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Synthesis and reactivity of organolanthanoid complexes containing N and S ligands

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Abstract

This paper provides a brief account of our recent researches in organolanthanoid chemistry containing N and S ligands. The first is concerned with the synthesis of organolanthanoid complexes, including anionic, supramolecular, neutral organolanthanoid amides and the organolanthanoid complexes supported by β-diketiminate, as well as organolanthanoid thiolates. The second deals with the reactivity of these organolanthanoid complexes, including the reaction with phenyl isocyanate, CS_2, and phenyl isothiocyanate, and the catalytic activity for the polymerization of polar monomers, such as methyl methacrylate, (dimethylamino)ethyl methacrylate and ε-caprolactone. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organolanthanoid complex; Synthesis; Reactivity; Activation small molecule; Polymerization

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1. Introduction

The chemistry of organolanthanoid complexes containing N and S ligand has been relatively unexplored. Actually, the absolute bond disruption enthalpies of Ln–N and Ln–S bonds are 48.2 and 73.4 kcal mol^{-1}, respectively. The former lies at an intermediate between those of Ln–O and Ln–C bonds, the latter is near that of lanthanoid oxide [1]. As a result, the Ln–N bond is less strong than the Ln–O bond and even comparable to Ln–C bonds, and the strength of Ln–S bond might be the same as that of Ln–O bond. The characteristic Ln–N and Ln–S bonds offers organolanthanoid amides and organolanthanoid sulfides an opportunity to get their reaction chemistry comparable to that of organolanthanoid alkyl complexes and organolanthanoid alkoxides, respectively. Therefore, a study of the reactivity of organolanthanoid amides and sulfides might be interesting both for understanding the chemistry of Ln–N and Ln–S bonds and for exploring their new reaction model. In recent years, we have focused our attention on the synthesis and reactivity of organolanthanoid containing N and S ligand. Here, we will present the results obtained in our laboratory.

2. Synthesis of organolanthanoid complexes containing N and S ligands

2.1. Synthesis of organolanthanoid amide

Anionic lanthanocene amide complexes, formulated as $[\mathrm{LiL}][\mathrm{Cp}_n\mathrm{Ln}(\mathrm{NR}_2)_{4-n}]$ ($n = 1, 2$; L = donor) are commonly isolated from the reaction of lanthanocene chloride with lithium amide in aprotic solvents [2]. By using a similar method, we have synthesized the following complexes $[\mathrm{Li(THF)}_4][(t\text{-}\mathrm{BuC}_5\mathrm{H}_4)\mathrm{Yb(NPh}_2)_3]$ [3], $[\mathrm{Li(DME)}_3][(t\text{-}\mathrm{BuC}_5\mathrm{H}_4)_2\mathrm{Nd(NPh}_2)_2]\cdot 1/2\mathrm{DME}$ [4].

$$\begin{aligned}&(t\text{-}\mathrm{BuC}_5\mathrm{H}_4)\mathrm{YbCl}_2\\&+\mathrm{LiNPh}_2\xrightarrow{\mathrm{THF}}[\mathrm{Li(THF)}_4][(t\text{-}\mathrm{BuC}_5\mathrm{H}_4)\mathrm{Yb(NPh}_2)_3]\end{aligned}\qquad(1)$$

$$\begin{aligned}&(t\text{-}\mathrm{BuC}_5\mathrm{H}_4)_2\mathrm{NdCl}\\&+\mathrm{LiNPh}_2\xrightarrow[2)\mathrm{DME}]{1)\mathrm{THF}}[\mathrm{Li(DME)}_3][t\text{-}\mathrm{BuC}_5\mathrm{H}_4)_2\mathrm{Nd(NPh}_2)_2]\end{aligned}\qquad(2)$$

Due to the lanthanide contraction, bis(cyclopentadienyl) or bis(methylcyclopentadienyl) early lanthanide

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chloride is well known to be not stable enough to be a precursor for the synthesis of their corresponding derivatives [5]. We use anionic compounds, $(C_5H_5)_2NdCl{\cdot}LiCl(THF)_n$ and $[(THF)_2Li(\mu\text{-}Cl)_2]_2[(MeC_5H_4)La(THF)]$, as precursors, and successfully synthesized first amide compounds with early lanthanide metals, $[Li(DME)_3][(C_5H_4)_2Nd(NPh_2)_2]$ [6] and $[Li(DME)_3][(MeC_5H_4)La(NPh_2)_3]$ [7], respectively.

$$(C_5H_5)_2NdCl{\cdot}LiCl(THF)_n + 2LiNPh_2 \xrightarrow[\text{2)DME}]{\text{1)THF}} [Li(DME)_3][(C_5H_5)_2Nd(NPh_2)_2] \tag{3}$$

$$(MeC_5H_4)LaCl_2{\cdot}2LiCl(THF)_3 + 3LiNPh_2 \xrightarrow[\text{2)DME}]{\text{1)THF}} [Li(DME)_3][(MeC_5H_4)La(NPh_2)_3] \tag{4}$$

X-ray structure determination shows that all these complexes synthesized have an ion-pair structure formed by lanthanide anion and lithium cation. Taking $[Li(DME)_3][(MeC_5H_4)La(NPh_2)_3]$ as an example, its molecular structure is shown in Fig. 1. The bond distances of Ln–N for the above complexes range from 2.234(1) to 2.459(7) Å.

When sodium diphenylamide, instead of lithium diphenylamide, was used as a reagent, a self-assembly of supramolecular lanthanide amide complexes bearing both diphenylamido and methylcyclopentadienyl ligands, $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2]_n$ (Ln = Sm, Er) was obtained [8].

$$n(MeC_5H_4)_2LnCl(THF) + 2nNaNPh_2 \xrightarrow{\text{THF}} [Na(THF)_2(MeC_5H_4)_2Ln(NPh_2)_2]_n$$

$$Ln = Sm, Er \tag{5}$$

These complexes possess a polymeric structure composed of units of $Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}MeC_5H_4)_2Ln(NPh_2)_2$, in which sodium is incorporated into the complex via bridging interactions of two η^5-MeC_5H_4 groups with lanthanide atoms (Fig. 2). The crystal structure is similar to those of $\{K[(\mu\text{-}C_5H_5)_2Nd(\mu\text{-}OAr)_2]\}_n$ [9] and $[(\mu{:}\eta^5\text{-}C_5Me_5)Sm(OAr)(\mu{:}\eta^5\text{-}C_5Me_5)K(THF)_2]_n$ [10].

The metathesis reaction of lanthanocene chloride with $LiNR_2$ takes place in aprotic solvents, such as toluene or hexane, the corresponding neutral lanthanocene amide was isolated in good yields. For example, $(MeC_5H_4)_2LnCl(THF)$ reacts with $LiN(i\text{-}Pr)_2$, $LiNC_5H_{10}$ (piperidine) in toluene to give the corresponding amide, $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln = Y, Er, Yb) [11], $(MeC_5H_4)_2LnNC_5H_{10}(HNC_5H_{10})$ (Ln = Y, Er, Yb) [12].

$$(MeC_5H_4)_2LnCl + LiNR_2 \xrightarrow{\text{toluene}} (MeC_5H_4)_2LnNR_2(L)$$

$$Ln = Y, Er, Yb;\ NR_2 = N(i\text{-}Pr)_2,\ NC_5H_{10} \tag{6}$$

Even use of $LiNPh_2$ as amido ligand, the neutral compounds free of $LiNPh_2$, $(MeC_5H_4)_2YbNPh_2(THF)$, $(t\text{-}BuC_5H_4)_2YbNPh_2(THF)$, and $(C_5Me_5)_2YbNPh_2$, are also isolated in good yield [13]. All the complexes, except $(C_5Me_5)_2YbNPh_2$, are solvated.

The indenyl amido complex for lanthanide was prepared by the reaction of $Ln[N(i\text{-}Pr)_2]_3$ and indene in toluene [14].

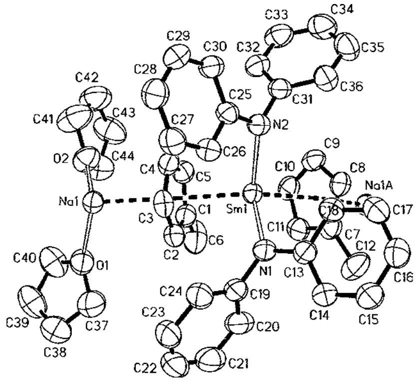


Fig. 2. Molecular structure of $[Na(THF)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}CH_3C_5H_4)_2Sm(NPh_2)_2]_n$.

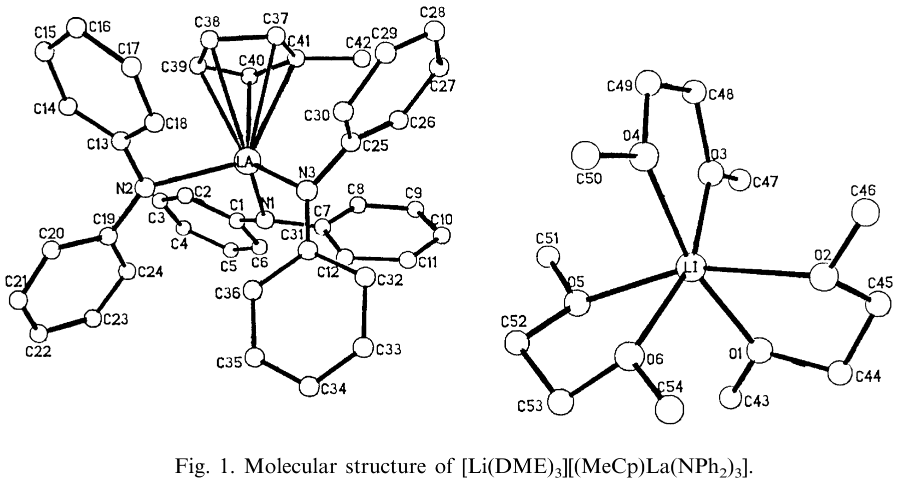


Fig. 1. Molecular structure of $[Li(DME)_3][(MeCp)La(NPh_2)_3]$.

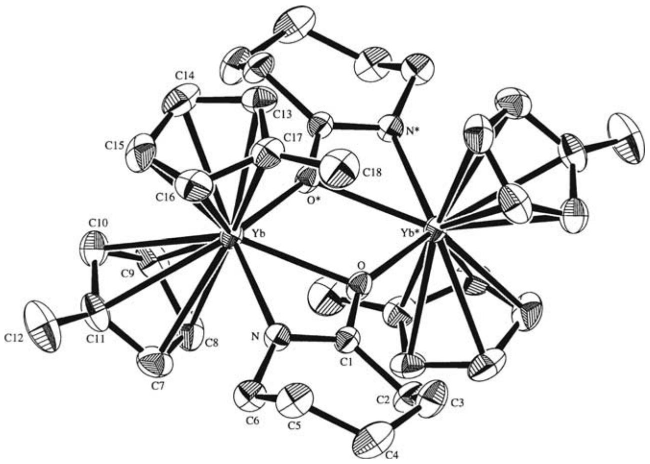


Fig. 3. Molecular structure of $(MeC_5H_4)_2YbOCN(CH_2)_4CH_2$.

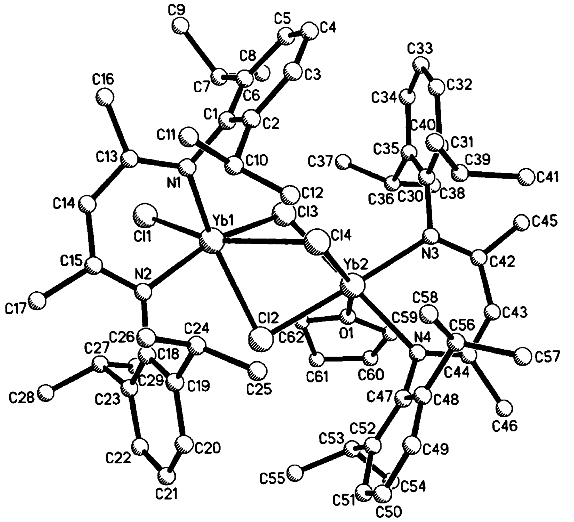


Fig. 4. Molecular structure of $\{[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)\}\cdot 1/2MePh$.

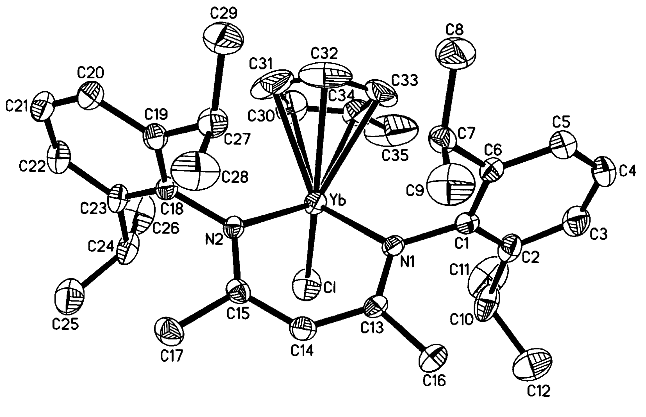
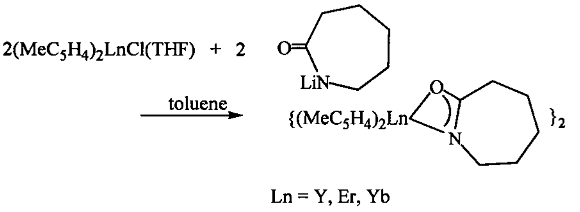


Fig. 5. Molecular structure of $(MeC_5H_4)[(DIPPh)_2nacnac]YbCl$.

$$Ln[N(i\text{-}Pr)_2]_3(THF) + 2C_9H_8 \xrightarrow{\text{toluene}} (C_9H_7)_2LnN(i\text{-}Pr)_2 + 2HN(i\text{-}Pr)_2 \quad Ln = Gd, Y, Er \tag{7}$$

Organolanthanoid derivatives bearing RCONR′ moiety have been reported to be synthesized by the insertion of CO into the Sm–N bond of complex $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$[15], phenyl isocyanate to the Ln–N bond of $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ [11], and the reduction coupling reaction of phenyl isocyanate mediated by $[(ArO)_2Sm(THF)_3](THF)$ [16], respectively. This kind of complex can also be synthesized straightforward by metathesis of lanthanocene chloride with corresponding alkali metal salts. Thus, $(MeC_5H_4)_2LnCl(THF)$ reacts with equivalent $LiOCN(CH_2)_4CH_2$ in toluene gives the complexes $(MeC_5H_4)_2LnOCN(CH_2)_4CH_2$ (Ln = Y, Er, Yb) [17] (Eq. (8)). The complex is an unsolvated dimer in which ligand $OCN(CH_2)_4CH_2$ donates four electrons to the lanthanide ion (Fig. 3).



(8)

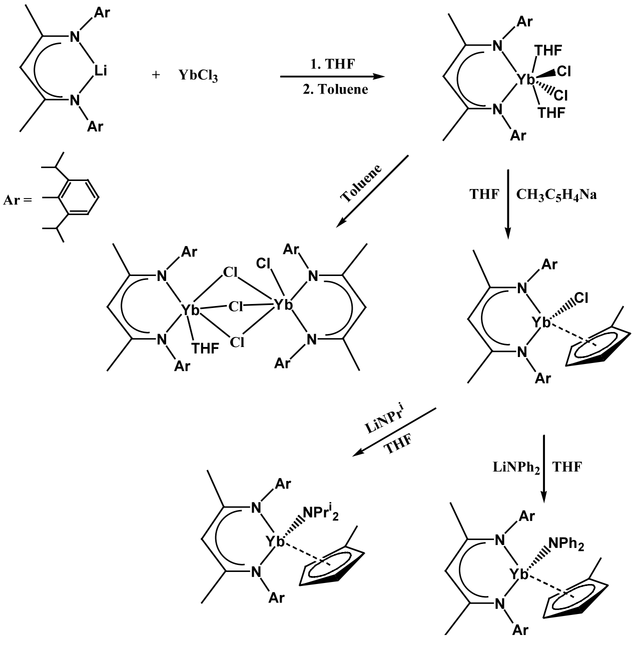
2.2. Synthesis organolanthanoid complex supported by β-diketiminate

Synthesis of organolanthanoid amide with β-diketiminate has also been studied in our laboratory. Using $(DIPPh)_2nacnac$ ($(DIPPh)_2nacnac = N,N$-diisopropylphenyl-2,4-pentanediimine) as an ancillary ligand, the β-diketiminate ytterbium dichloride $[(DIPPh)_2nacnac]YbCl_2(THF)_2$ was prepared by the metathesis reaction of $[(DIPPh)_2nacnac]Li$ with anhydrous $YbCl_3$ in a 1:1 molar ratio. Recrystallization of $[(DIPPh)_2nacnac]YbCl_2(THF)_2$ from toluene gave an unexpected complex $\{[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)\}\cdot 1/2MePh$, which has a rare triple chloride-bridge (Fig. 4). Reaction of $[(DIPPh)_2nacnac]YbCl_2(THF)_2$ with one equivalent of MeC_5H_4Na in THF, the mixed-ligand organolanthanoid chloride $(MeC_5H_4)[(DIPPh)_2nacnac]YbCl$ was isolated in high yield. Structure analysis reveals this complex to be a solvent-free monomeric species (Fig. 5). It is noteworthy that the spectator ligand, $(DIPPh)_2nacnac$, is coordinated to the metal ion in η^4 fashion. Moreover, treatment of $(MeC_5H_4)[(DIPPh)_2nacnac]YbCl$ with one equivalent of $LiNPh_2$ or $LiNi\text{-}Pr_2$ in THF smoothly allowed for the replacement of chloride and the production of the complexes $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbNPh_2$ and $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbN\textit{i}\text{-}Pr_2$ in good yields, respectively (Scheme 1). The molecular structure of $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbNPh_2$ is depicted in Fig. 6. This complex is a neutral unsolvated monomer, in which the spectator ligand adopts the η^2 coordinate fashion [18].

2.3. Synthesis of organolanthanoid thiolate

Organolanthanoid thiolate complex can be synthesized by the reaction of lanthanide metal with ArSSAr [19]; metathesis reaction of anhydrous $LnCl_3$ with MSR [20]; and the ligand exchange reaction of Cp'_3Ln with HSR [21]. In order to further study the reactivity of organolanthanoid thiolate, we use the third method to synthesize $[(MeC_5H_4)_2LnSPh(THF)]_2$ (Ln = Nd, Sm) as shown in Eq. (9) [22]. This complex is a centrosymmetric binuclear molecule, with the benzenethiol ligand as the bridging groups.

$$2(MeC_5H_4)_3Ln + 2HSPh \xrightarrow{THF} [(MeC_5H_4)_2LnSPh(THF)]_2 \qquad Ln = Nd, Sm \tag{9}$$



Scheme 1.

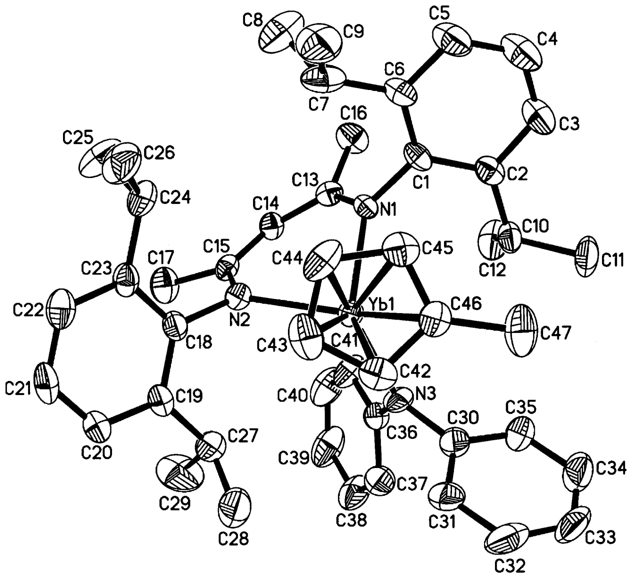


Fig. 6. Molecular structure of $(MeC_5H_4)[(DIPPh)_2nacnac]YbNPh_2$.

3. Reactivity of organolanthanoid complexes containing N and S ligands

3.1. Reactivity of organolanthanoid amide

Organolanthanoid amides have been widely used as precursor for synthesis of lanthanoid compounds [23]. However, their application in homogeneous catalysts was not known until 1989. Marks and coworkers first reported that the organolanthanoid amide is an efficient precatalyst for hydroamination/cyclization of N-unprotected aminoolefins [24]. The pioneering work indicated that organolanthanoid amide is potential in the homogeneous catalysts in the formation of C–N bond. During our study on the reactivity of organolanthanoid amide to phenyl isocyanate (PhNCO), CS_2, phenyl isothiocyanate (PhNCS), we have found that these molecules can be activated by organolanthanoid amide, and new C–N bonds are formed in these reactions.

3.1.1. Reactions with phenyl isocyanate

Organolanthanoid amides, like $(MeC_5H_4)_2LnN(\textit{i}\text{-}Pr)_2(THF)$, $(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$, and $(\textit{t}\text{-}BuC_5H_4)_2LnNC_5H_{10}(THF)$ (Ln = Y, Er, Yb), all exhibit good catalytic activity for phenyl isocyanate oligomerization. Taking $(MeC_5H_4)_2LnN(\textit{i}\text{-}Pr)_2(THF)$ as an example, when 300 equivalents of phenyl isocyanate was added to $(MeC_5H_4)_2LnN(\textit{i}\text{-}Pr)_2(THF)$ at 30 °C, the reaction took place rapidly, and solid products came down immediately. After work up, methanol insoluble and soluble fractions were obtained. The methanol soluble fraction was characterized mainly to be a trimer of PhNCO.

The active species for the reaction was studied by stoichiometric reaction of $(MeC_5H_4)_2LnN(\textit{i}\text{-}Pr)_2(THF)$ with PhNCO to be a complex formed from the insertion of PhNCO into Ln–N bond of $(MeC_5H_4)_2LnN(\textit{i}\text{-}Pr)_2(THF)$, in which a new group $NPhCON(\textit{i}\text{-}Pr)_2$ as bidentate ligand coordinated to the central metal (Eq. (10)).

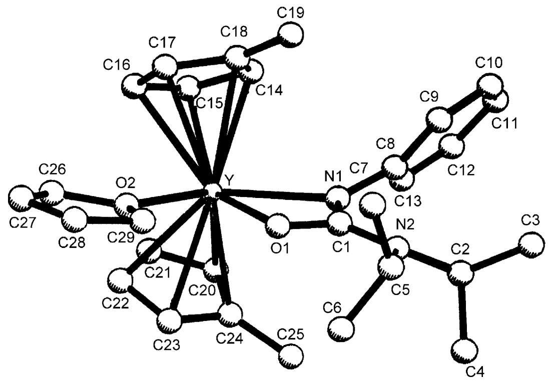


Fig. 7. Molecular structure of $(\text{MeC}_5\text{H}_4)_2\text{Y(THF)[O}\doteq\text{CN(i-Pr)}_2\doteq\text{NPh]}$.

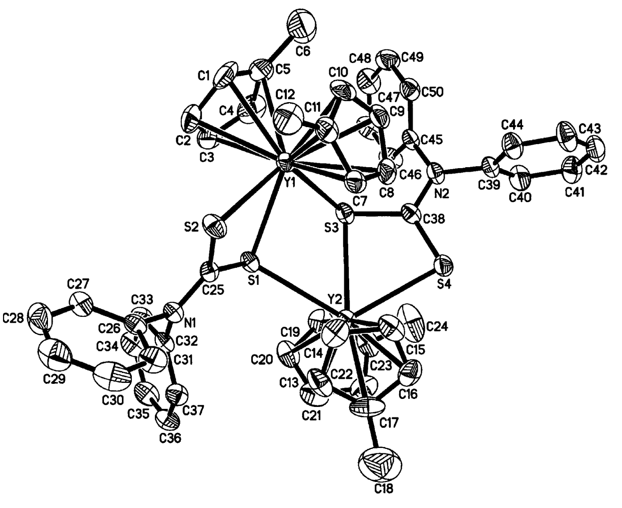
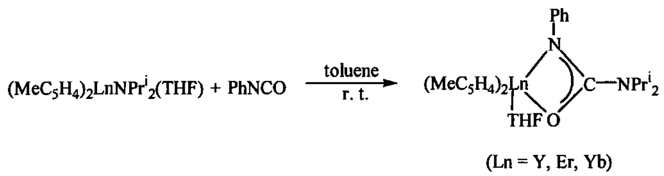


Fig. 8. Molecular structure of $[(\text{MeC}_5\text{H}_4)_2\text{Y}(\mu\text{-CS}_2)\text{NPh}_2]_2$.



(10)

The molecular structure of this complex is shown in Fig. 7. The complex $(\text{MeC}_5\text{H}_4)_2\text{Y(THF)[O}\doteq\text{CN(i-Pr)}_2\doteq\text{NPh]}$ shows the catalytic activity in PhNCO polymerization as good as the precatalyst $(\text{MeC}_5\text{H}_4)_2\text{YN}(i\text{-Pr})_2(\text{THF})$ does [11].

3.1.2. Reactions with CS_2

Activation reaction of CS_2 by organolanthanoid alkyl complex has been known to give the corresponding CS_2 insertion product [25]. Organolanthanoid amides, like organolanthanoid alkyl complex, can also activate CS_2 molecule. When $(\text{MeC}_5\text{H}_4)_2\text{YNPh}_2(\text{THF})$ is put together with CS_2 at room temperature, the color of the solution changed to red immediately. An insertion product of CS_2 into Y–N bond $[(\text{MeC}_5\text{H}_4)_2\text{Y}(\mu\text{-CS}_2)\text{NPh}_2]_2$ is isolated in good yield, in which a new C–N bond and dithiocarbamate group are formed (Eq. (11)). X-ray crystal structure determination shows this complex is a dimer (Fig. 8) [26].

$$2(\text{MeC}_5\text{H}_4)_2\text{YNPh}_2(\text{THF}) + 2\text{CS}_2 \rightarrow [(\text{MeC}_5\text{H}_4)_2\text{Y}(\mu\text{-CS}_2)\text{NPh}_2]_2 \qquad (11)$$

Analog complex $(\text{MeC}_5\text{H}_4)_2\text{YbNPh}_2(\text{THF})$ can also react with CS_2 to give a similar complex $(\text{MeC}_5\text{H}_4)_2\text{Yb}(\eta^2\text{-CS}_2)\text{NPh}_2$ (Eq. (12)), which has a monomeric structure (Fig. 9) [26].

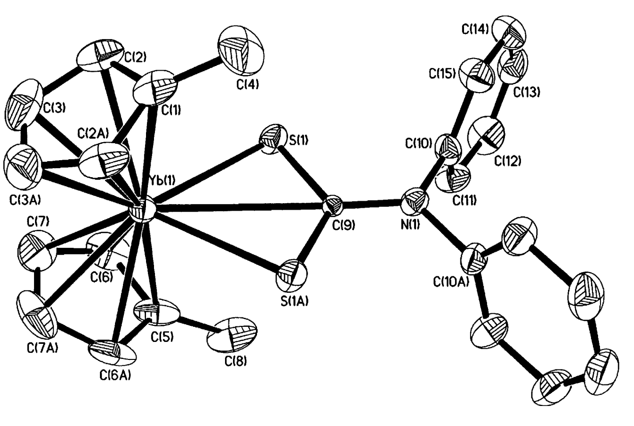


Fig. 9. Molecular structure of $(\text{MeC}_5\text{H}_4)_2\text{Yb}(\mu\text{-CS}_2)\text{NPh}_2$.

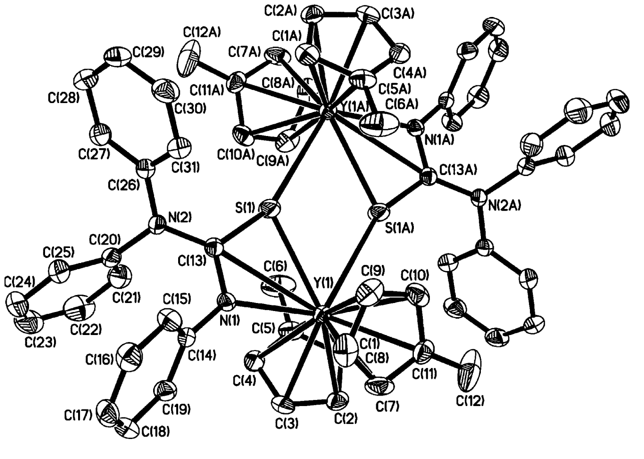


Fig. 10. Molecular structure of $\{(\text{MeC}_5\text{H}_4)_2\text{Y}[\mu\text{-}\eta^2\text{-SC(NPh}_2)\text{NPh}]\}_2$.

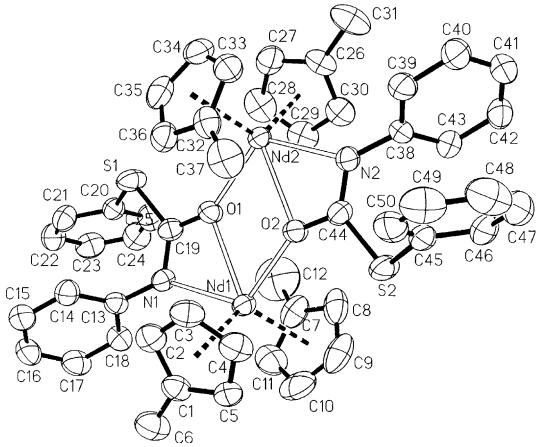


Fig. 11. Molecular structure of $[(CH_3C_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2$.

$$(MeC_5H_4)_2YbNPh_2(THF) + CS_2 \rightarrow (MeC_5H_4)_2Yb(\eta^2\text{-}CS_2)NPh_2 \quad (12)$$

3.1.3. Reactions with PhNCS

Organolanthanoid amide reacts with PhNCS, an isoelectronic analog of CS_2 and PhNCO, to provide a complex with $PhNC(NPh_2)S$ moiety. In this reaction, PhNCS inserts to Ln–N bond, and a new C–N bond ($C\text{-}NPh_2$) is formed (Eq. (13)).

$$2(MeC_5H_4)_2YNPh_2(THF) + 2PhNCS \rightarrow \{(MeC_5H_4)_2Y(\mu\text{-}\eta^2\text{-}SC(NPh_2)NPh]\}_2 \quad (13)$$

The characterization of molecular structure indicates the new ligand $PhNC(NPh_2)S$ donors four electrons to the central ion. The crystal structure is shown in Fig. 10 [26].

3.2. Reactivity of organolanthanoid thiolate

The synthesis of organolanthanoid thiolate has been extensively studied up to now [27]. However, the reactivity of these complexes has not been well understood [28]. Recently, we have found that organolanthanoid thiolate $[(MeC_5H_4)_2NdSPh(THF)]_2$ is able to activate small molecules, such as PhNCO and PhNCS, the new C–S bond was formed in these reactions.

3.2.1. Reaction with PhNCO

PhNCO can be activated by organolanthanoid thiolate $[(MeC_5H_4)_2NdSPh(THF)]_2$. Thus, the reaction of $[(MeC_5H_4)_2NdSPh(THF)]_2$ with one equivalent of PhNCO gives the product $[(MeC_5H_4)_2NdOC(SPh)NPh]_2$, which shows two strong absorptions at 1597 and 1520 cm^{-1} assigned to bidentate CN and CO vibrations in its IR spectrum. It is unambiguous that in this reaction a new C–S bond was formed through SPh group transferred to the isocyanate carbon atom in which the new amido ligand [OC(SPh)NPh] formed is coordinated to central metal Nd in η^2-fashion (Eq. (14)) (Fig. 11). X-ray determination shows the complex to be a dimer [22].

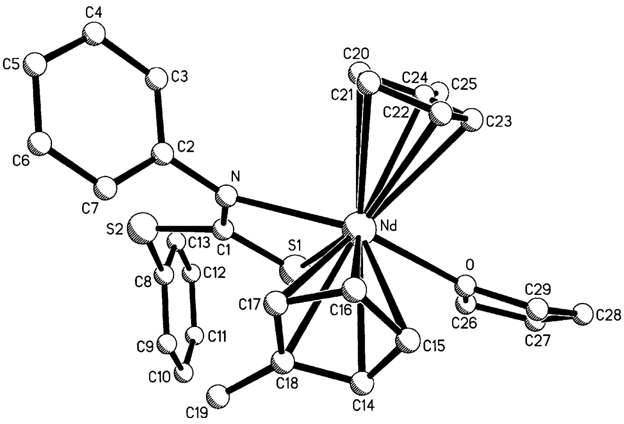


Fig. 12. Molecular structure of $(MeC_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh]$-(THF).

$$[(MeC_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2 + 2PhNCO \rightarrow [(MeC_5H_4)_2Nd]_2[\mu\text{-}\eta^2\text{-}OC(SPh)NPh]_2 \quad (14)$$

Both $[(MeC_5H_4)_2NdSPh(THF)]_2$ and $(MeC_5H_4)_2NdOC(SPh)NPh$ show good catalytic activity for oligomerization of PhNCO [29].

3.2.2. Reaction with PhNCS

The reaction of $[(MeC_5H_4)_2NdSPh(THF)]_2$ with PhNCS proceeds also smoothly at room temperature. An insertion product of PhNCS into Nd–S bond of $[(MeC_5H_4)_2NdSPh(THF)]_2$ $(MeC_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF)$ was obtained (Eq. (15)). X-ray determination shows that the new complex contains a thiocarbonate derivative, i.e. the CS_2N fragment of the dihapto-coordinated ligand, formed through SPh group linked to the isocyanate carbon atom (Fig. 12) [22].

$$[(MeC_5H_4)_2Nd(\mu\text{-}SPh)(THF)]_2 + 2PhNCS \rightarrow 2(MeC_5H_4)_2Nd[\eta^2\text{-}SC(SPh)NPh](THF) \quad (15)$$

3.3. Polymerization of polar monomers

Organolanthanoid complexes with Ln–C, Ln–H bond have been found to be the effective single component catalysts for ethylene polymerization without adding any cocatalyst [30]. Moreover, they can tolerate the existence of polar group in the monomer, and catalyze the living polymerization of alkyl methacrylate (acrylate) to give the polymer with high molecular weight and narrow molecular weight distribution [31]. The catalytic behavior of organolanthanoid amides in

Table 1
Polymerization of MMA catalyzed by organolanthanoid amides [a]

Entry	Catalyst	T (°C)	C (%)	M_n ($\times 10^3$)	M_w/M_n
1	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	40	97.1	268	2.10
2	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	0	99.9	431	1.79
3 [b]	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	0	96.2	–	–
4	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	−78	100	410	1.72
5	$(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$	0	100	125	1.14
6	$(MeC_5H_4)_2YbNPh_2(THF)$	0	95.0	253	1.67
7	$(C_5Me_5)_2YbNPh_2$	0	0	–	–
8	$(t\text{-}BuC_5H_4)_2YbNC_5H_{10}(THF)$	0	61.4	117	–
9	$(MeC_5H_4)_2YN(i\text{-}Pr)_2(THF)$	0	100	148	1.31
10	$(C_9H_7)_2YN(i\text{-}Pr)_2$	0	93.9	116	1.23
11 [c]	(R)-(neomenthyl)LaN(TMS)$_2$	0	36.0 [b]	50	7.9

[a] Polymerization conditions: catalyst concentration, 0.2 mol% MMA; solvent, toluene; solvent/$[MMA]_0 = 10$ V/V; 2 h.

[b] Catalyst concentration, 0.07 mol% MMA.

[c] 160 h.

polymerization of polar monomer was first found by Marks and coworkers [32]. Their work shows that the stereospecific polymerization of methyl methacrylate (MMA) can be carried out by use of chiral organolanthanoid amide. We found that organolanthanoid amides are also highly effective catalysts for the polymerization of polar monomers, such as MMA, (dimethylamino)ethyl methacrylate (DMAEMA) and ε-caprolactone.

3.3.1. Polymerization of MMA

Table 1 summarized the typical results of MMA polymerization catalyzed by a variety of organolanthanoid amides (Scheme 2) [12–14,33].

All these complexes, except $(C_5Me_5)_2YbNPh_2$, show high catalytic activity at a quite broad range of reaction temperature from − 78 to 40 °C, and give the polymer with high molecular weight. Taking complex $(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$ as an example, the polymerization gives the conversion as high as 96% at 0 °C for 2 h even though the catalyst concentration decreases from 0.2 to 0.07 mol% MMA [33]. π Ancillary ligand and amido groups both have an apparent effect on the activity. The activity increases with the decrease of the bulk of the π ligand, $C_5Me_5 < t\text{-}BuC_5H_4 < MeC_5H_4$ [34]. The activity order of amido group is $NPh_2 < Ni\text{-}Pr_2 < NC_5H_{10}$ which is contrary to the order of their bulk [33b]. The influence of the metal elements on polymerization activity has also been observed. For (diisopropylamido)-bis(methylcyclopentadienyl)lanthanoids, the observed increasing order, Y > Er > Yb, is in agreement with the order of eight-coordinate ionic radii, and is also consistent with the activity order for organolanthanoid hydride or alkyl complexes [33b].

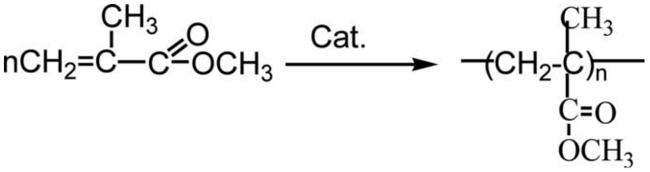
However, for the bis(methylcyclopentadienyl)-(piperidino)lanthanoids, the observed order is Yb > Er > Y, which is contrary to the order of the former. The real reason of these differences is not clear yet [12].

It should be noticed that the present polymerizations in comparable with the system with organolanthanoid alkyl is not well-controlled, resulting in broader molecular weight distribution, and greatly inflated number-average molecular weights. This might be due to side reactions of the electron-rich nitrogen anion with the highly functionalized monomer [35].

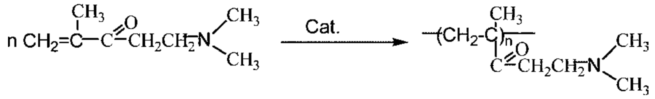
3.3.2. Polymerization of DMAEMA

All the work on the polymerization of methacrylates with organolanthanoid complexes published is restricted to the system of unfunctionalized methacrylates. Recently, we have first found that nitrogen-functionalized methacrylate, DMAEMA can also be polymerized effectively by organolanthanoid amide as catalyst without cocatalyst (Scheme 3) [36]. The typical results are given in Table 2.

All the amides, except the sterically crowded complex $(C_5Me_5)_2YbNPh_2$ tested have good activity. The poly-



Scheme 2.



Scheme 3.

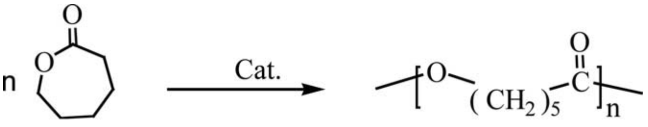
Table 2
Polymerization of DMAEMA catalyzed by organolanthanoid amides [a]

Entry	Catalyst	[I]/[M] (%)	T (°C)	C (%)	M_n (10^3)	M_w/M_n
1	$(MeC_5H_4)_2YN(i\text{-}Pr)_2(THF)$	0.2	0	100	121	1.22
2	$(MeC_5H_4)_2ErN(i\text{-}Pr)_2(THF)$	0.2	0	99.1	182	1.27
3	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	0.2	0	99.4	107	1.18
4	$(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$	0.2	0	100	178	1.16
5	$(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$	0.2	−78	100	151	1.11
6	$(MeC_5H_4)_2YbNPh_2(THF)$	0.2	0	99.0	256	1.70
7	$(t\text{-}BuC_5H_4)_2YbNPh_2(THF)$	0.2	0	99.7	104	1.20

[a] Polymerization conditions: solvent, toluene; solvent/monomer = 10 V/V; 2 h.

merization system can be carried out in a quite broad range of reaction temperature, and gives syndiotactic polyDMAEMA with high molecular weight and moderately molecular weight distribution. π-Ligand, amido group and central metal all have great effect on the polymerization activity. The active order is $C_5Me_5 < t\text{-}BuC_5H_4 < MeC_5H_4$, $NPh_2 < N(i\text{-}Pr)_2 < NC_5H_{10}$, $Yb < Er < Y$, which are consistent with those in MMA polymerization systems.

It is also observed that the activity decreases with the increase in polymerization temperature and number molecular weights of polyDMAEMA are deviated from the theoretic one. These results indicate that the side reaction might also take place together with the polymerization reaction in the present polymerization system.



Scheme 4.

Table 3
Ring-opening polymerization of ε-caprolactone by organolanthanoid amides [a]

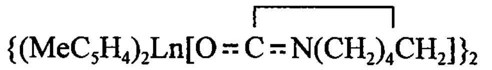
Entry	Catalyst	C (%)	M_n (10^3)	M_w/M_n
1	$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$	26.2	–	–
2	$(MeC_5H_4)_2ErN(i\text{-}Pr)_2(THF)$	66.4	117.5	1.14
3	$(MeC_5H_4)_2YN(i\text{-}Pr)_2(THF)$	84.4	180.0	1.24
4	$(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$	96.2	79.9	1.23
5	$(MeC_5H_4)_2ErNC_5H_{10}(HNC_5H_{10})$	99.1	118.0	1.28
6	$(MeC_5H_4)_2YNC_5H_{10}(HNC_5H_{10})$	100	123.4	1.28
7	$(t\text{-}BuC_5H_4)_2YbNC_5H_{10}(THF)$	100	133.6	1.41
8	$(t\text{-}BuC_5H_4)_2ErNC_5H_{10}(THF)$	100	139.2	1.42

[a] Polymerization conditions: $[M]_0/[I]_0 = 500$ mol/mol; solvent, toluene; solvent/$[M]_0 = 10$ V/V; 20 °C; 4 h.

3.3.3. *Ring-opening polymerization of ε-caprolactone*

Ring-opening polymerization of lactone catalyzed by lanthanoid complex have been reported extensively [31b,37]. However, almost all of the catalysts are those complexes containing Ln–O [38], Ln–C [39] and Ln–H [39] bonds, few are those containing Ln–N bonds [40]. We have found that bis(methylcyclopentadienyl)-lanthanide amides and related complexes are also efficient catalysts for the ring-opening polymerization of ε-caprolactone (Scheme 4), Table 3 listed the main results obtained by a variety of amides [41].

The polymers formed are generally of high molecular weight ($M_n > 100\,000$) with narrow polydispersities ($M_w/M_n < 1.5$). Both the central elements and the amido group have an apparent effect on the catalytic activity. For the central elements, the observed increasing order, $Yb < Er < Y$, is in agreement with the order of eight-coordinate ionic radii; for the amido groups, the increasing order is $N(i\text{-}Pr)_2 < NC_5H_{10}$, which is consistent with the order of their bulk. In addition, the chelating ligand containing organolanthanoids


$$\{(MeC_5H_4)_2Ln[O{=}C{=}N(CH_2)_4CH_2]\}_2$$

(Ln = Yb, Er, Y) also show good catalytic activity for the ring-opening polymerization of ε-caprolactone [17].

Organolanthanoid thiolate is also effective catalyst for the ring-opening polymerization of ε-caprolactone. For example, using $[(MeC_5H_4)_2Sm(\mu\text{-}SPh)(THF)]_2$ as catalyst, the polymerization gives the conversion as high as 100% at 35 °C for 3 h under the catalyst amount of 0.1 mol% [29]. In these systems, transesterification reaction, as a side reaction, was also observed.

4. Conclusion

The results presented in this account show that the chemistry of organolanthanoid complexes with

Ln–N and Ln–S bonds is interesting. Especially, the ability of these complexes to promote C–N and C–S bonds formation might give them a promising future in lanthanoid catalysis, as 'C–N' and 'C–S' moieties are fundamental building blocks in organic chemistry.

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