



# Rare-earth metal complexes with tridentate linked amido-indenyl ligand: Synthesis, characterization, and catalytic properties for intramolecular hydroamination



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## ARTICLE INFO

### Article history:

Received 14 April 2014

Received in revised form

8 June 2014

Accepted 18 June 2014

Available online 8 July 2014

### Keywords:

Rare-earth metals

Amido-indenyl ligand

Half-sandwich complexes

Hydroamination

## ABSTRACT

The complexes of rare-earth metals (Y, Sm, Er and Yb) with a tridentate silicon-linked amido-indenyl ligand were synthesized and characterized. These complexes demonstrated high efficiency in catalyzing the intramolecular hydroamination of non-activated olefins under very mild conditions. Structure–reactivity relationship study revealed that the catalytic activities of these complexes decreased as the radii of the core metal ion decreased.

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## Introduction

The rare-earth metals of group 3 including Sc, Y and lanthanides occupy a unique position in catalytic chemistry due to their distinct structural characteristics such as the “lanthanide contraction”. The synthesis and structural study of myriad complexes of rare-earth metals with various organic ligands have not only spurred the development of coordination chemistry, but also led to many efficient catalysts for numerous reactions [1]. Since the pioneering works of Marks and co-workers [2], the hydroamination of non-activated olefins has been one of the most important applications of these complexes in organic synthesis, providing a highly atom-economic approach to nitrogen-containing structures widely occurring in compounds with important biological and pharmaceutical activities [3]. In this regard, the development of new ligands, the synthesis and characterization of corresponding rare-earth metal complexes and reactivity study has been the research focus, committing to a broader reaction scope, lower catalyst loading amount, milder reaction conditions as well as better stereoselectivity.

Compared to the widely used cyclopentadienyl group (Cp)-based sandwich metallocene catalysts in this field, half-sandwich rare-earth metal complexes with Cp ligands linked to a short side arm containing additional chelating functionalities have shown distinct reactivities, which has been referred to as constrained geometry complexes (CGCs) [4–6]. In this field, rare-earth metal complexes with the silicon-linked amido-cyclopentadienyl ligands initially developed by Bercaw [5] and Okuda [6] have been one of the most successful classes of CGCs.

Particularly, the yttrium complex **1** introduced by Okuda [6h] is intriguing in that the tridentate silicon-linked amido-cyclopentadienyl ligand allows great flexibility in structural modification, although the reactivities of this type of complexes in specific reactions remains largely unexplored (Fig. 1). Inspired by this, our group have recently developed a novel chiral yttrium complex **2** with a tridentate silicon-linked amido-indenyl ligand, which catalyzed the intramolecular hydroamination of non-activated olefins with up to 97% ee [7]. However, the presence of multiple chiral elements in this (R, R)-1,2-diaminocyclohexane-derived ligand leads to fluxionality in the corresponding catalyst structures, which adds to the difficulty in the structure–reactivity study of these complexes with this ligand. Nevertheless, a comparative study on the structure–reactivity of this type of tridentate ligands with different rare-earth metals would provide useful clues for the design of more efficient complexes for applications in relevant

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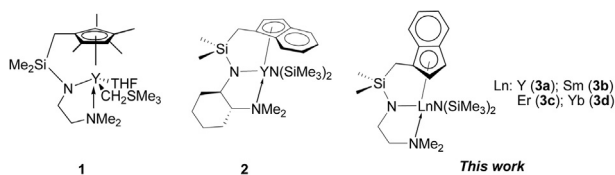


Fig. 1. Rare-earth metal complexes with silicon-linked tridentate ligands.

reactions. In this context, we designed and synthesized a novel silicon-linked tridentate amido-indenyl ligand from cheaply available indene and non-chiral diamine, and the corresponding complexes with rare-earth metals (Y, Sm, Er, Yb) were also easily accessed via a unified procedure for structure-reactivity study in the intramolecular hydroamination of non-activated olefins.

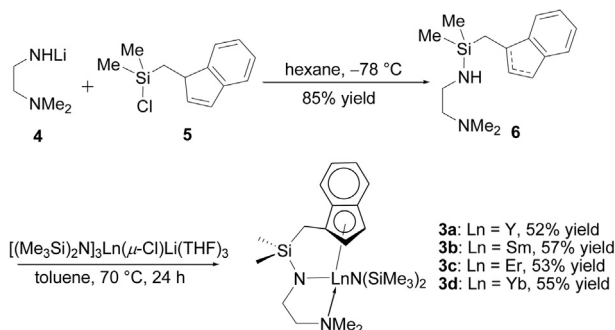
## Results and discussion

### Synthesis of rare-earth metal complexes **3**

The synthesis of rare-earth metal complexes **3** was performed following a similar procedure previously reported (Scheme 1) [7]. The reaction between equimolar lithium (2-(dimethylamino)ethyl) amide **4** and the known compound **5** gave the new tridentate ligand **6** in 85% yield as a mixture of two isomers. Subsequent treatment of **6** with corresponding  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (1.0 equiv.) in toluene provided the four complexes as microcrystalline solids in similar moderate yields after an appropriate work-up. These complexes are moderately soluble in *n*-hexane and highly soluble in THF and toluene, and could be stored at room temperature under inert atmosphere for several months without appreciable decrease in catalytic reactivities. The structures of complexes **3a** and **3b** were fully characterized by spectral methods, and the structures of all complexes were confirmed by single crystal X-ray crystallographic analysis.

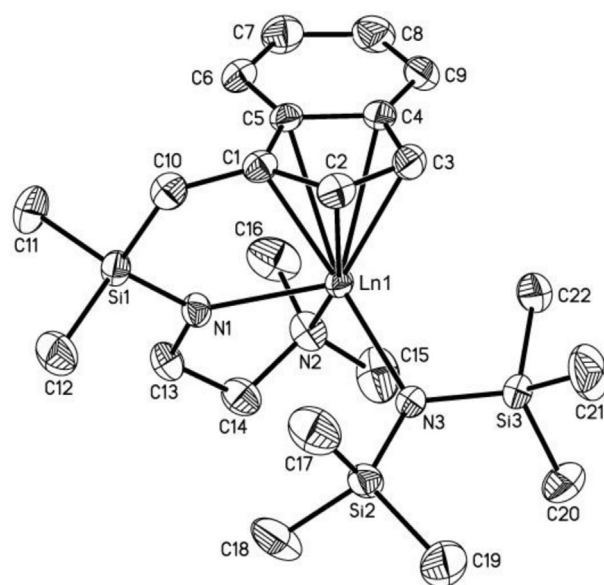
### Molecular structures of rare-earth metal complexes **3**

Single crystals of **3a–3d** were obtained by cooling the concentrated solution in toluene to  $-20^\circ\text{C}$ . Selected X-ray crystallographic data of these crystals were listed in Table 1. They all crystallized as mononuclear structures in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell, and the rare-earth metal atoms are about in tetrahedral coordination. The M–C bond distance of **3a** (2.640(2)–2.703(2) Å) between the yttrium atom and the indenyl carbon atom correlates well with those (2.642(2)–2.714(2) Å) of the corresponding Cp complex **1** reported by Okuda [6h]. The covalent M–N bond distances (M–N<sub>1</sub> and M–N<sub>3</sub>) are considerably



Scheme 1. Synthesis of rare-earth metal complexes **3**.

Table 1  
Selected bond lengths and angles for complexes **3a–3d**.



Complex	<b>3a</b> (Y)	<b>3b</b> (Sm)	<b>3c</b> (Er)	<b>3d</b> (Yb)
Bond lengths (Å)				
C1–Ln1	2.692(2)	2.753(2)	2.675(2)	2.655(2)
C2–Ln1	2.665(2)	2.747(2)	2.649(3)	2.621(2)
C3–Ln1	2.640(2)	2.713(2)	2.623(2)	2.599(2)
C4–Ln1	2.668(2)	2.717(2)	2.658(2)	2.645(2)
C5–Ln1	2.703(2)	2.738(2)	2.690(2)	2.674(2)
N1–Ln1	2.195(2)	2.246(2)	2.180(2)	2.161(2)
N2–Ln1	2.485(2)	2.555(2)	2.463(2)	2.447(2)
N3–Ln1	2.236(2)	2.291(2)	2.214(2)	2.194(2)
Bond angles (deg)				
N1–Ln1–N2	74.6(1)	73.0(1)	75.1(1)	75.5(1)
N1–Ln1–N3	110.2(1)	110.2(1)	109.5(1)	110.5(1)
N3–Ln1–N2	101.0(1)	100.7(1)	101.3(1)	100.9(1)

shorter than those of non-covalent ones (M–N<sub>2</sub>). Overall, an apparent lanthanide contraction effect on bond distances was observed: both the M–C and M–N bond lengths decreased as the radii of the rare-earth metal atoms decreased, while the bond angles showed no clear consistent trend.

An interesting feature of the structures of complexes **3a–3d** isolated in this work come from the asymmetry of the indenyl ring compared to the Cp ring. Although in our previous work with the chiral tridentate amido-indenyl ligand, we observed two epimers of the indenyl ring in the complexes of two different rare-earth metals (Y and Er) [7], the indenyl ring of the present four complexes adopts the same orientation. Such an observation implies that both the metal center and the diamine moiety might influence the coordination of the indenyl ring.

### Catalytic intramolecular hydroamination of non-activated olefins with complexes **3**

The catalytic activities of complexes **3a–3d** were then investigated in the intramolecular hydroamination of compound **7a** in C<sub>6</sub>D<sub>6</sub> (Table 2). In general, these complexes showed excellent reactivities in the reaction to provide the Markovnikov-type pyrrolidine product **8a** in excellent yield within a short time at ambient temperature. The reactivities of these complexes decreased as the radii of the metal atoms decreased, and this observation is

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