



A New Versatile Tool for Isomerization: Synthesis and Characterization of Lanthanide Chloride Tridendate Schiff base Derivatives

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The different types of the tridentate Schiff base N-(2-methoxyphenyl) salicylideneamine derivative of lanthanideindenyl chloride complexes [Ind·Ln-Schiff base·Cl·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 in a mixture of hexa-1, 4-diene, hexa-2,4-diene, methylenecyclopentane and methylcyclopentene. Hexa-1,4-diene and methylenecyclopentane were the major products while hexa-2,4-diene and methylcyclopentene were the minor ones. The results showed that ligand size and radius of the metal are important factors in determining the catalytic efficiency of the complexes.

Keywords: Schiff base, Indene, Lanthanocene, Hexa-1,5-diene, Isomerization.

INTRODUCTION

Recently the development in organolanthanoid chemistry has primarily focused on complexes stabilized by Schiff base ligands system. Moreover, the trend of extraction of metal complex ions by Schiff based ligands is increased day by day. It was also investigated that these types of complexes have great importance in natural ionospheres [1]. On the other hand, complexes of metal hydrides are considered as vital and fundamental compounds for metallic reactions. It was observed that lanthanide alkoxide complexes along with LiOt-But resulted in high yield with narrow polydispersity of syndiotactic-rich ($rr = 74$ to 80%) polymethylmethacrylate [2]. Similarly the ring opening polymerization was successfully catalyzed by the organosamarium(II) complex and stops the co-polymerization of monomer of L-lactide [3]. Alkyl and hydro complexes of yttrium result the atactic polymerization of *tert*-butylacrylate and acrylonitrile. The molecular weight (M_n) of acrylate polymer was found to be 720,000 with low distribution of molecular mass ($M_w/M_n = 1.50-2.00$) while the molecular mass of acrylonitrile polymer was observed to be greater than 105 but the polydispersity (M_w/M_n) was found to be greater than five [4]. The aryloxosamarium(II) complex showed high activity (yield = 99% , $M_n = 120,000$, $M_w/M_n = 1.40$) for the ring opening polymerization of ϵ -caprolactone

[5]. On the other hand organolanthanoid complexes can also be successfully cyclopolymerized the neat hexa-1,5-dieneto poly (methylene-1,3-cyclopentadiene) rather than promoting the cyclization of methylenecyclopentane [6]. The hydrides of the lanthanide metals were previously explained for interstitial metallic components and such types of simple hydrides were used for many years [7]. The literature survey verifies that lanthanide complexes are key factors for the rapid development in the field of organo lanthanoid chemistry. The investigations concerning lanthanide complexes with Schiff bases have been devoted to their syntheses, structural studies and biological application of metal enzymes or protein bondings. Schiff base ligands are privileged ligands because they can easily be synthesized by the condensation of imines and aldehydes. Schiff base ligands can coordinate different kinds of metals and stabilize these metals in different oxidation states, enabling the use of Schiff base complexes for the huge quality of important catalytic transformations [8]. Previously huge quantity of Schiff bases metal complexes were studied for investigating their different properties such as their reversibly binding of oxygen, activity of catalyst for the olefins's hydrogenation, transfer of amino group, photochromic properties, complexation ability towards toxic metals and catalytic synthesis of polymethylmethacrylate and isomerization of hexa-1,5-diene [9-12]. Schiff base derivatives of ruthenium(III)

complexes isomerized effectively the *o*-allyl systems such as 1,4-diallyloxybutane and 4-allyloxybutane-1-ol [13]. The catalysts showed the stereo-selectivity in the migration of double bond of allyl family to 1-propyl group and high selectivity of allyloxy alcohol's isomerization to cyclic acetal [14].

In another study, a high mass poly(β -pinene) having strong output efficiency was prepared by using Schiff base nickel complexes blended with methylaluminoxane. It was also found that ligand structure had a considerable impact on the polymerization with respect to its molecular mass and productivity [15]. Later on it was also observed that Schiff base ruthenium complexes reveal a high chemo-selectivity and high activity in a range of different catalytic processes such as dimerization of alkyne, ring closing and ring opening metathesis polymerization and synthesis of enol ester [16]. Keeping in mind the Schiff base derivatives of lanthanide complexes were prepared.

EXPERIMENTAL

Sodium hydride was washed with THF and dried under vacuum. Hexa-1,5-diene was dried over CaH_2 and was distilled under argon. Lanthanide complexes (Table-1) along with a co-catalyst (NaH) were used for the isomerization of hexa-1,5-diene. Following general procedure was used for this isomerization reaction. A 25 mL Schlenk flask fitted with a Teflon stopcock was charged under argon with 0.067 g (0.10 mmol) of the lanthanide complex and 0.15 g of NaH. Then THF (4 mL) was poured to it with constant stirring, cooled to -78°C . 0.165 g (0.24 mL) hexa-1,5-diene was introduced to it. The mixture was allowed to warm up to 60°C . The reaction mixture was quenched after the respected time (Table-4) with 1 mL of methanol. The mixture was distilled under reduced pressure condition and the distillate compound was collected in the Schlenk flask at -78°C . The distillate thus obtained was injected into the GLC equipment and the isomerized products were identified by comparing their chromatograms with that standard ones.

$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{SmCl}$ (1): m/z (%): 372.5 (M^+ -Indenyl-THF-Cl 100), 483.5 (M^+ -Schiff base-THF-Cl 56.5), 115 (indenyl 2.7), 226 (Schiff base 1.5), 72 (THF 2.5) Anal. $\text{C}_{31}\text{H}_{35}\text{NO}_4\text{SmCl}$. Calcd: C, 55.481; H, 5.225; N, 2.083. Found: C, 55.521; H, 5.024; N, 2.063.

$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{EuCl}$ (2): m/z (%): 374.5 (M^+ -Indenyl-THF-Cl 100), 485.5 (M^+ -Schiff base-THF-Cl 55.7), 115 (Indenyl 2.5), 226 (Schiff base 1.9) 72 (THF 2.1) Anal. $\text{C}_{31}\text{H}_{35}\text{NO}_4\text{EuCl}$. Calcd: C, 55.323; H, 5.205; N, 2.087 Found: C, 55.291; H, 5.212; N, 2.093.

$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{GdCl}$ (3): m/z (%): 379.5 (M^+ -Indenyl-THF-Cl 100), 490.5 (M^+ -Schiff base-THF-Cl 56.7), 115 (Indenyl 2.3), 226 (Schiff base 2.0) 72 (THF 2.5) Anal. $\text{C}_{31}\text{H}_{35}\text{NO}_4\text{GdCl}$. Calcd: C, 54.713; H, 5.175; N, 2.077 Found: C, 54.761; H, 5.203; N, 2.094.

$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{ErCl}$ (4): m/z (%): 389.5 (M^+ -Indenyl-THF-Cl 100), 500.5 (M^+ -Schiff base-THF-Cl 55.9), 115 (Indenyl 2.5), 226 (Schiff base 2.4) 72 (THF 2.9) Anal. $\text{C}_{31}\text{H}_{35}\text{NO}_4\text{ErCl}$. Calcd: C, 54.115; H, 5.097; N, 2.049 Found: C, 54.143; H, 5.125; N, 2.077.

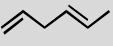
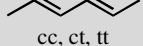
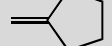
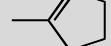
RESULTS AND DISCUSSION

The tridentate Schiff base [N-(2-methoxyphenyl)salicylideneamine] was synthesized by refluxing equimolar quantities of purified salicylaldehyde and anisidine in toluene for 5 h. The tridentate Schiff base derivatives of lanthanide complexes used for this study were synthesized and characterized with the help of elemental analyses and mass spectrometric technique. For this purpose equimolar quantity of the anhydrous chloride of the respective lanthanoid element (Sm, Eu, Gd and Er) was reacted with sodium salt of indene in THF in order to get the indenyl derivative of lanthanoid dichloride complex. Then this complex was reacted with an equimolar quantity of sodium salt of tridentate Schiff base in THF in order to get the tridentate Schiff base derivative of indenyl lanthanoidchloride complexes [17,18] (**Scheme-I**).

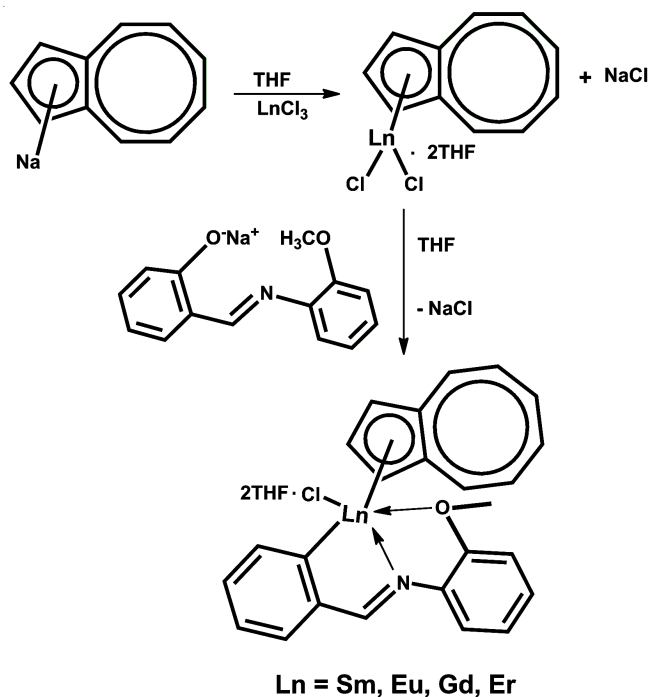
The titled lanthanide complexes **1-4** derived from tridentate Schiff base (Table-1) are applied in order to study the isomerization of hexa-1,5-diene (**Scheme-II**) under different reaction conditions viz. catalyst co-catalyst, reaction temperature and reaction time.

Since the catalytic efficiency of complex **1** ($\text{C}_{31}\text{H}_{35}\text{NO}_4\text{SmCl}$) was observed better than other attempted complexes (Table-1), therefore for simplification this complex was used as a representative of all the attempted complexes in order to study the effect of catalyst, temperature, catalyst/substrate ratio and time on the isomerization of hexa-1,5-diene. At 60°C all the complexes **1-4** favour the production of linear isomer such as hexa-1,4-diene. The percentage of 1, 4-hexadiene was maximum (84.6 %) in case of complex **1** while it was minimum (57.8 %) for complex **4**. Similarly, the conversion of hexa-1,5-diene 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 percentage of complex **1** was observed maximum (28.7 %) while other complexes (**2-4**) showed 25.8, 25.7 and 20.6 % respectively. The reason is the ionic radius of samarium is

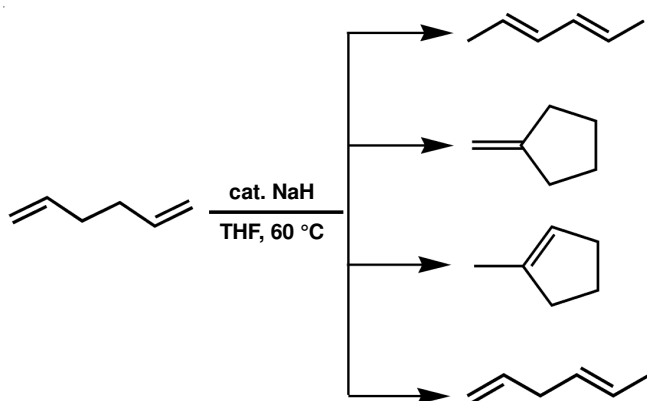
TABLE-1
EFFECT OF CATALYST ON ISOMERIZATION OF 1,5-HEXADIENE*

Catalyst	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{SmCl}$	29.6	84.6	2.6	13.5	5.6	87.2/19.1
$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{EuCl}$	26.8	80.3	2.9	11.8	4.9	83.2/16.7
$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{GdCl}$	25.7	74.0	8.4	14.1	4.6	82.4/18.7
$\text{C}_{31}\text{H}_{35}\text{NO}_4\text{ErCl}$	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), 24 h at 60°C in THF.



Scheme-I: Preparation of the catalyst



Scheme-II: Isomerization of hexa-1,5-diene in the presence of lanthanides complexes

larger than europium, gadolinium and erbium and hence the coordination sphere in case of complex **1** is larger than complexes **2**, **3** and **4**, respectively. The coordination sphere of the metal is directly proportional to the coordination number and hence the catalytic efficiency of catalyst is also increased. That is why, complex **1** exhibited maximum conversion (28.7 %) while catalyst **4** showed minimum (20.6 %). Further there was not found any remarkable activity with ErCl_3/NaH system.

Effect of temperature (Table-2), indicates that the conversion of hexa-1,5-diene into its isomers increases with the

temperature being maximum (29.6 %) at 60 °C and minimum (8.5 %) at 30 °C. Moreover the 1,4-hexadiene was observed the prominent isomer at higher temperature (60 °C) while at lower temperature methylene cyclopentane was found the major component. Conclusively the catalytic efficiency was observed appreciable at 60 °C (Fig. 1). Earlier similar types of the results were observed with organotitanium complexes [19].

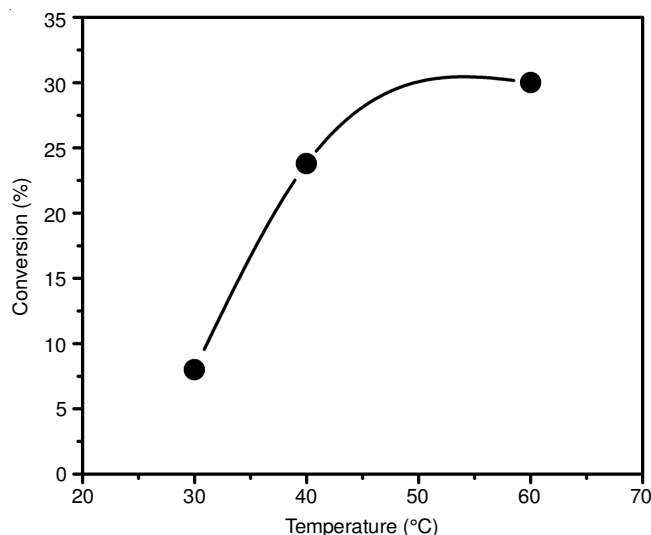


Fig. 1. Effect of temperature (°C) on the isomerization of hexa-1,5-diene

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 hexa-1,5-diene into either linear (85.5 and 81.6 %) products or cyclic (11.3 and 13.2 %) ones. However, a remarkable difference was found at 1:40 molar ratio. The percentage of 1,4-hexadiene was observed smaller (44.2 %) than others but the percentage of methylene cyclopentane was higher at this molar ratio than 1:10 and 1:20 respectively. This justifies that the product is directly depend on the amount of the catalyst, which is in accordance with results reported earlier [20].

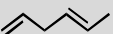
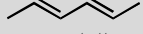
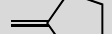
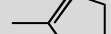
The effect of time (Table-4 and Fig. 3) shows that up to 10 h, the catalytic efficiency of the catalyst was very rapid, being 25.4 %, but during further 10 h, it was comparatively slower 26.8 %, after this there was no significant increase (27.5 %) in the converted products. Conclusively isomerization of 1,5-hexadiene can be completed during 20 h by using such type of catalytic system. The mechanism is proceeded by the reaction of the titled complex **1** with NaH in THF in order to produce indenyl lanthanide hydride derivative which is the active species for the isomerization of 1,5-hexadiene. At first step it interacts with the double bond of either 1-position or of

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

Temperature (°C)	Conversion (%)	Selectivity (%)				Linear/cyclic
			cc, ct, tt			
30	8.5	28.8	4.9	51.0	18.2	33.7/69.2
45	22.4	74.2	3.7	17.5	4.9	77.9/22.4
60	29.6	81.5	2.6	14.2	3.7	84.1/17.9

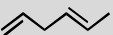
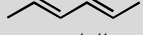
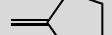
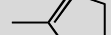
Reaction conditions: Catalyst/NaH (1:50) catalyst/1,5-hexadiene (1:20), 24 h, in THF.

TABLE-3
EFFECT OF MOLE RATIO OF CATALYST/HEXADIENE ON ISOMERIZATION OF 1,5-HEXADIENE

Mole ratio catalyst/HD	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
1:10	29.8	85.5	3.7	11.3	5.5	89.2/16.8
1:20	27.7	81.6	2.6	13.2	7.6	84.2/20.8
1:40	15.3	44.2	12.4	33.4	11.5	56.6/44.9

Reaction conditions: Catalyst/NaH (1:50) 24 h at 60 °C in THF.

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

Time (h)	Conversion (%)	Selectivity (%)				Linear/cyclic
			 cc, ct, tt			
1	4.9	6.2	17.4	53.7	19.7	26.6/73.4
5	8.5	6.5	33.2	41.9	19.4	38.4/61.3
10	25.4	77.7	3.2	11.2	9.0	84.8/15.2
20	26.8	83.2	2.3	11.1	4.2	84.7/15.3
30	27.5	80.6	2.4	12.4	4.6	83.0/17.0

Reaction conditions: Catalyst/NaH (1:50) catalyst/hexadiene (1:20) 60 °C, THF.

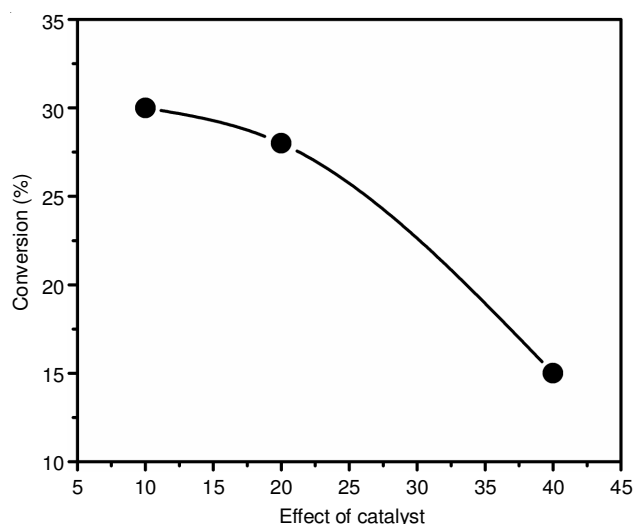


Fig. 2. Effect of catalyst/hexa-1,5-diene molar ratio on this isomerization reaction

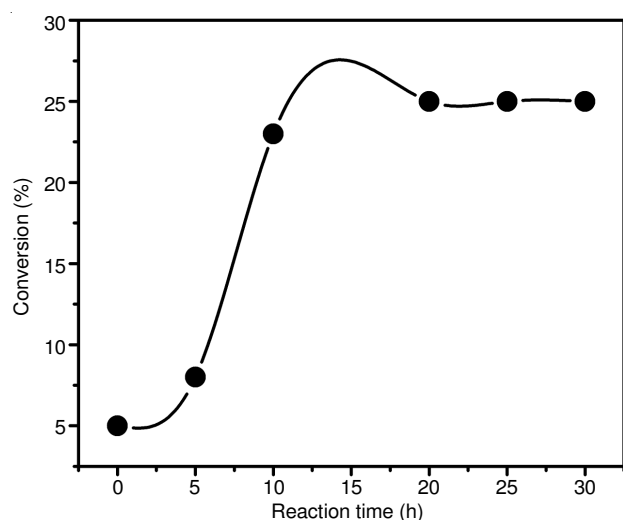
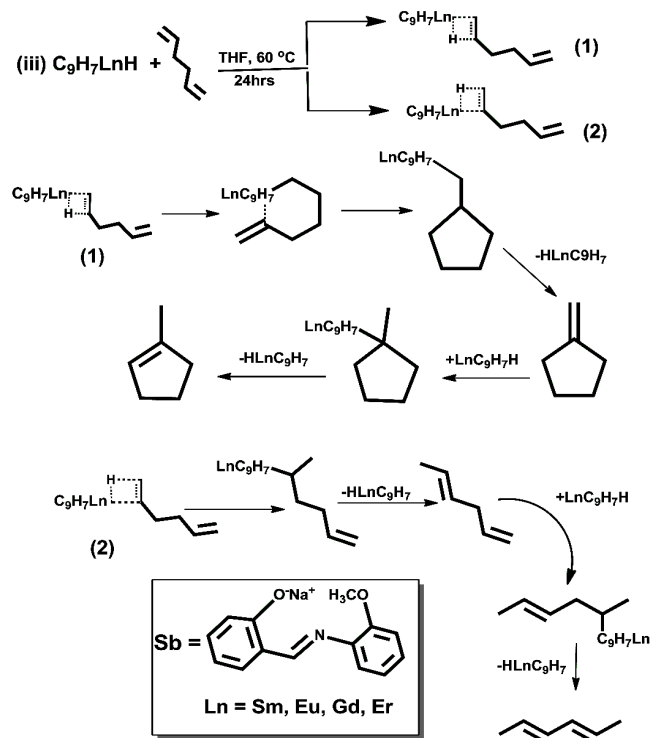
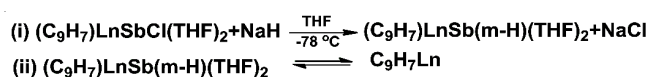


Fig. 3. Effect of time on the isomerization of hexa-1,5-diene

5-position in different fashions in order to produce two intermediates. The one intermediate is converted first into another intermediate (methylene cyclohexane) after passing through a chain process which is ultimately converted into an end product (methyl cyclohexene). The second intermediate migrate the double bond from 1-position to 2-position and then 3-position, respectively. The proposed mechanism is represented by the following reaction (Scheme-III).



Scheme-III: Mechanistic pathway of isomerization of hexa-1,5-diene

Conclusion

In conclusion, we found in the present work that the different types of tridentate Schiff base N-(2-methoxyphenyl)salicylideneamine derivative of lanthanideindenyl chloride complexes along with NaH are efficient for the isomerization of 1,5-hexadiene. The results showed that size and radius of the metal are important factors for the catalytic efficiency of the complexes. Further Schiff base ligands have ability to stabilize different types of metals in several oxidation states along with creating strong coordination between them. Continuing efforts will be focused on the syntheses of new kinds of Schiff bases with improved catalytic properties.

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