Synthesis, characterization and catalytic applications of tridentate Schiff base derivatives of bis and mono(cyclopentadienyl)-lanthanocene complexes

YOUSAF, Muhammad(约瑟夫·穆罕默德) LIU, Qian-Cai(刘乾才) HUANG, Ji-Ling(黄吉玲) QIAN, Yan-Long*(钱延龙)

Laboratory of Organometallic Chemistry, East China University of Science and Technology, Shanghai 200237, China

Seven kinds of lanthanocene complexes were prepared by the reaction of tridentate Schiff base {*N*-(2-methoxyphenyl)salicylideneamine} with tris(cyclopentadienyl)lanthanide tetrahydrofuranate or bis(cyclopentadienyl)lanthanide chloride tetrahydrofuranate in THF. All the complexes were characterized by MS, EA and IR respectively. The structure of {$Cp_2LnC_{14}H_{13}NO_2$) Ln = Sm, Dy, Y, Er} (1—4) was further confirmed by X-ray determination of $Cp_2Sm(C_{14}H_{13}NO_2)$ (1) which indicates that the complex is monomeric in which central metal is coordinatively saturated by two cyclopentadienyl rings, two oxygens and one nitrogen of the ligand. The isomerization of 1,5-hexadiene explains that complexes (1—4) isomerize this monomer into a mixture of 1,4-hexadiene, 2,4-hexadiene, 1,3-hexadiene, methylenecyclopentane and methylcyclopentene. Similarly complexes {$CpLn(Cl)C_{14}H_{13}NO_2$) (THF) (Ln = Sm, Dy, Y, Er)} (5—7) polymerize methylmethacrylate (MMA) to give polyMMA (PMMA) in 51.8% yield and high molecular weight (274×10^3), which shows narrow molecular weight distributions and partially syndiotactic.

Keywords Lanthanocene, tridentate Schiff base, synthesis, X-ray determination

Introduction

The coordination compounds formed by Schiff bases and *d*-transition elements have been extensively studied.[1] However, there has been only a very limited effort made in the study of the interaction between ligands of this type and lanthanide elements. Evans *et al*. revealed that bis(cyclopentadienyl) lanthanide alkyls could form organolanthanide enolate complexes {$Cp_2Ln(\mu\text{-}OCH=CH_2)$}$_2$.[2] The development of organolanthanide complexes with η^1-bonded ligands was only possible when the bis(cyclopentadienyl)lanthanide halides became available. Yu and coworkers[3] successfully prepared orthosubstituted benzoic acid derivatives of mono(cyclopentadieny) lanthanide chloride. Literature survey shows that Schiff base ligands are widely used to prepare such type of lanthanocene complexes. It shows their importance in chemical and biochemical fields.[4-6] So we are introducing firstly a tridentate Schiff base, *N*-(2-methoxyphenyl) salicylideneamine ligand that has electronic equivalency with cyclopentadienyl and are reporting Schiff base (SbH) derivatives of lanthanocene {$Cp_2Ln(C_{14}H_{13}NO_2)$ Ln = Sm, Dy, Y, Er} (**1—4**) and complexes {$CpLn(Cl)(C_{14}H_{13}NO_2)$(THF) Ln = Sm, Dy, Y, Er} (**5—7**) and then estimating their chemical efficiencies.

Experimental

All the reactions were carried out under an inert atmosphere of high purity argon on a vacuum line. Transfer and handling of complexes were facilitated by using Schlenk techniques. Tetrahedrofuran was refluxed and distilled over the sodium benzophenone ketyl immediately before use. Anhydrous $LnCl_3$, tris(cyclopentadienyl)-lanthanide tetrahydrofuranate and bis(cyclopentadienyl)-

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lanthanide chloride tetrahydrofuranate were prepared according to the literatures.[7,8] Schiff base, *N*-(2-methoxyphenyl) salicylideneamine, was prepared by reaction of equimolar 2-anisidine and salicylaldehyde in boiling toluene along with azeotropic distillation of water.

Synthesis of (η^5-Cp)$_2$Sm($C_{14}H_{13}NO_2$) (**1**)

To a stirring 40 mL of THF solution of Cp_3Sm(THF) (8.8 mmol) was added an equimolar solution of *N*-(2-methoxyphenyl) salicylideneamine in THF. After stirring for 16 h at room temperature, the orange yellow solution was concentrated under reduced pressure to get saturated THF solution which was set aside at room temperature for several days. The orange yellow crystals were obtained in 55% yield. *m/z* (%): 443(M^+ − Cp, 100), 362(M^+ − 2Cp, 59.9), 66(Cp, 18.3). Anal. $C_{24}H_{23}NO_2Sm$. Calcd: C, 56.69; H, 4.33; N, 2.76. Found : C, 55.72 ; H, 4.25 ; N, 2.8.

Synthesis of (η^5-Cp)$_2$Dy($C_{14}H_{13}NO_2$) (**2**)

This compound was prepared analogously to complex **1** from the reaction of equimolar Cp_3Dy(THF) (5.46 mmol) and *N*-(2-methoxyphenyl) salicylideneamine in THF. The yellow crystals were obtained in 48% yield. *m/z* (%): 455(M^+ − Cp, 100), 440 (M^+ − Cp-CH_3, 20.4), 374(M^+ − 2Cp, 52.1), 66 (Cp, 11.6). Anal. $C_{24}H_{23}NO_2Dy$. Calcd: C, 55.38; H, 4.23; N, 2.69. Found: C, 54.96; H, 4.26; N, 2.89.

Synthesis of (η^5-Cp)$_2$Y($C_{14}H_{13}NO_2$) (**3**)

This compound was prepared analogously to complex **1** from the reaction of equimolar Cp_3Y(THF) (7.51 mmol) and *N*-(2-methoxyphenyl) salicylideneamine in THF. The yellow crystals were obtained in 46% yield. *m/z* (%): 379(M^+ − Cp, 100), 364(M^+ − Cp − CH_3, 24.6), 299(M^+ − 2Cp, 43.9), 66(Cp, 11.6). Anal. $C_{24}H_{23}NO_2Y$. Calcd: C, 64.72; H, 4.94; N, 3.15. Found: C, 64.49; H, 4.95; N, 3.48.

Synthesis of (Cp)$_2$Er($C_{14}H_{13}NO_2$) (**4**)

This compound was prepared analogously to complex **1** from the reaction of equimolar Cp_3Er(THF) (2.82 mmol) and *N*-(2-methoxyphenyl) salicylideneamine in THF. The bright yellow crystals were obtained in 45% yield. *m/z* (%): 457(M^+ − Cp, 100), 442(M^+ − Cp-CH_3, 31.3), 376(M^+ − 2Cp, 66.4), 65(Cp, 10.6). Anal. $C_{24}H_{23}NO_2Er$. Calcd: C, 55.17; H, 4.21; N, 2.68. Found: C, 55.11; H, 4.22; N, 2.73.

Synthesis of (η^5-Cp)Dy(Cl)($C_{14}H_{13}NO_2$)(THF) (**5**)

To a stirring 40 mL of THF solution of Cp_2Dy(Cl)(THF) (5.8 mmol) was syringed a solution of equimolar *N*-(2-methoxyphenyl) salicylideneamine in THF. The mixture was stirred for 12 h at room temperature. After centrifugation, the yellow solution was concentrated under reduced pressure and was set aside at room temperature for several days. The yellow microcrystalline solids were obtained in 51.8% yield which were washed three times with *n*-hexane. *m/z* (%): 454(M^+ − Cl − THF, 100), 424(M^+ − Cp − THF, 5.3), 65(Cp, 37.2). Anal. $C_{23}H_{26}ClNO_3Dy$. Calcd: C, 49.11; H, 4.49; N, 2.49. Found: C, 48.66; H, 4.19; N, 2.70.

Synthesis of (η^5-Cp)Y(Cl)($C_{14}H_{13}NO_2$)(THF) (**6**)

This compound was prepared analogously to complex **5** from the reaction of equimolar Cp_2Y(Cl)(THF) (9.5 mmol) and *N*-(2-methoxyphenyl) salicyllideneamine in THF. A light yellow solids were obtained in 46% yield. *m/z* (%): 380(M^+ − Cl − THF, 1.5), 350(M^+ − Cp − THF, 2.9), 65(Cp, 100). Anal. $C_{23}H_{26}ClNO_3Y$. Calcd: C, 56.60; H, 5.13; N, 2.88. Found: C, 56.10; H, 4.97; N, 3.00.

Synthesis of (η^5-Cp)Er(Cl)($C_{14}H_{13}NO_2$) (THF) (**7**)

This complex was prepared analogously to **5** from the reaction of equimolar Cp_2Er(Cl)(THF) (5.8 mmol) and *N*-(2-methoxyphenyl) salicylideneamine in THF. The yellow solids were obtained in the yield of 42.5%. *m/z* (%): 458(M^+ − Cl − THF, 2.3), 428(M^+ − Cp − THF, 3.2), 65(Cp, 100). Anal. $C_{23}H_{26}ClNO_3Er$: C, 48.94; H, 4.43; N, 2.48. Found: C, 48.95; H, 4.16; N, 2.45.

All the complexes **1**—**7** are soluble in THF, sparingly soluble in toluene and are completely unsoluble in *n*-hexane. They have no melting points and the decomposition occurs at 190℃ in case of complexes **1**—**4** while complexes **5**—**7** decompose above 130℃.

X-*ray determination of complex* **1**

Suitable single crystal of **1** for crystal structure determination was sealed in thin-walled glass capillary. Unit cell and intensity data were obtained using standard procedures on a Siemens P4 four-cycle diffractometer. The intensities were corrected for L_p factors and semi-empirical absorptions. The details are given in Table 1. The samarium position was located by the Patterson method and other non-hydrogen atoms by Fourier difference techniques. All the positional and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-square techniques. All hydrogen atoms were introduced in the calculated positions with C—H bond distance of 0.096 nm. The calculations were completed by use of Siemens SHELXTL-Plus programs. Lists of final coordinates and thermal parameters, bond lengths and angles have been sent to the editors as supplementary materials.

Results and discussion

Reaction of anhydrous lanthanide trichloride with three or two equivalents of (cyclopentadienyl) sodium salt respectively and then with one equivalent of tridentate Schiff base ($C_{14}H_{14}NO_2$) in THF at room temperature followed by centrifugation, concentration and crystallization offered complexes **1**—**7** in reasonable yields.

$$\text{i. } LnCl_3 + NaCp \xrightarrow{THF} Cp_3Ln\cdot THF + NaCl$$

$$\text{ii. } LnCl_3 + NaCp \xrightarrow{THF} Cp_2Ln(Cl)(THF) + NaCl$$

$$\text{iii. } \left.\begin{matrix} Cp_3Ln\cdot THF \\ Cp_2Ln(Cl)(THF) \end{matrix}\right] + C_{14}H_{14}NO_2 \xrightarrow{THF} \underset{\mathbf{1-4}}{Cp_2Ln(C_{14}H_{13}NO_2)} / \underset{\mathbf{5-7}}{CpLn(Cl)(C_{14}H_{13}NO_2)(THF)} + CpH$$

Ln=Sm, Dy, Y, Er

Using this Schiff base ligand we have succeeded in synthesizing complexes with late rare earth metals in which the intramolecular coordination bonds from the oxygen and nitrogen atoms of the Schiff base to lanthanide metal are formed and efficiently satisfy the coordinating environment of these metal centers. This indicates that tridentate Schiff base behaves like cyclopentadienyl ligand in order to satisfy the coordination environment of the metal center. In the case of Schiff base derivatives of mono (cyclopentadienyl) lanthanide chloride complexes **5**—**7**, an additional coordination linkage through oxygen of THF was observed which was supported by MS, IR and EA analysis. These results justify that this linkage is very weak and can be cleaved easily. All these **1**—**7** complexes are monomeric and are different from the complexes derived from bidentate and tetradentate Schiff base ligands.[9-11] The composition of these complexes **1**—**7** were confirmed for MS, EA. The IR spectra of these new complexes exhibit similar characteristics. The typical absorption peaks for cyclopentadienyl rings occur at *ca*. 775, 1020, 1440 and 3085 cm^{-1}.[12,13] A strong peak due to asymmetric stretching vibration $\nu(C-O-C)$ occurs at 1045 cm^{-1} probably as a consequence of significant oxygen atom coordination, in accordance with the earlier work for the complex {$Ln(C_5H_5CH_2CH_2OMe)_2Cl$}.[14] Absorption bands in the region of 1100—1200 cm^{-1} and 1625 cm^{-1} may indicate the presence of C = N group of Schiff base.[15] The structure of complexes **1**—**4** was further confirmed by X-ray determination of {$Cp_2Sm(C_{14}H_{13}NO_2)$} (**1**). The crystal data and atom numbering scheme of **1** are shown in Table 1. The selected bond lengths, bond angles and the molecular structure are shown in Fig. 1 and Table 2. The crystal data justify that complex **1** is monomeric. The 9-coordinated samarium atom is bonded to one nitrogen atom and two oxygen atoms of the Schiff base and two Cp rings to form a distorted trigonal bipyramidal geometry. The Sm—C, bond distance ranges from 0.2686(7) to 0.2763(8) nm with an average of 0.2723(7) nm which is comparable to that of $[(\eta^5\text{-Cp})Sm(\mu\text{-}C_{20}H_{20}N_2O_2)]_2(\mu\text{-THF})(THF)_2$ (**8**)[10] 0.278 nm. The bond distances of Sm(1)—O(1) and Sm(1)—O(2) are 0.2232(4) nm and 0.2572(4) nm, respectively. The bond length of Sm(1)—O(2) is longer than that of Sm—O(1) with a difference of 0.034 nm, which indicates that Sm(1)—O(2) is coordination bond and Sm—O(1) is covalent one. Further these bond distances are *ca*. 0.006 nm shorter than those of **8** [0.229 and 0.263 nm]. The Sm(1)—N(1) bond distance 0.2534(4) nm is longer than that of complex **8**. The bond angles involving Schiff base and Sm center for O(1)-Sm(1)-N(1), O(1)-Sm(1)-O(2) and N(1)-Sm(1)-O(2) are 72.4(2)°, 134.94(14)° and 62.55(13)°, respectively.

Table 1 Crystal data for **1**

Formula	$C_{24}H_{22}NO_2Sm$
F_W	506.78
Crystal system	Orthorhombic
Space group	*Pbcn*
Cell constants	
a (nm)	2.2036(3)
b (nm)	1.4594(5)
c (nm)	1.2755(4)
$\alpha=\beta=\gamma$ (°)	90
V (nm^{-3})	410.8(2)
D_c ($g\cdot cm^{-3}$)	1.639
μ (mm^{-1})	2.877
Z	8
$F(000)$	2008
Radiation	Mo K_α
λ (nm)	0.071073
Crystal size (mm)	0.60 × 0.40 × 0.40
Data collection, 2θ range (°)	3—50
h, k, l	−1 to 26, −17 to 0,0 to 15
Reflections collected	3818
Unique reflections	3612
No. of parameters	253
R	0.0404
R_w	0.0550
Max. and min. transmission	0.1505 and 0.0797
Temperature (K)	293(2)

The catalytic effeciencies of these complexes were also checked. The results obtained from isomerization of 1,5-hexadiene explain that the complexes **1**—**4** showed no activity when were applied as a single component. But along with NaH as a cocatalyst, they exhibited reasonable efficiency. Complex **1** showed 28.7% conversion while that of complex **4** indicated 20.6%. These results explain that ionic radii of the central metals are responsible for the activity of these complexes. All the complexes gave positive response along with the temperature while that of substrate molar ratio affected the conversion negatively. Furthermore, results from microculture tetrozolium (MTT) study with complexes **1**—**4** showed 85.9% activity at 10^{-4} mol·L^{-1} concentration in P388 type cell after 48 h.

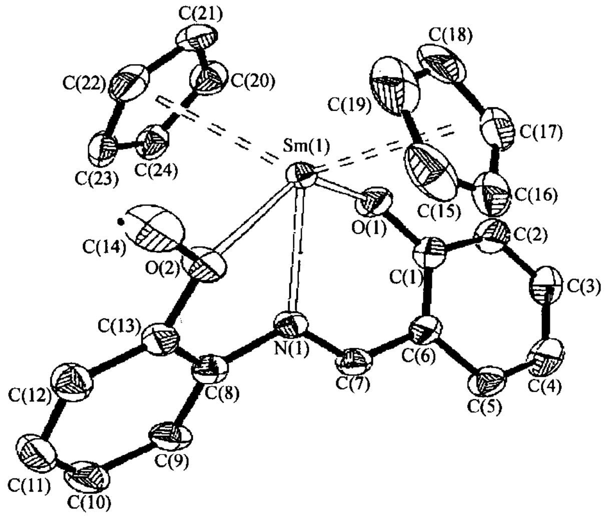

Fig. 1 Molecular structure of complex **1**.

Complexes **5**—**7** behaved in a similar manner. They catalyzed the polymerization of methylmethacrylate (MMA) only if were inoculated with $Al(i\text{-Bu})_3$. The complex **5** showed maximum conversion (51.8%) along with highest molecular weight (274×10^3) (M_n) while complex **7** exhibited minimum efficiency (43.94%). The molecular weight distribution for all the complexes was narrow ($M_w/M_n=1.71$—1.98). From the discussion it is concluded that ionic radii of the central metal play a significant role for specifying the activity of the complex. The results of our study are in agreement with the earlier work reported by Yasuda *et al*.[16] that the activity of the iniciator increases along with the ionic radii of the metals. Furthermore it was found that molar concentration of substrate and temperature exert positive effect on yield of PMMA which jutifies the living nature of polymerization. The ^1H NMR analysis of PMMA explains that the resulting polymer from all the complexes is partially syndiotactic (60—70%).

Table 2 Selected bond lengths (nm) and angles (°) for complex **1**

Sm(1)—O(1)	0.2232(4)	Sm(1)—O(2)	0.2572(4)
Sm(1)—N(1)	0.2534(4)	Sm(1)—C(15)	0.2763(8)
Sm(1)—C(16)	0.2741(7)	Sm(1)—C(17)	0.2713(7)
Sm(1)—C(18)	0.2685(7)	Sm(1)—C(19)	0.2703(7)
Sm(1)—C(20)	0.2700(7)	Sm(1)—C(21)	0.2711(6)
Sm(1)—C(22)	0.2730(7)	Sm(1)—C(23)	0.2750(6)
Sm(1)—C(24)	0.2730(6)	N(1)—C(8)	0.1421(7)
N(1)—C(7)	0.1282(7)		
O(1)-Sm(1)-N(1)	72.4(2)	O(1)-Sm(1)-O(2)	134.94(14)
N(1)-Sm(1)-O(2)	62.55(13)		

Conclusion

This study indicates that monomeric organolanthanocene complexes can be obtained by using tridenlate Schiff base ligand. These complexes can be effective for some biological and chemical processes. Further study is to synthesize novel lanthanocene complexes by changing the coordinating environment of the metal and to improve the catalytic effeciencies.

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