Lanthanide amidinates and guanidinates: from laboratory curiosities to efficient homogeneous catalysts and precursors for rare-earth oxide thin films†

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For decades, the organometallic chemistry of the rare earth elements was largely dominated by the cyclopentadienyl ligand and its ring-substituted derivatives. A hot topic in current organolanthanide chemistry is the search for alternative ligand sets which are able to satisfy the coordination requirements of the large lanthanide cations. Among the most successful approaches in this field is the use of amidinate ligands of the general type \([\text{RC(NR}^\text{0})_2\text{]}\) (R = H, alkyl, aryl; \(\text{R}^0\) = alkyl, cycloalkyl, aryl, SiMe\(_3\)) which can be regarded as steric cyclopentadienyl equivalents. Closely related are the guanidinate anions of the general type \([\text{R}_2\text{N(NR}^\text{0})_2\text{]}\) (R = alkyl, SiMe\(_3\); \(\text{R}^0\) = alkyl, cycloalkyl, aryl, SiMe\(_3\)). Two amidinate or guanidinate ligands can coordinate to a lanthanide ion to form a metalloocene-like coordination environment which allows the isolation and characterization of stable though very reactive amide, alkyl, and hydride species. Mono- and trisubstituted lanthanide amidinates and guanidinates are also readily available. Various rare earth amidinates and guanidinates have turned out to be very efficient homogeneous catalysts e.g. for ring-opening polymerization reactions. Moreover, certain alkyl-substituted lanthanide tris(amidinates) and tris(guanidinates) were found to be highly volatile and could thus be promising precursors for ALD (= Atomic Layer Deposition) and MOCVD (= Metal-Organic Chemical Vapor Deposition) processes in materials science and nanotechnology.

This tutorial review covers the success story of lanthanide amidinates and guanidinates and their transition from mere laboratory curiosities to efficient homogeneous catalysts as well as ALD and MOCVD precursors.

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† Dedicated to Professor John W. Gilje on the occasion of his 70th birthday.

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1. Principles of organolanthanide chemistry

The very beginning of organolanthanide chemistry dates back to the year 1954, when Birmingham and Wilkinson reported the synthesis of the first tris(cyclopentadienyl) lanthanide complexes, \(\text{Cp}_3\text{Ln}\). However, a major drawback encountered in this young field of organometallic chemistry was the intrinsic instability of certain classes of organolanthanide complexes combined with their often extreme sensitivity towards traces of air and moisture. Thus until about 30 years ago organometallic compounds of the rare earth metals remained a curiosity. This situation changed slowly in the late 1970s and the early 1980s when more sophisticated preparative and analytical techniques became more generally available. Especially the use of dry-boxes and access to single crystal X-ray diffraction techniques made it possible to safely handle and characterize these compounds and to understand the structural features of these fascinating complexes. The area developed even faster in the late 1980s, largely stimulated by the discovery of the high potential of these compounds as reagents in organic synthesis and as very active homogeneous catalysts.

It should be emphasized at this point that the organometallic chemistry of the lanthanide (and actinide) elements differs significantly in several ways from that of the \(d\)-transition metals. Generally accepted principles of \(d\)-transition metal chemistry do not apply to organolanthanide compounds, including the well-known "18-electron rule", \(\sigma\)-donor/\(\pi\)-acceptor metal ligand bonding, the formation of stable carbylons and olefin, alkylene, carbene or carbyne...
complexes, as well as the formation of stable M=O, M=N or M≡N multiple bonds. In fact, even direct metal-metal bonds, a common phenomenon in $d$-transition metal chemistry, are virtually non-existent in organo-f-element chemistry. This is due to several intrinsic properties of the lanthanide ions imparting unique electronic and steric features to rare earth organometallics. The rare earth metals (= Ln) generally comprise the lanthanides La–Lu as well as the group 3 metals scandium and yttrium. The 14 elements of the lanthanide series represent the largest subgroup in the Periodic Table. All lanthanide metals are highly electropositive, comparable to the alkali and alkaline earth metals, so that metal-to-ligand bonding can be considered as predominantly ionic. Therefore, the spectroscopic and magnetic properties of lanthanide coordination compounds are largely uninfluenced by the ligands. According to the HSAB (= hard and soft acids and bases) concept, lanthanide ions are considered as hard acids. This hard acid character combined with the largely ionic bonding is the origin of the pronounced oxophilicity of the lanthanide ions which can be quantified in terms of the dissociation energy of LnO. This oxophilic nature of the metal centers strongly influences the reactivity of lanthanide compounds and leads to a preference for hard oxygen- or nitrogen-based ligands while coordination of softer ligands containing e.g. phosphorus or sulfur donor atoms is generally disfavored. In all cases, Ln$^{3+}$ is the most stable oxidation state as tetravalent cerium as well as the reduced Ln$^{2+}$ state for samarium, europium and ytterbium. However, in this chemistry the steric saturation of the coordination sphere around the large f-element ions is much more important than the number of valence electrons. Thus current research in this area is increasingly focussed on the development of alternative ligand sets. Amidinate and guanidinate anions play a central role in this area of research. An early account of lanthanide amidinate chemistry can be found in a 1995 review article entitled “Cyclopentadienyl-free Organolanthane Chemistry”.

Amidinate anions of the general formula [RC(NR)$_2$] (Scheme 1) are the nitrogen analogues of the carboxylates. They have been widely employed as spectator ligands in main group and transition metal coordination chemistry, with the latter encompassing both early and late transition metals as well as the lanthanides and actinides. As illustrated in Scheme 1, all three substituents at the heteroallylic N=C=N unit can be varied in order to meet a large range of steric (and, to a lesser degree, electronic) requirements.

In addition to the substituents listed in Scheme 1, chiral groups may be introduced, and unsymmetrically substituted amidinate anions are also possible. The amidinate anions may also contain additional functional groups, or two such anions can be linked with or without a suitable spacer unit. Yet another variety comprises the amidinate unit being part of an organic ring system.

Historically, the amidinate story begins with the discovery of N,N,N’-tris(trimethylsilyl)benzamidine, PhC(≡NSiMe$_3$)$_2$, by Sanger and co-workers. The compound was prepared by the reaction of benzonitrile with Li(N(SiMe$_3$)$_2$ followed by treatment with chlorotrimethylsilane (Scheme 2).

2. Amidinate anions: highly versatile cyclopentadienyl-alternatives

Following the early discovery of the tris(cyclopentadienyl) complexes of the lanthanide elements by Wilkinson and Birmingham, most of the organolanthane compounds studied were sandwich-type complexes containing unsubstituted or ring-substituted cyclopentadienyl ligands. Their relatively high stability against moisture and air motivated numerous research groups to develop the area of lanthanocene chemistry over the last three decades. A main drawback encountered with using unsubstituted Cp was certainly the difficulty in obtaining anything other than Cp$_2$Ln, the chemistry of which is rather limited. With the introduction of Cp* (= pentamethylcyclopentadienyl) ligands into organolanthane chemistry, more versatile compounds of the Cp*$_2$Ln type became more easily available and this opening of the coordination sphere led to the development of a much more diverse derivative chemistry. Subsequently, it was demonstrated that various lanthanocene complexes exhibit highly efficient catalytic activity for olefin transformations including hydrogenation, polymerization, hydroboration, hydrosilylation, hydroamination, and hydrophosphination.

However, this chemistry the steric saturation of the coordination sphere around the large f-element ions is much more important than the number of valence electrons. This new class of rare earth metal complexes containing amidinate and guanidinate ligands and their transition from softer ligands containing e.g. phosphorus or sulfur donor atoms is generally disfavored. In all cases, Ln$^{3+}$ is the most stable oxidation state as tetravalent cerium as well as the reduced Ln$^{2+}$ state for samarium, europium and ytterbium. However, in this chemistry the steric saturation of the coordination sphere around the large f-element ions is much more important than the number of valence electrons. Thus current research in this area is increasingly focussed on the development of alternative ligand sets. Amidinate and guanidinate anions play a central role in this area of research. An early account of lanthanide amidinate chemistry can be found in a 1995 review article entitled “Cyclopentadienyl-free Organolanthane Chemistry”.

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The method was later improved by Oakley et al. In their 1987 paper these authors also reported a series of p-substituted derivatives. In the following years these N-silylated ligands were extensively employed in main group and transition metal chemistry, and the first review article covering the field was published by Dehnicke in 1990. Since 1994 an incredible variety of differently substituted amidinate ligands has been developed and employed in the coordination chemistry of various elements throughout the Periodic Table. The main advantages of these ligands are twofold. Amidinate anions are generally readily accessible using commercially available or easily prepared starting materials. Furthermore, their steric and electronic properties can be readily modified in a wide range through variation of the substituents on the carbon and nitrogen atoms. These properties combined make the amidinate anions clearly almost as versatile as the ubiquitous cyclopentadienyl ligands.

Metal amidinato complexes are principally accessible through several synthetic routes. The most prevalent of them include:

(i) insertion of carbodiimides, R–N=C=N–R, into a metal–carbon bond;
(ii) deprotonation of an amidine using a metal alkyl;
(iii) salt metathesis reactions between a metal halide substrate and an alkali metal amidinate (with the latter normally being generated by one of the routes (i) or (ii));
(iv) reaction of metal halides with N,N,N-tris(trimethylsilyl)amidines.

It should be noted here that not all these synthetic routes are equally well applicable to the rare earth elements. Route (ii) is severely restricted by the paucity of simple lanthanide alkyls, while route (iv) is unsuitable in the lanthanide case as lanthanide trihalides are generally unreactive towards N,N,N’-tris(trimethylsilyl)amidines. Deprotonation of amidines by metal amides should also be a possible synthetic pathway since the delocalized structure of the resulting anion will increase the acidity. However, this route has apparently not yet been tried.

Closely related to the amidinate anions are the guanidinate derivatives (Scheme 3), which differ only in that they contain a tertiary amino group at the central carbon atom of the NCN unit. The beginning of their coordination chemistry dates back to the year 1970, when Lappert et al. reported the first transition metal guanidinate complexes. Like the amidinates, these anions too make attractive ligands because of the similar steric and electronic tunability through systematic variations of the substituents at the carbon and nitrogen atoms. The general synthetic methods for preparing metal amidinato complexes can in part be applied to the corresponding guanidinates and include the following:

(i) insertion of carbodiimides into a metal–nitrogen bond;
(ii) deprotonation of a guanidine using a metal alkyl;
(iii) salt metathesis reactions between a metal halide substrate and an alkali metal guanidinate (with the latter normally being generated by one of the routes (i) or (ii)).

Here too the same restrictions apply for the preparation of lanthanide guanidinates. This means that route (ii) especially is not generally applicable due to the very limited access to simple lanthanide alkyls.

The general coordination modes of amidinate and guanidinate (R = NR’2) ligands are shown in Scheme 4. Both ligands display a rich coordination chemistry in which both chelating and bridging coordination modes can be achieved. By far the most common coordination mode is the chelating type A. In contrast, there are only rare examples of monodentate metal coordination (B). This type of bonding can be the result of severe steric crowding in certain amidinate or guanidinate ligands containing very bulky substituents. Also very common in transition metal chemistry is the bridging coordination mode C. The bridging coordination mode is often found in dinuclear transition metal complexes with short metal–metal distances, i.e. multiple bonding between the metal atoms. The majority of these complexes belong to the class of “paddlewheel”-type compounds with the general formula M2(amidinate)4 or M2(guanidinate)4. The fascinating chemistry of these complexes has been extensively investigated, mainly by Cotton and Murillo. However, this coordination mode, which is so characteristic for various d-transition metals, is completely unknown in lanthanide chemistry. The synthesis of dinuclear complexes comprising any type of direct Ln–Ln bonding (either single or multiple bonding) remains one of the big challenges in organolanthanide chemistry today. Even well-defined complexes containing an unsupported Ln–M bond (M = d-transition metal) are extremely rare.

The factors governing the formation of either chelating or bridging coordination modes in amidinate and guanidinate complexes have been analyzed in detail. Perhaps the greatest advantage of these ligands besides their easy availability is the possibility of tuning their steric requirements in a wide range by variation of the substituents at carbon and nitrogen. To
some extent, the electronic properties can also be influenced by introduction of suitable substituents such as SiMe₃ or 2,4,6-C₆H₃(CF₃)₃. Amidinate and guanidinate ligands have small N–M–N bite angles which are typically in the range of 63–65°. Tuning of the steric demand of the ligand by varying the substituents at nitrogen can also influence the coordination geometry of the metal center in bis(amidinato) complexes. Steric hindrance imparted by substituents on the nitrogen atoms has its main effects mainly within the heteroallylic N–M–N plane. Terphenyl substituents on the amidinate carbon atom have been successfully employed to effect steric shielding above and below the N–M–N plane, although this shielding is fairly remote from the metal center. Another approach to provide steric protection of the N–M–N coordination plane is the use of ortho-disubstituted aryl substituents on the nitrogen atoms. Especially useful in this respect is the 2,6-diisopropylphenyl group. Also a very important point to be noted is that in N,N'-bis(trimethylsilyl)-benzamidinates and related ligands the orientation of the phenyl ring on the central carbon atom with respect to the N–C–N unit is normally nearly perpendicular. This conformation accounts for the fact that such amidinate anions are not “flat” ligands such as the isoelectronic carboxylate anions, but also extend above and below the N–C–N plane. It was first pointed out by us that these ligands can be regarded as “steric cyclopentadienyl equivalents”. The concept of “steric cyclopentadienyl equivalents” was developed by Wolczanski et al. in connection with a series of tri-t-butyldimethylamido (“tritox”) complexes. The sterically demanding tri-t-butyldimethylamido ligand forms a steric cone about a metal, similar to bis(trimethylsilyl)amide or cyclopentadienyl. With 125 the cone angle of tritox approaches that of cyclopentadienyl (136°). Amidinate and guanidinate ligands, too, are monoaonic ligands, and their steric demand is tunable in a wide range similar to the transition from unsubstituted cyclopentadienyl to very bulky ring-substituted cyclopentadienyl ligands.

3. Synthesis and characterization of lanthanide amidinates and guanidinates

3.1 Lanthanide(II) amidinates and guanidinates

In (organo)lanthanide chemistry the divalent oxidation state is most readily accessible under normal conditions for samarium, europium, and ytterbium. Compounds of these elements in the +2 oxidation state are stronger reducing agents and undergo a large variety of interesting redox reactions. Just as in cyclopentadienyl–lanthanide chemistry, stable divalent species were of particular interest in amidinate and guanidinate lanthanide chemistry due to their anticipated high reactivity. In fact, soluble and very reactive ytterbium(II) benzamidinates containing [RC₆H₃C(NSiMe₃)₂]⁻ ligands were reported as early as 1990. As shown in Scheme 5, these compounds were readily prepared by treating freshly prepared YbI₂ in THF solution with two equivalents of sodium N,N'-bis(trimethylsilyl)amidinates and isolated as dark red, highly air-sensitive materials. X-Ray diffraction studies revealed the trans-coordination with two chelating amidinate ligands. A notable structural feature, characteristic also for many other complexes containing these ligands, is the large dihedral angle (77.3° for R = H) between the phenyl rings and the amidinate N–C–N units which precludes any conjugation between the two π-systems and is responsible for the cone-like overall shape of the amidinate ligands.

As expected, the ytterbium(II) benzamidinates shown in Scheme 5 were found to be strong reducing agents and to undergo various redox reactions e.g. with alkyl halides and dichalcogenides REER (E = S, Se, Te). For example, the S-S bond in [Me₂NC(S)S]₂ is readily cleaved to form an ytterbium(III) dithiocarbamate complex (Scheme 6). Facile cleavage of E–E bonds (E = Se, Te) was also observed (Scheme 7) giving rise to stable ytterbium(III) amidinate complexes comprising Yb–Se and Yb–Te bonds.
While ytterbium(II) benzamidinate complexes have been known for many years, the synthesis of the first divalent samarium bis(amidinate) required the use of a sterically hindered amidinate ligand, \(\text{[HC(NDipp)2]}\/\text{C0}\) (Dipp = C\(_6\)H\(_3\)Pr\(_2\)i-2,6). The dark green samarium(II) bis(amidinate) Sm(DippForm)\(_2\)(THF)\(_2\) (DippForm = \([\text{HC(NDipp)}\text{2}]\text{C0}\)) can be prepared by three different synthetic routes (Scheme 8). The trivalent diiodo samarate complex \([\text{Na(THF)}\text{5}]\text{[SmI2(DippForm)}\text{2(THF)}\text{2}]\) was isolated in small quantities as a colorless byproduct. Dissolution of this compound in hexane led to ligand redistribution to give Sm(DippForm)\(_3\) with concomitant precipitation of NaI and SmI\(_3\)(THF)\(_3\). The monofluoro-bis(amidinate) SmF(DippForm)\(_2\)(THF) could also be isolated from Sm(DippForm)\(_2\)(THF)\(_2\) via treatment with Hg(C\(_6\)F\(_5\))\(_2\). These results clearly show that carefully selected amidinate ligands are capable of stabilizing even the most strongly reducing “classical” lanthanide(II) ion, i.e. divalent samarium. Future investigations will show if similar complexes can also be synthesized with “non-classical” divalent lanthanide ions such as Tm\(_{\text{II}}\), Nd\(_{\text{II}}\) or Dy\(_{\text{II}}\). Apparently, analogous europium(II) amidinates too have not yet been reported, although they should be readily accessible through standard metathetical routes.\(^6\)

In 2007 the first homoleptic lanthanide(II) guanidinate complexes, Ln(Giso)\(_2\) (Ln = Sm, Eu, Yb; Giso = Cy\(_2\)N(NAr)\(_2\); Ar = C\(_6\)H\(_3\)Pr\(_2\)i-2,6), were reported and shown to have differing coordination geometries (including unprecedented examples of planar 4-coordination).\(^{23}\) In particular, X-ray studies revealed planar 4-coordinate coordination geometries for Sm and Eu derivatives (Fig. 1), while the ytterbium(II) species is distorted tetrahedral. In the case of Yb, two iodo-bridged dimeric lanthanide(II) guaninate complexes were also isolated from the reaction mixtures (Fig. 2). The reaction of equimolar amounts of Na([Me\(_2\)Si]\(_2\)NC(NCy)\(_2\)) (which was prepared in situ from NaN(SiMe\(_3\))\(_2\) and \(N,N'\)-dicyclohexylcarbodiimide) and YbI\(_2\)(THF)\(_2\) gave the closely related ytterbium(II) guaninate complex \([((\text{Me}_2\text{Si})_2\text{NC(NCy)}_2)\text{Yb(μ-I)}(\text{THF})_2]\) with bridging iodo ligands.\(^{6,23}\)

### 3.2 Lanthanide(III) amidinates and guaninates

#### 3.2.1 Homoleptic lanthanide(III) tris(amidinates) and -guanidinates

Homoleptic lanthanide(III) tris(amidinates) and -guanidinates are among the longest-known lanthanide complexes containing these chelating ligands. The first lanthanide amidinate complexes ever reported in the literature were homoleptic tris(amidinates) of the type \([\text{RC}_6\text{H}_4\text{C(NSiMe}_3)_2\text{]}\text{Ln}\) (Scheme 9), which can be regarded as the amidinate analogues of the homoleptic lanthanide tris(cyclopentadienyl) complexes Cp\(_3\)Ln.\(^{6,21}\)

A large number of such complexes were synthesized and fully characterized in the course of the early studies. However, at that time these compounds were mere laboratory curiosities without any apparent practical use. It also turned out that the derivative chemistry of these complexes is rather limited, resembling that of the parent Cp\(_3\)Ln complexes. It took many years until the promising catalytic activities of these compounds were discovered (see section 4).\(^{6,17}\)

In a similar manner, treatment of anhydrous rare earth chlorides with three equivalents of lithium 1,3-di-tert-butylacetamidinate (prepared in situ from di-tert-butylcarbodiimide, \(^1\text{Bu}-\text{N}=\text{C}=\text{N}^-\text{Bu},\) and methyllithium) afforded...
Ln[MeC(NBu)\textsubscript{2}]\textsubscript{3} (Ln = Y, La, Ce, Nd, Eu, Er, Lu) in 57–72% isolated yields.\textsuperscript{6,24} X-Ray crystal structures of these complexes demonstrated monomeric formulations with distorted octahedral geometry about the lanthanide(III) ions (Fig. 3, Ln = La). The new complexes are thermally stable at >300 °C, and sublime without decomposition between 180–220 °C/0.05 Torr. Other series of homoleptic lanthanide tris(amidinates) include the N-cyclohexyl-substituted derivatives [RC(NCy)\textsubscript{2}]\textsubscript{3}Ln(THF)\textsubscript{n} (R = Me, Ln = Nd, Gd, Yb, n = 0; R = Ph, Ln = Nd, Y, Yb, n = 2). A sterically hindered homoleptic samarium(III) tris(amidinate), Sm[HC(NC\textsubscript{6}H\textsubscript{3}Pr\textsubscript{2}i-2,6)\textsubscript{2}]\textsubscript{3}, was obtained by oxidation of the corresponding Sm(II) precursor (cf. Scheme 8).\textsuperscript{6}

In this area the carbodiimide insertion route is usually not applicable, as simple well-defined lanthanide tris(alkyls) and tris(dialkylamides) are not readily available.\textsuperscript{3–5} A notable exception is the formation of homoleptic lanthanide guanidinates from anionic lanthanide amido complexes and carbodiimides (Scheme 10).\textsuperscript{6}

The major synthetic route leading to homoleptic lanthanide tris(amidinates) and -guanidinates, however, is the metathetical reaction between anhydrous lanthanide trichlorides and preformed lithium amidinates or guanidinates, respectively, in a molar ratio of 1 : 3 (Scheme 11).\textsuperscript{6}

The six-coordinate tris(benzamidinates) [PhC(NSiMe\textsubscript{3})\textsubscript{2}]\textsubscript{3}Ln form 1 : 1 adducts with donor ligands such as THF, MeCN, or PhCN. In the case of benzonitrile it was possible to isolate and structurally characterize two of these seven-coordinate nitrile-adducts. They are most readily isolated when the original preparation is directly carried out in the presence of one equivalent of benzonitrile (Scheme 12). The facile adduct formation with small donor molecules is yet another analogy between the tris(amidinates) and the tris(cyclopentadienyl) complexes.\textsuperscript{6,17}

In recent years homoleptic lanthanide(III) tris(amidinates) and -guanidinates have been demonstrated to exhibit extremely high activity for the ring-opening polymerization of polar monomers such as ε-caprolactone and trimethylene carbonate (cf. section 4.1). Another promising field of application is their use in CVD and ALD processes (cf. section 5).\textsuperscript{6}

3.2.2 Lanthanide(III) bis(amidinates) and -guanidinates: metalloocene analogues. Bulky heteroallylic ligands such as the benzamide anions [RC\textsubscript{6}H\textsubscript{5}C(NSiMe\textsubscript{3})\textsubscript{2}]\textsuperscript{−} soon became well established as useful alternatives to the cyclopentadienyl ligands. Shortly after the successful synthesis and characterization of various lanthanide(III) tris(amidinate) derivatives the first disubstituted lanthanide(III) amidinate species were reported. Such compounds appeared to be interesting synthetic targets due to their metalloocene-like coordination environment which was expected to allow the isolation and characterization of stable though reactive amide, alkyl, and hydride species. In this respect the bulky amidinate and guaninate ligands resemble more the substituted cyclopentadienyl ligands such as Cp*\textsuperscript{+.} One of the first representatives of this class of compounds was a sky-blue neodymium complex containing the very bulky nonafluoromesityl-substituted benzamidinate ligand [2,4,6-(CF\textsubscript{3})\textsubscript{3}C\textsubscript{6}H\textsubscript{2}C(NSiMe\textsubscript{3})\textsubscript{2}]\textsuperscript{−} (Scheme 13).\textsuperscript{17}

Retention of LiCl led to formation of an “ate” complex which is an amidinate analogue of the well known neodymium metalloocene complex Cp\textsuperscript{+}\textsubscript{2}Nd(μ-Cl)\textsubscript{2}Li(THF)\textsubscript{2} (Cp\textsuperscript{+} = η\textsuperscript{3}-pentamethylecyclopentadienyl).\textsuperscript{3} While in the case of the large Nd\textsuperscript{3+} ion the use of a sterically bulky amidinate ligand was required, it soon turned out that...
bis(benzamidinate) lanthanide chlorides could be accessed in a more straightforward manner using scandium and yttrium as smaller central ions. Teuben et al. were able to show that the selective formation of lanthanide bis(amidinates) could also be achieved by adjusting the steric requirements of the ligands to the ionic radius of the lanthanide. Metathetical reactions between ScCl$_3$(THF)$_3$ or YCl$_3$(THF)$_3.5$ with two equivalents of the silyl-substituted amidinate ligands afforded the corresponding bis(amidinato) complexes [RC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$LnCl(THF). A similar approach using yttrium triflate as starting material was used to prepare the first bis(amidinato) lanthanide triflate complexes (Scheme 14).

Following the successful isolation of these chloro and triflate precursors, a major synthetic goal was the preparation of reactive alkyl, amide, and hydride species based upon the lanthanide bis(amidinate) moiety. This would further establish a close analogy between lanthanide bis(amidinates) and Cp$^*$_2Ln-type lanthanide metallocenes. For example, the yttrium(III) benzamidinates [RC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ are analogues of the metallocene alkyls Cp$^*$_2YCH(SiMe$_3$)$_2$. Indeed, it proved possible to employ the same synthetic routes which were well established in lanthanide metallocene chemistry to prepare the corresponding amidinate complexes. For example, alkyl derivatives were found to be easily accessible by alkylation of the corresponding chloride or triflate precursors (Scheme 15). Following their successful syntheses, it was demonstrated that these compounds exhibit comparable catalytic activities e.g. in olefin polymerizations as their metallocene counterparts (cf. section 5).

Other σ-alkyl yttrium complexes of this type include [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph(THF) and [PhC(NSiMe$_3$)$_2$]$_2$Y-(µ-Me)Li(TMEDA). The p-methoxy-substituted derivative [MeOC$_6$H$_4$C(NSiMe$_3$)$_2$YCH(SiMe$_3$)$_2$ was characterized by an X-ray structure determination confirming that the bis[N,N'-bis(trimethylsilyl)benzamidinate] ligand system sterically most resembles the bulky bis(pentamethylcyclopentadienyl) rather than the bis(cyclopentadienyl) ligand set. The reactivity of the benzamidinate-stabilized yttrium complexes towards various reagents including hydrogen, ethylene, terminal alkynes, nitriles, and pyridine derivatives was investigated in detail. Hydrogenolysis of the yttrium alkyls in benzene under 4 bar of H$_2$ afforded the dimeric hydride [[RC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Y(µ-H)]$_2$. Both [PhC(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph(THF) and [[RC$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Y(µ-H)]$_2$ were modestly active in ethylene polymerization but did not react with propylene and 1-hexene. The alkyls and the hydride were found to react with α-picoline to give an α-picoly derivative via C–H activation of a methyl group (Scheme 16).

Closely related benzamidinate chemistry has also been investigated with scandium. Due to its small ionic radius, Sc$^{3+}$ forms disubstituted benzamidinate complexes which give rise to interesting derivative chemistry. The main starting material is [PhC(NSiMe$_3$)$_2$]$_2$ScCl(THF), which is available from the reaction of Na[PhC(NSiMe$_3$)$_2$] with ScCl$_3$(THF)$_3$ in THF. The preparation of alkyl and aryl derivatives is illustrated in Scheme 17 (Mes = mesityl).

In the case of the methylolithium reaction the product is a THF solvate while, with bulky hydrocarbys, unsolvated complexes were obtained. The compound [PhC(NSiMe$_3$)$_2$]$_2$ScCH$_2$SiMe$_3$ readily reacts with H$_2$ to form the dimeric hydride [[PhC(NSiMe$_3$)$_2$]$_2$Sc(µ-H)]$_2$. 


\[
\begin{align*}
[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_2\text{YX(THF)} &+ \text{LiCH(SiMe}_3)_2 \\
\text{X} &= \text{Cl}, \ n = 1 \\
\text{X} &= \text{O}_2\text{SCF}_3, \ n = 0 \\
\rightarrow \ [\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_2\text{YCH(SiMe}_3)_2 \\
\text{R} &= \text{H}, \ \text{OMe}, \ \text{CF}_3 \\
- \text{LiX} \\
\end{align*}
\]
Metathetical routes using bulky lithium guanidinates as starting materials have also been employed to synthesize bis(guanidinato) lanthanide halides (Scheme 18) as well as reactive alkyls and hydrides. 6

Treatment of $\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Ln}(\mu-\text{Cl})_2\text{Li}(\text{THF})_2$ with methyllithium in the presence of TMEDA afforded the methyl bridged “ate” complexes $\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Ln}(\mu-\text{Me})_2\text{-Li}(\text{THF})_2$ (Ln = Nd, Yb) which also have analogues in Cp*-Ln chemistry. With Ln = Y and Nd the unsolvated, chloro-bridged dimers $\left(\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Ln}(\mu-\text{Cl})_2\right)_2$ were also synthesized. Amination of these complexes with two equivalents of LiNPri gave the amido derivatives $\left(\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Ln}(-\text{BH}_4)\right)_2\text{Li}(\text{THF})_2$ (Scheme 19). Treatment of the alkyl with an equimolar amount of PhSiH$_3$ in hexane led to formation of the first known dimeric lanthanide hydride in a bis(guanidinato) coordination environment (Scheme 20). 6

Mutual ligand arrangement in binuclear lanthanide guanidinate complexes of types $\left[\left(\text{guanidinate}\right)_2\text{Ln}(\mu-\text{Cl})_2\right]_2$, $\left[\left(\text{guanidinate}\right)_2\text{Ln}(\mu-\text{H})_2\right]_2$, and $\left(\text{guanidinate}\right)\text{Ln}(\mu-\text{Cl})_2\text{Li}(\text{THF})_2$ was quantitatively analyzed based on the ligand solid state angle approach. In complexes of the larger early lanthanides Nd, Sm, and Gd the guanidinate ligands shield up to 87% of the metal, and the bidentate ligands on opposite metal centers are in an eclipsed arrangement. In complexes of lanthanides with smaller ionic radii such as Y, Yb, and Lu the guanidinate ligands shield over 88.3% of the metal surface, and their staggered conformation is observed. The same ligand sets, i.e. the guanidinate anions $\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NR})_2\right)_2$ with $\text{R} = \text{Pr}$ and $\text{Cy}$, were utilized to synthesize novel guanidinate borohydride derivatives of lanthanides. For example, the heterobimetallic Sm bis(guanidinate) complex $\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Sm}(\mu-\text{BH}_4)_2\text{Li}(\text{THF})_2$ was obtained by a reaction of $\text{Sm}(\text{BH}_4)_3(\text{THF})_2$ with two equivalents of the corresponding lithium guanidinate. Subsequent treatment of the bimetallic “ate” complex, in which Sm and Li are linked by two bridging borohydride ligands, with 1,2-dimethoxyethane (DME) afforded the ionic complex $\left[\text{Li}(\text{DME})\right]_2\left[\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NPri})_2\right)_2\text{Sm}(\text{BH}_4)_2\right]$ (Scheme 21). The heterobimetallic “ate” complexes $\left(\text{Me}_3\text{Si}_2\text{NC}(\text{NCy})_2\right)_2\text{Ln}(\mu-\text{BH}_4)_2\text{Li}(\text{THF})_2$ (Ln = Nd, Sm, Yb) were found to catalyze methyl methacrylate polymerization (cf. section 4.1). 6

Bulky formamidinate ligands were also successfully employed to prepare lanthanide bis(amidinates). Reaction of La metal with Hg(C$_6$F$_5$)$_2$ and bulky N,N$^0$-bis(2,6-diisopropylphenyl)formamidine (HDippForm) in THF (Scheme 22) afforded (DippForm)$_2\text{LaF}(\text{THF})_2$ with a rare terminal La–F bond. A novel functionalized formamidine, resulting from ring-opening of THF, was formed as a by-product in this reaction. More recently these studies have been extended to other lanthanide elements such as Ce, Nd, Sm, Ho, Er, and Yb in order to gain a better understanding of the steric modulation of coordination number and reactivity in the synthesis of lanthanide(III) formamidinates. 6

3.2.3 Lanthanide(III) mono(amidinates) and -guanidinates.

The last group of lanthanide(III) amidinates and guanidinates to be synthesized were mono-substituted derivatives. As in cyclopentadienyl lanthanide chemistry, saturating the coordination sphere of the large lanthanide ions using just one chelating or cyclic ligand proved the most difficult task and often requires careful ligand design. For example, a novel amidinate ligand incorporating a bulky terphenyl group was used to prepare low-coordinate yttrium mono(amidinate) complexes (Scheme 23). 6

Especially notable among the most recent developments in lanthanide amidinate chemistry is the successful synthesis of stable mono(amidinate) yttrium dialkyls. The synthetic strategy involved the use of the sterically hindered amidinate ligand $[\text{Bu}^\text{t}^\text{C}(\text{NPri})_2]_2$. The first complex was prepared by a sequential reaction of YCl$_3$(THF)$_3.5$ with Li[ButC(NPri)$_2$] (1 equiv.) and two equivalents of LiCH(SiMe$_3$)$_2$ followed by pentane extraction. Large crystals of $[\text{Bu}^\text{t}^\text{C}(\text{NPri})_2]_2\text{Y}[\text{CH(SiMe}_3)_2]$($\mu-\text{Cl})\text{Li}(\text{THF})_3$
were isolated in 83% yield and structurally characterized by X-ray methods. Coordination of LiCl to the Y center results in a five-coordinated molecule. Such a retention of alkali metal halides which are formed during the course of reactions is a characteristic phenomenon in organolanthanide chemistry leading to the formation of so-called “ate” complexes. Subsequent reactions of neutral bis(alkyl) lanthanide benzamidinates with [NMe2HPh][BPh4] resulted in the formation of thermally robust ion pairs (Scheme 24).6

In a systematic study it was demonstrated that, using a specially designed bulky benzamidinate ligand, it is possible to prepare mono(amidinato) dialkyl complexes over the full size range of the Group 3 and lanthanide metals, i.e. from Sc to La (Fig. 4). The synthetic routes leading to the neutral and cationic bis(alkyls) are summarized in Scheme 25.6

Mono(guanidinato) complexes of lanthanum and yttrium were synthesized as illustrated in Scheme 26.6

![Scheme 23](image)

**Scheme 23**

![Scheme 24](image)

**Scheme 24**

![Scheme 25](image)

**Scheme 25**

![Scheme 26](image)

**Scheme 26**

The La compounds were made starting from La[N(SiMe3)2]3 and dicyclohexylcarbodiimide, Cy–N=C–N–Cy. Both mono(guanidinate) derivatives are monomeric in the solid state with a four-coordinate La center. In the case of yttrium it was recently reported that even the less bulky guanidinate ligand [(Me3Si)2NC(NPri)2]/C0 stabilizes mono(guanidinato) complexes. Closely related mono(guanidinato) lanthanide borohydride complexes of the type [(Me3Si)2NC(NCy)2]Ln(BH4)2(THF)2 (Ln = Nd, Sm, Gd, Er, Yb) were prepared by reactions of the corresponding borohydrides Ln(BH4)3(THF)3 with the sodium guanidinate Na[(Me3Si)2NC(NCy)2]. Scheme 27 illustrates the synthetic route leading to the Gd derivative which was crystallized as an adduct with 1,2-dimethoxyethane (DME).6

Bis(phenolate) ligands are present in the lanthanide guanidinate complexes shown in Scheme 28, which were prepared by insertion of disopropylcarbodiimide into the Ln–N bonds of appropriate neutral lanthanide amide precursors.6

**Fig. 4** Molecular structures of [PhC(NAr)2]Ln(CH2SiMe3)(THF)n cations (Ln = Sc, n = 2; Ln = Gd, n = 3, Ln = La, n = 4)
Brightly colored mono(benzamidinato) cyclooctatetraenyl lanthanide(III) complexes were prepared by treatment of either \([\text{C}_8\text{H}_8]\text{Ln}[\mu-\text{Cl}](\text{THF})_2]\) or \([\text{C}_8\text{H}_8]\text{Ln}[\mu-\text{OSCF}_3](\text{THF})_2]\) with \(\text{Na}[\text{R}\text{C}_6\text{H}_4\text{C}(-\text{SiMe}_3)_2]\) \((\text{R} = \text{H}, \text{OMe}, \text{CF}_3)\) (Schemes 29 and 30). According to X-ray structural analyses of \([\text{PhC}(-\text{SiMe}_3)_2]\text{Tm}(\text{C}_8\text{H}_8)(\text{THF})\) and \([\text{MeOC}_6\text{H}_4\text{C}(-\text{SiMe}_3)_2]\) Lu(\text{C}_8\text{H}_8)(\text{THF})\) these compounds are monomeric in the solid state.6,10

Insertion of carbodiimides into the Ln–C σ-bond of organolanthanide complexes was also reported to provide straightforward access to organolanthanide amidinates and guanidinates. The complexes \(\text{Cp}_2\text{Ln}[\text{Bu}^\circ\text{C}(-\text{NBut})_2]\) \((\text{Ln} = \text{Y}, \text{Gd}, \text{Er})\) were prepared this way from \(\text{Cp}_2\text{LnBu}^\circ\) and \(N,N^0\)-di-tert-buty carbodiimide. The analogous insertion of carbodiimides into Ln–N bonds has been shown to be an effective way of making lanthanide guanidinate complexes. For example, insertion of \(N,N^0\)-dicyclohexyl carbodiimide into one of the \(\text{Y}–\text{N}\) bonds of \(\text{Y}[\text{SiMe}_3]_2\) afforded the monoguanidinate diamide derivative \([\text{Me}_3\text{Si}]_2\text{NC}(-\text{NCy})_2\) \([\text{Y}–\text{N}[\text{SiMe}_3]_2]\). Complexes of the type \(\text{Cp}_2\text{Ln}[\text{Pri}^\circ\text{NC}(-\text{Pri})_2]\) \((\text{Ln} = \text{Y}, \text{Gd}, \text{Dy}, \text{Yb})\) have been prepared analogously.6

3.2.4 Lanthanide(III) complexes containing functionalized amidinate ligands

(a) Pendant-arm type amidinate ligands. In order to further explore the amidinate/cyclopentadienyl analogy, various amino-functionalized amidinate ligands have been synthesized with the aim of mimicking the well-known pendant-arm half-metalloocene catalysts. For example, benzamidinate ligands incorporating a pendant amine functional group were prepared as shown in Scheme 31. Instead of using \(\text{Me}_3\text{SiCl}/\text{NEt}_3\) in the first step, the starting amine can also be converted into the monosilylated derivative by successive reaction with \(^{11}\text{BuLi}\) followed by treatment with \(\text{Me}_3\text{SiCl}\).6

Reactions of \(\text{Li}[\text{Me}_3\text{SiNC}(-\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}_2](=\text{LiL})\) with \(\text{MCl}_3\) in appropriate stoichiometry led to the dinuclear \([\text{L}_2\text{M}(-\mu-\text{Cl})_2]\) \((\text{M} = \text{La}, \text{Ce})\) complexes. The potentially tridentate ligands \([\text{Me}_3\text{SiNC}(-\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}_2]\) \((\text{Scheme 32, } n = 2; \text{B}, n = 3; \text{C})\) have also been employed in the synthesis of yttrium alkyl and benzyl complexes.6

While the dialkyl complexes \([\text{Me}_3\text{SiNC}(-\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}_2][\text{Y}(-\text{CH}(-\text{SiMe}_3)_2)_2]\) could be isolated salt-free, attempts to prepare analogous benzyl or trimethylsilylmethyl complexes with ligand \(\text{B}\) yielded the \(\text{ate-complexes Li}[\text{Me}_3\text{SiNC}(-\text{Ph})\text{N}(\text{CH}_2)_3\text{NMe}_2][\text{Y}(-\text{CH}_2\text{Ph})\text{N}(-\text{CH}_2\text{SiMe}_3)_2][\text{PhCN}](\text{R} = \text{CH}_2\text{Ph}, \text{CH}_2\text{SiMe}_3)\) in which the \(\text{Li}\) ion is encapsulated by two amidinate and two amine nitrogens. The increased spacer length between the amidinate
and amine functionalities in ligand C prevented encapsulation of the Li ion, but still produced a bis(amidinate) yttrium benzyl complex, \([\text{Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_3\text{NMe}_2\text{]}_2\text{YCH}_2\text{Ph}\). In this compound only one of the two NMe\(_2\) functionalities is coordinated to the metal center.\(^6\)

\(\text{(b) Bis(amidinate) ligands.}\) Yet another interesting variation of the amidinate theme is the design and use of bis(amidinate) ligands. This can for example involve the reductive dimerization of carbodiimides to give oxalamidinate ligands of the type \([\text{C}_2\text{N}_4\text{R}_4]\)\(^2\). In the case of lanthanides, the reductive coupling of carbodiimides was achieved with the use of samarium(II) bis(trimethylsilyl)amides. The reaction of \(\text{Sm}[\text{N(SiMe}_3\text{)}_2\text{]}_2(\text{THF})_2\) with carbodiimides \(\text{RN} = \text{C} = \text{NR}\) \((\text{R} = \text{Cy, C}_6\text{H}_3\text{Pr}_2\text{]}\) led to formation of dinuclear Sm(III) complexes. For \(\text{R} = \text{Cy}\) (Scheme 33), the product has an oxalamidinate \([\text{C}_2\text{N}_4\text{Cy}_4]\)\(^2\) ligand resulting from coupling of two CyN=CH=C=N-Cy moieties at the central C atoms. The same product was obtained when the Sm(II) “ate” complex \(\text{Na[SmN(SiMe}_3\text{)}_2\text{]}_2\text{]}\) was used as divalent Sm precursor.\(^6\)

The dilithium salt of a linked bis(amidinate) dianionic ligand, \(\text{Li}_2[\text{Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_3\text{NMe}_2\text{]}_2\text{Y}[\text{CH(SiMe}_3\text{)}_2\text{]}(\text{THF})\).\(\text{Li}_2\text{L}\) was prepared by reaction of dilithiated \(\text{N}_2\text{N}'\text{-bis(trimethyl}-\text{silyl)l-1,3-diaminopropane with benzonitrile (Scheme 34).}\(^6\)

Reaction of the dilithium salt of the linked bis(amidinate) dianionic ligand \(\text{[Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_3\text{NMe}_2\text{]}_2\text{Y}[\text{CH(SiMe}_3\text{)}_2\text{]}(\text{THF})\) with \(\text{YCl}_3(\text{THF})_3\) gave \(\text{[Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_3\text{NMe}_2\text{]}_2\text{YCl(THF)}_2\), which, by reaction with \(\text{LiCH(SiMe}_3\text{)}_2\), was converted to an alkyl complex (Scheme 35). A structure determination of this compound (Fig. 5) showed that linking together the amidinate functionalities opens up the coordination sphere to allow for the bonding of an additional molecule of THF not present in the unbridged bis(amidinate) analogue \(\text{[PhC(NSiMe}_3\text{)}_2\text{]}_2\text{Y}[\text{CH(SiMe}_3\text{)}_2\text{]}\).\(^6\)

Analogous reaction of \(\text{Li}_2[\text{Me}_3\text{SiNC(Ph)N(CH}_2\text{)}_3\text{NMe}_2\text{]}_2\text{Y}[\text{CH(SiMe}_3\text{)}_2\text{]}(\text{THF})\) with \(\text{YbCl}_3\) afforded the linked...
bis(amidinato) ytterbium chloride LYb(μ-Cl)₂YbL(THF). The chloro-bridges in this compound are easily cleaved upon treatment with THF. Further reaction of the resulting monomeric chloro complex with NaCp in DME gave LYbCp(DME) in high yield (Scheme 36, Cp = η⁵-cyclopentadieny1).⁶,²⁷

In an extension of this work the steric effect of an amide group on the synthesis, molecular structures and reactivity of ytterbium amides supported by the linked bis(amidinate) ligand was investigated. Reactions of the chloro precursor with sodium arylamides afforded the corresponding monometallic amide complexes in which the linked bis(amidinate) is coordinated to the ytterbium center as a chelating ligand (Scheme 37). In contrast, the reaction with NaN(SiMe₃)₂ gave a bimetallic amide complex in which two linked bis(amidinates) act as bridging ancillary ligands connecting two YbN(SiMe₃)₂ fragments in one molecule.⁶,²⁷

3.3 Lanthanide(IV) amidinates and guanidinates

Most recently it was discovered in our lab that benzamidinate ligands are also capable of stabilizing novel cerium(IV) species. Thus they belong to the limited number of organic ligands which allow the stabilization of lanthanide complexes in all possible oxidation states (+2, +3, and +4). In analogy to the reaction shown in Scheme 9, treatment of anhydrous cerium(III) trichloride with three equivalents of the lithium amidinate precursor Li[p-MeOC₆H₄C(NSiMe₃)₂] first afforded the bright yellow p-anisoinitrile adduct of the homoleptic cerium(III) amidinate (Scheme 38). Oxidation to the corresponding cerium(IV) amidinate [p-MeOC₆H₄C(NSiMe₃)₂]₃CeCl was readily achieved using the reagent phenyliodine(III) dichloride. The advantage of this method is that iodobenzene is formed as the only by-product. This way the almost black cerium(IV) species could be isolated by simple crystallization directly from the concentrated reaction mixture. A single-crystal X-ray analysis clearly established the presence of the first amidinate complex of tetravalent cerium (Fig. 6).⁶

4. Lanthanide amidinates and guanidinates in homogeneous catalysis

At the time when the first lanthanide amidinates were reported in the early 1990s, these compounds appeared to be just laboratory curiosities for which nobody could envisage any practical uses. This situation changed completely when in 2002 it was discovered that homoleptic lanthanide tris(amidinate) complexes show extremely high activity for the ring-opening polymerization of ε-caprolactone at room temperature.²⁸ This was the first time that promising catalytic activity was found for lanthanide amidinates and it stimulated further work in the field. Certain aspects of catalytic applications of lanthanide amidinate complexes have already been summarized in review articles.⁶,¹²

4.1 Polymerization reactions catalyzed by lanthanide amidinate and guanidinate complexes

The use of amidinato catalyst systems for the polymerization of olefins was first reported in a patent application by us in cooperation with BASF.⁶ Since then various other patents dealing with the use of amidinato metal complexes as catalysts for olefin polymerizations have appeared. However, the main focus of these studies was on the use of group 4 metal amidinates as these have been found to exhibit very promising activities as homogeneous polymerization catalysts. This area has recently been compiled in an excellent review article by Eisen and Smolensky.²⁹ It took several more years until lanthanide amidinates and guanidinates successfully entered catalysis research and proved to be effective catalysts especially for polymerization reactions. The majority of the work published thus far involves the polymerization of polar monomers such as ε-caprolactone (CL), D,L-lactide or
methylmethacrylate (MMA), but promising results have also been achieved with simple olefins. For example, the dimeric bis(guanidinato) lutetium hydride complex \([[(\text{Me}_3\text{Si})_2\text{N}](\text{NC})_2]_2\text{Lu}(-\text{H})\) was found to catalyze the polymerization of ethylene, propylene, and styrene. Moderate activity in ethylene polymerization was observed with the mono(guanidinate) yttrium dialkyl \([((\text{Me}_3\text{Si})_2\text{N})(\text{NPri})_2]_2\text{Y}(-\text{CH}_2\text{SiMe}_3)_2\text{(THF)}_2\). The mono(amidinato) lanthanide \([\text{Ph}_2\text{NMe}_2\text{H}][\text{B}((\text{C}_6\text{F}_5)_4])\) and excess isobutyl alumoxane dialkyl precursors in combination with the Brønsted activator \([\text{La}[\text{N(SiMe}_3)_2]]_2\). Although a high molecular weight polymer was obtained, polydispersities were broad and no control over the stereochemistry of the polymer was observed.

The methyl bridged “ate” complexes \([(\text{Me}_3\text{Si})_2\text{N}](\text{NPri})_2]_2\text{Ln}(-\text{Me})_2\text{Li}(\text{THF})_2\) \((\text{Ln} = \text{Nd}, \text{Yb})\) exhibit extremely high activity for the ring-opening polymerization of \(\varepsilon\)-caprolactone to give high molecular weight polymers. The Nd derivative also showed good catalytic activity for the syndiotactic polymerization of methacrylate. Other metal amidinates and guanidinates, for which high activity in the polymerization of polar monomers such as \(\varepsilon\)-caprolactone (CL), lactide, and methylmethacrylate (MMA) have been reported, include the homoleptic lanthanide amidinates \([\text{Ln}[\text{RC}(\text{NCy})_2]_3](\text{THF})_n\) \((R = \text{Me, Ln = Nd, Gd, Yb, } n = 0; R = \text{Ph, Ln = Y, Nd, Yb, } n = 2)\) and the bis(guanidinate) lanthanide amides \([(\text{Me}_3\text{Si})_2\text{N}](\text{NPri})_2]_2\text{Ln}[\text{NPri}]=\text{Nd}\) was studied by Ephritikhine et al., and compared to the catalytic activity of its uranium(III) counterpart, \([\text{MeC}(\text{NCy})_2]_2\text{U}\). The Nd complex showed again extremely high activity in the ring-opening polymerization of \(\varepsilon\)-caprolactone (CL). In the presence of 0.5% mol equiv. of \([\text{MeC}(\text{NCy})_2]_2\text{Nd}\) in toluene, polymerization of CL was achieved in less than 2 min, giving a viscous gel of poly(\(\varepsilon\)-caprolactone). It was found that the uranium(III) complex was much less efficient because of its rapid oxidation into U(IV) species.

Recently the guanidinate lanthanide borohydrides \([(\text{Me}_3\text{Si})_2\text{N}](\text{NCy})_2]_2\text{Ln}(\text{BH}_4)_2\text{Li}(\text{THF})_2\) \((\text{Ln} = \text{Nd, Sm, Er, Yb})\) and \([(\text{Me}_3\text{Si})_2\text{N}](\text{NCy})_2]_2\text{Ln}(\text{BH}_4)_2\text{Li}(\text{THF})_2\) \((\text{Ln} = \text{Nd, Sm, Yb})\) were reported to be promising monoinitiators for the ring-opening polymerization of racemic lactide as well as methyl methacrylate polymerization. Recently ytterbium amide complexes stabilized by linked bis(amidinate) ligands (cf. Scheme 35) were reported to be efficient initiators for the polymerization of \(l\)-lactide. The catalytic performance was found to be highly dependent on the amido groups and molecular structures.

The ring-opening polymerization of trimethylene carbonate (TMC) using the homoleptic lanthanide aminate complexes \([\text{RC}(\text{NCy})_2]_2\text{Ln}\) \((R = \text{Me, Ph}; \text{Ln} = \text{La, Nd, Sm, Yb})\) as single-component initiators was investigated in detail. It was found that the substituents on the aminate ligands and the metal centers had a great effect on the catalytic activities of these complexes, i.e. Me > Ph, and La > Nd > Sm > Yb. Thus the lanthanum acetamidinate \([\text{MeC}(\text{NCy})_2]_2\text{La}\) showed the highest catalytic activity. The ring-opening polymerization of trimethylene carbonate was also achieved using homoleptic lanthanide guanidinate complexes \([\text{R}[\text{N}](\text{NR})_2]_2\text{Ln}\). Here too, the metal centers and the substituents on the guanidinate ligands showed a marked effect on the catalytic activities with...
[Ph2NC(NCy)2]Yb being the most active catalyst in this case. The copolymerization of TMC with ε-caprolactone initiated by [Ph2NC(NCy)2]Yb was also tested. The other members of this series of homoleptic lanthanide(III) guanidinates also exhibited extremely high activity for the ring-opening polymerization of ε-caprolactone giving polymers with high molecular weights. In this case, too, the different substituents at the guanidinate ligands have a great effect on the catalytic activity.6

Although polymerization catalysis using lanthanide amidinates and guanidinates is still in its infancy, the present results clearly show the great potential this class of rare earth complexes offers. Catalytic activities can be tuned in a wide range by using various group 3 and lanthanide metals and different substituents at the ligand backbone. A major advantage of the amidinates and guanidinates over the established lanthanide metalloocene catalysts is their significantly improved air-stability especially in the case of the tris(amidinates).

4.2 Other reactions catalyzed by lanthanide amidinate and guanidinate complexes

An interesting organolanthanide-catalyzed reaction which has been studied in recent years is the addition of terminal alkynes to carbodiimides leading to the novel class of N,N'-disubstituted propiolamidines. It was found that half-sandwich rare earth metal complexes bearing silylene-linked cyclopentadienyl-amido ligands can act as excellent catalysts in this addition reaction. As illustrated in Scheme 40, a rare earth amidinate species has been confirmed to be a true catalytic species.

This organolanthanide-catalyzed reaction provides the first example of efficient preparation of well defined propiolamidines, a new family of amides which are difficult to access by other means and may show unique reactivity. A wide range of terminal alkynes could be used for this catalytic cross-coupling reaction which was not affected by either electron-withdrawing or -donating substituents or their positions at the phenyl ring of the aromatic alkyne.33

More recently it was demonstrated that this organolanthanide-catalyzed reaction is more general in nature and can be extended to other lanthanide precatalysts as well as the addition of N–H bonds to carbodiimides.34,25 For example, the ring-bridged metalloccenes (EBI)LnN(SiMe3)2 (Ln = Y, Sm, Yb; EBI = ethylene-bis(η5-indenyl)) were found to exhibit versatile catalytic activities with high efficiency toward the addition of the N–H bonds of amines and the C–H bonds of terminal alkynes to carbodiimides, thereby providing access to various substituted guanidines and propiolamidines. Here again lanthanide guanidinate and amidinate species are the key intermediates in the proposed catalytic cycle.34 Various divalent lanthanide complexes such as Ln[N(SiMe3)2]2(THF)3 (Ln = Sm, Eu, Yb) or (MeC5H4)2Sm(THF)2 were also found to be highly active precatalysts for the addition of N–H and C–H bonds to carbodiimides. Scheme 41 illustrates the proposed catalytic cycle for a samarium(II) silylamide precursor. The first step in both reactions is supposed to be the formation of a bimetallic samarium bis(amidinate) species originating from the reductive coupling of carbodiimide promoted by the Ln(II) complex. The active species is proposed to be a lanthanide guanidinate and a lanthanide amidinate.35

The catalytic activity of bulky amidinato bis(alkyl) complexes of scandium and yttrium (cf. section 3.2.3) in the intramolecular hydroamination/cyclization of 2,2-dimethyl-4-pentenylamine has also been investigated and compared to the activity of the corresponding cationic mono(alkyl) derivatives. Cyclotrimerization of aryl isocyanates leads to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates). Another good catalyst for the cyclotrimerization of phenyl isocyanate was found in the organoyttrium amidinate complex Cp2Y[Bu4N(C(NBu1)3)].6 These initial results indicate that lanthanide amidinates and guanidinates may exhibit interesting catalytic activities in reactions other than polymerizations. Clearly more work in this direction would be highly desirable.

5. Lanthanide amidinate and guanidinate complexes in materials science

Even more surprising than the discovery of lanthanide amidinate and guanidinate catalysis was the finding that such complexes may turn out to be valuable precursors in materials science and nanotechnology. Although this field of application too is still in its infancy, the first results are promising and indicate that volatile lanthanide amidinates could play a significant role as ALD precursors in the future.
Atomic layer deposition (= ALD) is a modified chemical vapor deposition (= CVD) process for the deposition of highly uniform and conformal thin films by alternating exposures of a surface to vapors of two chemical reactants. Such uniform, conformal thin films have a wide variety of applications in modern technology, including microelectronics. In 2003, Gordon et al. first reported that pure metals can be deposited by using volatile homoleptic N,N′-dialkylacetamidinato metal complexes and molecular hydrogen gas as the reactants. A series of homoleptic metal amidinates of the general type [M(RC(NR)2)]3 (R = Me, Bu; R = Pr, Bu) was prepared for numerous metals (e.g. Ti, V, Mn, Fe, Co, Ni, Cu, and Ag), including lanthanum (Scheme 42). The new compounds were found to have properties well-suited for use as precursors for atomic layer deposition of thin films. They have high volatility, high thermal stability, and high and properly self-limited reactivity with molecular hydrogen, depositing pure metals, or water vapor, depositing metal oxides. Following this discovery, several patents dealing with the use of volatile metal amidinate complexes in MOCVD or ALD processes have meanwhile appeared in the literature.6

ALD in the presence of water vapor has been successfully employed for the deposition of lanthanide oxide thin layers. There is considerable current interest in lanthanide oxides such as La2O3 due to their potential applications as insulators for memory and logic devices. Winter et al. first reported the use of lanthanide amidinate complexes in the fabrication of lanthanide-doped inorganic phases by CVD methods. In the course of this work several new lanthanide tris(amidinates) were prepared which sublime at temperatures as low as 90 °C at low pressure. It was pointed out that lanthanide amidinate complexes are extremely promising CVD precursors due to their all-nitrogen coordination spheres, relatively low molecular weights, and variability of the amidinate ligand. Rare earth oxides, including Er2O3, have high permittivities and are promising candidates to replace SiO2 in future microelectronics devices. The atomic layer deposition of Er2O3 films has been demonstrated using [MeC(NBu)t]3Er and ozone with substrate temperatures between 225–300 °C. The growth rate increased linearly with substrate temperature from 0.37 Å per cycle at 225 °C to 0.55 Å per cycle at 300 °C (Fig. 7). The as-deposited films were amorphous below 300 °C, but showed reflections due to cubic Er2O3 at 300 °C.

Most recently, eight novel homoleptic tris(guanidinato) complexes M[NPr]2CNR23 [M = Y, Gd, Dy; R = Me, Et, Pr] have been synthesized and characterized by NMR, CHN-analysis, mass spectrometry and IR spectroscopy. Single crystal structure analyses revealed that all these compounds are monomers with the rare-earth metal center coordinated to six nitrogen atoms of the three chelating guanidinato ligands in a distorted trigonal prism geometry. With the use of TGA/DTA and isothermal TGA analysis, the thermal characteristics of all tris(guanidinates) were studied in detail to evaluate their suitability as precursors for thin film deposition by MOCVD and ALD. The Pr-Me2N-guanidinates of Y, Gd and Dy showed excellent thermal characteristics in terms of thermal stability and volatility. Additionally, the thermal stability of the Pr-Me2N-guanidinates of Y and Dy in solution was investigated by carrying out NMR decomposition experiments and both the compounds were found to be remarkably stable. All these studies indicated that Pr-Me2N-guanidinates of Y, Gd, and Dy have the prerequisites for MOCVD and ALD applications which was confirmed by the successful deposition of Gd2O3 and Dy2O3 thin films on Si(100) substrates. The MOCVD grown films of Gd2O3 and Dy2O3 were highly oriented in the cubic phase, while the ALD grown films were amorphous.

Yet another exciting application of the same erbium amidinate precursor, [MeC(NBu)t]3Er, is its use as a dopant source in the preparation of silicon nanocrystals. These nanocrystals were prepared by the co-pyrolysis of [MeC(NBu)t]3Er and disilane in a dilute helium stream at 1000 °C. Under conditions identical to those used previously for β-diketonate precursors, nanocrystals doped using this amidinate source were larger in size, of a narrower size distribution, and contained more erbium in the nanocrystal on average, making them attractive for possible optoelectronic device structures.

6. Conclusions
This tutorial review describes the success story of lanthanide amidinates and guanidinates. First reported almost two decades ago, these compounds have undergone a transition from mere laboratory curiosities to efficient polymerization catalysts and ALD precursors in recent years. Thus this article provides a good example for purely academic research eventually turning out to become the basis for unexpected practical uses. Initial results clearly show that certain lanthanide amidinates and guanidinates show very high catalytic activity...
in polymerization reactions of olefins and polar monomers while other lanthanide amidinates are starting a career as novel precursors in materials science and nanotechnology. Besides these exciting applications, the synthetic and structural chemistry of lanthanide amidinates is surprisingly diverse and far from being fully exploited. Amidinate and guanidinate ligands rival the ubiquitous cyclopentadienyl ligands in their accessibility and versatility. Important aspects of lanthanide cyclopentadienyl chemistry can now be realized using the amidinate and guanidinate anions as “steric cyclopentadienyl equivalents”. Mono-, di- and trisubstitution products are available as are complexes containing pendant-arm amidinates and bis(amidinate) ligands. All three possible oxidation states (+2, +3, and +4) of the lanthanide ions can be stabilized with the use of amidinate ligands. Future preparative work will show if e.g. novel divalent lanthanide amidinate and guanidinate complexes (Nd$^{2+}$, Eu$^{2+}$, Dy$^{2+}$, Tm$^{2+}$) can be prepared and fully characterized. Further investigation of the recently discovered cerium(IV) benzamidinates is also clearly warranted. Another point worthy of a more thorough investigation would be if and when there is any marked difference in catalytic activities between analogous cyclopentadienyl and amidinate/guanidinate chemistry. It would be interesting to see if there are examples of compounds belonging to the same class of compounds (e.g. L$_2$LnX) where the reactivity is different or polymerization is better with one class or other. This could be a good subject for more systematic future studies. In any case it needs no prophet to foresee that the most significant future development in this area lies in the practical exploration of lanthanide amidinates and guanidinates in catalysis, materials science and, perhaps, as novel reagents in organic synthesis.

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