Introduction

1.1 Rare earth metals:

"Lanthanons ……

These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us – mocking, mystifying and murmuring strange relevations and possibilities."

Sir William Crookes (February 16, 1887)

There are fourteen elements that follow lanthanum are together called the lanthanide metals. These elements have not been investigated for a long time in organometallic chemistry unlike the transition metals. Only in the eighties, a number of research laboratories began to focus on the lanthanides and their close relatives scandium and yttrium. At this time selected members of this group of elements were well established in a huge number of applications. Particularly "high-tech materials" division is widely dependent on rare earth components to a significant extent. They are known to tune magnetic/electric properties of metallic and oxidic materials, posses optical properties for color television and electric lighting, have mechanical properties of hard materials (metal oxides and nitrides), and can act as catalysts in mineral oil cracking, methanol synthesis, olefin polymerization, Fisher-Tropsch synthesis and exhaust gas chemistry (e.g. lambda sensors). An annual increase of more than 15% in high-tech applications of lanthanides is expected in the near future. As a matter of fact, these broad-scope applications have motivated the recent intense research into the coordination and organic chemistry of the rare earth elements.

The rare earth elements along with some of their principle characteristics are listed in the Table 1.1.[1] In passing from lanthanum to the last of lanthanides, lutetium, the electronic configuration changes from $[Xe]5d^16s^2$ to $[Xe]4f^{14}5d^16s^2$. That is, fourteen $4f$-electrons are added, although as shown in Table 1.1, with slight irregularities in case of some elements. The highly electropositive character of the lanthanide metals, which is comparable to that of the alkali and alkaline earth metals, is responsible for the formation of predominantly ionic compounds, Lanthanide(III) being the most stable oxidation state.[2]

Table 1.1 Some properties of rare earth atoms and ions.

Atomic number	Name	Symbol	Outer Shell Electronic configuration		$E^0(V)^a$
			Atom	M^{3+}	
57	Lanthanum	La	$5d^1 6s^2$	[Xe]	- 2.38
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$	- 2.34
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$	- 2.35
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$	- 2.32
61	Promethium	Pm	$4f^5 6s^2$	$4f^4$	- 2.29
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$	- 2.30
63	Europiam	Eu	$4f^7 6s^2$	$4f^6$	- 1.99
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$	- 2.28
65	Terbium	Tb	$4f^9 6s^2$	$4f^8$	- 2.31
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$	- 2.29
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$	- 2.33
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$	- 2.32
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$	- 2.32
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$	- 2.22
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$	- 2.30

[a]$Ln^{3+} + 3e = Ln$

The Lanthanide(III) cations of the series Ce-Lu possess the extended Xe-core electronic configuration $[Xe]4f^n$ (n = 1-14), a symbol which perfectly pictures the limited radial extension of the f-orbitals: The $4f$-shell is embedded in the interior of the ion, and is well shielded by the $5s^2$ and $5p^6$ orbitals.[3] Ionization energies of these elements,[4] optical properties[5] and magnetic moments of numerous complexes[6] reveal that the f-orbitals are perfectly shielded from the effects of the field of surrounding anions. Complexes with dipolar molecules results in minimal perturbation of the electronic transitions between the energy levels of the f-orbitals. In contrast to the broad $d \rightarrow d$ absorption bands of the transition metals, the $f \rightarrow f$ bands of the lanthanides in solid and in solution are almost as narrow as they are for gaseous ions. The pale colors of the lanthanide (Ln) complexes are due to the "Laporte forbidden" transitions which result in weak intensities. Due to limited interaction of the "hidden orbitals," with ligand orbitals, the colors of the trivalent species in general do not vary with the change in the nature of the ligand. The σ-donor/π-acceptor bonding mode is

absent and lanthanides do not form classic carbene, carbine, or carbon monoxide complexes (no 18 electron rule). On the other hand the lack of orbital restrictions, e.g., the necessity to maximize orbital overlap as in d-transition element chemistry, allows "symmetry forbidden" reactions. Due to very small crystal-field splitting and very large spin-orbit coupling (high Z), the energy states of the $4f^n$-electronic configurations are usually approximated by the Russel-Saunders coupling scheme.[7]

Table 1.2 Effective ionic radii for Ln(III), Ln(IV) and Ln(II) after Shannon.[8]

Ln^{x+}/CN	6	7	8	9	10	12
Sc^{3+}	0.745 R*		0.870 R*			
Y^{3+}	0.900 R	0.96	1.019	1.075		
La^{3+}	1.032 R	1.10	1.160	1.216	1.27	1.36 C
Ce^{3+}	1.01 R	1.07 E	1.143 R	1.196 R	1.25	1.34 C
Pr^{3+}	0.99 R		1.126 R	1.179 R		
Nd^{3+}	0.983 R		1.109 R	1.163 R		1.27 E
Pm^{3+}	0.97 R		1.093 R	1.144 R		
Sm^{3+}	0.958 R	1.02 E	1.079 R	1.132 R		1.24 C
Eu^{3+}	0.947 R	1.01	1.066 R	1.120 R		
Gd^{3+}	0.938 R	1.00	1.053 R	1.107 RC		
Tb^{3+}	0.923 R	0.98 E	1.040 R	1.095 R		
Dy^{3+}	0.912 R	0.97	1.027 R	1.083 R		
Ho^{3+}	0.901 R		1.015 R	1.072 R	1.12	
Er^{3+}	0.890 R	0.945	1.004 R	1.062 R		
Tm^{3+}	0.880 R		0.994 R	1.052 R		
Yb^{3+}	0.868 R*	0.925 E	0.985 R	1.042 R		
Lu^{3+}	0.861 R		0.977 R	1.032 R		
Sm^{2+}		1.22	1.27	1.32		
Eu^{2+}	1.17	1.20	1.25	1.30	1.35	
Tm^{2+}	1.03	1.09				
Yb^{2+}	1.02	1.08 E	1.24			
Ce^{4+}	0.87		0.97		1.07	1.14
Tb^{4+}	0.76 R		0.88			

Abbreviations: R from r^3 vs V plots (r = cation radius, V = volume of unit cell), C calculated, E estimated, * most reliable.

The term rare earth element is sometimes applied to La →Lu along with yttrium and scandium. The reason for including Y is that, Y has radii (atomic, metallic, and ionic) that are comparable to those of erbium and holmium and its chemistry is dominated by the trivalent state. Hence it resembles the later lanthanides very closely in its property and occurs with them in nature. Scandium on the other hand, far smaller than any of the lanthanides (Sc^{3+}

radius, 87 pm, CN 8). The chemical behavior of Sc deviates in many ways from that of the lanthanides, rather it resembles to that of aluminum and gallium.

The contracting nature of the 4*f*-orbitals and the concomitant poor overlap with the ligand orbitals contribute to the predominantly ionic character of organolanthanide complexes. Normally metal ligand interactions are determined by electrostatic factors. According to the HSAB classification of Pearson,[9] lanthanide cations are considered as *hard acids* and are located between Sr(II) and Ti(IV). Consequently, alkoxide, amide and cyclopentadienyl ligands show almost constant effective ligand anion radii[10] and therefore fit into the evaluation criteria for ionic compounds according to Eigenbroth and Raymond.[11] The ionic-bonding contributions cause the strong oxophilicity of the lanthanide cations.[12] The interaction of the oxophilic metal center with oxygen containing substrate molecules is an important factor for governing chemo-, regio- and stereoselectivities in organolanthaide-catalyzed transformations.[13] "Softer" phosphorus and sulfur counterions are applied for complexation to detect extended covalency in these molecular systems.[14]

Normally Ln(III) cations have a tendency to form more unusual oxidation states in solution.[15] Organometallic compounds of Ce(IV), Eu(II), Yb(II) and Sm(II) have been isolated. Charge dependent properties, such as ionic radii and Lewis acidity, significantly differ from those of the trivalent species (Table 1.2). Ln(II) and Ce(IV) show very intense and ligand dependent colors which is attributed to Laporte-allowed 4*f*→5*d* transitions.[5b] Complexes of Ce(IV) and Sm(II) have considerable importance in organic synthesis due to their strong oxidizing and reducing behavior, respectively.[16-20]

The fascinating steric features of lanthanide elements are most impressively expressed in the lanthanide contraction.[21] Lanthanide contraction is often simply explained as being the phenomena responsible for similar chemical properties, in particular between the pairs of the *d*-transition metal homologues Zr/Hf, Nb/Ta, and Mo/W. However the atomic (with exceptions) and the ionic radii decrease monotonically with increasing atomic number. It is only this feature of contraction that decisively favors the industrial separation of these elements. Of course this unique behavior which originates from the directional characteristics of the 4*f*-orbitals is enhanced by the electrons added along the series between La and Lu. The 4*f*-electrons do not shield each other effectively from the growing nuclear charge and as a result contraction occurs.

The formal coordination number of rare earth metal cations is in the range of 8-12.[22] Examples of the various coordination numbers and stereochemistries are presented in Table 1.3.[1]

Table 1.3 Oxidation states, Coordination Numbers and Geometry of Lanthanide Ions.

Oxidation states	Coordination number	Geometry	Examples
+2	6	NaCl type	EuTe, SmO; YbSe
	6	CdI_2 type	YbI_2
	6	Octahedral	$[Yb(PPh_2)_2(THF)_4]$
	7	Pent. bipyramid	$SmI_2(THF)_5$
	8	CaF_2 type	SmF_2
+3	3	Pyramidal	$[Ln\{N(SiMe_3)_2\}_3]$
	4	Distorted tetrahedral	$[Ln\{N(SiMe_3)_2\}_3OPPh_3]$
	4	Tetrahedral	$[Lu(mes)_4]^-$, $[Y(CH_2SiMe_3)_4]^-$
	6	Octahedral	$[Er(NCS)_6]^{3-}$, $[Ln_2Cl_9]^{3-}$, LnX_6^{3-}
	6	$AlCl_3$ type	$LnCl_3$ (Tb- Lu)
	6	Distorted trigonal prism	$[Pr\{S_2P(C_6H_{11})_2\}_3]$
	7	Monocapped trigonal prism	Gd_2S_3, $[Y(acac)_3.H_2O]$
	7	ZrO_2 type	ScOF
	8	Distorted square anti prism	$[Y(acac)_3(H_2O)_3]$, $[La(acac)_3(H_2O)_2]$
	8	Dodecahedral	$[Cs\{Y(CF_3COCHCOCF_3)_4\}]$
	8	Distorted dodecahedral	$[Na\{Lu(S_2CNEt_2)_4\}]$
	8	Cubic	$[La\{bipyO_2)_4\}]^{3+}$
	8	Bicapped trigonal prism	Gd_2S_3, LnX_3 (PuBr$_3$ type)
+3	9	Tricapped distorted trigonal prism	$[\{Nd(H_2O)_9\}]^{3+}$, $Y(H_2O)_3$, $[K\{La(ETDA)\}(H_2O)_8]$, $[La_2(SO_4)_3(H_2O)_9]$
	9	Capped square anti prism	$[Ln(NO_3)_3(H_2O)_3]$
	9	UCl_3 type	LaF_3, $LnCl_3$ (La-Gd)
	10	Complex	$[La_2(CO_3)_3(H_2O)_8]$
	10	Bicapped dodecahedron	$[Ce(NO_3)_5]^{2-}$, $[La(NO_3)_3(DMSO)_4]$
	11	Complex	$[La(NO_3)_3(H_2O)_5H_2O]$
	12	Distorted icosahedron	$[Pr(1,8-naphthyridine)_6]^{3+}$, $[Ce(NO_3)_6]^{3-}$
+4	6	Octahedral	$[Cs_2CeCl_6]$
	8	Square antiprism	$[Ce(acac)_4]$
	8	Distorted sqare antiprism (chains)	$[(NH_4)_2CeF_6]$
	8	CaF_2 type	CeO_2
	10	Complex	$[Ce(NO_3)_4(OPPh_3)_2]$

The considerable change in size of the Ln^{3+} ions from La^{3+} to Lu^{3+} implies that homologous compounds of lanthanides with appreciably different radii may differ in structure.

There are few examples.

(i)   The anhydrous halides MCl_3 (M = La-Gd) are all 9-coordinated with an UCl_3 type lattice; $TbCl_3$ and one form of $DyCl_3$ are of the $PuBr_3$ type, and the Ho-Lu chlorides have the octahedral $AlCl_3$ type geometry.

(ii)   For the M_2S_3 series there are three main structure types: La to Dy (orthorhombic, 8- or 7-coordinate); Ho_2S_3 actually has half its atoms 6- and half 7-coordinate); Yb and Lu (corundum type, 6-coordinate).

(iii)   The sublimation enthalpies of certain volatile chelates show irregular decrease from Pr to Lu, owing to structural differences.

(iv)   There is great structural diversity for the solvated $LnCl_3$.[23]

The aqua ions $[Ln(H_2O)_n]^{3+}$ are either 8- or 9-coordinate but this may vary with ionic strength and concentration of the solution.[24] The number, in 1 M perchlorate solution, appears to change from 9-for the largest Ln^{3+} ions to 8-for the smallest with a middle one such as Sm^{3+} The aqua ions $[Ln(H_2O)_n]^{3+}$ are either 8- or 9-coordinate but this may vary with ionic strength and concentration of the solution.[24] The number, in 1 M perchlorate solution, appears to change from 9-for the largest Ln^{3+} ions to 8-for the smallest with a middle one such as Sm^{3+} showing both coordination numbers.[25] There are many lathanide complexes with polydentate macrocyclic ligands (e.g. crown ether), anions and H_2O etc. with high coordination numbers.[26]

1.2 Divalent lanthanides and heavier alkaline earth metals:

Among the group 2 elements (Be, Mg, Ca, Sr, Ba, Ra) beryllium has unique chemical behavior with a predominantly covalent chemistry, although it forms an aqua ion $[Be(H_2O)_4]^{2+}$. Magnesium has a chemistry intermediate between that of Be and heavier elements and has considerable tendency to covalent bonds, consistent with the high charge/radius ratio. All the isotopes of radium are radioactive. Calcium, Sr and Ba are collectively termed as heavier alkaline earth metals. The structure and chemical behavior of these heavier alkaline earth metal complexes[27] have often been compared to that of early d- and f-block metal complexes.[28-37] In particular, similarities have been observed with "hot" Ln(II) complexes.[38] Lanthanide complexes are d^0-species with a limited radial extension of their f-orbitals. Therefore, orbital factors do not affect their chemistry as much as in transition

metal chemistry. Just like the complexes of the heavier alkaline-earth metals, their bonding and structures are mainly determined by electrostatic and steric factors.

Table 1.4 Comparison of ionic radii between divalent lanthanides and heavier alkaline earth metal ions.

Ions	Outer Shell Electronic configuration	Ionic radius (pm) CN 6
Eu^{2+}	$[Xe]4f^7$	117
Yb^{2+}	$[Xe]4f^{14}$	102
Ca^{2+}	$[Ar]$	100
Sr^{2+}	$[Kr]$	118
Ba^{2+}	$[Xe]$	135

There are ample evidences that demonstrate the striking similarity in the chemistry of Ca(II) and Yb(II) : (i) crystal structure of Ca and Yb analogues are always isomorphous and have exponentially similar cell constants,[33,34,36] (ii) the observation of nearly identical IR spectra of Ca and Yb analogues suggest a striking similarity in bonding,[28] (iii) Ca and Yb analogues displays similar gas-phase behavior: electron-diffraction studies of $[Cp_2{}^*Ca]$ and $[Cp_2{}^*Yb]$ reveal similar $Cp^*{}_{centroid}$-M-$Cp^*{}_{centroid}$ angle of 154(3)^o and 158(4)^o, respectively,[39] (Cp^* = pentamethylcyclopentadienyl), (iv) analogous reactivities of Ca(II) and Yb(II) complexes have been reported.[34,35] Similar kind properties also found in the chemistry of Sr(II) and Eu(II). Because of this fortuitous chemical similarity europium is frequently found in nature with Group 2 minerals, this is a good example of the geochemical importance of such chemical similarity.

1.3 Coinage metals:

Copper, silver and gold, termed as Coinage metals, have a single *s*-electron outside the completed *d*-shell. In the +1 oxidation state, they each has close shell d^{10}-configuration. In spite of the similarity in electronic structures and ionization potential, the chemistry of Ag, Au and Cu differs to a great extent.[40] There are no simple explanations for most of the differences although some of the differences between Ag and Au may be attributed to the relativistic effect on the 6*s*-electrons of the latter. Gold has about the same or a slightly smaller covalent radius than silver in comparable compounds, a phenomenon frequently referred to as "relativistic contraction".

Apart from similar stoichiometries of compounds in the same oxidation state, there are some similarities within the group or at least between two of the three elements:

(i)   All the metals crystallize with the same face centred cubic (*ccp*) lattice.

(ii) Cu_2O and Ag_2O have the same body centred cubic structure where the metal atom has two close oxygen neighbors and every oxygen atom is tetrahedrally surrounded by four metal atoms.

(iii)   Though the stability constant sequence for the halide complexes of most metals is $F > Cl > Br > I$, Cu(I) and Ag(I) belong to the group of ions of the more noble metals for which it is the reverse.

(iv)   Cu(I) and Ag(I) (and to a lesser extent Au(I)) form similar types of complex ions and compounds, such as K_2MCl_3, $[Et_3AsMI]_4$ and $[MCl_2]^-$.

(v)   A close comparison among the stereochemistries of closed-shell coinage metals Cu(I), Ag(I) and Au(I) can be seen from the Table 1.5.[1]

**Table 1.5** Stereochemistries of different coinage metal ions.

Metal ion	Coordination number	Geometry	Examples
Cu^I, d^{10}	2	Linear	Cu_2O, $KCuO$, $[CuCl_2]^-$, $[CuBr_2]^-$
	3	Planer	$K[Cu(CN)_2]$, $[Cu(SPMe_3)_3]ClO_4$
	4^a	Tetrahedral	$[CuI\{Cu(CN)_4\}_3]^-$, $[Cu(MeCN)_4]^+$
	4	Distorted planer	CuL^b
	5	Square pyramidal	$[CuLCO]^b$
Ag^I, d^{10}	2^a	Linear	$[Ag(CN)_2]^-$, $[Ag(NH_3)_2]$, $AgSCN$
	3	Trigonal	$[Ag(PCy_2Ph)_3]BF_4$
	4^a	Tetrahedral	$[Ag(SCN)_4]^{3-}$
	5	Distorted pentagonal plane	$[Ag(L)]^{+\,c}$
	5	Pentagonal pyramidal	$[Ag(L)]_2^{2+\,c}$
	6	Octahedral	AgF, $AgCl$, $AgBr$
Au^I, d^{10}	2^a	Linear	$[Au(CN)_2]^-$
	3	Trigonal	$AuCl(PPh_3)$
	4	Tetrahedral	$[Au(diars)_2]^+$

^{a}Most common states.

^{b}L = a macrocyclic N_4 anionic ligand, ^{c}L = a macrocyclic N_5 anionic ligand.

1.4 Amide complexes of rare earth metals:

The design of an appropriate ligand sphere is the most important part in organolanthanide chemistry. The nature of ligand (type, size, basicity, capabilities of hard/soft ligand functionalities) promptly affects mononuclearity, cation size, Lewis acidity, etc all of which co-determine the reactivities of the complex. Assuming electrostatic ligand interaction, optimal charge balance of the Ln(III) cations should be achieved by three stable anionic ligands. Identical anions will accomplish homoleptic systems of neutral type $(MR_n)_x$ or ate type $[MR_n]^{z-}[X_m]^{z+}$.[41] Bulky ligands should favor monomeric and volatile complexes. In earlier time homoleptic organolanthanide complexes of cyclopentadieneyl (Cp)[42] and pentamethylcyclopentadienyl (Cp^*)[43] were obtained.[44] Other Ln-C type complexes e.g. with pentadienyl-,[45] indenyl-,[46] cycooctatetraene- (COT),[47] aren-,[48] allyl-[49] and alkyl-[50] were also synthesized. Besides these organolanthanide complexes, coordination compounds having Ln-P-,[51] Ln-S-,[52] Ln-O-[53] and Ln-N-[54] linkage are also known. The last two type of coordinating ligands (i.e alkoxy and amido) (Scheme 1) are frequently used to stabilize rare earth metals besides the cyclopentadienyl or its derivatives.[55] Among these ligands the amides offer a wide possibility for designing the ligands and subsequent lanthanide complexes by varying two fold substitutions on the donor N atom.
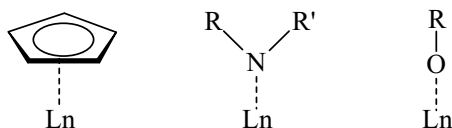
Scheme 1: Three important ligand-metal co-ordination modes in rare earth chemistry.

According to Pearson's HSAB concept,[9] the hard Lewis acid Ln^{3+} ions ideally can make stable Ln-N bonds with amides which posses the property of being hard Lewis bases. These can be used for the activation of well defined reaction centers, thereby allowing the use of the resulting compounds for different applications. The activation of the small unreactive molecules, the homogeneous catalysis and some organic transformations are some of the many examples known.[56]

In Scheme 2 the classification of the rare earth metal amides into inorganic and organic amide ligands are shown, where the classical amides, being accessible by "wet chemistry"(e.g. acids and sulfonamides) are excluded. In many cases an exact attribution is hardly possible as the single ligand can be assigned to multiple subgroups. In the usual