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Intramolecular enantioselective hydroamination catalyzed by rare earth binaphthylamides

Jérôme Hannedouche [a,b], Jacqueline Collin [a,b,*], Alexander Trifonov [c], Emmanuelle Schulz [a,b,*]

[a] Univ Paris-Sud, Laboratoire de Catalyse Moléculaire, ICMMO, UMR 8182, Orsay, F-91405, France
[b] CNRS, Orsay, F-91405, France
[c] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod GSP-445, Russia

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ABSTRACT

Asymmetric intramolecular hydroamination reaction is a stately way to prepare chiral nitrogen-containing heterocyclic compounds. We report in this account our personal contribution in this field with the synthesis of chiral amido rare-earth complexes. A new family of structurally defined heterobimetallic rare earth lithium ate complexes based on N-substituted binaphthylamido ligands was discovered that promoted the hydroamination/cyclization of aminoolefins with up to 87% ee.

Neutral rare earth amido and amido alkyl complexes could also be prepared and led to very active species. A more simple and reliable synthetic procedure was discovered towards the preparation of heterobimetallic rare earth amido alkyl ate complexes. They proved to be also active and enantioselective catalysts, as a good compromise between efficiency and practicability issues.

1. Introduction

Chiral nitrogen-containing heterocyclic structures are present as a recurrent scaffold in naturally occurring molecules or in biologically active compounds. Their usefulness for numerous applications is no more to be demonstrated and their preparation in an economic and environmentally friendly way remains a current challenge. Direct hydroamination reaction that consists in the straight addition of amine functionality onto a carbon–carbon unsaturation is an atom economic reaction which perfectly meets the requirements of "green chemistry" and "sustainable development" for the synthesis of valuable compounds. In this context, this reaction has known a great expansion in the last twenty years, with the development of numerous catalysts, promoters for this transformation in a selective manner either in an inter- or intramolecular way [1]. In 1989, Marks and his group were the first to discover the ability of lanthanide-based catalysts to promote efficiently the hydroamination/cyclization of aminoalkene derivatives [2]. A few years later, they proposed an enantioselective version of this transformation (AIH, Asymmetric Intramolecular Hydroamination) for the preparation of scalemic pyrrolidines and piperidines with lanthanocene-based catalysts modified by a menthyl or neomenthyl moiety [3]. New results for such reactions were reported only almost ten years later, in 2001, when Livinghouse and Bercaw found out that simple lanthanide trisamides catalyzed powerfully the intramolecular hydroamination of aminoalkenes [4]. This discovery opened the way to the search for new chiral catalysts, and different teams then proposed the use of several catalytic systems based on non-cyclopentadienyl structures [5]. Thus in the last ten years, the number of reports dealing with the enantioselective intramolecular hydroamination reaction has considerably increased and it is not possible to be exhaustive here [6]. Some seminal advanced work was however published in 2003 by Marks, describing the usefulness of *in situ* prepared bis(oxazoline) lanthanide complexes as active catalysts leading rapidly at room temperature to targeted heterocycles in up to 67% ee [7]. The same year, Scott described the preparation and isolation of lanthanum phenoxide catalysts possessing an amidobiphenyl backbone as chiral moiety that allowed the cyclization of aminopentene derivatives with up to 61% ee [8]. A chiral-bridged aminotroponiminate complex of lutetium was isolated and characterized by Roesky et al. and reported to be an active but moderately enantioselective catalyst for the cyclization of

* Corresponding authors. Univ Paris-Sud, Laboratoire de Catalyse Moléculaire, ICMMO, UMR 8182, Orsay, F-91405, France.
E-mail addresses: jacqueline.collin@u-psud.fr (J. Collin), emmanuelle.schulz@u-psud.fr (E. Schulz).

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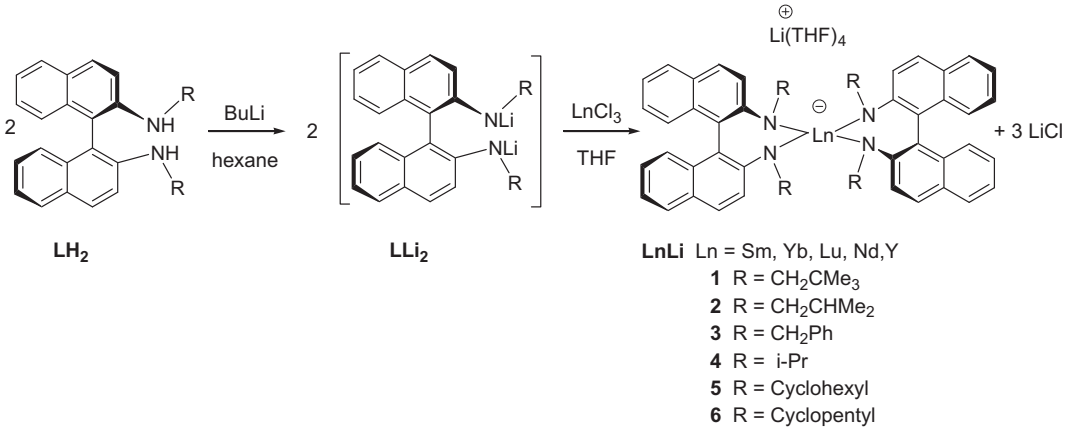

Scheme 1. Synthesis of rare earth *N*-substituted-(*R*)-binaphthylamine lithium ate complexes **LnLi**.

terminal aminoalkenes [9]. Chiral scandium and yttrium complexes were also prepared by the groups of Livinghouse [10] and Hultzsch [11], respectively, for which the chirality was introduced through a binaphthyl backbone, either from binaphthylamine or binaphthol type. Those new catalysts were mainly tested for the transformation of aminoalkene derivatives and led to the preparation of scalemic pyrrolidines and piperidines with various efficiencies in terms of yield and enantioselectivity according to the substrate structure. Nevertheless and as far as we know, the chiral binaphthol alkyl scandium complex delivered the highest enantioselectivity reported up to now in the enantioselective intramolecular hydroamination reaction and led thus to the isolation of 2-methyl-4,4-diphenyl-pyrrolidine in 95% ee [11]. More recently, the group of Zi reported the synthesis of new chiral amidolanthanides derived from pyrrole-chelating moieties modified by a binaphthyl core and their moderate efficiency for the hydroamination/cyclization of aminoalkenes [12].

There is thus to date no general solution for promoting the enantioselective hydroamination/cyclization of various aminoalkene derivatives under smooth conditions to deliver the corresponding heterocycles in high enantioselectivities. We started our research in this field aiming at the preparation of new chiral amido rare-earth-based complexes. Our main purpose was to propose a synthetic procedure that could led to the easy preparation of these new chiral species, starting from readily available lanthanide salts, for instance. At the same time, the search of efficient chiral ligands was acutely based on their commercial accessibility, in both enantiomeric pure forms. We were further aware about their facile derivatization by common synthetic procedures to be able, at best, to adapt their structure to expected enhanced activity and/or enantioselectivity of the corresponding targeted lanthanide complexes.

Driven by these motivations, we report here our efforts towards the discovery of new families of binaphthylamido-based catalysts and their use to promote the asymmetric cyclization of aminoalkenes.

2. Heterobimetallic rare earth amido ate complexes: first generation of catalysts for intramolecular hydroamination

We have synthesized a new family of structurally defined heterobimetallic rare earth lithium ate complexes based on *N*-substituted binaphthylamido ligands **LH_2**. These complexes **LnLi** were readily obtained from binaphthylamido lithium salts **LLi_2** and rare earth chlorides $LnCl_3$ (Scheme 1). The first complexes of the series were prepared from the *N*-neopentyl substituted (*R*)-binaphthylamide bis lithium salt and samarium, neodymium, ytterbium or lutetium chlorides in tetrahydrofuran and recrystallized after elimination of lithium chloride [13]. X-ray structures indicated these **LnLi** species are isostructural ionic complexes composed of a discrete cation $\{Li(THF)_4\}^+$ and a discrete complex anion $\{Ln[(R)\text{-}C_{20}H_{12}N_2R_2]_2\}^-$. The Ln atoms coordinated by four nitrogen atoms adopt a distorted tetrahedral geometry. The vicinal substituents of the nitrogen atoms are all placed in a *trans* orientation. The average Ln–N bond lengths are very similar despite the differences in the ionic radii of trivalent lanthanides and are noticeably longer than those reported for neutral lanthanide amido complexes. This common structure was obtained for all the complexes that could be crystallized with different *N*-substituted ligands (see Fig. 1).

This new family of complexes proved to be efficient for the asymmetric cyclization of aminoalkenes yielding pyrrolidines and a piperidine with significant enantiomeric excesses. We indeed focused on the optimization of these catalysts by varying the rare earth, the nature of the nitrogen substituents and the alkali metal.

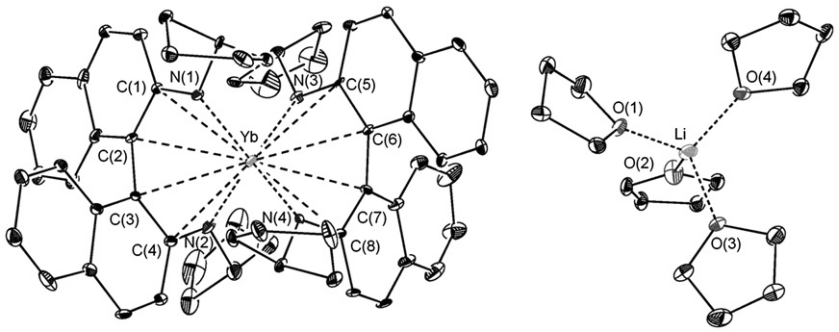

Fig. 1. ORTEP drawing of complex $\{Li(THF)_4\}\{Yb[(R)\text{-}C_{20}H_{12}(NC_5H_9)_2]_2\}$ **YbLi6**.