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Chiral rare-earth metal complexes with a tridentate amido-fluorenyl ligand: Syntheses, structures and catalytic performance

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ABSTRACT

The complexes of rare-earth metals (Y, La, Sm and Lu) with a chiral tridentate amido-fluorenyl ligand were synthesized and characterized. These complexes demonstrated high efficiency in catalyzing both the intramolecular hydroamination of non-activated olefins and the cyanosilylation of ketones under very mild conditions, however, with no enantiocontrol being achieved. ^{1}H NMR monitoring of the reaction process suggests the weak coordination capacity of the fluorenyl moiety might be responsible for the lack of asymmetric inducing power of the chiral complexes in such transformations.

1. Introduction

The development of rare-earth metal complexes for coordination chemistry studies and applications in organic synthesis has been an important research topic attracting considerable interests among organic chemists [1]. In this regard, half-sandwich rare-earth metal complexes with cyclopentadienyl group (Cp) or indenyl group-based ligands bearing a side arm containing additional coordinative functionalities, known as constrained geometry complexes (CGCs), have showed some intriguing structures and unique reactivities for useful organic transformations [2,3]. Particularly, several chiral rare-earth metal CGCs have demonstrated good to excellent chiral induction power in the intramolecular hydroamination of unactivated alkenes with free amines [4–7].

Our group has recently developed a new type of chiral rare-earth metal CGCs bearing silicon- or carbon-linked tridentate amido-indenyl ligands derived from enantiopure 1,2-diaminocyclohexane (Fig. 1) [7]. Although such complexes have exhibited high efficiency in catalyzing the asymmetric intramolecular hydroamination of olefins with free amines, the enantioselectivity turned out to be very unpredictably dependent on substrate structures. In this course, we realized that the flexible planar chirality of the indene ring in these complexes with multiple chiral elements might be highly influential on their chiral induction power. We then reasoned that the replacement of the indene ring with a fluorene ring would eliminate such a precarious planar chirality and might provide a better shielding effect due to the extended aromatic system. It should be noted that rare-earth metal CGCs containing a fluorenyl group have found applications in some useful organic transformations. For example, Cui and co-workers have reported the syntheses of such CGCs featuring a carbon-linked N-heterocyclic carbine-fluorenyl ligand, which have proved to be efficient precatalysts for highly 3,4-selective living polymerization of isoprene [8]. Herein, we report the preparation of four rare-earth metal complexes featuring a novel chiral tridentate amido-fluorenyl ligand and their catalytic activity in intramolecular hydroamination of alkenes and cyanosilylation of ketones.

2. Results and discussion

2.1. Syntheses of rare-earth metal complexes 3

The synthetic route to chiral rare-earth metal complexes **3** is shown in Scheme 1. Different from the one adopted in the synthesis of complex **2** in our previous work [7], this route is more practical in that a late-stage formation of the dimethylamino moiety in the key intermediate amide **5** enables the direct use of more cheaply available chiral (1*R*, 2*R*)-cyclohexane-1,2-diamine, instead of (1*R*,

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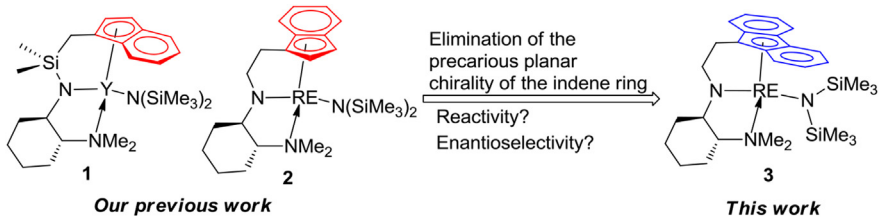
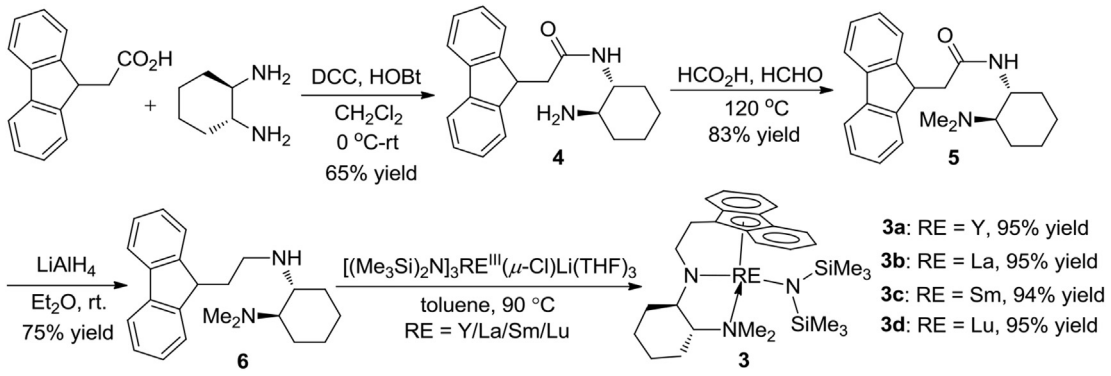


Fig. 1. Chiral half-sandwich rare-earth metal complexes with a tridentate ligand.



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

2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine, as starting material. Routine reduction of **5** with $LiAlH_4$ furnished the desired ligand **6**, which was reacted with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ in toluene to provide the four chiral half-sandwich rare-earth metal complexes **3** in excellent yields.

2.2. Molecular structures of rare-earth metal complexes *3*

Single crystals of **3a**-**3d** suitable for X-ray crystallographic analysis were obtained by recrystallization in toluene. Selected bond data of these crystals were listed in Table 1. They all crystallized as mononuclear structures in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The rare-earth metal atoms are about in a tetrahedral coordination mode with the compound **6** serving as a tridentate ligand as expected. The bond lengths of covalent RE-N bonds (RE-N1 and RE-N3) are considerably shorter than those of non-covalent ones (RE-N2). Overall, both the RE-C and RE-N bond lengths decreased as the radii of the rare-earth metal atoms decreased, which is consistent with the lanthanide contraction effect on bond distances.

A notable point of the structures of complexes **3** obtained in this work resides in the RE-C bond lengths of **3a** (Y-C bond, 2.614(3)-2.765(3) Å), **3c** (Sm-C bond, 2.671(4)-2.815(4) Å) and **3d** (Lu-C bond, 2.572(3)-2.719(3) Å) being longer on overall than their counterparts with the chiral tridentate amido-indenyl ligand in our previous work [7]. Such a phenomenon suggests that the coordination power of the fluorenyl ring to the rare-earth metal center might be weaker than that of the indene ring.

2.3. Catalytic asymmetric intramolecular hydroamination of a non-activated olefin with complex *3a*

The asymmetric intramolecular hydroamination of non-activated olefins with free amines represents a touchstone reaction for developing new chiral rare-earth metal complexes for asymmetric catalysis [4]. Therefore, the catalytic activity of the chiral amido-fluorenyl yttrium complex **3a** was then probed in the asymmetric hydroamination of olefin **7** (Scheme 2). The pyrrolidine product **8** of this reaction was transformed to the amide **9** for the determination of ee value by chiral HPLC as previously described [7a]. Compared to the previously developed chiral yttrium complex bearing a tridentate amido-indenyl ligand (5.0 h, 67% ee) [7b], complex **3a** demonstrated much lower catalytic efficiency with no enantioselectivity. This result is surprising and very frustrating, given the high structural similarity between these two types of complexes.

In light of the above results and the X-ray crystallographic data, we presumed that the very poor enantiocontrolling power of the complex might be ascribed to the relatively weaker coordination power of the fluorenyl group, which may disassociate from the metal center in the presence of a large excess of the primary amine substrate **7**, leading to the decomposition of the chiral catalyst. To test this assumption, we selected simple isopropyl amine to investigate its interaction with complex **3a** by ^1H NMR monitoring under similar reaction conditions. As shown in Fig. 2, the ^1H NMR signal of complex **3a** disappeared shortly after mixing with 5.5 equivalent of isopropyl amine, while signals congruent with those of the free ligand **6** predominated. This observation is clearly indicative of the decomposition of the chiral catalyst in the system involving disassociation of the fluorenyl group (or even the whole chiral ligand), which might explain the complete lack of enantioselectivity in the asymmetric hydroamination of **7** using complex **3a** as precatalyst.

2.4. Catalytic intermolecular cyanosilylation of ketones with complexes *3*

The cyanosilylation of ketones represents one of the most straightforward ways to cyanohydrins, which are very important synthetic intermediates with applications in the syntheses of a myriad of pharmaceuticals and agrochemicals [9–10]. We then tested the catalytic activities of complexes **3a-3d** in the cyanosilylation of 2-acetonaphthone **10a** under solvent-free conditions (Table 2). In general, these complexes showed excellent reactivities