

Synthesis and Characterization of Tridentate Schiff Base Derivative of Indenyl Lanthanoid Chloride Tetrahydrofuranate Complexes for Catalytic Applications

MUHAMMAD YOUSAF¹, AMEER FAWAD ZAHOR^{1*}, ANBREEN ANJUM², TANVEER HUSSAIN BOKHARI¹, KULSOOM GHULAM ALI¹, BUSHRA PURVEEN¹, SHAZIA NAHEED¹, ABDUL JABBAR¹ and HAFIZ BADARUDDIN AHMAD³

¹Department of Chemistry, Government College University, Allama Iqbal Road, Faisalabad, Pakistan

²Department of Applied Chemistry, Government College University, Allama Iqbal Road, Faisalabad, Pakistan

³Department of Chemistry, Bahauddin Zikaria University, Multan, Pakistan

*Corresponding author: E-mail: fawad.zahoor@gmail.com

(Received: 12 January 2012;

Accepted: 2 August 2012)

AJC-11915

Four kinds of novel lanthanocene complexes were synthesized in reasonable yield by the reaction of equimolar quantity of sodium salt of tridentate Schiff base [N-(2-methoxyphenyl)salicylideneimine] with indenyl lanthanoid dichloride tetrahydrofuranate in tetrahydrofuran. All the complexes after purification were characterized by MS and EA, respectively. These complexes isomerized successfully the 1,5-hexadiene into a mixture of products such as 1,4-hexadiene, 2,4-hexadiene, 1,3-hexadiene, methylenecyclopentane and methylcyclopentene. Similarly they also proved effective for the polymerization of methylmethacrylate (MMA), 56.45 % yield and high molecular weight (355×10^3).

Key Words: Indene, Tridentate Schiff base, Lanthanoid complexes.

INTRODUCTION

The literature survey explains that metal complexes of Schiff bases occupy a central role in coordination chemistry for analytical, physical and biological properties¹.

A contemporary theme in modern lanthanoid chemistry is the design of new ligand environments of lanthanoid complexes which are capable of saturating the coordination sphere of lanthanoid (Ln^{3+}) ions and exhibiting high reactivity. Accordingly Schiff bases have the advantages of ease of synthesis, low cost, a hard donor atom framework and tunable steric and electronic effects.

The recent growth in organolanthanoid chemistry has primarily focused on complexes stabilized by tridentate 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 Schiff base derivative of lanthanocene complexes may serve as biologically important, naturally occurring ionophores. Literature verifies that lanthanocene hydride complexes are fundamental components in a wide range of stoichiometric and catalytic organometallic reactions². A large number of Schiff bases and their complexes with lanthanoids have been studied for their interesting and important properties, such as, their ability to reversibly bind oxygen³, catalytic activity in hydrogenation of olefins⁴, transfer

of amino group⁵. Catalytic synthesis of polymethylmethacrylate⁶, isomerization of 1, 5-hexadiene into various products⁷ and so on. Similarly a series of Schiff base derivative of lanthanoid complexes with β -diketone hydrazone derivatives were synthesized which exhibited the antibacterial and antifungal potential activity⁸. A large number of lanthanoid complexes with cyclopentadiene/its substituted products and different types of the Schiff bases such as monodentate, bidentate, tridentate, tetradentate, *etc.* have exhibited their importance in industrial as well as biological fields. Schiff bases derivative of lanthanoid complexes with indenyl are not so much reported. In this work, new series of tridentate Schiff base derivative of lanthanoid complexes with indenyl ligand have been reported. After characterization, their catalytic potential have been studied for the polymerization of methylmethacrylate and isomerization of 1,5-hexadiene.

EXPERIMENTAL

Standard Schlenk techniques, a vacuum atmosphere and N_2 filled glovebox were used through the isolation and handling of metal complexes. All the analytical grade solvents were dried over sodium metal, refluxed and distilled over blue sodium benzophenone under argon immediately before use. Anhydrous LnCl_3 and indenyl lanthanoid dichloride tetrahydrofuranate complexes were prepared according to the

literature method⁹. Tridentate Schiff base, N-(2-methoxyphenyl)salicylideneimine was prepared by the condensation of equimolar quantities of purified salicylaldehyde and anisidine in toluene at room temperature. The resulting Schiff base was purified by recrystallization in petroleum ether, dried and was used to prepare its salt with sodium metal in tetrahydrofuran (THF).

Synthesis of (Ind)Sm(C₁₄H₁₃NO₂)Cl·2THF (1): To a stirring 40 mL of THF solution of indenyl (Ind) samarium dichloride tetrahydrofuranate (8 mmol) was syringed an equimolar solution of sodium salt of N-(2-methoxyphenyl)-salicylideneimine in THF. After stirring for 16 h at room temperature, the orange yellow solution was concentrated under reduced pressure in order to get saturated THF solution which was set aside at room temperature for several days. The orange yellow microcrystalline solid was deposited in the bottom which was separated from the solution and after drying yield was calculated to be 48 %. 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. C₃₁H₃₅NO₄ClSm. Calcd: C, 55.48; H, 5.22; N, 2.08. Found: C, 55.52; H, 5.02; N, 2.06.

Synthesis of (Ind)Eu(C₁₄H₁₃NO₂)Cl·2THF (2): This compound was prepared analogously to complex **1** from the reaction of equimolar indenyl europium dichloride tetrahydrofuranate (7.5 mmol) and sodium salt of N-(2-methoxyphenyl)salicylideneimine in THF. The yellow microcrystalline solid was obtained in 52 % yield. 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. C₃₁H₃₅NO₄ClEu. Calcd: C, 55.32; H, 5.20; N, 2.08 Found: C, 55.29; H, 5.21; N, 2.09.

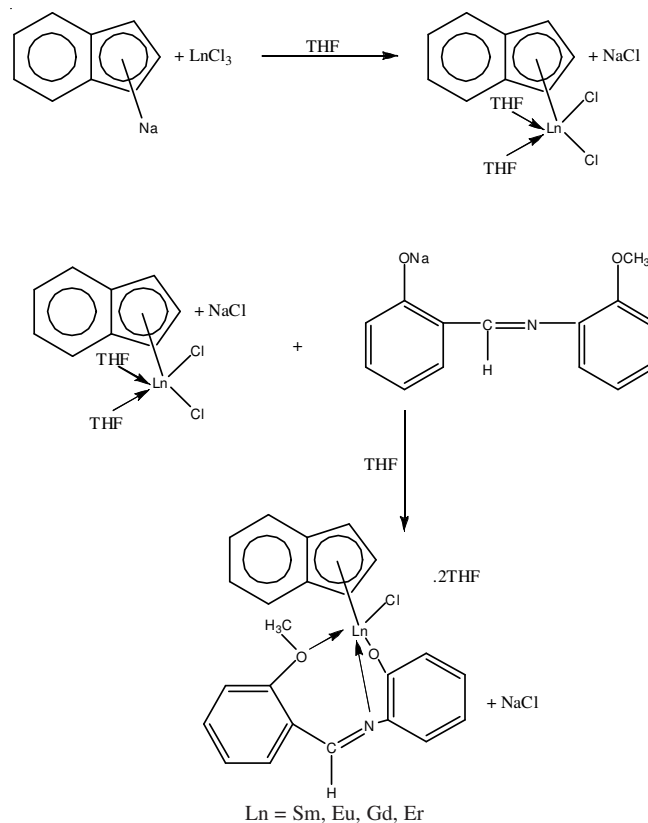
Synthesis of (Ind)Gd(C₁₄H₁₃NO₂)Cl·2THF (3): The complex **3** was also synthesized analogously to complex **1** by reacting equimolar indenyl-gadoliniumdichloride tetrahydrofuranate (8.8 mmol) with sodium salt of N-(2-methoxyphenyl)salicylideneimine in THF. The deep yellow microcrystalline solid in 49 % yield was obtained. 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. C₃₁H₃₅NO₄ClEu. Calcd: C, 54.71; H, 5.17; N, 2.07 Found: C, 54.76; H, 5.20; N, 2.09.

Synthesis of (Ind)Er(C₁₄H₁₃NO₂)Cl·2THF (4): Similarly this complex was prepared analogously to complex **1** from the reaction of equimolar amount of indenyl erbiumdichloride tetrahydrofuranate (6.5 mmol) with sodium salt of N-(2-methoxyphenyl)salicylideneimine in THF. The Orange yellow microcrystalline solid in 51 % yield was obtained. 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. C₃₁H₃₅NO₄ClEu. Calcd: C, 54.11; H, 5.09; N, 2.04 Found: C, 54.14; H, 5.12; N, 2.07.

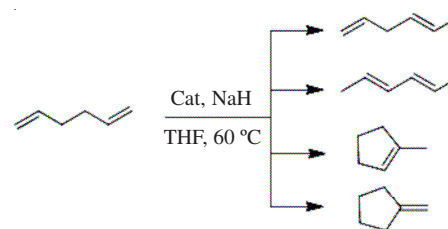
RESULTS AND DISCUSSION

The synthetic route of all the complexes (**1-4**) is explained in the **Scheme-I**.



Scheme-I: Synthesis of tridentate Schiff base derivative of indenyl lanthanoid complexes

These complexes along with NaH successfully isomerized the 1,5-hexadiene (**Scheme-II**) into various products such as 1,4-hexadiene, 2,4-hexadiene, methylenecyclopentene and methylenecyclopentane Table-1.



Scheme-II: Isomerization of 1,5-hexadiene in presence of lanthanide complexes

TABLE-1
EFFECT OF CATALYST ON THE ISOMRIZATION OF 1,5-HEXADIENE

S. No.	Catalyst	Conversion (%)	1,4-Hexadiene (%)	2,4-Hexadiene (%)	Methylene cyclopentane (%)	Methyl cyclopentene (%)	Linear/Cyclic
1	C ₃₁ H ₃₅ NO ₄ ClSm	29.2	83.5	2.5	12.8	4.9	86.0/17.7
2	C ₃₁ H ₃₅ NO ₄ ClEu	25.7	80.7	2.9	12.1	4.3	83.6/16.4
3	C ₃₁ H ₃₅ NO ₄ ClGd	24.9	74.9	6.7	14.7	5.0	81.6/19.7
4	C ₃₁ H ₃₅ NO ₄ ClEr	21.4	56.5	7.5	24.6	8.5	64.0/33.1
5	ErCl ₃	0.6	40.0	20.0	Traces	Traces	—

Reaction conditions: Catalyst/Hexadiene (1:20), Catalyst/NaH (1:50), time (20 h), temperature (60 °C), solvent (THF).

The complex **1** expressed better activity than all other attempted ones, which may be due to greater ionic radius of samarium metal than any other metal used (Gd, Eu and Er). It means that greater the ionic radius greater will be the coordination sphere of the metal. Hence, the easier the monomeric unit will make attachment with metal during isomerization.

Similarly these catalysts along with Al(*i*-bu)₃ yielded high molecular weight (355×10^3) polymethylmethacrylate with narrow polydispersity (1.70) (Table-2). Among all the catalysts the complex **1** exhibited better efficiency than others which again is due to the greater ionic radius of the samarium metal than other used during the formation of complexes (**1-4**).

TABLE-2
EFFECT OF CATALYSTS ON THE POLYMERIZATION
OF METHYLMETHACRYLATE (MMA)

S. No.	Catalyst	Conversion (%)	$M_n \times 10^3$	M_w/M_n
1	IndenylSmCl(C ₃₄ H ₃₃ NO ₂)·2THF	56.45	355	1.70
2	IndenylEuCl(C ₃₄ H ₃₃ NO ₂)·2THF	53.70	310	1.80
3	IndenylGdCl(C ₃₄ H ₃₃ NO ₂)·2THF	51.45	280	1.75
4	IndenylErCl(C ₃₄ H ₃₃ NO ₂)·2THF	40.50	195	1.83
5	SmCl ₃ *	9.5	13	-
6	Al(<i>i</i> -Bu) ₃ *	15.5	15	-

Reaction conditions: Time = 20 h, cat/MMA = 1:1000, cat/Al = 1:20, Temp. = 70 °C, blank = *

ACKNOWLEDGEMENTS

Financial Support from the University Research Fund (URF) of Government College University, Faisalabad, Pakistan is highly acknowledged.

REFERENCES

1. K. Desai and B.T. Thaker, *J. Indian Chem. Soc.*, **67**, 667 (1990).
2. R.G. Teller and R. Bau, *Structural Bonding*, Berlin Springer Press, Berlin, Germany, end. 1. pp. 44-60 (1981).
3. R.D. Jones, D.A. Summerville and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).
4. G. Hinrici-Olie and S. Olive, *The Chemistry of Catalysed Hydrogenation of Carbon Monoxide*, Berlin Springer Press, Berlin, Germany, p. 152 (1984).
5. H. Dugas and C. Penny, *Bioorganic Chemistry*, Springer Press, New York, USA, edn. 5, pp. 435-475 (1981).
6. M. Yousaf, J. Huang, F.Z. Feng, Y. Qian, S.J. Quan and P. Zhida, *Chin. J. Chem.*, **18**, 779 (2000).
7. M. Yousaf, G.A. Kulsoom, B. Bushra, A. Jabbar, H.B. Ahmad and H. Ma, *Asian J. Chem.*, **22**, 5254 (2010).
8. W.H. Hegazy and I.H. Al-Motawaa, *Bioinorg. Chem. Appl.*, **2011**, 1 (2011).
9. M. Yousaf, L. Qian-Cai, J. Huang and Y.L. Qian, *Chin. J. Chem.*, **18**, 740 (2000).