

Homolysis of the Ln–N bond: Synthesis, characterization and catalytic activity of organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands

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Abstract

A series of new organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands were synthesized via one-electron reductive elimination reaction. Treatments of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb, Eu) with 2 equiv. of $\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_7$ (**1**) or $\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_7$ (**2**), respectively in toluene at moderate high temperatures produced, after workup, the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**5**), Ln = Eu (**6**)) and $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**7**), Ln = Eu (**8**)) in reasonable to good yields. Treatments of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb, Eu) with 2 equiv. of $\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6\text{SiMe}_3$ (**3**) or $\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6\text{SiMe}_3$ (**4**), respectively, in toluene at moderate high temperatures afforded, after workup, the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**9**), Ln = Eu (**10**)) and $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**11**), Ln = Eu (**12**)) in good to high yields. All the compounds were fully characterized by spectroscopic methods and elemental analyses. The structure of complex **9** was additionally determined by single-crystal X-ray analyses. Studies on the catalytic activities of complexes showed that the complexes having silyl group functionalized indenyl ligands have high catalytic activities on ϵ -caprolactone polymerization. The temperatures, substituted groups on the indenyl ligands of the complexes, and solvents effects on the catalytic activities of the complexes were examined.

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1. Introduction

The chemistry of organolanthanide complexes is one of the most active fields among the transitional metal chemistry for their unique structures and reactivity [1]. It has been found that organolanthanide complexes

behaves a diverse chemistry including catalytic transformations of olefins and lactones polymerization [2], hydroamination/cyclization [3], hydrosilylation [4], hydrophosphination [3b,5], and hydroboration [6]. Organolanthanide(II) complexes are one of the family among the organolanthanide complexes, which can effect various reactions including activation of small molecules such as N_2 [7], CO [8], unsaturated hydrocarbons [9], carbonyl [10], as well as polymerization of ethylene [2], styrene [2], acrylonitrile [11], methyl methacrylate and lactones [2,12]. Among the reactivity of

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organolanthanide(II) complexes, the ring-opening polymerization of lactones provides a convenient route to biodegradable polyesters, which are of interest for a variety of practical applications [1,13].

We have reported that the interactions of functionalized indene compounds having internal donor substituted groups such as *N,N*-dimethylaminoethyl group [12b,12c], methoxyethyl groups [12d] with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) afforded organolanthanide(II) complexes. Interactions of $\text{C}_9\text{H}_6\text{-1-R-3-CH}_2\text{SiMe}_2\text{NC}_4\text{H}_8$ ($\text{R} = \text{H}, \text{CH}_3$) with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ resulted in the isolation and characterization of a series of novel tetranuclear triple-decker and monomeric europium(II) complexes [12e]. The reaction pathway was proposed to involve tandem silylamine elimination/homolysis of the Ln-N ($\text{Ln} = \text{Yb}, \text{Eu}$) bond based on the experimental results. It is found that organolanthanide(II) complexes prepared by this method can function as single-component of MMA polymerization catalysts.

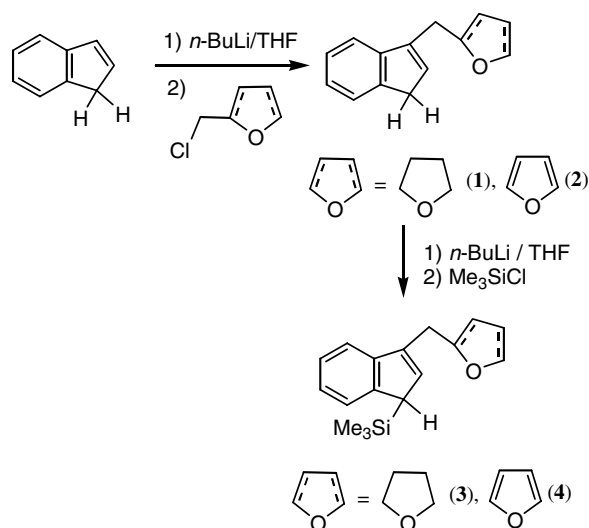
In this paper, we will report the synthesis, characterization and catalytic activities of a series of new organolanthanide(II) complexes having furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands. The studies on the catalytic activities of the complexes indicated that the complexes having both trimethylsilyl and furfuryl- or tetrahydrofurfuryl substituents on the indenyl ligands showed high catalytic activities on ring-opening polymerization of ϵ -caprolactone, while the complexes with only furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands cannot catalyze the ϵ -caprolactone polymerization. To the best of our knowledge, the complexes **10** and **12** represent the first examples of europium(II) complexes as the single-component of ring-opening polymerization of ϵ -caprolactone catalysts with high catalytic activities [2,13]. The solvents, polymerization temperatures, and solvent/monomer and monomer/catalyst ratio effects on the catalytic activities of the complexes and polymerization were examined.

2. Results and discussion

2.1. Synthesis and characterization of the ligands

The furfuryl- and the tetrahydrofurfuryl-substituted indene compounds **1** and **2** were synthesized according to the literatures with slightly modified procedures [14,15]. The substituted indene compounds were then transferred to the corresponding lithium salts, treatment of the freshly prepared indenyl lithium with excess of Me_3SiCl gave, after workup, the corresponding indene compounds **3** and **4** in good yield. The full synthetic procedures were outlined in Scheme 1.

The indene compounds were fully characterized by spectroscopic and high-resolution MS methods. ^1H



Scheme 1.

NMR analyses showed that the furfuryl or the tetrahydrofurfuryl-substituted group connects to the sp^2 carbon of the five-membered ring of the indene ring, and the Me_3Si functional group of the compounds **3** and **4** connected to the sp^3 carbon of the indene ring.

2.2. Synthesis and characterization of organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-substituted indenyl ligands

Treatment of lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) with 2 equiv. of the corresponding tetrahydrofurfuryl-substituted indene compound **1** or the furfuryl-substituted indene compound **2** in toluene at moderate high temperatures produced, after workup, the organolanthanide(II) compounds with formula $[\eta^5\text{:}\eta^1\text{-(C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6\text{)}]_2\text{-Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**5**), Eu (**6**)), and the organolanthanide(II) complexes with general formula $[\eta^5\text{:}\eta^1\text{-(C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6\text{)}]_2\text{Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**7**), Eu (**8**)) (Scheme 2). The complexes were fully characterized by IR and elemental analyses. The complexes **5** and **7** were also characterized by ^1H NMR spectra analyses; the diamagnetic properties of complexes **5** and **7** from the ^1H NMR spectra indicated that the central ytterbium metals in complexes are in the oxidation state +2. The ^1H NMR spectra of complexes **6** and **8** were not informative due to lack of locking signal for the paramagnetic property of the complex. The complexes were extremely air and moisture sensitive solid, they are soluble in polar solvents such as THF, DME and pyridine, slightly soluble in toluene, and insoluble in *n*-hexane.

The formation of divalent complexes **5–8** is believed to go through one-electron reductive elimination process. To extend the reaction scopes, to improve the solubility of the organolanthanide(II) complexes in nonpolar solvent such as toluene, the interactions of indene

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