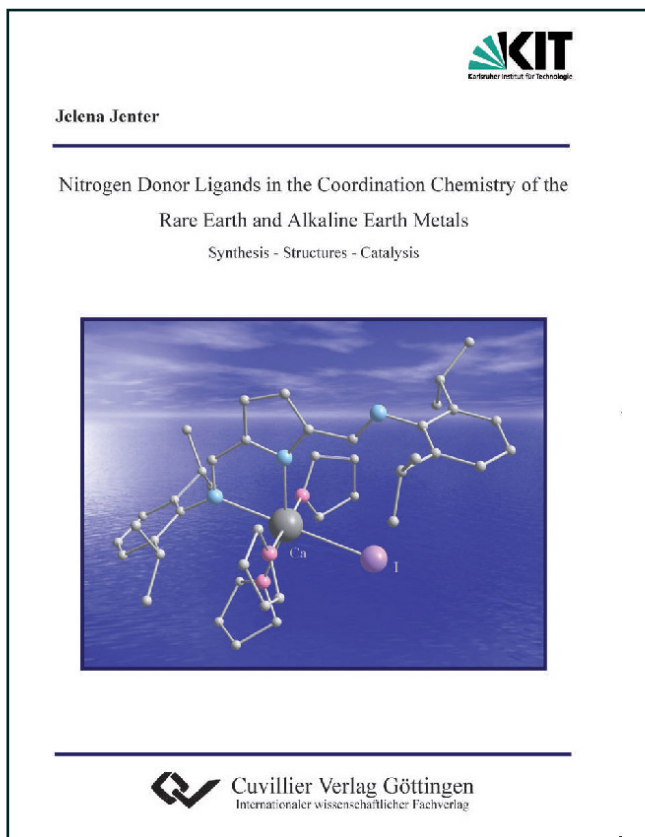




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**Nitrogen Donor Ligands in the Coordination  
Chemistry of the Rare Earth and Alkaline Earth  
Metals**  
Synthesis - Structures - Catalysis



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## 1. Introduction

### 1.1 Rare earth elements

The family of rare earth elements includes scandium, yttrium and the lanthanides. The lanthanides are the 15 elements (La-Lu), which are set apart together with the actinides from the other elements in the periodic table. Throughout the presented work, the general symbol Ln will be used to refer to all rare earth metals. The name “rare earth”, which describes the metal oxides, derives from the historically late discovery of these elements. Although this term implies that these metals are less abundant than the other elements, in fact, even thulium, which is the least common lanthanide except for the radioactive promethium is more abundant in the Earth’s crust than silver, mercury and the precious metals.<sup>[1]</sup> Rare earth metal compounds found versatile applications as laser materials, luminescent substances (for example in colour television sets) and permanent magnets.<sup>[2, 3]</sup> In addition, they are famous for their high activity in homogeneous catalysis as low-cost, low-toxicity and Lewis acidic catalysts.<sup>[4-8]</sup> Differently from the transition metals, the f-elements arise from the successive occupation of the f-orbitals with electrons. Regarding the lanthanides, the inert 4f shell lies deeply inside the ion and is well shielded from the 5s and 5p orbitals. This results in the lack of orbital interaction and back-bonding capability, which are important in transition metal chemistry. For this reason, lanthanides were assumed to have uninteresting chemistry. Because of their high electropositive character and the resulting tendency to form mainly ionic compounds, they were considered to be the trivalent extensions of the alkali and alkaline earth metals. The most stable oxidation state for all of the rare earth metals is +3. For a very long time, the only non-trivalent states considered accessible in coordination chemistry were Ce<sup>4+</sup>, Eu<sup>2+</sup>, Yb<sup>2+</sup> and Sm<sup>2+</sup>.<sup>[9, 10]</sup> In 2002 Evans reported molecular structures of LnI<sub>2</sub>(solv) (Ln = Tm<sup>2+</sup>, Dy<sup>2+</sup> and Nd<sup>2+</sup>).<sup>[11, 12]</sup> Recently, organometallic complexes of divalent lanthanum were prepared.<sup>[13, 14]</sup> Due to their stability, Eu<sup>2+</sup>, Yb<sup>2+</sup>, and Sm<sup>2+</sup> are still the most common divalent lanthanides. An important feature of the 4f-elements is called the lanthanide contraction which arises from the poor ability of f electrons to shield the other valence electrons from the nuclear charge.<sup>[2, 3]</sup> Consequently, the effective nuclear charge increases with the atomic number and the atoms/ions of the lanthanides contract. Table 1 shows the ionic radii of nine-coordinate trivalent ions of yttrium and the lanthanides.<sup>[15]</sup>

**Table 1** Ionic radii for nine-coordinate trivalent rare earth metal ions.

Ln	Ionic radius [Å]	Ln	Ionic radius [Å]
La	1.216	Tb	1.095
Ce	1.196	Dy	1.083
Pr	1.179	Y	1.075
Nd	1.163	Ho	1.072
Pm	1.144	Er	1.062
Sm	1.132	Tm	1.052
Eu	1.120	Yb	1.042
Gd	1.107	Lu	1.032

Except for the late actinides, there is no other series of so many elements that exhibits similar reactivity but different ionic radii. When lanthanide complexes are applied in homogeneous catalysis, this property affords the opportunity to control catalytic reactions not only by varying the ligands, but also by altering the center metal. In comparison to transition metal ions, lanthanide ions  $\text{Ln}^{3+}$  exhibit large ionic radii and thus tend to high coordination numbers. They are strong Lewis acids, highly oxophilic and consequently very reactive towards moisture and air. The coordination chemistry of rare earth metals was dominated by cyclopentadienyl complexes for a long time. Wilkinson's pioneering work showed that there is no 18-electron rule for the cyclopentadienyl lanthanide complexes  $(\text{C}_5\text{H}_5)_3\text{Ln}$ .<sup>[16, 17]</sup> The triscyclopentadienyl compounds were synthesized for all of the lanthanides except for the radioactive promethium with electron counts ranging from 18 for  $(\text{C}_5\text{H}_5)_3\text{La}$  to 32 for  $(\text{C}_5\text{H}_5)_3\text{Lu}$ . Similarly to alkali metal or alkaline earth metal cyclopentadienyl reagents, the ionic nature of the lanthanide compounds was confirmed by the reaction with iron halides to give ferrocene. The preparation of cyclopentadienyl lanthanide chlorides<sup>[18]</sup> and dichlorides<sup>[19]</sup> gave new perspectives concerning the development of organolanthanide chemistry. Subsequently, numerous cyclopentadienyl rare earth metal complexes were synthesized<sup>[20-29]</sup> and are still of great interest in homogeneous catalysis.<sup>[4-6, 28, 30-33]</sup> During the last two decades, cyclopentadienyl ligands were successfully replaced by new ligand systems to form the so-called post-metallocenes.<sup>[26, 27, 34-37]</sup> These systems are comprehensively described in the literature and some of them will be presented in the following sections.

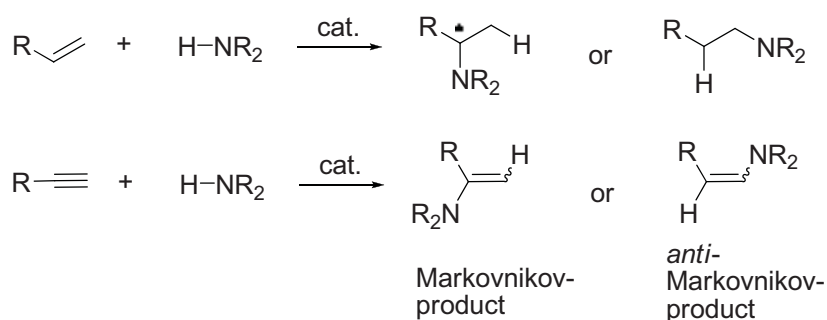
As already mentioned, lanthanide complexes are often compared to alkaline earth metal compounds, since the bonding and structures in both species are based on electrostatic and

steric factors. Regarding the divalent lanthanides, it is remarkable that the ionic radii are similar to those of the heavier alkaline earth metal ions (for six-coordinate ions:  $\text{Ca}^{2+}$  1.00 Å,  $\text{Yb}^{2+}$  1.02 Å,  $\text{Sr}^{2+}$  1.18 Å,  $\text{Eu}^{2+}$  1.17 Å,  $\text{Ba}^{2+}$  1.35 Å).<sup>[15, 38]</sup> Therefore, it is not astounding that the coordination chemistry of these metals is related. This theory is verified by crystal structures of Ca and Yb(II) analogues, which are mostly isomorphous and have similar cell constants.<sup>[39]</sup> In addition to metallocene derivatives,<sup>[40, 41]</sup> aminotroponimino<sup>[42]</sup> and bis(phosphinimino)methanide complexes<sup>[43]</sup> of divalent lanthanides and the heavier alkaline earth metals were prepared and all of them showed the expected similarities.

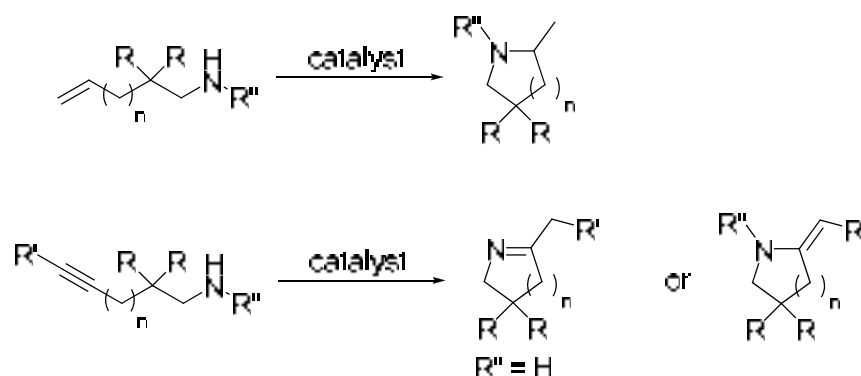
In the last decades, a great progress was achieved in the coordination chemistry of the rare earth metals. Against the initially manifested assumptions, rare earth metal compounds turned out to be widely applicable and the search for new ligand systems for creating catalytically active post-metallocenes of the rare earth metals is still in progress.

## 1.2 Hydroamination

Nitrogen-containing compounds, such as amines and imines, have been largely applied in the industries such as bulk chemicals, fine chemicals and pharmaceuticals.<sup>[44]</sup> Hydroamination, the addition of an amine to an unsaturated C-C bond, offers an ideal access to nitrogen-containing molecules in one step and has been intensely studied for the last decades.<sup>[33, 44-60]</sup> The direct 2+2 cycloaddition of N-H bonds to unsaturated C-C bond is orbital-forbidden. However, new reaction pathways can be achieved by using catalysts and the direct addition can be avoided. Intermolecular and intramolecular hydroamination reactions of non-activated alkenes and alkynes have been explored. As shown in Scheme 1, the intermolecular hydroamination of alkenes and alkynes can produce the Markovnikov and the anti-Markovnikov products as different regioisomers.<sup>[47, 59]</sup> In intramolecular hydroamination reactions primary and secondary aminoalkenes and aminoalkynes were used (Scheme 2). Secondary amines are more nucleophilic and thus undergo the hydroamination more facile. In general, intramolecular reactions are faster than intermolecular reactions and can be affected by varying the substituents in  $\beta$ -position of the amine. By using bulkier substituents, the substrate is bent into a conformation, in which the formation of the ring is facilitated; this phenomenon is established as the Thorpe-Ingold effect.<sup>[61-64]</sup>



**Scheme 1** Intermolecular hydroamination of alkenes and alkynes.



**Scheme 2** Intramolecular hydroamination of aminoalkenes and aminoalkynes.

Hydroamination has an enormous reaction scope and can be catalyzed by acids, bases and organometallic compounds.<sup>[59]</sup> Brønsted acids have been used as heterogeneous<sup>[44]</sup> and homogenous<sup>[44, 59, 65]</sup> catalysts, but for latter the reaction scope is limited to amines with low basicity; otherwise the formation of ammonium salts is favoured over the protonation of the C-C double or triple bond, which is the initial step of the catalytic reaction.<sup>[59]</sup> Base catalyzed hydroamination reactions were mainly explored for alkali metals and their amides.<sup>[44, 45, 66]</sup> These basic compounds are able to deprotonate amines to give more nucleophilic metal amides which can be added to alkenes. The activation energy of these reactions is high, which is mainly caused by weak coordinative interactions between non-functionalized alkenes and alkali metal ions, and unfavorable interactions between the N lone pair and the  $\pi$ -system of the unsaturated C-C bond. Complexes of highly electropositive metals, such as alkaline earth and rare earth elements, show the same activation of the amine in the initial step of the catalysis and can also be classified as basic catalysts. They will be discussed more detailed later in this section. Catalytic hydroaminations were investigated for a wide range of complexes of various metals, such as alkali<sup>[45, 48, 57, 66, 67]</sup> and alkaline earth metals,<sup>[44, 48, 59]</sup> early transition metals,<sup>[44, 52, 66]</sup> late transition metals,<sup>[44, 50, 52, 54, 56, 57, 66]</sup> lanthanides and