1. Introduction

1.1. Rare earth elements

1.1.1. General

Nowadays, it is impossible to imagine life without lanthanides. Being of great significance for scientific research, industry and daily life, lanthanides have been widely used not only in phosphor and laser materials due to their unique luminescence properties, such as sharp line emission, long lifetime and high quantum yield;[1-4] but also for a variety of nuclear applications (shielding materials for instance) owing to their neutron capture property.[5-8] In addition, lanthanides possess large magnetic moments and this thereby gives a rich number of related compounds with fascinating magnetic properties.[9] Recently, Single Molecule Magnets (SMMs) (more information can be found in section 1.4), up conversion nanoparticles, chiral catalysts (further details discussed in section 1.3) and metal-organic frameworks (MOFs) based on lanthanides have drawn extensive attention due to their potentially applications in data storage, photo therapy and catalysis, respectively.[10-15]

Lanthanides, known as a family of elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu with gradually filled 4f orbitals, normally share exchangeably used concepts with rare earth metals. Precisely, however, the rare earth metals encompass Y, Sc and lanthanides. Thus, the general symbol Ln will be used to refer to all rare earth metals throughout the presented work. As a matter of fact, the properties of the rare earth elements are very similar to each other and it took about 160 years before people could fully isolate all the rare earth elements. In 1787, a black mineral was discovered from the mine in Ytterby, near Stockholm, Sweden, by Carl Axel Arrhenius (1757-1824). Then 1794 witnessed Johan Gadolin(1760-1852)'s discovery of a new oxide material being later named Yttria[16] from the aforementioned black mineral. As a metal oxide mixture virtually, more lanthanides had been discovered from this mixture within the next century. The last lanthanide element, Pm, was isolated in 1947.[17] Although the name of rare earth include "rare", these elements are in fact not as rare as the name suggests. The terrestrial abundance of rare earth metals is varying from 0.2 ppm for Tm to 46 ppm for Ce, which are higher than Au (0.004 ppm), Hg (0.08 ppm) and Se (0.05 ppm).[18, 19]

1.1.2. Electron configurations and oxidation states

The similarity of lanthanides and their ions derived come from their electronic configurations. As shown in Table 1.1, the electron configurations of lanthanides contain a xenon core ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$).[20] Both of energy and spatial extension of

4f orbitals decrease abruptly after La. For instance, the binding energy of a single 4f electron drops from -0.95 eV for La to -5 eV for Nd.[21] The 4f orbitals of lanthanides are gradually filled from La to Lu (Table 1.1). Given the fact that the energy of a La 5d orbital is lower than that of its 4f counterpart, when filled with the outermost electron, La does not contain 4f electron. The first 4f electron appears in Ce. The stability of half-filled 4f orbitals allows Gd to have a 5d electron. Lu shows fully filled 4f orbitals and 5d orbitals with single electron.

The main oxidation state of all the lanthanides is +3, by losing two electrons in 6s orbital and one from either 5d (La^{III}, Ce^{III}, Gd^{III} and Lu^{III}) or 4f (Pr^{III}, Nd^{III}, Pm^{III}, Sm^{III}, Eu^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III} and Yb^{III}) orbitals. The other oxidation states of some lanthanides can be explained on the basis of the stability of empty (Ce^{IV}), half-filled (Eu^{II} and Tb^{IV}) and fully filled orbitals (Yb^{II}).

Table1.1 Electron configurations of the lanthanide atoms and ions[20]

	atom	Ln^{2+}	Ln^{3+}	Ln^{4+}
La	$[Xe]5d^1 6s^2$		$[Xe]$	
Ce	$[Xe]4f^1 5d^1 6s^2$		$[Xe]4f^1$	$[Xe]$
Pr	$[Xe]4f^3 6s^2$		$[Xe]4f^2$	$[Xe]4f^1$
Nd	$[Xe]4f^4 6s^2$	$[Xe]4f^4$	$[Xe]4f^3$	$[Xe]4f^2$
Pm	$[Xe]4f^5 6s^2$		$[Xe]4f^4$	
Sm	$[Xe]4f^6 6s^2$	$[Xe]4f^6$	$[Xe]4f^5$	
Eu	$[Xe]4f^7 6s^2$	$[Xe]4f^7$	$[Xe]4f^6$	
Gd	$[Xe]4f^7 5d^1 6s^2$		$[Xe]4f^7$	
Tb	$[Xe]4f^9 6s^2$		$[Xe]4f^8$	$[Xe]4f^7$
Dy	$[Xe]4f^{10} 6s^2$	$[Xe]4f^{10}$	$[Xe]4f^9$	$[Xe]4f^8$
Ho	$[Xe]4f^{11} 6s^2$		$[Xe]4f^{10}$	
Er	$[Xe]4f^{12} 6s^2$		$[Xe]4f^{11}$	
Tm	$[Xe]4f^{13} 6s^2$	$[Xe]4f^{13}$	$[Xe]4f^{12}$	
Yb	$[Xe]4f^{14} 6s^2$	$[Xe]4f^{14}$	$[Xe]4f^{13}$	
Lu	$[Xe]4f^{14} 5d^1 6s^2$		$[Xe]4f^{14}$	

1.1.3. Ionic radius and coordination numbers

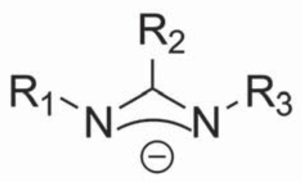
The ionic radius of lanthanides decreases smoothly with increasing atomic number from 57 (La) to 71 (Lu), this behaviour is known as “lanthanide contraction”. The lanthanide contraction derived from the imperfect shielding of 4f electrons by other 4f electrons.[22]

With the atomic number increasing from La to Lu, more 4f orbitals are filled and the imperfect shielding is occasioned. The 4f electrons experience more attraction by nucleus. Besides, the ionic radius of lanthanides is strongly related to the coordination numbers, the radius difference between lanthanide ions with coordination number 6 and 12 is around 30 pm.[23]

Although many publications deal with the divalent lanthanides (Eu^{II}, Yb^{II} and Sm^{II}) and Ce^{IV} complexes, most publications related to lanthanide complexes are about trivalent lanthanides compounds, due to +3 being the most characteristic oxidation of the lanthanides. Lanthanide in +3 oxidation states (Ln^{III} or Ln^{3+}) act as a hard Lewis acids, and anionic ligands with hard Lewis base atoms like O and N are preferred for coordination. Unlike d-block metal complexes, the coordination geometry and numbers of Ln mainly depend on the steric of ligands rather than crystal field effects. A study on 1389 trivalent lanthanide coordination compounds from 1935 to 1995, revealed that most lanthanide coordination compounds have the coordination numbers of 8 or 9, although coordination numbers can be varied from 3 to 15.[24] Lanthanides complexes show low coordination stabilization energy. The stability of coordination bonds increases from La to Lu due to the increasing charge density and the decreasing lanthanide ion size.

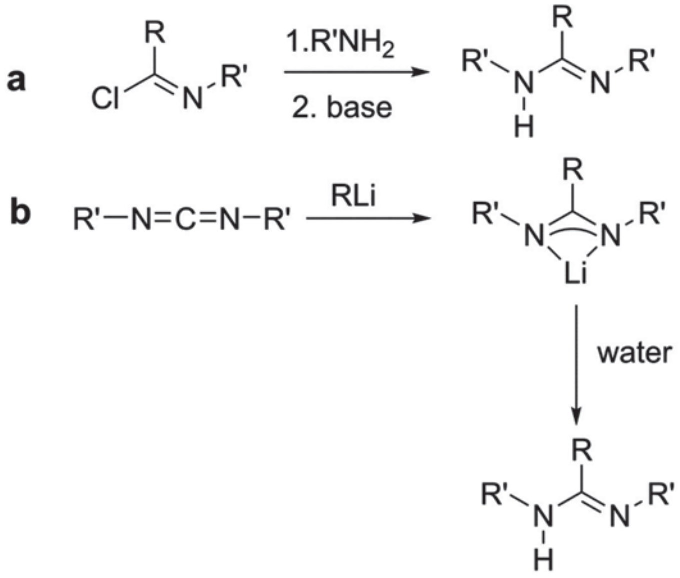
1.2. Amidinate

In the last decades, amidinate and guanidinate anions have attracted much attention due to both easy accessibility and their application as ligands in main group, transition metals, lanthanides and actinides coordination chemistry.[25-29] The amidinate anion is the nitrogen analogue of the carboxylate anion. By modifying the three substituents R_1, R_2 and R_3, a large variety of sterically and electronically different amidinates are accessible (Scheme 1.1).[29-32] This broad variety of the substituent pattern, the ease of accessibility, and the flexible coordination mode made amidinates and the closely related guanidinates a popular and very well-established class of ligands, which were used for almost all metals in the periodic table.[33, 34]



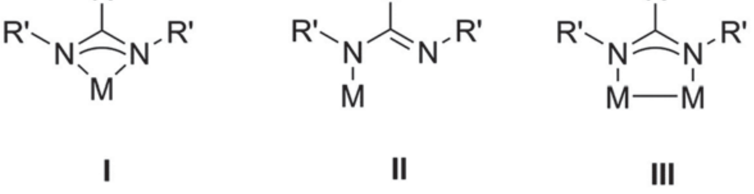
Scheme 1.1. The amidinate anion structure.

Two methods are commonly used for obtaining amidinates and guanidinates (Scheme 1.2).[35, 36] Firstly, amidinates and guanidinates can be obtained from imidoyl chloride, which is a good intermediate for the synthesis of amidinates and guanidinates (route a, scheme 1.2). Alternatively, by the insertion of carbodiimides into M–C or M–N bonds (route b), amidinates and guanidinates can be also obtained.



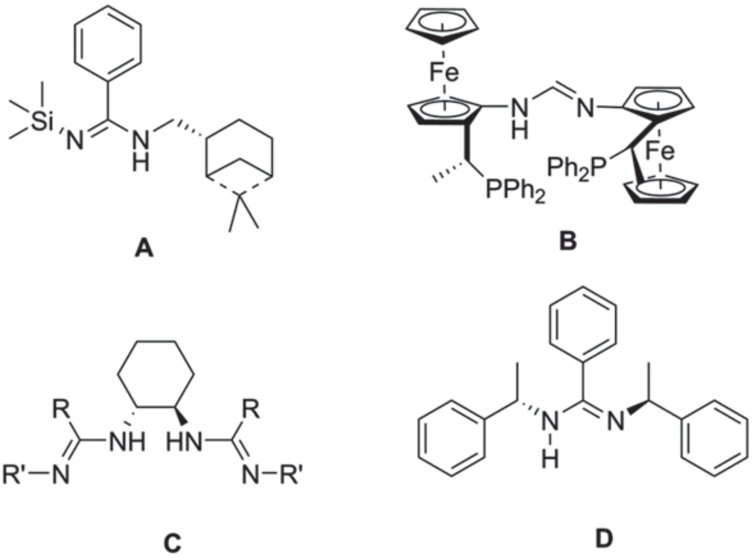
Scheme 1.2. a) imidoylchloride and b) carbodiimides routes for amindines and amidinates synthesis. [35 36]

Amidinate and guanidinate ligands are bidentate ligands and usually show three coordination modes in their metal complexes (Scheme 1.3). These ligands are versatile, and can either chelating one metal center or bridging two metal centers. In most cases, coordination mode **I** is observed. In transition metal clusters, the coordinating mode **III** is often found with short M-M distance. Coordination mode **II** is rarely reported and mainly exists in the complexes formed by ligands with steric bulky groups.



Scheme 1.3. The coordination modes of amidinate.[31, 36]

Although the complexes containing amidinates and guanidinates have been extensively studied both in structure and catalysis, chiral amidinate complexes are rarely reported. Several chiral amidinate ligands reported are showed in Scheme 1.4. In 1998 Averbuj et al. reported a series of group 4 metal complexes with a chiral benzamidinate ligand (ligand A, Scheme 1.4), which exhibit high catalytic activity for highly stereospecific polymerization of propylene.37 In 2006 Togni et al. described a novel Ru complex based on ligand **B** in Scheme 1.4.[38] With ligand **C** (Scheme 1.4), Li *et al.* synthesized several Zr and Ti complexes.[39] Recently our group reported several rare earth metal complexes containing chiral amidinate ligand (Ligand D, Scheme 1.4)[35, 36] which was first reported by H. Brunner in 1980.[40, 41]



Scheme1.4. Chiral amidinate ligand reported in literature. [35-41]

The amidinate complexes can be achieved *via* four routes, which are listed below.[31, 42]

1. Direct insertion of σ-alkyl M-C bond into carbodiimides, R–N=C=N–R'.
2. Deprotonation of amidine with metal alkyl. This method is mainly adopted by preparation of alkali, alkaline-earth and transition metal complexes. Due to the difficulties of making lanthanide alkyl, this route is not used for lanthanide amidates synthesis.
3. Salt metathesis between metal halides and alkali metal amidinates.
4. Reaction of metal halides and N,N,N'-tris(trimethylsilyl)-amidine. For lanthanide amidates, this route does not lead to Ln-amidates, since the lanthanide trihalides generally do not react with N,N,N'-tris(trimethylsilyl)-amidines.

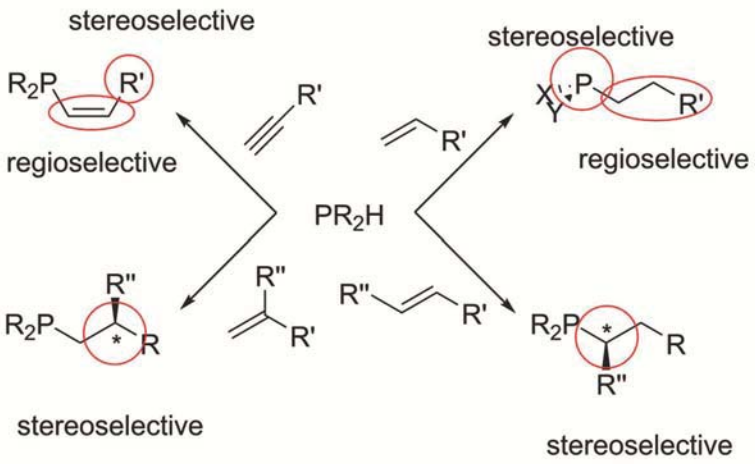
In rare earth metal chemistry, amidinate and guanidinate ligands almost exclusively coordinate in a *N,N'*-chelating mode.[29, 31, 42] Amidinates and guanidinates are a very common and well established class of ligands in rare-earth metal chemistry,[30, 42-44] e.g. the most intensively studied amidinate ligand *N*,*N*'-bis-(trimethylsilyl)benzamidinate[45, 46] can stabilize lanthanide complexes in all three accessible oxidation states (+II, +III, +IV).[42] Numerous applications of rare-earth metal amidinate complexes are known today, such as homogeneous catalysts, atomic layer deposition (ALD) and metal–organic chemical vapor deposition (MOCVD) precursors.[29, 44, 47-49] In homogeneous catalysis, transformations such as ethane[50] and isoprene polymerization,[51-53] ring open polymerization of polar monomers, e.g. ε-caprolactone and trimethylene carbonate,[54, 55] hydroboration,[56] hydrosilylation,[57] and intramolecular hydroamination / cyclization[58] catalyzed by lanthanide amidinate complexes were reported.[42, 44, 54, 59]

1.3. Hydrophosphination

The tertiary phosphines is an important class of compounds widely used in transition metal catalysis and organic synthesis.[60, 61] Hydrophosphination, with the formation of P-C bonds through the addition of the P-H across an unsaturated C-C bond, is an significant and atom-efficient route to synthesisize such phosphines (Scheme 1.5). Unlike the other C-X (X = B, H, N and Si) hererofunctionalizaiton reaction (hydroboration, hydroformylation, hydroamination and hydrosiylation), hydrophosphination is poorly studied.

Scheme 1.5. Hydrophosphination reaction.

The substrates and products of hydrophosphination may act as ligands, which coordinate *via* the P atom. Thus poisoning the catalyst may occur during or in the end of reaction. In contrast to the analog hydroamination reaction, hydrophosphination reaction can take place even without catalyst. The homolytic cleavage of P-H bonds can be initiated and enhanced by light, radicals, or thermal heating. Subsequently 1, 2-addition of the radicals to C-C multiple bonds may occur. The heterolytic P-H activation can also be catalyzed by bases or acids.[62-64] The low yield and efficiency of these reactions inspire the studies for new organometallic catalysts. The hydrophosphination can be carried out in the presence of main group metal, transition metal and rare-earth metal.[63, 65] Besides the enhancement of reaction efficiency, the main purpose of using metal catalysts is the introduction of region- and stereo-selectivity, thereby avoid the further separation of regioisomers or enantiopure chiral products (Scheme 1.6).



Scheme 1.6. Examples of selectivity in hydrophosphination reactions.[66]

1.3.1. *Trivalent rare earth metal complexes as catalysts*

There have been extensive studies in the adootion of trivalent rare-earth metal catalysts in various catalytic reactions, such as polymerization,[67, 68] hydrogenation,[69, 70] hydrosilylation,[71] hydroboration,[56, 72] hydroamination,[73, 74] hydroalkoxylation[75] and hydrothiolation[75] reactions of substrates containing unsaturated C-C bonds. The lanthanide complexes are attractive catalysts for hydrophosphination as well, due to the stereoelectronic tunability of lanthanide coordination spheres, the high electrophilicity, the absence of oxidative-addition/reductive-elimination pathways, and high kinetic liability.[76]

In 2000, Marks *et al*. reported the first lanthanide catalyst for intramolecular hydrophosphination of alkynes.[76, 78] In this kind of hydrophosphination reaction, there is no change in oxidation state of Ln^{III}. The catalytic cycle of lanthanide complexes catalyzed hydroamination is mechanistically and thermochemically well-defined.[79, 80] The mechanism of hydrophosphination, scheme 1.7, is similar to that of hydroamination.[77] The catalytic cycle is proposed to involve the P-C bond formation step. The P-H bond is activated by σ-bond metathesis *via* a four-center transition state that relies on the relative acidity of the P-H bond and the basicity of the alkyl fragment.[66] The insertion of C-C bond in Ln-P bond is the turnover limiting step of the whole process. Due to the hard acid (lanthanide ion) and soft base (phosphorus) interaction, the Ln-P bond is relatively weak. This facilitates the cleavage of P and insertion in the C-C unsaturated bond.[66]