/18.7
<b>4</b> $C_{30}H_{35}NO_4Er$	20.6	57.8	9.6	24.2	9.6	67.4/33.8
$ErCl_3$	0.8	50.0	50.0	trace	trace	–

Reaction conditions: catalyst/hexadiene = 1:20; catalyst/NaH; 1:50; time: 24 h; temperature: 60 °C; solvent: THF.

At 60 °C, all the the complexes (**1-4**) favour the production of linear isomer such as 1,4-hexadiene. The percentage of 1,4-hexadiene was observed maximum (84.6 %) in case of complex **1** while it was seen minimum (57.8 %) in case of the complex **4**. Similarly the conversion of 1,5-hexadiene into cyclic isomers especially methylenecyclopentane was found maximum (24.2 %) in case of complex **4** while was observed minimum (11.8 %) for the complex **2**. Overall the conversion rate of complex **1** was observed maximum (29.6 %) while the other complexes (**2-4**) showed 26.8, 25.7 and 20.6 %, respectively. The reason is the ionic radius of the samarium metal is larger than europium, gadolinium and erbium and hence the coordination sphere in case of complex **1** is larger than complex **2**, **3** and **4**, respectively. The greater the coordination sphere of the metal, the greater is the coordination number and hence greater is the catalytic efficiency of the catalyst. That is the reason, complex **1** exhibited maximum conversion (29.6 %) while catalyst **4** showed minimum (20.6 %). Further there was not found any remarkable activity (0.8 %) with  $ErCl_3/NaH$  system.

Effect of temperature (Table-2), indicates that the conversion of 1,5-hexadiene into its isomers increases with the temperature being maximum (30.6 %) at 60 °C and minimum (23.4 %) at 45 °C. Moreover the 1,4-hexadiene was observed the prominent isomer (81.5 %) at 60 °C temperature while at 45 °C temperature, methylenecyclopentane was found the major component. Conclusively the conversion ratio different isomers (linear/cyclic) was observed maximum (84.8/18.9) at 60 °C (Fig. 1). Earlier similar type of the results were observed with organotitanium complexes<sup>9</sup>.

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

Temp. (°C)	Conv. (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
45	23.4	74.2	3.2	18.5	4.9	77.4/23.4
60	30.6	81.5	3.3	15.2	3.7	84.8/18.9
75	33.8	80.5	2.5	17.1	3.5	83.0/20.6
45	23.4	74.2	3.2	18.5	4.9	77.4/23.4
60	30.6	81.5	3.3	15.2	3.7	84.8/18.9

\*: Reaction conditions: Cat/NaH: 1:50; cat/hexadiene: 1:20; time = 24 h; solvent: THF.

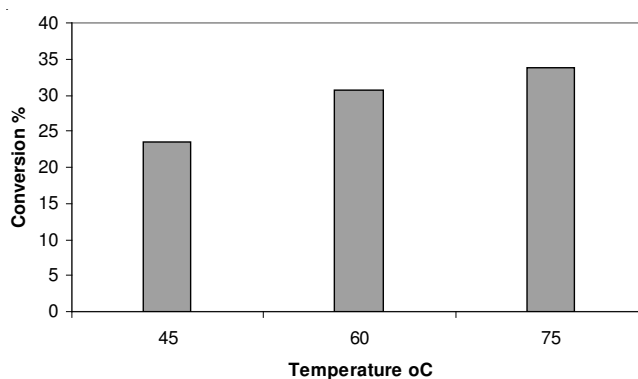

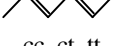




Fig. 1. Effect of temperature (°C) on the isomerization of 1,5-hexadiene

The effect of catalyst/substrate molar ratio explains (Table-3 and Fig. 2) that in case of 1:10-1:20 molar ratio, there was no significant difference in the conversion of 1,5-hexadiene into either linear (82.5 and 81.6 %) products or cyclic (11.5 and 12.2 %) ones. However, a remarkable difference was found at 1:40 molar ratio. The percentage of 1,4-hexadiene was observed less (47.2 %) than others but the percentage of methylenecyclopentane was more (30.4 %) at this molar ratio than 1:10 and 1:20, respectively. This justifies that the more the catalyst, the more the products which is in accordance with results reported earlier<sup>13</sup>.

TABLE-3  
EFFECT OF CATALYST/HEXADIENE MOLAR RATIO  
ON ISOMERIZATION OF 1,5-HEXADIENE\*

Mole ratio cat./HD	Conv. (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
1:10	27.8	82.5	3.1	11.5	5.2	85.6/16.7
1:20	29.7	81.6	2.9	12.2	6.6	84.5/18.8
1:40	21.3	47.2	11.4	30.4	10.5	58.6/40.9

\*: Reaction conditions: Cat/NaH; 1:50; time = 24 h; temp = 60 °C; solvent: THF.

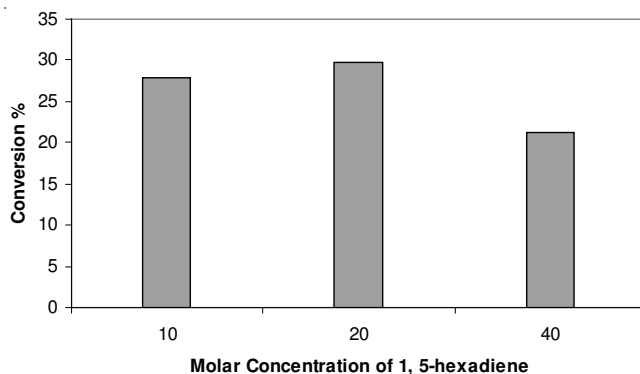
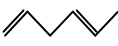
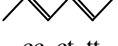




Fig. 2. Effect of catalyst/cocatalyst molar ratios on the isomerization of 1,5-hexadiene

The effect of time (Table-4 and Fig. 3) shows that uptill 10 h, the conversion rate was very rapid, being 20.4 % but during further 10 h, it was comparatively slower, 27.5 % and after this there was no significant increase (30.8 %) in the converted products. Conclusively isomerization of 1,5-hexadiene can be completed during 20 h by using such type of catalytic system.

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

Time (h)	Conv. (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
0	1.5	traces	–	traces	–	–
5	5.5	6.1	30.2	25.5	20.4	36.3/45.9
10	20.4	56.7	6.2	15.2	9.5	62.9/24.7
20	27.5	83.2	5.3	13.1	4.2	88.5/17.3
30	30.8	80.6	2.1	11.4	4.6	82.7/16.0

\*: Reaction conditions: Cat/NaH; 1:50; cat/hexadiene: 1:20; temp =60 °C; solvent: THF.

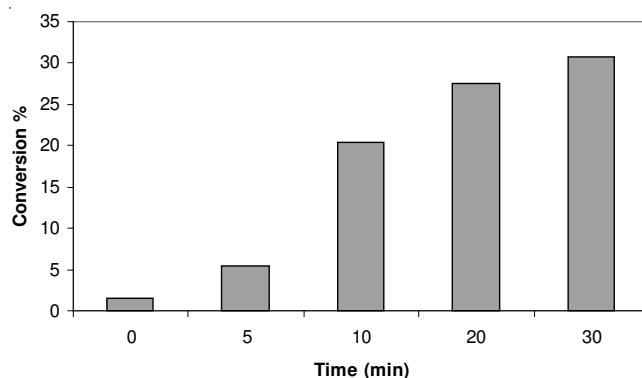
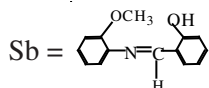
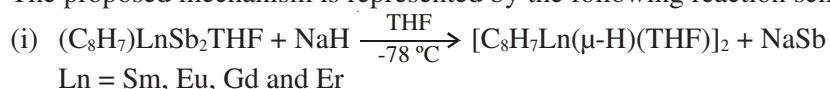


Fig. 3. Effect of time on the isomerization of 1,5-hexadiene

The proposed mechanism is represented by the following reaction scheme.



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