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Review

Guanidinate and amidopyridinate rare-earth complexes: Towards highly reactive alkyl and hydrido species

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ABSTRACT

The review summarizes advances in the chemistry of organo rare-earth complexes containing bulky guanidinate and amidopyridinate ligands. The methods of synthesis, structures, reactivities and catalytic activities of various types of alkyl and hydrido complexes and their precursors are considered.

1. Introduction

Alkyl and hydrido rare-earth complexes posses a unique set of properties and fairly rich chemistry, which make them intriguing objects for investigation of structural, reactivity and catalytic patterns. Large ionic radii of rare-earth elements [1], Lewis acidity and the presence of unoccupied 5d and 6s orbitals provide a marked tendency of rare-earth compounds to complexation resulting in high coordination numbers [2]. Combination in one molecule of Lewis acidity and of high reactivity of M–H and M–C bonds which undergo facile multiple carbon–carbon bond insertions [3] sets up a basis for high potential of rare-earth alkyl and hydrido complexes in various catalytic reactions, especially those involving unsaturated substrates. High catalytic activity in reactions of hydrogenation [3b,4], polymerization [5], hydrosilylation [6], hydroboration [7], hydroamination [8], hydrophosphination [9] of alkenes demonstrated by metallocene-type rare-earth alkyl and hydrido complexes maintain permanent interest to these compounds. Another important feature relevant to catalytic applications is gradual variation of the ionic radius within the rare-earth

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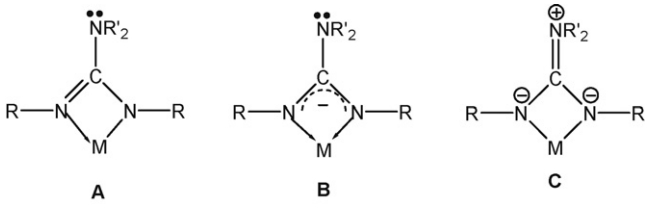
metals series in the range from 0.89 Å (Sc^{3+}) to 1.17 Å (La^{3+}) [1b] when the redox and chemical properties remain substantially similar. This affords an unique opportunity for tuning the reactivity of metal complex by designing the metal coordination sphere and selecting the central atom with appropriate radius according to specific requirements of the catalyzed reaction.

Electropositivity of rare-earth metals [10] and predominantly ionic character of the metal–ligand interactions in their organic derivatives have favored employment of ligands forming stable anions such as cyclopentadienyl and led to extensive growth of sandwich and half-sandwich classes of compounds during the past three decades [2,11]. In recent years the trend has been toward the development of new supporting ligand environments which would allow to overcome the limitations inherent to the cyclopentadienyl system and to extend the means for design of metal coordination sphere [12,15]. The aims of development of new ligand systems are to increase stability of rare-earth complexes under the condition of maintenance of high reactivity, to increase the complex tolerance to functional groups of substrates (or monomers), to extend the scope of the design and control of the geometry of the metal coordination sphere and to control the selectivity of catalytic reactions. The stability and reactivity of rare-earth organometallic compounds are known to be largely determined by the degree of saturation of the coordination sphere of metal atom that is why the ancillary ligand frameworks destined for synthesis of thermally stable and isolable species should meet a series of requirements. The ancillary ligand should be completely inert, non-labile and bulky enough to provide steric saturation of the metal atom coordination sphere and therefore the kinetic stability of the metal complex. Considerably ionic nature of rare-earth metal–carbon bond, ability to aggregation results in low energy pathways for ligand exchange that facilitates ligand redistribution and may preclude stabilization of a defined ligand sphere. In order to prevent this process multidentate ligands containing donor sites that do not tend to form bridging bonds are preferable, but at the same time one should bear in mind that a fine balance is necessary since excessive steric bulk and ligand denticity can dampen reactivity. Another challenge—synthesis of kinetically stable complexes containing central atoms with low coordination numbers can be overcome if the ancillary ligand provides solubility in non-polar non-coordinating solvents what allows to avoid the presence of coordinated Lewis bases such as THF in the molecule of complex. This can lead to enhanced catalytic activity of complexes as a result of exclusion of the competition between the Lewis base and the substrate for a site in the metal coordination sphere. Moreover, investigation of the influence of coordination environment of the rare-earth metal atom on the reactivities of M–C and M–H bonds is of considerable fundamental concern.

In this review the recent developments in the synthesis, structure determination, reactivity and catalytic activity of alkyl and hydrido rare-earth complexes supported by guanidinate and amidopyridinate ligands will be covered. The synthetic methods which allow introduction of guanidinate and amidopyridinate ligands into rare-earth complexes will be also considered.

2. Complexes containing guanidinate ligands

Tetrasubstituted guanidinate ligands of general formula $[RNC(NR'_2)NR'']^-$ are built around a central sp^2-hybridized carbon atom to which an imine (RN) and two amine groups (NR'_2 and deprotonated NR″) are bonded. The nitrogen lone pairs are involved in intramolecular π-bonding thus resulting in negative charge delocalization in NCN-fragment. Tetrasubstituted guanidinate ligands belong to bidentate monoanionic ligands and can be considered as isoelectronic alternatives to cyclopentadienyl anions. Due to the fact that both steric bulk and electronic properties of guanuidinate ligand can be easily modified through variations of the organic substituents on the nitrogen atoms this system presents high potential interest as a supporting ligand framework which allows control over the metal atom coordination sphere and metal mediated chemical processes. Another important features of guanidinate ligands $[RNC(NR'_2)NR'']^-$ which provide their attractiveness for coordination chemistry are flexibility and variety of coordination modes (Scheme 1) whose combination with a range of donor properties result in compatibility with a wide number of metal ions across the periodic table [13].



Scheme 1. Possible coordination modes of momoanionic guanidinate ligands.

Neutral, mono- and dianionic guanidinate ligands were successfully employed in coordination chemistry of transition and non-transition metals [13,14] but in rare-earth metal chemistry they appeared very recently [13c,d,15]. Application of closely related amidinate ligands $[RC(NR)_2]^-$ which were introduced in organometallic chemistry of rare-earth metals in pioneering works of Edelmann et al. [16] and Teuben and co-workers [17] gave a strong impact to the development of this area and allowed synthesis and characterization of new series of highly reactive species. Mono-, bis(alkyl), cationic alkyl and hydrido rare earth complexes supported by amidinate ligands were described and some of them demonstrated high catalytic potential in reactions of transformation of unsaturated substrates (olefin polymerization [17f,g], isoprene polymerization [18], acetylene dimerization [17c], olefin hydroboration [19], and hydrosilylation [20]). The interaction of the lone pair of the R_2N-group with the conjugated NCN ligand moiety augments guanidinates π-donor ability and makes them stronger donors than amidinates [11]. This also increases guanidinates compatibility with electron deficient metal ions and allows to decrease electron deficiency of the metal center and probably to modify catalytic activity.

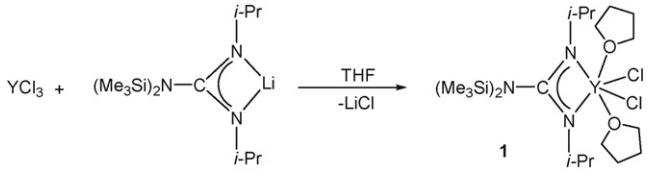
One of substantial advantages of guanidinate ligands is the ease with which the representatives of this family bearing various substituents can be synthesized by a number of routes from readily available starting materials [21]. A convenient method of synthesis of alkaline metal guanidinates is the reaction of appropriate amides with carbodiimides [22].

There are three synthetic routes which allow to introduce the monoanionic guanidinate fragment into rare-earth metal complex. The first method is metathesis reaction of anhydrous rare-earth metal halides with lithium or sodium guanidinates and the second one is insertion of carbodiimides into the Ln–N bond of appropriate amides. The only example of the synthesis of guanidinate complex via the alkane elimination under the treatment of tris(alkyl) yttrium derivative with guanidine was recently published by Hessen and co-workers [20].

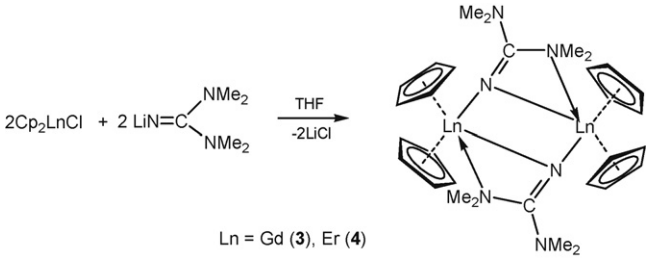
2.1. Synthesis of rare earth guanidinate halo complexes by salt metathesis reaction from halide precursors

2.1.1. Mono(guanidinate) rare-earth complexes

The guanidinate chloro derivatives are the most widely used precursors for synthesis of rare earth alkyl complexes supported by guanidinate ligands. To date complexes belonging to both mono(guanininate) dichloro and bis(guanidinate) chloro types



Scheme 2.



Scheme 4.

of compounds are known. Noteworthy the first examples of structurally characterized rare-earth mono(guanininate) dichloro complexes were reported very recently. Mono(guanidinate) dichloro yttrium complex $[(Me_3Si)_2NC(Ni\text{-}Pr)_2]YCl_2(THF)_2$ (**1**) was synthesized by reaction of YCl_3 and lithium N,N′-diisopropyl-N″-bis(trimethylsilyl)guanidinate $Li[(Me_3Si)_2NC(Ni\text{-}Pr)_2]$ in 1:1 molar ratio in THF at 20 °C (Scheme 2) [23].

The X-ray crystallographic study revealed that complex **1** is a monomeric salt-free compound. The coordination sphere of the yttrium atom consists of two nitrogen atoms from the bidentate guanidinate ligand, two chlorine atoms and two oxygen atoms from the two THF molecules. This results in a formal coordination number of six with the coordination geometry of the yttrium atom which can be described as a distorted octahedron.

Surprisingly the analogous synthetic pathway and workup procedure in the case of related dicyclohexyl substituted guanidinate ligand resulted in the formation of monoguanidinate dichloro yttrium derivative which was isolated as a dimeric heterobimetallic ate-complex $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ (**2**) (Scheme 3) in 95% yield [24].

Compound **2** turned out a dimeric ate-complex containing a bimetallic tetranuclear core $[Li(\mu\text{-}Cl)_2Y(\mu\text{-}Cl)]_2$ in which all six chlorine atoms are μ^2-bridging. Two of chlorine atoms form bridges between two yttrium atoms while four others connect yttrium and lithium atoms.

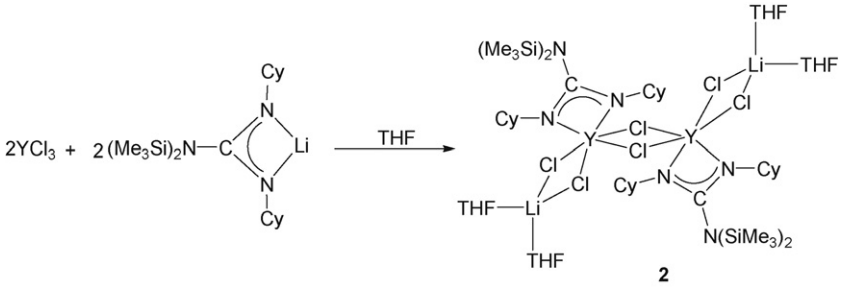
Monoguanidinate lanthanide complexes of metallocene type $[Cp_2Ln(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N{=}C(NMe_2)_2)]_2$ (Ln = Gd (**3**), Er (**4**)) were obtained by the salt metathesis reactions of Cp_2LnCl with N^1,N^1,N^2,N^2-tetrasubstituted lithium guanidinate $LiN{=}C(NMe_2)_2$ (Scheme 4) [25]. As provided by the X-ray single crystal diffraction study **3** is a salt-free compound which adopts a dimeric structure with an unusual μ-bridging coordination of the guanidinate ligands bonding two metal centers. Both gadolinium atoms are coordinated by two η^5-Cp ligands, one chelating guanidinate ligand and one nitrogen atom of the second guanidinate fragment. In complex **3** just one of two NMe_2-fragmetns is involved into coordination to metal atom as a terminal group, while the second one remains non coordinated. The N atom which does not bear organic radicals acts as a μ-bridging ligand bonding two metal centers. Unlike complexes **1** and **2** coordination of the guanidinate ligand in **3** is asymmetric. The double character of the bond between the central carbon atom and the bridging nitrogen atom [26] and the analysis of the Gd–N and C–N bond distances within NCN fragments indicate the negative charge localization on the imino nitrogen atom.

The synthesis of the mono(guanidinate) iodo Yb(II) derivatives bearing the guanidinate ligands with different steric bulk $[\{(Me_3Si)_2NC(NCy)_2\}YbI(THF)_2]_2$ (**5**) [27] (Scheme 5) and $[\{Cy_2NC(2,6\text{-}^iPr_2C_6H_3)_2\}YbI(THF)]_2$ (**6**) [28] (Scheme 6) were published recently.

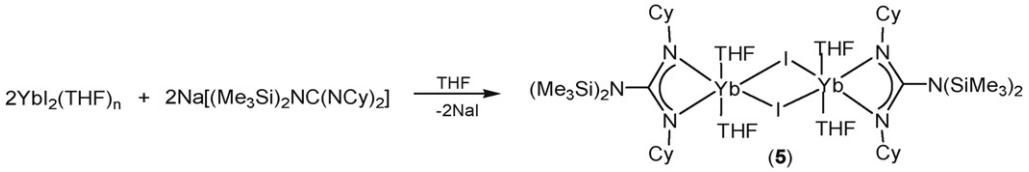
Complexes **5** and **6** were synthesized by the salt metathesis reactions of $YbI_2(THF)_n$ with equimolar amounts of $Na[(Me_3Si)_2NC(NCy)_2]$ or $K[Cy_2NC(2,6\text{-}^iPr_2C_6H_3)_2]$ respectively in THF at ambient temperature. Complex **5** was isolated after recrystallization from hexane in 66% yield. It is worthy to note that in the reactions of $K[Cy_2NC(2,6\text{-}^iPr_2C_6H_3)_2]$ containing bulkier guanidinate ligand with $LnI_2(THF)_n$ (Ln = Eu, Sm, Yb) despite of the reactions stoichiometry the homoleptic bis(guanidinate) derivatives $[Cy_2NC(2,6\text{-}^iPr_2C_6H_3)_2]_2Ln$ (Ln = Yb (**7**), Sm (**8**), Eu (**9**)) were the major products due to redistribution reactions advancing. However, small amounts (6%) of heteroleptic **6** were isolated from both 1:1 and 2:1 reactions. When complex **6** is kept in THF solution at room temperature over several hours it is redistributed to give **7** and $YbI_2(THF)_2$. The authors [28] suppose that the samarium and europium analogues can not be isolated due to their higher instability resulted from the more facile redistribution linked to the larger ionic radii of Sm and Eu (values for 7-coordinate Ln: Sm^{2+} 1.22 Å, Eu^{2+} 1.20 Å, Yb^{2+} 1.08 Å) [1b].

Both complexes **5** and **6** were found to be dimeric in crystalline state, their NMR spectra are consistent with proposed structures. Each of the ytterbium atoms is coordinated by one guanidinate ligand and two μ-bridging iodine atoms. Increase of steric demand of guanidinate ligand does not prevent dimer formation but allows to diminish the number of THF molecules coordinated to ytterbium atom (two THF molecules for complex **5** and one for **6**) and to reach lower extent of coordination saturation of the central atom.

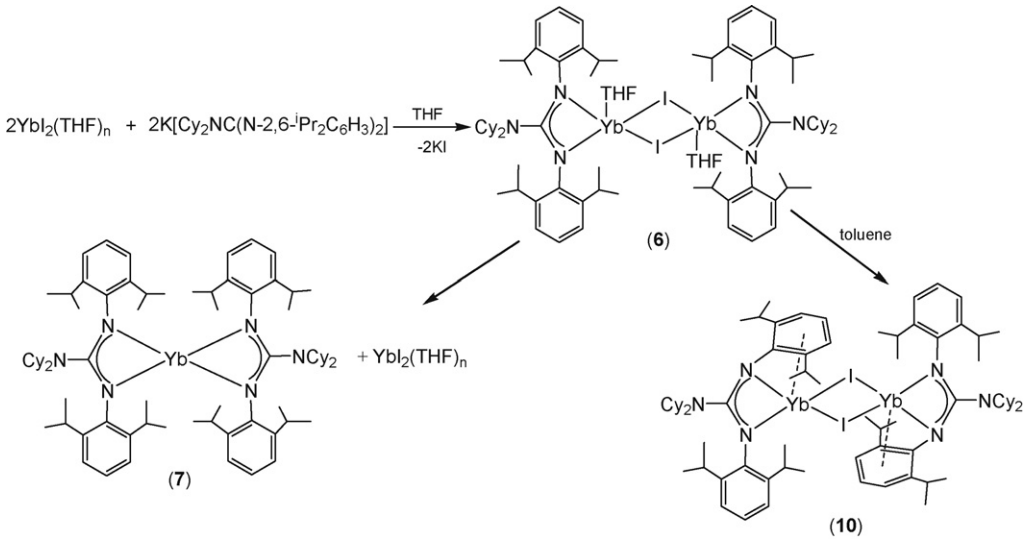
When complex **6** in solid state was subjected to reduced pressure at 25 °C and subsequently recrystallized from toluene the THF molecules were removed from the coordination sphere of ytterbium. That results in the change in the coordination mode of the guanidinate ligand involving η^6-coordination of arene to the ytterbium atom. This rearrangement can be reversed by dissolving **10** in THF.



Scheme 3.



Scheme 5.



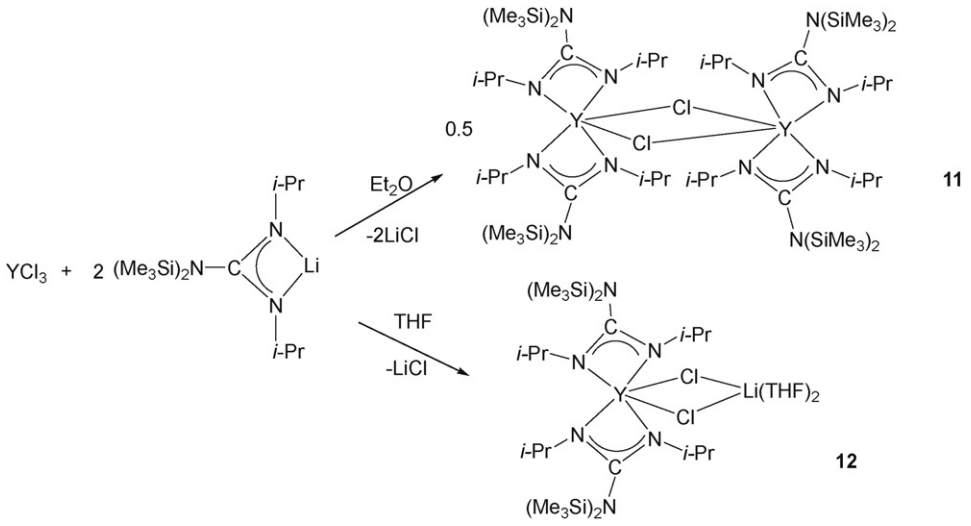
Scheme 6.

2.1.2. Bis(guanidinate) rare-earth complexes

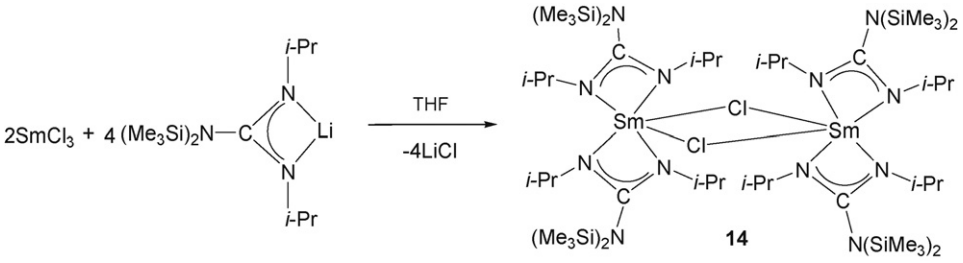
Rare-earth bis(guanidinate) chloro complexes are more numerous and are better investigated compared to mono(guanidinate) species. It was found that the reactions of anhydrous $LnCl_3$ with two equivalents of alkaline metal guanidinates can afford different types of bis(guanidinate) chloro complexes and namely: neutral monomeric $[R_2NC(NR'_2)_2]LnCl(L)$, ionic monomeric $[R_2NC(NR'_2)_2]Ln(\mu\text{-}Cl)_2Li(L)_n$ and neutral dimeric $\{[R_2NC(NR'_2)_2]LnCl\}_2$. The analysis of the data published on this subject clearly shows that a whole number of factors (guanidinate ligand steric demand, rare-earth metal ion size, reaction solvent, workup method, nature of alkaline metal cation in starting guanidinate) is crucial for this reaction and determines the composition and structure of the complex formed.

Thus Richeson and co-workers have found that the reaction of YCl_3 with $Li[(Me_3Si)_2NC(Ni\text{-}Pr)_2]$ (1:2 molar ratio) in ether resulted in the isolation of the neutral solvent- and salt-free dinuclear guanidinate complex $\{[(Me_3Si)_2NC(Ni\text{-}Pr)_2]Y(\mu\text{-}Cl)_2\}_2$ (**11**) which was isolated after recrystallization from hexane in 73% yield. The same reaction carried out in THF afforded the ate-complex $[(Me_3Si)_2NC(Ni\text{-}Pr)_2]Y(\mu\text{-}Cl)_2Li(THF)_2$ (**12**) (Scheme 7) [29].

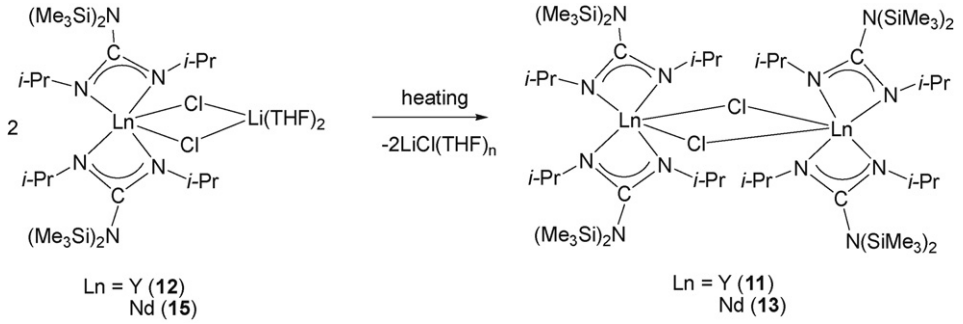
The structures of complexes **11** [29] and **12** [30] were confirmed by X-ray diffraction studies. The observed nonequivalence of the two *i*Pr groups in the ^1H NMR spectrum for complex **11** was explained by retention of the dinuclear structure in solution.



Scheme 7.



Scheme 8.



Scheme 9.

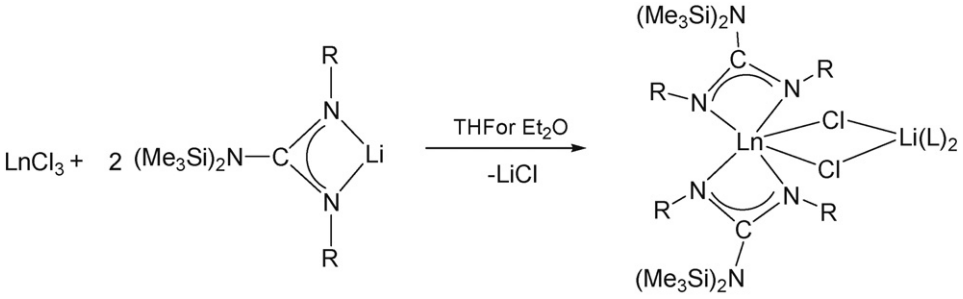
The synthesis and structures of dimeric bis(guanidinate) chloro complexes $\{[(Me_3Si)_2NC(Ni\text{-}Pr)_2]Ln(\mu\text{-}Cl)_2\}_2$ (Ln = Nd (**13**), Sm (**14**)) were described in articles [31,30] respectively. The samarium complex **14** was synthesized by reacting $SmCl_3$ with two equivalents of $Li[(Me_3Si)_2NC(Ni\text{-}Pr)_2]$ in THF at 40 °C. Subsequent recrystallization of the reaction product from hexane allowed isolation of yellow crystals of **14** in 82% yield (Scheme 8).

The synthetic approach to the neodymium containing analogue **13** was less straightforward. Complex **13** [31] was obtained as a result of prolonged refluxing of a toluene solution of $[(Me_3Si)_2NC(Ni\text{-}Pr)_2]Nd(\mu\text{-}Cl)_2Li(THF)_2$ (**15**) [31] which lead to remove the coordinated LiCl. It was also reported that prolong heating of complex **12** in hexane (60 °C) resulted in elimination of $LiCl(THF)_n$ and formation of dimeric **11** (Scheme 9) [30].

X-ray crystal structure investigations revealed that dimeric complexes **11** [29], **13** [31], **14** [30] have similar structures and consist of two edge-shared distorted octahedral moieties. Each of the metal atoms is coordinated by two μ-bridging chloride ligands and two chelating guanidinate ligands. The Ln–Cl bonds in the planar four-membered Ln_2Cl_2 fragments have similar lengths. Coordination of each guanidinate ligand to the metal center is slightly asymmetric: one Ln–N bond is somewhat longer than the second one. The orientation of the $N(SiMe_3)_2$ groups relative to the NCNLn plane is approximately perpendicular thus obviously reflecting steric repulsion between the *i*Pr- and trimethylsilyl groups.

Heterobimetallic bis(guanidinate) chloro lanthanide complexes $[(Me_3Si)_2NC(Ni\text{-}Pr)_2]Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Nd (**15**) [31], Gd (**16**) [30], Yb (**17**) [32], Lu (**18**) [33]) containing di(isopropyl) substituted guanidinate ligands were also prepared by the salt metathesis reactions of $LnCl_3$ with two equivalents of lithium N,N′-diisopropyl-N″-bis(trimethylsilyl)guanidinate in THF. Extraction of the reaction crude product with toluene (**16**, **18**) or ether (**15**, **17**) and subsequent recrystallization from hexane (**16**, **18**) or ether (**15**, **17**) allowed isolation of these complexes in 76–83% yields (Scheme 10).

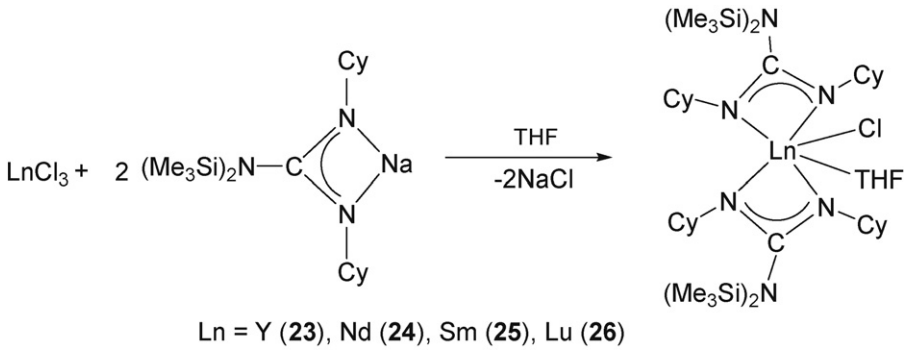
For the bulkier guanidinate ligand bearing cyclohexyl substituents on the nitrogen atoms of the NCN fragment $[(Me_3Si)_2NC(NCy)_2]^-$ no dimeric bis(guanidinate) chloro deriva-



Ln	L	R = *i*Pr
Nd	THF	(**15**)
Gd	THF	(**16**)
Yb	THF	(**17**)
Lu	THF	(**18**)

Ln	L	R = Cy
Y	THF	(**19**)
Sm	Et_2O	(**20**)
Yb	Et_2O	(**21**)
Lu	THF	(**22**)

Scheme 10.



Scheme 11.

tives were described. The reactions of $LnCl_3$ (Ln = Y, Sm, Yb, Lu) with a two-fold molar excess $Li[(Me_3Si)_2NC(NCy)_2]$ in THF or ether afforded heterobimetallic complexes $[(Me_3Si)_2NC(NCy)_2]Ln(\mu\text{-}Cl)_2Li(L)_2$ (Ln = Y (**19**) [34], Sm (**20**) [35], Yb (**21**) [35], Lu (**22**) [34], L = THF, Et_2O) (Scheme 10).

Though $LaCl_3$ clearly reacts with sodium or lithium N,N′-dicyclohexyl-N″-bis(trimethylsilyl)guanidinate under similar conditions no THF-soluble lanthanum complexes could be isolated [32]. Treatment of complex **16** with DME or **20** and **21** with TMEDA resulted in the substitution of coordinated donor ligands and formation of corresponding adducts $[(Me_3Si)_2NC(NCy)_2]Y(\mu\text{-}Cl)_2Li(DME)$ (**23**) [34] and $[(Me_3Si)_2NC(NCy)_2]Ln(\mu\text{-}Cl)_2Li(TMEDA)$ (Ln = Sm (**24**), Yb (**25**)) [35].

Ate-complexes containing di(isopropyl) substituted guanidinate ligands **12**, **17**, **18** and their cyclohexyl containing analogues **22** and **23** were characterized by X-ray crystallography which revealed that these compounds have similar structures. The coordination environment of the lanthanide atom in these compounds is defined by four nitrogen atoms of the bidentate guanidinate ligands, and two chlorine ligands which form μ^2-bridges to the lithium atom. The lithium atom is also bonded to two oxygen atoms of two THF or one DME molecules.

Application of the sodium derivative of bulky guanidinate $Na[(Me_3Si)_2NC(NCy)_2]$ in the reactions with anhydrous $LnCl_3$ in 2:1 molar ratio allowed synthesis of monomeric and salt-free bis(guanidinate) chloro lanthanide complexes $[(Me_3Si)_2NC(NCy)_2]LnCl(THF)$ (Ln = Y (**23**), Nd (**24**), Sm (**25**), Lu (**26**)) [34] (Scheme 11).

The solid state structure of complex **23** was proved by X-ray crystallography, which revealed that the complex adopts monomeric structure with the formal coordination number of 6 of the metal atom.

Tris(guanidinate) lanthanide complexes $[R_2NC(NR')_2]_3Ln$ (R = *i*Pr, R′ = Cy, Ln = Yb (**27**), Nd (**28**); R = *i*Pr, R′ = *i*Pr, Ln = Nd (**29**); R = 0.5 $(CH_2)_5$, R′ = *i*Pr, Ln = Nd (**30**) [36]. R = Ph, R′ = Cy, Ln = Nd (**31**), Sm (**32**), Yb (**33**) [37]. R = *i*Pr, R′ = *i*Pr, Ln = Tb (**34**) [38]. R = Me_3Si, R′ = *i*Pr, Ln = Nd (**35**); R = Me_3Si, R′ = Cy, Ln = Lu (**36**) [39]) were also synthesized by employing salt metathesis reactions.

2.2. Formation of guanidinate fragment by means of carbodiimide insertion into Ln–N bonds

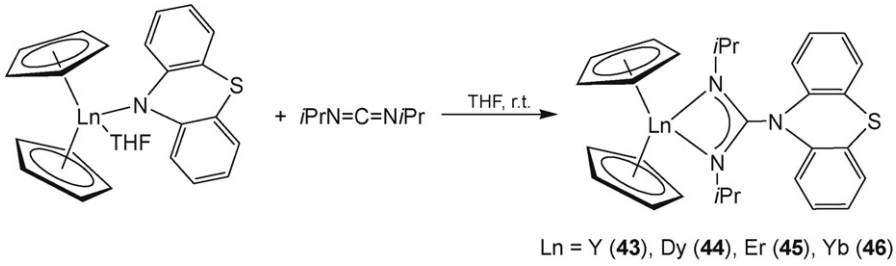
An introduction of a guanidinate fragment into rare earth complex may be also achieved by insertion of disubstituted carbodiimide into Ln–N bonds.

Arnold and co-workers have shown that the reaction of $La[N(SiMe_3)_2]_3$ with 1 equivalent of CyN=C=NCy in refluxing toluene yields a mixture of mono-$La[(Me_3Si)_2NC(NCy)_2][N(SiMe_3)_2]_2$ (**37**) and bis(guanidinate) amido $La[(Me_3Si)_2NC(NCy)_2]_2[N(SiMe_3)_2]$ (**38**) complexes. The mono(guanidinate) complex **37** predominates (60%) and can be separated from **38** (15%) by crystallization [40]. Metallocene-type amido complexes $Cp_2LnNiPr_2(THF)$ undergo mono-insertion under treatment with N,N′-diisopropylcarbodiimide which affords corresponding mono(guanidinate) derivatives $Cp_2Ln[iPr_2NC(NiPr)_2]$ (Ln = Y (**39**) [41], Yb (**40**), Dy (**41**), Gd (**42**) [42]).

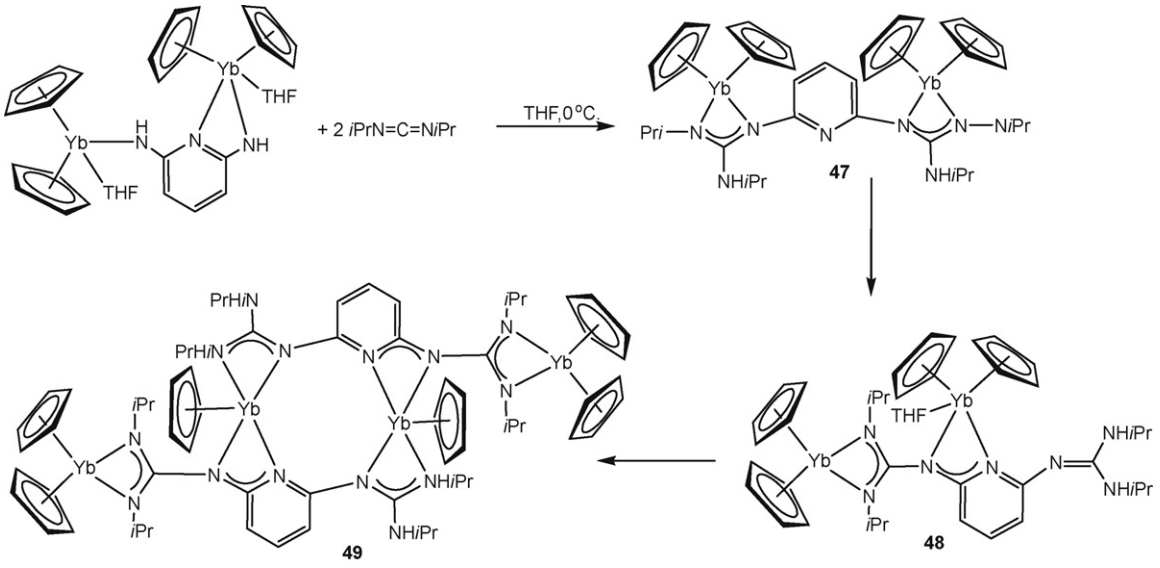
The related phenothiazine (Ptz) complexes $Cp_2Ln(Ptz)(THF)$ react with N,N′-diisopropylcarbodiimide in the similar fashion resulting in formation of bis(cyclopentadienyl) guanidinates $Cp_2Ln[PtzC(NiPr)_2]$ (Ln = Y (**43**), Dy (**44**), Er (**45**), Yb (**46**)) [43] (Scheme 12).

Insertion of two equivalents of N,N′-diisopropylcarbodiimide into covalent Yb-N bonds of dinuclear Yb(III) complex containing μ-bridging doubly deprotonated 2,6-diaminopyridine ligand $[Cp_2Yb(THF)]_2[\mu\text{-}\eta^1\text{:}\eta^2\text{-}(NH)_2(C_5H_3N\text{-}2,6)]$ allows formation of new linked bis(guanidinate) ligand system (Scheme 13) [44]. When a THF solution of **47** was kept during two weeks at room temperature disproportionation of the bis(guanidinate) system occurs: symmetrization of the coordination mode within one of the guanidinate $[Cp_2Yb(NC(NiPr)_2)]$ moieties and migration of the second Cp_2Yb group towards the amidopyridinate fragment resulted in the formation of complex **48** containing unusual dianionic pyridine substituted guainidinate ligand. The second guanidine fragment in **48** remains neutral.

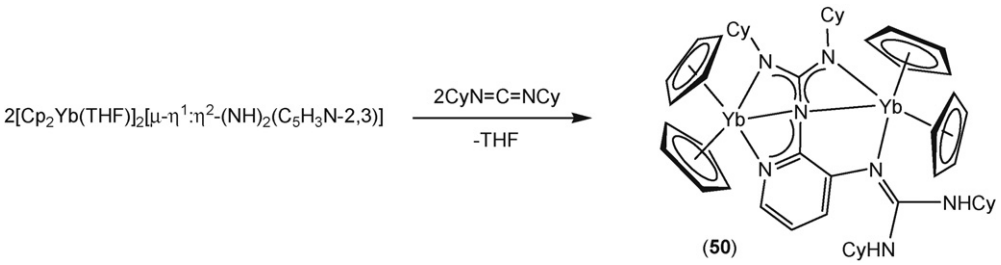
However, heating of **48** at 70 °C allows deprotonation of this neutral guanidine functional group by Cp_2Yb fragment which results in CpH elimination and formation of tetranuclear com-



Scheme 12.



Scheme 13.



Scheme 14.

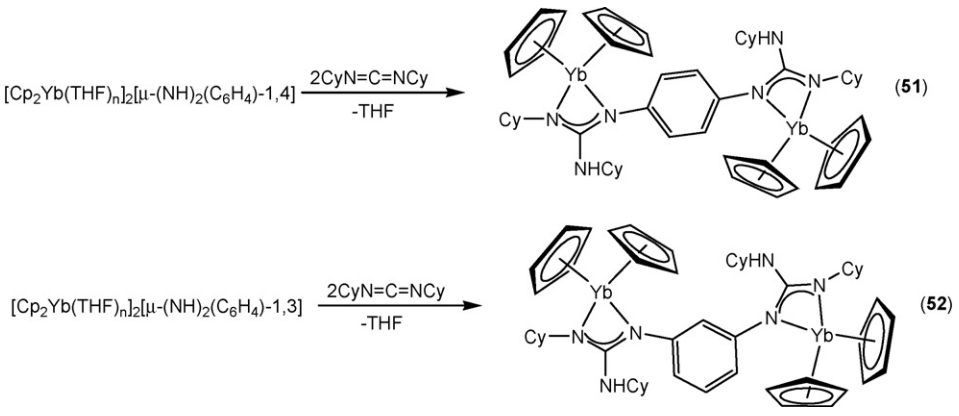
plex **49** with trianionic linked bis(guanidinate) ligands. Reaction of $[Cp_2Yb(THF)]_2[\mu\text{-}\eta^1\text{:}\eta^2\text{-}(NH)_2(C_5H_3N\text{-}2,6)]$ with CyN=C=NCy occurs in the similar way [45].

The dinuclear ytterbium complex $[Cp_2Yb(THF)]_2[\mu\text{-}\eta^1\text{:}\eta^2\text{-}(NH)_2(C_5H_3N\text{-}2,3)]$ containing 2,3-diamido substituted pyridyl ligand reacts with 2 equivalents of CyN=C=NCy giving the addition/isomerization product **50** (Scheme 14) [45].

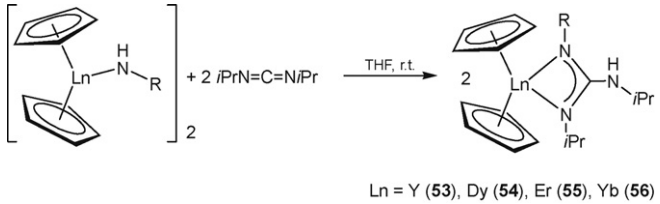
The dinuclear derivatives in which two ytterbium atoms are linked by 1,3- or 1,4-diaminobenzene ligands under treatment with two moles of CyN=C=NCy undergo double insertions which afford dianionic bis(guanidinate) ligands (Scheme 15) [45].

In the case of the derivatives of primary amines $[Cp_2LnNHR]_2$ (R = *t*Bu, Ph; Ln = Y, Dy, Er, Yb) insertion of N,N-diisopropylcarbodiimide afforded guanidinate complexes $Cp_2Ln[(i\text{PrNH})C(NR)(N i\text{Pr})]$ (R = *t*Bu, Ln = Y (**53**), Dy (**54**), Er (**55**), Yb (**56**); R = Ph, Ln = Yb (**54**)) with unsymmetrical coordination of the guanidinate ligand (Scheme 16) [41].

Insertions of carbodimides RN=C=NR (R = *i*Pr, Cy) into Ln–N bonds of functionalized amido complexes of ytterbium $[Cp_2YbNHR]_2$ (R = 8-quinolyl, 2-pyridyl, 2-aminophenyl, 3-amino-2-pyridyl) were described in article (Scheme 17, a) [46]. Reactions of 8-quinolyl derivative with 2 equivalents of carbodimides RN=C=NR (r = *i*Pr, Cy) afford the products of insertion into the N–H bond of the Yb-bonded amido group **57** and **58**. Treatment of 2-pyridyl compound with RN=C=NR yielded dinuclear species **59** and **60** in which two ytterbium centers are bridged by dianionic



Scheme 15.



Scheme 16.

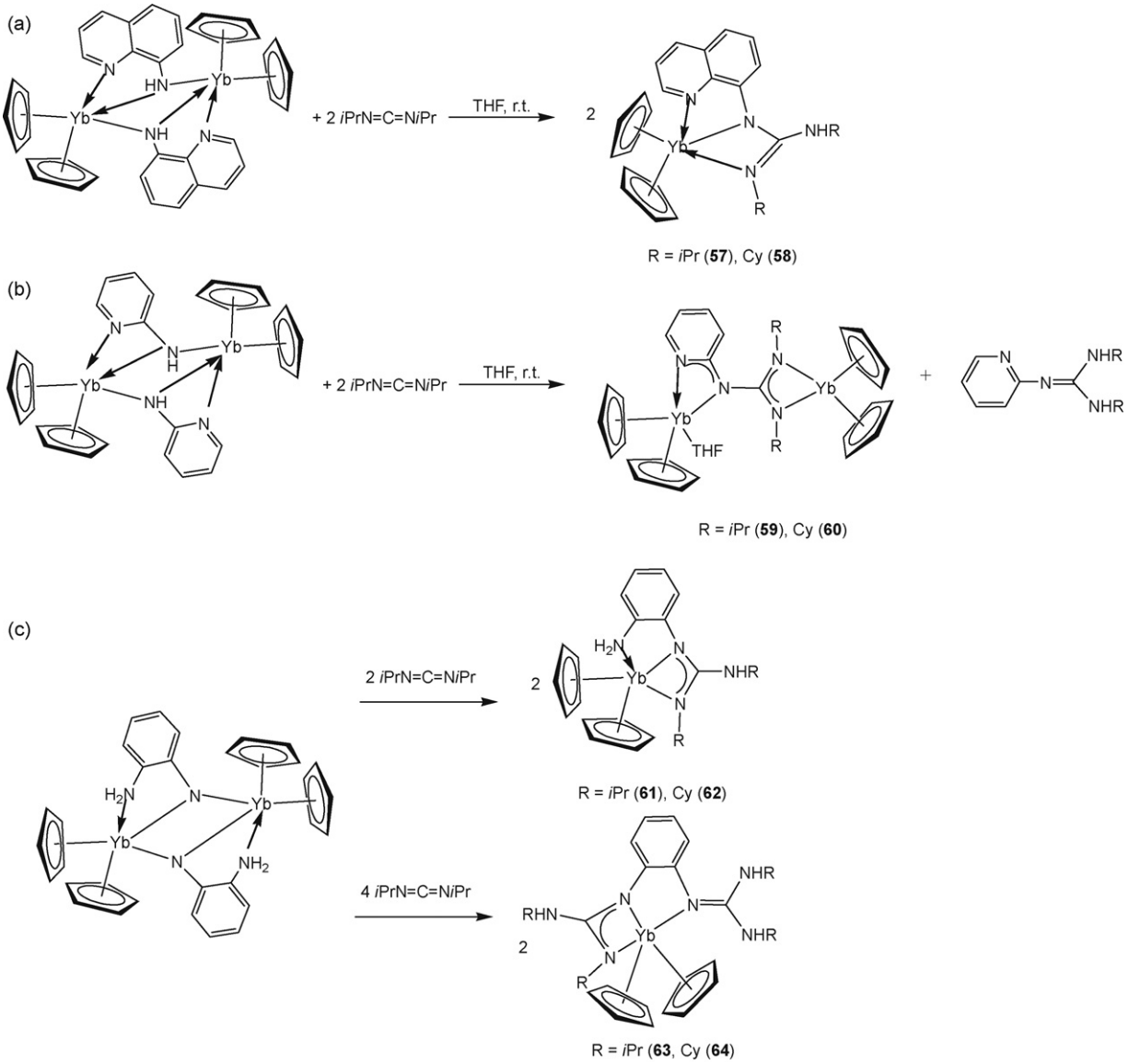
guanidinate ligand resulted from carbodiimide insertion into metal-coordinated N–H bond (Scheme 17, b). One of the ytterbium atoms is coordinated to NCN fragment of guanidinate moiety while the second one to that of amidopyridinate moiety. Reactions of the 2-aminophenyl complex with RN=C=NR depending on the stoichiometry can occur with formation of single and double insertion products (Scheme 17, c). Investigation of multiple N–H bond activation of both metal-bound neutral NH_2 and anionic nitrogen-containing fragments allowed the authors to propose a mechanistic insight for the metal-mediated mono- and diguanilation of primary amines and elucidate factors that affect the chemo- and regioselectivities of the addition and protonation steps.

Carbodiimides insertions into N–H bonds of lantanocene derivatives containing the o-aminothiophenolate ligand were reported in articles [47,48].

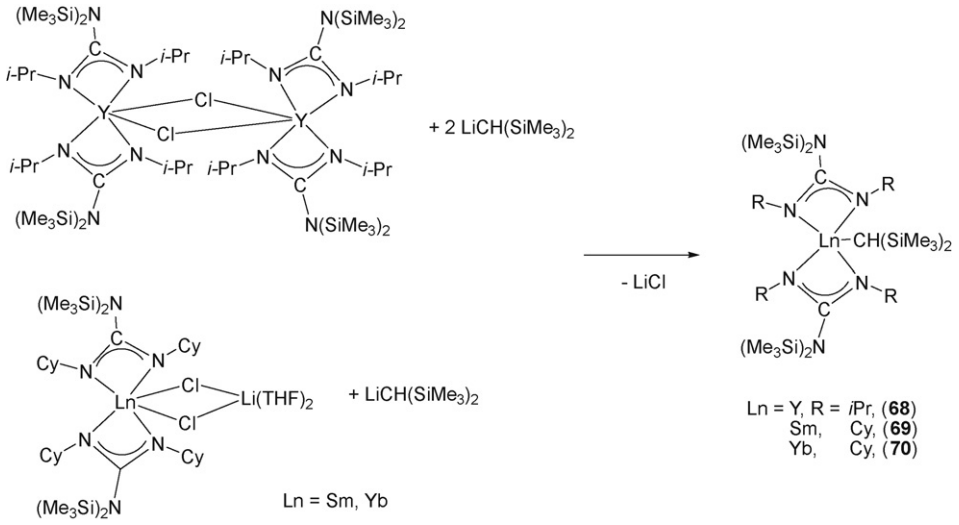
Reaction of tris(amide) lanthanide complexes $[Li(THF)_4][Ln(NPh_2)_4]$ (Ln = Nd, Sm, Yb) with a three-fold molar excess of CyN=C=NCy allowed synthesis of tris(guanidinate) derivatives $[Ph_2NC(NCy)_2]_3Ln$ (Ln = Nd (**65**), Sm (**66**), Yb (**67**)) in 65–78% yield [37].

2.3. Mono(alkyl) bis(guanidinate) rare-earth complexes

To date both neutral and ate-hydrocarbyl bis(guanidinate) rare-earth species have been described. Synthesis of neutral bis(guanidinate) alkyl derivatives $[(Me_3Si)_2NC(NR)_2]_2LnCH(SiMe_3)_2$ (Ln = Y, R = *i*Pr, (**68**) [29]; Ln = Sm, R = Cy, (**69**) [35]; Ln = Yb, R = Cy, (**70**) [35]) was published by Richeson and co-workers. Alkyl species **68**–**70** were obtained in high yields (73–87%) by reacting dimeric $\{[(Me_3Si)_2NC(NiPr)_2]_2Y(\mu\text{-}Cl)\}_2$ or monomeric $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)Li(L)_n$ (Ln = Sm, Yb,



Scheme 17.



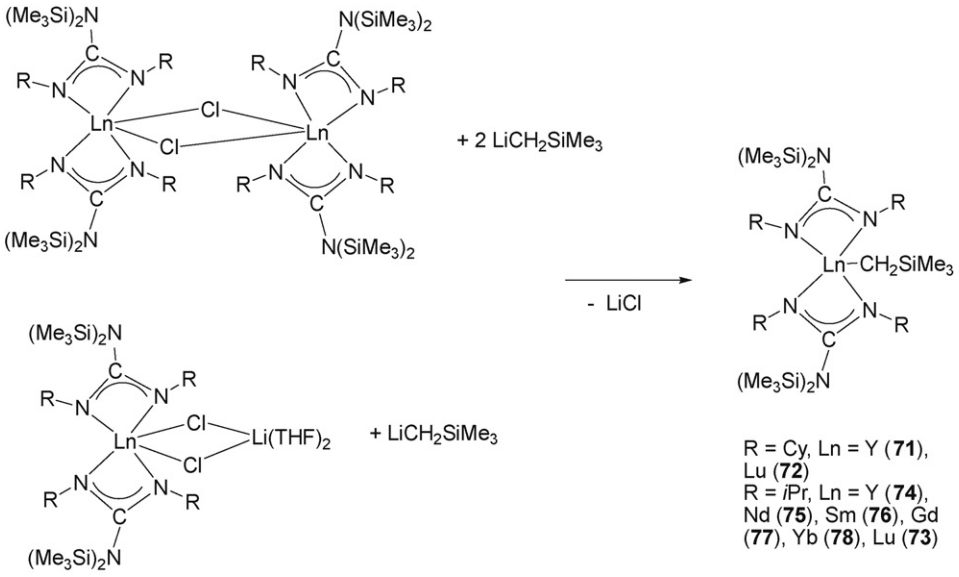
Scheme 18.

L = Et_2O, $n = 2$, L = TMEDA, $n = 1$) bis(guanidinate) chloro complexes with one or two equivalents of $LiCH(SiMe_3)_2$ respectively (Scheme 18). Unfortunately stabilities of complexes **68**–**70** were not described.

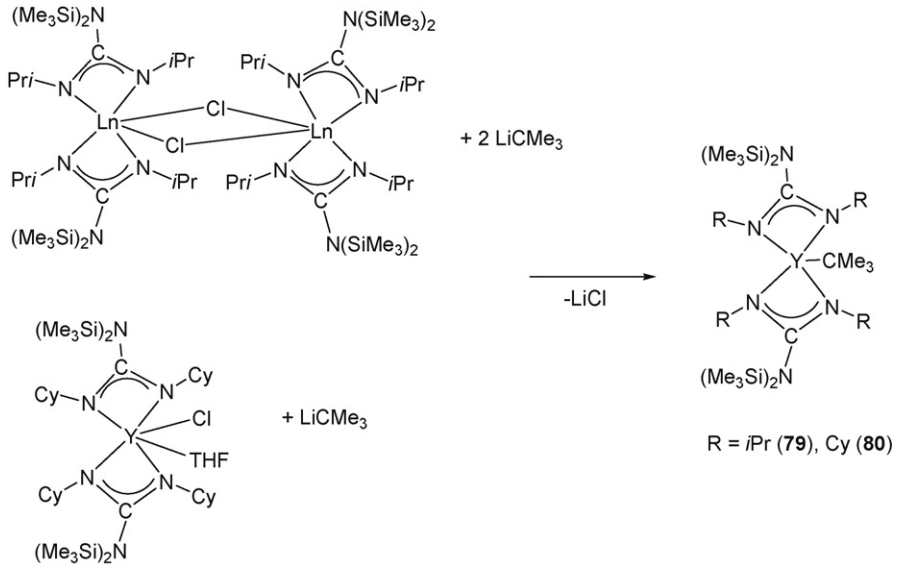
The ^1H and ^{13}C spectra of complex **68** display a single set of resonances corresponding to guanidinate ligands and are consistent with a non-rigid monomeric structure and high rate of fluxionality. Complexes **68** and **69** as provided by the X-ray diffraction analysis are monomeric, salt and Lewis base free with the coordination spheres of metal centers composed of the four nitrogen atoms of two guanidinate anions and the one carbon of alkyl group. Both complexes have approximately C_2 symmetric molecular geometry in which the pseudo-2-fold axis lies along the Ln–C(alkyl) bond. The metal atoms in complexes **68** and **69** adopt the low formal coordination number 5. The geometry distortion of alkyl group was described for **68** and was attributed to an agostic interaction between the metal center and β-SiC and γ-CH σ bonds. No such an interaction was observed for **69**.

The attempts of synthesis of bis(guanidinate) lanthanide complexes containing less bulky alkyl CH_2SiMe_3 group were described in papers [33,34,49,50] (Scheme 19). The alkylation of bis(guanidinate) chloro yttrium complex $[(Me_3Si)_2NC(NCy)_2]_2Y(\mu\text{-}Cl)Li(THF)_2$ with one equivalent of $LiCH_2SiMe_3$ in hexane at 0 °C afforded the alkyl derivative $[(Me_3Si)_2NC(NCy)_2]_2YCH_2SiMe_3$ (**71**) which was isolated as a microcrystalline solid in 64% yield [50]. Formation of **71** was also observed in the NMR tube reaction of $[(Me_3Si)_2NC(NCy)_2]_2YCl(THF)$ with $LiCH_2SiMe_3$ (toluene, 0 °C), however the reaction carried out on a preparative scale (hexane, 0 °C) yielded an inseparable mixture of **71** and compounds which were supposed to be thermal decomposition products [33]. The lutetium analogue $[(Me_3Si)_2NC(NCy)_2]_2LuCH_2SiMe_3$ (**72**) was isolated from the reaction of $[(Me_3Si)_2NC(NCy)_2]_2Lu(\mu\text{-}Cl)Li(THF)_2$ with $LiCH_2SiMe_3$ under the similar conditions in 90% yield and was characterized by ^1H, ^{13}C NMR and IR spectroscopy [50]. In an inert atmosphere complexes **71** and **72** can be stored in the crystalline state at −20 °C without decomposition, while in C_6D_6 solution at 20 °C they completely decompose in three days.

Alkyl lutetium complex $[(Me_3Si)_2NC(NiPr)_2]_2LuCH_2SiMe_3$ (**73**) containing isopropyl substituted guanidinate ligands was obtained by alkylation of $[(Me_3Si)_2NC(NiPr)_2]_2Lu(\mu\text{-}Cl)Li(THF)_2$



Scheme 19.

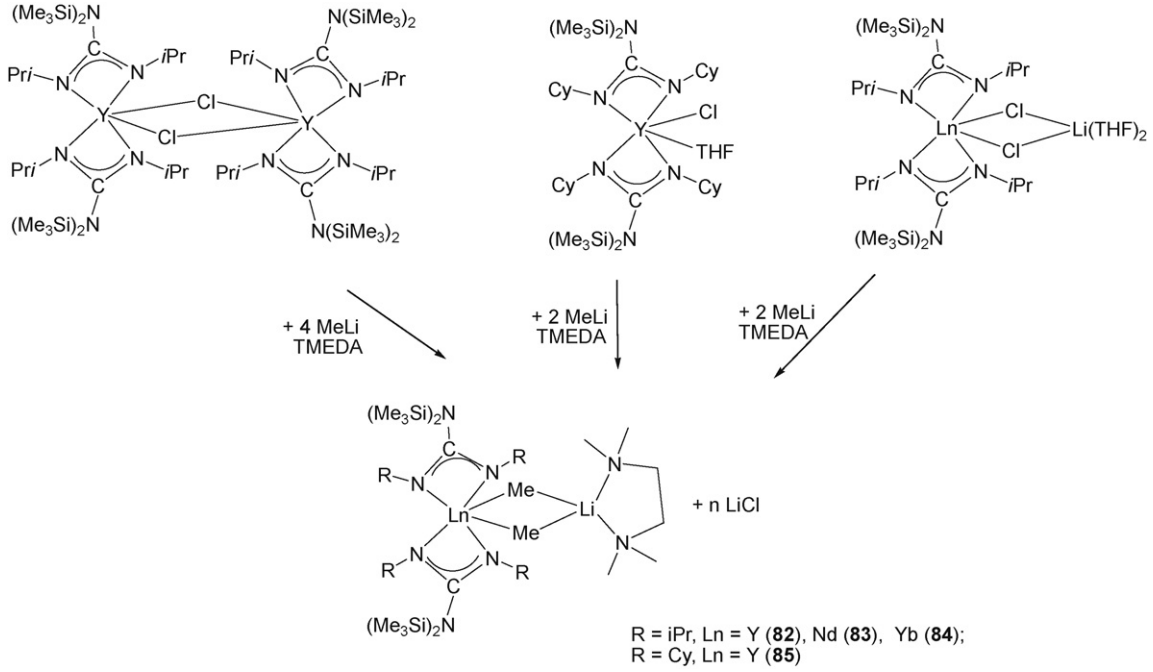


Scheme 20.

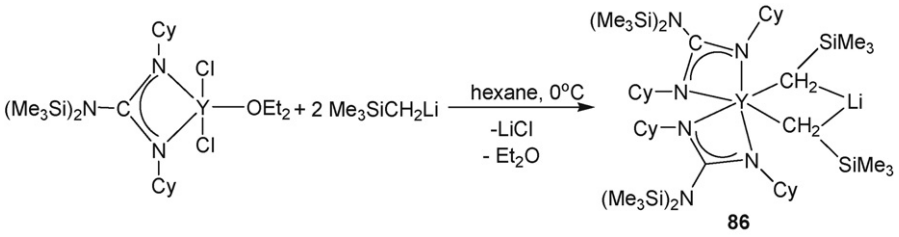
with $LiCH_2SiMe_3$ in toluene at 0 °C and isolated in 71% yield [33]. Formation of analogous complexes of the larger lanthanide metals $[(Me_3Si)_2NC(NiPr)_2]_2LnCH_2SiMe_3$ (Ln = Y (**74**), Nd (**75**), Sm (**76**), Gd (**77**), Yb (**78**)) was suggested in article [49]. These complexes were prepared by reactions of dimeric $\{[(Me_3Si)_2NC(NiPr)_2]_2Ln(\mu\text{-}Cl)\}_2$ (Ln = Nd, Sm) or monomeric $[(Me_3Si)_2NC(NCy)_2]_2Ln(\mu\text{-}Cl)Li(THF)_2$ (Ln = Y, Gd, Yb) chloro complexes with two or one equivalents of $LiCH_2SiMe_3$ respectively and were used "in situ" for preparation of related hydrido species.

Tert-butyl complexes of lanthanides still remain a rather rare class of compounds [51] due to their instability and pronounced tendency to decomposition via β-hydride mechanism. Guanidinate ligands turned out a suitable coordination environment which allows synthesis and isolation of monomeric salt and Lewis base free tert-butyl yttrium species. Alkylation of bis(guanidinate) chloro complexes $\{[(Me_3Si)_2NC(NiPr)_2]_2Y(\mu\text{-}Cl)\}_2$ and $[(Me_3Si)_2NC(NCy)_2]_2YCl(THF)$ with *t*BuLi in 1:2 (in diethyl ether) or 1:1 molar ratio (in hexane) resulted in the formation of tert-butyl derivatives $[(Me_3Si)_2NC(NR)_2]_2YCMe_3$ (R = *i*Pr (**79**) [29] Cy (**80**) [34]) which were isolated in 70 and 52% yields respectively (Scheme 20). Complex **80** proved to be rather robust: no decomposition was observed during three days in C_6D_6 solution at ambient temperature.

Complexes **79** and **80** appear to be sterically rigid at room temperature as indicated in their ^1H and ^{13}C NMR spectra. For complex **79** the *t*Bu methyl groups give rise to a singlet at 1.36 ppm, and a signal at 39.9 ppm in the ^{13}C NMR spectra coupled to yttrium ($^1J_{Y-C}$ = 46 Hz) was assigned to the tertiary carbon of the tert-butyl fragment. Surprisingly in complex **80** the methyl protons appear as a singlet at 1.48 ppm and the corresponding carbon atoms cause



Scheme 21.



Scheme 22.

the appearance of two ^{13}C NMR signals. The tertiary carbon atom bonded to the yttrium atom gives rise to a doublet at 37.5 ppm ($^1J_{Y-C}$ = 56 Hz). The single crystal X-ray diffraction analysis of **79** revealed different coordination modes for guanidinate ligands: in one of the guanidinate anions the negative charge is delocalized within the NCN fragment, while the second one can be considered rather as imino amido –N–C(NR_2) = NR′ ligand. For complex **80** agostic interactions between the yttrium atom and the the tert-butyl group in the solid state as well as in solution have been substantiated.

The guanidinate supported phenyl yttrium complex [$(Me_3Si)_2$NC$(NCy)_2$]$_2$YPh(THF) (**81**) was synthesized by treatment of [$(Me_3Si)_2$NC$(NCy)_2$]$_2$YCl(THF) with equimolar amount of PhLi in THF and was isolated in 61% yield [34].

Alkyl bis(guanidinate) ate-complexes [$(Me_3Si)_2$NC$(NR)_2$]$_2$Ln(μ-Me)$_2$Li(TMEDA) (R = *i*Pr, Ln = Y (**82**) [29], Nd (**83**) [52,32] Yb (**84**) [32]; R = Cy, Ln = Y (**85**) [34]) containing cyclohexyl and isopropyl substituted guanidinate ligands can be easily obtained by the reactions of appropriate bis(guanidinate) chloro derivatives with MeLi in hexane in the presence of TMEDA (Scheme 21). Complexes **82**–**85** were isolated in 61–79% yields. This class of compounds is of special interest due to combination of several advantages: easy availability, rather high thermal stability and high reactivity.

Definitive formulations of the structural features of complexes **82**–**84** were provided by single-crystal X-ray studies which revealed that they are monomeric heterobimetallic compounds with two μ-bridging methyl ligands bonding lanthanide and lithium atoms. The methyl ligands appear in the ^1H NMR spectra of diamagnetic yttrium derivatives (**82**, $\delta = -0.65$ ppm; **85**, $\delta = -0.51$ ppm) as broad singlets and give rise to broad resonances with no resolvable yttrium coupling in the ^{13}C NMR spectra (**82**, δ = 11.8 ppm; **85**, δ = 11.6 ppm).

Unusual bimetallic alkyl ate-complex {$(Me_3Si)_2$NC$(NCy)_2$}$_2$Y(μ-CH_2SiMe_3)$_2$Li (**86**) was unexpectedly obtained in the reaction of {$(Me_3Si)_2$NC$(NCy)_2$}$YCl_2(Et_2O)$ with two molar equivalents of $LiCH_2SiMe_3$ (hexane, 0 °C) instead of expected neutral dialkyl derivative (34% yield) (Scheme 22) [24].

As it was demonstrated by the X-ray diffraction study compound **86** is a monomeric *ate*-complex, where the yttrium atom is coordinated by two nitrogen atoms of two bidentate guanidinate ligands and two carbon atoms of alkyl groups bridging the yttrium and lithium atoms. The most interesting feature of this compound is an extremely low formal coordination number of the lithium atom which is coordinated just by two methylene carbon atoms. Obviously coordination sphere of the lithium atom is saturated due to agostic interaction with two methyl groups of the trimethylsilyl substituents.

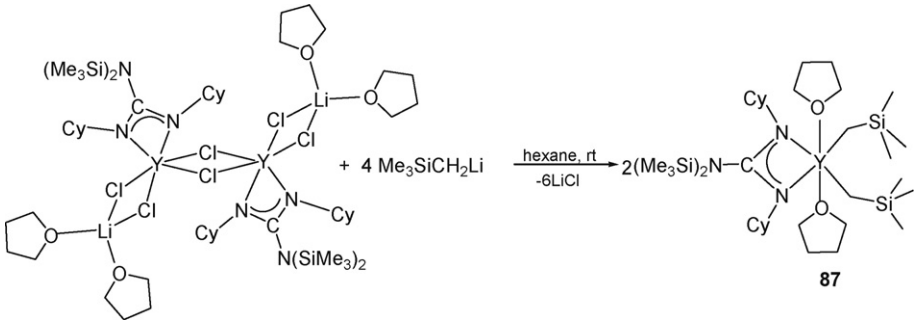
2.4. Bis(alkyl) mono(guanidinate) rare-earth complexes

Bis(alkyl) rare-earth complexes have recently attracted significant attention as potential precursors to cationic mono(alkyl) species [53] that were found to be efficient catalysts of homo- and copolymerization of olefins [54]. The first example of bis(alkyl) rare-earth complex supported by guanidinate ligand {$(Me_3Si)_2$NC$(NCy)_2$}$Y(CH_2SiMe_3)_2(THF)_2$ (**87**) was published in 2006 [24]. Treatment of complex [{$(Me_3Si)_2$NC$(NCy)_2$}Y{(μ-Cl)$_2$Li$(THF)_2$}(μ-Cl)]$_2$ with four molar equivalents of $LiCH_2SiMe_3$ in hexane at 0 °C yielded the monomeric salt-free dialkyl complex **87** in 96% yield (Scheme 23).

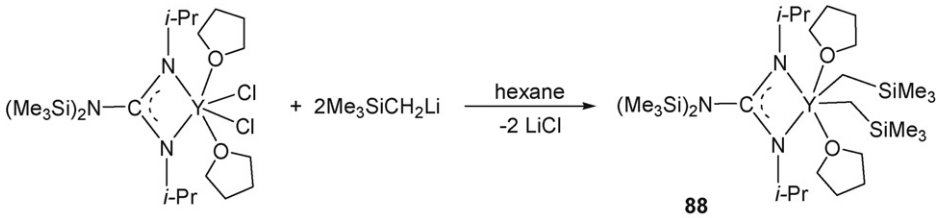
In an inert atmosphere, **87** can be stored in crystalline state at 0 °C without decomposition while in the C_6D_6 solution at 20 °C it slowly decomposes with elimination of Me_4Si.

The analogue containing isopropyl substituted guanidinate ligand {$(Me_3Si)_2$NC(N*i*-Pr)$_2$}$Y(CH_2SiMe_3)_2(THF)_2$ (**88**) was obtained by using the same synthetic approach (84% yield) (Scheme 24).

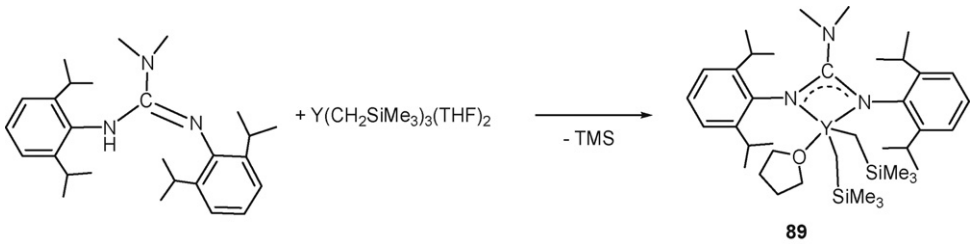
Complex **88** is rather stable. In an inert atmosphere, at −18 °C it can be kept without decomposition during three months. Complete decomposition of **88** in solution (C_6D_6 solution, 20 °C) took ~20 days [23]. Complexes **87** and **88** are monomeric, the coordination spheres of the yttrium atoms consist of two nitrogen atoms of the bidentate guanidinate ligand, two carbon atoms of the alkyl groups and two oxygen atoms of two THF molecules resulting in the formal coordination number of 6. The coordination geometries of the yttrium atoms can be described as distorted octahedrons with two carbon and two nitrogen atoms in equatorial positions and two oxygen atoms in apical positions. The attempts to generate cationic alkyl species by reacting **87** and **88** with $(C_6H_5)_3B$, $(C_6F_5)_3B$ or [$NHMe_2Ph$][$B(C_6F_5)_4$] (THF or toluene, −78 °C, 1:1 molar ratio) afforded intractable mixtures of products. Complex **86** activated



Scheme 23.



Scheme 24.



Scheme 25.

by equimolar amount of $(C_6H_5)_3B$ or $(C_6F_5)_3B$ in toluene sluggishly oligomerizes ethylene (20 °C, 0.5 bar), while the systems **88**-Ph_3B, **88**-Ph_3B-MAO in toluene do not catalyze ethylene polymerization.

Application of more sterically demanding guanidinate ligand $(Me_2N)C[N(2,6\text{-}iPr_2C_6H_3)]_2^-$ allows to decrease the number of THF molecules coordinated to the yttrium atom and to obtain coordinatively more unsaturated species $\{(Me_2N)C[N(2,6\text{-}iPr_2C_6H_3)]_2\}Y(CH_2SiMe_3)_2(THF)$ (**89**) [20]. Complex **89** was obtained by alkane elimination reaction under the treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with equimolar amount of guanidine $(2,6\text{-}iPr_2C_6H_3)NH\text{-}C(Me_2N)=N(2,6\text{-}iPr_2C_6H_3)$ in toluene at room temperature (85% yield) (Scheme 25).

It is noteworthy that the resonance corresponding to the carbon atom of the methylene group attached to yttrium YCH_2 in the ^{13}C NMR of **89** (δ = 37.6 ppm, dt, J_{CH} = 98.5 Hz, J_{YC} = 38.9 Hz) is upfield-shifted relative to the equivalent signal in the related amidinate complex $\{PhC[N(2,6\text{-}iPr_2C_6H_3)]_2\}Y(CH_2SiMe_3)_2(THF)$ (**90**) (δ = 39.5 ppm, dt, J_{CH} = 100.1 Hz, J_{YC} = 40.3 Hz) [17f] reflecting higher electron donating ability of guanidinate ligand. Less electron deficiency of the yttrium center in **89** can be also suggested from the data of the X-ray study which reveal considerable interaction of the lone pair of Me_2N with the conjugated NCN moiety. Unlike in complexes **87** and **88** in **89** the three C–N distances in the CN_3 moiety are very similar and the value of the dihedral angle formed by the planes CNC and NCN is only 27.3(4)°.

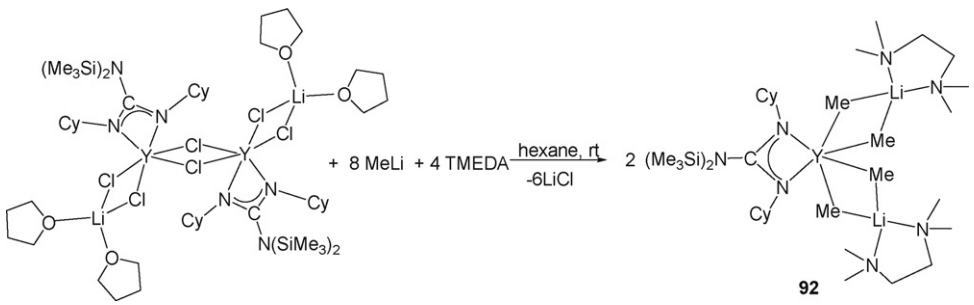
Synthesis and characterization of the first bis(tert-butyl) rare-earth complex $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}Y(t\text{Bu})_2(THF)$ (**91**) was reported in publication [23]. Complex **91** was obtained by the salt metathesis reaction of $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}YCl_2(THF)_2$ with a two-fold molar excess of *t*BuLi in hexane at 0 °C. Complex **91** decomposes completely in one day in C_6D_6 at ambient temperature. The reaction of $\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}YCl_2(THF)_2$ with two equivalents of Ph_2CHK in THF did not afford isolable alkyl yttrium complexes [23].

The monoguanidinate alkyl ate-complexes still remain very rare. Tetramethyl derivative $\{(Me_3Si)_2NC(NCy)_2\}Y[(\mu\text{-}Me)_2Li(TMEDA)]_2$ (**92**) was prepared by the reaction of dimeric complex $[\{(Me_3Si)_2NC(NCy)_2\}Y\{(\mu\text{-}Cl)_2Li(THF)_2\}(\mu\text{-}Cl)]_2$ with eight equivalents of MeLi in the presence of excess of TMEDA in toluene at 20 °C and was isolated in 44% yield (Scheme 26) [24].

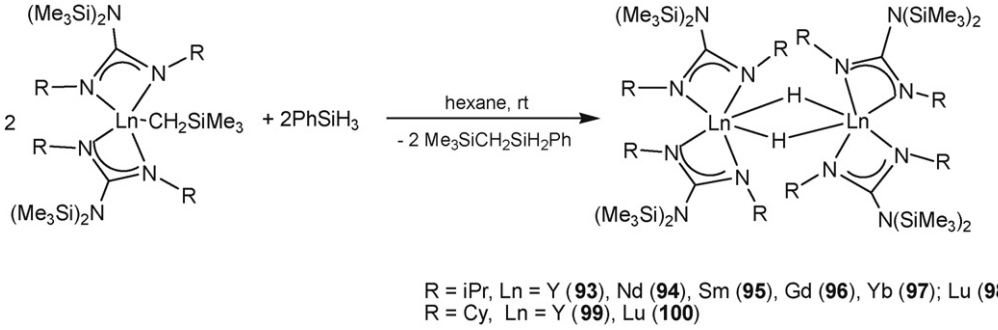
The structure of complex **92** was proved by X-ray single crystal analysis. Complex **92** is a monomeric trinuclear species in which the yttrium atom is coordinated by two nitrogen atoms of the chelating guanidinate ligand, as well as by four methyl ligands which bridge yttrium and two lithium atoms. Complex **92** is inactive in ethylene and styrene polymerizations at ambient temperature.

2.5. Hydrido rare-earth complexes supported by guanidinate ligands

Organolanthanide sandwich and half-sandwich type hydrido complexes possess very rich and unique chemistry [11,55] which have attracted a great deal of attention since the discovery of the first hydride in early 1980s [56]. Extensive research of catalytic activity and stoichiometric reactions of hydrido complexes have played an important role in the development of organolanthanide chemistry. However, despite the high potential of rare-earth hydrido derivatives their analogues in coordination environment alternative to the cyclopentadienyl one are still poorly investigated [15,57] and synthesis of new types of hydrido species remains



Scheme 26.



R = iPr, Ln = Y (**93**), Nd (**94**), Sm (**95**), Gd (**96**), Yb (**97**); Lu (**98**)
R = Cy, Ln = Y (**99**), Lu (**100**)

Scheme 27.

a challenge. Most of the rare earth hydrides known to date are dimeric [2,11,55], synthesis of the only structurally characterized momomeric hydride [1,3,4-*t*Bu$_3$C$_5$H$_2$]$_2$CeH containing the bulky cyclopentadienyl ligands was reported as late as in 2005 [58].

Sandwich and half-sandwich rare-earth hydrido complexes are most often synthesized by the σ-bond metathesis reaction of parent alkyls under treatment with dihydrogen [4b,56,59] or phenylsilane [60]. The same approaches were employed for synthesis of non-cyclopentadienyl hydrido species.

The family of Lewis base free hydrido complexes of rare earth metals supported by isopropyl and cyclohexyl substituted guanidinate ligands [Ln{(Me$_3$Si)$_2$NC(NR)$_2$}$_2$(μ-H)]$_2$ (R = *i*Pr, Ln = Y (**93**) [49], Nd (**94**) [49], Sm (**95**) [49], Gd (**96**) [49], Yb (**97**) [49], Lu (**98**) [33]; R = Cy, Ln = Y (**99**) [50], Lu (**100**) [50]) is the most systematically investigated among post-metallocene derivatives. Complexes **93**–**100** were synthesized by the reactions of alkyl species {(Me$_3$Si)$_2$NC(NR)$_2$}$_2$LnCH$_2$SiMe$_3$ with PhSiH$_3$ in 1:1 molar ratio in hexane at ambient temperature (Scheme 27) and were isolated in high yields.

The single crystal X-ray of complexes **93**–**100** and solution NMR studies of the yttrium derivatives **93** and **99** revealed that these complexes are dimeric in both solid state and [D$_6$]-benzene solution. Employment of the guanidinate ligands containing bulkier cyclohexyl groups at nitrogen atoms did not allow synthesis of monomeric species however in the case of yttrium complexes **93** and **99** in contrast resulted in the shortening of the M-M distance (**93** – 3.682(5) Å [49]; **99** – 3.6522(5) Å [50]). The hydrido complexes **93**–**100** have dimeric structures with similar coordination environment of the metal atom. Nevertheless in this series of dimeric hydrides depending on the metal atom size the reciprocal orientation of the Ln[(Me$_3$Si)$_2$NC(NR)$_2$]$_2$ fragments in dimer can be different and they can adopt eclipsed (Nd, Sm, Gd) or staggered (Y, Yb, Lu) conformation. The value of the dihedral angles between two planes defined by the central carbon atoms of the guanidinate ligand and metal atom C–Ln–C were used for quantitaive estimation of mutual disposition of these moieties. For yttrium, ytterbium and lutetium, which have smaller ion sizes, these planes are nearly orthogonal (point group C_2), while in the complexes of larger lanthanides, these planes are nearly coplanar and the dimers are close to adopt eclipsed conformation (point group D_{2h}).

In the series of hydrides supported by isopropyl-substituted guanidinate ligands **93**–**97** the all four guanidinate ligands are symmetrically coordinated to the metal atoms while the bonding parameters of the lutetium derivative **98** demonstrate non-equivalence of the Lu[(Me$_3$Si)$_2$NC(N*i*Pr)$_2$]$_2$ moieties [33]. Such a structural particularity was explained by a greater steric encumbrance of the metal coordination sphere in the lutetium compound, resulting from the smaller ion sizes of Lu. Despite of the fact that steric bulk of substituents by nitrogen atoms (*i*Pr or Cy) of the NCN fragments does not influence the reciprocal disposition of the Ln{(Me$_3$Si)$_2$NC(NR)$_2$}$_2$ fragments of the dimeric core it effects dramatically the coordination fashion of guanidinate ligands to the metal atoms and results in lengthening of the Ln–N bonds. Unlike complexes **93**–**97** the difference of the Ln–N bond distances in **99** and **100** and the bonding situation within the NCN fragments of the guanidinate ligands show evidence of a localized π-system and are consistent with a resonance structure depicted in Fig. 1.

Scrambling of the hydrido complexes **99** and **100** in C$_6$D$_6$ resulted in an equilibrium mixture containing the heterobimetallic species [{(Me$_3$Si)$_2$NC(NCy)$_2$}$_2$Y(μ-H)$_2$Lu{(Me$_3$Si)$_2$NC(NCy)$_2$}$_2$] indicating the dissociation of dimers and the presence of monomeric species in solution.

The attempts of generation and isolation of monomeric hydrido species were described in publication [50]. The treatment of complex **93** with [D$_8$]-THF in deuterobenzene and registration of its ^{1}H NMR spectrum in [D$_8$]-THF gave evidence of the formation of monomeric THF-adduct [Y{(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$}$_2$(H)(THF)$_n$] containing terminal hydrido ligand. All the efforts to isolate the THF-adduct failed because of its low stability in solution. The treatment of **93** with a twenty-fold molar excess of PMe$_3$ did not result in coordination of a Lewis base to the metal atom [49]. Complex **93** turned out to be rather inert *vs* addition to multiple carbon–carbon bonds of substituted olefins, it does not react with styrene, stilbene, tolane and bis(trimethylsilyl)acetylene ([D$_6$]-benzene, 20 °C, 96 h). Obviously the bis(guanidinate) ligand system creates steric saturation of the coordination sphere of the metal atom providing its kinetic stability but also dampening reactivity [48].

The attempt of the synthesis of dihydride species coordinated by diisopropylguanidinate ligands using the reaction of complex [(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (**88**) with two molar equivalents of PhSiH$_3$ or with H$_2$ (1 bar) in hexane was described in article [23]. The reactions afford crystalline precipitate insoluble in common organic solvents which was supposed to be a polyhidrido cluster [{(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$}YH$_2$]$_n$.

2.6. Borohydride rare-earth complexes supported by guanidinate ligands

Rare-earth borohydride complexes are of great interest because of their structural diversity and high catalytic activity [55]. The

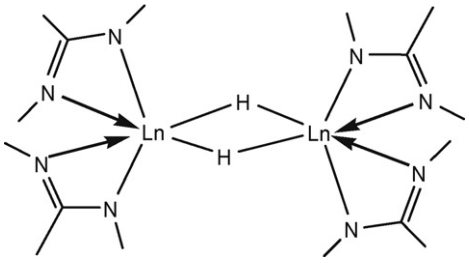
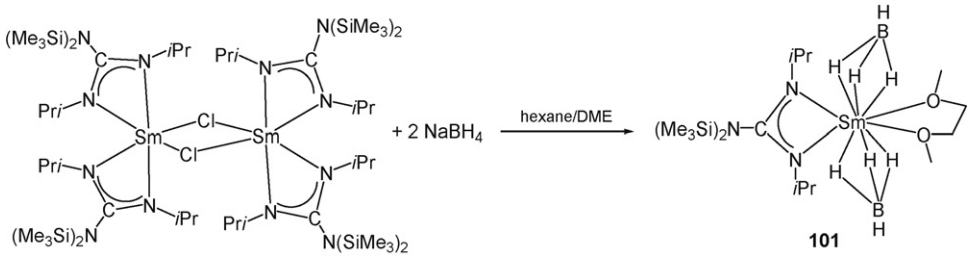


Fig. 1. Coordination mode of guanidinate ligands to Lu atom in complex 98.



Scheme 28.

borohydride groups can serve as bridging and terminal ligands having different dentation. Depending on the ionic radius of the central atom and its coordination environment, borohydride groups can serve as bidentate [61], tridentate [61a, 62] or tetradentate [61b, 61c] ligands. A high level of interest in rare earth borohydride complexes was stimulated by their high catalytic activity in polymerization of lactones [63], methylmetcrylate [64] and isoprene [65]. Borohydride complexes of d-transition metals, with the exception of those of group IV, are generally unstable and readily decompose into the corresponding hydrides with elimination of diborane [66]. In contras, f-elements borohydrides can be easily isolated [55]. Metallocene-type borohydride complexes are generally synthesized by the reactions of the corresponding chloride derivatives with $NaBH_4$ or $LiBH_4$ in THF or diethyl ether [55]. A convenient procedure for the synthesis of both bis(borohydride) and monoborohydride complexes is based on the reactions of lanthanide tris(borohydrides) $Ln(BH_4)_3(THF)_n$ (n = 2,3) [67] with alkali metal salts LM (M = Li, Na or K) of the corresponding ligand [63b,17a,68]. The yttrium bis(amidinate) complex $[PhC(NSiMe_3)_2]_2YBH_4(THF)$ [17a] and lanthanide derivatives containing polydentate diphenoxide O,O,N,N-ligands [63b,64] until recently were the rare examples of cyclopentadienyl-free lanthanide borohydride complexes.

It was reported that the reactions of bis(guanidinate) chloride derivatives $[\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}_2LnCl]_2$ (Ln = Nd, Sm) with $NaBH_4$ are more complex than those of cyclopentadienyl derivatives and they were found to be inefficient as a synthetic pathway to bis(guanidinate) borohydrides. Thus in the reaction of $[\{(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2\}_2SmCl]_2$ with $NaBH_4$ (1:2 molar ratio) the redistribution of the ligands was observed, producing monoguanidinate bis(borohydride) derivative $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]Sm(BH_4)_2(DME)$ (**101**) instead of the expected bis(guanidinate) borohydride complex regardless of the molar ratio of starting reagents (Scheme 28) [30].

The reactions of $Ln(BH_4)_3(THF)_2$ (Ln = Nd, Sm, Yb) with a twofold molar excess of the lithium guanidinate $Li[(Me_3Si)_2NC(NR)_2]$ (R = Cy, *i*Pr) in toluene at 65 °C (Scheme 29) proved to be a good method which allows synthesis of bis(guanidinate) borohydride complexes of the metals both from the beginning and the end the rare earth series $[(Me_3Si)_2NC(N\text{-}R)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (R = Cy, Ln = Nd (**102**) [69], Sm (**103**) [69], Yb (**104**) [69]; R = *i*Pr, Ln = Nd (**105**) [70], Sm (**106**) [70]) in reasonable yields (Scheme 29).

The X-ray crystal structure investigations have revealed that compounds **102**–**106** are heterobimetallic complexes in which the lanthanide and the lithium atoms are connected by two μ-bridging BH_4-groups. In complexes **102**–**104** coordination modes of borohydride groups are different: one group is tridentate with respect to the lanthanide atom and bidentate with respect to the lithium, while the second one is $\mu\text{-}\eta^2\text{:}\eta^2$-bridging in complexes **102** and **103**, but $\mu\text{-}\eta^2\text{:}\eta^1$-bridging in complex **104** [69]. In complexes containing isopropyl substituted guanidinate ligands **105** and **106** the both borohydride groups are $\mu\text{-}\eta^2\text{:}\eta^2$-coordinated to the lanthanide and lithium atoms [70].

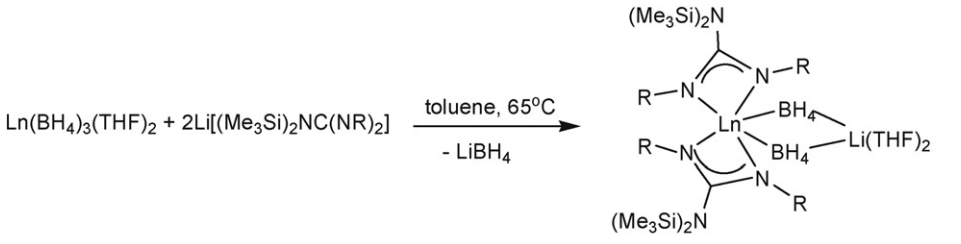
Obviously, the direction of salt metathesis reaction is sensitive to the nature of the alkaline metal in the starting guanidinate. When sodium guanidinate $Na[(Me_3Si)_2NC(NCy)_2]$ was used in the reaction with $Gd(BH_4)_3(THF)_2$ in 2:1 molar ratio (THF, 65 °C) monoguanidinate bis(borohydride) derivative $[(Me_3Si)_2NC(NCy)_2]Gd(BH_4)_2(DME)$ (**107**) was obtained [71] regardless the reaction stoichiometry, while the analogous reaction with $Nd(BH_4)_3(THF)_2$ (THF, 20 °C) occurs with guanidinate ligand fragmentation and resulted in the formation of mixed-ligand bis(guanidinate) formamidinate complex $[(Me_3Si)_2NC(NCy)_2]_2Nd[HC(NCy)_2]$ (**108**) (Scheme 30) [39].

Synthesis of monoguanidinate bis(borohydride) complexes $[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(THF)_2$ (Ln = Yb (**109**), Er (**110**)) by the reaction of equimolar amounts of $Ln(BH_4)_3(THF)_3$ and sodium guanidinate $Na[(Me_3Si)_2NC(NCy)_2]$ was reported in publication [72].

The treatment of the heterobimetallic complex of samarium **103** with an excess of DME affords the ionic complex $[\{(Me_3Si)_2NC(N\text{-}\textit{i}Pr)_2\}_2Sm(BH_4)_2]^-[Li(DME)_3]^+$ (**111**) (Scheme 31) [71].

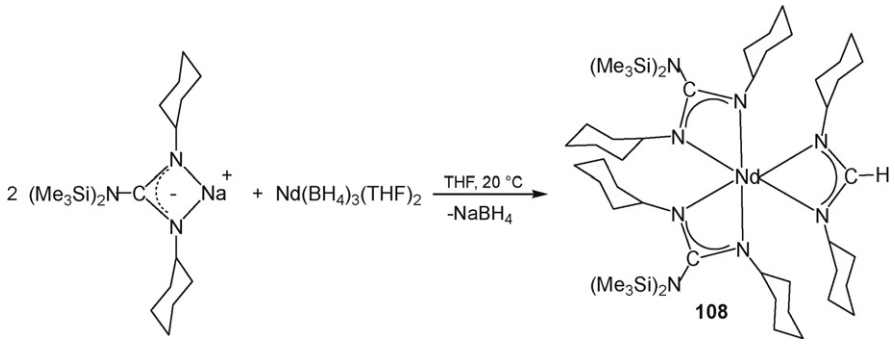
Compound **111** contains the complex anion $[\{(Me_3Si)_2NC(N\text{-}\textit{i}Pr)_2\}_2Sm(BH_4)_2]^-$ resulted from the coordination of two guanidinate and two terminal η^3-borohydride groups to the trivalent samarium cation.

The monoguanidinate bis(triethylborohydride) complex $[(Me_3Si)_2NC(N\textit{i}\text{-}Pr)_2]Y[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]_2(THF)$ (**112**) was pre-

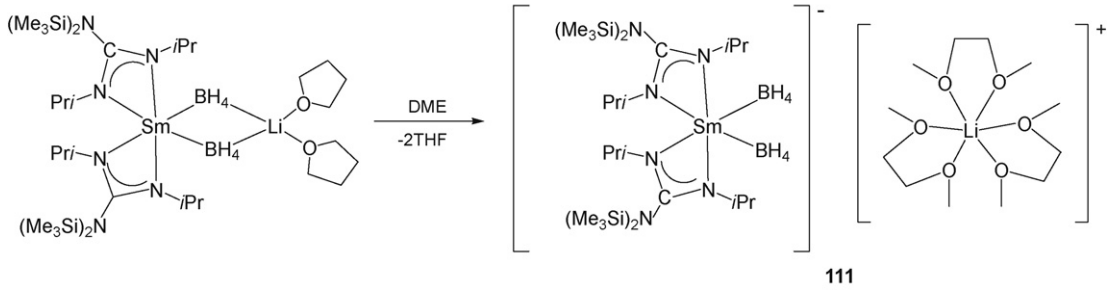


R = Cy, Ln = Nd (**102**), Sm (**103**), Yb(**104**)
R = *i*Pr, Ln = Nd (**105**), Sm (**106**)

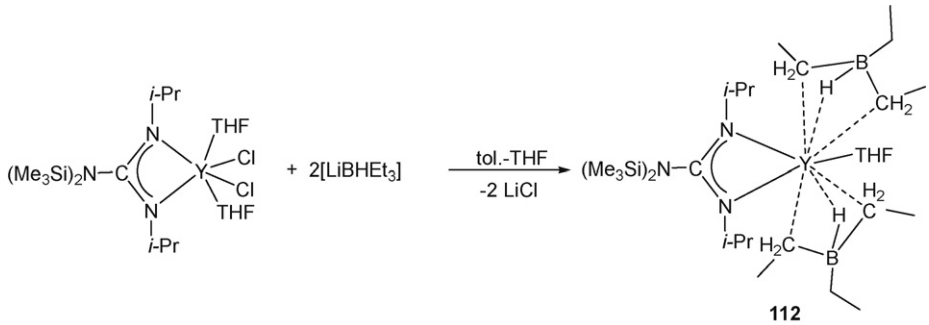
Scheme 29.



Scheme 30.



Scheme 31.



Scheme 32.

pared by the reaction of complex $[(Me_3Si)_2NC(Ni\text{-}Pr)_2]YCl_2(THF)_2$ with two equivalents of $Li[BHEt_3]$ in toluene–THF mixture at 0 °C (Scheme 32) [23].

The X-ray diffraction study revealed that **112** is a monomeric complex. The yttrium atom in **112** is coordinated by chelating guanidinate ligand, two triethylborohydride anions and one THF molecule. Each of triethylborohydride groups in **112** is bound to the yttrium atom by two μ^2-ethyl and one μ^2-hydrido ligands.

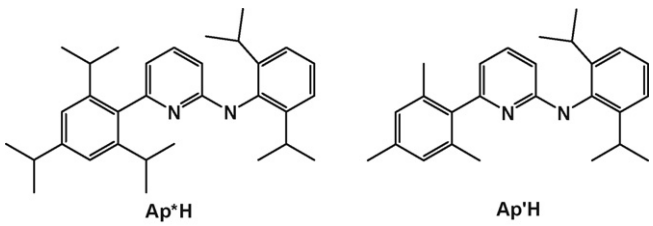
3. Complexes containing amidopyridinate ligands

3.1. Rare-earth amidopyridinate halo complexes

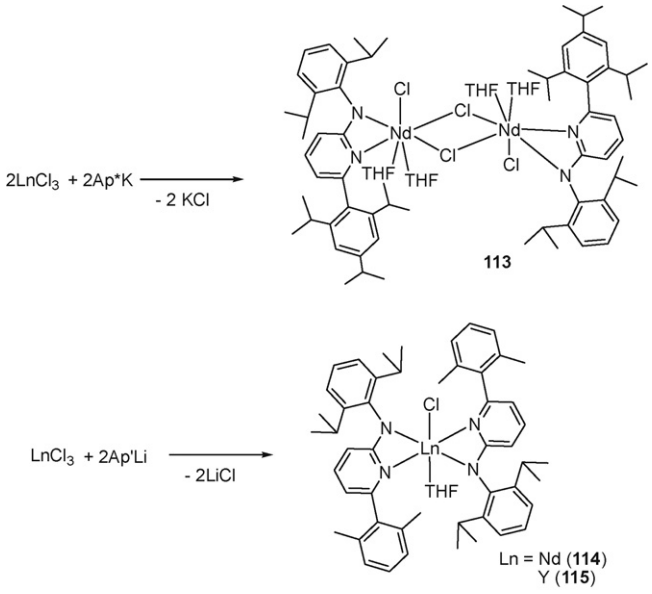
Amidopyridinate ligands having a common feature with guanidinate framework and namely a chelating monoanionic planar NCN moiety were introduced into organolanthanide chemistry by Kempe et al. and were successfully used as a suitable coordination environment for stabilization of lanthanide species [73]. A steric demand of amidopyridinate ligands, especially in the plane perpendicular to the pyridine moiety, turned out crucial for synthesis of monomeric and salt-free lanthanide complexes [74]. The preparation of sterically demanding aminopyridines (Scheme 33) as well as the synthesis, structure and dynamic behavior in solution of their lithium and potassium derivatives were described in article [75].

Polymeric $[Ap^*K]_n$ and $[Ap'K]_n$ undergo clean salt metathesis reactions with $NdCl_3$ in THF affording $[Ap^*NdCl(\mu\text{-}Cl)(THF)_2]_2$ (**113**) and $[Ap'_2NdCl(THF)]$ (**114**) respectively [76]. The reaction of $[Ap^*K]_n$ with $NdCl_3$ regardless the molar ratio of reagents (2:1 or 1:1) gives rise to the same product **113** (Scheme 34). The steric bulk of Ap^* seems to favor the formation of a one to one Ap to Ln complex.

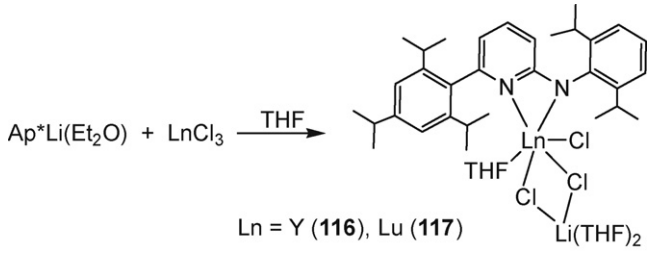
Reaction of anhydrous YCl_3 with a two-fold molar excess of Ap′K in THF at 50 °C afforded complex $[Ap'_2YCl(THF)]$ (**115**) which was



Scheme 33.



Scheme 34.

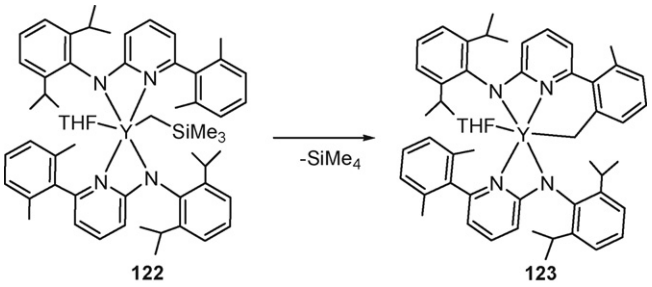


Scheme 35.

isolated after recrystallization from THF–hexane mixtures in 87% (Scheme 34). No ate-complex formation was observed [77].

Monoamidopyridinate dichloro complexes of yttrium and lutetium [Ap*Ln(Cl)(THF)(μ-Cl)$_2$Li(THF)$_2$] (Ln = Y (**116**), Lu (**117**) were synthesized by the reactions of equimolar amounts of $LnCl_3$ and Ap*Li(Et$_2$O) in THF at 20 °C (Scheme 35) [78].

Complex **116** has been characterized by an X-ray diffruction study, which revealed its monomeric structure. One of three chloro ligands in **116** is terminal, while two others are μ-bridging between the yttrium and the lithium atoms. Dimeric heteroleptic amido-iodo complexes of divalent ytterbium and samarium [Ap*Ln(μ-I)(THF)$_2$]$_2$ (Ln = Yb (**118**), Sm (**119**)) were synthesized using the same synthetic approach [76] Reactions of ytterbium metal with Ap′H and (2,4,6-trimethylphenyl)-[6-(2,4,6,-trimethylphenyl)pyridine-2-yl)amine (Ap^{Me}H) in the presence of



Scheme 37.

metallic mercury at elevated temperatures allow synthesis of homoleptic divalent [(Ap′)$_2$Yb] (**120**) and trivalent [(Ap^{Me})$_3$Yb] (**121**) ytterbium complexes [79].

3.2. Rare-earth alkyl complexes supported by amidopyridinate ligands

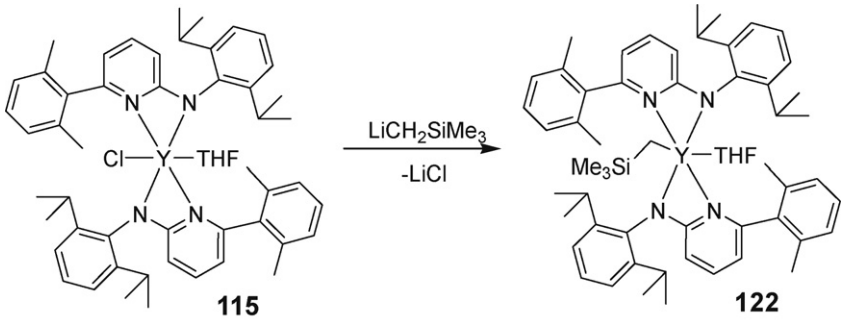
The first reports on synthesis and characterization of alkyl complexes supported by amidopyridinate ligands appeared very recently. Alkylation of complex **115** with $LiCH_2SiMe_3$ was carried out in hexane at 20 °C and resulted in the formation of the monomeric salt-free alkylyttrium derivative [Ap′$_2$YCH$_2$SiMe$_3$(THF)] (**122**) (Scheme 36), which was isolated in 65% yield [77].

Complex **122** was found to be rather thermally robust, nevertheless even at ambient temperature slow process of intramolecular activation of sp^3-hybridized C–H bond takes place leading to the formation of "benzylic" complex Ap′(Ap′$_{-H}$)Y(THF) (**123**) (Scheme 37). A linear decrease of ln(C/C_0) with time was observed, which is consistent with a rate law involving first-order dependence on **122**. The rate constant at 296 K was found to be $k = 0.0038\ h^{-1}$ and a half-time of a reaction of about 181 h was observed.

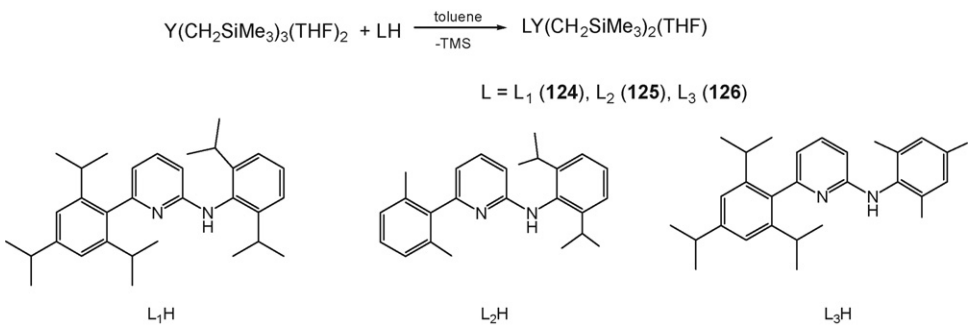
X-ray diffraction study of **123** revealed that unlike the parent alkyl compound **122**, one aminopyridinato ligand of complex **123** is tridentate due to metallation of the methyl group of one of the Me$_2$C$_6$H$_3$-fragment with formation of the new "benzylic" Y–C σ-bond.

In the tridentate Ap$_{-H}$′ ligand, formation of the Y–C bond dramatically influences the bonding situation. The covalent bond between yttrium and the amido nitrogen atom (2.432(8) Å) becomes longer than the coordination bond between yttrium and the pyridine nitrogen atom (2.338(7) Å) hence a switch from the amidopyridine to the aminopyridinate form is observed.

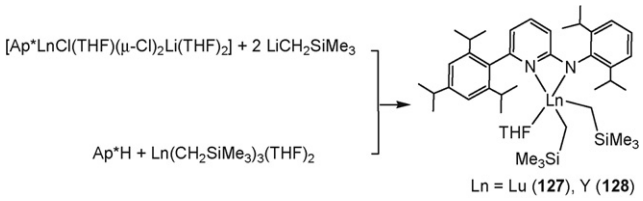
Bis(alkyl) rare earth species supported by amidopyridinate ligands were synthesized by using alkane elimination reaction under the treatment of complex Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with aminopyridines [80] or by salt metathesis reaction [78]. In publication



Scheme 36.



Scheme 38.



Scheme 39.

[80] bis(alkyl) yttrium complexes $LY(CH_2SiMe_3)_2(THF)$ (**124**–**126**) (Scheme 38) were obtained and characterized by ^1H and ^{13}C NMR techniques. The lutetium analogue $Ap^*Lu(CH_2SiMe_3)_2(THF)$ (**127**) was obtained following the same synthetic approach [78]. Alkylation of chloro complexes $[Ap^*Ln(Cl)(THF)(\mu\text{-}Cl)_2Li(THF)_2]$ (Ln = Y (**116**), Lu (**117**) with two equivalents of $LiCH_2SiMe_3$ (hexane, 0 °C) allowed synthesis of bis(alkyl) derivatives $Ap^*Ln(CH_2SiMe_3)_2(THF)$ (Ln = Lu (**127**), Y (**128**) (Scheme 39) [78].

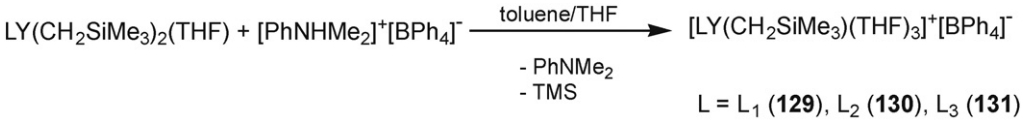
X-ray crystal structure investigations revealed that **127** and **128** are isostructural monomeric complexes. The coordination sphere of the metal atom consists of two nitrogen atoms of the bidentate amidopyridinate ligand, two carbon atoms of the alkyl groups and one oxygen atom of the THF molecule resulting in the formal coordination number of five. Complex **127** despite of the low coordination number of the central metal atom is surprisingly stable at room temperature in C_6D_6 solution: no decomposition evidences have been observed in one month. The stability of complex **128** is somewhat lower: under the similar conditions in one week ~10% of the compound was decomposed [78].

Complexes **124**–**126** were used as starting reagents for preparation of cationic alkyl derivatives. The reactions of **124**–**126** with $[PhNHMe_2]^+[B(C_6H_5)_4]^-$ in toluene–THF mixture lead selectively and quantitatively to an elimination of one of two alkyl groups and formation of cationic alkyl species $[LY(CH_2SiMe_3)(THF)_3]^+[B(C_6H_5)_4]^-$ (**129**–**131**) (Scheme 40) [80].

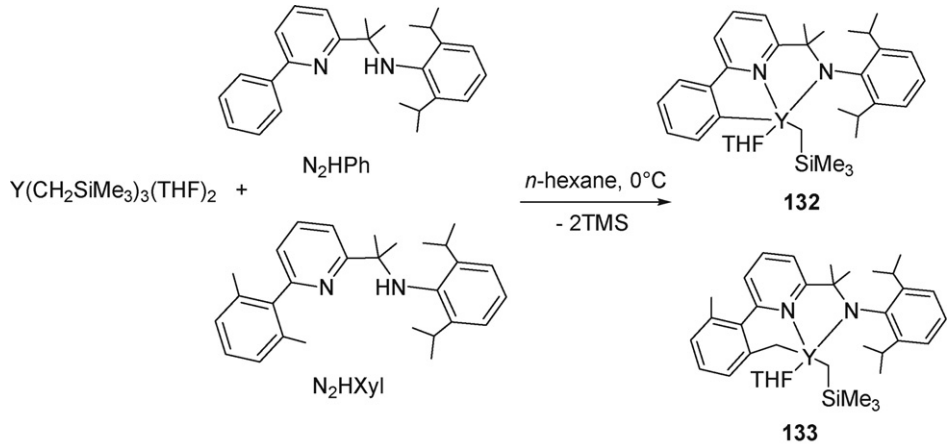
The single crystal X-ray structure determinations of complexes **129** and **131** revealed that both compounds are discrete ionic pairs.

It was reported that the reactions of $Y(CH_2SiMe_3)_3(THF)_2$ with aminopyridines bearing an additional CMe_2 group in the backbone (N_2H^{Ph} and N_2H^{Xyl}) under the same conditions (*n*-hexane, 0 °C) occur with intramolecular sp^2 or sp^3 C–H bond activation and result in the formation of alkyl-aryl or alkyl-benzyl complexes **132** and **133** (Scheme 41) [81].

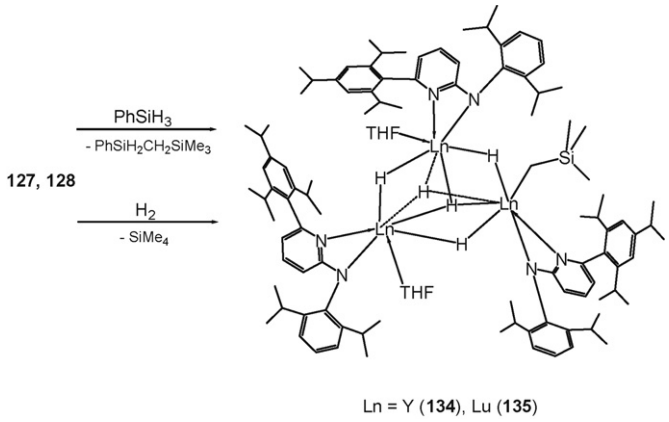
The coordination environment of the yttrium atom in monomeric complex **133** is set up by two nitrogen atoms of the chelating aminopyridinate ligand, one sp^3 carbon atom from the residual alkyl group, one further sp^3 carbon atom from the "benzylic" group and one oxygen atom from a THF molecule. Moreover, a close contact between the yttrium and the *ipso*-carbon on the



Scheme 40.



Scheme 41.



Scheme 42.

"benzylic" group is finally observed, which increases to six the coordination number.

Thereby length of a linker between two functional groups of amidopyridinate ligands was demonstrated to play a crucial role in stability of resulted bis(alkyl) yttrium species and their tendency to undergo intramolecular C–H bond activations (compare ligand L_2H [80], Scheme 38 and ligand N_2H^{Xyl} [81], Scheme 41).

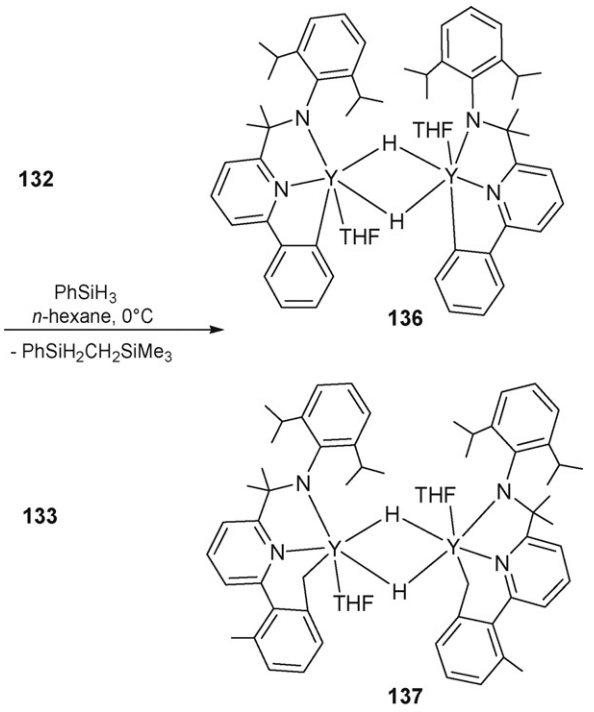
3.3. Rare-earth hydrido complexes supported by amidopyridinate ligands

The attempt of synthesis of yttrium amidopyridinate hydrido species by reacting alkyl complex [Ap′$_2$YCH$_2$SiMe$_3$(THF)] (**122**) with $PhSiH_3$ (toluene, 20 °C) was described in [77]. This reaction instead of formation of expected hydrido complex afforded the product of intramolecular C–H bond activation Ap′(Ap′$_{-H}$)Y(THF) (**123**) similar to that obtained in thermal decomposition of **122** (Scheme 37). The mechanistic and kinetic studies showed that the transient hydride, generated by the reaction of the alkyl with $PhSiH_3$ undergo an intramolecular metallation reaction very fast at room temperature. Intramolecular sp^3-hybridized C–H activation of a hydride was found to be more than 500 times faster than that of an alkyl.

The reactions of dialkyl complexes [Ap*Ln(CH$_2$SiMe$_3$)$_2$(THF)] (Ln = Y, Lu) with both $PhSiH_3$ (1:2 molar ratio, hexane, 0 °C) and H_2 (5 atm, 15 °C, 24 h) were found to result in the formation of a novel family of trinuclear alkyl-hydrido clusters [(Ap*Ln)$_3$(μ^2-H)$_3$(μ^3-H)$_2$(CH$_2$SiMe$_3$)(THF)$_2$] (Ln = Y (**134**), Lu (**135**)) supported by bulky Ap* ligands (Scheme 42). The use of a 10-fold molar excess of $PhSiH_3$ or increasing the reaction time with H_2 do not allow to remove the remaining alkyl group and to obtain polyhydrido clusters consisting of Ap*LnH$_2$ [78].

X-ray structural determination for the yttrium complex **134** revealed that it adopts a trinuclear structure, where three Ap*Y-fragments are bound by three μ^2-H- and two μ^3-H-bridging ligands, while the alkyl group remains terminal.

Treatment of alkyl-aryl (**132**) or alkyl-benzyl (**133**) complexes with an equimolar amount of $PhSiH_3$ (*n*-hexane, 0 °C) was demonstrated to result in rapid and selective σ-bond metathesis of the residual Y-CH$_2$SiMe$_3$ bonds to give the novel aryl-hydrido and benzyl-hydrido complexes **136** and **137** (Scheme 43) [81]. The Y–C(Aryl) and Y–C(Bn) bonds in **132** and **133** do not react with $PhSiH_3$, even after 24 h at room temperature and in the presence of a two-fold excess of silane. The reactions of **132** and **133** with H_2 lead to their decomposition with formation of a white-off material that does not contain any amidopyridinate ligand and is insoluble in common organic solvents.



Scheme 43.

Complex **136** adopts a binuclear structure with two six-coordinate yttrium atoms. The metal coordination sphere is determined by the two nitrogen and one carbon atoms from the tridentate amidopyridinate ligand, two bridging hydrido ligands and one oxygen atom from a residual THF molecule. Unlike the dimeric bis(guanidinate) yttrium hydrides the tetranuclear Y_2H_2-core in **136** is not planar, the dihedral angle between Y(1)H(1)H(1A) and Y(1A)H(1)H(1A) planes is 20.1°.

4. Alkyl and hydrido rare-earth complexes supported by guanidinate and amidopyridinate ligands in homogeneous catalysis

Catalytic activity of alkyl and hydrido complexes coordinated by guanidinate and amidopyridinate ligands is much less investigated compared to that of related amidinate supported species. This field still remains in its infancy and no systematic studies of catalytic properties have been carried out yet. Nevertheless, the data which were recently published demonstrate their high potential in diverse branches of homogeneous catalysis.

Alkyl ate-complexes [(Me$_3$Si)$_2$NC(NR)$_2$]$_2$Ln(μ-Me)$_2$Li(TMEDA) (R = *i*Pr, Nd (**83**) [52,32] Yb (**84**) [32]) exhibit high activity for ring-opening polymerization of ε-caprolactone to give high molecular weight polymers ($M_n > 10^4$). However, molecular mass distributions were found to be quite broad (1.92–2.96) [32]. Complexes **83** and **84** initiate styrene polymerization in the temperature range 70–100 °C [52]. The yields and reaction rates are nearly equal for **83** and **84**. The polystyrenes obtained demonstrate rather narrow molecular weight distributions ($M_w/M_n < 2$) with molecular weights (M_n) ranging from 1.72×10^4 to 5.89×10^4 and have atactic/syndiotactic rich microstructures. Complex **83** showed good catalytic activity for the syndiotactic polymerization of methyl methacrylate [32].

Dialkyl complex {(Me$_2$N)C[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$}Y(CH$_2$SiMe$_3$)$_2$(THF) (**89**) appeared to be a highly active and selective catalyst for terminal alkene hydrosilylation with $PhSiH_3$ (tof > 600 h^{-1} at 23 °C) [20]. For unfunctional-

ized olefins full selectivity towards anti-Markovnikov products was obtained. The more electron donating guanidinate ligand affords the highest activities with heteroatom-functionalized substrates than those observed for related amidinate complex $\{PhC[N(2,6\text{-}iPr_2C_6H_3)]_2\}Y(CH_2SiMe_3)_2(THF)$ (**90**) [17f].

The estimation of ethylene polymerization activities of hydrido complexes $[Ln\{(Me_3Si)_2NC(NR)_2\}_2(\mu\text{-}H)]_2$ (R = *i*Pr, Ln = Y (**93**) [49], Nd (**94**) [49], Sm (**95**) [49], Gd (**96**) [49], Yb (**97**) [49], Lu (**98**) [33]; R = Cy, Ln = Y (**99**) [50], Lu (**100**) [50]) has shown that that of samarium hydrido complex **95**, 1268 g mmol^{-1} atm^{-1} h^{-1} was the highest among tested compounds [49]. In the case of the yttrium derivative **93** the polymerization process was less rapid (442 g mmol^{-1} atm^{-1} h^{-1}). Complexes of gadolinium, ytterbium and lutetium have shown modest catalytic activities (281, 77 and 76 g mmol^{-1} atm^{-1} h^{-1} respectively). The neodymium complex **94** has shown very low activity. Yttrium hydrido complex **99** supported by cyclohexyl substituted guanidinate ligand was found to be less active (65 g mmol^{-1} atm^{-1} h^{-1}) compared to $(Me_3Si)_2NC(NiPr)_2$ containing analogue **93**. The catalytic activity of complex **100** is comparable to the activity of the isopropyl substituted analogue **98** (7.83 g mmol^{-1} atm^{-1} h^{-1}). Complexes **93**–**98** sluggishly oligomerize propylene. In styrene polymerization only derivatives of smallest lanthanide metals (Yb and Lu) have shown catalytic activity. Complex **98** initiates polymerization of styrene (20 °C, neat styrene, 5% of **98**). 90% conversion was reached in 6 days; the polystyrene obtained has a high molecular weight (M_n = 811,000 g mol^{-1}, M_w = 1,250,000 g mol^{-1}), narrow molecular weight distribution (M_w/M_n = 1.54), and melting temperature 255–260 °C. In the case of **97** (20 °C, neat styrene, 1 mol% of **97**, total conversion in 3 days) the obtained polymer had higher molecular weight distribution M_w/M_n = 2.6 (M_n = 90,000 g mol^{-1}, M_w = 237,700 g mol^{-1}; melting temperature 289–293 °C). Both polystyrenes have high degree of syndiotactisity [49]. Complexes **99** and **100** are inactive in propylene and styrene polymerizations [50].

Hydrides **93**, **98**–**100** were shown to catalyze efficiently the hydrosilylation of 1-nonene with $PhSiH_3$ (the substrates molar ratio: 1:1) to give the terminal silane $^nC_9H_{19}SiH_2Ph$ exclusively. If the hydrosilylation reaction is carried out in the presence of a two-fold molar excess of 1-nonene double addition takes place and leads to the formation of tertiary silane $(^nC_9H_{19})_2SiHPh$ which was obtained in 96% yield. Complexes **93**, **98**–**100** do not initiate neither 1-nonene polymerization nor $PhSiH_3$ dehydrogenative coupling. No reaction was observed for $PhSiH_3$ with cyclohexene, styrene and norbornene under similar conditions in the presence of **93**, **98**–**100**. The hydride complexes **93** and **98** efficiently initiate the ring-opening polymerization of ε-caprolactone to give polymers with molar mass up to 80,000 [50].

Borohydrido complexes $[(Me_3Si)_2NC(N\text{-}R)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (R = Cy, Ln = Nd (**102**) [69], Sm (**103**) [69], Yb (**104**) [69]) act as monoinitiators for the ring-opening polymerization of racemic lactide providing atactic polymers with a good degree of control (controlled molecular weights and relatively narrow polydispersities $1.09 < M_w/M_n < 1.77$), provided moderate substrate-to-initiator ratios are used. The neodymium complex **102** demonstrated the best results in terms of efficiency and degree of control [69]. Borohydrides $[(Me_3Si)_2NC(N\text{-}R)_2]_2Ln(\mu\text{-}BH_4)_2Li(THF)_2$ (R = Cy, Ln = Nd (**102**) [69], Sm (**103**) [69], Yb (**104**) [69]; R = *i*Pr, Ln = Nd (**105**) [70], Sm (**106**) [70]) and $[(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(THF)_2$ (Ln = Yb (**109**), Er (**110**)) [72] exhibited from moderate up to high catalytic activities in polymerization of methyl metacrylate [69,71,72].

For cationic alkyl species coordinated by amidopyridinate ligands $[LY(CH_2SiMe_3)(THF)_3]^+[B(C_6H_5)_4]^-$ (**129**–**131**) in the presence of small amounts of aluminium alkyl compounds, very high activities in ethylene polymerizations were observed at 80° if very bulky amidopyridinate ligands were used. The reduction of the steric demand of the Ap ligand (2,6-dimethylphenyl instead of 2,4,6-triisopropylphenyl substituents at the pyridine ring of the Ap ligand) goes along with a decrease of the ethylene polymerization activity by about 60%. During polymerization a reversible polyethylene chain transfer was observed between the organoyttrium cations and aluminium alkyls. The present catalytic system is able to produce relatively long-chain (up to 4000 g mol^{-1}) Al-terminated polyethylene with a molecular weight distribution <1.1 [80].

Alkyl-hydrido cluster compounds $[(Ap^*Ln)_3(\mu^2\text{-}H)_3(\mu^3\text{-}H)_2(CH_2SiMe_3)(THF)_2]$ (Ln = Y (**134**), Lu (**135**)) are single component ethylene polymerization catalysts. The ethylene polymerization activity of the yttrium complex was found to be 560 g mmol^{-1} bar^{-1} h^{-1}, but the catalyst was desactivated in 3 h. The lutetium complex was less active (168 g mmol^{-1} bar^{-1} h^{-1}) but did not demonstrate loss of the reaction rate during one day [78].

The results for ethylene polymerization (10 bar C_2H_4, 25 mL toluene, 30 °C) indicate that both hydrido complexes **136** and **137** do not generate very active catalytic systems as the highest turn-over frequency observed was 870 mol of C_2H_4 converted (mol metal)$^{-1}$ h^{-1} [80].

5. Conclusion

The data summarized in the present review show that the bulky guanidinate and aminopyridinate ligand frameworks are well-suited for coordination to large ions of rare-earth metals and provide diverse and rich synthetic and structural chemistry. Application of these ligands enables the synthesis of various types of isolable rare-earth alkyl and hydrido species. The progress achieved in this field demonstrates great possibilities for stabilization of highly reactive organo rare-earth derivatives and for regulating the reactivity of these compounds by the design of ligand systems and the coordination sphere of the central atom. Formerly scarce mono- and bis(alkyl) and hydrido derivatives became easily accessible and surprisingly stable. The examples of catalytic applications cited in the review confirm considerable perspectives of alkyl and hydrido rare-earth complexes supported by guanidinate and amidopyridinate ligands in polymerization of both polar and non-polar monomers, ring-opening polymerization of cyclic esters and hydrosilylation of olefins. Application of amidopyridinate ligands allowed synthesis of novel family of trinuclear alkyl hydrido clusters and cationic alkyl species featuring high catalytic activity in ethylene polymerization and reversible polyethylene chain transfer between rare earth and aluminum atoms. A number of intramolecular metallations of sp^2- and sp^3-hybridized C–H bonds was documented for mono-, bis(alkyl) and hydride complexes which present considerable interest due to their ability to activate inert chemical bonds. Despite of the progress which was done during past five years this field still leaves space for further development. Alkyl hydrido clusters of larger rare-earth metals, cationic hydrido species and especially their catalytic activity are expected to attract attention in near future. Synthesis of monomeric non-cyclopentadienyl hydrides still remains a challenge that necessitates design of bulkier guanidinate and amidopyridinate ligand systems. Bulky guanidinate and aminopyridinate ligands can serve as good candidates for stabilization of complexes of rare earth metals in non-conventional oxidation states and for synthesis of species containing the metal–metal atom bonds. A considerable progress can be provided in development of efficient catalysts especially for cyclic esters ring-opening polymerization and synthesis of novel precursors for materials science and nanotechnology.

References

[1] (a) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fourth ed., Wiley, New York, 1980;
(b) R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.
[2] M.N. Bochkarev, L.N. Zakharov, G.S. Kalinina, Organoderivatives of Rare Earth Elements, Kluwer Academic Publishers, Dordrecht, 1995.
[3] (a) W.J. Evans, J.H. Meadows, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 106 (1984) 1291;
(b) D. Stern, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 112 (1990) 9558;
(c) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623;
(d) K.C. Hulzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228;
(e) A.A. Trifonov, T.P. Spaniol, J. Okuda, Organometallics 20 (2001) 4869;
(f) C.P. Casey, J.A. Tunge, T.-Y. Lee, D.W. Carpenetti, Organometallics 21 (2002) 389;
(g) C.P. Casey, J.A. Tunge, T.-Y. Lee, M.A. Fagan, J. Am. Chem. Soc. 125 (2003) 2641;
(h) A.A. Trifonov, T.P. Spaniol, J. Okuda, Dalton Trans. (2004) 2245;
(i) Y. Luo, Z. Hou, Organometallics 26 (2007) 2941.
[4] (a) V.P. Conticello, L. Brard, M.A. Giardello, Y. Tsuji, M. Sabat, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 2761;
(b) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 811;
(c) W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 105 (1983) 1401.
[5] (a) Z. Hou, Y. Wakatsuki, Coord. Chem. Rev. 231 (2002) 1;
(b) H. Yasuda, J. Organomet. Chem. 647 (2002) 128;
(c) Y. Nakayama, H. Yasuda, J. Organomet. Chem. 689 (2004) 4489.
[6] G.A. Molander, J.A.C. Romero, Chem. Rev. 102 (2002) 2161.
[7] (a) E.A. Bijpost, R. Duchateau, J.H. Teuben, J. Mol. Catal. 95 (1995) 121;
(b) K.N. Harrison, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 9220.
[8] (a) K.C. Hultzsch, Adv. Synth. Catal. 347 (2005) 367;
(b) S. Hong, T.J. Marks, Acc. Chem. Res. 37 (2004) 673;
(c) I. Aillaud, J. Collin, J. Hannedouche, E. Schulz, Dalton Trans. (2007) 5105;
(d) K.C. Hultzsch, Org. Biomol. Chem. 3 (2005) 1819;
(e) P.W. Roesky, T.E. Müller, Angew. Chem. Int. Ed. 42 (2003) 2708.
[9] (a) A. Kawaoka, T.J. Marks, J. Am. Chem. Soc. 127 (2005) 6311;
(b) A. Kawaoka, T.J. Marks, J. Am. Chem. Soc. 126 (2004) 12764;
(c) M.R. Douglass, T.J. Marks, J. Am. Chem. Soc. 122 (2000) 1824.
[10] L.R. Morss, Chem. Rev. 76 (1976) 827.
[11] (a) H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865;
(b) S. Arndt, J. Okuda, Chem. Rev. 102 (2002) 1953;
(c) J. Okuda, Dalton Trans. (2003) 2367.
[12] F.T. Edelmann, D.M.M. Freckmann, H. Schumann, Chem. Rev. 102 (2002) 1851.
[13] (a) P.J. Bailey, S. Pace, Coord. Chem. Rev. 214 (2001) 91;
(b) D.A. Kissounko, M.V. Zabalov, G.P. Brusova, D.A. Lemenovskii, Russ. Chem. Rev. 75 (2006) 351;
(c) F.T. Edelmann, Adv. Organomet. Chem. 57 (2008) 183;
(d) F.T. Edelmann, Chem. Soc. Rev. 38 (2009) 2253.
[14] M.P. Coles, Dalton Trans. (2006) 985.
[15] (a) W.E. Piers, D.J.H. Emslie, Coord. Chem. Rev. 131 (2002) 233;
(b) A.A. Trifonov, Russ. Chem. Rev. 76 (2007) 1051.
[16] (a) C. Hagen, H. Reddmann, H.-D. Amberger, F.T. Edelmann, U. Pegelow, G.V. Shalimoff, N.M. Edelstein, J. Organomet. Chem. 462 (1993) 69;
(b) M. Wedler, F. Knosel, U. Pieper, D. Stalke, F.T. Edelmann, H.-D. Amberger, Chem. Ber. 125 (1992) 2171;
(c) A. Recknagel, F. Knosel, H. Gornitzka, M. Noltemeyer, F.T. Edelmann, U. Behrens, J. Organomet. Chem. 417 (1991) 363;
(d) M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke, F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 29 (1990) 894;
(e) M. Wedler, A. Recknagel, J.W. Gilje, M. Notelmeyer, F.T. Edelmann, J. Organomet. Chem. 426 (1992) 295.
[17] (a) R. Duchateau, C.T. Van Wee, A. Meetsma, P.T. Van Duijnen, J.H. Teuben, Organometallics 15 (1996) 2279;
(b) R. Duchateau, C.T. Van Wee, A. Meetsma, J.H. Teuben, J. Am. Chem. Soc. 115 (1993) 4931;
(c) R. Duchateau, C.T. Van Wee, J.H. Teuben, Organometallics 15 (1996) 2291;
(d) S. Bambirra, M.J.R. Brandsma, E.A.C. Brussee, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 3197;
(e) S. Bambirra, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 20 (2001) 782;
(f) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J.H. Teuben, Chem. Commun. (2003) 522;
(g) S. Bambirra, M.W. Bouwkamp, A. Meetsma, B. Hessen, J. Am. Chem. Soc. 126 (2004) 9182.
[18] L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, Angew. Chem. Int. Ed. 47 (2008) 2642.
[19] E.A. Bijpost, R. Duchateau, J.H. Teuben, J. Mol. Catal. 95 (1995) 121.
[20] S. Ge, A. Meetsma, B. Hessen, Organometallics 27 (2008) 3131.
[21] S. Patai, Z. Rapoport, The Chemistry of Amidines and Imidinates, vol. 2, Wiley, New York, 2000 (Chapter 10).
[22] F.T. Edelmann, Coord. Chem. Rev. 137 (1994) 403.
[23] D.M. Lyubov, G.K. Fukin, A.A. Trifonov, Inorg. Chem. 46 (2007) 11450.
[24] A.A. Trifonov, D.M. Lyubov, G.K. Fukin, E.V. Baranov, Yu.A. Kurskii, Organometallics 25 (2006) 3935.
[25] J. Zhang, X. Zhou, R. Cai, L. Weng, Inorg. Chem. 44 (2005) 716.
[26] S. Mullins, A.P. Dunkan, R.G. Bergman, J. Arnold, Inorg. Chem. 20 (2001) 6952.
[27] A.A. Trifonov, D.M. Lyubov, E.A. Fedorova, G.G. Skvortsov, G.K. Fukin, Yu.A. Kurskii, M.N. Bochkarev, Russ. Chem. Bull. Int. Ed. 55 (2006) 435.
[28] D. Heitmann, C. Jones, P.C. Junk, K.-A. Lippert, A. Stasch, Dalton Trans. (2007) 187.
[29] Z. Lu, G.P.A. Yap, D.S. Richeson, Organometallics 20 (2001) 706.
[30] A.A. Trifonov, G.G. Skvortsov, D.M. Lyubov, G.K. Fukin, E.A. Fedorova, M.N. Bochkarev, Russ. Chem. Bull. Int. Ed. 54 (2005) 2511.
[31] Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang, Q. Shen, J. Organomet. Chem. 679 (2003) 229.
[32] Y. Luo, Y. Yao, Q. Shen, K. Yu, L. Weng, Eur. J. Inorg. Chem. (2003) 318.
[33] A.A. Trifonov, E.A. Fedorova, G.K. Fukin, M.N. Bochkarev, Eur. J. Inorg. Chem. (2004) 4396.
[34] A.A. Trifonov, D.M. Lyubov, E.A. Fedorova, G.K. Fukin, H. Schumann, S. Mühle, M. Hummert, M.N. Bochkarev, Eur. J. Inorg. Chem. (2006) 747.
[35] Y. Zhao, G.P.A. Yap, D.S. Richeson, Organometallics 17 (1998) 4387.
[36] Ch. Jing-Lei, Y. Ying-Ming, L. Yun-Jie, Zh. Li-Ying, Z. Yong, Sh. Qi, J. Organomet. Chem. 689 (2004) 1019.
[37] L. Zhou, Y. Yao, Y. Zhang, M. Xue, J. Chen, Q. Shen, Eur. J. Inorg. Chem. (2004) 2167.
[38] X. Pang, H. Sun, Y. Zhang, Q. Shen, H. Zhang, Eur. J. Inorg. Chem. (2005) 1487.
[39] G.G. Skvortsov, D.M. Lyubov, M.V. Yakovenko, G.K. Fukin, A.V. Cherkasov, A.A. Trifonov, A.N. Izv, Ser. Khim. (2009) 1098.
[40] G.R. Giesbrecht, G.D. Whitener, J. Arnold, J. Chem. Soc., Dalton Trans. (2001) 923.
[41] J. Zhang, R. Cai, L. Weng, X. Zhou, Organometallics 23 (2004) 3303.
[42] J. Zhang, R. Cai, L. Weng, X. Zhou, J. Organomet. Chem. 672 (2003) 94.
[43] L. Ma, J. Zhang, R. Cai, Z. Chen, L. Weng, X. Zhou, J. Organomet. Chem. 690 (2005) 4926.
[44] C. Pi, Z. Zhu, L. Weng, Z. Chen, X. Zhou, Chem. Commun. (2007) 2190.
[45] C. Pi, R. Liu, P. Zheng, Z. Chen, X. Zhou, Inorg. Chem. 46 (2007) 5252.
[46] C. Pi, Z. Zhang, Z. Pang, J. Zhang, J. Luo, Z. Chen, L. Weng, X. Zhou, Organometallics 26 (2007) 1934.
[47] L. Ma, J. Zhang, Z. Zhang, R. Cai, Z. Chen, X. Zhou, Organometallics 25 (2006) 4571.
[48] J. Zhang, L. Ma, Y. Han, F.H.Z. Zhang, R. Cai, Z. Chen, X. Zhou, Dalton Trans. (2009) 3298.
[49] A.A. Trifonov, G.G. Skvortsov, D.M. Lyubov, N.A. Skorodumova, G.K. Fukin, E.V. Baranov, V.N. Glushakova, Chem. Eur. J. (2006) 5320.
[50] D.M. Lyubov, A.M. Bubnov, G.K. Fukin, F.M. Dolgushin, M.Yu. Antipin, O. Pelcé, M. Schappacher, S.M. Guillaume, A.A. Trifonov, Eur. J. Inorg. Chem. (2008) 2090.
[51] (a) W.J. Evans, A.L. Wayda, W.E. Hunter, J.L. Atwood, J. Chem. Soc., Chem. Commun. (1981) 292;
(b) H. Schumann, W. Genthe, N. Bruncks, J. Pickardt, Organometallics 1 (1982) 1194;
(c) W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 104 (1982) 2008.
[52] Y. Luo, Y. Yao, Q. Shen, Macromolecules 35 (2002) 8670.
[53] (a) C.J. Schaverien, Organometallics 11 (1992) 3476;
(b) S. Arndt, T.P. Spaniol, J. Okuda, Organometallics 22 (2003) 775.
[54] (a) H. Yasuda, E. Ihara, Bull. Chem. Soc. Jpn. 70 (1997) 1745;
(b) H. Yasuda, Polym. Sci., Part A: Polym. Chem. 39 (2001) 1955;
(c) Y. Luo, J. Baldamus, Z. Hou, J. Am. Chem. Soc. 126 (2004) 13910;
(d) X. Li, J. Baldamus, Z. Hou, Angew. Chem. Int. Ed. 44 (2005) 962.
[55] M. Ephritikhine, Chem. Rev. 97 (1997) 2193.
[56] W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 104 (1982) 2008.
[57] M. Konkol, J. Okuda, Coord. Chem. Rev. 252 (2008) 1577.
[58] L. Maron, E.L. Werkema, L. Perrin, O. Eisenstein, R.A. Andersen, J. Am. Chem. Soc. 127 (2005) 279.
[59] G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103.
[60] A.Z. Voskoboinikov, I.N. Parshina, A.K. Shestakova, K.P. Butin, I.P. Beletskaya, L.G. Kuz'mina, J.A.K. Howard, Organometallics 16 (1997) 4041.
[61] (a) T.J. Marks, G.W. Grynkewich, Inorg. Chem. 6 (1976) 1302;
(b) Y.K. Gun'ko, B.M. Bulychev, G.L. Soloveichik, V.K. Belsky, J. Organomet. Chem. 424 (1992) 289;
(c) E.B. Lobkovsky, Y.K. Gun'ko, B.M. Bulychev, G.L. Soloveichik, V.K. Belsky, J. Organomet. Chem. 424 (1991) 289;
(d) H. Schumann, W. Genthe, J. Organomet. Chem. 213 (1983) C7;
(e) H. Schumann, W. Genthe, N. Brunks, J. Pickardt, Organometallics 1 (1982) 1194;
(f) D. Deng, X. Zheng, C. Qian, J. Sun, L. Chang, J. Organomet. Chem. 466 (1994) 95;
(g) H. Schumann, M.R. Keitsch, J. Demtschuk, S. Mühle, Z. Anorg, Allg. Chem. 624 (1998) 1811.
[62] M. Mancini, P. Bougeard, R.C. Burns, M. Mlekuz, B.G. Sayer, J.I.A. Thompson, J. McGlinchey, J. Inorg. Chem. 23 (1984) 1082.
[63] (a) I. Pallard, A. Soum, S.M. Guillaume, Chem. Eur. J. 10 (2004) 4054;
(b) F. Bonnet, A.R. Cowley, P. Mountford, Inorg. Chem. 44 (2005) 9046.
[64] F. Bonnet, A.C. Hilier, A. Collins, S.R. Dubberley, P. Monutford, Dalton Trans. (2005) 421.

[65] D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, M. Visseaux, Eur. J. Inorg. Chem. (2000) 2333.
[66] T.J. Marks, J.R. Kolb, Chem. Rev. 77 (1977) 263.
[67] U. Mirsaidov, I.B. Shaimuradov, M. Khikmatov, J. Inorg. Chem. USSR 31 (1986) 1321.
[68] M. Visseaux, T. Chenal, P. Roussel, A. Mortreux, J. Organomet. Chem. 691 (2006) 86.
[69] G.G. Skvortsov, M.V. Yakovenko, P.M. Castro, G.K. Fukin, A.V. Cherkasov, J.-F. Carpentier, A.A. Trifonov, Eur. J. Inorg. Chem. (2007) 3260.
[70] G.G. Skvortsov, M.V. Yakovenko, G.K. Fukin, E.V. Baranov, Yu.A. Kurskii, A.A. Trifonov, Russ. Chem. Bull. Int. Ed. 56 (2007) 456.
[71] G.G. Skvortsov, M.V. Yakovenko, G.K. Fukin, A.V. Cherkasov, A.A. Trifonov, Russ. Chem. Bull. Int. Ed. 56 (2007) 1742.
[72] F. Yuan, Y. Zhu, L. Xiong, J. Organomet. Chem. 691 (2006) 3377.
[73] R. Kempe, H. Noss, T. Irrgang, J. Organomet. Chem. 647 (2002) 12.
[74] R. Kempe, Eur. J. Inorg. Chem. (2003) 791.
[75] N.M. Scott, T. Schareina, O. Tok, R. Kempe, Eur. J. Inorg. Chem. (2004) 3297.
[76] N.M. Scott, R. Kempe, Eur. J. Inorg. Chem. (2005) 1319.
[77] G.G. Skvortsov, G.K. Fukin, A.A. Trifonov, A. Noor, C. Döring, R. Kempe, Organometallics 26 (2007) 5770.
[78] D.M. Lyubov, C. Döring, G.K. Fukin, A.V. Cherkasov, A.S. Shavyrin, R. Kempe, A.A. Trifonov, Organometallics 27 (2008) 2905.
[79] S. Qayyum, K. Haberland, C.M. Forsyth, P.C. Junk, G.B. Deacon, R. Kempe, Eur. J. Inorg. Chem. (2008) 557.
[80] W.P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, Chem. Eur. J. 12 (2006) 8969.
[81] D.M. Lyubov, G.K. Fukin, A.V. Cherkasov, A.S. Shavyrin, A.A. Trifonov, L. Luconi, C. Bianchini, A. Meli, G. Giambastiani, Organometallics 28 (2009) 1227.